# AN EVALUATION OF FOURIER TRANSFORM INFRARED SPECTROSCOPY FOR THE CHARACTERIZATION OF ORGANIC COMPOUNDS IN ART AND ARCHAEOLOGY

by

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# ABSTRACT

The application of Fourier transform infrared spectroscopy (FT-IR) to the characterization of materials in art and archaeology is evaluated. The diffuse reflectance accessory was used extensively and an infrared microscope was utilized for microscopic samples. The development and theory of diffuse reflectance FT-IR spectroscopy are given and a brief outline of previous use of infrared spectroscopy in archaeological and art conservation is included. The experimental procedures and sample handling used in the research are explained in detail. Diffuse reflectance spectra of several classes of organic materials available in antiquity are presented. The classes of organic materials include waxes, fats and oils, bituminous materials, resins, amber, shellac, pitch, gums and gum resins and proteins. The spectra of the reference materials are interpreted in the light of the known information on chemical structure. Several examples of archaeological specimens which have been characterized are included. Two large groups of modern materials, a group of plastic sculptures and a collection of early plastic objects were characterized. Areas for future work include an expanded reference collection of modern materials and

the use of J-CAMP-DX programming language for interlaboratory exchange of data which is independent of the brand of spectrometer used.

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# PREFACE

The purpose of this research was to evaluate FT-IR spectroscopy for samples encountered in art and archaeology. A large number of samples of known provenance or identity were analysed to serve as a reference collection. Spectra were also obtained of unknown materials from a variety of sources and objects and attempts were made to identify the materials on the basis of their spectra.

The laboratory work was done outside the Institute of Archaeology and it was not certain at the beginning of the project how much time on the spectrometer would be available to the author. Thus, speed of sample preparation and acquisition was an important consideration. Also, the assessment of the technique was made on the basis of what might be useful to conservators and conservation students who were not analytical chemists. As a result, few pretreatment or separation techniques were carried out with the samples. The few exceptions are noted in the text. It was possible to run a large number of spectra of both reference material and unknown samples. The appendix is a catalogue of the reference materials used in this research.

The first chapter is a review of the literature of applications of infrared spectroscopy in art and archaeology. The publications concern several types of materials and applications, so the works were reviewed in chronological order. The second chapter is a review of the diffuse reflectance technique. Although little quantitative work was carried out in this research, it was considered wothwhile to include in the second chapter a brief review of the quantitative aspects of diffuse reflectance spectroscopy. This was considered to be necessary as this is the first application of diffuse reflectance to art and archaeological research. Also, this project is interdisciplinary in nature and some future workers referring to this text may not be familiar with the technique. Chapter 3 is a description of the methods used in the laboratory work undertaken in this project.

The natural products examined in this thesis are divided into five chapters on waxes, fats and oils, bituminous materials, resinous materials and proteins (Chapters 4 - 8). A brief summary of the source and composition of each material was included. The spectra of the reference materials are interpreted in terms of the band frequency assignments to determine if the spectra provide a valid means of assessing the composition of the material. The unknown spectra which were identified are then compared to those of the reference materials. Tables of the band assignments for both reference and unknowns and the figures are located at the end of each chapter. The spectra which are presented in this thesis were reproduced using a graphics software program which assigned arbitrary values to the ordinate axis. Since the work was qualitative in nature and spectral expansion was utilized with small samples, the ordinate axis is marked in the direction of increasing diffuse reflectance (R) and no numerical values are shown.

Chapter 9 is a background chapter which discusses the history of manufacture, structure, method of production and uses of four early plastics. The next chapter analyzes the reference spectra of these four plastics and chapter 11 discusses the three groups of early plastics which were identified using diffuse reflectance spectroscopy. Chapter 12 reviews the degradtion of polymers and chapter 13 is a case study in which a collection of plastics of known date or composition are analyzed to provide a larger reference collection. Chapter 14 is a summary of samples identified as synthetic materials on archaeological objects which seem to be old conservation treatments.

## CHAPTER 1 LITERATURE SURVEY ON THE USE OF INFRARED SPECTROSCOPY IN MUSEUM WORK

### Introduction

A literature survey was conducted on the applications of infrared spectroscopy to archaeology and conservation. A summary of the publications is presented in this chapter. The majority of the work has been concerned with the analysis of materials used in the fine arts such as pigments and binding media. Other work has included studies of bronze corrosion products, but very little material has been published on the application of infrared spectroscopy to archaeological analysis or conservation research. An exception is the extensive analysis of amber by Beck utilizing infrared spectroscopy. The articles are reviewed in chronological order.

### 1953 - 1960

Infrared spectroscopy was utilized in a study of the surviving materials from Turner's paint boxes which included dry pigments, pigment pastes and three samples of either media or varnish (Hanson, 1953). The media were extracted from the pigment pastes with either tetrahydropyran or trichloroethylene. In some cases, it was necessary to saponify the sample in the presence of alkali. The infrared spectra of the unsaponified fractions were found to be similar to those of vegetable oils. The ether-insoluble portions had spectra which were characteristic of a resin. The paper concluded that there were two types of media, one which consisted of drying oil and a resin and a second of drying oil. One of the varnish samples was identified as impure, aged turpentine and a second was identified as dammar resin in turpentine at a concentration of 68%. A third material was found to be a mixture of drying oil and resin with spectra similar to those found for the pigment paste extracts.

An early report of infrared analysis applied to studies in fine arts is given by Feller in 1954. The paper presented spectra of dammar resin (Singapore No 1) and mastic. The spectra are very similar to each other. The only difference is the presence of a band at 890 $cm^{-1}$ in the dammar which is not apparent in that of the mastic. The spectra obtained were of cast films which were prepared from chloroform solvent. The residual solvent is thought to cause the strong band which is evident at 760 $cm^{-1}$ and the weaker band at 1220 $cm^{-1}$. Samples which were dried under a vacuum gave spectra with a band of reduced intensity at 760 $cm^{-1}$, but the solvent bands were not completely removed.

In the study (Feller, 1954), spectra were obtained of different grades of mastic and dammar, including poor grades which were coloured. All were found to be extremely similar. Also, a sample of Batava dammar stored for 35 years was found to have a spectrum which was very similar to that of Batavia and Singapore dammars which were recently obtained. This similarity is expected as the resins are composed of the same types of constituents such as resin acids. Thus, it is difficult to obtain spectra which are characteristic for each type of dammar or mastic.

Infrared spectra were also obtained of samples which were artificially aged in a Fade-O-Meter (National Accelerated Fading Unit, Type XV) (Feller, 1954). Their spectra were measured to see if changes due to degradation could be seen in the infrared spectra. The spectra of the artificially aged materials were similar to the unaged samples in spite of the severe discolouration and cracking of the samples. The region between 1200 - 800 $cm^{-1}$ in both types of aged resins exhibited a loss in detail. This was explained by a greater complexity in the aged material. In the spectrum of the mastic, the relative intensities of the bands at 1450 and 1375 $cm^{-1}$ are reversed in the aged sample spectrum. This change in relative intensities may be indicative of chemical change caused either by a decrease in the methylene groups due to oxidation or an increase in the methyl groups which result from chain scission or a combination of both. A second explanation is that the molecular environment near the groups might have been altered which would change the intensity of the group. Feller concluded that infrared may have limited use in museum work due to the difficulties in the analysis of complex mixtures and in the detection of additives in trace quantities.

The use of infrared spectroscopy was later evaluated by Feller (1959) in a review of analysis methods for resins and varnishes. The difficulties which were encountered were listed and it was pointed out that natural resins are actually mixtures of compounds and thus it is difficult to isolate small amounts of other materials. In spectra of varnish/stand oil mixtures containing 20 - 50% oil, the presence of the oil does not strongly affect the spectrum. Also, it was emphasized that aging changes the composition and that reference samples of aged standards are necessary for characterization (Feller, 1959).

Another early report of infrared analysis in conservation is the study of waxes by Kuhn (1960). The analyses were performed with a double beam spectrometer with a NaCl prism equipped with a microscope with NaCl lenses which condensed the infrared beam. In order to obtain good quality spectra, it is desirable to fill as much of the infrared beam as possible with the sample. The concentration of the infrared beam allows the analysis of milligramme and microgramme samples. In this study, the samples studied were paint media from three Fayum mummy portraits and a wall painting from Pompeii in addition to a replica of the wall painting produced using a new encaustic technique (The term encaustic means using paint in a wax medium.) The presence of pigment in the samples causes a scattering of the infrared radiation and interferences in the resulting spectra so the sample had to be separated from the colouring matter in each case. This was performed by placing the sample in a micro-crucible or in a dimpled microscope slide with chloroform for one day at room temperature. The solution was then deposited onto a NaCl cell and the solvent was removed using hot air which left the sample as a film on the surface of the cell. Benzyl alcohol was utilized to separate the wax from wax-resin mixtures and wax may be removed from bituminous materials with warm monochlorohydrin ($CH_2OHCHOHCH_2Cl$).

In addition to the identification of the examples mentioned above, spectra were published of the following standard materials: beeswax, two relining mixtures, (one of beeswax with colophony and one of beeswax with a synthetic resin called A.W.2), carnauba wax, esparto wax, crude montan wax, stearin wax and paraffin wax (Kuhn, 1960). These are discussed in the section on waxes in Chapter 4. The substance known from antiquity as Punic wax, which was produced from beeswax, was made following an ancient recipe and spectra were published of the material and the alcohol extract.

## 1961 - 1970

In a further example of the application of infrared spectroscopy in the field of fine arts, the technique was used to examine the applique relief brocade from several examples of late Gothic wooden polychrome statues (Frinta, 1963). An applied material was used to imitate rich fabric and it was thought that gesso was used exclusively for this purpose. Some examples were tentatively identified as beeswax or a wax-resin mixture and small samples were taken for infrared and microscopic examination. Infrared analysis showed that samples were indeed wax or wax-resin mixtures. It was not known before this work that wax had been utilized for this technique, perhaps because of the poor state of preservation of the relief material and the small number of pieces that have survived. The polychrome figures which were incorporated into shrines were repaired and repainted from time to time. It is thought that the replacement of the wax brocade as it became damaged may not have been possible after the skills associated with its production had become obsolete. It is likely that the wax-resin material lost its adherance to the sculpture and became brittle. Another problem resulted from successive coats of overpainting which would progressively obscure the relief. It is thought that much of the delicate brocade was lost during restoration in the late nineteenth century when the paint layers (and much of the underlying relief) were removed mechanically. Also, the beeswax would be harmed by solvent treatment to remove the paint layers. Beeswax would also be adversely affected by the wax immersion conservation techniques which are also used for statuary. This article (Frinta, 1963) illustrates two of the advantages of infrared analysis. In addition to providing further insight into early technology, infrared spectroscopy provides a reliable method for identification of old materials before conservation to help ensure that no important information or detail is lost.

The infrared analysis in Frinta (1963) was carried out utilizing a very similar method to that ad opted by Kuhn (1960)(Mills and Plesters, 1963). The sample size was given in terms of size not weight. The size of the pieces was generally 2 to 3 $mm^2$, although some were smaller. Chloroform was used to extract the wax material. In this work, the solvent was warmed to facilitate dissolution of the wax and the chloroform-sample solution was centrifuged to precipitate the mineral matter. The solution was then deposited onto a NaCl plate. The solvent was evaporated by placing the NaCl disk in an oven for one hour at 110° C and the remaining sample material formed a film after cooling. The materials in the applied brocade samples were identified as beeswax and beeswax-resin mixture by comparison to spectra of known compounds. No spectra were presented in the article but reader was refered to spectra of the pure beeswax and the beeswax colophony mixture presented by Kuhn (1960).

Another early reference to infrared analysis was published by Keck and Feller (1964). During examination, a painting was found to have a coating which was observed to be insoluble in common organic solvents, water and dilute bases such as $NH_4OH$ and NaOH. The painting was found to be extensively overpainted and the insoluble coating, which was thought to have been used to disguise the retouching, was coated with a thin film of soluble varnish. The insoluble hard material was identified using infrared spectroscopy as a high molecular weight epoxy resin of the bisphenyl variety. The article presents spectra of the unknown and of a known specimen of epoxy resin. The spectra of the samples are very similar to each other although they show very minor differences in detail. The spectra were recorded using the split mull technique which eliminates interference from the dispersing agent but requires that two spectra are measured (Chapter 2). In the spectrum of the unknown sample, two minor bands occur at 5.9 and 6.05 um which are not evident in the reference spectrum. Natural products which may have become attached to the epoxy such as oil, dammar or mastic which contain carbonyl groups are suggested as possible assignments for the band at 5.9 um. The absorption was removed from the sample spectrum after lengthy extraction in warm chloroform. The extraction failed to eliminate the band at 6.05 um which subsequently was assigned to an imino or amide functional group. This might be caused by residual traces in the resin of the material used to cure the resin. A spectrum of a polyamide cured epoxy resin was observed to match the sample spectrum in the area fairly closely.

The authors of this article (Keck and Feller, 1964) draw the important conclusion that analytical instruments may be utilized to differentiate between original and modern materials in works of art. In this instance, analysis confirmed the suspicion that a less valuable painting had been extensively modified to resemble a more valuable one (Keck and Feller, 1964). It is now vital to be able to identify synthetic materials which have been used in conservation in the recent past as these materials have become widely available.

An extensive study has been was undertaken by Beck in an attempt to identify the source of the amber using infrared spectroscopy (Beck et al., 1964; Beck et al., 1965; Beck, 1970; Beck et al., 1971). A large deposit of amber is located beneath the North

Sea and the material obtained from this source was widely exploited in antiquity. Secondary deposits from this source are found throughout northern Europe. Amber from these regions is refered to as Baltic amber. There are also smaller, local sources of amber which were not derived from the North Sea scattered throughout Europe. The source of amber artifacts is of great interest in the elucidation of ancient trade routes and it was highly desirable to find a reliable technique to distinguish between ambers of various sources. Previous attempts to classify the materials were not reliable.

A large number of mineralogical amber specimens of known provenance were examined with infrared spectroscopy by Beck and his collegues (Beck et al., 1964; Beck et al., 1965; Beck, 1970; Beck et al., 1971). They established that amber from Baltic sources has a characteristic absorption pattern in the region 1250 - 1100 $cm^{-1}$ which has not been observed in the spectra of European ambers of non-Baltic origin (Chapter 7). In spectra of weathered samples, oxidation of the material changes the spectrum and the characteristic region becomes less distinct. This important region is masked in many archaeological samples by mineral contaminants such as silicates, sulphates and phosphates which also absorb in the the region and by the use of consolidants with strongly absorbing ester groups such as beeswax and poly (vinyl acetate). A computer program has been devised to analyse the characteristic region in order to eliminate any subjective element in the analysis of weathered or degraded samples. The computer analysis method has been found to be very accurate in identifying the provenance of mineralogical reference samples achieving a success rate of (97.5%) (Beck et al., 1964; Beck et al., 1965; Beck, 1970; Beck et al., 1971).

Infrared spectroscopy was selected for the research into amber provenance for a number of reasons. The instrumentation was readily available and the sample size required (0.5 - 2.0 mg) was considered to be within reason. The time required to acquire a spectrum was twenty minutes which allowed a large number of samples to be analysed. Acquisition of the data was simple and did not require an experienced chemist to carry them out. Also, the resulting spectrum produced a variety of absorptions which might act as characteristic markers (Beck et al., 1964; Beck et al., 1965; Beck, 1970; Beck et al., 1971).

Beck also emphasized that the technique is merely a fingerprinting system which has been shown to be a statistically valid way of distinguishing Baltic amber from non-Baltic amber. The only difficulty is with badly degraded specimens which exhibit spectra which are not clear in the characteristic region. The system is not dependent on extensive knowledge of the chemical structure of amber (Beck et al., 1978).

In 1966, a review article of infrared spectroscopy in museum research was published which presented some of the work that had published and outlined several areas for possible future research (Olin, 1966). The article reported several results from the author's laboratory (Conservation Analytical Laboratory, Smithsonian Institution) obtained on a Perkin-Elmer model 521 dispersive spectrometer equipped with optics that allowed measurements to 200 $cm^{-1}$. The instrument was also fitted with a Perkin-Elmer dual beam condensing system which provided a sixfold demagnification of the infrared beam. The beam condenser could be utilized to perform differential spectroscopy with microsamples.

The article (Olin, 1966) reported the identification of two samples, one of which was a paint varnish layer which was insoluble in organic solvents and the other an unknown adhesive. The varnish sample was found to have a spectrum which was indicative of a protein material and lacked bands which would be expected of natural and synthetic varnishes. It was also found to be soluble in water which supported the identification of animal glue. The second sample was found to be shellac: this information was useful in selecting the conservation treatment. Both samples were characterized as KBr pellets and the sample size was reported as 0.1 mg.

The article (Olin, 1966) also gives an example of identification of materials using comparison of unknown spectra to those of known samples. A sample spectrum of an unknown corrosion product was found to compare well to that of sampleite which is a copper phosphate complex. This identification was aided by the extended low wavenumber capability of the instrument (200 $cm^{-1}$) which is useful for inorganic analysis. Olin believes that infrared spectroscopy is a useful adjunct to x-ray diffraction analysis which is not always sufficient for conclusive characterization of an unknown. The spectra of natural cochineal from the coccus cacti and commercial "madder lake" which was composed of synthetic alizarin were compared to illustrate the possible applications of the technique in textile analysis.

Olin also suggested that the differential technique would be useful in the identification of the colouring agent in the pigment maya blue. The material had been found to consist primarily of attapulgite which is a white clay. Conventional infrared spectroscopy was found to be insufficiently sensitive to identify the colouring matter and no results were reported. Infrared spectroscopy was also recommended for analysis of pigment mixtures and pigments of different shades which have identical elemental composition such as Naples yellow. It was also suggested that natural and synthetic ultramarine could be distinguished by their infrared spectra. It was also mentioned that a microsampling stategy was being developed to perform X-ray emission, X-ray diffraction and infrared analysis on a sample of 50 ug or less, but no further details were given. The review also refers to the work of Kuhn (1960), Keck and Feller (1964) and Beck and his collegues.

The article (Olin, 1966) suggested several worthwhile roads of enquiry, but only a few actual results and spectra were published. The review does illustrate the potential of infrared spectroscopy for comparison of unknown sample spectra to those of known standards and for the differentiation of synthetic and natural materials. The conclusion does make the important point that the success of the technique relies upon obtaining a large quantity of reference material and that specific analytical procedures need to be developed for the types of samples encountered in art and archaeology. Olin predicts that infrared spectroscopy will become more important in the future analysis of paintings and historical and archaeological materials.

In a paper by Masschelein-Kleiner et al. (1968), infrared spectroscopy was incorporated into an analysis programme for old varnishes, media and adhesives. The scheme utilized solubility tests, infrared spectroscopy, thin layer chromatography (TLC) and gas chromatography. The system separates the samples first on the basis of solubility and then infrared spectroscopy is utilized to determine the functional groups present. The addition analytical techniques are used to confirm the results of the infrared analysis and to make a more detailed identification. The article acknowledges the difficulties inherent in this type of study, the small sample size available and the chemical complexity of the materials. The samples were analysed after solubility tests as solid materials in KBr micropellets. The spectra were recorded using a Perkin-Elmer 221 spectrometer with a beam condenser which creates a sixfold demagnification of the beam.

Two case studies were given of water soluble samples (Masschelein-Kleiner et al., 1968). Three water soluble substances from an Egyptian sarchophagus were thought to be polysaccharides as the infrared specta were reported to contain bands due to hydroxyl groups and no evidence of the peptide linkages which result in characteristic bands. A second example was given of a water soluble material which was thought to be a protein based on the infrared spectrum which exhibited bands at 1640 and 1540 $cm^{-1}$ which are characteristic of the peptide bond (Chapter 8). The spectrum was presented in the paper.

In the classification scheme (Masschelein-Kleiner et al., 1968), the samples soluble in chloroform could have been waxes, resins, bitumenous materials and oils. The preliminary differentiations were made with infrared spectroscopy. Each of the four types of material is characterized by certain band frequencies which are indicative of the functional groups present. These criteria are discussed in detail in Chapters 4 - 7 of this thesis where the analysis of natural products is discussed. Spectra were presented of the butanol extract and the chloroform extract of a resin and a wax-resin mixture. The authors acknowledge the difficulties which are encountered in the analysis of mixtures and recommend separation of components. The wax resin mixture was cited as an example where solubility differences may be exploited. The major drawback of this approach is that it is geared to the identification of materials which have not been severely altered over time and no provision was made for identification of degradation products (Masschelein-Kleiner et al., 1968).

Another paper from the same laboratory (Masschelin-Kleiner and Heylen, 1968) presented the analysis of natural red dyes and the infrared spectra of lac, brazilline, bois du Bresil, cochineal, and carminic acid (carmine) as well as madder, alizarin and purpurin. However, the article states that the requirements for infrared spectroscopy include that sufficient sample is available to allow for extraction of the organic material. Thin layer chromatography is recommended for very small samples such as those obtained from illuminated manuscripts and paintings which are usually too small for infrared analysis. Infrared spectroscopy was utilized with ultraviolet and visible spectroscopy to characterize red dyes extracted from wool fibres.

Similar difficulties in sample size were encountered in a study where infrared spectroscopy was utilized for the study of the materials used in illuminated manuscripts (Flieder, 1968). It was hoped to identify the materials before conservation treatment. Infrared spectroscopy was utilized to examine the organic pigments. The article presents reference spectra of several organic pigments with some spectra obtained from various illuminated manuscripts. There were major problems with the size of sample required for analysis with infrared spectroscopy which for this study was 1 mg. This amount of sample is very rarely available from manuscripts. It was not possible to identify the green colourant from a manuscript as either malachite or verdigris and analysis of purple colourants was not successful.

Infrared analysis has been included in a study of natural dyestuffs (Hofenk-de Graf, 1969). The report presents the history of use, source, composition, structure and terminology of natural dyes such as weld, fustic, madder, cochineal, lac dye, henna and others. Several spectral methods of identification are discussed and the infrared spectrum of many of the samples are included.

A Perkin-Elmer 13 spectrometer which was fitted with the Perkin-Elmer microscope 85 was utilized in the analysis of old painting materials (van't Hul-Ehrnreich, 1970). The instrument is a single beam system because the microscope is positioned behind the monochromator where the optical path is the same for both the sample and the reference beam. Thus, the spectra also contain bands near 2360 and 1460 $cm^{-1}$ which result from atmospheric $CO_2$ and $H_2O$ vapour respectively. The microscope was flushed with nitrogen gas to reduce the atmospheric interferences. The microscope used for this project was that designed by Coates et al., (1953) (Chapter 2). The spectrometer utilized as Nernst-glower infrared source and the monochromator was a NaCl prism. The microscope was equiped with a small target thermocouple to act as a detector and the numerical aperture of 0.75 was used. The energy transmitted to the detector was estimated to be 35% of that generated by the instrument. The article also mentioned the difficulty of scattering of the light energy which often occurs with non-homogenous sample distribution on KBr pellets or with large grains of pigment. Scattering lessens the amount of energy which reaches the detector.

Samples from test paintings and from several Dutch paintings from the 18th and 19th centuries were studied using the infrared microscope (van't Hul-Ehrnreich, 1970). Several different sampling approaches were attempted. KBr micropellets of 1 - 3 mm in diameter were prepared. However, grinding the sample with the KBr in a mortar which is the usual procedure was inefficient and some sample was lost. The second approach was to simply add the sample to the KBr in a die and press. In some cases, the microscope was used to select a layer for analysis. A third method involved dissolving the sample in an organic solvent and mixing with the KBr in a lyophilization apparatus. However, old paint samples are often insoluble. The second technique was utilized most for the study. Attempts were also made to prepare cross-sections of the samples. This is difficult for infrared spectroscopy as most resins used for conventional preparation of cross-sections are strong absorbers in the infrared. The sample spectrum would then contain strong bands due to the resin which would mask weaker absorptions and confuse the identification of the unknown. In the study, paraffin wax was utilized as an embedding materials as it has only a few infrared absorptions. Polyethylene was also suggested as a harder material which might be useful for embedding samples for infrared spectroscopy. The sample which has been embedded is then sliced with a microtome and the resulting layers are placed on AgCl sheets in the microscope. The samples often crumbled, however. A second method was attempted to eliminate the need for a mounting material. The sample was frozen in water on a cooled microtome. The material was then sliced and the mounting material was removed by warming. However, the freezing further increased the brittleness of the sample which caused crumbling of the sample during cutting.

The detection limits of the microscope system were estimated to be 1.5 - 3 ug (van't Hul-Ehrnreich, 1970). However, the presence of atmospheric bands caused difficulties. With the sample sizes given above, it was possible to differentiate the carbonyl region from the water bands. This would indicate the presence of oils or resins, but other absorptions would be necessary to differentiate between the oils and resins. However, the bands which are used to characterize proteins such as egg white and glue are blocked by the absorptions arising from the atmospheric water bands in concentrations of this magnitude. For old paintings, the amount of sample needed may be higher to allow for the scattering of the light. With the paraffin sections, a surface area of 37.5 by 500 um with a thickness of 20 um was found to be sufficient if the sample does not scatter a large portion of the energy. The paraffin causes problems as it absorbs in the range of the C-H stretching absorptions of aliphatic hydrocarbons (3000 - 2800 $cm^{-1}$). These bands may be used in a general qualitative sense to distinguish between gums, egg tempera and animal glue (weak bands) on the one hand and oils, waxes and resins (stronger bands reflecting greater quantity) on the other.

The analyses of the cross-sections from the test paintings were partially successful (van't Hul-Ehrnreich, 1970). The varnish layers were too thin to be characterized by the system as the necessary diaphragm size is too small to allow sufficient energy to pass to the detector. Also, there was a considerable amount of interference from other components. For example, the evidence of the binder utilized in the ground was completely masked in the spectrum by the absorption bands due to the chalk (calcium carbonate). The medium could be seen in the spectrum of the vermillion paint layer as the pigment is transparent in the infrared. The results from the Dutch paintings were less conclusive. The system has the advantage of allowing the operator to see and select the portion of the sample to be analysed, which is a feature not available with a beam condenser (van't Hul-Ehrnreich, 1970). However, the inability to remove atmospheric contributions and bands from supporting media from the sample spectra lessens the advantage of the system severely.

Infrared analysis was utilized in a study of verdigris and copper resinate pigments (Kuhn, 1970). In the report, infrared spectroscopy was used in conjunction with microscopic analysis, emission spectroscopy, X-ray diffraction, X-ray fluorescence, electron probe analysis and X-radiography to characterize verdigris which is the copper salt of acetic acid. There are four different structures of basic verdigris, three of which are blue and one of which is green. Basic verdigris may contain one of the four types or be a mixture of several structures. Neutral verdigris is blue-green and has one structure. The spectra of neutral and one type of basic verdigris were given in the paper and it was reported that deviations are seen in the spectra of basic verdigris when varying compositions are analysed. The presence of verdigris in paint samples was indicated by the presence of a band in the region 1560 - 1610 $cm^{-1}$ which has been assigned to the ionized carboxyl group. It was reported that 30 - 100 ug of paint sample are required for detection when ordinate scale expansion and a beam condenser are utilized. The article lists the results from paintings.

Copper resinate is composed of the copper salts of resin acids and its identification is somewhat difficult (Kuhn, 1970). The material appears as a transparent green glaze which does not exhibit distinct particles when examined by microscope. TLC and gas chromatography were suggested for identification and the results of infrared examination were reported. 0.1 mg of sample was prepared as a KBr micropellet. The spectra contain a characteristic absorption near 1600 $cm^{-1}$ which is assigned to the ionized carboxyl group. Unfortunately, this is also a characteristic absorption for verdigris and copper resinate when mixed with verdigris and consequently copper resinate may not be identified with certainty by infrared spectroscopy alone. Also, it is necessary to mention that verdigris forms copper salts of fatty acids when mixed with oil media and the infrared spectrum of this material exhibits a broad band in the region of 6.2 um. The spectra also contain bands at 1710 and 1240 $cm^{-1}$ which were assigned to the carboxylic acids and the resin acids. The spectrum of copper resinate prepared by a procedure dating from the 16th century was compared to material from a commercial source. The probable preparation method of the commercial sample was thought to be the treatment of a copper salt solution with and aqueous solution of sodium resiate or by melting resin with reactive copper salts (Kuhn, 1970). It is interesting that the commercial material gives a spectrum with more detail most notably in the region 1500 - 1400 $cm^{-1}$ where three distinct bands are visible in addition to the other bands which were mentioned as characteristic of copper resinate.

## 1971 - 1980

Infrared spectroscopy was utilized in conjunction with a report on the conservation treatment of wax sculpture (Murrell, 1971). The study included two case studies of an allegorical tableau and two 17th century ecclesiastical dolls. Wax has been used as a modeling material for polychrome relief portraits, tableaux, anatomical models and wax dolls. The author of the article believed that most wax sculptures were contructed with beeswax which was unadulterated except for bleaching and the addition of pigments and inert filler material. Recipes survive for beeswax mixtures in which substances such as Venice turpentine, animal fat or pitch were added as plasticizers, but the author stated that these mixtures were utilized for modeling objects such as medallions at room temperature and seldom for finished wax sculptures. It was also suggested that an additive such as resin was incorporated to produce thin sheets for draping effects. However, no extensive analytical work had been performed on wax models and sculpture which would confirm the theory. A small number of samples were analysed for the Murrell study (1971) by Mills and Plesters at the National Gallery, London. The samples were identified using infrared spectroscopy and microscopy and the pigments and inert materials were characterized by chemical tests. Ten samples were taken from four pieces with dates that ranged from the 17th to the 19th centuries. Seven samples were found to contain beeswax and pigments only and three were resin wax mixtures. Two of the mixed samples were from wax used to attach pieces in the tableau and the third was a green wax which gained its colour from copper resinate. Although it is not stated, it is assumed that the methods used and the criteria for identification were similar to those given in the earlier reference (Mills and Plesters, 1963).

In a rare example of analysis of archaeological samples, infrared spectroscopy was utilized in conjunction with thin layer chromatography and gas chromatography to identify the contents of two Roman glass bottles as a partially degraded oil (Basch, 1972). The bottles were found in Jerusalem. The results obtained in this study are discussed in detail in the section on fats and oils.

Infrared spectroscopy was recommended as basic equipment for museum laboratories which may have to examine organic materials in a paper presented at a conservation conference in 1972 (Mills, 1972). The technique was described as particularly useful for the analysis of waxes. The sample preparation was described previously by the author (Mills and Plesters, 1963) by which the wax is extracted from the sample mixture with chloroform and then dropped onto a NaCl disk. The solvent was removed by evaporation and the spectrum is acquired from the solid residue. Several examples of wax identified with infrared spectroscopy were presented including wax from an Egyptian sarcophogus, a Roman candle, a medieval seal and a 19th century tableau. The spectra of these samples which are of varying antiquity ranging over several thousand years are very similar to that of fresh beeswax. The material is very stable over long periods of time which permits easier identification. Beeswax and later paraffin wax were used in restoration, so care must be taken in deciding if the material is original.

Several case studies were discussed (Mills, 1972) in which mixtures of waxes were analysed. Several sculptures which date from the 19th century were found to be made of hydrocarbon wax (Chapter 4) but one was found to be composed of a mixture. The initial identification was made by comparison with published spectra and then mixtures of several different proportions were prepared to obtain reference spectra. The composition with the best match was found to be ceresine wax with smaller amounts of beeswax and stearin wax. Analysis was also made of a relining wax which dates from between the First and Second World Wars to reline several very large pictures. The spectrum was found to be very similar to that of a mixture of paraffin and beeswax. However, there was a small band which was not assigned in the spectrum of the mixture. A small amount of a resinous material was retrieved after extraction of the sample with methanol. The infrared spectrum of the extract was measured and found to correspond closely to that of an aged sample of Venice turpentine which is similar to the spectrum of the unaged compound. The band which was apparent in the original unknown spectrum was assigned to the acetate functional group of larixyl acetate which is a diterpene component of Venice turpentine. The paper also mentions that infrared spectroscopy may be used to distinguish between bitumen and pitch, but no examples were presented (Mills, 1972).

Infrared spectroscopy has been utilized in conjunction with mineralogical methods such as X-ray diffraction (Debye-Scherrer) in a study of Egyptian pigments (Reiderer, 1974). An example was given of the characterization of a white pigment, hunite ($CaCO_3 \cdot 3MgCO_3$), and the article presents frequency values for dolomite, calcite and magnesite as well as those for hunite to illustrate that various carbonates may be distinguished by their infrared spectra. Infrared spectroscopy was described as "a useful method for subdividing similar pigments because of structural differences."

A study (Birstein, 1975) was carried out to identify the media of wall paintings located in Central Asia. Preliminary studies of the wall paintings did not include media analysis. Infrared spectroscopy was utilized in addition to thin layer chromatography and gas chromatography for the characterization of samples which ranged in age from the 2nd - 1st century B.C. to 1830. Fairly large samples were taken for the analysis, 1 - 2 g. The oldest samples from the wall paintings of Manser Depe were identified as degraded protein by quantitative amino acid analysis. The protein was thought to be gelatin which would come from the use of animal glue as the binder. The remaining samples were identified as polysaccharides. These samples were extracted in boiling water and the residues were treated with both acid and base and the extracts were combined. After water dialysis, the water was removed under vacuum and the infrared spectra was obtained of the residue which was prepared as KBr pellets. The infrared spectra will be discussed in more detail in the chapter on resins and gums although it should be noted that the specific type of gum could not be isolated with infrared spectroscopy. Thin layer chromatography and gas chromatography of the materials was utilized to further characterize the samples. It was concluded on the basis of the chromatographic evidence, that two of the samples were of cherry or apricot gum origin and the Prunoideae species were suggested as origins for two other specimens. No origin was suggested for the remaining sample (Birstein, 1975).

Infrared spectroscopy has also been utilized in conservation research problems (Baer and Indictor, 1976). Infrared spectroscopy was used to monitor linseed oil films containing dissolved metal acetylacetonates as part of a study of linseed oil-pigment model systems. A Perkin-Elmer 337 grating infrared spectrometer was used to measure samples of 3 mg linseed oil with a $10^{-3}$ M acetyl acetonate concentration which were held between flat AgCl disks. Measurements were made at intervals of two sets of samples which were kept at 23 and 100° C. The ratio of the absorbance at 3450 $cm^{-1}$ and 2940 $cm^{-1}$ was used as a measure of the relative absorbance of the samples (Baer and Indictor, 1976).

In spite of the early predictions, conventional infrared spectroscopy was not widely utilized and few applications were reported in the literature. In 1977, a study was published in which the advantages of the recently developed Fourier transform infrared spectroscopy (FT-IR) were discussed (Low and Baer, 1977). The new type of spectroscopy was inherently more sensitive than dispersive spectroscopy and it was thought that this would overcome some of the difficulties presented by art and archaeological samples, namely the small size and the chemical complexity of the substance. A description of the FT-IR system was given and compared to conventional dispersive infrared spectroscopy to emphasize the advantages of the new technique. Sample spectra were presented of a variety of pigments which were powdered and placed between KBr disks. It was recommended that liquids be analysed as film between KBr disks. Transmission spectra were then obtained of the powders and the films without further sample preparation. The spectra which were published included linseed oil, indigo, madder lakes, alizarin, Indian yellow, purpurin, egg yolk, albinum and paper. The sampling technique was described as 'crude', but it was emphasized that bands due to mulling oils or possible reactions of the sample with the KBr when pellets are prepared are eliminated. However, scattering effects and sloping backgrounds are often observed in the spectra of powdered materials prepared in this manner. When significant expansion of the ordinate scale is required, the sloping background causes difficulties. The quality of the spectra in terms of high resolution, low noise and minimal sample preparation was emphasized.

The article (Low and Baer, 1977) presented the 'trading rules' which can be exploited with FT-IR. The distance of the moving mirror, the sample size and the total time required to collect the multiple scans are factors which may be "traded". The time required for one scan may be increased by increasing the displacement of the mirror to increase the signal-to-noise ratio (SNR) for the analysis of a small sample. However, the SNR may be improved by multiple scanning which lenghthens the total time required to measure the sample spectrum, but improves the spectrum. This is also advantageous for the analysis of small samples. Spectra of Indian yellow were used to illustrate the refinement of weak and overlapping bands with increased resolution. Another example shows the reduction in spectral noise with multiple scans in spectra of indigo. FT-IR was also used to examine the effects of ultraviolet radiation on films of linseed oil. Spectra of various madder lakes are utilized to point out that even in spectra where the bands may not be assigned with certainty, it is possible to use the infrared traces as fingerprints of the compounds. The article concludes with an illustration of the improvements in SNR which can be obtained in much shorter time periods. A scan which may be obtained in one hour with FT-IR would require almost two weeks with conventional infrared spectroscopy to obtain the same SNR (Low and Baer, 1977). The article provides a very good summary of the FT-IR technique which illustrates its advantages. However, it does not actually show results from objects which would illustrate a 'real-life' situation.

The studies which have been published since the publication of "Application of infrared Fourier transform spectroscopy to problems in conservation", (Low and Baer, 1977), have been largely concerned with pigments and painting materials. Low and Baer followed up their review of FT-IR with two conference presentations on the application of FT-IR (Low and Baer, 1978a; Low and Baer, 1978b). In the first paper (Low and Baer, 1978a), the FT-IR spectra of dammar and mastic, which were prepared as films cast from chloroform onto KCl plates, were compared. The paper emphasized that the greatly improved sensitivity of FT-IR spectroscopy results in spectra with greater detail. The spectra which are presented are similar in many respects especially in the strong bands. However, variations are observed in the shape of the bands, shoulders and relative intensities. Also, the region 1500 - 800 $cm^{-1}$ was found to vary considerably between samples and seven sample spectra were presented. Also, the spectrum of an artificially aged resin was compared to that of the fresh material and differences are evident. Low and Baer point out that very little research has been performed on specific explainations for the differences in the spectra. The spectra which may be obtained with FT-IR are useful as unique fingerprints for each sample and it is hoped that further work may include study of aging and light exposure. FT-IR may possibly be used to determine the source of resins. This work improves upon the gloomy conclusions reached by Feller in 1954 when less sensitive instrumentation was used. The work concluded with a similar prediction to that made in their earlier review (1977) that FT-IR would become more widely utilized in museum work. The paper concentrates on the technique and does not present examples of identification of naturally aged samples.

A further report was made of FT-IR applied to the study of pigments (Low and Baer, 1978b). It was emphasized that sensitive instrumentation is important to obtain fingerprint spectra of materials which have similar chemical structures. An example is given of three anthraquinoid lake pigments, two of which exhibited similar spectra which require minor spectral details to be differentiated. A second example was presented of several alizarin lakes. It was shown that pure Ca-Al-alizarin complex, the same material on an alumina base and a K-Al-alizarin compound on an alumina base exhibit very similar spectra differentiated only by small variations in the spectra. A sample of pigment was shown to be more similar to that of the Ca-Al-alizarin deposited onto alumina than the other two in terms of the minor features in the spectra. It is emphasized that various alizarin mixtures exhibit identical spectra when analysed with less sensitive, conventional spectrometers. Low and Baer conclude with the observation that published spectra which have been obtained using less sensitive spectrometers are inadequate in light of the spectra of high resolution and precision which may be recorded with FT-IR. Thus, new reference collections should be accumulated of pigments and other materials of interest in art and archaeology using uniform conditions and sensitive instrumentation (Low and Baer, 1978b).

An alternative sampling technique has been suggested for the analysis of small samples in conservation work (Laver and Williams, 1978). A diamond cell is used to analyse small samples by utilizing pressure to spread the sample into a thin layer. The method has been used with sucess (Laver and Williams, 1978), although the application of high pressure may result in alterations to the sample structure which may affect the spectrum.

A paper was published by Newman (1980) which analysed several pigments which were somewhat difficult to analyse using X-ray diffraction. An example was presented of a synthetic organic pigment, phthalocyanine blue which occurs in two different crystal forms. The alpha and beta forms may be distinguished by the strong band which occurs at 723 $cm^{-1}$ in the alpha form and at 730 $cm^{-1}$ in the beta polymorph. The spectra of pigments containing polyatomic ions were discussed. The study included several examples of chrome or Brunswick green pigments which are actually mixtures of Prussian blue, chrome yellow and often $BaSO_4$ or kaolinite which were utilized as extenders. The pigments were identified using infrared spectroscopy. A distinctive characteristic is the presence of a band in the region of 2080 -

2070 $cm^{-1}$ which is indicative of the carbon-nitrogen triple bond in the ferrocyanide ion $Fe(CN)_6^{4-}$. This is a fairly distinctive feature which is not characteristic of any other common organic or inorganic substance and permits the detection of Prussian blue even when present in small amounts. The report also lists the absorptions which result from the $CrO_4^{2-}$ ions which may be masked by the presence of large quantities of sulphate ions. Infrared spectroscopy may be used to differentiate between the two forms of green earth pigments, celadonite and glauconite. A spectrum from an sample taken from a painting is presented which is difficult to interpret. Band assignments for carbonate ions, sulphate ions, alpha-$SiO_2$, green earth pigment and a possible proteinaceous medium are suggested, but further analysis such as microscopy were recommended for confirmation of the identity of such samples and the infrared spectrum should not be used as conclusive evidence. The pigments $Cr_2O_3$ and veridian ($Cr_2O_3 \cdot 2H_2O$) are amorphous and each exhibit characteristic absorptions in the region 800 - 400 $cm^{-1}$. Newman concludes that infrared is a useful technique in the analysis of materials used in art, but is somewhat less useful for actual painting samples due to difficulties in characterizing mixtures and the size of the sample required.

## 1981 - 1988

A relatively recent application of FT-IR in conservation research is the characterization of corrosion products. A study was presented of the components of Bronze disease (Tennent and Antonio, 1981), copper chloride, which exists as a mixture of materials which have the identical chemical composition but different structures, namely, botallackite, paratacamite and atacamite. Although infrared spectroscopy was not widely used for corrosion products at that time, the extended range which allows analysis in the far infrared suggested its use for inorganic materials. Conventional dispersive infrared spectroscopy was utilized to characterize synthetic corrosion products which were produced in the study by comparison to those obtained of mineralogical standards. It was found to be and effective technique to differentiate between the three polymorphs which were of known identity. The spectra were published and the frequencies and band assignments were given. It was reported that mixtures of the minerals could be detected. The further uses of infrared incorporate its ability to characterize organic materials. For example, the reactions of the corrosian stabilizer, benzotriazole (BTA) are being studied (Tennent and Antonio, 1981).

A further report presents a large reference collection of minerals which may be found in bronze patinas (Matteini et al., 1984). It is emphasized that corrosion products are often complex, especially if the object is located out-doors. Spectra were recored with a conventional dispersive spectrometer (Perkin-Elmer 157G) with the range of 4000 - 625 $cm^{-1}$ and the samples were prepared as KBr pellets. Sample sizes of 1.5 - 2 mg were used and acquisition times of 30 minutes are reported. The reference materials were obtained from commercial sources (analytical grade), laboratory preparation and mineralogical standards. Reference spectra included copper salts such as chlorides, sulphates, nitrates, carbonates and oxalates. Other minerals considered were quartz and silicates, calcium carbonates, oxalates, nitrates and sulphates, and lead sulphate. The paper presents the spectra and tabulated frequency data. The use of conventional dispersive spectroscopy and the inability to measure the extended range result in the loss of important detail. Also, only one reference was mentioned of specific application, Fiorentino et al., 1982, when detection of copper nitrate on the bronze 'Door of Paradise' in Florence using infrared spectroscopy indicated that the object had been cleaned with nitric acid.

FT-IR with a microscope attachment was utilized in a report published on the examination of samples from an unattributed painting 'Virgin and Child' which was thought to date from the 15th century (Shearer et al., 1983). The article discusses the the difficulty of evaluating the authenticity of paintings which have been restored in the past or covered by old, discoloured varnish. Treatment usually includes the removal of old varnish and retouchings, and weakened areas and flaking paint need to be stabilized. The treatment may involve the repainting of missing areas and revarnishing. The necessity for conservators to identify the materials incorporated into works of art before carrying out any treatment is emphasized in the article. The ability of infrared spectroscopy to characterize both inorganic and organic compounds was emphasized in comparison to other techniques commonly used in art conservation such as polarized light microscopy, X-ray diffraction, X-ray fluorescence and electron probe microanalysis for characterization of inorganic components and gas chromatography for organic materials. The advantages of using a FT-IR spectrometer equipped with a microscope are illustrated by the analysis of two microscope samples removed from the painting 'Virgin and Child'.

A core showing a cross-section of the paint and varnish layers was removed from the upper right quadrant of the painting and a small sample of the red material was taken from the lower left corner. The samples were collected with a scalpel and dissecting needle under a stereo zoom microscope. The samples were analysed with a FT-IR system which included a beam condenser and a wide-band mercury-cadmium-tellurium (MCT) detector (Analect fX-6201 FT-IR spectrometer and an fXK-635 detector and an fXA-510 aspheric beam condenser). The wide band detector was chosen over a more sensitive narrow band detector as it measures a wider range, down to 450 $cm^{-1}$. The sample preparation used in this study was that published by Cournoyer et al., (1977) in which small salt crystals are prepared by multiple cleaving of commercial crystals until plates of 1-2 by 3-4 mm dimensions and thickness of 200 - 500 um are obtained. An aperture disk is made from a sheet of brass or stainless steel which is 1 mm thick and a aperture is made with a diameter of 20 - 200 um. The sample is placed between two cystal sheets and mounted with a small amount of wax onto the aperture disk. The sample is positioned to fill as much of the aperture as possible (Cournoyer et al., 1977; Shearer et al., 1983). The minimum sample size required for conventional infrared spectroscopy is reported to be 0.5 ug and the limits of detection are three orders of magnitude less for FT-IR (Shearer et al., 1983).

The publication includes the spectra obtained of the samples (Shearer et al., 1983). The red material was found to be shellac. The cross-section was found to have four layers. The base layer or ground was identified as calcium sulphate dihydrate, but it was not possible to identify the binder. The first paint layer was blue and the pigment was identified as Prussian blue by the appearance of a band at 2091 $cm^{-1}$ (characteristic of the ferrocyanide ion (Newman, 1980)). The spectrum is also thought to contain evidence for the presence of natural resins. The spectrum of the second paint layer was interpreted as containing kaolinite and an organic material which was not identified. This is thought to be an example of lake red which is prepared by combining an inorganic support with a red organic substance and then a binder is added. The last layer is a thin gilding. The spectrum is characteristic of kaolinite. This material was often used as a ground for the gilding. The gilding material is thought to be elemental gold which does not exhibit distinctive absorptions in the infrared region.

The conclusions which were reached in the study exemplify the methods used to determine authenticity in works of art. Evidence of materials which were known to have been available during the period in which the object was thought to have been produced is taken as an indication of authenticity. Also, knowledge of conservation techniques utilized in the past is used to evaluate whether the presence of certain materials might be indicative of treatment. This is necessary as it has only recently become standard practice to kept records of conservation treatment. The presence of Prussian blue pigment which was not available until after 1704 and the presence of resin as a medium indicate that the picture was heavily restored original or a copy. This supported the opinion of the art historian without the removal of large samples or other damage to the painting. The article reports that the presence of oil or resin medium also suggests a later date for the painting as egg tempera was the predominant material in use until the beginning or middle of the 16th century when oil came to be widely used. No evidence of protein material was seen in the spectra obtained in the study (Shearer et al., 1983). Proteins are easily masked by the strongly absorbing pigments, however, and their presence may not be detected.

Infrared spectroscopy was utilized in conjunction with gas chromatography/mass spectrometry (GC-MS) to characterize six examples of pitch recovered from the Mary Rose shipwreck (Evershed et al., 1985). A sample of a tarry substance from an early medieval site in York and a further sample from an Etruscan shipwreck located off the coast of Giglio, Italy were also examined. Infrared spectroscopy was incorporated into this investigation as a preliminary technique. The samples which were adhered to fragments of rope, wood or animal hair were collected by solvent extraction with dichloromethane in an elution tube. The other Mary Rose samples were examined with no further sample preparation. The samples were examined as films cast from the melt or from the dichloromethane solution. No mention was made of sample size, but microsampling did not seem to have been used. The samples were identified by comparison to standard spectra obtained of wood, coal, peat and petroleum tars including commercial Stockholm tar which was produced from Pinus sylvestris wood. All of the samples from the Mary Rose were observed to be very similar to each other. No spectra or specific frequency values were given, but the presence of carboxylic acid groups, aliphatic and aromatic C-H groups was reported. The sample spectra were said to resemble that of Stockholm tar very closely both in the frequency values and the relative intensity of the absorption bands. The infrared spectra of the York and Etruscan samples were reported to be similar to the Mary Rose sample spectra and that of the Stockholm tar. The Mary Rose sample spectra were also found to be somewhat comparable to the peat tar spectrum. The spectra of the petroleum bitumen and coal tar, however, were found to be dissimilar to the Mary Rose sample spectra.

A sequel to the original report on the application of FT-IR to conservation (Low and Baer, 1977) appeared in 1986 (Low and Varlashkin, 1986). In this study, the use of photothermal beam deflection spectroscopy (PBDS) was examined as a non-destructive method for the analysis of surfaces. PBDS is a type of photoacoustic spectroscopy where infrared radiation is introduced to the interferometer and then directed to the object surface. The sample surface, which is estimated to be 2 mm in diameter, absorbs radiation which then degrades to heat. Some of the heat energy travels to the air and changes the refractive index. A helium-neon laser is utilized as a probe beam which is used to monitor the changes caused by the infrared beam. The spectrum is processed from the information which reaches the detector by a data processing program which is similar to that of conventional FT-IR and a reference spectrum of carbon is used. Examples are given of analysis of a Moroccan dagger hilt. Several inlays were identified as mother of pearl, celluloid, ivory or horn and the varnish was characterized as a cellulose coating. The technique is physically limited by the size of the sample compartment but this could be overcome in theory. The sample surface area which is analysed may be reduced with a concomitant loss of energy throughput. A serious drawback is that the sample must be extremely near the surface or the beam is prevented from reaching the detector. Inlays which were as little as 0.1 mm below the surface of the object could not be examined. The texture of the material is a factor. As the porosity increases and particle size decreases, the photothermal signal increased. For example, mother-of-pearl gives a weak signal. Smooth, non-porous samples require longer scanning times. Another problem with the method is that the sample is heated. The temperature is estimated to reach 50° C. The PBDS technique is useful for materials which scatter or absorb infrared very strongly, materials which are difficult to study with conventional infrared spectroscopy.

Recent applications of FT-IR spectroscopy to archaeology include an extensive study of resinous materials from Southeast Asia, primarily from the Maylasian peninsula (Gianno et al., 1987). The study includes analysis of a botanical reference collection of resinous tree products which were obtained from resin producing trees from the region. The project is being carried out to gain a better understanding of trade in the region by monitoring the occurrence of resins which formed part of the economy. FT-IR spectroscopy was selected for this analysis because the large number of samples to be analysed required a fairly rapid technique. Gas chromatography and gas chromatography/mass spectrometry analysis give more information, but are more time consuming and the instrumentation is more expensive than FT-IR spectrometers. The samples were analysed as KBr pellets. The sample size used for the reference materials was 2 - 3 mg in 200 mg of KBr. The mixture was ground in a vibration mill and then formed into 13 mm diameter disks. For the samples from ethnographic materials, 0.3 - 0.5 mg of sample were taken and mixed with 20 mg KBr and formed into micropellets. Three types of samples were examined: the extensive botanical reference collection, archaeological specimens which were obtained from four sites and samples from items from the Smithsonian Institution ethnographic collection. A cluster analysis program was developed using coefficients of similarity which was utilized to classify the spectra. The majority of the botanical samples seemed to fall into groups characteristic of each botanical family. The archaeological samples were found to fit into clusters of the reference materials which resulted in the assignment of a resin family to the unknowns and a genus characterization was also made for three of the samples. The analysis of the ethnographic samples was less successful and only a few sample spectra were found to correspond to those of the reference material. The variations in spectra between the ethnographic and the reference collections are thought to result from several factors which include conservation treatment to the objects and possible processing of the materials by the manufacturers of the artefacts (Gianno et al., 1987).

The problem of identification of bronze corrosion products has also been recently addressed (Giangrande, 1987). In this study, conventional dispersive infrared spectroscopy (Perkin-Elmer 225 double beam grating spectrometer) with an extended range of 4000 - 200 $cm^{-1}$ was utilized. Cesium chloride was used as the alkali halide matrix. Eighteen mineral reference standards were collected and seven mixtures of known composition were prepared. In addition, 35 samples of corrosion products from objects were collected. The spectra of the standard minerals were discussed with assignment of the bands to specific bonds, vibrations or specific atomic or molecular structures. The analysis of the mixtures illustrates the difficulty encountered when bands overlap. Inorganic materials absorption bands are typically broad and the bands may overlap. Often in inorganic mixtures, bands overlap to such an extent that broad areas of absorption are observed which are not very characteristic. This is illustrated in the mixture of 75% atacamite and 25% paratacamite where the principal bands of paratacamite are masked by bands resulting from atacamite. This problem was not observed with combinations composed of malachite and cuprite as the bands which are considered characteristic do not overlap. Sucess was reported in the identification of some of the unknowns. Spectral subtraction of FT-IR spectra was recommended for unknown mixtures. The article discusses the advantages of infrared spectroscopy over X-ray diffraction. These include the ability to measure samples which are non-cystalline in some phases, to detect water in the structure, and to identify anions such as carbonates and silicates in the structures. The speed and simplicity of the technique are emphasized and the possibility of utilizing infrared spectroscopy in stabilization research is proposed (Giangrande, 1987).

The growing interest in FT-IR in museum work is reflected in a recent conference publication (Martin, 1988) in which the technique is explained and several examples of "real life" museum applications are presented.

## Conclusion

In light of the gaps which exist in the analysis of archaeological samples, the focus of this research project was placed on the analysis of organic materials which were found as or in conjunction with archaeological objects. Samples such as pigments were not included in the reference collection. As the project progressed, it became necessary to add synthetic materials to the library as they frequently appear as a result of old or field conservation treatments. Also, objects composed entirely of modern materials are beginning to present urgent conservation problems and attempts were made to identify these materials.

In many of the papers which were summarized above, the results were quite promising. In most cases however, the advantages of infrared spectroscopy have been substantially improved by the introduction of FT-IR. For example, the study of amber by Beck and his collegues is a very good illustration of how a wide survey of a well documented reference collection may be used as a reliable fingerprinting technique and it also indicates the advantages of computer analysis in this type of work. The sample size and sample preparation and acquisition time which were more than acceptable at the time may be significantly reduced using FT-IR. However, few publications have as yet appeared using the new technique and the intial reports which rightly point out the obvious advantages do not actually illustrate their arguments with examples of analysis in practice. Thus in this work, the emphasis has been placed on the analysis of a large number of samples from objects which have undergone a variety of degrees of degradation.

# CHAPTER 2 DIFFUSE REFLECTANCE SPECTROSCOPY

## Fourier transform infrared spectroscopy

The principle of Fourier transform infrared spectroscopy (FT-IR) is based on the two beam interferometer developed by Michelson in 1891. The design is basically the same for all instruments although the principle has been modified for special purposes (Figure 2.1) (Griffiths and de Haseth, 1986).

The interferometer has two plane mirrors placed perpendicular to each other. One is fixed (F) and the other one (M) moves in the direction which is perpendicular to its plane (Figure 2.1). A semi-transparent beamsplitter (B) is located between the mirrors and this reflects a portion of the light to the fixed mirror and transmits a portion of light to the moveable mirror. The moving mirror causes varying path differences which introduce an interference between the beams when they are combined. The beams return to the beamsplitter where they recombine and again are partly transmitted to the detector (D) and partly reflected to the source (S). For a single frequency and constant mirror velocity, the signal is a sine wave with the maxima occurring when the beams are in phase and the minima when they are 180° out of phase. The beam directed to the detector is passed through the sample where portions of the radiation are absorbed, hence the intensities are changed. The spectral information obtained from FT-IR spectrometry is measured from the change in intensity of the beam directed to the detector. This variation is measured as a function of the path difference (Griffiths and de Haseth, 1986).

The signal measured by the detector is called an interferogram and the information is transformed mathematically into a spectrum using the Fourier transform. The interferogram of monochromatic radiation (single frequency) is a sine wave and the Fourier transform is a fairly simple mathematical operation. If, however, the source emits a continuum, as is necessary to obtain an infrared spectrum, the resulting interferogram is the sum of the interferograms of each wavenumber. This complex interferogram requires a digital computer to extract the spectral information and this factor prohibited the development of the technique until the computer age (Low and Baer, 1977).

An FT-IR spectrometer measures all frequencies simultaneously unlike dispersive instruments which obtain them sequentially. Thus, many FT-IR spectra can be accumulated in the time required to measure one spectrum with a dispersive infrared spectrometer. Interferometers do not have slits which restrict the amount of energy which reaches the detector. The energy throughput is thus higher in a spectrometer using an interferometer than in a conventional machine at the same resolution. It is possible to obtain the same signal to noise ratio (SNR) as a dispersive spectrometer in a significantly shorter time period. The short scanning time of interferometers makes multiple scanning feasible. This also improves the signal to noise ratio which allows for smaller sample sizes. The interferometer has a helium-neon laser which acts as an internal reference for the frequency scale. The calibration of an interferometer can be more accurate and is more stable over the long term than that of a dispersive instrument. Dispersive instruments utilize slits to separate the light into wavelength components. The programs used to control the slits causes the resolution to vary during the scan period. The resolution of an interferometer is constant over all wavelengths. There are no discontinuities in a FT-IR spectrum because there are no grating changes (Perkin-Elmer, 1984).

In addition to being able to measure spectra at high SNR or in a short period of time, the introduction of FT-IR has also led to a much greater variety of forms in which a sample can be presented to the spectrometer through the development of various new sampling accessories. Many of these new devices have been developed in theory for conventional dispersive spectrometers, but could not be used effectively with them because the accessories greatly reduce the energy reaching the detector. These methods include gas chromatography (GC) and high performance liquid chromatography (HPLC)/FT-IR interfaces, infrared microscopy and diffuse reflectance spectroscopy (DR). (Griffiths, 1986).

It was envisaged that this thesis would examine one or more of these techniques applied to the types of samples which frequently occur in art and archaeology. A large number of samples would be run to evaluate the technique for use in a museum or conservation laboratory. The choice of techniques was limited to what was available to the author in terms of instrumentation and also by what seemed to be valid for the types of samples to be analysed. As almost all art and archaeological samples come to the laboratory in the solid form, it was desirable to use a technique which examines solid samples in the solid state. As the opportunity occurred to use diffuse reflectance, a relatively new technique for powdered solids, it was chosen and extensively used. A FT-IR spectrometer equipped with a microscope was also used and evaluated.

## Diffuse reflectance spectroscopy

### Development of diffuse reflectance spectroscopy

There are several traditional methods of sample preparation for solid samples for infrared analysis. Each type has certain drawbacks. The best known technique is to grind the sample with an alkali halide such as potassium bromide (KBr) and then to press the sample/alkali halide mixture into a disk by the application of pressure. The problem with the KBr disks is that alterations to the crystal structure of the sample may occur due to the pressure used to produce the disk. Ion exchange between the sample and the potassium and bromide ions has also been observed (Fuller and Griffiths, 1980; Griffiths and Fuller, 1982). It is essential that the sample is well dispersed in the KBr matrix to prevent uneven backgrounds due to scattering [illegible] and poor line shapes in the sample spectra (Turner and Horres, nd).

Another widely used method is to disperse the powdered sample in mineral oil by forming mulls. All mineral oils have some absorption bands in the infrared and it is usually necessary to measure two spectra using mulling oils which absorb in different regions of the infrared (usually Nujol and Fluorolube). This method is called the split mull technique and the obvious drawback is that it is time consuming (Fuller and Griffiths, 1980; Griffiths and Fuller, 1982).

If the sample is soluble, the material may be examined as a solution. The solvent will affect the spectrum and thus, a solvent should be chosen which has few bands in the infrared. The best solvents are $CCl_4$ and $CS_2$ which have few absorptions in the infrared. As with the mineral mulls, two spectra of each sample are required to obtain a complete spectrum of the sample. A further drawback is that many materials are insoluble in $CCl_4$ and $CS_2$ (Griffiths and Fuller, 1982).

Polymers may be hot pressed into a film, but such treatment may alter the structure of the material. Films may also be cast from solution if the sample is soluble in a volatile solvent (Fuller and Griffiths, 1978). It is difficlut to completely remove the solvent from the film.

In an effort to develop a method to analyse solids in powder form, research was pursued into diffuse reflectance spectroscopy (Fuller and Griffiths, 1978; Fuller and Griffiths, 1980; Griffiths and Fuller, 1982). Diffuse reflectance is a widely accepted method for ultraviolet-visible spectroscopy of powders and turbid liquids. It has been applied to clinical measurements, pharmaceutical quality control, heat tranfer studies and food science. It was thought that insufficient radiation would be reflected from a powdered sample to obtain satisfactory infrared spectra (medium resolution, 2-4 $cm^{-1}$, and high SNR), so diffuse reflectance had not been considered feasible for infrared analysis (Fuller and Griffiths, 1978).

An integrating sphere device is used to collect the diffusely reflected ultraviolet-visible and near infrared radiation. In such a device, the sample and detector are usually positioned at the interior sphere surface which has been coated with a nonabsorbing, diffusing powder such as MgO or $BaSO_4$ (Fuller and Griffiths, 1978).

The integrating sphere could not be directly adapted for measurements in the mid-infrared. Infrared detectors are much less sensitive than the photo-multiplier tubes which are used in ultraviolet-visible spectroscopy. The integrating spheres do not efficiently collect the radiation and the resulting SNR is low. Also, efficient coatings for the sphere interior had not been developed for infrared spectroscopy (Fuller and Griffiths, 1978).

Until 1978, there were few reports of diffuse reflectance spectroscopy in the mid-infrared. Willey (1976) was among the first to interface an integrating sphere to a FT-IR. Long measurement times were needed to achieve spectra of high SNR and at only moderate resolution, however (Fuller and Griffiths, 1978; Krishnan and Ferraro, 1982). Several different experimental designs have been tested and hemiellipsoidal and ellipsoidal collecting mirrors are thought to be the most efficient in collecting and transmitting diffusely reflected radiation to the detector (Fuller and Griffiths, 1978). In 1978, Fuller and Griffiths (1978) published their results using a fairly efficient ellipsoidal collecting mirror interfaced to a rapid scanning FT-IR. They were able to obtain spectra at medium resolution and high SNR using fairly short measurement times.

Quantitative Analysis

Although quantitative analysis was not utilized for this thesis, a short summary of the theory as presented by Fuller and Griffiths (1978; 1980) is included. The Kubelka-Munk theory may be used to describe diffuse reflectance at scattering layers in powdered samples. Scattered radiation can be linked to sample concentration in a similar fashion to that embodied by the Boucher-Beer law in transmission spectroscopy. The Kubelka-Munk equation is written as follows for an "infinitely thick" sample:

$$f(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} = \frac{k}{s} \qquad \text{(Equation 2.1)}$$

where $R_\infty$ is the absolute reflectance of the sample layer, s is a scattering coefficient and k is the molar absorption coefficient. An ideal standard for diffuse reflectance has not been determined experimentally. A ratio (Equation 2.2) is created where the single-beam reflectance spectrum of the sample, $R_\infty'$ (sample), is divided by the single-beam reflectance spectrum of some nonabsorbing standard, $R_\infty'$(standard).

$$R_\infty' = \frac{R_\infty'\text{(sample)}}{R_\infty'\text{(standard)}} \qquad \text{(Equation 2.2)}$$

The standard must show high diffuse reflectance through the entire the wavelength region being measured (Fuller and Griffiths, 1978). In practice, $R_\infty$ is then replaced in Equation 2.1 by $R_\infty'$.

A linear relationship is suggested to exist between the molar absorption coefficient, k, and the peak value of $f(R_\infty)$ for each band by the Kubelka-Munk theory. The scattering coefficient, s, must be kept constant. The parameters of particle size and range should be kept as consistent as possible since the scattering coefficient is dependent on these factors. For low concentrations of sample in a matrix of low absorbance, it has been proven that:

$$k = 2.303 \epsilon c \qquad \text{(Equation 2.3)}$$

where $\epsilon$ is the molar absorptivity and c is the molar concentration. Thus, Equation 2.1 can be rewritten as:

$$f(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} = \frac{c}{k'} \qquad \text{(Equation 2.4)}$$

where k' is equal to s/2.303 .

The authors (Fuller and Griffiths, 1978) conclude that "diffuse reflectance spectra of samples dispersed in finely powdered KBr or KCl might be expected to be quite similar to the absorbance spectra of the same samples prepared as a KBr disk." Spectra of cholic acid and carbazole were presented in which this was observed to be true (Fuller and Griffiths, 1978).

The relationship between SNR and sample concentration in the limit of low concentration is somewhat different in diffuse reflectance spectroscopy than in transmission spectroscopy (Fuller and Griffiths, 1980). The Beer-Lambert Law describes the relationship between concentration and transmittance,

$$-\log_{10} T = abc \qquad \text{(Equation 2.5)}$$

where T is the transmittance, a is the absorptivity, and b is the path length. The equation may be written as:

$$T = 10^{-abc} = e^{-2.303abc}$$

$$= 1 - 2.303abc + 2.651a^2b^2c^2 \qquad \text{(Equation 2.6)}$$

The signal of the absorbing sample, 1 - T, is given as the limit as 2.303abc as c tends to zero. Thus, the SNR has a linear relationship to c at low concentrations. The Kubelka-Munk equation describes the relationship for diffuse reflectance for "infinitely deep" samples (Equation 2.4) which can be written as follows:

$$f(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} = \frac{2.303ac}{s} \qquad \text{(Equation 2.7)}$$

where s represents the scattering coefficient and $R_\infty$ is the ratio of the diffuse reflectance of the dilute sample "at infinite depth" to that of the nonabsorbing matrix alone. $R_\infty$ approaches unity as the sample concentration within the non-absorbing matrix is decreased, Thus:

$$(1 - R_\infty) = \left(\frac{4.605ac}{s}\right)^{1/2} \qquad \text{(Equation 2.8)}$$

and the SNR becomes proportional to the square root of the sample concentration. This phenomenon is thought to be unique to diffuse reflectance spectroscopy and is an obvious improvement in the analysis of very small samples (Fuller and Griffiths, 1980).

The diffuse reflectance of powdered gold, germanium and some alkali halides was measured in an attempt to select a suitable material for the nonabsorbing background (Fuller and Griffiths, 1978). Powdered KCl was found to exhibit the highest reflectance with the least interferences. The particle size of KCl was found to affect the reflectance. The smallest average particle size was observed to give the highest reflectance at high wavenumbers. A standard dispersing matrix of KCl at a particle size less than 10 μm has been recommended (Fuller and Griffiths, 1978).

It is important to note that the Kubelka-Munk equation is only valid for moderately absorbing materials having a limited particle size range (Fuller and Griffiths, 1978). A "Kubelka-Munk law" plot of $f(R_\infty)$ versus weight percent of sample becomes non-linear at high sample concentrations. Particle size affects both bandwidths and relative intensities. A decrease in particle diameter is observed to reduce bandwidths significantly. Variation in particle size has been observed to affect the intensity of certain bands to a greater extent than others (Fuller and Griffiths, 1978).

It is necessary to keep particle size constant when comparing diffuse reflectance spectra of a series of similar substances. It is vital that pure alkali halide powder should be used for diffuse reflectance, especially for microsampling. The same stock of alkali halide should be used for comparison of related compounds (Krishnan and Ferraro, 1982).

Experiments suggest (Fuller and Griffiths, 1978) that spectral subtractions of diffuse reflectance spectra are valid if the $f(R_\infty)$ is low for both spectral components. Attempts to subtract the entire spectrum of one sample from another which were not diluted with KCl were not successful. A later reference indicates that diffuse reflectance can be used quantitatively only over narrow concentration ranges (Krishnan and Ferraro, 1982). Quantitative results have been reported (Turner and Horres, nd) using a Bruker FT-IR spectrometer with a Harrick "praying mantis" type diffuse reflectance unit. In the study, spectra were obtained of finely ground ascorbic acid at concentrations of 1, 2, 4 and 8% in KBr. The peak heights of four bands were plotted against concentration. A nonlinear relationship was observed for the raw data and linear plots were found for data corrected by the Kubelka-Munk equation which is in agreement with the results of Fuller and Griffiths (1978).

Particle size and concentration are not the only factors which affect the spectrum by causing deviations from the theoretical Kubelka-Munk situation. There is a specularly reflected component in the radiation that is sent to the detector that is caused by the radiation which bounces off the surface of the sample without penetrating into the sample. For specular or regular reflectance, the angle of incidence is equal to the angle of reflectance. In diffuse reflectance, the direction of reflected light is random with respect to the incoming beam (angle of incidence) (Figure 2.2)(Willey, 1976). Diffuse transmittance and regular transmittance have a similar relationship to diffuse and regular reflectance. For diffuse reflectance, the depth of penetration is a function of the internal scattering of the material. The total reflectance spectrum is due to the reflection from the surface plus the scattering and absorption of the particles in the medium (Willey, 1976).

The specular reflectance for most organic compounds from a single crystal is very small at all wavelengths. This is attributed to the relatively small absorptivity of the absorption bands which leads to only small changes in the refractive index across the spectrum (Griffiths and Fuller, 1982).

Specular reflectance is a concern for many inorganic compounds, the absorptivity of the stronger bands can be very large and the refractive index can change dramatically across the band. This is called anomalous dispersion which leads to the appearance of spurious reststrahlen bands in the specular reflectance spectrum. If small, irregular crystallites are examined instead of a single crystal, the resulting spectrum contains a combination of diffuse and specular reflectance. The larger the absorptivity of a particular band and the larger the crystal, the more closely the spectrum will resemble the specular reflectance spectrum. The specular component decreases and the diffuse reflectance radiation increases as particle size decreases. However, there is still an element of specularly reflected radiation which does not penetrate into the bulk of the sample, but instead reflects off of the particles on the top layer of the sample. Band inversion or when a negative absorption appears above the baseline may occur in the region of intense bands in the spectrum. When inorganic samples are ground with an inert, nonabsorbing matrix such as KCl, the diffuse reflectance spectrum more closely resembles the typical absorption spectrum. If quantitative information on minerals is to be obtained with diffuse reflectance, the sample should be ground with KCl in a concentration of 1% (Griffiths and Fuller, 1982).

### Qualitative analysis

Diffuse reflectance is a powerful qualitative technique for rapid identification of powdered solid samples with little or no sample preparation (Fuller and Griffiths, 1978). The amount of sample needed is very small. A strong spectrum may be obtained from only 100 µg of sample in most cases and as little as 200 ng of sample is sufficient to record a spectrum for moderately absorbing substances. A spectrum has been observed from 2 ng of sample in KCl in a few rare cases. A matrix thickness of less than 5 mm is reported to be the point where a further increasing thickness does not change the spectrum, ie "infinite thickness". There seems to be very little difference in band intensity between sample thicknesses of 2 to 5 mm (Fuller and Griffiths, 1978).

The microsampling capabilities of diffuse reflectance were compared to those of transmission spectroscopy using KCl disks. Two mixtures of carbazole and KCl were prepared, one with a carbazole concentration of 0.37% and one with a concentration of 53 ppm. KCl disks were prepared from both mixtures and transmission spectra were obtained of each disk. Diffuse reflectance spectra were obtained of both concentrations without any further sample preparation. All of the major bands appear in both the transmission spectrum of the KCl disk and the diffuse reflectance spectrum of the 0.37% mixture. A clear diffuse reflectance spectrum was also obtained of the very dilute mixture. Only the strongest bands, however, appear in the transmission spectrum of the KCl disk of the 53 ppm concentration. The spectra were collected under identical instrumental conditions. The band intensity of the diffuse reflectance spectrum of the 53 ppm concentration is about one order of magnitude greater than in the transmission spectrum of the KCl disk of the same concentration (Fuller and Griffiths, 1980). The detection limits were further investigated by recording the spectra of mixtures of a given amount of KCl with 11 μg, 250 ng and 11 ng of caffeine (1000 scans and 4 min scanning time). The stronger absorption bands are easily seen above the noise level in the spectrum of the 11 ng sample (Fuller and Griffiths, 1980).

One microsampling problem with infrared spectroscopy is measuring solutes at low concentration. The traditional method requires that the concentration of the solute is first increased either by evaporation of the solvent or by extraction of the solute into a smaller volume of an immiscible solvent. A small amount of KBr is added and the residual solvent is removed by boiling away or freeze-drying. The sample remains on the surface of the KBr and the material is then pressed into a micropellet. The diffuse reflectance spectrum could instead be obtained from the unpressed powder sample. The above procedure has been automated and utilized in the interface between a HPLC and a diffuse reflectance spectrometer (Fuller and Griffiths, 1980). The detection limits for such measurements are very low (approximately 100 ng). The intensity of the bands of a 1% sample of carbazole deposited on the KCl from solution was observed to be greater than those from a spectrum of finely ground carbazole mixed with powdered KCl at a concentration of 1% (Fuller and Griffiths, 1980).

The relative intensities of analyte mixed with KBr are different from those for the sample pressed into a KBr disk. The effect is particularly noticeable in aromatic compounds when the relative intensities of bands in the overtone region 1700 - 2000 $cm^{-1}$ and the fundamental modes are compared. The overtone bands are condiderably stronger in the diffuse reflectance spectrum. However, the relative intensities in the diffuse reflectance spectrum of the samples prepared by depositing the analyte from the solution onto the KBr powder seem to be much more similar to those observed in the transmission spectrum of the KBr pellet (Fuller and Griffiths, 1980). " This effect is thought to be due to the small thickness of the solute film on the KCl particles relative to the wavelength of the infrared radiation when the analyte is deposited from solution as opposed to the comparatively large particle diameter of the sample when mixed with the KCl." However, no thoery was presented describing the reasons for this phenomenon (Fuller and Griffiths, 1980).

Diffuse reflectance is an easy way to measure infrared spectra of solids and obtain high quality results. It is particularly effective for materials such as coal and minerals that are difficult to study as alkali halide pellets. It is hard to grind such materials into the fine uniform powders which are needed to produce pellets without scattering effects (Krishnan and Ferraro, 1982). The sample preparation time is reduced, the complete spectrum can be measured and the chance of ion exchange is lessened. It is possible to obtain spectra of neat samples, but it is preferable to grind organic samples in approximately twenty times their weight of KCl for one to three minutes. Inorganic samples need to be mixed with more alkali halide to yield an acceptable spectrum (Fuller and Griffiths, 1980).

There are some problems which are associated with the use of alkali halides as reference materials for diffuse reflectance. Alkali halides tend to adsorb water which causes bands at 3300 and 1640 $cm^{-1}$. It also adsorbs organic materials from the air if it is left in a powdered state for several hours. Thus, the alkali halide material should be stored as lumps and ground as needed shortly before use (Griffiths and Fuller, 1982). Other materials were examined to see if they could be used to replace alkali halides. Silicon and germanium were tested because of their purity and ease of grinding. When the ratio of a spectrum of KCl to that of finely ground silicon or germanium was calculated, absorption bands indicating water (3300 and 1640 $cm^{-1}$) and organics (2950 $cm^{-1}$) appeared. Unfortunately, silicon and germanium exhibit strong bands at 1100 and 900 $cm^{-1}$ respectively which are thought to be due to oxide layers on the powder surface. Also, the overall reflectance of these materials is substantionally less than that of KCl. When a ratio of a diffuse reflectance spectrum of an organic compound in silicon or germanium to that of silicon or germanium was calculated, the baseline was often found to be above 100% which causes difficulty with quantitative work (Griffiths and Fuller, 1982).

### Silicon carbide paper sampling technique

A new method of collecting powdered material for infrared analysis has been suggested (Sharp, 1982; Jansen, 1983) where silicon carbide abrasive paper is used to grind the sample. The first report (Sharp, 1982) recommended the use of "wet and dry" paper. Three drops of deionized water are placed on a small piece of silicon carbide paper. The sample is rubbed onto the paper until a fine suspension of sample is collected in the water. The sample suspension is rinsed with 1-2 $cm^3$ water into a centrifuge tube and centrifuged for one minute. After decanting the water, the material is added to 0.7 g KBr, mixed, gently dried and then it is ground and pressed into a pellet. If the object is large or cannot be sampled in the lab, its surface may be moistened and rubbed with the wet and dry paper (Sharp, 1982). Another report (Jansen, 1983) suggests that the sample and the KBr be ground together with a pestle on the abrasive paper. Water is not used and the resulting mix is then pressed into a pellet. Dichloroethane is recommended for use with rubber materials. The author points out that the use of silicon carbide paper allows a small amount of sample to be removed at positions where little or no harm is done to the appearance or function of the object. The technique is also useful for objects which cannot be destroyed (Jansen, 1983).

A further refinement of the silicon carbide technique occurred when it was suggested that the diffuse reflectance spectrum could be measured directly from the surface of the powder <u>in situ</u> on the silicon carbide paper (Spragg, 1984; Perkin Elmer, 1986). The technique is suggested for materials which may be difficult and time consuming to grind instead of using a vibration mill or mortar and pestle. The sample is rubbed onto the paper until sufficient sample has been accumulated and the spectrum is measured directly from the paper. The preparation time is very short, usually only a few seconds and very little sample is needed. It has been mentioned before that diffuse reflectance spectra are most similar to transmission spectra when the samples are mixed with a nonabsorbing matrix. When neat samples are measured, the relative band intensities and band shapes may vary considerably from those in a transmission spectrum. The spectra are however, often adequate for qualitative indentification or quality control (Spragg, 1984).

There does not seem to be much if any, spectral interference from the silicon carbide paper. A spectrum can be obtained by calculating the ratio of the spectrum of the paper against the spectrum of the plane mirror (Perkin-Elmer, 1986). A spectrum was obtained of the silicon carbide paper used in this thesis and is reproduced in Shearer, 1987. A number of different silicon carbide papers were tried and 200 grit was found to be satisfactory for a variety of materials (Spragg, 1984; Perkin-Elmer, 1986). In some types of paper, the spectra only exhibited a silicon carbide reflectance peak near 800 $cm^{-1}$ and very little evidence of other materials such as organic adhesives. In the spectra of other examples, the presence of organic binders is stronger. The spectrum of English Abrasives paper "p220C" contains many weak bands due to organic components, but the peak at 800 $cm^{-1}$ is less intense than in the spectra of most other examples of silicon carbide paper (Spragg, 1984). There is a considerable difference in the intensity of the background spectra of various papers. A variety of examples from different sources should be examined to minimize the possible interferences. Very stiff paper provides ease of handling.

Spectra were measured of a plastic moulding material which was identified as an acrylonitrile-butadiene-styrene copolymer (Spragg, 1984). A diffuse reflectance sample was prepared by abrasion of the material by silicon carbide coated paper. The spectrum of the powdered sample on the surface of the paper was measured. The amount of sample on the paper was 150 µg on an area of 35 $mm^2$. The spectrum was compared to that of a film cast from a solution of 1,2-dichloroethane on a KBr window. The spectra were collected at a resolution of 5 $cm^{-1}$ and one scan was collected. There are no features in the diffuse reflectance spectrum which can be attributed to the silicon carbide paper. The bands observed in the diffuse reflectance spectrum correspond very closely with those in the transmission spectrum of the cast film (Spragg, 1984). The relative intensities of the corresponding bands are very similar. The similarity between the transmission spectrum and the diffuse reflectance spectrum is thought to be due to the sample being thinly distributed on the silicon carbide paper. The infrared radiation still has to travel different path lengths, but they are all fairly short (Perkin-Elmer, 1986) Thus, the silicon carbide paper has a similar effect to diluting the sample in a nonabsorbing matrix.

This observation agrees with that of Griffiths (1986) who states that diffuse reflectance spectroscopy is most successful when the sample is in the form of a very thin layer on the surface of a diffusely reflecting support.

The sample loading or amount on the paper does not need to be closely contolled for qualitative spectroscopy. The sample in the above illustration was obtained from sample loading of approximately 5 $\mu g/mm^2$. At this concentration, most of the sample is trapped within the crevices of the surface and the silicon carbide is still visible. (Spragg, 1984). The reflectance at this level is 1 - 2% in contrast to approximately 10% for finely powdered KBr in the diffuse reflectance accessory. The reflectance can be increased by adding more powdered sample (Perkin-Elmer, 1986). The reflectance in the areas where the sample does not absorb increases by as much as a factor of 2 (Spragg, 1984). However, the contrast between weak and strong bands is reduced (Spragg, 1984; Perkin-Elmer, 1986). An effect similar to measuring the diffuse reflectance of a neat powdered sample is achieved. The reflectance can also increase by rubbing the silicon carbide paper with powdered KBr although this somewhat reduces the convenience of the method (Perkin-Elmer, 1986).

In the diffuse reflectance accessory used in the experiment (Spragg, 1984), the infrared beam is focussed down to an area approximately of 2 $mm^2$. When the sample is collected by being rubbed on the surface of the silicon carbide paper, it will be distributed over a larger area than is needed. The amount of sample taken can be reduced by cutting a piece of silicon carbide paper to the appropriate size and rubbing the smaller piece on the surface of the bulk sample. The sample size taken can be reduced to 20 ug or less (Spragg, 1984).

The silicon carbide sampling technique is fast and convenient. It is useful for polymeric materials which are difficult to grind and is appropriate for large objects (Spragg, 1984). The least success was obtained with very soft materials and substances which are torn into particles which are too large for direct measurement by diffuse reflectance spectroscopy.

The use of the silicon carbide technique is also mentioned in an article on industrial applications of diffuse reflectance FT-IR spectroscopy (Chalmers and Mackenzie, 1985). It was suggested for use with materials which were difficult to prepare by other more conventional techniques. Examples included poly (aryl ether sulphone)(PES) which is a high temperature thermoplastic which is difficult to compression mould into a film which is sufficiently thin to obtain a satisfactory spectrum. It is also difficult to remove the last traces of solvent from a cast film of the material. Another example cited was surface analysis of corrugated glass-reinforced plastic sheeting which does not form good contact with the reflection element for MIR (multiple internal reflectance) analysis. The silicon carbide paper was also used for identification of minerals. It was recommened that the surface of the silicon carbide paper should be dusted with KBr when analyzing inorganic materials. Although the technique is primarily of qualitative interest, it was suggested that it would be useful in industrial situations (Chalmers and Mackenzie, 1985).

### Other applications of diffuse reflectance spectroscopy

It has been found that sufficient SNR can be obtained with a Harrick praying mantis type accessory linked to a high performance Perkin-Elmer model 983 conventional dispersive spectrometer and lower performance machines such as the Perkin-

Elmer model 1430 conventional dispersive spectrometers (Hannah and Anacreon, 1983). The silicon carbide paper technique was originally developed using a diffuse reflectance accessory and a conventional dispersive infrared spectrometer (Spragg, 1984).

A diffuse reflectance accessory has been designed to allow _in situ_ analysis of a small surface area of large objects without the need to take samples (Korte and Otto, 1988). The design requirements included that the specularly reflected radiation component be directed away from the detector and that the optical energy throughput be high enough to obtain satisfactory spectra. A large portion of the reflected radiation from samples with smooth surfaces such as varnishes and coatings is due to specular reflection. The authors concluded that the reflectance for compact samples is low when compared to that of powdered samples in an alkali halide powder matrix. The diffuse reflectance spectra of different thicknesses of an acrylate/isocyanate varnish with metallic flake pigment were found to fairly closely resemble the absorbance spectrum of the material. However, samples of a weakly scattering polyester varnish gave a low reflectance, although it was possible to measure spectra. There are, however, significant variations in the relative band intensities between spectra of various thicknesses and in comparison to the transmittance spectrum of the material. The location of certain strong bands has also been observed to shift to higher wavenumbers. The authors concluded that the distortions are caused by Fresnel reflection (specular reflectance component) and that the device does not reject all of the specularly reflected radiation. When samples of low reflectance are analysed, it is necessary to obtain as high an energy throughput as possible. In this system however, higher energy throughput would result in a greater specular reflectance component in the total radiation. It was concluded that varnishes and coatings are not idealy suited for diffuse reflectance spectroscopy, but that acceptable spectra could be measured in moderate scanning times with no removal of sample (Korte and Otto, 1988). This technique is obviously ideal for extremely valuable objects which cannot be sampled, but if a very small amount of sample may be taken, it is possible to obtain higher energy throughput without severe specular reflectance.

## Multicomponent analysis

### Introduction

One drawback of the diffuse reflectance method is that it produces a spectrum of the total sample and it is difficult to distinguish several substances, especially if the materials are similar chemically. The obvious solution is spectral subtraction, although this is difficult with diffuse reflectance measurements that are not strictly controlled for quantitative analysis. It is of limited validity with the silicon carbide method. Three possible alternatives will also be discussed: thin layer chromatography (TLC) for separation of sample components before FT-IR analysis, the infrared microscope and high performance liquid chromatography-FT-IR interface.

### Thin layer chromatography/FT-IR

Early attempts to measure the infrared spectra of materials separated by thin layer chromatography directly from the spots on the TLC plates using emission spectroscopy, specular reflectance and ATR spectroscopy were not successful. A technique was developed where the spot could be analysed <u>in situ</u> on the plate without eluting the sample spot by transmission spectroscopy. The plates used were composed of silver chloride with a thin layer of silica gel or alumina. The thickness of the adsorbent was kept as thin as possible and the interferences from the silica gel and the alumina were removed by using the ratio of the sample spectrum to a spectrum of the plate (Percival and Griffiths, 1975). The method was successful, but the adsorbent caused scattering at high frequencies which reduced the signal to noise ratio. It was found that treatment of the plate after development with a substance whose refractive index approximately matches that of the adsorbent such as Nujol or Fluorolube improved the sensitivity of the method in the higher wavelength regions (Gomez-Taylor et al., 1976). The sensitivity of the method was further increased by the use of programmed multiple development which reduced the sample spot size which increased the chromatographic resolution and the utilization of a MCT detector which decreased the sample scanning time needed (Gomez-Taylor and Griffiths, 1977).

It was suggested that since the strong bands of an adsorbed species can be detected in strongly absorbing matrices such as silica gel, that it should be possible to obtain spectra of components separated by TLC without sample preparation. A spectrum of 1.2 μg of methylene blue on a silica gel plate was obtained (Fuller and Griffiths, 1978), however, further research by the same workers was not successful (Fuller and Griffiths, 1980). The spectrum of the adsorbent must be either subtracted or used to obtained a ratio in order to record a satisfactory spectrum of the adsorbate (Griffiths and Fuller, 1982). The absorptivity of silica gel is much higher than that of charcoal or XE-340 graphitized polymer beads in several diagnostic areas of the spectrum. Also, it is very difficult to see the bands resulting from the adsorbates due to the high attenuation of the beam in the region of the silica absorption bands. It was also observed that the exposure of the silica gel to a solvent tends to change its surface and cause small shifts in frequency and intensity changes. This results in a very uneven background in the ratio spectrum. The choice of reference material is vital in order to obtain an adequate spectrum (Fuller and Griffiths, 1980). It does not seem to be possible to adequately compensate for the very strong bands due to the adsorbent (Griffiths and Fuller, 1982).

Fuller and Griffiths (1980) concluded that better results were observed when the sample was extracted from the silica gel before the spectrum was measured. Each spot was scraped off the support and extracted with about 0.5 ml of acetone. The slurry was stirred and centrifuged for one minute. The solvent was then decanted, evaporated in air to 150 µl and deposited onto a sample cup packed with KCl. The diffuse reflectance spectrum was then obtained from the powder after the residual solvent had evaporated. It was also found that some silica gel remained suspended in the solution and intense silica bands could be observed in the spectrum. The residual silica gel was removed by passing the supernatent liquid through a sintered glass filter after centrifuging. It was also concluded that there is a high degree of susceptibility to interferences due to the very high sensitivity of diffuse reflectance microsampling. One has to be very careful during sample preparation and spectral interpretation when the sample amounts being measured are near the detection limit of the technique (Fuller and Griffiths, 1980). The same conclusions on measuring the spectra of TLC spots <u>in situ</u> were reached by other workers (Chalmers and Mackenzie, 1985).

## HPLC/FT-IR

The interface between HPLC or GC and diffuse reflectance FT-IR seems to be a more promising method for examining multicomponent systems. These techniques were not available for this research, but a certain amount of work has been published on the subject. Gas chromatographs (GC) have also been interfaced with FT-IR spectrometers for on-line measurements of infrared spectra of peaks as they elute from the GC colum. The sensitivity of the systems are now high enough to recommend an FT-IR spectroscopy interface as an alternative or complement to a mass spectrometer interface for qualitative analysis of multicomponent mixtures which are sufficiently volatile and thermally stable to be separated by GC. HPLC is usually used to separate nonvolatile or thermally labile components. However, the interface between HPLC and FT-IR is more difficult than for GC and FT-IR. The detection limits of an early commercial model were greater than those of equivalent GC/FT-IR systems (Kuehl and Griffiths, 1980).

The difficulty with sensitivity in HPLC/FT-IR systems is caused by the strong infrared absorption of the mobile phase. In conventional systems, the effluent passes through a flow cell and the spectrum of each HPLC peak is recorded and stored during the chromatographic run. After the chromatogram has run, the solution spectra are computed and the solvent bands are removed by subtraction. It is necessary to keep the pathlength of the flow-cell very small to prevent the solvent absorption bands from "blacking out" very large regions of the spectrum. The recommended pathlength for most solvents used for normal phase HPLC is about 100 µm. The volume of 3 mm diameter cells is less than 1 µl and less than 1% of each sample is present in the cell at any time during the collection of the solute spectrum. This severely limits the sensitivity of the system (Kuehl and Griffiths, 1980). Kuehl and Griffiths (1980) describe a system where the effluent from the column is concentrated and deposited onto KCl powder. The residual solvent is removed by rapid evaporation and the solute remains on the KCl. The diffuse reflectance spectrum of each fraction is then measured.

The detection limits of the system are determined by chemical interferences and not by the noise level of the instrument. Solvent which has not been evaporated can cause interferences depending the nature of the solvent. The best results are obtained with highly volatile, fairly nonpolar solvents. A second problem is atmospheric moisture which can become adsorbed to the KCl powder. The water can usually be removed by treating a reference cup of KCl in the same manner as the samples, but on humid days or when very large ordinate expansion is needed, bands due to water are sometimes seen in the spectra. Only very pure KCl should be used. Since diffuse reflectance spectroscopy results in much more intense bands than conventional transmission measurements, it is essential to minimize comtaminants from all sources in order to obtain low detection limits (Kuehl and Griffiths, 1980).

There are several disadvantages to the HPLC/diffuse reflectance system. The solutes must be much less volatile than the solvent. This is not a serious limitation as most volatile samples are analysed by GC. The second difficulty is that water cannot be completely eliminated because of its high surface tension and latent heat of evaporation. This limits the application of FT-IR to size exclusion or normal phase HPLC. Systems which require an aqueous phase cannot be used in conjunction with FT-IR because of the strong absorption bands due to water. The third and most serious problem is due to the fact that in this system, the detector signal of the HPLC acts as a trigger mechanism for the recording of an FT-IR spectrum so the solute must be detected by the detector for the system to work. The authors discuss the possiblity of a fully automated system (Kuehl and Griffiths, 1980).

The HPLC/FTIR system has another advantage which is of interest with archaeological samples or other samples of limited availability. Each component is collected into sample cups and not destroyed. If the spectrum obtained by the on-line method is unsatisfactory, the sample can be re-run with the signal averaged over a longer period of time to improve the SNR or it may be recovered from the KCl with a nonaqueous solvent and analysed by a different technique (Kuehl and Griffiths, 1980).

The use of HPLC with diffuse reflectance FT-IR is mentioned by other workers (Chalmers and Mackenzie, 1985). In their paper, the separation was carried out using reverse phase chromatography with a water/methanol mobile phase and the separated fractions were collected into vials. The aqueous solvent was evaporated using a steam bath and the solute was redissolved in a minimum quantity of dichloroethane and deposited by a capillary pipette onto powdered KCl. Satisfactory spectra were obtained of 20 and 2 ug quantities of sample (Chalmers and Mackenzie, 1985).

Until the development of the diffuse reflectance FT-IR system, FT-IR instruments had not been sufficiently sensitive to identify minor constituents of mixtures separated by adsorption chromatography due to problems with the mobile phase (Kuehl and Griffiths, 1980). However, one technique in which the solvent does not need to be removed before infrared measurement of each fraction is size exclusion chromatography where the choice of solvent does not seriously alter the separation. Solvents with good infrared transmittance such as $CCl_4$ and $CS_2$ may thus be used as the mobile phase for size exclusion chromatography. However, these solvents are not completely transparent in the infrared and spectral subtraction techniques are not yet sophisticated enough to remove all solvent bands when gradient elution is required for chromatographic separation (Kuehl and Griffiths, 1980).

### FT-IR microscopy

Although microscope accessories have only been widely available since 1983, the idea is not new and the model introduced by Cole and Jones shows similarities to the microscopes which are now available (Griffiths, 1986). A microscope interfaced to a ultraviolet-visible spectrometer and a quartz refracting instrument was used to measure spectra in the ultraviolet region. However, the instrument had to be refocused as the wavelength changed and the system of lenses absorbed in certain regions which limited the range which could be examined (Barer et al., 1949). In 1947, Burch developed a reflecting microscope which was achromatic and no absorbing materials were used in the construction. The instrument was applicable to spectrometry from the ultraviolet to the infrared regions. The Burch microscope was attached to a Perkin-Elmer infrared spectrometer by Barer et al. (1949) and spectra of particles were obtained from 2 to 15 um without the need for large slit widths which would severely reduce the the spectral resolution. The instrument was fitted with sodium chloride and lithium fluoride prisms, and the radiation from a Nernst glower source was passed through the microscope and sample. The image was magnified 100 - 1000 times. The sample was held on a thin plate of rock salt, quartz or other infrared transparent material. A small, adjustable preliminary slit was used to select the area to be analysed and the radiation was directed by focusing mirrors through the sample area selected onto the entrance slit of the spectrometer. The sample size used was $10^{-7}$ - $10^{-8}$ g. The minimum sample size was controlled by the resolving power of the microscope which varied with the wavelength. Results were obtained with crystals and fibres which were 20 - 50 um in diameter. Polarization effects were studied with a selenium mirror (Barer et al., 1949).

The experiment was repeated by Gore (1949). A Bausch and Lomb Grey design Type IV microscope was interfaced to a Perkin-Elmer Model 12B infrared spectrometer. The microscope was equipped with a 0.4 numerical aperture condenser and objectives and only reflecting elements were used. An auxillary source was used to collect the radiation and direct it to the condensing system. After the radiation passed through the sample, it was collected by the objective and directed through a draw tube. The radiation was then collected by a spherical mirror in the spectrometer which directed the magnified image onto the entrance slit. The diameter of the image was made equal to the length of the slit by adjusting the physical dimensions of the slit. The size of the image could also be controlled by adjustment of the sample on the microscope stage. The suggested sample preparation methods included suspension of specimen in mineral oil on a NaCl plate or between two plates. The material may also be placed in solution or attached to a stretched fine wire. The sample size used was estimated to be 0.3 $\mu$g at 4000 $cm^{-1}$ to 3.0 $\mu$g at 650 $cm^{-1}$. The black body characteristics of the energy source required that the slit width be increased as the wavelength increased. Macro and micro sample spectra were obtained of sodium benzyl penicillin and it can be seen that the wide slit widths needed adversely affect the resolution near 2400 and 1325 $cm^{-1}$ (Gore, 1949).

Coates et al. (1953) introduced a modified design for an infrared microscope interfaced to a Perkin-Elmer single beam spectrometer. In this design, the microscope is mounted so that the radiation passes from the exit slit of the monochromator to the microscope and then to the detector. This inovation decreased the possible damage to the sample from the heat and photochemical reactions. The condenser and objective pair were of the Schwarzschild type and the numerical aperture is 0.75 and the obscuration ratio is 0.4. Accurate selection and measurement of sample area is provided by a viewing and manipulation system. Approximately 35% of the radiation from the monochromator is passed through the microscope system by minimizing the number of reflecting surfaces. Field mirrors were used to provide more efficient transfer of energy. The radiation is measured by a separate detector and preamplifier which were subsequently connected to the system amplifier and recorder. The minimum sample size was dependent on the wavelength and limited by the energy available. The system was used to provide spectra of fibres, crystals, biological tissues and small volumes of solution in cells (Coates et al., 1953). The system was marketed under the name Perkin-Elmer model 85, but it was not a commericial success with only limited production (Reffner et al., 1987).

The introduction of computers facilitated the growth of microspectroscopy. In 1980, V. Coates and his firm (Nanometrics) introduced the NanoSpec 20IR which consists of a single beam monochromator instrument, a computer and an infrared microscope. The computer facilities are used to generate a double beam format spectrum from the single beam sample spectrum and a background spectrum which is stored in its memory. The resulting spectrum does not contain absorptions due to the atmosphere or instrument background which appear in conventional single beam spectra. The scanning time needed for this instrument is two minutes or less. The use of FT-IR spectrometers also promoted the growth of microspectroscopy. The advantages over conventional dispersive spectrometers provided by FT-IR also apply to the use of the microscope. These include high energy throughput, good spectral resolution, high signal to noise ratio, rapid data collection and digital processing of spectral data. The interface was first demonstrated in 1982 by McCrone Associates (Reffner et al., 1987) and in 1983, Digilab introduced the first commercial microscope accessory for FT-IR (Griffiths, 1986) and Analect also produced a version that year (Reffner et al., 1987). Microscope accessories can now be obtained for all FT-IR spectrometers (Reffner et al., 1987). The Digilab model was originally only able to measure transmission spectra. It was later updated to perform reflectance measurements as well. There are two types of microscope accessory available. The most expensive high performance microscope systems are equipped with their own mercury cadmium tellurium MCT detector. The less expensive models use the MCT detector within the spectrometer (Griffiths, 1986).

When utilizing infrared microscopy, the sample to be analysed usually covers a much smaller dimensional area than the total area of the instrument light beam which is projected onto the sample plane of the microscope. The dimensions of the radiation must be decreased to match those of the sample. This is usually accomplished with four moveable slit edges located at an auxiliary light focus. The result is that the image of the sample covers only a small part of the area of the detector. The detector is optimized to take advantage of the superior throughput and the SNR can be significantly increased by the use of a MCT detector which has been optimized for the microscope. Reasonable spectra can be obtained from a sample of 20 um square with a scanning time of a few minutes. Smaller samples present a difficult problem as the sample size is then equal to or smaller than the wavelengths of the light being used. The diffracted light will bypass the sample if the beam is blocked in some way by slit edges at an auxiliary focus. One solution is to mount the sample on a pin-hole in an opaque plate in the sample plane, but care must be taken that the plate is thin to avoid obscuring the beam (Griffiths, 1986).

The thickness of the sample is important to obtain satifactory transmission spectra. The sample thickness should be of the correct magnitude, between 5 and 50 μm, to yield an acceptible spectrum. For specimens which are too thick, the material can be squeezed between two type II diamonds. This reduces the thickness and increases the cross-sectional area of the sample. A larger quantity of the radiation is then able to pass through the sample since there is more open area. Thus, the SNR and the quality of the resulting spectrum are increased. This technique is thought to be more successful than mounting the sample behind a pin-hole (Griffiths, 1986).

A microscope has been developed by Spectra-Tech which combines high quality visual imaging with the reflecting optics necessary for infrared measuring. The other available infrared microscopes do not have the capability to perform high quality research light microscopy. The accessory is known as the IR-PLAN has both transmission and reflection capabilities so spectra may be measured through the sample and by reflection of the surface. The visual light path is coaxial with the infrared light path so the image selected is the same that is analysed. The sample area is defined and stray light is reduced by remote variable apertures which are located at conjugate image planes. This technique is refered to as redundant aperturing (Spectra-Tech)(Reffner et al., 1987).

There is a very wide variety of uses for the infrared microscope and the advantages for archaeological and art samples are obvious. The microscope can be used for cross-sectional analysis. It is useful for identifying components in layers without chemical separation or "peeling" of layers which is difficult and often incomplete. An example was given of analysis of a plastic laminate. A thin cross-section was prepared by microtomy and infrared analysis of each layer including the adhesives was obtained after each material was optically isolated with the dual remote variable apertures. The separation achieved with the redundant aperturing technique seems to be very efficient. The report did not indicate the support used for the cross-section (Reffner et al., 1987).

The microscope in reflecting mode may be used to analyse surfaces _in situ_. The method is similar to reflection accessories used with FT-IR. The method can be nondestructive with no sample preparation but the sample geometry must be correct. The object may be analysed either directly on the stage where the size of the sample is limited by its space available between the objective and the stand or using a sideways facing external objective port. This may be used to examine large or bulky samples. The reflection microscopy method is best suited for studies of surface coatings and contaminant films (Reffner et al., 1987).

Another sampling advantage of infrared microscopy is found with the identification of fibres. In the past, the identification of monofilament fibres was difficult with infrared spectroscopy due to band distortions caused by diffraction effects. This problem is overcome by the remote aperturing system. Also, bicomponent systems can be studied. The light imaging facilities can be used to measure the morphology and optical properties to distinguish the sample from other fibres. Conventional infrared sample preparation techniques cannot be used to identify the microstructure of bicomponent fibres. Techniques such as grinding the material into KBr pellets, dissolving and casting it into films or infrared reflection destroy the microstructure of the fibre. Both microscopy and spectroscopy are thus desirable for complete characterization (Reffner et al., 1987).

Another advantage of the microscope is the ability to characterize solid mixture system without physical separation or bulk analysis of all components. The sample can be separated into its components by differences in crystallinity or morphology. The crystals may be differentiated by shape or birefringence using cross polarized light. If the crystal is too large, it is necessary to crush it to obtain a sample of the optimum size (Reffner et al., 1987).

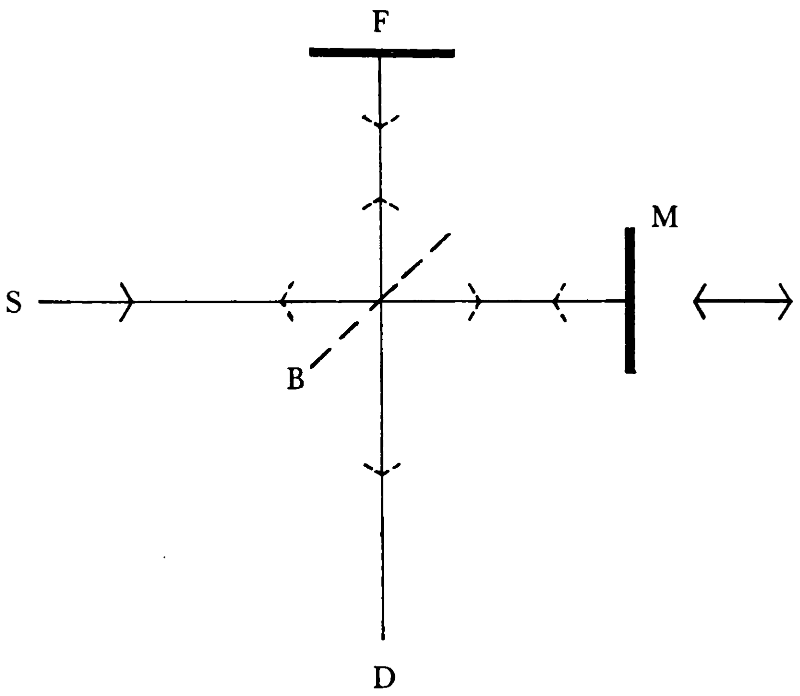


Figure 2.1 Diagram of the Michelson interferometer (Griffiths and de Haseth, 1986). (F) is the fixed mirror, (M) is the moveable mirror, (B) is the beamsplitter, (S) is the source and (D) is the detector.

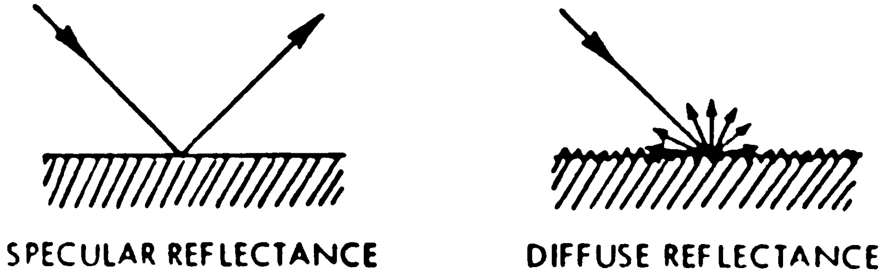


Figure 2.2 Illustration of specular and diffuse reflectance (Willey, 1976).

# CHAPTER 3 EXPERIMENTAL PROCEDURE

## Instrument Specifications

### FT-IR Spectrometers

The diffuse reflectance measurements were carried out using a Perkin-Elmer 1710 infrared Fourier transform spectrometer. The machine design is an improved single beam Michelson interferometer with rotary scan and bi-directional data collection (Perkin-Elmer, 1984).

The optical unit, which contains a Michelson interferometer system similar to that described in Chapter 2, is sealed and filled with molecular sieve dessicant to reduce absorptions due to atmospheric contaminants. The beam splitter is coated with germanium and a variable Jacquinot stop is utilized. The infrared source is a temperature stabilized ceramic source which operates at 1400° K. The detector is a temperature stabilized, coated fast recovery deuterated triglycine sulphate (FR-DTGS) detector with moisture resistant CsI windows. The instrument was not fitted with a more sensitive mercury cadmium tellurium (MCT) detector, but, the FR-DTGS detector was found to be more than adequate for this research. The beam size at the focus is 8 mm at the first sample position. The frequency range that may be measured with this machine is 4400 - 400 $cm^{-1}$ and the frequency accuracy is 0.01 $cm^{-1}$. A helium/neon laser is used as a reference. The ordinate precision is better than 0.1% and is usually limited by the noise level. The signal-to-noise ratio is higher than 0.1% transmittance from peak to peak. The resolution may be changed and is available from 2 to 64 $cm^{-1}$. The scanning times are very short, about one second is need for a scan at a resolution of 4 $cm^{-1}$. The sample alignment when an accessory is used is carried out with the laser and the facility exists for energy transmitted optimum alignment (Perkin-Elmer, 1984). The spectrometer is equipped with a Barnes Analytical/Spectra-Tech "Collector" diffuse reflectance accessory which will be discussed in greater detail in the next section.

The initial diffuse reflectance measurements for this research were made with a Bruker IFS 45 bench top spectrometer. However, the data handling software available with the Perkin-Elmer was more compatible with the goals of this research. Thus, the diffuse reflectance measurements were made on the Perkin-Elmer and the Bruker FT-IR was used exclusively for infrared microscopy.

The Bruker FT-IR instrument utilizes a high throughput Michelson interferometer with single air bearing controlled by a helium/neon laser. The beam splitter is KBr coated with germanium and the detector is a deuterated triglycine sulphate (DTGS) type with a KBr window. The frequency range covered by the instrument is 4800 - 400 $cm^{-1}$ and the highest resolution available, 2 $cm^{-1}$, is constant over the entire range. The frequency precision is 0.01 $cm^{-1}$ and the accuracy and repeatability is 0.1% transmittance. The aperture ratio is f/4.5 and the beam size at the sample position is 10 mm (Bruker Technical Information). The Bruker FT-IR system does not have a microprocessing unit with specialized software for data handling, although, the spectra data may be stored on floppy disks.

### Diffuse reflectance accessory

There are several designs for diffuse reflectance accessories which vary in the optical alignment. The system developed by Fuller and Griffiths (1978) is shown in Figure 3.1. It is an on-axis reflectometer with ellipsoidal collection mirrors. In the original system, the collimated beam from the interferometer is reflected by two plane mirrors to a paraboloidal mirror which is at 90° to the axis of the radiation beam. This mirror focuses the beam onto the powdered sample in a sample cup which is located at one focus of an ellipsoidal mirror. There is a small hole drilled in the ellipsoidal collection mirror at the centre on the major axis which permits the radiation from the paraboloid to pass onto the sample. With this arrangement, the specularly reflected radiation component from the sample passes back through the hole. The diffusely reflected radiation is collected by the ellipsoid and focused at the other principal focus of the ellipsoid mirror. A second paraboloid mirror positioned 90° off-axis is used to focus the radiation into a beam of about 2 mm in diameter onto the detector. A trigylcine sulphate (TGS) and a MCT detector were both used, the MCT detector requiring less scanning time. It was suggested that a state-of-the-art FT-IR equipped with a new TGS detector could be used satisfactorily, however (Fuller and Griffiths, 1978).

In later work, the ellipsoidal collecting mirror is replaced by a paraboloidal mirror with the hole drilled at the vertex. A wide beam MCT detector is also substituted for the narrow beam detector so the beam does not need to be attenuated (Fuller and Griffiths, 1980).

There are several diffuse reflectance accessories available commercially which fit into the sample compartment of FT-IR spectrometers. The accessory used for this thesis was manufactured by Barnes Analytical/Spectra-Tech Corporation and is known as the "Collector". Another commercial accessory which is often ecountered in the literature is the "Praying Mantis" which is marketed by Harrick Scientific Corporation. The designs of the various commericial accessories are illustrated in Griffiths and de Haseth (1986).

Each of the commercial accessories is designed to collect the total reflectance of the sample which is all of the specularly reflected portion and part of the diffusely reflected radiation unlike the Fuller and Griffiths design which eliminates the specular element. In several of the commercial accessories, the spectral component can be eliminated. The Spectra-Tech design incorporates a post or blocker to deflect the specular component, which will be discussed in more detail below. The Harrick design reduces the specular reflection by rotation of the plane of the sample cup (Griffiths and de Haseth, 1986).

The high efficiency of the Fuller and Griffiths design and of the commercial designs make it possible to record high quality spectra with the use of a DTGS detector as well as an MCT detector (Griffiths and de Haseth, 1986).

The optical system and the path of the radiation through the "Collector" accessory are illustrated in Figure 3.2. In this design, four flat and two aspherical reflectors are used with an alignment mirror which may be placed in the sample position (M4). The aspheric mirrors are off-axis ellipsoids which focus and collect infrared radiation with a 6x condensation of the beam. A FT-IR beam normally has a 3 to 18 mm spot size at the focus. Thus, the spot size with the diffuse reflectance accessory will range from 0.5 to 3.0 mm. The collection angle is a full pi steradians which captures 50% of the available diffuse energy. The collector accessory has been designed for high energy throughput (Barnes Analytical Technical Information).

The sample cup is removable for sample loading and can be put in place by sliding the ellipsoids apart. The sample cup is mounted on a sliding arm which brings the cup forward under the ellipsoidal mirrors so it may be removed by moving the ellipsoids. The sample height is adjustable. The mirrors are uncoated aluminium and care must be taken not to scratch them. Four sample cups are supplied with the accessory, two macro cups which are a 13 mm in diameter and 2 mm in depth, and two micro cups which are 3 mm in diameter and 2 mm in depth. There is no vignetting of the beam with the macro cups, but some vignetting of the diffuse energy is caused by the rim of the micro cup which lowers the energy throughput. The surface of the powder in the cups should be smooth. The "Collector" may also be utilized to measure high quality specular reflectance spectra of films and coatings by positioning the sample at a 50° mean angle of incidence.

The problem of the specularly reflected component of the total energy which reaches the detector is eliminanted by the use of a blocker device on the "Collector" accessory. The device blocks the front surface of reflected energy directly at the sample. This prevents the energy from reaching the collection mirror and the detector. The effect is illustrated in Figure 3.3. A thin metal blade just touches the surface of the sample and perpendicularly bisects the sample surface without penetrating into the sample. Thus, only the infrared energy which penetrates to some extent into the powdered sample can reach the detector. The specular component or energy reflected without penetration into the sample is prevented from reaching the collection mirror (Messerschmidt, 1985). The use of the blocker also reduces the energy throughput to only 15% of the throughput without the blocker. Thus longer measurement times and the use of a high sensitivity MCT detector are recommended. The blocker device may be moved out of position for higher energy throughput measurements when Kubelka-Munk calculations (quantitative measurements) are not necessary (Messerschmidt, 1985).

### FT-IR microscope

The microscope used in the project was designed by Bruker. The accessory was designed to have high sensitivity, easy conversion between sampling modes, visible control of measured area and easy sample handling. The microscope was designed with reflecting optical elements only in the measurement channel. The instrument is fitted with interchangeable horizontal sample stages which may be controlled with computer guided stepping motors for "sample mapping" and manual switchover between reflectance and transmittance modes of measurement. The microscope has binocular optics and a movable field of view which permits convenient inspection of the sample area. The optical system provides optimum sample illumination for reflectance and transmittance measurements. There are three types of aperture: iris, various fixed round apertures or four independent knife edges which may be utilized to isolate the desired sampling area. Sensitive detection is provided by a cryogenic detector. The detector element size may be specifically chosen for sample diameters in the range of 20 - 500 microns. The magnification and measurement area may be altered for specific purposes by exchanging objectives and apertures. The sample area space may be enlarged when the reflection mode is utilized for analysis of large or bulky samples (Simon, nd).

## Experimental procedure for diffuse reflectance

### General procedure

Krishnan and Ferraro (1982) have outlined a procedure for measuring diffuse reflectance spectra with a KBr powder matrix. A background spectrum of the stock powdered alkali halide powder is recorded and stored. The spectrum of the sample is then measured. The material may be diluted in stock alkali halide at a sample concentration of about 5 - 10% to obtain optimum spectra, but the spectra of undiluted samples may be measured if necessary. The reflectance spectrum may be determined from the ratio of the sample spectrum to the reference spectrum. The procedure used for the research reported in this thesis is similar, but there are differences, mainly in sample preparation.

A preliminary report on the technique developed in this thesis has been published (Shearer, 1987). A reference spectrum of the blank silicon carbide paper is recorded in the background memory channel. The blank silicon carbide paper is then rubbed against the object or substance to be analysed until a small, but visible amount of powder adheres to the silicon carbide paper. When a sample has been removed from the object, it may be held with forceps and rubbed directly onto the paper. The sample spectrum is then measured directly from the silicon carbide paper. The Perkin-Elmer FT-IR is equipped with a microcomputer with sample handling software designed to store the reference material in a library and to compare sample spectra to the data base. If the spectrum is that of a reference material of a known identity, it is added to the reference spectra library database in the computer using the software. A spectrum of an unknown is compared to the reference library using the search software and a list of possible structural units present in the unknown compound and a list of possible identities are produced along with a factor which gives an indication of the closeness of the fit of the unknown with each of the reference spectra. The spectrum of the unknown is then compared visually with those suggested by the search before an identification is made (Shearer, 1987).

### Instrument preparation

The instrument is first aligned with the diffuse reflectance accessory and the alignment mirror in the sample position. The alignment adjusts the beamsplitter for maximum energy throughput (Barnes Analytical Technical Information) and this procedure was carried out at the beginning of each experimental session.

### Background spectra collection

It is necessary to measure a background spectrum to remove the bands which result from water and carbon dioxide in the atmosphere within the instrument from the sample spectrum. If a sample medium is used, any contributions to the spectrum from the medium may be removed by including the material in the reference spectrum. The reference spectrum is collected in the background memory channel and is used for each sample measurement until it is replaced by a new background spectrum. A new reference spectrum should be acquired if the amounts of water vapour or atmospheric carbon dioxide have changed since the last background measurement (Perkin-Elmer, 1984). This may be determined by the presence of a doublet or a valley in the region of 2360 $cm^{-1}$ in the spectrum due to the carbon dioxide in the atmosphere.

For improved background subtraction in transmittance measurements, a sample shuttle may be used which consists of two sample holders on a stage which is controlled by a motor. The rear holder is used for the reference material with no sample and the front holder is used for the sample. The shuttle may be manipulated by the computer to move back and forth to collect a series of sample and background spectra. This allows for the sample spectra to be compared to very recently acquired background spectra and eliminates the atmospheric interferences from the final spectrum (Perkin-Elmer, 1984).

For diffuse reflectance measurements, the sample shuttle cannot be used. The background spectrum must be measured through the instrument because the pathlength through the accessory is longer than the open beam pathlength. In this work, the blank silicon carbide paper was included in the reference spectrum. The overall reflectance of the abrasive paper is not as high as KBr and most of the sample measurements were above 100% absorption. However, the focus of this work is qualitative identification and it was considered to be more important to have consistent subtraction of background interferences than to achieve circumstances appropriate for quantitative analysis.

Slight changes in pathlength of the accessory such as a change in the position of the ellipsoidal mirrors result in inadequate subtraction of the background interferences. It is thus desirable to remove the reference material and replace it with the sample by sliding the arm out rather than by moving the ellipsoidal mirrors apart. Theoretically at least, a number of sample spectra may be measured against one background measurement. In the accessory used for this research, however, the ellipsoidal mirrors were not held together tightly and the very light disturbances which are caused by moving the sliding arm cause changes in the pathlength and the appearance of bands due to atmospheric carbon dioxide. This also sometimes occurs when the reference is removed causing interferences in the first spectrum which is measured. Owing to the time constraints within which the experimental work was conducted and the fact that the carbon dioxide bands occur approximately in the region of 2360 $cm^{-1}$ which is not an important diagnostic area, a reference spectrum was obtained at the beginning of each experimental session. A new reference spectrum was collected only when the carbon dioxide absorption was as intense as the weak absorption bands in the sample. Thus, the appearance of a doublet in the region of 2360 $cm^{-1}$ in the data in this work is simply due to experimental difficulties and not in any way characteristic of the sample.

### Sample spectra collection

The energy throughput should be maximized before each measurement of the reference or sample. With the "Collector" accessory, the energy throughput may be monitored in the throughput mode where the amount of energy passing to the detector is displayed. The height of the sample stage is adjusted until the reading is maximized. The sample stage height must be readjusted for each sample because the infrared radiation penetrates to different depths depending on the sample loading which affects the optical path of the attachment (Barnes Analytical Technical Information).

The instrument measures the interferogram of the sample and the spectrum is calculated by the electronic unit using the Fourier transform. The interferometer is a single beam instrument, thus the sample spectrum must be calculated from the ratio of the spectrum obtained with the sample in the beam against the background spectrum measured without the sample. The resulting spectrum is stored in one of the three memory channels and displayed on the VDU. When multiple scanning is utilized, the average spectrum is automatically calculated. (Perkin-Elmer, 1984)

The reference and sample spectra were collected under uniform instrumental conditions. One hundred scans were recorded at 8 $cm^{-1}$ resolution in 5.2 minutes. The operational parameters were set by the engineers for optimal normal usage when the machine was installed (Perkin-Elmer, 1984). It is beyond the scope of this thesis to discuss these parameters in depth. They are, however, reviewed in the book by Griffiths and de Haseth (1986).

### Sample preparation for diffuse reflectance

The silicon carbide paper used in this research was English Abrasives Waterproof silicon carbide paper, grit size p320A. In order to maintain consistent particle size, the same grit size was used for all reference material and sample spectra. Although the interferences from the silicon carbide paper are very slight, silicon carbide paper from the same roll of paper was used for all measurements. The standard size of paper used was a 12 mm diameter circle. This size of paper was used for all standard reference spectra and for most of the unknown samples.

The majority of the unknown samples were removed by the conservator treating the object and given to the author for analysis. The sample was placed on the circle of silicon carbide paper and crushed with the back of a microspatula. If the silicon carbide was no longer visible under the powdered sample, the silicon carbide disk was held by forceps and shaken slightly to remove excess sample. A minimum of sample is required to avoid distortion of the spectra as discussed in the previous chapter. In many instances, more sample was provided than was needed. It was desirable to remove the sample with the silicon carbide paper directly from the object whenever possible. It was frequently possible to take a scraping from the reverse or an edge which was not visible while on display. The silicon carbide paper method caused minimal scratches on the objects. It was especially suitable for varnishes or other coatings on large objects such as furniture. The method is portable, objects could be analysed without bringing them to the laboratory. Decisions on sampling method were made individually for each object in consultation with the conservator.

The basic technique was adapted to sample a series of modern sculptures in the Tate Gallery made of plastic materials. The samples are discussed in greater detail in chapter 11. It was necessary to minimize the amount of sample removed and the marks left by the silicon carbide paper as most of the plastic was transparent. The sampling marks were only visible under a microscope (Heuman, personal communication). Smaller circles of a diameter of 5 mm were punched from a finer grit of silicon carbide paper (p400). The small circles were mounted onto wooden dowels with Blue Tack adhesive and used to remove the sample. The dowels were then secured in foam and transported to the laboratory where they were measured against the background of the same blank silicon carbide paper.

### Difficulties with the silicon carbide paper technique

The silicon carbide sampling technique was most successful with solid materials which powdered easily. There were three types of samples which were more difficult to handle, samples which did not grind easily, sticky materials and specimens which contained a large proportion of inorganic matter.

Care must be taken in the interpretation of spectra of materials which are difficult to grind. Very hard materials sometimes removed some of the grit from the paper. Thus, there was a risk of interferences from the organic adhesive. Samples of birch bark bistre (hardwood pitch) were difficult to grind because of their hardness and a spectrum with very little detail was obtained. A possible solution for very hard samples is to grind the material in an agate mortar and pestle before spreading onto the silicon carbide paper.

Several samples of aged adhesive were removed as slivers of thin films and were rubbed against the paper with the back of a microspatula. The samples did not powder well. The resulting spectra were difficult to interpret and probably not representative of the intended sample as an identical spectrum was obtained by rubbing a blank silicon carbide disk with the back of a clean microspatula. In an attempt to deal with this problem, the thin films of adhesive were held with a pair of very fine tweezers and the films were very gently rubbed onto the paper until a thin deposit formed. This technique is much more time consuming, but excellent spectra were obtained (Chapter 14).

Another problem was encountered with liquid or sticky samples. Reference materials such as Venice turpentine, gum labdanum, softwood pitch and certain waxes formed a coating on the silicon carbide paper and the resulting spectrum showed indications of specular reflectance. The problem was not remedied by the use of the blocker device as the silicon carbide paper sat in the base of the cup and the blade did not come into contact with the sample surface. A solution to the problem was found by rubbing the sticky material with powdered KBr on the silicon carbide paper. The spectrum is then recorded after a reference spectrum of the blank silicon carbide paper rubbed with powdered KBr was first measured. The effect may be seen in Figure 3.4 where a sample spectrum which was obtained with no treatment is compared to a spectrum which was measured with the sample mixed with powdered KBr. Although none of the samples taken from objects were in a liquid form, some were sticky. The samples which were extracted from the ship luting (Chapter 7) were observed to be very sticky after the evaporation of the solvent. The samples were mixed with ground KBr and satisfactory results were obtained. Some samples taken from Egyptian jars (Chapter 5) were also very sticky.

The third class of materials which were difficult to characterize were samples which were largely inorganic in composition. Materials were classified as inorganic by the absence of bands due to C-H stretching and bending vibrations and by the presence of very broad, intense and ill-defined bands in the spectrum especially below 1200 $cm^{-1}$ which may be due to silicate materials. Mineral matter often causes specular reflectance and a more realistic spectrum may be obtained by diluting the sample on the silicon carbide paper with powdered KBr. The focus of this research was the characterization of organic materials and no collection of inorganic reference samples was attempted for this study.

## Data handling

After the spectrum was recorded, it was transferred to the microcomputer system and then saved on a floppy disk. This storage method was used as a large number of spectra were acquired for this project. The data may then be recalled from the disk and placed in the memory of the computer for further data manipulation, printout or computer library searches. The software, CDS-3, was written by Perkin-Elmer engineers specifically for infrared spectroscopy. The expansion function was used extensively for this work to enhance detail in the spectrum especially when a small sample was used. The calculation of frequency values by the PEAK function is more precise than reading from the chart and the frequency values quoted in the thesis are those given by the computer. The spectra subtraction function was only used in a few cases when one component of a system was easily identified in the spectrum. These examples are noted in the text.

The SEARCH-3 program was developed as an aid to interpretation and identification of infrared spectra. The software contains a large data file of absorption bands which are characteristic of particular functional groups. In the interpretive section of SEARCH-3, the peak table which is generated from the sample spectrum is compared to the data base. This gives an indication of the functional groups within the molecule. The list of possible function groups or structural units (PSU) are compared to those of the sample and the PSU's which fulfill the criteria are listed on the screen. The identification is further assisted by the comparison of the sample peak table to those contained in the SEARCH libraries. A general spectral library is included with the system and other libraries may be purchased. The software also enables the analyst to build libraries with spectra measured in the laboratory (Perkin-Elmer, 1984).

The computerized SEARCH-3 results are not conclusive and are merely intended to assist in identification of compounds. The complete list of possible structural units is compiled along with possible sources of interference in a reference manual provided with the the software and should be consulted. A definite characterization should only be made after comparison of the unknown spectrum to those in the reference volumes which were suggested by the SEARCH program or with reference spectra acquired by the analyst.

### Identification of unknowns

Two methods for characterization of unknowns were used in this thesis. The first involves the SEARCH software described above and reference spectra libraries. The second technique is to assign the absorption bands in the spectrum to specific functional groups using tables and books compiled from the characterization work in the scientific literature. The principal source for the band assignments is The Infrared Spectra of Complex Molecules, by L. J. Bellamy and the references contained therein. A combination of both methods has been used.

The commercial libraries of infrared spectra consist principally of pure chemical compounds used in chemical laboratories. They do not, however, contain materials such as the natural products which are of interest to museum scientists. A library of spectra was thus compiled incorporating the diffuse reflectance spectra of the natural product reference materials. The commercial libraries were very useful, however, for the identification of the semi-synthetic and synthetic polymer samples (Hummel, 1978; Chicago Society of Coatings Technology, 1980; Hanson, 1987).

The identification of natural products is, however, somewhat more complicated. For pure chemical compounds, an exact match between the unknown sample and the reference spectrum is required for identification. With natural products, it is more difficult because there is a great deal of similarity in infrared spectra between a related series of compounds. The absorption bands characteristic of certain functional groups are well documented. The assignment of every band in the spectrum to a specific functional group is not always possible, however, due to spread and overlap of bands. The infrared spectrum of a complex mixture such as a natural resin contains a large number of absorption bands and they often overlap to a great degree and result in broad envelopes or bands of absorption with few distinctive peaks (Mills and White, 1987).

An example is given in Mills and White (1987) which compares the spectrum of a pure compound, hydroxydammarenone I, which is present in fresh dammar resin, unaged dammar resin and a dammar varnish film which is 50 years old. There are many strong, sharp bands in the region of 1300 - 625 $cm^{-1}$. The same region is somewhat blurred in the spectrum of the fresh dammar resin, although there are bands present which may be assigned to individual substituents. The aged sample is increased in chemical complexity and this results in several broad, indistinct bands in the spectrum (Mills and White, 1987).

## Experimental procedure for thin layer chromatography samples

### Preparation of thin layer chromatography samples

An attempt was made to measure the diffuse reflectance spectrum of spots from high performance TLC separations. A CAMAG HP-TLC Arid Chamber system was used with precoated silica gel plates (60F254). Two different solvent phases were used, a 50:50 (v/v) solution of heptane and t-butylmethylether and a 50:50 (v/v) solution of methanol and t-butylmethylether. Various materials which are typical of the natural products being analysed from archaeological collections were analysed using both solvent systems. These include glance pitch, frankincense, stick lac, abietic acid and *Pistacia lentiscus*. The resulting plates were allowed to dry and the plates were examined under fluorescent and ultraviolet light without any chemical development. The spots were scored around with a scalpel blade under the fluorescent light and removed by sliding the scalpel blade under the spot and lifting it from the glass support. A blank was obtained in the same manner and a reference spectrum was measured of the silica gel. A spectrum of the sample spot was then recorded, but the spectrum was distorted, perhaps by specular reflectance from the surface of the sample. The sample spots were then analysed using silicon carbide paper. The reference was obtained by rubbing the silicon carbide paper with silica gel which had been treated with the solvent system, but not the sample. The sample spots were removed and measured in the same way. The resulting spectra were very similar to one another and characterized by a broad band centered at about 3400 $cm^{-1}$ and broad, indistinct bands from 1650 - 400 $cm^{-1}$ with a very strong, wide band in the region of 1200 - 1000 $cm^{-1}$. In some cases, a very weak sample spectrum was observed but after abscissa expansion, the compensation for the broad band at 3400 $cm^{-1}$ was too strong in relation to the other bands resulting in a negative absorption. The general similarity of the spectra to each other and the complete absence of bands due to C-H stretching indicated that there were spectral interferences from the silica gel. The commercial plates contain inorganic fluorescing agents and binders which may cause interferences. Also, rubbing the spot onto the silicon carbide paper is an inefficient way of handling small samples and most natural products such as those used for this study do not absorb more strongly than the silica gel compound matrix.

Extraction of the sample spots from the silica gel was attempted using AnalaR diethyl ether. One trial TLC plate was made of glance pitch, hydrocarbon wax, and abietic acid and a second plate was prepared of hexatriacontan, umbelliferone and Pistacia lentiscus. Selected spots were removed with a scalpel in the same manner and placed in a small amount of ether in capped vials overnight. The solutions were then put through a pipette which contained a plug of silica glass wool to remove the silica gel. The solutions were then placed in a fume cupboard and the ether was allowed to evaporate.

### Interpretation of thin layer chromatography sample spectra

The resulting spectra were obtained by rubbing the solute left after evaporation onto the silicon carbide paper. The reference for this experiment was the blank silicon carbide paper. The spectra were similar to each other and to those obtained directly from the sample spots. However, there may be evidence of the sample in the spectra in the form of bands in the C-H stretching region (2960 - 2920 $cm^{-1}$) which are present in all of the spectra but not in the spectra of the blanks. The spectra do not bear a close similarity to the standard spectra of the reference materials. The spectrum of the residue extracted from the abietic acid is marked by the absence of the strong band expected in the carbonyl region (1700 $cm^{-1}$). The standard spectrum of umbelliferone shows a series of many sharp, strong bands from 1510 - 400 cm$^{-1}$ which are absent in both of the sample spectra of the umbelliferone spots which were extracted from both solvent systems. The spectrum of the umbelliferone extract from the heptane/t-butylmethylether solvent system had a very intense, broad band with its most intense region centred at 1064 cm$^{-1}$. (This band is probably due to the silica gel.) Likewise, the standard spectrum of the hydrocarbon wax is very simple and marked by strong bands in which are discussed in chapter 4. Only the bands due to the C-H stretching vibrations are present in the spectra of both of the extracted samples of the hydrocarbon wax where broad, intense bands are observed in the region from 1300 to 400 cm$^{-1}$ due to interferences from inorganic materials.

The spectrum of the extracted sample spot of the glance pitch contains bands in the C-H stretching region (centered at 2917 cm$^{-1}$) and bands at 1607, 1475, 1361 and 1209 cm$^{-1}$ which correspond to bands in the standard diffuse reflectance spectrum of glance pitch at 2926, 1603, 1461, 1377 and 1203 cm$^{-1}$. There is, however, very little similarity between the spectra in the area from 1150 - 400 cm$^{-1}$. There is a strong band centred at 3358 cm$^{-1}$ and one at 787 cm$^{-1}$ in the extract spectrum which are interferences which are most probably caused by silica gel. The most promising results were found with the hexatriacontane, a long chain hydrocarbon with a very simple diffuse reflectance spectrum. There are strong bands in the reference spectrum at 2956, 2931, 2894, and 2857 $cm^{-1}$ (C-H stretching vibrations), 1471 and 731 $cm^{-1}$. The spectrum of the extract of the hexatriacontan spot from the methanol/t-butylmethylether solvent system has bands at 2920 (multiplet), 1461 and 726 $cm^{-1}$. There are, however, several bands in the region of 1731 - 1580 $cm^{-1}$ and intense bands in the region from 1200 to 1000 $cm^{-1}$ which are not evident in the standard spectrum and are probably due to elements in the silica gel. The characteristic bands are not present in the spectrum of the extracted spot from the heptane/t-butylmethylether system where they seem to be masked by several broad, intense bands at 1434, 1352, 1196, 1004, 814 and 523 $cm^{-1}$.

There are several possible sources for the interferences. The contamination bands might be due to residual solvent. However, the plates were dried briefly with hot air after the chromatographic run and heated in an oven at 38°C for 30 minutes before the samples were removed. The most probable causes are the silica gel and the inorganic fluorescing agents, particularly as the spectral features are similar to those observed with inorganic materials, i.e. broad, ill-defined, very intense bands. It is possible that the background subtraction is not entirely adequate in compensating for the silica gel. This difficulty was encountered by other workers (Fuller and Griffiths, 1980). The extraction process could also be improved by filtering the solution through a sintered glass filter to remove finely suspended silica gel from the solvent as suggested by Fuller and Griffiths (1980). The extraction might also be more efficient if a solvent in which the solute is more highly soluble were chosen. The choice of such a solvent is, however, difficult with unknown samples. The treatment of the silica gel plate with a releasing agent might also improve the recovery of the specimen.

The difficulty in obtaining satisfactory spectra of standard materials of known identity and the problems encountered by other workers (Fuller and Griffiths, 1980) suggested that this method is not suitable for analysis of archaeological specimens. It would be more desirable to perform a sensitive separation technique such as HPLC or GC-MS if a multicomponent system is suspected.

**Experimental procedure for FT-IR microscopy**

The procedure for obtaining spectra with the microscope is similar to that for measuring diffuse reflectance spectra. Infrared microscopy is single beam transmission spectroscopy and it is necessary to record a reference spectrum. The supporting material for the sample is included in the background spectrum which is stored in the background channel. The sample interferogram is then recorded and the computer calculates the spectrum, subtracts the background and displays the spectrum. The spectrum is then stored on magnetic disks for future reference, although no software facilities existed on the machine for the collection and storage of a search library. The spectrum may be manipulated on the screen and enlarged printouts may be made.

The major difficulty with the microscope is the sample preparation. There are two problems with sample preparation for infrared microscopy. The first difficulty is in mounting the sample and the second is in obtaining satisfactory sample thickness and transparency. Most conventional mounting techniques for microscopic specimens require synthetic resins or glass slides, both of which would cause too much contamination to achieve a worthwhile spectrum. High pressure diamond anvil cells are one possible solution, but one was not available for this research. The original analyses in this thesis were carried out using blank KBr disks (13 mm in diameter). The sample was placed on the disk and then a small amount of solvent was deposited onto the disk. It was hoped that the solvent would dissolve all or part of the sample and the transmission spectrum could easily be measured. The difficulties encountered with this technique were loss of sample and insoluble samples. The method which was adopted involved the use of copper transmission electron microscopy (TEM) grids. The sample was transfered to the grid with microforceps and pressed with manual pressure with the back of a clean microspatula. The small particles of sample adhered to the grid which left portions of sample supported, but with no backing which would cause spectral interference in the infrared. The grid was supported in an aluminium disk which had a 2 mm hole drilled through it and a 4 mm shallow depression to hold the grid in place. The aluminium disk was placed on the microscope stage which could be moved by two micrometers to align the sample. This method allowed for the examination of materials with very little sample manipulation. Although the sample thickness was not measured directly, the amount of energy throughput was used to determine if the sample was thin enough. The reference spectrum was collected by moving the circular aperture to 1.05 microns and position the aperture in one of the empty square openings in the grid. The reference spectrum of 200 scans was obtained at 8 $cm^{-1}$ resolution and had an energy throughput of approximately 2000 counts per unit time. The sample spectrum was obtained by moving the sample using the movable stage so that a fairly transparent section of the sample within an open square of the grid was visible in the aperture. The energy throughput of the various references and unknowns were different. Very thin, transparent samples could range from 1000 - 1500 counts per unit time. Some spectra were obtained with counts as low as 262, but the sample was then usually pressed a second time or a different location on the sample was chosen to obtain an energy throughput of 400 counts per unit time or more. In some cases, the sample did not fill the grid entirely and a small amount of light passed through. This resulted in the presence of bands in the region of 2360 $cm^{-1}$ which are due to inadequate compensation for the carbon dioxide from the atmosphere.

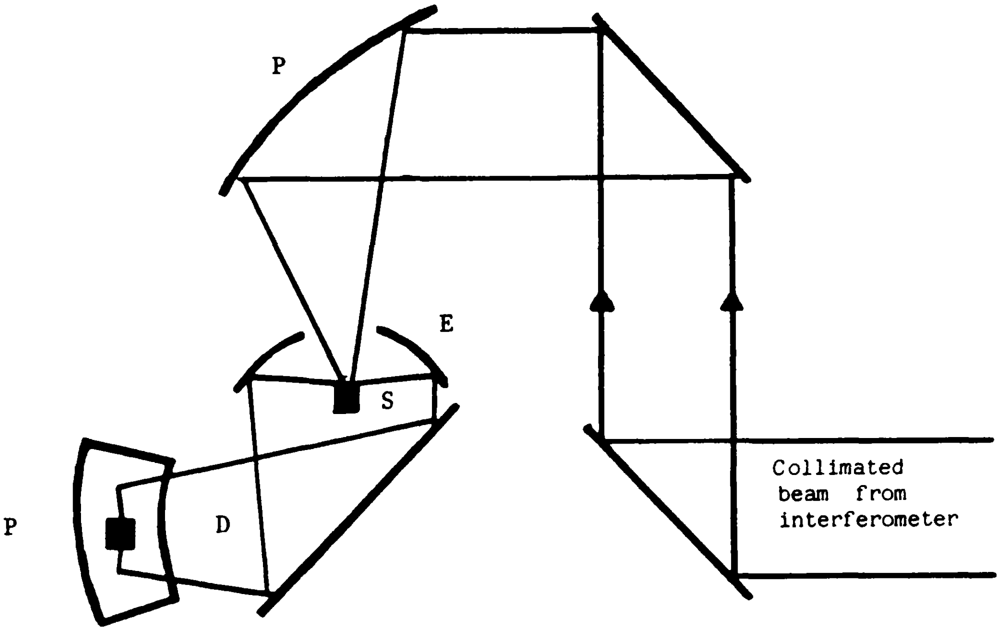


**Figure 3.1** Diagram of diffuse reflectance FT-IR system developed by Fuller and Griffiths (1978). (S) is the sample, (P) are the paraboloidal mirrors, (E) is ellipsoidal mirror and (D) is the detector.

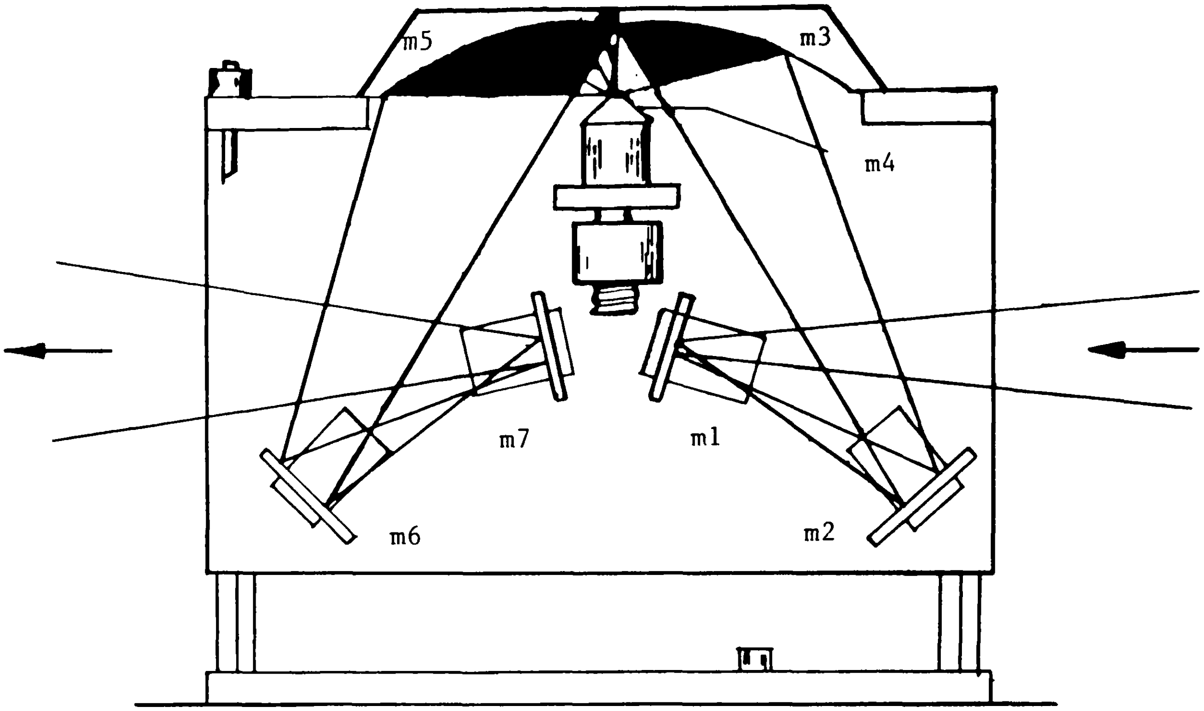


**Figure 3.2** Optical diagram of the "Collector" diffuse reflectance unit (Spectra-Tech Corporation) (Griffiths and de Haseth, 1986).

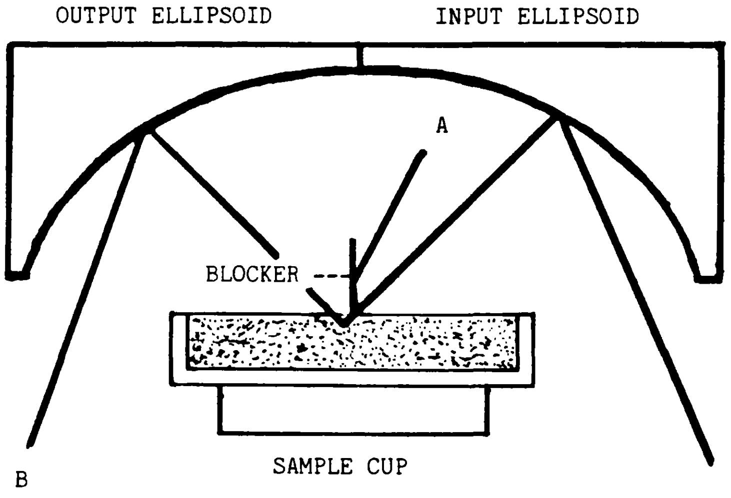


Figure 3.3 Diagram of blocker device for use with the "Collector" accessory (Messerschmidt, 1985). (A) represents the specularly reflected radiation reflected back to the source by the blocker and (B) represents the diffusely reflected radiation directed to the detector.

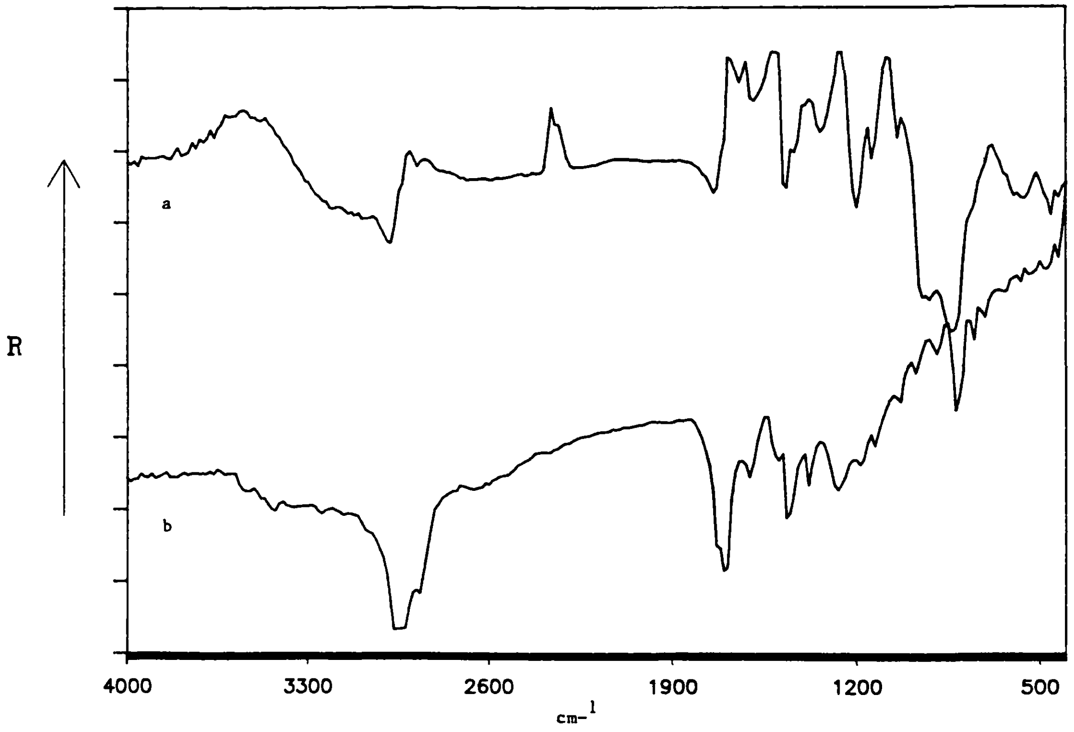


Figure 3.4 Diffuse reflectance FT-IR spectra of (a) softwood pitch (RW1 Pix liquida) (gsva0015) and (b) softwood pitch mixed with KBr powder (RW1) (gsva0615).

# CHAPTER 4 WAXES

## Beeswax

### Source

Wax is produced by species of the Apis bees (Mills and White, 1987). It is manufactured by the bees using wax glands in their abdominal wall. The thin scales of wax are used to construct the comb and then it is filled with honey. To recover the wax, the honey is removed by draining and centrifuging. The wax is then heated in water and filtered. The natural product is a pale yellow colour and may be bleached by the sun or by oxidizing agents (Tooley, 1971).

### Composition

The chemical composition of beeswax seems to be consistent. Eighty samples of Canadian beeswax were examined (Tulloch and Hoffman, 1972) to determine the quantitative values of acid, ester and hydrocarbon composition. The values were observed to fit into narrow ranges. There was little variation between values obtained from old comb waxes and pure capping wax. The percentage of hydrocarbons was found to be slightly higher for older waxes. There were no significant differences between waxes collected from different regions of Canada (Tulloch and Hoffman, 1972). Beeswax is produced by bees and not collected from plants and the composition is determined biogenetically and is thus consistent (Mills and White, 1987). The differences in composition between different species of bee have not been examined, however. It is known that beeswax from the African species _Apis mellifera adansonii_ is very similar in composition to that of the common _Apis mellifera_. In contrast, ghedda wax which is obtained from Asiatic bees was found to be similar in qualitative composition, but very different in quantitative composition (Mills and White, 1987). The principal components of beeswax are mono-, di-, poly- and hydroxy esters, free acids, and hydrocarbons (Tulloch, 1972). The composition of beeswax is given in Table 4.1 (Tulloch, 1971).

Beeswax is one of the first ancient materials to have been identified with a reasonable degree of certainty. Early samples were identified using the melting point. The melting point range for the eighty Canadian wax samples was 63.5 - 65 °C (Tulloch and Hoffman, 1972) and it is fairly consistent for aged samples as well (Mills and White, 1987). Infrared spectroscopy (Kuhn, 1960) and later gas chromatography (White, 1978) were recommended for identification of waxes. Infrared spectroscopy is suggested for relatively pure samples if sufficient sample is available as the spectrum is not affected much by oxidation. Exposure to water during burial may cause partial hydrolysis (Mills and White, 1987).

### Identification and interpretation of standard spectra

Kuhn (1960) has published spectra of various waxes including pure and adulterated beeswax. The standard spectra measured in this study are very similar to those given by Kuhn. For this thesis, two commercial beeswaxes and six obtained from the British Museum (Natural History) of various *Apis* species were analysed and the ranges of major bands are given in Table 4.2. A sample of wax produced by a *Trigona* species was also measured and the frequency values are listed separately in Table 4.2. The samples obtained from the British Museum (Natural History) were taken from the combs. In one case, the comb had been abandoned and bleached white by the sun. In the other examples, the comb was coated with material thought to be a combination of residual polysaccharide and dust. The spectrum of the naturally bleached sample is given in Figure 4.1a and was found to be most similar to those of the commercial beeswaxes and those published by Kuhn. The spectra of the other samples from the combs are also very similar, but they exhibit a more pronounced absorption in the hydroxyl region and several of the spectra exhibit two absorptions in the region of 1650 and 1550 $cm^{-1}$. These interferences may be due to residual polysaccharide material or, more probably due to hydrolysis of the sample. These spectra also exhibit a lower relative intensity of the bands in the region 1400 - 400 $cm^{-1}$ which may result from inorganic interferences from dust.

The major difference between the spectra measured in this study and that of Kuhn is that the resolution in the C-H stretch region is much better in the more recent spectra. In Kuhn's spectra, there is one absorption band with maximum intensity in the region of 2850 $cm^{-1}$. In the reference spectra in this study, the separate bands are more distinct and occur in the ranges of 2932 - 2935 $cm^{-1}$, 2894 - 2904 $cm^{-1}$ and 2856 - 2859 $cm^{-1}$. The bands in the ranges 2932 and 2856 $cm^{-1}$ result from the C-H stretches in the methylene groups and the band in the region of 2894 $cm^{-1}$ is due to a combination of methyl groups and methine C-H stretches (Bellamy, 1975).

The band which appears in the carbonyl region at 1736 - 1741 $cm^{-1}$ in this study occurs at 1730 $cm^{-1}$ in the spectrum published by Kuhn and assigned to the C=O stretch in the ester functional group. The range given by Bellamy (1975) is 1750 - 1730 $cm^{-1}$ for normal saturated esters. Kuhn also mentions a second, weak band at 1709 $cm^{-1}$ which appears as a shoulder on the band at 1730 $cm^{-1}$. Mills and White (1987) have published a spectrum with two distinct bands located at 1738 and 1711 $cm^{-1}$ with the latter band having a weaker intensity. The second carbonyl band results from the C=O stretch in the un-ionized free carboxylic acids present (Kuhn, 1960; Mills and White, 1987). The carbonyl region in the spectra obtained in this study resemble those in Kuhn with a weak shoulder present on the carbonyl band near 1710 $cm^{-1}$. The range for C=O vibrations in saturated aliphatic acids is 1725 - 1700 $cm^{-1}$ (Bellamy, 1975).

The beeswax standard spectra exhibit bands in the ranges 1474 - 1470 $cm^{-1}$ and 1379 - 1377 $cm^{-1}$ which are due to C-H deformations or bending vibrations. The absorption band in the region 1474 - 1470 $cm^{-1}$ is due to a combination of the -CH2- groups and the asymmetrical deformations in the -CH3 groups and the band in the region of 1379 - 1377 $cm^{-1}$ results from the symmetrical -CH3 bending vibration (Bellamy, 1975). The values quoted in the literature for beeswax are 1470 and 1388 $cm^{-1}$ (Kuhn, 1960). The spectra obtained in this study also contain weak absorptions in the region 1420 - 1418 $cm^{-1}$ and near 1347 $cm^{-1}$. They appear in the spectrum in the literature, but are not assigned. They fall beyond the usual limits for C-H deformation frequencies which rarely deviate more than ± 20 $cm^{-1}$ from the values 1450 and 1465 $cm^{-1}$ or from 1380 - 1370 $cm^{-1}$ except in the presence of a strongly electronegative atom (Bellamy, 1975).

An intense absorption occurs in the region of 1179 - 1176 $cm^{-1}$ in the spectra obtained in this study which corresponds to the band at 1177 $cm^{-1}$ in the literature and is assigned to the C-O stretch in the ester functional group (Kuhn, 1960). This band occurs in addition to that in the region of 1730 $cm^{-1}$ which are characteristic of the ester group. The range for the C-O stretching vibration is 1200 - 1150 $cm^{-1}$ for propionates and higher esters (Bellamy, 1975).

The spectrum given in the literature (Kuhn, 1960) exhibits weak absorptions at 962, 918, 890 $cm^{-1}$ and a series of six absorptions between 1333 - 1190 $cm^{-1}$ which are unattributed, but are thought to be characteristic of solid beeswax as they disappear when the substance is examined in the molten state. Nine bands are present in the spectra obtained in this study in the regions 959 - 958 $cm^{-1}$, 922 - 921 $cm^{-1}$, 891 - 866 $cm^{-1}$, 1331 - 1330 $cm^{-1}$, 1312 -1311 $cm^{-1}$, near 1267 $cm^{-1}$, 1246 - 1245, near 1221 and 1198 - 1197 $cm^{-1}$. The bands in the region 1350 - 1180 $cm^{-1}$ may be assigned to a phenomenon known as a band progression present in fatty acids and fatty acid esters which result in a series of evenly spaced bands in this region. They are thought to be due to rocking and twisting motions of the methylene groups (-CH2-) in the trans- configuration in the aliphatic chains, (Jones et al., 1952). Conditions which modify the structure affect the spectrum. The disappearance of the absorptions in spectra of material in the liquid state is thought to result from a continuous and random distribution of the aliphatic chains (Bellamy, 1975, Corish and Davison, 1955). One trial spectrum of commercial beeswax which was not included in the values given in the table was obtained when the sample was still very sticky. As a result, the spectrum showed evidence of specular reflection in the higher frequency region. However, all of the major absorptions were present at slightly varying frequency values and the bands which are characteristic of solid beeswax in the region of 1330 - 1190 cm$^{-1}$ were absent in the spectrum of the sticky wax.

Kuhn's report mentions the presence of a doublet at 730 and 719 cm$^{-1}$ in the beeswax spectrum which was attributed to the presence of long chain hydrocarbons. These absorptions appear as a single band in the reference spectra in this study in the region 729 - 722 cm$^{-1}$. The range given by Bellamy (1975) is 750 - 720 cm$^{-1}$ for a chain of four methylene groups or more.

In the report published by Kuhn, spectra were presented of beeswax mixtures. The first example was that of Punic wax. The process of preparing Punic wax has been reported by ancient sources. By this method, beeswax is heated with seawater and soda (Pliny, Book XXI, line 84). The soda reacts with some of the esters producing sodium salts of the fatty acids (soaps). The resulting mixture can be emulsified with water and used as a paint medium. Punic wax was produced by Kuhn with beeswax, water, and sodium carbonate, and a spectrum was obtained of the dried film. The spectrum is similar to that of beeswax with several minor discrepancies. The band at 1480 cm$^{-1}$ is widened on the low wavenumber side, and a new band appears near 1570 $cm^{-1}$. The changes are the result of the presence of ionized carboxyl groups of the salts of the fatty acids (Kuhn, 1960). These groups are characterized by absorption bands in the region between 1610 and 1550 $cm^{-1}$ and near 1430 $cm^{-1}$ (Colthup, 1950). The greater width of the band at 1480 $cm^{-1}$ in the Punic wax spectrum as compared to the corresponding absorption in the beeswax spectrum is thought to be due to the influence of the band from the ionized carboxyl group. The spectrum of the alcohol extract of the punic wax shows weak indications of the characteristic beeswax spectrum. The bands due to the ionized carboxylic acid are stronger (Kuhn, 1960).

Two spectra were also obtained of wax-resin canvas relining mixtures (Kuhn, 1960). The mixtures were studied as films without any solvent extraction. The band at 2859 $cm^{-1}$ in the spectra of the colophony and beeswax mixture was observed to be widened on the high wavenumber side due to additional O-H groups present. Extra carboxyl groups widen the carbonyl band on the higher wavenumber side. An increase in carboxyl groups also generates a fairly strong series of bands between 1274 - 1250 $cm^{-1}$ which are superimposed on those resulting from the solid beeswax. An absorption due to the $R_2C=CHR$ configuration of the resin acids also appears in the region 833 - 820 $cm^{-1}$. The spectrum of a beeswax and A.W.2 resin mixture (A.W.2 is a ketone resin produced as a condensation product of cyclohexanone and methyl cyclohexanone) was observed to have a strong band at 3450 $cm^{-1}$ due to the increase in O-H groups present. Kuhn (1960) assigned the band at 1053 $cm^{-1}$ to O-H absorptions. A weak band appears in this region in the standard spectrum and in all of the beeswax spectra obtained in this study and is probably the result of hydrolysis. The band at 1730 $cm^{-1}$ is widened on the low wavenumber side due to the increase in ketone groups in the mixture (Kuhn, 1960).

Kuhn concludes that the infrared spectra of beeswax mixtures only indicate whether the beeswax is adulterated in some way and that separation by solvent extraction is required to identify other additives (Kuhn, 1960).

It has been noted (Mills and Plesters, 1963) that in the spectra of wax-resin mixtures, the carboxylic acids present in the resin cause a widening of the base of the C-H band in the region of 2900 $cm^{-1}$ and that the hydroxyl absorption appears as a shoulder on the higher wavenumber side of the bands near 2900 $cm^{-1}$. This was evident in sample spectra published by these authors and in the spectrum of wax-colophony mixture published by Kuhn (1960).

### Identification of unknown samples

### Unadulterated beeswax

A sample of a waxlike coating was removed from a Gaudier-Brezska sculpture constructed in red sandstone, Redstone Dancer (c. 1913). No record of previous conservation treatment exists and the coating may not be original. The sample was rubbed onto the silicon carbide paper for analysis. The resulting spectrum was found to correspond very closely with that of beeswax (Shearer, 1987). Characteristic bands occur in the region of 2900, 1739, 1471, 1377, 1177 and 724 $cm^{-1}$. The series of six bands occurs near 1330, 1312, 1290, 1266, 1220 and 1198 $cm^{-1}$ and bands are observed at 957 and 922 $cm^{-1}$. A weak band occurs in the region of 890 $cm^{-1}$ (Table 4.2). The only evidence of adulteration is a broad O-H shoulder on the C-H stretching bands which is centered at 3400 $cm^{-1}$ which may result from hydrolysis.

A sample was removed from a large Chinese inlaid bronze vase (Victoria and Albert Museum M1154-1296) with multiple repairs.

The material of interest was a green waxy filler that fluoresced yellow and a sample was taken along a vertical edge of the neck with silicon carbide paper. The sampling marks were easily removed by gently smoothing the surface with a soft cloth. The spectrum obtained from the silicon carbide paper was very similar to that of the beeswax spectra. (Table 4.2). The only evidence of impurities present is the rounded absorption centered at 3331 $cm^{-1}$ and several weak absorptions around 779 $cm^{-1}$. However, the remaining regions of the spectrum are very sharp and there is very little other evidence of adulteration.

A sample was taken with silicon carbide paper of an Egyptian figurine which was thought to be made of wax (Boston Museum of Fine Arts 72.4783). The sample was obtained on silicon carbide paper in Boston and transported to England to be analysed. The resulting spectrum is extremely similar to that of pure beeswax. (Table 4.2). There is only a small shoulder on the C-H stretching bands in the region of 3350 $cm^{-1}$ and a slight shoulder on the carbonyl absorption at 1715 $cm^{-1}$. There is no strong evidence of adulteration in the spectrum.

A sample was collected from a large block of wax at the probable site of a metal casters workshop from the Maligawa excavations at Kandy, Sri Lanka. (The site dates from around the 16th century.) The sample had a sandy crust on the outside and the interior more closely resembled fresh wax. A spectrum was recorded of both the exterior crust and the interior. The spectra were found to be very similar (Figure 4.2) in spite of the differences in appearance of the samples. Both of the plots contain a rounded absorption in the region of 3300 - 3360 $cm^{-1}$ which is more intense in relation to the other absorptions in the spectrum of the weathered crust (Figure 4.2b). The band in the region of 1050 $cm^{-1}$ is also stronger in the spectrum of the crust. These changes are probably due to hydrolysis of the material. Also, they may be the result of natural impurities such as residual carbohydrates which are visible in some of the reference spectra collected from the combs. The spectrum of the exterior material also contains weak bands at 1646 $cm^{-1}$ (with a shoulder which ends at 1520 $cm^{-1}$) and at 1102 $cm^{-1}$ which are not seen in the spectrum of the material taken from the interior of the block. These absorptions are more likely to be caused by the presence of minor impurities than by ageing.

## Beeswax mixtures

An ethnographic knife handle from central Australia was examined. It was thought that the wax used to produce the handle was obtained from Trigona bees whose wax has been reported (Dickson, 1981) to have superior working properties to that of Apis species for the manufacture of experimental tools. It was also found (Dickson, 1981) that the wax prepared by Aboriginals was loaded with vegetable matter and ochre to an extent of 70% by weight. It is necessary to adulterate the wax to prevent shrinkage and add mechanical strength (Dickson, 1981). The spectrum obtained of the handle material in this study contains absorptions which are characteristic of beeswax with some unusual bands. The spectrum exhibits the series of six absorptions in the region 1330 - 1190 $cm^{-1}$ which have been observed in the spectra of the wax of the Apis species, but not in the spectrum of the wax of the Trigona species. It would seem that the handle was produced from wax from an Apis species. However, not enough samples were available of Trigona species wax to make a firm judgement on this sample. The spectrum also contains bands at 1631, 1577, 1544 and 877 $cm^{-1}$ which may be caused by additives and a broad band centred at 3331 $cm^{-1}$ which may caused by residual polysaccharide material and pollen, but more likely to be caused by hydrolysis.

A sample from a Minbar at Shiraz, Iran was examined. The sample was contaminated having been wrapped in adhesive tape for transport. The sample was removed from the adhesive tape and an attempt was made to find a fresh surface. A scraping of the adhesive tape was taken with the silicon carbide paper and included in the background spectrum in order to subtract any contribution to the spectrum from the adhesive tape. The resulting sample spectrum exhibits similarities to the beeswax spectra, but there is an overall loss of relative intensity which may be due to interferences from the adhesive tape or to the presence of other additives. However, there are bands in the region of 2900 $cm^{-1}$ and one at 1736 $cm^{-1}$ with a slight shoulder. Absorptions are present at 1466, 1377, 1174 and 723 $cm^{-1}$. There are five weak absorptions visible in the region between 1330 - 1190 $cm^{-1}$.

A sample was obtained of the black resinous material (MFA1) found outside the mummy Nesmin (Rhode Island School of Design). The spectrum of the sample indicated beeswax with additives (Figure

4.3a). The bands in the region of 2900 $cm^{-1}$, at 1736 and 1713 $cm^{-1}$, at 1464, 1379, 1173 and 722 $cm^{-1}$ are indicative of beeswax and there are six very weak bands in the region 1330 - 1190 $cm^{-1}$. However, the band centred at 3300 $cm^{-1}$ merges with the C-H stretching absorption which is widened at the base. The absorptions in the carbonyl region are also widened and the band at 1713 $cm^{-1}$ is of equal intensity and indicative of the presence of carboxylic acids (Mills and Plesters, 1963). The additional carboxylic acids are evidence of a resin mixture. Also, the bands at 1464 and 1379 $cm^{-1}$ are not as distinct as in the pure beeswax spectra and there is a shoulder to the right of the band at 1464 $cm^{-1}$. The mixture was analysed by gas chromatography/mass spectroscopy and found to be composed principally of beeswax with additions of resin and bitumen (White, personal communication).

Spectral subtraction with the interactive difference function was utilized with the diffuse reflectance spectrum of the sample MFA1 (Figure 4.3a) and a spectrum of beeswax from Apis mellifera (NHM19) (Figure 4.3b). The resulting spectrum (Figure 4.4) contains features which are indicative of a resin. Characteristic resin spectra are discussed in chapter 7.

A sample of wax from the surface of a burnt fragment of a Nimrud ivory was analysed (See Chapter 14). The spectrum contains evidence of beeswax and other additives. Bands are present in the region of 2900, 1739, 1477, 1379, 1176, 958, 920 and 729 $cm^{-1}$. There are also bands evident at 1312, 1290, 1266, 1244, 1220 and 1197 $cm^{-1}$. However, the region near 1500 - 1350 $cm^{-1}$ is indistinct and not similar to the region in beeswax. The weak absorptions near 1420 and 1340 $cm^{-1}$ are not present. There is a shoulder on the low wavenumber side of the band at 1477 $cm^{-1}$ and two absorptions at 1539 and 1504 $cm^{-1}$ which have been assigned by Kuhn to ionized carboxyl groups. There is also a shoulder on the C-H stretching absorption band which is centred near 3350 $cm^{-1}$. In addition, the spectrum also contains weak bands at 2551, 2524, 1786, 874 and 857 $cm^{-1}$ (See Chapter 6).

**Spermaceti wax**

Source

Spermaceti wax is obtained from the oil present in the head cavity of the sperm whale, Physeter macrocephalus L. and the oil contains 11% of the hard wax material. It has been available since the advent of whaling and was utilized in 15th century England (Mills and White, 1987).

### Composition

The literature indicates that it is composed of cetyl palmitate (cetyl alcohol is the C16 alcohol as palmitic acid is the C16 acid), but further investigation with gas chromatography indicates that it contains a series of long chain fatty acid esters including ceric acid (White, 1978). The material was saponified and methylated and the resulting gas chromatography analysis gave C12 as the major acid and others were found to be present including C10 to C18 with lesser amounts of higher acids. The principal alcohols present were found to be C18, C14 and C16 and smaller amounts of C13, C15 and C17 were detected (Mills and White, 1987).

### Identification of standard spectrum

A sample of spermaceti wax (British Museum Research Laboratory) was obtained and the spectrum is shown in Figure 4.5. The spectrum is characterized by bands at 2960, 2935, 2860 and 2838 $cm^{-1}$ which correspond to the values given by Bellamy (1975) for C-H stretching vibrations (See Table 4.3). Bands are also observed at 1474 and 1378 $cm^{-1}$ which result from the C-H deformation frequencies and correspond to the values listed in the literature (Bellamy, 1975). There are also weak bands at

1418 and 1348 $cm^{-1}$ which occur in the beeswax spectra. There is a band in the spermaceti spectrum at 730 $cm^{-1}$ which is characteristic of the rocking vibration of long aliphatic chains.

The spermaceti spectrum is also characterized by a strong absorption at 1741 $cm^{-1}$ which corresponds to the C=O linkage in the ester functional group. A band is observed at 1184 $cm^{-1}$ which is due to the C-O stretch in the ester linkage. The values correspond with the value ranges in the literature of 1750 - 1730 $cm^{-1}$ for the C=O stretch and 1200 - 1150 $cm^{-1}$ resulting from the C-O.

There is a pattern evident in the spectrum which is similar, but not identical, to that of solid beeswax. There are a series of weak, sharp bands at 1330, 1309, 1284, 1223 and 1202 $cm^{-1}$ and at 984, 958, 922, 890, 851, 816 and 776 $cm^{-1}$. The values are not exactly the same as for the beeswax and the region between 984 - 776 $cm^{-1}$ is more complex in the spermaceti spectrum than in that of the beeswax. The band progression in the region 1350 - 1180 $cm^{-1}$ in solid fatty acids is thought to be related to the rocking or twisting motions of the methylene groups in the chains (Jones et al., 1952). Thus, it is possible to differentiate between the two materials using spectra of pure samples.

The spermaceti wax spectrum is also characterized by a slight shoulder in the hydroxyl region on the the C-H stretching vibrations near 3450 $cm^{-1}$ and a shoulder on the high wavenumber side of the carbonyl absorption which is indicative of a small quantity of carboxylic acid. The band at 1418 $cm^{-1}$ falls within the range of the C-O- stretching of carboxylic acids, however, the band which should characteristically accompany it (a fairly intense band in the region of 1320 - 1211 $cm^{-1}$) is absent in the spermaceti wax spectrum. One of the bands in the region of 950 - 900 $cm^{-1}$ may be the result of O-H out of plane deformation in carboxylic acids (Bellamy, 1975).

### Carnauba wax

Source

Carnauba wax is obtained from the leaves of the palm *Copernicia cerifera* Mart. which is grown mainly in Brazil. The waxy coating is collected by shredding and beating the leaves which causes the wax to come off as a powder (Mills and White, 1987). This material is collected, melted with a small amount of water and poured into moulds. The resulting commercial product is the grey impure wax. The pure wax is almost colourless with a melting point range of 82 - 90 °C (Tooley, 1971). It is used in conservation mixed with beeswax to produce a harder product with a higher melting point for relining canvases and other uses. Carnauba wax is a major constituent of wax polishes and is often mixed with less expensive waxes such as paraffin (Mills and White, 1987).

Composition

The composition of carnauba is esters of long chain alcohols and acids with longer carbon chains than in beeswax. Thus, the materials are easily separated by gas chromatography. The substance also contains triterpenes and about 50% of the material is too involatile for analysis with gas chromatography (Mills and White, 1987). The composition determined by gas chromatography as given in the literature is listed in Table 4.4 (Tulloch, 1973). The volatile portion was reported as 47% with 11% free alcohols and 36% monoesters. After methylation, the composition was found to be 27% acids, 57% alcohols, 13% omega-hydroxy esters and 3% alpha,omega-diols (Tulloch, 1973). It has also been suggested that the involatile fraction contains hydroxyesters, p-hydroxy and p-methoxycinnamic acid diesters (Vandenburg and Wilder, 1970) although these were not detected by the gas chromatography (Tulloch, 1973).

### Interpretation of standard spectra

Spectra were obtained of grey and yellow carnauba wax obtained from commercial sources and yellow carnauba wax (*Copernicia prunifera*) from the Museum of Economic Botany, Kew. The spectra were extremely similar and the range of observed frequency values and assignments are listed in Table 4.5. A carnauba wax spectrum is given in Figure 4.6a (Kew sample *Copernicia prunifera*).

There is a rounded band with maximum intensity in the region of 3337 - 3354 $cm^{-1}$ which is due to the O-H groups in the alcohol present in the structure. There are bands in the region of 2925 - 2927 $cm^{-1}$ and 2852 - 2853 $cm^{-1}$ which correspond to the values given by Bellamy (1975) for C-H stretching vibrations. The spectrum also contains bands at 1470 and 1376 $cm^{-1}$ which fall within the ranges for C-H bending vibrations listed in Bellamy. There is a relatively strong absorption at 724 $cm^{-1}$ in the spectra that is due to the rocking vibration of the long aliphatic chains (Bellamy, 1975).

The spectra are characterized by strong absorptions in the ranges 1736 - 1737 $cm^{-1}$ and 1173 - 1174 $cm^{-1}$ which fall into the values quoted by Bellamy (1975) for aliphatic esters.

The carnauba wax spectra contain absorptions which indicate the presence of an aromatic ring. In the spectrum reported by Kuhn (1960), the bands fall at 1612, 1515 and 833 $cm^{-1}$. In the standard spectra reported in this thesis, the bands fall at 1633, 1606 - 1607, 1516 and 832 - 833 $cm^{-1}$. The band at 1633 $cm^{-1}$ is a shoulder on the band at 1606 $cm^{-1}$ corresponding to the band recorded at 1612 $cm^{-1}$ in the literature. The vibrations are due to skeletal ring breathing modes. The values listed by Bellamy (1975) are 1625 - 1575 $cm^{-1}$ (1650 - 1585 $cm^{-1}$ for para-substituted materials), 1600 - 1560 $cm^{-1}$, 1525 - 1475 $cm^{-1}$ and in the area of 1450 $cm^{-1}$. The band at 1450 $cm^{-1}$ is often masked in spectra of materials with methylene groups which also absorb in the region. The presence of aromatic compounds is also supported by absorptions in the region of 3030 - 3079 $cm^{-1}$ which are due to aromatic C-H stretching absorptions in these spectra. They are often masked by the strong aliphatic C-H vibrations. A shoulder can be seen at the left side of the C-H stretching absorptions which may result from the aromatic compounds.

## Identification of unknown sample

A sample of the material used for reconstruction of a copper alloy vessel rim (Bedford Museum 1712) was analysed (Figure 4.6b). The sample was removed from the object for analysis and rubbed against the silicon carbide paper. The sample contained a green colouring matter which lowered the baseline in the fingerprint region of the spectrum. However, it was possible to see evidence of a wax material. The presence of bands in the region of 2922, 2852, 1734, 1469, 1419, 1379, 1174 and 722 cm$^{-1}$ comfirmed the presence of a wax. The spectrum was not marked by the series of bands between 1330 and 1190 cm$^{-1}$, only two are visible at 1312 and 1243 cm$^{-1}$. Also, the spectrum exhibits bands at 1608 and 1588 cm$^{-1}$ which are indicative of aromatic compounds. The absence of the sharp bands in the region 1330 - 1190 may be the result of adulteration of the material with resin, but the bands due to the aromatic compounds are suggestive of carnauba wax. The presence of a broad band at 3341 cm$^{-1}$ which appears as a shoulder on bands centred at 2922 cm$^{-1}$ and the second carbonyl absorption at 1713 cm$^{-1}$ which is of equal intensity to the band at 1734 cm$^{-1}$ are characteristic of carboxylic acids which may result from a resin mixture.

## Candelilla wax

### Source

Candelilla wax is obtained from various species of the Euphorbia which grow in Mexico and the southern United States (Mills and White, 1987). The wax which coats the stems is obtained by boiling the plants in water and skimming the wax off the surface. The product is a brownish liquid which is poured into moulds to solidify, and is then broken up (Tooley, 1971).

The wax is used in conservation to harden other waxes without increasing the melting point (Mills and White, 1987).

### Composition

The composition of candelilla wax (Table 4.4) has been found by gas chromatography to be 41% hydrocarbons, 8% free acids, 4% free alcohols and 6% monoesters. After methylation, the composition was found to be primarily acids and alcohols. The non-hydrocarbon content increased by 50% after methylation which is thought to be due to acids and alcohols present in the nonvolatile fraction (Tulloch, 1973). The original nonvolatile portion was 37% and is thought to contain triterpenoid esters (Mills and White, 1987).

Identification of standard spectrum

The spectrum of candelilla wax (Figure 4.7) from Euphorbia cerifera contains a shoulder centred near 3350 cm$^{-1}$ which may be due to the O-H groups in the alcohol component. The spectrum exhibits bands at 2927 cm$^{-1}$ and 2852 cm$^{-1}$ which result from C-H stretching absorptions and bands at 1469 and 1381 cm$^{-1}$ which are due to C-H deformations. The spectrum is also characterized by an absorption at 724 cm$^{-1}$ which results from a rocking vibration of long aliphatic chains (Bellamy, 1975). The spectrum also contains strong evidence of the ester functional group with bands at 1736 and 1173 cm$^{-1}$. There is a second band of almost equal intensity in the carbonyl region (1714 cm$^{-1}$) which may be due to unionized carboxyl groups in the material. There are no distinct bands in the region 1330 - 1190 cm$^{-1}$, but a shoulder is observed which may be due to overlapping of bands in the region. There are weak bands at 1645 and 1606 cm$^{-1}$ which may indicate the presence of aromatic compounds, but there is no evidence of an absorption in the region of 1515 cm$^{-1}$. The frequency values and band assignments for candelilla wax are listed in Table 4.6.

### Paraffin wax

#### Source

Paraffin wax is obtained the distillation of petroleum, giving various grades which have melting point ranges between 52 and 57 °C.

#### Composition

Paraffin wax is composed entirely of hydrocarbons, most of which are long chain saturated compounds. The higher molecular weight fractions in paraffin have a tendency to crystallize out as very small crystals. This material is used to produce microcrystalline waxes (Mills and White, 1987).

#### Interpretation of standard spectra

The identification of pure paraffin wax is not difficult with infrared spectroscopy. The spectrum of the material is very simple as there is no oxygen in the structure. The spectrum shown in the literature (Kuhn, 1960) contains four absorptions at 2850, 1480, 1388 and 719 $cm^{-1}$. The sample spectra obtained in this study were very similar. A sample spectrum is given in Figure 4.8a and the observed frequency ranges are listed in Table 4.7. Difficulties in identification of paraffin wax arise when it in a mixture with other, more complex materials which make the spectrum more complicated and mask the presence of the mineral wax.

The paraffin wax spectra exhibit four bands in the regions of 2960 - 2961, 2935 - 2936, 2860 and 2833 - 2837 $cm^{-1}$ which are characteristic of C-H stretching vibrations. The spectra also contain bands at 1471 - 1472 $cm^{-1}$ and 1379 $cm^{-1}$ which are due to C-H deformations. The band located at 727 - 728 $cm^{-1}$ is the result of the rocking vibration of long aliphatic chains of 4 or more methylene units. The spectrum of commercial microcrystalline wax is very similar and contains bands at 2932, 2902, 2855, 1464, 1378 and 729 $cm^{-1}$.

Identification of unknown samples

A sample (MF2) was removed from a the coating of a modern, bronze cast figure of a cello player (Fitzwilliam Museum). The piece was suffering from corrosion in which white salts were appearing in sheltered areas. The surface was thought to have been varnished and then waxed and the salts seem to be coming up through the wax. The sample of the waxy coating was rubbed onto the silicon carbide paper and the resulting spectrum shows some evidence of specular reflectance as some of the strong absorptions come up past the base line of the spectrum (Figure 4.8b). However, it is still recognizable as paraffin wax as it is a simple spectrum with absorptions at 2936, 2860, 1475, 1378 and 732 $cm^{-1}$ which are characteristic of paraffin wax (Table 4.7). There is a doublet at 1197 and 1142 $cm^{-1}$ which is not characteristic of paraffin wax, but may result from minor impurities. These bands have been observed in some of the other reference spectra of commercial paraffin wax. There is no evidence in the spectra of the presence of varnish.

A spectrum was measured of a sample (MFA17) taken from the back of a model mummy mask (Boston Museum of Fine Arts 23-11-453/4). The sample was rubbed onto the silicon carbide paper and the diffuse reflectance spectrum was obtained. The spectrum (Figure 4.9a) contains strong bands at 2935, 2859, 1470, 1378 and 724 $cm^{-1}$ (Table 4.7). The spectrum also contains broad bands of weaker intensity with maximum intensity at 1721, 1647, 1109, 1044 and a very weak absorption at 891 $cm^{-1}$. This spectrum indicated a paraffin wax mixture. The sample was also examined with the infrared microscope and found to have two distinct areas, a transparent area and a dark yellow area. The spectrum of the white area alone was the distinctive simple one of paraffin wax. The spectrum of the yellow area contained the bands due to paraffin and other absorptions and the spectrum resembled that of the diffuse reflectance spectrum of the entire sample. The microscope investigation suggests that the paraffin and the yellow material are in layers. The yellow material has not been identified.

Spectral subtraction was utilized with the diffuse reflectance spectrum of sample MFA17 (Figure 4.9a). A diffuse reflectance spectrum of paraffin wax (BM20) was subtracted from the sample spectrum. The resulting difference spectrum, shown in Figure 4.9b, is not immediately suggestive of a particular class of compound. However, the rounded band centred at 3384 $cm^{-1}$, the weak band at 2122 $cm^{-1}$, the broad absorption at 1647 $cm^{-1}$, the broad band with maximum intensities at 1109 and 1040 $cm^{-1}$ and the weak band at 912 $cm^{-1}$ are suggestive of a gum or gum resin (see Chapter 7).

A sample (MFA12) from the back of a New Kingdom mummy mask (Boston Museum of Fine Arts 23.1475) was rubbed onto silicon carbide paper and the spectrum was obtained. The resulting diffuse reflectance spectrum was very similar to that of sample MFA17 which was discussed above. The spectrum is marked by absorptions at 2931, 2898, 2857, 1469, 1377 and 723 $cm^{-1}$ which are characteristic of the paraffin wax. The spectrum also contains a broad, rounded absorption centred at 3354 $cm^{-1}$, a weak absorption at 2135 $cm^{-1}$, a band at 1431 $cm^{-1}$ and a broad absorption in the region 1200 - 980 $cm^{-1}$ with maximum absorptions at 1115 and 1048 $cm^{-1}$. A weak band is observed at 895 $cm^{-1}$. These bands are characteristic of plant gums which are described in chapter 7. The paraffin wax is a later treatment as it was not available to the ancient Egyptians. The gum, however, may be ancient or modern. The similarity of this spectrum to the one of sample MFA17 indicates that it may reflect a similar early conservation treatment.

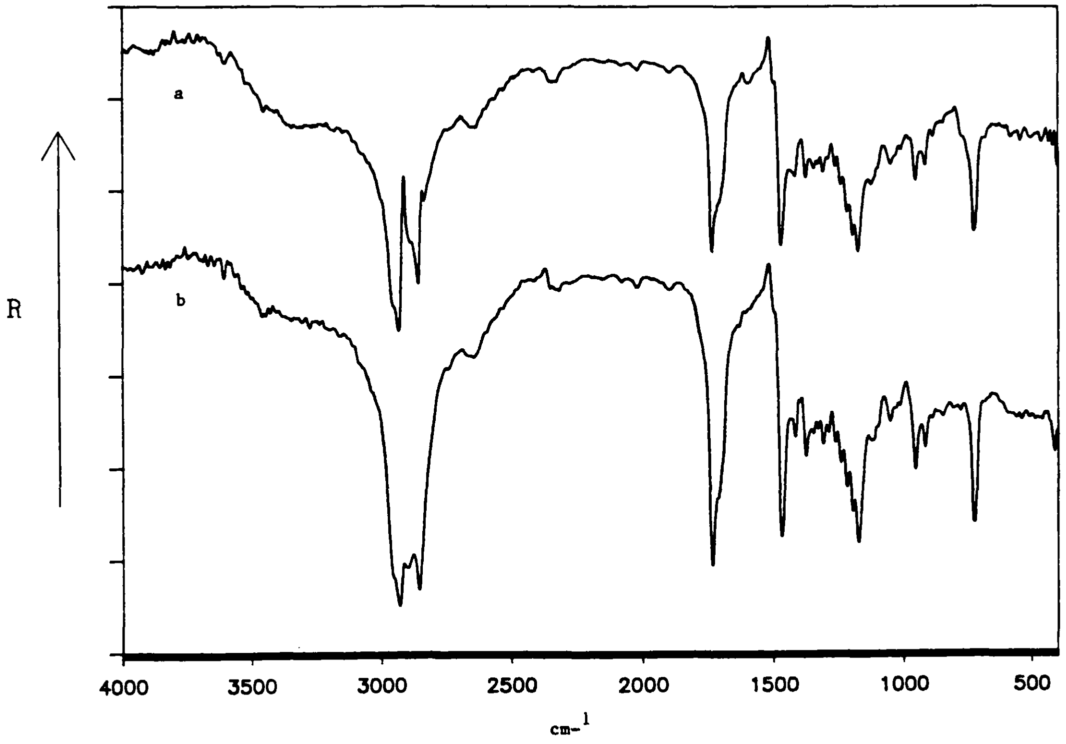


Figure 4.1 Diffuse reflectance FT-IR spectra of (a) beeswax (Apis mellifera) from an abandoned comb which was bleached in the sun (NHM19 gsva0318) and (b) a sample from an Egyptian figurine (mfa12, Boston Museum of Fine Arts 72.4783)

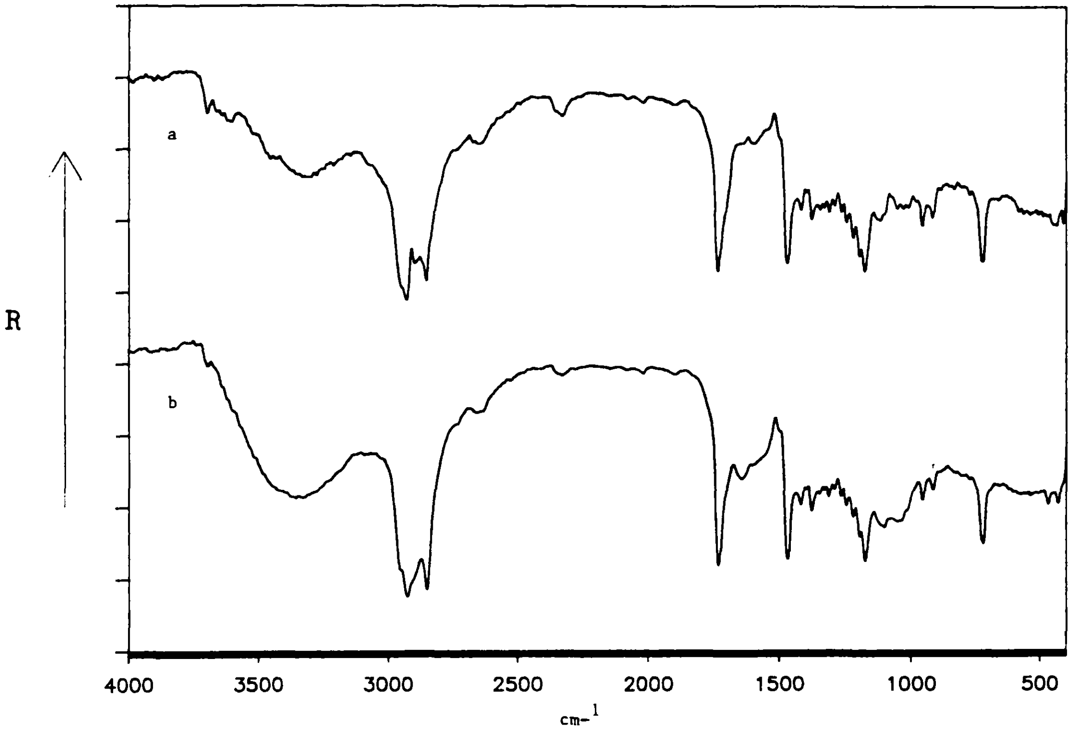


Figure 4.2 Diffuse reflectance FT-IR spectra of a wax sample (NJS8) from the site of a metal caster's workshop in Kandy, Sri Lanka, (a) interior material (gsva0233) and (b) crust (gsva0235).

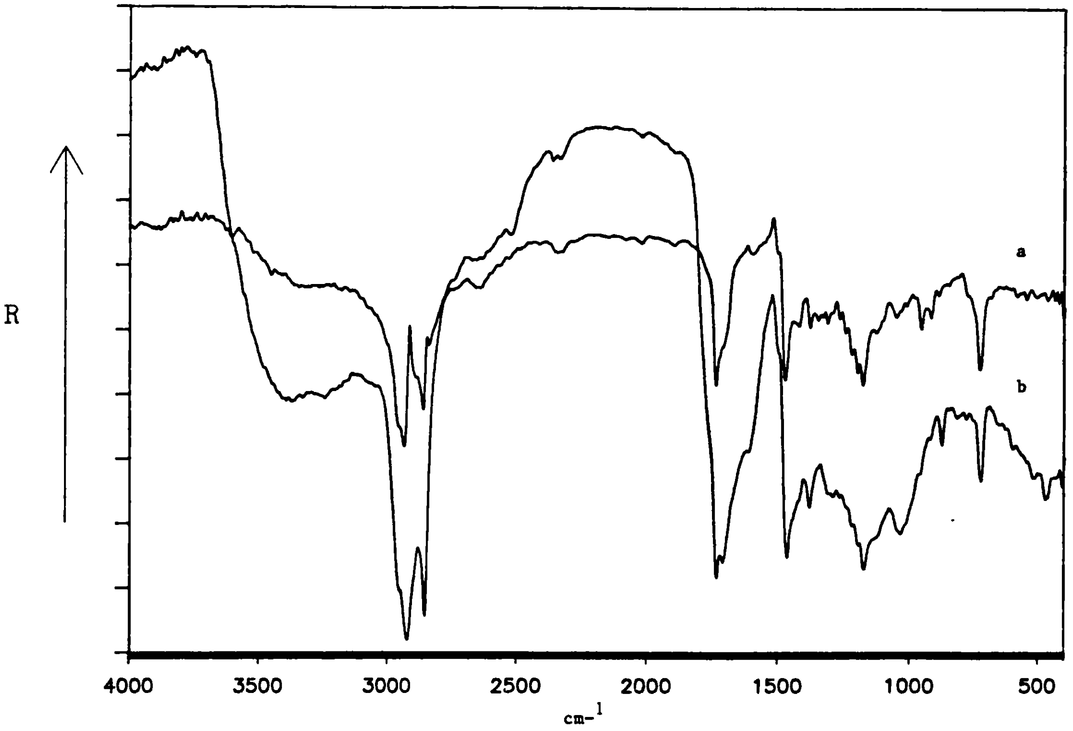


Figure 4.3 Diffuse reflectance FT-IR spectra of (a) coating sample taken from the outside of mummy Nesmin (mfa1)(Rhode Island School of Design) and (b) beeswax (Apis mellifera) (see Figure 4.1a).

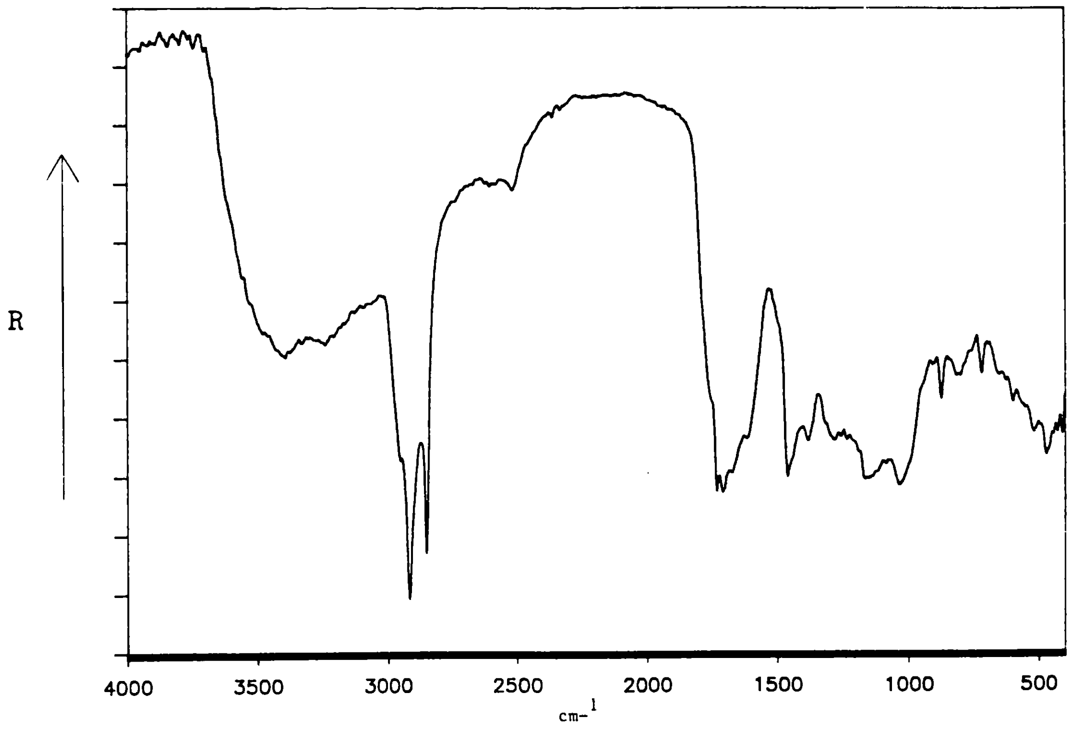


Figure 4.4 Diffuse reflectance FT-IR difference spectrum of Figure 4.3a minus Figure 4.3b obtained using interactive difference function (gsva0625).

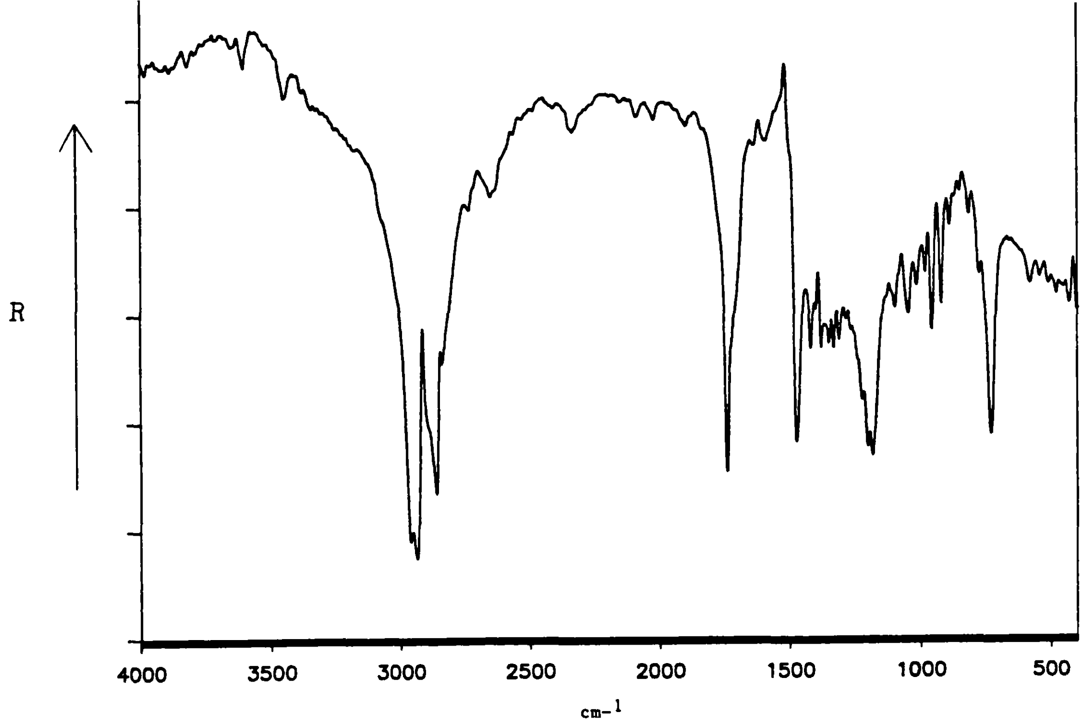


Figure 4.5 Diffuse reflectance FT-IR spectrum of spermaceti wax (BM9) (gsva0166).

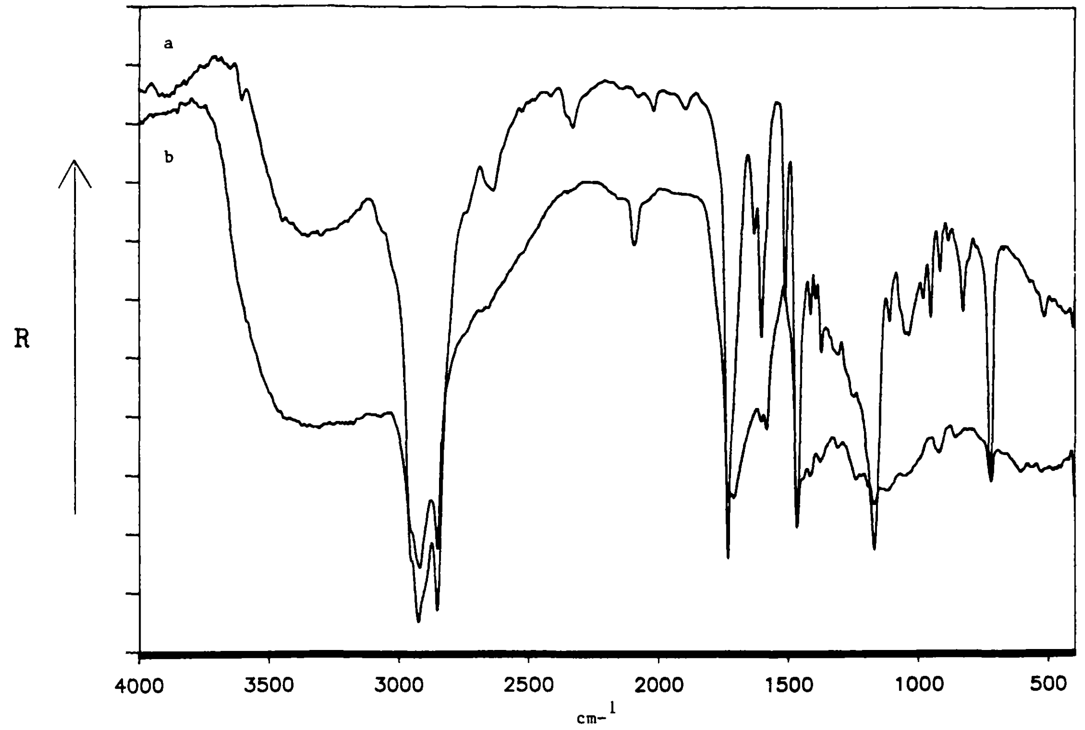


Figure 4.6 Diffuse reflectance FT-IR spectra of (a) carnauba wax (Copernicia prunifera) (Kew26 Museum of Economic Botany, Kew) (gsva0197) and (b) reconstruction material from a copper alloy vessel rim (MF4 Bedford Museum 1712) (gsva0244).

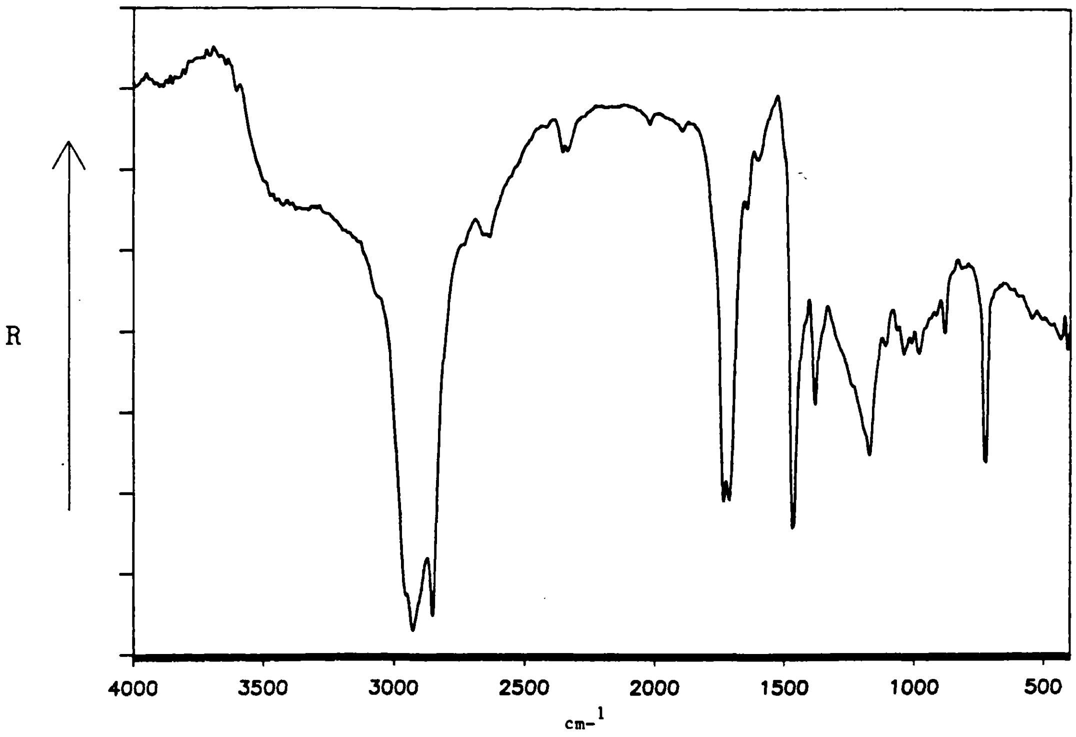


Figure 4.7 Diffuse reflectance FT-IR spectrum of candelilla wax (Euphorbia cerifera) (Kew 27, Museum of Econimic Botany, Kew) (gsva0198).

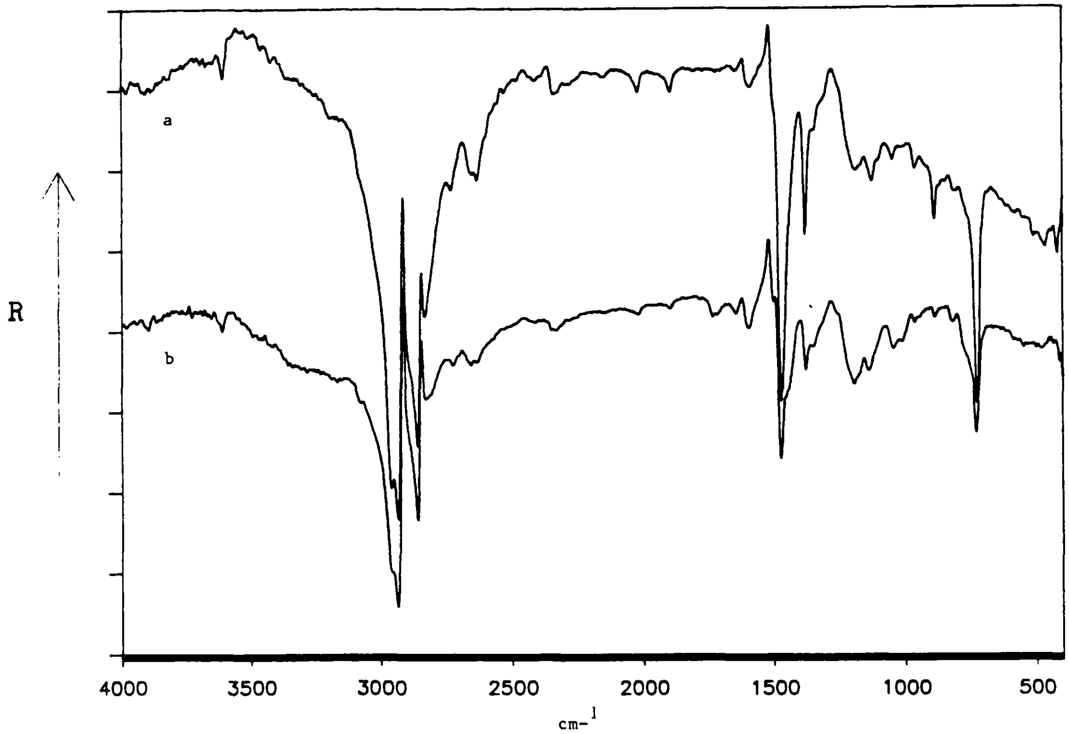


Figure 4.8 Diffuse reflectance FT-IR spectra of (a) paraffin wax (BM20 BDH) (gsva0183) and (b) wax coating from a figure of a cello player (MF2 Fitzwilliam Museum).

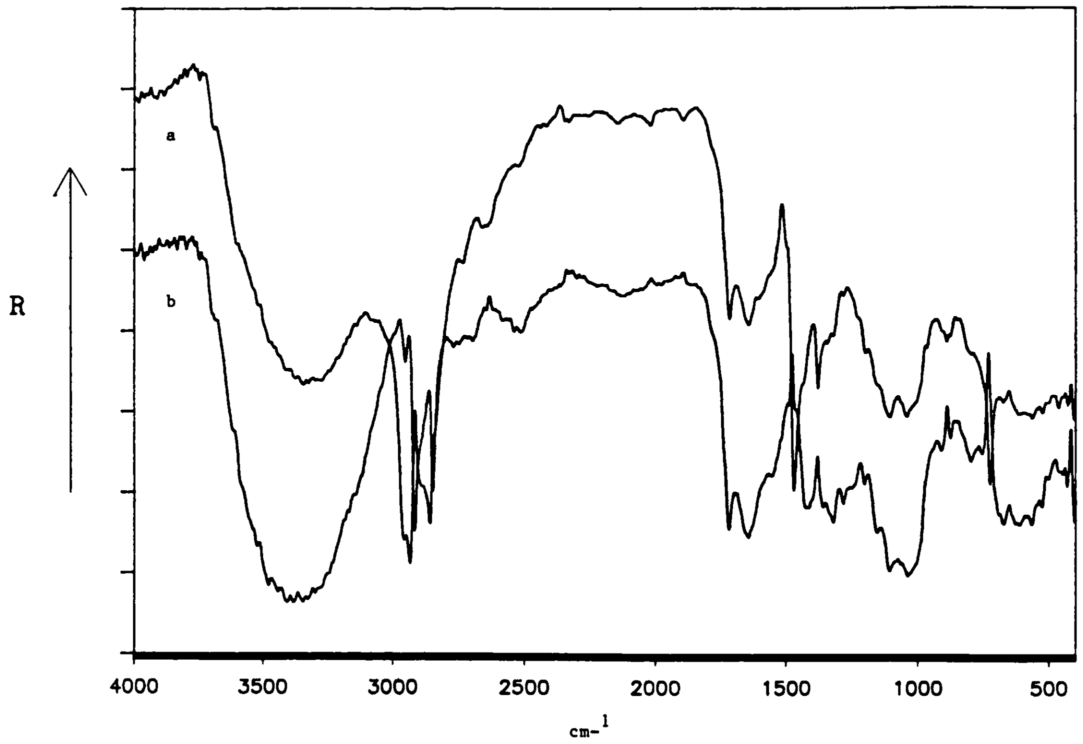


Figure 4.9 Diffuse reflectance FT-IR spectrum of (a) material from the back of a model mummy mask (mfa17, Boston Museum of Fine Arts 23-11-453/4) and (b) the difference spectrum of Figure 4.9a minus Figure 4.8a obtained using the interactive difference function.

Table 4.1

Composition of beeswax (Tulloch, 1971)

| Component | | Percent by weight |
|---|---|---|
| Hydrocarbons | | 14.0 |
| Monoesters | | 34.7 |
| Diesters | | 13.7 |
| Triesters | | 3.3 |
| Hydroxy monoesters | | 3. |
| Hydroxy polyesters | | 7.7 |
| Free acids | | 11.9 |
| Acid monoesters | | 0.8 |
| Acid polyesters | | 1.7 |
| Unidentified | Recovered from column | 2.1 |
| | Not recovered from column | 6.5 |

Table 4.4

Composition of carnauba and candelilla waxes
(Tulloch, 1973)

| Components | Wax<br>Carnauba<br>(%) | Candelilla<br>(%) |
|---|---|---|
| Hydrocarbons | -- | 41 |
| Free acids | -- | 8 |
| Free alcohols | 11 | 4 |
| Monoesters | 36 | 6 |
| Hydroxy esters | -- | -- |
| Unidentified * | -- | 6(2) |
| Total volatile | 47 | 65 |

* Number of components in parentheses.

TABLE 4.2

Frequency values and band assignments for beeswax and unknowns identified as beeswax

| Reference samples cm-1 | Trigona sample cm-1 | Unknown samples beeswax cm-1 | Unknown samples mixtures cm-1 | Vibration | Functional group | Frequency range given in literature cm-1 | Ref. |
|---|---|---|---|---|---|---|---|
| 3345 - 3310(sh) | 3435(m) | 3461 - 3277(sh) | 3375 - 3323(m) | O-H stretch | alcohol | 3450 | 1 |
| 2935 - 2932(s) | 2921(s) | 2933 - 2924(s) | 2935 - 2922(s) | C-H stretch | methyl, methylene and methine groups | 2850 | 1 |
|  |  |  |  | C-H stretch | methylene groups | 2926 ± 10(s) | 2 |
| * 2904 - 2894(va) |  | 2904 - 2899(va) |  | C-H stretch | methine groups | 2890 ± 10(w) | 2 |
| 2859 - 2856(s) | 2851(s) | 2857 - 2852(s) | 2860 - 2852(s) | C-H stretch | methylene groups | 2853 ± 10(s) | 2 |
| 1741 - 1736(s) | 1735(s) | 1739 - 1737(s) | 1739 - 1736(s) | C=O stretch | ester | 1730 | 1 |
|  |  |  |  | C=O stretch | ester | 1750 - 1730(s) | 2 |
| ** nr 1710(vw sh) | near 1710(sh) | ** nr 1710(vw sh) | **1713(s) | C=O stretch | carboxylic acids non-ionized | 1709 | 1 |
|  |  |  |  | C=O stretch | carboxylic acids non-ionized | 1725 - 1700(s) | 2 |
| 1474 - 1470(s) | 1463(s) | 1472 - 1470(s) | 1477 - 1464(s) | C-H deformation | methyl and methylene groups | 1470 | 1 |
|  |  |  |  | C-H asym. deformation | methyl groups | 1450 ± 20(m) | 2 |
|  |  |  |  | C-H deformation | methylene groups | 1465 ± 20(m) | 2 |
| 1420 - 1418(w) | near 1420(w) | 1420 - 1418(w) |  | C-H deformation | methylene group next to carboxylic acid | 1410 - 1405 | 4,5 |
| 1379 - 1377(w) | 1383(s) | 1378 - 1377(w) | 1379 - 1377(w) | C-H deformation | methyl groups | 1388 | 1 |
|  |  |  |  | C-H sym. deformation | methyl groups | 1380 - 1370(s) | 2 |

TABLE 4.2 contd.

Frequency values and band assignments for beeswax and unknowns identified as beeswax

| Reference samples cm-1 | Trigona sample cm-1 | Unknown samples beeswax cm-1 | Unknown samples mixtures cm-1 | Vibration | Functional group | Frequency range given in literature cm-1 | Ref. |
|---|---|---|---|---|---|---|---|
| near 1347(w) | | * 1348 - 1347(w) | | unassigned | solid samples | 1333 - 1190 | 1 |
| 1331 - 1330(w) | | 1332 - 1331(w) | 1325 - 1312(w) | C-H 'wagging and twisting'vibrations | methylene groups in fatty acids | 1350 - 1180 | |
| 1312 - 1311(w) | near 1285(sh) | 1292 - 1290(w) | 1291 - 1290(w) | | | band progression series of weak evenly spaced bands | 3 |
| near 1267(w) | | 1267 - 1266(w) | near 1266(sh) | | | | |
| 1246 - 1245(w) | near 1240(sh) | 1246 - 1244(w) | near 1244(sh) | | | | |
| near 1221(w) | | 1221 - 1220(w) | near 1220(sh) | | | | |
| 1198 - 1197(w) | | 1198 - 1197(w) | near 1197(sh) | | | | |
| 1179 - 1176(s) | 1176(s) | 1178 - 1176(s) | 1176 - 1173(s) | C-O stretch | ester | 1177 | 1 |
| | | | | C-O stretch | ester | 1200 - 1150(s) | 2 |
| 1056 - 1053(w) | 1046(m) | 1055 - 1052(va) | 1052 - 1036(va) | unassigned | | | |
| 959 - 958(m) | near 965(vw) | 959 - 957(m) | * 958(va) | unassigned | solid samples | 962 | 1 |
| 922 - 921(m) | near 925(vw) | 922 - 920(m) | * 920(va) | unassigned | solid samples | 918 | 1 |
| 891 - 866(w) | near 890(sh) | | | unassigned | solid samples | 890 | 1 |
| 729 - 722(s) | 724(s) | 726 - 723(s) | 729 - 722(s) | chain vibration | long chain hydrocarbons | 730 | 1 |
| | | | | | | 719 | 1 |
| | | | | chain rocking vibration | long chain hydrocarbons with four or more methylene groups | 750 - 720(m) | 2 |

* Absorption is weak or occurs as a shoulder in some spectra.
** Absorption is not apparent in some spectra.

1. Kuhn, 1960
2. Bellamy, 1975
3. Jones et al., 1952
4. Sinclair et al., 1952a
5. Sinclair et al., 1952b

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp; nr = near

## TABLE 4.3

Frequency values and band assignments for spermaceti wax

| Spermaceti wax cm-1 | Vibration | Functional group | Frequency range given in literature cm-1 | Ref. |
|---|---|---|---|---|
| near 3450(vw sh) | O-H stretch | alcohol (polymeric) | 3400 - 3200(vs,b) hydrogen bonded | 1 |
| | | carboxylic acid hydrogen bonded | 3000 - 2500(b) | 1 |
| 2960(s) | C-H stretch | methyl group | 2962 ± 10(s) | 1 |
| 2935(s) | C-H stretch | methylene group | 2926 ± 10(s) | 1 |
| 2860(s) | C-H stretch | methyl group | 2872 ± 10(s) | 1 |
| | | methylene group | 2853 ± 10(s) | 1 |
| 2838(s) | C-H stretch | methylene group | 2853 ± 10(s) | 1 |
| 2650(w) | O-H stretch | carboxylic acid hydrogen bonded | near 2650(w) | 1 |
| 1741(s) | C=O stretch | ester | 1750 - 1730(s) | 1 |
| near 1700(sh) | C=O stretch | carboxylic acid | 1725 - 1700(s) | 1 |
| 1474(s) | C-H asym. deformation | methyl group | 1450 ± 20(m) | 1 |
| | C-H deformation | methylene group | 1465 ± 20(m) | 1 |
| 1418(w) | C-O stretch or O-H deformation | carboxylic acid | 1440 - 1395(w) | 1 |
| 1378(w) | C-H sym. deformation | methyl group | 1380 - 1370(s) | 1 |
| 1348(w)<br>1330(w)<br>1309(w)<br>1284(w)<br>1223(w)<br>1202(s) | C-H 'wagging and twisting' vibrations | methylene groups in fatty acids | 1350 - 1180 band progression series of weak evenly spaced bands | 2 |
| 1184(s) | C-O stretch | ester | 1200 - 1150(s) | 1 |
| 1099(w) | unassigned | | | |
| 1048(w) | unassigned | | | |
| 984(w) | unassigned | | | |
| 958(m) | unassigned | | | |
| 922(m) | O-H out-of-plane deformation | carboxylic acid | 950 - 900(va) | 1 |
| 890(w) | unassigned | | | |
| 851(w) | unassigned | | | |
| 816(w) | unassigned | | | |
| 776(w) | unassigned | | | |
| 730(s) | chain rocking vibration | long chain hydrocarbon with four or more methylene units | 750 - 720(m) | 1 |

1. Bellamy, 1975
2. Jones et al., 1952

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; s

(TABLE 4.4 see page 202)

TABLE 4.5

Frequency values and band assignments for carnauba wax and unknown sample identified as carnauba wax

| VA1 cm-1 | BM22 cm-1 | Kew26 cm-1 | MF4 unknown cm-1 | Vibration | Functional group | Frequency range given in literature cm-1 | Ref. |
|---|---|---|---|---|---|---|---|
| 3337(m,b) | 3354(m,b) | 3353(m,b) | 3341(m,sh) | O-H stretch | alcohol (polymeric) | 3400 - 3200(vs,b) hydrogen bonded | 1 |
|  |  |  |  | O-H stretch | carboxylic acid | 3000 - 2500(b) | 1 |
| 2927(s) | 2925(s) | 2927(s) | 2922(s) | C-H stretch | methylene group | 2926 ± 10(s) | 1 |
| 2852(s) | 2852(s) | 2853(s) | 2852(s) | C-H stretch | methylene group | 2853 ± 10(s) | 1 |
| 2642(w) | 2641(w) | 2637(w) | near 2600(vwsh) | O-H stretch | carboxylic acid | near 2650(w) | 1 |
| 1737(s) | 1736(s) | 1736(s) | 1734(s) | C=O stretch | ester | 1750 - 1730(s) | 1 |
| near 1700(sh) | near 1700(sh) | near 1700(sh) | 1713(s) | C=O stretch | carboxylic acid | 1725 - 1700(s) | 1 |
| 1633(w) | 1633(w) | 1633(w) |  | skeletal ring stretch | aromatic ring | 1625 - 1575(va) | 1 |
| 1607(m) | 1606(s) | 1606(s) | 1608(w)<br>1588(w) | skeletal ring stretch | aromatic ring | 1600 - 1560(w unless conjugated) | 1 |
|  |  |  |  | skeletal ring stretch | aromatic ring | 1612 | 2 |
| 1516(m) | 1516(s) | 1516(s) |  | skeletal ring stretch | aromatic ring | 1525 - 1475(va)<br>1515 | 1<br>2 |
| 1470(s) | 1470(s) | 1470(s) | 1469(s) | C-H asym. deformation | methyl group | 1450 ± 20(m) | 1 |
|  |  |  |  | C-H deformation | methylene group | 1465 ± 20(m) | 1 |
| 1417(w) | 1417(w) | 1417(w) | 1419(w) | C-O stretch or O-H deformation | carboxylic acid | 1440 - 1395(w) | 1 |
| 1397(vw) | 1396(w) | 1397(w) |  | unassigned |  |  |  |
| 1376(w) | 1376(w) | 1376(w) | 1379(w) | C-H sym. deformation | methyl group | 1380 - 1370(s) | 1 |
| 1316(w) | 1316(w) | 1310(w) | 1312(w) | unassigned |  |  |  |
|  |  |  | 1243(w) | unassigned |  |  |  |
| 1174(s) | 1173(s) | 1173(s) | 1174(s) | C-O stretch | ester | 1200 - 1150(s) | 1 |

TABLE 4.5 contd.

Frequency values and band assignments for carnauba wax and unknown sample identified as carnauba wax

| VA1<br>cm-1 | BM22<br>cm-1 | Kew26<br>cm-1 | MF4 unknown<br>cm-1 | Vibration | Functional group | Frequency range given in literature<br>cm-1 | Ref. |
|---|---|---|---|---|---|---|---|
| 1115(w) | 1114(w) | 1115(w) |  | unassigned |  |  |  |
| 1040(m) | 1040(m) | 1041(m) |  | unassigned |  |  |  |
| 957(m) | 957(m) | 957(m) |  | unassigned |  |  |  |
| 921(w) | 922(w) | 921(w) | 924(w) | O-H out-of-plane deformation | carboxylic acid | 950 - 900(va) | 1 |
| 888(w) | 888(w) | 889(w) | 864(w) | C-H out-of-plane deformation | aromatic ring | 900 - 860(m) one free H atom | 1 |
| 833(m) | 832(m) | 832(m) |  | C-H out-of-plane deformation | aromatic ring | 860 - 800(vs) para-substitution | 1 |
|  |  |  |  | C-H out-of-plane deformation | aromatic ring | 833 | 2 |
| 724(s) | 724(s) | 724(s) | 722(s) | chain rocking vibration | long chain hydrocarbons with four or more methylene units | 750 - 720(m) | 1 |

1. Bellamy, 1975
2. Kuhn, 1960

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp

## TABLE 4.6

Frequency values and band assignments for candelilla wax

| Kew27<br>cm-1 | Vibration | Functional group | Frequency range given in literature (1)<br>cm-1 |
|---|---|---|---|
| near 3350(m sh) | O-H stretch | alcohol (polymeric) | 3400 - 3200(vs,b) hydrogen bonded |
|  | O-H stretch | carboxylic acid hydrogen bonded | 3000 - 2500(b) |
| 2927(s) | C-H stretch | methylene group | 2926 ± 10(s) |
| 2852(s) | C-H stretch | methylene group | 2853 ± 10(s) |
| 2636(w) | O-H stretch | carboxylic acid hydrogen bonded | near 2650(w) |
| 1736(s) | C=O stretch | ester | 1750 - 1730(s) |
| 1714(s) | C=O stretch | carboxylic acid | 1725 - 1700(s) |
| 1645(s) | skeletal ring stretch | aromatic ring | 1625 - 1575(va) |
| 1606(w) | skeletal ring stretch | aromatic ring | 1600 - 1560(w unless conjugated) |
| 1469(s) | C-H asym. deformation | methyl group | 1450 ± 20(m) |
|  | C-H deformation | methylene group | 1465 ± 20(m) |
| near 1400(w sh) | C-O stretch or O-H deformation | carboxylic acid | 1440 - 1395(w) |
| 1381(s) | C-H sym. deformation | methyl group | 1380 - 1370(s) |
| 1173(s) | C-O stretch | ester | 1200 - 1150(s) |
| 1112(w) | unassigned |  |  |
| 1042(w) | unassigned |  |  |
| 985(w) | unassigned |  |  |
| near 900(vw) | O-H out-of-plane deformation | carboxylic acid | 950 - 900(va) |
| 885(w) | C-H out-of-plane deformation | aromatic ring | 900 - 860(m) one free H atom |
| near 830(vw) | C-H out-of-plane deformation | aromatic ring | 860 - 800(vs) para-substitution |
| 724(s) | chain rocking vibration | long chain hydrocarbon with four or more methylene units | 750 - 720(m) |

1. Bellamy, 1975

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder;
b = broad; va = variable; sp = sharp

## TABLE 4.7

Frequency values and band assignments for paraffin wax and samples identified as paraffin wax

| Paraffin wax | Microcrytalline wax | Unknown MF2 | Unknown MFA12 | Unknown MFA17 | Vibration | Functional group | **Frequency range given in literature (1)** |
|---|---|---|---|---|---|---|---|
| cm-1 | cm-1 | cm-1 | cm-1 | cm-1 | | | **cm-1** |
| 2961 - 2960(s) | | | | | C-H stretch | **methyl group** | **2962 ± 10(s)** |
| 2936 - 2935(s) | 2932(s) | 2936(s) | 2931(s) | 2935(s) | C-H stretch | **methylene group** | **2926 ± 10(s)** |
| | 2902(s) | | 2898(s) | | C-H stretch | **methine group** | **2890 ± 10(w)** |
| 2860(s) | 2855(s) | 2860(s) | 2857(s) | 2859(s) | C-H stretch | **methyl group** | **2872 ± 10(s)** |
| 2837 - 2833(s) | | | | | C-H stretch | **methylene group** | **2853 ± 10(s)** |
| 1472 - 1471(s) | 1464(s) | 1475(s) | 1469(s) | 1470(s) | C-H asym. deformation | **methyl group** | **1450 ± 20(m)** |
| | | | | | C-H deformation | **methylene group** | **1465 ± 20(m)** |
| 1379(s) | 1378(s) | 1378(m) | 1377(m) | 1378(m) | C-H sym. deformation | **methyl group** | **1380 -1370(s)** |
| 728 - 727(s) | 729(s) | 732(s) | 723(s) | 724(s) | chain rocking vibration | **long chain hydrocarbon with four or more methylene units** | **750 - 720(m)** |

1. Bellamy, 1975

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; **b = broad; va = variable; sp = sharp**

# CHAPTER 5 FATS AND OILS

## Source

Fats are classified as lipids (Tooley, 1971). Fats have been utilized by man since early times and sources include animal fat tissue (tallow) and various vegetable sources such as olives and nuts (Mills and White, 1987; Tooley, 1971).

## Composition

### Unaltered fats and oils

True fats or glyceryl esters of fatty acids are the principle components of fats and oils. Fatty acids are long chain carboxylic acids. Some fatty acids are completely saturated which means there are no C=C bonds in the structure and some other structures contain one or more double bonds. The structure of glycerol is given in Figure 5.1a. It is an alcohol with three hydroxyl groups (trihydric) and it may be mono-, di- or tri-substituted with fatty acids containing one carboxyl group. Fats and oils which have not undergone degradation contain tri-substituted esters only. The triglycerides may be substituted with the same kind of fatty acid. These materials are refered to as simple triglycerides (Figure 5.1b). However, most triglycerides from natural sources are mixed glycerides or esters with more than one type of fatty acid substituent. Oils are similar in basic structure, but are liquids at room temperature. The melting point is affected by the molecular weight of the fatty acids and the degree of saturation. For example, fats from vegetable sources are composed mainly of unsaturated fatty acids and have lower melting points than animal fat which consists primarily of saturated fatty acids (Tooley, 1971; Mills and White, 1987).

The majority of fatty acid esters are composed of only a few of the large number of fatty acids which are known to occur in fats. The important fatty acids are stearic, oleic and the other compounds composed of 18 carbon atoms. The common fatty acids are listed in Table 5.1. Natural products are made up of mixtures of the various triglycerides. The structures are very complex and have not been fully elucidated. Gas chromatography is not ideal as the triglycerides have a high molecular weight and low volatility. Most analyses are based on the fatty acid content which may be measured after the saponification or hydrolysis of the ester linkages. The composition for each type of oil is variable and is affected by such factors as the species of plant, soil environment and the climatic conditions. A table

(Table 5.2) (Mills and White, 1987) has been compiled of the ranges of fatty acid composition which have been obtained using gas chromatography which is the most reliable method. As mentioned earlier, only a few important fatty acid structures are incorporated into the structures and the differentiations are based on quantitative measurements (Mills and White, 1987).

### Effects of ageing

The ester linkages in fats and oils are susceptible to cleavage. The mechanism is the hydrolysis of the bonds which produces glycerol and free fatty acids. Archaeological specimens of fat or oils have often been found to consist entirely of the free fatty acids. The glycerol seems to be removed by water. The reaction may be caused by water over a long period of time although it may also be due to bacteria (Mills and White, 1987).

## **Identification and interpretation of standard spectra**

### Standard sample information

The principal method of analysis for fats is gas chromatography of the fatty acid content after hydrolysis or saponification of the ester linkages and methylation of the esters. The great similarity in composition of the materials makes their differentiation by infrared spectroscopy unlikely. For this thesis, transmission spectra of two types of olive oil and four kinds of seed oil were measured at high resolution (2 $cm^{-1}$) to determine if any differentiation might be made. A sample of lamb suet was analyzed as a solid utilizing diffuse reflectance spectroscopy. The fat was not examined until two weeks after it was obtained and although it was kept refrigerated, there is some evidence of decomposition in the spectrum. This is not unexpected and it was desirable to obtain the spectrum of degradation products as that is what is examined in archaeological specimens. Also, spectra were obtained of four fatty acids: oleic (transmission), myristic, palmitic and stearic acids (diffuse reflectance).

### Vegetable and seed oils

The spectra of the six oils were found to be extremely similar (Figure 5.2). Only very minor variations are visible in the region 1150 - 800 $cm^{-1}$. In the spectra of safflower oil (GS10), grapeseed oil (GS11) and walnut oil (GS12), there is a relatively weak band at 1100 $cm^{-1}$ with a less intense band which occurs in the region of 1120 $cm^{-1}$ as a shoulder on the strong band at 1163 - 1164 $cm^{-1}$. The band near 1120 $cm^{-1}$ is slightly more intense than the band at 1100 $cm^{-1}$ in the spectra of the two olive oils (GS9 and GS14) and the hazelnut oil (GS13). There is a minor band in the region of 915 $cm^{-1}$ in the spectra of the safflower, grapeseed and walnut oils which is not apparent in the other three materials.

The remaining bands in the spectra may be assigned to characteristic groups in triglycerides (Table 5.3). The spectra are characterized by bands in the regions of 2926 - 2925 $cm^{-1}$ (with a shoulder in the region of 2954 $cm^{-1}$), 2855 - 2854 $cm^{-1}$, 1466 and 1378 $cm^{-1}$ which are indicative of C-H stretching and bending vibrations. The values listed in the literature (Sinclair et al., 1952a) for saturated and monounsaturated fatty acids are 2920 and 2850 $cm^{-1}$ assigned to the C-H stretches in methylene groups with weaker bands near 2960 and 2870 $cm^{-1}$ which are assigned to the methyl group absorptions. The intensity of the methyl group bands increases in relation to those of the methylene groups in the spectra of materials with higher numbers of double bonds. The band in the region of 2870 $cm^{-1}$ is not evident in the spectra of the vegetable oils. The spectra of the oils are also marked by absorptions in the range 724 - 723 $cm^{-1}$ which correspond to values quoted in the literature for the rocking vibration which occurs in aliphatic hydrocarbon chains longer than four units, 750 - 720 $cm^{-1}$ (Bellamy, 1975). The values of 720 $cm^{-1}$ (Sinclair et al., 1952a; Sinclair et al., 1952b) and 719 $cm^{-1}$ (Shreve et al., 1950) have been given for the fatty acids, methyl esters of fatty acids and the triglycerides which were studied.

The spectra of unsaturated materials exhibit characteristic absorptions which are due to the double bond. The regions include the ethylenic C-H stretch which falls in the area 3100 - 3000 $cm^{-1}$, the C=C stretch which absorbs in the region 1580 - 1650 $cm^{-1}$ and the out-of-plane deformations of the =C-H bond which occur in the regions near 980 and 690 $cm^{-1}$ (Sinclair et al., 1952b). The oil standard spectra are characterized by absorptions in the region 3009 - 3005 $cm^{-1}$ which are assigned to the C-H stretch on the double bond carbons. The values given in the literature for fatty acids are 3020 $cm^{-1}$ (Sinclair et al., 1952b) and near 3030 $cm^{-1}$ (Shreve et al., 1950). The spectra of the oils contain a very weak absorption in the region 1657 - 1656 $cm^{-1}$ and several contain a second weak band at 1650 $cm^{-1}$. These bands may be representative of the C=C stretches, but, there is evidence of water in the spectra which is thought to be from the KBr plates used to hold the sample and it is difficult to say whether the bands are due to water or the sample. The literature reports that the band attributed to the C=C bond occurs as an unresolved shoulder at 1660 $cm^{-1}$ which occurs on the band near 1708 $cm^{-1}$ in the spectra of unsaturated fatty acids (Sinclair et al., 1952b). There are no strong bands in the region 980 - 690 $cm^{-1}$ except for the band in the region of 723 $cm^{-1}$. However, the band near 723 $cm^{-1}$ exhibits a broad shoulder on the right side which ends around 670 $cm^{-1}$. This may correspond to the presence of a cis-substituted double bond structure. Trans-substituted unsaturated fatty acids are characterized by a fairly strong absorption in the region 980 - 965 $cm^{-1}$ (Sinclair et al., 1952b) and small amounts of trans-structures may result in a weak band in this region. A very weak band is observed near 970 $cm^{-1}$ in the spectra of the vegetable oils. Unsaturated structures also effect the region between 1460 - 1400 $cm^{-1}$. The literature reports the presence of a band in the region of 1405 - 1410 $cm^{-1}$ in both saturated and unsaturated fatty acids which is thought to be due to the methylene group next to the carboxyl functional group (Sinclair et al., 1952a; Sinclair et al., 1952b). A second band which is attributed to the methylene group in the immediate vicinity of the C=C bond is located in the region of 1435 $cm^{-1}$ in the unsaturated fatty acid spectra (Sinclair et al., 1952a). The intensity of the band was observed to increase as the number of double bonds increase. The vegetable oils, which are predominantly composed of triglycerides, have ester functional groups instead of carboxyl groups which may result in the appearance of the band in the region of 1405 - 1410 $cm^{-1}$. In the oil spectra, two very weak bands occur in the region of 1430 $cm^{-1}$ which occurs as a shoulder on the band at 1466 $cm^{-1}$ and near 1417 $cm^{-1}$.

The spectra of the vegetable oils are characterized by bands which result from the ester linkages. The frequencies of several triglycerides have been reported (Shreve et al., 1950). The values for the C=O stretch fall into the range 1751 - 1748 $cm^{-1}$. The region 1250 - 1100 $cm^{-1}$ is characteristic of triglycerides and thought to be related to the C-O stretching vibration in the ester functional group. The region is marked by a strong absorption near 1163 $cm^{-1}$ with less intense absorptions near 1250 and 1111 $cm^{-1}$. In the spectra which are presented (Shreve et al., 1950), those of the unsaturated tri-elaidon and tri-olein exhibited patterns which consist of a strong band near 1163 $cm^{-1}$

and one at 1236 and 1239 $cm^{-1}$ respectively. However, instead of one absorption at 1111 $cm^{-1}$ which is evident in the two spectra of the triglycerides composed of saturated fatty acids (trimyristin and tripalmitostearin), the spectra of the trielaidon and tri-olein exhibit two bands at 1121 $cm^{-1}$ and 1101 - 1099 $cm^{-1}$ (Shreve et al., 1950). This pattern is evident in the spectra of the oils examined in this thesis where bands occur in the ranges 1239 - 1238 $cm^{-1}$, 1164 - 1163 $cm^{-1}$, 1100 - 1097 $cm^{-1}$ and a band in the region 1120 - 1119 $cm^{-1}$ which is very weak in three of the spectra which were discussed earlier. The oil spectra also exhibit a very strong band in the region of 1747 - 1746 $cm^{-1}$ which is only slightly beyond that given in the literature for triglycerides (Shreve et al., 1950).

### Lamb suet

The spectrum of the lamb suet (Figure 5.3) is marked by absorptions at 2940 $cm^{-1}$ with a shoulder in the region of 2960 $cm^{-1}$ and absorptions at 2862 and 2835 $cm^{-1}$ with a shoulder on the band at 2862 $cm^{-1}$ which may represent the band expected at 2870 $cm^{-1}$. These bands are due to the C-H stretching vibrations. The spectrum also exhibits bands 1471 $cm^{-1}$ and 1379 $cm^{-1}$ which result from C-H deformation vibrations. The spectrum also contains a band at 727 $cm^{-1}$ which is the result of aliphatic chain rocking vibration. The only major variation between this spectrum and those of the oils is that the bands due to the methyl group C-H stretches, the shoulders near 2960 $cm^{-1}$ and 2870 $cm^{-1}$, are more pronounced. The frequency values are given with the band assignments in Table 5.3.

Although animal fats are composed predominantly of saturated fatty acid esters, they contain a certain amount of unsaturated material. Mutton tallow has been found to contain 30% oleic acid and 1.5% linoleic acid (Mills and White, 1987). The spectrum of the lamb suet exhibits certain bands which may be assigned to the double bond structure. A weak shoulder appears in the region of 3010 $cm^{-1}$ which probably corresponds to the ethylenic C-H stretch which has been reported to fall near 3020 - 3030 $cm^{-1}$ (Sinclair et al., 1952b; Shreve et al., 1950). The spectrum also exhibits a band at 1654 $cm^{-1}$ which is of greater relative intensity than those in the oil spectra and is probably due to the C=C stretch. The band at 964 $cm^{-1}$ is of medium intensity in relation to the other bands in the spectrum and falls into the range given for trans-isomer structures, 980 - 965 $cm^{-1}$ (Sinclair et al., 1952b). There is no strong evidence for a cis-isomer structure: a very weak shoulder appears from approximately 710 to 670 $cm^{-1}$ which may indicate traces of cis-substituted materials. The range reported for cis-isomers is near 690 $cm^{-1}$ (Sinclair et al., 1952b). Also, a weak band appears at 1418 $cm^{-1}$ in the suet spectrum which corresponds to the weak bands observed near 1417 $cm^{-1}$ in the oil spectra and are probably due to the C-H deformations of the methylene groups which are adjacent to the carboxyl group. The band at 1471 $cm^{-1}$ has a shoulder in the region of 1445 $cm^{-1}$ which may be due to the methylene groups in the immediate vicinity of the C=C bonds which have been reported to occur in the region (Sinclair et al., 1952b).

The spectrum of the suet also contains evidence for the ester linkage. There is a very intense band at 1756 $cm^{-1}$ and a second intense band at 1184 $cm^{-1}$ which are due to the C=O and the C-O stretch respectively. The band is flanked by a weak absorption at 1121 $cm^{-1}$, but the band which is expected near 1239 $cm^{-1}$ is not apparent. A wide shoulder occurs near 1200 $cm^{-1}$ which reaches to almost 1300 $cm^{-1}$.

There is some evidence for the presence of carboxylic acid functional group in the spectrum which would indicate the break down of some of the triglyceride structure. A band appears as a shoulder on the C-H stretching absorptions with a maximum intensity at 3304 $cm^{-1}$ and a further band occurs at 2671 $cm^{-1}$. These bands are representative of the O-H bond in carboxylic acids which form hydrogen bonded dimers in the solid and liquid state. The absorption has been described as a shoulder on the bands due to the C-H stretching vibration (Shreve et al., 1950; Sinclair et al., 1952a). Also, the band has been reported to occur near 2703 $cm^{-1}$ which was assigned as "a branch of the O-H···O 'association' band" which is part of the total O-H absorption" (Shreve et al., 1950). Bellamy (1975) refers to the band in the region 2700 - 2500 $cm^{-1}$ as a satellite band of the bonded O-H absorption. A shoulder is observed on the band at 1756 $cm^{-1}$ in the suet spectrum in the region of 1735 - 1680 $cm^{-1}$ which may be due to small amounts of carboxylic groups which exhibit carbonyl stretches in the region 1701 - 1698 $cm^{-1}$ (Sinclair et al., 1952a and 1715 - 1709 $cm^{-1}$ (Shreve et al., 1950). Also, fatty acid spectra contain a series of evenly spaced weak bands in the region 1350 - 1180 $cm^{-1}$ which are due to wagging and twisting vibrations of the methylene groups (Jones et al., 1952). Small amounts of fatty acids may result in the broad shoulder which is observed in this region in the suet spectrum and mask the weak absorption expected in the region 1250 - 1238 $cm^{-1}$.

Fatty acids

The spectrum of oleic acid was obtained by transmission and the spectra of the saturated fatty acids were recorded using diffuse reflectance. The spectra exhibit characteristic carboxylic acid absorptions in addition to the absorptions due to aliphatic functional groups and there is no evidence of ester linkages. The major spectral frequency ranges are reported with the assignments in Table 5.4.

The oleic acid spectrum contains bands at 2925 and 2854 $cm^{-1}$ which are due to aliphatic C-H stretching vibrations. The spectrum also exhibits absorptions at 1466 and 1378 $cm^{-1}$ which correspond to those of aliphatic C-H deformations. The band which occurs at 723 $cm^{-1}$ in the spectrum is due to the rocking vibration of aliphatic chains of four or more methylene groups. In addition to the aliphatic absorptions, the spectrum contains a band at 3006 $cm^{-1}$ which may be assigned to the C-H stretches on the C=C groups. Bands appear at 1434 and 1413 $cm^{-1}$ which may be assigned to the C-H deformations of the methylene groups adjacent to the C=C groups and the carboxyl groups respectively (Sinclair et al., 1952b). The strong band at 1711 $cm^{-1}$ exhibits a slight widening at base on the right hand side which may be the result of C=C stretching vibrations which have been reported to absorb weakly in the region of 1660 $cm^{-1}$ (Sinclair et al., 1952b). Also, the band at 723 $cm^{-1}$ has a broad shoulder in the approximate region of 705 - 660 $cm^{-1}$ which may be indicative of the presence of cis-isomer structures (Sinclair et al., 1952b).

The presence of carboxyl groups is indicated by the band which occurs at 1711 $cm^{-1}$ which is above the range given by Sinclair et al. (1952a), but fits within the values reported by Shreve et al. (1950), 1715 - 1709 $cm^{-1}$. This region has been assigned to the C=O of the carboxylic acid group and the shift from the values for the triglycerides (1751 - 1748 $cm^{-1}$) is diagnostic (Shreve et al., 1950). The spectrum also exhibits a slight shoulder from about 3500 - 3080 $cm^{-1}$ which is probably the result of a combination of water from the KBr plates and the hydrogen bonded O-H stretch in the carboxyl group. The band at 2675 $cm^{-1}$ is also diagnostic of carboxylic acids. There are two very weak bands on the shoulder of the band at 1378 $cm^{-1}$ at 1285 and 1247 $cm^{-1}$. Bands have been reported near 1282 and 1250 $cm^{-1}$ (Shreve et al.,

1950) which have tentatively been assigned to the C-O stretching vibration in the carboxyl group. The oleic acid spectrum exhibits a band of medium intensity at 939 $cm^{-1}$ which may be assigned to the deformation of the O-H linkage in the carboxylic acid group which is reported to occur near 935 $cm^{-1}$ (Shreve et al., 1950). There are two very weak absorptions at 1119 and 1091 $cm^{-1}$ in the spectrum which are difficult to assign.

Saturated fatty acids have a slightly different spectrum (Figure 5.4). The spectra are all very similar which is not surprising as the structures only vary by the length of the carbon chain. The spectra exhibit bands in the ranges 2958 - 2955 $cm^{-1}$, 2930 - 2929 $cm^{-1}$ and 2857 - 2856 $cm^{-1}$ which are due to aliphatic C-H stretches and in the range 1470 - 1469 $cm^{-1}$ which is indicative of aliphatic C-H deformations. The spectrum of stearic acid (VA21) contains an additional band at 2899 $cm^{-1}$. The band which is expected to occur near 1378 $cm^{-1}$ is not evident, but a band appears in the range 1352 - 1351 $cm^{-1}$. A band is evident in the region 1413 - 1412 $cm^{-1}$ which has been assigned to the C-H deformations in the methylene groups in the immediate vicinity of the carboxyl group. The spectra are also characterized by a band of medium intensity in the range 727 - 725 $cm^{-1}$ which is representative of the rocking vibrations of long chain aliphatic compounds.

The spectra of myristic (VA19) and palmitic (VA20) acid exhibit weak bands at 1599 $cm^{-1}$ and all three fatty acid spectra contain an absorption in the range 1435 - 1433 $cm^{-1}$ and one in the area 691 - 689 $cm^{-1}$ which are regions which have been discussed earlier as being related to structures containing C=C bonds. These bands may result from impurities in the standard material. (They were obtained from Aldrich and were general purpose reagent quality). The spectrum may also be affected by polymorphism. It has been found that fatty acids may exist in more than one crystal structure. Two orientations of the hydrocarbon chain have been found with respect to the axes of the crystal and the hydrogen bonding within the molecule has been found to be different for the two forms. A spectrum of a mixture of alpha and beta forms of stearic acid was found to vary considerably from a spectrum of the beta polymorph only (Sinclair et al., 1952a). The spectrum of the mixture contains an absorption with maximum intensity centred at approximately 875 $cm^{-1}$ which shifts to approximately 930 $cm^{-1}$. Unfortunately, the region between 1430 and 1500 $cm^{-1}$ is not clearly presented in the figures published in the literature and the region between 1320 and 1400 $cm^{-1}$ is blocked by the absorptions due to the carbon disulphide solvent. Thus, it is not possible to see what effect polymorphism has in this region.

The spectra exhibit bands due to the carboxyl group. A very broad, weak shoulder is observed in all three spectra which commences near 3000 $cm^{-1}$ and ends near 3400 $cm^{-1}$ in the spectrum of myristic acid. The band goes off scale in the other two spectra. The spectra also contain a band in the region of 2669 - 2661 $cm^{-1}$ which is characteristic of carboxylic acids. The carbonyl absorption falls in the range 1714 - 1711 $cm^{-1}$ which corresponds with the value for fatty acids and a broad band occurs in the region 948 - 945 $cm^{-1}$. The width of the band may be due to the polymorphism. There is also a series of bands which occur in the following regions: near 1329 $cm^{-1}$ (which occurs as a shoulder near 1330 $cm^{-1}$ in the spectra of palmitic (VA20) and stearic (VA21) acids), 1312 - 1301 $cm^{-1}$, 1275 - 1262 $cm^{-1}$, 1251 - 1237 $cm^{-1}$, 1229 - 1213 $cm^{-1}$, 1208 - 1204 $cm^{-1}$ (except for myristic acid) and 1192 - 1188 $cm^{-1}$. These bands are most probably related to the band progression which has been described for fatty acids and attributed to the wagging and twisting motions of the methylene groups (Jones et al., 1952). The broad multiplet in the region of 1310 $cm^{-1}$ is probably due to the coupled absorptions of the band progression and the C-O stretching vibrations (Jones et al., 1952). The number of bands in the progression is thought to be related to the length of the carbon chain, but this is often obscured by the C-O stretching mode in the carboxylic acid group (Jones et al., 1952). The bands are reported to be fairly evenly spaced (Jones et al., 1952), but the variations observed in these spectra may be due to the presence of more than one crystal form.

The spectra of the saturated fatty acids display sharp, fairly weak bands in the regions 1126 - 1125 $cm^{-1}$, 1104 - 1094 $cm^{-1}$, 817 - 812 $cm^{-1}$, 786 - 782 $cm^{-1}$ and 552 - 551 $cm^{-1}$. In addition, the spectrum of palmitic acid (VA20) exhibits a band at 852 $cm^{-1}$ and the spectra of myristic (VA19) and stearic (VA21) acids contain bands at 755 and 762 $cm^{-1}$ respectively. The three spectra also show extremely weak bands in the region 1787 - 1785 $cm^{-1}$ which appear as shoulders on the strong carbonyl absorption. These bands do not correspond to absorptions which are characteristic for fatty acid structures and consequently are difficult to assign. They may result from impurities or the effects of polymorphism.

## Identification of unknown samples

A survey was made of the surviving contents of a variety of ceramic and stone jars from the Egyptian collections of the British Museum and the Petrie collection (University College, London). The resulting spectra were grouped by similarities in the spectra and there were several groups which were thought to be mixtures. One of the groups showed similarities to the spectra of the saturated fatty acid spectra obtained by diffuse reflectance. The similarities are in the frequency values. The shape of the sample spectra are somewhat different. The variations may be due in part to the various degrees of degradation of the samples and possibly to the original material being a mixture. Also, other materials may have been added: many of the samples contained some chaff-like material and other contaminants. Because of the time constraints and the large number of samples, the specimens were not pretreated in any way. The ranges of frequency values are listed in Table 5.4 compared with those of the fatty acids and the oils. The sample details are listed at the end of the chapter.

The spectra contain absorptions due to C-H stretching and deformation vibrations in the regions 2943 - 2922 cm$^{-1}$, 2861 - 2852 cm$^{-1}$ and 1474 - 1464 cm$^{-1}$. The spectra also exhibit a band in the region 1435 - 1420 cm$^{-1}$ which was tentatively assigned to the methylene group stretches which were adjacent to the C=C. However, this absorption is also present in the saturated fatty acid spectra. The absorption which is expected near 1412 cm$^{-1}$ is only present in one sample spectrum (MS15P) at 1413 cm$^{-1}$ and as a weak shoulder in a few of the other sample spectra. The band which is expected in the region 1380 - 1370 cm$^{-1}$ does not occur in the saturated fatty acid spectra, but is apparent in that of the unsaturated oleic acid. In the unknown sample spectra, it is apparent in only a few cases. The band which is present near 1352 cm$^{-1}$ in the saturated fatty acid spectra appears in only a few of the sample spectra. The sample spectra all contain an absorption in the region 729 - 720 cm$^{-1}$ which results from the aliphatic chain rocking vibration.

The spectra were subdivided into two groups based on the shape of the O-H stretching absorption. In the first group, which contains samples MS11, MS12, MS33, MS14, MS14P, MS18P and MS15P (Figure 5.4c), the O-H band appears as a broad band which begins in the region of 3700 cm$^{-1}$ and runs into the C-H absorptions at 3000 cm$^{-1}$. It is thought that part of this absorption may be due to moisture in the sample, but the same range appears for this absorption in the spectrum of myristic acid. The second group, which consists of samples MS38, MS2 (Figure 5.4b), MS30, MS10, MS5P, MS25, MS1 and MS26, exhibits a rounded absorption with maximum intensity which falls in the range 3495 - 3127 cm$^{-1}$. The band seems to run into the C-H bands. All of the spectra contain bands which correspond to those in the fatty acid spectra. There is, however, some variation and some evidence of ester content in a few of the sample spectra.

The group I samples all display the shoulder in the region between 3700 - 3000 cm$^{-1}$ which was described above (Figure 5.4). The spectra also contain an absorption in the region 2683 - 2659 cm$^{-1}$ which is characteristic of carboxylic acids. The spectra also contain the absorption centred near 945 cm$^{-1}$ which is due to the O-H deformation in the carboxylic acid functional group. The evidence for a mixture of ester and carboxylic acid materials is seen in the carbonyl stretching region. In the spectra of samples MS11, MS14P, MS18P and MS15P, a band is observed in the region 1718 - 1714 cm$^{-1}$ with a very weak shoulder on the higher frequency side of the band. This is representative of the C=O stretch in the carboxylic acid group and the shoulder falls into the region which is characteristic for ester carbonyl stretches. The other samples, MS12, MS33 and MS14, exhibit bands with maximum intensity in the region of 1743 - 1742 $cm^{-1}$ with weaker bands or shoulders (in the spectra of MS12, the bands are of equal intensity) in the region 1721 - 1719 $cm^{-1}$ which indicate the presence of both types of carbonyl groups, esters and carboxylic acids. The region between 1330 - 1180 $cm^{-1}$ shows some variation in the sample spectra. A characteristic band progression appears in the spectra of carboxylic acids in this region as does the C-O stretch in ester groups. In the spectra of group I which contain the maximum carbonyl absorption near 1717 $cm^{-1}$, bands occur in the regions 1314 - 1296 $cm^{-1}$ and 1205 - 1189 $cm^{-1}$ with three to four very weak bands in between these absorptions. In the spectra of MS12 and MS33 which contain the strong ester absorption, a broad shoulder appears from approximately 1314 $cm^{-1}$ to 1195 $cm^{-1}$ and from near 1318 $cm^{-1}$ to 1188 $cm^{-1}$ respectively. In the spectrum of MS14, a very indistinct absorption occurs in this region with maximum intensities at 1252 and 1190 $cm^{-1}$. It is interesting that the spectra which seem to contain a greater amount of carboxylic acid, MS11, MS14P, MS18P and MS15P, exhibit indications of the fatty acid band progression and that in the spectra of the materials which seem to contain ester groups, the corresponding region is blurred. This may be due to the interference of the C-O absorptions which have been observed in triglyceride esters. Also, the complexity of the mixtures probably causes the general loss of resolution in this area.

The group I spectra are also characterized by fairly consistent absorptions in the regions of 813 - 811 $cm^{-1}$, 784 - 782 $cm^{-1}$, 693 - 687 $cm^{-1}$ and 565 - 547 $cm^{-1}$ with a weak shoulder in the region of 880 $cm^{-1}$. The bands were not assigned except for the band near 690 $cm^{-1}$ which was assigned to the cis-isomer structure in unsaturated fatty acids, although it is also apparent in the saturated fatty acid spectra. Bands occur in the other regions in the spectra of the saturated fatty acids.

The group II spectra (Figure 5.4) contain some evidence for the presence of carboxylic acids, but it is less strong in most of the sample spectra. For example, only two spectra, MS5P and MS25, contain a carbonyl absorption with maximum intensity at

1703 and 1712 cm$^{-1}$ respectively with weak shoulders in the higher frequency region. In the other sample spectra (MS38, MS2, MS30, MS10, MS1 and MS26), the maximum intensities in the carbonyl region fall between 1749 and 1736 cm$^{-1}$ with a less intense band or shoulder in the area of 1717 - 1716 cm$^{-1}$. The spectra contain a shoulder in the area of 2685 - 2668 cm$^{-1}$ which is, for many of the samples, less well defined than in the group I spectra. The spectra in group II also contain an absorption in the region of 957 - 938 cm$^{-1}$ which is less distinct in some of the some spectra.

In the region of the band progression, 1350 - 1180 cm$^{-1}$, there is much variation. The spectra of samples MS1 and MS26 contain multiple bands with a band of maximum intensity at 1184 and 1185 cm$^{-1}$ respectively. The spectra of MS25 and MS1 exhibit absorptions near 1319 - 1299 cm$^{-1}$ and near 1195 cm$^{-1}$ with several very weak bands in between. In the remaining four sample spectra, the region is less distinct with a shoulder which commences near 1327 - 1318 cm$^{-1}$ and ends with the absorption in the range 1203 - 1184 cm$^{-1}$. In the spectrum of MS30, the region is fairly indistinct.

The group II spectra also exhibit absorptions near 812 - 804 cm$^{-1}$, 784 - 780 cm$^{-1}$, 690 - 657 cm$^{-1}$ and near 557 - 552 cm$^{-1}$ with a weak shoulder or band in the region of 893 - 850 cm$^{-1}$. However, there is a greater variation in the occurence of these bands.

The presence of bands in some of the spectra from both groups in the regions 1652 - 1621 cm$^{-1}$ and 1598 - 1582 cm$^{-1}$ may be indicative of the C=C stretches in unsaturated materials. However, with the absorption near 1502 - 1500 cm$^{-1}$, they may represent the presence of aromatic compounds as components of the mixture.

A possible explanation is that the samples are partially degraded triglycerides which would explain the presence of characteristic absorptions of both ester and fatty acid groups. The complexity of these samples causes variations in the spectra and makes it difficult to identify them with certainty. However, the appearance of certain characteristic bands of both fatty acids and esters in all of the spectra indicates the identity of the major components of the sample. The presence of fatty acids and esters suggests that the original material contained oils or fats of some kind. However, it is not possible to identify the oil or oils and the identity of any minor constituents such as might occur in ungents cannot be determined. It would be necessary to use a sensitive separation technique such as gas chromatography to further elucidate the identity of the samples.

The conclusions reached from these samples may be compared with a report of the analysis of the contents of two glass bottles (Barag, 1972; Basch, 1972). In this study, the surviving contents of two glass vessels of uncertain provenance which were reported to have been found in the northern region of Jerusalem were analysed. The objects were thought to have been obtained from a tomb site. The contents which were thought to be original have survived (Barag, 1972). The contents consisted of a liquid residue with a covering which was described as a "dark brownish-red resinous material" (Basch, 1972). Samples were obtained of both and were analysed by infrared spectroscopy, thin layer chromatography and gas chromatography.

The infrared spectra were not shown, but the wavelengths of the major bands were reported. The liquid material, after the water and other volatiles were removed, gave spectra which exhibited a broad band in the region of 3333 - 2500 $cm^{-1}$ which was assigned to a bonded O-H vibration and a strong absorption at 1709 $cm^{-1}$. The conclusion was reached that the material contained a carboxylic acid functional group. Absorptions were also reported to have occurred at 1111 and 1031 $cm^{-1}$ which were said to be indicative of glycerine. The conclusion was reached that fatty acids and glycerine in an aqueous solution were the major constituents of the liquid as there were no bands in the spectra which resulted from functional groups which do not occur in fatty acids and glycerol (Basch, 1972).

The infrared spectra of the brownish-red samples were similar to each other and were reported to exhibit bands which were characteristic of both organic acids and esters (Basch, 1972). Bands were observed in the regions of 2941, 2857, 1460, 1379 and 722 $cm^{-1}$ which were reported to be characteristic of "a long linear aliphatic chain," (Basch, 1972) although only the band at 722 $cm^{-1}$ is specifically due to long aliphatic chains. Also, a flattened, broad O-H band was found in the region 3571 - 2500 cm-1 in addition to a strong band at 1709 $cm^{-1}$. The absorptions are characteristic of a carboxylic acid. The description of the carbonyl absorption is interesting as a shoulder is reported to occur at 1733 $cm^{-1}$ which was assigned as an ester absorption. This spectral feature is very similar to those found for the jar contents examined in this study. The spectra also contained bands in the region 1250 - 1111 $cm^{-1}$ which were assigned to ester C-O vibrations and were described as "diffuse absorptions" (Basch, 1972). This pattern may also correspond to the same region in the spectra obtained for this thesis where a variety of absorption patterns were observed. The conclusion reached by Basch based on the infared results was that the materials were probably a fat or oil which had undergone a large degree of hydrolysis.

In the study (Basch, 1972), thin layer chromatography was used to analyse the "resins" and the samples were found to contain mono- and di-glycerides as well as fatty acids. Triglycerides were not observed. The gas chromatography results suggested olive oil as a possible original material due to the high ratio of palmitic acid to stearic acid which was found and the high amount of oleic acid which has survived. Oleic acid would be expected to alter over time due to the reactivity of the double bond (Basch, 1972).

One of the jar samples in this thesis, MS18P, was analysed by gas chromatography/mass spectrometry (White, personal communication). The material was examined before and after saponification and it was found that almost all of the fatty acid material exists as free fats. No triterpenoid or diterpenoids were isolated which indicates that no resinous compound is present (Chapter 7). The principal components were found to be palmitate and stearate which result from palmitic and stearic acid. Evidence was found of the C-8, C-9 and C-10 dicarboxylic acids which indicate that the original material contained semi-drying, unsaturated oils. This suggests either a fruit or seed oil as vegetable oils are higher in polyunsaturated fats. Some animal fat may have been present. No sterols or cholesterol were isolated. However, such materials are susceptible to bacteria action and would have degraded if the sterols had been present originally. No ketone or aldehyde functional groups were present in the sample. The conclusion was reached that the original material was probably a seed or fruit oil with the possible addition of animal fat (White, personal communication).

**Unknown sample information**

Group I

MS11 Medium brown, gummy residue from one handled, alabaster (?) jug with peg base. Provenance - unknown. Date - New Kingdom (XVIIIth dynasty). British Museum Department of Egyptology 26962.

MS12 Dark brown, waxy residue from one handled, sepentine vase with lid. Provenance - unknown. Date - New Kindom (XVIIIth dynasty). British Museum Department of Egyptology 24417.

MS14 Orange waxy residue from one handled alabaster (?) jug with lid. Provenance - unknown. Date - (New Kingdom) XVIIIth dynasty. British Museum Department of Egyptology 24418.

MS33 Buff pink, soft residue from imitation (?) alabaster (?) barrel jar on stand with lid. Provenance - unknown. Date - New Kingdom (?). British Museum Department of Egyptology 69024.

MS14P Brown, sticky residue from thin wavy handled pottery cylinder jar. Provenance - Hu. Date - Predynastic. British Museum Department of Egyptology 30902.

MS15P As above, lighter brown, loose residue which had been removed from jar previously and stored in polythene bag.

MS18P Black, shiny, friable residue from "Abydos ware" pottery jar. Provenance - Abydos, tomb of Djer. Date - Protodynastic (Ist dynasty). British Museum Department of Egyptology 35549.

Group II

MS1 Yellow-brown, sticky residue from alabaster (?) globular vase with flattened base. Provenance - Reqoquah ?? tomb 1. Date - New Kingdom, (XVIIIth dynasty). University College London Petrie Collection 38053.

MS2 Orange-brown, compact residue from large alabaster (?) jar with two loop handles on body. Provenance - unknown. Date - New Kingdom (XVIII - XIX th dynasty). University College London Petrie Collection 38052.

MS10 Medium brown residue from blue anhydrite cylinder jar. Provenance - unknown. Date - Middle Kingdom (XIIth dynasty). British Museum Department of Egyptology 4490.

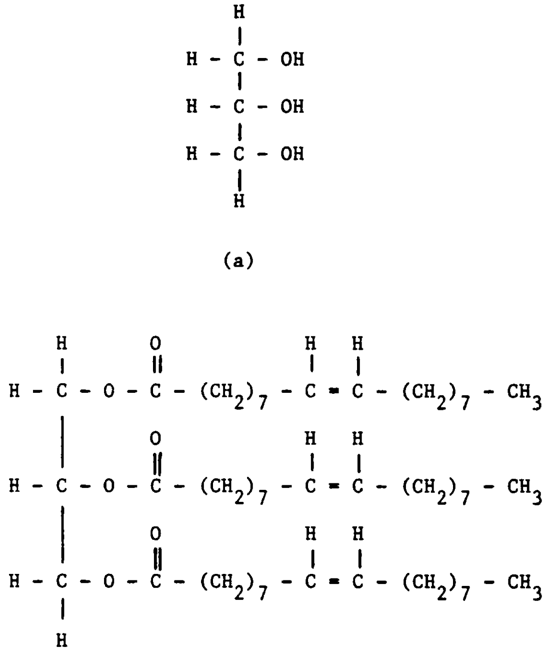
MS25 Light brown, powdery residue from rounded anhydrite jar with moulded rim. Provenance - unknown. Date - Middle Kingdom (XIIth dynasty). British Museum Department of Egyptology 4705.

MS26 Pale yellow, waxy residue which appears black on the surface from an alabaster (?) wide neck globular vase on base. Provenance - unknown. Date - ?New Kingdom. British Museum Department of Egyptology 32067.

MS30 Orange, friable residue which appears black on the surface from a round, alabaster (?) jar. Provenance - unknown. Date - Late Old Kingdom to Early Middle Kingdom (?)(VI - XIth dynasty). British Museum Department of Egyptology 35319.

MS38 Reddish-brown, soft residue from alabaster (?), one handled toilet jar with a wide neck. Provenance - Thebes, toilet box of Tutu. Date - New Kingdom (XVIIIth dynasty). British Museum Department of Egyptology 24708 (number for entire box and contents).

MS5P Black/brown fibrous residue from one handled pottery jug with loop handle on body. Provenance - unknown. Date - New Kingdom (XIX - XXIIth dynasty). British Museum Department of Egyptology 4902.



(a)

(b)

Figure 5.1 Structure of (a) glycerol and (b) triolein, a simple triglyceride.

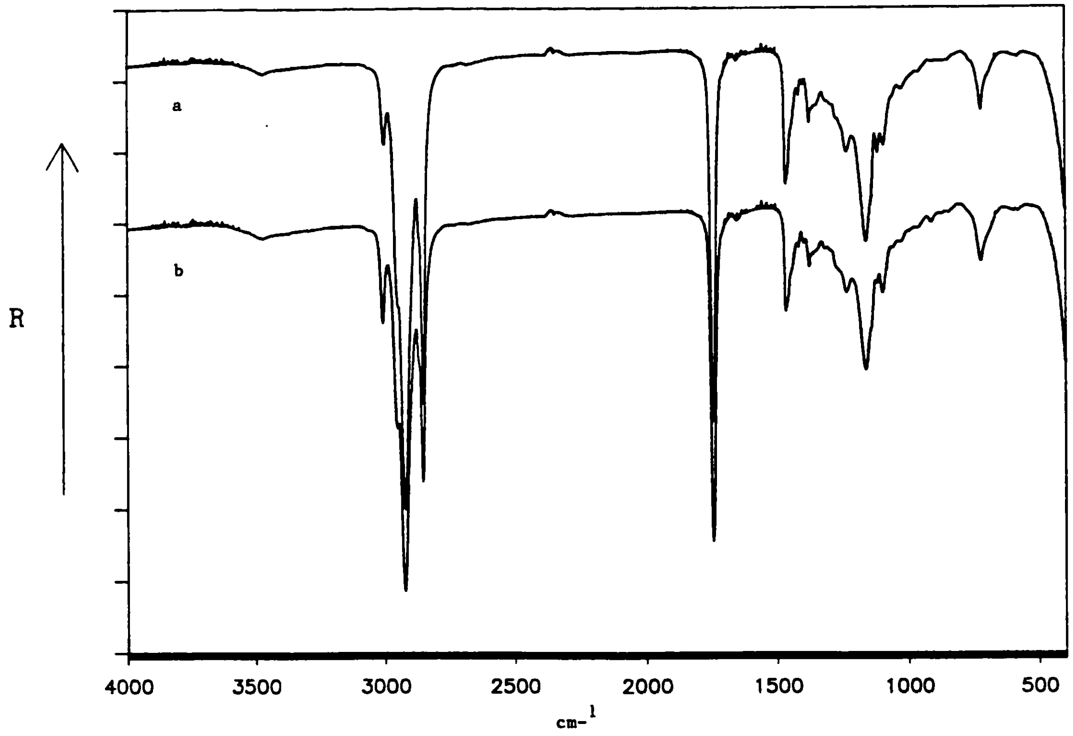


Figure 5.2 Transmission spectra of (a) olive oil (GS9 Commericial source) (gsva0465) and (b) grapeseed oil (GS11 Commercial source) (gsva0467)

Figure 5.3 Diffuse reflectance FT-IR spectrum of lamb's suet (GS8) (gsva0434).

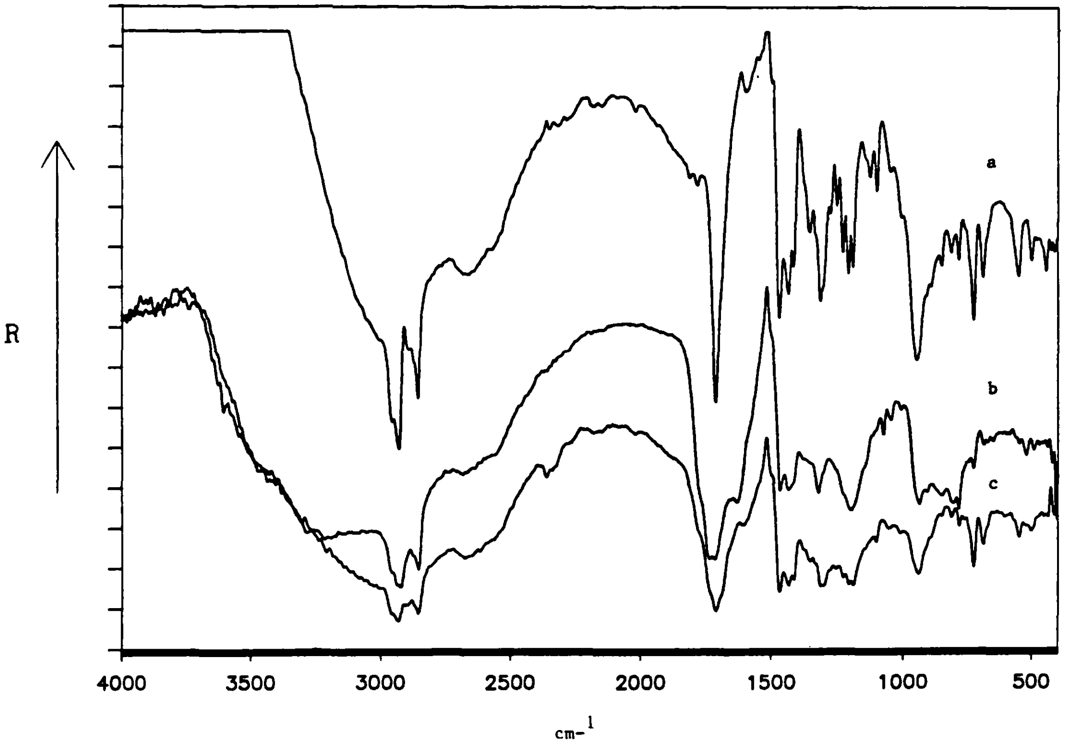


Figure 5.4 Diffuse reflectance FT-IR spectra of (a) palmitic acid (VA20 BDH Chemicals Ltd.) (gsva0473), (b) residue from Egyptian calcite jar - Group II (MS2 UC38052) (gsva0409) and (c) residue from Egyptian ceramic jug - Group I (MS15P BM30902) (gsva0458).

TABLE 5.1

**Major fatty acids of oils and fats (Mills and White, 1987)**

| Formula | Systematic name | Common name | Structure | M.p. °C |
|---|---|---|---|---|
| $C_{12}H_{24}O_2$ | Dodecanoic | Lauric | $HOOC-(CH_2)_{10}-CH_3$ | 44 |
| $C_{14}H_{28}O_2$ | Tetradecanoic | Myristic | $HOOC-(CH_2)_{12}-CH_3$ | 54 |
| $C_{16}H_{32}O_2$ | Hexadecanoic | Palmitic | $HOOC-(CH_2)_{14}-CH_3$ | 63 |
| $C_{16}H_{30}O_2$ | 9-Hexadecenoic | Palmitoleic | $HOOC-(CH_2)_7-CH=CH-(CH_2)_5-CH_3$ | 0.5 |
| $C_{18}H_{36}O_2$ | Octadecanoic | Stearic | $HOOC-(CH_2)_{16}-CH_3$ | 70 |
| $C_{18}H_{34}O_2$ | 9-Octadecenoic | Oleic | $HOOC-(CH_2)_7-CH=CH-(CH_2)_7-CH_3$ | 16 |
| $C_{18}H_{32}O_2$ | 9,12-Octadecadienoic | Linoleic | $HOOC-(CH_2)_7-CH=CH-CH_2CH=CH-(CH_2)_4-CH_3$ | -5 |
| $C_{18}H_{30}O_2$ | 9,12,15-Octadecatrienoic | Linolenic | $HOOC-(CH_2)_7-CH=CH-CH_2CH=CH-CH_2-CH=CH-CH_2-CH_3$ | -11 |
| $C_{18}H_{30}O_2$ | cis,trans,trans-9,11,13-Octadecatrienoic | α-Elaeostearic | $HOOC-(CH_2)_7-CH=CH-CH=CH-CH=CH-(CH_2)_3-CH_3$ | 49 |
| $C_{18}H_{34}O_2$ | 12-Hydroxy-9-octadecenoic | Ricinoleic | $HOOC-(CH_2)_7-CH=CH-CH_2-CHOH-(CH_2)_5-CH_3$ | |

TABLE 5.2

**Fatty acid composition of some oils and fats (Mills and White, 1987)**

| | 8:0 | 10:0 | 12:0 | 14:0 | 16:0 | 18:0 | 18:1 | 18:2 | 18:3 | Others |
|---|---|---|---|---|---|---|---|---|---|---|
| Olive | | | | tr | 8-18 | 2-5 | 56-82 | 4-19 | 0.3-1 | |
| Sunflower seed | | | | tr | 5-6 | 4-6 | 17-51 | 38-74 | tr | |
| Coconut | 5-9 | 6-10 | 44-52 | 13-19 | 8-11 | 1-3 | 5-8 | 1-2 | | |
| Poppyseed | | | | | 10 | 2 | 11 | 72 | 5 | |
| Walnut | | | | | 3-7 | 0.5-3 | 9-30 | 57-76 | 2-16 | |
| Linseed | | | | tr | 6-7 | 3-6 | 14-24 | 14-19 | 48-60 | |
| Hempseed | | | | | 6-7 | 2-3 | 12-17 | 55-65 | 14-20 | |
| Perilla | | | | | 7 | 2 | 13 | 14 | 64 | |
| Tung | | | | | 3 | 2 | 11 | 15 | 3 | elaeostearic 59% |
| Castor | | | | | 1-2 | 1-2 | 3-6 | 4-7 | | ricinoleic 83-89% |
| Pig | | | | 1-2 | 20-28 | 13-16 | 42-45 | 8-10 | 0.5-2 | |
| Beef tallow | | | | 2-3 | 23-30 | 14-29 | 40-50 | 1-3 | 0-1 | |
| Mutton tallow | | | | 6 | 26 | 30 | 30 | 1.5 | 0.2 | |
| Cow's milk | 1-2.5 | 2-3 | 2-3 | 9-11 | 22-30 | 11-15 | 25-31 | 1-2.5 | 1-2.5 | |
| Hens eggs | | | | tr | 27 | 9 | 44 | 13.5 | 0.5 | |

The headings, 18:0, 18:1, etc. indicate chain lengths:number of double bonds. These data were all obtained by gas chromatography, and are from several sources notably T. P. Hilditch and P. N. Williams, The Chemical Constitution of Natural Fats and D. Swern (editor), Bailey's Industrial Oil and Fat Products. For several oils there are few reliable data and it is not possible to give a range of compositions.

TABLE 5.3

Frequency values and band assignments for vegetable oils and lamb suet

| Vegetable oils cm-1 | Lamb suet GS8 cm-1 | Vibration | Functional group | Frequency values given in literature cm-1 | Ref. |
|---|---|---|---|---|---|
| 3477 - 3472(w) | 3468(w) | O-H stretch | water | | |
| | 3304(w) | O-H stretch | carboxylic acid | 3000 - 2500(b) | 4 |
| | | | | 3333 - 3030 | 3 |
| | | | | 3500 - 3000 | 1 |
| 3009 - 3005(m) | 3010(w) | C-H stretch | C=C bond | 3100 - 3000(va) | 2 |
| | | | | (3020) | |
| | | | | 3030(s) | 3 |
| 2954(sh) | 2940(s) | C-H stretch | methyl group | 2960(m) | 1 |
| 2926 - 2925(s) | | C-H stretch | methylene group | 2920(s) | 1 |
| 2855 - 2854(s) | 2862(s) | C-H stretch | methylene group | 2850(s) | 1 |
| | 2835(m) | C-H stretch | methylene group | 2850(s) | 1 |
| | 2671(w) | O-H stretch | carboxylic acid | near 2650(w) | 4 |
| | | | | 2703 | 3 |
| 1747 - 1746(s) | 1756(s) | C=O stretch | ester (triglyceride) | 1751 - 1748 | 3 |
| | 1735 - 1680(sh) | C=O stretch | carboxylic acid | 1701 - 1698 | 1 |
| | | | (fatty acid) | 1715 - 1709 | 3 |
| 1657 - 1656(vw) | 1654(w) | C=C stretch | C=C bond | 1650 - 1580(sh) | 2 |
| * 1650(vw) | | C=C stretch | C=C bond | 1650 - 1580(sh) | 2 |
| 1466(m) | 1471(s) | C-H asym. deformation | methyl group | 1450 ± 20(m) | 4 |
| | | C-H deformation | methylene group | 1465 ± 20(m) | 4 |
| near 1430(sh) | near 1440(sh) | C-H deformation | methylene group next to C=C bond | 1435 | 2 |
| near 1417(vw) | 1418(w) | C-H deformation | methylene group next to carboxylic acid | 1410 - 1405 | 1,2 |
| 1378(w) | 1379(w) | C-H deformation | methyl group | 1389 - 1351 | 3 |

TABLE 5.3 contd.

Frequency values and band assignments for vegetable oils and lamb suet

| Vegetable oils cm-1 | Lamb suet GS8 cm-1 | Vibration | Functional group | Frequency values given in literature cm-1 | Ref. |
|---|---|---|---|---|---|
| | 1300 - 1200(sh) | C-H 'wagging and twisting' vibration | methylene groups in fatty acids | 1350 - 1180 band progression series of weak evenly spaced bands | 5 |
| 1239 - 1238(w) | | C-O stretch | ester (triglyceride) | near 1250 | 3 |
| 1164 - 1163(m) | 1184(s) | C-O stretch | ester (triglyceride) | near 1163 | 3 |
| ** 1120 - 1119(w) | 1121(w) | C-O stretch | ester (triglyceride) | 1121 | 3 |
| 1100 - 1097(w) | | C-O stretch | ester (triglyceride) | 1101 - 1099 | 3 |
| | 1060(w) | unassigned | | | |
| near 970(vw) | 964(m) | C-H out-of-plane deformation | C=C bond (trans-) | 980 - 965(s) | 2 |
| | 922(m) | unassigned | | | |
| | 840(w) | unassigned | | | |
| 724 - 723(m) | 727(m) | chain rocking vibration | long chain hydrocarbons with four or more methylene units | 750 - 720(m)<br>719 | 4<br>3<br>1,2 |
| near 670(sh) | near 690(vw sh) | C-H out-of-plane deformation | C=C bond (cis-) | near 690 | 2 |

* Absorption is not apparent is some spectra.

** Absorption occurs in spectra of samples GS10, GS11 and GS12.

1. Sinclair et al., 1952a
2. Sinclair et al., 1952b
3. Shreve et al., 1950
4. Bellamy, 1975
5. Jones et al., 1952

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp

## TABLE 5.4

Frequency values and band assignments for fatty acids and samples from Egyptian jars

| Fatty acids | | | | Unknown jar contents cm-1 | Vibration | Functional group | Frequency value given in literature cm-1 | Ref. |
|---|---|---|---|---|---|---|---|---|
| VA18 cm-1 | VA19 cm-1 | VA20 cm-1 | VA21 cm-1 | | | | | |
| ************* (see text) *************** | | | | see text | O-H stretch | carboxylic acid | 3000 - 2500(b) | 4 |
| | | | | | | hydrogen bonded | 3333 - 3030 | 3 |
| | | | | | | | 3500 - 3000 | 1 |
| 3006(m) | | | | | C-H stretch | C=C bond | 3100 - 3000(va)<br>(3020) | 2 |
| | | | | | | C=C bond | 3030(s) | 3 |
| | 2958(s) | near 2955(sh) | 2955(s) | | C-H stretch | methyl group | 2960(m) | 1 |
| 2925(s) | 2929(s) | 2930(s) | 2930(s) | 2943 - 2922(s) | C-H stretch | methylene group | 2920(s) | 1 |
| | | | 2899(m) | | C-H stretch | methine group | 2890 ± 10(w) | 4 |
| 2854(s) | 2856(s) | 2857(s) | 2856(s) | 2861 - 2852(s) | C-H stretch | methylene group | 2850(s) | 1 |
| 2675(w) | 2669(w) | 2661(w) | 2668(w) | * 2685 - 2659(w) | O-H stretch | carboxylic acid hydrogen bonded | near 2650(w) | 4 |
| | 1786(sh) | 1785(sh) | 1787(sh) | | unassigned | | | |
| | | | | * 1749 - 1736(s) | C=O stretch | ester (triglyceride) | 1751 - 1748 | 3 |
| 1711(s) | 1713(s) | 1714(s) | 1711(s) | * 1721 - 1703(s) | C=O stretch | carboxylic acid | 1701 - 1698 | 1 |
| | | | | | | (fatty acid) | 1715 - 1709 | 3 |
| | | | | * 1652 - 1621(w) | C=C stretch | C=C bond | 1650 - 1580(sh) | 2 |
| | 1599(w) | 1599(w) | | * 1598 - 1582(w) | C=C stretch | C=C bond | 1650 - 1580(sh) | 2 |
| | | | | * 1502 - 1500(w) | | | | |
| 1466(m) | 1470(m) | 1470(m) | 1469(m) | 1474 - 1464(s) | C-H asym. deformation | methyl group | 1450 ± 20(m) | 4 |
| | | | | | C-H deformation | methylene group | 1465 ± 20(m) | 4 |
| 1434(m) | 1435(m) | 1434(m) | 1433(m) | 1435 - 1420(va) | C-H deformation | methylene group next to C=C bond | 1435 | 2 |
| 1413(m) | 1412(m) | 1413(m) | 1412(m) | * 1413(va) | C-H deformation | methylene group next to carboxylic acid | 1410 - 1405 | 1,2 |
| 1378(w) | | | | * 1391 - 1376(va) | C-H deformation | methyl group | 1389 - 1351 | 3 |

TABLE 5.4 contd.

Frequency values and band assignments for fatty acids and samples from Egyptian jars

| Fatty acids<br>VA18<br>cm-1 | <br>VA19<br>cm-1 | <br>VA20<br>cm-1 | <br>VA21<br>cm-1 | Unknown jar contents<br>cm-1 | Vibration | Functional group | Frequency value given in literature cm-1 | Ref. |
|---|---|---|---|---|---|---|---|---|
| | 1352(m) | 1351(w) | 1352(m) | * 1352(va) | C-H 'wagging and twisting' vibration | methylene groups in fatty acids | 1350 - 1180 band progression series of weak evenly spaced bands | 5 |
| | 1329(w) | near 1330(sh) | near 1330(sh) | 1337 - 1296(va) | | | | |
| | 1310(m) | 1312(m) | 1301(m) | | | | | |
| 1285(m) | 1263(m) | 1275(w) | 1262(m) | see text | | | | |
| 1247(m) | 1237(m) | 1251(w) | 1241(m) | | | | | |
| | 1213(m) | 1229(m) | 1223(m) | | | | | |
| | | 1208(m) | 1204(m) | * 1205 - 1184(s) | C-O stretch | ester (triglyceride) | near 1163 | 3 |
| | 1192(m) | 1190(m) | 1188(m) | | | | | |
| | | | | 1140(va) | unassigned | | | |
| 1119(w) | 1126(w) | 1125(w) | 1125(w) | 1116 - 1102(va) | unassigned | | | |
| 1091(w) | 1094(w) | 1100(w) | 1104(w) | | unassigned | | | |
| 939(m) | 945(m) | 948(s) | 947(s) | * 957 - 938(va) | O-H deformation | carboxylic acid | near 935 | 3 |
| | | 852(w) | | | unassigned | | | |
| | 817(m) | 814(w) | 812(m) | * 813 - 804(va) | unassigned | | | |
| | 782(w) | 784(w) | 786(w) | 784 - 780(va) | unassigned | | | |
| | 755(m) | | 762(m) | | unassigned | | | |
| 723(m) | 725(m) | 727(m) | 726(m) | 729 - 720(m) | chain rocking vibration | long chain hydrocarbons with four or more methylene units | 750 - 720(m)<br>719 | 4<br>3 |
| | 689(m) | 691(m) | 690(m) | * 693 - 675(va) | C-H out-of-plane deformation | C=C bond (cis-) | near 690 | 2 |
| | 552(m) | 552(m) | 551(m) | * 565 - 547(va) | unassigned | | | |
| | 506 - 501(m) | | | | unassigned | | | |

* Absorption is weak or not apparent in some spectra.

1. Sinclair et al., 1952a
2. Sinclair et al., 1952b
3. Shreve et al., 1950
4. Bellamy, 1975
5. Jones et al., 1952

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp

# CHAPTER 6 BITUMINOUS MATERIALS

## Bitumen

### Source

Bitumen has been defined (Abraham, 1938) as "a generic term applied to native substances of variable colour, hardness and volatility; composed principally of saturated hydrocarbons substantially free from oxygenated bodies; sometimes associated with mineral matter, the non-mineral constituents being fusible and largely soluble in carbon disulphide."

Bituminous materials are fractions of petroleum which is fossilized organic material. The materials are produced over a very long period of geological time from biological remains which were deposited in layers. Chemical and biological reactions alter the structure of the organisms. The composition of the lower sections were subsequently affected by the anaerobic conditions, increased temperature and pressure. The reactions involved the eventual loss of functional groups and molecules were broken up. Other alterations included the loss of side chains and the transfer of hydrogen atoms from one molecule to another which produced saturated and unsaturated materials. Functional groups may still exist in more recent layers which have been exposed to relatively mild environments (Mills and White, 1987). Thus, the composition of bitumens is related to that of the original organisms (Mills and White, 1987).

The classification and nomenclature is not clear for these materials. Writers in antiquity used many terms and often only distinguished between liquid, solid or semi-solid. Also, modern nomenclature has not been consistent (Forbes, 1936). The term asphalt is the Greek name and bitumen is the Roman word for the same substance (Mills and White, 1987). The material may be considered in four groups, the bitumens, pyrobitumens, the pyrogeneous distillates and the pyrogeneous residues. The bitumen group includes petroleums, native asphalts and bitumens and the asphaltites which include gilsonite and glance pitch. The pyrobitumens include peat, lignite and coal (Forbes, 1936). The third and fourth groups are artificial materials made by pyrolysis of wood, coal or resin. The distillate produced by the pyrolysis is known as tar and the residue is referred to as pitch (Forbes, 1936; Mills and White, 1987). The term bitumen is now used for the material which is composed of a large quantity of hydrocarbon components known as maltenes which are soluble in organic solvents and a low percentage of insoluble constituents known as asphaltenes. Bitumens contain little or no inorganic material (Mills and White, 1987), and the term is utilized to describe both the substances which occur naturally and the involatile substance left by petroleum distillation. In contrast, asphalts are considered to be the native deposits which occur as outcrops. They are classified by mineral content: true asphalts which contain less than 10% inorganic matter and rock asphalts which contain mineral matter in quantities greater than 10% (Forbes, 1936; Mills and White, 1987). Asphaltites are materials with a higher melting point and are sometimes infusible (Mills and White, 1987).

The ancient civilizations were not aware of the geological structure beneath the earth and obtained the bitumenous materials from surface deposits. The layers or strata beneath the earth's surface which contain petroleum hold natural gas and water in their pores along with the oil. The gas, which is a product of the decomposition of the materials which form the petroleum, results in high pressures which are held underground by impervious cap rock layers of clay or shale. If the cap rocks are disturbed by movements of the earth, fissures or gaps are created and the petroleum, gas and water can reach the surface to form pools or seepages on the surface (Forbes, 1936). Layers nearer the surface may also be uncovered by erosion. The volatile portions evaporate over time leaving the heavy oil residue. (Mills and White, 1987) Also in some cases, oil strata do not stay underground and veins extrude to the surface. The natural gases escape and the volatile fractions evaporate slowly. The heavier fractions remain in the rock. Rock asphalt outcrops which contain 4 - 20% bitumen occur all over the world and were possible sources in antiquity. Veins of asphaltites and asphaltic pyrobitumen are much less common, but surface deposits may have been exploited in antiquity (Forbes, 1936).

Crude oil, asphalt, rock asphalt, petroleum asphalt, wood tar and wood tar pitch are the bitumenous materials which are believed to have been exploited in antiquity. Bitumen, wood tar and pitch were mixed with mineral matter to use as mortar, plaster and waterproofing material. The artificial mixture is referred to as mastic by archaeologists (Forbes, 1936) and care must be taken with the interpretation of the term. Certain forms of Pistacia resins are also referred to as mastic. There are a few classical records of bitumen collection and almost none on refinement techniques. It is assumed that heating was used to refine crude asphalts and to prepare mastic. The major area of surface deposits in the Old World is in the fertile cresent, but other sources are found in Syria and in the Dead Sea. The material was used by the Assyrians for construction. Deposits have also been found in India and Eastern Europe (Forbes, 1936). As small deposits are located all over the world and may have been exploited on a small scale, identification of a bitumen is not strictly limited to objects from the Middle East.

## Composition

The composition of bitumenous material is very complex and the fairly recent development of gas chromatography and subsequently, gas chromatography/mass spectroscopy has enabled workers to separate and identify the many hundreds of constituents (Mills and White, 1987). A detailed discussion of the many structures is beyond the scope of this thesis. However, the major families of compounds which are listed in the literature include normal, branched chain and cyclic hydrocarbons; diterpenoids; tetracyclic and pentacyclic triterpanes; and the acyclic isoprenoids, phytane and pristane. Examples of the principal groups, sterane (tetracyclic) and hopane (pentacyclic) skeleton structures are given in Figure 6.1. The diasteranes, which are structural analogs of sterane in which there is a rearrangement of the configuration along the sterane backbone, have also been isolated. Bitumens may be characterized by the presence of hopanes of an analogous series of 17 beta (H),21 beta (H) hopanes. The diasteromers at positions R-22 and S-22 of the extended hopanes containing 31-35 carbon atoms have also been isolated. Monoaromatic analogs of steroid structures and polynuclear aromatic hydrocarbons have been cited. (Douglas and Grantham, 1974; Simoneit, 1977; Seifert and Moldowan, 1978; Simoneit and Lonsdale, 1982; Richardson and Miller, 1982; Venkatesan et al., 1982).

The compositions reported in the literature listed above vary widely quantitatively. They are affected by the depositional conditions, the age of the sample and the type of material which was deposited. For example, the presence of diterpenoids which have structures that are analogous to abietane and pimarane (constituents of higher plants) are thought to result from deposits of terrestrial material (Simoneit, 1977; Richardson and Miller, 1982). Geological deposits which contain large quantities of pentacyclic triterpenoids are thought to results from decay of marine material as the pentacyclic materials are found in the structure of algae (Mills and White, 1987). The composition is also affected by the age of the deposit. Geologically older petroleums contain a higher amount of saturated material. Also, the concentration of tricyclic and pentacyclic triterpanes decreases with increasing age of the deposits (Seifert and Moldowan, 1978). The extent of biodegradation is also associated with the age of the deposit. For example, isoprenoid compounds degrade more swiftly than steranes and terpanes which have been observed to withstand moderate amounts of biological attack. However, steranes are completely degraded in very old crude petroleums. While the diasterane content also decreases, they survive to a certain extent (Seifert and Moldowan, 1979). The hopane compounds are thought to be a ubiquitous component of sediments as hopane structures have been isolated in every sediment analysed thus far (Ourisson et al., 1979; Ourisson et al., 1984). It is thought that the hopanes are incorporated in the cell membranes of the bacteria which instigate the decay of plant and animal matter. Thus, when the bacteria are buried, they die and form part of the fossil layers (Ourisson et al., 1984). In spite of the difficulties of degradation, it seems to be possible to identify bituminous substances by isolating the biological markers which are analogues of the original deposited materials (Mills and White, 1987).

## Identification and interpretation of standard spectra

The identification of bituminous materials from several archaeological specimens was made by isolation of hopane species utilizing gas chromatography/mass spectrometry (Mills and White, 1987). The complexity and variation in composition coupled with the lack of distinctive functional groups makes FT-IR an unlikely choice for the characterization of bituminous materials. Nevertheless, series of bitumens from various sources was obtained and the diffuse reflectance spectra of the samples were recorded. An added difficulty with this study is that although most of the samples were obtained from the British Museum (Natural History) and the Institute of Archaeology mineralogy collection, the materials were not adequately catalogued and there is no record of how the identity (ie bitumen or asphalt), was determined. Most of the samples used in the study did have some sort of geological provenance (see appendix). However, no clear pattern was established between those samples marked bitumen and those labelled as asphalt. The samples were classified according to similarities in the spectra and not by the original designation. Three samples obtained from Raymond White (National Gallery) were known to be bitumen, asphaltum and asphaltite and these samples were utilized to classify the other samples. Seventeen samples were found to have similar spectra, but they were further classified as group I (seven samples) and group II (ten samples) based on slight differences in the spectra. The samples of asphaltum and asphaltite fell into group II. A third group of samples was marked by further differences. Two spectra were marked with strong bands which may be due to inorganic matter.

The majority of the bitumen/asphalt sample spectra from groups I (Figure 6.2a) and II (Figure 6.3a) are simple spectra which indicate the nature of the materials as hydrocarbon mixtures. The characteristic strong bands occur in the regions of 2933 - 2924 $cm^{-1}$, 2866 - 2855 $cm^{-1}$, 1464 - 1459 $cm^{-1}$ and 1379 - 1376 $cm^{-1}$ for group I and in the regions of 2929 - 2923 $cm^{-1}$, 2869 - 2855 $cm^{-1}$, 1461 - 1457 $cm^{-1}$ and 1379 - 1377 $cm^{-1}$ for those in group II. These absorptions are due to the C-H stretching and bending vibrations (see Table 6.1) These band regions are also characteristic for the paraffin waxes and may be differentiated by the fact that the wax is a fairly simple chemical structure compared to the mixture in the asphalts. The presence of a melange of materials results in fairly broad bands which are generally less intense than the bands due to the C-H stretching modes. Both of the groups are also sometimes characterized by bands in the regions of 882 - 860 $cm^{-1}$, 820 - 813 $cm^{-1}$ and 753 - 744 $cm^{-1}$ for group I and 879 - 871 $cm^{-1}$, 821 - 800 $cm^{-1}$ and 758 - 743 $cm^{-1}$ for group II. These bands vary considerably in intensity between samples and all three absorptions are not always present in every sample spectrum. They are thought to be due to the C-H out-of-plane deformations arising from the aromatic ring and are characteristic of the substitution pattern (see Table 6.1).

Groups I and II are differentiated by the region between 1700 - 1600 $cm^{-1}$ in the spectra. In the group I spectra, the region is characterized by the presence of a band in the region 1605 - 1598 $cm^{-1}$ and a less intense band located in the region 1652 - 1647 $cm^{-1}$ which is very weak in some of the sample spectra. The spectra in group II contain a band in the region of 1706 - 1695 $cm^{-1}$ and one in the region of 1607 - 1598 $cm^{-1}$. Some of the spectra in the second group also exhibit a band in the area of

1660 - 1645 cm$^{-1}$. The relative intensities of the bands in this group are variable. The spectra in group I are characterized by an absence or only a very weak shoulder in the region of 1706 - 1695 cm$^{-1}$. The bands in the region of 1607 - 1598 cm$^{-1}$ and 1605 - 1598 cm$^{-1}$ may be the result of the skeletal ring breathing mode in aromatic compounds, although the other bands which are normally associated with it are not present. The other two bands are more difficult to assign. The band in the region of 1700 cm-1 occurs in a region which is normally characteristic of oxygenated functional groups, such as the carbonyl group. There are very few other possibilities for identification and the assignment of this absorption is not clear. Although the range is slightly high for the values given by Bellamy (1975) of 1625 - 1575 cm$^{-1}$, the band in the region of 1645 - 1660 cm$^{-1}$ and 1652 - 1647 cm$^{-1}$ may be one of the degenerate pair of aromatic skeletal ring breathing modes.

The very weak bands in the region between 1209 and 1143 cm$^{-1}$ may be due to vibrations arising from branched chain alkanes which are reported to be uncharacteristic due to wide ranges of possible frequency and very weak intensity (Bellamy, 1975). However, these bands occur near regions which are characteristic of isopropyl groups (1170 ± 5 $cm^{-1}$, 1170 - 1140 $cm^{-1}$) and of tertiarybutyl groups (1250 ± 5 $cm^{-1}$, 1250 - 1200 $cm^{-1}$)(Bellamy, 1975). The two bands in the regions of 1049 - 1018 $cm^{-1}$ and 958 $cm^{-1}$ (group I) and in 1043 - 1014 $cm^{-1}$ and 960 - 917 $cm^{-1}$ (group II) fall into the ranges given by Bellamy (1975) for the pair of absorptions due to cyclohexane (1055 - 1000 $cm^{-1}$ and 1005 - 925 $cm^{-1}$). There is only one spectrum which exhibits a band at 727 $cm^{-1}$ in addition to the band in the region of 758 - 743 $cm^{-1}$. However, a shoulder often occurs on the band near 758 - 743 $cm^{-1}$. This indicates that there is not a high percentage of long straight chain hydrocarbons in the structure.

The third group includes three spectra which show some similarities, but are somewhat variable. This group contains the sample identified as bitumen from the National Gallery. All three of the spectra exhibit bands in the region of 2928 - 2925 $cm^{-1}$ and near 2857 $cm^{-1}$ which are characteristic of the C-H stretch vibration. The band which occurs within the range (1465 - 1446 $cm^{-1}$) is in agreement with the values given by Bellamy (1450 ± 20 $cm^{-1}$ and 1465 ± 20 $cm^{-1}$) for C-H deformation vibrations. However, the band which is expected to occur in the region of 1380 - 1370 $cm^{-1}$ is only evident in the first sample spectrum at

1382 $cm^{-1}$. The samples are characterized by a band which is centred in the region of 1617 - 1595 $cm^{-1}$ and is probably the result of aromatic skeletal stretching mode. There is great variation in the spectra in the region 1250 - 700 $cm^{-1}$ which is indicative of a variation in chemical composition. Also, the bands are observed to be broad which also suggests the presence of a mixture. The first sample, RW2 is also characterized by weak bands at 2516, 1796, 874 and 715 $cm^{-1}$ which are characteristic of calcium carbonate (Miller and Wilkins, 1952).

Two of the samples which were labelled as bitumen and rock asphalt were found to exhibit strong bands in the regions 2530 - 2516 $cm^{-1}$, 1817 - 1797 $cm^{-1}$, 880 - 878 $cm^{-1}$ and 730 - 715 $cm^{-1}$ which are characteristic of calcium carbonate (Miller and Wilkins, 1952). In addition, the rock asphalt spectrum has a very broad band with maximum intensities of 1433 and 1400 $cm^{-1}$ which correspond to a strong absorption at 1430 cm-1 recorded in the literature for calcium carbonate The spectra also have evidence of an organic component with two absorptions in the regions of 2926 - 2925 $cm^{-1}$ and 2860 - 2855 $cm^{-1}$. The C-H deformation absorptions, however, seem to be masked by the strong absorption near 1430 $cm^{-1}$. Also, there are bands which occur in the region of 1200 - 1020 cm$^{-1}$ which may be due to organic materials. The presence of the inorganic matter interferes with the interpretation of the spectrum.

Identification of unknown samples

Although there is some difficulty in identifying bituminous materials using infrared, two samples were tentatively identified as bituminous by the simplicity of their spectra and comparison with spectra in groups I and II. The first sample (KA4) was of material which was purchased in a street market in Ankara, Turkey and thought to be refined asphalt. It was desirable to confirm the identification as the material was to be used for experimental tool making. A spectrum was obtained and the values of the frequencies are listed in Table 6.1. The spectrum (Figure 6.2b) was found to resemble those in group I most closely. The sample spectrum exhibited bands at 2947, 2920, 1600, 1465, 1378, 865, 812 and 750 cm$^{-1}$ which correspond to those observed for the group I materials. Also, there are weak absorptions in the area of 2850, 1210, 1030 and 725 cm$^{-1}$ which support the possible identification of the sample as a bituminous substance.

The second sample was a black residue (KA1) which was parallel to the unpolished edge of a flint sickle blade from the Institute of Archaeology Mallowan collection from the site Arpachiyah dating from the Halaf period (possible 5th mellenium) . The blade is truncated at one end and broken at the other. The edge exhibits a gloss and is retouched with slight irregular denticulation. The location of the black deposit indicated that it might have been utilized as hafting material. A small sample was removed with the silicon carbide paper and the spectrum was obtained. The spectrum (Figure 6.3b) was fairly simple and is similar to those of the bituminous material in group II. The spectrum is characterized by absorptions at 2928, 2855, 1702, 1460, 1379, 1119, 1033 and 754 $cm^{-1}$. Also, there is a band in the region of 1600 $cm^{-1}$ and there are several very weak bands in the region of 900 - 800 $cm^{-1}$ which further support the identification.

### Shale, jet and dopplerite

#### Source

Shale and jet are bituminous materials which have been used since antiquity for decorative objects. Jet has been defined as "essentially a very hard coal" (Mills and White, 1987). Shale is sedimentary rock composed of clay minerals and quartz, calcite, pyrite and (carbonaceous) organic substances. However, the composition is variable, the clay content ranges from nearly 100% to 40% and the other constituents are not constant. Although these materials are formed in strata beneath the surface of the earth, several sources were exploited in early times. For example in Great Britain, jet was obtained from the Whitby beach area and shale from deposits in the Kimmeridge area.

### Composition

Shale may vary considerably in composition. The Kimmeridge deposits include strata of clays, shales and the material known as Kimmeridge coal which is oil shale with a high bitumen content (Arkell, 1947). The organic extract of shale from Green River, Colorado was found to contain isoprenoid paraffins (12%), carotenoids (13%) terpenoids (20%) and steroids (20%) with a further 10% which seem to be the same types of compounds (Gallegos, 1971). The types of organic material are very similar to those discussed in the section on bitumens and asphalts.

### Identification and interpretation of standard spectra

The similarity of the organic content of shale and jet to other bituminous materials and the variations in compostion between shale strata from the same geographic location make the identification of materials such as jet or shale very difficult. An infrared spectrum was published (Gallegos, 1971) of the organic extract of the Green River shale. The infrared spectrum coupled with the nuclear magnetic resonance (NMR) spectrum were reported to give evidence for large quantities of branched chain alkanes and multiple ring constituents and small amounts of olefinic materials. The infrared spectrum was fairly simple and had strong bands located approximately at 2930, 2850, 1458, 1445, 1370 and 1360 $cm^{-1}$ which are due to the C-H stretching and bending vibrations. The literature spectrum also exhibited weak bands near 1305, 1205, 1165, 970, 950, 930, 850, 810, 760 and 720 $cm^{-1}$. The diffuse reflectance technique has both advantages and disadvantages. It examines the whole sample and therefore gives a fingerprint which may be useful in identification of a material from a particular source. However, with the shale materials, the presence of inorganic materials may distort the spectra and cause alterations due to specular reflectance. The other difficulty is that only a few samples were obtained and a far larger collection of samples from a wider area is needed to make conclusive decisions about identity and provenance.

Two samples of dopplerite were obtained from the Institute of Archaeology mineralogical collection. The labels indicated that the materials came from Ireland and defined the dopplerite as secondary bituminous minerals formed as a humic acid gel by percolation in fissures of peat. The materials were classified with the shale and jet due to the similarities in the spectra.

Two samples of jet were obtained from different sources, one from the Whitby Museum and a second which was also said to be Whitby jet. Two samples of shale were also examined. One sample was a brown material which was thought to come from Kimmeridge and the second was obtained from Kimmeridge. The spectra of the Whitby jet were found to be very similar: the spectra of the two jet samples are shown in Figure 6.4. The spectra of the two shale samples (Figure 6.5) were observed to be different from each other and from the jet spectra. The dopplerite spectra were similar to each other with variations from the other types of material (Figure 6.6).

The jet spectra (Figure 6.4) are characterized by bands in the region of 2928 and 1446 $cm^{-1}$ and a weak band in the region of 1375 $cm^{-1}$. These absorptions are due to the C-H stretching and bending deformations which have been described earlier. The spectra are also characterized by absorptions near 1609 and 1510 $cm^{-1}$ and near 824 and 754 $cm^{-1}$ which are characteristic of aromatic compounds. The spectra also contain a weak absorption in the region of 3060 $cm^{-1}$ which results from aromatic C-H stretches. The spectra contain a broad doublet centred near 3294 $cm^{-1}$ which is indicative of O-H groups. The materials are unlikely to contain oxygenated compounds, so the bands are thought to result from hydrolysis of the samples over the period of time since they have been exposed to the atmosphere. The spectra contain a broad absorption centred at 1224 $cm^{-1}$ and a weaker band at 1041 $cm^{-1}$ which are probably due to the contribution of several compounds which are difficult to characterize.

The Kimmeridge shale spectrum (Figure 6.5b) contains the usual characteristic absorptions of the aliphatic C-H stretching vibrations at 2927, 2858 and 1379 $cm^{-1}$. The spectrum also exhibited bands at 1605, 781, 752 and 715 $cm^{-1}$ which are indicative of substituted aromatic systems. The spectrum also contains a fairly intense band at 1705 $cm^{-1}$ which probably results from the non-organic shale constituents. There is a broad band centred at 1038 $cm^{-1}$ with shoulders located near 1100 and 1180 $cm^{-1}$ which are probably due to more than one component. The band at 1038 $cm^{-1}$ may be representative of overlapping bands due to ring hydrocarbons which absorb in this region. For example, cyclohexane exhibits two absorptions in the regions 1005 - 925 $cm^{-1}$ and 1055 - 1000 $cm^{-1}$. The spectrum contains evidence for the presence of calcium carbonate (calcite). The spectrum exhibits a strong absorption at 1450 $cm^{-1}$ which corresponds to the band reported to occur at 1430 $cm^{-1}$ in the literature (Miller and Wilkins, 1952). This band is broad and very intense and consequently masks the C-H deformation which is expected near 1465 $cm^{-1}$. The spectrum also contains a weak band at 2514 $cm^{-1}$ and a medium, sharp band at 878 $cm^{-1}$ which also correspond to those reported in the literature at 2530 and 877 $cm^{-1}$ (Miller and Wilkins, 1952).

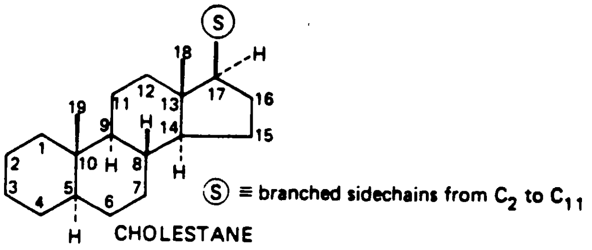
The spectrum of the brown shale (Figure 6.5a) which is suspected to be from Kimmeridge is somewhat different from that of the sample of known provenance. There is no evidence for the presence of calcite in the spectrum of the brown shale. The spectrum exhibits the bands expected of aliphatic hydrocarbons at 2889 and 1468 $cm^{-1}$, but the band expected in the region 1380 -

1370 cm$^{-1}$ falls at 1345 cm$^{-1}$ with a shoulder near 1360 cm$^{-1}$. The region between 1500 and 1200 cm$^{-1}$, which is dominated by the band at 1450 cm$^{-1}$ with a weak band at 1379 cm$^{-1}$ in the Kimmeridge shale spectrum, contains four sharp bands located at 1468, 1345, 1282 and 1241 cm$^{-1}$ in the spectrum of the brown shale. There is a very broad absorption band with maximum intensities at 1104 and 1017 cm$^{-1}$ which is probably the result of overlapping bands due to the complexity of the mixture. The spectrum contains a broad absorption which exhibits maximum intensity at 1606 cm$^{-1}$ with a shoulder in the region of 1710 cm$^{-1}$, and weak bands at 844, 780 and 696 cm$^{-1}$ which are indicative of aromatic compounds.

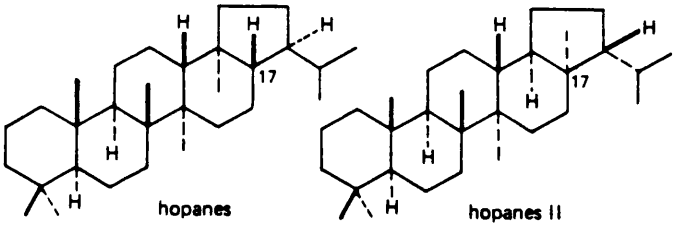
The dopplerite spectra are characterized by very broad absorptions (Figure 6.6). The two samples which are from different locations do not give identical spectra. There are similarities between the spectra which include a strong broad band centred at 3385 (IA3) and 3336 cm$^{-1}$ (IA4), a very weak absorption near 2929 cm$^{-1}$ in the spectrum of IA4 which appears as a shoulder on the broad band and is extremely weak in the spectrum of IA3. Both spectra exhibit a broad band with maximum intensity at 1613 cm$^{-1}$ (IA3) and 1608 cm$^{-1}$ (IA4) with a shoulder in the region of 1700 cm$^{-1}$ which is similar to the region in the spectra of the jet samples and in the brown shale spectrum. This absorption is probably due to the skeletal ring breathing mode in aromatic compounds. The spectra of the dopplerite samples also contain a weak absorption at 1511 $cm^{-1}$ (IA3) and 1510 $cm^{-1}$ (IA4) which could also result from skeletal ring breathing modes. The spectrum of IA3 has an absorption at 1429 $cm^{-1}$ which has an extremely broad shoulder which masks the second absorption expected near 1480 $cm^{-1}$. The spectrum of IA4 has two bands located at 1431 and 1378 $cm^{-1}$, but the bands are fairly broad. The region between 1100 and 900 $cm^{-1}$ is marked by three broad absorptions with maxima at 1086, 993 and 917 $cm^{-1}$ in the spectrum of IA3 while the region in the spectrum of IA4 is also a very broad absorption with maxima at 1220, 1148 and 1064 $cm^{-1}$. The spectrum of IA3 is marked by a sharp absorption at 3621 $cm^{-1}$ and has three weak absorptions located at 829, 753 and 695 $cm^{-1}$. In the spectrum of IA4, the absorptions are visible, but the strongest band is located at 754 $cm^{-1}$.

### Identification of unknown samples

Eight black beads from a Roman cemetery site at Verulamium, St Albans (Verulamium Museum V7532, numbers 146, 166, 127, 149, 152, 164, 168 and 131) were sampled with silicon carbide paper. The sample was removed from the side of the beads to protect the drill marks which are evident in the holes. The spectra obtained were found to be almost identical, indicating that the material for the beads was probably obtained from the same source. The spectra were characterized by absorptions in the ranges 2928 - 2927 cm$^{-1}$, 2860 - 2858 cm$^{-1}$, 1453 - 1438 cm$^{-1}$ and 1379 - 1377 cm-1 in addition to a broad absorption in the region 1607 - 1596 cm$^{-1}$ shoulders near 1700 and 1651 cm$^{-1}$, a shoulder which is apparent on the strong C-H band in the region of 3066 cm$^{-1}$, and bands at 887 - 886 cm$^{-1}$, 822 - 820 cm$^{-1}$ 752 - 739 cm$^{-1}$ and 707 - 694 cm$^{-1}$ (Figure 6.7a). There is a broad band with maximum absorption near 1261 and 1216 - 1198 cm$^{-1}$ which in addition to the other bands are characteristic of almost all of the bituminous materials which have been discussed. Visual comparison of the bead sample spectra with those of the standard spectra showed the jet spectra to be the most similar in general shape and intensity. The only major variation is that the strong band in the region of 1014 - 1001 cm$^{-1}$ in the spectra of the bead samples is not evident in the jet spectra where a much less intense band occurs at 1041 cm$^{-1}$. Without extensive numbers of samples from various locations, it is difficult to make a definite identification. However, a tentative identification may be made based on the evidence obtained thus far that the beads are made of jet as their sample spectra is more similar to those of the Whitby jet than those of the two shale samples. The spectrum of one of the samples (V7532 #127) is compared to the jet from Whitby museum (GS17) in Figure 6.7.



I



II

Figure 6.1 Structures of the cholestane (tetracyclic) (I) and hopane (pentacyclic) (II) skeletons (Mills and White, 1987).

Figure 6.2 Diffuse reflectance FT-IR spectra of (a) glance pitch (IA5) from the Dead Sea, Jordan (Group I) (gsva0149) and (b) material purchased from a market in Ankara, Turkey (KA4) (gsva0261).

Figure 6.3 Diffuse reflectance FT-IR spectra of (a) asphalt (NJS24) from Khurbet Qumran, Jordan (Group I) (gsva0608) and (b) residue from flint sickle blade from Arpachiyah (KA1) (gsva0245).

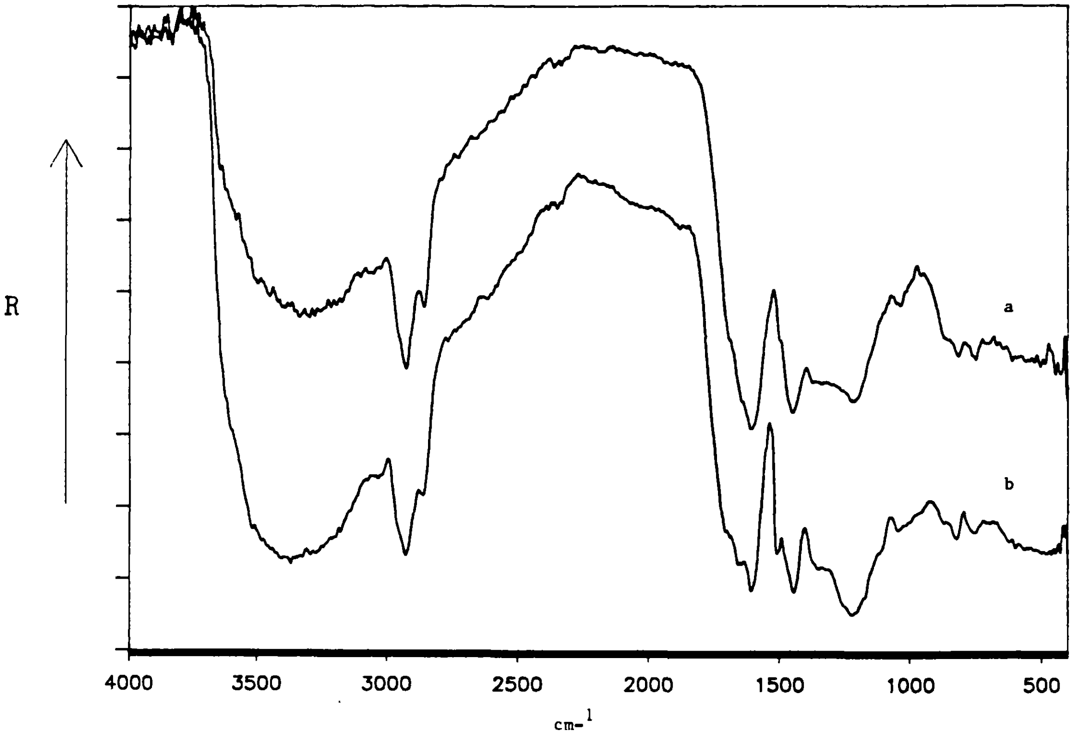


Figure 6.4 Diffuse reflectance FT-IR spectra of (a) jet from Whitby beach (NJS10) (gsva0230) and (b) jet from Whitby Museum (GS16) (gsva0517).

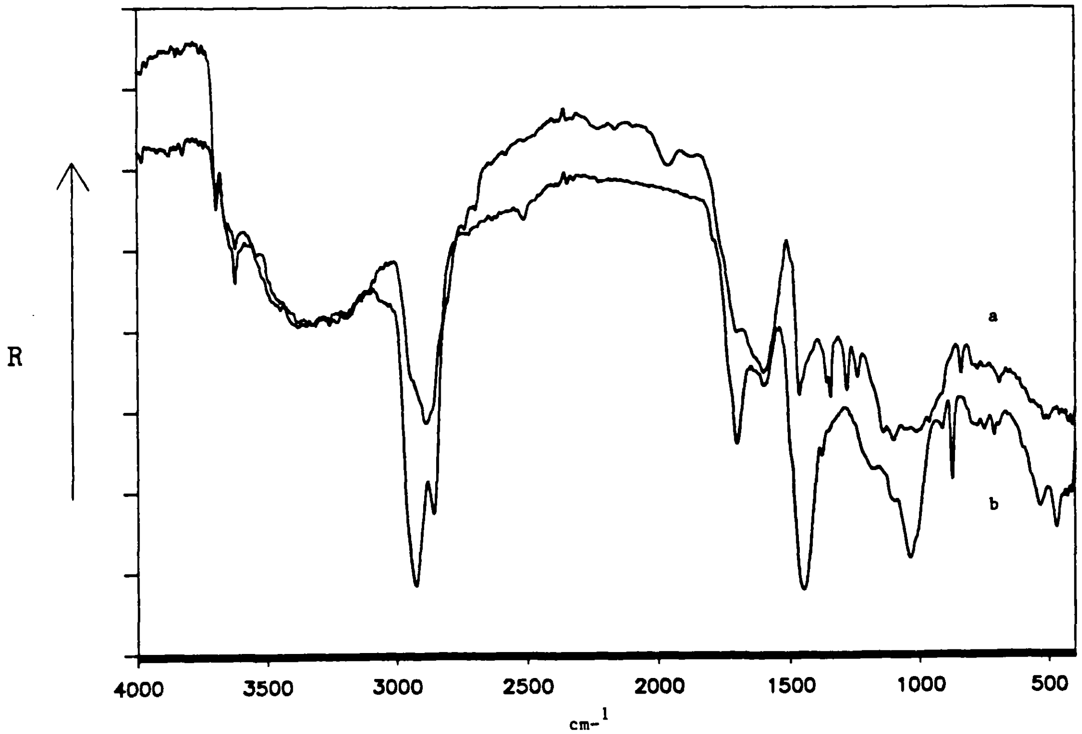


Figure 6.5 Diffuse reflectance FT-IR spectra of (a) brown shale thought to originate from Kimmeridge (GS15) (gsva0546) and (b) black shale from Kimmeridge (GS17) (gsva0547).

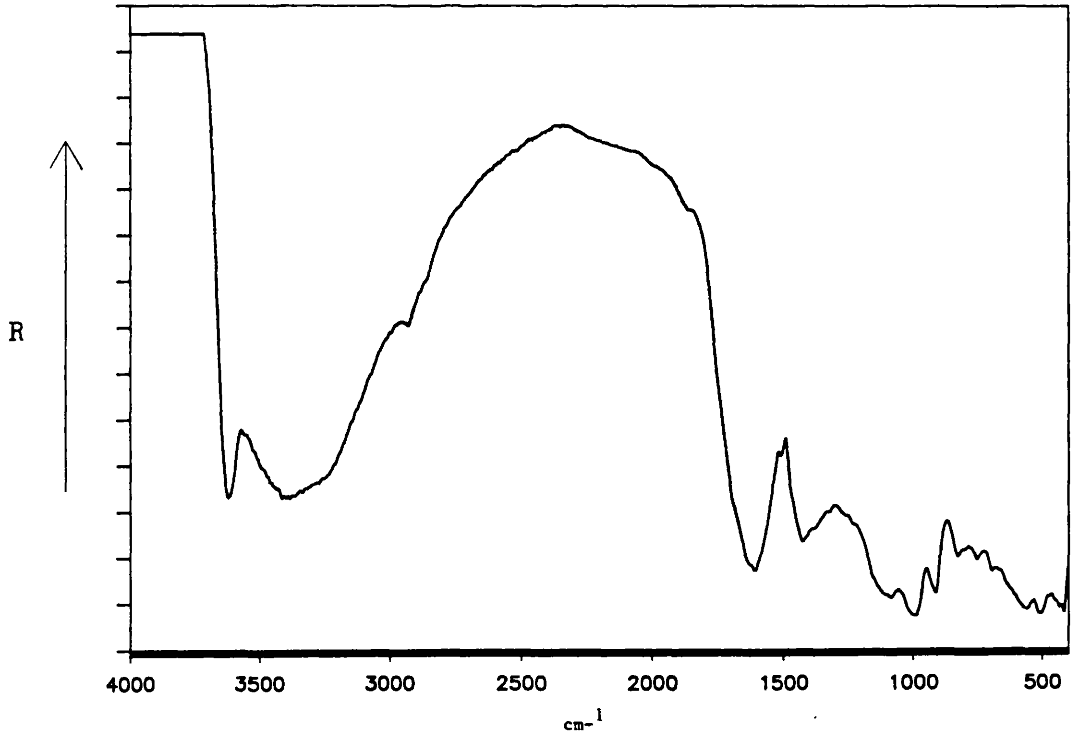


Figure 6.6 Diffuse reflectance FT-IR spectrum of dopplerite (IA3) from Garry Castle, County Westmeath, Althone (gsva0147).

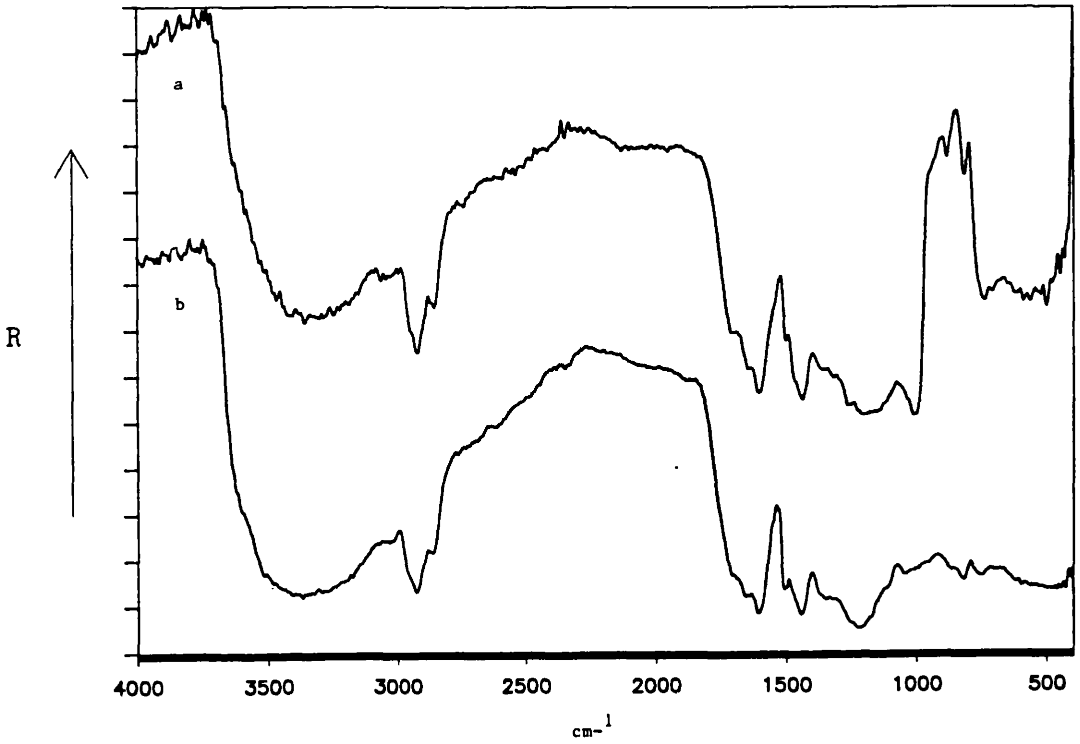


Figure 6.7 Diffuse reflectance FT-IR spectra of (a) black bead (DM3) found in cemetery at Verulamium, St. Albans (V7532 #127) (gsva0413) and (b) jet from Whitby Museum (GS16) (gsva0517).

## TABLE 6.1

Frequency values and band assignments for bitumens and unknowns identified as bitumen

| Group I | Group II | KA4 | KA1 | Vibration | Functional group | Frequency range given in literature (1) |
|---|---|---|---|---|---|---|
| cm-1 | cm-1 | cm-1 | cm-1 | | | cm-1 |
| 3295 - 3190(m) | 3368 - 3174(va) | 3180(sh) | 3217(m,b) | O-H stretch | water | |
| * 2959(s) | * 2953(s) | 2947(s) | | C-H stretch | methyl group | 2962 ± 10(s) |
| 2933 - 2924(s) | 2929 - 2923(s) | near 2920(s) | 2928(s) | C-H stretch | methylene group | 2926 ± 10(s) |
| 2866 - 2855(s) | 2869 - 2855(s) | near 2850(s) | 2855(s) | C-H stretch | methylene group | 2853 ± 10(s) |
| * 2730 - 2727(w) | * 2732 - 2727(w) | near 2730(w) | near 2730(sh) | unassigned | | |
| | 1706 - 1695(va) | | 1702(m) | unassigned | | |
| * 1652 - 1647(va) | * 1660 - 1645(va) | | | skeletal ring stretch | aromatic ring | 1650 - 1585(s) unsym. tri-substitution |
| | | | | C=C stretch | C=C bond non-conjugated | 1680 - 1620(va) |
| 1605 - 1598(va) | 1607 - 1598(va) | 1600(m) | near 1600(m) | skeletal ring stretch | aromatic ring | 1600 - 1560(w unless conjugated) |
| | | | | C=C stretch | C=C bond phenyl conjugated | near 1625(s) |
| | | | | C=C stretch | C=C bond, aliphatic conjugated | near 1600(s) |
| 1464 - 1459(s) | 1461 - 1457(s) | 1465(s) | 1460(s) | C-H asym. deformation | methyl group | 1450 ± 20(m) |
| | | | | C-H deformation | methylene group | 1465 ± 20(m) |
| 1379 - 1376(s) | 1379 - 1377(s) | 1378(s) | 1379(m) | C-H sym. deformation | methyl group | 1380 - 1370(s) |
| 1209 - 1203(w) | * 1205 - 1185(w) | near 1210(b) | near 1200(sh) | skeletal vibrations | branched chain alkanes | see text |
| | 1164 - 1143(w) | | | skeletal vibrations | branched chain alkanes | see text |
| | | | 1119(s) | unassigned | | |

TABLE 6.1 contd.

Frequency values and band assignments for bitumens and unknowns identified as bitumen

| Group I<br>cm-1 | Group II<br>cm-1 | KA4<br>cm-1 | KA1<br>cm-1 | Vibration | Functional group | **Frequency range given in literature (1) cm-1** |
|---|---|---|---|---|---|---|
| 1049 - 1018(w) | 1043 - 1014(w) | 1030(m) | 1033(s) | ring deformation | cyclohexane | **1055 - 1000(m)** |
| * 958(w) | * 960 - 917(w) | near 950(sh) | | ring deformation | cyclohexane | **1005 - 925(m)** |
| * 882 - 860(va) | * 879 - 871(va) | 865(m) | | C-H out-of-plane deformation | aromatic ring | **900 - 860(m) one free H atom** |
| * 820 - 813(va) | * 821 - 800(va) | 812(m) | | C-H out-of-plane deformation | aromatic ring | **860 - 800(vs) para-substitution** |
| * 772(w) | | | | C-H out-of-plane deformation | aromatic ring | **810 - 750(vs) meta-substitution** |
| * 753 - 744(va) | 758 - 743(va) | 750(m) | 754(w,b) | C-H out-of-plane deformation | aromatic ring | **770 - 735(vs) ortho-substitution** |
| | | | | C-H out-of-plane deformation | aromatic ring | **770 - 730(vs) mono-substitution** |
| near 727(sh) | | near 725(m) | | C-H out-of-plane deformation | aromatic ring | **710 - 690(s) mono-substitution** |

* Absorption is very weak or absent in some spectra.

1. Bellamy, 1975

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp

TABLE 6.2

Frequency values and band assignments for jet, shale, dopplerite, and unknown beads

| Jet GS16 cm-1 | Jet NJS10 cm-1 | Shale GS15 cm-1 | Shale GS17 cm-1 | Dopplerite IA3 cm-1 | Dopplerite IA4 cm-1 | Unknown beads cm-1 | Vibration | Functional group | Frequency range given in literature (1) cm-1 |
|---|---|---|---|---|---|---|---|---|---|
| | | | | 3621(sp) | | | unassigned | | |
| 3294(b) | 3299(b) | 3328(b) | 3384(b) | 3385(s,b) | 3336(s,b) | 3419 - 3310(m,b) | O-H stretch | water | |
| nr 3060(sh) | nr 3060(sh) | nr 3060(sh) | nr 3060(sh) | | | * 3066(w) | C-H stretch | aromatic ring | 3070 and 3030(w) |
| 2928(s) | 2926(s) | | 2927(s) | nr 2920(sh) | 2929(w) | 2928 - 2927(s) | C-H stretch | methylene group | 2926 ± 10(s) |
| nr 2850(w) | 2861(m) | | 2858(s) | | | 2860 - 2858(m) | C-H stretch | methylene group | 2853 ± 10(s) |
| | | | 2514(w) | | | | calcium carbonate | | 2530(vw) (2) |
| nr 1700(sh) | nr 1700(sh) | nr 1710(sh) | 1705(s) | nr 1700(sh) | nr 1700(sh) | nr 1700(sh) | unassigned | | |
| nr 1650(sh) | nr 1650(sh) | | | | | nr 1651(sh) | skeletal ring stretch | aromatic ring | 1650 - 1585(s) unsym. tri-substitution |
| | | | | | | | C=C stretch | C=C bond non-conjugated | 1680 - 1620(va) |
| 1609(s) | 1610(s) | 1606(s) | 1605(m) | 1613(s,b) | 1608(s,b) | 1607 - 1596(s) | skeletal ring stretch | aromatic ring | 1600 - 1560(w unless conjugated) |
| | | | | | | | C=C stretch | C=C bond phenyl conjugated | near 1625(s) |
| | | | | | | | C=C stretch | C=C bond aliphatic conjugation | near 1600(s) |
| 1510(w) | nr 1500(w) | nr 1500(vw sh) | nr 1500(vw sh) | 1511(w) | 1510(w) | nr 1504(w) | skeletal ring stretch | aromatic ring | 1525 - 1475(va) |
| 1446(s) | 1452(s) | 1468(s) | | nr 1480(sh) | | 1453 - 1438(s) | C-H asym. deformation | methyl group | 1450 ± 20(m) |
| | | | | | | | C-H deformation | methylene group | 1465 ± 20(m) |
| | | | 1450(s) | 1429(s,b) | 1431(s,b) | | calcium carbonate | | 1430(vs,b) (2) |
| nr 1375(w) | nr 1375(w) | nr 1360(sh) | 1379(w) | | 1378(s,b) | * 1379 - 1377(m) | C-H sym. deformation | methyl group | 1380 - 1370(s) |
| | | 1345(s) | | | | | unassigned | | |

TABLE 6.2 contd.

Frequency values and band assignments for jet, shale, dopplerite, and unknown beads

| Jet<br>GS16<br>cm-1 | Jet<br>NJS10<br>cm-1 | Shale<br>GS15<br>cm-1 | Shale<br>GS17<br>cm-1 | Dopplerite<br>IA3<br>cm-1 | Dopplerite<br>IA4<br>cm-1 | Unknown beads<br>cm-1 | Vibration | Functional group | Frequency range given in literature (1)<br>cm-1 |
|---|---|---|---|---|---|---|---|---|---|
| | | 1282(s) | | | | | skeletal | branched chain | see text |
| nr 1260(sh) | nr 1260(sh) | 1241(s) | | | | nr 1261(sh) | vibrations | alkanes | |
| 1224(s) | 1226(s) | | | | 1220(s,b) | 1216 - 1198(s) | unassigned | | |
| | | | nr 1180(sh) | | 1148(s,b) | | unassigned | | |
| | | 1104(s,b) | nr 1100(sh) | 1086(s,b) | 1064(s,b) | | unassigned | | |
| 1041(w) | nr 1040(w) | 1017(s,b) | 1038(s) | 993(s,b) | | 1014 - 1001(s) | ring deformation | cyclohexane | 1055 - 1000(m) |
| | | | 916(w) | 917(s,b) | | | ring deformation | cyclohexane | 1005 - 925(m) |
| nr 880(w) | nr 880(w) | | 878(m) | | | 887 - 886(m) | C-H out-of-plane | aromatic ring | 900 - 860(m) |
| | | | | | | | deformation | | one free H atom |
| | | | 878(m) | | | | calcium carbonate | | 877(s,sp) (2) |
| 824(m) | 817(m) | 844(m) | nr 820(sh) | 829(w) | | 822 - 820(m) | C-H out-of-plane | aromatic ring | 860 - 800(vs) |
| | | | | | | | deformation | | para-substitution |
| | | 780(w) | 781(w) | | | | C-H out-of-plane | aromatic ring | 810 - 750(vs) |
| 754(w) | 751(w) | | 752(w) | 753(w) | 754(w) | 752 - 739(w) | deformation | | meta-substitution |
| | | | | | | | C-H out-of-plane | aromatic ring | 770 - 735(vs) |
| | | | | | | | deformation | | ortho-substitution |
| | | | | | | | C-H out-of-plane | aromatic ring | 770 - 730(vs) |
| | | | | | | | deformation | | mono-substitution |
| nr 700(vw) | nr 700(vw) | 696(w) | 715(w) | 695(w) | nr 690(vw) | 694 - 707(w) | C-H out-of-plane | aromatic ring | 710 - 690(s) |
| | | | | | | | deformation | | mono-substitution |

* Absorption is weak in some sample spectra

1. Bellamy, 1975
2. Miller and Wilkins, 1952

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp; nr = near

# CHAPTER 7 RESINS AND RELATED MATERIALS

## Resins

### Source

Resin is the general term which is used for the exudate of many varieties of plants and trees. The sticky materials are not soluble in water and are produced as by-products of plant metabolism. They have been used by man since antiquity, primarily as adhesives, varnishes and binding media. The materials are found in both archaeological and art objects (Mills and White, 1987). The initial tree product is often referred to as an oleo-resin or balsam which may be distilled to produce turpentine as the distillate and rosin or colophony as the residue (Gettens and Stout, 1966).

### Composition

Resins are composed of mixtures of complex chemical compounds. Little information was obtained on the structure of resins until the development of modern chromatographic methods which are capable of separating the various components. The primary components are terpenoids (Mills and White, 1977). Terpenoids are composed of isoprene building blocks. (The structure of isoprene is given in Figure 7.1.) Monoterpenoids are composed of two isoprene units and contain 10 carbon atoms. Similarly, sesqui-, di- and triterpenoids are compounds which contain 3, 4 and 6 isoprene units and contain 15, 20 and 30 carbon atoms respectively (Mills and White, 1987). At normal temperatures, the C-10 and C-15 compounds occur in the liquid state and act as solvents for the C-20 and C-30 compounds which are solid. The di- and triterpenoids have not been found in the same resin and this criteria is used to classify the materials. However, the mono- and sesquiterpenoids may appear in the same resin (Mills and White, 1977; Mills and White, 1987).

One of the best known monoterpenoid mixtures is oil of turpentine which is the distillate of crude resin and widely used as a painting material and contains several monoterpenoid compounds. Many of the Pinaceae genera produce a similar monoterpenoid product, but the largest producers are the species of the Pinus genus. Thus, the other products are less abundant and more expensive. Also, essential oils which provide the characteristic odour of flowers and herbs are composed of oxygenated monoterpenoids (Mills and White, 1987).

Until recently, detailed knowledge of the chemical composition of various resins was not known. Although this type of information is now available, it is not of great use in analysis of art and archaeological samples. The reactions which occur over time alter the original composition and make a specific identification difficult. In some cases when a large amount of sample has been preserved or if the sample has not undergone extensive oxidation, the specific Pinus species may be identified. This is very rare. In some cases, the presence of a specific chemical compound may be used to identify a specific resin. For example, the presence of larixol and larixyl acetate indicates the presence of the Larch resin, Larix decidua Miller, commonly known as Venice turpentine, and only this resin and and Larix gmelinii have been found to have this composition. However, this type of analysis is dependent on an efficient separation technique. As with the bituminous materials, FT-IR presents the infrared spectrum of the entire compound and does not distinguish between various components. However, the resins as a group are characteristic and may be differentiated from other materials on the basis of the infrared spectra. Thus, a detailed analysis of the chemistry of resins is not appropriate in this thesis and only a general outline is presented. A more complete summary of resin chemistry as it relates to art and archaeology is given by Mills and White (1977; 1987).

## Diterpenoid resins

The principal sources of diterpenoid resins are Coniferales and the Leguminosae sub-family, Caesalpinioideae. The families of the Coniferales which produce resins which are believed to be the major sources for art and archaeology are summarized in Table 7.1 (Mills and White, 1987). Only the major resin producers are listed. Among the diterpenoid resins, there are several important skeletons which include the abietane and pimarane series which have three rings and the labdane series which have two rings and a side chain. The principal form of the materials contain the carboxylic acid functional group, although alcohol and aldehydes occur in small quantities. Examples are given in Figure 7.2 of laevopimaric, palustric, neoabietic and abietic acids which are abietadienes. The structures are very similar with variations in the position of the double bonds. The pimaradiene structures are similar to those of other series, but contain double bonds in different positions which may not be conjugated (Mills and White, 1977).

The most important labdane compound is trans-communic acid and others include cis-abienol, agathic acid, manool, lambertianic acid and pinusolide in addition to larixol and larixyl acetate (Figure 7.3). In the Leguminosae resins, the mirror-image structures or enamtiomers of the labdane series compounds are found. In these materials, the stereochemistry is reversed at the three asymmetric centers (Mills and White, 1977).

In summary, the resins of the Pinaceae are characterized by large quantities of the pimarane and abietane acid compounds. The Cupressaceae resins are composed primarily of labdane structures and those of the Araucariaceae contain a large amount of labdane compounds with smaller amounts of pimarane and abietane materials. As mentioned above, the Leguminosae resins are characterized by the presence of labdane structures (Mills and White, 1987).

## Triterpenoid resins

The major sources of the triterpenoid resins are the tropical Dipterocarpaceae sub-family, the Dipterocarpoidaeae which are known as the dammars. The sub-family contains 15 genera with more than 500 species and the harder resins, known as dammars, have become popular as picture varnishes and may possibly occur in conjunction with ethnographic and archaeological objects. The second important type is the resin known as mastic which is obtained primarily in the Mediterranean coast from *Pistacia lentiscus* L. (Anacardiaceae family). A resin is obtained from the tree known as *P. terebinthus* var. *atlantica* or *P. atlantica* which is found in Turkey, Cyprus and the Near East and this resin is known as Chian turpentine. Several resins are obtained from the Burseraceae family. The genera Canarium, Bursera and Protium produce resins which have been known as elemi resins. The Commiphora and Boswellia families produce the gum resins myrrh and frankincense which will be discussed in a later section (Mills and White, 1977; Mills and White, 1987).

The triterpenoids are usually tetracyclic or pentacyclic structures. The major tetracyclic compounds contain the dammarane or euphane skeletons (Figure 7.4). The dammarane and euphane structures are characterized by a ketone functionality or a hydroxyl group at position three and the side chain often contain double bonds and other functionalities. The major pentacyclic structures include the ursane and the oleanane compounds (Figure 7.4) and lupane and hopane series are found in lesser quantities and are less important (Mills and White, 1977). The ursane and oleanane when hydroxyl substituted at position 3, are refered to as alpha- and beta-amyrin and often occur in the same resin (Mills and White, 1977).

It is not known from what specific source the dammar used in Europe and the United States comes, however it is thought to be from either the Hopea or Shorea species and it has been found to contain primarily dammarane skeleton structures and polymeric hydrocarbons. Mastic has been found to have a greater variety of consitituents which have not been fully examined. The compounds which have been found include the euphane skeleton acids and a few oleanane materials (Mills and White, 1987).

## Ageing

As mentioned before, the composition of resins alters considerably with time. The structures of the abietane series which have been discussed differ by the location of the conjugated double bonds. The heating process causes alterations of the structure and the resulting product is composed of abietic acid with little or no laevopimaric acid. Also, as the materials age, the acids are converted by dehydrogenation to dehydroabietic acid (Figure 7.2) The material, 7-oxodehydroabietic acid (Figure 7.2) is formed from dehydroabietic acid by autoxidation. The structure of the material contains a ketone functional group (Mills and White, 1977). The presence of the two degradation products has been detected by gas chromatography and gas chromatography/mass spectroscopy and used to identify the materials as being a pine resin (Mills and White, 1977; Mills and White, 1987).

The labdane compound trans-communic acid has a conjugated carbon double bond in the side chain which is susceptible to polymerization. This is also the case for other compounds in the series. Resins which contain large amounts of trans-communic acid are transformed over a period of time to polycommunic acid which is a polymer of low molecular weight.

### Interpretation of standard spectra

A number of resins from the families listed in Table 7.1 were obtained from the Museum of Economic Botany, Kew, and the diffuse reflectance spectra were obtained of the original surface of the sample and from a freshly exposed surface. The resins analyzed in this study are listed in Table 7.2. The samples of the natural surfaces of the conifer resins show a fair amount of detail and thus, the resins are not thought to have been heavily degraded. For the most part, the region between 1300 - 400 cm$^{-1}$ shows evidence of overlapping due to the large number of components in the resins. However, some distinct bands are evident and quite a large amount of variation in the occurrence of bands which does not appear to be consistent within families. The spectra of the natural surfaces exhibit bands in very similar ranges and show a similar degree of variation. The frequencies of the various families for both natural and fresh surfaces are listed in Table 7.3. It must be stressed that there is a great deal of variation in the occurrence of the bands between the various samples. The spectra of the _Hymenaea_ species, _verrucosa_ and _courbaril_, show slightly less detail than the conifer resins. The mastic resin spectra, however, are marked by very broad, indistinct absorptions and a loss of detail in the region 1300 - 400 cm$^{-1}$ in comparison to those of the conifer resins. There is even less detail present in the spectra of the natural surface samples.

It is difficult to make specific band assignments for extremely complex mixtures such as resins. Also, several bands in a particular region may be due to the same functional group which is present in several different components of a mixture. However, several regions are characteristic for resins. The primary functional group which is present in most resins is the carboxylic acid group. This functional group which has been discussed in earlier sections is marked by the presence of bands in the region of 3000 - 2500 $cm^{-1}$ for samples in the solid state. In this region, a broad band is observed as a shoulder on the high frequency side of the C-H stretching bands and a "satellite band" is observed in the region 2700 - 2500 $cm^{-1}$, usually near 2650 $cm^{-1}$. The group also contains a carbonyl group. The general range for absorptions due to this group for aryl acids is listed as 1700 - 1680 $cm^{-1}$ and the range listed for alpha-, beta-unsaturated acids is 1705 - 1690 $cm^{-1}$. There are several other characteristic absorptions which include a weak band in the region of 1440 - 1375 $cm^{-1}$ with a second, stronger band located in the region of 1300 $cm^{-1}$ which are thought to result from a coupled C-O stretching vibration and an O-H in-plane deformation. Carboxylic acids are often marked by a second, more intense band which has been observed to occur at a lower frequency in the wide range 1320 - 1211 $cm^{-1}$. However, the band assignment has not been fully elucidated. The group is also marked by a fairly intense, broad band in the region 950 - 900 cm$^{-1}$ which is due to the O-H out-of-plane bending vibration (Bellamy, 1975).

Other functional groups which may contribute to the spectra are the ketone group and the hydroxyl group. The hydroxyl group is very polar in nature and forms hydrogen bonds with other polar materials. Intermolecular bonded O-H groups result in a broad, strong band in the region 3400 - 3200 cm$^{-1}$ (Bellamy, 1975). The presence of O-H groups may cause a band with a higher frequency than would be expected for carboxylic acids alone. The ketone group which is attached to six-carbon rings results in absorptions in the range expected for open chain, aliphatic ketones, 1725 - 1705 cm$^{-1}$. The presence of alpha-, beta-unsaturation has been observed to lower the frequency range to 1684 - 1674 cm$^{-1}$. However, higher frequencies are observed in fused ring systems and this may counteract the shift caused by the unsaturation (Bellamy, 1975). Thus, carbonyl absorptions which have higher frequencies than would be expected for carboxylic acids may be the result of both types of functional groups.

The spectra of the resins may also be affected by the presence of carbon-carbon double bonds. The characteristic regions were discussed in the section on fatty acids and include 3040 - 3010 cm$^{-1}$ for -CH=CH- C-H stretches and 3095 - 3075 cm$^{-1}$ for terminal =CH2 groups and 1680 - 1620 cm$^{-1}$ for the C=C stretches. The regions of 1310 - 1295 cm$^{-1}$ and 970 - 960 cm$^{-1}$ are characteristic of trans-substituted isomers and near 690 cm$^{-1}$ are expected of cis-substituted compounds (Bellamy, 1975).

The resin spectra, in general, are marked by a broad absorption in the region 3500 - 3100 cm$^{-1}$ (the ranges of values are listed for each family in Table 7.3). Often, the band has a maximum intensity near 3400 cm$^{-1}$ which then runs into the C-H absorptions. The band appears as a shoulder on the C-H absorptions in only a few spectra. The band is probably due to the presence of both bonded hydroxyl stretches and carboxylic acid stretches. The resin spectra also contain a band or shoulder in the region of 2650 cm$^{-1}$ which corresponds to the "satellite band" which is characteristic of carboxylic acids. The band tends to appear as a shoulder in the spectra of the Pistacia and in some of the resin sample spectra. The spectra are also marked by an absorption in the carbonyl region. In general, the absorptions fall into the range listed for alpha-,beta-unsaturated carboxylic acids, 1705 - 1690 $cm^{-1}$, but in some spectra, the frequency value may be as high as 1719 $cm^{-1}$. The higher values agree with the range given for saturated, aliphatic acids, 1725 - 1700 $cm^{-1}$, also, the frequency shift may be caused by the presence of additional ketone groups.

In the spectra of both the fresh and natural surfaces of the conifer resins, bands are apparent which may be assigned to other characteristic absorptions in the carboxylic acid group. Bands are observed near 1400 $cm^{-1}$, 1300 $cm^{-1}$ (except in the Pinaceae resins) and near 950 $cm^{-1}$. Also, in almost all spectra, a very intense band is observed near the region of 1280 - 1230 $cm^{-1}$ with most occurring near 1240 $cm^{-1}$. Although these bands are not all apparent in every spectrum, they may be tentatively assigned to absorptions due to the carboxyl group.

In the _Hymenea_ species, the fresh surface sample spectra exhibit bands in the regions 1266 - 1253 $cm^{-1}$ and 944 - 942 $cm^{-1}$, however, the bands are less distinct in the spectrum of the natural surface of _H. verrucosa_ where only a shoulder is apparent in the region of 1250 $cm^{-1}$. In the natural surface spectrum of

H. courbaril, bands appear at 1241 $cm^{-1}$ and 949 $cm^{-1}$. There is less detail in the mastic spectra. In both the fresh and aged sample spectra (except the fresh P. terebinthus), a broad band is observed with a maximum intensity in the region 1194 - 1184 $cm^{-1}$. The bands near 960 $cm^{-1}$ are only observed in the spectra of the fresh surfaces of the two P. lentiscus samples. The bands which are expected near 1400 and 1300 $cm^{-1}$ are not apparent in any of the Hymenea or Pistacia spectra. The loss of these bands and the band near 960 $cm^{-1}$ is probably due to the increased complexity of the resins which cause band overlap and subsequent masking of expected bands.

There is some evidence of the C=C group in some of the diterpene resin spectra. There are weak absorptions visible in the region 3080 - 3060 $cm^{-1}$ in certain spectra which may be indicative of C-H stretches of carbon double bonds. However, the values fall slightly between the ranges of 3095 - 3075 $cm^{-1}$ and 3040 - 3010 $cm^{-1}$ given by Bellamy (1975). The spectra are also marked by weak bands or shoulders in the regions near 1600 and 1650 $cm^{-1}$ which may be due to C=C stretching vibrations. These bands are not apparent in either the fresh or natural surface spectra of the Pistacia resins. The regions which are characteristic of C-H deformations for double bond trans- structures, 1310 - 1295 and 970 - 960 $cm^{-1}$, are also characteristic for carboxylic acids and the assignments for regions which have been made may in fact include these absorptions as well. Many of the diterpenoid spectra contain a weak absorption near 700 $cm^{-1}$ which may correspond to the C-H deformation in cis-substituted isomers which is expected near 690 $cm^{-1}$. None of the C=C characteristic absorptions occur in the triterpenoid Pistacia spectra.

The resin spectra are also characterized by absorptions which are typical of C-H stretches and deformations. The second absorption is centred near 2870 $cm^{-1}$ in most of the resin spectra and sometimes appears as a shoulder on the lower frequency side of the stronger band in the region of 2940 $cm^{-1}$. The resin spectra are also characterized by two absorptions of approximately equal intensity in the region of 1467 - 1450 $cm^{-1}$ and 1388 - 1365 $cm^{-1}$ which may be assigned to the C-H deformations.

## Identification of unknown samples

When samples from archaeological contexts were examined, it became evident that the amount of detail which was observed in the resin standards was not retained in aged samples. This was not surprising. However, the spectra retained a sufficient number of characteristic absorptions of carboxylic acid to be classified as resins. Also, the resin spectrum has a characteristic shape which is also indicative (see Figure 7.5). Twenty samples from various provenances were identified as resins and the ranges of frequencies which were observed to be characteristic of resins are listed in Table 7.4. The frequency values were found to be somewhat similar to those of a commercial sample of colophony which have been included for comparison. In addition to the samples which were identified as resins, a further twelve samples were tentatively assigned as resin mixtures. The spectra contain bands which are indicative of the carboxyl group, but the presence of other interfering bands from admixed materials or degradation products of the resin itself has obscured the spectra. Thus, the identification of these samples is merely tentative. The differentiation was made by visual and consequently subjective means. The details of the individual samples are listed at the end of the section.

The samples which were identified as resins are characterized by a broad absorption with maximum intensity in the region 3437 - 3221 $cm^{-1}$, a weak shoulder in the region 2641 - 2627 $cm^{-1}$, a strong band in the region 1726 - 1701 $cm^{-1}$ and a band in the region of 985 - 958 $cm^{-1}$ which are characteristic of carboxylic acids and have been discussed in detail. The spectra are also marked by a very intense, but somewhat ill-defined absorption with maximum intensity in the region of 1215 - 1179 $cm^{-1}$. In a few cases, a second absorption was observed in the region of 1138 - 1132 $cm^{-1}$ or 1238 - 1223 $cm^{-1}$ and in two samples, the maximum absorption occurred in the region of 1236 - 1223 $cm^{-1}$ instead of 1215 - 1179 $cm^{-1}$.

The spectra are also marked by a broad band at 1050 - 1039 $cm^{-1}$ which appears in almost all of the reference resin spectra, but has not been assigned to a specific functional group. The sample spectra also contain two bands of fairly equal intensity in the regions of 1463 - 1450 $cm^{-1}$ and 1387 - 1379 $cm^{-1}$.

The remaining absorptions which have been noted in the standard resin spectra do not occur consistently in the sample spectra. Weak bands are evident in some of the spectra in the region 3084 - 3071 $cm^{-1}$ and 1610 - 1607 $cm^{-1}$ which may be due to C=C structures. Also, the band in the region 985 - 958 $cm^{-1}$ may be due to both the O-H out-of-plane deformation in carboxylic acids and the C-H deformation due to trans-substituted ethylenic bonds. A weak band is apparent in some spectra near 1420 - 1416 $cm^{-1}$ which is due to carboxylic acids, and a few spectra contain an absorption in the region 708 - 695 $cm^{-1}$ which may be representative of cis-substituted isomers of C=C compounds. However, it must be noted that the region 1300 - 400 $cm^{-1}$ is marked by only a few broad maxima with very weak bands in the region 900 - 400 $cm^{-1}$. An area of absorption is evident in the region of 769 - 747 $cm^{-1}$ for some of the samples. As can be seen in Table 7.4, there is a great variation in the occurrence of absorptions in this region.

In general, the sample spectra are marked by a very broad band near 1200 $cm^{-1}$ and the carbonyl band is also observed to become broader in addition to the slight shift to higher frequencies. This may be explained in part by the increasing complexity of the aged material. The broad absorption near 1200 $cm^{-1}$ is probably due to a variety of absorptions which overlap The production of 7-oxodehydroabeitic acid in pine resins would result in the presence of ketone groups which may affect the shape and frequency of the carbonyl absorption. Also, there is a general loss of detail in the region 1300 - 400 $cm^{-1}$ which is the result of the great complexity of the mixture and has been described by Mills and White (1987).

The spectra of the materials which were tentatively assigned to resin mixtures were identified on the basis of presence of a broad band with a maximum intensity in the region of 3544 - 3229 $cm^{-1}$, a fairly weak shoulder on the lower frequency side of the C-H stretching vibration bands in the region of 2650 $cm^{-1}$, a strong band with maximum intensity in the region 1744 - 1706 $cm^{-1}$, a broad band with maximum intensity in the region of 1217 - 1174 $cm^{-1}$ (some maxima are located between 1126 and 1125 $cm^{-1}$) and a band in the region 1076 - 1039 $cm^{-1}$. The remaining bands are variable in occurrence and the region between 950 - 400 $cm^{-1}$ is very indistinct.

A sample was obtained from the non-reflecting side of a Chinese bronze mirror (Victoria and Albert Museum, FE87 1982) which was produced in Huzhou. A small amount of sample, which formed a black particulate inlay on the surface, was removed using a scalpel and rubbed on silicon carbide paper. The resulting spectrum was observed to resemble a resin spectrum upon visual examination and the computerized search selected the spectrum of

Pinus massoniana fresh surface as the closest match. The resin sample spectrum exhibited a greater degree of detail in the region 900 - 400 $cm^{-1}$ than has been observed for other resins (Figure 7.5). However, the identification of the resin to a specific species must be treated with caution due to the similarity of the various resin spectra to each other. Also, no references have been found on the exploitation of P. massoniana. (Rupert Hastings, Museum of Economic Botany, Kew, personal communication). It is most probable that the sample is some sort of conifer resin which is native to China.

A second example illustrates the danger of making a precise identification based on the infared spectra of resins. A sample of material incorporated into the embalmed internal organs was obtained from the tomb of Djehuty Nakht located at Deir el Bersheh (XI dynasty). The spectrum of the material was observed to be a resin and the computer search suggested either the spectra of Juniperus phoenicia or Pistacia lentiscus as the closest match. However, the sample was characterized by gas chromatography/mass spectroscopy and both dehydroabietic acid and

7-oxodehydroabeitic acid were identified which indicated the presence of a pine resin (R. White, personal communication).

Unknown sample information

Resins

RK3 Sample taken of light brown residue/old repair from base of Chinese bronze vase, possible sealant. Provenance - unknown. Date - 12th - 13th century. Victoria and Albert Museum Far Eastern Department 121-1876.

RK4 Black particles on reverse of Chinese bronze mirror. Provenance - Huzhou. Date - unknown Far Eastern Department, Victoria and Albert Museum, FE87 1982.

MFA2a Black funerary resin?/residue from coffin of Nesptah. Provenance - unknown. Date - XXII - XXVIth dynasty Boston Museum of Fine Arts 72.4838.

MFA2b as for MFA2a sample taken with silicon carbide paper.

MFA3b Black resin from pectoral. Provenance - unknown. Date - Late period Boston Museum of Fine Arts 72.769.

MFA4 Black resin from embalmed internal organs. Provenance - Tomb of Djehuty Nakht, Deir el Bersheh. Date - XIth dynasty Boston Museum of Fine Arts.

MFA8 Black residue from back of shawabti of Merneptah. Provenance - unknown. Date - unknown Boston Museum of Fine Arts W29. Sample taken with silicon carbide paper.

MFA10 Yellow ?resin sample with aromatic odor. Provenance - unknown. Date - unknown. Boston Museum of Fine Arts, Meyer Collection, no number.

MFA15 Sample of surface coating over painted design on dummy stone jars. Provenance - unknown. Date - unknown. Boston Museum of Fine Arts 72.4268.

MFA18 Sample of black ?resin from back of gilded bracelet of Nefetari. Provenance - unknown. Date - unknown. Boston Museum of Fine Arts 04.1955.

MFA20 Red residue from black Egyptian coffin. Provenance - unknown. Date - Middle Kingdom. Boston Museum of Fine Arts no number.

NJS11 Sample of adhesive used to hold inlays in gold relic box. Provenance - Gandhara region. Date - 1st - 2nd Century, A.D. Institute of Archaeology conservation laboratory number 3900.

AH1 Sample of orange residue from Egyptian textiles. Provenance - unknown. Date - unknown. Insitute of Archaeology conservation laboratory number 6108 via Petrie Museum.

KA7 Ethnographic knife with black ?resin handle. Provenance - central Australia. Date - unknown. Institute of Archaeology collection 52/1972 LP.4251. Sample compared to spectrum of hafting material composed of spinifex resin prepared by Aboriginals. Sample taken with silicon carbide paper.

SMC1 Sample of varnish from surface of Egyptian coffin lid described as uneven brownish/reddish varnish. Provenance - unknown. Date - ?XXI - XXIIth dynasty. Aberdeen University Anthropological Museum collection, via Scottish Museums Council SMC A194.

MS16 Golden yellow, brittle residue from model alabaster (?) cylinder jar. Provenance - unknown. Date - Old Kingdom (?). British Museum Egyptology Department 4481.

MS23 Golden orange, dry residue from alabaster (?) model one handled jar Provenance - unknown. Date - unknown. British Museum Egyptology Department 4567.

MS39 Reddish-brown, shiny, brittle residue with aromatic odour from small alabaster (?) cylinder jar with lid. Provenance - Kahun. Date - Middle Kingdom (XIIth dynasty). University College London Petrie Collection 7318.

MS40 as for MS39

MS41 Red-orange, sticky residue which appears dark brown on the surface from small alabaster (?) cylinder jar inscribed with titulary. Provenance - Hatshepsut Deir el Bahari foundation deposit. Date - New Kingdom (XVIIIth dynasty). University College London Petrie Collection 15862.

MS42 as for MS41, sample taken of dark material on surface.

## Resin mixtures

IG1 Sample of resin used to hold stone blades in ethnographic adze, traditional design with chair spindle used in place of wooden shaft. Provenance - unknown, probably central Australia.

Date - unknown - probably late 19th to early 20th century. Ian Glover, Institute of Archaeology, Prehistory Department.

NJS14 Sample of residue from inside wooden hilt. Provenance - unknown. Date - unknown. Institute of Archaeology Department of Conservation laboratory number 1593.

MS31P Black/brown, friable residue from ceramic cylindrical jar with narrowing mouth. Provenance - Gebelain. Date - New Kingdom (late XVIIIth dynasty). British Museum Department of Egyptology 22198.

MS34P Black, friable residue from pottery brownware globular jar with white slip. Provenance - Buhen. Date - Middle Kingdom. British Museum Department of Egyptology 65686.

MS36P Brown/black, brittle residue form large ceramic globular jar with two small lugs on shoulders. Provenance - Tell Nebesheh. Date - Late Period (XXVIth dynasty). British Museum Department of Egyptology 22354 (166A).

MS38P Brown, powdery residue from large ceramic amphora with stippled lines and Hieratic inscription. Provenance - unknown. Date - unknown. British Museum Department of Egyptology. 30334.

MS34 Black, gritty residue from large alabaster (?) cylinder jar. Provenance - unknown. Date - unknown. British Museum Department of Egyptology 29866.

MS43 Medium brown, powdery residue from alabaster (?) cylinder jar with lid, both inscribed with titulary. Provenance - Hatshepsut Deir el Bahari foundation deposit. Date - New Kingdom (XVIIIth dynasty). University College London Petrie Collection 15863.

MFA7 Sample of orange resin and possibly some orpiment from beard. Provenance - ? Date - ? Boston Museum of Fine Arts 72.4798.

MFA9 Black contents from Egyptian alabaster jar. Provenance - unknown. Date - Old Kingdom. Boston Museum of Fine Arts 04.1887. Sample taken with silicon carbide paper.

MFA11 Red ?resin sample with aromatic odor. Provenance - unknown. Date - unknown. Boston Museum of Fine Arts, Meyer Collection, no number.

**Amber**

Source

Amber is a fossil resin. Although 'fossil' resin has not been well defined, it refers to material which has existed for a very long period of geological as opposed to historical time. The material has been subjected to pressure and weathering from water and soil. The principle source for Baltic amber is the Eastern coast of the Baltic sea (modern day Poland and Lithuania). It has been found on other Baltic country coasts and on the Eastern shore of England as well as near the region of the Dnieper River and the Black Sea. In addition to the Baltic amber, smaller deposits have been found throughout Europe including Sicily, Rumania and Spain. The mineralogical name for Baltic amber is Succinite (Beck et al, 1965; Mills and White, 1987).

The source of the resin has long been credited to an extinct conifer species which was named _Pinus_ _succinifera_, however, amber is not similar to modern resins from the _Pinus_ family. However, recent research has shown that the chemical structure of amber is more similar to resins of the Araucariaceae species (Mills and White, 1987).

Amber was prized by early cultures and amber artifacts have been found in many grave sites from Neolithic times. The provenance of amber artifacts found in Europe, Baltic or non-Baltic, has been an important question for many years and was one of the first applications of scientific research in archaeology (Beck et al, 1965).

### Composition

### Baltic amber

Amber has a non-crystalline structure and is not very soluble in organic solvents. Amber is about 20% soluble in ether. The ether soluble fraction has been examined by gas chromatography and found to have a characteristic chromatogram containing several hundred components (Mills and White, 1987). The insoluble portion has been found to be a high molecular weight, crosslinked polymer. The structure is similar to a natural alkyd resin formed by the esterification reaction of a polyvalent alcohol and a dibasic acid (Mills and White, 1987). The amber contains a communic acid/ communol copolymer which acts as the polyvalent alcohol and succinic acid which is the dibasic acid. The structure is similar to that of kauri resin which contains the copolymer of communic acid and communol. Amber also contains free carboxylic acid groups (Mills and White, 1987).

### Other ambers

There has been very little analysis performed on other fossil resins (Mills and White, 1987).

## Interpretation of standard spectra

### Literature values

As mentioned above, Baltic amber may be identified by gas chromatography of the ether-soluble components (Mills and White, 1987). In addition, infrared spectroscopy has been used extensively to establish the provenance of European amber (Beck et al., 1965). The band assignments published by Beck have been made on the basis of almost 600 spectra of amber from Baltic and non-Baltic regions (Beck et al., 1965). It is emphasized in the article that that it is not possible to make very specific functional group assignments for spectra of natural products such as amber. The composition of this material is complex and there are many structurally similar components which result in broad bands and shoulders. The study also mentions that a wide range of frequency values (20 - 50 $cm^{-1}$) and intensities were observed between different spectra of the same sample. Larger variations in frequency were observed for different samples from the same geological source (Beck et al., 1965).

The amber spectra in the literature (Beck et al., 1965) are marked by absorptions due to C-H, C=O, C-O and O-H bonds. The spectra contain absorptions due to C-H stretches and deformations which fall in the expected frequency ranges for methyl and methylene groups (Table 7.5). The presence of C=C bonds are suggested by the bands near 3095 and 885 $cm^{-1}$.

The broad band observed in the range 1770 - 1695 $cm^{-1}$ is assigned to the C=O stretching mode due to both ester and ketone functional groups. Differences in the shape of the bands suggest that the material is a mixture of several different esters and ketones (Beck et al., 1965). The range for this band also includes the C=O absorption in carboxylic acids (Table 7.5) (Bellamy, 1975). The bands in the region 1250 - 1100 $cm^{-1}$ are characteristic of the C-O stretching vibration in esters and are discussed below.

The broad band in the region 3700 - 3100 $cm^{-1}$ is representative of various kinds of hydroxyl groups (Beck et al., 1965) including those in carboxylic acids (Bellamy, 1975). The band near 1640 $cm^{-1}$ is normally assigned to the O-H deformation. However, both the O-H vibrations increase in intensity with prolonged grinding time which indicates that amber is sensitive to reactions with water and/or oxygen in the air (Beck et al., 1965). The presence of the broad band in the region 3700 - 3100 $cm^{-1}$ and a shoulder in the region of 2650 $cm^{-1}$ indicate the presence of carboxylic acids (Table 7.5) (Bellamy, 1975).

The region between 1250 - 1100 $cm^{-1}$ has been observed to be characteristic of Baltic amber. Absorptions in this region are due to the C-O stretching vibration in the ester group (Bellamy, 1975). The spectra of Baltic amber exhibit a broad, horizontal absorption between 1250 and 1175 $cm^{-1}$ which appears as a shoulder on a band near 1150 $cm^{-1}$. The band near 1150 $cm^{-1}$ has been assigned to saturated aliphatic esters (Beck et al., 1965; Bellamy, 1975). These bands have not been observed in the spectra of amber from European non-Baltic locations which show great variation in the region. The pattern has been observed in some spectra of ambers from the North American continent (Beck et al, 1965).

In some sample spectra, the horizontal absorption is not evident and a shoulder with what is described as a negative slope is apparent which slants downwards to the right. The cause given for this variation is that exposure to air will cause new C-O bonds to be formed which will absorb in the same region, but not in the identical area which would result in a change of shape of the broad band in the region (Beck et al., 1965).

The Baltic amber spectra also contain a band in the region of 885 $cm^{-1}$ which has been assigned to the C-H out-of-plane deformation of a terminal olefin group. It is thought that the structure may be CR1R2=CH2. It has been suggested that the band may result from an exocyclic double bond on a agathic acid diterpene derivative (Beck et al., 1965).

The band near 885 $cm^{-1}$ is affected by oxidation. The band appears as a shoulder in some spectra. It is apparent in all Baltic amber spectra obtained by Beck et al. (1965), and may be used to differentiate, to a certain extent, between European non-Baltic fossil resins (Beck et al., 1965).

## Reference sample information

For this thesis, three samples of mineralogical amber were obtained. Two specimens were thought to be from Russia (LA1 yellow opaque, LA2 transparent orange) and a third was reported to be from Denmark (LA3). The locations suggest that the ambers are of Baltic origin, but the lack of precise provenance limits the validity of the samples. The sample from Denmark seems to have been cut from a larger piece, the inside section was an opaque yellow which was surrounded by a red crust. Diffuse reflectance spectra were obtained of both the centre and the crust.

## Interpretation of standard spectra

The resulting infrared spectra correspond very closely to that described by Beck et al. (1965) and Mills and White (1987). The region between 1300 - 1100 $cm^{-1}$ which has been described as characteristic for Baltic amber is clearly evident in all four sample spectra. The shoulder from 1250 - 1200 slants downwards which indicates that all of the samples have undergone some oxidation. In the spectrum of the weathered crust (LA3), the bands at 1028 and 888 $cm^{-1}$ are somewhat masked by other absorptions near 950 $cm^{-1}$ and a multiplet occurs with bands near

850, 830 and 805 cm$^{-1}$ which are not apparent in the other spectra. The frequency values are compared to those given by Beck et al. (1965) in Table 7.5.

### Identification of unknown samples

### Unknown sample information

Two examples of archaeological amber artifacts were also examined. The first was an ochre stained object from a gravesite in Lieto, Finland (KM 19727: 465) (Airola, 1980). The sample was removed from the surface and no additional treatment was performed. The second object was a bead found during an excavation at High Down Hill, Sussex (1988.459 136). The outer surface of the bead was sandy in appearance and did not resemble amber. The bead was broken during excavation and the interior was observed to be a transparent red material thought to be amber. Spectra were obtained of both the interior and the exterior of the object.

### Interpretation of unknown sample spectra

The spectrum of the amber from Lieto was very similar to those obtained for amber in this study and those which have been published (Beck et al., 1965; Mills and White, 1987). The band in the region of 890 is very weak in relation to the other bands in the spectrum. However, there are no serious interferences due to the ochre. In particular, the characteristic region 1300 - 1100 cm$^{-1}$ is not affected.

The spectrum of the High Down Hill bead interior is also very similar to those published in the literature including the characteristic region 1300 - 1100 cm$^{-1}$. The spectrum of the bead exterior, however, gives indications of contaminants. The spectrum is marked by weak bands at 2514 and 1794 cm$^{-1}$, a very strong, broad band with maximum intensity at 1451 cm$^{-1}$, a sharp band at 876 cm$^{-1}$ and a weak band at 713 cm$^{-1}$ which are characteristic of calcium carbonate (Miller and Wilkins, 1952). The region 1300 - 1100 cm$^{-1}$ is somewhat obscured. The band at 1162 cm$^{-1}$ is present but the broad shoulder between 1260 and 1200 cm$^{-1}$ is not present. A steep shoulder is seen with a weak absorption near 1250 cm$^{-1}$. Also, the band at 1032 cm$^{-1}$ is more intense than the band at 1162 cm$^{-1}$ and may also be due to an inorganic constituent. The frequency values observed in this study are compared to the other ambers and the values given by Beck et al. (1965) in Table 7.5.

## Shellac

### Source

Lac is produced by the insect, Laccifer lacca Kerr (Family: Lacciferidae Cockerell) which is native to India (Wadia et al, 1969). The insects infest host trees and secrete the substance on the twigs and branches. The material is retrieved by scraping the stick-lac from the branches. The composition of lac is believed to be related to the type of host tree and the major tree is the Butea monosperma Lamk (Mills and White, 1987).

The major application of shellac is as a varnish material for a variety of objects and it was widely used in early conservation practice as an adhesive and for mending broken pottery (Mills and White, 1987).

### Composition

### Structure of fresh shellac

The raw material, known as stick lac, is processed by mechanical crushing, sieving and washing in water to remove tree and insect debris and this material is referred to as seedlac. Further purification is used to give various grades of shellac of commerce (Wadia, et al, 1969). The stick-lac is composed of 6 -

7% wax, 4 - 8% colouring matter, 70 - 80% resin and the remaining material consists of insect remains, water and other extraneous matter such as woody material (Wadia, et al., 1969).

The composition of the lac resin has been elucidated only in the past twenty years. It is known to be a polyester material formed from certain hydroxy acids (Wadia, et al., 1969). The identity and structure of two of the acids were established as aleuritic acid and shelloic acid (Figure 7.6). Further work estabished the identity of butolic acid (6-hydroxytetradecanoic acid) and jalaric acid which is a monobasic dihydroxy acid with an aldehyde functional group as components of lac resin (Wadia, et al., 1969). Jalaric acid is an alicyclic acid which is a derivative of the sesquiterpene cedrene (Mills and White, 1987). Other compounds isolated (Wadia et al., 1969) included epishellolic acid and epilaksholic acid and their epimers, shellolic acid and laksholic acid. The acids are very similar in structure to jalaric acid (Figure 7.6). In epishellolic and shellolic acids, the aldehyde functionality is replaced by a carboxyl group. In epilaksholic and laksholic acid, it is replaced by a hydroxymethylene group (Wadia, et al., 1969). The four acids are formed when jalaric acid is treated with 20% alkali for 10 days (Wadia, et al., 1969) and they may actually be products of the alkali saponification treatment. Jalaric acid may also be autoxidized to epishelloic acid as the aldehyde functional group is susceptible to conversion to the carboxylic acid (Mills and White, 1987). Jalaric acid is thought to be the primary acid (Wadia, et al., 1969).

A second primary acid was identified as laccijalaric acid which was found to be a derivative of the cedrene sesquiterpenoids, and structurally very similar to jalaric acid with the primary hydroxyl group replaced by a methyl group (Singh, et al., 1969). Derivatives of laccijalaric acid similar to those mentioned above for jalaric acid were isolated. These derivatives include laccishellolic acid and laccilaksholic acid in which the aldehyde group is replaced by a carboxylic acid group and a hydroxymethylene group respectively and their epimers. However, it was not possible to isolate these derivatives in lac which had been subjected to a short (5 hour) period of saponification. This fact led the workers to conclude that the laccijalaric acid is the primary acid of the series in the resin (Singh, et al., 1969). The compounds are probably formed as artefacts during the saponification, however, epilaccishallolic acid may be formed as an autoxidation product (Mills and White, 1987).

The resin component may be separated into "hard" and "soft" fractions by ether extraction as the hard resin is insoluble in ether (Khurana, et al., 1970). The hard resin was used to determine the probable structure of lac resin. The material is termed pure lac resin (Khurana, et al., 1970) and the workers concluded that the polyester molecule should contain four terpene acid groups and four aleuritic acid units. The terpene acid seems to be mainly jalaric acid. The molecular weight of the theoretical model is 2210 which is very close to that of the molecular weight experimentally obtained for the pure lac resin, 2095 ± 110. The proposed structure is given in Figure 7.7 (Singh, et al., 1974b). The proposed sequence is an average of the possible constituents (Mills and White, 1987). The soft resin fraction was found to consist primarily of dimer acid esters composed of aleuritic acid and a sesquiterpene compound (Singh, et al., 1974a). It has been suggested that the pure lac resin and the soft resin are fractions of a mixture of oligomers with a range of molecular weights (Mills and White, 1987).

## Effects of ageing

Aldehydes are susceptible to oxydation and the aldehyde groups in shellac are converted to carboxylic acid groups over time. There are also a large number of free hydroxyl groups which are susceptible to further esterification. This would result in cross-linking and an increase in the average molecular weight. The process is thought to continue in shellac coatings. There has been little study of aged shellacs, but it has been observed that shellac is less soluble in alcohol over time (Mills and White, 1987).

## Identification and interpretation of standard spectra

There is a chemical test for the identification of shellac (Vollman, 1957). Lac contains erythrolaccin of which traces are still present in bleached or decolourized shellac. Erythrolaccin forms a violet coloured salt when reacted with alkali. In decolourized shellacs, the colour ranges from pink to light brown in chlorine bleached material. However, the recommended procedure (Vollman, 1957) requires that the sample be soluble in ethanol which may be a problem with old samples.

Analysis of lac with gas chromatography is difficult. The reaction of jalaric acid with diazomethane is complicated and produces a number of products (Wadia, et al., 1969; Upadhye, et al., 1970). The hydroxy acid methyl esters were observed to produce multiple peaks indicating decomposition (Upadhye, et al., 1970). However, several old samples have been characterized using gas chromatography (Mills and White, 1987).

Shellac may be identified by the infrared spectrum (Mills and White, 1987). Five samples of lac were analysed, one of natural stick-lac and four of commercial lac including a sample of bleached shellac. The spectra were very similar (Figure 7.8a), with differences in the region of 800 - 400 $cm^{-1}$ which may be due to the cross-linking which occurs as a result of age. The samples are of indeterminate age, a certain amount of ageing is thought to have occurred. The carbonyl absorption in the stick lac spectrum is more broad with three shoulders in the regions of 1640, 1610, and 1560 $cm^{-1}$ and a slight band near 1510 $cm^{-1}$ and resembles that in the spectrum of one of the commercial shellacs (BM1) in the region of 1640 - 1600 $cm^{-1}$. The shoulders in the spectrum of the crude material occur in characteristic aromatic regions and are probably due to the dyestuff still present in the material. The other three spectra have bands at approximately 1715 and 1640 $cm^{-1}$ with a slight shoulder on the band at 1640 cm-1. The region between 1500 and 900 $cm^{-1}$ is very characteristic for shellac, however, in the spectrum of one of the commercial shellacs, the relative intensities are affected and the band in the region of 1140 $cm^{-1}$ is much weaker and more narrow. Also, the band in the region of 1200 $cm^{-1}$ falls at 1235 $cm^{-1}$ which is somewhat beyond the range.

The spectra are characterized by absorptions in the regions of 2923 - 2933 $cm^{-1}$ and 2854 - 2858 $cm^{-1}$ which are due to C-H stretching and 1464 - 1469 $cm^{-1}$ and 1375 - 1377 $cm^{-1}$ which result from C-H bending deformations (Bellamy, 1975).

The spectra exhibit a broad absorption in the region of 3326 - 3421 $cm^{-1}$ in the hydroxyl region. The spectra of solid carboxylic acids give rise to a broad absorption with a series of minor peaks in the range 3000 - 2500 $cm^{-1}$. The bands are usually partially superimposed on C-H absorptions (Bellamy, 1975) leading to the effect described by Mills and Plesters (1963). The proposed structure also contain a large number of hydroxyl groups which give rise to absorptions in the hydroxyl region.

The OH groups are very polar and will bond with other OH groups. The range of values for polymeric intermolecular bonds of alcohols is 3400 - 3200 $cm^{-1}$ and is very broad (Bellamy, 1975). The band in the sample spectra is probably a combination of both types of vibrations.

The absorption in the carbonyl region is due to several sources. The proposed structure (Figure 7.7) is primarily a polyester with aldehyde, hydroxyl and carboxylic acid groups. It is thought that the aldehydes are oxidized to carboxylic acids and that some of the hydroxyl groups may form further esters (Mills and White, 1987). It is probable that the spectrum reflects the presence of esters and carboxylic acids. The range of values for the carbonyl stretch in aryl esters is given by Bellamy as 1730 - 1717 $cm^{-1}$ and the value for aryl aldehyde C=O stretch is 1715 - 1695 $cm^{-1}$. The range for the carbonyl absorptions in aryl carboxylic acids is 1700 - 1680 $cm^{-1}$. The range observed in the spectra obtained in this study is 1713 - 1717 $cm^{-1}$ and is thought to be due to a combination of carboxyl and ester carbonyl absorptions.

The aldehyde functional group can be characterized by the C-H stretching frequency of the aldehyde group. The C-H frequency is fairly independent of the molecule due to the influence of the carbonyl oxygen. The aldehydic stretching mode is usually two bands in the region of 2900 - 2700 $cm^{-1}$ with one near 2720 $cm^{-1}$. The C-H in-plane and out-of-plane deformations are less characteristic. The out-of-plane deformation falls in the region of 975 - 780 $cm^{-1}$ and the in-plane deformation falls near 1400 $cm^{-1}$, but it is fairly weak and often masked by other absorptions in the region. There is no strong evidence of the C-H stretching absorption in the region of 2900 - 2700 $cm^{-1}$, however, there is a shoulder on the right side of the bands in the C-H region near 2700 $cm^{-1}$ in two of the commercial shellac spectra. The band which is located in the region of 945 - 947 $cm^{-1}$ in the sample spectra (and appears as a doublet in the spectrum of one of the commercial shellacs, NJS2) may be due to the C-H out-of-plane deformation. It may also be due to the out-of-plane O-H deformation in the carboxylic acid which falls in the range of 950 - 900 $cm^{-1}$ (Bellamy, 1975) or a combination of both.

There are three broad bands in the spectra of the shellac samples which occur in the ranges of 1235 - 1253 $cm^{-1}$, 1162 - 1170 $cm^{-1}$, and 1030 - 1048 $cm^{-1}$ which are thought to result from a combination of bands due to the C-O stretching vibrations in the carboxylic, hydroxyl and ester functional groups. The band in the range of 1235 - 1253 $cm^{-1}$ is thought to be due to a combination of the C-O stretch and O-H deformation in a primary or secondary alcohol, the range of which is given by Bellamy (1975) as 1350 - 1260 $cm^{-1}$ and the C-O stretch and O-H deformation in carboxylic acids which is listed as a strong absorbance at 1320 - 1211 $cm^{-1}$ (Bellamy, 1975). The absorption in the region of 1147 - 1170 $cm^{-1}$ probably results from the C-O stretch in the ester functional groups which is reported to fall in the range 1200 - 1100 $cm^{-1}$ (Bellamy, 1975). There is a very weak absorption in the region of 1114 $cm^{-1}$ in the shellac spectra which may be due to the second absorption of the O-H deformation and C-O stretch of a secondary alcohol which is expected to fall near 1100 $cm^{-1}$ (Bellamy, 1975). The absorption in the region 1040 - 1048 $cm^{-1}$ are thought to result from the second O-H deformation and C-O stretch which is expected to occur near 1050 $cm^{-1}$ in primary alcohols.

The absorption in the region of 945 - 948 $cm^{-1}$ may be due to either the O-H out-of-plane deformation in carboxylic acids or the C-H out-of-plane deformation in aldehydes which occur in the range of 950 - 900 $cm^{-1}$ and 975 - 780 $cm^{-1}$ respectively. It may also be a combination of both. The weak absorption which occurs in some of the spectra in the region of 772 - 799 $cm^{-1}$ may be related to the aldehyde functional group instead. (The absorption which occurs at 772 $cm^{-1}$ in one of the commercial shellac spectra (BM1) is of stronger relative intensity than in the other spectra.) The shellac spectra also exhibit an absorption in the region 723 - 725 $cm^{-1}$ which results from the rocking vibrations of aliphatic chains of four or more methylene groups often observed in the region of 720 - 750 $cm^{-1}$. This is caused by the aliphatic acids which make up the lac resin molecule.

## Identification of unknown sample

A schist relic box (2nd century B. C. - 2nd century A. D.) produced in the Gandhara region (present day Pakistan and Afganistan) was decorated with an incised design which was filled with a pale yellow paste. A small sample was removed for analysis. The sample was placed onto the silicon carbide paper and crushed with the back of a microspatula. The resulting diffuse reflectance spectrum (Figure 7.8b) was observed to resemble the spectra of the shellac standards. The computerized search utilizing the SEARCH (peak) mode produced a list which included five of the reference spectra of shellac as the top five possible identifications. The first choice was commercial white shellac (Figure 7.8a). It is assumed that the commercial product was bleached in some way and perhaps contained a colouring agent of some type. However, the pale yellow colour of the unknown sample suggested that it had been processed in some way before use.

The characteristic frequencies of the diffuse reflectance spectrum of the unknown sample are listed in Table 7.6 with the ranges of the known samples. The frequencies fall within the ranges fairly consistently, but there are some differences in the C-O stretching region which may be due to ageing. The band which appears in the region of 1162 - 1170 $cm^{-1}$ in the standard spectra occurs as two shoulders on the band at 1249 $cm^{-1}$ which itself appears as a doublet in the sample spectrum. The band in the region of 1040 - 1048 $cm^{-1}$ in the shellac reference spectra appears as a doublet near 1040 and 1019 $cm^{-1}$ with the maximum intensity at 1019 $cm^{-1}$ in the sample spectrum. This absorption is also more intense in relation to the other absorptions in the spectrum of the unknown material than in the shellac spectra. Also, the band in the region of 945 -947 $cm^{-1}$ in the reference spectra is not evident in the unknown sample spectrum where a shoulder appears on the band at 1019 $cm^{-1}$. Also, two weak bands occur near 760 and 780 $cm^{-1}$ in the unknown sample spectrum. The changes in the spectrum are probably due to alterations in the structure due to cross-linking. It was thought that perhaps the differences may be due to the bleaching process, however, the sample of commercial bleached shellac, which is reported to have become insoluble in alcohol exhibits a spectrum which is very similar to the other shellacs in the region discussed above. The differences in the band assigned to the O-H deformation and C-O stretch in primary alcohols may be affected by the transition of these groups to esters in the cross-linking process. However, the corresponding ester C-O stretching absorption is less intense and occurs as a shoulder in the region of 1175 $cm^{-1}$. It may be that excessive cross-linking has resulted in a large polyester molecule with restricted vibrational movement.

## Tar and pitch

### Source

As mentioned above, tar is the distillate of the destructive distillation of hard or soft woods and pitch is the residue left from distillation (Forbes, 1936; Mills and White, 1987). Hard wood tars are obtained from broad leaf, deciduous trees such as maple, birch, beech, oak and ash and soft wood tars are produced from conifer trees such as pine, fir , cedar, spruce and larch. Pitch may also be prepared from tree resin (oleo-resin) by destructively distilling the rosin (Abraham, 1936). Pitch may be prepared by heating the tar to reduce the volatile components and thicken the substance. This produces a material which is more highly polymerized and known as pitch (Evershed et al., 1985).

The destructive distillation of wood was known in antiquity (Abraham, 1938). Pliny records a production method for softwood tar (Natural History, XVI, 52 - 53): "In Europe tar is obtained from the torch-pine by heating it, and is used for coating ships' tackle and many other purposes. The wood of the tree is chopped up and put into ovens and heated by means of a fire packed all round outside. The first liquid that exudes flows like water down a pipe; in Syria this is called 'Cedar-juice' and it is so strong that in Egypt it is used for embalming the bodies of the dead. The liquor that follows is thicker and now produces pitch; this in turn is collected in copper cauldrons and thickened by means of vinegar, as making it coagulate, and it has been given the name of Bruttian pitch; it is only useful for casks and similar receptacles, and differs from other pitch by its viscosity and also by its reddish colour and because it is greasier than all the rest."

Pliny also mentions the production of pitch from resin (Natural History, XVI, 53): ".. caused to boil by means of red-hot stones in casks made of strong oak, or if casks are not available, by piling up a heap of billets, as in the process of making charcoal." He also wrote that this product was used for seasoning wine.

## Composition

The chemical composition of wood and resin tars has not been extensively studied. However, it is thought that the structure would be similar for both materials as during the distillation process, the wood tar is created from the resin in the wood. The major constituents of coniferous resin are abietane acids which will be discussed in a later section. Gas chromatography was utilized (Mills and White, 1987) to examine methylated samples of tar produced from softwood tar and tar made from rosin. The primary component of wood and resin tars was observed to be methyl dehydroabietate. Other components which were isolated in lesser amounts in both samples include retene, 1,2,3,4-tetrahydroretene, 18-nor and 19-norabietatriene. Methyl abietate was observed in the spectrum of the softwood pitch which is not strongly evident in that of the rosin pitch and both spectra contain a peak due to methyl 7-oxodehydroabietate. There is evidence of residual cellulose and lignin in the chromatogram of the tar produced from softwood (Mills and White, 1987).

In the study of the pitch from the Mary Rose (Evershed et al., 1985), the samples were analysed by gas chromatography/mass spectrometry. The samples were observed to contain methyl dehydroabietate, dehydroabietic acid, retene and minor amounts of other alkyl substituted tricyclic diterpenoid hydrocarbons. Stockholm tar prepared from wood from Pinus sylvestris was analysed in the same manner and the similarity in composition of the Mary Rose samples to that of the Stockholm tar strongly supported pine wood as the starting material of the pitch samples from the Mary Rose. In these samples, no evidence of the underivatized abietic acid was found in the pitch samples or in the standard Stockholm tar. It was suggested that the derivatives of the resin acid are created by the destructive distillation which modifies the original resin acid by dehydrogenation and a certain amount of decarboxylation (Evershed et al., 1985). The methyl ester of abietic acid was found by Mills and White (1987) in the chromatogram of the softwood tar. It is possible that the degree of change is affected by the duration of the distillation process.

Tar and pitch may also be produced from coal. The material may be pyrolyzed to produce a tar as a distillate and a higher molecular weight pitchy material fuses and separates from the coke residue. Phenols, heterocyclics and polynuclear aromatic hydrocarbons are constituents of the tar. Coal tar was first prepared in the nineteenth century (Mills and White, 1987).

### Interpretation of standard spectra

Spectra were obtained of softwood tar, pine rosin tar and softwood tar which had been aged for 11 years (Samples provided by R. White, National Gallery). Samples which were labelled as wood tar pitch and wood or Stockholm tar (Institute of Archaeology Mineralogical collection) and a commercial specimen of Stockholm tar (British Museum Research Lab) were examined. Spectra were obtained of the fresh softwood tar, pine rosin tar and wood tar and further spectra were obtained after the liquid samples had been allowed to dry for two weeks and for nine months. In addition to the softwood tars, two samples of hardwood pitch or bistre from birch bark and beech wood were examined and one sample of aged coal tar (samples provided by R. White).

Ten spectra of the various softwood tars were obtained and the range of frequency values is given in Table 7.7. The values for the commercial Stockholm tar are listed separately. Figure 7.9 compares the spectrum of softwood pitch dried for nine months to one of softwood pitch aged for eleven years. The spectra exhibit bands in the regions of 2962 - 2958 $cm^{-1}$, 2935 - 2928 $cm^{-1}$ and 2874 - 2867 $cm^{-1}$ which correspond to the C-H stretching regions given by Bellamy, 2962 and 2872 $\pm$ 10 $cm^{-1}$ for methyl groups and 2926 and 2853 $\pm$ 10 $cm^{-1}$ for methylene groups. The band which is expected near 2872 $cm^{-1}$ is masked and the band near 2962 $cm^{-1}$ is weaker and not always evident in the spectra. This indicates that there is a higher amount of methylene groups than methyl groups in the structure. An absorption is evident in the region 1464 - 1458 $cm^{-1}$ and in the region 1384 - 1382 $cm^{-1}$ which result from the deformations of the C-H linkages. The band near 1464 $cm^{-1}$ is probably a combination of the asymmetrical stretch in the methyl group (1450 ± 20 $cm^{-1}$) and the deformation of the methylene group (1465 ± 20 $cm^{-1}$) and the second absorption is due to the symmetrical stretch of the methyl functional group (1380 - 1370 $cm^{-1}$)(Bellamy, 1975).

There is evidence of aromatic groups in the spectra. There is a shoulder on the left side of the strong C-H stretching absorptions which is thought to be due to the aromatic C-H stretch. The regions given in the literature for this group are sharp, weak absorptions near 3030 and 3070 $cm^{-1}$. The weak bands appear as shoulders in these spectra. The absorptions are difficult to see when carboxylic acids are present as the O-H stretch appears as a shoulder on the C-H stretching absorptions. The tar spectra exhibit absorptions in the regions of 1607 - 1604 $cm^{-1}$ and 1500 - 1498 $cm^{-1}$ and sometimes a weak band is evident near 1646 $cm^{-1}$ and 1515 $cm^{-1}$. These bands may be assigned to the skeletal ring breathing vibrations. In the literature, two strong bands are observed in the regions 1625 - 1575 $cm^{-1}$ and 1525 - 1475 $cm^{-1}$ with two weaker bands, one near 1600 - 1560 $cm^{-1}$ which often occur as a shoulder on the band near 1600 $cm^{-1}$ and one near 1450 $cm^{-1}$ which is often masked by the C-H bending vibrations. However, the range of the first band is extended to 1650 - 1585 $cm^{-1}$ for some para-substituted and certain unsymmetrical tri-substituted compounds (Bellamy, 1975). Also in the case of fused ring systems, the band in the region 1600 - 1560 $cm^{-1}$ is much more intense and appears as a distinct band (Bellamy, 1975).

The standard tar spectra exhibit a series of bands in the region of 900 - 700 $cm^{-1}$ which may represent the C-H out-of-plane deformations in the aromatic ring. The band in the region of 888 - 886 $cm^{-1}$ indicates the presence of rings with only one free hydrogen atom (900 - 860 $cm^{-1}$), the band in the area 825 - 819 $cm^{-1}$ corresponds to rings with two adjacent free hydrogen atoms (860 - 800 $cm^{-1}$) and the band in the region of 758 - 755 $cm^{-1}$ may be the result of either rings with four adjacent free hydrogen atoms (770 - 730 $cm^{-1}$) or five adjacent free hydrogen atoms (770 - 730 $cm^{-1}$). When five adjacent free hydrogen atoms are present, the band is accompanied by a second band in the region of 710 - 690 cm$^{-1}$ which corresponds to the band in the region of 718 - 703 cm$^{-1}$ in the standard tar spectra. There is a considerable variation in intensity in this region between spectra and this may be explained by the differences in composition between the sample spectra.

The presence of dehydroabietic acid in the softwood tar (Evershed et al., 1985; Mills and White, 1987) should give rise to bands which are characteristic of the carboxylic acid functional group. The tar standard spectra exhibit a broad absorption in the O-H stretching region with a maximum intensity in the region 3400 - 3250 cm$^{-1}$ which appears as a shoulder on the C-H stretching absorption. In some cases, there is an additional maximum in the region 3198 - 3157 cm$^{-1}$. This corresponds to the O-H stretching absorption in carboxylic acids. The region given in the literature for this absorption in solid and liquid samples is 3000 - 2500 cm$^{-1}$ with a pattern that includes a broad absorption in the region of 3000 cm$^{-1}$ with several weaker bands which are masked by the C-H stretching absorptions. A characteristic weak absorption which is not hidden has been observed to occur near 2650 cm$^{-1}$. The spectra of the tars contain a weak absorption in the region 2660 - 2640 cm$^{-1}$ which is indicative of a carboxylic acid. The range of values observed for the tar spectra is higher than expected for the major absorption. This may be due to hydrolysis of the materials which would cause a broadening of the band.

Carboxylic acids are characterized by a C=O stretching vibration and absorptions which result from C-O stretching and O-H deformations. The region given by Bellamy (1975) for aryl carboxylic acids is 1700 - 1680 cm$^{-1}$. The tar spectra exhibit a band in the region 1702 - 1695 cm$^{-1}$ with a less intense shoulder in the region of 1727 - 1725 cm$^{-1}$. The stronger band is thought to be due to the carbonyl group within the carboxyl functional group. Carboxylic acids also exhibit vibrations which arise in the regions 1440 - 1395 cm$^{-1}$ and 1320 - 1211 cm$^{-1}$. The former region contains two fairly weak absorptions near 1430 cm$^{-1}$ and 1300 cm$^{-1}$ which are conventionally assigned to the C-O stretch and the O-H in-plane deformation respectively, although the bands are thought to be due to a combination of both vibrations which cannot be specifically assigned (Bellamy, 1975). These bands are not evident in the spectra of the tars and may be masked by the vibrations which occur in the neighbouring regions. The second band which occurs in the region 1320 - 1211 $cm^{-1}$ is somewhat more intense and is thought to be due to C-O stretching vibration, but the assignment is somewhat tentative (Bellamy, 1975). A band occurs in the region of 1279 - 1254 $cm^{-1}$ in the tar spectra which is fairly intense and may correspond to the band in the region 1320 - 1211 $cm^{-1}$. There are bands which occur in the region of 979 - 966 $cm^{-1}$ and, in some cases, in the region 910 - 908 $cm^{-1}$ in the spectra of the tar standards which may be related to the absorption in the area 950 - 900 $cm^{-1}$ assigned to the O-H out-of-plane deformation.

The methyl dehydroabietate reported to occur in tar produced from pine (Evershed et al., 1985) should result in absorptions due to the ester group in the spectra. Esters produce two strong bands in the infrared spectrum which result from to the C=O and the C-O functional groups (Bellamy, 1975). The range given for the carbonyl stretch is 1730 - 1717 $cm^{-1}$ for alpha, beta-unsaturated and aryl esters. The weak absorption which occurs in the region of 1727 - 1725 $cm^{-1}$ and sometimes appears as a shoulder on the band arising from the carboxylic acid has been assigned to the ester carbonyl absorption. This indicates that the acid component is present in greater amounts in the tar standards.

The second absorption due to the C-O stretch is more difficult to assign even though it is a strong band. Absorptions which occur in the region 1300 - 1000 $cm^{-1}$ may result from a variety of C-O vibrations from acids, alcohols, ethers and esters. The frequency of the band is strongly affected by the environment of the group and may be altered by changes in the groups. Also, it is thought that the C-O stretching vibration is affected by neighbouring atoms and is not due to a C-O stretching motion alone (Bellamy, 1975). The spectra of the tar standards exhibit a strong absorption in the region 1193 - 1176 $cm^{-1}$ with two medium absorptions in the region of 1133 - 1128 $cm^{-1}$ and 1041 - 1037 $cm^{-1}$. It is not possible to assign the bands exactly, but some esters have been found to display more than one absorption in this region. Also, the complexity of the material and changes which take place during heating might cause changes in the frequencies. Thus, one or more of the bands are probably due to the C-O stretch in the ester groups.

## Identification of unknown samples

Seventeen samples of luting material were analysed. The samples were obtained from five different ships which were reused as revetements in the Thames valley area in Medieval times. The samples consisted of animal hair coated with a black substance. The black material was extracted using ethanol or methanol and the solvent was removed by evaporation. A yellowish black residue was left after evaporation of the solvent and diffuse reflectance spectra were obtained of these samples. In certain samples, the residue was still sticky after the solvent was removed and the samples were mixed with KBr to obtain a satisfactory spectrum.

Thirteen of the sample spectra were found to resemble those of the softwood tar. These included JS1, JS2, JS5, JS6, JS12, JS15, JS23,JS24, JS25, JS35, JS41, JS42 and JS43. The details of the samples are listed at the end of the section. Figure 7.10 compares the spectrum of the softwood pitch which has been aged for 11 years with sample JS1 which was found to have the closest fit. The spectrum of fresh softwood pitch is shown with one of sample JS43 in Figure 7.11. The range of frequency values are listed in Table 7.7 along with those of the softwood tars. The ship samples exhibit absorptions in the regions 3409 - 3209 $cm^{-1}$, 3082 - 3049 $cm^{-1}$, 2934 - 2927 $cm^{-1}$, 2871 - 2856 $cm^{-1}$, 1608 - 1603 $cm^{-1}$, 1468 - 1452 $cm^{-1}$, 1383 - 1364 $cm^{-1}$, 1207 - 1171 $cm^{-1}$, 1075 - 1036 $cm^{-1}$, 889 - 874 $cm^{-1}$, 825 - 805 $cm^{-1}$, 757 - 752 $cm^{-1}$ and

706 - 700 cm$^{-1}$ which correspond to those observed in the spectra of the softwood tar standards. There is widening of the ranges in some cases, but these variations may reflect the degradation which is expected in archaeological samples. The samples were exposed to waterlogged conditions which may have resulted in other reactions.

The sample spectra also contain absorptions in the regions 3192 - 3181 cm$^{-1}$, 2960 - 2957 cm$^{-1}$, 1651 cm$^{-1}$, 1507 - 1500 cm$^{-1}$, 968 - 953 cm$^{-1}$ and 926 - 925 cm$^{-1}$ which occur as weak absorptions or do not appear in every sample spectrum. The band which is evident in the region of 1279 - 1254 cm$^{-1}$ in the standard spectra only appears as a very slight shoulder on the band in the region of 1207 - 1171 cm$^{-1}$ in all but two of the sample spectra. Also, the band in the region of 1133 - 1128 cm$^{-1}$ in the standard spectra which is not present in all of the compounds appears in most of the sample spectra in the region of 1145 - 1140 cm$^{-1}$ with a shoulder near 1100 cm$^{-1}$. In certain cases, the band near 1140 cm$^{-1}$ is not evident, but a weak, but distinct band is evident in the region of 1128 - 1113 cm$^{-1}$. Both bands were evident together in only one sample spectrum. A band is apparent in the region of 1229 -1227 cm$^{-1}$ in two of the sample spectra.

The major variation observed is in the absorption band in the carbonyl region. In the sample spectra, the carbonyl region has a maximum absorption in the range 1733 - 1696 $cm^{-1}$ with a slight shoulder in the area of 1695 $cm^{-1}$. In the standard spectra, the maximum intensity is observed in the region 1702 - 1695 $cm^{-1}$ with a weak band in the region 1727 - 1725 $cm^{-1}$. This phenomenon coupled with the loss of the band in the region of 1279 - 1254 $cm^{-1}$ indicates that the carboxylic component in the sample has been severely decreased. This may be due to reactions which occur during degradation. A second explanation is that the carboxylic acids were ionized during burial forming salts and the treatment of the sample with acid before extraction was not sufficiently strong to convert the salts to the acid and subsequently the carboxylic acid was not extracted.

Four of the samples, JS3, JS7, JS14 and JS19, which were analysed did not result in spectra which compared well with those of the softwood tars. The frequencies were similar, but the relative intensities of the bands in the region of 1700 - 1600 $cm^{-1}$ were different. A visual inspection of the spectra indicated that they were more similar to those of the bitumen standards. It is possible that the material was more of a pitch-like material which had been heated for a longer period of time or had undergone more severe degradation.

Two samples, JS2 and JS22, were analysed by gas chromatography/mass spectrometry. JS2 was found to contain dehydroabietic acid and some evidence of 7-oxodehydroabietic acid. Traces of retene-like compounds and fats were also observed. JS22 was found to contain evidence of animal fats and dehydroabietic acid as major components and possible traces of retene-like compounds. This information indicates that the material was a pine resin and supports the theory that a softwood pitch was used for the luting.

## Unknown sample information

The terms "luting" and "caulking" are sometimes confused, but luting is a "distinct technique for waterproofing the wooden hulls of clinker (or lapstrake) built boats" (Sanson, 1988). The samples were originally obtained from the Museum of London and formed the basis of an undergraduate research project in the Department of Human Environment, University College London Institute of Archaeology (Sanson, 1988). There were a total of 43 samples, but due to the amount of time needed for extraction of the samples, the samples which might be representative of various repairs were chosen. They are summarized below.

JS1 HOR 86 F1230 S525 Site - Kingston Horsefair Date - Medieval

JS2 245 BR 269 204 Site - 245 Blackfriars Road Date - Medieval

JS3 ABB 86 21 10 Site - Falstaff House Date - Medieval

JS5 HOR 86 F1230 Scarf in S454 Site - Kingston Horsefair Date - Medieval

JS6 HOR 86 F1230 S451 Site - Kingston Horsefair Date - Medieval

JS12 ABB 86 21 9 Setwork Site - Falstaff House Date - Medieval

JS15 ABB 86 21 12 Frag A Site - Falstaff House Date - Medieval

JS23 HOR 86 F1230 from under tingle Frag C Site - Kingston Horsefair Date - Medieval

JS24 HOR 86 F1230 S524 Frag B under tingle Frag D Site - Kingston Horsefair Date - Medieval

JS25 HOR 86 F1230 S542 under tingle Site - Kingston Horsefair Date - Medieval

JS35 HOR 86 from lap on boat plank 1008 sub-sample 1008A Site - Kingston Horsefair Date - Medieval

JS41 CUS 73 1.18 Site - Custom House Date - probably med. 13th century.

JS42 TL 74 1136/1 1383 Site - Trig Lane Date - before 1330 - 1380

JS43 Blackfriars III Site - bed of river Thames near Blackfriars Date - 15th century

Summary of sites (Sanson, 1988)

Falstaff House - located in Abbot's Lane which is off Tooley Street, London, S.E.1. Several boat planks were reused as waterfront revetments in Medieval era. Planks had tarred hair luting between overlaps.

245 Blackfriars Road - located on the Southwark side of Blackfriars Bridge, London. The tarred hair luting was obtained from a portion of a clinker built boat which was reused as revetments in Medieval times.

Blackfriars III - Samples came from a 15th century wreck which was excavated within a cofferdam located in the bed of the Thames near Blackfriars. The luting was tarred hair.

Customs House - located between Lower Thames Street in the City of London and the Thames river. The site contained a flat boat bottom with the keel removed leaving two half-moon shapes which had been reused as a revetment. The luting was composed of tarred hair and the date of the boat is thought to be mid 13th century as the revetments were dated to the late 13th or early 14th century.

Trig Lane - located in City of London. Two small revetments were found to have been made from boat planks. The luting was composed of tarred hair. The boat would seem to have a date some time before 1330 - 1380 which was the date of material found behind the revetments.

The luting from the clinker-built boats excavated from New Fresh Wharf, Lower Thames Street, London was composed of moss. No samples were analysed in this study.

## Gums and gum resins

### Gums

#### Source

Certain plants produce an exudate which is either soluble in water or a dispersible in water. These materials are high molecular weight polysaccharides (Mills and White, 1987). The materials which are referred to as hydrocolloids are viscous and gummy when obtained and become glassy masses when dried in air (Glicksman, 1996). The production mechanism is not understood. It is, however, thought to be related to a defence mechanism within the plant. For example, Acacia trees produce a greater quantity of exudate when grown in poor climatic conditions such as high elevation than when grown in optimum conditions. Acacia trees are often slashed to produce the gum (Glicksman, 1969). In some cases, plant seeds contain polymers composed of sugars other than glucose in addition to the starch (glucose polymers) reserves which serve as stored nutrition for growing plants. These materials have properties similar to those of the gums and may be utilized for similar purposes (Glicksman, 1969).

The materials which are of interest in this study are materials which are known or thought to have been exploited in antiquity.

The most important material is gum arabic which is the exudate from *Acacia* species. It was utilized in Ancient Egypt (Mills White, 1987) and is also referred to as gum acacia, Turkey gum and gum Senegal (Glicksman, 1969). Gum arabic is utilized today in applications such as the food industry and the primary source of the material is the Sudan. However, species of the *Acacia* are also found in India, Australia, Central America and southwestern North America in addition to Africa (Mills and White, 1987; Glicksman, 1969).

Gum tragacanth was known at least several centuries before Christ when it was mentioned by Theophrastus. The botanical sources for the material are varieties of the *Astragalus* genus of the family Leguminosae. Other terms for the material include bassora gum, hog gum, goat's thorn, leaf gum and Syrian gum. The material is collected from shrubs located in Asia Minor and in Iran, Syria and Turkey in the mountainous arid regions. The gum is produced by wounding the bark of the plant and collecting the exudate (Glicksman, 1969).

The occurrence of gum karaya is limited to India where there is widespread use of this exudate of the species *Sterculia* *urens*.

The material is also referred to as gum kadaya, Indian tragacanth, India gum and Sterculia gum. It is obtained by tapping the trees and collecting the lumps of exudate after it has hardened (Glicksman, 1969).

The only seed gum which is of interest is the material known as locust bean gum. The material is obtained from the fruit of the Ceratonia siliqua L. which is known as the locust or carob tree. The plant is the only species of the Ceratonia genus which is a member of the Leguminosae family. The long pod-shaped fruit contain seeds from which the gum is obtained. The tree originated in the Near East and Mediterranean, but it was introduced to Greece and Italy by the Greeks who transported it from Syria. Utilizing their trade routes, the Arabs brought the plant to Spain and Northern Africa. The material is known by various local names which include St. John's bread (Johannisbrot), gum gatto, gum hevo, janda gum, lakol gum, rubigum, lupogum, luposol, gum tragon, tragasol, tragarab, honey locust and algaroba. Ancient sources indicate that the material was used as food for both animals and humans and perhaps the most important known archaeological use is in ancient Egypt. The material was incorporated as a paste used for mummy wrappings (Glicksman, 1969).

## Composition

Gum arabic is a polysaccharide with a molecular weight which ranges from 250,000 to 1,000,000. The material is heterogeneous and it is thought that several different molecular compounds are present. It is thought to occur as a slightly acidic or neutral salt of a polysaccharide and calcium, magnesium and potassium ions are thought to be present. The principal structure has been described as a chain of beta-galactopyranose rings linked at positions 1 and 3 with side chains of galactopyranose units. The terminal groups are described as glucuronic acid or 4-O-methylglucuronic acid. The galactose side-groups are also substituted in the C-3 location by glucuronic acid and 4-O-methylglucuronic acid. The sugars D-galactose, L-arabinose, L-rhamnose and D-glucuronic acid are detected after the hydrolysis of gum arabic. The proportions of the four compounds are different for different Acacia species, but all are present (Glicksman, 1969).

The precise chemical structure of gum tragacanth has not been elucidated. The approximate molecular weight is 840,000. The substance is thought to be a mixture of polysaccharides and the sugars which have been found to be present include D-galacturonic acid, D-galactose, L-fructose, D-xylose and L-arabinose. As with gum arabic, the acids are thought to exist as calcium, magnesium and potassium salts (Glicksman, 1969). Gum tragacanth is characterized by a water soluble portion which is called tragacanthin and a portion which swells which is known as bassorin. The tragacanthin is a relatively minor component with the bassorin constituting 60 -70%. The tragacanthin structure is described as ring of three molecules of glucuronic acid and one molecule of arabinose. Two arabinose structures are also present as a side chain. The bassorin is thought to be made of polymethoxylated acids with a complex structure. A minor amount of cellulose, starch and protein are reported to occur in gum tragacanth (Glicksman, 1969).

Gum karaya is also a complex polysaccharide. The molecular weight is very large, approximately 9,500,000. The material is partially acetylated and L-rhamnose, D-galactose and D-galacturonic acid in a ratio of 4: 6: 5 have been detected after acid hydrolysis of the gum (Glicksman, 1969).

The seed gum, locust bean gum, has been observed to have a molecular weight in the region of 310,000. The structure has been reported to be a straight chain polymer of D-mannose units which form linkages at the C-1 and C-4 positions. The structure is characterized by a single side group of D-galactose on position C-6 on every fourth or fifth mannose ring, and is illustrated in Figure 7.12. Differences in the growth stage of the plant at the time of collection and other variations in plant locations are thought to explain the variations in relative amounts of D-galactose and D-mannose which have been reported. Locust bean gum may also contain small amounts of cellulose, protein, ash, and pentosan (Glicksman, 1969).

## Identification and interpretation of standard spectra

Polysaccharides or sugars may be characterized by the furfural reaction in which the unknown material is treated with acid which produces furfural compounds by dehydration. These compounds produce Schiff bases when combined with aromatic amines such as aniline. The Schiff bases are marked by characteristic colours.

The classical method of analysis for polysaccharide materials is to hydrolyze the material using acid and then measure the sugar and uronic acid products. The materials may be separated by various types of chromatography. The sugars must be converted into derivatives before gas chromatographic analysis (Mills and White, 1987).

The infrared spectra of gums are very similar in the high frequency region. This is expected as the substances contain the same functional groups (Glicksman, 1969). It has been suggested that an infrared spectrum may be used to identify gums as a class of materials. For example, the spectrum of a polysaccharide is different from that of a protein which is soluble in water (Mills and White, 1987). Previous infrared analysis of polysaccharides (Birstein, 1975) were obtained using rather large amounts of sample and were described as uninformative (Mills and White, 1987). Also, water extraction which was used to purify the sample might contain water soluble salts which would distort the spectrum. This effect may be eliminated by treating the sample with methanolic hydrochloric acid (Mills and White, 1987). However, this problem is not encountered in this study which utilizes solid sample analysis.

The region near 1667 $cm^{-1}$ is reported to be affected by techniques used to purify the materials and is thus not useful for identification (Glicksman, 1969). The archaeological samples are unlikely to have been treated by processes used in modern day purification methods. However, it is not certain what treatment may have been used with the samples used as standards.

The region 1429 - 667 $cm^{-1}$ is thought to be characteristic for gums and correlations and variations in this region were used to divide the materials into groups. The materials designated as group I include locust bean gum while group II includes gum karaya and group III contains both gum arabic and gum tragacanth (Glicksman, 1969).

The gum diffuse reflectance spectra obtained for this thesis are characterized by broad bands. The bands which are common to all four spectra include a broad, rounded band with maximum intensity in the region 3436 - 3290 $cm^{-1}$ which is representative of the many hydroxyl groups in the polysaccharide structures. An indistinct band occurs in the region 2939 - 2923 $cm^{-1}$ which is the result of C-H stretching vibrations and is less intense in relation to the O-H absorption. The spectra are also marked by a weak absorption in the region 2161 - 2140 cm$^{-1}$. This band is not evident in the spectra which have been published by Glicksman (1969) and may be a result of the differences in spectra acquisition such as sample handling. The spectra exhibit a stong absorption in the region 1651 - 1607 cm$^{-1}$, but a wide variation is observed in the location of the maximum intensity. A broad band is observed in the region of 1250 - 1000 cm$^{-1}$, but there are variations in the shape and the location of the maximum intensity which occurs in the range 1251 - 1227 cm$^{-1}$ and 1150 - 1117 cm$^{-1}$. The region is most similar in the spectra of gum tragacanth and locust bean gum. All of the spectra are marked by a broad indistinct envelope which reaches from about 800 - 400 cm$^{-1}$, and is due to the overlap of many absorptions in the region. The frequency values and band assignments which have appeared in the literature (Birstein, 1975) are compared with those of the spectra obtained in this thesis in Table 7.8.

The spectrum of locust bean gum is marked by bands in the regions 866 and 810 cm$^{-1}$ with a "trough" in between (Glicksman, 1969). This pattern is evident in the diffuse reflectance spectrum obtained in this study where bands are evident in the regions of

876 and 815 cm$^{-1}$. A valley is present in the region centred near 850 cm$^{-1}$.

The gum karaya spectrum is reported to contain intense absorptions near 1724 and 1250 cm$^{-1}$ (Glicksman, 1969) which are evident at 1725 and 1251 cm$^{-1}$ in the diffuse reflectance spectrum of the material obtained in this study. The bands may be the result of the acetyl groups which are thought to be included in the structure of the material. Acetate esters are reported to exhibit a C-O stretching absorption in the region 1250 - 1230 cm$^{-1}$, but the frequency 1725 cm$^{-1}$ is slightly below the range for normal saturated esters, 1750 - 1730 cm$^{-1}$ (Bellamy, 1975). The location of the band may be affected by differences in the molecular structure. The spectrum is also said not to contain a band at 1333 cm$^{-1}$ (Glicksman, 1969). This is true for the diffuse reflectance spectrum of gum karaya, but it is not characteristic as the band is not evident in the spectrum of gum arabic and appears at 1315 cm$^{-1}$ in the locust bean gum spectrum. There are differences reported in the relative intensities in the area 1176 - 833 cm$^{-1}$ (GLicksman, 1969) and this region corresponds in part to the variation observed in the region 1250 - 1000 cm$^{-1}$ which has been discussed. Variations are also said to occur in the region between 833 - 667 $cm^{-1}$. In the spectrum of gum karaya which was reproduced (Glicksman, 1969), the region is very weak. In the spectra of gum arabic and gum tragacanth, there are minor bands evident. The detail is very hard to see and no precise bands were reported (Glicksman, 1969). However, the corresponding region in the diffuse reflectance spectra in this study are not very useful.

The spectra of gum arabic and gum tragacanth are said to correspond closely in the region 1176 - 909 $cm^{-1}$ (Glicksman, 1969). In the diffuse reflectance spectra, however, the gum tragacanth spectrum is marked by a band with a maximum intensity at 1117 $cm^{-1}$ and a second absorption at 1055 $cm^{-1}$ with a broad shoulder which ends near 980 $cm^{-1}$. The band has a different shape in the gum arabic spectrum with distinct absorptions located near 1050 $cm^{-1}$ and at 984 $cm^{-1}$. Also, there are variations between the materials in the regions 1429 - 1250 $cm^{-1}$ and 909 - 526 $cm^{-1}$ (Glicksman, 1969). The diffuse reflectance spectrum of gum tragacanth exhibits bands at 1372 and 1332 $cm^{-1}$ which are absent in that of gum arabic. However, the region 909 - 526 $cm^{-1}$ is not very informative. The gum tragacanth spectrum obtained in this study is characterized by a strong absorption at

1744 $cm^{-1}$ which indicates a possible ester linkage in the structure. The doublet observed at 1744 and 1637 $cm^{-1}$ in this study is visible in that reported by Glicksman (1969), but the feature is not mentioned, nor are any frequencies given.

## Gum resins

### Source

Gum resins are materials which contain both a resin component and a gum or water soluble polysaccharide portion. The materials of interest in this group include the species of Commiphoria and Boswellia in the Burseraceae family which are better known as myrrh and frankincense respectively. These materials were exploited in antiquity as perfumes and medicines and the sources are located in the Middle East. Also, some species of the conifer Araucaria family have been found to produce gum resins (Mills and White, 1987).

### Composition

The resin component of the Commiphoria and Boswellia materials has been found to consist of triterpenoids. However, the composition of the polysaccharide components has not been elucidated (Mills and White, 1987).

## Interpretation of standard spectra

For this study, two samples were obtained of gum myrrh (MW1 and MW9) and one of frankincence (MW2). In addition, samples were obtained of a material labelled "gum dammar" (MW5) and gum olibanum (frankincense) (MW3). With the exception of one gum myrrh sample (MW9), the diffuse reflectance spectra were observed to be very similar in form to those of the resins. The frequencies of the four spectra are listed in Table 7.9. They may be compared with those of the resins which are listed in Table 7.3. In general, the spectra have bands which are characteristic of the carboxylic functional group, which include a broad band with maximum intensity in the region of 3420 - 3395 $cm^{-1}$ which runs into the strong C-H stretching absorptions, a weak shoulder on the low frequency side of the C-H bands in the region of 2700 - 2500 $cm^{-1}$, and a strong absorption in the region 1714 - 1704 $cm^{-1}$. In addition to these bands, the bands which occur in the region 1459 - 1455 $cm^{-1}$ and 1383 - 1381 $cm^{-1}$ are of nearly equal intensity. The spectra are also marked by bands or shoulders in the regions 1246 - 1230 $cm^{-1}$ (except gum dammar), 1150 - 1139 $cm^{-1}$ and 1052 - 1032 $cm^{-1}$. The region 1300 - 400 $cm^{-1}$1 in the gum dammar spectrum is marked by fairly distinct bands and a doublet is observed with maximum intensity at 1285 $cm^{-1}$.

The spectrum of the second sample of gum myrrh (MW9) was found to resemble those of the gums (Table 7.8). The spectrum is characterized by a strong, rounded band with maximum intensity at 3416, a relatively weak band at 2936 $cm^{-1}$, a weak absorption at 2160 $cm^{-1}$, a broad band centred at 1607 $cm^{-1}$ and a broad absorption in the region in between 1200 - 1000 $cm^{-1}$ with maximum intensity at 1086 $cm^{-1}$. Also, the region 800 - 400 $cm^{-1}$ appears as a rounded envelope with maximum intensities occurring at 729 and 623 $cm^{-1}$. The spectrum is also marked by a wide, weak absorption at 912 $cm^{-1}$ which may correspond to absorptions evident in the spectrum of gum tragacanth at 921 $cm^{-1}$ and of locust bean gum at 876 $cm^{-1}$.

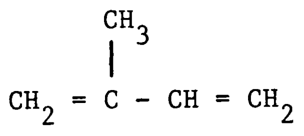
### Identification of unknown samples

An example of characterization of an unknown by diffuse reflectance FT-IR is a sample of linen from the reverse of an Egyptian cartonnage (Shearer, 1987). The date of the object is uncertain and may range from 300 B. C. to 4th century A. D. (Ptolemaic to Roman period). A preliminary spectrum was obtained by rubbing the linen against the silicon carbide paper and recording the spectrum from the powder. The sample was extracted in both deuterated chloroform and diethyl ether to eliminate possible interferences from the linen. The sample was insoluble in the diethyl ether, but an orange residue was left after the evaporation of the deuterated chloroform. The diffuse reflectance spectrum of this material was found to resemble those of the gums. It is difficult to precisely identify specific gums from the infrared spectra and the unknown spectrum did not match any of the spectra exactly. However, the closest fits were observed with the unknown spectrum and those of gum arabic and gum myrrh (MW9). The spectrum of the unknown has been published with the spectra of gum arabic and gum myrrh (Shearer, 1987). The unknown spectrum is marked by a strong, rounded band centred at 3363 $cm^{-1}$, a weaker band located at 2914 $cm^{-1}$, a weak absorption at 2134 $cm^{-1}$ and a broad absorption between 1200 - 980 $cm^{-1}$ which are characteristic of the gums. In this spectrum, the maximum intensity of the band between 1200 - 980 $cm^{-1}$ is 1110 $cm^{-1}$ and a second, less intense maximum occurs at 1044 $cm^{-1}$ which varies slightly from the gum spectra. Also, the broad, intense band with maximum intensity at 1648 $cm^{-1}$ is somewhat higher than the frequencies observed for the standards. The only other variations are that the band at 1323 $cm^{-1}$ in the unknown spectrum is not very strong in the gum arabic and gum myrrh spectra and that the three shoulders located near 1282, 1233 and 1203 $cm^{-1}$ in the spectrum of the unknown differ slightly from the gum spectra where a single band is evident in the region 1251 - 1227 $cm^{-1}$. The band at 905 $cm^{-1}$ in the unknown spectrum may correspond to that observed at 912 $cm^{-1}$ in that of gum myrrh. Also, there is more detail in the region between 700 - 400 $cm^{-1}$ in the unknown spectrum which may be a result of the solvent treatment. The variations in the sample spectrum from those of the reference material may be due to either degradation or the presence of small amounts of additives.

A sample of red colouring matter (MFA14) was taken from the body of a Ptah sokar osiris figure (Boston Museum of Fine Arts 03.1625). The sample was rubbed onto silicon carbide paper and the diffuse reflectance spectrum was obtained. It was observed to correspond closely to those of the gums and gum myrrh (MW9). The spectrum exhibits a rounded, strong band with maximum intensity at 3379 $cm^{-1}$, a band at 2932 $cm^{-1}$, a weak absorption at 2136 $cm^{-1}$, an intense band at 1606 $cm^{-1}$ and a strong, broad band located between 1200 and 950 $cm^{-1}$ which has two maximum absorptions near 1150 and at 1064 $cm^{-1}$. Also, a weak band with maximum intensity is located at 904 $cm^{-1}$ which may correspond to similar absorptions in the spectra of gum tragacanth, gum myrrh, locust bean gum and in unknown HK4. The region 700 - 400 $cm^{-1}$ appears as a rounded hump with no strong absorptions. It is not possible to make a certain identification, but the spectrum is most similar to those of the locust bean gum and gum arabic in the region between 1500 and 900 $cm^{-1}$. The sample spectrum (Figure 7.14a) may be compared to those of locust bean gum and gaum arabic (Figure 7.13). It is possible that the gum material was utilized as a medium for the colouring matter.

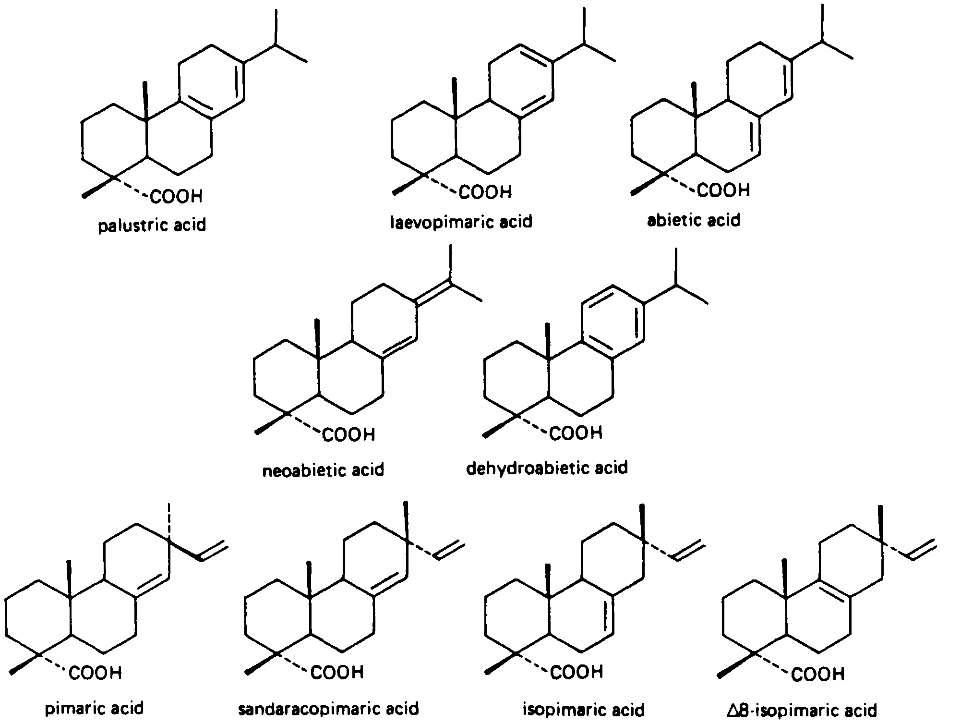
A sample of black, brittle resin (MFA16) from the Anubis figure on the outermost coffin of Nesmutaatneru (Boston Museum of Fine Arts 95.1407) was examined. The sample was rubbed onto silicon carbide paper and the diffuse reflectance spectrum was measured from the paper. The resulting spectrum (Figure 7.14b) was found to exhibit bands which are considered characteristic of the gums. In addition to the bands located at 3354, 2923, 2135 and 1607 cm-1 and a broad absorption with maximum absorption at 1138 and 1050 $cm^{-1}$ which correspond to spectra which have been discussed, the spectrum contains a band at 1713 $cm^{-1}$. This feature is evident in the spectra of gum tragacanth and gum karaya, however, the frequency of the band in the former spectrum is much higher (1744 $cm^{-1}$) and the geographical provenance would indicate that the latter material is an unlikely match. It is more likely that the sample contains a minor component which has a carbonyl group. The remaining regions of the unknown spectrum are similar to those of the gum resins with a weak band centred at 883 $cm^{-1}$ and a broad, indistinct region from 700 to 400 $cm^{-1}$. The region between 1500 and 900 $cm^{-1}$ in the unknown spectrum (Figure 7.14b) is most similar to the corresponding region in those of gum arabic and locust bean gum (Figure 7.13).

A sample (NJS12) was obtained from the residue inside a gold relic box (Institute of Archaeology laboratory number 3900) from the Gandhara region, which is present day Pakistan and Afganistan. The material was examined by diffuse reflectance and the resulting spectrum was found to correspond closely to those of the gums. The unknown sample spectrum exhibits bands at 3299 $cm^{-1}$ (rounded, broad), 2930, 2141 and 1629 $cm^{-1}$. The spectrum also contains a weak band at 932 $cm^{-1}$ and a broad area of absorption from 700 to 400 $cm^{-1}$. The region of intense absorption between 1200 and 980 cm$^{-1}$ is marked by three fairly distinct bands at 1153, 1080 and 1030 cm$^{-1}$ and the shape of the band is somewhat different from those of the standard gum spectra. Also, the region between 1500 - 1200 cm$^{-1}$ is marked by a series of weak absorptions which also differs from the corresponding regions in the gum spectra. The region 1500 - and 1200 cm$^{-1}$ in the unknown spectrum is most similar to the corresponding regions in the gum arabic and gum myrrh (MW9) spectra. The sample was identified as myrrh by gas chromatography/mass spectroscopy (Raymond White, personal communication). The spectrum of the unknown is compared to that of gum myrrh in Shearer, 1988 .



$$CH_2 = \overset{\overset{\displaystyle CH_3}{|}}{C} - CH = CH_2$$

Figure 7.1 Structure of isoprene (Mills and White, 1987).



palustric acid
laevopimaric acid
abietic acid
neoabietic acid
dehydroabietic acid
pimaric acid
sandaracopimaric acid
isopimaric acid
Δ8-isopimaric acid

Figure 7.2 Structures of some abietane and pimarane diterpenoid components of conifer resins (Mills and White, 1987).

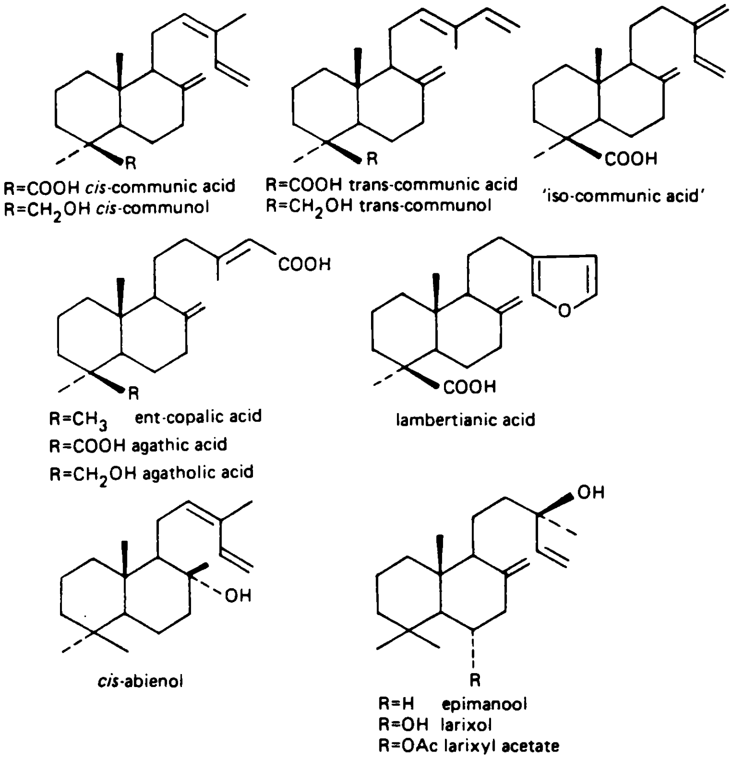


**Figure 7.3** Structures of some labdane diterpenoid components of conifer resins (Mills and White, 1987).

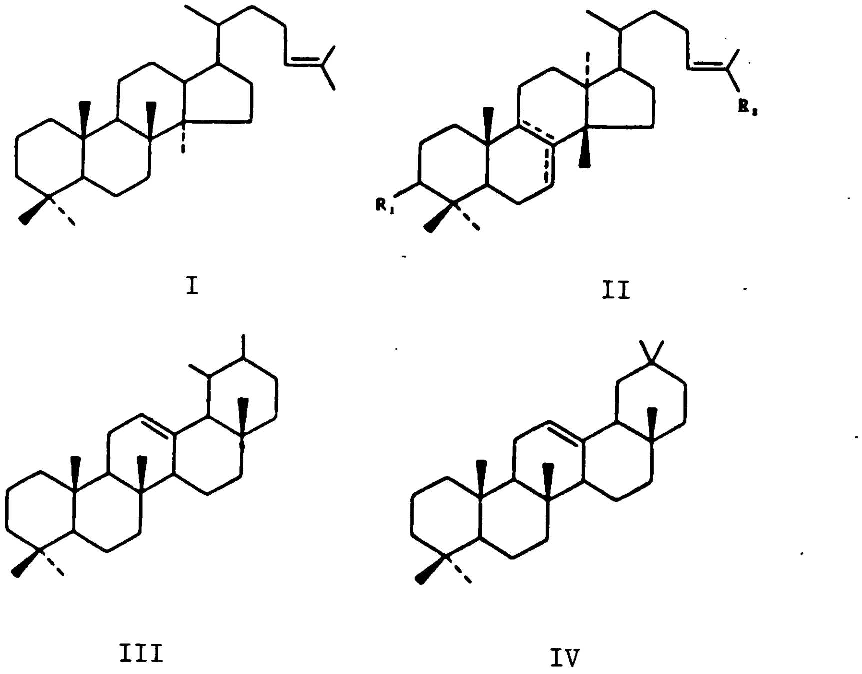


**Figure 7.4** Structures of the dammarane (I), euphane (II), ursane (III) and oleanane (IV) skeletons (Mills and White, 1977).

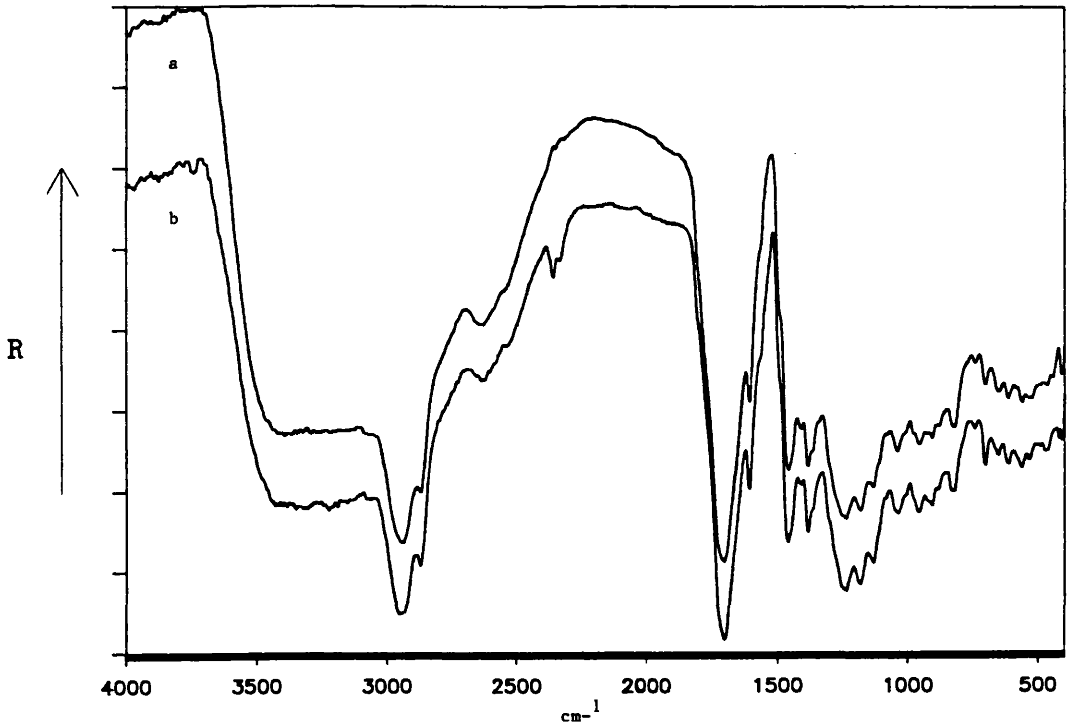
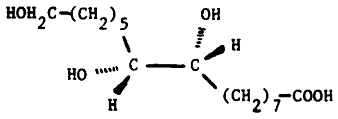
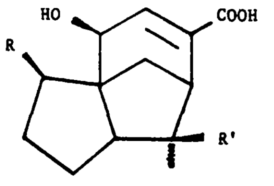


Figure 7.5 Diffuse reflectance spectra of (a) resin from <u>Pinus massoniana</u> (Kew10 Museum of Economic Botany, Kew) (gsva0070) and (b) material from reverse of Chinese bronze mirror (RK4 Victoria and Albert Museum FE87 1982) (gsva0349).

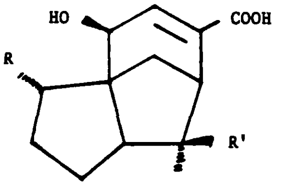


II



V: R = COOH; R' = $CH_2OH$

VI: R = R' = $CH_2OH$



I: R = CHO; R' = $CH_2OH$

III: R = COOH; R' = $CH_2OH$

IV: R = R' = $CH_2OH$

Figure 7.6 Structures of lac acids: jalaric acid (I), aleuritic acid (II), epishelloic acid (III), epilaksholic (IV), shelloic acid (V) and laksholic acid (VI) (Singh et al., 1974b).

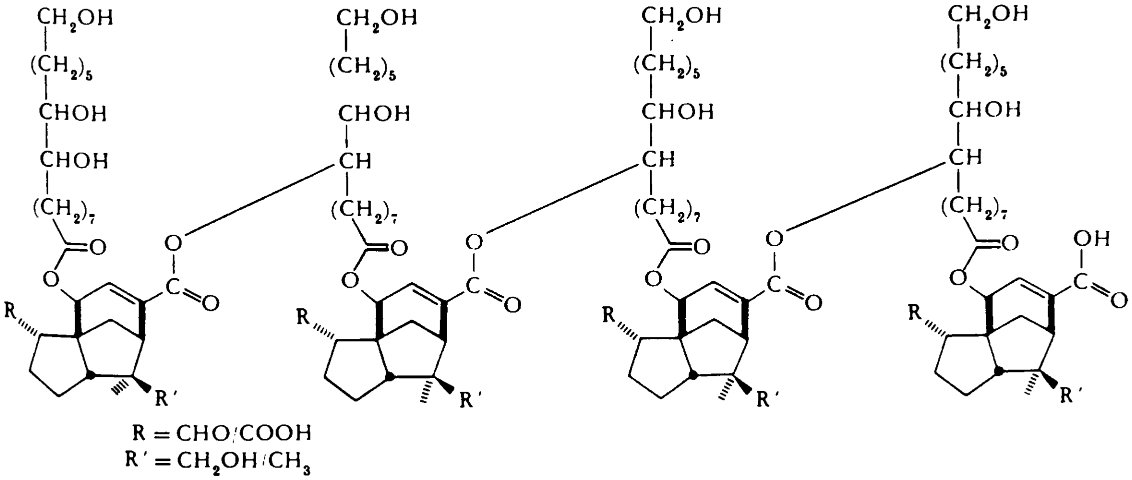


Figure 7.7 Proposed structure of "pure lac resin" (Singh et al., 1974b).

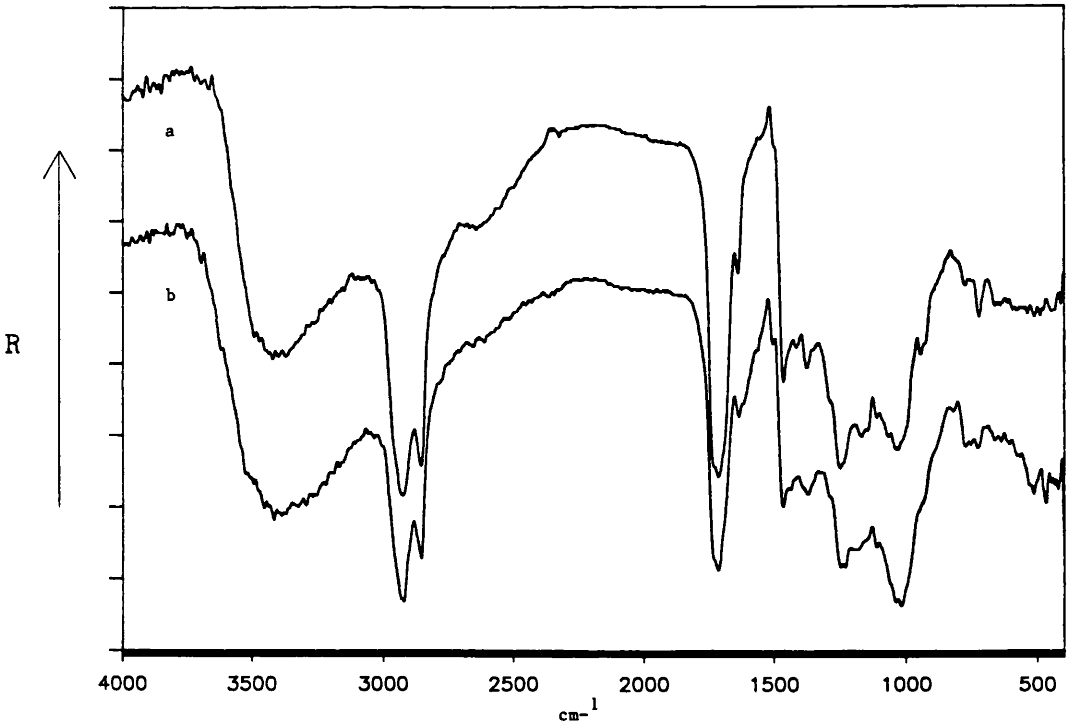


Figure 7.8 Diffuse reflectance FT-IR spectra of (a) commercial white shellac (VA4) (gsva0223) and (b) inlay paste from schist relic box from the Gandhara region (NJS7) (gsva0209).

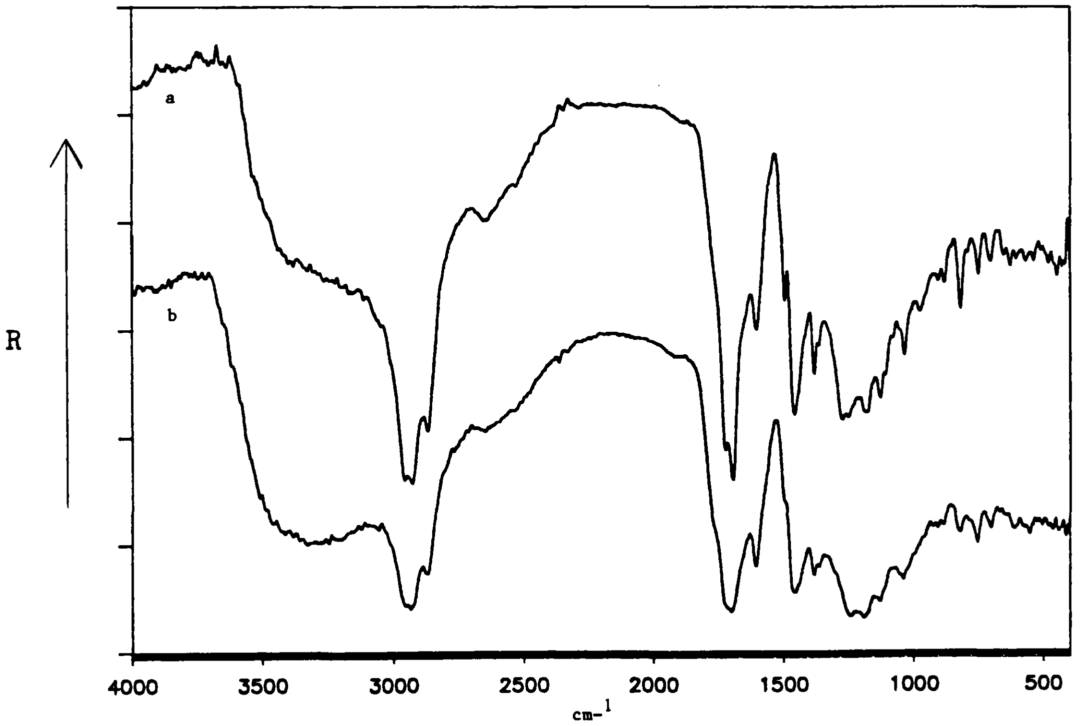


Figure 7.9 Diffuse reflectance FT-IR spectra of (a) softwood pitch (<u>Pix liquida</u>) dried for nine months (RW1) (gsva0387) and (b) softwood pitch (pix liquida) aged for eleven years (RW9) (gsva0228).

Figure 7.10 Diffuse reflectance FT-IR spectra of (a) softwood pitch (see Figure 7.9b) and (b) sample from ship luting (JS1 HOR 86 F1230 S525) (gsva0374).

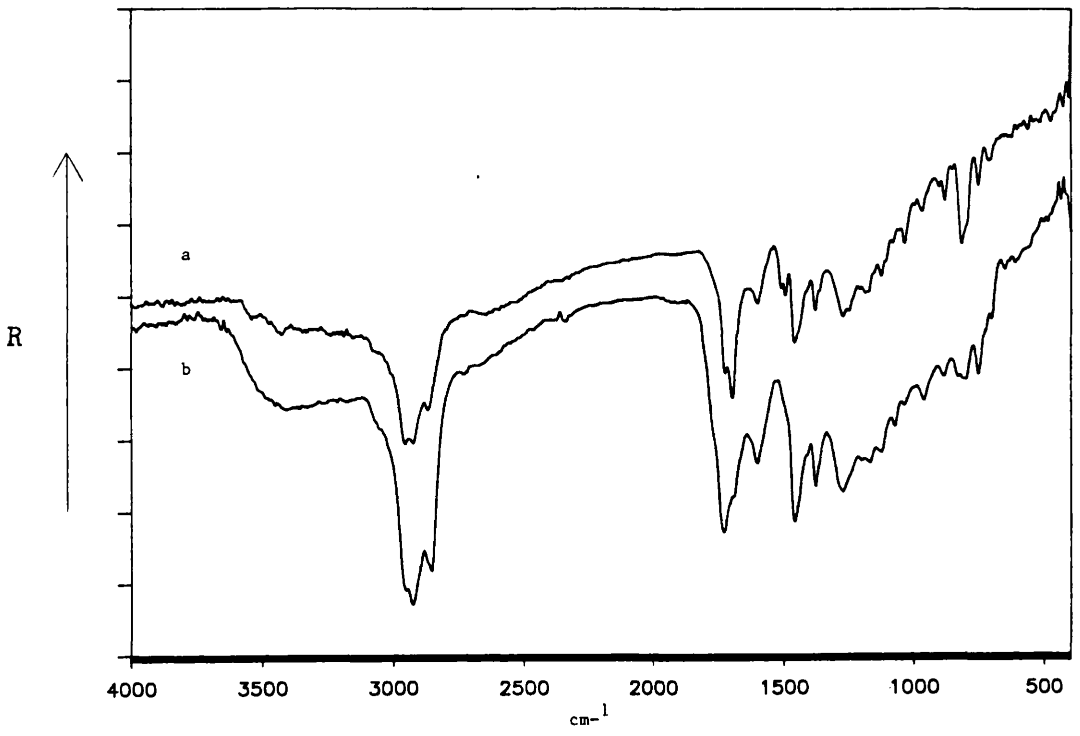


Figure 7.11 Diffuse reflectance FT-IR spectra obtained using KBr powder with silicon carbide paper of (a) fresh softwood pitch (<u>Pix liquida</u>) (RW1) (gsva0615) and (b) sample from ship luting (JS43 Blackfriars III) (gsva0562).

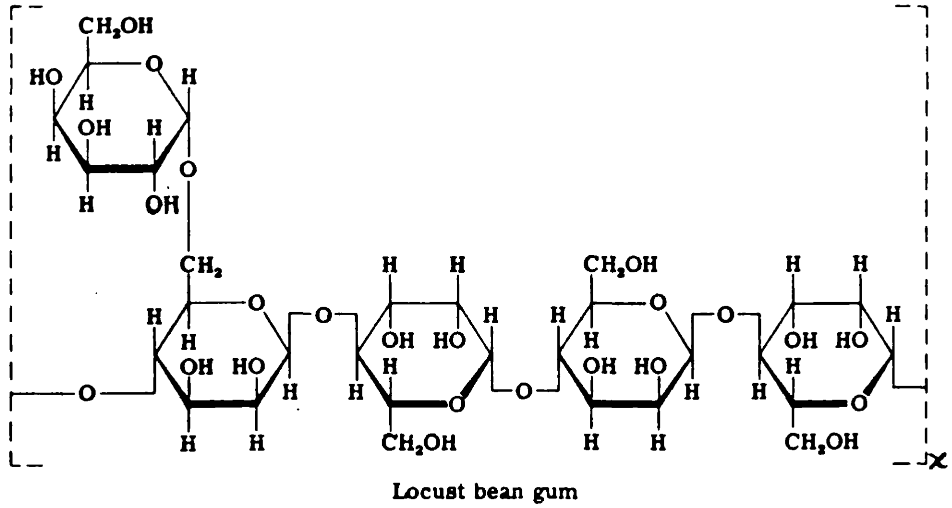


Figure 7.12 Structure of locust bean gum (Glicksman, 1969).

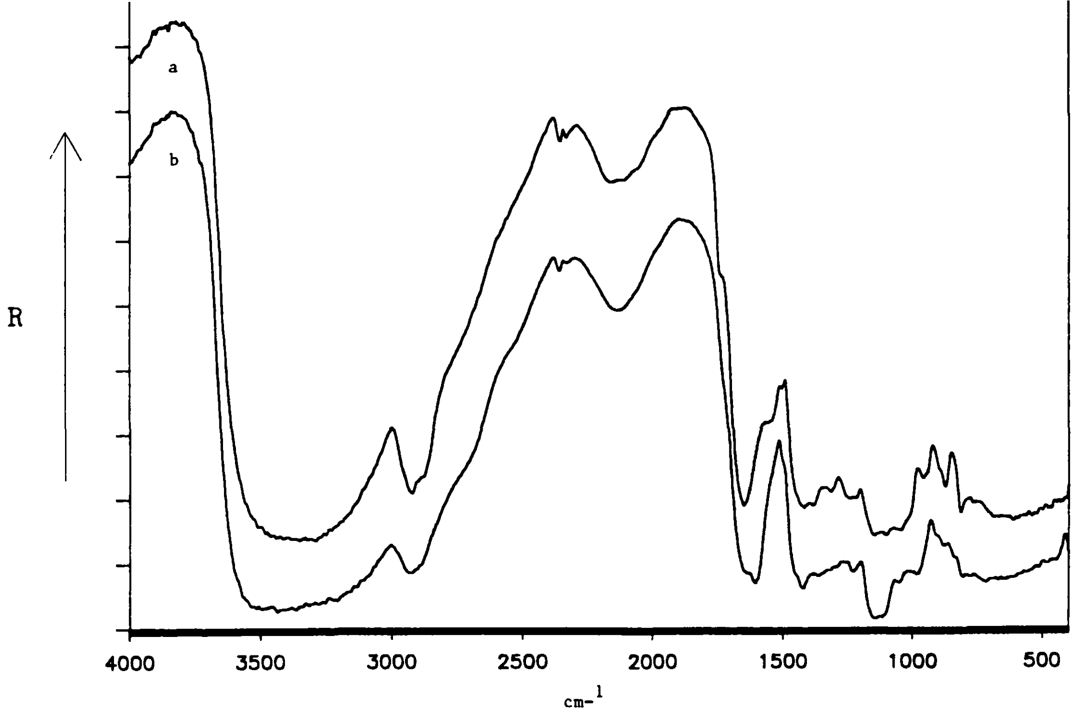


Figure 7.13 Diffuse reflectance FT-IR spectra of (a) locust bean gum (MW6) (gsva0028) and (b) gum arabic (MW8) (gsva0030).

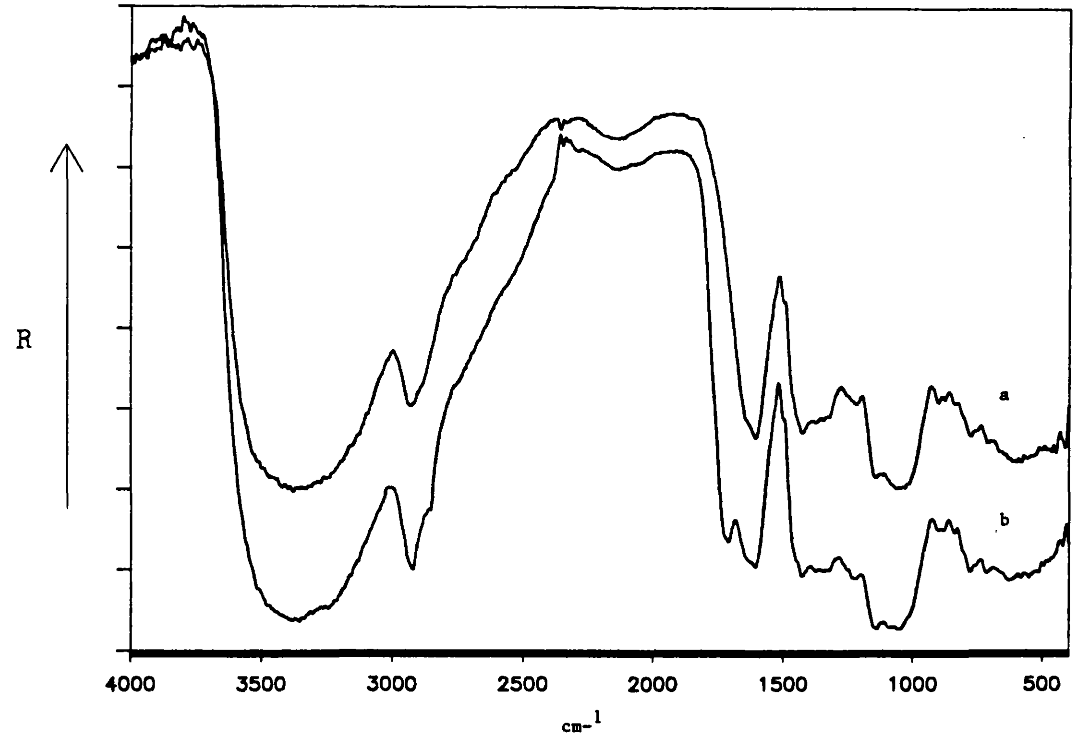


Figure 7.14 Diffuse reflectance FT-IR spectra of (a) red colouring matter from Ptah sokar osiris figure (mfa14 Boston Museum of Fine Arts 03.1625) (MFA14) and (b) black material from Anubis figure on the outermost coffin of Nesmutaatneru (mfa16 Boston Museum of Fine Arts 95.1407) (MFA16).

TABLE 7.1

Diterpenoid natural resins and their sources (Mills and White, 1987)

| *Coniferae* | | | *Leguminosae* |
|---|---|---|---|
| *Pinaceae* | *Cupressaceae* | *Araucariaceae* | |
| *Pinus* species (Common or Bordeaux turpentine, rosin or colophony) | *Tetraclinis articulata* (sandarac) | *Agathis* species (kauri, manila) | *Hymenaea* species (East African or Zanzibar copal; Brazil copal) |
| *Picea* species (Burgundy pitch; scrape resin) | *Juniperus* species | *Araucaria* species | *Copaifera* species (copaibas) |
| *Abies* species (Strasbourg turpentine; Canada balsam) | *Cupressus* species | | *Guibourtia*; *Tessmannia*; *Daniellia*; (other African copals; Congo, Accra, Benguela, Sierra Leone, etc.) |
| *Larix* species, notably *L. decidua* (Venice turpentine)<br>*Pseudotsuga menziessii* (Oregon balsam) | | | |

TABLE 7.2

Di- and triterpenoid resins obtained for this study from Kew

| Diterpenoids | | | | | | | |
|---|---|---|---|---|---|---|---|
| Coniferae | | | | | | Leguminosae | |
| Pinaceae | | Cupressaceae | | Araucariaceae | | | |
| *Pinus kesiya* | Kew9 | *Tetraclinis articulata* | Kew17 | *Agathis australis* | Kew1 | *Hymenaea verrucosa* | Kew18 |
| *Pinus massoniana* | Kew10 | | | *Agathis dammara* | Kew2 | *Hymenaea courbaril* | Kew19 |
| *Pinus merkusii* | Kew11 | | | *Agathis dammara* | Kew3 | | |
| *Pinus roxburghii* | Kew12 | *Juniperus phoenicea* | Kew16 | | | | |
| *Pinus sylvestris* | Kew13 | | | *Araucaria columnaris* | Kew4 | | |
| *Pinus palustris* | Kew25 | | | | | | |
| | | *Callitris endlichen* | Kew14 | | | | |
| *Picea abies* | Kew7 | *Callitris verrucosa* | Kew15 | | | | |
| *Picea glauca* | Kew8 | | | | | | |
| *Abies spectabilis* | Kew5 | | | | | | |
| *Cedrus brevifolia* | Kew6 | | | | | | |
| | Kew28 | | | | | | |

| Triterpenoids | |
|---|---|
| Anacardiaceae | |
| *Pistacia lentiscus* | Kew20 |
| *Pistacia lentiscus* | Kew21 |
| *Pistacia terebinthus* | Kew22 |

TABLE 7.3

Frequency ranges and band assignments for resin standards (natural surfaces)

| Coniferales | | | Leguminosae | Anacardiaceae | Assignment | | |
|---|---|---|---|---|---|---|---|
| Araucariaceae cm-1 | Pinaceae cm-1 | Cupressaceae cm-1 | Hymenea cm-1 | Pistacia cm-1 | Vibration | | Frequency range given in literature (1) cm-1 |
| 3454 - 3250(sh) | 3467 - 3164(sh) | 3419 - 3188(sh) | 3413 - 3375(sh) | 3442 - 3419(sh) | O-H stretch hydrogen bonded | carboxylic acid | 3000 - 2500(b) |
| | | | | | O-H stretch | O-H group intermolecular bonded | 3400 - 3200(b,vs) |
| 3079 - 3076(w) | 3075 - 3066(w) | 3079 - 3077(w) | 3080 - 3079(w) | | C-H stretch | C=C bond | 3095 - 3075(m)<br>3040 - 3010(m) |
| 2954 - 2917(s) | 2942 - 2932(s) | 2939 - 2925 | 2940 - 2938(s) | 2957 - 2953(s) | C-H stretch | methyl group | 2962 ± 10(s) |
| | | | | | | methylene group | 2926 ± 10(s) |
| 2873 - 2872(s) | 2875 - 2871(s) | | 2873 - 2871(s) | | C-H stretch | methyl group | 2872 ± 10(s) |
| near 2850(s) | | | | | | methylene group | 2853 ± 10(s) |
| near 2680(w) | 2650 - 2639(w) | 2676 - 2672(w) | near 2659(w) | | O-H stretch hydrogen bonded | carboxylic acid | near 2650(w) |
| 1719 - 1698(s) | 1704 - 1695(s) | 1714 - 1697(s) | 1715 - 1704(s) | 1713 - 1712(s) | C=O stretch | carboxylic acid aryl | 1700 - 1680(s) |
| | | | | | C=O stretch | carboxylic acid , unsaturated | 1705 - 1690(s) |
| | | | | | C=O stretch | ketone | 1725 - 1705 |
| 1645 - 1644 | near 1643 | near 1653 | near 1645 | | C=C stretch | C=C bond non-conjugated | 1680 - 1620(v) |
| | 1611 - 1607 | | | | C=C stretch | C=C bond C-O or C=O conjugated | near 1600(v) |
| | 1556 - 1496 | | | | unassigned | | |
| 1467 - 1450(1) | 1462 - 1453 | 1455 - 1451 | 1452 - 1451 | 1462 - 1461 | C-H asym. deform. | methyl group | 1450 ± 20(m) |
| | | | | | C-H deformation | methylene group | 1465 ± 20(m) |

TABLE 7.3 contd.

Frequency ranges and band assignments for resin standards (natural surfaces)

| Coniferales | | | Leguminosae | Anacardiaceae | Assignment | | |
|---|---|---|---|---|---|---|---|
| Araucariaceae | Pinaceae | Cupressaceae | <u>Hymenea</u> | <u>Pistacia</u> | Vibration | | Frequency range given in literature (1) |
| cm-1 | cm-1 | cm-1 | cm-1 | cm-1 | | | cm-1 |
| near 1413 | 1417 - 1402 | 1413 - 1412 | | | C-O stretch/O-H deformation | carboxylic acid | 1440 - 1375(w) |
| 1385 - 1371 | 1388 - 1365 | 1385 - 1380 | 1387 | 1384 - 1383 | C-H sym. deform. | methyl group | 1380 - 1370(s) |
| near 1330 | | | | | unassigned | | |
| 1315 - 1308 | | 1316 | | | C-O stretch/O-H deformation | carboxylic acid | near 1300(s) |
| 1235 - 1223(s) | 1278 - 1235(s) | 1237 - 1236(s) | 1241(s) | | unassigned | carboxylic acid | 1320 - 1211(s) |
| 1183 - 1179(s) | 1186 - 1176(s) | 1181 - 1177(s) | 1194 - 1176(s) | 1191 - 1184 | unassigned | | |
| | | | 1104 | | unassigned | | |
| 1047 - 1032 | 1049 - 1036 | 1051 - 1032 | near 1043 | 1058 - 1040 | unassigned | | |
| 964 - 961 | 960 - 950 | 960 - 950 | near 949 | | O-H out-of-plane deformation | carboxylic acid | 950 - 900(v) |
| 751 - 750 | 747 - 743 | 752 - 750 | 747 - 746 | | unassigned | | |
| 713 - 702 | 715 - 705 | 703 - 699 | near 701 | | C-H out-of-plane deformation | C=C bond (cis) | near 690 |

Unless otherwise indicated, the intensity of the bands are variable. Some absorptions are not present in all spectra.

1. Bellamy, 1975

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp

TABLE 7.4

Frequency ranges and band assignments for colophony and unknowns identified as resin or resin mixtures

| Colophony BM16 | Resins cm-1 | Resin mixtures cm-1 | Vibration | | Frequency range given in literature (I) cm-1 |
|---|---|---|---|---|---|
| 3396(sh) | 3437 - 3181(sh) | 3544 - 3229(sh) | O-H stretch hydrogen bonded | carboxylic acid | 3000 - 2500(b) |
| | | | O-H stretch | O-H group intermolecular bonded | 3400 - 3200(b,vs) |
| near 3060(w) | 3084 - 3071(w) | 3064 - 3031(w) | C-H stretch | C=C bond | 3095 - 3075(m) |
| | | | | | 3040 - 3010(m) |
| 2937(s) | 2970 - 2924(s) | 2965 - 2923(s) | C-H stretch | methyl group | 2962 ± 10(s) |
| | | | | methylene group | 2926 ± 10(s) |
| 2872(s) | 2876 - 2854(s) | 2866 - 2853 | C-H stretch | methyl group | 2872 ± 10(s) |
| | | | | methylene group | 2853 ± 10(s) |
| 2650(w) | 2641 - 2627(w) | near 2650(vw sh) | O-H stretch hydrogen bonded | carboxylic acid | near 2650(w) |
| 1703(s) | 1726 - 1701(s) | 1744 - 1706(s) | C=O stretch | carboxylic acid aryl | 1700 - 1680(s) |
| | | | C=O stretch | carboxylic acid , unsaturated | 1705 - 1690(s) |
| | | | C=O stretch | ketone | 1725 - 1705 |
| | | 1660 - 1652 | C=C stretch | C=C bond non-conjugated | 1680 - 1620(v) |
| | 1610 - 1607 | near 1609 | C=C stretch | C=C bond C-O or C=O conjugated | near 1600(v) |
| 1497 | 1499 | 1551 - 1507 | unassigned | | |
| 1462 | 1463 - 1450 | 1463 - 1450 | C-H asym. deform. | methyl group | 1450 ± 20(m) |
| | | | C-H deformation | methylene group | 1465 ± 20(m) |

TABLE 7.4 contd.

Frequency ranges and band assignments for colophony and unknowns identified as resin or resin mixtures

| Colophony BM16 | Resins cm-1 | Resin mixtures cm-1 | Vibration | | Frequency range given in literature (1) cm-1 |
|---|---|---|---|---|---|
| | 1420 - 1416 | near 1431 | C-O stretch/O-H deformation | **carboxylic acid** | **1440 - 1375(w)** |
| 1387 | 1387 - 1379 | 1386 - 1373 | **C-H sym. deform.** | **methyl group** | **1380 - 1370(s)** |
| | | 1322 - 1319 | C-O stretch/O-H deformation | **carboxylic acid** | **near 1300(s)** |
| 1236(s) | 1238 - 1223(s) | | unassigned | **carboxylic acid** | **1320 - 1211(s)** |
| 1184(s) | 1215 - 1179(s) | 1217 - 1174(s) | unassigned | | |
| | 1138 - 1132 | 1142 - 1125(s) | unassigned | | |
| 1041 | 1050 - 1039(b) | 1076 - 1039 | unassigned | | |
| 956 | 985 - 958 | near 958 | O-H out-of-plane deformation | **carboxylic acid** | **950 - 900(v)** |
| 744 | 769 - 747 | 749 - 747 | unassigned | | |
| | 730 - 728 | 728 - 698 | C-H out-of-plane deformation | **C=C bond (cis-)** | **near 690** |
| 709 | 708 - 695 | | | | |

Unless otherwise indicated, the intensity of the bands are variable. **Some absorptions are not present in every spectrum in range.**

1. Bellamy, 1975

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; **b = broad; va = variable; sp = sharp**

TABLE 7.5

Frequency values and band assignments for amber samples

| LA1<br>cm-1 | LA2<br>cm-1 | LA3 interior<br>cm-1 | LA3 crust<br>cm-1 | Lieto<br>cm-1 | High Down Hill interior<br>cm-1 | High Down Hill crust<br>cm-1 | Vibration | Functional group | Frequency range given in literature<br>cm-1 | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|
| 3262(sh) | 3406(sh) | 3250(sh) | 3262(sh) | 3351(sh) | 3426(sh) | 3413(s,b) | O-H stretch | O-H groups free and bonded | 3700 - 3100(b) | 1 |
| | | | | | | | O-H stretch hydrogen bonded | carboxylic acid | 3000 - 2500(b) | 2 |
| | 3078(w) | near 3070(w) | near 3070(w) | 3090(w) | 3089(w) | | C-H stretch | C=C bond | 3095(w) | 1 |
| 2932(s) | 2935(s) | 2931(s) | 2942(s) | 2932(s) | 2932(s) | 2933(s) | C-H stretch | methyl group | 2962 ± 10(sh) | 1,2 |
| | | | | | | | C-H stretch | methylene group | 2926 ± 10(s) | 1,2 |
| near 2870(s) | 2871(s) | 2871(s) | near 2870(s) | 2870(s) | 2868(s) | 2871(s) | C-H stretch | methyl group | 2872 ± 10(sh) | 1,2 |
| | | | | | | | C-H stretch | methylene group | 2853 ± 10(s) | 1,2 |
| ********************** (shoulder near 2700 - 2650) **************** | | | | | 2648(sh) | 2600(sh) | O-H stretch hydrogen bonded | carboxylic acid | near 2650(w) | 2 |
| | | | | | | 2514(w) | | calcium carbonate | 2530(vw) | 3 |
| | | | | | | 1794(w) | | calcium carbonate | 1785(vw) | 3 |
| 1735(s) | 1723(s) | 1736(s) | 1733(s) | 1714(s) | 1724(s) | 1704(s) | C=O stretch | esters and ketones | 1770 - 1695(s) | 1 |
| | | | | | | | C=O stretch | carboxylic acid | 1725 - 1700(s) | 2 |
| near 1650(sh) | near 1650(sh) | 1646(w) | near 1650(sh) | near 1650(sh) | near 1650(sh) | 1651(s) | O-H deformation | O-H group | 1640 | 1 |
| | | | | | | | C=C stretch | C=C bond | 1680 - 1620(va) | 2 |
| 1452(m) | 1453(m) | 1454(m) | 1460(m) | 1454(m) | 1452(m) | | C-H deformation | methylene group | 1465 ± 20(m) | 1,2 |
| | | | | | | | C-H sym. deform. | methyl group | 1450 ± 20(m) | 1,2 |
| | | | | | | 1451(vs) | calcium carbonate | | 1430(vs,b) | 3 |
| 1381(m) | 1382(m) | 1377(m) | 1383(m) | 1382(m) | 1381(m) | near 1380(sh) | C-H asym. deform. | methyl group | 1380 - 1370(s) | 1,2 |

# TABLE 7.5 contd.

Frequency values and band assignments for amber samples

| LA1<br>cm-1 | LA2<br>cm-1 | LA3 interior<br>cm-1 | LA3 crust<br>cm-1 | Lieto<br>cm-1 | High Down Hill interior<br>cm-1 | High Down Hill crust<br>cm-1 | Vibration | Functional group | Frequency range given in literature<br>cm-1 | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|
| *************** (broad shoulder from 1260 - 1200 into band near 1165) ********** | | | | | | 1250(vw sh) | C-O stretch | ester<br>see text | 1250 - 1175(sh) | 1 |
| 1162(s) | 1168(s) | 1161(s) | 1164(s) | 1169(s) | 1169(s) | 1162(s) | C-O stretch | ester<br>see text | 1150(s) | 1 |
| 1015(m) | 1028(m) | 1004(m) | 1028(m) | 1027(s) | 1019(m) | 1032(s) | C-H deformation | cyclohexane | 1050 - 950(b) | 1 |
| | | | near 950(m,b) | | | | unassigned | | | |
| 890(m) | 890(m) | 889(m) | 888(m) | near 890(w) | 880(w) | | C-H out-of-plane deformation | terminal olefin<br>see text | 885(va) | 1 |
| | | | | | | 876(sp) | | calcium carbonate | 877(s,sp) | 3 |
| near 860(w) | near 860(w) | near 859(w) | near 850(m) | | | | unassigned | | | |
| | | | near 830(m) | | | | unassigned | | | |
| | | | near 805(m) | | | | unassigned | | | |
| | near 748(w) | | | | 748(w) | | unassigned | | | |
| | | | | | 710(w) | 713(w) | | calcium carbonate | 715(w) | 3 |

1. Beck et al., 1965
2. Bellamy, 1975
3. Miller and Wilkins, 1952

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp

TABLE 7.6

Frequency values and band assignments for reference shellac specimens and unknown sample

| Reference shellacs cm-1 | Unknown cm-1 | Vibration | Functional group | Frequency range given in literature (1) cm-1 |
|---|---|---|---|---|
| 3421 - 3326(b) | 3416(b) | O-H stretch hydrogen bonded | carboxylic acid | 3000 - 2500(b) |
| | | O-H stretch | alcohol | 3400 - 3200(vs,b) polymeric intermolecular bonds |
| 2933 - 2923(s) | 2922(s) | C-H stretch | methylene group | 2926 ± 10(s) |
| 2858 - 2854(s) | 2855(s) | C-H stretch | methylene group | 2853 ± 10(s) |
| 1717 - 1713(s) | 1714(s) | C=O stretch | ester, aryl | 1730 - 1717(s) |
| | | C=O stretch | carboxylic acid aryl | 1700 - 1680(s) |
| | | C=O stretch | aldehyde, aryl | 1715 - 1695 |
| * 1641 - 1638(m) | 1634(m) | unassigned | | |
| 1469 - 1464(m) | 1466(m) | C-H asym. deformation | methyl group | 1450 ± 20(m) |
| | | C-H deformation | methylene group | 1465 ± 20(m) |
| * 1418 - 1414(w) | 1435(vw) | C-H in-plane deformation | aldehyde | near 1400(w) |
| 1377 - 1375(m) | 1371(m) | C-H sym. deformation | methylene group | 1380 - 1370(s) |
| 1253 - 1235(s) | 1249(s) | C-O stretch/O-H deformation | alcohol primary or secondary | 1350 - 1260(s) |
| | | C-O stretch/O-H deformation | carboxylic acid | 1320 - 1211(s) |
| 1170 - 1147(s) | 1193(sh) | C-O stretch | ester | 1300 - 1000(s) |
| | 1148(sh) | C-O stretch | ester | 1300 - 1000(s) |
| * 1114(vw) | 1113(w) | C-O stretch/O-H deformation | alcohol, secondary | near 1100(s) |
| 1048 - 1030(s) | 1019(s) | C-O stretch/O-H deformation | alcohol, primary | near 1050(s) |
| 948 - 945(m) | 937(sh) | O-H out-of-plane deformation | carboxylic acid | 950 - 900(va) |
| | 885(sh) | unassigned | | |
| * 799 - 772(w) | 776(w) | C-H out-of-plane deformation | aldehyde | 975 - 780(m) |
| | 757(w) | unassigned | | |
| * 725 - 723(m) | 730(w) | chain rocking vibration | long chain hydrocarbons with four or more methylene units | 750 - 720(m) |
| * 664 - 639(w) | 641(w) | unassigned | | |
| * 565 - 513(w) | 515(w) | unassigned | | |

* Absorption is weak, occurs as a shoulder or is not apparent in some sample spectra

1. Bellamy, 1975

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp

TABLE 7.7

Frequency values and band assignments for tar standards and unknown ship luting samples

| softwood tars cm-1 | unknown ship samples cm-1 | hardwood pitch cm-1 | coal tar cm-1 | Vibration | Functional group | Frequency range given in literature (1) cm-1 |
|---|---|---|---|---|---|---|
| 3400 - 3250(sh,b) | 3409 - 3209(sh,b) | 3404 - 3325(m,b) | 3284 - 3259(m,b) | O-H stretch | water | |
| *3198 - 3157(sh,b) | *3192 - 3181(sh,b) | | | O-H stretch hydrogen bonded | carboxylic acid | 3000 - 2500(b) |
| near 3070(sh) | 3082 - 3049(w) | | 3054 - 3052(m) | C-H stretch | aromatic ring | 3070 and 3030(w) |
| 2962 - 2958(sh) | * 2960 - 2957(sh) | | 2955(s) | C-H stretch | methyl group | 2962 ± 10(s) |
| 2935 - 2928(s) | 2934 - 2927(s) | @ 2929 - 2927(m) | 2928 - 2926(s) | C-H stretch | methylene group | 2926 ± 10(s) |
| 2874 - 2867(s) | 2871 - 2856(s) | 2856 - 2855(w) | 2859 - 2858(s) | C-H stretch | methylene group | 2872 ± 10(s) |
| | | | | C-H stretch | methyl group | 2853 ± 10(s) |
| 2660 - 2640(w) | | | | O-H stretch hydrogen bonded | carboxylic acid | near 2650(w) |
| | | | 1922 - 1918(w) | unassigned | | |
| 1727 - 1725(sh) | 1733 - 1696(s) | | | C=O stretch | ester , unsaturated | 1730 - 1717(s) |
| | | | | C=O stretch | ester, aryl | 1730 - 1717(s) |
| 1702 - 1695(s) | * near 1695(sh) | @ near 1700(sh) | | C=O stretch | carboxylic acid aryl | 1700 - 1680(s) |
| | | | | C=O stretch | carboxylic acid , unsaturated | 1705 - 1690(s) |
| * near 1646(sh) | * 1651(w) | | 1649(sh) | skeletal ring stretch | aromatic ring | 1650 - 1585(s) unsym. tri-substitution |
| 1607 - 1604(m) | 1608 - 1603(s) | 1610 - 1606(s) | 1605 - 1603(s) | skeletal ring stretch | aromatic ring | 1625 - 1575(va) |
| | | | | skeletal ring stretch | aromatic ring | 1600 - 1560(w unless conjugated) |
| * near 1515(sh) | | @ 1513(m) | | unassigned | | |
| 1500 - 1498(m) | * 1507 - 1500(w) | | 1501(sh) | skeletal ring stretch | aromatic ring | 1525 - 1475(va) |

## TABLE 7.7 contd.

Frequency values and band assignments for tar standards and unknown ship luting samples

| softwood tars cm-1 | unknown ship samples cm-1 | hardwood pitch cm-1 | coal tar cm-1 | Vibration | Functional group | Frequency range given in literature (1) cm-1 |
|---|---|---|---|---|---|---|
| 1464 - 1458(s) | 1468 - 1452(s) | 1478 - 1465(s) | 1461 - 1457(s) | C-H asym. deformation | methyl group | 1450 ± 20(m) |
| | | | | C-H deformation | methylene group | 1465 ± 20(m) |
| 1384 - 1382(s) | 1383 - 1364(w) | @ 1333 - 1332(s) | 1379 - 1378(s) | C-H sym. deformation | methyl group | 1380 - 1370(s) |
| * 1279 - 1254(s) | ** 1274 - 1267(s) | | | C-O stretch | carboxylic acid | 1320 - 1211(s) |
| | ***1229 - 1227(s) | | | C-O stretch | carboxylic acid | 1320 - 1211(s) |
| 1193 - 1176(s) | 1207 - 1171(s) | 1207 - 1193(s) | 1205 - 1199(s) | C-O stretch | ester | 1300 - 1100(s) |
| * 1133 - 1128(s) | * 1145 - 1113(s) | @ 1158 - 1150(s) | | C-O stretch | ester | 1300 - 1100(s) |
| 1041 - 1037(s) | 1075 - 1036(s) | 1054 - 1043(s) | 1038 - 1036(m) | C-O stretch | ester | 1300 - 1100(s) |
| * 979 - 966(m) | * 968 - 953(va) | # 965(s) | 956 - 952(m) | O-H out-of-plane deformation | carboxylic acid | 950 - 900(va) |
| * 910 - 908(va) | * 926 - 925(va) | | | O-H out-of-plane deformation | carboxylic acid | 950 - 900(va) |
| 888 - 886(va) | * 889 - 874(va) | @ 880(w) | 869(sh) | C-H out-of-plane deformation | aromatic ring | 900 - 860(m) one free H atom |
| 825 - 819(va) | 825 - 805(va) | | 816 - 815(s) | C-H out-of-plane deformation | aromatic ring | 860 - 800(vs) para-substitution |
| 758 - 755(va) | * 757 - 752(va) | @ 782 - 780(m) | 754 - 752(s) | C-H out-of-plane deformation | aromatic ring | 770 - 735(vs) ortho-substitution |
| | | | | C-H out-of-plane deformation | aromatic ring | 770 - 730(vs) mono-substitution |
| 718 - 703(va) | * 706 - 700(va) | @ 697(m) | | C-H out-of-plane deformation | aromatic ring | 710 - 690(s) mono-substitution |

* Absorption is weak or not apparent in some spectra.

** Absorption occurs in sample spectra of JH42 and JH43 only.

*** Absorption occurs in sample spectra of JH41 and JH42 only.

1. Bellamy, 1975

@ Absorption occurs in spectra of beechwood bistre only.

\# Absorption occurs in spectrum of birch bark bistre only.

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp

TABLE 7.8

Frequency values and band assignments for gum standards

| MW8 cm-1 | MW7 cm-1 | MW4 cm-1 | MW6 cm-1 | MW9 cm-1 | Vibration | Functional Group | Frequency value given in literature cm-1 | Ref. |
|---|---|---|---|---|---|---|---|---|
| 3436(s,b) | 3405(s,b) | 3397(s,b) | 3290(s,b) | 3416(s,b) | O-H stretch | O-H group hydrogen bonded | 3400(s,b) | 1 |
| 2923(m) | 2938(m) | 2939(m) | 2924(m) | 2936(m) | C-H stretch | methyl and methylene groups | 3000 - 2800 | 1 |
| 2143(w,b) | 2144(w,b) | 2140(w,b) | 2161(w,b) | 2160(w,b) | unassigned | | | |
| | 1744(m) | 1725(m) | | | C=O stretch | carboxylic acid non-ionized | 1740(w) | 1 |
| near 1650(sh) | | | | | | | | |
| 1607(m) | 1637(m,b) | 1608(m) | 1651(m) | 1607(m) | C=O stretch | carboxylic acid ionized | 1640 - 1620(m) | 1 |
| | | | | | | carboxylic acid ionized anti-symmetrical | 1610 - 1550 | 2 |
| 1422(m) | 1440(m) | 1421(m) | 1421(m) | 1433(m) | C-H deformation | methyl and methylene groups | 1500 - 1400(m) | 1 |
| | | | | | C=O stretch | carboxylic acid ionized symmetrical | 1400 - 1300 | 2 |
| | 1372(w) | 1375(w) | | 1378(w) | C-H sym. deformation | methyl group | 1380 - 1370(s) | 2 |

## TABLE 7.8 contd.

Frequency values and band assignments for gum standards

| MW8<br>cm-1 | MW7<br>cm-1 | MW4<br>cm-1 | MW6<br>cm-1 | MW9<br>cm-1 | Vibration | Functional Group | Frequency value given in literature cm-1 | Ref. |
|---|---|---|---|---|---|---|---|---|
| | 1332(w) | | 1315(w) | | unassigned | | | |
| 1227(m) | 1236(m) | 1251(m) | 1243(m) | 1237(s) | unassigned | | | |
| 1148(s,b) | near 1150(sh) | 1148(s) | 1149(s,b) | | unassigned | | | |
| | 1117(s,b) | | | | unassigned | | | |
| near 1050(s,b) | 1055(s,b) | 1056(s,b) | | 1086(m) | inorganic components | | 1100 - 1000(s,b) | 1 |
| 984(m) | | | 960(m) | | unassigned | | | |
| | 921(m) | 894(m) | 876(m) | 912(m) | unassigned | | | |
| near 810(w) | | near 810(w) | 815(m) | near 810(sh) | unassigned | | | |
| 717(w) | | | | 729(w) | unassigned | broad area of absorption - see text | | |
| | 639(w) | | 614(w) | 623(w) | unassigned | | | |

1. Birstein, 1975
2. Bellamy, 1975

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp

## TABLE 7.9

Frequency values and band assignments for gum resin standards

| MW1<br>cm-1 | MW2<br>cm-1 | MW3<br>cm-1 | MW5<br>cm-1 | Vibration | Functional group | Frequency values given in literature (1)<br>cm-1 |
|---|---|---|---|---|---|---|
| 3420(m,b) | 3397(m,b) | 3395(m,b) | 3414(m,b) | O-H stretch | O-H group intermolecular bonded | 3400 - 3200(b) |
| | | | | O-H stretch hydrogen bonded | carboxylic acid | 3000 - 2500(b) |
| 2953(s) | 2950(s) | 2953(s) | 2953(s) | C-H stretch | methyl group | 2962 ± 10(s) |
| 2873(s) | 2873(s) | | 2870(s) | C-H stretch | methyl group | 2872 ± 10(s) |
| 1704(s) | 1714(s) | 1704(s) | 1706(s) | C=O stretch | carboxylic acid , unsaturated | 1705 - 1690(s) |
| | | | | C=O stretch | ketone | 1725 - 1705 |
| | | | | C=O stretch | carboxylic acid aryl | 1700 - 1680(s) |
| 1672(m) | 1663(m) | 1662(m) | 1645(m) | C=C stretch | C=C bond non-conjugated | 1680 - 1620(v) |
| 1508(w) | | | | skeletal ring stretch | aromatic ring | 1525 - 1475(v) |
| 1455(m) | 1459(m) | 1455(m) | 1459(m) | C-H asym. deform. | methyl group | 1450 ± 20(m) |
| | | | | C-H deformation | methylene group | 1465 ± 20(m) |
| 1382(m) | 1382(m) | 1381(m) | 1383(m) | C-H sym. deform. | methyl group | 1380 - 1370(s) |
| | | | 1310(w) | C-O stretch/O-H deformation | carboxylic acid | near 1300 |
| near 1230(sh) | 1246(s) | 1245(s) | 1285(m) | C-O stretch or O-H deformation | carboxylic acid | 1320 - 1211(s) |
| | 1204(s) | | 1184(s) | unassigned | | |
| near 1150(sh) | 1140(s) | 1139(s) | 1147(s) | unassigned | | |
| | | | 1114(s) | unassigned | | |

TABLE 7.9 contd.

Frequency values and band assignments for gum resin standards

| MW1<br>cm-1 | MW2<br>cm-1 | MW3<br>cm-1 | MW5<br>cm-1 | Vibration | Functional group | Frequency values given in literature (1) cm-1 |
|---|---|---|---|---|---|---|
| | | | 1082(m) | unassigned | | |
| 1044(b) | 1032(b) | 1052(b) | 1046(b) | unassigned | | |
| | 993(w) | | 988(w) | unassigned | | |
| | | | 966(w) | unassigned | | |
| near 920(w) | | | 924(w) | O-H out-of-plane deformation | carboxylic acid | 950 - 900(v) |
| | | | 892(w) | unassigned | | |
| | 824(w) | | 832(w) | unassigned | | |
| | | | 812(w) | unassigned | | |
| 752(w) | | 777(w) | 757(w) | unassigned | | |
| | 667(w) | 665(w) | 661(w) | unassigned | | |

1. Bellamy, 1975

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp

TABLE 7.10

Frequency values and band assignments for unknowns identified as gums

| HK4<br>cm-1 | MFA14<br>cm-1 | MFA16<br>cm-1 | NJS12<br>cm-1 | Vibration | Functional Group | Frequency value given in literature cm-1 | Ref. |
|---|---|---|---|---|---|---|---|
| 3363(s,b) | 3379(s,b) | 3354(s,b) | 3299(s,b) | O-H stretch | O-H group hydrogen bonded | 3400(s,b) | 1 |
| 2914(m) | 2932(m) | 2923(m) | 2930(m) | C-H stretch | methyl and methylene groups | 3000 - 2800 | 1 |
| 2134(w,b) | 2136(w,b) | 2135(w,b) | 2141(w,b) | unassigned | | | |
| | | 1713(m) | | C=O stretch | carboxylic acid non-ionized | 1740(w) | 1 |
| 1648(m,b) | 1606(m,b) | 1607(m) | 1629(m) | C=O stretch | carboxylic acid ionized | 1640 - 1620(m) | 1 |
| | | | | | carboxylic acid ionized anti-symmetrical | 1610 - 1550 | 2 |
| 1429(m) | 1430(m) | 1430(m) | 1459(m) | C-H deformation | methyl and methylene groups | 1500 - 1400(m) | 1 |
| | | | | C=O stretch | carboxylic acid ionized symmetrical | 1400 - 1300 | 2 |
| near 1371(sh) | near 1375(w) | | 1377(m) | C-H sym. deformation | methyl group | 1380 - 1370(s) | 2 |
| 1323(m) | near 1345(w) | 1346(w) | | unassigned | | | |
| near 1282(w) | | | | unassigned | | | |
| near 1233(w) | | near 1230(m) | 1237(s) | unassigned | | | |
| near 1203(w) | 1218(m) | | | unassigned | | | |
| | near 1150(s,b) | 1138(s,b) | 1153(s) | unassigned | | | |
| 1110(s,b)<br>1044(s) | 1064(s,b) | 1050(s,b) | 1080(s)<br>1030(s) | inorganic components | | 1100 - 1000(s,b) | 1 |

TABLE 7.10 contd.

Frequency values and band assignments for unknowns identified as gums

| HK4<br>cm-1 | MFA14<br>cm-1 | MFA16<br>cm-1 | NJS12<br>cm-1 | Vibration | Functional Group | Frequency value given in literature<br>cm-1 | Ref. |
|---|---|---|---|---|---|---|---|
| 905(m) | 904(m) | | 932(m) | unassigned | | | |
| | | 883(m) | 864(m) | unassigned | | | |
| | | 841(w) | | unassigned | | | |
| | 776(w) | 780(w) | 771(m) | unassigned | | | |
| 614 | (broad area of absorption 700 - 400) | | | unassigned | | | |

1. Birstein, 1975
2. Bellamy, 1975

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp

# CHAPTER 8 PROTEINS

## Source

Proteins are a class of compounds which occasionally may be encountered as or with archaeological objects. Proteinacious materials are susceptible to degradation processes and are not often found in archaeological contexts. However, some materials survive in special burial microenvironments. The most common example of an archaeological protein is leather. Also, proteins have been utilized as binding media and adhesives. Examples include animal glue, egg white (albumen), egg yolk (tempera) and casein (Kuhn, 1986). In addition, proteins are natural plastics and may be deformed under pressure. Materials such as horn and tortoiseshell have been moulded into objects which are beginning to appear in social history collections (see chapters 9 and 13 on plastics).

## Structure and identification

Proteins are complex structures which are composed of amino acids linked together by peptide bonds (Figure 8.1). Proteins as a class of materials may be identified by the presence of certain bands in the infrared. The bands result from the peptide bonds which link the amino acid "building blocks" in the polymer chain.

The infrared spectra of proteins are fairly similar. A more sensitive technique such as gas chromatography is needed to make a more specific identification. Several methods of protein analysis are not feasible for art and archaeological specimens due to the large sample required (Mills and White, 1987).

## Interpretation of standard spectra

### Standard sample information

In this study, diffuse reflectance spectra were obtained of egg white, animal glue, rabbit skin glue, and hide glue in addition to three objects made of pressed horn and one object of tortoiseshell (Hawksbill turtle) (Chapter13). The frequency values and band assignments are listed in Table 8.1.

### Interpretation of spectra

The characteristic protein spectrum is discussed in the casein section of chapter 10. In general, protein spectra are marked by several strong bands (Figure 8.2). The N-H groups are susceptible to hydrogen bonding within the polymer chain and with other polymer molecules. A strong, broad band is observed in the region of 3330 $cm^{-1}$ and is thought to be characteristic of both the inter- and intramolecular hydrogen bonded N-H groups in the protein structure. The spectra also contain two bands in the approximate areas 1650 and 1550 $cm^{-1}$ which are referred to as the amide I and amide II bands respectively. The amide I band results from the C=O stretch and the amide II band is thought to be caused by a coupled C-N stretch and a N-H deformation. Differences in structure, such as change in conformation, may cause variations in frequency values. Protein spectra may also contain a weak absorption in the region of 3080 $cm^{-1}$ which is thought to be an overtone of the amide II absorption. The other areas of the spectrum result from functional groups on the amino acid side chains (Bellamy, 1975).

The region near 1270 $cm^{-1}$ is sometimes characteristic of secondary amides and is referred to as the amide III band. It may fall in the wide region of 1305 - 1200 $cm^{-1}$ and is usually weaker in relation to the amide I or II bands. It is often blocked by other absorptions which occur in the region. The band is assigned to a coupled C-N stretch and N-H deformation (Bellamy, 1975). Absorptions in this region in a protein spectrum may be due to C-N or N-H vibrations.

The spectra of proteins are marked by a broad area of absorption in the region 800 - 400 cm$^{-1}$. This is probably the result of the overlap of many bands due to the complex structure of the proteins.

**Identification of unknown sample**

An archaeological specimen which was thought to be untanned skin (York2) was tentatively identified as a protein. Skin is composed of protein (33%) and water (65%) and will decay rapidly. However, skin may survive in a dry environment where it becomes brittle (Kuhn, 1986).

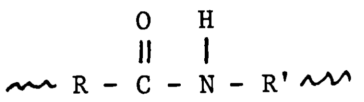
The band frequencies and band assignments are summarized in Table 8.1. The spectrum of the unknown sample is compared to that of tortoiseshell and pressed horn in Figure 8.2. The broad band with maximum intensity at 3308 cm$^{-1}$ in the spectrum of the unknown is assigned to the bonded N-H stretching vibration. The unknown sample spectrum has bands at 1662, 1606 and 1422 cm$^{-1}$ with a shoulder in the region of 1550 cm$^{-1}$ on the band at 1606 cm$^{-1}$.

In addition to the amide bonds, the presence of bands near 1608 and 1400 cm$^{-1}$ have been found in the spectra of dipeptides and have been assigned to the $COO^-$ group which is the ionized form of the peptide linkage. The band near 1600 $cm^{-1}$ is assigned to the anti-symmetrical vibration and the absorption near 1400 $cm^{-1}$ is assigned to the symmetrical vibration. The band near 1608 $cm^{-1}$ often masks or partially obscures the amide II absorption and it is difficult to assign frequencies in this area. These band frequencies correspond well with the values given for the amide I band (1680 - 1630 $cm^{-1}$) and the ionized carboxyl group (1608 $cm^{-1}$). The shoulder near 1550 $cm^{-1}$ is probably the partially obscured amide II band. The spectrum of the unknown material has an absorption at 1422 $cm^{-1}$ which may relate to the band near 1400 $cm^{-1}$ listed in the literature for the ionized carboxyl group. It would seem that the material is a protein which has undergone partial degradation (hydrolysis) which has resulted in the formation of ionized compounds.

In the unknown spectrum, a complex absorption with maximum intensities at 1270 and 1233 $cm^{-1}$ is evident. It is possible that one or both of these bands are due to C-N stretching or N-H deformation vibrations. The weak absorption near 3080 $cm^{-1}$ which has been tentatively identified as an overtone of the absorption in the region of 1550 $cm^{-1}$ (amide II) is not particularly evident in the unknown spectrum, but a weak shoulder may be seen on the right side of the N-H stretching absorption at 3308 $cm^{-1}$ which may correspond to this absorption.

The other regions in the spectrum result from vibrations of the various amino acid groups. In complex proteins, a broad area of absorption is expected to occur in the region 800 - 400 $cm^{-1}$. This is not particularly evident in this unknown spectrum, but the presence of inorganic materials such as hair or dirt seems to cause loss of relative intensity which lowers the baseline severely in the region between 1600 - 400 $cm^{-1}$ in the unknown sample spectrum.

The sample was identified on the basis of chemical information obtained from the frequencies as a partially degraded protein. This type of identification is usually aided by comparison with spectra of standard material of known identity. This is less useful with proteins as their infrared spectra tend to be very similar. Also, it is very difficult to recreate or estimate the reactions which take place during burial.



$$\sim R - \overset{\overset{O}{\|}}{C} - \overset{\overset{H}{|}}{N} - R' \sim$$

**Figure 8.1** Structure of a peptide bond.

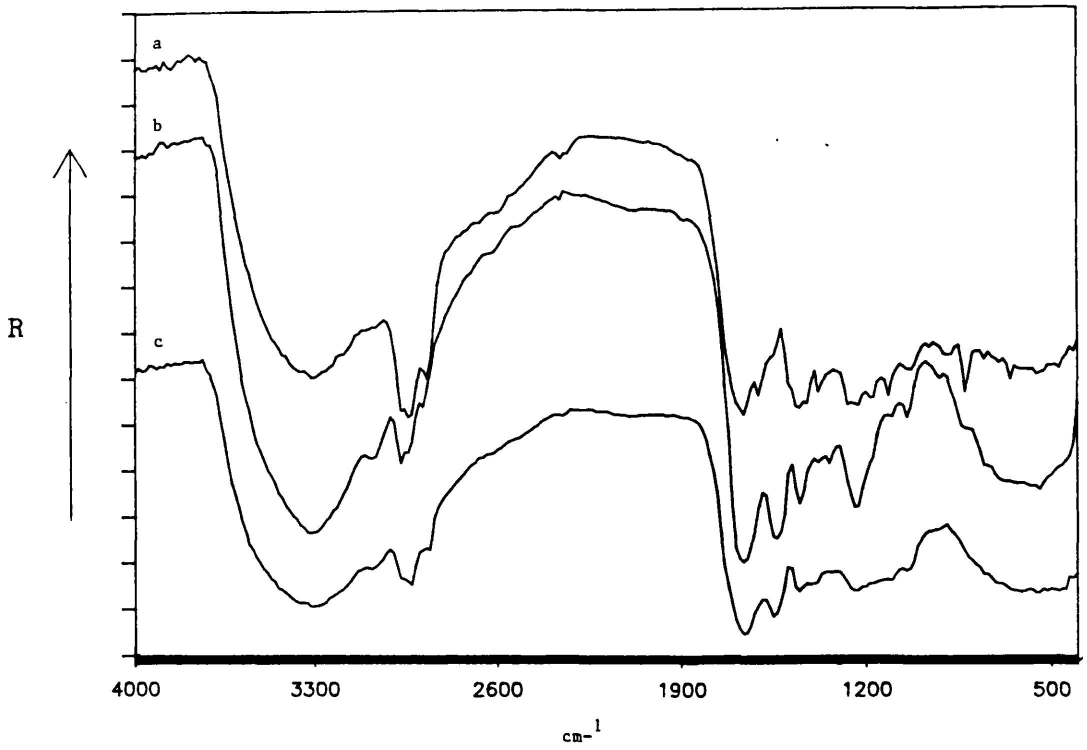


**Figure 8.2** Diffuse reflectance FT-IR spectra of (a) unknown sample (York2) identified as a protein (York Archaeological Trust Conservation Laboratories) (gsva0573), (b) tortoiseshell hairbrush (PHS55) from Hawksbill turtle (Plastics Historical Society (phs0058) and (c) pressed horn seal (PHS25) (Plastics Historical Society) (phs0028).

TABLE 8.1

Frequency values and band assignments for proteinaceous materials

| Albumen GS1 cm-1 | Rabbit skin glue VA10 cm-1 | Animal glue VA11 cm-1 | Hide glue VA12 cm-1 | Horn PHS25 cm-1 | Horn PHS26 cm-1 | Horn PHS27 cm-1 | Tortoise-shell PHS55 cm-1 | Unknown York2 cm-1 | Vibration | Functional group | Frequency range given in literature (1) cm-1 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 3276(s,b) | 3333(s,b) | 3333(s,b) | 3339(s,b) | 3297(s,b) | 3282(s,b) | 3291(s,b) | 3319(s,b) | 3308(m,b) | N-H stretch hydrogen bonded | peptide bond (trans-) | 3320 - 3270(m) |
| 3071(w) | nr 3070(s) | nr 3070(vw) | | nr 3070(w) | nr 3070(w) | nr 3070(w) | | nr 3080(sh) | amide II overtone | peptide bond (cis- and trans-) | 3100 - 3070(w) |
| | | | | | 2961(m) | | 2963(m) | 2960(s) | C-H stretch | methyl group | 2962 ± 10(s) |
| 2942(w) | 2938(w) | 2940(w) | 2944(w) | 2926(m) | 2927(m) | 2922(m) | | 2929(s) | C-H stretch | methylene group | 2926 ± 10(s) |
| | | | | 2855(w) | | 2854(w) | 2878(w) | 2870(s) | C-H stretch | methylene group | 2853 ± 10(s) |
| | | | | | | | | | C-H stretch | methyl group | 2872 ± 10(s) |
| | nr 2100(w,b) | 2132(w,b) | 2129(w,b) | | | | | | unassigned | | |
| 1648(s) | 1649(s) | 1673(s) | 1698(vs) | 1659(s) | 1652(s) | 1658(s) | 1661(s) | 1662(s) | amide I C=O stretch | peptide bond | 1680 - 1630(s) |
| | | | | | | | | 1606(s) | COO- vibration anti-symmetric | ionized carboxylic acid | near 1600(s) |
| 1554(s) | nr 1550(w) | 1541(s) | 1573(s) | 1548(s) | 1545(s) | 1548(s) | 1536(s) | nr 1550(sh) | amide II-coupled N-H deformation and C-N stretch | peptide bond | 1570 - 1515(s) |
| | 1510(s) | | | | | | | | unassigned | | |
| 1449(m) | 1454(s) | 1452(s) | 1472(s) | 1451(m) | 1450(m) | 1451(m) | 1449(s) | 1454(s) | C-H deformation | methylene group | 1465 ± 20(m) |
| | | | | | | | | | C-H asym. deformation | methyl group | 1450 ± 20(m) |
| | | | | | | | | 1422(s) | COO- vibration symmetric | ionized carboxylic acid | near 1400(s) |
| | | | | | 1400(w) | 1394(w) | 1388(m) | 1382(s) | C-H sym. deformation | methyl group | 1380 - 1370(s) |
| 1309(m) | 1335(m) | 1338(m) | 1344(m) | | | | 1341(m) | | unassigned | | |

TABLE 8.1 contd.

Frequency values and band assignments for proteinaceous materials.

| Albumen | Rabbit skin | Animal | Hide | Horn | Horn | Horn | Tortoise- | Unknown | Vibration | Functional group | Frequency range given |
|---|---|---|---|---|---|---|---|---|---|---|---|
|  | glue | glue | glue |  |  |  | shell | York2 |  |  | in literature (1) |
| GS1 | VA10 | VA11 | VA12 | PHS25 | PHS26 | PHS27 | PHS55 |  |  |  |  |
| cm-1 | cm-1 | cm-1 | cm-1 | cm-1 | cm-1 | cm-1 | cm-1 | cm-1 |  |  | cm-1 |
|  |  |  |  |  |  |  |  | 1270(s) | amide III-coupled | peptide bond | 1305 - 1200(m) |
|  | 1238(s) | 1237(s,b) | 1256(m) | 1234(m) | 1233(m) | 1235(m) | 1235(s) | 1233(s) | N-H deformation |  |  |
|  |  |  | 1203(m) |  |  |  |  |  | and C-N stretch |  |  |
|  |  |  |  |  |  |  |  | 1177(s) | unassigned |  |  |
|  | nr 1100(w) |  |  | nr 1100(sh) | nr 1100(sh) | 1104(w) | 1107(w) | 1116(s) | unassigned |  |  |
|  |  | 1084(s) | 1089(m) |  |  |  |  |  | unassigned |  |  |
| 1049(m) | nr 1050(w) |  |  | nr 1050(sh) | nr 1050(sh) | 1046(w) | 1044(w) | 1037(m) | unassigned |  |  |
| nr 1000(sh) |  | nr 1000(w) |  |  |  |  |  | 961(m) | unassigned |  |  |
| nr 940(sh) |  | nr 930(vw) |  |  |  |  | 921(w) | 925(m) | unassigned |  |  |
|  |  |  |  |  |  |  |  | 900(m) | unassigned |  |  |
|  | nr 875(w) |  |  |  |  |  |  | 874(m) | unassigned |  |  |
|  |  | nr 850(vw) |  |  |  |  |  |  | unassigned |  |  |
|  | nr 810(w) |  |  |  |  |  | nr 800(sh) | 820(s) | unassigned |  |  |
|  |  |  |  |  |  |  | nr 750(sh) | 754(m) | unassigned |  |  |
|  |  |  |  |  |  |  |  | 701(m) | unassigned |  |  |
|  |  |  |  |  |  |  |  | 654(m) | unassigned |  |  |
|  |  |  |  |  |  |  |  | 556(m) | unassigned |  |  |

1. Bellamy, 1975

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp; nr = near

# CHAPTER 9 HISTORY AND DEVELOPMENT OF EARLY PLASTICS

## Introduction

The purpose of this chapter is to give an outline of the background information regarding the development of plastics including the history, structure, production method, additives, uses and tradenames. The characterization of these materials using diffuse reflectance FT-IR and a short section on the sources of degradation of the materials will be discussed in subsequent chapters.

## Polymerization

The term plastic is used to describe a property of certain materials able to be moulded or deformed. Plastics has come to be known as a collective noun for semi-synthetic and synthetic materials which are capable of being moulded. However, it should be remembered that there are natural polymers that have been used to make objects by moulding under heat and pressure since antiquity. Thus, conservators and other museum staff should be aware of both natural and synthetic polymers and how to characterize the material. The diffuse reflectance FT-IR technique was thought to be very promising for the characterization of both natural and synthetic polymers and this chapter is concerned with the application of the technique to both objects and works of art made from polymers.

Polymers are long chains of repeating structural units called monomers. The chains are produced by chemical reactions which cause the monomers to join and a catalyst is frequently necessary to facilitate the reaction. Monomers must have at least two functional groups and bifunctional monomers form linear polymers. Polyfunctional monomers give branched chain and three-dimensional network systems. There are two types of polymerization reactions, condensation and addition. In condensation reactions, the monomer molecules are broken up and certain parts are joined together to form the polymer. The process produces waste products. An example is nylon which is a family of polymers which are of the polyamide type and water is produced as a by-product. In addition reactions, chemical reactions of molecules with multiple bonds are utilized. The presence of double or triple bonds or regions of unsaturation increases the reactivity of the molecule because the Pi bond is susceptible to attack (Cotterill, 1985). There are two types of catalyst for this reaction which utilize either an ionic mechanism or a free-radical mechanism. The ionic mechanism uses certain metallic or non-metallic halides

($AlCl_3$, $SnCl_4$ or $BF_3$) or sulphuric acid. The free-radical mechanism utilizes chain reactions and the catalyst must create free-radicals. These catalysts include organic and inorganic peroxides and the salts of peracids (benzoyl peroxide, acetyl peroxide, hydrogen peroxide and potassium perborate (Finar, 1963). The resulting polymer is made up of repeating units of the monomer and there are no by-products produced in the reaction. The presence of an electronegative group also increases the reactivity of the monomer. For example, vinyl chloride is more reactive than ethylene. Sulphur is a divalent molecule and it is used to replace hydrogen and forms sulphide bonds of the -C-S-C- and disulphide bonds of the -C-S-S-C- type. The sulphur link is very common as a cross-link in biological polymers. Cross-links or bonds that form between molecular chains cause the polymer to become rigid. Disulphide bonds are strong covalent links, but weaker hydrogen bonds which form in nylon polymers are sufficiently strong if there are large numbers of them (Cotterill, 1985).

### Natural plastics

There are numerous examples of natural plastics used in antiquity and the chemistry of these materials have been discussed in earlier chapters. Materials such as bitumen, amber, shellac and albumen may be moulded into objects (Brydson, 1975). Some natural plastics are discussed in Chapter 13.

## Gutta percha

Several natural polymeric materials were brought to Europe as a result of exploration of the new world and southeast Asia. John Tradescant (1608 - 1662) was an English traveller and gardener who brought gutta percha back from his travels (Brydson, 1975). The material is obtained from the bark of the palaquium tree which is grown in Malaysia and it can be manipulated after dipping in hot water. The Gutta Percha Company was formed in London in 1845 and it produced extruded mouldings which were to be imitations of those made of wood for panels and friezes. It was utilized during the second half of the nineteenth century for casting medals, decorative ornaments, buttons, clock cases and jugs. It is resistant to acids and was used for bottles for hydrofluoric acid. It was used as a substitute for papier maché, leather and wood and became a popular material for the production of golf balls (Hillman, 1986). Gutta percha was also widely used as underwater cable insulation material and was used for this purpose until 1940 (Brydson, 1975).

## Natural rubber

Natural rubber was observed by sailors on Columbus' expedition to Central America where they found the natives playing with lumps of the material. The first written reference appeared around 1535. La Condamine was sent on a misson by the French government to study the shape of the earth in 1731. He obtained rubber coated cloth which was produced by the native tribes of the Amazon basin and used to make waterproof shoes and flexible bottles. Natural rubber is collected by coagulation from a latex and was at first only a novelty since it could not be shaped by moulding or extrusion. However in 1820 in England, Thomas Hancock found that the highly elastic material could be made plastic and capable of flow through shearing or mastication of the rubber. Nineteen years later in the USA, Charles Goodyear discovered that the addition of sulphur to heated rubber resulted in a product which was elastic over a wider range of temperature than untreated rubber and was more resistant to the action of solvents. Hancock also found somewhat later that masticated rubber mixed with molten sulphur produced an elastic material. Although Goodyear made the initial discovery and the work of Hancock was to a certain extent based on that of Goodyear, Hancock took out a British patent in 1843 and Goodyear did not patent his discovery in America until 1844. The process was termed vulcanization by a friend of Hancock, William Brockendon (Brydson, 1975).

The vulcanization process only required the addition of a few percent sulphur. Both Hancock and Goodyear observed that the addition of sulphur in a ratio of one part sulphur to two parts rubber resulted in a very hard product. Nelson Goodyear patented the method for making hard rubber, as the product was known, in 1851 (Brydson, 1975). It was also known as vulcanite or ebonite in England. The hard rubber or vulcanite was used to produce buttons, jewelry, combs, cutlery handles, buckets, smoking pipe mouthpieces, telephone receivers, dentures and fountain pens (Hillman, 1986). Charles Mackintosh began to produce ebonite in 1851 and several plants were in operation by 1860. This discovery is considered to be an important one in the history of rubber, but it is also very important in the history of plastics. It is the first chemical modification of a natural material to produce a thermosetting plastic (Brydson, 1975).

## Twentieth century

The term plastics came into general use during the late 1920's when these new substances were being invented and utilized to make objects for a large variety of industrial, commercial and domestic uses. For example, celluloid or cellulose nitrate plastic was first exploited as a substitute for natural materials like ivory, hard rubber, amber and tortoise-shell and used to make small domestic objects which were considered to be novelties. However, plastics have come to be considered as important materials with properties which are often better than natural materials for many applications (Hillman, 1986). After the Second World War, there were large excess supplies of synthetic resins. They were used to make versions of many household objects, most of which were inexpensive and of poor quality. Thus, the term plastic has gained the reputation of being cheap, artificial and of poor quality. They are becoming increasingly necessary as natural sources are exhausted. Conveniences which have become part of recent culture such as automobiles, telephones and television would not be possible without the use of plastics (Brydson, 1975; Hillman, 1986). Plastic objects are already appearing in social history collections and in works of art and will become more prevalent in the future, especially in history of technology collections. Plastic materials are generally refered to as a group, but it important to realize that different types of plastic have unique properties and to be able to distinguish between various kinds of plastics.

### Cellulose nitrate

#### History

Cellulose nitrate was first prepared by Braconnet in 1833 by reacting sawdust and linen with nitric acid. Shortly thereafter, Pelouze also produced cellulose nitrate by treating paper with nitric acid (Yarsley et al., 1964). In 1845, Schonbein discovered that the reaction of cotton with sulphuric and nitric acids resulted in an explosive material, cellulose trinitrate. He immediately realized the political implications of the explosive material (Kaufman, 1963). The discovery stimulated governmental interest and France, Russia, Germany and Austria set up commissions to develop the military applications of this branch of explosives chemistry (Yarsley et al., 1964). When it was found that the cellulose nitrate material was soluble in ether alcohol mixtures, cellulose nitrate could be made into films and coatings and this material was known as collodion (Yarsley et al., 1964). In the mid-nineteenth century, F. Scott Archer began to use the collodion for photographic work. The cellulose nitrate was mixed with potassium iodide and spread on a glass plate. The plate was then coated with silver nitrate then exposed while wet. The film was removed during processing and replaced on the glass after the final washing (DeMare, 1957).

Great advances in the manufacture of cellulose nitrate were made by Alexander Parkes in England. In 1852, he presented the first cellulose nitrate lacquer, pyroxylin, at the London Exposition. (Yarsley et al., 1964). The process was patented in 1856 (BP 1123/1856) (Kaufman, 1963). A mouldable, thermoplastic material produced from cellulose nitrate was shown at the universal exhibition in London (1862) which was awarded a bronze medal. In 1865, a formulation for cellulose nitrate using camphor as a plasticizer was patented by Parkes (BP 1313/1865) which was thought to have been the process utilized for the objects presented at the 1862 exhibition. He called the plastic Parkesine. This was a major breakthrough in the development of the plastic (Kaufman, 1963).

In 1866, the Parkesine Company was founded by Parkes. It was not successful and lasted only two years. The production method adopted by the company did not contain vital steps which are now known to be important in producing a stable product. Parkes was concerned with lowering the cost of his product and used cheap materials including poor quality cellulose. Also, he did not find a good solvent system for the material (Kaufman, 1963).

In the USA, the Hyatt brothers became involved with cellulose nitrate as a result of a contest to find a replacement material for ivory billiard balls. The Hyatts began to work with collodion mixtures and took out three patents on cellulose nitrate in 1869, USP88,634/1869 (for production of billiard balls), USP 89,582/1869 and USP 91,341/1869. In 1870, the Hyatts made an important discovery. They found that the use of camphor in large quantities was an effective solvent for cellulose nitrate (USP 105,338/1870). The patent suggests the use of two parts cellulose nitrate to one part camphor. The brothers used the material to produce dental plates and began the Albany Dental Plate Company. In 1872, the company name was changed to the Celluloid Manufacturing Company (Kaufman, 1963).

Cellulose nitrate production was resumed in England by Daniel Spill who had been the works manager of the ill-fated Parkesine Company. In 1869, he established the Xylonite Company on the premises of the Parkesine Company, however, this company was liquidized in 1874. Spill was perseverent and found backing for a new company which he named the Daniel Spill Company. In 1876, the British Xylonite Company was created in conjunction with L. P. Merriam with backing from three other businessmen. The new company was not immediately successful. In 1877, Spill initiated a legal suit for patent infringement against the Hyatt brothers claiming that the camphor/alcohol solvent and the bleaching processes used by them were covered by Spill's patents USP 97,454/1869 and USP 101,175/1870. After a three year legal battle, the judge decided in favor of Spill. He set up a company in the USA called the American Zylonite Company. The Hyatt brothers changed the formulation slightly and requested a new hearing. The case was reopened and in 1884, the judge reversed the earlier decision. He stated that no limitations could be put on the cellulose nitrate/camphor /alcohol formula and this allowed for competition and growth in the industry. Meanwhile, the British Xylonite Company finally achieved financial success with the manufacture of cellulose nitrate collars and cuffs in 1885 (Kaufman, 1963).

## Chemical structure and nomenclature

Cellulose is a high molecular weight polymer found in nature which is made up of many anhydro-beta-glucose (Figure 9.1a) units bonded together in an extended open-chain structure. The number of glucose units in the structure (degree of polymerization) is dependent on the degradation that occurs during the purification of the cotton linters. The cellulose chains contain from 1,000 to 3,000 glucose molecules after the chemical treatment of the cotton. The six-atom ring glucose molecules are fairly rigid which are bonded by primary valence bonds or glucoside bonds through oxygen bridges in the 1:4 positions (ether linkages)(Figure 9.1b)(Yarsley et. al., 1964).

Cellulose has very little internal flexibility. This is due to the limited movement at the oxygen bridges resulting from stearic hinderence from the groups in the vicinity of the bond and the rigidity of the glucose rings. The cellulose chains are aligned approximately parallel to each other in the direction of the fibre axis. The chains are held together by hydrogen bonds which form between the hydroxyl groups in the glucose molecules. The bonds which hold the chains together are strong enough to resist mechanical deformation of the fibres and thus no permanent alteration results from the temperature and pressure used for moulding plastics. Thus, cellulose cannot be processed as other plastics. Also, cellulose cannot be plasticized because it is soluble only in very strongly acidic or basic solvents. Plasticizers act by separating the chains and may be considered as high boiling point solvents which remain incorporated in the structure of the plastic (Yarsley et al., 1964).

The treatment of the cellulose with nitric and sulphuric acids results in a change in the chemical nature of the material which allows it to be manipulated as a plastic. The reaction is often refered to as a nitration, but this term is misleading. The chemical process is an esterification. Although the term nitrocellulose is used, the product is actually an ester and it will be refered to as cellulose nitrate. The plasticized product will be refered to as cellulose nitrate plastic or celluloid (Yarsley et al., 1964).

The anhydroglucose unit in cellulose has three hydroxyl groups which may be substituted. Commercially produced cellulose nitrate (Figure 9.2) has a nitrogen content of between 10 - 14 % and the degree of substitution is determined by the intended use of the material (Table 9.1). Cellulose nitrate for plastics production is close to the value for a dinitrate with a nitrogen content of 10.7 to 11.1 %. A slightly higher degree of substitution desirable for the production of lacquers to obtain a decrease in water sensitivity. Material for the explosive cordite has a degree of substitution close to the theoretical value for trinitrate (Yarsley et al., 1964).

The substitution of the hydroxyl groups by the nitrate groups reduces the hydrogen bonding which results in compatibility of cellulose nitrate with a large number of plasticizers and the solubility of the material in common solvents. Camphor is the most widely used plasticizer and the structure of camphor is given in Figure 9.3 (Bean, 1972). X-ray diffraction and optical birefringence results (Yarsley et al., 1964) indicate that the camphor and the cellulose nitrate form a fairly stable complex with the camphor bonding to the cellulose nitrate molecule. Camphor and the substituted glucose ring are thought to react in equal molecular proportions to form a complex structure. It is thought that a hydrogen bond is created between the carbonyl group in the camphor molecule and the hydroxyl group which is not nitrated on the glucose molecule. As an excess of cellulose nitrate is used in proportion to the camphor, the mixture probably contains both cellulose nitrate and cellulose nitrate-camphor complex (Yarsley et al., 1964).

Plasticity results from increased movement of the chain. This enables the material to move or be deformed under pressure. The action of the plasticizer can be illustrated as having a solvent effect. The plasticizer is thought to become attached to the polar groups on the cellulose chain. This increases the distance between the cellulose chains which in turn decreases the bonding between them. However, there is still some bonding between adjacent chains which keeps the material from flowing at ordinary temperatures (Yarsley et al., 1964).

## Production Method

### Preparation of cellulose linters

The source for cellulose which is used for the plastics industry is cotton linters which are obtained as a by-product from the cotton industry. The cotton is passed through a gin which removes the cotton staple fibre from the seeds. Short buff coloured fibres remain attached to the seed hull which are known as linters. They are separated from the hull by a linter machine. There are three grades of linters, first cuts, second cuts and mill runs. The cotton staple fibre and the first cut linters are used in the textile industry and the second cut linters are used to produce chemical cellulose (Yarsley et al., 1964).

The cellulose is prepared for use by a process of mechanical cleaning, digesting, bleaching, washing and drying. The first step of mechanical cleaning takes place in a breaker. The bales of linters ae broken up by bronze spikes attached to rotating cylinders. The linters are then picked up in an air stream which carries them up into an air separator at the top of the building. The air blowing process removes the heavy impurities. The linters are then deposited onto a conveyor where the are treated with a 3% caustic soda solution and introduced into the digester (Yarsley et al., 1964).

The digestion process ensures that seed hull remnents and other non cellulosic impurites are chemically changed to substances which can be eliminated with water. In a typical example, 7,000 lbs of linters are placed in a digester with 10 times the weight of the linters of 3% caustic soda . The alkaline mixture is then boiled under pressure for two to six hours. The steam is introduced below the level of the solution and the the air in the digester is then displaced. The time required is determined by the desired viscosity and the content are thoroughly mixed during the entire process. The contents are released through a valve and taken up through a steam separator. The linters and the alkali solution are then directed into a steel wash tank where the liquid is drained off. The linters are rinsed very thoroughly at this stage to remove the alkali and the degradation products of the impurities. 30,000 gallons of water are used for one ton of linters (Yarsley et al., 1964).

A continuous operation process for digestion and washing has been found to be more efficient in promoting chemical reaction and washing. The continous Dorr-Oliver digester is equipped with a rotary table with a spray jet and removes the alkali and small grit particles more rapidly (Yarsley et al., 1964).

The next step is the bleaching of linters. It is usually done in two or more steps to lessen the possible degradation of the cellulose fibres. The treatment is carried out in wooden tubs with perforated false bottoms. Bleaching agents employed are gaseous chlorine and sodium or calcium hypochlorites with chlorine content ranging from 0.75 to 1.25%. The bleach is most often acidified with sulphuric acid. It is vital that the time, temperature, pH and concentration be strictly monitered throughout the bleaching procedure to ensure that the resultant product has a white colour and is not degraded. Continuous bleaching methods are also being developed to obtain a more uniform product.

After each step of the bleaching procedure, the product is thoroughly rinsed. The purity of the water is important. Impurities such as iron have a pronounced effect on the colour of the product. The product is washed with an oxalic acid solution to lower the iron content after bleaching.

The linters are introduced into a large container where they are blended thoroughly to ensure a chemically and physically uniform product. The linters are then put into a solution of water with a concentration less than 0.5% and the slurry is pumped through a machine where the last of the heavy impurities settle out of the slurry (Yarsley et al., 1964).

The linters are then dried to lower the water content to 50% of the dry weight. The material is drained through rubber covered rolls. The linters are then introduced to a continuous tunnel-drier in which heated air 150 - 160 °F is circulated. When the moisture content falls below 5%, the dried linters are pressed compressed into bales (Yarsley et al., 1964).

### Esterification or "nitration" of cellulose

To produce cellulose nitrate, the cellulose must be dried and then reacted with a solution of concentrated sulphuric and nitric acids. The acid is then recovered and the resultant ester is stabilized, bleached, rinsed and then dehydrated by replacing the water with ethyl alcohol (Yarsley et al., 1964).

The moisture content of the linters must be lowered as the water content is often raised to 7 - 8% during transportation and storage. It is critical to remove as much of the excess moisture as possible before treatment. Excess water decreases the acidity of the solution and irregular nitration results. This causes reduced solubility of the product. The heat generated during the dilution of the acid in the fibre structures causes degradation and thus decreased product. The material is dried in the same manner as in the final step of the purification process by passing the material through a tunnel heated by circulating air. The final moisture level should be 0.5 - 1.0 % (Yarsley et al., 1964).

The cellulose can be converted to various derivatives by either homogeneous or heterogeneous techniques. The production of cellulose nitrate is a heterogeneous technique where the fibre structure is retained throughout the process. This differs from the methods used to produce cellulose acetate where the product dissolves into the solution as it is produced, and ethyl cellulose where the fibre structure is destroyed, but the material does not disperse into the medium. Cellulose nitrate may be produced by direct esterification with concentrated nitric acid or with nitric acid vapour under reduced pressure. However, the standard technique is to use concentrated sulphuric acid as a condensing agent in addition to the concentrated nitric acid. A solution consisting of 25% nitric acid, 55% sulphuric acid and 20% water is typical for the production of 11% nitrogen. The composition is very similar to that used by Schonbein (Yarsley et al., 1964).

There have been many improvements in the nitrating procedure. The DuPont process, which was first developed in the USA and is now commonly used, employs a mechanical dipping process. The stainless steel unit is composed of four dipping pots called dippers, a centrifuge and a drowning tank which are positioned vertically with the dipping pots at the top. The actual chemical reaction takes place in the dippers where 30 lbs. of cotton are combined with 1,200 lbs. of the acid mixture at a temperature of 35-40 °C for 30 - 60 minutes. The product is then dropped into the centrifuge and the acid is "spun off" and retained to be reused. The cotton, which still contains a high percentage of acid, is then dropped into a drowning tank where the acid is diluted in a large quantity of water. The resultant slurry is then transferred into large stainless steel vessels where large quantities are collected for further processing (Yarsley et al., 1964).

The next stage is the stabilization of the cellulose nitrate. This is a very important step as the unstabilized material is explosive. Several early disasters led to research, and in 1865 Abel found that the instability was caused by traces of the nitrating acids which were retained in the structure of the material. It was found that the nitration reaction produced sulphuric-nitric mixed esters as a secondary product of the nitration reaction. Sulphuric acid was created as the groups "split off" which instigated autocatalytic decomposition. In 1906, Robertson discovered that boiling the cellulose nitrate in weakly acidic water would almost completely eliminate the acid ester groups. The material is stabilized in the large collection vats. The slurry is washed and the water continously replaced until the acidity of the water is about 0.2%. The solution is then brought to a boil using steam and heated for 5 to 12 hours. If a product with high stability is needed, the process is carried on for a much longer time. The stabilizing process slightly decreases the nitration content and viscosity of the resulting cellulose nitrate (Yarsley et al., 1964).

Bleaching is necessary to produce clear transparent and light coloured plastic. The natural cellulose nitrate plastic has a brownish yellow tinge. The stabilized cellulose nitrate is placed in lined wooden vessels at low temperatures. Gaseous chloride or sodium hypochlorite are the common bleaching agents. The concentration used is about 0.5% available of the weight of the cellulose nitrate and the treatment lasts from 30 to 60 minutes. The product should be treated with sodium sulphite or weak nitric acid to remove residual chlorine from the material. This is important as residual chlorine would cause breakdown of the product. The cellulose nitrate is rinsed until the wash water is neutral and then the product is transfered into a tile-lined draining stall where the water is drained through holes in the floor. As with the preparation of cotton linters for commercial production, it is important that the water is pure. Cellulose nitrate can absorb metallic ions from water with great ease. For example, iron damages both the appearance and the heat stability of the product. Thus, there must be constant quality control of water supply and it must be treated as necessary (Yarsley et al., 1964).

The cellulose nitrate contains a high percentage of water (35 - 40% of the wet weight) after the draining procedure. It is necessary to remove as much of the water content as possible before it can be used to produce cellulose nitrate plastic. It is necessary to replace as much of the water as possible with denatured ethyl alcohol. There are two methods for this process, the first which involves putting the cellulose nitrate into a centrifuge consisting of two concentric baskets. The alcohol is introduced as a spray while it is in motion. The dehydrated product should contain about 30% alcohol and 5% water. In the second method, the cellulose nitrate is pressed into a cylindrical mass in a hydraulic press at a pressure of 2000 - 3000 lb/in$^2$. The alcohol is added to the system at a pressure of 600 - 800 lb/in$^2$. The solution is then forced out under full pressure. This method is more efficient, the dehydration is more complete and less alcohol is needed (Yarsley et al., 1964).

The dehydration also has a stabilizing effect as the cellulose nitrate is not entirely insoluble in the alcohol and about 1% of the material is lost in the process. The material which goes into solution has been found to have a lower nitrogen content (Yarsley et al., 1964).

### Production of cellulose nitrate plastic and additives

The dehydrated cellulose nitrate is mixed with camphor to create a uniform dispersion or dough. The material is subjected to hydraulic pressure and then the solvent is partially removed by rolling. The bulk is pressed into a block by heat and pressure in a hydraulic press. The block is cut into sheets, the residual solvent is removed by a process called stoving. The sheets are then polished (Yarsley et al., 1964).

The mixing of the cellulose nitrate with the camphor takes place in cast iron, bronze or stainless steel mixers which are boxes with two pairs of blades which "rotate" in opposite directions, and with external heating components. The average composition of the raw material is three parts cellulose nitrate to one part camphor, however, different amounts of camphor are used for special applications. In some cases, plasticizers such as triphenyl phosphate and diethyl or dibutyl phthalate have been used as a partial substitute for camphor. However, camphor is still the most widely used plasticizer for cellulose nitrate. The mixer is steam heated at the beginning of the reaction, but it is usually turned off as the reaction proceeds as heat resulting from the internal friction in the cellulose nitrate keeps the temperature at 104 - 122 °F. The ethyl alcohol in the cellulose nitrate becomes an effective solvent in the presence of camphor. The cellulose nitrate fibres swell and lose their structure as the material gels. Other additives which include colouring agents and occasionally stabilizers are introduced at the beginning of the mixing process. Colouring agents include soluble dyes and pigments which are either added dry or as a paste. For clear transparent plastics, a small amount of soluble dye or very finely dispersed pigment is used to counteract the yellow tinge in natural cellulose nitrate. It is necessary to obtain a uniform dispersion of colourants to prevent "colour spots" in the finished product. Stabilizers are added in small amounts to neutralize acids which may form which gives greater stability. These include urea or a urea derivitive and zinc oxide which is also utilized in opaque pigments. The mixing process takes 1-2 hours until the colouring matter is uniformly dispersed throughout the mixture (Yarsley et al., 1964).

After nitration, the dust and other impurities are eliminated by passing the dough through a calico sieve under hydraulic pressure of 1.5 tons /in$^2$. The filtered material is then rolled between differentially heated cylinders for 30 - 40 minutes in a two step process to reduce the solvent (ethyl alcohol) concentration in the compound from 28 - 30% to 12 - 15%. During the first part, the movement of the rolls repeatedly exposes fresh surfaces of the material creating a situation where the solvent is evaporated quickly. It is important to not remove too much solvent and the timing is still based on the experience of the operator. The second step is to roll the material on slower, cooled rolls also known as calenders where the plastic is rolled into 1/2 inch thick sheets which are cut to fit the block press.

The Parkes technique called for squeezing the dough between rolls and then eliminating the volatile solvent content. The Hyatt brothers improved on this procedure by first pressing sheets of plastic into a block in a press and then slicing sheets from the mass. This produced a substance with greater toughness than that produced by earlier methods. In modern processes, the sheets are placed on a steel base scored with grooves in which the cellulose nitrate plastic is firmly attached for the subsequent slicing step. The base is placed inside a steel box which is then put in a hydraulic press. The press is heated to 200 °F and put under 350 $lb/in^2$ pressure. The period of time necessary is dependent on the thickness of the block, the average time required is usually 4 - 5 hours. It is necessary to allow the apparatus to cool thoroughly. If the block is released from the press while still hot, solvent bubbles form in the material and it must be repressed. After the cooled blocks are removed from the box, they are placed in a cool atmosphere for 24 hours to reach a uniform temperature.

The block is fastened to a movable table which is manipulated by a reversible screw. The screw moves the plastic block backwards and forwards under a knife which is programmed to cut certain thicknesses of sheet. An allowance must be made for the final thickness as a certain amount of shrinkage occurs during seasoning. The thickness of sheet can range from 0.005 to 1.0 inch.

There are two methods for seasoning of the cellulose nitrate, one for thin sheets, up to 0.100 in and a modified one for thick sheets. After slicing, the sheets are hung in a heated chamber where the temperature is kept at 122 °F and the air is circulated ultimately into a solvent recovery system. A hard surface layer forms which does not cause a problem with the curing of thin materials. However, the creation of a hard surface layer makes the seasoning of the interior more difficult. The solvent must diffuse through the outer coating which requires a greater length of time. Thick sheets, 0.100 in and greater, are hung in an unheated chambers for three days to allow the bulk of the solvent to diffuse from the material. Then, the sheets are hung in heated rooms as for thin sheets. This prevents the formation of bubbles when the sheets are placed in the heated rooms. There is a certain amount of distortion due to shrinkage as the solvent is removed. The damage is most evident around the edges of thin sheets. The final moisture content is 2% water and some ethyl alcohol which is almost impossible to eliminate because of the strong affinity of the camphor and alcohol and cellulose nitrate.

The final step in the production of sheet cellulose nitrate is polishing. The knife edge used for slicing leaves marks which make transparent cellulose nitrate plastic appear translucent. It must be polished to remove the imperfections on the surface. The seasoned sheets are press polished by heating the sheet between highly polished, nickel plated steel plates in a hydraulic press. The temperature, pressure and time of polishing are carefully controlled so that only the surface material is affected. The plates are quickly chilled to prevent a reduction in thickness of the sheet. Cellulose nitrate sheets with impressed or etched designs can also be produced by using etched or embossed metal plates (Yarsley et al., 1964).

## Trade names and applications

The short lived Parkesine Company (1865-1867) produced buckles, clasps, buttons, beads, mirror backs, medallions, book covers, bracelets, handles, shoe-horns and door knobs. In the USA, the Hyatt brothers first manufactured flesh toned dental plates to be used in place of those made of dark hard rubber (1870). In 1872, the new Celluloid Manufacturing Company produced knife handles, harness trimmings and brush backs. In 1878, their production was extended to manufacture jewelry, necklaces, pendants, earrings, watch chains, pins, buttons, charms, bracelets, checkers, dominoes, thimbles, soap dishes and other domestic objects. The Merchant's Manufacturing Company (Newark, New Jersy) had already been set up in 1881 and produced cellulose nitrate under the name Pasbosene. The trademark was changed to Cellonite in 1883 and in 1885, the company was moved and renamed as Arlington Manufacturing Company. The product was then called Pyralin. The Celluloid Manufacturing Company took over the American Zylonite Company in 1890 and with the Arlington Company, were the major producers of cellulose nitate plastic for 25 years. Dupont eventially took over the Arlington Company, but continued to use the trade-mark Pyralin. In 1927, the Celluloid Manufacturing

Company merged with the Celanese Corporation of America (Kaufman, 1963).

More than 1,200 patents had been taken in the USA and Great Britain by 1911 on cellulose nitrate plastic application and production. It is impossible to list them all, but an indication of the scope may be summarized. Natural material were sucessfully substituted by cellulose nitrate. These included grained ivory (1883), horn (1891), tortoise-shell (1875), mother of-pearl (1884), coral, amber, onyx (1895) and marble (1898) (Hillman, 1986).

In addition to the early uses of cellulose nitrate plastic for dentures and "linen" collars and cuffs, other uses included knife handles, printers blocks, and "fancy goods" such as hand mirrors (1890's), dressing cases, trinket boxes, photo frames, dolls, car windsheilds, table tennis balls, lacquers, shoe heels, and corset stays (1881). It was widely used for combs and brush backs which were an important part of the market. Different types of brushes made include hair, nail, shaving, clothes, hat, baby and tooth brushes. Other objects made included piano key linings (1878), ice pitcher linings, playing cards, eye-glass frames, pen holders

(1879), syringes (1880), chocolate and bon-bon boxes (1893), trays and dishes (1895), shoe eyelets (1902), golf balls (1903-1905), and "amber" cigar holders (1904). It was also used to manufacture children's toys including the Kewpie doll, baby rattles, straight razor handles. Artificial leathers utilized for upholstry, bookbindings, raincoats, suitcases, dressing cases, automobile trimming and handbags and waterproof coatings for posters, show bills, and exterior sign s were other applications of celluloid. The first important industrial use was in the new photographic and cinematographic industries. Kodak introduced cellulose nitrate film in 1889 (Kaufman, 1963; Yarsley et al., 1964).

The early trademark Celluloid has come to be used for all cellulose nitrate plastics, but there are many other trade-names which have been used. Certain trademarks were only used for a short time while others were used for many years. The trademarks include Bonesilate, Cellonite, Celluline, Cellulodine, Cellulosine, Coraline, Crolithion, Crytalloid, Fiberloid, Fibrolithoid, Ivaleur, Ivoride, Ivorine, Ivoryide, Lignoid, Lithoxyl, Parkesine, Pasbosene, Pearl-Tone, Pegamoid, Pulveroid, Pyralin, Pyrantin, Pyroxyline, Rubberine, Shell Tone, Shelleur, Viscoloid, Vitroloid, Xylonite, Zylonite and Zyl. Artificial leather was first marketed as Tannette (1890) which was later known as Morrocoline (1892). Later tradenames which date from the turn of the century include Fabrikoid, Keretol, Marokene, Meers, Case and Texaderm (Hillman, 1986).

## Cellulose acetate

### History

The acetylation of cellulose is a more difficult chemical reaction and the development of cellulose acetate was not as straight forward as that of cellulose nitrate plastic (Kaufman, 1963). Cellulose was first acetylated by Schutzenberger in 1865. He treated cotton with acetic anhydride in a sealed tube and heated it to 130 - 140 °C (Kaufman, 1963; Yarsley et al., 1964). The resulting product was severly degraded and the reaction was difficult to control. Brydson, 1975). Sulphuric acid was first used as a catalyst by Francimont. Cross and Beavan developed the first commercial production method of cellulose acetate in the form of spinnable fibres from regenerated cellulose in 1904. The material was known as viscose rayon (Kaufman, 1963, Hillman, 1986). The initial material was cellulose triacetate which is soluble in chloroform and other toxic solvents. In 1905, Miles found that an acetone soluble product could be produced by the treatment of the triacetate with a weak acid. The hydrolysis created a diacetate. This development helped lead to commercial success. The Dreyfus brothers first achieved success with the production of cellulose acetate used to stiffen fabric aeroplane wings during World War I. After the war, the brothers used surplus stocks to develop a cellulose acetate fibre (Kaufman, 1963). With the introduction of plasticizers in 1927, cellulose acetate could be used for a wider range of applications. It became a non-flammable alternative for cellulose nitrate. It was used more extensively for injection moulding during the subsequent ten years and was the leading material for this purpose until the early years of the 1950s (Kaufman, 1963; Brydson, 1975).

### Chemical structure and nomenclature

The structure of cellulose has been discussed above. Like cellulose nitrate, cellulose acetate is an ester where one or more of the available hydroxyl groups on the anhydroglucose molecule is replaced with an acetate group (Figure 9.4). The substitution of the hydroxyl groups with the acetyl groups has a similar effect to the replacement in cellulose nitrate, the hydrogen bonding between the cellulose chains is reduced and the space between the chains is increased by the bulk of the acetate groups. Thus, the polarity of the molecule is reduced. Cellulose acetate may be characterized by the degree of substitution and different degrees are required for different uses. Also, the solubility in various solvents changes according to the degree of substitution (Table 9.2).

### Production method

### Acetylation of cellulose

There are two types of production techniques, the homogeneous method where the acetylated cellulose is dissolved in a solvent as it is produced and a heterogeneous one where the fibrous structure of the material is kept as it is acetylated. The former method is the most common for the manufacture of cellulose diacetate (Yarsley et al., 1964).

The production method for acetylating cellulose consists of five steps, pretreatment, acetylation, saponification or 'ripening', precipitation and after-treatment. The pretreatment is necessary to "open up" the cellulose structure, otherwise only the hydroxyl groups on the surface will be acetylated. Pretreatment is a mild acetylation where the material is usually treated with glacial acetic acid. This precedure ensures faster and more uniform acetylation. It also helps insure that the cellulose structure does not degrade during acetylation (Yarsley et al., 1964).

The acetylation method usually involves three components, the acetylating agent, a catalyst and a diluent. Acetic anhydride is most commonly used as the acetylating agent, however, acetyl chloride and ketene ($CH_2=C=O$) are also mentioned in the literature. Sulphuric acid, which was first used by Francimont in 1879 is the most commonly used catalyst, although other acids have been reported. The diluent increases the homogeneity of the acetylation reaction, and the most common diluent is glacial acetic acid. It is often combined with methylene chloride (which came into use in the 1940's) which, as the solvent boils, can remove excess heat from the reaction as latent heat of evaporation (Brydson, 1975). The bubbling action also increases the mixing of the reactants (Brydson, 1975; Yarsley et al., 1964). There are an extremely large number of patents for the production of cellulose acetate which incorporate acetic anhydride, acetic acid and a catalyst. They vary in the type and amount of catalyst used and the method and degree of temperature control. The mechanism for the chemical reaction which takes place can be represented in Equation 9.1 where X equals the glucose molecule in cellulose (Brydson, 1975).

$$X\text{-}OH + CH_3\text{-}CO\text{-}O\text{-}CO\text{-}CH_3 \longrightarrow X\text{-}O\text{-}CO\text{-}CH_3 + CH_3\text{-}COOH \qquad \text{Equation 9.1}$$

However, the mechanism is not completely understood (Yarsley et al., 1964). It is thought that perhaps the catalyst combines with the cellulose in some way and thus, the reaction is not purely catalytic. It has been suggested that acetyl sulphuric acid ($CH_3\text{-}CO\text{-}O\text{-}SO_3H$) is formed when sulphuric acid is used as the catalyst and that this compound causes the acetylation (Yarsley et al., 1964).

The next step is refered to as saponification, ripening or hydrolysis. The acetylation reaction produces a product with a degree of substitution greater than the diacetate. The ripening stage converts the product to the acetone soluble diacetate. The material is treated with dilute acetic acid or water. The length of treatment and conditions are determined by the desired properties for the cellulose acetate. The reaction is continued until the material displays the desired solubility. The solubility indicates the degree of substitution (Brydson, 1975;

Yarsley et al., 1964). Different degrees of acetylation result in different properties (Table 9.2) (Brydson, 1975)

After saponification, the cellulose acetate must be precipitated from solution. If a low boiling solvent such as methylene chloride is used, it can be removed by evaporation. The usual diluent also contains nonvolatile acetic acid. Water is added to the solution to bring down the cellulose acetate. This must be done carefully to avoid the formation of lumps (Yarsley et al., 1964).

The final step in the acetylation process is the after-treatment which includes washing, stabilizing and drying of the material. The cellulose acetate must be washed to remove free acetic acid and excess mineral acid. Some of the sulphuric acid is incorporated into the cellulose acetate structure as acetosulphate. Thus, stabilization is required. After several washings, the cellulose acetate is boiled with stirring in weak acid (0.02%) sulphuric acid) until the acidity of the water is observed to be constant. Then, the material is washed until no more acid is detected in the water. The resulting powder is then dried at temperatures not exceeding 100 °C until the moisture content is between 2 - 3%. This step was not performed in early manufacturing methods and the sulphur content was found to result in an unstable product. If the cellulose is required for photographic or other purposes for which greater clarity is required, the material undergoes further purification. Otherwise, the material is ready for compounding (Yarsley, et al., 1964).

### Compounding of cellulose acetate and additives

The acetylated cellulose is then prepared for commercial use by compounding. The aim of this process is to create a homogeneous mixture of the cellulose acetate, plasticizers, colouring matter and fillers in a form which may be used for production methods such as moulding. The most important additive is the plasticizer which changes the properties of the cellulosic material so that it can be manipulated and the plasticizer has a large effect on the properties of the resulting plastic (Yarsley et al., 1964).

The addition of plasticizers is important because cellulose acetate has a high softening point which is very near its decomposition point and will not flow under heat and pressure.

Thus, unplasticized cellulose acetate cannot be used for extrusion or injection moulding. Although some unplasticized material is produced for specialized applications, most film and all moulding powders are plasticized. The plasticizer has four important effects on the cellulose acetate. It decreases the fusion temperature of the cellulose acetate sufficiently so that the materials can be worked without severe degradation of the cellulose structure. It also increases the ability of the cellulose acetate to flow. The plasticizer adds pliability to films and increases the toughness of finished moulded objects (Yarsley et al., 1964).

There are two types of plasticizer, solvent and non-solvent. The theory of solvent action plasticizer is very similar to that of solution. Cellulose and cellulose ester molecules are composed of glucose rings which are attached by glycosidic bonds which form long chains. Hydrogen bonds formed between the hydroxyl groups cause attraction of the chains to each other. The hydrogen bonding thus reduces the movement of the molecules which prevents flexibility. The solvent type plasticizer is thought to become absorbed to the hydroxyl groups in the cellulose molecule. This would decrease the hydrogen bonding and increase the distance between the chains. A greater mobility between the adjacent molecules would be expected to increase in flexibility and a decrease of the softening point of plasticized cellulose acetate (Yarsley et al., 1964).

Non-solvent plasticizers do not act as solvents, but as extending agents. It is thought that they have a mechanical action instead of a chemical reaction. The distance between the cellulose threads is increased by the bulk of the plasticizer molecule. The bulking process is more effective if the intermolecular attraction between the chains has been reduced by forming hydrogen bonds with the plasticizers. Thus, they are almost always used with solvent action plasticizers (Yarsley et al., 1964).

The properties of cellulose acetate materials are largely affected by the plasticizer. For example, cellulose acetate with 53% acetic acid combined in the structure were observed to have high compatibility with plasticizers which have keto or carboxylic ester groups. The terminal groups should contain three or fewer carbon atoms, the most favourable groups should have two or less. For example, methyl esters such as dimethyl phthalate are highly compatible with cellulose acetate, ethyl esters are slightly less compatible and butyl esters exhibit very poor compatibility. Likewise, acetates demonstrate greater compatibility than propyl esters and proprionates which are in turn more compatible that butyrates. Four types of plasticizer have been defined, linear, planar, pyramidal and complex three dimensional. Pyramidal and complex plasticizers result in a hard, more brittle material than linear and planar compounds. Also, plasticizers which are solid at room temperature give harder and more brittle results than liquid ones (Yarsley et al., 1964).

Yarsley et al. (1964) list the requirements of the ideal plasticizer.

1. It would have a high permanent degree of compatibility with the polymer.
2. It would be substantially non-volatile.
3. It would be resistant to extraction by materials with which the plastic would be likely to come into contact in service.
4. It would be colourless, odourless, tasteless and non-toxic.
5. It would be efficient in preventing brittleness in the plastic at sub-zero temperatures.
6. It would be stable at processing temperatures.
7. It would be stable under the influence of ultraviolet light.
8. It would be cheap and readily available.

It has been difficult to find a compound which would fulfill these requirements and research into the problem is still being pursued. Over several hundred substances have been suggested in the patent literature, but only a small number of plasticizers have been used commercially (Table 9.3)(Yarsley et. al., 1964). One of the major plasticizers in use is dimethyl phthalate. In addition to the very high level of compatibility mentioned before, it is cheap and improves flexibility, toughness and ease of flow. Unfortunately, it is highly volatile which makes the resulting plastic more flammable. Diethyl phthalate is sometimes used as it is less volatile and compatible. It is, however, less effective. Triphenyl phosphate is a crystalline solid which, although it has a lower compatibility with cellulose acetate, is often used with dimethyl phthalate to increase water resistance and give flame retardance. It has been shown to be more permanent than dimethyl phthalate. Triacetin was widely used in the past as it was compatible. However, it lessens the water resistance of the plastic material and is also volatile. It has become necessary to use the cheapest materials to keep cellulose acetate production competitive with that of synthetic polymers. Thus, expensive plasticizers such as ethyl phthalyl ethyl glycollate which are compatible are seldom used (Brydson, 1975).

The structures of three common plasticizers are given in Figure 9.5.

The second important additive is the colouring matter or dye. Untreated cellulose acetate has a yellow tinge that is present even in the highest quality grades. It is necessary to add a small amount of blue dye to produce clear films and sheets. Also, it can be made into a wide variety of colours. Organic dyestuffs are used to produce transparent colours. The choice of colouring agents is difficult, since the material must withstand heat and pressure generated during production and it should not induce degradation of the plastic. The dyestuff should be light-fast and it is important that it not be extracted by compounds which come into contact with the cellulose acetate. Although oil and water soluble dyes are sometimes utilized, the principal dyes used are spirit soluble anthraquinones (Yarsley et al., 1964).

Opaque colours are obtained using pigments and organic lakes. Inorganic pigments are entirely light-fast, but less intense than the organic lakes. More pigment must be used to obtain an equivalent intensity. Opaque shades may also be made from soluble dyestuffs used in conjunction with white pigments. However, in some cases, the use of white pigments reduces the light stability of organic dyes (Yarsley et al., 1964).

Cellulose acetate plastics are usually unfilled, however, powdered mica (in quantities up to 25%) is occasionally utilized. In some cases, carbon black, zinc oxide and wood flour are added as fillers. Mineral fillers increase hardness, the modulus of elasticity and flexural strength of the plastic and water absorption is lessened. Impact strength is lessened and the appearance is affected (Yarsley et al., 1964). Castor oil is sometimes used as a cheap extender (Brydson, 1975).

Ultraviolet light can act as an initiator causing the degradation of the cellulose chains. This causes brittleness of the material and oxygen enhances the reaction. Thus, stabilizers which reverse or retard this reaction must be added to cellulose acetate which is to be used out of doors. Plasticizers which contain aromatic groups such as triphenyl phosphate have a stabilizing effect. The use of compounds such as phenol salicylate (salol), hydroquinone (quinol), monobenzyl ether and other phenolic compounds impart more effective retardation (Yarsley et al., 1964; Brydson, 1975). A very small amount of a weak acid such a tartaric acid is added to clear cellulose acetate before processing to reduce the risk of colour change and this additive is also thought to retard the effect of ultraviolet light. Other stabilizers reported include menthyl phenol, amyl phenols, octyl phenols and other derivitives of phenol (Yarsley et al., 1964).

A lubricant is sometimes added to cellulose acetate to aid in the removal of objects from the mould. It also imparts a surface gloss. It is important to add only a very small amount or it will exude to the surface of the finished article. A plasticizer of low compatibility (dibutyl phthalate for example) is used sometimes as it migrates to the surface to a small extent during moulding. Waxes such as paraffin, spermaceti and carnauba wax are also sometimes utilized as lubricants in quantities of 0.03 - 0.3% (Yarsley et al., 1965).

## Trade names and applications

In 1904, spinnable fibres were first produced from regenerated cellulose and marketed as viscose rayon. The Dreyfus brothers developed a manufacturing technique using excess stocks of acetate lacquer from World War One and the acetate fibre was first marketed in England under the trade-name Celanese in 1921. The acetate fibres were first manufactured in the USA in 1924 (Hillman, 1986). After the introduction of plasticizers, cellulose acetate was produced in sheet, rod and tube and some of the common trade-names include Bexoid, Lumarith, Rhodoid, Cellon, Tenite Acetate and Fibestos. It was increasingly used as a cellulose nitrate replacement during the 1930's and 1940's and was widely utilized until the early 1950's. It was used to produced toothbrushes, eye-glass frames, brush backs, tool handles, knobs, dresserware sets, bracelets, game pieces, combs, football helmets, toys, shoe heels, flashlight cases, telephone receivers and steering wheels in motor cars. It was utilized for sunglasses which became fashionable in the late 1930's. Cellulose acetate plastic served as a replacement for parchment lampshades and as 'crystal' buttons and was utilized as packaging for other substances, namely flexible tubes for creams and lotions. The plastic could be made to imitate marble, mother-of-pearl, tortoise-shell and onyx and could be made into any translucent or opaque colour and a fluorescent product could be manufactured (Hillman, 1986).

## Casein plastic

### History

The development of casein plastic was first sparked by a need for white blackboards in German schools (1897). The concept of producing a casein film on white cardboard which would then be rendered water resistant by chemical treatment was developed by a printer from Hanover named W. Krische. A. Spitteler, a chemist from Bavaria, discovered that casein and formaldehyde form a hard, waterproof material which was resistant to acid. The two collaborated and patents were taken out in 1899 in Germany and 1900 in the USA. The material was first produced in Germany and France under the name Galalith (milkstone). In 1904, the International Galalith Gesellschaft Hoff & Co. was formed and was the only producer of casein plastic until the beginning of World War I. The Spitteler and Krische technique is known as the dry method (Kaufman, 1963).

In the United Kingdom, the technique for the production of casein plastic was patented by a Russian student (V. Schutze) in 1909, a method known as the "wet process". The Syrolit company was founded to produce the material which was called Syrolit. The wet process was not economically viable and the company nearly failed. However, the company was placed under new management and the factory was converted to the dry production method. The new company which was called Erinoid gained stability during World War I (Kaufman, 1963). Casein plastic was not produced in America until 1919 by Christensen. The material was called Aladdinite (Kaufman, 1963).

## Chemical structure

Casein is a member of a class of natural products known as proteins which are discussed in Chapter 8. They are similar to polyamides, but their structure is more complex. Polyamides such as Nylon 6,6 or 11 have only one omega amino acid in their structure (Figure 9.6a) whereas proteins are composed of a variety of different alpha amino acids (Figure 9.6b) ( Brydson, 1975). The structure of casein has not been fully elucidated, but hydrolysis of the protein has produced over 30 amino acids including glutamic acid, hydroxyglutamic acid, proline, valine, leucine and lysine which make up approximately 60% of the total. Also, arginine seems to play a part in the crosslinking of casein with formaldyhyde. Proteins are highly stereospecific, the amino acids have the L-configuration. The casein molecule is associated with nonprotein material called prosthetic groups and known as a conjugated protein. The casein molecule is associated with phosphoric acid. Calcium is involved in the molecule as well. The presence of inorganic components influences the processing and the use of casein polymers. Casein is present in many animal and vegetable substances, but only cow's skimmed milk is used as a commercial source. There is about 3% casein in milk and it is present as colloidally dispersed micelles with a diameter of approximately $10^{-5}$ cm (Brydson, 1975).

### Production method

### Isolation of casein from milk

Although casein can be precipitated from milk using heat, alcohols, acid salts, or the enzyme action of rennet, only precipitation by acid or rennet coagulation methods are used for commercial processes. Casein obtained from acid precipitation is not widely used for plastics production as casein isolated by rennet retains the calcium and phosphates and is more desirable for the manufacture of plastics (Brydson, 1975). In a typical process, the milk is treated as soon as possible after collection. The milk is skimmed to remove the cream. The milk is then placed in vats and steam heated to 100 °F. The rennet is then added and the mixture is agitated. The stirring is controlled to obtain the desired curd size which is the size of peas. After the reaction has finished, the remaining greenish liquid whey is drained and the casein is washed three times with warm water, drained, pressed to remove excess water and dried at temperatures of 110 - 115 °F (Yarsley, 1943). It is thought that the calcium caseinate is changed to the calcium paracaseinate which is insoluble and thus coagulates. It is critical to control the temperature and the entire coagulation process as impurities such as other proteins may be precipitated along with the casein under adverse conditions. These contaminants have a negative effect on the transparency of the plastic product. The size of the curd is important. If the agitation is too slow, the resulting product will be large clots, if the agitation is too fast, the curd will be too fine. In both cases, the precipitate is difficult to wash effectively. In additon to controlling the agitation, inorganic ions are added to improve the quality of the product. Phosphorus ions are introduced to prevent a flaky curd and calcium ions may be required for calcium deficient casein which will not coagulate properly. It is also necessary to dry the finished polymer carefully (Brydson, 1975). The moisture content should be 10 -12%. If the casein is dried at too high a temperature, the product will have too little moisture and would not be usable for plastics production (Yarsley, 1943). If the material is dried too rapidly, an impervious outer layer is formed and the interior of the particles would not be dried. Also, if the drying process is too slow, the product will sour (Brydson, 1975).

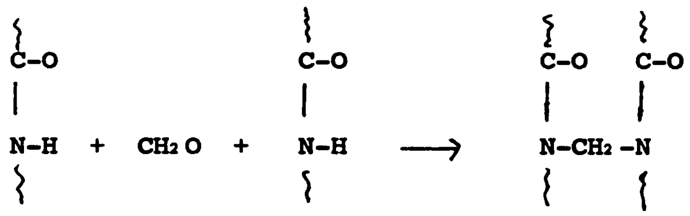
### Production of casein plastic and additives

Casein plastic is prepared by mastication of the casein curds under heat and pressure in the presence of moisture. The product is a homogenous plastic mass which can be treated with formaldehyde to create a hard, hornlike material (Yarsley, 1943).

The casein is sieved and then ground in a roller mill. The ground material is then introduced to a purifier where it is sifted and separated from light particles. The final powder should pass through a 40-mesh sieve, but not an 80-mesh sieve. The final cleaning involves the passing the material through a magnetic separator to remove metallic impurities. The ground casein is placed in a dough mixer. In a typical process, 100 kilograms of casein with 10% moisture content are combined with 26 kilograms of distilled water which is introduced as a spray over a period of fifteen minutes. Any dyes or other additives are added at this point. The material is then mixed for one hour. The mixture is then extruded using a horizontal screw extrusion press to produce rods of casein plastic. The material hardens as it is extruded and is cut into the desired lengths and cooled in water. Sheets are produced using two methods. The mixed, coloured casein powder is placed in a mould and pressed or the rods produced by extrusion are cut into uniform lengths and placed in a mould which is heated under high pressure. After the moulds have been filled, the are placed in a multiple hydraulic press and the press is heated to between 180 and 190 °F at a pressure of 600 pounds per square inch (psi) for three minutes. The pressure is increased to two tons psi for three minutes. The moulds are then cooled with cold water while still under pressure for six minutes before the sheets are removed. Initially, the material is soft, but dries and becomes brittle after exposure to the air (Yarsley, 1943).

The next step is to cure the plastic by treating it with formalin which makes the material hard and waterproof. Formalin is a solution of 40% formaldehyde diluted to 5-6%. The concentration used is slightly stronger for thick sheets or rods and weaker for thin sheets. The concentration is important as an excess of formaldehyde will result in a rapid curing of the surface and consequently, insufficient hardening of the center as the formalin cannot permeate the hardened surface. A low concentration lengthens the time needed for hardening (Brydson, 1975). The casein is soaked in the formalin in a cement lined brick tanks and the solution is kept moving by pumps. The amount of time required ranges from two days for very thin sheets of 2 mm in thickness to two months for thich rods of 25 mm in diameter. The reaction between the casein and the formaldehyde is not fully understood and has been described as a condensation reaction (Yarsley, 1943). It is thought that the following three reactions occur (Brydson, 1975).

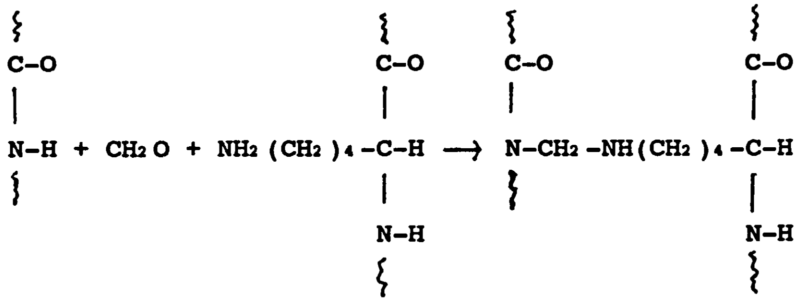
1. There is a crosslinking between the peptide groups.



$$\begin{array}{c}\mathrm{C{-}O}\\ |\\ \mathrm{N{-}H}\end{array} + \mathrm{CH_2O} + \begin{array}{c}\mathrm{C{-}O}\\ |\\ \mathrm{N{-}H}\end{array} \longrightarrow \begin{array}{ccc}\mathrm{C{-}O} & & \mathrm{C{-}O}\\ | & & |\\ \mathrm{N} & \mathrm{{-}CH_2{-}} & \mathrm{N}\end{array}$$

(Equation 9.2)

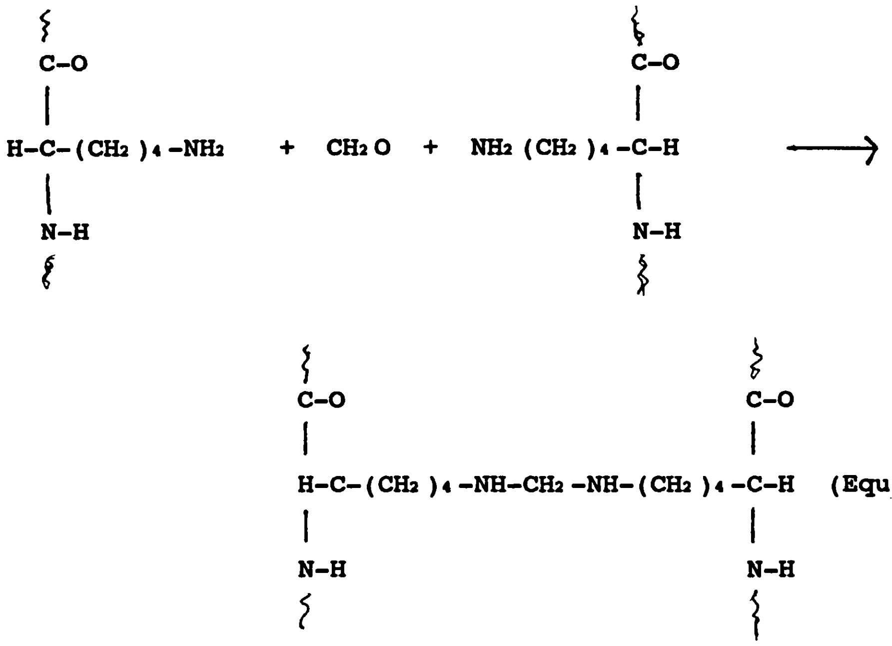
2. There are reactions between the lysine side chains and the peptide groups.



$$\overset{\overset{\wr}{\text{C-O}}}{\overset{|}{\text{N-H}}} + CH_2O + NH_2(CH_2)_4\text{-}\underset{\underset{\wr}{\text{N-H}}}{\underset{|}{\overset{\overset{\wr}{\text{C-O}}}{\overset{|}{\text{C}}}}}\text{-H} \longrightarrow \overset{\overset{\wr}{\text{C-O}}}{\overset{|}{\text{N}}}\text{-}CH_2\text{-}NH(CH_2)_4\text{-}\underset{\underset{\wr}{\text{N-H}}}{\underset{|}{\overset{\overset{\wr}{\text{C-O}}}{\overset{|}{\text{C}}}}}\text{-H}$$

(Equation 9.3)

3. There are similar reactions between the amino groups on side chains.



$$\text{H-}\underset{\underset{\wr}{\text{N-H}}}{\underset{|}{\overset{\overset{\wr}{\text{C-O}}}{\overset{|}{\text{C}}}}}\text{-}(CH_2)_4\text{-}NH_2 + CH_2O + NH_2(CH_2)_4\text{-}\underset{\underset{\wr}{\text{N-H}}}{\underset{|}{\overset{\overset{\wr}{\text{C-O}}}{\overset{|}{\text{C}}}}}\text{-H} \longrightarrow \text{H-}\underset{\underset{\wr}{\text{N-H}}}{\underset{|}{\overset{\overset{\wr}{\text{C-O}}}{\overset{|}{\text{C}}}}}\text{-}(CH_2)_4\text{-NH-}CH_2\text{-NH-}(CH_2)_4\text{-}\underset{\underset{\wr}{\text{N-H}}}{\underset{|}{\overset{\overset{\wr}{\text{C-O}}}{\overset{|}{\text{C}}}}}\text{-H}$$

(Equation 9.4)

These hypothesized reactions do not explain all of the reactions that occur during formalization. Thus, there are other reactions which are taking place during the process (Brydson, 1975). The formalization can be described as both a physical process of swelling and absorption and as a chemical reaction of consensation in which the hydrogen of the amino group is replaced by a methylene group. They are opposing reactions, the absorption results in swelling and the condensation in shrinkage. Thus, an equilibrium is reached which is determined by the formaldehyde concentration (Yarsley, 1943).

It has been found that the formalization process can be accelerated by adding approximately 1% sodium carboxymethyl cellulose or other water soluble cellulose compounds to the casein mixture. It is thought that a fibrous compound is produced which acts as a wick and provides a network of channels for the formalin to spread more quickly through the structure. The time required is reduced by 25%, but the clarity of the finished material is slightly reduced (Brydson, 1975).

Several alternate methods of hardening have been described by Yarsley (1943). The casein is mixed with 5% water and trithanolamine or a mixture of ethanolamines, or with glyoxal or a homologue. The casein may also be put into alkaline solution with a phenol and an aldehyde in the presence of ammonia. It may also be cured during hot pressing by the addition of methyl ureas and urethanes.

The hardened casein is washed to remove excess water and free formaldehyde and then carefully dried. The drying process must be done slowly to prevent cracking and warping. The product is then polished before manufacture into objects. Only rods and slabs are produced successfully on a large scale. Objects are produced using three techniques; softening the sheet and then shaping, sawing or moulding. It can be turned, drilled, polished, stamped, moulded and engraved like horn and ivory (Yarsley, 1943).

Additives as colouring agents or to add transparency are incorporated during the mixing stage. They include acid dyes, and glycerine (2% of the weight of the casein) has been found to be a successful plasticizer and adds transparency. Tricresyl phosphate and methyl-diphenylamine have also been used as plasticizers (Yarsley, 1943). A later source (Brydson, 1975) lists alkaline water soluble dyes, pigments, and titanium dioxide as a white pigment or a colour base for colouring agents. Clearing agents added to give tansparency include ethyl benzyl aniline, tritolyl phosphate, trixylyl phosphate and chlorinated diphenyls.

### Trade names and applications

Casein plastic is rigid and hornlike. It has a pleasant feel and appearance. The material is hygroscopic and can be dyed by acidic or basic alkaline water soluble dyes to obtain a wide range of colours (Brydson, 1975) It is not flammable, harder than cellulose nitrate and easily and economically produced from abundant raw materials. It is also affected by excess humidity Although casein has properties which were more desirable than cellulose nitrate, it never replaced celluloid. it was too brittle to be made into very thin sheets which limited its use for moulding and the sensitivity to water led to cracking and warping in regions of high humidity (Brydson, 1975; Kaufman, 1963). Objects often develop faults due to shrinkage in warm dry atmospheres (Yarsley, 1943). The material could not be used for electrical insulation in outdoor or high tension situations due to its hydroscopic property. Thus it was superceded by synthetic plastics with superior properties as they were developed, but it continued to be widely used for buttons and other decorative objects up until the 1960's.

The trade names Galalith and Erinoid became synonyms for casein in the plastics field (Kaufman, 1963). A related material was manufactured under the trademark Lactoid by the British Xylonite Ltd. (Langton, 1943). In the USA, it first appeared as Aladdinite in 1919. During the 1920's, casein plastics were produced under the trademanes Karolith, Kyloid, Erinoid (Kaufman, 1963) and as India (Langton, 1943). The Button Corporation of America became concerned with the new material and thus assumed control of the Kyloid Company in 1929. The American Plastics Corporation was formed from the combination of the Erinoid Company of America and the Karolith Corporation of America and other firms in 1931 and used the trade-name of Ameroid (Kaufman, 1963). Other trade-marks for casein plastics can be identified by the prefix lac meaning milk (Hillman, 1986).

The climate in the USA limited its use to buttons, buckles and other small objects (Langton, 1943; Kaufman, 1963). It has been used in England to produce buttons, cutlery, combs, spectacle, umbrella handles, fancy goods and electrical units (Yarsley, 1943). In the early years of the twentieth century, it was utilized to produce beads, buckles, poker chips, cigarette holders, boxes and bracelets (Hillman, 1986). It was also used to produce knitting pins, pens and barrels for propelling pencils. A casein fibre was produced in Italy between the two wars which was known as Lanital. Widespread development of synthetic polymers over the past thiry years has sharply decreased the use of casein plastics, but it is still used for buttons, buckles, slides and hair pins. The largest user of casein is the button industry. Casein which has not been treated with formaldehyde is utilized as an adhesive, as a stabilizers for rubber latex and for paper coatings and uses in textile manufacture (Brydson, 1975).

### Poly (methyl methacrylate)

#### History

The history of acrylic polymers began in 1873 when Caspary and Tollens first synthesized methyl, ethyl and allyl acrylate and found that the allyl acrylate polymerized. Methyl acrylate was polymerized by Kahlbaum in 1880, at the same date, it was discovered that methacrylic acid and several of its derivitives polymerize. Otto Rohm researched acrylic polymers and in 1901, published the results of his doctoral dissertation. In 1927, Rohm and his collegue Haas produced poly (methyl acrylate) at their plant in Darmstadt, Germany. It was marketed under the names Acryloid and Plexigum and the gummy material was used for coatings. It was not suitable for producing objects. R. Hill developed poly (methyl methacrylate) (1930) a polymer which had rigid, transparent properties and it was predicted to be of interest to the aircraft industry as glazing material. Early methacrylate esters were produced by dehydration of hydroxyisobutyric esters which were too expensive to be used for commercial processes. A major breakthrough occurred in 1932, when J. W. C. Crawford (ICI) developed a new synthesis of the monomer which utilized acetone, hydrocyanic acid, methanol and sulphuric acid. These materials were inexpensive and easily obtained and this process is still used today worldwide with only minor changes. It was used extensively for aircraft glazing during the Second World War and has found many other uses (Brydson, 1975).

## Chemical structure

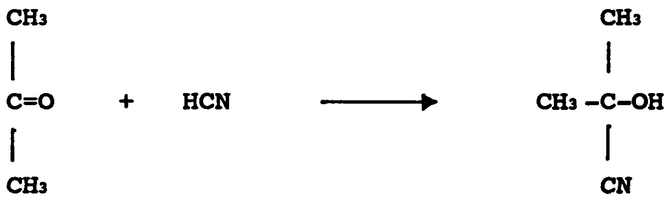
Acrylic polymers are structural derivitives of acrylic acid (Figure 9.7a). Although poly (methyl methacrylate) (Figure 9.7b) is the best known polymer in commercial use, other families of interest include a variety of derivitive polyacrylates (Figure 9.7c) and polymethacrylates (Figure 9.7d). Polyacrylonitrile

(Figure 9.7e) is a widely used polymer for fibre production (Brydson, 1975).

Production method

Synthesis of methyl methacrylate monomer

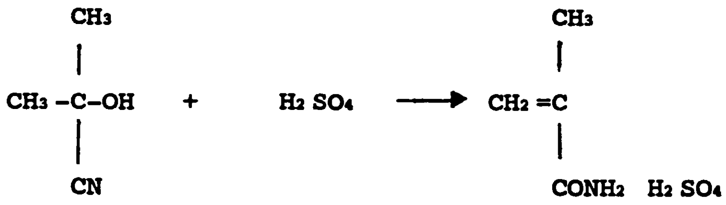
The chemical process which was developed by Crawford is outlined below (Brydson, 1975). The initial step is to add the acetone and the hydrogen cyanide which produces acetone cyanohydrin (Equation 9.5).



$$\overset{CH_3}{\underset{CH_3}{C=O}} + HCN \longrightarrow CH_3-\overset{CH_3}{\underset{CN}{C}}-OH$$

(Equation 9.5)

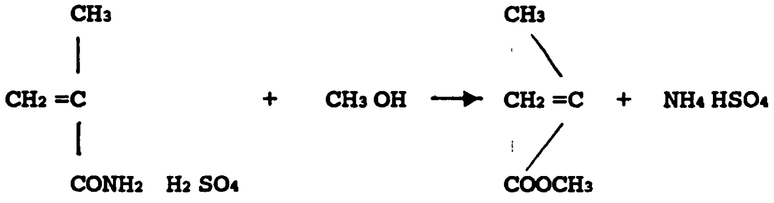
The acetone cyanohydrin is next reacted with 98% sulphuric acid in a cooled hydrolysis container to give methacrylamide sulphate (Equation 9.6).



$$CH_3-\overset{CH_3}{\underset{CN}{C}}-OH + H_2SO_4 \longrightarrow CH_2=\overset{CH_3}{\underset{CONH_2\ H_2SO_4}{C}}$$

(Equation 9.6)

The mixture is then reacted with methanol in an esterification vessel without isolation of the sulphate to produce the monomer (Equation 9.7). Inhibitors to prevent polymerization may be added during this step.



$$CH_2{=}C(CH_3)CONH_2\;H_2SO_4 + CH_3OH \longrightarrow CH_2{=}C(CH_3)COOCH_3 + NH_4HSO_4$$

(Equation 9.7)

The esterified material is introduced into a stripping column to remove the residual sulphuric acid, ammonium bisulphate and some of the excess water from the methyl methacrylate, methanol and additional water. The monomer is recovered and purified by additional distillation (Brydson, 1975).

Polymerization

Methyl methacrylate polymerizes easily and the solution should be inhibited to prevent polymerization during storage. An inhibitor such as hydroquinone is added in a concentration of up to 0.10% to the monomer. This is removed before use by distillation under reduced pressure or by treating the monomer with an alkaline solution (Brydson, 1975). For commercial production, a free radical mechanism with peroxides or azo-diisobutyronitrile at temperatures up to 100 °C are used. Methacrylate peroxides are produced in a side reaction if polymerization is carried out in the presence of oxygen. This affects the rate of reaction and the nature of the products. Polymerization should be carried out in a full cell or under an inert gas to exclude oxygen. The rate of conversion accelerates after approximately 20% of the monomer has reacted. This phenomenon is known as the gel effect, the Tromsdorf effect or the autoacceleration effect (Brydson, 1975).

The bulk polymerization method is used on a wide scale to produce sheet polymer and is also used to make a certain amount of rods and tubes. There are several problems in production that must be taken into consideration in order to produce a satisfactory product. It is necessary for commercial success that the product is of even thickness and constant quality and that it contains no impurities or imperfections. Also, excess energy is created during the exothermic reaction and the polymerization rate increases during the course of the reaction. There is also approximately 20% shrinkage of the material after polymerization and the problem of oxygen must be considered (Brydson, 1975).

The first step is to make a 'prepolymer'. This step will decrease the shrinkage in the casting cell and limit the leakage from the cell. After the inhibitor is removed, the monomer is heated for eight minutes at 90 °C in the presence of 0.5% benzoyl peroxide, then returned to room temperature. Additives such as plasticizers, colouring matter and ultraviolet light stabilizers are then added if needed. The product is then filtered and can be stored, if necessary, in a refrigerator. The prepolymer syrup may be considered a solution of the polymer in the monomer. It is thought that the dissolved oxygen in the monomer is reduced by the heating step in the process. This step is difficult to control in large scale commercial situations and must be carefully monitered. Another method is to dissolve some of the polymer in the monomer with some peroxide which will achieve the same results as the preparation of a prepolymer (Brydson, 1975).

Poly (methyl methacrylate) sheet is produced using a casting cell which is made of two sheets of heat resistant polished glass. The glass plates are sealed with a hollow, tube made of rubber or plasticized poly (vinyl alcohol). The syrup is added to the cell making certain that the cell is completely filled. The unit is held together by spring loaded clamps or spring clips. This arrangement allows the glass sheets to come closer together as the material decreases in bulk during polymerization. Thus, the sheet will not have sink marks or voids. The use of rigid glass sheets and even pressure ensures a product of uniform thickness (Brydson, 1975).

The prepared cells are passed through a heating tunnel. The rate of polymerization is slow in the early stages as the temperature is kept at 40 °C. Thus, a rise in temperature due to the exothermic reaction or viscosity-chain termination will have a minor effect on the rate of reaction at this temperature. After 14 hours, most of the monomer has been converted and the cell is exposed to higher temperatures in the heating tunnel. The temperature is raised to approximately 97 °C during a period of one hour and then it is kept at 97 °C for one half an hour. The cell is allowed to cool and then the product is removed from the cell. It is then annealed by heating to 140 °C to decrease internal stress. The sheets are covered with paper attached with gelatine or a pressure sensitive adhesive to protect the surfaces. Large blocks of poly (methyl methacrylate) are difficult to produce because of the excess exothermic energy which builds up during polymerization. In such cases, the process is carried out inside a pressure vessel which elevates the boiling point of the monomer (Brydson, 1975).

Rods of poly (methyl methacrylate) are produced by filling vertical aluminium tubes with the syrup, and then placed in a water bath at 40 °C. As the material at the base of the tube polymerizes, it shrinks and the syrup nearer the top sinks down. The tube is filled from a chamber above. This process allows for shrinkage of the material during polymerization. Tubes are manufactured by placing a given amount of the syrup into a horizontal aluminium tube which is subsequently sealed. the tube is purged with nitrogen, rotated and the apparatus is heated. Polymerization of the material occurs on the wall of the hollow cylinder. The shrinkage problem is not critical and allows the plastic tube to be removed without difficulty (Brydson, 1975).

The average molecular weight of poly (methyl methacrylate) produced by bulk polymerization is too large for the material to have flow properties suitable for applications such injection moulding. The molecular weight can be decreased by mechanical grinding, however, it is not commercially viable the additional cost of mechanical scission increases the price of the already expensive bulk polymerization process. The technique of suspension polymerization was developed to produce material with lower molecular weight. There is no difficulty with excess exothermic energy, thus the process is rapid. The only problems are the control of particle size and agglomeration of the beads. Factors such as the shape and size of the reaction vessel, type and speed of agitation and the suspending agents and protective colloids used control particle size. Talc, magnesium carbonate and aluminium oxide are common suspending agents and poly (vinyl alcohol) and sodium polymethacrylate are frequently utilized protective colloids (Brydson, 1975).

The suspension polymerization process has been described as follows (Brydson, 1975): methylmethacrylate and water in a ratio of one to two are combined with 0.2% benzoyl peroxide as a catalyst and agitated. Eight to 18 grams of Magnesium carbonate in a quantity of eight to 18 grams per litre of reactants is then introduced. A larger quantity is used to produce smaller beads and the use of a smaller amount gives larger particle sizes. The reaction temperature rises from an initial 80 °C to 120 °C due to the excess energy produced in the reaction. Sulphuric acid is added after polymerization is complete (usually after one hour) to eliminate the magnesium carbonate. The beads are then collected, washed thoroughly and dried. The reaction process is sometimes modified by the addition of certain materials. The pH of the reaction may controlled by the addition of a buffer such as sodium hydrogen phosphate. The molecular weight may be modified by chain transfer agents which include lauryl mercaptan or trichloroethylene. Stearic acid and sodium lauryl sulphate may also be added as a lubricant and an emulsifier respectively.

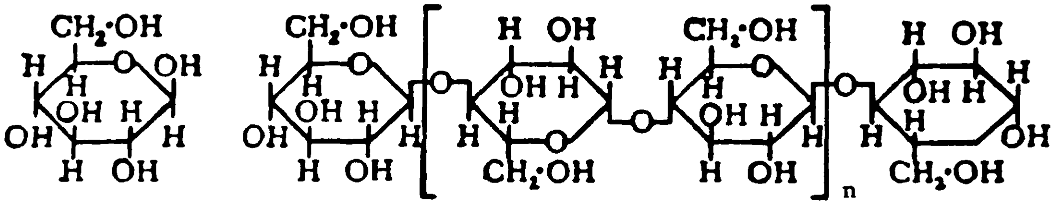
### Processing methods for poly (methyl methacrylate) and additives

Acrylic plastics may be processed in the melt phase by injection moulding and extrusion, by mechanical manipulation of sheet, rod and tube, and with monomer-polymer doughs (Brydson, 1975). Production of objects using injection moulding or extrusion is successful as the shrinkage observed after moulding is very low. However, the polymer beads must be stored in dry conditions as the beads absorb water up to 0.3%. The water vapourizes in the heating cylinders creating bubbles and subsequently, a frothy appearance. Also, the equipment used for extrusion or injection moulding must be capable of producing high pressures because the melt viscosity of poly (methyl methacrylate) at the processing temperatures are much higher than those of polystyrene, polyethylene and plasticized poly (vinyl chloride). Also, dependable temperature control throughout the process is vital for consistent quality. Products are frequently made by mechanical manipulation of sheet, rod and tube acrylics using drills, circular saws and bandsaws. It is important not to overheat the plastic. Various forms of cementing have been described as the material cannot be welded together easily. The pieces may be attached by treating the surfaces to be joined with chloroform or by a solution of polymer in a solvent. The use of a monomer-polymer solution has been found to be the most effective technique especially if it is necessary to gap fill. The cement usually contains a photocatalyst which results in polymerization activated by ultraviolet light or a promoter which reacts upon the addition of peroxide to result in rapid polymerization. The manufacture of dentures has been the primary use for monomer and polymer doughs. A plaster of Paris mould is made. The monomer is combined with the polymer powder and an initiator. This results in a dough which is put into the mould. The mould is clamped closed and heated for approximately one half hour and then cooled and opened (Brydson, 1975).

A variety of additives may be incorporated into poly (methyl methacrylate). THe most important are dyes and pigments which must be chosen carefully. They should be stable during processing and use. They should not interfere with polymerization during casting and should exhibit resistance to weathering. Plasticizers are sometimes utilized. Dibutyl phthalate is often used at a composition of approximately 5% It increases the melt properties when used with moulding powders, but impairs the mechanical properties of the object. The inclusion of small amounts of ultraviolet light absorbers such as phenyl salicylate, 2:4-dihydroxy benzophenone, resorcinol monobenzoate, methyl salicylate or stilbene increases the protection against ultraviolet radiation (Brydson, 1975).

## Trade names and applications

Poly (methyl methacrylate) in sheet form is marketed under the names Perspex by ICI, Plexiglass by Rohm and Haas, USA and Oroglass by Rohm and Haas, GmbH, Germany. Commercial moulding powders are Diakon by ICI, Acry-ace by Fudow Chemical Co, Japan, Lucite by DuPont, USA and Vedril by Montecatini, Italy (Brydson, 1975).



(a) (b)

Figure 9.1 (a) Structure of anhydro-beta-glucose unit (b) structure of cellulose (Yarsley et al., 1964).

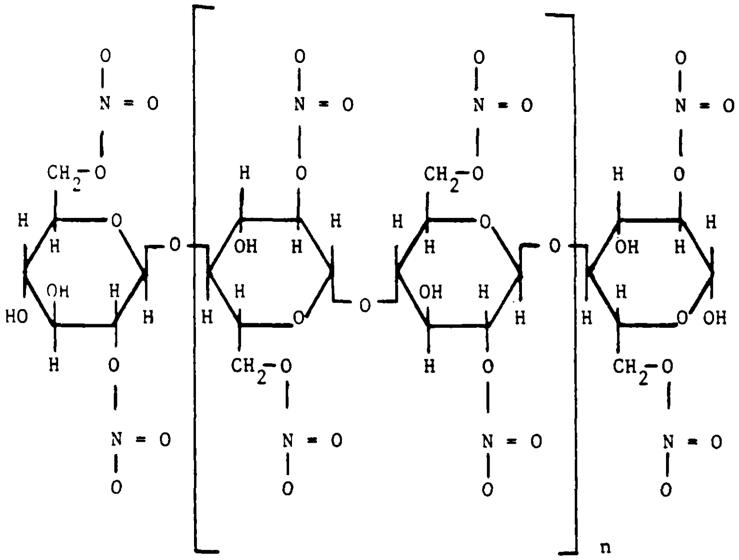


Figure 9.2 Structure of cellulose nitrate.

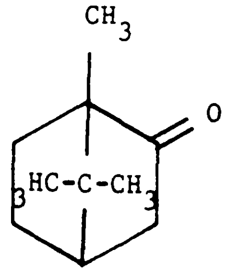


Figure 9.3 Structure of camphor (Bean, 1973).

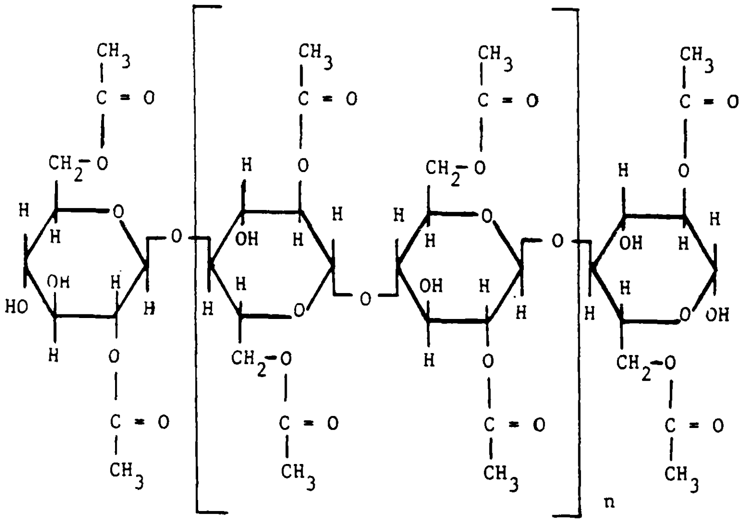


Figure 9.4 Structure of cellulose acetate.

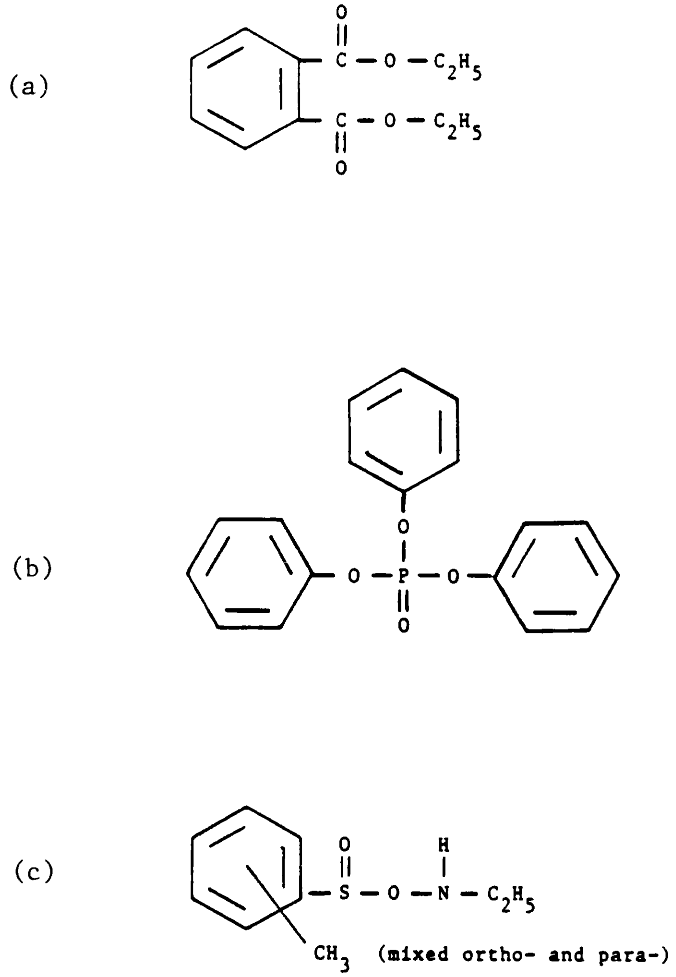
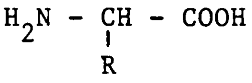


Figure 9.5 Structure of three important plasticizers of cellulose acetate, (a) diethyl phthalate (b) triphenyl phosphate and (c) N-ethyl o,p-toluenesulphonamide.

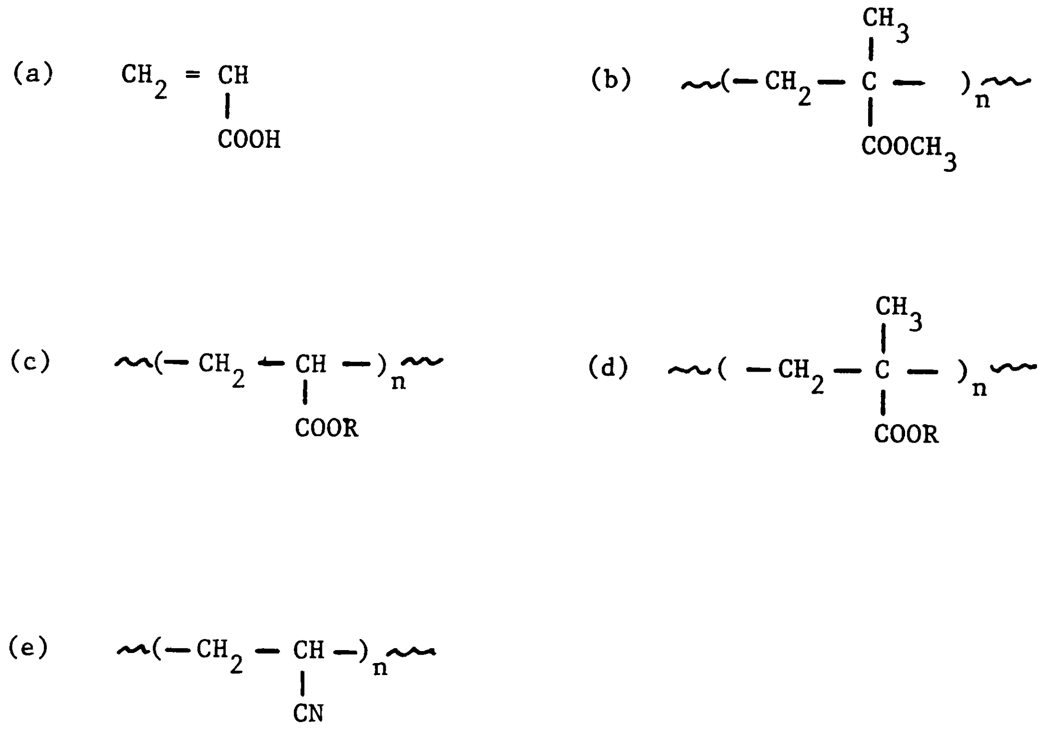
$H_2N - R - COOH$



$$H_2N - \underset{\displaystyle R}{\underset{|}{CH}} - COOH$$

(a) (b)

Figure 9.6 Structure of (a) omega amino acid and (b) an alpha amino acid (Brydson, 1975).



(a) $CH_2=CH(COOH)$

(b) $\sim(-CH_2-C(CH_3)(COOCH_3)-)_n\sim$

(c) $\sim(-CH_2-CH(COOR)-)_n\sim$

(d) $\sim(-CH_2-C(CH_3)(COOR)-)_n\sim$

(e) $\sim(-CH_2-CH(CN)-)_n\sim$

**Figure 9.7** Structure of (a) acrylic acid, (b) poly (methyl methacrylate), (c) polyacrylates, (d) polymethacrylates and (e) polyacrylonitrile (Brydson, 1975).

TABLE 9.1

Degree of nitration and typical usage for cellulose nitrate (Yarsley, et al., 1964)

| Degree of nitration | Nitrogen content (%) | Typical usage |
|---|---|---|
| Cellulose mononitrate | 6.76 (theor.) | Not made commercially |
| Cellulose dinitrate | 11.11 (theor.) | |
| | 10.7 - 11.1 | Plastics, lacquers |
| | 11.2 - 12.3 | Lacquers |
| | 12.4 - 13.5 | Cordite |
| Cellulose trinitrate | 14.14 (theor.) | Not made commercially |

TABLE 9.2

Influence of degree of substitution on the properties and uses of cellulose acetate (Brydson, 1975)

| Degree of substitution | Acetyl content (% - $COCH_3$ | Acetic acid yield (%) | Solubility | Uses |
|---|---|---|---|---|
| 2.2 - 2.3 | 36.5 - 38.0 | 52.1 - 54.3 | soluble in acetone | injection moulding |
| 2.3 - 2.4 | 38.0 - 39.5 | 54.3 - 56.4 | | film |
| 2.4 - 2.6 | 39.5 - 41.5 | 56.4 - 59.3 | | lacquers |
| 2.8 - 3.0 | 42.5 - 44.0 | 60.7 - 62.8 | insoluble in acetone, soluble in chloroform | triacetate film and fibre |

TABLE 9.3

Plasticizers of cellulose acetate

(Yarsley et al., 1964)

| Plasticizer | Molecular Weight | Boiling point (°C) | Maximum Permanent Compatibility (1) |
|---|---|---|---|
| Triethyl acetylcitrate | 318 | 127/0.7 mm | -- |
| Butyl phthalyl butyl glycollate | 336 | 219/5 mm | 50 |
| Butyl stearate | 340 | 360 | -- |
| Dibutyl phthalate | 278 | 325 | 30 |
| Dibutyl sebacate | 314 | 345 | <10 |
| Diethyl phthalate | 222 | 295 | 30 |
| Di(2-ethoxyethyl) phthalate | 310 | 345 | 25 |
| Diethyl sebacate | 258 | 308 | 10 |
| Dimethyl phthalate | 194 | 285 | 15 |
| Di(2-methoxyethyl) phthalate | 282 | 209-261/20 mm | 25 |
| Dioctyl phthalate | 390 | 229/5 mm | -- |
| Ethyl phthalyl ethyl glycollate | 280 | 190/5 mm | 40 |
| Methyl phthalyl ethyl glycollate | 266 | 189/5 mm | 40 |
| N-ethyl o- and p-toluene sulphonamides | 199 | -- | 35 |
| Triacetin | 218 | 259 | 12 |
| Tributyl phosphate | 266 | 289 | 17 |
| Triolyl phosphate | 368 | 295/13 mm | 20 |
| Triphenyl phosphate | 326 | 245/11 mm | 30 |
| Tripropionin | 260 | 177-182/20 mm | 35 |

1. Expressed as parts of plasticiser per 100 parts of cellulose acetate (56.5% acetic acid).

## CHAPTER 10 INTERPRETATION OF REFERENCE PLASTIC SPECTRA

### Description of reference materials

The unknown plastic samples were identified by comparison of their spectra with those of reference material, and the absorption frequencies of the major bands with those given in the literature. The standard materials were obtained from chemical companies and in some cases, samples of commercial plastics were also used. Spectra were also obtained from several known plasticizers which were obtained from chemical companies (see appendix). The commercial spectral atlases were used to confirm the validity of the reference spectra (Hummel, 1978; Chicago Society of Coatings Technology, 1980; Hanson, 1987). All of the spectra were collected using diffuse reflectance spectroscopy unless noted otherwise. The band assignments given in this chapter are summarized in Tables 11.4 - 11.9.

A spectrum was obtained of cellulose powder from Whatman. A cellulose nitrate sample of Millipore SC (8 micron) was used as one standard and a sample of fresh scrap cellulose nitrate was obtained from the Wardle-Storey factory in Brantham, Essex. A spectrum of camphor was also obtained of material marketed by P. Boulton, dispensing chemist.

The cellulose acetate systems were identified by comparison with two types of chemical cellulose acetate produced by Aldrich; cellulose triacetate and cellulose acetate, acetyl content 39.8%. An example of commercial sheet triacetate, Bexfilm, was also used. Transmission spectra were also obtained of three known plasticizers of cellulose acetate; o,p-toluenesulphonamide (Ketjenflex, Monsanto), diethyl phthalate (Aldrich) and triphenyl phosphate (Aldrich).

The two spectra used to identify casein plastics were spectra of casein which has not been masticated or formalized. The chemical casein was obtained from BDH and probably precipitated by rennin. The second sample was prepared by R. White of the National Gallery by acid precipitation in the presence of lime.

The identification of poly (methyl methacrylate) plastics was accomplished by comparison of the spectra with a transmission spectrum of poly (methyl methacrylate) obtained from Aldrich and two diffuse reflectance spectra of commercial acrylic plastics, one of Visijar Tuckers Perspex and one of Plexiglass given by the Conservation Analytical Laboratory (Smithsonian Institution, USA).

## Interpretation of reference spectra

### Cellulose nitrate

The spectrum of cellulose nitrate may be identified by absorption bands arising from the cellulose structure and the nitrate groups. The standard cellulose nitrate spectra (Millipore SC 8 micron; Wardle-Storey) are compared with that of cellulose powder in Figure 10.1. The broad absorption band which is centered at 3460 $cm^{-1}$ which is due to the O-H stretching vibration. The extremely polar nature of the hydroxyl group results in hydrogen bonding with any molecules that are even slightly polar. Thus it is only possible to see the free O-H stretching absorption when examining the material in the vapour phase or in dilute solution in a non-polar solvent. The band observed in most examples is due to the O-H stretches of the hydrogen bonds. In certain rare cases, the free hydroxyl stretching mode can be observed in molecules where there is steric hindrance reduces or stops the hydrogen bonding. In the cellulose nitrate spectra (Figures 10.1b and 10.1c), the frequencies of the hydroxyl absorption (3447 $cm^{-1}$ and 3442 $cm^{-1}$) are slightly higher than the range given in the literature for polymeric intermolecular bonds (3400 - 3200 $cm^{-1}$)(Bellamy, 1974) and higher than the value observed for cellulose in Figure 10.1a (3358 $cm^{-1}$) and the range quoted in the literature (3347 $cm^{-1}$ - 3324 $cm^{-1}$)(Marrinan and Mann, 1954). Although it is difficult to make quantitative comparisons due to the effects of sample loading, the intensity of the O-H band relative to the carbon-hydrogen stretching absorptions and the ether linkage absorptions is much greater in the cellulose powder spectrum than in the cellulose nitrate spectra. The loss of intensity is probably caused by the loss of hydrogen bonding between the cellulose chains by the introduction of the nitrate groups and the plasticizer camphor. The increase in frequency may result from the hydrogen bonds which are thought to form between the camphor molecules and the free hydroxyl groups.

The most characteristic features in the spectrum are the absorption bands arising from the stretching of the N-O linkages in the nitrate groups. The literature (Brown, 1955) lists the range of values and the assignments for nitrate esters including cellulose nitrate and the values of the standard spectra are listed with the band assignments in Table 11.4. The first band is very strong and occurs in the region 1653 - 1629 $cm^{-1}$ which results from the asymmetric N-O stretch in the nitrate group. Brown also observed that the value for polynitrates can range to

1667 $cm^{-1}$. The second band is also very intense and falls within the range 1285 - 1272 $cm^{-1}$ and is assigned to the symmetric stretch of the N-O bond. The third intense band occurs from 872 to 841 $cm^{-1}$ and is due to the N=O bond stretch in the nitrate ester. Brown also states that the range extends to 833 $cm^{-1}$ in polynitrates. There are two bands of medium intensity which occur in the regions of 761 - 745 $cm^{-1}$ and 710 - 689 $cm^{-1}$ and are assigned to an out of plane deformation and a N-O bond bending mode respectively. The spectra of the cellulose nitrate samples have bands which correspond to these regions, but some of the frequencies are beyond the range stated in the literature. The value of the band at 1671 $cm^{-1}$ in the spectrum of the Milipore sample is somewhat beyond the upper range for cellulose nitrate (1667 $cm^{-1}$) and the absorptions at 1288 $cm^{-1}$ and 1286 $cm^{-1}$ are slightly beyond the limit of 1285 $cm^{-1}$. However, the spectrum of cellulose nitrate has absorption bands at 846, 751 and 692 $cm^{-1}$ which fall well within the ranges stated by Brown (1955). The deviations in the cellulose nitrate spectrum may be caused by differences in conformation of the samples, the resolution of the instrument and by degradation of the standard cellulose nitrate material.

A strong band occurs at 1748 $cm^{-1}$ (Millipore) and 1732 $cm^{-1}$ (Wardle-Storey) in the reference spectra of cellulose nitrate which has been identified as the carbonyl stretching frequency arising from the camphor. It corresponds to the band at 1735 cm-1 in spectra of cellulose nitrate plastic (Sirkis, 1982). Sirkis noted that the frequency of the carbonyl band of the camphor combined with the cellulose nitrate was slightly lower than the band in the spectrum of free camphor. This was also observed in this study. A diffuse reflectance spectrum of camphor gave a strong, sharp absorption band at 1757 $cm^{-1}$.

### Cellulose acetate

Cellulose acetate plastics have an infrared spectrum which is characterized by absorptions of the hydroxyl groups and ether linkages of the glucose units in the cellulose and the ester linkages between the acetate groups and the cellulose. It is possible to see bands indicative of the plasticizer which do not occur in the unplasticized chemical cellulose acetate.

The three reference spectra include two of chemical cellulose acetate (Figures 10.2a and 10.2b) and one commercial sheet cellulose triacetate plastic (Figure 10.2c) which have certain bands in common which are characteristic of the cellulose acetate structure. The broad absorption band which ranges from 3499 - 3482 $cm^{-1}$ is due to the O-H stretching modes which are similar in nature to the hydroxyl groups in cellulose nitrate plastic. The same behaviour is observed with a slightly higher frequency and much less relative intensity than polymeric intermolecular bonds and in cellulose and the probable causes are also the same. The presence of the acetate groups and the hydrogen bonding of the free hydroxyl group with the plasticizers reduce the hydrogen bonding between the cellulose chains.

There are bands present in all three spectra which are characteristic of C-H stretching modes due to the methyl functionalities in the acetate groups. The stronger absorption falls at 2959 $cm^{-1}$ in all three cases and the less intense band ranges from 2892 - 2893 $cm^{-1}$. The ranges quoted in the literature for the methyl group are 2962 $\pm$ 10 $cm^{-1}$ (asymmetrical stretch) and 2872 $\pm$ 10 $cm^{-1}$. The bands at 2959 $cm^{-1}$ fall within the range, but the symmetrical stretch is 10 $cm^{-1}$ beyond the limit of the standard values. This may be caused by the adjacent carbonyl group in the ester linkage, although the literature (Bellamy, 1975) states the presence of a carbonyl group linked to the methyl group does not result in very significant frequency shifts. It is possible that the absorption includes the weak tertiary C-H band which occurs at 2890 $cm^{-1}$ and that it is not possible to resolve the bands. The C-H deformation bands in the reference spectra occur at 1433 - 1434 $cm^{-1}$ and 1373 - 1374 $cm^{-1}$ which falls within the range for the methyl group asymmetrical (1450 ± 20 $cm^{-1}$) and symmetrical (1380 - 1370 $cm^{-1}$) C-H deformations (Bellamy, 1975).

The cellulose acetate can also be characterized by the absorptions due to the ester linkage. There is an intense band which results from the C=O stretching mode and one or more bands in the region of 1250 - 1100 $cm^{-1}$ which are caused by the carbon-oxygen single bond stretching absorption. The strong band which occurs in the standard spectra at 1758 - 1764 $cm^{-1}$ is outside the range for most esters (1750 - 1730 $cm^{-1}$). The standard spectra contain a very intense, split absorption band which is centered at 1245 $cm^{-1}$ which is characteristic for an acetate ester (1250 - 1230 $cm^{-1}$)(Bellamy, 1975). There is a second, less intense band which is also due to the C-O stretch which has been observed to appear in the region 1060 - 1000 $cm^{-1}$ (Bellamy, 1975). This peak would be impossible to see in cellulose acetate, because it falls in the region of the ether linkages in the glucose units. In the cellulose acetate spectra, the ether linkages form a broad band which is centered at 1065 $cm^{-1}$ in the chemical cellulose triacetate spectrum (Figure 10.2b) and at 1087 $cm^{-1}$ in the other two spectra (Figures 10.2a and 10.2c). The frequencies of the ether link in large ring systems is equivalent to values for open chain compounds (1150 - 1060 $cm^{-1}$)(Bellamy, 1975).

There are two sharp bands in the regions 904 - 905 $cm^{-1}$ and 604-605 $cm^{-1}$ which appear in all three spectra. The former is unassigned, but the latter absorption has been described as a skeletal vibration of the acetate group which reported to occur at 605 $cm^{-1}$ (Hummel, 1966) and 612 $cm^{-1}$ (Thompson and Torkington, 1945).

The commercial cellulose acetate sheet contains plasticizers and other possible additives. It would be difficult to identify them from the diffuse reflectance spectrum. However, the absorption bands at 1591, 1490, 1189, 963, 782 and 760 $cm^{-1}$ appear in the spectrum of the commercial cellulose triacetate (Figure 10.2c) which do not occur in the spectra of chemical cellulose acetate which are not plasticized (Figures 10.2a and 10.2b). The bands may be attributed to plasticizers of cellulose acetate (Figure 9.5). There is strong evidence in the spectrum for the presence of an aromatic compound. The aromatic ring is identified by the C-H stretching mode which results in sharp, weak bands near 3070 and 3030 $cm^{-1}$ and four bands in the region 1650 - 1450 $cm^{-1}$ which represent the skeletal ring breathing modes. In the spectrum of the commercial cellulose triacetate, there is a weak band at 3069 $cm^{-1}$ which corresponds to the conjugated C-H stretching mode in an aromatic compound. The band expected at 3030 $cm^{-1}$ is masked in this spectrum by the aliphatic C-H stretching vibrations.

The four bands resulting from skeletal breathing modes are actually two pairs which are degenerate in benzene and thus appear as two bands in the spectrum. When the ring is substituted, the bands split to form four bands. The first band at 1591 $cm^{-1}$ in Figure 10.2c occurs within the range stated in the literature, 1625 - 1575 $cm^{-1}$ and the band at 1490 $cm^{-1}$ is in good agreement for values suggested for monosubstituted aromatics, 1510 - 1480 $cm^{-1}$ (Bellamy, 1975). There are two other bands which are the pairs to the bands near 1600 and 1500 $cm^{-1}$ which may be resent in aromatic compound, one in the region of

1600 - 1560 $cm^{-1}$ and one in the area of 1450 $cm^{-1}$. The absorption band in the 1600 - 1560 $cm^{-1}$ region is often not present or only appears as a weak shoulder on the band near 1600 $cm^{-1}$ in the spectra of most compounds. The band at 1450 $cm^{-1}$ is often masked by the C-H deformation modes which occur in the same region. In the commercial cellulose triacetate sheet spectrum (Figure 10.2c), there is a shoulder on the band at 1434 $cm^{-1}$ which does not occur in the spectra of chemical cellulose acetate. The absorptions in the region of 1600 and 1500 $cm^{-1}$ coupled with the bands in the area of 3060 - 3030 $cm^{-1}$ are considered good evidence for the presence of an aromatic ring (Bellamy, 1975).

In addition, the presence of an aromatic compound is supported by several bands in the fingerprint region. There is a band of medium intensity which is split at 782 and 760 $cm^{-1}$ which corresponds to the out of plane C-H bending mode for monosubstituted aromatic rings. The band is reported to fall in the 770 - 730 $cm^{-1}$ region and has been observed to be split in the spectra of several compounds. The presence of a monosubstituted aromatic ring is furthur supported by the presence of a sharp band at 692 $cm^{-1}$ in the commercial cellulose triacetate spectrum which falls in the region quoted in the literature (700 - 675 $cm^{-1}$) and is used to differentiate between monosubstituted and orthosubstituted aromatic systems (Bellamy, 1975). There are absorptions in this region in the chemical cellulose acetates, but they are very weak shoulders near 692 $cm^{-1}$ (Figures 10.2a and 10.2b).

The band at 1189 $cm^{-1}$ in the commercial cellulose triacetate spectrum occurs in the range 1242 - 1100 $cm^{-1}$ which is characteristic of the P-O-C (aromatic) system asymmetric stretch in aromatic phosphates (Thomas and Chittenden, 1964). There is a second band in the region 996 - 905 $cm^{-1}$ which is also due to the P-O-C aromatic system (Thomas and Chittenden, 1964). There is a strong band in the commercial cellulose triacetate spectrum at 963 $cm^{-1}$ which coreesponds to the literature value.

Casein

Proteins, although they are complex structures, can be characterized by bands which correlate to the peptide bond. Other bands are due to the amino acid side chains and in more complex peptides and proteins, it is difficult to elucidate the structure further on the basis of the infrared spectrum. A broad absorption band in the region of 3450 - 3300 $cm^{-1}$ occurs in protein spectra and is assigned to the N-H stretches in the molecule (Bellamy, 1975). It has been suggested that a band near 3300 $cm^{-1}$ is due to the trans- type hydrogen bonding between chains and that a weaker bands near 3200 $cm^{-1}$ is due to intramolecular bonds (Bellamy, 1975). In the reference casein spectrum (Casein I) (Figure 10.3a), there is a broad band centred at 3287 $cm^{-1}$ which may be due to an overlapping of peaks in the region 3450 $cm^{-1}$ - 3200 $cm^{-1}$. There is a weak band at approximately 3100 $cm^{-1}$ which at one time was thought to be due to the intramolecular hydrogen bonds of the N-H groups, but is now assigned as an overtone of the amide II absorption.

The bands in the 1650 and the 1550 $cm^{-1}$ regions are characteristic of the amide bonds which occur in all proteins and can be useful in differentiating between proteins and other classes of compounds. The band that absorbs in the 1650 $cm^{-1}$ region is due to the C=O in the amide bond and is referred to as the amide I band (Bellamy, 1975). This occurs in the casein I spectrum (Figure 10.3a) at 1661 $cm^{-1}$. The value for alpha casein given in the literature (D'Esposito and Koenig, 1978) for the amide I band in the solid state is 1656 $cm^{-1}$. The absorption band in the area of 1550 $cm^{-1}$ is referred to as the amide II band and is thought to be due to a N-H bending mode coupled with a C-N stretching mode. In the casein standard spectrum obtained in this study (Figure 10.3a), this absorption appears at 1546 $cm^{-1}$. The literature value for this absorption is 1538 $cm^{-1}$ (D'Esposito and Koenig, 1978).

The casein I spectrum contains absorptions at 1450 and 1400 $cm^{-1}$. The literature lists two bands of medium intensity at 1448 and 1399 $cm^{-1}$ which are assigned to C-H deformations of the methyl and methylene groups and the ionized carboxyl groups (COO-) respectively (D'Esposito and Koenig, 1978).

There is a band that occurs in the 1305 - 1200 $cm^{-1}$ region in the secondary amides which is called the amide III band and is less intense than the amide I and II absorptions. The amide III band is also due to a coupling of the C-N stretching mode and a N-H bending vibration. In the casein I spectrum, there is a band at 1315 $cm^{-1}$ and one at 1241 $cm^{-1}$ which are both relatively weak and one or both may be indicative of a mixed vibration in this region. The literature lists two bands at 1312 and 1242 $cm^{-1}$

which are assigned to methylene deformations and the amide III absorption respectively (D'Esposito and Koenig, 1978).

The casein I spectrum exhibits bands at 1175, 1106 and 950 $cm^{-1}$ which are difficult to assign but correspond somewhat to the values reported for solid alpha-casein, 1158, 1101 and 980 $cm^{-1}$ (D'Esposito and Koenig, 1978). The rather significant variations in frequency are probably caused by the variations in conformation. There is an ill-defined absorption that is reported to occur in the region of 700 $cm^{-1}$ that is considered characteristic of proteins and secondary amides and has been assigned to an out-of-plane N-H deformation (Bellamy, 1975). In the standard spectrum, there is a very weak peak centred at 703 $cm^{-1}$. The region between 800 - 400 $cm^{-1}$ in the casein spectrum is a broad, ill-defined band which is caused by the overlapping of many absorptions due to overtones from the amide bonds and the vibrations of the amino acid side chains.

The second casein standard which was prepared by acid precipitation in the presence of lime (White) has a spectrum (Figure 10.3b) which is somewhat different than that of the casein I sample (Figure 10.3a). In the N-H stretching region, the broad band has three distinct peaks at 3495, 3399 and 3246 $cm^{-1}$. The bands at 3246 and 3399 $cm^{-1}$ are characteristic of bonded N-H structure. The band at the higher frequency of 3495 is credited to free N-H stretches in secondary amides in the trans configuration. The differences between the two spectra in this region may be due to differences in hydrogen bonding and configuration resulting from the alternate method of preparation. The spectrum of casein II does not have the weak band in the region of 3080 $cm^{-1}$ and has relatively weak bands at 2925 and 2854 $cm^{-1}$ which indicate C-H stretches. There are two bands at 2228 and 2117 $cm^{-1}$ which do not appear in the first standard spectrum.

The carboxyl absorption or the amide I band is also slightly different in the casein II spectrum. There is a strong absorption centred at 1621 $cm^{-1}$, a less intense band at 1684 cm-1 and a very weak band at 1501 $cm^{-1}$ which is almost completely masked. The appearance of two bands in the carbonyl region may be indicative that the protein exists in two conformations, folded and the extended forms. This would affect the bonding. This splits the band and shifts the frequencies. The weak band at 1501 $cm^{-1}$ is probably the amide II band. The band at 1621 $cm^{-1}$

may also be due to the presence of an ionized carboxyl group which have been observed to absorb in the region of 1600 $cm^{-1}$ (Bellamy, 1975).

The remaining absorption bands are difficult to assign with certainty, but there are some similarities to the casein I spectrum. The absorption at 1431 $cm^{-1}$ is a broad, ill-defined band which may relate to the doublet at 1450 and 1400 $cm^{-1}$ in casein I and correlate to a nitrogen-hydrogen deformation mode. There is a band at 1235 $cm^{-1}$ which has a parallel in the casein I spectrum at 1241 $cm^{-1}$ which may be the result of a coupled N-H bending mode and a carbon-nitrogen stretching vibration. The band that absorbs at 1099 $cm^{-1}$ in casein II may correspond to the band at 1106 $cm^{-1}$ in casein I, however, the casein II absorption is much more intense in relation to the other bands than the band at 1106 $cm^{-1}$. In the casein II spectrum, there are weak absorptions at 1007, 958, 869 and a very weak band at approximately 700 $cm^{-1}$ which may be due to a number of factors either by the side chains or deformations of the peptide bonds. The band around 700 $cm^{-1}$ is indicative of and out of plane N-H deformation which is characteristic of proteins, but it is extremely weak. Unlike the casein I spectrum, the region between

700 and 400 $cm^{-1}$ is not a broad, ill-defined band. This region has three distinct bands at 667, 592 and 433 $cm^{-1}$, but it is impossible to assign these bands.

Poly (methyl methacrylate)

Unlike the natural polymers such as proteins, acrylic plastics are composed of uniform monomers and it is possible to interprete the spectra more clearly. The structure of the poly (methyl methacrylate) unit is shown in Figure 9.7. The absorption bands are due to the C-H stretching and deformation vibrations and the stretching modes of the ester linkages.

The transmission spectrum of the secondary standard poly (methyl methacrylate) (Figure 10.4) was compared to the plexiglass (Figure 10.5a) and the perspex (Figure 10.5b) sample spectra and no additional bands appear in the spectra of the commercial materials. In these examples, the additives are not present in sufficient quantities in the diffuse reflectance spectrum. The diffuse reflectance spectrum of the secondary standard poly (methyl methacrylate) was somewhat distorted, most probably due to the fact that the sample was not finely enough ground. The baseline in the transmission spectrum is slanted upwards which is due to the KBr cell whereas the diffuse reflectance spectra slant downwards which may be caused by the influence of the silicon carbide paper. The spectra of the commercial products are very similar to the transmission spectrum. There are differences in relative intensities, the most striking being the increased intensities of the C-H stretching absorptions in the diffuse reflectance spectra. This is caused by the sample overloading effects discussed in Chapter 3. The resolution of the transmission spectrum is slightly better. A doublet is apparent at 1450 and 1436 cm$^{-1}$ which appears as a single band at 1448 cm$^{-1}$ in the perspex spectrum (Figure 10.5b) and at 1450 cm$^{-1}$ in the plexiglass spectrum (Figure 10.5a). A weak band is observed in the transmission spectrum of the secondary standard at 703 cm$^{-1}$ which does not appear in the spectra of the commercial products which may be due to residual solvent used to make the thin film.

The standard spectra have three absorptions in the C-H stretching region. The frequency values range from 2995 - 2997 cm$^{-1}$, 2951 - 2952 cm$^{-1}$ and 2843 - 2844 cm$^{-1}$. The values of the latter two bands fall within the ranges for the carbon-hydrogen stretches given in the literature (Bellamy, 1975) for the methyl group (2962 and 2872 + 10 cm$^{-1}$) and for the methylene groups (2926 and

2853 ± 10 $cm^{-1}$). However, the bands at 2872 and 2926 $cm^{-1}$ are not evident. The band in the 2995 - 2997 $cm^{-1}$ region is also due to a C-H stretching mode. The values quoted above have been obtained from measurements of unstrained hydrocarbons where the atoms adjacent to the carbon are also carbon atoms. The presence of electronegative atoms attached to the carbon cause a shift in the frequency (Bellamy, 1975). The band in the 2995 - 2997 $cm^{-1}$ region is most probably due to the C-H stretching in the methyl group that is adjacent to the oxygen atom in the ester linkage. McKean et al. (1973) obtained values of 3010 (s) and 2976 $cm^{-1}$ (a) for the methyl group which is adjacent to the single bonded oxygen atom in acetate group where a and s refer to the skeletal plane of the molecule.

The region between 1485 and 1370 $cm^{-1}$ is characteristic of the C-H deformation frequencies. The frequency values for the standard spectra are 1479 - 1484 $cm^{-1}$, 1448 - 1450 $cm^{-1}$ and 1386 - 1389 $cm^{-1}$. The transmission spectrum has an extra band at 1436 $cm^{-1}$. There is a shoulder on the peak in in the region 1386 - 1389 $cm^{-1}$ in all three spectra. The range for the asymmetrical C-H deformation in a methyl group is 1450 + 20 $cm^{-1}$ and the C-H bending resulting from a methylene group is 1465 ± 20 $cm^{-1}$.

Variations greater than ± 20 $cm^{-1}$ are very unusual except when there is a strongly electronegative atom adjacent to the carbon atom. The range for the symmetrical C-H deformation is 1380 - 1370 $cm^{-1}$ (Bellamy, 1975). Also, it is very difficult to differentiate between the bands in the 1460 $cm^{-1}$ region. The absorption bands in the reference spectra regions 1479 - 1484 and 1448 - 1450 $cm^{-1}$ in the reference spectra fall within the ranges given in the literature. The second band which is found at 1436 $cm^{-1}$ in the transmission spectrum may be indicative of the second type of methyl group in the structure. The frequency values for the symmetrical deformation in the methyl group are higher than those given in the literature, (1380 - 1370 $cm^{-1}$). This range is fairly consistant for methyl groups which are adjacent to carbon atoms and the frequency can be affected by the presence of electronegative groups in adjacent positions. The band in the region of 1386 - 1389 $cm^{-1}$ with the shoulder may also be indicative of the two types of methyl groups present in the poly (methyl methacrylate) structure.

The poly (methyl methacrylate) can also be distinguished by the presence of absorptions due to the ester linkage. Esters normally have two characteristic bands which are due to the C=O and the C-O bonds in the ester linkage. The frequencies of the carbonyl band in the samples range from 1730 to 1734 $cm^{-1}$ which fit into the range of saturated esters given in the literature (1750 - 1730 $cm^{-1}$). Esters are characterized by a second band in the region 1200 - 1100 $cm^{-1}$ which is due to the carbon-oxygen single bond stretch. The spectra of the poly (methyl methacrylates) have a common pattern of two bands which are split at 1269 - 1273 $cm^{-1}$ and 1241 - 1243 $cm^{-1}$ and at 1193 - 1194 $cm^{-1}$ and 1150 - 1154 $cm^{-1}$. The literature indicates that acrylates give two strong bands in the approximate regions of 1310 - 1250 $cm^{-1}$ and 1200 - 1100 $cm^{-1}$ (Colthup, 1950). Although no band assignments are given, the frequency values 1282, 1235, 1170 and 1149 $cm^{-1}$ are given as characteristic for the poly (methyl methacrylate) spectrum (Urbanski et al., 1977).

The standard spectra have a characteristic fingerprint in the region 1065 - 754 $cm^{-1}$ which may be useful in the identification of poly (methyl methacrylate). A band appears as a shoulder on the ester linkage band at 1065 $cm^{-1}$. In the transmission spectrum of the secondary standard poly(methyl methacrylate), a doublet occurs at 980 and 967 $cm^{-1}$ which appears as a band in the region of 992 - 991 $cm^{-1}$ with a weak shoulder in the diffuse reflectance spectra of the commercial material. A weak band occurs is the area of 913 $cm^{-1}$ in all three spectra. Also, a band falls at 843 $cm^{-1}$ with very weak shoulders around 811 and 827 $cm^{-1}$. A strong band occurs at 754 $cm^{-1}$ in the diffuse reflectance spectra and at 737 $cm^{-1}$ with a weak shoulder in the transmission spectrum. This band corresponds to the band at 749 $cm^{-1}$ which has been described as characteristic for the poly (methyl methacrylate) spectrum (Urbanski et al., 1977). There is a broad weak band centered at 485 - 482 $cm^{-1}$ in all three. The Visijar Perspex spectrum contains a series of weak bands which are not present in the other spectra from 650 to 485 $cm^{-1}$ which may result from the presence of additives.

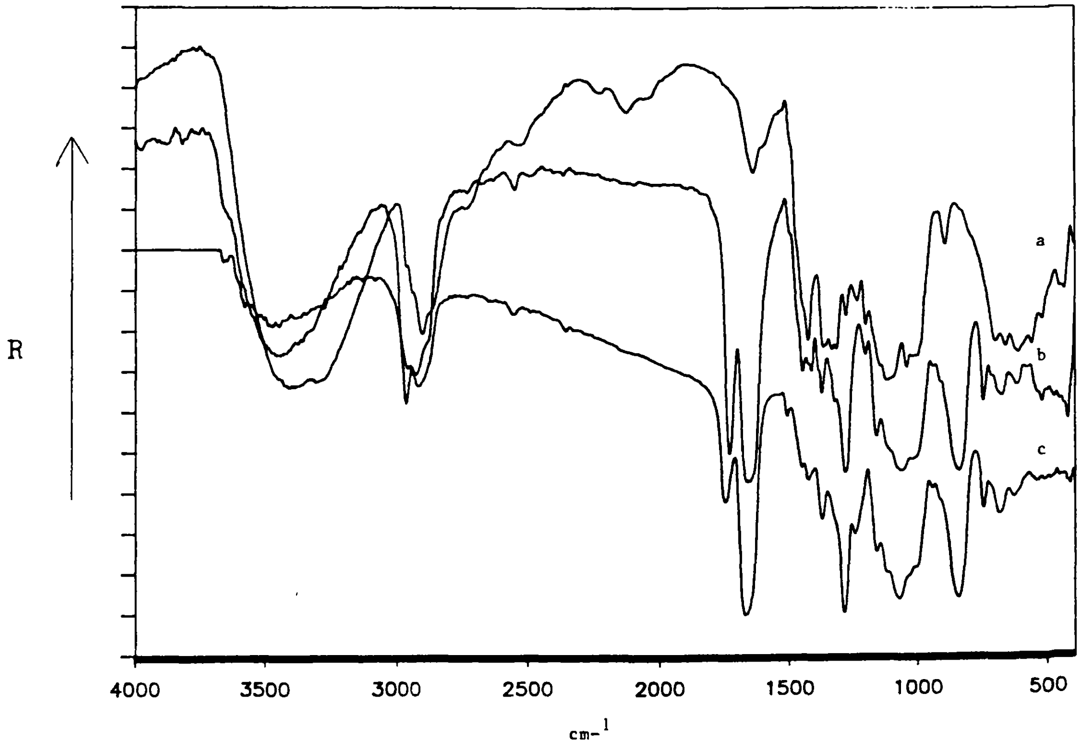


Figure 10.1 Diffuse reflectance FT-IR spectra of (a) cellulose powder, (b) cellulose nitrate plastic (Wardle Storey) and (c) cellulose nitrate plastic (Millipore).

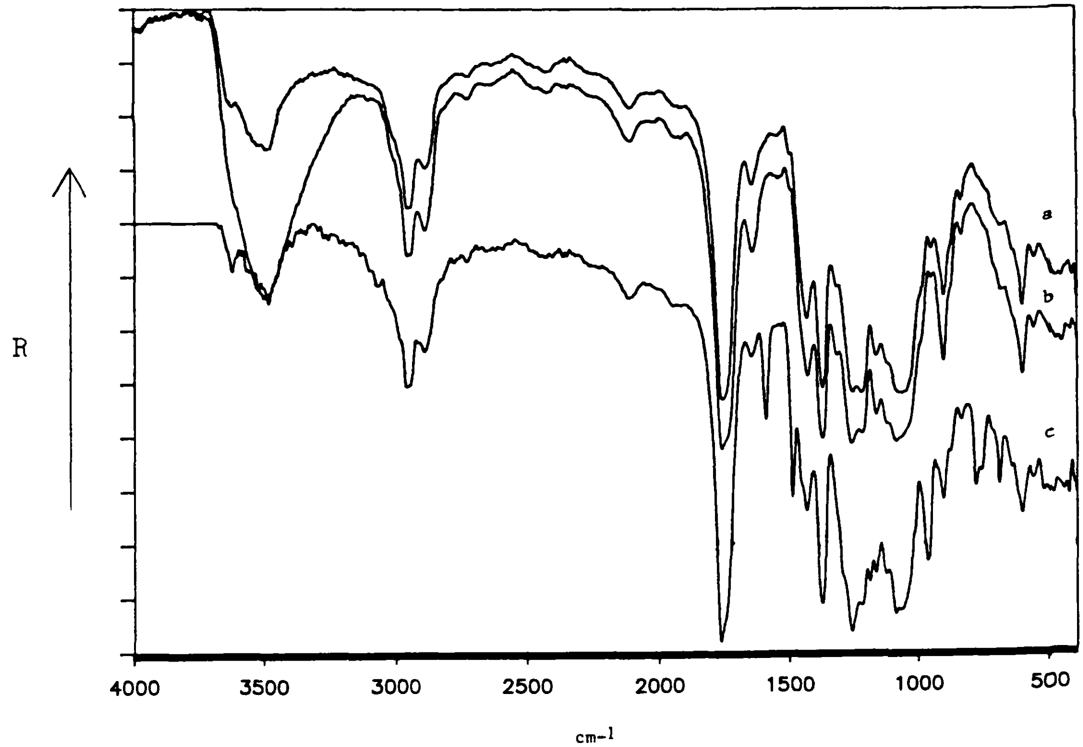


Figure 10.2 Diffuse reflectance FT-IR spectra of (a) chemical cellulose diacetate (acetyl content 39.8%), (b) chemical cellulose triacetate and (c) commercial sheet cellulose triacetate (Bexfilm).

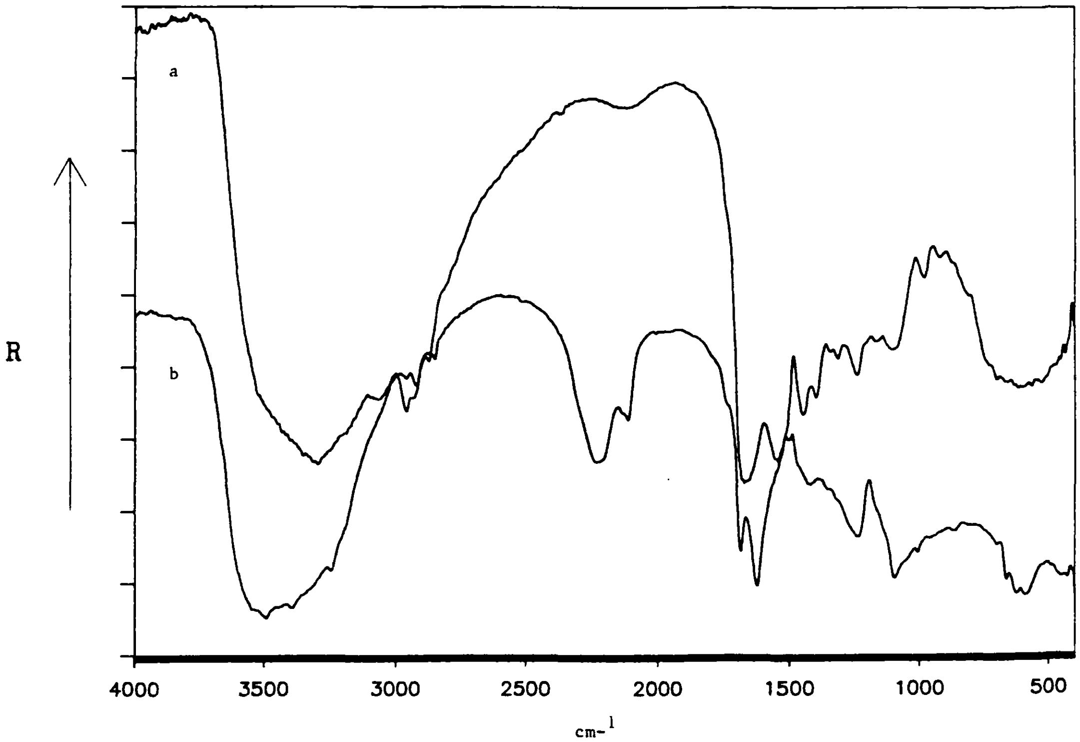


Figure 10.3 Diffuse reflectance FT-IR spectra of (a) commercial casein (BDH) and (b) casein prepared by acid precipitation in the presence of lime.

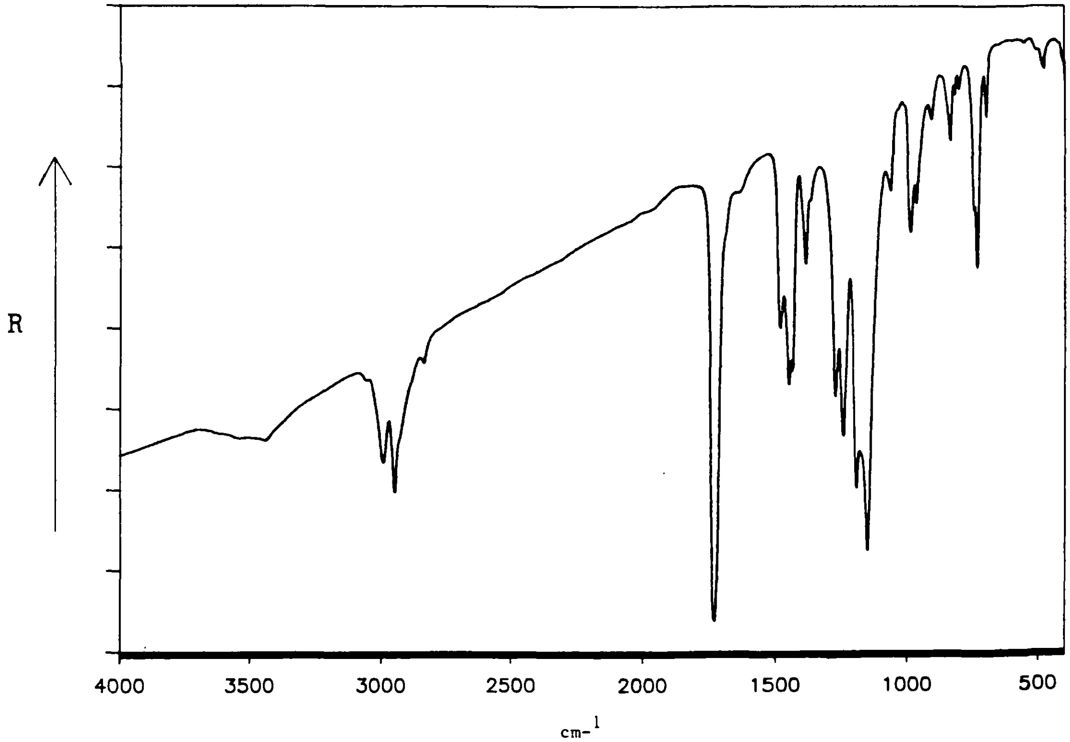


Figure 10.4 Transmission FT-IR spectrum of secondary standard poly(methyl methacrylate).

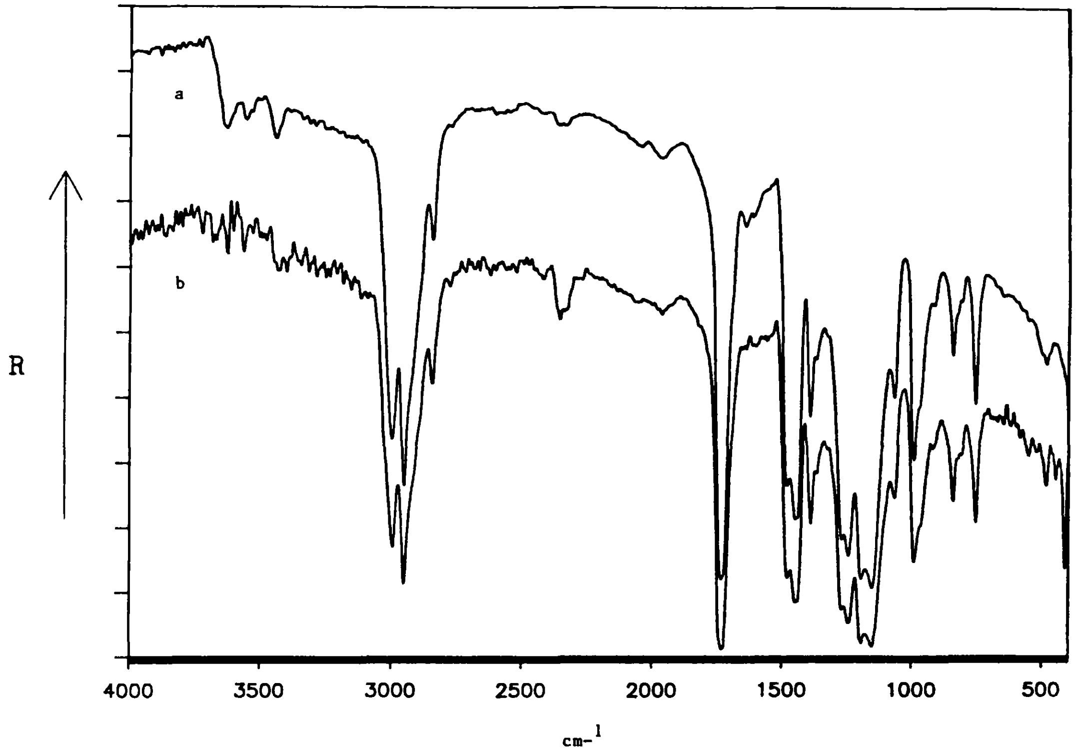


Figure 10.5 Diffuse reflectance FT-IR spectra of (a) commercial sheet "plexiglass" and (b) Visijar Tucker perspex.

# CHAPTER 11 IDENTIFICATION OF SCIENCE MUSEUM, VESTRY HOUSE MUSEUM AND TATE GALLERY SAMPLES

## Description of samples

### Science Museum samples

Six objects from the collection of Parkesine (cellulose nitrate plastic) which were given to the Science Museum by Alexander Parkes in 1934 were sampled using silicon carbide paper. The objects chosen for analysis exhibited no signs of deterioration. There was no exudate visible on the surface and no deformation in shape. The specimens (Science Museum # 1937-30) included a lump of crude Parkesine (#1) (1855-1868). a green marbled door handle (#8) (1855-1868), a billiard ball (#7), and a set of three disks (#3)(1865). The yellow and green disks were stamped with the patent and the green, brown and red marbled one was not.

### Vestry House Museum samples

In contrast to the samples taken from the Science Museum, the objects chosen for analysis from the Vestry House Museum were in an advanced state of degradation. Several samples were taken from a hand mirror frame (DB 30.9.65/46) which had broken apart. The plastic was crizzled and cracked and there was a strong odour of camphor given off when the storage box was opened.

Also, the sweat was observed to react with the tissue paper in the box. The mirror frame was composed of an amber coloured plastic on which there was a thin layer of blue and a thicker layer of green plastic on either side. The amber material had discoloured to light yellow. The blue plastic changed to a dark green colour. As the object was severely deteriorated, small samples of each of the three plastics was obtained in addition to the sample removed by silicon carbide paper. An abrasive paper sample was taken from a light green hairbrush (DB 30.9.65/73) which was marked with the Halex trademark and had beads of 'sweat' visible on the surface. A sample of the sweat was collected by rubbing the surface with a cotton swab. A silicon carbide paper sample was taken from the rim of a cylindrical box (DB 30.9.65/97).

### Tate Gallery samples

### Gabo sculpture samples

Diffuse reflectance spectroscopy was used to identify the polymer system used in a number of sculptures executed in plastic by Naum Gabo located at the Tate Gallery. Several of these sculptures are displaying signs of degradation including distortion and the presence of an exudate or 'sweat' on the surface. The pieces need urgent conservation and the first step was to identify the materials. It was thought that the first piece which was degrading was constructed of cellulose nitrate which is known to be unstable. Initial analysis (Martin, 1987 unpublished results) revealed that the degrading polymer system was in fact cellulose acetate. Thus, the identification of the plastics became an urgent first step (Pullen and Heuman, 1988). A survey of the the sculptures was undertaken using small circles of a finer grade silicon carbide paper to minimize the amount of sample removed. The samples were taken by the conservator by attaching the silicon carbide paper to a wooden dowel and rubbing against the area to be sampled. The sampling marks were visible only under a microscope (Heuman, personal communication). The samples were then taken to the Victoria and Albert Museum to be analysed as soon as possible after sampling. The details of the samples including the works from which they were taken are listed in Table 11.1.

### Other Gabo samples

In addition to the pieces of sculpture, several samples plastic from Gabo's workshop were provided for analysis by the Gabo family (Pullen and Heuman, 1988) (Table 11.2). The plastics were subjected to artifical ageing and spectra were obtained of both the unaged and the artificially aged samples. Samples of the exudate or 'sweat' which appeared on the surface of the samples after ageing were also examined. Surface exudate samples from two sculptures were also analysed (Table 11.3). The 'sweat' samples were removed from the surface by using a cotton wool swab and then the swab was rubbed against a potassium bromide cell. The spectrum is obtained by transmission spectroscopy. A sample of adhesive from one of the sculptures was examined using diffuse reflectance spectroscopy. The sample details are presented in Tables 11.2 and 11.3.

**Interpretation of sample spectra**

Science Museum samples

The six sample spectra from the Parkesine objects all exhibit bands which have been described as characteristic of cellulose nitrate (Figure 11.1), namely in the regions of 1667 - 1693 $cm^{-1}$, 1272 - 1285 $cm^{-1}$, 833 - 872 $cm^{-1}$ and 761 - 745 cm-1 which result from vibrations of the nitrate bonds (See Table 11.4). The band which is expected in the region of 710 - 689 $cm^{-1}$ is masked, possibly by overlapping bands in the region, in each of the sample spectra except SM5 (Marbled disk #3) (Figure 11.1b) where a weak band appears at 696 $cm^{-1}$. There is a weak band at 677 $cm^{-1}$ in SM1 (lump of crude Parkesine)(Figure 11.1a) and in SM4 (green disk #3). However, there are several other indistinct bands in the region which overlap and are difficult to interpret.

In all of the sample spectra, there is a broad band which centred in the range 3441 - 3383 $cm^{-1}$ due to O-H stretches and a broad band in the range 1066 - 1059 which is assigned to the C-O stretch in the ether linkage of the glucose molecules.

The most interesting feature in these spectra is that the band which has been assigned to the C=O stretch due to the camphor molecule is absent in the spectra of sample SM3 (yellow disk #3), SM5 (marbled disk #3) and SM6 (billiard ball). In addition, a band appears at 1541 and 1544 $cm^{-1}$ in the spectra of SM5 and SM6 respectively. In the spectrum of SM4 (green disk #3), the band at 1724 $cm^{-1}$ is very weak in relation to the other bands in the spectrum and there is a weak shoulder in the region of 1550 $cm^{-1}$. The absence of the absorption credited to the camphor molecule can be explained by the fact that although Alexander Parkes used camphor and other materials as plasticizers, he did not utilize it in large quantities.

Vestry House Museum samples

Four of the five silicon carbide samples from the Vestry House Museum collection were identified as cellulose nitrate. The spectra of the different plastics from deteriorated hand mirrors and the cylindrical box were found to have the bands which are characteristic of the nitrate ester (see Table 11.5) as well as the absorption bands in the O-H stretching region and the C-O ether stretches (Figure 11.2). As in the Science Museum sample spectra, the band in the region 710 - 689 cm$^{-1}$ seems to be masked by multiple overlap in the region 700 - 400 cm$^{-1}$. In the spectrum of VHN5, the band at 1670 cm$^{-1}$ is slightly beyond the range suggested in the literature, but it is within the range observed experimentally in other samples.

The spectrum of sample VHM3 shows some signs of degradation (Figure 11.2b). The spectrum was identified as cellulose nitrate on the basis of the bands at 1643, 1283, 830 and 752 cm$^{-1}$. There some differences in band shape between the sample spectrum and those of the cellulose nitrate plastics. The band at 830 cm$^{-1}$ is slightly beyond the range in the literature, but this may be due to degradation. However, the band in the carbonyl region credited to the presence of the camphor molecule is not evident in the spectrum. Also, the band in the C-H stretching region is very weak and a broad ill defined band appears at 2227 $cm^{-1}$.

The sample taken from the Halex hairbrush (DB 30.9.65/73) was found to be cellulose acetate. The spectrum was identified by the very intense bands at 1758 and 1239 $cm^{-1}$ which are due to the carbonyl stretch and the C-O stretch of the ester linkage (Figure 11.3). The value of the frequency at 1239 $cm^{-1}$ is within the range of acetate esters and both values agree closely with those in the standard spectra of cellulose acetate. The fingerprint bands which occur at 905 and 605 $cm^{-1}$ in the standard cellulose acetate spectra also appear in the spectrum of VHM4. Also, the bands which are observed in the commercial plasticized cellulose acetate sheet can be observed in the Halex spectrum at 1592, 1490, 966, 782, 758 and 692 $cm^{-1}$ which are indicative of an aromatic compound.

The Halex hairbrush was observed to have a surface residue which appeared as a skin. The spectrum of the material seems to indicate an aromatic compound due to the presence of sharp bands at 1604, 1506 and 1456 $cm^{-1}$.

The identification of the Halex hairbrush illustrates the value of the FT-IR technique. Objects which are stamped with the Halex trademark are considered to be cellulose nitrate, but both cellulose acetate and cellulose nitrate were marketed under the Halex name. As both materials have a tendency to degrade, it is no longer possible to classify all Halex objects as cellulose nitrate without chemical analysis.

## Tate Gallery samples

### Gabo sculpture samples

The identity of samples taken from the Gabo sculptures are summarized in Table 11.1. There were four polymer systems which were identified in the sculpture, cellulose nitrate, cellulose acetate, casein and poly (methyl methacrylate).

Thirteen samples were identified as cellulose nitrate and are listed in Table 11.1. The spectra were identified by the presence of bands due to the nitrate group bonds and the carbonyl stretch owing to the camphor (Figure 11.4). The range of the frequencies for each characteristic absorption for the samples is listed in Table 11.6.

The sample spectra show some variation in the 630 - 400 $cm^{-1}$ region. This may be due to additives such as pigments and dyes. The spectra of two samples of crizzled cellulose nitrate were not visibly different from the other samples (Figure 11.4b). In sample JH18, the bands in the C-H bending region are very weak. All of the nitrate bands used for identification are not affected. There is a band in the region of 1500 $cm^{-1}$ in the spectra of I-6, I-11, I-13, II-4, II-5, II-13, II-16 and JH17. This may be due to an aromatic additive such as a plasticizer, but there is no other evidence in the spectra.

The samples which were identified as cellulose acetate are listed in Table 11.1. The samples were identified by the presence of bands which have been assigned to features of cellulose acetate structure (Figure 11.5a). The spectra of samples which are visibly degrading are very similar to those of apparently stable plastic (Figure 11.5b). The bands which may be due to aromatic plasticizers are also present. The range of frequency values for the characteristic bands in the sample cellulose acetate spectra are listed in Table 11.7.

The range of the absorption frequencies are slightly greater than the reference spectra, however, they fall within the literature values. Minor variations in composition owing to different manufacturers, age and degradation would affect the infrared spectra slightly, but the frequency values are still valid for identification purposes. The C-H stretching absorptions appear as two bands in the standard spectra. These bands are less resolved in most of the sample spectra where only one band centred from 2920 - 2960 $cm^{-1}$ occurs. Also, there is a band at 839 - 841 $cm^{-1}$ in the reference spectra which appears as a weak band or shoulder in the sample spectra from 828 - 819 $cm^{-1}$.

The samples which were identified as casein plastic were characterized by comparison to the spectrum of commercial casein (Figure 10.3). Two of the samples taken from the Gabo sculptures were found to be casein and are listed in Table 11.1. The sample spectra (Figure 11.6) have bands which correspond with the standard spectrum in the regions of 3287, 3100, 2962, 1661, 1546, 1450 and 1400 (Table 11.8). Also, there is a band at 1175 $cm^{-1}$ in the standard spectrum of casein which has not been assigned, but which occurs in the sample spectra. There is an absorption at 1106 $cm^{-1}$ in the casein spectrum which may be related to the bands which occur at 1088 and 1084 $cm^{-1}$ in samples I-8 (Figure 11.6a) and II-12 (Figure 11.6b) respectively.

In the standard casein spectrum, there are bands at 1350, 1315 and 1241 $cm^{-1}$. The latter two were tentatively assigned to a coupled C-N stretching mode and a N-H bending vibration. The bands at 1350 and 1315 $cm^{-1}$ are not present in the sample spectra and a new band occurs in the region 1231 - 1233 $cm^{-1}$. This effect may be due to several factors. The change in the spectra may be a result of weathering of the polymer structure. It may also be due to changes in the structure caused by the hardening process. It is difficult to say as a sample of fresh casein plastic was not obtained.

In the sample spectra, the amide II band is split with a second band at 1507 and 1511 $cm^{-1}$. This region is sensitive to changes in conformation and may be due to changes in structure resulting from the hardening process. The region between 800 - 400 $cm^{-1}$ is a broad, ill-defined band with maximum intensity occuring at 826, 656 and 540 $cm^{-1}$. These are not observed in the standard spectrum and the differences may be due to the hardening process or to additives in the plastic.

The samples which were identified as poly (methyl methacrylate) are listed in Table 11.1. These samples were characterized by comparison of the sample spectra with those of the standard materials (Figure 11.7). The absorptions which have been described as characteristic for poly (methyl methacrylate) are present in the sample spectra except for the band which occurs at 1193 - 1194 $cm^{-1}$ in the standard spectra is not evident in the sample spectra. The sample spectra also have bands in the region 1066 - 1077, 990 - 991 and 753 - 754 $cm^{-1}$ which correspond to those in the reference spectra. The bands which appear near 967 and 913 $cm^{-1}$ in the standards appear as very weak shoulders in some of the sample spectra and the bands at 843, 827 and 811 $cm^{-1}$ do not occur in all of the sample spectra. The frequency values of the Gabo sculpture samples are compared to those of the standards in Table 11.9.

The sample spectra have weak spikey bands from 3900 to 3500 $cm^{-1}$ and a broad band centred in the region 3440 - 3443 $cm^{-1}$. These bands are most probably due to moisture which is absorbed by the poly (methyl methacrylate) powdered sample from the atmosphere between the time that the sample is collected and the time the spectrum was measured. Poly (methyl methacrylate) beads can absorb 0.3% moisture (Brydson, 1975) and the samples were not kept in a dessicator.

The sample spectra also exhibit very weak bands between 1600 - 1550 $cm^{-1}$. The bands are characteristic of aromatic compounds and fall in a range where they are not masked by other absorptions. There is a band at 1602 - 1606 $cm^{-1}$ and one in the area 1542 - 1547 $cm^{-1}$ in each example. There is also a band in the region of 1580 $cm^{-1}$, but it is extremely weak. These absorptions may be skeletal ring breathing modes of the aromatic ring. They would result from the presence of either plasticizers or stabilizers. The plasticizer dibutyl phthalate is an aromatic compound which is sometimes used in poly (methyl methacrylate). The ultraviolet light stabilizers such as phenyl salicylate and 2:4-dihydroxy benzophenone are also aromatic compounds.

The spectrum of sample I-17 has certain anomalies. There are two sharp bands at 3549 and 3408 $cm^{-1}$, a medium intense band at 1622 $cm^{-1}$ with a shoulder at 1605 and two bands at 672 and 605 $cm^{-1}$ which may result from the presence of additives which cannot be specified.

Gabo experimental plastic samples

Sample G is a transparent grey plastic that resembles the bottom section of the sculpture "Construction in space, Two cones" (T.2143). The material used in the sculpture is reported to be "Rhodoid", a cellulose diacetate, although the sample plastic is of uncertain commercial origin. The grey plastic in the "Two cones" piece is showing signs of degradation. The infrared spectra of samples taken from the surface of the plastic sample G (Figure 11.8a) did show some variations from those of the cellulose acetate standards and those of the sculpture samples identified as cellulose acetate. The strong band in the carbonyl region appears in the range 1724 - 1725 $cm^{-1}$ in the sample spectra which is somewhat lower than in the standard cellulose acetate spectra (1758 - 1764 $cm^{-1}$). It is also much less intense in relation to the other bands in the spectrum. The strong band in the region of 1240 $cm^{-1}$ in the reference spectra is also much less intense and the frequency has shifted to 1233 - 1235 $cm^{-1}$. This change indicates that a number of the ester linkages between the acetate groups and the glucose units have been broken. However, several samples were taken at one end after grinding to obtain a fresh surface. The spectra of these samples resemble those of the standard cellulose acetate (Figure 11.8b). The carbonyl band which ranges from 1744 - 1745 $cm^{-1}$ is very intense and the band which falls in the region of 1235 $cm^{-1}$ is also very strong. Thus, the degradation process is not consistent throughout the sample and the degradation seems to be occurring at the surface first.

The grey plastic sample G was subjected to several types of accelerated ageing. Samples were placed in an oven at 50 °C for 30 days under various conditions of relative humidity (RH). Two of the pieces which were aged in 100% RH were examined, one which turned a light brown colour and one which became blue. Both samples had severe lengthwise cracks and sweat was produced on the surface. A third sample was kept at 35% RH but not heated. No significant colour change was noted, but internal cracks occurred. Three spectra were obtained of the low RH material from various locations on the sample and one spectrum was collected of each of the high RH samples (Figure 11.9). The spectra were characterized by a weak band or shoulder in the region of 1723 - 1724 $cm^{-1}$. The band due to the C-O stretch falls at 1233 - 1234 $cm^{-1}$ and is weak in relation to the other bands in the spectrum (Figure 11.9).

The spectra of the aged samples are very similar to the surface sample spectra of the unaged samples (Figures 11.8 and 11.9). However, the bands in the regions of 1650, 1600 and 1500 $cm^{-1}$ seem to be unaffected by the ageing. A band appears in the region 1315 - 1322 $cm^{-1}$ in the spectra of the surface samples of the unaged and in all of the aged samples. This band is not apparent in the spectra of the fresh surfaces of sample G or in any of the sculpture samples identified as cellulose acetate. The band may reflect the structural changes which result as the cellulose acetate molecule loses acetyl groups. There are some variations in the bands in the region of 800 - 400 $cm^{-1}$ in the aged samples which may be due to weathering.

Sample A is a black plastic and when examined initially, was observed to be cellulose acetate (Table 11.2, sample I-1). However, it was examined a second time and the spectrum was slightly different. The carbonyl band occurred at 1729 $cm^{-1}$ and was less intense in relation to the other bands in the spectrum than the corresponding band in the initial spectrum (Figure 11.10a). After heat ageing at 100% RH and 50 °C there was a dramatic change in the spectrum (Figure 11.10b). The carbonyl band appeared at 1732 $cm^{-1}$ and the relative intensity was sharply decreased. The band at 1652 $cm^{-1}$ is very weak and the bands which occurred at 1236 and 1298 $cm^{-1}$ have disappeared. A new band is present at 1315 $cm^{-1}$ and the broad band in the ether region is replaced by a weak band at 1039 $cm^{-1}$.

Sample plastic B is a yellowed transparent material which distorted dramatically after heat ageing (Table 11.2). The unaged sample was identified as cellulose acetate (Figure 11.11a). The spectrum of the aged sample shows some variation from those of the unaged plastic (Figure 11.11b). The carbonyl band is shifted from 1758 $cm^{-1}$ in the spectra of the unaged sample to 1732 $cm^{-1}$ in the aged sample spectrum and it is less intense in relation to the other bands in the spectrum. The band at 1246 $cm^{-1}$ in the unaged spectrum is very broad and strong. The corresponding band occurs at 1236 $cm^{-1}$ with a weak shoulder at 1293 $cm^{-1}$ in the aged sample spectrum. The intensity of this band is not greatly affected.

Sample C is a very slightly yellowed, transparent plastic which did not show signs of distortion or signs of sweat on the surface (Table 11.2). It was identified as cellulose acetate and found to be soluble in methylene chloride. Thus, the greater stability is explained as the material is the more stable cellulose triacetate. Sample B was insoluble in both acetone and methylene chloride, but is thought to be the diacetate ester due to its instability. Unfortunately, the spectrum of the unaged sample B is almost identical to that of unaged sample C, thus it does not seem that the degree of substitution can be determined by the diffuse reflectance spectrum.

Sample D is a very yellowed transparent material. The sample did not show signs of degradation. The spectrum indicated that it was cellulose nitrate (Table 11.2).

The red plastic E was identified as casein. The spectrum (Figure 11.12a) exhibits bands at 3313, 3072, 2962, 1671, 1552, 1452 and 1409 $cm^{-1}$ which correspond to the standard casein spectrum (Figure 10.3). Bands are also found at 1510, 1236 and 1176 $cm^{-1}$ which correspond to the spectra of the sculpture samples which were identified as casein plastic. In addition, the bands which are observed at 1350 and 1315 $cm^{-1}$ in the standard casein spectrum and are not apparent in the casein plastic sample spectra are also missing in the sample E spectrum. The region from 800 - 400 $cm^{-1}$ is a broad, ill-defined band, but an absorption occurs at 826 $cm^{-1}$ which corresponds to the bands at 826 and 824 $cm^{-1}$ in the spectra of the samples I-8 and II-12.

After heat ageing at 50 °C and 100% RH for 30 days, sample E was observed to expand and when left to cool returned to almost the same weight as before ageing (Heuman, personal communication). The spectrum of the aged material is somewhat different to that of the unaged sample (Figure 11.12b). Two sharp absorptions occur at 3539 and 3488 $cm^{-1}$ and a broad band is observed at 3311 $cm^{-1}$. The amide I and amide II bands occur at 1659 and 1549 $cm^{-1}$ but there is no evidence of a band in the 3070 - 3100 $cm^{-1}$ region. There are also bands at 1508, 1452 and 1408 $cm^{-1}$ which occur in the unaged sample. However, there are variations in the region 1230 - 400 $cm^{-1}$. The band at 1236 $cm^{-1}$ in the unaged sample is shifted to 1225 $cm^{-1}$ after ageing. The band at 1099 $cm^{-1}$ in the unaged sample spectrum does not occur, but two bands appear at 1141 and 1081 $cm^{-1}$ in the aged sample spectrum. The band at 1140 $cm^{-1}$ masks the band which occurs at 1176 $cm^{-1}$ in the unaged sample spectrum. New bands occur at 990, 873, 797 and 665 $cm^{-1}$ in the aged sample spectrum and a broad band which occurs at 559 $cm^{-1}$ in the unaged sample spectrum is split into bands at 577 and 550 $cm^{-1}$ in the spectrum of the aged plastic.

Gabo plastic sample F is a transparent sheet of mustard yellow plastic. The diffuse reflectance FT-IR spectrum of the material is not similar to those of the four polymer systems identified in the the Gabo sculptures and samples. The polymer was tentatively identified by comparison of the spectrum to an infrared atlas of polymers (Hanson, 1987). The sample F spectrum (Figure 11.13) is similar to the spectrum of poly (vinyl chloride) (PVA) in the region 1450 - 400 $cm^{-1}$, but also has a carbonyl absorption at 1733 $cm^{-1}$ which is not expected in a spectrum of PVA. The spectrum was found to be most similar that of a vinyl chloride/vinyl acetate copolymer which contained 97.5% vinyl chloride. Copolymers of vinyl chloride and vinyl acetate exhibit properties similar to those of PVC, but are more flexible. The copolymer has between 97 and 85% chloride (Sax and Lewis, 1987). The spectral atlas contained spectra of several copolymers with increasing percentages of vinyl acetate (Hanson, 1987). The region 1450 - 400 $cm^{-1}$ is altered by increasing amounts of vinyl acetate. The similarity of the sample F spectrum to that of PVC and the copolymer with a small percentage of vinyl acetate indicates that the material also contains a small amount of vinyl acetate.

The sample F spectrum (Figure 11.13) contains a fairly strong absorption at 1733 cm$^{-1}$ which corresponds to a band in the literature spectrum which occurs near 1735 cm$^{-1}$. It is slightly more intense in relation to the other bands in the sample F spectrum than the comparable band in the reference spectrum. This variation may be caused by the sample loading on the silicon carbide paper. The literature spectrum was collected by transmission of a cast film. The sample F spectrum contains a strong band at 616 cm$^{-1}$ with a less intense absorption at 700 cm-1. This pattern corresponds to the doublet near 630 and 605 cm$^{-1}$ and the band near 685 cm$^{-1}$ in the atlas spectrum. These bands fall in the C-Cl stretching frequency range for poly (vinyl chloride), 768 - 540 cm$^{-1}$ (Krimm et al., 1963).

The bands at 1433, 1330, 1250, 1103 and 971 cm$^{-1}$ in the spectrum of sample F correspond fairly well with those occurring in the region of 1420, 1325, 1245, 1095 and 955 cm$^{-1}$ in the literature spectrum. The literature spectrum also contains a valley in the region of 1145 cm$^{-1}$ which is absent in the diffuse reflectance spectrum. The diffuse reflectance spectrum has a band at 1197 cm$^{-1}$ which appears as a shoulder near 1195 cm$^{-1}$ in the literature spectrum.

The sample F plastic underwent a dramatic colour change after heating at 50 °C and 100% RH (Table 11.2). The material became an opaque peach colour. The spectrum of the aged material was not dramatically altered from that of the unaged material. The band at 1197 $cm^{-1}$ in the original spectrum appears as a doublet shoulder near 1201 $cm^{-1}$ which is much less intense. The shoulder near 900 $cm^{-1}$ in the original sample F spectrum occurs as a sharp band at 831 $cm^{-1}$ which is similar to the band near 830 $cm^{-1}$ in the literature spectrum. Also, the band at 971 $cm^{-1}$ in the original sample F spectrum occurs at 970 $cm^{-1}$ and is much less intense in the artificially aged spectrum. The sample spectrum of the artificially aged material is slightly more similar to the literature spectrum than that of the unaged material.

The crizzled plastic sample 801 was found to be poly (methyl methacrylate) (Table 11.9). The spectrum of the material (Figure 11.14) is very similar to those of the visibly undegraded sample spectra of poly (methyl methacrylate)(Figure 11.7). There are no new bands which might indicate the creation of degradation products. There is an absence of bands in the region 845 - 810 $cm^{-1}$. However, there is a fourth C-H stretching band present at 2925 $cm^{-1}$ which is also evident in the sample spectrum of II-7.

## Gabo surface exudate samples

The sculptures "Construction in space, Two cones" and "Circular relief" are displaying signs of physical distortion and the presence of a material on the surface. The material was thought to be plasticizer exudate and is described as "sweat". Two samples were collected from "Two cones", one clear substance from the transparent grey plastic and one black substance from the black plastic, by rubbing the surface of the plastic gently with a cotton swab. The swab was then rubbed against a potassium bromide cell and the transmission spectrum of the material was recorded at 2 $cm^{-1}$ resolution and 10 scans. The initial analysis of the "Two cones" samples were performed at the Victoria and Albert Museum (Martin, 1987, unpublished results).

The report on the sweat samples from the "Two cones" sculpture concluded that the spectra of the two samples were similar, but that there were variations in intensity between the two. Several of the absorption bands occurred in different ratios. It was concluded that the samples consisted of two or more substances which have exuded from the polymer system. Also, the sweat mixture may have undergone chemical alteration such as oxidation. It was not possible to make a conclusive identification of the samples, however, there were indications that the mixture may contain a sulphonamide, a phthalate ester or triphenyl phosphate. All three of the materials are documented plasticizers of cellulose acetate and mixtures of phthalates and triphenyl phosphate are often used. It is thought that triphenyl phosphate which is known to sweat out of polymers, is migrating from the polymer system and bringing a certain amount of the other plasticizers to the surface (Martin, 1987, unpublished results).

Four samples of exudate were examined in this study which were obtained using the same sampling technique and examined under the same conditions as the samples from the "Two Cones" sculpture (Table 11.3). The samples JH4 (black) (Figure 11.15a) and JH5 (clear) (Figure 11.15b) were obtained from the artificially aged plastic samples A and G. Sample JH34 was collected from the surface of "Circular Relief" (T.2142) (Figure 11.16a) where it appeared as crystals on the surface. Sample JH40 was a black exudate which appeared on the surface of the "Construction in Space, Two Cones" sculpture which has appeared since the initial analysis (Figure 11.16b). The sample spectra of the artificially induced sweat and the samples from the sculptures were compared to those obtained from the earlier samples. In general, the four sample spectra show similarities to those of the earlier samples and to each other, but there are differences in band intensities. The spectra of samples JH34 and JH5 are not as strong as the other two as less sample was available.

The spectra of the four samples were compared visually with those of triphenyl phosphate (Figure 11.17), diethyl phthalate (Figure 11.18), and Ketjenflex which is N-ethyl o,p-toluenesulfonamide (Figure 11.19). The comparisons must be approached with caution as all three of the types of plasticizer are aromatic compounds and there are certain similarities in all of the spectra which result from aromatic compounds. However, there are some variations in the spectra which can be used to interpret the sample spectra. A table of the absorption frequencies for the four samples are compared to those of the standard materials in Table 11.10.

There is a weak absorption in the region of 3070 $cm^{-1}$ which corresponds to the C-H stretch in an aromatic system. In the spectra of samples JH5 and JH34, the band is very weak. There is a band in the range 1588 - 1590 $cm^{-1}$ and one in the range 1488 - 1489 $cm^{-1}$ which are characteristic of an aromatic system resulting from the skeletal ring breathing modes. In substituted aromatics, these two bands are split to produce four bands. The band in the region of 1600 $cm^{-1}$ is usually strong and the band in the area of 1560 - 1600 $cm^{-1}$ is often weak or non-existent in the infrared spectrum. In the spectrum of triphenyl phosphate and in the four sample spectra, the band near 1580 is strong with the band in the region of 1600 $cm^{-1}$ occurring as a shoulder. In the spectrum of N-ethyl o,p-toluenesulphonamide, there is one sharp band at 1599 $cm^{-1}$. The diethyl phthalate spectrum has two sharp bands at 1600 and 1580 $cm^{-1}$. The second set of bands occurs in the range 1510 - 1480 $cm^{-1}$ and at approximately 1455 $cm^{-1}$. The band in the region of 1455 $cm^{-1}$ is often masked by C-H bending vibrations which occur in the same area. In the spectrum of triphenyl phosphate, the bands occur at 1484 $cm^{-1}$ and 1455 $cm^{-1}$. The sulphonamide spectrum has a single sharp band at 1495 $cm^{-1}$ and the diethyl phthalate has a multiplet of bands at 1488, 1476, 1466 and 1448 $cm^{-1}$. In the spectra of sample JH5 and JH34, there is a strong absorption at 1489 and 1488 $cm^{-1}$ with a weak band in the region of 1450 $cm^{-1}$. In the sample JH4 and JH40 spectra, there are two bands at 1489 and 1450 $cm^{-1}$ and 1489 and 1457 $cm^{-1}$ respectively.

Aromatic compounds exhibit a series of low intensity absorptions in the region 1225 - 950 $cm^{-1}$. Bands in the regions of 1175 - 1125 $cm^{-1}$, 1110 - 1070 $cm^{-1}$ and 1070 - 1000 $cm^{-1}$ are characteristic of C-H in-plane deformations in mono-substituted aromatic compounds. Ortho and para-substituted compounds exhibit weak bands in the region 1225 - 1175 $cm^{-1}$, 1125 - 1090 $cm^{-1}$ and 1070 - 1000 $cm^{-1}$ (two bands). In addition, ortho-substituted compounds also absorb in the region 1000 - 960 $cm^{-1}$. This region is less useful for identification as the bands are weak. They are used to confirm evidence from other regions in the spectrum (Bellamy, 1975). In the spectrum of triphenyl phosphate, bands occur at 1176, 1162, 1153, 1071, 1030, 1023 and 1009 $cm^{-1}$. Diethyl phthalate, which is an ortho-substituted compound, has absorptions at 1174, 1124, 1097, 1074, 1041 and 1018 $cm^{-1}$. The spectrum of Ketjenflex, which is a mixture of ortho and para-substituted compounds contains bands at 1162, 1120, 1095, 1067, 1037 and 1019 $cm^{-1}$. In the sample spectra of JH4 and JH40, there are bands at 1162 - 1163 $cm^{-1}$, 1123 - 1124 $cm^{-1}$, 1072 - 1073 $cm^{-1}$, 1041, 1026 and 1011 $cm^{-1}$. Some but not all of these bands are also apparent in the weaker spectra of JH5 and JH34.

The region 1000 - 650 $cm^{-1}$ is characteristic for aromatic compounds and strong bands appear which result from C-H out-of-plane deformations. The occurrence of these bands is due to the position of the substituents and is characteristic of the substitution pattern of the ring (Bellamy, 1975). Mono-substituted aromatic materials absorb very strongly in the region 770 - 730 $cm^{-1}$ with an additional strong band in the region 710 - 690 $cm^{-1}$. Ortho-substituted compounds also absorb in the region 770 - 735 $cm^{-1}$, however, the compound does not absorb in the region 710 - 690 $cm^{-1}$ which makes this band diagnostic for mono-substituted compounds. Para-substituted aromatics are characterized by a strong band in the region 860 - 800 $cm^{-1}$. The spectrum of mono-substituted triphenyl phosphate contains a strong doublet at 770 and 752 $cm^{-1}$ and a strong band at 691 $cm^{-1}$. The diethyl phthalate spectrum has strong absorptions at 745, 706, and 651 $cm^{-1}$. The spectrum of the sulphonamide, which is a mixture of ortho and para compounds, exhibits strong bands at 815 and 664 $cm^{-1}$ with a band of medium intensity at 707 $cm^{-1}$. The sample spectra exhibit an intense doublet in the region of 770 $cm^{-1}$ and another band at 689 - 690 $cm^{-1}$ and are most similar to that of triphenyl phosphate. However, smaller amounts of ortho-substituted compounds may be present as one of the two bands in the region 770 $cm^{-1}$ may be due to both ortho and mono substitution. There is no evidence of para substitution which may indicate that if it is present, it is only in very small quantities.

The three types of plasticizer have unique functional groups which can be used to differentiate between them in the infrared spectrum. Triphenyl phosphate can be characterized by the phosphorus linkages. The P=O vibration is recorded in the literature as absorbing in the region 1300 - 1250 $cm^{-1}$ (Bellamy, 1975). The band occurs at 1295 $cm^{-1}$ in the triphenyl phosphate spectrum. However, there is a very strong band in this region in the diethyl phthalate spectrum, so it is not useful for isolating triphenyl phosphate. The P-O-C (aromatic) stretching vibration results in two absorptions in the regions 1242 - 1110 $cm^{-1}$ and 996 - 905 $cm^{-1}$ (Thomas and Chittenden, 1964). There is a band in the region of 1185 $cm^{-1}$ in the spectrum of Ketjenflex, but there are no possible interferences from diethyl phthalate. The second band, however, is very diagnostic. It is a strong and often complex band. In the spectrum of triphenyl phthalate, a strong multiplet occurs in this region with a maximum intensity at 953

$cm^{-1}$. There are no strong bands in this region in the spectrum of the sulphonamide mixture or the diethyl phthalate. The sample spectra have bands at 1187 - 1188 $cm^{-1}$ and 954 - 964 $cm^{-1}$. In the sample spectra JH5, JH34 and JH40, the band occurs from 954 - 964 $cm^{-1}$ and is the strongest absorption in relation to the other bands in the spectrum. In the spectrum of JH4, the band occurs at 961 $cm^{-1}$ and is less intense than the bands at 1728 and 1288 $cm^{-1}$. The band in the area of 1187 - 1188 $cm^{-1}$ may be due to a combination of the P-O-C (aromatic) vibration and the absorption in the sulphonamide mixture.

Diethyl phthalate is an ester which is distinguished by the presence of two strong absorptions resulting from the ester linkage. The ester linkage in phthalate esters are characterized by absorptions in the regions 1730 - 1717 $cm^{-1}$ (C=O stretch in aryl esters), 1310 - 1250 $cm^{-1}$ and 1150 - 1100 $cm^{-1}$ (C-O stretching vibration) (Bellamy, 1975). In the diethyl phthalate spectrum, there are strong absorptions at 1728, 1284 and 1124 $cm^{-1}$. The band in the region 1310 - 1250 $cm^{-1}$ is subject to confusion due to the P=O absorption in phosphates, although in the phthalate spectrum, it is very broad. The band in the region of 1150 - 1100 $cm^{-1}$ is not diagnostic as there is a strong multiplet in the area of 1200 - 1140 $cm^{-1}$ which might mask the absorption in a mixture. The carbonyl absorption is useful, however. In the spectrum of triphenyl phosphate, there are very weak absorptions at 1952, 1881, 1800 and 1739 $cm^{-1}$ which are aromatic overtone and combination bands. In the Ketjenflex spectrum, these bands occur at 1920, 1808, 1765, 1726, 1709 and 1687 $cm^{-1}$ and are also very weak. Thus, the presence of a strong absorption in the region of 1726 - 1728 $cm^{-1}$ is indicative of a phthalate.

It is slightly harder to characterize the sulphonamide when in combination with other aromatic compounds. There are strong bands at 1325 $cm^{-1}$ (with shoulders at 1306 and 1290 $cm^{-1}$) and 1161 $cm^{-1}$ in the standard spectrum of Ketjenflex which may be used. The bands correspond to the characteristic regions for sulphonamides which exhibit strong bands, one in the region 1180 - 1160 $cm^{-1}$ and one in the region 1360 - 1330 $cm^{-1}$. The bands are assigned to S=O stretches in the sulphone group ($-SO_2-$) (Bellamy, 1975). The band at 1162 $cm^{-1}$ is not as diagnostic as it may be confused with the C-H in-plane deformations of the aromatic ring in all the compounds. The band in the region of 1325 $cm^{-1}$ is possibly more diagnostic as there are no strong bands in the corresponding region of the other plasticizer spectra. A weak band occurs at 1350 $cm^{-1}$ in the spectrum of JH5, but no absorption is evident in the spectrum of JH35. In the spectrum of sample JH4, there are bands at 1339 and 1369 $cm^{-1}$ which are medium in intensity and a band occurs at 1369 $cm^{-1}$ in the spectrum of sample JH40.

The exudate sample spectra give indications of an aromatic material and although it is not possible to match the spectra with that of a pure compound, it is possible to determine the identity of the mixture by characteristic bands of each material. The identification of triphenyl phosphate as one of the possible components is supported by the literature as it has been reported to exude from cellulose acetate. It is also reported to be used in conjunction with phthalate plasticizers, so the identification of a phthalate plasticizer as one of the components is also supported. It is also possible that the phthalate is being carried out with the triphenyl phosphate. The physical appearance of sample JH34 as crystals on the surface indicated that the material was triphenyl phosphate which is a solid at room temperature. However, the presence of weak bands in the aliphatic C-H stretching region in addition to the strong band at

1726 $cm^{-1}$ indicate that a second compound must be present which is probably a phthalate ester. The presence of the sulphonamide is more difficult to confirm. It is very compatible with cellulose acetate, so it is not expected to exude in great quantities. It is difficult to say whether or not the sweat samples actually contain a sulphonamide from the spectra obtained in this study.

### Gabo sculpture adhesive sample

A sample of adhesive was removed from the sculpture "Construction in space, Two cones" and analysed by diffuse reflectance spectroscopy (Table 11.3). The sample was held with forceps and lightly rubbed against the silicon carbide paper. The sample spectrum was found to resemble those of the poly (methyl methacrylate) standards and a diffuse reflectance spectrum of an acrylic resin adhesive (HMG) which is made of Paraloid B-72 acrylic resin. The sharp bands in the C-O region which are evident in the poly (methyl methacrylate) standard spectra are not as distinct in the sample spectra where two bands appear 1235 and 1173 $cm^{-1}$. The same effect is evident in the spectrum of the acrylic adhesive where absorptions occur at 1237 and 1169 $cm^{-1}$. The sample spectrum is very similar to that of the acrylic resin adhesive with only minor variations and they are compared in Figure 11.20. There is a band at 1475 $cm^{-1}$ in the Paraloid B-72 spectrum which appears as a shoulder on the band at 1450 $cm^{-1}$ in the sample spectrum. A weak band occurs near 1525 $cm^{-1}$ in the Paraloid B-72 spectrum which is very indistinct in the sample spectrum. The band which appears at 837 $cm^{-1}$ as a shoulder on the band at 863 $cm^{-1}$ in the acrylic resin spectrum occurs at 828 $cm^{-1}$ in the sample spectrum and a new, weak band occurs at 691 $cm^{-1}$ in the sample spectrum. There are slight variations in the region 600 - 400 $cm^{-1}$ between the spectra, however, the agreement between the strong bands in the spectra is strong evidence for the identity of the unknown adhesive to be an acrylic resin.

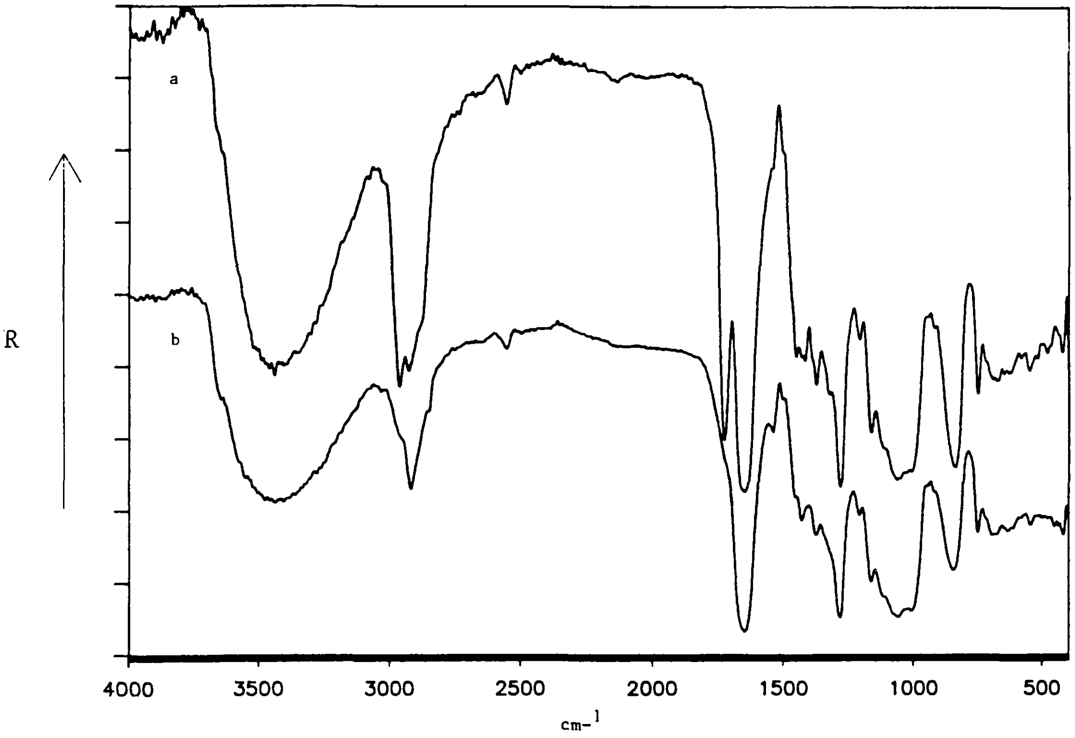


Figure 11.1 Diffuse reflectance FT-IR spectra of (a) lump of crude Parkesine (SM1) and(b) Parkesine marble coloured disk (SM5).

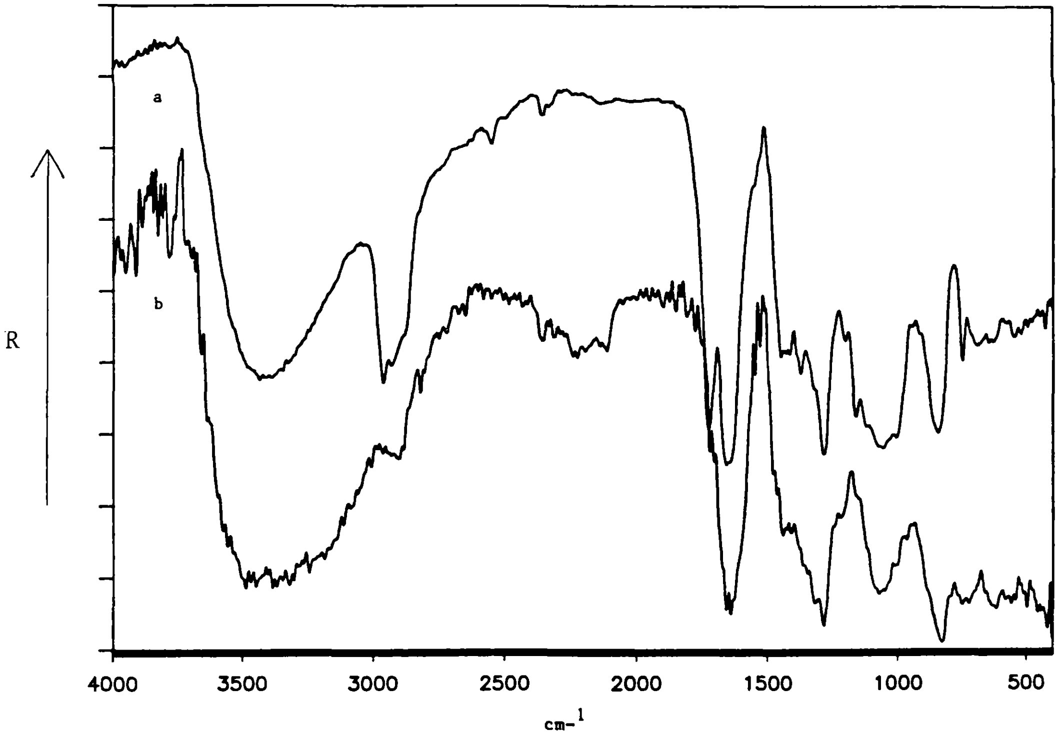


Figure 11.2 Diffuse reflectance spectra of samples from a degraded hand mirror from Vestry House Museum(a) yellow section (vhm1) and (b) dark green section (vhm3).

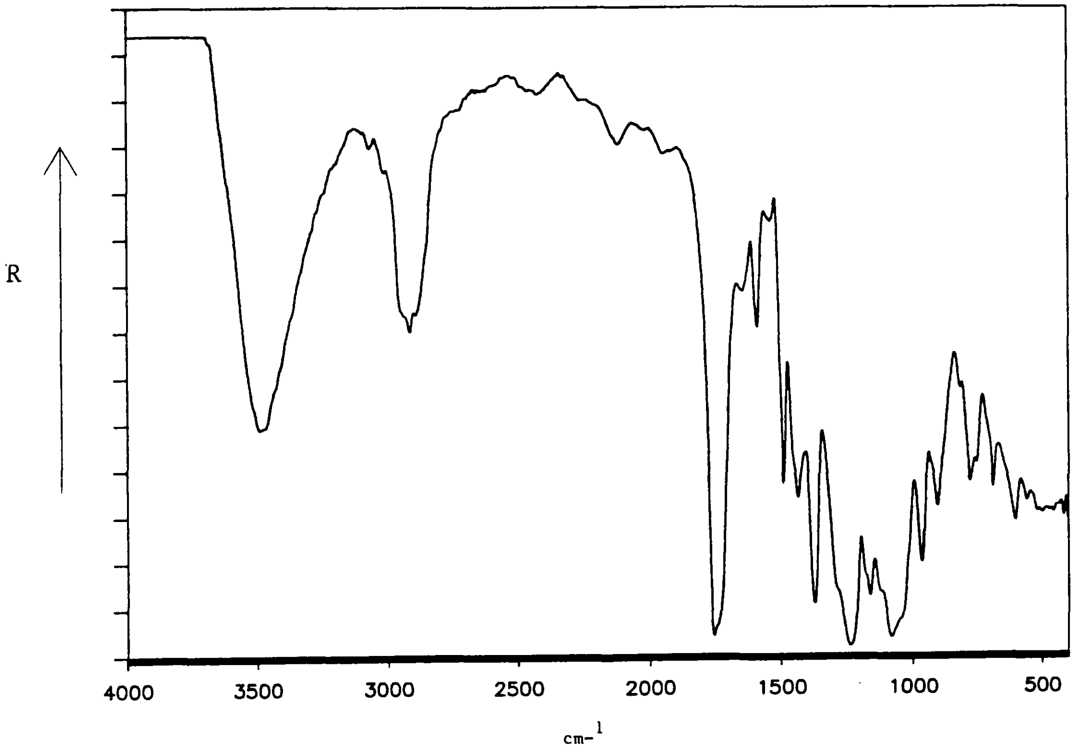


Figure 11.3 Diffuse reflectance FT-IR spectrum of a "Halex" hairbrush (vhm4) from Vestry House Museum.

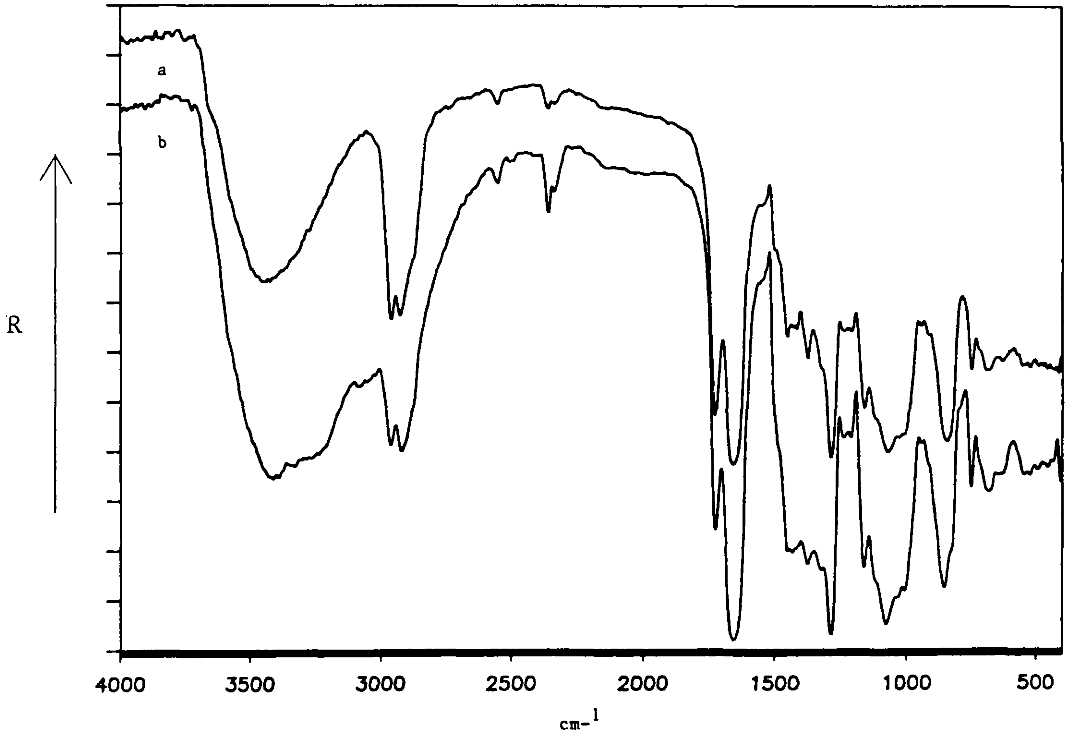


Figure 11.4 Diffuse reflectance FT-IR spectra of two Gabo samples identified as cellulose nitrate plastic. (a) Material in good condition from Model for 'Monument for an Airport' (T.2168) and (b) Crizzled plastic from Model for 'Double relief in a niche' (T.2170).

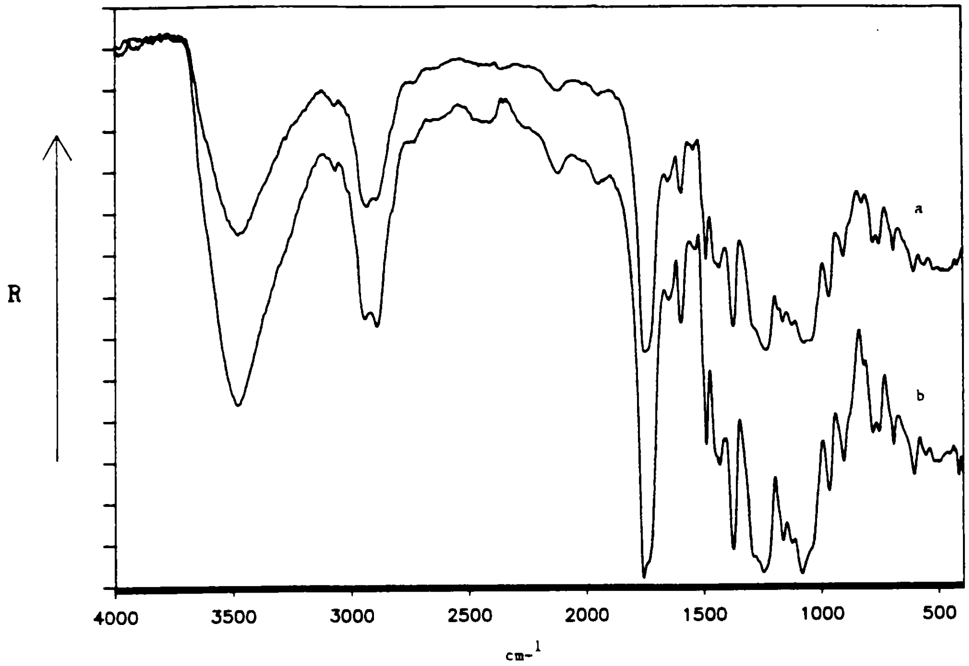


Figure 11.5 Diffuse reflectance FT-IR spectra of samples from Gabo sculptures which were identified as cellulose acetate plastic, (a) material in good condition from 'Torsion' (T.2146) and (b) Material observed to "sweat" from 'Construction in space, Two cones' (T.2143).

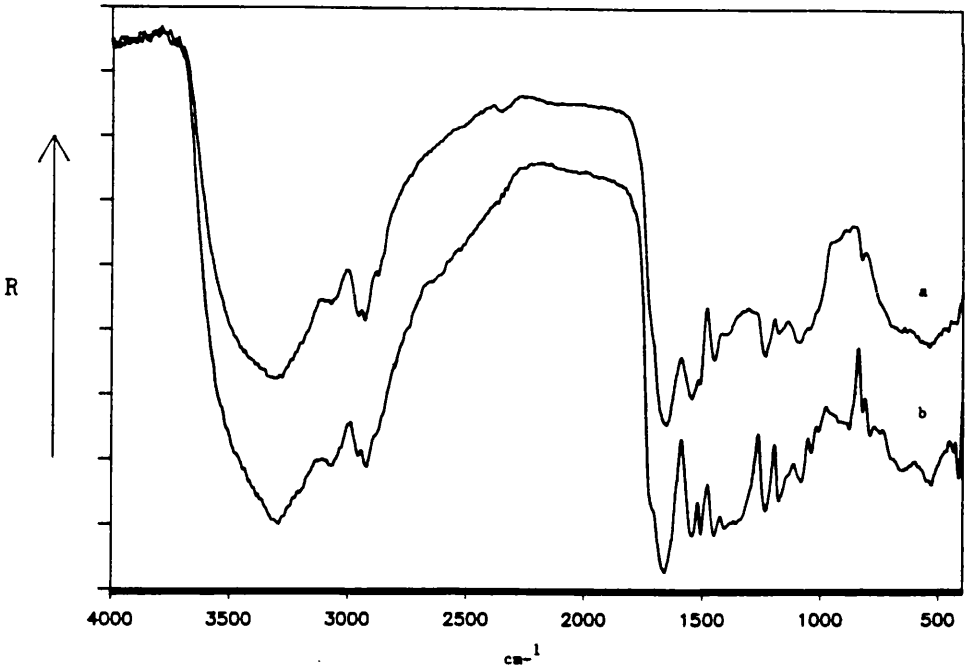


Figure 11.6 Diffuse reflectance FT-IR spectra of samples from Gabo sculptures identified as casein plastic, (a) material from Model for 'Construction in space, Two cones' (T.2169) and (b) sample from Model for 'Double relief in a niche' (T.2170).

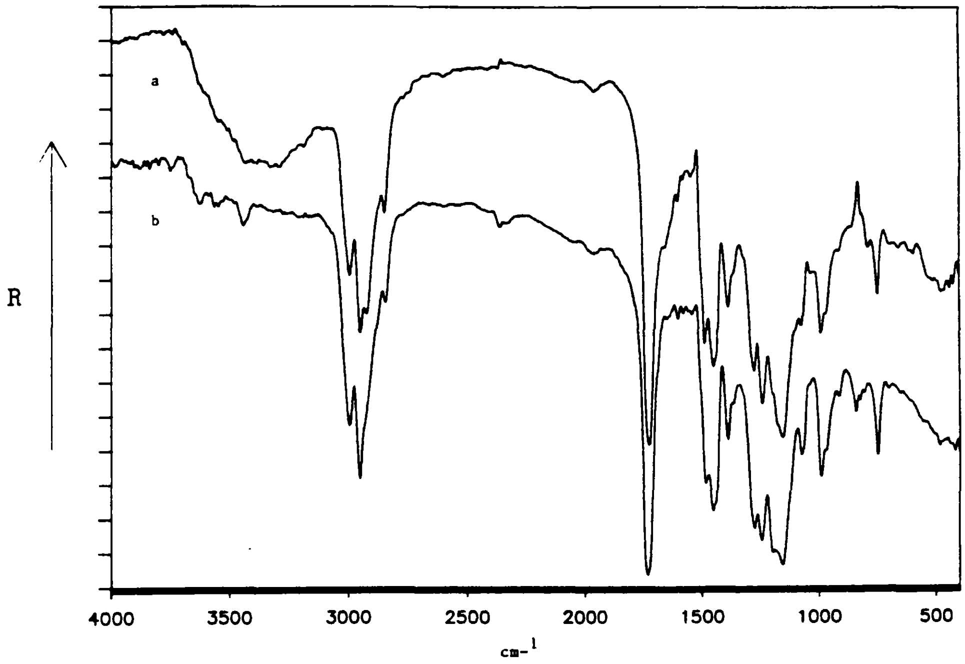


Figure 11.7 Diffuse reflectance FT-IR spectra of samples from Gabo sculptures identified as poly(methyl methacrylate), (a) material from First model for 'Monument to the unknown political prisoner' (T.2186) and (b) sample from Model for 'Monument to the unknown political prisoner' (T.2187).

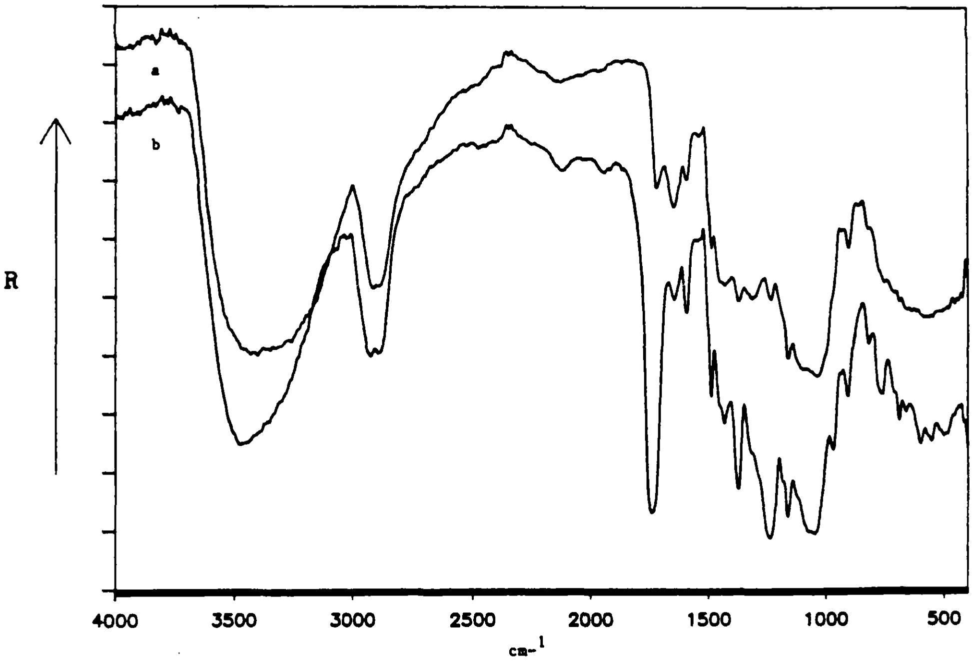


Figure 11.8 Diffuse reflectance FT-IR spectra of Gabo sample plastic G (transparent grey) identified as cellulose acetate, (a) sample taken from original surface and (b) sample obtained after grinding to obtain a fresh surface.

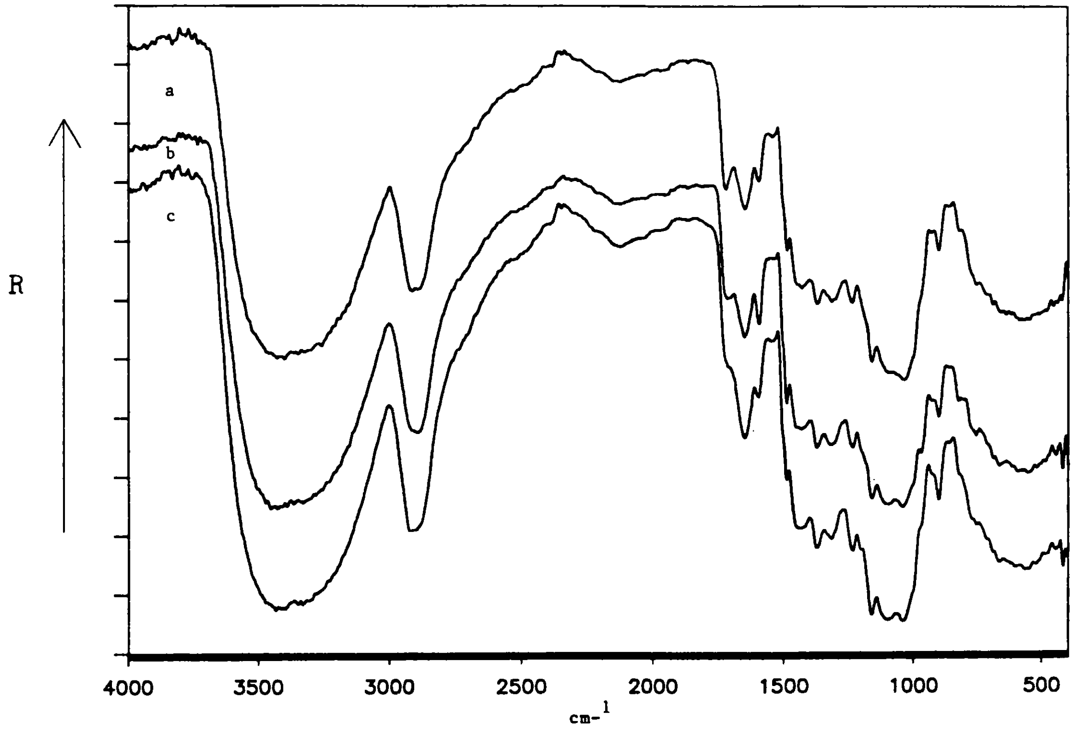


Figure 11.9 Diffuse reflectance FT-IR spectra of artificially aged samples of Gabo sample plastic G, (a) sample aged at 35% RH, (b) sample aged at 100% RH and 50 °C and (c) sample aged at 100% RH and 50 °C which turned blue.

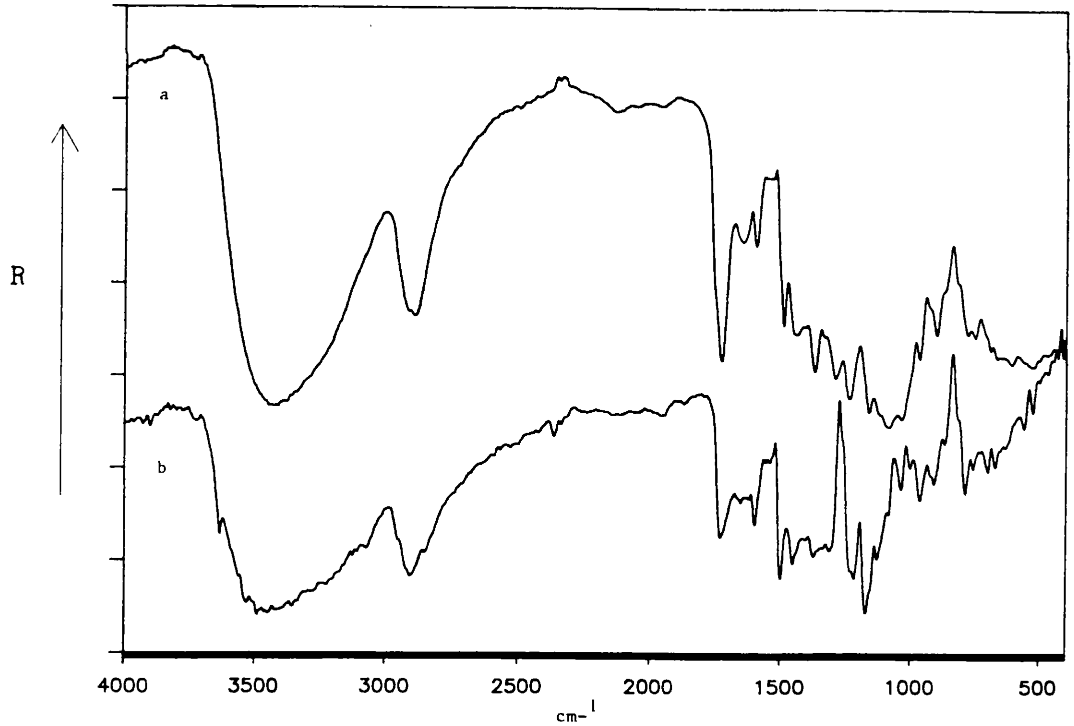


Figure 11.10 Diffuse reflectance FT-IR spectra of Gabo sample plastic A (black) identified as cellulose acetate (a) before artificial ageing and (b) after ageing at 100% RH and 50 °C.

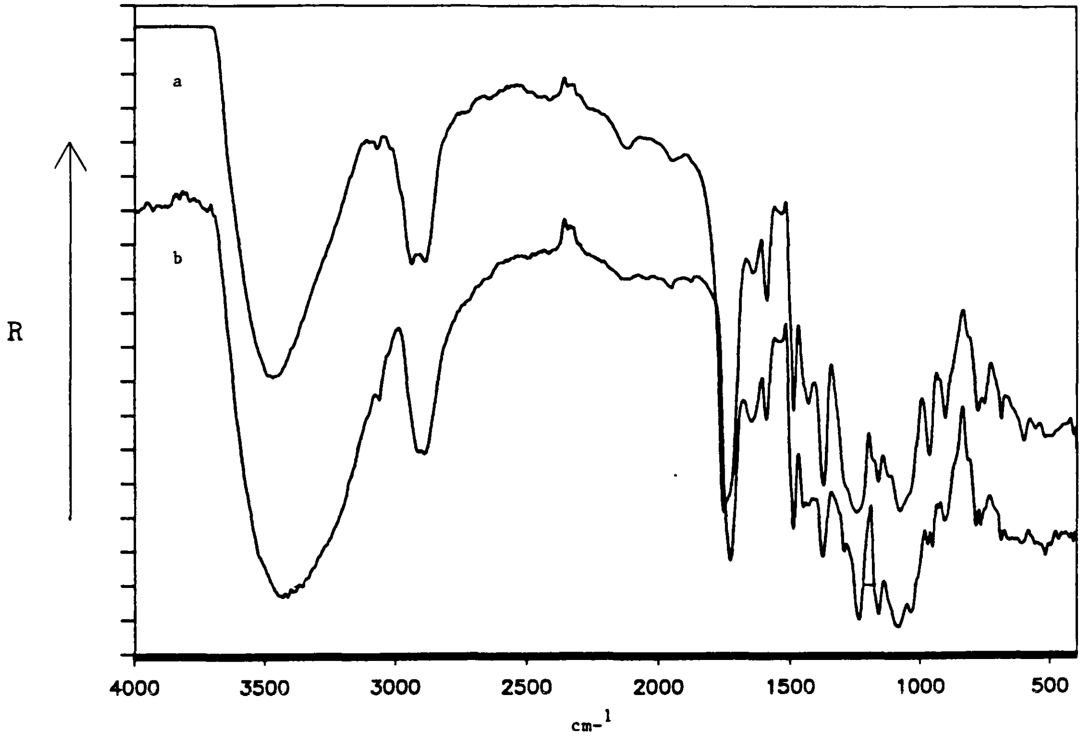


Figure 11.11 Diffuse reflectance FT-IR spectra of Gabo sample plastic B (clear) idnetified as cellulose acetate (a) before artificial ageing and (b) after ageing at 100% RH and 50 °C.

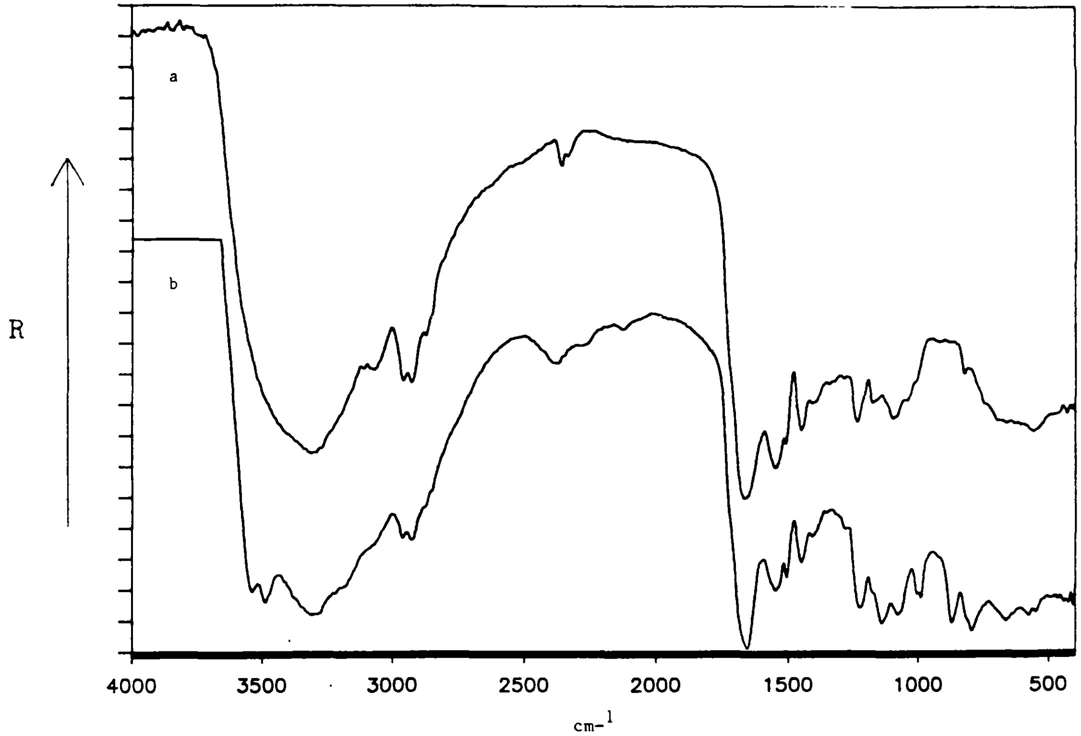


Figure 11.12 Diffuse reflectance FT-IR spectra of Gabo sample plastic E (red) identified as casein (a) before artifical ageing and (b) after ageing at 100% RH and 50 °C.

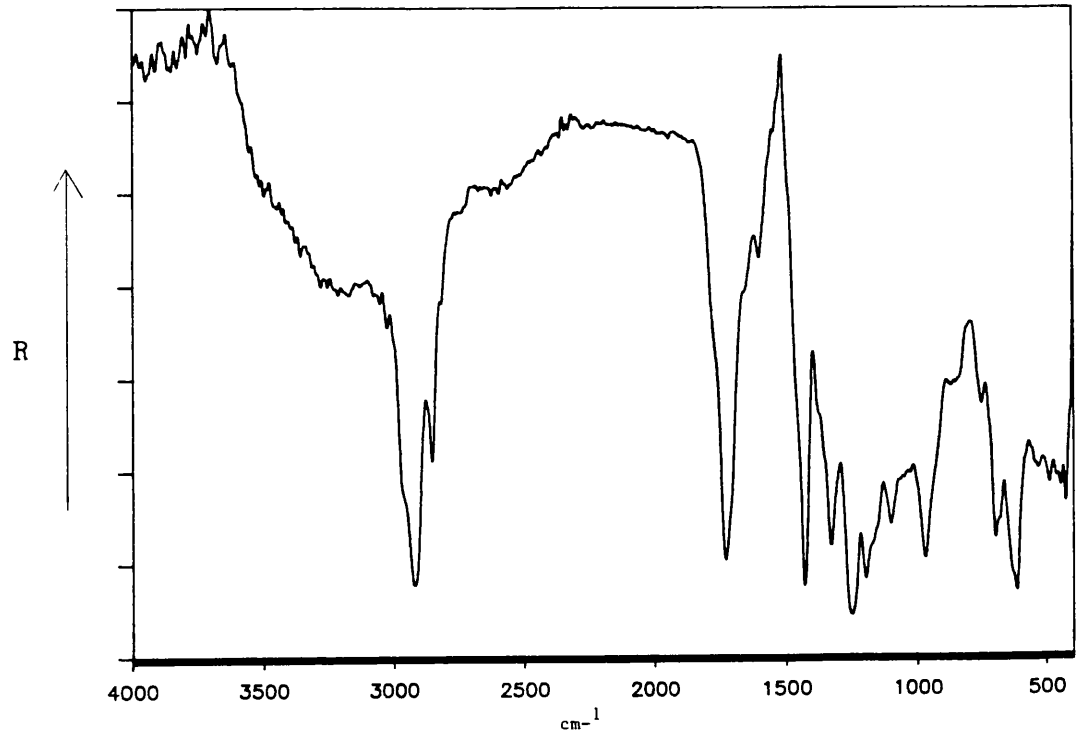


Figure 11.13 Diffuse reflectance FT-IR spectrum of Gabo sample plastic F (transparent yellow).

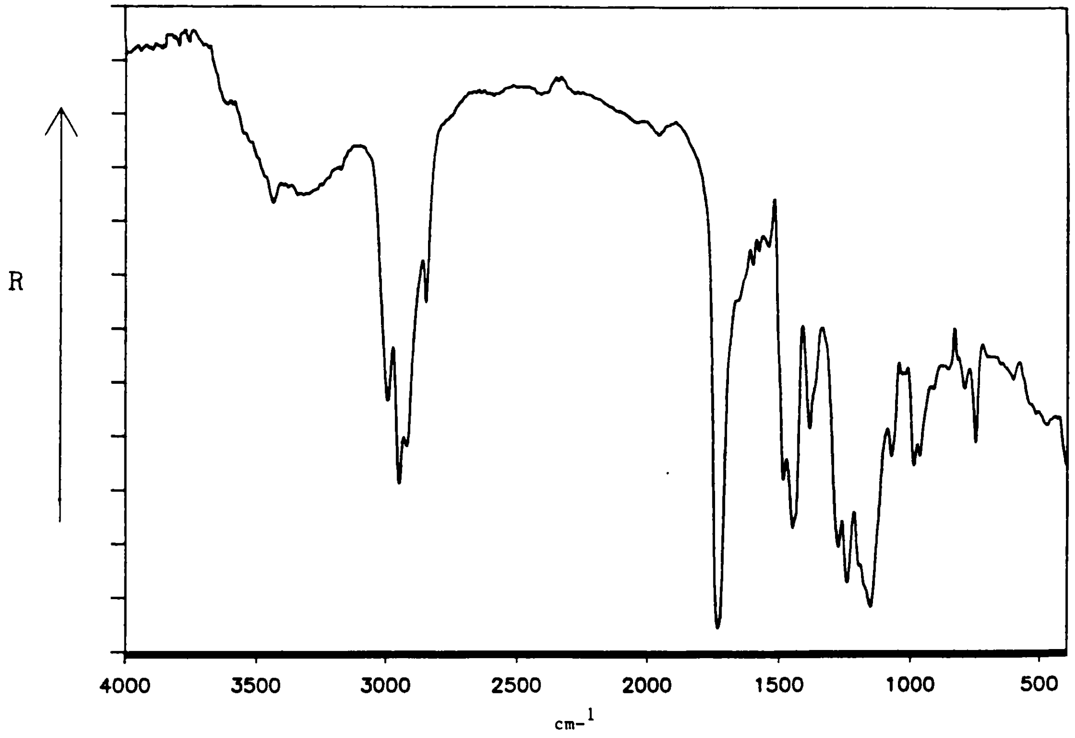


Figure 11.14 Diffuse reflectance FT-IR spectrum of Gabo archive sample 801 identified as poly (methyl methacrylate).

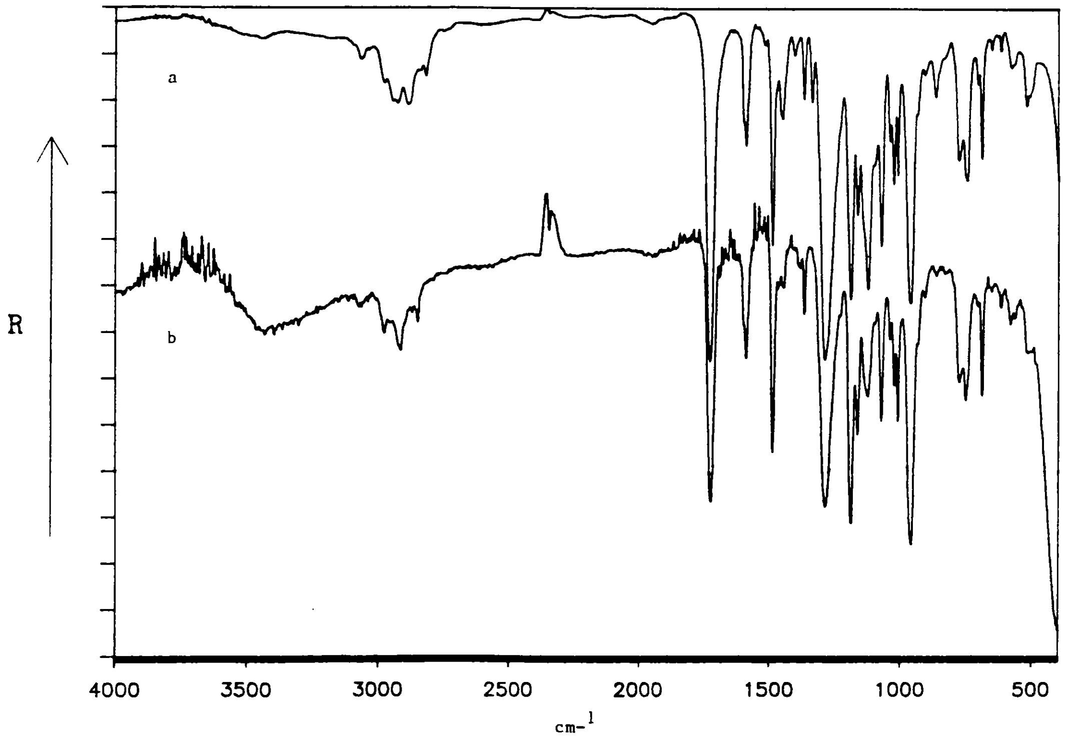


Figure 11.15 Transmission FT-IR spectra of surface exudate produced after artificial ageing of (a) Gabo plastic sample A and (b) Gabo plastic sample G.

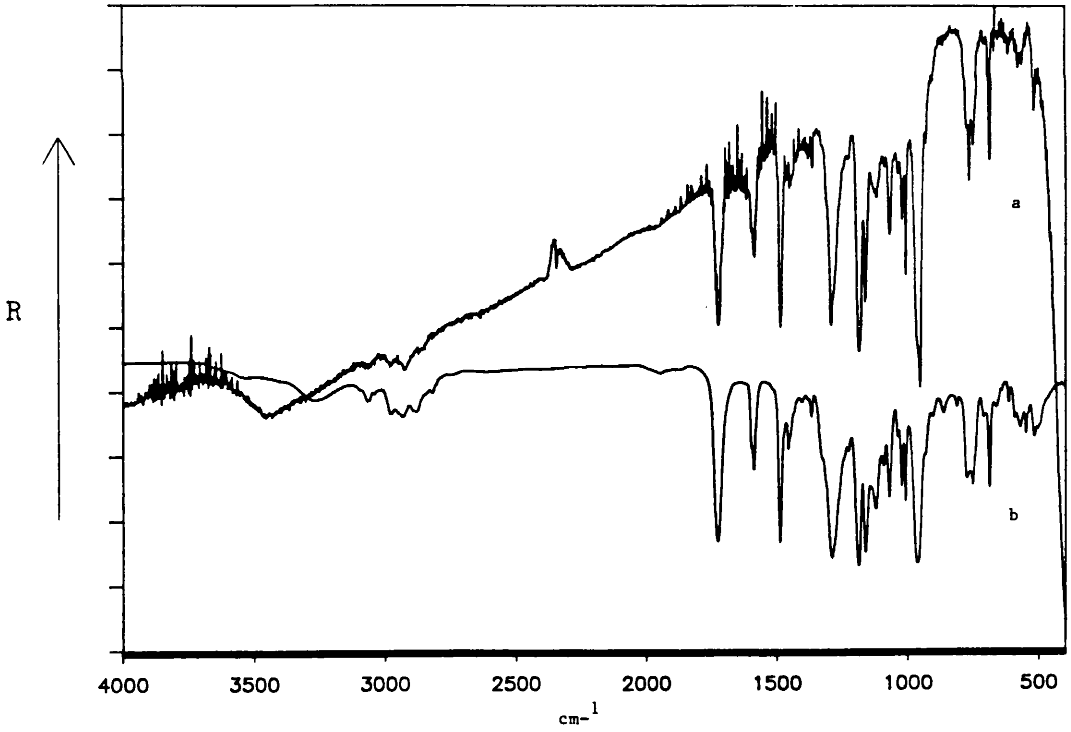


Figure 11.16 Transmission FT-IR spectra of surface exudate observed on the surface of (a) 'Circular relief' (T.2142) as crystals and (b) 'Construction in space, Two cones' (T.2143).

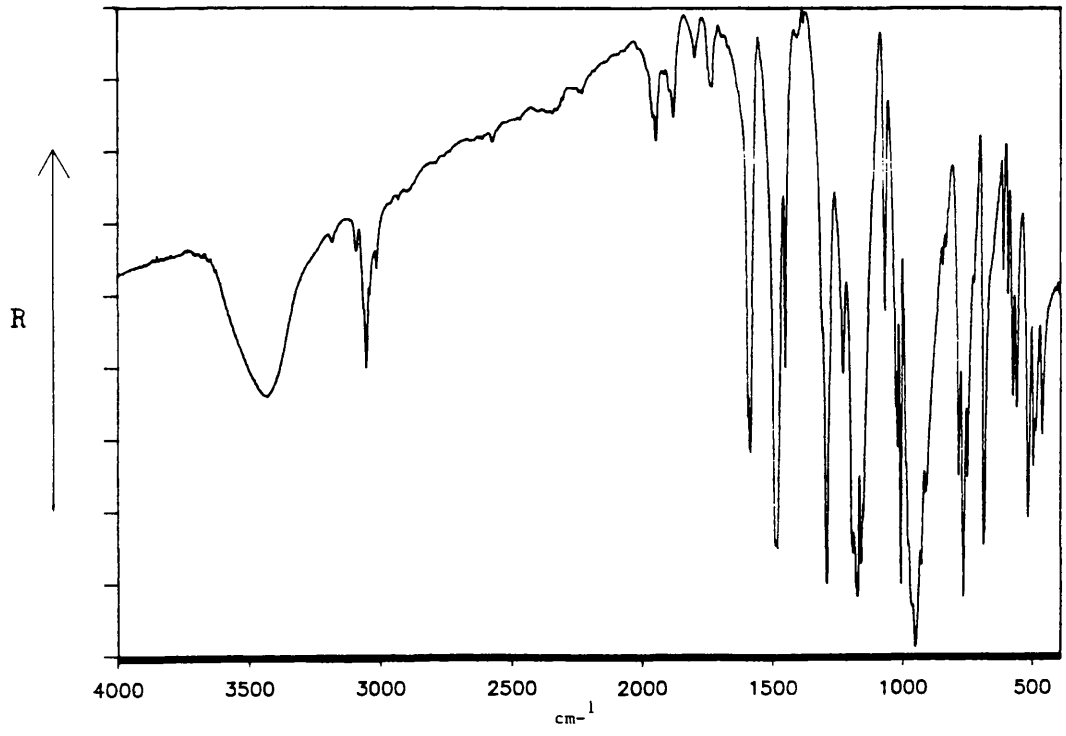


Figure 11.17 Transmission FT-IR spectrum of triphenyl phosphate.

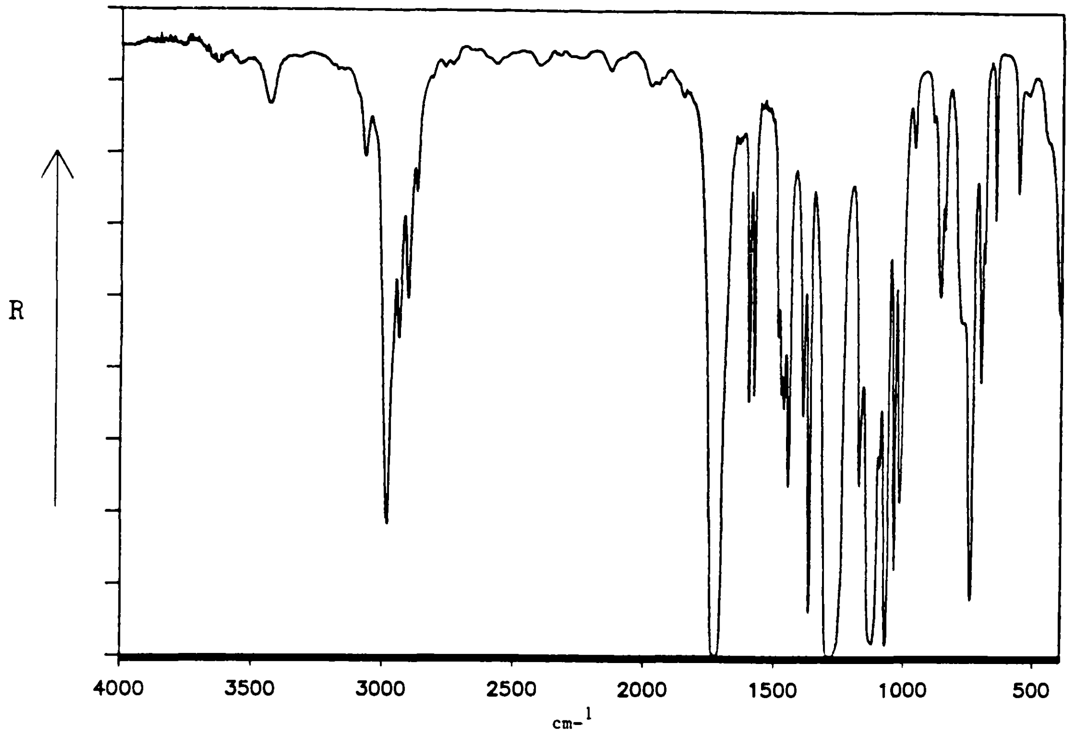


Figure 11.18 Transmission FT-IR spectrum of diethyl phthalate.

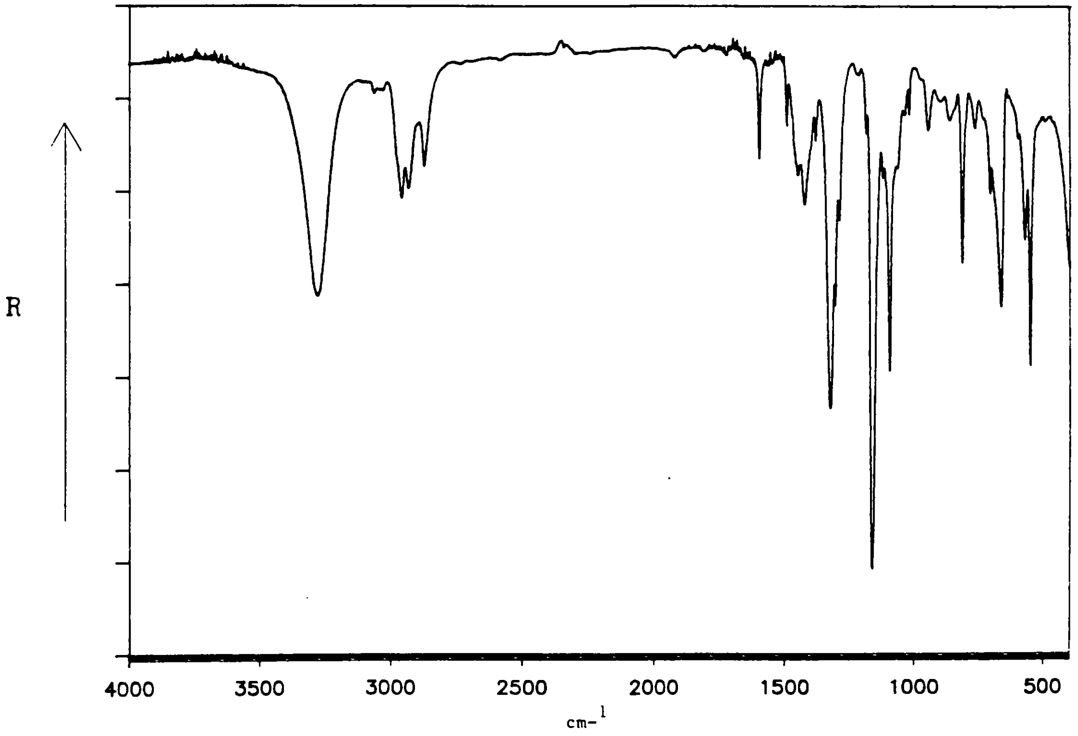


Figure 11.19 Transmission FT-IR spectrum of Ketjenflex 8 (N-ethyl o,p-toluenesulphonamide).

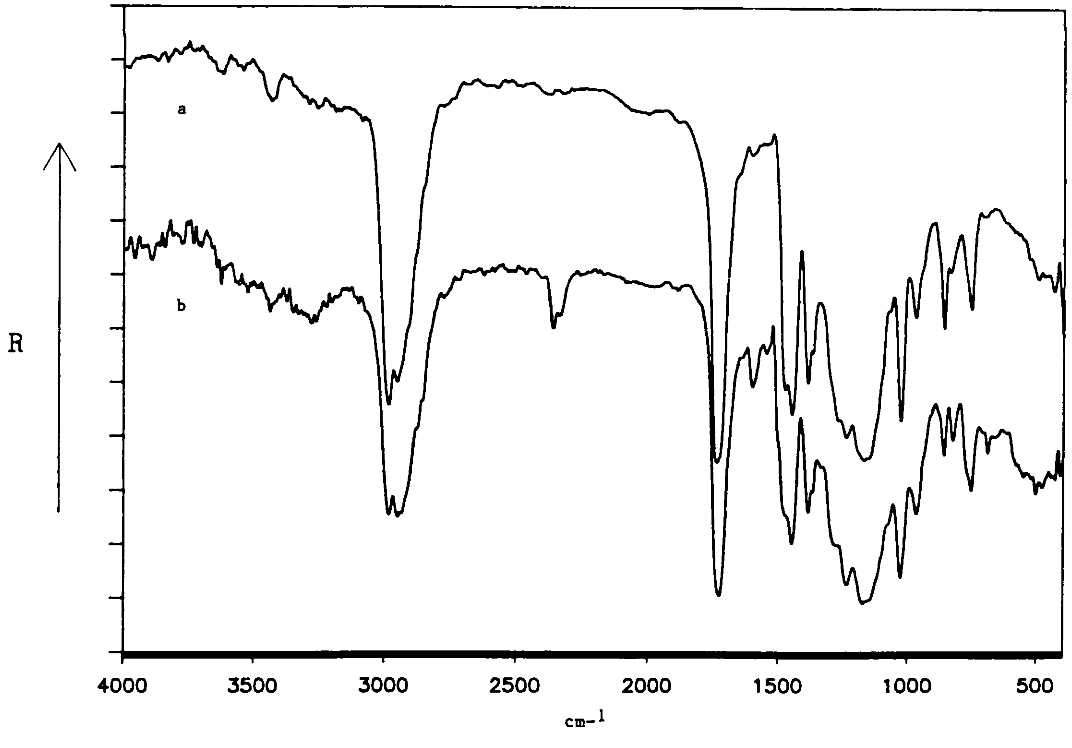


Figure 11.20 Diffuse reflectance spectra of (a) HMG Paraloid B-72 acrylic adhesive and (b) adhesive sample (JH3) from 'Construction in space, Two cones' (T.2143).

TABLE 11.1

Description and identification of Gabo sculpture samples

| Sample number | Museum number | Title | Date | Location of sample | Colour | Condition | Identification |
|---|---|---|---|---|---|---|---|
| I-3 | T.2168 | Model for 'Monument for an airport' | c.1932 | black parallelogram | black | OK | cellulose nitrate |
| I-4 | T.2178 | Model for 'Construction on a line' | c.1937 | clear plastic in front | clear, yellowed | distorted with bubbles | cellulose acetate |
| I-5 | T.2178 | Model for 'Construction on a line' | c.1937 | thin clear back sheet | clear | distorted | cellulose acetate |
| I-6 | T.2178 | Model for 'Construction on a line' | c.1937 | black strip | black | slightly distorted | cellulose nitrate |
| I-7 | T.2169 | Model for 'Construction in space, Two cones' | c.1927 | bottom layer of base section | black | OK | cellulose nitrate |
| I-8 | T.2169 | Model for 'Construction in space, Two cones' | c.1927 | triangular section inside cones | red | OK | casein |
| I-9 | T.2169 | Model for 'Construction in space, Two cones' | c.1927 | grey upper layer of base section | trans grey | OK | cellulose acetate |
| I-10 | T.2145 | Construction in a niche | c.1930 | large curved backdrop section | trans orange | OK | poly(methyl methacrylate) |
| I-11 | T.2167 | Model for 'Column' | c.1920-21 | long black strip | black | OK | cellulose nitrate |
| I-12 | T.2179 | Model for 'Construction in space' crystal | c.1937 | thick base section | clear, yellowed | slight distortion | cellulose acetate |
| I-13 | T.2170 | Model for 'Double relief in a niche' | c.1929-30 | strip at bottom of rectangular section | black | OK | cellulose nitrate |
| I-14 | T.2142 | Circular relief | c.1925 | black strip | black | slight distortion crystals of sweat | cellulose acetate |
| I-15 | T.2146 | Torsion | c.1929-37 | black top | black | OK | cellulose acetate |
| I-16 | T.2146 | Torsion | c.1929-37 | upper arm | clear | OK | poly(methyl methacrylate) |
| I-17 | T.2187 | Model for 'Monument to the unknown political prisoner' | c.1952 | black wedge | black | OK | poly(methyl methacrylate) |
| I-18 | T.190 | Spiral theme | c.1941 | thick side section | clear, slightly yellowed | OK | cellulose acetate |
| I-19 | T.2187 | Model for 'Monument to unknown prisoner' | c.1952 | center section, scratched | clear | OK | poly(methyl methacrylate) |
| I-20 | T.190 | Spiral theme | c.1941 | thin side section, not bloomed | clear | OK | cellulose acetate |
| II-1 | T.2206 | Model for 'Construction in space, arch' | c.1937 | transparent side | clear, yellowed | collapsed | cellulose acetate |
| II-3 | T.2177 | Model for 'Construction through a plane' | c.1935-37 | outer surround | clear | slight distortion | cellulose acetate |
| II-4 | T.2177 | Model for 'Construction through a plane' | c.1935-37 | triangle in front | clear, slightly yellowed | distorted | cellulose nitrate |
| II-5 | T.2177 | Model for 'Construction through a plane' | c.1935-37 | star in center | black | OK | cellulose nitrate |
| II-6 | T.2181 | Model for 'Spiral theme' | c.1941 | top section | clear | OK | cellulose acetate |

TABLE 11.1 contd.

Description and identification of Gabo sculpture samples

| Sample number | Museum number | Title | Date | Location of sample | Colour | Condition | Identification |
|---|---|---|---|---|---|---|---|
| II-7 | T.2187 | Model for 'Monument to the unknown political prisoner' | c.1952 | N/A | clear | OK | poly(methyl methacrylate) |
| II-8 | T.2145 | Construction in a niche | c.1930 | orange shape | orange | OK | poly(methyl methacrylate) |
| II-9 | T.2145 | Construction in a niche | c.1930 | curved shape at top | clear, slightly yellowed | OK | cellulose acetate |
| II-10 | T.2145 | Construction in a niche | c.1930 | wedge shape in rear | frosted | OK | poly(methyl methacrylate) |
| II-11 | T.2145 | Construction in a niche | c.1930 | curved spiral section at bottom | clear, slightly yellowed | OK | cellulose nitrate |
| II-12 | T.2170 | Model for 'Double relief in a niche' | c.1929-30 | rectangle base | orange | OK | casein |
| II-13 | T.2170 | Model for 'Double relief in a niche' | c.1929-30 | plastic beneath cone | clear, yellowed | OK | cellulose nitrate |
| II-14 | T.2144 | Red cavern | c.1926 | black strip | black | OK | cellulose nitrate |
| II-15 | T.2144 | Red cavern | c.1926 | triangle shape | frosted | OK | cellulose nitrate |
| II-16 | T.2144 | Red cavern | c.1926 | long, thin rectangle at front | white | OK | cellulose nitrate |
| II-17 | T.2142 | Circular relief | c.1925 | top section | white | OK | poly(methyl methacrylate) |
| II-18 | T.2142 | Circular relief | c.1925 | large circular panel | black | slight distortion where laminated | cellulose acetate |
| JH13 | T.2143 | Construction in space 'Two cones' | c. 1968 | base section | trans grey | distorted, sweat | cellulose acetate |
| JH15 | T.2143 | Construction in space 'Two cones' | c. 1968 | base section | black | distorted, sweat | cellulose acetate |
| JH17 | T.2168 | Model for 'Monument for an airport' | c. 1932 | vertical plane, yellow piece | yellow | crizzled | cellulose nitrate |
| JH18 | T.2170 | Model for 'Double relief in a niche' | c.1929-30 | adhered on base | orange | crizzled | cellulose nitrate |
| JH26 | T.2142 | Circular relief | c.1925 | top section | clear | OK | poly(methyl methacrylate) |
| JH29 | T.4146 | stage set 'La Chatte' (Pevsner) | c.1925-26 | model in back | clear, slightly yellowed | OK | cellulose acetate |
| JH30 | T.4146 | state set 'La Chatte' | c.1925-26 | back piece | black | OK | see text |
| JH32 | T.4146 | state set 'La Chatte' | c.1925-26 | diamond riveted in #B | clear, yellowed | OK | cellulose nitrate |
| JH38 | T.2188 | Model for 'Construction outside Bijenkorf building, Rotterdam | c. 1955 | greenish clear base | clear | OK | cellulose acetate |
| JH39 | T.2186 | First model for 'Monument to the unknown political prisoner | c. 1952 | clear section at bottom edge | clear | OK, acrylic appearance | cellulose acetate |

## TABLE 11.2

Description and identification of Gabo plastic samples

| Sample | Sample number | Treatment | Colour | Condition | Identification | Comments |
|---|---|---|---|---|---|---|
| A | I-1 | none | black | OK | cellulose acetate | |
| | JH21 | none | black | OK | cellulose acetate | **some loss of C=O band** |
| | JH22 | heat + 100% RH | black | sweat + distortion | | **spectrum much altered see text** |
| B | II-2 | none | yellowed | OK | cellulose acetate | |
| | JH19 | none | yellowed | OK | cellulose acetate | |
| | JH20 | heat + 100% RH | yellowed | sweat + distortion | | **spectrum altered - some loss of C=O and C-O bands** |
| C | JH33 | none | very slightly yellowed | OK | cellulose acetate | |
| | JH36 | heat + 100% RH | no change | OK | cellulose acetate | |
| D | JH16 | none | yellowed transparent | OK | cellulose nitrate | |
| E | I-1 | none | red | OK | casein | |
| | JH31 | heat + 100% RH | red | expanded see text | casein | **some alteration in spectrum see text** |
| F | JH8 | none | mustard yellow transparent | OK | poly(vinyl chloride)/ poly(vinyl acetate) copolymer | |
| | JH37 | heat + 100% RH | opaque peach | OK | poly(vinyl chloride)/ poly(vinyl acetate) copolymer | **slight alteration in spectrum** |

TABLE 11.2 contd.

Description and identification of Gabo plastic samples

| Sample | Sample number | Treatment | Colour | Condition | Identification | Comments |
|---|---|---|---|---|---|---|
| G | JH2 | none | transparent grey | OK | cellulose acetate | loss of C=O and C-O bands |
| | | none-ground end | | | cellulose acetate | loss of C=O and C-O bands |
| | | none-smooth side surface | | | cellulose acetate | loss of C=O and C-O bands |
| | | none-rough side surface | | | cellulose acetate | loss of C=O and C-O bands |
| | | none-ground end | | | cellulose acetate | |
| | | none-further grinding | | | cellulose acetate | |
| | JH10 | 35% RH | transparent grey | internal cracks | cellulose acetate | loss of C=O and C-O bands |
| | | | | | cellulose acetate | loss of C=O and C-O bands |
| | | | | | cellulose acetate | loss of C=O and C-O bands |
| | JH11 | heat + 100% RH | transparent light brown | sweat + lengthwise cracks | cellulose acetate | loss of C=O and C-O bands |
| | JH12 | heat + 100% RH | transparent blue | sweat + lengthwise cracks | cellulose acetate | loss of C=O and C-O bands |
| 801 | II-1A | none | transparent | crizzled | poly (methyl methacrylate) | |

TABLE 11.3

Description and identification of Gabo adhesive and surface exudate samples

| Sample number | Museum number | Title/Sample | Date | Sample | Sampling technique | Sample location | Colour | Identification |
|---|---|---|---|---|---|---|---|---|
| JH3 | T.2143 | Construction in space 'Two cones' | c. 1968 | adhesive | sample removed, rubbed onto silicon carbide paper | between laminated layers in base | clear | acrylic adhesive |
| JH4 | | Gabo plastic sample A artificially aged - see text | N/A | sweat | removed with swab, rubbed onto KBr plate | surface | black | plasticizers see text |
| JH5 | | Gabo plastic sample B artificially aged - see text | N/A | sweat | removed with swab, rubbed onto KBr plate | surface | clear | plasticizers see text |
| JH34 | T.2142 | Circular relief | c. 1925 | sweat | removed with swab, rubbed onto KBr plate | black circular section see text | crystals | plasticizers see text |
| JH40 | T.2143 | Construction in space 'Two cones' | c. 1968 | sweat | removed with swab, rubbed onto KBr plate | base | black | plasticizers see text |

# TABLE 11.4

Frequency values and band assignments for cellulose nitrate and Parkesine samples

| Milli-pore | Wardle-Storey | Parkes SM1 | SM2 | SM3 | SM4 | SM5 | SM6 | Inten-sity | Vibration | Functional group | Frequency range given in literature | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| cm-1 | cm-1 | cm-1 | cm-1 | cm-1 | cm-1 | cm-1 | cm-1 | | | | cm-1 | |
| 3447 | 3442 | 3441 | 3406 | 3400 | 3397 | 3438 | 3383 | m,b | O-H stretch hydrogen bonded | O-H group | 3400 - 3200(vs) polymeric intermolecular | 1 |
| 2961 | 2965 | | | | | | | m | C-H stretch | methyl group | 2962 ± 10(s) | 1 |
| 2917 | 2928 | 2929 | 2921 | 2918 | 2933 | 2919 | 2920 | m | C-H stretch | methylene group | 2926 ± 10(s) | 1 |
| 1748 | 1732 | 1731 | 1728 | | 1724 | | | s | C=O stretch | carbonyl group | 1735(s,sp) | 2 |
| 1671 | 1663 | 1651 | 1652 | 1651 | 1652 | 1652 | 1651 | s | N-O asym. stretch | nitrate group | 1667 - 1629(vs) | 3 |
| 1511 | | | | | | 1541 | 1544 | w | unassigned | | | |
| 1455 | 1452 | | | | | | | m | C-H asym. deformation | methyl group | 1450 ± 20(m) | 1 |
| | | | | | | | | | C-H deformation | methylene group | 1465 ± 20(m) | 1 |
| 1429 | 1418 | 1419 | 1431 | | 1428 | 1429 | 1400 | m | unassigned | | | |
| 1374 | 1376 | 1375 | | | 1375 | 1375 | | m | C-H sym. deformation | methylene group | 1380 - 1370(s) | 1 |
| 1288 | 1286 | 1280 | 1281 | 1282 | 1281 | 1282 | 1283 | s | N-O sym. stretch | nitrate group | 1285 - 1272(vs) | 3 |
| 1246 | | | | | | | | m | unassigned | | | |
| | 1205 | 1206 | | | | 1207 | | m | unassigned | | | |
| 1162 | 1163 | 1162 | | | 1163 | 1163 | | s | C-O stretch | ether linkage | 1150 - 1060(vs) | 1 |
| 1073 | 1066 | 1066 | 1062 | 1062 | 1059 | 1061 | 1064 | s,b | C-O stretch | ether linkage | 1150 - 1060(vs) | 1 |
| 945 | near 945 | | | | | | | w | unassigned | | | |
| 846 | 846 | 840 | 841 | 843 | 846 | 847 | 846 | s | N=O stretch | nitrate group | 872 - 833(s) | 3 |
| 751 | 752 | 752 | 750 | 753 | 752 | 752 | 749 | m | out-of-plane deformation | nitrate group | 761 - 745(m) | 3 |
| 692 | 683 | 677 | | | 677 | 696 | | m | N-O deformation | nitrate group | 710 - 689(m) | 3 |

1. Bellamy, 1975 2. Sirkis, 1982 3. Brown, 1955

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp

TABLE 11.5

Frequency values and band assignments for cellulose nitrate and Vestry House Museum samples

| Millipore | Wardle-Storey | Vestry House Museum Samples | | | | Intensity | Vibration | Functional group | Frequency range given in literature | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|
| | | VHM1 | VHM2 | VHM3 | VHM5 | | | | | |
| cm-1 | cm-1 | cm-1 | cm-1 | cm-1 | cm-1 | | | | cm-1 | |
| 3447 | 3442 | 3437 | 3386 | 3488 | 3445 | m,b | O-H stretch hydrogen bonded | O-H group | 3400 - 3200(vs) polymeric intermolecular | 1 |
| 2961 | 2965 | 2964 | 2963 | | | m | C-H stretch | methyl group | 2962 ± 10(s) | 1 |
| 2917 | 2928 | 2934 | | | 2928 | m | C-H stretch | methylene group | 2926 ± 10(s) | 1 |
| 1748 | 1732 | 1739 | 1728 | | 1728 | s | C=O stretch | carbonyl group | 1735(s,sp) | 2 |
| 1671 | 1663 | 1661 | 1643 | 1643 | 1670 | s | N-O asym. stretch | nitrate group | 1667 - 1629(vs) | 3 |
| 1511 | | | | | | w | unassigned | | | |
| 1455 | 1452 | 1451 | 1451 | | | m | C-H asym. deformation | methyl group | 1450 ± 20(m) | 1 |
| | | | | | | | C-H deformation | methylene group | 1465 ± 20(m) | 1 |
| 1429 | 1418 | | | | 1420 | m | unassigned | | | |
| 1374 | 1376 | 1375 | 1368 | | 1378 | m | C-H sym. deformation | methylene group | 1380 - 1370(s) | 1 |
| 1288 | 1286 | 1285 | 1283 | 1283 | 1282 | s | N-O sym. stretch | nitrate group | 1285 - 1272(vs) | 3 |
| 1246 | | | | | | m | unassigned | | | |
| | 1205 | 1204 | 1204 | | | m | unassigned | | | |
| 1162 | 1163 | 1162 | 1161 | | 1162 | s | C-O stretch | ether linkage | 1150 - 1060(vs) | 1 |
| 1073 | 1066 | 1058 | 1061 | 1075 | 1053 | s,b | C-O stretch | ether linkage | 1150 - 1060(vs) | 1 |
| 945 | near 945 | | | | | w | unassigned | | | |
| 846 | 846 | 847 | 840 | 830 | 845 | s | N=O stretch | nitrate group | 872 - 833(s) | 3 |
| 751 | 752 | 752 | 753 | 752 | 752 | m | out-of-plane deformation | nitrate group | 761 - 745(m) | 3 |
| 692 | 683 | 694 | | | 674 | m | N-O deformation | nitrate group | 710 - 689(m) | 3 |

1. Bellamy, 1975  2. Sirkis, 1982  3. Brown, 1955

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp

## TABLE 11.6

Frequency values and band assignments for cellulose nitrate standards and Gabo sculpture samples

| Millipore cm-1 | Wardle-Storey cm-1 | Gabo samples cm-1 | Intensity | Vibration | Functional group | Frequency range given in literature cm-1 | Ref. |
|---|---|---|---|---|---|---|---|
| 3447 | 3442 | 3494 - 3411 | m,b | O-H stretch hydrogen bonded | O-H group | 3400 - 3200(vs) polymeric intermolecular | 1 |
| 2961 | 2965 | 2964 - 2962 | m | C-H stretch | methyl group | 2962 ± 10(s) | 1 |
| 2917 | 2928 | 2929 - 2915 | m | C-H stretch | methylene group | 2926 ± 10(s) | 1 |
| 1748 | 1732 | 1732 - 1728 | s | C=O stretch | carbonyl group | 1735(s,sp) | 2 |
| 1671 | 1663 | 1678 - 1662 | s | N-O asym. stretch | nitrate group | 1667 - 1629(vs) | 3 |
| 1511 |  | 1504 - 1488 | w | unassigned |  |  |  |
| 1455 | 1452 | 1454 - 1451 | m | C-H asym. deformation | methyl group | 1450 ± 20(m) | 1 |
|  |  |  |  | C-H deformation | methylene group | 1465 ± 20(m) | 1 |
| 1429 | 1418 | *1419 - 1416 | m | unassigned |  |  |  |
| 1374 | 1376 | 1378 - 1375 | m | C-H sym. deformation | methylene group | 1380 - 1370(s) | 1 |
| 1288 | 1286 | 1297 - 1287 | s | N-O sym. stretch | nitrate group | 1285 - 1272(vs) | 3 |
| 1246 |  | *1240 - 1230 | m | unassigned |  |  |  |
|  | 1205 | *1213 - 1208 | m | unassigned |  |  |  |
| 1162 | 1163 | 1166 - 1162 | s | C-O stretch | ether linkage | 1150 - 1060(vs) | 1 |
| 1073 | 1066 | 1095 - 1073 | s,b | C-O stretch | ether linkage | 1150 - 1060(vs) | 1 |
| 945 | near 945 | * 945 | w | unassigned |  |  |  |
| 846 | 846 | 870 - 846 | s | N=O stretch | nitrate group | 872 - 833(s) | 3 |
| 751 | 752 | 755 - 752 | m | out-of-plane deformation | nitrate group | 761 - 745(m) | 3 |
| 692 | 683 | 699 - 685 | m | N-O deformation | nitrate group | 710 - 689(m) | 3 |

* Absorption is weak or does not appear in some spectra

1. Bellamy, 1975 2. Sirkis, 1982 3. Brown, 1955

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp

TABLE 11.7

Frequency values and band assignments for cellulose acetate standards and Gabo samples identified as cellulose acetate

| cellulose acetate VA13 | VA14 | Bexfilm | Gabo samples | Inten-sity | Vibration | Functional group | Frequency range given in literature | Ref. |
|---|---|---|---|---|---|---|---|---|
| cm-1 | cm-1 | cm-1 | cm-1 | | | | cm-1 | |
| 3499 | 3494 | 3482 | 3493 - 3464 | m,b | O-H stretch | O-H group hydrogen bonded | 3400 - 3200 (b) | 1 |
| | | 3069 | 3073 - 3068 | w | C-H stretch | aromatic ring | near 3070 (w) | 1 |
| 2959 | 2959 | 2959 | 2960 - 2891 | m | C-H stretch | methyl group | 2962 ± 10 (s) | 1 |
| 2892 | 2893 | 2893 | | m | C-H stretch | methine group | 2890 ± 10 (w) | 1 |
| 1762 | 1758 | 1764 | 1760 - 1736 | s | C=O stretch | ester | 1750 - 1730 (s) | 1 |
| 1644 | 1647 | 1648 | 1651 - 1646 | m | unassigned | | | |
| | | 1591 | 1600 - 1592 | m | skeletal ring stretch | aromatic ring | 1625 - 1575(va) | 1 |
| 1547 | nr 1547 | nr 1535 | * 1551 - 1536 | vw | unassigned | | | |
| | | 1490 | 1492 - 1490 | m | skeletal ring stretch | aromatic ring | 1525 - 1475(va) | 1 |
| 1433 | 1434 | 1434 | 1436 - 1433 | m | C-H asym. deformation | methyl group | 1450 ± 20 (m) | 1 |
| 1374 | 1373 | 1374 | 1375 - 1373 | s | C-H sym. deformation | methyl group | 1380 - 1370 (s) | 1 |
| 1262 | 1258 | 1260 | 1246 - 1232 | s | C-O stretch | acetate ester | 1250 - 1230 (s) | 1 |
| 1221 | 1222 | | | | unassigned | | | |
| | | 1189 | | s | P-O-C (aromatic) | triphenyl phosphate | 1242 - 1110 (s) | 2 |
| 1164 | 1166 | 1166 | 1164 - 1162 | s | C-O stretch | ether linkage | 1150 - 1060 (vs) | 1 |
| 1087 | 1065 | 1087 | 1085 - 1040 | s,b | C-O stretch | ether linkage | 1150 - 1060 (vs) | 1 |

TABLE 11.7 contd.

Frequency values and band assignments for cellulose acetate standards and Gabo samples identified as cellulose acetate

| cellulose acetate VA13 cm-1 | VA14 cm-1 | Bexfilm cm-1 | Gabo samples cm-1 | Intensity | Vibration | Functional group | Frequency range given in literature cm-1 | Ref. |
|---|---|---|---|---|---|---|---|---|
| 954(vw) | 954(vw) | 963 | 975 - 965 | s | P-O-C (aromatic) | triphenyl phosphate | 996 - 905 (s) | 2 |
| 905 | 904 | 904 | 907 - 904 | m | unassigned | | near 901 (m) | 3 |
| 840 | 841 | 839 | * 828 - 819 | m | unassigned | | near 837 (vw) | 3 |
| | | 782 | 785 - 761 | m | C-H out-of-plane deformation | aromatic ring | 810 - 750 (vs) meta-substitution | 1 |
| | | 760 | | m | | | | |
| | | | | | | | 770 - 735 (vs) ortho-substitution | 1 |
| | | | | | | | 770 - 730 (vs) mono-substitution | 1 |
| nr 692(vw) | 692 (vw) | 692 | 692 - 691 | m | C-H out-of-plane deformation | aromatic ring | 710 - 690 (s) mono-substitution | 1 |
| 605 | 604 | 604 | 607 - 603 | m | bending vibration | acetate group | 605 (m) | 3 |
| | | | | | skeletal vibration | acetate group | 612 (s) | 4 |

* Absorption is absent in some sample spectra.

1. Bellamy, 1975
2. Thomas and Chittenden, 1964
3. Hummel, 1966
4. Thompson and Torkington, 1945

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp; nr = near

TABLE 11.8

Frequency values and band assignments for casein and Gabo samples identified as casein

| Casein I | Gabo samples | | | | Vibration | Functional group | Frequency range given in literature | Ref. |
|---|---|---|---|---|---|---|---|---|
| RW1 | I-8 | II-12 | I-1 | JH31 | | | | |
| cm-1 | cm-1 | cm-1 | cm-1 | cm-1 | | | cm-1 | |
| | | | | 3539(sp) | unassigned | | | |
| | | | | 3488(sp) | unassigned | | | |
| 3287(s,b) | 3313(s,b) | 3291(s,b) | 3313(s,b) | 3311(s,b) | N-H stretch hydrogen bonded | peptide bond | 3320 - 3270(m) (trans-) | 1 |
| 3100(sh) | 3076(sh) | 3068(sh) | 3072(sh) | | amide II overtone | peptide bond | 3100 - 3070(w) (cis- and trans-) | 1 |
| 2962(m) | 2959(m) | 2959(m) | 2962(m) | 2962(m) | C-H stretch | methyl group | 2962 ± 10(s) | 1 |
| | 2932(m) | 2923(m) | 2931(m) | 2927(m) | C-H stretch | methylene group | 2926 ± 10(s) | 1 |
| 2876(m) | | | | | C-H stretch | methyl group | 2872 ± 10(s) | 1 |
| 2120(w) | | | | 2129(w) | unassigned | | | |
| 1661(s) | 1652(s) | 1661(s) | 1671(s) | 1659(s) | amide I C=O stretch | peptide bond | 1680 - 1630(s) | 1 |
| | | | | | amide I | peptide bond | 1656(vs) | 2 |
| 1546(s) | 1544(s) | 1544(s) | 1552(s) | 1549(s) | amide II - coupled N-H deformation and C-N stretch | peptide bond | 1570 - 1515(s) (solid) | 1 |
| | | | | | amide II | peptide bond | 1538(s) | 2 |
| | 1511(s) | 1507(s) | 1510(s) | 1508(s) | unassigned | | | |
| 1450(m) | 1453(s) | 1452(s) | 1452(s) | 1452(s) | C-H deformation | methyl and methylene groups | 1448(m) | 2 |
| 1400(m) | near 1400(m) | 1408(s,b) | 1409(s,b) | 1408(m) | C-O resonance bond | carboxylic acid ionized | 1399(m) | 2 |
| 1350(m) | | | | | unassigned | | | |
| 1315(m) | | | | | C-H deformation | methylene groups | 1312(w) | 2 |

TABLE 11.8 contd.

Frequency values and band assignments for casein and Gabo samples identified as casein

| Casein I<br>RW1<br>cm-1 | Gabo samples<br>I-8<br>cm-1 | <br>II-12<br>cm-1 | <br>I-1<br>cm-1 | <br>JH31<br>cm-1 | Vibration | Functional group | Frequency range given in literature<br>cm-1 | Ref. |
|---|---|---|---|---|---|---|---|---|
| 1241(m) | 1233(s) | 1231(s) | 1236(s) | 1225(s) | amide III - coupled N-H deformation and C-N stretch | peptide bond | 1305 - 1200(m) | 1 |
|  |  |  |  |  | amide III | peptide bond | 1242(m) | 2 |
| 1175(m) | 1177(m) | 1176(s) | 1176(m) | 1141(s) | unassigned |  | 1158(w) | 2 |
| 1106(m) | 1088(m) | 1084(m) | 1099(s) | 1081(s) | N-H deformation | peptide bond | 1101(m) | 2 |
|  | near 1050(m) | 1040(m) |  |  | unassigned |  |  |  |
| 950(w) |  | 1009(m) |  | 990(s) | unassigned |  | 980(m) | 2 |
| 900(w) |  | 880(m) |  | 873(s) | unassigned |  |  |  |
|  | 826(w) | 824(w) | 826(m) |  | unassigned |  |  |  |
|  |  | 793(m) |  | 797(s) | unassigned | broad area of absorption - see text |  |  |
| 703(b) |  |  |  |  | unassigned |  |  |  |
| 626(b) | 656(b) | 650(b) |  | 665(s) | unassigned |  |  |  |
| 569(b) | 540(b) | 532(b) | 559(b) | 577(s) | unassigned |  |  |  |

1. Bellamy, 1955
2. D'Esposito and Koenig, 1978

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp

TABLE 11.9

Frequency values and band assignments for poly (methyl methacrylate) standards and Gabo samples identified as poly (methyl methacrylate)

| Aldrich trans cm-1 | Plexiglass DR cm-1 | Perspex DR cm-1 | Gabo samples cm-1 | Vibration | Functional group | Frequency range given in literature cm-1 | Ref. |
|---|---|---|---|---|---|---|---|
| 2995 | 2997 | 2995 | 2998 - 2995 | C-H stretch | methyl group | 3010; 2976 | 2 |
| 2951 | 2952 | 2952 | 2953 - 2951 | C-H stretch | methyl group | 2962 ± 10 (s) | 3 |
| 2843 | 2844 | 2844 | 2852 - 2844 | C-H stretch | methylene group | 2853 ± 10 (s) | 3 |
| 1730 | 1734 | 1734 | 1739 - 1729 | C=O stretch | ester | 1750 - 1730 (s) | 3 |
|  | 1641 | 1601 |  | unassigned |  |  |  |
| 1484 | 1480 | 1479 | 1489 - 1485 | C-H deformation | methylene group | 1465 ± 20 (m) | 3 |
| 1450 | 1450 | 1448 | 1453 - 1451 | C-H asym. deformation | methyl group | 1450 ± 20 (m) | 3 |
| 1436 | nr 1430(sh) | nr 1430(sh) |  | C-H asym. deformation | methyl group | 1450 + 20 (m) | 3 |
| 1386 | 1389 | 1389 | 1389 - 1388 | C-H sym. deformation | methyl group | 1380 - 1370 (s) | 3 |
| 1273 | 1269 | 1270 | 1276 - 1271 | C-O stretch | ester | 1310 - 1250 (s) | 4 |
|  |  |  |  | unassigned |  | 1282 | 5 |
| 1242 | 1243 | 1241 | 1243 - 1239 | C-O stretch | ester | 1310 - 1250 (s) | 4 |
|  |  |  |  | unassigned |  | 1235 | 5 |
| 1193 | 1193 | 1194 | **1196 - 1195 | C-O stretch | ester | 1200 - 1100 (s) | 4 |
|  |  |  |  | unassigned |  | 1170 | 5 |
| 1150 | 1152 | 1154 | 1161 - 1153 | C-O stretch | ester | 1200 - 1100 (s) | 4 |
|  |  |  |  | unassigned |  | 1149 | 5 |
| 1065 | 1065 | 1065 | 1077 - 1066 (1) | unassigned |  |  |  |
| 990 | 991 | 992 | 991 - 990 | unassigned |  |  |  |
| 967 | nr 960(sh) | nr 960(sh) | * 968 | unassigned |  |  |  |
| 913 | nr 910(sh) | nr 910(sh) | * 915 - 911 | unassigned |  |  |  |
| 843 | 843 | 843 | * 844 - 843 | unassigned |  |  |  |

TABLE 11.9 contd.

Frequency values and band assignments for poly (methyl methacrylate) standards and Gabo samples identified as poly (methyl methacrylate)

| Aldrich trans cm-1 | Plexiglass DR cm-1 | Perspex DR cm-1 | Gabo samples cm-1 | Vibration | Functional group | Frequency range given in literature cm-1 | Ref. |
|---|---|---|---|---|---|---|---|
| 827 | nr 825(sh) | nr 825(sh) | * 828 - 827 | unassigned | | | |
| 811 | nr 810(sh) | nr 810(sh) | * 810 | unassigned | | | |
| | | | * 795 - 793 | unassigned | | | |
| 737 | 754 | 754 | 754 - 753 | unassigned | | 749 | 5 |
| 703 | | | | unassigned | | | |

* Absorption is weak or does not appear in some spectra  ** Absorption only appears in sample spectra I-19 and II-10.

1. Band appears at 1035 cm-1 in spectrum of sample II-8
2. McKean et al., 1973
3. Bellamy, 1975
4. Colthup, 1950
5. Urbanski et al., 1977

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp; nr = near

TABLE 11.10

Frequency values and band assignments for plasticizer standards and unknown 'sweat' samples

| JH4<br>cm-1 | JH5<br>cm-1 | JH34<br>cm-1 | JH40<br>cm-1 | Triphenyl phosphate cm-1 | Sulphon-amide* cm-1 | Diethyl phthalate cm-1 | Vibration | Functional group | Frequency range given in literature (1) cm-1 |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | 3281(s) | | | unassigned | |
| | | | | 3097(w) | | | C-H stretch | aromatic carbon | 3070 and 3030(w) |
| 3070(w) | near 3070(w) | near 3070(w) | 3070(w) | 3059(m) | 3064(w) | 3072(w) | C-H stretch | aromatic carbon | 3070 and 3030(w) |
| | | | | 3019(w) | | | C-H stretch | aromatic carbon | 3070 and 3030(w) |
| | | | 2980(w) | | 2960(m) | 2983(s) | C-H stretch | methyl group | 2962 ± 10(s) |
| 2931(m) | 2918(m) | near 2900(w) | 2936(w) | | 2934(m) | 2939(m) | C-H stretch | methylene group | 2926 ± 10(s) |
| | | | | | | 2906(m) | C-H stretch | methine group | 2890 ± 10(w) |
| 2891(m) | | | 2882(w) | | 2874(m) | 2874(m) | C-H stretch | methyl group | 2872 ± 10(s) |
| 2821(w) | | | 2821(w) | | | | unassigned | | |
| | | | | 1739(w) | | | unassigned | | |
| 1728(s) | 1726(s) | 1726(s) | 1727(s) | | | 1728(s,b) | C=O stretch | ester, aryl | 1730 - 1717(s) |
| | | | 1597(sh) | 1598(s) | 1599(m) | 1600(s) | skeletal ring stretch | aromatic ring | 1625 - 1575(va) |
| 1590(m) | 1590(m) | 1588(m) | 1589(m) | 1588(s) | | 1580(s) | skeletal ring stretch | aromatic ring | 1600 - 1560(w unless conjugated) |
| 1489(s) | 1489(s) | 1488(s) | 1489(s) | 1484(s) | 1495(w) | 1488(m) | skeletal ring stretch | aromatic ring | 1525 - 1475(va) |
| | | | | | | 1476(s) | C-H asym. deformation | methyl group | 1450 ± 20(m) |
| 1450(m) | | | 1457(m) | 1455(m) | 1453(m) | 1466(s) | | | |
| | | | | | 1426(m) | 1448(s) | C-H deformation | methylene group | 1465 ± 20(m) |
| | | | | | | | skeletal ring stretch | aromatic ring | near 1450((m) |
| 1405(w) | | | 1405(w) | | | | unassigned | | |
| | | | | 1384(w) | 1383(m) | 1391(s) | unassigned | | |
| 1369(m) | | | 1369(w) | | | 1369(s) | C-H sym. deformation | methyl group | 1380 - 1370(s) |

TABLE 11.10 contd.

Frequency values and band assignments for plasticizer standards and unknown 'sweat' samples

| JH4<br>cm-1 | JH5<br>cm-1 | JH34<br>cm-1 | JH40<br>cm-1 | Triphenyl phosphate<br>cm-1 | Sulphon- amide*<br>cm-1 | Diethyl phthalate<br>cm-1 | Vibration | Functional group | Frequency range given in literature (1)<br>cm-1 |
|---|---|---|---|---|---|---|---|---|---|
| 1339(m) | | | | | 1325(s) | | S=O stretch | sulphonamide | 1358 - 1336(s) |
| | | | | | 1306(sh) | | unassigned | | |
| | | | | | 1290(sh) | | unassigned | | |
| 1289(s) | 1287(s) | 1294(s) | 1289(s) | 1295(s) | | 1284(s,b) | P=O stretch | phosphate | 1300 - 1250(s) |
| | | | | | | | C-O stretch | phthalate ester | 1310 - 1250(s) |
| | | | 1227(m) | 1233(m) | | | unassigned | | |
| 1188(s) | 1188(s) | 1187(s) | 1188(s) | 1194(s) | 1185(w) | | P-O-C (ar)/ | phosphate | 1242 - 1110(s) (2) |
| | | | | | | | P-O stretch | aromatic | |
| | | | | 1176(s) | | 1174(s) | C-H in-plane | aromatic ring | 1225 - 950(w) |
| | | | | | | | deformation | | |
| 1163(s) | near 1160(s) | 1163(s) | 1162(s) | 1162(s) | 1161(s) | | S=O stretch | sulphonamide | 1169 - 1152(s) |
| | | | | 1153(s) | | | unassigned | | |
| 1123(s) | 1124(s) | near 1125(m) | 1124(s) | | 1120(m) | 1124(s) | C-O stretch | phthalate ester | 1150 - 1100(s) |
| | | | 1094(m) | | 1094(s) | 1097(s) | C-H in-plane | aromatic ring | 1225 - 950(w) |
| 1073(s) | 1073(s) | near 1080(m) | 1072(s) | 1071(m) | 1067(w) | 1074(s) | deformation | | |
| 1041(m) | near 1040(m) | near 1040(w) | 1041(m) | 1030(s) | 1037(w) | 1041(s) | | | |
| 1026(m) | near 1025(m) | near 1025(m) | 1026(s) | 1023(s) | 1019(w) | 1018(s) | | | |
| 1011(m) | 1011(s) | 1010(s) | 1011(s) | 1009(s) | | | | | |
| | | | | 981(s) | | | P-O-C (ar) | phosphate | 996 - 905(s) (2) |
| 961(s) | 959(s) | 954(s) | 964(s) | 953(vs) | 948(w) | 963(w) | | aromatic | often complex |
| | | | | 931(s) | | | | | |
| | | | 906(w) | 913(s) | | 893(w) | | | |
| 866(m) | | | 866(w) | | 864(w) | 864(m) | unassigned | | |
| | | | | 846(w) | | 847(m) | unassigned | | |
| | | | | 835(w) | | | unassigned | | |

TABLE 11.10 contd.

Frequency values and band assignments for plasticizer standards and unknown 'sweat' samples

| JH4<br>cm-1 | JH5<br>cm-1 | JH34<br>cm-1 | JH40<br>cm-1 | Triphenyl phosphate cm-1 | Sulphon- amide* cm-1 | Diethyl phthalate cm-1 | Vibration | Functional group | Frequency range given in literature (1) cm-1 |
|---|---|---|---|---|---|---|---|---|---|
| | | | 817(w) | | 815(s) | | unassigned | | |
| | | | | 787(s) | | | unassigned | | |
| 779(m) | 770(m) | 770(m) | 778(s) | 770(s) | 767(w) | | C-H out-of-plane | aromatic ring | 770 - 730(vs) |
| 747(m) | 753(s) | near 750(m) | 755(s) | 752(s) | | | deformation | | mono-substitution |
| | | | | | | 745(s) | C-H out-of-plane | aromatic ring | 770 - 735(vs) |
| | | | | | | | deformation | | ortho-substitution |
| 706(w) | | | 714(w) | | 707(m) | 706(s) | C-H out-of-plane | aromatic ring | 710 - 690(s) |
| 690(m) | 689(s) | 690(m) | 689(s) | 691(s) | | 692(sh) | deformation | | mono-substitution |
| 652(w) | | | 663(w) | | 664(s) | 651(m) | unassigned | | |
| 618(w) | | | 617(w) | 616(w) | | | unassigned | | |
| | | | 595(w) | 596(w) | | | unassigned | | |
| 579(m) | | | 573(m) | 579(s) | 572(s) | | unassigned | | |
| | | | 551(m) | 564(s) | 551(s) | 563(m) | unassigned | | |
| 520(sh) | | | 519(m) | 519(s) | | | unassigned | | |

* N-ethyl o,p-toluenesulphonamide (Monsanto)

1. Bellamy, 1975
2. Thomas and Chittenden, 1964

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp

# CHAPTER 12 POLYMER DEGRADATION MECHANISMS

## Introduction

A detailed study of the degradation of polymers was not undertaken in this research. However, most samples which are examined in the conservation context will have undergone some degradation and a brief discussion of degradation mechanisms is appropriate.

Degradation is defined as a change of properties or loss of characteristics which generate the specific requirements necessary for the product to fulfil its desired function (Crighton, 1988). The most important characteristic is mechanical performance. In the polymer industry, it is necessary to produce materials with mechanical properties which are specific to its intended use. The mechanical properties are dependent on the polymer type, length of polymer chain and the structural arrangements of the molecules such as areas of crystallinity, cross links between chain and preferred orientation of the chains affect the properties (Crighton, 1988). A variation in molecular size, namely chain length, has the greatest effect on properties and these changes in turn affect the chain interactions and areas of ordered structure.

Variations in appearance resulting from creation or loss of a chromophore can be undesirable and are considered to be degradation (Crighton, 1988). This is especially true in works of art and objects in museum collections.

Some of the properties which are affected by chain length include strength, toughness, elasticity, abrasion resistance, processability and clarity (in films). Breakage of bonds in the polymer backbone causes changes in mechanical properties. There are two types of reactions, a step reaction and a chain reaction. The step reaction involves breakage of bonds in random locations in the chain to produce large fragments. This results in a rapid alteration of the properties which are dependent on chain length as only a few reactions are needed to reduce the chain length by 50%. In the chain degradation mechanism, the terminal backbone linkage is repeatedly broken producing the monomer. It has been described as an unzipping depolymerization. This is a slower degradation process as 50% of the reactions must occur before the chain length is reduced by half. The crosslinks between polymer chains affect the mechanical properties and are also affected by the step degradation process. Crosslinks give strength and elastic recovery and prevent excessive movement of the chains. There is a favoured concentration of crosslinks for desired properties and an excess causes greater stiffness and brittleness. Thus, the rapid reduction of chain length by random scission will result in a higher percentage of crosslinks for each molecule (Crighton, 1988).

### Sources of energy for bond scission

Chemical bond scission requires a discrete amount of energy. In certain molecules there are imperfections in the chain structure which often provide weak bonds which are more susceptible to breakage. Thus, the energy required is reduced. The sources of energy are mechanical, thermal or electromagnetic radiation. The energy from the ultraviolet region (<320 nm) causes much damage and is a major source of degradation energy. Chemical reactions also cause degradation by weakening links in the back bone or by direct reaction with the bond. Examples of chemical reaction include hydrolysis which occurs in the presence of water and oxidation which requires oxygen or ozone (Crighton, 1988).

Hydrolysis is the reverse of the reaction used to produce polymers by the condensation process. Water is often a byproduct of condensation polymerization and polymers such as polyesters and polyamides which are produced by condensation are particularly subject to hydrolysis by scission of the ester or amide backbone linkages. The rate of degradation is controlled by the severity of the environmental conditions, the chemical structure of the monomer units and the ease of access of the linkages to the reactive agents (Crighton, 1988).

Thermal or heat energy is a second source of energy which can break chemical bonds. Weak bonds due to structural irregularities and "activated" bonds in the polymer backbone are susceptible to thermal degradation. In addition-type polymers, thermal degradation produces one polymer chain with a free radical end which is very reactive. In polymers which are produced by a free radical initiated chain reaction, the presence of a free radical end can cause a depolymerization or unzipping reaction. The chain length of the polymer gradually reduces and monomers are liberated. Poly (methyl methacrylate) is particularly susceptible to thermal degradation, the polymers is entirely reduced to monomer units where poly (ethylene) is only degraded by 3%. Other degradation reactions can be caused by thermal energy. For example, poly (vinyl chloride) loses hydrochloric acid. After a large amount of the acid is lost, the remaining polymer absorbs energy from the visible region of the electromagnetic spectrum and the residual polymer darkens and turns black (Crighton, 1988).

The presence of oxygen increases the rate of thermal degradation. The oxygen reacts chemically at the reactive sites in the polymer chain causing backbone scission. Areas of unsaturation in the polymer chain are susceptible to oxidation. Peroxides are easily attacked at the O-O bond and a very reactive free radical is formed. This type of reaction is accelerated by heat, light or metal ions. The free radicals which are produced then react with other polymer chains causing further degradation. The rate of degradation is related to both the chemical structure of the polymer system and the physical changes which result from the degradation. Thus, there is no antioxidant which will be efficient for all polymers. In vulcanized rubber, the crosslinks are sensitive to heat and oxygen. The properties of rubber are severely affected by the number of crosslinks and too few or too many result in a degraded product. Ozone which is present in the atmosphere in small quantities and other materials such as oxidizing acids ($H_2SO_4$) can have the same effect (Crighton, 1988).

When a molecule is exposed electromagnetic radiation, the molecule absorbs some of the energy and becomes 'excited'. The energy in the region 290 - 400 nm is the most critical as many of the bond energies fall within this region. If the radiation is equal to the bond energies of 'weak' chemical bonds due to structural irregularities, the bond may break. Also, free radical species are often produced by this reaction which cause further chain scission. The free radicals are referred to as photo-initiators. Additives in the polymer matrix such as dyes, pigments, delustrants and other additives. can also act as sensitizers when they absorb light energy and transfer it to the polymer by molecular collisions. Impurities which include residues of catalysts used in the polymerization, trace metals absorbed during productions or processing and atmospheric pollutants have a similar sensitizing effect (Crighton, 1988).

If the impurity in the polymer structure when activated by the light energy removes a hydrogen atom from the polymer creating a radical which then in turn may remove a hydrogen atom from another chain. It can also react with oxygen in the air or form a crosslink with another polymer radical (Crighton, 1988).

Photo-oxidation is a chain reaction which creates further light absorbing molecules which cause degradation. Thus, the presence of only a few radicals can result in a significant variation in the mechanical properties of the polymer (Crighton, 1988).

The oxidation reaction also forms carbonyl groups which are potentially very reactive and after a quantity is formed, they absorb a large amount of active incident light. This energy absorption causes bond scission or it may activate another oxygen molecule which causes further oxidation (Crighton, 1988).

When polymers are subjected to tensile stress, the polymer chains which are in an amorphous arrangement are extended which causes strain in localized lengths. These bonds are more reactive and susceptible to attack. It is possible to observe localized differences in degradation rates in strained fibres and fabrics (Crighton, 1988).

Plasticizers modify mechanical properties of polymers such as stiffness and hardness (Chapter 9). They are only active in the amorphous areas within the polymer. With mobile chains, some of the plasticizer is lost by diffusion over time which will change the properties. Fillers such as carbon black, which are added to reinforce polymer systems, result in increased stiffness, strength, toughness and abrasion resistance. This occurs due to forces between the additive molecules and those of the polymer Loss of filler additives will also alter the properties. Liquids which come into contact with polymers cause them to swell and extract additives (Crighton, 1988).

Polymers of natural origin, such as cellulose or protein derivatives, are also susceptible to bacterial and insect attack in a warm and moist environment. Polymers may be treated by an insecticide or a bacteriocide and should be stored in a dry cool air environment to retard degradation (Crighton, 1988).

## Degradation of plastics

### Cellulose nitrate

Cellulose nitrate is affected by both thermal and photochemical decomposition. In thermal degradation, it is thought that the primary reaction is the breaking of the N-O bond of the nitrate ester (Sirkis, 1982).

$$R{-}O{-}NO_2 \longrightarrow R{-}O\bullet + NO_2\uparrow \qquad \text{(Equation 12.1)}$$

However, the secondary reactions are not fully understood. One possible situation is that the free radicals may form an aldehyde and an alcohol (Equation 12.2).

$$R{-}O\bullet + R{-}O\bullet \longrightarrow ROH + RCHO \qquad \text{(Equation 12.2)}$$

The free radical may attack the remaining nitrate to form an aldehyde and $NO_2$ gas.

$$R{-}CH_2{-}O\bullet + R{-}CH_2{-}O{-}NO_2 \longrightarrow R{-}CH_2{-}OH + R{-}\dot{C}H{-}O{-}NO_2 \qquad \text{(Equation 12.3)}$$

$$R{-}\dot{C}H{-}O{-}NO_2 \longrightarrow R{-}CHO + NO_2\uparrow \qquad \text{(Equation 12.4)}$$

where $R{-}\dot{C}H{-}O{-}NO_2$ is a radical nitrate (Sirkis, 1982).

The reactions are strongly exothermic at room temperature and are autocatalyzed by unstable sulphate esters which are formed as a byproduct of the nitration, residual acids remaining from the nitration, and free radicals. The presence of moisture further accelerates the degradation as moisture swiftly converts the $NO_2$ to nitric acid which causes additional denitration and hydrolysis of the cellulose chain. It is thought that the glucose ring is destroyed as well (Ott, 1943). The number of terminal aldehydes which are possible reducing agents is increased each time the cellulose chain is shortened.

Ultraviolet radiation is thought to cause dramatic colour changes to cellulose nitrate by the production of nitrogen dioxides. Photochemical degradation also causes scission of the backbone bonds which results in a loss in viscosity and embrittlement. All of the wavelengths in the ultraviolet result in denitration. Shorter wavelengths, however, cause changes in viscosity and the most rapid change is seen with light of 253.6 nm. The presence of oxygen with light causes photo-oxidation and fluctuating environmental conditions increase the rate of degradation. The exact reactions of photodegradation are not fully elucidated. They are thought to be a series of peroxide and free radical reactions (Sirkis, 1982).

The cellulose chain is sensitized by metal ions, anthraquinone dyes, azo dyes, reactive and dispersive dyes which make the material more sensitive to ultraviolet radiation. The mechanism for the sensitization can be represented either by Equation 12.5

$$\text{DYE} + O_2 \xrightarrow{\text{light}} O_2^* + \text{DYE}^* \qquad \text{(Equation 12.5)}$$

or by Equations 12.6 and 12.7

$$\text{DYE} \xrightarrow{\text{light}} \text{DYE}^* \qquad \text{(Equation 12.6)}$$

$$\text{DYE}^* + \text{Cell-H} \rightarrow \text{Cell}^* + \text{DYE-H} \xrightarrow{O_2} \text{Cell}^*\text{-}O_2 \qquad \text{(Equation 12.7)}$$

The metal ions are incorporated into the cellulose as trace metals and catalyst residues from the production method and these "foreign atoms" are found in most polymers after production (Crighton, 1988).

It is interesting to note that as the most complete experiments on cellulose nitrate degradation have been performed with pure uncombined cellulose nitrate, the effect of camphor is not known. It has been assumed that camphor could be involved in a number of possible reactions. The role of camphor in cellulose nitrate degradation should be studied to obtain a better understanding of cellulose nitrate deterioration (Sirkis, 1982).

The progress of cellulose nitrate film degradation has been studied and the stages are documented. The stages of object deterioration are more complex because of compositional differences such as the presence of fillers, dyes, and stabilizers and the shape of the object. Also, the production method and what the object was utilized for will have an effect on the degradation and will differ from object to object. The first sign of deterioration may be observed in the packing materials. Paper, which is mainly composed of cellulose, is sensitive to gaseous $NO_2$ and the hygroscopic nature of the paper provides a matrix for the manufacture of nitric acid from the NO2 given off by the objects (Weseloh, 1981). The paper darkens and/or becomes brittle. Acid-free tissue paper can almost completely disintegrate after contact of less than 48 hours with actively deteriorating cellulose nitrate. Other observable deterioration in objects include increased brittleness, cracking, discolouration, especially yellowing, a greasy feel on the surface, droplets of sticky moisture appearing on the surface and a strong odour. More severe degradation includes excessive warping and cracking and a characteristic crizzling pattern. The object may after a time completely fall apart (Sirkis, 1982).

The conventional dispersive infrared analysis of cellulose nitrate in the Sirkis study did not show any marked changes between the spectra of visibly stable and degraded material. No new bands were formed and there was no evidence of major destruction of the glucose rings or of the ether linkages between them. Nor was there any evidence of aldehyde formation. Another study using FT-IR to analyse artificially aged fresh cellulose nitrate films concluded that there were no differences apparent in the spectra of six modern cellulose nitrates after heat or light ageing. However, there was some visible yellowing of the samples (Green and Bradley, 1988). In the same study, severely deteriorated cellulose nitrate Somali beads were examined. The degradation was not uniform and there were three deterioration 'zones' which were straw coloured, dark yellow and brown which were analysed separately by FT-IR. The spectrum of the brown material did show evidence of degradation. The bands which are due to the nitrate bonds were much less intense in relation to other bands in the spectrum than in the straw coloured material or the other cellulose nitrate sample spectra. The ratio of the carbonyl peak height to that of the nitrate band in the region of 1660 $cm^{-1}$ is higher in the spectrum of the brown sample than in that of the straw coloured sample. The authors concluded that the age of the sample does not seem to be related to the degree of deterioration and that the non-uniformity of the deterioration seems to be due to the bulk of the sample (Green and Bradley, 1988).

The results of the studies by Sirkis (1982) and Green and Bradley (1988) are similar to those observed in this research. No strong evidence of degradation can be seen in the spectra. The Tate samples JH17 and JH18 are described as crizzled, but there are no major variations between the spectra of the samples and those of the visibly undegraded cellulose nitrate and the cellulose nitrate standards. The Gabo sample D was very yellowed, but no change was observed in the spectrum (see Chapter 11).

### Cellulose acetate

Cellulose acetate is generally considered to be more stable than cellulose nitrate and shortly after it was invented, it was widely used as a replacement for cellulose nitrate. Since the early 1950's, cellulose triacetate has completely replaced cellulose nitrate as an archival material for cinema and photographic film. It is one of the few polymer systems which meets specifications for use as a photographic film support as it is considered to have archival permanence (physical and chemical stability over long periods of time when stored under a controlled environment). Images from older cellulose nitrate films have been transferred to cellulose acetate film. However, it is now evident that cellulose acetate is also subject to degradation. The decomposition is characterized by the release of acetic acid when the film container is opened and by the appearance of liquid/crystalline plasticizer deposits on the surface of the film. The phenomenon has become known as the "vinegar syndrome" in the film industry (Allen et al., nd).

The degradation mechanism of cellulose acetate is described as a deacetylation reaction in which acid is produced, which in turn causes chain scission. As the acetate groups are lost, and subsequently, the degree of substitution is lowered, the rate of reaction increases. Thus, an autocatalytic effect similar to that in cellulose nitrate degradation seems to be occurring. The reaction is thought to be acid catalyzed as the maximum rate of hydrolysis occurs at a pH of 4 and the degradation increases with increasing moisture concentration and temperature (Edge et al., 1988).

Work is being carried out on degradation of photographic film (Allen, et al., 1988; Edge, et al., 1988). Samples of naturally aged and artifically aged films were analysed. The study found that the rate of degradation was higher in the presence of 1M acetic acid than in 100% RH and that the slowest rate was observed in dry conditions. It was also found that the rate of degradation increases with increasing temperature and that the atmosphere is more critical than the temperature in degradation. The presence of acetic acid accelerates or perhaps catalyzes the hydrolytic degradation of the films. The effect of film storage materials were also examined and the enclosure of reels in metal storage cans was found to accelerate the degradation. Analysis of cross sections revealed that degradation was more extensive near to the spool and at the outer edges of the reel where the film would come into contact with the metal. The degradation of polymeric materials is known to be catalyzed by transition metals such as iron and decomposition was observed to be delayed by the use of inert glass containers. The emulsion layer was observed to inhibit deterioration of the base polymer to a certain extent, probably due to its acting as an acid neutralizer.

Plasticizers are used in cinematographic film to make the base more flexible. Triphenyl phosphate is usually used at a concentration of 20% of the weight of the acetate base. Diffusion or migration of the plasticizer was found to be associated with hydrolysis and deacetylation of the film and was observed to be dominant in the regions of the film reel which show higher moisture regain after dessication. White crystalline deposits, which were identified as triphenyl phosphate, were found on films which have characteristics of lowered acetyl content (i.e. high degree of insoluble polymer, high moisture regain and low pH) (Edge et al., 1988).

The results of the study support the mechanism of acid catalyzed hydrolytic deacetylation and degradation of the polymer structure and the subsequent loss of plasticizer. Moisture absorption was found to be the most important controlling factor in the decomposition process. Also, the build up of acetic acid in the film containers is thought to promote the degradation.

The stability of cellulose acetate is related to its structure. Different degrees of substitution result in differences in physical and chemical properties. Solubility can be used to distinguish between undegraded cellulose triacetate and diacetate. Cellulose triacetate with a substitution factor of 2.7 is soluble in methylene chloride/methanol and insoluble in ketonic solvents where the diacetate with a substitution factor of 2.3 is soluble in ketonic solvents such as acetone and not soluble in the methylene chloride/methanol solution (Edge et al., 1988). The absorption of moisture by cellulose acetate is attributed to hydrogen bonding between water molecules and available hydroxyl groups of the glucose units. The greater the degree of substitution, the lower the uptake of moisture ( Edge et al., 1988). The chemical stability of cellulose diacetate was found to be lower than that of cellulose triacetate. Analysis of cellulose diacetate and cellulose triacetate dispersed in buffer solutions of pH rangeing from 2 - 10 at 30 °C indicated that the overall rate of hydrolysis was faster for the diacetate than that of the triacetate. This is an important consideration as the degradation mechanism in cellulose acetate is thought to be a hydrolysis reaction.

The initial methods used in the studies (Allen et al., 1988; Edge et al., 1988) were infrared and Fourier transform infrared spectroscopy. The spectroscopic methods were not successful owing to the thickness of the photographic film and its insolubility in the later stages of degradation (Allen et al., 1988). It was decided that cast thin films from a solvent would not be used as it would not be indicative of the real situation and because of the solubility problems of the heavily degraded film stock. Also, thin films that were made were poor in quality and there was a loss in clarity (Allen et al., 1988). The infrared results did not give detailed data on the changes in structure due to degradation. No obvious chemical or functional group variation was noted in the spectra. Only small decreases in acetate content and "variable" qualitative change in the hydroxyl region were seen. Thus, indirect measurement of deacetylation was made by monitoring changes in physical properties. This included changes in moisture regain, solubility, and pH (formation of free acetic acid) and the molecular weight was measured by dilute solution viscometry which gave an indication of chain scission.

The degradation of cellulose acetate used in Gabo's sculpture "Construction in Space, Two Cones" has been recorded. The sculpture was made in 1968 as a replica of a piece originally constructed in 1937 (material unidentified) which had fallen apart. The replica was produced from a variety of cellulose acetate sheets of different thicknesses and colours which are joined together with a solvent based adhesive. The deterioration of the replica has been described (Pullen and Heuman, 1988) as follows:

1. Distortion and warping without damage to adhered joints (1982).
2. Acetic acid odour (first detected in 1982).
3. The appearance of small beads of an oily substance on the laminate base (2/87).
4. Minor crack appeared on base (5/87).
5. Severe cracking and delamination on base, pH 3.5 (6/87).
6. Advanced deterioration and internal cracking (12/87).

The changes which are due to oxidation and hydrolysis are thought to have been occurring over a long period of time even when the sculpture appeared stable. The deterioration seems to be related to the induction phenomenon which has been observed in studies of organic polymer degradation (Pullen and Heuman, 1988). During the induction period, apparent stability suddenly ceases and rapid deterioration is observed. In the "Two Cones" piece, the warping and cracking of the base has completely changed it from its original form and it was necessary to make detailed photographic documentation. Little research has been done on the effect of light on cellulose acetate. It is thought that ultraviolet and possibly visible radiation can supply the activation energy for degradation reactions of oxidation and chain scission. As stabilizers are lost or altered over time, the polymer system is more vulnerable to photolytic degradation (Pullen and Heuman, 1988).

There are several factors which might have affected the stability of the "Two Cones" sculpture. The composition of the material is important. As mentioned earlier, the triacetate form is more stable, but the use of triacetate has in the past been limited to the production of photographic film and fibres. The sheet acetate used in the sculptures is thought to be the diacetate which is inherently less stable. Stability varies from batch to batch and may be masked by the addition of stabilizers (Pullen and Heuman, 1988).

Additives such as fillers, pigments, anti-oxidants and ultraviolet light absorbers are added to cellulose acetate to change properties and extend the lifespan of the product. Additives influence polymer stability, but are gradually lost over time by evaporation, volatilization on heating, or leaching out by water or other solvents. This results in brittleness, shrinkage, warping and lower resistance to moisture penetration (Pullen and Heuman, 1988). A lower resistance to moisture will lead to hydrolysis of the polymer material.

A third element affecting stability is the environmental history of the object. The "Two Cones" piece was exposed to a wide range of unrecorded conditions (temperature, relative humidity and light levels) before coming to the gallery and was subjected to some variations afterwards. The original "Two Cones" was kept in an air-tight case for many years and when the case was removed, a strong odour was noted and cracks developed on parts of the piece. On the following day, the base and the thick centre section were shattered. The Tate replica had also been kept stored under an acrylic cover and acetic acid was detected as having built up. Attempts were made to ventilate the piece, but the degradation continued. The cover was removed, but rapid deterioration has followed (Pullen and Heuman, 1988).

It is interesting to note that although the replica was made 40 years after the original, the initial degradation appeared in the same area. The first signs of break-down occurred on the laminated structure of the base. The sculpture base was constructed with a 4 mm thick transparent sheet "sandwiched" between two opaque black layers adhered with a solvent based acrylic adhesive system. It is thought that internal stresses are created by shrinkage as the solvent evaporates from the laminated joint and are relieved by cracking. The stresses remain locked into the polymer and make the system more susceptible to degradation (Pullen and Heuman, 1988).

In the artificial weathering tests, beads of exudate were only visible on the surface of samples kept at 100% RH at 50° C and 19° C. At 50 ° C, sweat appeared after 5 days followed by severe cracking and yellowing. At 19 ° C, plasticizer appeared after 16 days and slight cracking occurred without colour change. However, although 0% RH has been recommended for photographic film, the 4 mm thick samples which were exposed to 35% RH exhibited severe cracking. Gradual reconditioning of samples from 50 to 40 ° C over 72 hours has resulted in samll cracks extending inwards from the cut edges. The effect of cyclic variations of humidity have not yet been investigated (Pullen and Heuman, 1988).

As with the cellulose nitrate samples, no strong evidence of the cellulose acetate degradation can be seen in the diffuse reflectance spectrum of the samples taken from "Construction in space, Two cones", JH13 (transparent grey) and JH15 (black). In the Gabo plastic sample G (see chapter 11), there is strong evidence for the hydrolysis of the acetate ester bond on the surface of the unaged sample and the aged sample. The degradation did not seem to be uniform throughout the sample. The question remains as to why the sample spectra from the actively degrading sculpture did not show evidence of degradation. As mentioned before, only a few random breaks in the backbone polymer chain drastically reduces the molecular weight and adversely affects the physical properties of the plastic. The plastics used in the sculpture have been subjected to stresses that the samples have not, and a change in the physical properties may be more evident in the material subjected to stress. The number of broken ester linkages needed to catalyze or accelerate the degradation are probably just a few of the total within the molecule and the loss of the ester linkages would not be seen in the spectrum until after the degradation has proceeded to a large degree.

## Casein

The casein samples from the Gabo pieces seem to be in good condition (Pullen and Heuman, 1988) and casein is considered to be fairly stable. Casein is hygroscopic and tends to warp and shrink in warm, dry conditions (Langton, 1943; Yarsley, 1943). Thus, extreme environmental conditions are harmful, but ambient conditions seem to be satisfactory for the plastic. As no acids are involved in the production method for obtaining casein by the rennin method or by the hardening process, there does not seem to be an inherent risk of autocatalyzed degradation. The chemical reactions involved in compounding the plastic and hardening with formaldehyde seem to affect the conformation of the protein and cause crosslinking between elements along the chain. They do not seem to derivatize the protein as in the modification of cellulose. Additives such as dyes or pigments may affect long term stability which has not become evident as yet.

The Gabo sample plastic E which was identified as casein returned to almost the same size after expansion during ageing in high humidity. The material seems to recover from the ageing process. This situation is not realistic for objects as stresses in construction would cause cracks and warping. There are also differences in the diffuse reflectance spectra measured before and after the artificial ageing. Namely, the sharp bands which appear in the region of 3600 $cm^{-1}$ in the aged sample spectra which indicate that water molecules have been incorporated into the structure. The spectrum of the aged plastic does not show any evidence of significant amino acid production which would indicate hydrolysis of the protein chain.

### Poly (methyl methacrylate)

Poly (methyl methacrylate) is considered to be extremely stable. The longterm stability may be due to the fact that the structure is less susceptible to autocatalyzed degradation. Acid is used in the production of the monomer, but care is taken in its removal. Also, potential acid forming functional groups in the structure seem to be more stable. However, surface crazing has been observed on several of the Gabo sculptures and the archive piece which have been identified as poly (methyl methacrylate) (Pullen and Heuman, 1988). Several organic materials such as aliphatic alcohols (but not solvents) cause crazing and cracking in poly (methyl methacrylate)(Brydson, 1975; ICI 1987). The crazing in the Gabo pieces is thought to be due to treatment with propan-2-ol. Isopropyl alcohol was "commonly used" to clean Gabo's work (Pullen and Heuman, 1988).

# CHAPTER 13 SURVEY OF OBJECTS FROM THE PLASTICS HISTORICAL SOCIETY

## Introduction

A series of plastic objects from the collection of the Plastics Historical Society was surveyed using silicon carbide paper and diffuse reflectance spectroscopy. The objects which were selected for analysis were stamped or marked with a patent or trademark which enabled identification of the material and an approximate date. In some cases, the objects were identified on the basis of examination by plastic experts (Plastics Historical Society, Publishers of "Plastiquarian - Journal of the Plastics Historical Society). The collection was to form a reference library for the identification of a wide range of early plastics. The types of plastic identified may be separated into three major groups, natural plastics, semi-synthetic plastics and synthetic plastics.

## Natural plastics

### Proteins

This group includes protein containing materials such as horn and tortoiseshell which were discussed in chapter 8. Three objects identified as horn by Colin Williamson (Plastics Historical Society were sampled. They included a black stamp seal in the shape of a bust of John Wesley (PHS25) which was marked 'John Wesley Centenary, 1839', a black broach in the shape of a wreath (PHS26) which was marked 'reg. 18/5/1880' and a bow shaped broach (PHS27) with mother-of-pearl inlay which was stamped 'reg. 13/10/1880'. A spectrum of tortoiseshell was obtained from a hairbrush made from Hawksbill turtle (PHS55). The results are summarized in chapter 8.

Other natural products which have been used as moulding materials include gutta percha, rubber and shellac. The composition of these materials have been discussed in earlier chapters. Another protein, albumen, was also utilized. These materials are discussed in the following section.

### Gutta percha

Three objects of gutta percha of early date were sampled in addition to one example of modern gutta percha. The first example was an inkwell (PHS1) marked 'Gutta Percha Co. Patent' (c. 1860's), the second was a medallion (PHS2) marked 'Gutta Percha Company London' (c. 1860's), and the third was a photo frame (PHS3) impressed with 'Hancock's Patent West Ham, Essex' (c. 1850). The modern sample was a Silvertown Dental Impression

Sheet (1987)(PHS4). The three older samples were resinous and crystalline. Two samples were removed from the inkwell, one from the rough surface on the base and the second one from the rim around the inkwell where the black lacquer had broken away. A sample was taken from the medallion and the frame in a location where the brown coating had worn away to prevent the possibility of contamination from the lacquer and to minimize the damage to the object.

The spectra of the three older objects were observed to be very similar to each other and very different from that of the modern sample. The first three sample spectra are marked by several strong, broad bands in the regions 3452 - 3384 $cm^{-1}$, 2971 - 2970 $cm^{-1}$, 2942 - 2932 $cm^{-1}$, 1714 - 1712 $cm^{-1}$, 1453 - 1452 $cm^{-1}$, 1380 - 1379 $cm^{-1}$ and a broad, indistinct absorption with maximum intensities in the regions of 1172 - 1170 $cm^{-1}$ and 1097 - 1051 $cm^{-1}$ (Figure 13.1a). A weak absorption is evident in the area 1320 - 1319 $cm^{-1}$ and near 803 - 801 $cm^{-1}$. The region from 800 to 400 $cm^{-1}$ in the spectra is a broad area of absorbance with several weak bands. The band in the carbonyl region (1714 - 1712 $cm^{-1}$) has a distinct shape. The band has a slight shoulder in the region of 1770 $cm^{-1}$ and a stronger shoulder in the region near 1660 $cm^{-1}$.

The spectrum of the modern material is similar to those of the other gutta percha samples in the region 4000 - 1800 $cm^{-1}$. However, the carbonyl region of the modern material contains a series of bands which are less intense in relation to the remaining bands in the spectrum and exhibit frequencies of 1711, 1663, 1625 and 1600 $cm^{-1}$. This is in sharp contrast to the corresponding region in the older samples. In the modern sample spectrum, there are bands at 1449 and 1381 $cm^{-1}$ and a broad area of absorption with maximum absorptions at 1207, 1105 and 1032 $cm^{-1}$. The region from 950 to 400 $cm^{-1}$ is marked by a series of distinct, sharp bands at 878, 798, 752, 671, 603, 539 and 472 $cm^{-1}$. This area differs greatly from that observed in the spectra of the older gutta percha samples.

Crude gutta percha contains a portion of resinous material in addition to the rubber hydrocarbon. The spectrum of crude gutta percha has been published along with the spectra of the resinous extract and that of the residual elastomer (Saunders and Smith, 1949). The spectrum of the unextracted gutta percha has a complex area of absorption in the carbonyl region. Two bands of medium intensity are located near 1739 and 1709 $cm^{-1}$ with weaker bands in the regions of 1667 and 1639 $cm^{-1}$. With the exception of the band near 1667 $cm^{-1}$, the bands are not evident in the spectrum of the purified rubber hydrocarbon. The spectrum of the resinous material exhibits a strong band near 1709 $cm^{-1}$ with a shoulder in the region of 1739 $cm^{-1}$ and a weak band in the area of 1639 $cm^{-1}$. This pattern is similar to that observed in the carbonyl region in the spectra of the old gutta percha obtained in this study.

The spectra of the gutta percha objects contain bands which are characteristic of both the hydrocarbon elastomer and the resinous portion. The tentative band assignments are listed in Table 13.1.

The differences between the spectra of the older materials and the modern sample may be due to contamination of the sample by the presence of a resinous lacquer. However, this is unlikely as great care was taken to obtain samples from areas where the lacquer had worn away. Also, to confirm this, the sample of the photo frame (PHS3) (<0.5 mg) was taken from the back of the frame (PHS3) in a place where the brown coating material had worn away.

This sample was yellow, brittle and resinous and was crushed onto the silicon carbide paper to ensure that no lacquer was removed with the sample. The spectrum of this material was very similar to those obtained of the other objects. The differences in the spectra may also reflect changes which occur over time or during moulding. It is more likely that the objects made in earler times were produced from unextracted gutta percha. Thus, a resinous component would be present in the material. This would explain the presence of the strong carbonyl absorption and other bands which may be attributed to resins (carboxylic acids) in the diffuse reflectance spectra of the older objects examined in this study. Also, gutta percha exists in one of two possible crystalline orientations (alpha or beta) at room temperature (Saunders and Smith, 1949). The crystalline nature of gutta percha would explain the crystalline appearance of the material which is so different to that of the modern material. This difference in the spectra supports the opinion of plastics authorites that the material used in the past differs from that which may be obtained today.

## Rubber

### Vulcanized rubber

Two examples of rubber were examined, a piece of Spencer Moulton rubber hose (c. 1936) (PHS18) and a section of a Michelin tyre (PHS19). The rubber hose was exhibiting signs of degradation on the interior. The external surface of of the hose was black, but the interior was a grey colour and a strong odour was noticed. The tyre section was in good condition.

Two spectra were obtained of the rubber hose, one sample was taken from the interior and one from the exterior. The rubber materials examined in this study did not powder well. The diffuse reflectance spectra of the tyre and hose obtained in this study do not resemble those of natural rubber and vulcanized rubber which have been published (Linnig and Stewart, 1958). The variations in shape between the spectra are most probably due to differences in sample preparation. The silicon carbide paper did not produce a suitable sample to obtain a good quality spectrum. An early report of the silicon carbide method recommended moistening the silicon carbide paper with dichloroethane before obtaining the sample. This was not done in this study due to the possible detrimental effects of the solvent to the objects.

The spectrum of the exterior of the hose is similar to that of the Michelin tyre. The spectrum of the hose exterior has bands at 3375, 2926, 1662, 1429, 1138, 757, 672 and 606 $cm^{-1}$ which correspond to those at 3385, 2922, 1660, 1411 (very broad), 1141, 757, 670 and 602 $cm^{-1}$ in that of the tyre. However, the intensities are not consistent. The spectrum of the exterior of the hose has a band with maximum intensity at 1048 $cm^{-1}$ which is in contrast to the spectrum of the tyre which contains two distinct bands at 1099 and 1022 $cm^{-1}$. Also, the spectrum of the hose contains a sharp, weak absorption at 1377 $cm^{-1}$. In the tyre spectrum, a sharp, weak band appears at 1322 $cm^{-1}$ and a weak band occurs at 820 $cm^{-1}$.

The spectrum of the interior of the hose is similar to that of the gutta percha with bands at 3387, 2934, 1712, 1450, 1378 and 1085 $cm^{-1}$. The carbonyl band has a sharp absorption at 1712 $cm^{-1}$ with a very pronounced shoulder in the region of 1650 $cm^{-1}$. The band with maximum intensity at 1085 $cm^{-1}$ is very broad.

The frequency values for the vulcanized rubber obtained in this study are listed in Table 13.2 where they are compared to those given in the literature for vulcanized rubber (Linnig and

Stewart, 1958) and given tentative band assignments. The bands which are evident near 1661, 1639, 1631 and 1600 cm$^{-1}$ in the literature spectrum (Linnig and Stewart, 1958) are due to the presence of double bonds and suggest that a large number of double bonds exist after vulcanization. The band near 1661 cm$^{-1}$ in the literature is evident in both the spectrum of natural rubber and the vulcanized rubber and these absorptions are evident in the diffuse reflectance spectra in this study near 1661 cm$^{-1}$ (hose exterior) and at 1660 cm$^{-1}$ (tyre). The band at 1600 cm$^{-1}$ appears in the spectra of vulcanized rubber and is characteristic of conjugated double bonds.

Also, the band located at 837 cm$^{-1}$ in unvulcanized rubber (Linnig and Stewart, 1958) decreases in intensity in the spectra of vulcanized rubber. A band appears near 962 cm$^{-1}$ in the spectra of vulcanized rubber. The bands are assigned to the C-H deformations of hydrogens attached to double bonded carbons in the trans- configuration. The band at 962 cm$^{-1}$ is due to the double bonds which were shifted in the vulcanization process and the band near 837 cm$^{-1}$ results from the original double bonds (Linnig and Stewart, 1958). These bands are not evident in the spectra obtained in this study. A weak band is evident near 820

$cm^{-1}$ in the tyre spectrum and a medium band is seen at 808 $cm^{-1}$ in the spectrum of the hose exterior.

The literature also lists weak bands at 699 and 676 $cm^{-1}$ for rubber containing more than 12% sulphur and a single band at 690 $cm^{-1}$ for rubber containing between 2 and 12% sulphur which were assigned to the hydrogens on the carbon double bonds in the cis-configuration (Linnig and Stewart, 1958). These bands are evident in the hose exterior spectrum at 672 $cm^{-1}$ and in the tyre spectrum at 694 and 670 $cm^{-1}$.

In addition to these bands, a band is evident in the vulcanized rubber spectrum in the literature near 1111 $cm^{-1}$ which is not present in that of the natural rubber. This band has not been assigned and may be related to the strong band at 1099 $cm^{-1}$ in the tyre spectrum and 1138 $cm^{-1}$ in the hose exterior spectrum. Also, the literature spectrum contains a band near 1307 $cm^{-1}$ and the spectrum of the tyre contains a band at 1322 $cm^{-1}$ which may be assigned to the C-H in-plane deformation of the carbon double bond which falls in the region of 1310 - 1295 $cm^{-1}$.

The difference in the spectra of the interior and the exterior of the hose may represent the changes in structure which occur when rubber undergoes ageing. The similarity of the interior spectrum to that of gutta percha is interesting and may be due to the loss of sulphur linkages in the vulcanized structure.

## Vulcanite

The addition of large amounts of sulphur to natural rubber results in a very hard material known as ebonite, vulcanite or hard rubber. The ratio of rubber to sulphur in these materials is approximately 68 to 32. The material contains a large amount of cross linkage and the empirical formula indicates that one double bond is converted for every sulphur atom present (Brydson, 1975). Three objects of vulcanite were examined and one object which was thought to be a rubber mixture. A Vesta box (PHS14) with the image of Queen Victoria (1897), a Jubilee medal (PHS15) for Queen Victoria (1887) and a cigarette holder (PHS17) made by Dunhill (c. 1920's) which were identified as vulcanite (Williamson, personal communication) were sampled. Also, a medal copy (PHS16) which was stamped 'Facsimilie of Wm. Warne & Co. Prize Medal 1862, Manufactured from their patent Mineralite London and Tottenham'. The material was thought to be rubber plus some sort of additive.

The spectra of the vulcanite specimens obtained in this study resemble the published spectrum of vulcanized rubber (Linnig and Stewart, 1958) more closely than the spectra of vulcanized rubber obtained in this study. This is in fact due to the hardness of vulcanite which led to more satisfactory samples for diffuse reflectance. The frequency values observed for the vulcanite objects are listed with the vulcanized rubber and the literature values in Table 13.2 Tentative band assignments are also given. The spectra of the four objects have fairly simple spectra which exhibit five absorptions which may be considered characteristic (Figure 13.1b). The regions include 2929 - 2927 $cm^{-1}$, 1453 - 1451 $cm^{-1}$, 1379 - 1376 $cm^{-1}$, 1151 - 1129 $cm^{-1}$ and 1040 - 1032 cm-1. The absorptions in the regions 1453 - 1451 $cm^{-1}$ and 1379 - 1376 $cm^{-1}$ are strong and sharp. The absorptions in the regions 1157 - 1129 $cm^{-1}$ and 1040 - 1032 $cm^{-1}$ are very broad. There are variations between the spectra in other regions.

In the spectra of PHS14 and PHS17, the C-H stretching absorptions are very strong and much more intense in relation to the rounded absorption in the hydroxyl region. In the spectra of the samples PHS15 and PHS16, the C-H stretching vibrations are less intense in relation to the hydroxyl absorption. Also, the bands in the region of 1453 - 1451 $cm^{-1}$ and 1379 - 1376 $cm^{-1}$ are more intense than the broad absorption in the regions 1151 - 1129 $cm^{-1}$ and 1040 - 1032 $cm^{-1}$ in the spectra of PHS14 and PHS17. The broad bands are more intense than the bands at 1453 - 1451 $cm^{-1}$ and 1379 - 1376 $cm^{-1}$ in the spectra of samples PHS15 and PHS16. There is a great deal of variation in the carbonyl region in the spectra. The spectrum of PHS17 has very weak bands at 1710, 1652 and 1603 $cm^{-1}$, the spectrum of PHS16 has two absorptions of medium intensity at 1711 and 1623 $cm^{-1}$, the spectrum of PHS15 contains a broad band with maximum absorptions at 1709 and 1662 $cm^{-1}$ and the spectrum of PHS14 has a sharp band of medium intensity at 1743 $cm^{-1}$ and a weak band at 1652 $cm^{-1}$.

The region between 950 and 400 $cm^{-1}$ is fairly weak and there are some variations in the spectra. An exception is the spectrum of the medal copy (PHS16) which contains fairly strong absorptions at 672, 600 and 467 $cm^{-1}$. The C-S absorptions occur as weak bands in the approximate region 700 - 600 $cm^{-1}$ and S-S linkages are marked by very weak absorptions in the area 500 - 400 $cm^{-1}$ (Bellamy, 1975). The spectra of PHS14 and PHS15 contain weak bands at 598 and 610 $cm^{-1}$ respectively and the spectrum of PHS16 contains two bands at 672 and 600 $cm^{-1}$ which may be due to the

C-S linkage. The spectra of PHS14, PHS16 and PHS17 contain weak bands at 471, 467 and 466 $cm^{-1}$ respectively which may result from disulphide linkages. These bands are normally very weak and not considered to be diagnostic (Bellamy, 1975), however, the vulcanite structure contains a high number of sulphur linkages and it would be reasonable to assume that the weak bands may be due to these bonds.

The variation in the vulcanite spectra are probably due to the presence of colourants. It is interesting to note that the spectra of the two black objects, the Vesta box and the cigarette holder, are very similar with the exception of the band at 1743 $cm^{-1}$ in the spectrum of the vesta box (PHS14) which is apparent as only a weak band at 1710 $cm^{-1}$ in the spectrum of the cigarette holder. This similarity is encouraging from the stand point of identification of objects of unknown constitution. The date of the objects differs by about 20 years, however, the spectra are very similar which suggests similar composition. The spectra of PHS14 and PHS17 exhibit bands at 954 and 955 $cm^{-1}$, 848 and 822 $cm^{-1}$, 739 and 740 $cm^{-1}$ and 1312 and 1313 $cm^{-1}$ respectively. The spectrum of the medal copy (PHS16), which was composed of a material refered to as mineralite, displays similarities to that of vulcanite.

### Shellac

Several objects which were known or thought to be made from mineral filled shellac were examined. The objects included a union case (PHS9) marked 'S. Peck'. The frame section of the case contained a paper which listed the following information: 'S. Peck's Patent Oct 3d, 1854, Halverson's Patent, Feb 7th, 1855 assigned to S. Peck, S. Peck's Patent, Feb 5th, 1856'. Union cases were used to display ambrotypes and daguerreotypes and the patent disclosed that the objects were moulded from shellac mixed with wood flour (catalogue). The second object was a black hand mirror (PHS8) with an ornate flower pattern on the back which was identified as a filled shellac (Williamson, personal communication). The third object was a black knot brooch (PHS22) which was marked 'Mantons Ware Patent'. This material was described in the patent as a mineral filled shellac (Williamson, personal communication).

In addition to the objects described, three other objects were found to be shellac materials as the spectra obtained display bands which correspond to those obtained of the three objects previously described. These include a photograph frame (PHS6) stamped 'Smith's American Patent Composite', a belt buckle (PHS20) identified as D&C Patent and a brooch (PHS21) stamped with 'D&C Patent'.

The absorption frequencies and the band assignments of these samples are compared to those of shellac in Table 13.3. The spectra of the objects include a broad, strong band with maximum intensity in the range 3409 - 3353 $cm^{-1}$, strong bands in the region 2931 - 2922 $cm^{-1}$ and 2858 - 2855 $cm^{-1}$, a strong band in the region 1726 - 1713 $cm^{-1}$, a weaker absorption in the region 1658 - 1640 $cm^{-1}$ (a band occurs at 1605 $cm^{-1}$ is observed in the spectrum of PHS20) and weak bands in the regions 1465 - 1461 $cm^{-1}$ and 1379 - 1375 $cm^{-1}$. In the spectrum of PHS21, the band occurs at 1429 $cm^{-1}$ with a shoulder in the higher frequency region and the band at 1379 - 1375 $cm^{-1}$ is not apparent in the spectrum of PHS22. The regions observed in these pieces correspond to those observed in the spectra of the shellac standards (chapter 7); 3421 - 3326 $cm^{-1}$, 2933 - 2923 $cm^{-1}$, 2858 - 2854 $cm^{-1}$, 1717- 1713 $cm^{-1}$, 1641 - 1638 $cm^{-1}$, 1469 - 1464 $cm^{-1}$ and 1377 - 1375 $cm^{-1}$.

The presence of mineral fillers would be expected to affect the spectrum and this is seen in the variation in the spectra in the region 1250 - 400 cm$^{-1}$. The spectra of the reference shellacs exhibit a series of broad absorptions with maximum intensity at 1253 - 1235 cm$^{-1}$, 1170 - 1162 cm$^{-1}$ and 1048 - 1030 cm$^{-1}$. However, there is considerable variation in this region between the various object spectra. A weak band is evident at 723, 723 and 725 cm$^{-1}$ in the spectra of PHS9, PHS6 and PHS20 respectively which correspond to a weak band apparent in the range 725 - 723 cm$^{-1}$ in the reference shellac spectra.

The spectrum of the Manton's Ware sample (PHS22) is marked by bands at 2515, 1796, 878 and 753 cm$^{-1}$ which are indicative of calcium carbonate (Miller and Wilkins, 1952). The broad band which is expected near 1430 cm$^{-1}$ in the spectrum of calcium carbonate (Miller and Wilkins, 1952) is apparent in the broad, intense band with maximum intensity at 1465 cm$^{-1}$ which may be due to overlap of several absorptions due to different vibrations.

### Bois durci (Albumen and wood flour)

An early moulding material was produced from the combination of albumen from egg whites or dried blood with wood flour. The material was placed in steel moulds and transformed by high heat and pressure. The precess was developed by C. Lepage who established English and French patents in 1855. The material was refered to as Bois Durci and was used to manufacture commemorative plaques of famous personalities and royal personages in addition to items such as combs, jewelry, knife handles, pipes and frames. It is thought that the material was no longer produced by 1887 (Williamson, 1988).

A circular, dark brown plaque which depicts the head of Leopold (PHS13) and was thought to be Bois Durci was examined (c. 1860's). The resulting spectrum bears certain variations from that obtained of dry egg white which is probably the result of interference from the fillers. The Bois Durci spectrum is marked by a strong, broad band with maximum intensity in the region 3410 - 3304 $cm^{-1}$ and a band of medium intensity at 2921 $cm^{-1}$. This region is similar to that of the dried albumen spectrum where a strong band is apparent with maximum intensity at 3276 $cm^{-1}$ and a less intense absorption is present at 2942 $cm^{-1}$. However, the weak band at 3071 $cm^{-1}$ in the albumen spectrum is not evident in that of the Bois Durci. The amide I absorption in the Bois Durci spectrum is very wide and the amide II band expected near 1550

$cm^{-1}$ is not evident. The shape of the amide I region is very different to that observed in the albumen spectrum. The Bois Durci spectrum contains a sharp band at 1511 $cm^{-1}$ and a wide band with maximum intensities at 1463 $cm^{-1}$ and near 1430 $cm^{-1}$. The albumen spectrum has one broad absorption centered at 1449 $cm^{-1}$. The major difference between the spectra is in that of the Bois Durci, a very intense, broad area of absorption is evident in the region 1300 - 1000 $cm^{-1}$ with bands at 1235, 1115 and 1061 (very strong) $cm^{-1}$. The corresponding region in the albumen spectrum contains two broad, weak regions of absorption with maximum absorptions at 1309 and 1049 $cm^{-1}$. The region from 800 - 400 $cm^{-1}$ is a broad envelope of absorption in both spectra which is typical for proteins.

A second object , a black lacquered knot brooch (PHS23) which had the pin broken off, was examined. The small sample was removed from where the fastener broke off to avoid contamination from the lacquer. The spectrum of the material shows some similarities to that of the albumen although it does not closely resemble that of the Bois Durci plaque. The spectrum was thought to be of a protein material due to the strong, broad band in the region 3450 - 3298 $cm^{-1}$, a band of medium intensity at 2929 $cm^{-1}$, and bands at 1661 (amide I), 1549 (amide II) and 1431 cm$^{-1}$ which are found in the spectra of proteins (chapter 8). The band assignments are summarized in Table 13.4.

## Semi-synthetic plastics

### Cellulose nitrate

### Parkesine

Three objects which were identified as Parkesine were sampled: a black knife handle with a blade which was stamped 'Patent Parkesine Handle (PHS28), a mottled green and yellow knife handle with no blade (PHS29) and a white billiard ball (PHS30). The objects date from the 1860's. The objects were in good condition, only the green handle being slightly distorted.

All three pieces gave spectra which contained the characteristic nitrate absorptions near 1651, 1282, 846 and 752 cm$^{-1}$ (Brown, 1955). The band which is expected in the region 710 - 690 cm$^{-1}$, however, seems to be masked by overlapping bands in the region. The spectra contain broad bands in the range 3450 - 3394 cm$^{-1}$ and 1076 - 1031 cm$^{-1}$ which are due to the hydrogen bonded hydroxyl groups and the C-O ether linkages respectively in the cellulose molecule. The spectra are similar to those obtained from the

Parkesine objects from the Science Museum (Chapter 11). It is also interesting to note that the intense band in the carbonyl region which is characteristic of the camphor molecule is not apparent in these spectra (Chapter 10). In the spectrum of the black knife handle, a relatively weak band occurs at 1727 $cm^{-1}$ and only a very slight shoulder occurs in the region of 1725 $cm^{-1}$ in the other spectra. The frequency values and band assignments are listed in Table 13.5.

### Xylonite

Four examples which were identified as Xylonite were examined: a white cuff (PHS31) which was stamped with the elephant and tortoise Xylonite trademark (c. 1890's), a red photo developing tray (PHS32) which was marked 'Xylonite trademark' (c. 1900's) and a blue powder box (PHS34) stamped 'Xylonite trademark' (c. 1930's). The fourth object was a 'tortoise-shell' tray which was exhibiting signs of degradation, namely the appearance of plasticizer 'sweat' on the surface. Also, two of the four knob 'feet' had come loose. The tray had been treated with soya bean oil in an effort to arrest the degradation (Williamson, personal communication). The material beneath the knob feet was discoloured and cracked. The other three objects were in good condition.

A small sample was removed from the degraded material beneath the knob feet with a scalpel to avoid contamination from the vegetable oil. A spectrum was measured of the degraded material and two samples were taken of the surface with silicon carbide paper, one of the very top surface and one of the surface obtained by stronger rubbing. The spectra of the degraded material and the very top surace show some evidence of denitration. The bands located near 1660, 1290 and 850 cm$^{-1}$ are less intense in relation to the broad band in the region of 1065 cm$^{-1}$. This is in contrast to the intensities observed in the spectra of cellulose nitrate objects which do not show visible evidence of degradation. The degradation does not prevent the identification of the material as cellulose nitrate as the characteristic nitrate bands are still evident. The vegetable oil did not cause visible distortion of the spectrum.

The spectrum of the deeper surface contained strong nitrate bands. This spectrum and those obtained of the other Xylonite objects display the characteristic nitrate absorptions which are discussed in chapters 10 and 11. Also, the spectra of the Xylonite samples contain a strong absorption in the region of 1730 $cm^{-1}$ which is characteristic of camphor (Table 13.5).

Cellulose acetate

A transparent orange phonograph record (PHS47) was sampled. It was marked 'Filmophone Flexible Record Ltd. British Made Cat. No. 236 (F13 U7H I)'. The spectrum, which was identified as cellulose acetate, is characterized by bands at 3491, 2943, 1746, 1647, 1432, 1373, 1230, 1162, 1051, 905 and 603 $cm^{-1}$ which are indicative of the cellulose acetate structure (chapter 10). Bands are also evident at 1592, 1488, 970, 780 and 691 $cm^{-1}$ which are characteristic of aromatic structures and indicate the presence of aromatic plasticizers (Table 13.6).

Casein

Three objects were examined which were tentatively identified as casein (Williamson, personal communication). These included a green nail brush with a roughened, worn surface (PHS35), a flat circular hat adornment which depicts a woman's head (PHS36) and a mottled brown, blue and white pen which had a silver end pieces with an image of George V and Queen Mary (PHS37). The side was stamped 'Jubilee Souvenir 1910-1935'.

The spectra of the three materials exhibit the bands which are characteristic of proteins and which have been discussed in chapter 8. The values for these samples are summarized in Table 13.7. The spectra include a broad band in the range of 3320 - 3293 $cm^{-1}$ and a weak shoulder in the region of 3070 $cm^{-1}$. The spectra also contain the characteristic bands at 1662 - 1661 $cm^{-1}$ (amide I), 1551 - 1550 $cm^{-1}$ (amide II) and 1449 - 1447 $cm^{-1}$. The region between 1300 and 400 $cm^{-1}$ varies greatly between samples, however. The spectrum of the nail brush is marked by a broad, fairly flat band between 1235 - 1000 $cm^{-1}$ which is probably the result of several overlapping bands. There is also a broad area of absorption in the region 800 - 400 $cm^{-1}$. The spectrum of the hat adornment is characterized by a broad absorption centered at 1123 $cm^{-1}$ flanked by minor absorptions at 1234 and 999 $cm^{-1}$. The spectrum also contains a broad band of absorption from 800 to 400 $cm^{-1}$ with maximum intensity near 600 $cm^{-1}$. The spectrum of the pen is marked by a very strong, broad absorption centred at 1101 $cm^{-1}$. The spectrum contains several bands of medium intensity in the area 900 - 400 $cm^{-1}$ at 917, 799, 782, 696, 515, 468 and 414 $cm^{-1}$ which is in contrast to the region in the other spectra. The analysis of these objects indicates that the materials are indeed protein, but there is a great deal of variation between various objects which is most likely due to the presence of additives such as colourants.

### Synthetic plastics

#### Phenol formaldehyde

Phenol formaldehyde was the first synthetic plastic. The process was developed by Leo Baekeland. The patent for this material was taken out in 1899. It was already known that phenols and aldehydes form a resin-like material. In Baekeland's patent, the material which has come to be known as Bakelite is produced by a reaction of phenol and formaldehyde under high heat and pressure. The process also includes the addition of fillers, namely wood flour. The major difficulty with the material was that is was a dark colour which limited the colours to dark brown or black. A later development in the procedure involved heating the liquid resin in lead moulds at lower temperatures for a longer period of time. This material was not coloured and could be dyed to create both transparent and opaque colours (Kaufman, 1963). These materials are known as cast phenolics (Williamson, personal communication).

Two objects of Bakelite were examined. The first was a small, brown bowl (PHS45) which is marked with the Bakelite logo and marked 'Bakelite Limited reg'd trademark' (c. 1940's) and the second object was a black desk tidy (PHS46) made in the shape of the Bakelite logo. It was produced to commemorate the coronation of George VI and Queen Elizabeth (1937). It is marked with the Bakelite logo and trademark. A third example of phenol formaldehyde, a black aerial link (PHS44) which was produced by Mouldensite, was also sampled.

Several cast phenolic objects were also examined. These include a orange-red coloured napkin ring (PHS41), a Carvercraft ash tray marked with a mallet and chisel trademark (PHS42), a handle which was originally a pale amber colour which had turned black (c. 1925)(PHS43) and a bright orange sample plaque made by Dekorit and marked 'Dekorit L222' (PHS48)(c. 1987).

The spectra which were obtained are very similar for the dark phenol formaldehydes and the cast phenolics (Figure 13.2). This is not surprising as the chemical structure of the materials is similar. The structure consists of phenol groups linked by methylene groups (Candlin, 1988). The frequency values and band assignments are listed in Table 13.8.

A broad band is evident in the spectra which is centered in the region 3400 - 3305 cm$^{-1}$ which has been assigned to the intermolecular hydrogen bonded O-H groups. The value given in the literature for solid polymeric phenol is 3225 cm$^{-1}$ (Evans, 1960).

The spectra exhibit strong bands in the regions 1609 - 1597 cm-1, 1510 - 1508 cm$^{-1}$ and 1483 - 1477 cm$^{-1}$ with a less intense band or shoulder in the region 1652 - 1644 cm$^{-1}$. In the spectra of samples PHS43, PHS44, PHS45 (Figure 13.2b) and PHS46, there is a strong band in the region 1510 - 1508 cm$^{-1}$. In the spectra of the remaining samples (PHS41, PHS42 and PHS48(Figure 13.2a)), however, only a weak shoulder is apparent. In the spectra of samples PHS44 and PHS45, there is no strong band evident in the region 1483 - 1477 cm$^{-1}$ (see table 13.8). These bands are indicative of the skeletal ring stretching modes of the aromatic ring (chapters 10 & 11) (Bellamy, 1975). The frequency values recorded for solid phenol are 1605, 1598, 1501 and 1473 $cm^{-1}$ (Evans, 1960).

In the sample spectra, strong, fairly broad bands are observed in the regions 1369 - 1334 $cm^{-1}$ and 1234 - 1217 $cm^{-1}$. The first absorption corresponds to a band reported to occur at 1370 $cm^{-1}$ in the spectrum of solid phenol which has been assigned as a ring stretching mode coupled with an O-H deformation (Evans, 1960). The second absorption, which has a weak shoulder in the approximate region of 1250 $cm^{-1}$, may be related to the bands which have been reported to occur in solid phenols at 1252 and 1230 $cm^{-1}$. The bands have been assigned to the C-O stretch and to the in-plane O-H deformation coupled with ring stretch in polymeric phenols respectively (Evans, 1960).

A broad area of absorption is observed in the region 1200 - 1000 $cm^{-1}$ with maximum absorptions in the regions 1154 - 1152 $cm^{-1}$, 1102 - 1097 $cm^{-1}$ and 1065 - 1043 $cm^{-1}$. The band near 1102 - 1097 $cm^{-1}$ is not, however, evident in all of the spectra and the intensities vary somewhat. The bands are due to the C-H in-plane deformations of the aromatic ring (Bellamy, 1975) and correspond approximately to the frequency values reported for solid phenol, 1169, 1152, 1072 and 1024 $cm^{-1}$ (Evans, 1960).

The spectra are also marked by a band in the region of 897 - 883 $cm^{-1}$, a band at 826 - 822 $cm^{-1}$ (variable intensity) and a band of medium intensity in the region 763 - 757 $cm^{-1}$. The bands in this region are due to C-H out-of-plane deformations of the aromatic ring and are indicative of the substitution pattern on the ring (Bellamy, 1975). In a highly cross-linked polymer, the rings would be highly substituted and the pattern would not be consistent. This would explain the variation in the intensities of the bands in this region. The region would also be affected by the presence of fillers and the spectra of the cast phenolics might also by affected by the colouring matter. The values reported for solid phenol, 888, 828 and 754 $cm^{-1}$ (Evans, 1960), are fairly close to those observed for the phenolic plastics in this study.

Amino plastics

The condensation reaction between urea and formaldehyde was first discovered in 1884. The first commercially successful plastic (1928) was prepared from a mixture of urea and thiourea in equal parts, formaldehyde and wood flour or cellulose pulp. This material was dried and ground to form a moulding powder. The product was called Beetle and later Beatl. In 1931 - 1930, a technique was developed for the production of a urea formaldehyde plastic in which an accelerator was added to decrease the time needed for moulding. Plastics produced by the reaction of melamine with formaldehyde were established around 1935 (Kaufman, 1963).

Two objects of thiourea/urea formaldehyde were sampled. A yellow and green cup (PHS38) marked 'Beatl ML137 made in England' (1926 - 1935) and a green, blue and yellow marbled beaker (PHS39) stamped on the base with 'Bandalasta Ware Reg'd trademark Made in England' and the Bandalasta trademark (1928). The spectra of the urea formaldehyde plastics were obtained from a white sample plaque (PHS49) marked 'BIP x8132' (c. 1987) and a cream coloured shaving cream box (PHS50) stamped 'Wardonia Patent Nos 296,597, 376644 Reg'd trademark Made in England' (c. 1950's). A sample was also taken from a yellow saucer (PHS40) composed of melamine formaldehyde which was marked on the base 'Melaware'.

Thiourea/urea, urea and melamine formaldehyde plastics may be differentiated by their spectra (Urbanski et al., 1977) and the diffuse reflectance spectra obtained of these samples are observed to be characteristic for each type of plastic. The spectra of thiourea/urea formaldehyde (Figure 13.3a) and urea formaldehyde (Figure 13.3b) are fairly similar to each other and exhibit features also found in the spectra of proteins (chapter 8). The spectra of the urea formaldehyde plastics are marked by strong absorptions near 1650 and 1550 $cm^{-1}$ which correspond to the amide I and amide II bands and a broad band near 3335 $cm^{-1}$ which is indicative of N-H stretching vibrations. These absorptions are consistent with the structure of the urea molecule and agree well with values quoted in the literature for urea resins, 1639, 1563 and 3333 $cm^{-1}$ (Urbanski et al., 1977).

The spectra of the urea plastics obtained in this study also contain absorptions near 2922 $cm^{-1}$ (PHS50) and 1479 $cm^{-1}$ which indicate methylene linkages in the polymer structure. They also show a broad absorption in the region of 1048 - 1040 $cm^{-1}$ which corresponds to ether linkages and there is some evidence for methyl end groups due to the bands near 2961 $cm^{-1}$ (PHS49) (Bellamy, 1975) and 1380 $cm^{-1}$. These bands correspond with the values given in the literature for condensation polymerization of urea and formaldehyde carried out in butanol, 1087 and 1383 $cm^{-1}$ (Urbanski et al., 1977).

The thiourea/urea formaldehyde spectra exhibit absorptions due to both the urea and thiourea structures. The literature states that thiourea resin spectra contain two bands near 1538 and 1333 $cm^{-1}$ and that the amide I band is not present. The band at 1538 $cm^{-1}$ is assigned to a C=S vibration and the second band is also tentatively related to the C=S functional group (Urbanski et al., 1977). In the spectra of the thiourea/urea formaldehyde resins, the amide II absorption masks the absorption near 1538 $cm^{-1}$ in part but the band near 1333 $cm^{-1}$ is not blocked and is thus a characteristic feature for amino resins containing thoiurea (Urbanski et al., 1977). The spectra of the thiourea/urea formaldehyde plastics in this study contain absorptions at 1341 $cm^{-1}$. The bands at 1541 and 1548 $cm^{-1}$ in these spectra are probably due to both the amide II and C=S vibrations. This may explain why these bands are more intense in relation to the other bands in the spectra, than the amide II absorption in the urea formaldehyde spectra. The band assignments are summarized in Table 13.9.

Melamine formaldehyde has a somewhat different spectrum (Figure 13.3c) which is due to the melamine structure. The region 1667 - 1250 cm$^{-1}$ is characteristic for melamine formaldehyde spectra where a series of strong absorptions occur. A particularly characteristic band is observed near 1563 cm$^{-1}$ in the literature. These bands are assigned to the triazine ring and to methylene and ether linking groups in the structure (Urbanski et al., 1977). A band which is observed near 813 cm$^{-1}$ is also credited to the triazine ring. The ether group is also observed due to a weak band near 1064 cm$^{-1}$ (Urbanski et al., 1977).

The melamine formaldehyde spectrum obtained in this thesis is marked by strong bands at 1586, 1501 and 1478 cm$^{-1}$ which overlap to a great extent, in addition to an equally intense band apparent at 1356 cm$^{-1}$. The spectrum of the melamine formaldehyde has a strong, sharp band at 815 cm$^{-1}$ and a strong broad band at 1048 cm$^{-1}$. The frequency values are listed in Table 13.9.

All five spectra are marked by a broad envelope of absorption with no strong bands in the region 800 - 400 cm$^{-1}$. This feature is also observed in the protein spectra obtained in this study. The complex structures of the polymers would result in many overlapping bands.

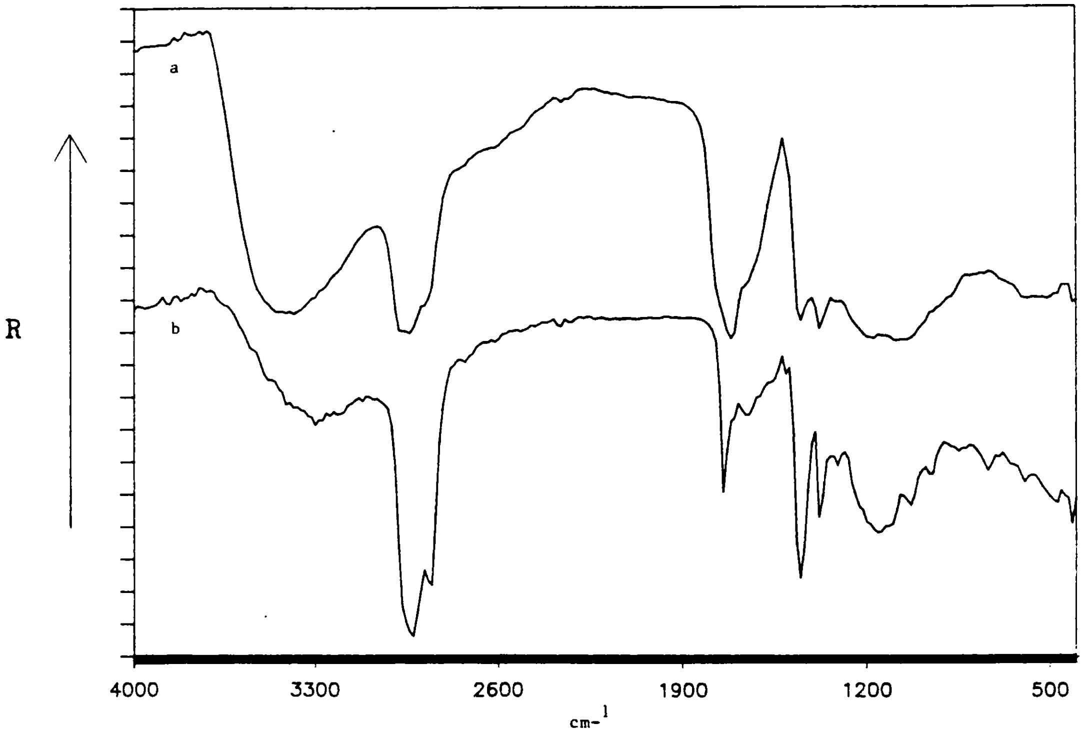


Figure 13.1 Diffuse reflectance FT-IR spectra of samples from (a) a gutta percha inkwell (PHS1) and (b) a vulcanite Vesta box (PHS14) from the Plastics Historical Society collection.

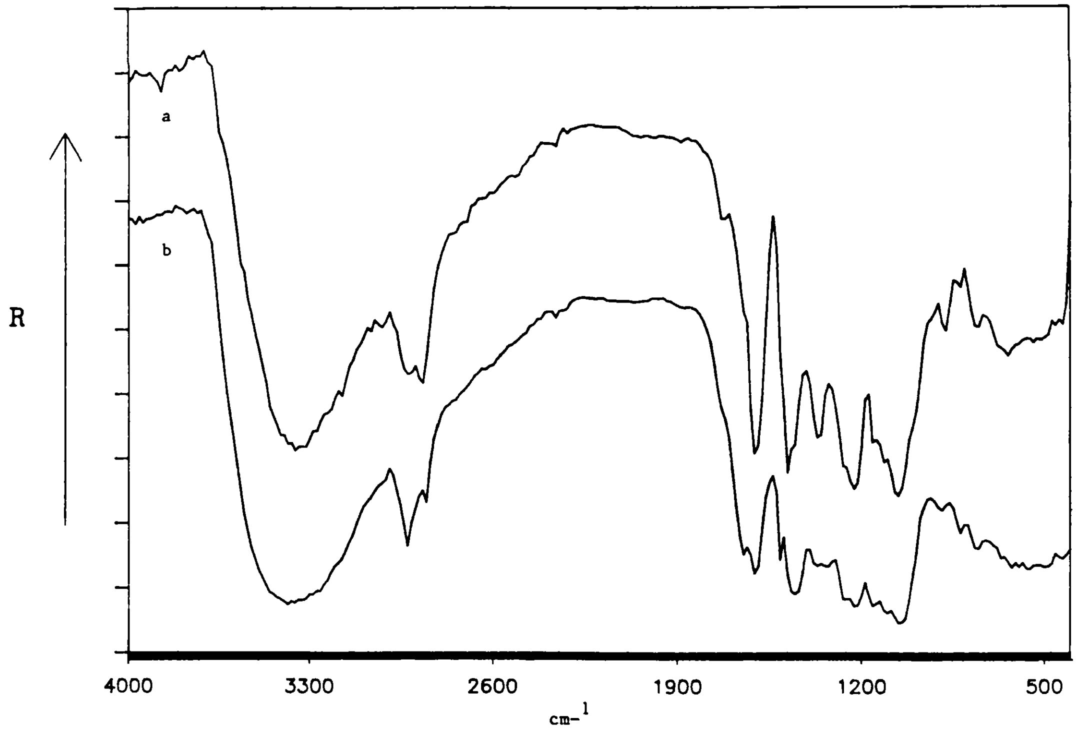


Figure 13.2 Diffuse reflectance FT-IR spectra of samples from (a) a 'Dekorit' cast phenolic sample plaque (PHS48) and (b) a Bakelite bowl (PHS45) from the Plastics Historical Society collection.

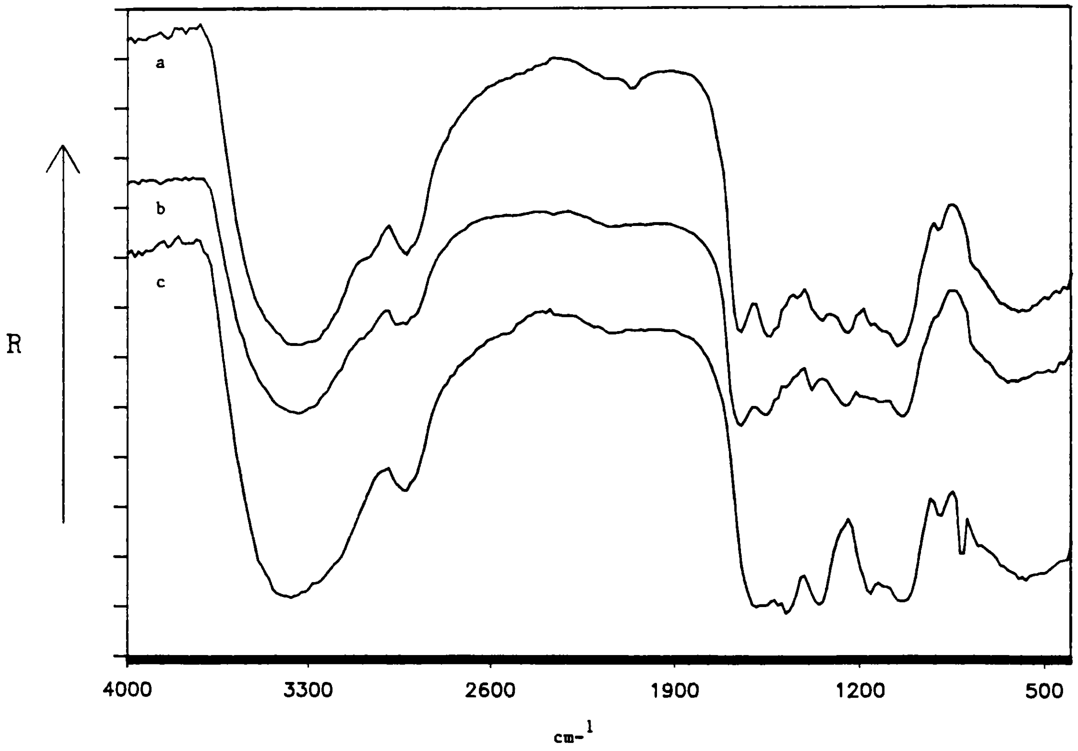


Figure 13.3 Diffuse reflectance FT-IR spectra of samples from (a) a thiourea/urea formaldehyde 'Beatl' cup (PHS38), (b) a urea formaldehyde BIP sample plaque (PHS49) and (c) a melamine formaldehyde 'Melaware' saucer (PHS40) from the Plastics Historical Society collection.

TABLE 13.1

Frequency values and band assignments for Plastics Historical Society gutta percha samples

| PHS1 cm-1 | PHS1 cm-1 | PHS2 cm-1 | PHS3 cm-1 | PHS4 cm-1 | Crude gutta percha (1) cm-1 | | Vibration | Functional group | Frequency range given in literature (3) cm-1 |
|---|---|---|---|---|---|---|---|---|---|
| 3421 | 3415 | 3421 | 3431 | 3414 | 3448(w,b) | | O-H stretch hydrogen bonded | carboxylic acid<br>water | 3000 - 2500(b) |
| 3387 | 3385 | 3387 | 3384 | 3390 | | | O-H stretch hydrogen bonded | carboxylic acid | 3000 - 2500(b) |
| near 2970(sh) | 2971(s) | near 2970(sh) | 2970(s) | near 2970(sh) | | | C-H stretch | methyl group | 2962 ± 10(s) |
| 2932(s) | 2941(s) | 2937(s) | 2942(s) | 2926(s) | 2941(s) | | C-H stretch | methylene group | 2926 ± 10(s) |
| | | | | 2857(s) | | | C-H stretch | methylene group | 2853 ± 10(s) |
| ********** (weak shoulder near 2700) ********* | | | | | 2740(sh) | | O-H stretch hydrogen bonded | carboxylic acid | near 2650(w) |
| ************ (shoulder near 1770) ************ | | | | | 1739(sh) | R | C=O stretch | ester | 1750 - 1730(s) |
| 1712(s) | 1714(s) | 1714(s) | 1714(s) | 1711(m) | 1709(s) | R | C=O stretch | carboxylic acid | 1725 - 1700(s) |
| ************ (shoulder near 1660) ************ | | | | 1663(m) | 1667(m) | E | C=C stretch | C=C bond non-conjugated | 1680 - 1620(va) |
| | | | | 1625(m) | 1639(w) | R | unassigned | | |
| | | | | 1600(m) | | | C=C stretch | C=C bond, C-O or C=C conjugated | near 1600(va) |
| 1452(s) | 1453(s) | 1452(s) | 1452(s) | 1449(s) | 1449(s) | | C-H asym. deform. | methyl group | 1450 ± 20(m) |
| | | | | | | | C-H deformation | methylene group | 1465 ± 20(m) |
| 1380(s) | 1380(s) | 1379(s) | 1380(s) | 1381(s) | 1379(s) | | C-H sym. deform. | methyl group | 1380 - 1370(s) |
| near 1320(sh) | 1320(w) | near 1320(w) | 1319(w) | | 1325(m) | E | C-H in-plane deformation | C=C bond | 1310 - 1295(s-w) |
| | | | | | 1242(s) | R | C-O stretch/ O-H deformation | carboxylic acid | 1320 - 1211(s) |
| | | | | 1207(s) | 1205(s) | E | unassigned | | |
| near 1170(sh) | 1172(s,b) | near 1170(b) | 1170(s,b) | | 1163(s) | R | C-O stretch | ester | 1300 - 1000(s) |
| | | | | | 1143(s) | E | unassigned | | |
| | | | | 1105(s) | | | unassigned | | |

TABLE 13.1 contd.

Frequency values and band assignments for Plastics Historical Society gutta percha samples

| PHS1<br>cm-1 | PHS1<br>cm-1 | PHS2<br>cm-1 | PHS3<br>cm-1 | PHS4<br>cm-1 | Crude gutta percha (1)<br>cm-1 | | Vibration | Functional group | Frequency range given in literature (3)<br>cm-1 |
|---|---|---|---|---|---|---|---|---|---|
| 1083(s,b) | 1051(s,b) | 1064(s,b) | 1097(s,b) | | 1093(s) | E | unassigned | | |
| | | | | 1032(s) | 1047(s) | E | unassigned | | |
| | | | | | 1026(s) | R | C-O stretch | ester | 1300 - 1000(s) |
| | | | | | 990(m) | E | C-H out-of-plane | C=C bond (trans-) | 970 - 960(s) |
| | | | | | 971(sh) | | deformation | | |
| | | | | | 922(w) | R | O-H out-of-plane | carboxylic acid | 950 - 900(va) |
| | | | | | | | deformation | | |
| | | | 881(w) | 878(m) | 885(m) | E | C-H out-of-plane | C=C bond | 1000 - 800(s) |
| | | | | | 862(m) | E | deformation | | |
| | | | | | 848(m) | E | | | |
| 803(w) | 803(w) | near 800(w) | 801(w) | 798(m) | 803(m) | E | | | |
| | | | 752(w) | 752(m) | 766(w) | R | unassigned | | |
| | | | | | 741(w) | E | unassigned | | |
| 660(w) | 659(w) | | | 671(m) | (2) | | C-H out-of-plane<br>deformation | C=C bond (cis-) | near 690 |
| 607(w) | 579(w) | | 601(w) | 603(m) | (2) | | unassigned | | |
| | 561(w) | | | | | | unassigned | | |
| | 516(w) | 544(w) | 517(w) | 539(m) | (2) | | unassigned | | |
| | | | | 472(s) | (2) | | unassigned | | |

1. The wavelength values were estimated to the nearest + 0.05 microns from an enlarged copy of the spectrum from Saunders and Smith, 1949. The wavenumber conversions were taken from the table in Hummel, 1966.
Bands which are marked R are apparent in the spectrum of the resinous extract only.
Bands which are marked E are apparent in the spectrum of the elastomer extract only. See text
2. Spectrometer range ends at 700 cm-1.
3. Bellamy, 1975

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp

TABLE 13.2

Frequency values and band assignments for vulcanized rubber and vulcanite Plastics Historical Society samples.

| Vulcanized rubber | | | Vulcanite | | | | | Vibration | Functional group | Frequency range given in literature | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| PHS18 int. cm-1 | PHS18 ext. cm-1 | PHS19 cm-1 | PHS14 cm-1 | PHS15 cm-1 | PHS16 cm-1 | PHS17 cm-1 | vulcanized rubber (1) cm-1 | | | cm-1 | |
| | | | | | 3483(sp) | | | unassigned | | | |
| | | | | | 3411(sp) | | | unassigned | | | |
| 3412(s,b) | 3375(s,b) | 3404(s,b) | 3304(m,b) | 3387(s,b) | 3304(m,b) | 3304(m,b) | 3279(w) | O-H stretch | water | | |
| | | | | | | | | O-H stretch hydrogen bonded | carboxylic acid (resin fraction) | 3000 - 2500(b) | 2 |
| 2963(s) | near 2960(s) | 2961(m) | | | | | | C-H stretch | methyl group | 2962 ± 10(s) | 2 |
| 2934(s) | 2926(s) | 2922(m) | 2928(s) | 2927(s) | 2927(s) | 2929(s) | * 2941(s) | C-H stretch | methylene group | 2926 ± 10(s) | 2 |
| | near 2850(sh) | 2853(m) | 2856(s) | near 2859(sh) | near 2850(sh) | 2858(s) | | C-H stretch | methylene group | 2853 ± 10(s) | 2 |
| | | | | | | | * 2740(w) | O-H stretch hydrogen bonded | carboxylic acid (resin fraction) | near 2650(w) | 2 |
| | | | | | | | 2041(w) | unassigned | | | |
| | | | 1743(s) | | | | 1739(w) | C=O stretch | carbonyls in hydrocarbon chain, | | 1 |
| 1712(s) | | | | 1709(s) | 1711(s) | 1710(m) | 1709(w) | C=O stretch | oxidation products or resinous fraction.<br>additives to plastic | | |
| 1650(sh) | 1662(s,b) | 1660(s,b) | 1652(m) | 1662(s) | 1623(m) | 1652(m) | 1661(m) | C=C stretch | C=C bond | 1680 - 1620(va) | 2 |
| | | | | | | | 1639(m) | C=C stretch | C=C bond | 1680 - 1620(va) | 2 |
| | | | | | | | 1631(m) | C=C stretch | C=C bond | 1680 - 1620(va) | 2 |
| | | | 1505(w) | | | 1603(m) | 1600(m) | C=C stretch | C=C bond conjugated | near 1600(va) | 1,2 |
| | | | | | | | 1538(w) | unassigned | | | |
| 1450(s) | | | 1453(s) | 1452(s) | 1451(s) | 1452(s) | * 1449(s) | C-H deformation | methylene group | 1465 ± 20(m) | 2 |
| | 1429(s) | 1411(s,b) | | | | | | C-H asym. deform. | methyl group | 1450 ± 20(m) | 2 |
| 1378(s) | 1377(s) | | 1376(s) | 1379(s) | 1378(s) | 1376(s) | * 1379(s) | C-H sym. deform. | methyl group | 1380 - 1370(s) | 2 |

TABLE 13.2 contd.

Frequency values and band assignments for vulcanized rubber and vulcanite Plastics Historical Society samples.

| Vulcanized rubber | | | Vulcanite | | | | | Vibration | Functional group | Frequency range given in literature | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| PHS18 int. | PHS18 ext. | PHS19 | PHS14 | PHS15 | PHS16 | PHS17 | vulcanized rubber (1) | | | | |
| cm-1 | cm-1 | cm-1 | cm-1 | cm-1 | cm-1 | cm-1 | cm-1 | | | cm-1 | |
| | | 1322(m) | 1312(m) | | | 1313(m) | * 1307(m) | C-H in-plane deformation | C=C bond | 1310 - 1295(s-w) | 2 |
| | | | | | | | * 1227(m) | unassigned | | | |
| | | | | | | 1194(s) | | unassigned | | | |
| | 1138(s,b) | 1141(s) | 1151(s,b) | 1129(s,b) | 1147(s,b) | 1139(s) | * 1136(sh) | unassigned | | | |
| | | | | | | | * 1111(m) | unassigned | not present in natural rubber spectrum | | 1 |
| 1085(s,b) | | 1099(s) | | | | | * 1087(m) | unassigned | | | |
| | 1048(s) | 1022(s) | 1034(s) | 1040(s) | 1039(s) | 1032(s) | * 1036(m) | unassigned | | | |
| | | | | | | | * 1020(sh) | unassigned | | | |
| | | | 954(m) | | | 955(w) | 962(s) | C-H out-of-plane deformation | C=C bond (trans-) | | 1 |
| | | | | | | | | C-H out-of-plane deformation | | 970 - 960(s) | 2 |
| | | | | | | | * 889(m) | unassigned | | | |
| | 808(m) | 820(w) | 848(m) | | 872(m) | 822(w) | 837(s) | C-H out-of-plane deformation | C=C bond (trans-) | | 1 |
| | | | | | | | | | C=C bond (trans-) | 1000 - 800(s) | 2 |
| | 757(w) | 757(m) | 739(m) | | | 740(w) | * 761(m) | unassigned | | | |
| | | | | | | | * 741(m) | unassigned | | | |
| | | 694(m) | | | | 701(w) | 699(w) | C-H out-of-plane deformation | C=C bond (cis-) | | 1** |
| | | | | | | | | C-H out-of-plane deformation | C=C bond (cis-) | near 690 | 2 |
| | 672(w) | 670(m) | | | 672(s) | | 676(w) | C-H out-of-plane deformation | C=C bond (cis-) | | 1** |

TABLE 13.2 contd.

Frequency values and band assignments for vulcanized rubber and vulcanite Plastics Historical Society samples.

| Vulcanized rubber |  |  | Vulcanite |  |  |  |  | Vibration | Functional group | Frequency range given | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| PHS18 int. cm-1 | PHS18 ext. cm-1 | PHS19 cm-1 | PHS14 cm-1 | PHS15 cm-1 | PHS16 cm-1 | PHS17 cm-1 | Vulcanized rubber (1) cm-1 |  |  | in literature cm-1 |  |
| 617(m) | 606(m) | 602(m) | 598(w) | 610(m) | 600(s) |  | 588(w) | unassigned |  |  |  |
|  |  |  |  |  |  |  | 571(w) | unassigned |  |  |  |
| 493(w) |  |  |  | 512(w) |  |  | 505(w) | unassigned |  |  |  |
| 467(w) | 467(m) | 452(m) | 471(w) |  | 467(m) | 466(w) | 472(w) | S-S linkages |  |  | 1 |
|  |  |  |  |  |  |  | 441(w) | S-S linkages |  |  | 1 |
|  |  |  |  |  |  |  | 410(w) | S-S linkages |  |  | 1 |

1. Linnig and Stewart, 1958. Wavenumber conversions were made using the table in Hummel, 1966.
2. Bellamy, 1975

* Absorption values were estimated from enlarged copy of spectrum in Linnig and Stewart, 1958.

** Reference also suggests bands may be due to C-S linkages or non-characteristic skeletal vibrations.

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp

TABLE 13.3

Frequency values and band assignments for shellac and mineral filled shellac objects from Plastics Historical Society

| Shellac samples<br>cm-1 | PHS8<br>cm-1 | PHS9<br>cm-1 | PHS6<br>cm-1 | PHS20<br>cm-1 | PHS21<br>cm-1 | PHS22<br>cm-1 | Vibration | Functional group | Frequency range in literature (1)<br>cm-1 | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|
| 3421 - 3326(b) | 3388(m,b) | 3390(s,b) | 3387(s,b) | 3353(m,b) | 3353(s,b) | 3405(m,b) | O-H stretch hydrogen bonded | carboxylic acid | 3000 - 2500(b) | 1 |
| | | | | | | | O-H stretch | alcohol | 3400 - 3200(vs,b) polymeric inter-molecular bonds | 1 |
| 2933 - 2923(s) | 2924(s) | 2922(s) | 2931(s) | 2930(s) | 2925(s) | 2928(s) | C-H stretch | methylene group | 2926 ± 10(s) | 1 |
| 2858 - 2854(s) | 2855(s) | 2857(s) | 2855(s) | 2858(s) | 2856(s) | 2856(s) | C-H stretch | methylene group | 2853 ± 10(s) | 1 |
| | | | | | | 2515(w) | calcium carbonate | | 2530(vw) | 2 |
| | | | | | | 1796(w) | calcium carbonate | | 1785(vw) | 2 |
| 1717 - 1713(s) | 1724(s) | 1726(s) | 1714(s) | 1713(s) | 1726(s) | 1717(s) | C=O stretch | ester, aryl | 1730 - 1717(s) | 1 |
| | | | | | | | C=O stretch | carboxylic acid aryl | 1700 - 1680(s) | 1 |
| | | | | | | | C=O stretch | aldehyde, aryl | 1715 - 1695 | 1 |
| * 1641 - 1638(m) | 1642(w) | 1642(m) | 1640(w) | 1605(m) | 1658(m) | 1640(m) | unassigned | | | |
| 1469 - 1464(m) | 1465(w) | 1464(w) | 1465(m) | 1461(m) | nr 1450(sh) | 1465(s,b) | C-H asym. deformation | methyl group | 1450 ± 20(m) | 1 |
| | | | | | | | C-H deformation | methylene group | 1465 ± 20(m) | 1 |
| | | | | | 1429(m) | | calcium carbonate | | 1430(vs,b) | |
| * 1418 - 1414(w) | | | nr 1420(sh) | nr 1420(sh) | | | C-H in-plane deformation | aldehyde | near 1400(w) | 1 |
| 1377 - 1375(m) | 1379(w) | 1375(w) | 1378(m) | 1375(m) | 1375(m) | | C-H sym. deformation | methylene group | 1380 - 1370(s) | 1 |
| | | | | | 1319(w) | | unassigned | | | |
| 1253 - 1235(s) | nr 1230(sh) | 1237(s) | 1236(s) | | | 1253(s) | C-O stretch/O-H deformation | alcohol primary or secondary | 1350 - 1260(s) | 1 |
| | | | | | | | C-O stretch/O-H deformation | carboxylic acid | 1320 - 1211(s) | 1 |
| 1170 - 1147(s) | 1197(m) | nr 1160(sh) | 1166(s) | 1166(s) | 1163(s) | 1149(s) | C-O stretch | ester | 1300 - 1000(s) | 1 |

TABLE 13.3 contd.

Frequency values and band assignments for shellac and mineral filled shellac objects from Plastics Historical Society

| Shellac samples<br>cm-1 | PHS8<br>cm-1 | PHS9<br>cm-1 | PHS6<br>cm-1 | PHS20<br>cm-1 | PHS21<br>cm-1 | PHS22<br>cm-1 | Vibration | Functional group | Frequency range in literature (1)<br>cm-1 | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|
| * 1114(vw) | | nr 1120(sh) | 1115(w) | nr 1115(s) | 1112(s) | 1111(s) | C-O stretch/O-H deformation | alcohol, secondary | near 1100(s) | 1 |
| 1048 - 1030(s) | 1085(s) | 1048(s) | 1041(s) | 1059(s) | 1058(s) | 1037(s) | C-O stretch/O-H deformation | alcohol, primary | near 1050(s) | 1 |
| 948 - 945(m) | 970(vs) | | 947(w) | | nr 950(w sh) | 921(s) | O-H out-of-plane deformation | carboxylic acid | 950 - 900(va) | 1 |
| | 882(w) | | | | | 878(s) | calcium carbonate | | 877(s) | 2 |
| **799 - 772(w) | | 803(m) | 781(w) | | | 791(w) | C-H out-of-plane deformation | aldehyde | 975 - 780(m) | 1 |
| * 725 - 723(m) | | 723(m) | 723(m) | 725(w) | | 753(w) | chain rocking vibration | long chain hydrocarbons with four or more methylene units | 750 - 720(m) | 1 |
| | | | | | | 714(m) | calcium carbonate | | 715(w) | 2 |
| **664 - 639(w) | 617(s) | 662(m) | 660(w) | 607(w) | 613(w) | | unassigned | | | |
| **565 - 513(w) | 572(s) | 536(m) | 518(w) | 564(w) | 521(w) | 543(s) | unassigned | | | |

* Absorption is weak or occurs as a shoulder in some sample spectra.

** Absorption is not present is some sample spectra.

1. Bellamy, 1975

2. Miller and Wilkins, 1952

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp; nr = near

TABLE 13.4

Frequency values and band assignments for Bois Durci and albumen Plastics Historical Society samples

| Albumen GS1 cm-1 | PHS13 cm-1 | PHS23 cm-1 | Vibration | Functional group | Frequency range given in literature (1) cm-1 |
|---|---|---|---|---|---|
| 3276(m,b) | 3410(s,b) | 3450(s,b) | N-H stretch | peptide bond | 3320 - 3270(m) |
|  | 3304(s,b) | 3298(s,b) | hydrogen bonded |  | trans- |
| 3071(m) |  |  | amide II | peptide bond | 3100 - 3070(w) |
|  |  |  | overtone |  | cis- and trans- |
| 2942(m) | 2921(m) | 2929(m) | C-H stretch | methylene group | 2926 ± 10(s) |
| nr 2050(w) | 2139(w) | 2151(w) | unassigned |  |  |
| 1648(s) | 1661(m,b) | 1661(s) | amide I | peptide bond | 1680 - 1630(s) |
|  |  |  | C=O |  |  |
| 1554(s) |  | 1549(m) | amide II - coupled | peptide bond | 1570 - 1515(s) |
|  |  |  | N-H deformation |  |  |
|  |  |  | and C-N stretch |  |  |
|  | 1511(m) | 1502(w) | unassigned |  |  |
| 1449(m,b) | 1463(m,b) | 1431(m,b) | C-H deformation | methylene group | 1465 ± 20(m) |
|  | nr 1430(m,b) |  | C-H asym. | methyl group | 1450 ± 20(m) |
|  |  |  | deformation |  |  |
|  | 1372(m) | 1345(m) | C-H sym. | methyl group | 1380 - 1370(s) |
|  |  |  | deformation |  |  |
| 1309(m,b) | nr 1310(m) |  | unassigned |  |  |
|  | 1235(s) |  | amide III - coupled | peptide bond | 1305 - 1200(m) |
|  |  |  | N-H deformation |  |  |
|  |  |  | and C-N stretch |  |  |
|  | nr 1160(s) | 1164(s,b) | unassigned | possible interference from mineral fillers |  |
|  | 1115(s) |  | unassigned |  |  |
| 1049(m,b) | 1061(vs) | 1060(s) | unassigned |  |  |
|  |  | 926(m) | unassigned |  |  |
|  | 899(w) |  | unassigned |  |  |
|  |  | 848(s) | unassigned |  |  |
| **** (see text) **** |  | 804(s) | unassigned |  |  |
|  |  | 716(s) | unassigned |  |  |

1. Bellamy, 1975

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder;
b = broad; va = variable; sp = sharp; nr = near

# TABLE 13.5

Frequency values and band assignments for Plastics Historical Society Parkesine and Xylonite samples

| Millipore | Wardle-Storey | PHS28 | PHS29 | PHS30 | PHS31 | PHS32 | PHS33 | PHS34 | Intensity | Vibration | Functional group | Frequency range given in literature | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| cm-1 | cm-1 | cm-1 | cm-1 | cm-1 | cm-1 | cm-1 | cm-1 | cm-1 | | | | cm-1 | |
| 3447 | 3442 | 3450(m,b) | 3448(m,b) | 3394(m,b) | 3453(m,b) | 3441(m,b) | 3406(m,b) | 3448(m,b) | m,b | O-H stretch hydrogen bonded | O-H group | 3400 - 3200(vs) polymeric intermolecular | 1 |
| 2961 | 2965 | | | | | 2965(m) | 2964(m) | 2965(m) | m | C-H stretch | methyl group | 2962 ± 10(s) | 1 |
| 2917 | 2928 | 2927(m) | 2924(m) | 2922(m) | 2929(m) | 2928(m) | 2925(m) | 2930(m) | m | C-H stretch | methylene group | 2926 ± 10(s) | 1 |
| 1748 | 1732 | 1727(m) | | | 1729(m) | 1731(s) | 1730(m) | 1732(s) | s | C=O stretch | carbonyl group | 1735(s,sp) | 2 |
| 1671 | 1663 | 1651(s) | 1651(s) | 1651(s) | 1662(s) | 1662(s) | 1662(s) | 1671(s) | s | N-O asym. stretch | nitrate group | 1667 - 1629(vs) | 3 |
| 1511 | | | | | | | | | w | unassigned | | | |
| 1455 | 1452 | 1452(m) | | | 1453(m) | 1452(m) | | 1452(m) | m | C-H asym. deformation | methyl group | 1450 ± 20(m) | 1 |
| | | | | | | | | | | C-H deformation | methylene group | 1465 ± 20(m) | 1 |
| 1429 | 1418 | | 1426(m) | 1428(m) | 1430(m) | 1419(m) | 1430(m) | 1418(m) | m | unassigned | | | |
| 1374 | 1376 | 1378(m) | 1377(m) | 1377(m) | 1376(m) | 1376(m) | 1376(m) | 1376(m) | m | C-H sym. deformation | methylene group | 1380 - 1370(s) | 1 |
| 1288 | 1286 | 1280(s) | 1282(s) | 1282(s) | 1284(s) | 1286(s) | 1288(s) | 1290(s) | s | N-O sym. stretch | nitrate group | 1285 - 1272(vs) | 3 |
| 1246 | | | | | | | | | m | unassigned | | | |
| | 1205 | | | | | 1206(m) | 1207(m) | 1205(m) | m | unassigned | | | |
| 1162 | 1163 | 1162(m) | 1163(m) | near 1160(w) | 1163(s) | 1163(s) | 1162(s) | 1163(s) | s | C-O stretch | ether linkage | 1150 - 1060(vs) | 1 |
| 1073 | 1066 | 1031(s,b) | 1061(s,b) | 1076(s,b) | 1061(s,b) | 1065(s,b) | 1061(s,b) | 1066(s,b) | s,b | C-O stretch | ether linkage | 1150 - 1060(vs) | 1 |
| 945 | near 945 | | | | | | | 946(w) | w | unassigned | | | |
| 846 | 846 | 842(m) | 846(s) | 847(s) | 840(s) | 841(s) | 848(s) | 850(s) | s | N=O stretch | nitrate group | 872 - 833(s) | 3 |
| 751 | 752 | 750(m) | 752(m) | 752(m) | 752(s) | 752(m) | 752(m) | 752(m) | m | out-of-plane deformation | nitrate group | 761 - 745(m) | 3 |
| 692 | 683 | | 676(m) | | 695(s) | 694(m) | 695(m) | 695(m) | m | N-O deformation | nitrate group | 710 - 689(m) | 3 |

1. Bellamy, 1975 2. Sirkis, 1982 3. Brown, 1955

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp

TABLE 13.6

Frequency values and band assignments for cellulose acetate standards and Plastics Historical Society sample

| cellulose acetate VA13 cm-1 | VA14 cm-1 | Bexfilm cm-1 | Intensity | PHS47 cm-1 | Vibration | Functional group | Frequency range given in literature cm-1 | Ref. |
|---|---|---|---|---|---|---|---|---|
| 3499 | 3494 | 3482 | m,b | 3491(m,b) | O-H stretch | O-H group hydrogen bonded | 3400 - 3200 (b) | 1 |
| | | 3069 | w | | C-H stretch | aromatic ring | near 3070 (w) | 1 |
| 2959 | 2959 | 2959 | m | 2943(m) | C-H stretch | methyl group | 2962 ± 10 (s) | 1 |
| 2892 | 2893 | 2893 | m | near 2890(m) | C-H stretch | methine group | 2890 ± 10 (w) | 1 |
| 1762 | 1758 | 1764 | s | 1746(s) | C=O stretch | ester | 1750 - 1730 (s) | 1 |
| 1644 | 1647 | 1648 | m | 1647(m) | unassigned | | | |
| | | 1591 | m | 1592(m) | skeletal ring stretch | aromatic ring | 1625 - 1575(va) | 1 |
| 1547 | nr 1547 | nr 1535 | vw | | unassigned | | | |
| | | 1490 | m | 1488(m) | skeletal ring stretch | aromatic ring | 1525 - 1475(va) | 1 |
| 1433 | 1434 | 1434 | m | 1432(m) | C-H asym. deformation | methyl group | 1450 ± 20 (m) | 1 |
| 1374 | 1373 | 1374 | s | 1373(s) | C-H sym. deformation | methyl group | 1380 - 1370 (s) | 1 |
| 1262 | 1258 | 1260 | s | 1230(s) | C-O stretch | acetate ester | 1250 - 1230 (s) | 1 |
| 1221 | 1222 | | | | unassigned | | | |
| | | 1189 | s | near 1190(w) | P-O-C (aromatic) | triphenyl phosphate | 1242 - 1110 (s) | 2 |
| 1164 | 1166 | 1166 | s | 1162(s) | C-O stretch | ether linkage | 1150 - 1060 (vs) | 1 |
| 1087 | 1065 | 1087 | s,b | 1051(s,b) | C-O stretch | ether linkage | 1150 - 1060 (vs) | 1 |

TABLE 13.6 contd.

Frequency values and band assignments for cellulose acetate standards and Plastics Historical Society sample

| cellulose acetate | | | Inten- sity | PHS47 | Vibration | Functional group | Frequency range given in literature | Ref. |
|---|---|---|---|---|---|---|---|---|
| VA13 | VA14 | Bexfilm | | | | | | |
| cm-1 | cm-1 | cm-1 | | cm-1 | | | cm-1 | |
| 954(vw) | 954(vw) | 963 | s | 970(s) | P-O-C (aromatic) | triphenyl phosphate | 996 - 905 (s) | 2 |
| 905 | 904 | 904 | m | 905(m) | unassigned | | near 901 (m) | 3 |
| 840 | 841 | 839 | m | 834(m) | unassigned | | near 837 (vw) | 3 |
| | | 782 | m | 780(m) | C-H out-of-plane deformation | aromatic ring | 810 - 750 (vs) meta-substitution | 1 |
| | | 760 | m | | | | | |
| | | | | | C-H out-of-plane deformation | aromatic ring | 770 - 735 (vs) ortho-substitution | 1 |
| | | | | | C-H out-of-plane deformation | aromatic ring | 770 - 730 (vs) mono-substitution | 1 |
| nr 692(vw) | 692 (vw) | 692 | m | 691(m) | C-H out-of-plane deformation | aromatic ring | 710 - 690 (s) mono-substitution | 1 |
| 605 | 604 | 604 | m | 603(m) | bending vibration | acetate group | 605 (m) | 3 |
| | | | | | skeletal vibration | acetate group | 612 (s) | 4 |

1. Bellamy, 1975
2. Thomas and Chittenden, 1964
3. Hummel, 1966
4. Thompson and Torkington, 1945

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp; nr = near

TABLE 13.7

Frequency values and band assignments for Plastics Historical Society samples identified as casein

| Casein I RW1 | PHS35 | PHS36 | PHS37 | Vibration | Functional group | Frequency range given in literature | Ref. |
|---|---|---|---|---|---|---|---|
| cm-1 | cm-1 | cm-1 | cm-1 | | | cm-1 | |
| 3287(s,b) | 3320(s,b) | 3305(s,b) | 3293(s,b) | N-H stretch hydrogen bonded | peptide bond | 3320 - 3270(m) (trans-) | 1 |
| 3100(sh) | near 3070(sh) | near 3070(sh) | near 3070(sh) | amide II overtone | peptide bond | 3100 - 3070(w) (cis- and trans-) | 1 |
| 2962(m) | | 2963(m) | | C-H stretch | methyl group | 2962 ± 10(s) | 1 |
| | 2929(m) | 2934(m) | 2920(s) | C-H stretch | methylene group | 2926 ± 10(s) | 1 |
| 2876(m) | | 2877(sh) | 2852(s) | C-H stretch | methyl group | 2872 ± 10(s) | 1 |
| 2120(w) | near 2100(w) | 2130(w) | 1879(w) | unassigned | | | |
| 1661(s) | 1661(s) | 1662(s) | 1661(s) | amide I C=O stretch | peptide bond | 1680 - 1630(s) | 1 |
| | | | | amide I | peptide bond | 1656(vs) | 2 |
| 1546(s) | 1550(s) | 1551(s) | 1550(s) | amide II - coupled N-H deformation and C-N stretch | peptide bond | 1570 - 1515(s) (solid) | 1 |
| | | | | amide II | peptide bond | 1538(s) | 2 |
| 1450(m) | 1448(m) | 1447(m) | 1449(s) | C-H deformation | methyl and methylene groups | 1448(m) | 2 |
| 1400(m) | | | | C-O resonance bond | carboxylic acid ionized | 1399(m) | 2 |
| 1350(m) | | | | unassigned | | | |
| 1315(m) | | 1320(m) | | C-H deformation | methylene groups | 1312(w) | 2 |
| 1241(m) | 1235(m,vb) | 1234(m) | | amide III - coupled N-H deformation and C-N stretch | peptide bond | 1305 - 1200(m) | 1 |
| | | | | amide III | peptide bond | 1242(m) | 2 |

TABLE 13.7 contd.

Frequency values and band assignments for Plastics Historical Society samples identified as casein

| Casein I RW1 | PHS35 | PHS36 | PHS37 | Vibration | Functional group | Frequency range given in literature | Ref. |
|---|---|---|---|---|---|---|---|
| cm-1 | cm-1 | cm-1 | cm-1 | | | cm-1 | |
| 1175(m) | | | | unassigned | | 1158(w) | 2 |
| 1106(m) | | | 1101(vs,b) | N-H deformation | peptide bond | 1101(m) | 2 |
| 950(w) | | | | unassigned | | 980(m) | 2 |
| 900(w) | | | 917(m) | unassigned | | | |
| | | | 799(s) | unassigned | broad area of absorption - see text | | |
| | | | 782(s) | unassigned | | | |
| 703(b) | | | 696(s) | unassigned | | | |
| 626(b) | | | | unassigned | | | |
| 569(b) | | | 515(s) | unassigned | | | |
| | | | 468(s) | unassigned | | | |

1. Bellamy, 1955

2. D'Esposito and Koenig, 1978

KEY: v = very; s = strong; m = medium; w =weak; sh = shoulder; b = broad; va = variable; sp = sharp

TABLE 13.8

Frequency values and band assignments for phenolic plastic samples from Plastics Historical Society

| PHS45 | PHS46 | PHS41 | PHS42 | PHS43 | PHS44 | PHS48 | Vibration | Functional group | Frequency range given in literature | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|
| cm-1 | cm-1 | cm-1 | cm-1 | cm-1 | cm-1 | cm-1 | | | cm-1 | |
| 3353(s) | 3335(b) | 3305(b) | 3344(b) | 3400(b) | 3351(b) | 3334(s) | O-H stretch | phenol polymeric | 3225 | 1 |
| | 3013(w) | | | 3017(m) | | | C-H stretch | aromatic ring | 3019 | 1 |
| 2921(m) | 2922(m) | 2923(m) | near 2920(m) | 2915(m) | 2925(m) | near 2920(m) | C-H stretch | methylene group | 2926 ± 10(s) | 2 |
| 2853(m) | near 2860(sh) | near 2860(sh) | 2876(m) | 2843(w) | | 2869(m) | C-H stretch | methylene group | 2853 ± 10(s) | 2 |
| 1646(m) | near 1650(sh) | 1651(m) | 1652(m) | near 1650(sh) | 1644(w) | near 1640(w) | unassigned | | | |
| 1604(s) | 1606(s) | 1609(s) | 1608(s) | 1598(s) | 1597(s) | 1600(s) | skeletal ring stretch | aromatic ring | 1605 | 1 |
| 1509(s) | 1508(s) | near 1500(sh) | near 1500(sh) | 1510(s) | 1510(s) | near 1500(sh) | skeletal ring stretch | aromatic ring | 1501 | 1 |
| | 1477(s) | 1483(s) | 1483(s) | 1477(s) | | 1483(s) | skeletal ring stretch | aromatic ring | 1473 | 1 |
| 1450(s) | near 1450(sh) | near 1450(sh) | near 1450(sh) | 1442(s) | 1457(s) | near 1450(sh) | C-H deformation | methylene group | 1465 ± 20(m) | 2 |
| 1334(b) | 1338(b) | 1359(s) | 1362(s) | 1337(s) | 1369(b) | 1363(s) | coupled ring stretch and O-H deformation | phenol | 1370 | 1 |
| near 1250(sh) | near 1250(sh) | near 1250(sh) | near 1250(sh) | near 1250(sh) | near 1250(sh) | near 1250(sh) | C-O stretch | phenol | 1252 | 1 |
| 1220(s) | 1217(s) | 1234(s) | 1232(s) | 1225(s) | 1228(s) | 1223(s) | coupled O-H deform. and ring stretch | phenol polymeric | 1230 | 1 |
| 1154(s) | 1153(s) | 1153(s) | 1152(s) | | 1154(s) | 1153(s) | C-H in-plane deformation | aromatic ring | 1152 | 1 |
| near 1100(s) | 1099(s) | near 1100(sh) | | 1102(s) | 1097(s) | | C-H in-plane deformation | aromatic ring | 1072 | 1 |
| 1051(s) | 1054(s) | 1064(s) | 1060(s) | 1043(w) | 1048(s) | 1065(s) | C-H in-plane deformation | aromatic ring | 1024 | 1 |
| | | | | 1000(w) | | | unassigned | | | |

## TABLE 13.8 contd.

Frequency values and band assignments for phenolic plastic samples from Plastics Historical Society

| PHS45 | PHS46 | PHS41 | PHS42 | PHS43 | PHS44 | PHS48 | Vibration | Functional group | Frequency range given in literature | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|
| cm-1 | cm-1 | cm-1 | cm-1 | cm-1 | cm-1 | cm-1 | | | cm-1 | |
| 895(w) | near 900(w) | 885(m) | 885(m) | 887(w) | 897(w) | 883(m) | C-H out-of-plane deformation | aromatic ring | 888 | 1 |
| 822(m) | 823(m) | 826(m) | 826(m) | 823(s) | 822(m) | 825(m) | C-H out-of-plane deformation | aromatic ring | 828 | 1 |
| 757(m) | 758(m) | 763(m) | 757(m) | 758(s) | 759(m) | 759(m) | C-H out-of-plane deformation | aromatic ring | 754 | 1 |

1. Evans, 1960
2. Bellamy, 1975

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp

TABLE 13.9

Frequency values and band assignments for amino plastic samples from Plastics Historical Society

| PHS38 T/UF cm-1 | PHS39 T/UF cm-1 | PHS49 UF cm-1 | PHS50 UF cm-1 | PHS40 MF cm-1 | Vibration | Functional group/ compound | Frequency value given in literature cm-1 | Ref. |
|---|---|---|---|---|---|---|---|---|
| 3334(s,b) | 3335(s,b) | 3337(s,b) | 3335(s,b) | 3369(s,b) | N-H stretch | urea, thiourea melamine | 3333(b) | 1 |
|  |  | 2961(m) |  |  | C-H stretch | methyl group | 2962 ± 10(s) | 2 |
| 2922(m) | 2923(m) |  | 2922(m) | 2925(m) | C-H stretch | methylene group | 2926 ± 10(s) | 2 |
| 2061(w,b) | 2059(w,b) |  | 2151(w,b) |  | unassigned |  |  |  |
| 1650(s) | 1647(s) | 1650(s) | 1644(s) |  | amide I C=O stretch | urea | 1639(s) | 1 |
|  |  |  |  | 1586(s) | triazine ring | melamine | * 1667 - 1250(s) | 1 |
| 1541(s) | 1548(s) | 1550(s) | 1553(s) |  | amide II C-N stretch | urea | 1563(s) | 1 |
|  |  |  |  |  | C=S vibration | thiourea | 1538(s) | 1 |
|  |  |  |  | 1501(s) | triazine ring | melamine | * 1667 - 1250(s) | 1 |
|  |  |  |  | 1478(s) | triazine ring | melamine | * 1667 - 1250(s) | 1 |
| 1434(w) | 1433(w) | 1479(m) | nr 1479(m) |  | C-H deformation | methylene group | 1443 | 1 |
|  |  | 1381(m) | 1380(m) |  | C-H deformation | methyl group | 1383 | 1 |
|  |  |  |  | 1356(s) | triazine ring | melamine | * 1667 - 1250(s) | 1 |
| 1341(m) | 1341(m) |  |  |  | C=S vibration | thiourea | 1333 | 1 |
| 1238(s) | 1237(s) | 1251(s) | 1244(s) |  | unassigned |  |  |  |
|  | 1159(m) |  |  | 1161(s) | unassigned |  |  |  |
| 1056(s) | 1059(s) | 1048(b) | 1040(b) | 1048(s,b) | C-O stretch | ether linkage | nr 1087(s) | 1 |
|  |  |  |  |  | C-O stretch | ether linkage melamine | 1064(vw) | 1 |
| 901(m) | 900(m) | nr 900(sh) | nr 900(sh) | 899(m) | unassigned |  |  |  |
|  |  |  |  | 815(s) | triazine ring | melamine | 813(s) | 1 |
|  |  | nr 800(sh) | nr 800(sh) |  | unassigned |  |  |  |

T/Uf = thiourea/urea formaldehyde UR = urea formaldehyde MF = melamine formaldehyde

* A series of strong bands occur in region 1667 - 1250 cm-1

1. Urbanski et al., 1977; Wavelengths were converted using table from Hummel, 1966 2. Bellamy, 1975

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp; nr = near

# CHAPTER 14 IDENTIFICATION OF OLD CONSERVATION MATERIALS FOUND ON OBJECTS

## Introduction

In addition to being able to identify the synthetic materials used to construct objects (discussed in the previous chapter), it is also important to be able to identify the synthetic materials that have been used in conservation treatments. Modern materials have been used extensively in conservation almost from the time that they became available (Horie, 1987). Unfortunately, it has only recently become standard procedure to keep detailed treatment records. Several materials were encountered during the course of this research project which were identified as synthetic substances and the results of the infrared spectroscopy of these samples will be summarized below.

## Nimrud ivories

Some Nimrud ivory writing boards were examined as part of an undergraduate dissertation (Norman, 1988). Several types of materials applied during previous conservation, including consolidants, adhesives and gap filling materials were present on the objects. No records had been kept of the treatments carried out during the period 1958 - 62 and the person who performed much of the early conservation treatment is no longer alive. Ivory has a tendency to laminate. Some of the treatment materials had yellowed and were pulling away from the surface and causing damage by bringing some of the ivory with it. FT-IR was utilized in an attempt to identify the materials which were used.

It was thought that the residues might be poly (vinyl acetate) (PVAC) as it was known to have been used as a consolidant when the objects were excavated (Norman, 1988). The use of PVAC homopolymers in conservation was first published in 1932 and the material was widely used by the mid 1950's (Horie, 1987). PVAC has been observed to be stable to light aging. It oxidizes to a certain extent in air, but has not been observed to severely crosslink or otherwise degrade. It has been reported that PVAC can be dissolved after 30 to 40 years. PVAC is also made as a dispersion and dispersions of vinyl copolmers have been used in conservation. However, they have been found to be less stable and more susceptible to yellowing due to the emulsifiers used which are somewhat unstable. Early emulsions used in conservation were plasticized and the plasticizers are thought to be lost after several decades. Also, PVAC dispersions have been observed to degrade and produce acetic acid (Horie, 1987).

A summary of the field conservation of the Nimrud ivories is given as an appendix in the publication on Nimrud (Mallowan, 1966). After uncovering and preliminary cleaning, the objects were coated with PVAC in acetone. When the solvent had evaporated, the piece was lifted and the other side was consolidated. The post excavation treatment of the ivories incorporated further cleaning and consolidation. Also, the pieces were reinforced and the lost portions were filled if necessary (Wales, 1966). It has been recorded that PVAC was used to consolidate the fragile ivories which were excavated at Fort Shalmaneser during the final seasons (cir. 1958 - 1962). The ivories had to be consolidated in the field as the original condition was described as having the consistency of processed cheese (Reade, 1982).

A further material which could have been used on the ivories was cellulose nitrate. Cellulose nitrate in solution can be used as an adhesive. A solution of celluloid dissolved in a 50/50 solution of acetone and amyl acetate was first recommended in 1926 for use as an adhesive and consolidant. However, cellulose nitrate has long been recognized as an unstable material and its use in other fields such as the film industry has been superceded by more stable materials. As early as 1867, it was discovered that cellulose nitrate became acidic in the presence of strong light. The degradation products included nitric, formic and oxalic acids, cyanogen and glucose. Cellulose nitrate is sensitive to acid and alkaline hydrolysis which produces a reduction of chain length and denitration. This may be catalyzed by residual acid impurities retained from the nitration process. Also, the loss of volatile stabilizers and plasticizers produce a brittle film with impaired mechanical properties. Thus, in addition to a loss of adhesion qualities with time, acidic degradation products are formed which are harmful to the objects. However, cellulose nitrate is still widely used in conservation (Koob, 1982).

The composition of a typical cellulose nitrate adhesive includes 100 parts by weight cellulose nitrate (11.4% nitrogen content), 40 parts camphor, 75 parts acetone, 300 parts ethyl alcohol and 165 parts amyl acetate (Skeist, 1977). Different solvents are utilized by manufacturers to achieve various working properties. The solvents make up the largest portion of the composition by weight. Camphor is not used by every company as a plasticizer (Koob, 1982)

There are two methods which can be used to identify cellulose nitrate. The first technique is a spot test utilizing acidic diphenylamine which turns a very intense blue colour in the presence of cellulose nitrate (Koob, 1982; Haslem et al., 1972; Braun, 1982). The second method is infrared spectroscopy. Cellulose nitrate has a distinctive spectrum which has been discussed in detail in chapter 10.

Fourteen samples were removed from the ivories by the conservator for analysis. The sample details are listed in table 14.1. The samples were prepared for analysis by the standard procedure of rubbing them gently onto a piece of silicon carbide abrasive paper and measuring the spectrum directly from the paper. In many cases, the samples were thin films, but they were too thick to obtain a satisfactory transmission spectra when mounted in a microaperture holder. It was difficult to generate a powder by rubbing the film on to the abrasive paper. The samples were held with fine forceps and very gently rubbed against the silicon carbide paper. The hard waxlike materials were simply crushed onto the paper with the back of a microspatula and the excess was shaken off and retained.

The results of the infrared analysis are summarized in Table 14.1. Six of the samples were identified conclusively as cellulose nitrate. In all of these spectra, the bands characteristic of the nitrate group (Chapter 10) appear, except for the absorption in the region 689 - 710 $cm^{-1}$ (Table 14.2). It is thought that the band in that region is masked by the overlapping of several bands. The spectra were also compared to a diffuse reflectance spectrum of a fresh cellulose nitrate adhesive (HMG) (Figure 14.1). In sample CWN1 (Figure 14.2b), the bands at 1673 and 1296 $cm^{-1}$ fall slightly above the regions suggested in the literature for cellulose nitrate, but the second absorption occurs at 1298 $cm^{-1}$ in the HMG spectrum. The frequencies of the absorption bands are affected by the immediate environment of the of the functional group it represents. The value may be shifted by the crosslinking and denitration which occur on ageing or by plasticizers and additives present. Two types of cellulose nitrate adhesive seem to have been used, as spectra of samples CWN5 (Figure 14.2a) and CWN12 have a strong band at 1737 and 1735 $cm^{-1}$ respectively which is characteristic of the plasticizer camphor (Sirkis, 1982). In the other four spectra, only a very weak shoulder appears at 1720 - 25 cm$^{-1}$ which may be due the presence of other additives (Figure 14.2b).

Two of the sample spectra, CWN6 (Figure 14.3b) and CWN11, have very similar spectra which are somewhat difficult to interpret. There are bands at 1647 - 1651 cm$^{-1}$ and 1282 - 1284 cm$^{-1}$ which are less intense in relation to the other bands in the spectrum which may indicate a heavily denitrated cellulose nitrate. However, there are indications of a second material with very weak bands in the regions of 2516, 1797 and 875 cm$^{-1}$. These bands are characteristic of calcium carbonate (Miller and Wilkins, 1952).

The spectra of CWN9 and CWN 14 are extremely difficult to interpret. There is an absence of sharp or intense bands. There is a broad band centered at 3374 cm$^{-1}$, an indistinct band at 2924 cm$^{-1}$ and a broad band at 1646 cm$^{-1}$ which correlate with those in the spectrum of cellulose powder. There is also a doublet at 988 and 921 cm$^{-1}$ which may be due to the ether linkages in the cellulose. There is no evidence of bands at 1280 and 840 cm$^{-1}$, so it is difficult to say that it is severely degraded cellulose nitrate. None of the sample spectra resembled that of ivory.

Only one sample, CWN13, was identified as poly (vinyl acetate) which has been recorded as being used. It was identified by comparison with a diffuse reflectance sectrum of chemical poly (vinyl acetate) (Aldrich secondary standard) and to a spectrum of PVAC adhesive (UHU, Beecham). The spectrum of CWN13 (Figure 14.4b) has absorptions at 1435, 1375, 1265, 1227, 1125, 1026, 948, 631 and 606 $cm^{-1}$ which correspond very closely to absorptions in the spectrum of the secondary standard poly (vinyl acetate) (Figure 14.4a). The spectra are compared in Figure 14.4. The sample spectrum has a strong band which is most intense at 1739 $cm^{-1}$; however,the corresponding absorption in the standard spectrum is a broad band with the maximum intensity occurring at 1752 $cm^{-1}$. The frequency values are compared in Table 14.3.

Sample CWN3 was described as a wax fill and identified as beeswax. The sample spectrum is discussed in the chapter on wax. However, there are several bands at 2522, 1788, 874 and 857 $cm^{-1}$ and are due to some sort of impurity or additive. A spectrum of beeswax taken from a comb of Apis dorsata was subtracted from the sample spectrum by the computer and the difference spectrum was obtained. It was found to have the bands at 2522, 1788, 874, 857

$cm^{-1}$ and a very strong band at 1539 $cm^{-1}$. The beeswax sample CWN3 contains other components which may include calcium carbonate, which is characterized by bands which occur at 2530, 1785, 1430, 877 and 715 $cm^{-1}$ (Miller and Wilkins, 1952).

Two samples which were described as a hard waxlike substance (CWN7) and a possibly original grey wax (CWN10) were found to have similar, distinctive spectra. The spectrum is characterized by four sharp bands which fall in the regions 2515 - 2516 $cm^{-1}$ (doublet), 1797, 875 - 877 and 715 - 716 $cm^{-1}$. These bands fall into the regions given above for calcium carbonate. Initially, the identification of this spectrum was difficult. The confusion is due to the the effect of specular reflectance which causes the bands near 2530 and 1785 $cm^{-1}$ to be disproportionately intense. There is no strong evidence for the presence of cellulose nitrate in these spectra. However, the description of the materials as a hard wax-like substance (CWN7) and possibly original wax indicate that the consistancy of the material was somewhat different to that of the adhesive and consolidants. In an early textbook on conservation (Plenderleith, 1956), a recipe is given for a mixture of cellulose nitrate in a solution of amyl acetate and acetone (50/50) and fine white sand. This mixture was described as having the "consistancy of soft putty" and was recommended as a anhydrous cement which would not shrink. The dry material had the colour of light sandstone and was recommended for stone. However, it might have been used for these materials as it would have been desirable to have a gap filling material which would not shrink. Presumably calcium carbonate was used in place of sand as a filler.

It is not surprising that many of the samples were identified or thought to be cellulose nitrate because it has been a popular conservation material and was available from the date of excavation of the ivories. Although the Nimrud ivories were not specifically mentioned, commercial cellulose nitrate adhesives such as Durofix and HMG were "safely recommended" as an adhesive for ivories in a textbook on conservation (Plenderleith and Werner, 1971). It is interesting to note that samples which were described both as yellowed and as white were identified as cellulose nitrate. Also, there seem to be two types of cellulose nitrate used, one with camphor as a plasticizer and one with very little or none. There may also be samples of denitrated cellulose nitrate. It is important to be able to detect whether cellulose nitrate has been used on objects such as the ivories so that it can be removed. It has been noted in the literature that the acidity of the cellulose nitrate may be harmful to sensitive materials such as ivory (Koob, 1982).

The weak bands which have been assigned to the presence of calcium carbonate in several of the spectra may indicate that a mineral filler was prepared with cellulose nitrate. It is also possible that the traces of calcium carbonate result from the traces of soil which were found to adhere in some cases to the ivory and consolidant (Norman, 1988).

The presence of PVAC and beeswax on the object are also not surprising as both materials have been widely used in conservation for many years. There is no evidence of degradation in the CWN13 spectrum and it has been reported that poly (vinyl acetate) can be dissolved after 30 - 40 years (Horie, 1987).

### Stone consolidation material from marble frieze

A sample of gap filling material was taken from a marble frieze located at the British Museum. The material was thought perhaps to be a resin of some sort. The restoration was thought to have been carried out in the nineteenth century. The diffuse reflectance spectrum of the material is characterized by bands at

2516, 1797, 1442 (very strong), 877 and 714 $cm^{-1}$ which are characteristic of calcium carbonate. The spectrum also contains a shoulder which commences near 3400 $cm^{-1}$ and runs into the band at 2934 $cm^{-1}$. Also, a strong band is observed at 1696 $cm^{-1}$. These bands are indicative of an organic acid which suggests that the material contains a resin of some sort. It may be that an material similar to the later putty material described by Plenderleith (1956) was prepared with a resin and a filler containing calcium carbonate.

### Materials from glass painting sample

A sample was analyzed which had been separated from the inorganic pigments from a painting on glass. The material was thought to be an organic binder. A diffuse reflectance spectrum was measured and it was found to correspond very closely to that of cellulose nitrate adhesive. This was somewhat surprising as it was not obvious from a visual inspection that the painting had been treated. It is not known if cellulose nitrate was used as the medium. The material was also examined with the infrared microscope to see if traces of the painting media were evident in the cellulose nitrate. The sample examined appeared to be homogeneous and was found to be cellulose nitrate.

### Coating from glass lithograph fragment

A sample (York3) was analyzed from a fragment of glass which was thought to be a lithograph which was attached to the glass with turpentine and then covered with a white material which was thought to be paint (Skeldergate, York, 1983.25 context 2005, small finds number 96). The glass fragments were found in a fill from the cellar of a building erected between 1718 and 1786. There are a wide range of dates given to the material in the fill, however, the picture represents a building which was not built until around 1833. It is thought that the fill material was deposited in the 1880's. The material was excavated in 1983 and the surface was consolidated with a PVAC emulsion. The material is almost certainly Vinamul (poly (vinyl acetate) dispersion) (Little, 1988, personal communication).

A fragment was sent for identification and a small sample was removed for analysis. Diffuse reflectance spectroscopy was not successful as the material did not powder well. A sliver of the thin film was transfered to a copper TEM grid and examined with FT-IR microscopy without any mounting medium which might have obscured the spectrum. The sample was transparent in some areas and appeared to be folded over in others forming grey areas.

There were also several yellowed areas which were thought to be residual adhesive, perhaps resin. Spectra were recorded of the very transparent section and one of the yellowed sections. A second set of two samples of the white material thought to be paint was also examined. The paint samples appeared as an opaque grey colour under the microscope.

The first sample was the clear, transparent section and the resulting spectrum (Figure 14.5) was identified as PVAC by comparison with reference spectra. The unknown sample spectrum contains absorptions due to the C=O and the C-O stretching vibrations of the acetate ester functional group which are assigned in Table 14.3. The spectrum was found to correspond closely to a published spectrum of poly (vinyl acetate) (Hummel, 1978). The sample spectrum was also observed to correspond to spectra of secondary standard poly (vinyl acetate) and of a PVAC adhesive (UHU, Beecham) which were collected using diffuse reflectance FT-IR spectroscopy. Minor variations in band intensity were observed between the published transmission spectrum and the diffuse reflectance. This effect is discussed in Chapter 2. The frequencies values of the diffuse reflectance spectra are fairly close to those of the transmittance spectrum in the literature. The frequency values of the unknown are compared with the standards in Table 14.3. The weaker bands at 1697 and 1433 $cm^{-1}$ in the unknown spectrum (Figure 14.5) are greater in relative intensity in the diffuse reflectance spectra of the secondary standard poly (vinyl acetate) (see Figure 14.4a). The band which occurs as a doublet near 1270 and 1224 $cm^{-1}$ in the diffuse reflectance spectra appears as a single band at 1238 $cm^{-1}$ in the unknown spectrum and as a single band near 1245 $cm^{-1}$ in the spectrum from the literature. The most serious variation between the spectrum of the unknown and the reference spectra is the shape of the band with maximum intensity at 1024 $cm^{-1}$. The band at 1127 and 1123 $cm^{-1}$ in the spectra of the chemical standard PVAC and the PVAC adhesive respectively are not apparent in the sample spectrum where a weak shoulder occurs at 1115 $cm^{-1}$. The presence of a broad band centered at 3458 $cm^{-1}$ which is indicative of hydroxyl groups suggested that the material might contain poly (vinyl alcohol) (PVAL). This absorption is not present in the PVAC reference spectra. PVAL is produced from PVAC and often actually contains some acetate groups in the structure (Horie, 1987). The diffuse reflectance FT-IR spectra obtained of two types of Gelvatol (poly (vinyl alcohol)) exhibited evidence of acetate content. It is more likely that the PVAC dispersion has undergone a degree of deacetylation through time resulting in the presence of some hydroxyl groups in the structure, or that the band may be due to residual water in the structure.

The second sample of the yellowed area was thicker and the resulting spectrum is less clear. The bands in the region 3454 - 2860 $cm^{-1}$ are more intense in relation to the other bands in the spectrum than in that of the clear sample. The band which occurs at 1738 $cm^{-1}$ is much wider in the thicker sample spectrum and the weak shoulder at 1697 $cm^{-1}$ is stronger and occurs at 1659 $cm^{-1}$. Also, the band at 1433 $cm^{-1}$ is stronger and the region between 1248 - 1024 $cm^{-1}$ is indistinct with no major bands. Several new, weak bands appear in the region between 2400 - 2000 $cm^{-1}$. However, the differences are probably due to the distortions caused by the thickness of the sample and not by the presence of additional materials. Unfortunately, the data processing capabilities of the microscope do not allow spectral subtraction which would remove the bands due to PVAC and so possibly reveal the presence of other materials.

The spectra of the paint material are very similar. Most of the bands present are due to the PVAC. However, two very broad, strong bands occur with maximum intensities at 3393 and 1074 $cm^{-1}$. The shape and the location of these very broad bands suggest that an inorganic compound is present. The only statement which can be made is that it is not calcium carbonate which is marked by a very strong, broad band near 1430 $cm^{-1}$ with lesser bands near 877, 1785 and 2530 $cm^{-1}$ (very weak). The broad band in the paint sample spectra is indicative of inorganic constituents.

**Paraffin wax**

Another type of synthetic treatment which has been discussed earlier is that of paraffin or hydrocarbon wax. It has been widely used in conservation since the end of the last century (Horie, 1987) and, as it is produced from petroleum distillation, has only been available since the nineteenth century (Mills, 1972). It has also been recommended for lifting fragile objects in an early text on archaeological excavation techniques (Droop, 1915). The wax is merely heated and then the hot wax is deposited over the object. Paraffin oil or wax was recommended in an early textbook on conservation (Plenderleith, 1956) as a treatment for corroded steel, coating for leather, and as a moisture barrier in the treatment of stone. Also, a recipe is given for a paraffin wax/polyethylene wax paste which is recommended as a polish for, among other things, paintings (Plenderleith, 1956). The use of paraffin wax has largely been discontinued. Thus, when identified on an art or archaeological object, it must be assumed to be the result of treatment and not original unless the object is of very recent date. Examples of the use of thiis material have been encountered in this study on the bronze figure from the Fitzwilliam Museum and the two mummy masks from the Boston Museum of Fine Arts (Chapter 4).

### Material from Mask of Thay

A very good example of the desirability of identifying old treatments may be seen with an object from the Fitzwilliam Museum, the Mask of Thay (E.198.1903). The object, a Middle Kingdom mummy mask, was excavated from the Tomb of Beni Hasan and acquired by the museum in 1903 as a gift of the excavation committee. It is thought that all subsequent treatment was performed at the museum and no documentation of any sort was kept. The piece was again conserved in 1987 in preparation for an exhibition. The mask was composed of three layers, a plaster layer which was thought to have been treated with shellac, linen which was coated with some sort of resin and the top layer which was plaster which had been painted. The bottom layer was cracked in some places, but was fairly intact. The top layer of plaster was made up of about forty fragments which were reassembled presumably at the museum. Several samples were removed from the mask to attempt to identify some of the early materials which had been utilized during conservation.

A sample of material which was thought to be modern was removed from the repair above the left eye (FW16). The diffuse reflectance spectrum of this material was found to resemble that of cellulose nitrate adhesive. It is interesting to note that the material does not show any evidence of degradation in the spectrum. All of the characteristic bands of the nitrate group are strong (Table 14.2) and a band which is indicative of camphor is present at 1714 $cm^{-1}$. A second sample (FW17) which was removed from the lower right cheek gave a very complex diffuse reflectance spectrum which was difficult to interpret. The sample was then examined by FT-IR microscopy. The sample was a dirty white colour with a few specks of a yellow-red material which may be shellac. The spectrum of the grey material (Figure

14.6) was observed to correspond closely with that of the PVAC from the painted glass (York3) and the PVAC standards (Table 14.3). The spectrum of the yellow area was much less clear. The spectrum was very difficult to interpret which indicates that a mixture is present.

### *In situ* analysis of coatings on metal objects

It was hoped that the FT-IR microscope could be used to examine coatings and residues on metal objects in the reflectance mode. Such an examination procedure could be carried out completely non-destructively. Earlier attempts to analyze black, presumably organic, deposits on highly burnished Cypriot ceramic ware were unsuccessful as an insufficient amount of energy was reflected back to the detector to record a signal. Two metal objects were also examined. The first object was a Saxon brooch (Institute of Archaeology laboratory number 5528) which had several organic inlays. It was thought that the object had been coated with a synthetic varnish. The metal surface was sufficiently reflective to record a signal and a spectrum was recorded against a background spectrum of an aluminum mirror. However, the resulting spectrum was very difficult to interpret. A series of sharp bands were observed above the baseline. These might arise from the metal of the brooch itself. The spectrum is not thought to be in any way related to that of a synthetic organic material. An attempt was made to examine one of the resinous inlays in the brooch but the inlay area was not sufficiently reflective to record a signal. The second piece which was examined was a bronze pin (Institute of Archaeology laboratory number 2743) which was known to have been coated with Incralac, an acrylic resin commonly used to coat bronze objects. The surface did not, however, reflect sufficient energy to record a spectrum.

It is thought that in the first case, a larger number of scans would improve the measurement from highly reflective surfaces. However, the problem of insufficiently reflective surfaces has yet to be overcome with the FT-IR microscope used in this research.

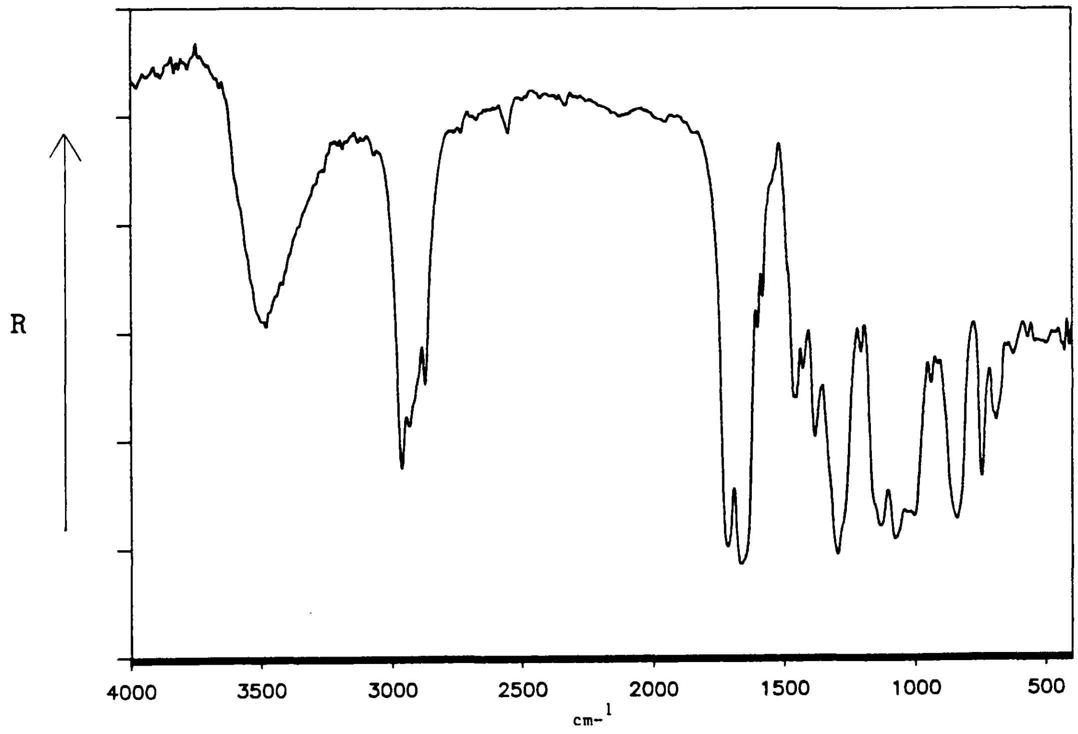


Figure 14.1 Diffuse reflectance FT-IR spectrum of HMG cellulose nitrate adhesive.

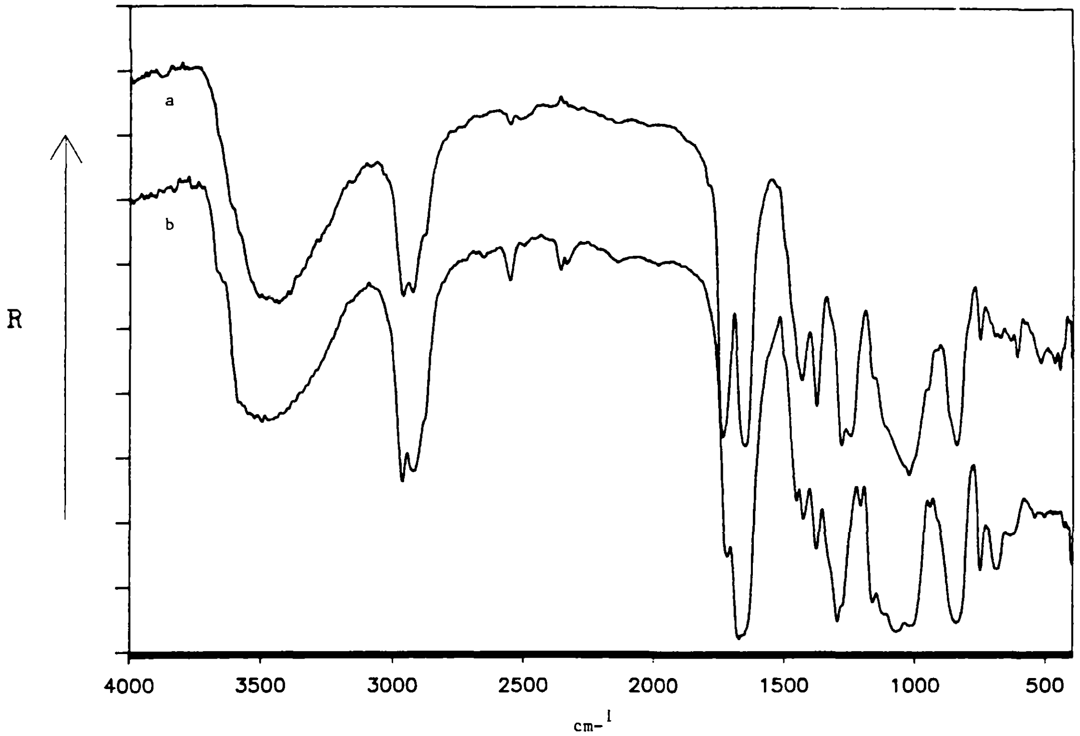


Figure 14.2 Diffuse reflectance FT-IR spectra of consolidant/adhesive samples from Nimrud ivories identified as cellulose nitrate, (a) CWN5 and (b) CWN1.

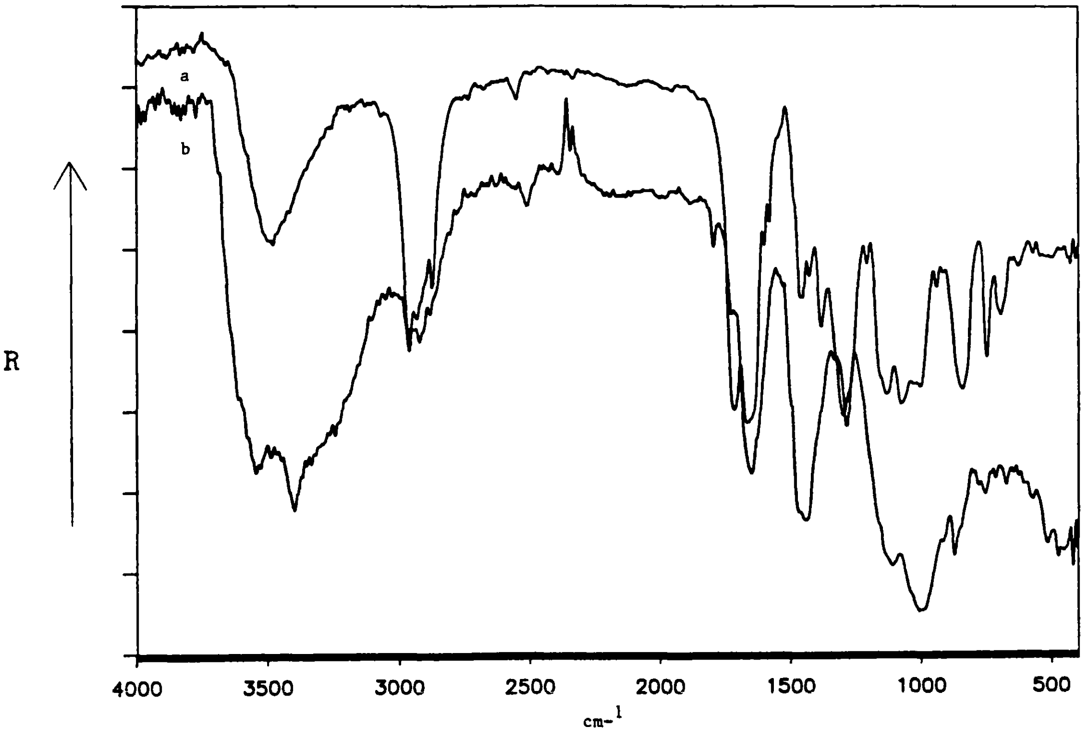


Figure 14.3 Diffuse reflectance FT-IR spectra of (a) HMG cellulose nitrate adhesive and (b) consolidant film from Nimrud ivories identified as degraded cellulose nitrate (CWN6).

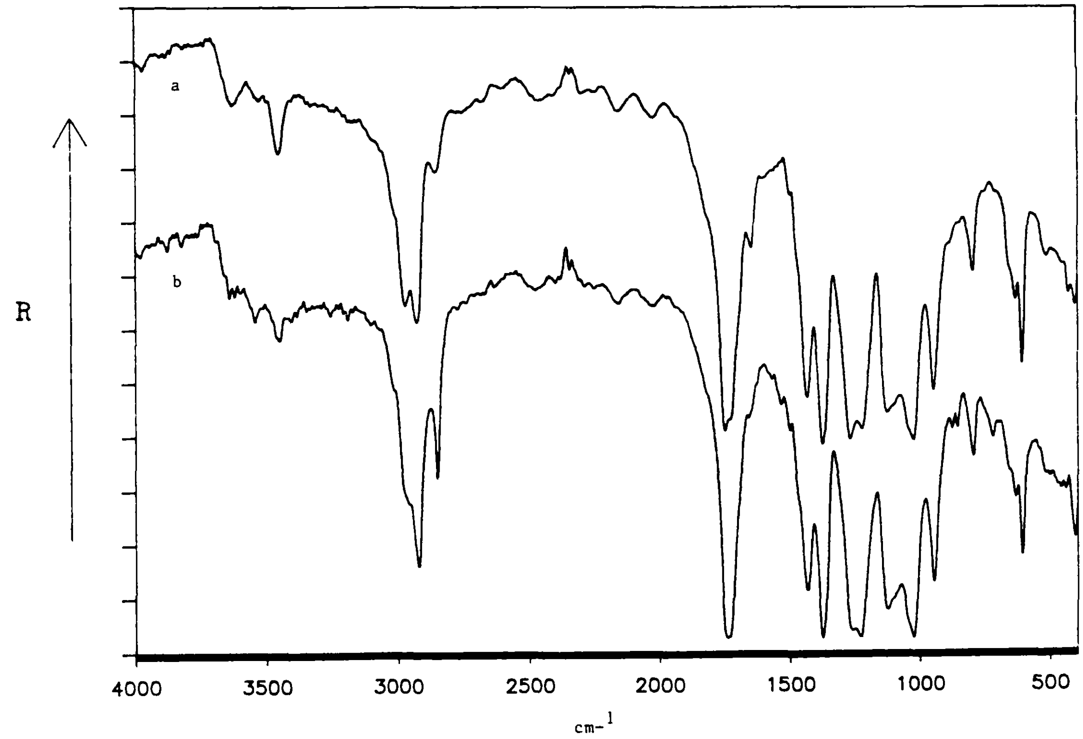


Figure 14.4 Diffuse reflectance FT-IR spectra of (a) secondary standard poly (vinyl acetate)(Aldrich) and (b) adhesive/consolidant from Nimrud ivories identified as poly (vinyl acetate)(CWN13).

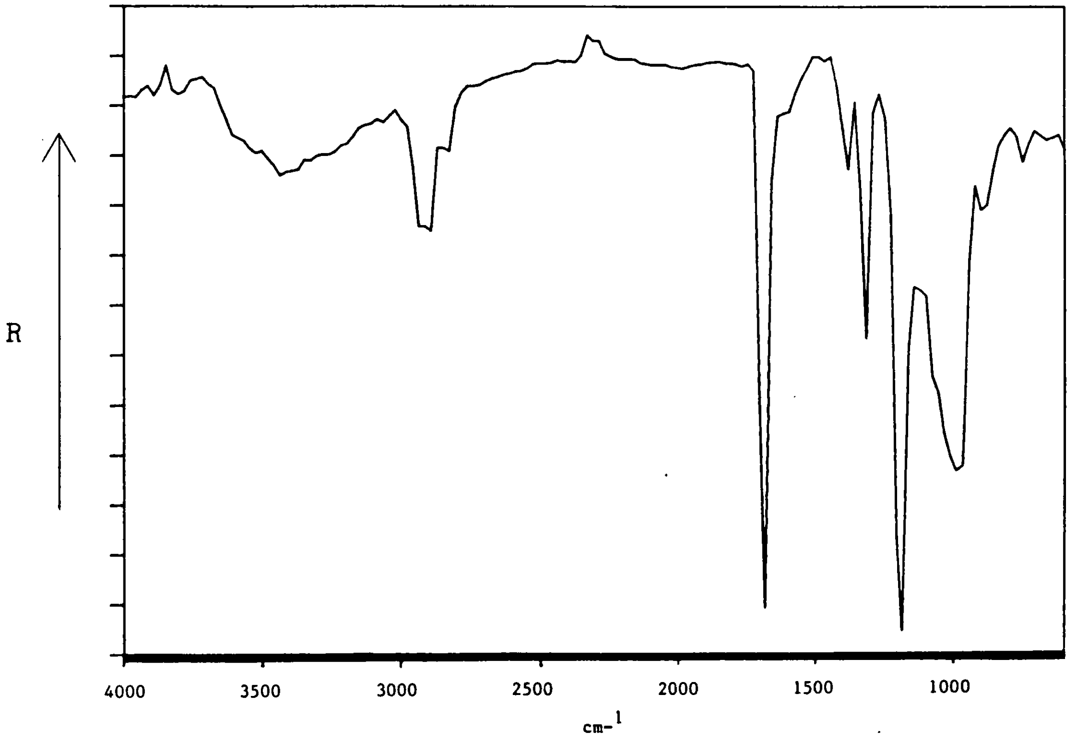


Figure 14.5 Transmission FT-IR spectrum of coating from glass lithograph (York3) obtained using Bruker FT-IR microscope. The material was identified as poly (vinyl acetate).

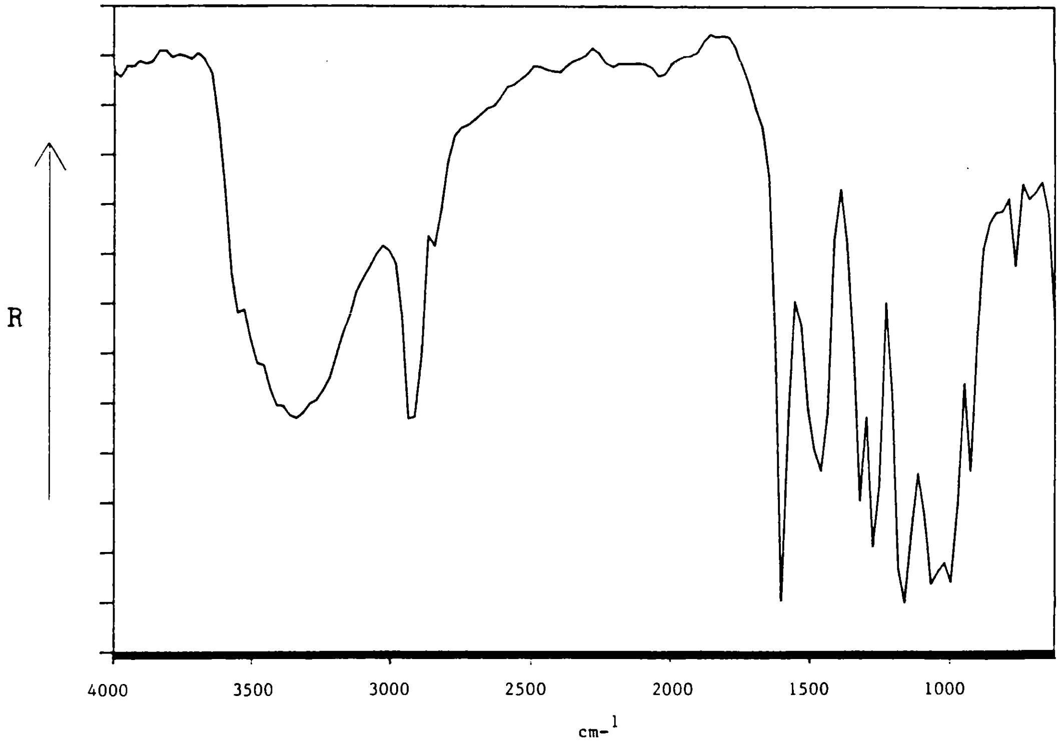


Figure 14.6 Transmission FT-IR spectrum of old restoration material from the lower reight cheek of the Mask of Thay (FW17) obtained using Bruker FT-IR microscope. The sample was identified as poly (vinyl acetate).

TABLE 14.1

Description and identification of Nimrud ivory samples

| Sample number | Sample description | Object number (1) | Identification | Spectrum number |
|---|---|---|---|---|
| CWN1 | consolidant/adhesive | | cellulose nitrate | gsva0356 |
| CWN2 | yellowed, hard adhesive | | cellulose nitrate | gsva0357 |
| CWN3 | waxfill from surface of burnt fragment w/ corner | | beeswax + calcium carbonate | gsva0358 |
| CWN4 | consolidant layer from wax surface of burnt fragment | | cellulose nitrate | gsva0553 |
| CWN5 | adhesive | | cellulose nitrate | gsva0360 |
| CWN6 | white consolidant film | | degraded cellulose nitrate | gsva0554 |
| CWN7 | hard waxlike substance from long point hinge fragment | | calcium carbonate | gsva0362 |
| CWN8 | adhesive from burnt fragment | | cellulose nitrate | gsva0548 |
| CWN9 | possible original wax from grey uneven surface of writing board | ND 3572 | possible degraded cellulose nitrate | gsva0564 |
| CWN10 | possible original wax from writing board | ND 3572 | calcium carbonate | gsva0522 |
| CWN11 | consolidant layer from writing board | ND 3572 | degraded cellulose nitrate | gsva0551 |
| CWN12 | white consolidant film from writing board | ND 3572 | cellulose nitrate | gsva0552 |
| CWN13 | adhesive/consolidant from reverse of writing board | ND 3572 | poly (vinyl acetate) | gsva0552 |
| CWN14 | Hard waxlike material | | possible degraded cellulose nitrate | gsva0526 |

1. If available

TABLE 14.2

Frequency values and band assignments for synthetic samples identified as cellulose nitrate

| Milli-pore | Wardle-Storey | HMG ad-hesive | Nimrud ivory samples | Mask of Thay | Inten-sity | Vibration | Functional group | Frequency range given in literature | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| cm-1 | cm-1 | cm-1 | cm-1 | cm-1 | | | | cm-1 | |
| 3447 | 3442 | 3482 | 3496 - 3404 | 3480 | m,b | O-H stretch hydrogen bonded | O-H group | 3400 - 3200(vs) polymeric intermolecular | 1 |
| 2961 | 2965 | 2964 | * 2966 - 2962 | 2963 | m | C-H stretch | methyl group | 2962 ± 10(s) | 1 |
| 2917 | 2928 | 2936 | 2928 - 2921 | 2935 | m | C-H stretch | methylene group | 2926 ± 10(s) | 1 |
| 1748 | 1732 | 1719 | **1737 - 1735 | 1714 | s | C=O stretch | carbonyl group | 1735(s,sp) | 2 |
| 1671 | 1663 | 1664 | 1673 - 1651 | 1673 | s | N-O asym. stretch | nitrate group | 1667 - 1629(vs) | 3 |
| 1511 | | | | | w | unassigned | | | |
| 1455 | 1452 | 1461 | * 1464 - 1455 | 1468 | m | C-H asym. deformation | methyl group | 1450 ± 20(m) | 1 |
| | | | | | | C-H deformation | methylene group | 1465 ± 20(m) | 1 |
| 1429 | 1418 | 1431 | 1433 - 1429 | | m | unassigned | | | |
| 1374 | 1376 | 1384 | 1376 - 1375 | 1379 | m | C-H sym. deformation | methylene group | 1380 - 1370(s) | 1 |
| 1288 | 1286 | 1298 | 1296 - 1278 | 1292 | s | N-O sym. stretch | nitrate group | 1285 - 1272(vs) | 3 |
| 1246 | | | * 1247 - 1243 | | m | unassigned | | | |
| | 1205 | 1208 | * 1209 - 1208 | | m | unassigned | | | |
| 1162 | 1163 | 1134 | * 1163 - 1161 | 1143 | s | C-O stretch | ether linkage | 1150 - 1060(vs) | 1 |
| 1073 | 1066 | 1079 | 1073 - 1022 | 1058 | s,b | C-O stretch | ether linkage | 1150 - 1060(vs) | 1 |
| 945 | near 945 | 944 | * 946 | near 945(sh) | w | unassigned | | | |
| 846 | 846 | 845 | 846 - 838 | 842 | s | N=O stretch | nitrate group | 872 - 833(s) | 3 |
| 751 | 752 | 749 | 753 - 750 | 751 | m | out-of-plane deformation | nitrate group | 761 - 745(m) | 3 |
| 692 | 683 | 694 | 694 - 670 | 693 | m | N-O deformation | nitrate group | 710 - 689(m) | 3 |

* Absorption is weak or does not appear in some spectra

** Strong band occurs in samples CWN5 and CWN12, a weak shoulder occurs near 1719 cm-1 in other sample spectra.

1. Bellamy, 1975 2. Sirkis, 1982 3. Brown, 1955

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp

TABLE 14.3

Frequency values and band assignments for samples identified as poly (vinyl acetate)

| PVAC standard cm-1 | PVAC adhesive cm-1 | PVAC (1) cm-1 | CWN13 diffuse reflect. cm-1 | York3 micro-scope cm-1 | FW17 micro-scope cm-1 | Inten-sity | Vibration' | Functional group | Frequency range given in literature cm-1 | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|
| 3457 | 3451 | 3470 | 3452 | 3458 | 3358 | w | O-H stretch hydrogen bonded | alcohol<br>water | 3400 - 3200 (b)<br>polymeric | 3 |
| 2975 | 2973 | 2985 | near 2960(sh) | 2961 | 2963 | m | C-H stretch | methyl group | 2962 ± 10 (s) | 3 |
| 2929 | 2927 | 2930 | 2922 | 2930 | 2935 | m | C-H stretch | methylene group | 2926 ± 10 (s) | 3 |
| 2861 | near 2860(sh) | near 2860(sh) | 2851 | 2860 | 2860 | w | C-H stretch | methyl group | 2872 ± 10 (s) | 3 |
| | | | | | | | C-H stretch | methylene group | 2853 ± 10 (s) | 3 |
| 1752 | 1730 | 1745 | 1739 | 1738 | 1749(b) | s | C=O stretch | ester | 1750 - 1730 (s) | 3 |
| | | | | | 1738(b) | s | C=O stretch | ester | 1750 - 1730 (s) | 3 |
| 1651 | 1656 | near 1650 | near 1650 | 1697(vw) | | sh | unassigned | | | |
| | | | | | 1582 | s | unassigned | | | |
| 1436 | 1435 | 1435 | 1435 | 1433 | 1433 | s | C-H asym. deformation | methyl group | 1450 ± 20 (m) | 3 |
| 1375 | 1374 | 1375 | 1375 | 1373 | 1373 | s | C-H sym. deformation | methyl group | 1380 - 1370 (s) | 3 |
| 1270 | near 1270(sh) | | near 1250(sh) | | 1250(b) | s | C-O stretch | acetate ester | 1250 - 1230 (s) | 3 |
| 1224 | 1225 | 1245(b) | 1227 | 1238 | 1238(b) | s | C-O stretch | acetate ester | 1245(s) | |
| | | | | 1171 | | w | unassigned | | | |
| 1127 | 1123 | 1130 | 1125 | 1115(w) | 1124 | s | unassigned | | | |
| 1028 | 1025 | 1025 | 1026 | 1025 | 1024 | s | C-O stretch | acetate ester | 1060 - 1000 (m) | 3 |

## TABLE 14.3 contd.

Frequency values and band assignments for samples identified as poly (vinyl acetate)

| PVAC standard cm-1 | PVAC adhesive cm-1 | PVAC (1) cm-1 | CWN13 diffuse reflect. cm-1 | York3 micro-scope cm-1 | FW17 micro-scope cm-1 | Inten-sity | Vibration | Functional group | Frequency range given in literature cm-1 | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|
| 948 | 948 | 950 | 948 | 947 | 947 | s | unassigned | | | |
| 798 | 797 | 795 | 797 | 795 | 795 | m | unassigned | | | |
| 632 | 632 | 630 | 631 | (2) | (2) | m | bending vibration | acetate group | 630 | 4 |
| | | | | | | | skeletal deformation | acetate group | 640(s) | 5 |
| 607 | 607 | 605 | 606 | (2) | (2) | s | bending vibration | acetate group | 605 | 4 |
| | | | | | | | skeletal deformation | acetate group | 612(s) | 5 |

1. Values were estimated to nearest 5 cm-1 from transmission spectrum in Hummel, 1978.
2. Microscope range ends at 650 cm-1
3. Bellamy, 1975
4. Hummel, 1966
5. Thompson and Torkington, 1945

KEY: v = very; s = strong; m = medium; w = weak; sh = shoulder; b = broad; va = variable; sp = sharp

# CHAPTER 15 CONCLUSIONS

For natural products, diffuse reflectance infrared spectroscopy was useful in identifying the type of material but rarely allowed a more specific identification. Waxes can be identified with a high degree of certainty and in several examples, waxes were identified as components of a mixture. Shellac and amber have distinct infrared spectra. Proteins and gums may be identified as a class of materials. Some samples of fats and resins were identified as being such, but no very specific identification could be made as to type of resin or fat. Bituminous materials were very difficult to identify because of their compositional complexity. These results support the conclusions of earlier workers (Chapter 1).

Many of the samples examined in this study which were not identified were characterized by several broad, overlapping bands. These broad features may be due to several factors. They may be indicative of severe degradation of the sample or of the presence of inorganic materials. Both of these factors are common in archaeological samples. As was mentioned in Chapter 3, the infrared analysis of complex substances is difficult due to overlapping bands and polymerization reactions that take place over time decrease the detail which may be observed in infrared spectra (Mills and White, 1987). More sensitive separation techniques such as GC-MS are required for more specific characterization of natural products. FT-IR can, however, be recommended as a preliminary screening technique as very little sample is required and the procedure is rapid.

In the case of semi-synthetic and synthetic materials, the technique was far more successful for the identification of these materials. All but one of the unknown plastic samples provided by the Museums was identified with certainty. The need for this type of analysis for both the identification of previous conservation treatments and the characterization of materials in twentieth century objects is vital. The identity of modern synthetics should be determined before any type of treatment is carried out and it is very difficult or impossible to identifiy the materials with certainty by visual or microscopic examination. The importance of this technique in the future of conservation cannot be underestimated.

The FT - IR microscopy did not produce the kind of results that were expected from reports in the literature. A major problem was sample preparation. It is very important to have a sufficiently transparent sample and many of the samples analysed in this thesis were not sufficiently transparent to produce acceptable spectra. Also there is the problem of finding a suitable sample support. The TEM grids used in this study were adequate for some samples, but were difficult to work with in the laboratory conditions available to the author. There is a wide area for future research using other types of FT-IR microscopes.

Other areas for future work in the application of FT-IR within conservation include gathering reference spectra of collection of early plastic materials and of early conservation treatments. Another important consideration is the use instruments which utilize J-CAMP-DX programming language (McDonald and Wilks, 1988). This language permits the interlaboratory exchange of spectra irrespective of the brand of spectrometer used. Readily exchangable data is an important consideration in the field of conservation research as there are few research laboratories in the field.

The results of this thesis indicate that FT-IR is a valid technique for the identification of modern organic materials of interest in conservation and has use in the characterization of natural product encountered in archaeological and art contexts. FT-IR is recommended for conservation research since, after the initial expenditure, it is cheap in terms of analyst time and running costs. Also, the speed and portabilty of the silicon carbide technique make the analysis of samples from other museums easily possible.

## REFERENCE COLLECTION

Sample Number: RW1
Sample Name/Common Name: Softwood tar
Chemical Name/Genus and Species: Pix liquida BP
Source: Raymond White
Museum/Laboratory: National Gallery, Trafalgar Square, London WC2N 5DN. Telephone: 01-839-3321 x 233.
Provenance: N/A
Number: N/A
Spectra: GSIA0010
GSIA0031
GSIA0069
GSIA0154
GSIA0155
GSVA0015
GSVA0097
GSVA0288
GSVA0387
Library Number: DR0015 (GSVA0015)
DR0142 (GSVA0097)
DR0207 (GSVA0387)

Sample Number: RW2
Sample Name/Common Name: Bitumen
Chemical Name/Genus and Species: N/A
Source: Raymond White
Museum Laboratory: National Gallery, Trafalgar Square, London WC2N 5DN. Telephone: 01-839-3321 x 233.
Provenance: Middle East
Number: N/A
Spectra: GSIA0001
GSIA0026
GSIA0032
GSIA0070
GSVA0016
GSVA0098

Library Number: DR0016 (GSVA0016)
DR0143 (GSVA0098)

Sample Number: RW3
Sample Name Common Name: Asphaltite
Chemical Name Genus and Species: N/A
Source: Raymond White
Museum/Laboratory: National Gallery, Trafalgar Square, London WC2N 5DN. Telephone: 01-839-3321 x 233.
Provenance: Middle East
Number: N/A
Spectra: GSIA0002
GSIA0027
GSIA0029
GSIA0030
GSIA0071
GSVA0017
GSVA0101
Library Number: DR0017 (GSVA0017)
DR0144 (GSVA0101)

Sample Number: RW4
Sample Name/Common Name: Pine rosin tar
Chemical Name/Genus and Species: N/A
Source: Raymond White
Museum/Laboratory: National Gallery, Trafalgar Square, London WC2N 5DN. Telephone: 01-839-3321 x 233.
Provenance: N/A
Number: N/A
Spectra: GSIA0011
GSIA0033
GSIA0072
GSIA0156
GSIA0157
GSVA0018
GSVA0102
GSVA0289
GSVA0388
Library Number: DR0018 (GSVA0018)
DR0145 (GSVA0102)
DR0208 (GSVA0388)

Sample Number: RW5
Sample Name/Common Name: Asphaltum
Chemical Name/Genus and Species: N/A
Source: Raymond White
Museum/Laboratory: National Gallery, Trafalgar Square, London WC2N 5DN. Telephone: 01-839-3321 x 233.
Provenance: N/A
Number: N/A
Spectra: GSIA0003
GSIA0028
GSIA0034
GSIA0073
GSVA0019
GSVA0103
Library Number: DR0019 (GSVA0019)
DR0146 (GSVA0103)

Sample Number: RW6
Sample Name/Common Name: Coal tar (aged film spread '78)
Chemical Name/Genus and Species: N/A
Source: Raymond White
Museum/Laboratory: National Gallery, Trafalgar Square, London WC2N 5DN. Telephone: 01-839-3321 x 233.
Provenance: N/A
Number: N/A
Spectra: GSIA0012
GSIA0035
GSIA0074
GSIA0098
GSVA0020
GSVA0104
Library Number: DR0020 (GSVA0020)
DR0147 (GSVA0104)

Sample Number: RW7
Sample Name/Common Name: Coarse birch bark bistre (Hardwood pitch)
Chemical Name/Genus and Species: from Betula species
Source: Raymond White
Museum/Laboratory: National Gallery, Trafalgar Square, London WC2N 5DN. Telephone: 01-839-3321 x 233.
Provenance: N/A
Number: N/A
Spectra: GSIA0013
GSIA0036
GSIA0075
GSIA0099
GSVA0021
GSVA0105
Library Number: DR0021 (GSVA0021)
DR0148 (GSVA0105)

Sample Number: RW8
Sample Name/Common Name: Egyptian mummy
Chemical Name/Genus and Species: N/A
Source: Raymond White
Museum/Laboratory: National Gallery, Trafalgar Square, London WC2N 5DN. Telephone: 01-839-3321 x 233.
Provenance: N/A
Number: N/A
Spectra: GSIA0004
GSIA0037
GSIA0076
GSVA0022
GSVA0106
Library Number: DR0022 (GSVA0022)
DR0149 (GSVA0106)

Sample Number: RW9
Sample Name/Common Name: Softwood pitch (aged 11 years)
Chemical Name/Genus and Species: Pix liquida BP
Source: Raymond White
Museum/Laboratory: National Gallery, Trafalgar Square, London WC2N 5DN. Telephone: 01-839-3321 x 233.
Provenance: N/A
Number: N/A
Spectra: GSIA0151
GSIA0152
GSVA0228

Library Number: DR0198 (GSVA0228)

Sample Number: RW10
Sample Name/Common Name: Casein
Chemical Name/Genus and Species: Casein
Source: Raymond White
Museum/Laboratory: National Gallery, Trafalgar Square, London WC2N 5DN. Telephone: 01-839-3321 x 233.
Provenance: BDH
Number: N/A
Spectra: GSIA0297
GSVA0322
Library Number: DR0191 (GSVA0322)
P00035 (GSVA0322)

Sample Number: RW11
Name/Common Name: Casein (precipitated with acid)
Chemical Name/Genus and Species: Casein
Source: Raymond White
Museum/Laboratory: National Gallery, Trafalgar Square, London WC2N 5DN. Telephone: 01-839-3321 x 233.
Provenance: N/A
Number: N/A
Spectra: GSIA
GSVA0323
Library Number: DR0199 (GSVA0323)
P00045 (GSVA0323)

Sample Number: RW12
Sample Name/Common Name: Abietic acid
Chemical Name/Genus and Species: 1,2,3,4,4a,4b,5,6,10,10a-Decahydro-1,4a-dimethyl-7-(1-methylethyl)-1-phenanthrene-carboxylic acid
($C_{20}H_{30}O_2$)
Source: Raymond White
Museum/Laboratory: National Gallery, Trafalgar Square, London WC2N 5DN. Telephone: 01-839-3321 x 233.
Provenance: N/A
Number: N/A
Spectra: GSIA0299
GSVA0324
Library Number: DR0200 (GSVA0324)

Sample Number: RW13
Sample Name/Common Name: Umbelliferone
Chemical Name/Genus and Species: 7-Hydroxy-2H-1-benzopyran-2-one $(C_9H_6O_3)$
Source: Raymond White
Museum/Laboratory: National Gallery, Trafalgar Square, London
WC2N 5DN. Telephone: 01-839-3321 x 233.
Provenance: Sigma U 7626
Number: N/A
Spectra: GSVA0336
Library Number: DR0192

Sample Number: RW14
Sample Name/Common Name: Hexatriacontane
Chemical Name/Genus and Species: Hexatriacontane $(CH_3(CH_2)_{34}CH_3)$
Source: Raymond White
Museum/Laboratory: National Gallery, Trafalgar Square, London
WC2N 5DN. Telephone: 01-839-3321 x 233.
Provenance: Fluka AG Bucks SG
Number: N/A
Spectra: GSVA0337
Library Number: DR0193

Sample Number: RW15
Sample Name/Common Name: Beechwood bistre (hardwood pitch)
Chemical Name/Genus and Species: from Fagus grandifolia Ehrh.
Source: Raymond White
Museum/Laboratory: National Gallery, Trafalgar Square, London
WC2N 5DN. Telephone: 01-839-3321 x 233.
Provenance:
Number: N/A
Spectra: GSVA0515
GSVA0516
Library Number:

Sample Number: MW1
Sample Name/Common Name: Gum myrrh
Chemical Name/Genus and Species: from Commiphora ssp.
Source: Margot Wright
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E OPY, 01-387-7050
Provenance: N/A
Number: RC1
Spectra: GSIA0014
GSIA0036
GSIA0077
GSVA0023
GSVA0107
Library Number: DR0023 (GSVA0023)
DR0150 (GSVA0107)

Sample Number: MW2
Sample Name/Common Name: Frankincense (olibanum)
Chemical Name/Genus and Species: from Boswellia species
Source: Margot Wright
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E OPY, 01-387-7050
Provenance: N/A
Number: RC2
Spectra: GSIA0015
GSIA0039
GSIA0078
GSVA0024
GSVA0108
Library Number: DR0024 (GSVA0024)
DR0151 (GSVA0108)

Sample Number: MW3
Sample Name/Common Name: Gum olibanum
Chemical Name/Genus and Species: from Boswellia species
Source: Margot Wright
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E OPY, 01-387-7050
Provenance: N/A
Number: RC3
Spectra: GSIA0016
GSIA0040
GSIA0079
GSVA0025
GSVA0109
Library Number: DR0025 (GSVA0025)
DR0152 (GSVA0109)

Sample Number: MW4
Sample Name/Common Name: Gum karaya
Chemical Name/Genus and Species: from Sterculia urens
Source: Margot Wright
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E OPY, 01-387-7050
Provenance: N/A
Number: RC4
Spectra: GSIA0005
GSIA0041
GSIA0080
GSVA0026
GSVA0110
Library Number: DR0026 (GSVA0026)
DR0153 (GSVA0110)

Sample Number: MW5
Sample Name/Common Name: Gum dammar
Chemical Name/Genus and Species: N/A
Source: Margot Wright
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E OPY, 01-387-7050
Provenance: N/A
Number: RC5
Spectra: GSIA0017
GSIA0042
GSIA0081
GSVA0027
GSVA0111
Library Number: DR0027 (GSVA0027)
DR0154 (GSVA0111)

Sample Number: MW6
Sample Name/Common Name: Locust bean gum
Chemical Name/Genus and Species: from Ceratonia siliqua L.
Source: Margot Wright
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E OPY, 01-387-7050
Provenance: N/A
Number: RC6
Spectra: GSIA0018
GSIA0043
GSIA0082
GSVA0028
GSVA0112
Library Number: DR0028 (GSVA0028)
DR0155 (GSVA0112)

Sample Number: MW7
Sample Name/Common Name: Gum tragacanth
Chemical Name/Genus and Species: from Astragalus species
Source: Margot Wright
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E OPY, 01-387-7050
Provenance: N/A
Number: RC7
Spectra: GSIA0019
GSIA0044
GSIA0083
GSVA0029
GSVA0113
Library Number: DR0029 (GSVA0029)
DR0156 (GSVA0113)

Sample Number: MW8
Sample Name/Common Name: Gum arabic
Chemical Name/Genus and Species: from Acacia species
Source: Margot Wright
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E OPY, 01-387-7050
Provenance: N/A
Number: RC8
Spectra: GSIA0006
GSIA0045
GSIA0084
GSVA0030
GSVA0114
Library Number: DR0030 (GSVA0030)
DR0157 (GSVA0114)

Sample Number: MW9
Sample Name/Common Name: Gum myrrh
Chemical Name/Genus and Species: from Commiphoria species
Source: Margot Wright
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E OPY, 01-387-7050
Provenance: N/A
Number: W62
Spectra: GSIA0020
GSIA0046
GSIA0085
GSVA0008
GSVA0031
GSVA0120
Library Number: DR0031 (GSVA0031)
DR0158 (GSVA0120)

Sample Number: MW10
Sample Name/Common Name: Gum benzoin sumatra
Chemical Name/Genus and Species: from Styrax benzoin
Source: Margot Wright
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E OPY, 01-387-7050
Provenance: N/A
Number: W63
Spectra: GSIA0007
GSIA0047
GSIA0053
GSIA0086
GSVA0032
GSVA0121
Library Number: DR0032 (GSVA0032)
DR0159 (GSVA0121)

Sample Number: MW11
Sample Name/Common Name: Gum tolu balsam
Chemical Name/Genus and Species: from Myroxylon balsamum (L.) Harms.
Source: Margot Wright
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: N/A
Number: W64
Spectra: GSIA0021
GSIA0048
GSIA0052
GSIA0087
GSVA0033
GSVA0122
GSVA0174
GSVA0291
Library Number: DR0033 (GSVA0033)
DR0160 (GSVA0122)
DR0180 (GSVA0291)
DR0196 (GSVA0174)

Sample Number: MW12
Sample Name/Common Name: Gum labdanum
Chemical Name/Genus and Species: from Cistus ladaniferus L.
Source: Margot Wright
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: N/A
Number: W65
Spectra: GSIA0008
GSIA0009
GSIA0050
GSIA0051
GSIA0088
GSVA0034
GSVA0123
GSVA0175
GSVA0290
GSVA0389
GSVA0390
Library Number: DR0034 (GSVA0034)
DR0161 (GSVA0123)
DR0179 (GSVA0290)
DR0197 (GSVA0175)
DR0209 (GSVA0390)

Sample Number: NJS1
Sample Name/Common Name: Natural stick lac
Chemical Name/Genus and Species: from Laccifer lacca Kerr.
Source: N. J. Seeley
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: N/A
Number: N/A
Spectra: GSIA0022
GSIA0054
GSIA0089
GSVA0002
GSVA0014
GSVA0124
GSVA0217
Library Number: DR0002 (GSVA0217)
DR0162 (GSVA0124)

Sample Number: NJS2
Sample Name/Common Name: Shellac
Chemical Name/Genus and Species: from Laccifer lacca Kerr.
Source: N. J. Seeley
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: N/A
Number: N/A
Spectra: GSIA0023
GSIA0055
GSIA0090
GSVA0001
GSVA0013
GSVA0125
GSVA0216
Library Number: DR0001 (GSVA0216)
DR0163 (GSVA0125)

Sample Number: NJS10
Sample Name/Common Name: Jet
Chemical Name/Genus and Species: N/A
Source: N. J. Seeley
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: Whitby beach
Number: N/A
Spectra: GSVA0230
Library number: DR0194

Sample Number: NJS20
Sample Name/Common Name: Hematite
Chemical Name/Genus and Species: Iron oxide ($Fe_2O_3$)
Source: N. J. Seeley
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: N/A
Number: N/A
Spectra: GSVA0335
Library number: DR0195

Sample Number: NJS24
Sample Name/Common Name: Ivory
Chemical Name/Genus and Species: N/A
Source: N. J. Seeley
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: N/A
Number: N/A
Spectra: GSVA0519
Library number: DR0227

Sample Number: NJS25
Sample Name/Common Name: Asphalt
Chemical Name/Genus and Species: N/A
Source: N. J. Seeley
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: Dead Sea, Khurbet Qumran, Jorden
Number: N/A
Spectra: GSVA0607
GSVA0608
Library number: DR0234 (GSVA0607)
DR0235 (GSVA0608)

Sample Number: VA1
Sample Name/Common Name: Carnauba wax (fatty grey)
Chemical Name/Genus and Species: from Copernicia cerifera
Source: J. Kitchin
Museum/Laboratory: Conservation Department, Victoria and Albert
Museum, Cromwell Road, London SW7
Provenance: John Myland, 18 Norwood High Street, London, SE29 9NW
Number: N/A
Spectra: GSIA0061
GSIA0092
GSVA0035
GSVA0036
GSVA0127
Library Number: DR0035 (GSVA0035)
DR0036 (GSVA0036)
DR0165 (GSVA0127)

Sample Number: VA2
Sample Name/Common Name: Paraffin wax
Chemical Name/Genus and Species: Hydrocarbon wax
Source: J. Kitchin
Museum/Laboratory: Conservation Department, Victoria and Albert
Museum, Cromwell Road, London SW7
Provenance: John Myland, 18 Norwood High Street, London, SE29 9NW
Number: N/A
Spectra: GSIA0062
GSIA0093
GSVA0037
GSVA0128
Library Number: DR0037 (GSVA0037)
DR0166 (GSVA0128)

Sample Number: VA3
Sample Name/Common Name: Beeswax
Chemical Name/Genus and Species: N/A
Source: J. Kitchin
Museum/Laboratory: Conservation Department, Victoria and Albert
Museum, Cromwell Road, London SW7
Provenance: John Myland, 18 Norwood High Street, London, SE29 9NW
Number: N/A
Spectra: GSIA0060
GSIA0094
GSVA0038
GSVA0129
Library Number: DR0038 (GSVA0038)
DR0167 (GSVA0129)

Sample Number: VA4
Sample Name/Common Name: White shellac
Chemical Name/Genus and Species: from Laccifer lacca Kerr
Source: J. Kitchin
Museum/Laboratory: Conservation Department, Victoria and Albert
Museum, Cromwell Road, London SW7
Provenance: N/A
Number: N/A
Spectra: GSIA0063
GSVA0039
GSVA0223
Library Number: DR0039 (GSVA0039)
DR0176 (GSVA0223)

Sample Number: VA5
Sample Name/Common Name: Sandarac
Chemical Name/Genus and Species: from Tetraclinis articulata
Source: J. Kitchin
Museum/Laboratory: Conservation Department, Victoria and Albert
Museum, Cromwell Road, London SW7
Provenance: N/A
Number: N/A
Spectra: GSIA0064
GSVA0040
Library number: DR0040 (GSVA0040)

Sample Number: VA6
Sample Name/Common Name: Mastic
Chemical Name/Genus and Species: from Pistacia lentiscus
Source: J. Kitchin
Museum/Laboratory: Conservation Department, Victoria and Albert
Museum, Cromwell Road, London SW7
Provenance: N/A
Number: N/A
Spectra: GSIA0065
GSVA0041
Library number: DR0041 (GSVA0041)

Sample Number: VA7
Sample Name/Common Name: English mandrak

**Chemical Name/Genus and Species:** N/A
**Source:** J. Kitchin
**Museum/Laboratory:** Conservation Department, Victoria and Albert
Museum, Cromwell Road, London SW7
**Provenance:** N/A
**Number:** N/A
**Spectra:** GSIA0066
GSIA0068
GSVA0042
**Library number:** DR0042 (GSVA0042)

**Sample Number:** VA8
**Sample Name/Common Name:** Kaolin
**Chemical Name/Genus and Species:** N/A
**Source:** J. Kitchin
**Museum/Laboratory:** Conservation Department, Victoria and Albert
Museum, Cromwell Road, London SW7
**Provenance:** N/A
**Number:** N/A
**Spectra:** GSIA0067
GSVA0043
**Library number:** DR0043 (GSVA0043)

**Sample Number:** VA9
**Sample Name/Common Name:** Microcrystalline wax
**Chemical Name/Genus and Species:** Hydrocarbon wax
**Source:** J. Kitchin
**Museum/Laboratory:** Conservation Department, Victoria and Albert
Museum, Cromwell Road, London SW7
**Provenance:** N/A
**Number:** N/A
**Spectra:** GSVA0100
GSVA0229
**Library Number:** DR0177 (GSVA0100)
DR0178 (GSVA0229)

**Sample Number:** VA10
**Sample Name/Common Name:** Rabbit skin glue
**Chemical Name/Genus and Species:** N/A
**Source:** G. Martin
**Museum/Laboratory:** Conservation Department, Victoria and Albert
Museum, Cromwell Road, London SW7
**Provenance:** N/A
**Number:** N/A
**Spectra:** GSVA0194
**Library Number:** DR0133

**Sample Number:** VA11
**Sample Name/Common Name:** Animal glue
**Chemical Name/Genus and Species:** N/A
**Source:** G. Martin
**Museum/Laboratory:** Conservation Department, Victoria and Albert
Museum, Cromwell Road, London SW7
**Provenance:** N/A
**Number:** N/A
**Spectra:** GSVA0195
**Library Number:** DR0134

**Sample Number:** VA12
**Sample Name/Common Name:** Hide glue
**Chemical Name/Genus and Species:** N/A
**Source:** G. Martin
**Museum/Laboratory:** Conservation Department, Victoria and Albert
Museum, Cromwell Road, London SW7
**Provenance:** N/A
**Number:** N/A
**Spectra:** GSVA0196
**Library Number:** DR0135

**Sample Number:** VA13
**Sample Name/Common Name:** Cellulose acetate acetyl content 39.8%
**Chemical Name/Genus and Species:** Cellulose diacetate
**Source:** G. Martin
**Museum/Laboratory:** Conservation Department, Victoria and Albert
Museum, Cromwell Road, London SW7
**Provenance:** Aldrich
**Number:** N/A
**Spectra:** GSVA0350
**Library number:** P00037

**Sample Number:** VA14
**Sample Name/Common Name:** Cellulose acetate
**Chemical Name/Genus and Species:** Cellulose triacetate
**Source:** G. Martin
**Museum/Laboratory:** Conservation Department, Victoria and Albert
Museum, Cromwell Road, London SW7
**Provenance:** Aldrich
**Number:** N/A
**Spectra:** GSVA0351
**Library number:** P00038

**Sample Number:** VA15
**Sample Name/Common Name:** Poly (vinyl acetate) PVAC
**Chemical Name/Genus and Species:** Poly (vinyl acetate)
**Source:** G. Martin
**Museum/Laboratory:** Conservation Department, Victoria and Albert
Museum, Cromwell Road, London SW7
**Provenance:** Aldrich secondary standard
**Number:** N/A
**Spectra:** GSVA0352
**Library number:** P00039

**Sample Number:** VA16
**Sample Name/Common Name:** Poly (vinyl chloride) PVC
**Chemical Name/Genus and Species:** Poly (vinyl chloride)
**Source:** G. Martin
**Museum/Laboratory:** Conservation Department, Victoria and Albert
Museum, Cromwell Road, London SW7
**Provenance:** Aldrich secondary standard
**Number:** N/A
**Spectra:** GSVA0353
pvc4
**Library Number:** P00040 (GSVA0353)
P00041 (pvc4)

**Sample Number:** VA17
**Sample Name/Common Name:** Cellulose acetate butyrate
**Chemical Name/Genus and Species:** Cellulose acetate butyrate
**Source:** G. Martin
**Museum/Laboratory:** Conservation Department, Victoria and Albert
Museum, Cromwell Road, London SW7
**Provenance:** Aldrich
**Number:** N/A
**Spectra:** GSVA0386
**Library Number:** P00043

**Sample Number:** VA18
**Sample Name/Common Name:** Oleic acid
**Chemical Name/Genus and Species:** 9-Octadecenoic acid
$(COOH(CH_2)_7CH{=}CH(CH_2)_7CH_3)$
**Source:** G. Martin
**Museum/Laboratory:** Conservation Department, Victoria and Albert
Museum, Cromwell Road, London SW7
**Provenance:** BDH Chemicals Ltd., Poole, England
technical grade
**Number:** N/A
**Spectra:** GSVA0471
**Library number:** DR0228

**Sample Number:** VA19
**Sample Name/Common Name:** Myristic acid
**Chemical Name/Genus and Species:** Tetradecanoic acid
$(COOH(CH_2)_{12}CH_3)$
**Source:** G. Martin
**Museum/Laboratory:** Conservation Department, Victoria and Albert
Museum, Cromwell Road, London SW7
**Provenance:** BDH Chemicals Ltd., Poole, England
biochemical grade, specially pure
**Number:** N/A
**Spectra:** GSVA0472
**Library number:** DR0229

**Sample Number:** VA20
**Sample Name/Common Name:** Palmitic acid
**Chemical Name/Genus and Species:** Hexadecanoic acid
$(COOH(CH_2)_{14}CH_3)$
**Source:** G. Martin
**Museum/Laboratory:** Conservation Department, Victoria and Albert
Museum, Cromwell Road, London SW7
**Provenance:** BDH Chemicals Ltd., Poole, England
general purpose reagent (GPR)
**Number:** N/A
**Spectra:** GSVA0473
**Library number:** DR0230

**Sample Number:** VA21
**Sample Name/Common Name:** Stearic acid
**Chemical Name/Genus and Species:** Octadecanoic acid
$(COOH(CH_2)_{16}CH_3)$
**Source:** G. Martin
**Museum/Laboratory:** Conservation Department, Victoria and Albert
Museum, Cromwell Road, London SW7
**Provenance:** BDH Chemicals Ltd., Poole, England
general purpose reagent (GPR)
**Number:** N/A
**Spectra:** GSVA0474
**Library number:** DR0231

**Sample Number:** VA22
**Sample Name/Common Name:** Poly (methyl methacrylate)
**Chemical Name/Genus and Species:** Poly (methyl methacrylate)
**Source:** G. Martin
**Museum/Laboratory:** Conservation Department, Victoria and Albert
Museum, Cromwell Road, London SW7
**Provenance:** Aldrich secondary standard
**Number:** N/A
**Spectra:** pmethmel
GSVA0530
**Library Number:** P00008 (pmethmel)

**Sample Number:** VA23
**Sample Name/Common Name:** Polycarbonate resin
**Chemical Name/Genus and Species:** Polycarbonate resin
**Source:** G. Martin
**Museum/Laboratory:** Conservation Department, Victoria and Albert
Museum, Cromwell Road, London SW7
**Provenance:** Aldrich secondary standard
**Number:** N/A
**Spectra:** carbonate
**Library Number:** P00032

Sample Number: VA24
Sample Name/Common Name: Cellulose nitrate
Chemical Name/Genus and Species: Cellulose nitrate
Source: G. Martin
Museum/Laboratory: Conservation Department, Victoria and Albert
Museum, Cromwell Road, London SW7
Provenance: Millipore SC 8 micron
Number: N/A
Spectra: cno3
Library number: DR0008
P00027

Sample Number: VA25
Sample Name/Common Name: Cellulose nitrate plastic
Chemical Name/Genus and Species: Cellulose nitrate
Source: G. Martin
Museum/Laboratory: Conservation Department, Victoria and Albert
Museum, Cromwell Road, London SW7
Provenance: Wardle-Storey Factory, Brantham, Essex
Number: N/A
Spectra: GSVA0555
Library number: P00049

Sample Number: VA26
Sample Name/Common Name: Camphor
Chemical Name/Genus and Species: from Cinnamomum camphorae Nees
$(C_{10}H_{16}O)$
Source: G. Martin
Museum/Laboratory: Conservation Department, Victoria and Albert
Museum, Cromwell Road, London SW7
Provenance: P. Bolton, Dispensing Chemist
Number: N/A
Spectra: camphor2
GSVA0531
Library number: P00031 (camphor2)

Sample Number: VA27
Sample Name/Common Name: Bexfilm T cellulose acetate sheet
Chemical Name/Genus and Species: Cellulose triacetate
Source: G. Martin
Museum/Laboratory: Conservation Department, Victoria and Albert
Museum, Cromwell Road, London SW7
Provenance: Bexford plc
Number: N/A
Spectra: Bexfilm
Library number: DR0175
P00029

Sample Number: VA28
Sample Name/Common Name: Triphenyl phosphate
Chemical Name/Genus and Species: Triphenyl phosphate
Source: G. Martin
Museum/Laboratory: Conservation Department, Victoria and Albert
Museum, Cromwell Road, London SW7
Provenance: Aldrich 99+%
Number: N/A
Spectra: Tripphos
Library number: N/A

Sample Number: VA29
Sample Name/Common Name: Diethyl phthalate
Chemical Name/Genus and Species: Diethyl phthalate
Source: G. Martin
Museum/Laboratory: Conservation Department, Victoria and Albert
Museum, Cromwell Road, London SW7
Provenance: Aldrich 99%
Number: N/A
Spectra: Diethylp
Library Number: N/A

Sample Number: VA30
Sample Name/Common Name: Santicizer 8 (Ketjenflex8)
Chemical Name/Genus and Species: N-ethyl o,p-toluenesulfonamide
mixture
Source: G. Martin
Museum/Laboratory: Conservation Department, Victoria and Albert
Museum, Cromwell Road, London SW7
Provenance: Monsanto
Number: N/A
Spectra: Ketjen8
Library Number: P00028

Sample Number: VA31
Sample Name/Common Name: Perspex (Plexiglass)
Chemical Name/Genus and Species: Poly (methyl methacrylate)
Source: G. Martin
Museum/Laboratory: Conservation Department, Victoria and Albert
Museum, Cromwell Road, London SW7
Provenance: Visijar Tuckers Perspex VE
Number: N/A
Spectra: Perspex
Library Number: P00030

Sample Number: VA32
Sample Name/Common Name: Plexiglass (Perspex)
Chemical Name/Genus and Species: Poly (methyl methacrylate)
Source: Furniture conservation
Museum/Laboratory: Smithsonian Institution, Conservation
Analytical Laboratory, Washington D.C.
Provenance: unknown commercial
Number: N/A
Spectra: plex320
Library Number: P00034

Sample Number: LA1
Sample Name/Common Name: Amber
Chemical Name/Genus and Species: Succinite (Baltic amber)
Source: Leena Airola
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: possibly from Russia
Number: 34
Spectra: GSIA0056
GSIA0095
GSVA0007
GSVA0011
GSVA0131
GSVA0219
Library Number: DR0004 (GSVA0219)
DR0169 (GSVA0131)

Sample Number: LA2
Sample Name/Common Name: Amber
Chemical Name/Genus and Species: Succinite (Baltic amber)
Source: Leena Airola
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: possibly from Russia
Number: 35
Spectra: GSIA0057
GSIA0096
GSVA0004
GSVA0132
GSVA0220
Library Number: DR0005 (GSVA0220)
DR0170 (GSVA0132)

Sample Number: LA3
Sample Name/Common Name: Amber
Chemical Name/Genus and Species: Succinite (Baltic amber)
Source: Leena Airola
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: Denmark
Number: 36
Spectra: GSIA0058
GSIA0059
GSIA0097
GSVA0005
GSVA0006
GSVA0130
GSVA0221
GSVA0222
Library Number: DR0006 (GSVA0221)
DR0007 (GSVA0222)
DR0168 (GSVA0130)

Sample Number: Kew1
Sample Name/Common Name: Kauri resin (white, rerasped)
Chemical Name/Genus and Species: from Agathis australis
Source: Rupert Hastings
Museum/Laboratory: Museum of Economic Botany, Kew
Provenance: New Zealand (T. Hedley Barry)
Number: 36.1932
Spectra: GSIA0103
GSIA0104
GSVA0044
GSVA0045
GSVA0213
Library Number: DR0044 (GSVA0044)
DR0045 (GSVA0045)

Sample Number: Kew2
Sample Name/Common Name: East Indian copal (medium-hard grade)
Chemical Name/Genus and Species: from Agathis dammara
Source: Rupert Hastings
Museum/Laboratory: Museum of Economic Botany, Kew
Provenance: Dutch East Indies (T. Hedley Barry)
Number: 36.1932
Spectra: GSIA0105
GSIA0106
GSVA0046
GSVA0047
GSVA0214
Library number: DR0046 (GSVA0046)
DR0047 (GSVA0047)

Sample Number: Kew3
Sample Name/Common Name: Resin
Chemical Name/Genus and Species: from Agathis dammara
Source: Rupert Hastings
Museum/Laboratory: Museum of Economic Botany, Kew
Provenance: Singapore (India Museum)
Number: N/A
Spectra: GSIA0107
GSIA0108
GSVA0048
GSVA0049
GSVA0215
Library number: DR0048 (GSVA0048)
DR0049 (GSVA0049)

Sample Number: Kew4
Sample Name/Common Name: Resin
Chemical Name/Genus and Species: from Araucaria columnaris
Source: Rupert Hastings
Museum/Laboratory: Museum of Economic Botany, Kew
Provenance: New Caledonia (J. McGillivray)
Number: N/A
Spectra: GSIA0109
GSIA0110
GSVA0050
GSVA0051
GSVA0239
GSVA0240
Library number: DR0050 (GSVA0050)
DR0051 (GSVA0051)

Sample Number: Kew5
Sample Name/Common Name: Resin
Chemical Name/Genus and Species: from Abies spectabilis
Source: Rupert Hastings
Museum/Laboratory: Museum of Economic Botany, Kew
Provenance: Simla, India (Indian Office, India Museum)
Number: 18.1898
Spectra: GSIA0111
GSIA0112
GSVA0052
GSVA0053
GSVA0054
Library number: DR0052 (GSVA0052)
DR0053 (GSVA0053)
DR0054 (GSVA0054)

Sample Number: Kew6
Sample Name/Common Name: Resin
Chemical Name/Genus and Species: from Cedrus brevifolia
Source: Rupert Hastings
Museum/Laboratory: Museum of Economic Botany, Kew
Provenance: Cyprus (Forest Exhibition, Edinburgh)
Number: 167.1884
Spectra: GSIA0113
GSIA0114
GSVA0055
GSVA0056
Library Number: DR0055
DR0056

Sample Number: Kew7
Sample Name/Common Name: Burgandy pitch (as sold in market)
Chemical Name/Genus and Species: from Picea abies
Source: Rupert Hastings
Museum/Laboratory: Museum of Economic Botany, Kew
Provenance: Geneva (Dr. Hanbury, 1874)
Number: N/A
Spectra: GSIA0115
GSIA0116
GSVA0057
GSVA0058
GSVA0059
Library Number: DR0057 (GSVA0057)
DR0058 (GSVA0058)
DR0059 (GSVA0059)

Sample Number: Kew8
Sample Name/Common Name: Resin
Chemical Name/Genus and Species: from Picea glauca
Source: Rupert Hastings
Museum/Laboratory: Museum of Economic Botany, Kew
Provenance: Carlton, Saskatchewan, Canada
Number: N/A
Spectra: GSIA0117
GSIA0118
GSVA0065
GSVA0066
Library Number: DR0062 (GSVA0065)
DR0063 (GSVA0066)

Sample Number: Kew9
Sample Name/Common Name: Htin Yoo resin (used for soldering)
Chemical Name/Genus and Species: from Pinus kesiya
Source: Rupert Hastings
Museum/Laboratory: Museum of Economic Botany, Kew
Provenance: India (Indian Forestry Department)
Number: N/A
Spectra: GSIA0119
GSIA0120
GSVA0067
GSVA0068
Library Number: DR0064 (GSVA0067)
DR0065 (GSVA0068)

Sample Number: Kew10
Sample Name/Common Name: Resin
Chemical Name/Genus and Species: from Pinus massoniana
Source: Rupert Hastings
Museum/Laboratory: Museum of Economic Botany, Kew
Provenance: Ningpo, China (W. M. Cooper)
Number: 149.1884
Spectra: GSIA0121
GSIA0123
GSVA0069
GSVA0070
Library number: DR0066 (GSVA0069)
DR0067 (GSVA0070)

Sample Number: Kew11
Sample Name/Common Name: Resin
Chemical Name/Genus and Species: from Pinus merkusii
Source: Rupert Hastings
Museum/Laboratory: Museum of Economic Botany, Kew
Provenance: Sumatra (T. Hedley Barry)
Number: 23.1938
Spectra: GSIA0124
GSIA0125
GSVA0071
GSVA0072
Library number: DR0068 (GSVA0071)
DR0069 (GSVA0072)

Sample Number: Kew12
Sample Name/Common Name: Resin
Chemical Name/Genus and Species: from Pinus roxburghii
Source: Rupert Hastings
Museum/Laboratory: Museum of Economic Botany, Kew
Provenance: India
Number: N/A
Spectra: GSIA0126
GSIA0127
GSVA0073
GSVA0074
Library number: DR0070 (GSVA0073)
DR0071 (GSVA0074)

Sample Number: Kew13
Sample Name/Common Name: Common yellow resin
Chemical Name/Genus and Species: from Pinus sylvestris
Source: Rupert Hastings
Museum/Laboratory: Museum of Economic Botany, Kew
Provenance: North Europe
Number: N/A
Spectra: GSIA0129
GSIA0130
GSVA0060
GSVA0061
Library number: DR0060 (GSVA0060)
DR0061 (GSVA0061)

Sample Number: Kew14
Sample Name/Common Name: Resin
Chemical Name/Genus and Species: from Callitris endlicheri
Source: Rupert Hastings
Museum/Laboratory: Museum of Economic Botany, Kew
Provenance: New South Wales, Australia (F. M. Bail)
Number: 73.1891
Spectra: GSIA0131
GSIA0132
GSVA0075
GSVA0076
Library Number: DR0072 (GSVA0075)
DR0073 (GSVA0076)

Sample Number: Kew15
Sample Name/Common Name: White pine resin
Chemical Name/Genus and Species: from Callitris verrucosa
Source: Rupert Hastings
Museum/Laboratory: Museum of Economic Botany, Kew
Provenance: New South Wales, Australia
Number: N/A
Spectra: GSIA0133
GSIA0134
GSVA0077
GSVA0078
Library Number: DR0074 (GSVA0077)
DR0075 (GSVA0078)

Sample Number: Kew16
Sample Name/Common Name: Gunisht resin
Chemical Name/Genus and Species: from Juniperus phoenicea
Source: Rupert Hastings
Museum/Laboratory: Museum of Economic Botany, Kew
Provenance: Morocco
Number: N/A
Spectra: GSIA0135
GSVA0079
GSVA0080
Library Number: DR0076 (GSVA0079)
DR0077 (GSVA0080)

Sample Number: Kew17
Sample Name/Common Name: Gum sandarach
Chemical Name/Genus and Species: from Tetraclinis articulata
Source: Rupert Hastings
Museum/Laboratory: Museum of Economic Botany, Kew
Provenance: Bombay, India
Number: N/A
Spectra: GSIA0136
GSIA0137
GSVA0081
GSVA0082
Library Number: DR0078 (GSVA0081)
DR0079 (GSVA0082)

Sample Number: Kew18
Sample Name/Common Name: East Africa gum copal
Chemical Name/Genus and Species: from Hymenaea verrucosa
(Trachylobium verrucosa)
Source: Rupert Hastings
Museum/Laboratory: Museum of Economic Botany, Kew
Provenance: N/A
Number: 66.1924
Spectra: GSIA0138
GSIA0139
GSVA0083
GSVA0084
Library number: DR0080 (GSVA0083)
DR0081 (GSVA0084)

Sample Number: Kew19
Sample Name/Common Name: Resin
Chemical Name/Genus and Species: from *Hymenaea courbaril*
Source: Rupert Hastings
Museum/Laboratory: Museum of Economic Botany, Kew
Provenance: Bahea, Brazil (Coll. T.S.)
Number: N/A
Spectra: GSIA0140
GSIA0141
GSVA0085
GSVA0086
Library number: DR0082 (GSVA0085)
DR0083 (GSVA0086)

Sample Number: Kew20
Sample Name/Common Name: Chio mastic
Chemical Name/Genus and Species: from *Pistacia lentiscus*
Source: Rupert Hastings
Museum/Laboratory: Museum of Economic Botany, Kew
Provenance: Turkey
Number:
Spectra: GSIA0142
GSIA0143
GSVA0088
GSVA0089
Library number: DR0084 (GSVA0088)
DR0085 (GSVA0089)

Sample Number: Kew21
Sample Name/Common Name: Mastic
Chemical Name/Genus and Species: from *Pistacia lentiscus*
Source: Rupert Hastings
Museum/Laboratory: Museum of Economic Botany, Kew
Provenance: N/A
Number: N/A
Spectra: GSIA0145
GSIA0146
GSVA0090
GSVA0091
Library number: DR0086 (GSVA0090)
DR0087 (GSVA0091)

Sample Number: Kew22
Sample Name/Common Name: Chian turpentine
Chemical Name/Genus and Species: from *Pistacia terebinthus*
Source: Rupert Hastings
Museum/Laboratory: Museum of Economic Botany, Kew
Provenance: N/A
Number: 7.1927 (Burroughs and Wellcome)
Spectra: GSIA0147
GSIA0148
GSVA0092
GSVA0093
Library Number: DR0088 (GSVA0092)
DR0089 (GSVA0093)

Sample Number: Kew23
Sample Name/Common Name: Larch manna
Chemical Name/Genus and Species: from *Larix decidua* Miller
Source: Rupert Hastings
Museum/Laboratory: Museum of Economic Botany, Kew
Provenance: Canton Valais, Switzerland (Prof. A. Henry)
Number: 51.1924
Spectra: GSIA0178
Library Number: DR0171

Sample Number: Kew24
Sample Name/Common Name: Swiss turpentine
Chemical Name/Genus and Species: from *Picea abies*
Source: Rupert Hastings
Museum/Laboratory: Museum of Economic Botany, Kew
Provenance: Messrs Menier and Co.
Number: N/A
Spectra: GSVA0292
GSVA0391
Library Number: DR0181 (GSVA0292)
DR0210 (GSVA0391)

Sample Number: Kew25
Sample Name/Common Name: American turpentine
Chemical Name/Genus and Species: from *Pinus palustris*
(*Pinus australis*)
Source: Rupert Hastings
Museum/Laboratory: Museum of Economic Botany, Kew
Provenance: N/A (D. Hanbury)
Number: N/A
Spectra: GSVA0293
GSVA0392
Library Number: DR0182 (GSVA0293)
DR0211 (GSVA0392)

Sample Number: Kew26
Sample Name/Common Name: Carnauba wax (yellow)
Chemical Name/Genus and Species: from *Copernicia cerifera*
(*Copernicia prunifera*)
Source: Rupert Hastings
Museum/Laboratory: Museum of Economic Botany, Kew
Provenance: Brazil (Prices patent candle Co.)
Number: 23.1853
Spectra: GSVA0197
Library number: DR0172

Sample Number: Kew27
Sample Name/Common Name: Candelilla wax
Chemical Name/Genus and Species: from *Euphorbia cerifera*
Source: Rupert Hastings
Museum/Laboratory: Museum of Economic Botany, Kew
Provenance: Coahula, Mexico
Number: 24.1935
Spectra: GSVA0198
Library number: DR0173

Sample Number: Kew28
Sample Name/Common Name: Resin
Chemical Name/Genus and Species: from *Cedrus libani* (var. *brevifo*
same as Kew6
Source: Rupert Hastings
Museum/Laboratory: Museum of Economic Botany, Kew
Provenance: Cyprus (Museum Pharm. Soc. of Great Britain)
Number: 167.1884
Spectra: GSVA0475
GSVA0476
Library number: DR0232 (GSVA0475)
DR0233 (GSVA0476)

Sample Number: NHM1
Sample Name/Common Name: Asphaltum
Chemical Name/Genus and Species: N/A
Source: Department of Mineralogy
Museum/Laboratory: British Museum Natural History, London, SW7
Provenance: Longmynd beds, Houghmond Hill, Shrewsbury, Shropshire
Number: 1911,298 (Bought of M. F. H. Butler, 1911)
Spectra: GSIA0182
GSVA0135
Library number: DR0090 (GSVA0135)

Sample Number: NHM2
Sample Name/Common Name: Asphalt
Chemical Name/Genus and Species: N/A
Source: Department of Mineralogy
Museum/Laboratory: British Museum Natural History, London, SW7
Provenance: Eastwell, Croftymine, Camborne, Cornwall
Number: 14433
Spectra: GSIA0183
GSVA0136
Library Number: DR0091 (GSVA0136)

Sample Number: NHM3
Sample Name/Common Name: Asphaltum
Chemical Name/Genus and Species: N/A
Source: Department of Mineralogy
Museum/Laboratory: British Museum Natural History, London, SW7
Provenance: floating on the Dead Sea, Palestine (Dr. J W. Evans
1928)
Number: 1928,245
Spectra: GSIA0184
GSVA0137
Library Number: DR0092 (GSVA0137)

Sample Number: NHM4
Sample Name/Common Name: Bitumen
Chemical Name/Genus and Species: N/A
Source: Department of Mineralogy
Museum/Laboratory: British Museum Natural History, London, SW7
Provenance: bitumen mines between Hasheya and Jezzen, Syria
(M. Davidson)
Number: 26775
Spectra: GSIA0185
GSVA0224
Library Number: DR0093 (GSVA0224)

Sample Number: NHM5
Sample Name/Common Name: Mineral pitch
Chemical Name/Genus and Species: N/A
Source: Department of Mineralogy
Museum/Laboratory: British Museum Natural History, London, SW7
Provenance: south beach of Mustique Island, (Grendine), West Indies)
Number: 80896
Spectra: GSIA0186
GSVA0225
Library Number: DR0094 (GSVA0225)

Sample Number: NHM6
Sample Name/Common Name: Asphalt or bitumen
Chemical Name/Genus and Species: N/A
Source: Department of Mineralogy
Museum/Laboratory: British Museum Natural History, London, SW7
Provenance: France
Number: 39698
Spectra: GSIA0187
GSVA0140
Library number: DR0095 (GSVA0140)

Sample Number: NHM7
Sample Name/Common Name: Bitumen
Chemical Name/Genus and Species: N/A
Source: Department of Mineralogy
Museum/Laboratory: British Museum Natural History, London, SW7
Provenance: Darbyshire (Alan-Gregg collection)
Number: AG5
Spectra: GSIA0188
GSVA0141
Library number: DR0096 (GSVA0141)

Sample Number: NHM8
Sample Name/Common Name: Asphaltum
Chemical Name/Genus and Species: N/A
Source: Department of Mineralogy
Museum/Laboratory: British Museum Natural History, London, SW7
Provenance: found as coating on quartz from chocdolomite, Strencno
(18.8°E, 49.3°N), Zilna, Slovakia (V. Rosicky, 1939)
Number: 1939,92
Spectra: GSIA0189
GSVA0142
Library number: DR0097 (GSVA0142)

Sample Number: NHM9
Sample Name/Common Name: Asphaltum
Chemical Name/Genus and Species: N/A
Source: Department of Mineralogy
Museum/Laboratory: British Museum Natural History, London, SW7
Provenance: Trinidad, West Indies (F. C. Garrett, 1904)
Number: 87147
Spectra: GSIA0190
GSVA0143
Library number: DR0098 (GSVA0143)

Sample Number: NHM10
Sample Name/Common Name: Bitumen
Chemical Name/Genus and Species: N/A
Source: Department of Mineralogy
Museum/Laboratory: British Museum Natural History, London, SW7
Provenance: in anhydrite rock, Billingham, Co. Durham (Directors of ICI, Ltd., 1943)
Number: 1943.9
Spectra: GSIA0191
GSVA0144
Library Number: DR0099 (GSVA0144)

Sample Number: NHM11
Sample Name/Common Name: Bitumen
Chemical Name/Genus and Species: N/A
Source: Department of Mineralogy
Museum/Laboratory: British Museum Natural History, London, SW7
Provenance: Mt. Sorrell, Leicestershire
Number: 48372
Spectra: GSIA0192
GSVA0145
Library Number: DR0100 (GSVA0145)

Sample Number: NHM12
Sample Name/Common Name: Beeswax
Chemical Name/Genus and Species: from comb of Apis dorsata
Source: Department of Entomology, Hymenoptera collection
Museum/Laboratory: British Museum Natural History, London, SW7
Provenance: Goalparah, Bengal
Number: N/A
Spectra: GSVA0311
Library Number: DR0185

Sample Number: NHM13
Sample Name/Common Name: Beeswax
Chemical Name/Genus and Species: from comb of Apis floralis
Source: Department of Entomology, Hymenoptera collection
Museum/Laboratory: British Museum Natural History, London, SW7
Provenance: N/A
Number: N/A
Spectra: GSVA0312
Library Number: DR0186

Sample Number: NHM15
Sample Name/Common Name: Resin
Chemical Name/Genus and Species: from tree which hosted Trigona loeviceps
Source: Department of Entomology, Hymenoptera collection
Museum/Laboratory: British Museum Natural History, London, SW7
Provenance: Singapore (Smith, 1857)
Number: N/A
Spectra: GSVA0314
Library number: DR0187

Sample Number: NHM16
Sample Name/Common Name: Beeswax
Chemical Name/Genus and Species: from Apis dorsata
Source: Department of Entomology, Hymenoptera collection
Museum/Laboratory: British Museum Natural History, London, SW7
Provenance: India
Number: N/A
Spectra: GSVA0315
Library number: DR0187

Sample Number: NHM17
Sample Name/Common Name: Beeswax
Chemical Name/Genus and Species: from Trigona species
Source: Department of Entomology, Hymenoptera collection
Museum/Laboratory: British Museum Natural History, London, SW7
Provenance: India and Burmah (East Indian Museum)
Number: N/A
Spectra: GSVA0316
Library number: DR0188

Sample Number: NHM18
Sample Name/Common Name: Beeswax
Chemical Name/Genus and Species: from queen cells of Apis mellif
Source: Department of Entomology, Hymenoptera collection
Museum/Laboratory: British Museum Natural History, London, SW7
Provenance: Southall (Abbott Brothers, 1902)
Number: N/A
Spectra: GSVA0317
Library number: DR0189

Sample Number: NHM19
Sample Name/Common Name: Beeswax
Chemical Name/Genus and Species: from comb of Apis mellifera
Source: Department of Entomology, Hymenoptera collection
Museum/Laboratory: British Museum Natural History, London, SW7
Provenance: Dorset, '77
Number: N/A
Spectra: GSVA0318
Library Number: DR0190

Sample Number: IA1
Sample Name/Common Name: Wood tar pitch
Chemical Name/Genus and Species: Pix liquida BP
Source: Mineralogical collection
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: N/A
Number: N/A
Spectra: GSIA0193
GSVA0146
Library Number: DR0101 (GSVA0146)

Sample Number: IA2
Sample Name/Common Name: Wood or Stockholm tar
Chemical Name/Genus and Species: Pix liquida BP
Source: Mineralogical collection
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: N/A
Number: N/A
Spectra: GSVA0177
GSVA0294
GSVA0393
Library Number: DR0174 (GSVA0177)
DR0183 (GSVA0294)
DR0212 (GSVA0393)

Sample Number: IA3
Sample Name/Common Name: Dopplerite
Chemical Name/Genus and Species: N/A
Source: Mineralogical collection
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: Garry castle, Althone, County Westmeath
Number: N/A
Spectra: GSVA0147
Library Number: DR0102

Sample Number: IA4
Sample Name/Common Name: Dopplerite
Chemical Name/Genus and Species: N/A
Source: Mineralogical collection
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: Mount shannon, Limerick
Number: N/A
Spectra: GSVA0148
Library number: DR0103

Sample Number: IA5
Sample Name/Common Name: Glance pitch
Chemical Name/Genus and Species: N/A
Source: Mineralogical collection
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: Dead Sea
Number: N/A
Spectra: GSIA0196
GSVA0149
Library number: DR0104 (GSVA0149)

Sample Number: IA6
Sample Name/Common Name: Gilsonite
Chemical Name/Genus and Species: N/A
Source: Mineralogical collection
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: Utah, USA
Number: N/A
Spectra: GSIA0197
GSVA0150
Library number: DR0105 (GSVA0150)

Sample Number: IA7
Sample Name/Common Name: Asphalt (refined)
Chemical Name/Genus and Species: N/A
Source: Mineralogical collection
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: Trinidad Lake
Number: N/A
Spectra: GSIA0198
GSVA0151
Library number: DR0106 (GSVA0151)

Sample Number: IA8
Sample Name/Common Name: Rock asphalt
Chemical Name/Genus and Species: N/A
Source: Mineralogical collection
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: Syria
Number: N/A
Spectra: GSIA0199
GSVA0152
Library Number: DR0107 (GSVA0152)

Sample Number: IA10
Sample Name/Common Name: Glycerol
Chemical Name/Genus and Species: 1.2.3-Propanetriol

Source: Department of Conservation
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: BDH General Purpose Reagent (GPR)
Number: N/A
Spectra: GSVA0379
Library number: DR0201

Sample Number: IA11
Sample Name/Common Name: Ketone Resin N
Chemical Name/Genus and Species: Probably cyclohexanone polymer
Source: Department of Conservation
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: F. W. Joel Ltd.
Number: N/A
Spectra: GSVA0380
Library number: DR0202

Sample Number: IA12
Sample Name/Common Name: Paraloid B-48N
Chemical Name/Genus and Species: Uncertain methyl methacrylate
copolymer
Source: Department of Conservation
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: Rohm & Haas (UK) Ltd.
Number: N/A
Spectra: GSVA0381
Library number: DR0203

Sample Number: IA13
Sample Name/Common Name: Poly (vinyl acetate) PVAC
Chemical Name/Genus and Species: Poly (vinyl acetate)
Source: Department of Conservation
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: F. W. Joel Ltd.
Number: N/A
Spectra: GSVA0382
Library Number: DR0204

Sample Number: IA14
Sample Name/Common Name: Dammar resin
Chemical Name/Genus and Species: N/A
Source: Department of Conservation
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: Hopkins and Williams Laboratory
Number: N/A
Spectra: GSVA0383
Library Number: DR0205

Sample Number: IA15
Sample Name/Common Name: Soluble nylon
Chemical Name/Genus and Species: N-methoxymethyl nylon
Source: Department of Conservation
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: Calaton
Number: N/A
Spectra: GSVA0563
GSVA0581
GSVA0583
GSVA0585
GSVA0598
GSVA0600
GSVA0602
Library Number: N/A

Sample Number: IA16
Sample Name/Common Name: Urea
Chemical Name/Genus and Species: Carbamide ($H_2NCONH_2$)
Source: Department of Conservation
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: Urea SLR Fisons Laboratory Reagent
Number: N/A
Spectra: GSVA0385
Library Number: DR0206
P00042

Sample Number: IA17
Sample Name/Common Name: HMG adhesive
Chemical Name/Genus and Species: Cellulose nitrate
Source: Department of Conservation
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: H. Marcel Guest Ltd. (HMG)
Number: N/A
Spectra: GSVA0540
GSVA0586
GSVA0587
GSVA0596

Library number: P00046 (GSVA0540)

Sample Number: IA18
Sample Name/Common Name: Paraloid B-72 adhesive
Chemical Name/Genus and Species: Methyl acrylate/ethyl methacrylate
copolymer
Source: Department of Conservation
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: H. Marcel Guest Ltd. (HMG)
Number: N/A
Spectra: GSVA0541
GSVA0595
Library number: P00047 (GSVA0541)

Sample Number: IA19
Sample Name/Common Name: UHU adhesive
Chemical Name/Genus and Species: Poly (vinyl acetate)
Source: Department of Conservation
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: Beecham UHU
Number: N/A
Spectra: GSVA0542
GSVA0597
Library number: P00048 (GSVA0542)

Sample Number: IA20
Sample Name/Common Name: Gelvatol 40:20
Chemical Name/Genus and Species: Poly (vinyl alcohol)
Source: Department of Conservation
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: F. W. Joel Ltd.
Number: N/A
Spectra: GSVA0622
Library number: N/A

Sample Number: IA21
Sample Name/Common Name: Gelvatol 20:90
Chemical Name/Genus and Species: Poly (vinyl alcohol)
Source: Department of Conservation
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: F. W. Joel Ltd.
Number: N/A
Spectra: GSVA0623
Library Number: N/A

Sample Number: BM1
Sample Name/Common Name: Shellac flakes
Chemical Name/Genus and Species: from *Laccifer lacca* Kerr.
Source: S. Bradley
Museum/Laboratory: British Museum Research Laboratory, London, WC1
Provenance: N/A
Number: N/A
Spectra: GSVA0158
Library Number: DR0108

Sample Number: BM2
Sample Name/Common Name: Bleached shellac (insoluble in alcohol)
Chemical Name/Genus and Species: from *Laccifer lacca* Kerr.
Source: S. Bradley
Museum/Laboratory: British Museum Research Laboratory, London, WC1
Provenance: N/A
Number: N/A
Spectra: GSVA0159
Library Number: DR0109

Sample Number: BM3
Sample Name/Common Name: Gum arabic
Chemical Name/Genus and Species: from *Acacia* species
Source: S. Bradley
Museum/Laboratory: British Museum Research Laboratory, London, WC1
Provenance: N/A
Number: N/A
Spectra: GSVA0160
Library Number: DR0110

Sample Number: BM4
Sample Name/Common Name: Gum sandarac
Chemical Name/Genus and Species: from *Tetraclinis articulata*
Source: S. Bradley
Museum/Laboratory: British Museum Research Laboratory, London, WC1
Provenance: N/A
Number: N/A
Spectra: GSVA0161
Library number: DR0111

Sample Number: BM5
Sample Name/Common Name: Gum ammoniacum
Chemical Name/Genus and Species: from *Dorema ammoniacum*
Source: S. Bradley
Museum/Laboratory: British Museum Research Laboratory, London, WC1
Provenance: N/A
Number: N/A
Spectra: GSVA0162
Library number: DR0112

Sample Number: BM6
Sample Name/Common Name: Gum acacia
Chemical Name/Genus and Species: from *Acacia* species
Source: S. Bradley
Museum/Laboratory: British Museum Research Laboratory, London, WC1
Provenance: N/A
Number: N/A
Spectra: GSVA0163
Library number: DR0113

Sample Number: BM7
Sample Name/Common Name: Copaiba balsam
Chemical Name/Genus and Species: from *Copaifera* species
Source: S. Bradley
Museum/Laboratory: British Museum Research Laboratory, London, WC1
Provenance: N/A
Number: N/A
Spectra: GSVA0164
Library number: DR0114

Sample Number: BM8
Sample Name/Common Name: Ketone resin
Chemical Name/Genus and Species: Probably cyclohexanone polymer
Source: S. Bradley
Museum/Laboratory: British Museum Research Laboratory, London, WC1
Provenance: BASF replacement for A.W.2, similar to M.S.2
Number: N/A
Spectra: GSVA0165
Library Number: DR0115

Sample Number: BM9
Sample Name/Common Name: Spermaceti wax (cetaceum)
Chemical Name/Genus and Species: from Physeter macrocephalus L.
Source: S. Bradley
Museum/Laboratory: British Museum Research Laboratory, London, WC1
Provenance: Trinity College, Dublin
Number: N/A
Spectra: GSVA0166
Library Number: DR0116

Sample Number: BM10
Sample Name/Common Name: Gum copal
Chemical Name/Genus and Species: possibly from Daniella similis
Source: S. Bradley
Museum/Laboratory: British Museum Research Laboratory, London, WC1
Provenance: N/A
Number: N/A
Spectra: GSVA0167
Library Number: DR0117

Sample Number: BM11
Sample Name/Common Name: Guaiacum resin
Chemical name/Genus and Species: from Guaiacum sanctum
Source: S. Bradley
Museum/Laboratory: British Museum Research Laboratory, London, WC1
Provenance: N/A
Number: N/A
Spectra: GSVA0168
Library Number: DR0118

Sample Number: BM12
Sample Name/Common Name: Gum benzoin
Chemical Name/Genus and Species: from Styrax benzoin
Source: S. Bradley
Museum/Laboratory: British Museum Research Laboratory, London, WC1
Provenance: N/A
Number: N/A
Spectra: GSVA0169
Library number: DR0119

Sample Number: BM13
Sample Name/Common Name: Gum dammar
Chemical Name/Genus and Species: N/A
Source: S. Bradley
Museum/Laboratory: British Museum Research Laboratory, London, WC1
Provenance: N/A
Number: N/A
Spectra: GSVA0170
Library number: DR0120

Sample Number: BM14
Sample Name/Common Name: Canada balsam
Chemical Name/Genus and Species: from Abies balsamea
Source: S. Bradley
Museum/Laboratory: British Museum Research Laboratory, London, WC1
Provenance: N/A
Number: N/A
Spectra: GSVA0171
Library number: DR0121

Sample Number: BM15
Sample Name/Common Name: Button shellac
Chemical Name/Genus and Species: from Laccifar lacca Kerr
Source: S. Bradley
Museum/Laboratory: British Museum Research Laboratory, London, WC1
Provenance: N/A
Number: N/A
Spectra: GSVA0172
Library number: DR0122

Sample Number: BM16
Sample Name/Common Name: Colophony (Rosin)
Chemical Name/Genus and Species: probably from Pinus species
Source: S. Bradley
Museum/Laboratory: British Museum Research Laboratory, London, WC1
Provenance: N/A
Number: N/A
Spectra: GSVA0179
Library Number: DR0123

Sample Number: BM17
Sample Name/Common Name: Asphalt
Chemical Name/Genus and Species: N/A
Source: S. Bradley
Museum/Laboratory: British Museum Research Laboratory, London, WC1
Provenance: N/A
Number: N/A
Spectra: GSVA0180
Library Number: DR0124

Sample Number: BM18
Sample Name/Common Name: Bitumen
Chemical Name/Genus and Species: N/A
Source: S. Bradley
Museum/Laboratory: British Museum Research Laboratory, London, WC1
Provenance: N/A
Number: N/A
Spectra: GSVA0181
Library Number: DR0125

Sample Number: BM19
Sample Name/Common Name: Stockholm tar
Chemical Name/Genus and Species: Pix liquida BP
Source: S. Bradley
Museum/Laboratory: British Museum Research Laboratory, London, WC1
Provenance: N/A
Number: N/A
Spectra: GSVA0182
Library Number: DR0126

Sample Number: BM20
Sample Name/Common Name: Paraffin wax
Chemical Name/Genus and Species: Hydrocarbon wax
Source: S. Bradley
Museum/Laboratory: British Museum Research Laboratory, London, WC1
Provenance: N/A
Number: N/A
Spectra: GSVA0183
Library number: DR0127

Sample Number: BM21
Sample Name/Common Name: Badische A wax
Chemical Name/Genus and Species: Hydrocarbon wax
Source: S. Bradley
Museum/Laboratory: British Museum Research Laboratory, London, WC1
Provenance: N/A
Number: N/A
Spectra: GSVA0184
Library number: DR0128

Sample Number: BM22
Sample Name/Common Name: Carnaube wax (yellow)
Chemical Name/Genus and Species: from Copernicia cerifera
Source: S. Bradley
Museum/Laboratory: British Museum Research Laboratory, London, WC1
Provenance: BDH
Number: N/A
Spectra: GSVA0185
Library number: DR0129

Sample Number: BM23
Sample Name/Common Name: Beeswax
Chemical Name/Genus and Species: N/A
Source: S. Bradley
Museum/Laboratory: British Museum Research Laboratory, London, WC1
Provenance: N/A
Number: N/A
Spectra: GSVA0186
Library number: DR0130

Sample Number: BM24
Sample Name/Common Name: PVAC vinylite
Chemical Name/Genus and Species: Poly (vinyl acetate)
Source: S. Bradley
Museum/Laboratory: British Museum Research Laboratory, London, WC1
Provenance: AYAF
Number: N/A
Spectra: GSVA0187
Library Number: DR0131

Sample Number: BM25
Sample Name/Common Name: Beeswax (yellow foreign)
Chemical Name/Genus and Species: N/A
Source: S. Bradley
Museum/Laboratory: British Museum Research Laboratory, London, WC1
Provenance: BDH
Number: N/A
Spectra: GSVA0188
Library Number: DR0132

Sample Number: BM26
Sample Name/Common Name: Hard wax mixture 1 part dammar resin, 1 part grey carnauba wax, 1 part paraffin and 3 parts beeswax
Chemical Name/Genus and Species: N/A
Source: S. Bradley
Museum/Laboratory: British Museum Research Laboratory, London, WC1
Provenance: National Museum of Copenhagen
Number: N/A
Spectra: GSVA0226
Library Number: DR214

Sample Number: BM27
Sample Name/Common Name: Venice turpentine
Chemical Name/Genus and Species: from Larix decidua Miller
Source: S. Bradley
Museum/Laboratory: British Museum Research Laboratory, London, WC1
Provenance: N/A
Number: N/A
Spectra: GSVA0227
GSVA0394
Library Number: DR0184 (GSVA0295)
DR0213 (GSVA0394)

Sample Number: GS1
Sample Name/Common Name: Egg white (3 hours UV exposure)
Chemical Name/Genus and Species: Albumen
Source: G. Shearer
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: N/A
Number: N/A
Spectra: GSVA0199
Library number: DR0136

Sample Number: GS2
Sample Name/Common Name: Egg yolk (3 hours UV exposure)
Chemical Name/Genus and Species: N/A
Source: G. Shearer
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: N/A
Number: N/A
Spectra: GSVA0200
Library number: DR0137

Sample Number: GS3
Sample Name/Common Name: Egg yolk and white (3 hours UV exposure)
Chemical Name/Genus and Species: N/A
Source: G. Shearer
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: N/A
Number: N/A
Spectra: GSVA0201
Library number: DR0138

Sample Number: GS4
Sample Name/Common Name: Egg white (3 hours UV exposure)
Chemical Name/Genus and Species: Albumen
Source: G. Shearer
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: N/A
Number: N/A
Spectra: GSVA0202
Library number: DR0139

Sample Number: GS5
Sample Name/Common Name: Egg yolk (12 hours UV exposure)
Chemical Name/Genus and Species: N/A
Source: G. Shearer
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: N/A
Number: N/A
Spectra: GSVA0203
Library Number: DR0140

Sample Number: GS6
Sample Name/Common Name: Egg yolk and white (12 hours UV exposure)
Chemical Name/Genus and Species: N/A
Source: G. Shearer
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: N/A
Number: N/A
Spectra: GSVA0204
Library Number: DR0141

Sample Number: GS7
Sample Name/Common Name: Cellulose powder
Chemical Name/Genus and Species: Cellulose
Source: Department of Conservation
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: Whatman standard grade, W & R Balston Ltd.
Number: N/A
Spectra: GSVA0334
Library Number: DR0010
P00044

Sample Number: GS8
Sample Name/Common Name: Lamb suet
Chemical Name/Genus and Species: N/A
Source: G. Shearer
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: N/A
Number: N/A
Spectra: GSVA0434
Library Number: DR0217

Sample Number: GS9
Sample Name/Common Name: Olive oil
Chemical Name/Genus and Species: N/A
Source: G. Shearer
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: Sainsbury's brand
Number: N/A
Spectra: GSVA0465
Library number: DR0218

Sample Number: GS10
Sample Name/Common Name: Safflower oil
Chemical Name/Genus and Species: N/A
Source: G. Shearer
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: Dove brand pure safflower oil
Number: N/A
Spectra: GSVA0466
Library number: DR0219

Sample Number: GS11
Sample Name/Common Name: Grapeseed oil
Chemical Name/Genus and Species: N/A
Source: G. Shearer
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: Dufrais Pure Grapeseed Oil
Number: N/A
Spectra: GSVA0467
Library number: DR0220

Sample Number: GS12
Sample Name/Common Name: Walnut oil
Chemical Name/Genus and Species: N/A
Source: G. Shearer
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: Planoix brand
Number: N/A
Spectra: GSVA0468
Library number: DR0221

Sample Number: GS13
Sample Name/Common Name: Hazelnut oil
Chemical Name/Genus and Species: N/A
Source: G. Shearer
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: 'La fleur de Noisetier' brand
Number: N/A
Spectra: GSVA0469
Library Number: DR0222

Sample Number: GS14
Sample Name/Common Name: Olive oil
Chemical Name/Genus and Species: N/A
Source: G. Shearer
Museum/Laboratory: Institute of Archaeology, 31 - 34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: N/A
Number: N/A
Spectra: GSVA0470
Library Number: DR0223

Sample Number: GS15
Sample Name/Common Name: Shale
Chemical Name/Genus and Species: N/A
Source: D. Moffat
Museum/Laboratory: Institute of Archaeology, 31-34 Gordon Square
London, WC1E 0PY, 01-387-7050
Provenance: possibly Kimmeridege
Number: N/A
Spectra: GSVA0512
GSVA0546
Library Number: DR0224 (GSVA0512)

Sample Number: GS16
Sample Name/Common Name: Jet
Chemical Name/Genus and Species: N/A
Source: John Leveson Gower
Museum/Laboratory: The Square, Winscombe, Avon, BS25 1DA
Provenance: Whitby Museum
Number: N/A
Spectra: GSVA0517
Library Number: DR0225

Sample Number: GS17
Sample Name/Common Name: Shale
Chemical Name/Genus and Species: N/A
Source: Dennis Sloper
Museum/Laboratory: Ringwood, Hampshire
Provenance: Kimmeridge
Number: N/A
Spectra: GSVA0518
GSVA0547
Library number: DR0226 (GSVA0518)

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