

Handbook of instrumental techniques from CCiTUB

Applications of Fourier transform infrared spectroscopy

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Abstract. This article summarizes the basic principles of Fourier Transform Infrared Spectroscopy, with examples of methodologies and applications to different field sciences.

1. Introduction

Infrared spectroscopy is an analytical technique applied to the characterization of molecules. It is based in the fact that molecules absorb specific frequencies that are characteristic of their structure. These absorptions are related to the strength of the bond.

In order for a vibrational mode in a molecule to be active in the infrared region, it must be associated with changes in the permanent dipole. The interaction between electromagnetic light and a molecule produce a change in its permanent dipole, and when the frequency of the infrared light is the same as the vibrational frequency of a bond, absorption occurs.

Although this technique has been used for many years, conventional dispersive infrared spectrometers have been replaced by Fourier Transform infrared equipment, which incorporates a Michelson interferometer and presents an improvement of energy and the simultaneous measurement of the whole spectral range.

The Michelson interferometer consists of a fixed mirror, a moving mirror and a beamsplitter. The beamsplitter is made of a material that transmits and reflects light equally. The two beams reflects back to the beamsplitter from the mirrors and interfere constructively and destructively according to the optical path difference produced by the moving mirror.

Owing to these improvements, infrared spectroscopy has undergone a marked development in the last years because of the possibility of adapting new accessories to the spectrometers and, therefore, of analyzing all kind of samples in the solid, liquid or gaseous state.

The possibility of analyzing and identifying macroscopic or microscopic samples, the accurate comparison of samples from different origins and the fact that the sample is not destroyed, have converted the FTIR technique into a valuable tool. Moreover, the possibility to obtain an infrared spectrum in few minutes and the selectivity of the technique, like a fingerprint of the substance, makes it a first step choice in any conventional analysis.

Kinetics, surface analysis, in vivo measurements are also fields of interest.

Mapping and imaging instrumentation, provide an interesting tool for obtaining large amount of spectra and applying chemometrics measurements.

2. Methodologies and main accessories

Depending on the size of the sample and difficulties regarding handling, different accessories and methodologies can be applied to Fourier Transform Infrared Spectrometers.

2.1. Accessories for macro samples

2.1.1. *Transmission*

Samples which are between 2 and 10 mm in diameter and below 100 microns thick, can be analysed placing them directly in the middle of the beam. In the same cases, they can be prepared mixing particles with an infrared transparent compound, such as potassium bromide, sodium chloride, cesium iodide or other ionic compounds, and pressing it to make a pellet.

Liquids and gases can also be measured by transmission using special cells with transparent windows in the infrared regions of interest.

2.1.2. *Diffuse reflection (DRIFT)*

Diffuse reflectance may be considered as a result of multiple reflection, refraction and diffraction processes on solid particles. It is a common accessory used for surface analysis when samples show a diffuse component of reflected light. Samples which can be a powder or a piece of paper or textile, or a stone, are placed on a cubette or flat support, and the diffuse light emitted is recovered by a semispheric mirror and sent to the detector.

Some good examples to be analysed using this accessory are gemstones. Specially cut gemstones like brilliants, show a very neat spectrum because of its property to diffuse light in all directions.

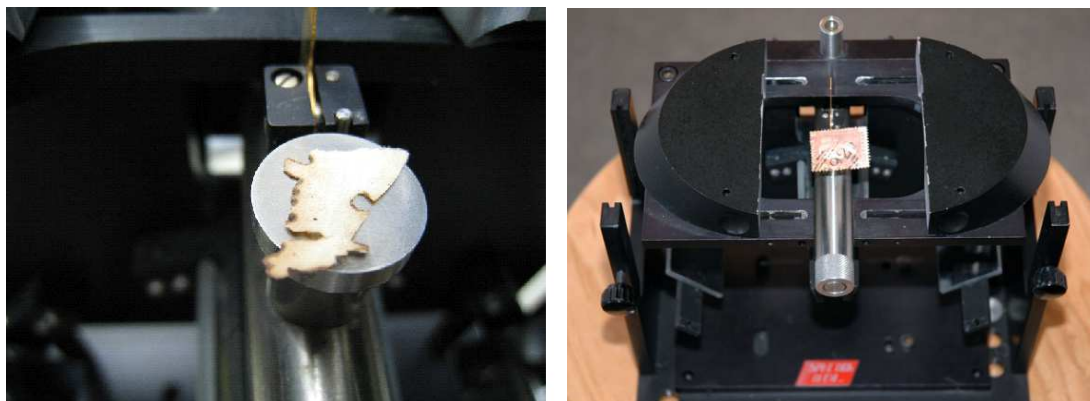


Figure 1. Detail of the sample holder for the DRIFT accessory

2.1.3. Specular Reflection

Samples that can not be manipulated at all and have a specular or polished surface, can be placed on a flat support and be analysed collecting the light reflected in the same direction that the one incident on the surface. Metal surfaces, thin organic or inorganic layers over metals, semiconductors, are commonly analysed using this methodology.

2.1.4. Attenuated Total Reflectance (ATR)

Internal reflection spectroscopy is an infrared technique in which the infrared radiation is passed through an infrared transmitting crystal of high-refractive index. Radiation is directed up to the input face of the crystal. It reflects through the crystal, passing into the sample a finite amount with each reflection along the top surface. The radiation is reflected one or more times depending on the length of the crystal, the refractive index and the angle of incidence of the light.

Attenuated total reflectance is applied to samples where the composition of the surface needs to be measured. It is applied to soft samples such as paper, polymers, textiles, which can achieve good contact with the crystal used. The only consideration to be borne in mind is the need to obtain good optical contact between the surface of the sample and the crystal of the accessory, which can be made of diamond, Germanium, Zinc Selenide, etc. It is also used for liquid, viscous or sticky samples.

When the sample is big enough to cover a long ATR crystal, the possibility of multiple reflections on the surface of the sample, makes it possible to obtain a good infrared spectrum. This is also a solution for liquid samples. Some macro ATR accessories, have a cuvette form to fit liquids inside.

Nowadays, many instruments have the unique internal reflection ATR crystal. The sample is just pressed against it or a drop is placed on the crystal, and a good spectrum can be obtained in few seconds.

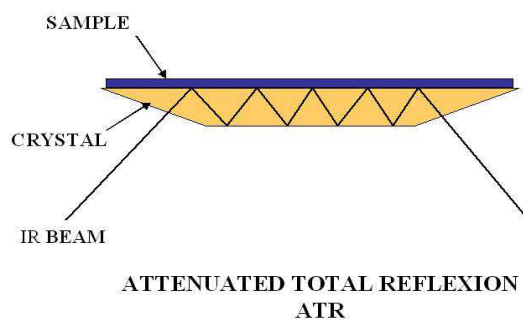


Figure 2. Detail of sample handling in a multireflection ATR accessory

2.2. Accessories for microscopes

2.2.1. *Diamond Cell*

Diamond cell is one of the most frequently used accessories in infrared microscopy. It is normally used when samples are very small, but can be separated from the matrix. The particle or fibre is placed on a diamond window and put under pressure with the help of another diamond window. The pressure of the cell allows the sample to spread over the diamond increasing its surface area while decreasing in thickness. In this way, the infrared radiation is able to go through the sample and, therefore, its infrared spectrum can be obtained by transmission.

Despite the absorption of diamond in the mid infrared, the excellent wavenumber reproducibility of Fourier Transform instruments, makes it possible to subtract the diamond spectrum and to obtain clean spectra of the sample.

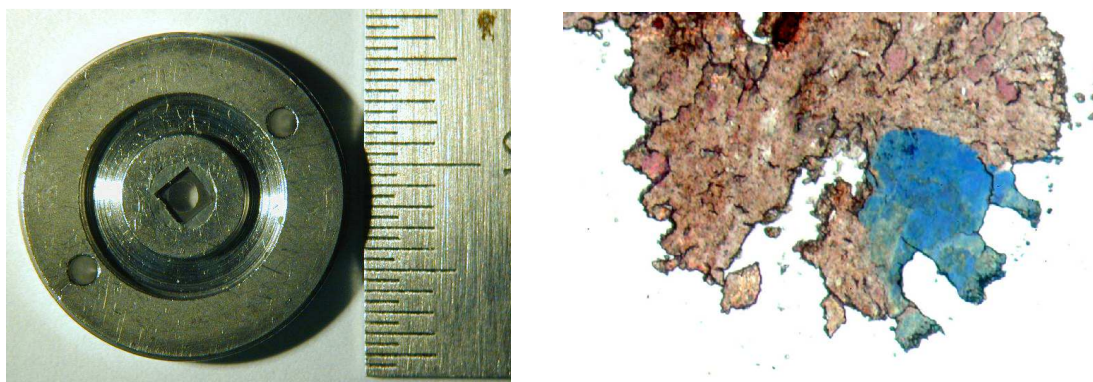


Figure 3. Diamond cell and a pressed sample on a diamond cell

2.2.2. *Micro Attenuated Total Reflectance (ATR)*

The ATR crystal is a part of an objective that can be coupled to the microscope. A unique internal reflection over the sample in touch with the crystal is enough to obtain the spectrum. This is the alternative when even a single particle cannot be removed from the matrix, which is the case for very ancient or valuable samples such as manuscripts, books or paintings. In forensic science, when the sample needs to be recovered for other analysis, ATR is a well known alternative.



Figure 4. ATR Germanium tip

2.2.3. *Cross sections*

In some cases, samples contain several thin layers of different materials. Layers can be as small as 5 microns, and can not be removed separately. This is the case of multilayer commercial polymers, multilayers from paintings or sculptures, etc. Embedding the sample in different materials, such as paraffin, polyester or epoxy resins, permits to cut it in thin layers with a microtome and therefore to analyse it in transmission. Another option is to polish the block where the multilayer is embedded until the sample appears on its surface and apply reflectance measurements.

2.2.4. *Mapping and Imaging*

Most of the modern infrared spectrometers with a coupled microscope, have a motorized stage for samples and therefore it is possible to analyse regions of samples. This can be accomplished by mapping or imaging.

In a mapping analysis, a sequential acquisition of adjacent regions is measured, either moving the stage to the last point of the previous regions, or overlapping it using a fixed step size.

In an imaging analysis, a region of the sample to be measured is focused on the array detector and each pixel is analysed simultaneously.

This has produced an enormous advantage both in speed, a big area can be measured without personnel intervention, and in spectral interpretation, because each band of interest shows an intense colour in the image. Distribution of colours through the image allows the location of its compounds.

3. Examples of applications

Applications to all fields have been developed in our laboratory [1]. They include subjects such as:

- Food analysis: additives, preservatives, colorants
- Environmental analysis: water, atmospheric particles, gases
- Conservation and restauration of heritage: paintings, sculptures, ceramics, fossils, ivories.
- Forensic science: paints, textiles, cosmetics,
- Semiconductor analysis
- Pharmaceuticals.
- Physiological samples: malignant cells, bones, hairs
- Multilayer compounds: polymers, paintings, films
- Geological samples: inclusions in stones

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3.1. Gemstones

Infrared spectroscopy applied to gemstones in order to distinguish natural or synthetic pieces, or even to analyze its composition, has provided an objective evidence for its characterization and has proved to be an important tool for both identification and certification purposes in commercial and legal practices. Emeralds, diamonds, topazs, aquamarines, show characteristic infrared absorptions. Gemstones, specially those with a brilliant cut, diffuse light in all directions, therefore, the diffuse reflectance accessory provides a useful way to analyse them quickly.

Natural diamonds without impurities have a characteristic spectrum with bands that are common to both natural and synthetic pieces, but most diamonds also present bands caused by defects in the crystalline lattice. Two different ranges in the infrared spectra are interesting for identification purposes: the first one corresponds to the interval between 5000 and 2700 cm^{-1} and is the range where the bands corresponding to hydrogen impurities in natural diamonds appear, the second one, between 1400 and 1000 cm^{-1} , identifies the impurities due to nitrogen (Figure 5). According to the type of nitrogen substitution, there are also different kinds of diamonds [2].

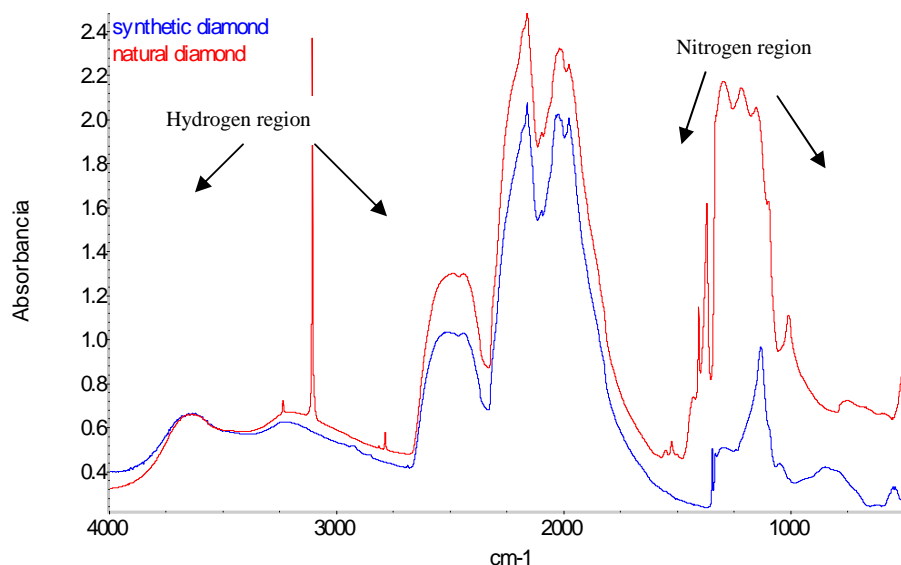


Figure 5. comparison between a natural and a synthetic diamond.

3.2. Analysis of multilayer samples

Some of the samples of interest to be measured using mapping or imaging infrared spectroscopy are those from pictures, walls, murals, sculptures...

The purpose is not only to know the pigment or substrate of the painting, but also the binding media used to fix pigments. A cross section of multilayer samples makes it possible to analyse the different layers. Figure 6 shows a little piece of a mural painting. Mapping of the sample allows us to place the different materials. Infrared spectra of the layers show calcium sulphate, calcium carbonate, Prussian blue, quartz and carboxilates coming from metal soaps, which makes it possible to recognize oil as a binding material.

Figure 7 shows the spectrum of the Prussian blue region. Figure 8 shows the spectrum of oil and carboxilates placed on the external surface of the mural painting. Figure 9 shows the spectrum of a quartz particle in the inner part of the painting.

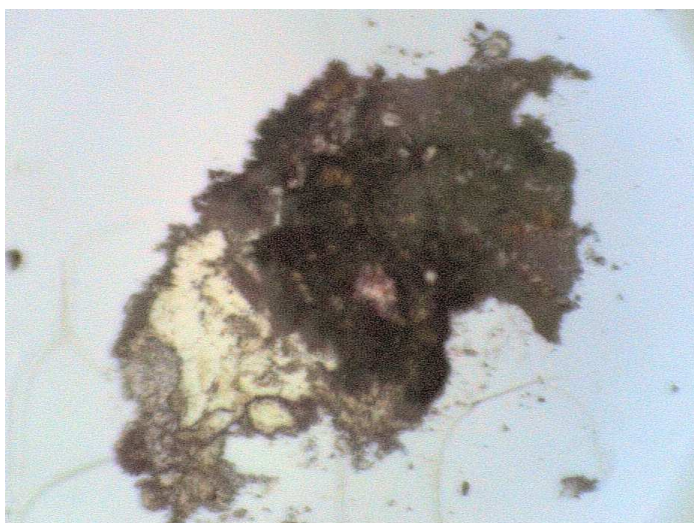


Figure 6. Cross section of a piece of a mural painting (about 300 microns long)

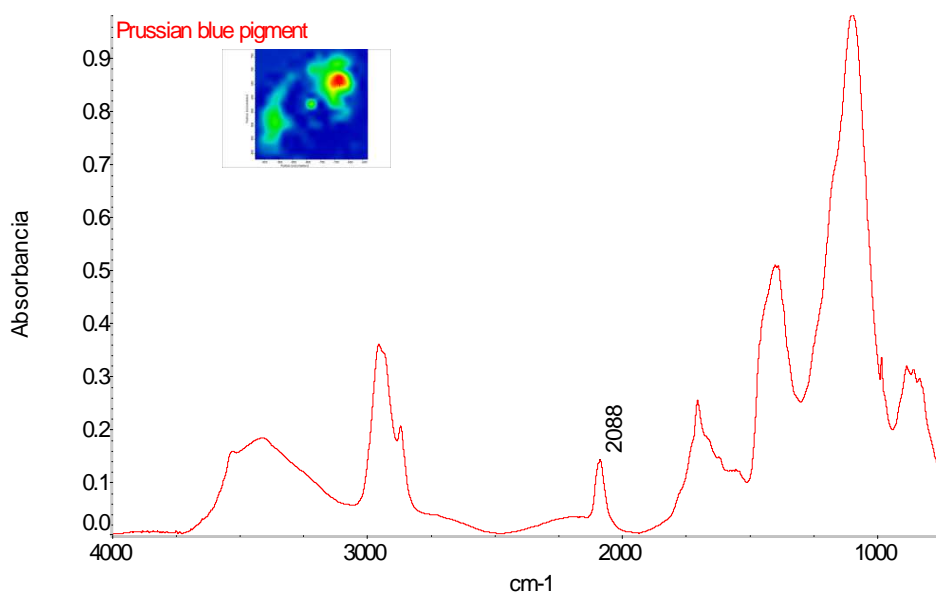


Figure 7. Spectrum of a region containing Prussian blue

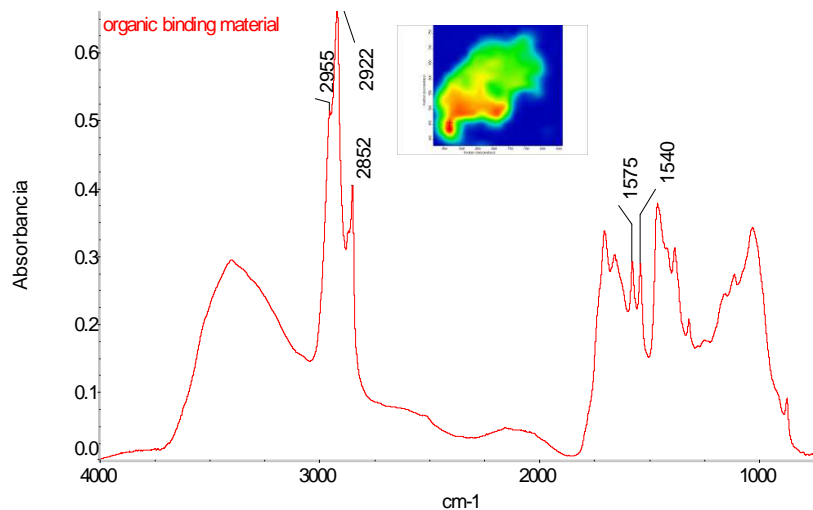


Figure 8. Spectrum of a region containing binding material

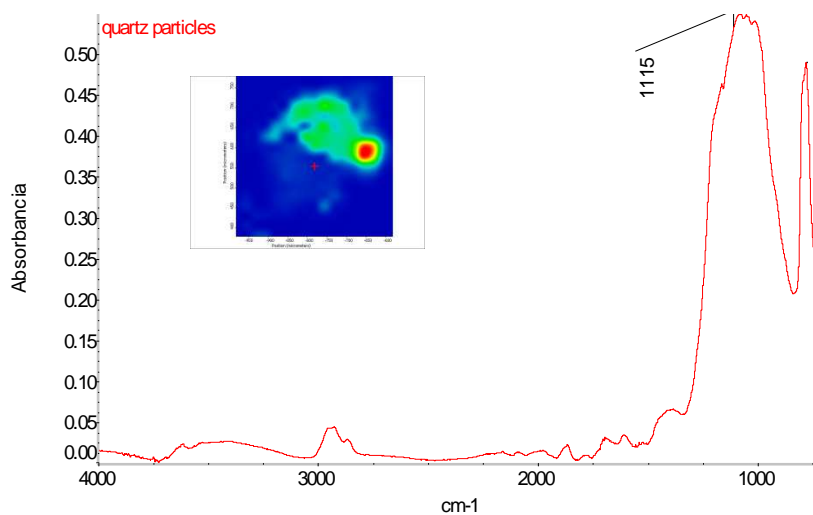


Figure 9. Spectrum of a region containing quartz

Multilayer films of polymers are also a common sample that can be analysed using mapping or imaging infrared spectroscopy. Figure 10 shows the image of a 3 component multilayer film used to contain farmaceuticals and figure 11 shows the spectra of polyethylene and polypropylene found in two layers.

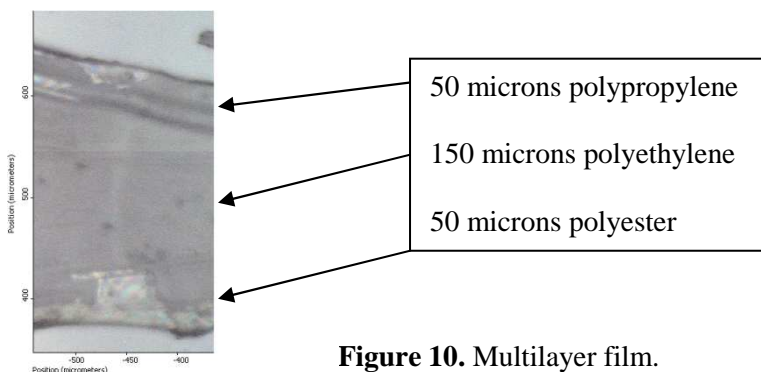


Figure 10. Multilayer film.

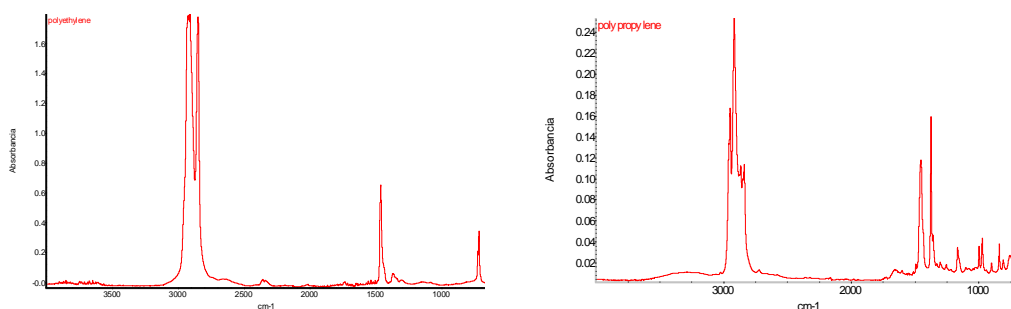


Figure 11. Spectra of polyethylene and polypropylene

3.3. Analysis of papers and inks

Analysis of papers, parchments and inks in ancient manuscripts which are nearly destroyed and need to be restored, has been one of the goals in archives and libraries containing valuable and incunabula books. Determining the composition of papers and inks is important to understand the reaction mechanisms involved in its damage [3]. Corrosion in manuscripts involves acidity and oxidation processes. Iron ions have an important role in the oxidation of cellulose. Acidity of paper is also another parameter to measure in order to postulate degradation mechanisms. Some compounds found over ferrogallic inks are: oxalates, sulfates, carbonate, etc.

Extraction of single particles as small as 10 microns in size, or micro ATR techniques are used for these samples whose handling needs to be not destructive at all. Figure 12 shows two pictures of parchment and paper with inks. Figure 13 shows a spectrum of a single particle from an ancient parchment. Bands at 1663, 1375, 1320 and 827 correspond to magnesium oxalate. Bands at 1195, 1080 and 999 correspond to iron sulphate.

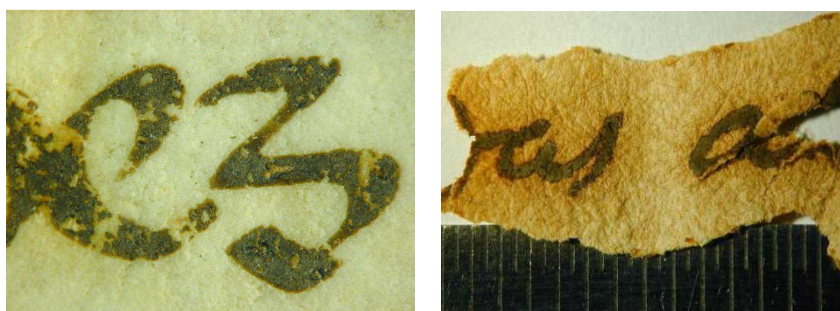


Figure 12. Pictures of a parchment manuscript and a paper manuscript. Both with ink.

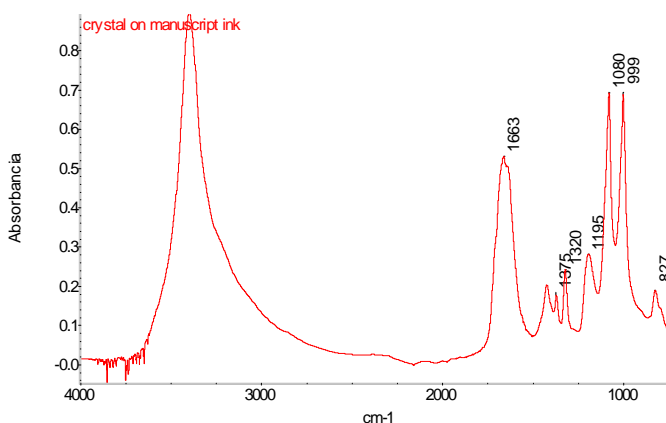


Figure 13. Spectrum of a single crystal on the surface of a parchment sample with ink

Analysis of modern printing inks has also been developed in our centre [4]. Analysis of inks in printings needs a special handling because of the cellulose matrix. Sometimes the accurate comparison between a clean fibre and a fibre with ink is enough to characterize the pigment. (Figure 14)

Figure 15 shows the spectra of blue and red pigments found in damaged stamps. Blue colour was associated to Prussian Blue and red colour to lead chromate.



Figure 14. One penny postage stamps printed 1841-1880 with a blueing effect

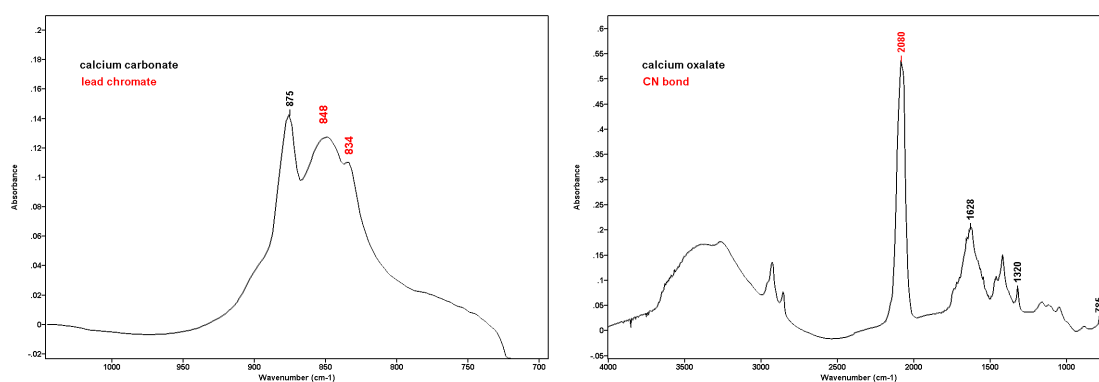


Figure 15. Spectra of Prussian blue and lead chromate. Both pigments were found in damaged stamps.

3.4. Quantitative and qualitative analysis of oils and greases

An alternative procedure using solid phase extraction for the analysis of oil and grease in waters was developed in our laboratory [5]. The use of a teflon filter as a solid phase allowed retention of oil and grease and further analysis of carbon-hydrogen bonds could be run over the filter. Teflon has only carbon-fluor bonds and therefore the region where carbon-hydrogen bands absorb is clean. This method avoided the use of any kind of solvent. Standard methods used carbon tetrachloride or trichlorotrifluoroethane extractions, which should be avoided according to the Montreal Protocol [6].

Experiments used n-hexadecane as a standard oil in different water matrices. The detection limit was 0.034 mg/l. Recoveries of diesel oil, pump vacuum oil, olive oil, sunflower oil and mixture of oils, depend strongly on the oil used for the calibration line, but in general satisfactory results were obtained. The method was fast, clean and sensitive, and represented a way of measuring oil and grease in water with high reproducibility. Qualitative differences could also be detected, depending on the relationship among the intensities of the CH₃ and CH₂ symmetric stretching bands. A small shift in the position of both bands, could also be seen.

Figure 16 shows the comparison among different oils used to prepare synthetic samples.

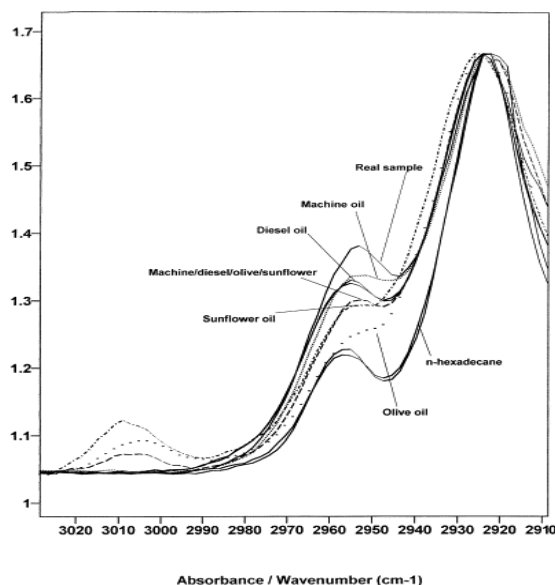


Figure 16. Comparison of infrared absorptions among different oils.

Acknowledgements

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