

**OXIDATION AT THE WET/DRY INTERFACE IN THE
DETERIORATION OF PAPER IN LIBRARY AND ARCHIVAL
COLLECTIONS IN HUMID CLIMATIC CONDITIONS**

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DECLARATION

I, the undersigned hereby declare that the work contained in this thesis is my own original work and has not previously in its entirety, nor in part, been submitted at any university for a degree.

Signature

Wolfgang Peltner

Date

12. 4. 99

Das Wissen allein ist nicht Zweck des Menschen auf der Erde;
das Wissen muß sich im Leben auch betätigen."

(H.Helmholtz)

ABSTRACT

Three primary mechanisms of paper deterioration in library and archival collections are driven by climatic conditions of excessive relative humidity. These are chemical reactivity, mechanical stress and biological deterioration. It is the view of the researcher that the role of chemical reactivity has not been adequately assessed in relation to the deterioration of paper.

The significance of an autoxidative phenomenon, similar to the brown tideline staining at the wet/dry interface, has not been previously recognised as a cause of deterioration as an accelerated function of time under humid conditions of the macroclimate, and as a function of the unstable equilibrium moisture content of materials in a microclimate, but has been obscured by the accepted explanation of biological deterioration.

An analytical procedure was developed to enable the comparison of oxidative degradation products found in stained areas of naturally aged samples with those formed during a dynamic simulated ageing programme to induce cellulosic discolouration. A relationship between the degradative mechanism and humid climatic conditions was established. Based on the findings of the analytical investigation, this study forms a contribution towards the development of a theory of deterioration.

Evidence is presented of a chemical process of degradation in the oxidation of paper at the wet/dry interface, following the condensation and evaporation kinetics induced by cycling relative humidity (RH) driven by temperature fluctuations in diurnal and seasonal ranges.

Sites of moisture accumulation at which the oxidative reaction readily take place, and which constitute a wet/dry interface, are identified at surface areas exposed to atmospheric exchange, in physical defects, in uneven adhesive lamination, in local wet treatments, in impervious storage enclosures or adjacent to an impervious surface which acts as a vapour barrier to the transudational force of capillary action.

In advancing the theory of a chemical response of library and archival materials in the fluctuating moisture content as an explanation for the causation of cellulosic staining, the evidence of foxing is redefined. Librarians, archivists and conservators are thus assisted in the identification of the basic chemical reactions involved in the process of deterioration, and in recognising the role of oxidative degradation relation to environmental conditions.

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LIST OF ACRONYMS

ACTAG	Arts and Culture Task Group
ATR	Attenuated total reflectance
CSD	Centre for Science Development
DRIFT	Diffuse reflectance infrared Fourier transform
EDX	Energy dispersive X-ray
EMC	Equilibrium moisture content
FTIR	Fourier transform infrared spectroscopy
GC/MS	Gas chromatography/mass spectrometry
HATR	Horizontal Attenuated Total Reflectance
HPLC	High performance liquid chromatography
HSRC	Human Sciences Research Council
IFLA	International Federation of Library Associations and Institutions
IR	Infrared
ISO	International Standards Organisation
NRF	National Research Foundation
NQF	National Qualification Framework
RH	Relative humidity
SAQA	South African Qualification Authority

SEM	Scanning electron microscopy
TLC	Thin layer chromatography
UV	Ultraviolet

CHAPTER ONE

STATEMENT OF THE DIRECTION OF STUDY

1.1 INTRODUCTION

A major function of the library is to preserve for future generations the thoughts and words, the ideas and artistic creations of humankind, often entrusted to something as fragile as a sheet of paper. The preservation of library and archival materials is focussed on the life expectancy of paper artefacts, and while some fragments of the first paper made, attributed to T'sai Lun in the fourth century, remain extant, modern paper is not expected to survive a single generation.

The quality of fibre furnish deteriorated dramatically in the nineteenth century with the introduction of groundwood pulp to paper manufacture. Acidity, introduced to the pulp in the alum/rosin sizing process, is now recognised as a major cause of deterioration. Storage conditions of temperature and humidity, the subject of this study, are equally important in paper permanence. The role of storage conditions has received far less attention, although these factors can be corrected in libraries and archives for the preservation of collections. (BANSA & HOFER, 1980; DESSAUER, 1989; HUDSON, 1976; standard..., 1993)

1.1.1 PRESERVATION AND CONSERVATION IN LIBRARY AND INFORMATION SCIENCE

Libraries and archives have fostered the development of paper preservation and conservation since its obscure beginnings in the last century. The first international conference held in St. Gallen, Switzerland in 1898, organised by Dr Franz Ehrle, then head of the Vatican Library and responsible for the restoration work carried out there, was convened to consider:

“the best methods of preserving and restoring manuscripts, parchments, maps, etc.” (EHRLE, 1898 p.45)

Preservation and conservation have developed rapidly in the past thirty years in recognition of the need to preserve the cultural heritage embodied in collections, precipitated by the devastation of the Florence floods in 1966. The International Federation of Library Associations and Institutions (IFLA) established, in response to the identification of preservation needs, a Core Programme on Preservation and Conservation in 1986, with the mandate:

“...to encourage and promote the search for the solutions to the serious problems of physical and chemical deterioration of library and information materials for the purpose of preserving these materials for the future.” (SMITH, 1987 p.1)

Never before in the history of South Africa has our society attached as much importance to the role of research and learning as it has since the political transformation in the early 1990's. Libraries are under pressure to meet an

overwhelming need, denied to many by the previous political regime, to be educated both formally and informally. (BADAT, BARENDS, & WOLPE, 1993; HINDLE, 1996) While South Africa had previously enjoyed a strong research tradition, support for research was previously concentrated within a minority group of the population. The Centre for Science Development (CSD) of the Human Sciences Research Council (HSRC), restructured under the National Research Foundation (NRF, 1998) has acknowledged the need to:

“... contribute to the shaping of a more representative research community in the country (in race and gender terms) and strengthen the link between research in the humanities and social sciences and social policy development.” (Centre for Science Development, 1998 p.1)

The flexible access into and between universities and colleges, afforded by the National Qualification Framework (NQF) has shifted the educational emphasis away from curriculum content towards the research process, in outcome-based learning and continued lifelong learning. The stated objectives of the NQF are, among others, to:

“...accelerate the redress of past unfair discrimination in education, training and employment opportunities; and thereby...contribute to the full personal development of each learner and the social and economic development of the nation at large.” (SAQA, 1998 p.1)

Resource-based learning requires a decisive response from the library and archival professional to ensure access to educational and information materials. The aim is to ensure that:

“...by the time they (students) graduate, they must all have acquired the skills and tools of independent inquiry that characterises research.” (NATAL, 1995 p.1-2)

The rich cultural heritage and diversity of South African society is increasingly acknowledged without political restriction, fostered by the democratic process of consultation, such as the Arts and Culture Task Group (ACTAG), initiated by the Department of Arts, Culture, Science and Technology in 1994, to propose ways of identifying and managing cultural resources in an equitable manner. (ACTAG, 1995) Four pillars of cultural tradition were identified: archives, museums, monuments and *amasiko*, or living culture. Libraries, archives and museums, the structures identified for the conservation and management of our cultural heritage, are charged with the responsibility to house the source materials and circumstantial evidence of the past. The preservation and conservation of cultural heritage collections is the responsibility of library, archive and museum professionals, whose role is moving away from the passive curatorial image of the past. Increasingly, they are required to possess a conceptual knowledge of the physical and intellectual nature of materials, encompassing an appreciation of the value of documentary artefactual heritage. (PALMER, 1995) In fulfilling the information needs of users,

librarians and archivists are required to demonstrate an understanding of modern scholarly processes, ranging from the relationship between print and electronic media and the technological access capabilities afforded by networked computer systems, to the simple information needs of the illiterate population. Faced with the exponential increase in demand on resources by the burgeoning educational drive in South Africa, librarians and archivists require a basic understanding of the interdependent role that the library building, the environment and the provision of appropriate storage conditions play in the preservation of collections, to ensure continued access to information in the most appropriate format.

1.1.2 A PRELIMINARY CONSIDERATION OF TERMINOLOGY

The terminology describing the field of study is often confusing, the terms conservation, preservation and restoration being seemingly interchangeable. The use of the terminology has evolved in recent years, as seen in a comparison of the present definitions offered by IFLA with those of 1986 :

Conservation is an umbrella term to denote the policies and practices involved in protecting cultural heritage from deterioration, including the functions of examination, preservation and restoration.

Preservation includes the managerial and financial considerations

in the storage and accommodation of collections.

Restoration denotes the techniques and professional judgements used by specialised conservators in the making good of materials damaged by time, use and related factors. Conservators are trained to the level of specialisation based on the nature of materials - painting, paper, textiles, furniture, or ceramics. (DUREAU & CLEMENTS, 1986)

The word *restoration* has fallen into disuse in the English language, the function of interventive treatment absorbed into that of *conservation*. It is still retained in some European languages to avoid confusion, for example, with the French term, *conservateur*, denoting a curatorial function. The current English terminology is applied in this study as defined by the IFLA Core Programme on Preservation and Conservation:

Preservation

“Includes all the managerial and financial considerations, including storage and accommodation provisions, staffing levels, policies, techniques and methods involved in preserving library and archival material and the information contained in them.”

Conservation

“Specific practices taken to slow deterioration and prolong the life of an object by directly intervening in its physical or chemical make-up. Examples would be repairing damaged bindings or deacidifying paper.” (ADCOCK, VARLAMOFF, & KREMP, 1998)p.4-5

This study of the conservation of library and archival material is concerned therefore with the formulation of practices and the application of techniques to limit the inevitable process of deterioration of organic materials. This requires an understanding of the manner in which the complex systems comprising library materials deteriorate. The identification of the causes of deterioration, focussed in this study on paper degradation, enables the development of sound practices of preventive conservation and appropriate conservation treatment for the long-term preservation of paper-based information.

1.2 HISTORICAL CONTEXT OF THE STUDY OF ENVIRONMENTAL CONDITIONS IN THE DETERIORATION OF PAPER

The effects of climatic conditions on the complex mechanisms of degradation in the ageing process of cultural artefacts of an organic nature have long been recognised. (BROMELLE, 1968; GRANT, 1937; GREATHOUSE & WESSEL, 1954; KIMBERLEY & SCRIBNER, 1937; LANGWELL, 1957; PETROVA, BELYAKOVA, & KOZULINA, 1964; WESSEL & THOM, 1954; WINK, 1961)

These early studies served to align anecdotal evidence of deterioration with scientific theory of ageing processes, and in quantifying the problem, to secure managerial support for collections conservation, which is preventive rather than remedial in nature. They focussed on an attempt to ensure the optimum environmental conditions for preservation, based on the chemical kinetics of the Arrhenius plot of accelerated ageing tests. (FELLER, 1973; THOMSON, 1964) Their success is measurable against the growing acceptance of the introduction of air-conditioning to document repositories in the past thirty years¹. The development of standard recommendations on suitable levels of temperature and relative humidity was thus stimulated by the demand for building design parameters of cultural heritage institutions, for good preservation management.

The three primary mechanisms of paper deterioration driven by excessive relative humidity (RH) are chemical reactivity, mechanical stress and biological deterioration. It is the view of this researcher that the relative importance of chemical reactivity has not previously been adequately assessed. Biological deterioration, immediately associated with humid conditions, has been thoroughly investigated and reported in the conservation literature - notably without consensus on the role of fungal

1

Environmental control by mechanical air-conditioning systems was introduced in the United Kingdom, initially to the House of Lords Records Office in the early 1960's. (STAZICKER, 1987)

infestation in the causation of foxing. (ARAI, MATSUMURA, & MURAKITA, 1990; ARAI, 1984; BECKWITH, SWANSON, & IIAMS, 1940; PRESS, 1976; SZCZEPANOWSKA, 1986) More recent research on mechanical stress has fuelled a concurrent debate on the efficacy of standard environmental recommendations. (MECKLENBURG & TUMOSA, 1995; MICHALSKI, 1996; REILLY, 1996; SCHULTZ, 1995)

1.2.1 CLIMATIC CONDITIONS IN SOUTHEAST AFRICA

The Campbell Collections of the University of Natal comprise an archival library and a museum housing books, documents, photographic materials and both modern and antiquarian works of art on paper. The conservation treatment of the varied materials in the Campbell Collections led the researcher to identify a predominant form of damage to the Collections and question the probability of a mechanism of deterioration in the ageing of paper artefacts that was specific to the ambient climatic conditions of the location.

Empirical observation of the author, based on fifteen years' experience as both a librarian and a paper conservator at the Campbell Collections, located in a subtropical climate, has supported this growing scepticism reflected in the conservation literature of a reliance on a standard recommendation for environmental control. Climatic conditions experienced in the subtropical marine climate of southeast Africa have been noted

consistently to elude the attainment of the recommended values of 20°C and 50% relative humidity (RH). Furthermore, it is possible that attempts in the past to achieve these values may have contributed to an increased chemical reactivity, in the excessive humidity levels resulting from repeated excursions to dewpoint, thereby contributing to the nature of the damage commonly perceived. The role of environmental factors in the chemical mechanisms of paper deterioration will be further investigated in 3.2 below.

The climate of the subtropical coastal region is characterised by mild temperatures, the narrow diurnal and seasonal ranges in temperature smoothed by alternating land breezes by day and sea breezes by night. Weather circulation systems are characterised by patterns of the Hadley cell, a giant convection cell in which warm air rises over the equatorial region and moves southward in the upper atmosphere, sinking to the ground in an anticyclonic pattern at latitudes of about 30°S. Durban is situated at latitude 29° 58' S and longitude 30° 57' E. The resulting high precipitation in the summer months is accompanied by extreme levels of humidity in the summer months, exceeding a mean of 65% RH from September to April, and peaking at 92% in March. A sharp drop in humidity to a low of 41% is experienced in the short winter months from May to August of each year. (BATTAN, 1983; Climate..., 1986; NIEUWOLT, 1977; PRESTON-WHYTE & TYSON, 1988; VAN HEERDEN & HURRY, 1987)

The climatic conditions described in this study are not limited to the small east coastal region of South Africa. Humid subtropics are found elsewhere, across practically the entire south and south-eastern parts of the United States, sweeping from central Texas through Oklahoma in a northeasterly direction to the Atlantic coast at approximately Atlantic City. A large portion of the South American continent experiences similar conditions along a strip of the east coast and extending a distance inland from approximately 23° to 38° latitude, in the region between Rio de Janeiro and Buenos Aires. Two small regions are located at the east and west ends of the Black Sea, as well as a stretch in Yugoslavia. A large portion of northern India, a great part of China; much of Japan; and a strip of east coastal Australia share similar humid subtropical conditions. (WESSEL & THOM, 1954)

The implications of these meteorological factors were taken into consideration in the experimental design to test the probability of the relationship between environmental conditions and the predominant form of damage identified, described in Chapter 4.

Existing theories of paper deterioration, determined largely by the measure of acid hydrolysis, are based on the effect of temperate climates of Europe and North America, with the result that the effect of this important chemical reaction, beyond the empirical evidence afforded under those conditions, has been overlooked in previous research. Indeed, there is no indication in the literature, beyond the association of tropical climates with

biodeterioration, (GILBERT & LOVELOCK, 1975; HEIM, FLIEDER, & NICOT, 1968; ICCROM, 1968; LEE, 1988; NAIR, 1972; SMITH, 1946), of previous research of South African conditions, or of oxidative reactions induced by similar climatic conditions . A literature review of the role of ambient humid environmental conditions in the causation of perceived damage will be presented in 2.4 below.

1.2.2 MANIFESTATION OF DAMAGE

A large body of experiential evidence was amassed by the researcher as a professional paper conservator over an extended period of fifteen years in the direct observation of the nature of paper deterioration under humid conditions.

Initial investigation by stereo microscopy revealed that some forms of staining, in particular those with dark concentrated centres were clearly visible, while the diffuse blotches were scarcely discernible from the substrate. No evidence of fungal growth could be identified at 100x magnification. Scanning electron microscopy did reveal minimal evidence of microbiological infestation in the presence of only isolated hyphae at some sites. Proliferation of the *Aspergillus niger* fungal species identified was not evident. (BERJACK, 1995) (See Figure 1.1) If microbiological degradation was the primary operative mechanism of paper deterioration, a more significant infestation could have been anticipated. Similar findings

are reported by other authors. (HEY, PASQUARIELLO, GALLO, GUIDI, & PIERDOMINICI, 1988) This, it has been argued, is related to the change in optimum conditions for sustained growth. (FLORIAN, 1994)

Instead, this study has sought to investigate an alternative causative effect of cellulosic staining in an oxidative reaction at the wet/dry interface. (See Figure 1.2) The reported association of brown tideline staining with the foxing phenomenon (LIGTERINK, PORCK, & SMIT, 1991) led this researcher to question the relationship of the oxidative reaction to the ambient humid climatic conditions, the investigation thereof is reviewed in Chapter 2. The minimal evidence of microbiological infestation clearly bore no correlation to the widespread discolouration present. Cellulosic discolouration commonly encountered under humid conditions, in the form of diffuse areas of brown staining, gives a blotched appearance rather than the spotted effect associated with foxing.

Such diffuse staining can be anticipated in the margins of books, predominantly but not exclusively adjacent to the exposed edges - the head, the tail and fore-edge of bound volumes. Tears and dog-eared corners were noted to be consistently associated with cellulosic discolouration, as were the frontispiece and illustration pages bearing graphic artistic techniques and the leaves adjacent to impervious coated paper used for photographic printing techniques.

The discolouration is commonly evidenced in highly porous papers, comprising for example, the illustration pages of books which lack surface sizing for better graphic printing. The smooth, hard surface of the clay coated pages is consistently unaffected, in comparison to the heavy staining of adjacent soft-sized and rough surfaced leaves. Notable is the three dimensional penetration of staining through adjacent leaves, diminishing over a number of leaves distanced from the coated paper insertion. The role of microbiological infestation was further questioned in this transudatory appearance of staining.

A similar effect was noted in the discolouration accordant with brush strokes of laminate adhesive on artworks apparently laid down unevenly. Glued lamination is commonly practised in commercial picture framing to prevent inevitable cockling and surface planar distortion of works on paper displayed under humid conditions. Routine conservation de-lamination of artworks led to a noted correlation of discolouration with air bubbles in un-laminated areas, giving rise to further dissatisfaction with the traditional explanation of microbiological infestation, and prompting the need for further investigation of the browning phenomenon.

The ephemeral nature of much rare archival material frequently dictates the necessity for protective enclosure for loose leaves. Of particular concern is the cellulosic discolouration noted on documents stored in partially-filled

boxes, while those stored in close-fitting enclosures seem unaffected. The implications for microclimate preservation strategies were of immediate concern in this study.

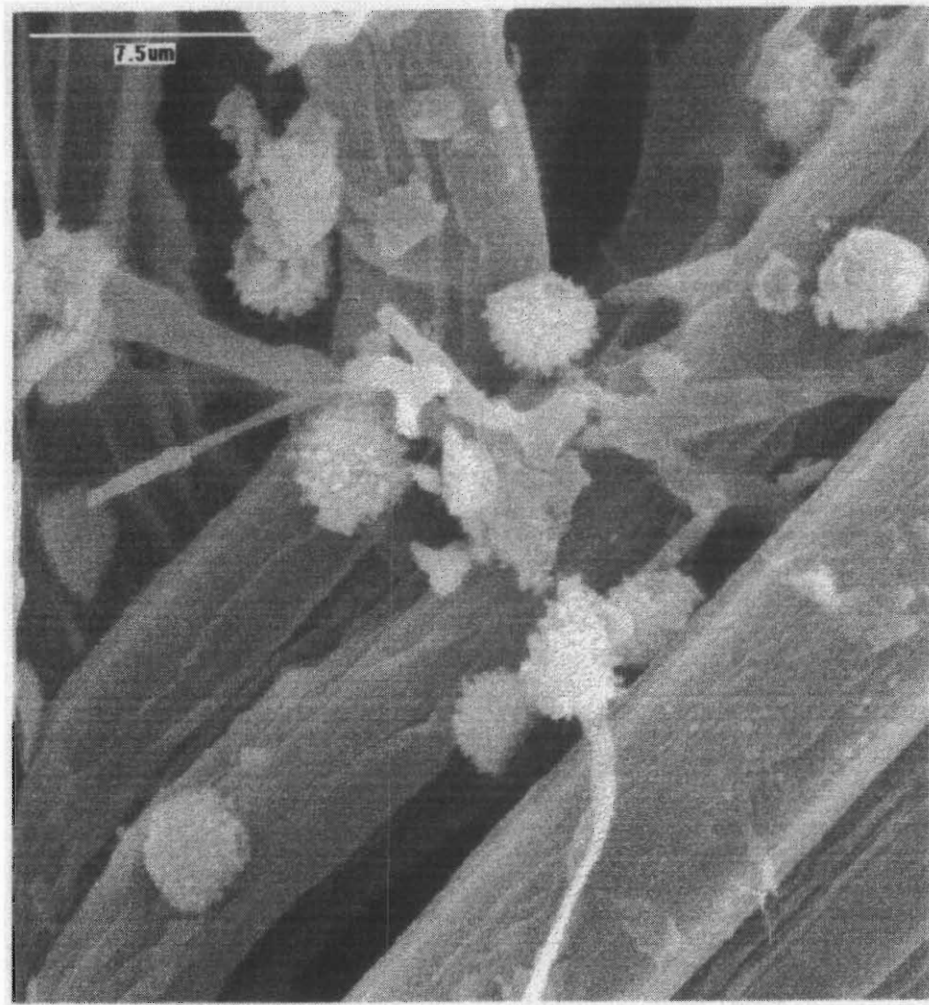


Figure 1.1 Scanning electron micrograph (SEM) of cellulosic discolouration

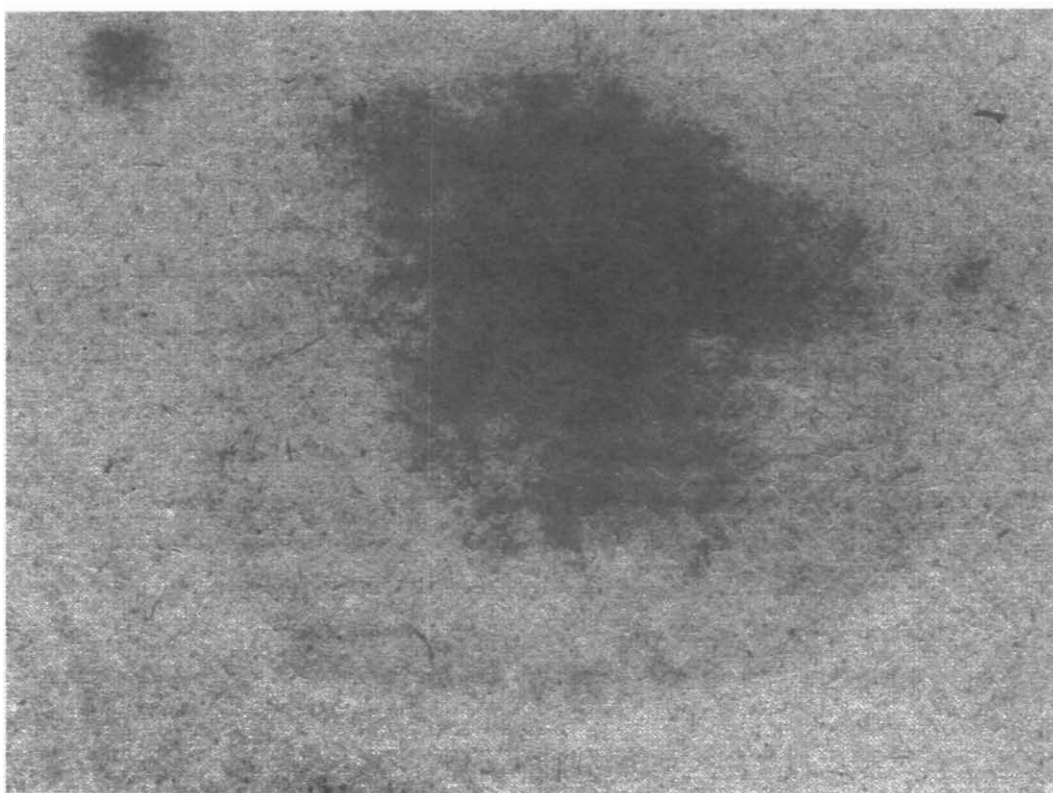


Figure1. 2 Digital image of cellulosic staining 2400dpi

1.2.3 POSSIBLE EXPLANATION FOR THE CAUSATION OF DAMAGE

It was this researcher's belief that the overwhelming factor in the causation of discolouration evident in a humid climate is resultant upon the evaporation kinetics in moisture sorption and desorption under fluctuating temperature and relative humidity. The significance of an autoxidative phenomenon, similar to that of oxidation at the wet/dry interface, has not previously been recognised as a cause of deterioration as an accelerated function of time under humid conditions of the macroclimate, and as a function of the unstable moisture content of materials in a microclimate, but has been obscured by the accepted explanation of biological deterioration.

1.3 STATEMENT OF THE PROBLEM

The abundant evidence of cellulosic discolouration, commonly known as foxing, led firstly to the differentiation between the various forms, and subsequently, to the question of their causation. Randomly distributed spotted discolouration with a dark centre did not respond positively to oxidative bleaching in the same positive manner as did the diffuse blotches in the page margins. Not satisfied that the various forms of staining met with the generally accepted theory that paper-based materials housed in a humid climate are susceptible to microbiological degradation, it was important to this researcher to investigate the evidence of the cellulosic discolouration.

Valuable personal communication in the development of the hypotheses was conducted, including that with Dr Judith Hofenk de Graaff, co-ordinator of the Scientific Department of the Central Research Laboratory for Objects of Art and Science in Amsterdam; Dr Elmer Eusman of the Conservation Department of the Baltimore Museum of Art, and previously of the National Gallery of Art in Washington; Dr M V Nair, Director of the National Research Laboratory for Conservation of Cultural Property in India; Dr Colin Pearson, Director of the School of Conservation, University of Canberra; Ms M-L Florian, Royal British Columbia Museum; Dr Vincent Daniels, Scientific Director of the Department of Conservation of the British Museum; Mr Graeme Scott, architect and conservator at the Australian Museum; Prof Dieter Holm, Professor of Architecture, University of Pretoria and Ms Anne-Laurence Dupont, Canadian Conservation Institute. This communication is appended as an indication of the research process. (See Appendix 1)

1.4 GENERAL AIM OF THE PRESENT INVESTIGATION

The poor correlation of the manifestation of damage with the traditional explanation for foxing gave rise to the search for an alternative explanation of damage. The aim of this study was to investigate the causation of cellulosic discolouration in the increased chemical reactivity evidenced in the phenomenon of autoxidation at the wet/dry interface at the paper surface under humid conditions. Reproducible laboratory experimental work has been presented in Chapter 4 to indicate a relationship between the process

of oxidation, and the condensation and evaporation kinetics induced by cycling relative humidity driven by fluctuations in diurnal and seasonal ranges of temperature and humidity.

1.4.1 RESEARCH OBJECTIVES

The research objectives were defined as follows:

- 1 To study the interaction between those factors affecting paper permanence which relate to conditions during storage and use, focussing on the role of humidity, while acknowledging the role of temperature, air movement, illumination intensity and distribution and atmospheric pollutants in the oxidation reaction.
- 2 To evaluate accepted preservation strategies of environmental control, ventilation and microclimate storage options, for the long-term maintenance of collections.
- 3 To review conservation treatment procedures applicable to the restorative intervention into the oxidative reaction.

1.5 THE RESEARCH HYPOTHESES

The causation of cellulosic discolouration was advanced under the following hypotheses:

- 1.5.1 A fluctuating equilibrium moisture content of the paper substrate causes cellulosic staining.

- 1.5.2 The nature and degree of staining can be evaluated by measurement of the formation of autoxidative degradation products.

- 1.5.3 The more stringent the control of environmental conditions, the slower the rate of autoxidative reaction.

1.6 RESEARCH METHODOLOGY

On the basis of published and unpublished research, these hypotheses were developed in relation to the phenomenon of oxidation at the wet/dry interface and the re-evaluation of recommendations for environmental control.

The background to the study of the relationship between environmental conditions and chemical degradation investigated environmental conditions, particularly relative humidity, as the determinant factor in cellulosic discolouration as evidence of damage to library and archival collections.

This investigation, presented in Chapter 3, was conducted in three steps:

- 1 An examination of the role of environmental control in the mechanism of chemical degradation;
- 2 the response of the equilibrium moisture content under conditions of fluctuating relative humidity, and
- 3 the role of accelerated ageing in measuring the effect of oxidative degradation for the prediction of paper permanence.

On the basis of these investigations, the research design and methodology employed to test these hypotheses are presented in Chapter 4. The experimental model was designed to induce the proposed mechanism of deterioration in a representative paper sample to allow for comparative analysis with observed examples of degraded library and archival materials of known provenance.

The challenge of this research project lay in the empirical testing of the relationship between the environmental conditions and the observed evidence of damage in the form of cellulosic discolouration. This was achieved by developing a theoretical experimental model determined by the psychrometric relationships experienced in the building envelope of the library under subtropical climatic conditions.

The testing of physical strength characteristics such as folding endurance, burst strength and tensile strength are normed standards widely used in the paper industry in the prediction of permanence. These are not appropriate measures of oxidative deterioration, measuring rather the consequence of the subsequent reaction of acid hydrolysis. An independent method of data collection under laboratory conditions was devised to monitor the initiation of the deterioration process.

The natural ageing process is too slow and the development of resultant degradation products too small to be monitored effectively within a reasonable space of time. The accelerated ageing procedure was adapted in a dynamic simulated climate ageing programme to monitor a possible oxidative reaction under reproducible laboratory conditions. It was hoped to establish a relationship between environmental fluctuations - measured in the response of the moisture content of the paper substrate to the dynamic simulated ageing programme - and the recognised phenomenon of oxidation at the wet/dry interface. In identifying the conditions under which the reaction is initiated, it was further anticipated that more effective environmental controls could be derived.

The experimental model is submitted as a tool in library research rather than a project in analytical chemistry. The first stage of the experimental design required the use of an environmental control chamber, critical to the induction of degradation. This was located at the Department of Textile

and Fibre Chemistry at the University of Stuttgart. The analytical procedure comprised the subsequent spectrophotometric measurement of naturally and artificially aged paper samples by Fourier transform infrared (FTIR) spectroscopy, following the development of degradation products associated with oxidative degradation. Finally the confirmation of the formation of degradation products, by means of staining reagents, completed the analytical procedure, reported in Chapter 4 below, was conducted by the researcher at the University of Stuttgart.

In order to reach an understanding of the phenomenon of oxidation at the wet/dry interface as a function of environmental conditions, the presentation of data and the analytical interpretation thereof in Chapter 5 had three related objectives:

- 1 To test the ambient range of environmental conditions to determine the effect of fluctuations in precipitating oxidative mechanisms of degradation.
- 2 To determine the significance of an oxidative reaction at the wet/dry interface in the manifestation of cellulosic discolouration known as foxing.
- 3 To evaluate the relationship between the fine structure of the cellulose substrate and its potential degradation by an oxidative

mechanism.

1.7 JUSTIFICATION AND SIGNIFICANCE OF THE PRESENT STUDY

The application of the phenomenon of oxidation at the wet/dry interface in relation to the deterioration of paper experienced under humid conditions is presented as a contribution towards the further development of a theory of deterioration, based on the reported findings of previous research, and on the results of an independent investigation utilising the analytical tools of conservation science.

As a professional librarian and a paper conservator, it was the view of this researcher that the amalgamation in the practitioner-research relationship indicated the necessity to devise relevant research applicable to the problem at hand, in the identification and treatment of various forms of cellulosic staining, and to design an analytical model to determine the effect of humid environmental conditions on the chemical mechanisms of paper deterioration.

The mechanisms of biodeterioration, while acknowledged as relevant to the process of environmentally induced degradation, were not included in the scope of the present study, as they have been adequately treated elsewhere. The study of foxing focussed on the debate between the probability of biological causation (ARAI, et al., 1990; ARAI, 1984;

BECKWITH, et al., 1940; BURGE, BOISE, SOLOMON, & BANDERA, 1980; CRAIG, 1986; FLORIAN, 1994; PANTKE & KERNER-GANG, 1988; PRESS, 1976; SZCZEPANOWSKA, 1986; SZCZEPANOWSKA & LOVETT, 1992) versus metal-induced staining. (DANIELS, 1988; HEY, et al., 1988; TANG & TROYER, 1981; TANG, 1978)

Physical stress, in the mechanical response of paper and other objects to fluctuations in relative humidity, has also been the subject of recent debate on the determination of standard recommendations for environmental control for cultural institutions, and has been adequately researched elsewhere and presented in the literature. (ERHARDT, MECKLENBURG, TUMOSA, & McCORMICK-GOODHART, 1995; McCORMICK-GOODHART, 1996; MECKLENBURG, McCORMICK-GOODHART, & TUMOSA, 1994; MECKLENBURG & TUMOSA, 1995; MECKLENBURG & TUMOSA, 1996; MECKLENBURG, TUMOSA, & McCORMICK-GOODHART, 1992; MICHALSKI, 1993)

This study has developed rather, a theoretical model for a preceding mechanism of cellulosic staining by autoxidation, first noted in 1935 (IIAMS & BECKWITH, 1935), and the subject of speculation by various authors since. (BECKWITH, et al., 1940; CAIN & KALASINSKY, 1983; CAIN & MILLER, 1982a; CAIN, 1983; CAIN & MILLER, 1982b; DANIELS, 1988; DEROW & DWAN, 1992; HUTCHINS, 1983; LIGTERINK, et al., 1991) In the investigation of the chemical process of degradation by the phenomenon

of oxidation at the wet/dry interface, this study has considered the effect of fluctuations in ambient environmental conditions in the causation of cellulosic discolouration. To this end, it was the researcher's view that the significance of the study lay in the application of psychrometric properties of a humid atmosphere to the experimental design, in the inducement of the oxidative phenomenon by means of environmental fluctuations.

In contributing to the understanding of the process of deterioration by determining the function of autoxidation in relation to climatic conditions, appropriate conservation techniques for the control of these mechanisms can be identified, providing recommendations for the development of effective preservation strategies for collections management.

A further contribution of the study was developed in the research process, in which a dearth of subject headings for the technical fields of preservation and conservation was noted in relation to library and archival material. It was therefore the researcher's anticipation that as a by-product of the study, a thesaurus of relevant keywords in the field could be developed.

It was also the researcher's intention that the research would not be directed at the development of a theory of kinetic laws governing the change exhibited in the natural degradation of paper, generally the result of complex simultaneous or sequential reactions. It was hoped that the study would serve primarily to permit librarians, archivists and conservators to identify

and come to terms with the basic chemical reactions involved in the process of deterioration experienced in inappropriate storage conditions.

1.8 SUMMARY OF THE SCOPE OF THE PRESENT STUDY

The role of environmental conditions, and particularly of relative humidity (RH) in the chemical deterioration of paper artefacts has been examined in relation to library and archival storage. This study focussed on the chemical response of the paper artefact in a fluctuating moisture content, as a possible explanation for the causation of cellulosic staining, that redefines the evidence of foxing.

This study investigated the process of deterioration experienced in the humid climatic conditions of southeast Africa by testing the relationship between the fluctuating equilibrium moisture content of the paper substrate and the formation of cellulosic staining. The total water content of the atmosphere under fluctuating humid climatic conditions was replicated under experimental conditions, and the moisture content of the sample monitored in an attempt to plot the causation of cellulosic staining in the inconstant rate of diffusion from the paper surface.

It was anticipated that the degree of cellulosic staining could be evaluated by the measurement of the formation of degradation products, and the effect of humid environmental conditions on the chemical mechanisms of paper deterioration thus quantified. The experimental sample was subjected to a simulation of ambient conditions to monitor the formation of degradation products, determined by photographic, chemical and spectral analysis,

compared with the empirical evidence of damage encountered under humid conditions. In the identification of the predominant deterioration process under these conditions, the analytical interpretation enables an assessment of risk that precedes and ultimately precludes costly conservation intervention. (ASHLEY-SMITH, 1998)

The implications for conservation in this investigation of the oxidative mechanism in the ageing process was therefore, to devise preventive conservation strategies to arrest the reaction, and to recover by conservation, those properties lost to the paper in the process of deterioration by this mechanism. The study sought further to develop preventive conservation strategies integral to collections management functions. In coming to terms with the chemical reactions taking place under conditions of high humidity, the implementation of appropriate preventive measures and the use of suitable storage materials in the housing of library and archival collections offer more effective alleviation of the natural and inevitable progress of deterioration.

It was the researcher's hope that the summary of research findings will provide library and information workers with the knowledge required to intervene in the natural and inevitable process of degradation of organic materials comprising collections. The application of preventive conservation strategies in response to evidence of damage caused under conditions of high humidity will extend the usable lifespan of materials in their original

format. Information workers are empowered to intervene more directly in fulfilling the information needs of users, in providing continued access to the source materials and the circumstantial evidence of the past. The technological options of reformatting irreversibly degraded material onto microfilm or fiche, and the possibility of information transfer by digital conversion either via the Internet or recorded on CD-ROM, greater enhance the ability of library and information workers to meet the needs of users. An understanding of the manner in which the complex systems comprising library materials deteriorate will further permit an informed decision to be taken, based on the condition of the original, of when to apply the technological advantages offered by an alternative format .

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CHAPTER TWO

REVIEW OF RELATED LITERATURE AND PREVIOUS RESEARCH

2.1 BACKGROUND TO THE PROBLEM OF PAPER DETERIORATION

The deterioration of library materials is a complex subject encompassing the ageing processes associated with books, maps, documents, photographs and works of art on paper.

Mechanical stress is exerted upon materials in the course of their use and handling by staff and researchers. The causation of physical damage resultant upon mechanical stress is that factor of paper deterioration most readily addressed as being self-evident to staff and users following careless handling. User awareness programmes are widely recommended and operate effectively from points of user interface, in circulation control and at the photocopy machine, where books and documents are vulnerable to inadvertent mechanical stress. (BROCK, 1975; FEATHER, 1991; HARVEY, 1993)

The second major factor in the preservation of library and archival collections is the environment. It is accepted that the rate at which paper will begin to deteriorate depends largely on the environment and conditions under which it is stored. (SEBERA, 1994) The investigation of a typical

form of deterioration evidenced in cellulosic staining, is focussed in this study on the organic fibrous structure of paper stored under humid environmental conditions. Environmental control forms the focus of this study, and will be considered in 2.2 below.

A third, no less important factor - albeit one over which the librarian or archivist has no control - the manufacture of impermanent paper - has long been recognised as a predominant factor in paper deterioration. (GRANT, 1937) A growing lobby to improve paper quality and the establishment of standards for modern paper with specific predictable permanence properties for use in the storage of information has brought to attention the defects inherent in the manufacturing processes. In 1977, Stuhrke commented on the need to establish standards for paper manufacture. (STUHRKE, 1977) By 1993, various national standards had been collated under the international standard, ISO 9706, stipulating the requirements for permanence according to pH value, alkaline reserve, tear resistance and resistance to oxidation. The strength of the ongoing lobby is reflected in the continued work of ISO Technical Committee 46/SC10 in the preparation of a standard to describe the qualities necessary not only for permanence but also for durability in the manufacture of a paper for documents for high historical, legal or other significant value. In co-operation with the paper industry, the effect of pulp composition on the deterioration of paper has been comprehensively addressed on an international level. (standard..., 1993)

The effect of the acid content of paper on the rate of deterioration by acid-catalysed hydrolysis has been established as the primary area of research in the development of the science of paper conservation. (BURGESS, 1990; FELLER, LEE, & CURRAN, 1985; FELLERS, IVERSEN, LINDSTROM, NILSSON, & RIGDAHL, 1989; LINDSTROM, 1990) Early work was carried out in this country by Venter, in identifying the effect of the rate of acid hydrolysis on the permanence of paper. (VENTER, 1966; 1967; 1968; 1978) The doctoral dissertation of Richard Smith investigated the effects of acid hydrolysis in establishing the accepted conservation technique of non-aqueous deacidification to counteract these effects. (SMITH, 1970) The latter study continues to direct conservation research today in the ongoing development of mass deacidification procedures. (BURGESS & GOLTZ, 1994; CARTER, 1996)

The considerable body of research on acid hydrolysis as the primary mechanism of deterioration has clearly indicated the effect of temperature and humidity conditions in increasing the rate of deterioration.¹ Some have even pointed to the accelerated rate of deterioration by this mechanism in tropical and sub-tropical conditions. (BANSA, 1981) The purpose of the present study however, is to indicate the environmental effect of

¹ The expression for the effect of temperature on the rate of reaction, written by the Arrhenius equation as :

$$S = Ae^{-AE/RT}$$

where S= rate of reaction, A=Constant, E=activation energy in cal/mole, R = gas constant. T=Absolute temperature in °C+273, e=base for natural logarithms. (THOMSON, 1964) Loosely extrapolated as a doubling in the rate of reaction for every 10° increase in storage temperature.

temperature, and particularly of high levels of humidity, in the direct causation of paper deterioration by an alternate oxidative mechanism.

2.2 ENVIRONMENTAL CONTROL IN THE DETERIORATION OF PAPER

A comprehensive preservation programme is an essential library and archival management strategy in the effective utilisation of personnel and of the most important material resource: that of its collection, in which the information sought by its users takes physical form. Environmental control is an acknowledged and well established preventive conservation strategy in collections management programmes, and is aimed at decreasing the rate of deterioration of entire collections of materials, thereby reducing the need for costly and invasive restoration treatment of individual items. Unlike the factors of mechanical stress and inherent paper quality, the passive or indirect prevention of paper deterioration by means of environmental control demands a substantial budgetary commitment, and since the effects of poor environmental control are not immediately apparent, is reliant upon an informed curatorial response by library and archival management and staff.

Environmental factors which affect the deterioration of library and archival materials include temperature, humidity, light, particulate and atmospheric pollution, vibration and insect pests; the effects of which have been comprehensively described in the classic works of conservation literature.

(CUNHA, TUCKER, & CUSHING, 1972; PLENDERLEITH & WERNER, 1971; THOMSON, 1986; WESSEL, 1978) Designed as guidelines for library managers, who might be unfamiliar with the technical requirements of environmental control, the often simplistic recommendations contained therein have been developed by more recent scientific research, reviewed here below.

The chemical response of paper under environmental conditions of high and of fluctuating humidity is of primary concern to this study. The determination of what might be termed stable, or appropriate environmental conditions is therefore pertinent, and merits some elaboration. With the application of airconditioning to library and archive environments in the early 1960's, recommendations for the preservation of artefacts were first promulgated, citing environmental values of 20°C and 50%RH. (STAZICKER, 1987) However, a growing awareness of the different requirements of different materials has led to a proliferation of seemingly conflicting recommendations.

The reliance on a single standard recommendation for museum and library climate control has been negated, amidst considerable controversy, by the research of the Preservation Science Group of the Conservation Analytical Laboratory at the Smithsonian Institute. (McCRADY, 1994) In measuring the natural physical response of organic materials, this research has advocated a relaxation in environmental control to contain diurnal ranges while

permitting a wider range of fluctuation in RH to accommodate seasonal drift.

A fixed recommended point takes no cognisance of the material response to conditions of local climate. While acknowledging the danger of extremes of RH, which result in mould growth and softening of materials at high RH, and in embrittlement at low RH, a broad range of allowable temperature and RH values is identified. The limitation of that body of research lies in the determination of an allowable range by the evaluation of the physical damage resulting from extreme fluctuations, equating restraint of the material under extreme environmental conditions with mechanical stresses in handling. The development of the theory based on chemical mechanisms of paper deterioration is lacking. (ERHARDT, 1989; ERHARDT, 1990; ERHARDT & MECKLENBERG, 1994; ERHARDT & MECKLENBURG, 1994; ERHARDT, MECKLENBURG, TUMOSA, & McCORMICK-GOODHART, 1995; McCORMICK-GOODHART & MECKLENBURG, 1993; MECKLENBURG, 1988; MECKLENBURG, McCORMICK-GOODHART, & TUMOSA, 1994; MECKLENBURG & TUMOSA, 1995; MECKLENBURG & TUMOSA, 1996; MECKLENBURG, TUMOSA, & McCORMICK-GOODHART, 1992)

The substantial body of research produced by the Conservation Analytical Laboratory of the Smithsonian Institute has brought into question the environmental regime followed in museums and libraries for the past thirty years. Based on the structural response of materials to fluctuating relative humidity, their investigation has shown that the attainment of what they term

'a universal environmental nirvana', might be less critical than was previously believed. They have recommended a continued control of diurnal ranges, but concede that a slow seasonal adjustment can be tolerated reasonably well by all but the most sensitive materials. Photographic materials are identified in that category. The particular relevance of the study of environmental conditions conducted by the Conservation Analytical Laboratory is the investigation of moisture content isolines in long term storage of photographic materials, which tests the assumption of constant moisture content at constant RH, (McCORMICK-GOODHART, 1995) and will be considered in further detail in 2.6.1 and 3.3 below.

Clarification of an environment beyond 'flatlining' - the attempt to maintain constant values of temperature and humidity - has been presented by Michalski, in research undertaken at the Canadian Conservation Institute. Bearing in mind the mixed materials of documentary heritage collections, (ranging from the ink, pencil and paints of the textual content, to supports of paper, plastic, parchment, metals or glass), most benefit is thought to derive from environmental control within the range of 50%RH ($\pm 20\%$) and 20°C ($\pm 20^\circ\text{C}$). This control, he explains, is aimed at maintaining RH within a realistic range, while allowing the temperature to float downwards in winter and return slowly in summer to a level that will ensure a steady response of the material to the surrounding RH. Short-term fluctuations, as in wide diurnal ranges are to be avoided, in the structural stress of the varied response rates of composite materials. (MICHALSKI, 1996)

The foregoing research has opened the debate on appropriate environmental control for the conservation of cultural artefacts. The question arises whether the current recommendations of an extended range of 30-70%RH and 0°C - 40 °C constitute any control at all? A conference sponsored by the Conservation Analytical Laboratory of the Smithsonian Institute and the National Centre for Preservation Technology and Training in September 1997 was unable to achieve its goal of clarifying the issue of guidelines for collections environments. (TUMOSA, MECKLENBURG, ERHARDT, & McCORMICK-GOODHART, 1998) The conclusions and recommendations of that conference called for the determination and quantification of the risks to library and archival collections by environmental settings and fluctuations. The contribution of this research to the current debate lies in the investigation of the potential risk of a chemical response of paper objects to the realistic ambient environmental fluctuations in humidity experienced in the sub-tropical coastal region of southeast Africa, as opposed to the mechanical stress measurements which have formed the conceptual basis of previous studies.

2.3 PREVIOUS RESEARCH INTO THE OXIDATIVE MECHANISMS OF PAPER DETERIORATION

A critical review of the benchmark papers on the role of environmental factors in paper deterioration, noted above, confirmed the relationship between climatic variables and manifestations of both chemical and physical damage to organic materials. In the course of the investigation of unique alternative factors in the causation of cellulosic staining under humid conditions, research has been directed in a linear pattern towards the role of oxidation at the wet/dry interface, indicating autoxidation at the surface boundary layer as a phenomenon separate from and preceding the biological deterioration traditionally associated with paper deterioration under humid environmental conditions.

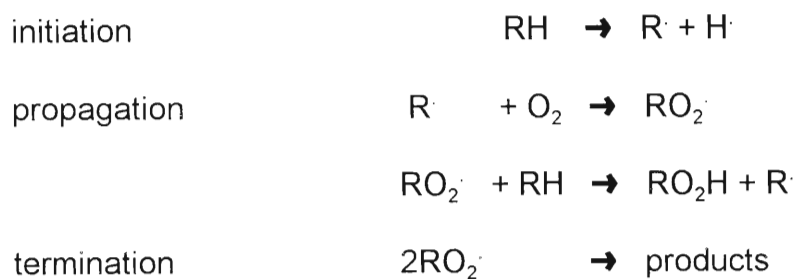
2.3.1 AUTOXIDATION IN ORGANIC CHEMISTRY

The literature reflects extensive research in organic chemistry related to the question of oxidation with atmospheric oxygen, known as autoxidation: electron transfer reactions thought to be responsible for the staining phenomenon, described as autoxidation reactions initiated by the formation of free radicals; the decomposition of peroxides; oxygen uptake and catalytic oxidation by transition metal ions. (GEORGE, 1954; GUNDERMANN & McCAPRA, 1987; LUNDBERG, 1961; SIMS & HOFFMAN, 1961; SWERN,

1961; TOBOLSKY, METZ, & MESROBIAN, 1950; TRYON & WALL, 1961; URI, 1961)

Oxidation reactions proceed in three steps, initiation, propagation and termination. Initiation may involve, either independently or simultaneously, light, photosensitive dyes, gamma and x-rays, autoxidation products, heavy-metal ions and free radical producing compounds. Oxidative reactions in paper are commonly recognised as being initiated by thermal, ultraviolet light, high energy radiations, and by chemical oxidation. The latter, a redox reaction resulting in the formation of short-lived free radicals, is pertinent to this study. (ARTHUR & HINOJOSA, 1971) Little attention has been paid to the dehydrogenation and oxidative polymerisation reactions, which increase the chemical reactivity of cellulose in a humid storage environment. While the importance of independent or simultaneous photochemical degradation as well as that of ozone and other oxidants is acknowledged, and undoubtedly play a role in the rate of oxidation in paper in archival storage, those sources of oxidation are treated adequately elsewhere and are not within the scope of the present study. (ANGIBEAUD, DEFAYE, & GADELLE, 1985; BOGARTY, CAMPBELL, & APPEL, 1952a; GODSAY & LEWIN, 1989; HERRERA, 1990; LAUNER & WILSON, 1949; OSAWA, ERBY, SARKANEN, CARPENTER, & SCHUERCH, 1963; OSAWA & SCHUERCH, 1962; WESSEL, 1970)

An accepted description of an autoxidation reaction is that carried by free radical intermediates, organic fragments (R) bearing an unpaired electron, the electron denoted as a dot, in association with hydrogen (H) and oxygen (O) at room temperature:



Kinetic studies have confirmed that organic peroxides appear among the first products of the reaction, and that the subsequent oxidation of the parent hydrocarbon is autocatalysed by the decomposition of peroxides, which produce free radical chain carriers for the chain reaction. The decomposition of peroxides also leads to the formation of secondary oxidation products such as ketones, aldehydes, acids, alcohols, water and carbon dioxide. (MESROBIAN & TOBOLSKY, 1961; TOBOLSKY, et al., 1950)

Direct oxidation is not considered an efficient reaction by either oxygen or hydrogen peroxide, however, both are autocatalysed by intermediate oxidants, of the free radical or peroxide type. (MINOR & SANYER, 1971) Free radical mechanisms, chain reactions and autoxidation as a chain reaction are complex reactions in which the significance of trace metals, and the role of metal catalysis are drawn into the theoretical consideration of

their effect on paper deterioration. (URI, 1961) The oxidative mechanism of paper deterioration initiated by free radicals in the decomposition of hydrogen peroxide is investigated in this study as a causative factor of cellulosic discolouration encompassing the previously unresolved debate on the causation of cellulosic staining, or foxing, by microbiological factors or by metal-induced catalysis.

The degradation of cellulose in oxygen formed the subject of an early study by Major in 1958. Accelerated ageing at elevated temperature in oxygen and nitrogen atmospheres provided a comparison of degraded residues, analysed chromatographically for carbonyl and carboxyl content, and for degree of polymerisation. Degradation was shown to be much higher in an oxygen atmosphere, apparently as a result of primary oxidation, with oxygen acting as a non-specific oxidant. Of importance to this study is the observation that the reaction takes place in the amorphous regions of the cellulose, since the crystalline regions are not readily accessible to moisture uptake, and continues after the degree of polymerisation has become constant. (MAJOR, 1958). A clear understanding of the mechanism of autoxidation of cellulose has been hampered however, by the complexity in the variety of basic repeating molecular units and the variety of forms in which cellulose occurs, which govern the degree of crystallinity and the moisture content of the material. (TRYON & WALL, 1961) Previous research is reflected across the wide range of cellulosic materials, in paper, cotton textiles and rayon fabric, a regenerated cellulose. This study will investigate the role of the crystalline /amorphous ratio in the relationship between storage environment, moisture content and the cellulose structure

of the paper substrate in 2.6.1 below.

2.3.2 THE ROLE OF ATMOSPHERIC OXIDATION IN PAPER AGEING

The study of the yellowing of aged paper conducted by the paper industry made important contributions to the development of a wider theory of cellulosic discolouration, much of which went unreported in the conservation literature. In 1938, Strachan explored the chemistry of browning in the solubility of cellulose in water, in which he proposed that the dispersion of cellulose in water probably accounted for some chemical breakdown in the cellulose molecule. Ironically, microbiological attack was considered, but was discarded on the basis of microscopic and other evidence. The exact nature of the reaction was undetermined. (STRACHAN, 1938) Simultaneously, Tongren published findings of a linear relationship of the influence of increasing RH of the ageing atmosphere on the rate of discolouration, accompanied by an increase in copper number. (TONGREN, 1938) The oldest known method of carbonyl group determination is the value of reduced copper in a defined amount of cellulose.² The linear relationship between the copper number and carboxyl content and the reversion rate of pulp was confirmed by Giertz, who further identified the lower colour stability of short fibres, or fines, of bleached sulphite pulp. (GIERTZ, 1945) The carbonyl function of carboxylic groups was adopted in this study as an indicator of the degree of oxidation of cellulose measured in response to environmental conditions in an experimental test environment, presented in 2.5.3 and 4.4.2 and 5.3.1

²Norm TAPPI T 215 m-50: Copper number of pulp. (KRAUSE, 1991)

below.

The work of Bone and Bogarty reported in 2.3.3 below, confirmed the deterioration at the brown line resulting from evaporation of water at the cellulose-water-air interface, the brown colour being formed by water-soluble substances. (BOGARTY, CAMPBELL, & APPEL, 1952b; BONE, 1934) The relationship between the paper substrate, the humid environment and the formation of oxidative degradation products was thus separately established in the phenomenon of discolouration.

The effect of salts of the metals, iron, copper and manganese on the colour stability of pulp and paper was investigated independently by Rollinson and Mesrobian, and found to accelerate the reversion rate. (MESROBIAN & TOBOLSKY, 1961; ROLLINSON, 1955)] Metal-induced reversion appeared to be greatly affected by conditions of temperature and moisture during the ageing process. (CZEPIEL, 1960) The effect of environmental conditions in metal-catalysed reactions is thus also substantiated, supporting the multiple and interdependent causation theory of cellulosic discolouration.

Sims and Hoffman point to film formation in transition from a liquid to solid state by three methods: by evaporation of the solvent, nonoxidative polymerisation and oxidative polymerisation. (SIMS & HOFFMAN, 1961) These mechanisms of drying find ready application in paper manufacture, and to a lesser extent, in conservation treatment procedures. Their implications of oxygen concentration on the mode of oxidation and radical

termination have been extended here to include the response of the moisture content of paper artefacts in archival storage under predominantly humid climatic conditions with seasonal excursion to low humidity.

The relative importance of oxidation by atmospheric oxygen in the ageing chemistry of paper was examined by Arney and others, in a series of studies in the late seventies and early eighties. Their primary investigation lay in the development of an experimental technique, based on the measurement of deterioration as a function of oxygen concentration. A quantitative evaluation of the ratio of atmospheric oxidation to the total rate of deterioration suggested the importance of the role of an oxidative mechanism of deterioration, possibly surpassing that of acid-catalysed hydrolysis, in the ageing process. (ARNEY & JACOBS, 1978)

A subsequent study of the influence of atmospheric oxygen on the rate of yellowing showed the rate of yellowing and strength loss to vary linearly with oxygen concentration, but did not go to zero in the absence of oxygen. The data indicated a competition between atmospheric oxidation and a undetermined process independent of oxygen, both contributing to the deterioration of paper. The rate of deterioration in both cases was accelerated by moisture, while the predominance of the competing processes depended on the fibre type, the humidity and the physical properties being measured. The data also reflected a surprising deviation from the norm of a retarded rate of atmospheric oxidation under a lowered humidity; the oxygen-independent process was accelerated in rag paper, but not in newsprint, by a *decrease* in humidity. (ARNEY & JACOBS, 1979)

These findings established a mechanism of atmospheric oxidation, relating a general discolouration, in the rate of yellowing, and the moisture content of the atmosphere. The oxygen-independent process was of particular interest in this study for the following reasons:

- 1 the accelerated reaction in response to a higher rate of evaporation resulting from a decrease in humidity;
- 2 the formation and decomposition of hydrogen peroxides in the brown line at the wet/dry interface as the oxygen independent process;
- 3 the possible effect of lignin in retarding the rate of oxidative degradation.

The subsequent study by Arney and others, on the relative importance of the oxygen-independent and oxygen-dependent processes of atmospheric oxidation, assessed the influence of the acidity in rag and newsprint papers. Measurement of the kinetic rate of change of properties of diffuse reflectance and tensile strength indicated the temperature dependence of the relative importance of the two processes and the pH dependence of the absolute rates of both processes, but was unable to prove a pH dependence of the relative importance of the oxygen-dependent and oxygen-independent processes of oxidation. (ARNEY & NOVAK, 1982) The final investigation of the predominance of the competing processes (according to the dependence on fibre type, humidity and physical properties) chose to evaluate the role of acid content. The present study aimed to investigate the relationship between humidity and fibre type in the role of the crystalline / amorphous ratio in the oxidative reaction in 3.3.2 below. The implications

of deacidification for effective treatment of paper deteriorated by atmospheric oxidation will be discussed further in Chapter 6.

A valuable contribution to the study of cellulosic discolouration associated with the ageing phenomena of paper was made by Kleinert and Marraccini. In a three part study on ageing and colour reversion of bleached pulps, they reported the formation of measurable amounts of hydrogen peroxide during the natural ageing of commercial paper pulps. (KLEINERT & MARRACCINI, 1963; KLEINERT & MARRACCINI, 1966; MARRACCINI & KLEINERT, 1962) They established, by means of air ageing at elevated temperatures, the concurrent formation and consumption of peroxide at a constant rate, the drop of the copper-number related to the peroxide increase indicating the oxidation of some of the aldehyde groups. The analytical techniques employed in this study to determine peroxide formation have sought to replicate those findings under simulated storage conditions, given that the presence of peroxide measured at any time would represent only a fraction of the total amount produced during the ageing process. The role of the fibre content was established in the relationship of the peroxide formation rate to the fibre length. A higher degree of oxidation found in low molecular pulp portions and in pulp fines, found to contain higher amounts of peroxide than did pure cellulose. Short fibre fractions and fines containing higher amounts of peroxide are thus sensitive to yellowing, but are commonly associated with woodpulp and the discolouration resulting from lignin content. The authors point out that with decreasing particle size the total surface of particles increases, as indicated by peroxide formation. The significant inference was made that atmospheric oxidation may be related

to surface reactions. The suggested mechanism of peroxide formation is attributed to peroxidation at reducing end groups, and in the process of the autoxidative reaction, the pulp materials degraded, and coloured substances were formed. (MARRACCINI & KLEINERT, 1962) Elsewhere, the role of lignin was found to induce cellulose oxidation in alkaline solutions, probably due to hydrogen peroxide liberated during the lignin oxidation. (ERICSSON, LINDGREN, & THEANDER, 1971)

On further investigation of the influence of moisture on the yellowing of pulp, Kleinert and Marracini concluded from moist accelerated ageing experiments, that the peroxide content of the pulp increased during moist ageing to values greater than those observed in dry ageing, while brightness, viscosity and copper-number dropped to lower levels, indicative of increased oxidative deterioration under humid conditions. Peroxide formation was found to be independent of the rate of autoxidation, following one mechanism in the presence of air and various others in the absence of air. This factor was not considered by Arnet *et al* in the differentiation between oxygen dependent and oxygen independent oxidation processes in the ageing of paper. Kleinert and Marracini were further able to confirm the increased peroxide formation in the brown zone of tideline staining. (KLEINERT & MARRACCINI, 1963) Finally, in extracting the coloured material from ageing pulps, ultraviolet and infrared spectra confirmed the presence of carbon to carbon double-bonds in the complex mixture obtained, containing peroxide groups as well as unsaturated chromophores, probably of an enediol ring type, involving intramolecular rearrangement. (KLEINERT & MARRACCINI, 1966) The formation of coloured materials

during the oxidative ageing process, established in this study, was subsequently and repeatedly confirmed by others, and will be further investigated in 2.3.3 below.

The first reference to a likely parallel phenomenon applicable to archival conservation was made in a series of studies by McCamy and Pope on the formation of redox blemishes on rolled microfilm during storage. They determined an oxidation-reduction reaction caused by peroxides and other gaseous degradation products emitted by the paper enclosures in which the film is stored. This highlights three points of interest:

- 1 Peroxide formation within the paper storage enclosure is positively linked to blemish formation in the film. The relationship between blemish formation on film and that on paper is pertinent, since blemish on film was noted at areas of dense emulsion, or where the substrate accumulated maximum moisture.
- 2 The absence of blemish formation at 50%RH and its abundance at 75%RH indicates the role of environmental conditions in this mechanism. Generally ascribed to an increased absorption of gaseous pollutants under fluctuating environmental conditions, a direct response to the moisture sorption and desorption kinetic resulting from that fluctuation is indicated.
- 3 Both staining techniques and microscopic examination reveal no evidence of microbiological attack in the causation of blemishes.

(McCAMY & POPE, 1965; McCAMY & POPE, 1970; POPE, 1968)

An early reference to the general role of oxidation in the preservation of library and archival materials are made in a comprehensive overview by Wessels, in which attention is drawn to the importance of water vapour both as a chemical and as a physical agent of deterioration. (WESSEL, 1970; WESSEL, 1972) Feller's consistent treatment of thermal and photochemical discolouration of organic materials were however, concerned with a recognition of the wider oxidative effect in the problem of brittle books, rather than the role of atmospheric oxidation mechanisms outlined in organic chemistry in the cellulosic discolouration, in the form of spotting or blemishes, specifically associated with foxing. (FELLER, 1994a; FELLER, 1973; FELLER, 1977; FELLER, 1987; FELLER, 1994b; FELLER, et al., 1985; LEE, BOGAARD, & FELLER, 1989; LEE & FELLER, 1986)

The contribution of the body of work presented by Feller lies rather in developing an understanding of the inevitability of the oxidative deterioration process, despite the slow and often imperceptible deterioration taking place during the long induction period. The study of the processes of deterioration were focussed in a study of the chemical reactions taking place as a function of time, while attempts to develop simple kinetic laws on the basis of changes in physical properties, as previously developed for the study of acid-catalysed hydrolysis, were reported to be inadequate for oxidative deterioration, often the net result of a multiplicity of chemical reactions. (FELLER, 1977) Feller pointed rather to the need to study the rates, concentrations and the order of reactions; the effect of moisture in oxidative

degradation, reactions proportional to the concentration of water, the regulation of relative humidity during experiments and the influence of temperature and humidity on oxidative reactions. (FELLER, 1994b)

These factors are considered in the experimental design of this study, outlined in Chapter Four.

The impact of the investigations in organic chemistry and those at the molecular level underway in the pulp and paper industry by Arney, Maraccini, Kleinert and others became evident in conservation science with the publication by Williams on the role of metallic catalysts in the oxidative degradation of paper. Williams pointed out the lack of predictive value of dry oven ageing for oxidative degradation, and the correlating effect on the rate of such deterioration under humid conditions, accelerated by the presence of transition metal catalysts such as iron, cobalt and copper as they enhance the decomposition of peroxides formed during free-radical oxidation. (WILLIAMS, FOWLER, LYON, & MERRILL, 1977) This work brought together the oxidative degradation of paper and the metal-induced theory of foxing.

The use of chemiluminescence was introduced in the study of paper permanence, using a single photon counting method to measure the feeble light emission which takes place in oxidation, as a non-destructive test to measure the rate of autoxidation in paper artifacts. The weak chemiluminescence produced when peroxide radicals mutually combine was recorded in the cycling effect of moist and dry air in paper. (KELLY,

WILLIAMS, MENDENHALL & OGLE, 1979) The autoxidation of paper under test conditions was thus experimentally measured. (See Figure 2.1)

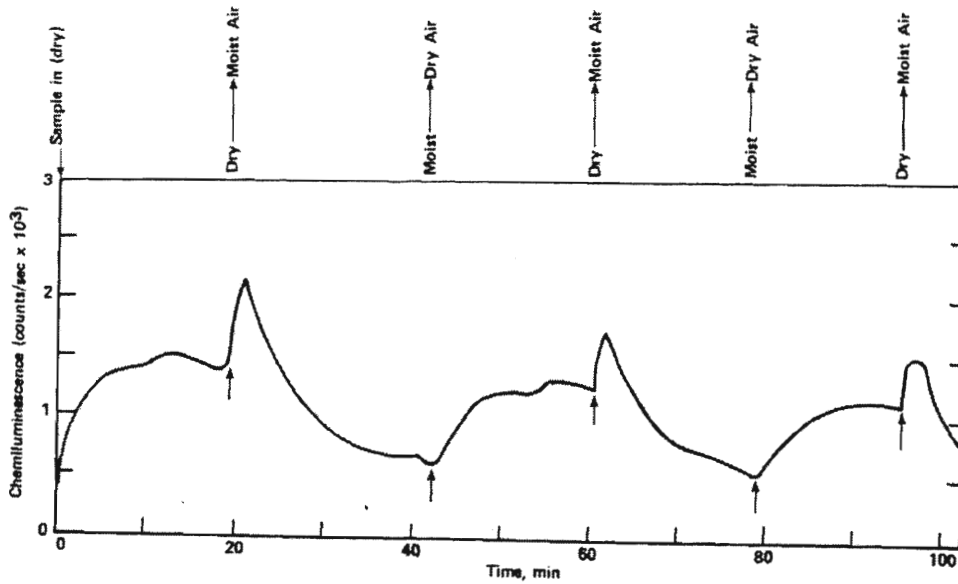


Figure 2. Effects of cycling moist and dry air on chemiluminescence from paper (Sample F, $70 \pm 0.4^\circ\text{C}$)

Figure 2.1 Effects of cycling moist and dry air on chemiluminescence from paper (KELLY, 1979)

Grattan added impetus to this concept in 1978 with a definitive article on the oxidative degradation of organic materials and its importance in the deterioration of artifacts. (GRATTAN, 1978) The phenomenon of oxidative deterioration, acknowledged as little understood or studied in the conservation profession despite its general occurrence, was rated equally important a cause of deterioration as biodeterioration for organic material.

The seriousness of the problem was emphasised in the dearth of preventive measures against oxidative mechanisms to which organic materials might be subject - even at room temperature. The alarming scope of the problem, previously unrecognised, was highlighted in this study, in the need for a better understanding of the possible forms which oxidative degradation might take in the library and archival context.

Despite the importance of this knowledge, the study of the degradation chemistry of paper ageing, including those presented above, has produced little direct evidence of the dominant scission route, either hydrolytic or oxidative, with resulting uncertainty over possible degradation paths. The implementation in libraries and archives of effective preservation strategies and of appropriate conservation treatment decisions demands however the reasonable inference of the feasible causation of degradation. Whitmore and Bogaard outlined the problems in the quantitative characterisation of cellulose that must be overcome if the degradation route is to be established. (WHITMORE & BOGAARD, 1994) ³ Such chemical

3

Whitmore and Bogaard recommend the identification of the degradation route in the determination of the extent of degradation measured primarily in the number of chain scissions, determined by molar mass measurements; and the monitoring of functional group changes during the degradation process. However, most functional group analyses have been incapable of a quantitative, selective assay for mildly degraded cellulose.

investigation was not the aim of the present study, and is rather a wider consideration of conservation science. (BLAZEJ & KOSÍK, 1985; LINDSTROM, 1990; NEVELL, 1959; NEVELL, 1985; WILLIAMS, et al., 1977)

The general study of autoxidation and the effect thereof on paper preservation and conservation has been developed by various conservators and conservation scientists in recent years. A paper was presented by Daniels of the British Museum, introducing to paper conservation the non-destructive technique of monitoring the deterioration of materials in the negative image formed by the interaction of silver halides of photographic film with an oxygen - containing species, tentatively identified as hydrogen peroxide. The Russell effect was developed by Daniels to follow the rate of deterioration of materials, to test storage materials for photographs and to detect local treatments in artworks. (DANIELS, 1984a; DANIELS, 1984b; DANIELS, 1986)

Confirmation of the role of light and water on the degradation of paper was again provided in the evidence of Russell effect photography. In determining the substances which gave a strong Russell image, a correlation was established between the formation of redox blemishes on microfilm, and the incidence of cellulosic discolouration in paper. (McCAMY & POPE, 1965; McCAMY & POPE, 1970; POPE, 1968)

Cellulose degradation was subsequently measured by Eusman, Conservator at the National Gallery in Washington, DC, in the tideline region of local

wetting, using the Russell effect. His findings were supported by reagent analysis in the increased methylene blue absorption and formation of water soluble fluorescent and coloured compounds in the tideline region. In repeated wetting, Russell effect photography proved the formation of new peroxides at every boundary thus formed, indicating the potential cumulative damage of fluctuating environmental conditions. (EUSMAN, 1994a; EUSMAN, 1994b; EUSMAN, 1995)

2.3.3 THE FORMATION OF A BROWN LINE AT THE WET/DRY INTERFACE

This study is aimed at the investigation of the role of the brown line phenomenon in the formation of diffuse circular areas of cellulosic discolouration within the pages of a volume, commonly known as foxing. The studies into the formation of foxing, reviewed below, have relied upon the identification of degradation products to relate causation to biological growth or to metal catalysis. It is therefore expedient to trace the development of our understanding of the reaction mechanism and resultant identification of oxidation products in the study of the brown line at the wet/dry interface.

Early investigations in the application of dyes to textile fabrics form the basis of the supporting evidence that the staining phenomenon at the wet/dry interface is resultant upon the amount of water evaporated through the fabric, with the exposed part of the bundle tending to adjust continually to equilibrium with the atmosphere. Claims to have proven the formation of

hydrogen peroxide by the evaporation of water were first made in an investigation into the effects of water on reactions in the gas phase, as reported by Dixon in the *Journal of the Chemical Society* in 1886, and form the basis of the first published observation of the development of a brown line at the wet/dry interface by Bone in 1934. (BONE, 1934; DIXON, 1886) Bone claimed that the evaporation of water was capable of creating tidelines in highly purified cotton cloth, noting the presence of cellulose modification not visible in daylight or under ultraviolet (UV) light, by which oxycellulose is formed in a manner similar to the formation of hydrogen peroxide. This early study noted that the change in the cotton was dependent primarily on the amount of water evaporated through the sample rather than on temperature, suggesting the role of the equilibrium moisture content as a parameter of paper permanence. A continued investigation on modification of cellulose at the brown tideline on both bleached and unbleached samples established that the formation thereof was unaltered when the sample was pre-washed to remove soluble compounds, indicating that the brown line appeared to be formed by the evaporative process rather than by the chromatographic migration of impurities which might be concentrated at the boundary.(BONE & TURNER, 1950)

Of particular interest to this study are two findings of Bogarty *et al* :

- 1 that the brown line formed by capillary action is comparable to the effect of repeated wetting and drying in terms of the constant production of fluorescent material at the brown line, which;

2 seems to be independent of biological activity, being formed on fabric pre-treated with antiseptic agents, such as thymol. However, subsequent inoculation with the fungal organism, *Aspergillus niger*, resulted in rapid growth along the brown line which spread to the other areas of the fabric only after 4-5 days. (BOGARTY, et al., 1952b)

The apparent predisposition of oxidised paper to subsequent biodeterioration possibly clarifies the general acceptance of visible degradation in the form of cellulosic discolouration as a biological effect of humid conditions. This factor may also account for the correlation of two separate reactions in the subsequent spotted discolouration in areas which constitute a wet/dry interface.

The early investigations conducted in the textile industry set out to create tidelines for experimental purposes by dipping samples of cloth into water and examining the extract of the brown product formed at the wet/dry interface. Bone *et al* found that in addition to water soluble coloured products, insoluble products containing carboxylic groups are formed. (BONE & TURNER, 1950) Bogarty *et al* determined that oxidation takes place at the primary hydroxyl groups with the formation of polyglucuronic acid and that chain scission occurs resulting in the formation of water soluble fractions of low molar mass. From the extract they were further able to detect the presence of glucuronic acid, formaldehyde and formic acid. (BOGARTY, et al., 1952b) The presence of these compounds can be

anticipated in materials that have undergone the oxidative mechanism described.

The experiments were extended to an investigation of the role of oxygen in the formation of the brown line. The inhibition of the formation of the brown line *in vacuo*, despite evidence of the continued oxidation of the cellulose would suggest that minute amounts of free oxygen from the water-cellulose system itself provides enough oxygen to effect the browning reaction. (MADARAS & TURNER, 1953) Replacing water with organic solvents revealed an absence of acidic groups at the former brown line location after the sample had been washed in the solvent in which it had been originated, while the cellulose appeared to be unchanged. It is suggested that the solvent itself is oxidised at the wet/dry boundary, and not the cellulose substrate in this case. (SCHAFFER, APPEL, & FORZIATI, 1955) Later evidence of dehydrogenation would dispute that finding, but both these studies unequivocally point to water - oxygen - cellulose relationship in the reaction mechanism, as described by Arney *et al*, who showed the rate of yellowing and strength loss to vary linearly with oxygen concentration, but which did not go to zero in the absence of oxygen. (ARNEY & JACOBS, 1979)

The chemistry of the browning reaction was treated comprehensively in a seminal paper by Hodge, in which the phenomenon of browning in food dehydration was examined. Browning is explained as the result of the formation of unsaturated compounds with the presence of conjugated double bonds occurring in chemical systems containing carbonyl groups as the

reducing sugars, which are further transformed into unsaturated coloured compounds. Food technology recognises three types of browning reactions, the most common being carbonyl-amino reactions, including the reaction of aldehydes, amino acids and the reducing sugars identified in degraded paper with amines, amino acids, peptides and the proteins of gelatine sized papers. Sugar-amine condensation in the nearly-dry state accounts for the accelerated production of brown pigment, indicating the critical role of water content in the browning reaction. Termed the Maillard reaction, the sugar-amine reaction is thought to give rise to the distinctive “Maggi”⁴ odour of aged paper. (ANGRICK & REWICKI, 1980; HODGE, 1953)

Measurement by Hodge of the browning of thoroughly dehydrated food was found to increase and pass through a maximum as the water content increases. The need to plot browning against moisture content in a simulated ageing process was therefore a primary aim of the present study. Claiming that dehydration and fission go hand in hand, Hodge further established the independence of sugar-amine browning from atmospheric oxidation, the relative importance of each he felt might vary with controlling conditions. Later confirmation was again forthcoming provided by Arney *et al* in distinguishing of an oxygen-independent process, the relative importance of which was found to alternate with the oxygen-dependent process as a function of temperature. (ARNEY & NOVAK, 1982)

The browning reaction has also been studied in the effect frequently seen in paper chromatography. The early investigation by Strachan determined

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Food flavour enhancer. (BANIK, 1998)

a slight solubility of pure cellulose in water from the constant mass of residue from repeated extracts. In attributing this dispersion to a probable breakdown in the cellulose molecule, the feasibility of microbiological attack was considered, but discarded on the basis of a lack of microscopic evidence. (STRACHAN, 1938) The lack of microscopic evidence of biological activity noted similarly by this researcher gave rise to the present study, in an investigation of possible alternative causes of discolouration. Intensive investigation by Huffman *et al* distinguished small amounts of water-soluble carbohydrates, particularly when slow air drying of chromatography samples was used, apparently related to the deterioration of cellulose caused by alternate wetting and drying and by the action of ozone at high moisture levels. The constant amount of discoloured material extracted by Huffman suggests that degradation products are formed every time that paper dries. (HUFFMAN, REBERS, SPRIESTERSBACH, & SMITH, 1955) The subsequent conclusion of Ambler and Finney sums up the contemporary understanding, that the effect seen in paper chromatography was probably a combination of a then unexplained oxidative reaction and the capillary concentration of degradation products in relation to the age of the paper. (AMBLER & FINNEY, 1957) The relevance of these findings to the archival storage of paper artefacts points to the hazard of a fluctuating environmental control, and yet again to the role of a high equilibrium moisture content (EMC) in the wet/dry oxidative reaction. The rate of drying is a factor of interest, in the unstable moisture content of hygroscopic paper-based materials. Fluctuations of EMC can be expected in the seasonal drift from high summer levels of humidity, ranging from a recorded high of 92%RH to a recorded low of 41%RH, a difference of 51%RH within a limited

time span of four months between March and July within the ambient annual cycle. (Climate..., 1986)

A resurgent interest of the textile industry in the phenomenon at the wet/dry interface arose from the problem of browning observed in the drying of dyed textiles, as noted by Fox when ambient temperatures were high, and was thought to be seasonal. (FOX, 1965b) These observations are apparently contradictory to the recommendation for wider environmental control to allow for seasonal drift, advocated by recent environmental research carried out at the Conservation Analytical Laboratory of the Smithsonian Institute, described in 2.2 above. Seasonal drift may accommodate less drastic physical changes of dimension but it would seem that the psychrometric relationship of temperature to humidity and the resultant effect on the EMC acts as a catalyst of oxidative degradation at the wet/dry boundary in the repeated wetting and drying of paper-based collections. Fox further advanced the theory of the brown line phenomenon by successfully conducting the tideline experiment in sunlight, daylight, artificial light and in total darkness, thereby dismissing photochemical reactions as a major contributor to the tideline formation at the wet/dry interface.

The relevance of the two studies by Fox lies specifically in the identification of the reaction as confined to points of maximum evaporation, and in indicating the complexity of the problem arising from the natural sorption and desorption property of the fibres. The aqueous extract of the brown line region was shown to be acidic, and while the presence of glucuronic acid was not confirmed by infrared spectra, absorption bands of an inorganic salt

of carboxylic acid and bands due to long chain aliphatic compounds and probably aliphatic ether groups were identified. Both secondary and primary hydroxyl groups seemed to take part in the browning reaction. (FOX, 1965a; FOX, 1965b)

Sporadic investigation of the problem of foxing in paper gathered momentum in the mid 1970's and the 1980's, with opposing views on the causation of the small circular reddish-brown stains. The subject is of relevance in the identification of various forms of foxing and their classification, by methods comparable with those employed in the study of brown line formation and will be examined in depth in 2.4 below. The first description of published research into the phenomenon of water stained cellulose, and which suggests a new line of enquiry into whether certain types of staining, known as foxing, are related to the brown line reaction, was presented in a literature review by Hutchins in 1983. (HUTCHINS, 1983) In questioning the effect of fluctuating moisture content on the cellulose substrate, and the possibility of slow drying page edges acting as an oxidative interface under humid conditions, the review introduced the concept, developed in this study, that mould might be a result of discolouration rather than a cause.

The Russell effect technique was developed by Daniels and applied to the study of the discolouration of paper on ageing, as described in 2.3.2 above. A comprehensive investigation resulted in a classification of stains and the mechanisms of their formation - by foxing; tidemark stains; the migration of acids; image transfer of ink inscriptions; the discolouration caused by light and metal induced discolouration, as well as the degradation of deposited

volatile materials. (DANIELS, 1986) The mechanism of browning at the wet/dry interface was investigated in the form of the tidemark stains resulting from localised wetting, either accidental or in localised conservation treatment. The application of Russell effect photography is positively linked to the identification of the formation of hydrogen peroxide. The investigation of discolouration is pursued in later research, pointing to the role of inorganic compounds in metal-induced foxing and the photochemical oxidation of zinc oxide pigments, whereby atmospheric oxygen and water vapour combine in the presence of zinc oxide to form hydrogen peroxide, eventually causing discolouration. Related research examined above had indicated that the combination of oxygen and water vapour alone lead to the formation of hydrogen peroxide at the region of evaporation at the brown line. (DANIELS, 1990; DANIELS & MEEKS, 1992)

A need for a comprehensive definition of cellulosic discolouration was expressed by the Dutch researchers, Ligterink, Porck and Smit, in their study of the staining of paper surrounding printing ink. (LIGTERINK, PORCK, & SMIT, 1991) Discolouration was described as a three dimensional spatial process within and between adjacent pages of a book, with spotted stains developing at sites of temporary moisture accumulation, caused by local condensation processes related to the wet/dry interface. Personal communication supported the speculated relationship between the phenomenon at the wet/dry interface and the empirical evidence of discolouration noted under the humid ambient conditions of southeast Africa. (PORCK, 1992) This publication is acknowledged as a major impetus for the present study to develop an understanding of the mechanism of

discolouration of paper artefacts under humid environmental conditions that is not adequately explained by the current definition of foxing. It also formed the basis of further important research at the Centraal Laboratorium voor Onderzoek van Voorwerpen van Kunst en Wetenschap in Amsterdam.

Application of the theory of textile tendering to archival storage was pursued in a study to determine the relationship between the storage microclimate and the deterioration mechanism at the wet/dry interface due to the evaporation of water. In libraries, archives and museums, documents and works of art are frequently stored in protective enclosures, including framed and unframed mounts, boxes and display cases. The Municipal Archives of Amsterdam commissioned the Centraal Laboratorium to investigate the cause of browning of mounted paper artefacts stored vertically in boxes. The limited volume of air within a microclimate, it was found, is unable to respond in the expected manner and the reverse phenomenon of fluctuations in relative humidity following the rise and fall of temperature was experimentally measured. The degree of browning observed at the surface within the window opening of the mounted works was found to increase with the frequency of these humidity fluctuations, and was influenced by the porosity of the mounting board. (HOFENK DE GRAAFF, 1994; HOFENK DE GRAAFF, VAN BOMMEL, & PORCK, 1993) It is presumed therefore that the mechanism of oxidative degradation experienced in the ambient humid macro climate is analogous with that identified at the paper surface in the microclimate of mounts stored in protective enclosures. The effect of microclimate storage options will be considered, as a potential factor in the oxidative deterioration of library and archival materials. (see 6.3 below)

Further investigation into the formation of a brown line at the wet/dry interface was undertaken by Eusman, in response to the concern of paper conservators over possible side effects in the tideline staining surrounding localised wet treatment. The resulting production of discolouration at the wet/dry boundary, commonly believed to be evidence of migration of water-soluble compounds was shown to be accompanied by a stationary oxidative degradation process taking place in the same region, the high concentration of peroxides at the tideline indicating an oxidative reaction in organic materials. (EUSMAN, 1995)

The degradation of cellulose at the wet/dry interface formed the subject of a recent study by Dupont of the effect of some conservation treatments on the brown lines encountered by textile and paper conservators. This study was subsequently supported by the identification of oxidation compounds formed at the interface. (DUPONT, 1996a; DUPONT, 1996b) The first part of the study sought to induce the phenomenon, in much the same manner as conducted previously by Hofenk de Graff and Eusman, and thereby contributes to the reproducible standard methodology also employed in this study. Qualitative visual methods of detection of the resultant degradation were used in an assessment of the effect of artificial ageing and the effect of the conservation treatments of washing and bleaching with the reducing agent, sodium borohydride. The results showed that any process resulting in an uneven moisture content of the artefact may be a potential source of oxidative degradation:

“a very particular micro environment... at the wet/dry interface might be necessary for oxidation to occur at this location.”
(DUPONT, 1996b p.1)

The second part of the study comprised a chemical analysis of the degradation compounds formed at the wet/dry interface, using the analytical techniques of thin layer chromatography (TLC), Fourier transform infrared spectroscopy (FTIR) and gas chromatography coupled with mass spectrometry (GC/MS). The various compounds identified by the different techniques speak more for the limitations of these analytical techniques than for the causation of the phenomenon observed. This study constitutes a considerable advance in the affirmation of the chemical mechanism, a matter of conjecture in much of the earlier literature. (DUPONT, 1996a) The relevance of this study will be elaborated upon in 2.5 below in relation to the methodologies employed in previous research.

2.4 APPLICATION OF THE RESEARCH TO HUMID CLIMATIC CONDITIONS

The investigation of the role of oxidation in paper ageing, presented in 2.3.2 above has revealed that light, heat and moisture are known to affect the reaction between oxygen and organic compounds, but the seemingly different results are difficult to evaluate because several of those factors may operate simultaneously. (SWERN, 1961). A description of the manifestation of oxidative damage in the climatic conditions of southeast Africa was presented in 1.3 above, based on the experiential evidence amassed by the researcher as a professional paper conservator in the direct observation of the nature of paper deterioration under humid conditions.

The absorption of excessive water vapour under humid conditions provides an interface on the fibrous paper substrate with intimate contact between air and liquid with a large surface area for autoxidative reaction. (TRYON & WALL, 1961) The fluctuating moisture content of paper stored under excessively humid climatic conditions, and exposed to seasonal variations is thought to approach a phase transition parallel to the formation of a brown line at the wet/dry interface, presented in 2.3.3 above. It is therefore this researcher's belief that the overwhelming factor in the causation of discolouration evident in a humid climate is resultant upon the evaporation kinetics in moisture sorption and desorption under fluctuating temperature and relative humidity. The effect of increased chemical reactivity under humid climatic conditions, beyond the empirical evidence afforded under temperate conditions, has been overlooked in previous research. The significance of an autoxidative phenomenon, similar to that of oxidation at the wet/dry interface, has therefore not previously been recognised as a function of an unstable moisture content of materials, generated by excessive levels of RH in a humid climate. The phenomenon of oxidation at the wet/dry interface has been identified rather, in relation to various aspects of conservation, including the detection watermarks, and of potentially harmful materials for application in archival storage (DANIELS, 1984a; DANIELS, 1984b), and the effect of localised wet treatment. (EUSMAN, 1994b; EUSMAN, 1995) Furthermore, the mechanism of the resultant increased chemical reactivity has been obscured by the accepted explanation of biological deterioration in a humid climate. The application of the phenomenon of oxidation at the wet/dry interface to the cellulosic discolouration evidenced under humid climatic conditions is an original

contribution to the field, in the development of a theory of the deterioration of paper.

The direction of study is supported by a literature review of the causation of cellulosic discolouration in the form of foxing, which has revealed an area of persistent uncertainty regarding the formation mechanisms, despite ongoing research and analysis. It was therefore necessary to review the previous research in the areas of both cellulosic discolouration and the specific formation mechanisms of foxing, to determine a possible relationship between what is proposed by the researcher as two separate, but interrelated phenomena.

2.4.1 CAUSATIVE FACTORS IN EVIDENCE OF FOXING

“Foxing of paper is indicated by brown colour, the sensation of moisture, loosened texture, and weakness of structure.”
(BECKWITH, SWANSON, & IIAMS, 1940 p.332)

The same definition is equally applicable to the evidence of oxidation of paper. The study of foxing, based on the definition above, is relevant to this study in the possible explanation of the localised nature of discolouration. The preferred terminology of cellulosic discolouration is applied to the broader visual, chemical and physical change that occurs as a manifestation of the degradation of paper, including the effects of phenomena described by the traditional understanding of foxing. The literature review of the causative factors of foxing is presented here in support of an alternative mechanism of cellulosic discolouration, in the chemical response of paper to humid climatic conditions. Related areas of research on discolouration

on the ageing of paper pursued in the paper industry were presented in 2.3.2.

The mechanisms of the formation of foxing have been widely reported and classified according to the analytical evidence of areas of discolouration. The debate on the causation of foxing has advanced two principle theories of causation, biological infestation, (ARAI, MATSUMURA, & MURAKITA, 1990; ARAI, 1984; BECKWITH, et al., 1940; BURGE, BOISE, SOLOMON, & BANDERA, 1980; CRAIG, 1986; FLORIAN, 1994; PANTKE & KERNER-GANG, 1988; PRESS, 1976; SZCZEPANOWSKA, 1986; SZCZEPANOWSKA & LOVETT, 1992) and metal-induced catalysis resulting from paper impurities. (DANIELS, 1988; HEY, PASQUARIELLO, GALLO, GUIDI, & PIERDOMINICI, 1988; TANG & TROYER, 1981; TANG, 1978) Both theories are well supported by analytical procedures presented in 2.5.1 below. Notable is a further category of discolouration identified by conservators as being related to the tidemark staining caused by uneven evaporation noted during localised treatment procedures. (DEROW & DWAN, 1992; DUPONT, 1996b; EUSMAN, 1994b) A wider description of these mechanisms is warranted under the collective terminology of cellulosic discolouration.

The literature reflects a lack of conclusive evidence for a single causative factor, suggesting the possibility of variable causation, resulting in a classification of the visual evidence of foxing in microfilm, paper and textiles. (CAIN & MILLER, 1982a; CAIN & MILLER, 1982b; CARTER, 1984; McCAMY & POPE, 1965) Blemishes are described as “atolls”, “bullseyes”,

“hoshi”, “stars”, “snowflakes”, “stains”, “offprints” and “shadows”. The variety of terms applied to the phenomenon of foxing is indicative of the imprecise current understanding of the mechanism or the interrelationship of mechanisms resulting in cellulosic discolouration.

An early discussion of foxing in the preservation of rare books and manuscripts, published in 1932, raises the question of “ideal” atmospheric conditions in the prevention of foxing. A consequent study of fungal inoculation of spots points to the phenomenon of continued staining when atmospheric conditions and moisture content of the paper are no longer encouraging to mould growth. (IIAMS, 1932; IIAMS & BECKWITH, 1935) Significant is the evidence of fungal growth once the moisture in the paper has dried out, indicating an intermediate reaction in the drying process. A high humidity, resulting in a damp substrate appears to be insufficient to justify the causation of foxing in a proliferation of fungal growth. The theory was later advanced by the authors in the evaluation of the presence of iron in paper, which concluded that the iron content was identical in foxed and unfoxed areas. An unchanged chemical state was confirmed by reagent staining, indicating rather an oxidation of the ferric iron present. The interaction of trace metals with the environment is evident in an oxidative reaction.

An interesting parallel was noted in paper which had been exposed to moisture and subsequently become brown. The positive presence of non-viable fungi was found to be accompanied by aggregates of brown coloured material of undetermined nature scattered throughout the foxed area, or of

a uniform brown discolouration, with evidence of the brown particulate aggregates, believed to be degradation products. (BECKWITH, et al., 1940) The combination of a wet/dry interface at the surface of the paper with evidence of non-viable fungi mirrors the evidence of paper deterioration experienced by this researcher. Various questions arise from these findings with regard to the unsatisfactory explanation of fungal causation:

- 1 The predominant, or preceding mechanism of discolouration;
- 2 The process of interaction between the two distinct mechanisms;
- 3 The unsustained development of fungal growth as a result of either inappropriate environmental conditions, or of chemical modification of the substrate.

The present study has sought to develop the theory of cellulosic discolouration to increase an understanding of the issues raised. The presence of fungi is undisputed, but the exclusive role of biological factors in the causation of cellulosic discolouration under humid conditions is questioned in this study. The lack of visible manifestation of fungal growth in association with areas of discolouration is reported by various authors and is accepted here as support for a wider theory of multiple causation mechanisms.(BECKWITH, et al., 1940; GALLO, 1963; IIAMS & BECKWITH, 1935; WAGSTAFF, 1977) It is not the aim of this study to evaluate the accepted mechanisms of foxing, but rather to investigate an alternative mechanism of oxidative degradation, resulting in visible evidence of brown discolouration in the chemical modification of the cellulose molecule,

possibly preceding and precipitating both fungal infestation and metal-induced catalysis.

The association of blemishes with a chemical reaction was first made in relation to the preservation storage of microfilm, when the peroxide formation in the ageing degradation of the microfilm storage boxes was found to cause blemishes on the film, the tendency increasing with humidity. (McCAMY & POPE, 1965; McCAMY & POPE, 1970) These findings were based on the research of Marracini and Kleinert, on the ageing and colour reversion of bleached pulps by peroxide formation, continued in the study of the effect of air and moisture, and finally, of high humidity. (KLEINERT & MARRACCINI, 1963; KLEINERT & MARRACCINI, 1966; MARRACCINI & KLEINERT, 1962) Peroxide formation was related to brightness reversion, or discolouration of bleached pulps and to the viscosity drop indicating loss of physical strength during ageing. The body of research is outlined in 2.3.2 above.

The debate in conservation circles continued unabated, limited to the causation of staining by fungal infection versus metal content, as pursued by various authors. (ARAI, 1987b; BAYNES-COPE, 1976; CARTER, 1984; HEY, et al., 1988; MEYNELL, 1978; MEYNELL, 1979; NOL, HENIS, & KENNETH, 1983; PRESS, 1976; TANG & TROYER, 1981) (SZCZEPANOWSKA, 1986) The classification of foxing proposed by Cain and Miller in 1982 and subsequent characterisation of aged papers, using Fourier transform infrared spectroscopy and thin-layer chromatography, was a significant advance of the theory of foxing as caused by various

mechanisms . The identification of little difference in the character of foxed spots and associated paper resulted in a proposal of foxing as the localised manifestation of an ageing process, catalysed by some agent at the foxing site. (CAIN & KALASINSKY, 1983; CAIN & MILLER, 1982b) Even very diffuse types of blemish had often been noted to have a particle of foreign matter at the centre. Some could be identified as metal, others as dust particles. In a marine climate it is suggested by the researcher that such particles might be salt. Even where these do not penetrate the surface, they may act as condensation centres where the effective humidity exceeds that in the ambient air. (McCAMY & POPE, 1970)

The foxing debate was opened to wider enquiry in the work of Hutchins, who introduced the phenomenon of water-stained cellulose and questioned the effect of a fluctuating moisture content on a cellulose substrate of uneven thickness. (HUTCHINS, 1983)

The biochemical formation mechanism of foxing was investigated by the determination of the components of discoloured areas, which were found to be related to the browning reaction known as the Maillard reaction described in 2.3.3 above. (ARAI, MATSUI, & MURAKITA, 1988) Experimentation with environmental conditions to induce the browning reaction revealed the following points of interest:

- 1 Glucose and amino acids reacted together (Maillard reaction) on paper causing browning, and foxing was subsequently formed. This would suggest the concentration of a nutrient source for fungal

growth at the site of browning. The inference is one of two concurrent reactions at the brown line, supported by the evidence of Kleinert of water soluble degradation products containing both peroxide groups and unsaturated chromophores, probably of an enediol ring type, and that intramolecular rearrangement is involved. (KLEINERT & MARRACCINI, 1966)

- 2 The browning reaction was more marked at lower water activity and at higher temperature, suggesting discolouration as a result of drying in the evaporation kinetics of moisture sorption and desorption;
- 3 The amino acids in foxed areas may be supplied by the fungal body of foxing-causing fungi.

The source of amino acids in proteinaceous sizing agents may be an additional variable in the causation of the reaction, and forms a further research project beyond the scope of this study. Relevant to the present study is the association of a chemical browning reaction with environmental conditions, noted in (2), approaching the formation mechanism of a brown line at the wet/dry interface.

The interdependence of formation mechanisms is stressed in an investigation of the enzymatic destruction of cellulose in biodeterioration:

" The dependence of fungal development on the presence of iron in the substrate may link the divergent concepts of the formation of foxing, both as the result of the oxidation of metallic inclusions in the substrate and as the direct result of fungal growth, but further research is needed to establish a direct link" (SZCZEPANOWSKA, 1986 p.38)

The correlating effect on the rate of oxidative degradation under humid conditions, accelerated by the presence of transition metal catalysts such as iron, cobalt and copper as they enhance the decomposition of peroxides formed during free-radical oxidation, has also been described. (WILLIAMS, et al., 1977)

The relationship between the identified causative factors of cellulosic discolouration, in which the oxidative mechanism akin to formation of a brown line at the wet/dry interface precipitates both metal-induced catalysis, and subsequently, also fungal growth, is thus apparent. This relationship is confirmed by Koenigs, in the use of some fungi of an hydrogen peroxide (H_2O_2) and ferrous iron (Fe^{++}) system to attack cellulose in the catalysis to the ferric state (Fe^{+++}). The increased swelling and alkali solubility of residual cellulose also increased the susceptibility of the fibre to the active enzyme of the fungal preparation. (KOENIGS, 1975)

The literature review of the formation mechanisms of foxing has revealed a growing recognition of multiple factors in the causation of cellulosic staining, promoting an understanding of the nature and processes of degradation, which may operate simultaneously and probably sequentially. Research has been directed in this study towards the role of oxidation at the wet/dry interface as found at the surface boundary layer as a unique phenomenon separate from and preceding the biological deterioration traditionally associated with paper deterioration in a humid climate. The phenomenon is thought to precipitate the causation of foxing.

2.5 METHODOLOGIES EMPLOYED IN PREVIOUS RESEARCH

In devising an experimental model to test the research hypothesis, it was necessary to evaluate the analytical techniques applied in the two relevant areas of study, in the investigation of the causation of foxing, and the formation of a brown line at the wet/ dry interface.

A standard reproducible test methodology was developed, with the objective of induced degradation resembling empirical evidence of cellulosic discolouration, and determination of the formation of oxidative degradation products resultant upon the induction process. The importance lay in effectively testing the causation of cellulosic discolouration in the increased chemical reactivity evidenced in the phenomenon of autoxidation at the wet/dry interface at the paper surface under humid conditions.

The oxidative phenomenon is induced in this study in accordance with the developed standard accelerated moist ageing procedure, with an additional dynamic simulated climate ageing programme variation representing ambient climatic conditions to which aged paper is exposed in local library and archival environments. The selection of appropriate analytical techniques in the identification of oxidative degradation products in sample material of known previous history and exposed to this procedure was considered critical to this study.

The experimental design approached the actual storage parameters of environment experienced in a humid climate. The selection of reproducible

experimental techniques in the identification of an oxidative mechanism of degradation served to related the laboratory- controlled experimentation of previous research into the phenomenon at the wet/dry interface with the evidence of deterioration witnessed under conditions of high humidity.

2.5.1 METHODOLOGIES APPLIED TO THE OBSERVATION OF FOXING.

The techniques applied in identification of the formation mechanisms of foxing are relevant to this study for reasons of comparison, in testing the research hypothesis that the evaluation of the nature and degree of staining induced in the experimental design can be measured in the formation of autoxidative degradation products.

The study of the role of biological activity in the causation of foxing has relied on a methodology of fungal inoculation of existent areas of discolouration and the isolation, in culture, of fungi from foxed spots. (ARAI, 1984; BECKWITH, et al., 1940; IIAMS & BECKWITH, 1935) The resultant development of fungal growth has been accepted as proof of causation, but this methodology serves only as proof of the positive presence of fungal spores in areas of cellulosic discolouration. The development of techniques such as X-ray fluorescence analysis and scanning electron microscopy (SEM) enabled a correlation of foxing with iron content embedded in the paper fibres and the microscopic identification of iron and fungal spores on the surface. (BAYNES-COPE, 1976; CAIN & MILLER, 1982a; PRESS, 1976)

The identification of fungal growth in relation to foxing has been limited to visible identification by microscope and ultraviolet (UV) fluorescence screening. UV fluorescence has been consistently employed and has enabled a classification of foxing based on the identification of the presence of fungal activity. (CAIN & MILLER, 1982a; DANIELS & MEEKS, 1992; MEYNELL, 1978; PRESS, 1976)

Analytical sampling of foxed areas has employed methods applicable to this study such as Fourier transform infrared spectroscopy (FTIR) and combinations of spectroscopic with chromatographic techniques. (CAIN & KALASINSKY, 1983; CAIN, 1983; CARDAMONE, 1991)

The determination of metal elements in foxed areas has been successfully achieved by flameless atomic absorption spectroscopy, (TANG & TROYER, 1981; TANG, 1978), and energy dispersive X-ray (EDX) analysis. (ARAI, 1987a; CAIN & MILLER, 1982a) The differentiation between organic and inorganic foxing is achieved in conservation treatment with oxidising bleaches, effective only in the removal of organic foxing. Chlorine was found to be present in ferrous foxing. (DANIELS & MEEKS, 1992)

Reagent testing has been employed in the observation of foxing. Tests for the presence of iron in foxed paper have employed chemical reagents, including potassium thiocyanate and potassium ferrocyanide. (CARTER, 1984) The comparison of foxed and unfoxed areas showed no difference in the quantities of ferric iron present. Ferrous and organically combined iron were found to be absent. (BECKWITH, et al., 1940) This is confirmed by the

findings of Koenigs of ferrous iron catalysed to the ferric state in a hydrogen peroxide system. (KOENIGS, 1975) Positive reaction to phenolic reaction has been presented as a reagent test in support of fungal causation . (NOL, et al., 1983)

2.5.2 COMPARATIVE EXPERIMENTAL TECHNIQUES IN DETERMINING THE OCCURRENCE OF OXIDATIVE DEGRADATION.

The difficulty of monitoring relatively low oxidation rates of materials under simulated ambient environmental conditions in a controlled experimental environment is addressed in this study in applying analytical techniques reported in the investigation of the formation of the brown line at the wet/dry interface. Previous research into the formation of a brown line at the wet/dry interface has been outlined in 2.3 above.

From the earliest investigation of evaporation of water from cellulose, a marked increase in methylene blue reagent absorption has been noted in the boundary region at the wet/dry interface, indicating the chemical modification of the cellulose in the presence of oxycellulose in that region. (BOGARTY, et al., 1952b; BONE, 1934; BONE & TURNER, 1950; DUPONT, 1996b; FOX, 1965b; LIGTERINK, et al., 1991; MADARAS & TURNER, 1953) Methylene blue reagent and Tollens' reagent were reported to be sensitive enough to detect the small amounts of degradation products evolved, (HOFENK DE GRAAFF, 1994) and methylene blue was reported to be an excellent visual tool in disclosing the presence of carboxylic groups in cellulose materials. (EUSMAN, 1995)

The measurement of increased cuprammonium fluidity in determining the viscosity of cellulose as an indicator of a loss in fibre strength was accepted on the basis of early investigations of the evaporation of water brown line . (BOGARTY, et al., 1952b; BONE, 1934; BONE & TURNER, 1950; MADARAS & TURNER, 1953) The physical chemistry inherent in this technique was impractical for use in this study.

Fluorescent material at the wet/dry interface was consistently reported. (BOGARTY, et al., 1952b; BONE & TURNER, 1950; CAIN & MILLER, 1982a; DUPONT, 1996b; EUSMAN, 1995; FOX, 1965a; SCHAFFER, et al., 1955; TRYON & WALL, 1961) The presence of fluorescence is thought to precede the development of browning. (DUPONT, 1996b; HODGE, 1953)

The additional use of fluorescence in the identification of fungal mechanisms of foxing formation is of additional interest value in this project, although Eusman claimed to have found no further connection between tidelines and foxing. (EUSMAN, 1994b)

Chromatographic extraction was also jointly employed in foxing studies and in the investigation of the discoloured material formed each time the paper dries. (AMBLER & FINNEY, 1957; HUFFMAN, et al., 1955) While pertinent to this study, the technique of thin layer chromatography could not be employed in this study because of the danger of confusion between tideline formation in the induced environmental procedure and those reported to be formed in analysis.

The analysis of drying rates determined a definite pattern of lateral order changes in cellulose during ageing. The slope of the log of the drying rate versus the moisture regain curve gave an indication of the intercrystalline fibre structure. This technique was considered imperative to this study in indicating the response of the substrate to conditions of high humidity in the swelling of the ordered regions, permitting water vapour to penetrate into the fibres, facilitating diffusion. (LAUER & CHAO-WU, 1961)

The measurement of the autoxidation of organic materials by the detection of hydrogen peroxide was recommended by a technique using sensitised photographic film, Russell effect photography, presented in 2.3.2 above. (DANIELS, 1984a; EUSMAN, 1994a; LECKIE & WILLIAMS, 1994) William Russell had found that some organic materials could produce an image on a photographic plate in the dark, and thought that somehow hydrogen peroxide evolved from certain materials was responsible for forming the image. Russell effect photography was developed by Daniels using sensitised photographic film, and found to be sensitive enough to follow slow deterioration reactions at ambient conditions. The application of the technique was considered in this study to follow the oxidative reaction and the effect of the environmental factors influencing the rate of oxidation. (DANIELS, 1984b; DANIELS, 1986; DANIELS, 1996) The technique was not adopted in this study because of the unavailability of the unstabilised grade of photographic film required. The difficulty in applying the Russell effect was exacerbated by the transient nature of the formation and decomposition of hydrogen peroxide.

Chemiluminescence has been applied to the problem of the detection of deterioration at very early stages and at small levels of change with remarkable success. (DANIELS, 1996; GRATTAN, 1978; GROMEK & DERRICK, 1993; KELLY, et al., 1979; MENDENHALL, 1977) The slow reaction of organic compounds with atmospheric oxygen at room temperature has been measured by chemiluminescence with humidity cycling being reported to increase the degradation rate by means of mechano-chemical chain scission inducing free radicals (R.) and subsequent autoxidation over formed peroxides (ROO.) (MENDENHALL, 1977) The further evaluation of chemiluminescence as a technique for monitoring deterioration is under current research by the Getty Conservation Institute. (GROMEK, DERRICK, GINELL, STULIK, & PREUSSER, 1998) The technique seems appropriate in assessing the low oxidative degradation rates that were anticipated in this study, obtained under experimental conditions designed to simulate normal conditions. However, the technique is not yet well developed in conservation analysis, the instrumentation is not widely available, and could not be located for use in this study.

The analysis of degradation products of aged papers by FTIR was originally applied in the investigation of foxing, both independently, with an attenuated total reflectance (ATR) attachment, and in conjunction with chromatographic methods to determine the chemical nature of products found in areas of discolouration. (CAIN & KALASINSKY, 1983; CAIN, 1983; CARDAMONE, 1991) The similar objectives of the current study were supported in the reported use of FTIR spectroscopy to measure the oxidation of cellulose in browned paper mounted in mats. (HOFENK DE GRAAFF, 1994)

The problems encountered in the quantification of degradation products are recorded in the advantages and disadvantages of the analytical techniques employed in the identification of oxidation compounds conducted most recently by DuPont. The difficulty of labourious sampling techniques is pointed out in the use of thin layer chromatography (TLC), FTIR using ground samples in KBr pellets; gas chromatography in conjunction with mass spectrometry(GC/MS) and high performance liquid chromatography (HPLC). (DUPONT, 1996a)

2.5.3 THE SELECTION OF EXPERIMENTAL TECHNIQUES USED IN THIS STUDY

The phenomenon of a brown line has been previously studied in the visible form by the capillary action of wicking, either suspending a sample in water or by dropper action to induce the degradative mechanism. (DUPONT, 1996b ; EUSMAN, 1995; HOFENK DE GRAAFF, 1994) This methodology was applied both directly and indirectly in the development of an experimental project to study the formation of a wet/dry interface resulting from the uneven sorption and desorption of atmospheric moisture at points of moisture accumulation related to conditions of high humidity. Points of moisture accumulation are typically noted at areas of penetration at the page margins and endpapers of volumes; at physical defects such as tears and dog-eared corners, and at areas of uneven adhesion as evidenced in the lamination of artworks. The sample was thus prepared to represent potential areas of moisture accumulation, by the direct application of moisture, as outlined in 4.3.1 below.

The second stage of the experimental design comprised the dynamic simulated ageing programme to represent the ambient climatic conditions thought to induce oxidative degradation in the response of the paper substrate. In testing the hypothesis that a fluctuating equilibrium moisture content of the paper substrate causes cellulosic staining, it was necessary to monitor the chemical modification of the cellulose caused during the simulated ageing programme.

The selection of experimental techniques applied in this study to monitor chemical modification was influenced by similar experience reported in previous investigations in the area of cellulosic staining. The results of the present study would thus conform with a reproducible standard, and enable a useful comparison with the results of previous studies. (DUPONT, 1996a; EUSMAN, 1995; HOFENK DE GRAAFF, 1994) The preliminary visual inspection of the phenomenon of cellulosic staining in paper conservation, using stereo and scanning electron microscopy (SEM), and inspection under UV light in the course of routine conservation, revealed a need for the characterisation of cellulose at the areas of discolouration for the purposes of this study.

The characterisation of cellulose by FTIR was selected as the primary analytical technique, the application of FTIR being well developed in conservation. (BAKER, VON ENDT, HOPWOOD, & ERHARDT, 1988; CAIN & KALASINSKY, 1983; FERRETTI, 1993; LOW & BAER, 1977; SHEARER, 1987; SHEARER, PETERS, GOEPFNER, & NEWTON, 1983) The spectrophotometric measurement by diffuse reflectance infrared Fourier

transform (DRIFT) spectroscopy was applied to the investigation of the development of carbonyl groups on the cellulose molecule, as evidence of an oxidative mechanism of degradation precipitated by environmental conditions. However, Daniels had reported of a lack of success in the FTIR measurement of aged paper samples, and advocated the supportive analysis by chemical reagents, sensitive to detect the small amount of degradation products evolved. (DANIELS, 1995) This recommendation was accepted on the basis of supportive experience reported elsewhere. (EUSMAN, 1995; HOFENK DE GRAAFF, 1994)

Chemical reagent staining was thus employed to confirm the findings of spectrophotometric analysis. The determination of carbonyl groups by ionic exchange with cationic dyes, including methylene blue are described, (KRAUSE, 1991) and the use of methylene blue as a redox indicator dye is well documented in the literature, and was presented in 2.5.2 above.

The formation of hydrogen peroxide in the autoxidative reaction was well supported in the literature. Previous techniques applied included Russell effect photography and chemiluminescence, in the detection of free radicals. The selection of a chromatographic indicator of hydrogen peroxide, Naphtorin, was made in adaptation of the use of Tollens' reagent (naphtoresinol), reported to be of limited success applied in an aqueous extraction. (HOFENK DE GRAAFF, 1994)

The structural modification of the fine structure of cellulose was followed in this study as evidence of an oxidative reaction in response to environmental

conditions. The limitation of chemical reactivity to the accessible hydroxyl groups in the amorphous fraction provided a useful tool in the study of the oxidative reaction in the quantitative measurement of the degree of crystallinity as an indicator of cellulose degradation. The data obtained in this procedure enabled an investigation of a further area of interest in the critical interaction of air, water and cellulose.

2.6 AN ASSESSMENT OF THE OUTSTANDING FACTORS TO BE DEALT WITH IN THIS STUDY

Previous investigation of cellulosic staining has been limited to the repeated formation, by induced capillary action or wicking of paper strips suspended in water, of a brown line at the wet/dry interface. The study of foxing in the conservation literature has been limited to the debate between fungal or metal catalysed causation, while oxidative degradation of pulp and paper has been treated in the literature of the paper industry in relation to colour reversion. These interrelated factors were tested in the investigation of the wet/dry interface in the causation of the proposed oxidative mechanism of paper degradation noted in library and archival material stored under humid climatic conditions.

The conceptual basis for the investigation of an alternate mechanism of causation of cellulosic staining is the noted modification of cellulose at the brown line, which appeared to be formed by the evaporative process in the interaction of air, water and cellulose. The limitations of standard recommendations for environmental control were presented in 2.2 above.

An area of study which has not received full attention in the preservation of library and archival materials is the relationship between the storage environment, the paper substrate and the resultant modification of the cellulose structure.

2.6.1 THE RELATIONSHIP BETWEEN STORAGE ENVIRONMENT, PAPER SUBSTRATE AND CELLULOSE STRUCTURE

Finally, the assertion of the researcher that the damage perceived in the library and archival collection housed in a humid sub-tropical climate does not stem from mould growth alone, relies on anecdotal evidence of the disruptive role of ventilation. Varied air circulation rates on the stability of surface layers of air surrounding organic artefacts act in restricting mould growth. Scott has reported on the validity of high ventilation rates in the control of available moisture in the paper substrate as supported by the lack of evidence of universal damage by fungal rot which might otherwise be anticipated in warm humid climates. (SCOTT, 1994) Since relative humidity is psychrometrically controlled as a function of temperature, fluctuations, particularly seasonal fluctuations, result in marked decrease in relative humidity, and resultant changes in equilibrium moisture content. As the moisture content responds to changes in vapour pressure, or more specifically absolute humidity, the transfer of water from hygroscopic material to the surrounding air is reliant on the motive power in the difference in partial pressure, of water vapour in one direction, and heat in the opposite direction. (POLLACK, 1961) The response of the equilibrium moisture content to environmental conditions will be investigated in 3.3

below.

In an important contribution to the understanding of the structural response of various classes of materials to change in temperature and specifically to change in RH, the research of the Preservation Science Group of the Conservation Analytical Laboratory at the Smithsonian Institute opened the discussion on climatic conditions that might be considered suitable for preservation. The relevance of their research is seen in relation to the mechanical stress experienced by organic materials. The physical response of the material results not only in mechanical stress, but also in an irreversible chemical modification of the fine structure. The determination of a crystallinity index from the FTIR spectra, reflecting the chemical modification, was therefore included in the selection of experimental techniques applied in this study. The crystalline/amorphous ratio of the cellulose structure will be investigated further in 3.3.2, in the determination of a relationship between environmental conditions and the chemical degradation evidenced in the fine structure of the cellulose.

The measure of permanence applied in this study lies in the investigation of climatic conditions suitable for preservation, as determined by the response of the moisture content of the material, rather than simply the monitoring of the RH of the surrounding air.

2.7 SUMMARY

Three major factors were identified in the deterioration of paper, mechanical stress, the acid content inherent in the manufacturing process, and the storage environment. Environmental control is acknowledged as an effective preservation management strategy, and under the given ambient conditions of high humidity, formed the focus of this investigation into the potential risk of an oxidative reaction at the wet/dry interface.

The free radical mechanism, initiated in the decomposition of hydrogen peroxide formed at the wet/dry interface, and the complex chain reactions in which the presence of trace metals is significant, was considered. The study of the yellowing of paper conducted by the paper manufacturing industry was examined, in which the formation and consumption of measurable amounts of hydrogen peroxide were reported to be formed on the ageing of paper, and that the peroxide content increased during moist ageing to values higher than those noted in dry ageing.

The role of autoxidation in the deterioration of library and archival collections was recognised in the formation of a brown line at the wet/dry interface, and the early investigations in the textile industry applied to this study in the capillary action of repeated wetting and drying as induced by fluctuating environmental conditions. The chemistry of the browning reaction, known as the Maillard reaction, was found to be linked to the moisture content in the dehydration of foodstuffs, and poses an interesting area of further investigation.

The theory of paper ageing, textile dyeing and the dehydration of foodstuffs has been applied to the conservation of paper in the discolouration noted in mounted works housed in storage boxes, and the tideline formation resulting from local treatment procedures. Peroxide formation was confirmed in the analytical investigation of the degradation products extracted from the brown line. The absorption of excessive water vapour in humid conditions, and the desorption kinetics of a seasonal decrease in RH was proposed by the researcher as an oxidative reaction, equivalent to the formation of brown line at the wet/dry interface, as the predominant factor in the causation of deterioration, previously obscured by the accepted explanation of biological deterioration in a humid climate.

Despite the lack of consensus on the causative factors in the evidence of foxing, the role of both fungal infection and metal-induced catalysis were both found to be associated with hydrogen peroxide formation. The oxidative mechanism is proposed as a precipitating factor in the causation of foxing.

The methodologies adopted in the previous study of both the brown line formation and the causation of foxing were compared, in the selection of experimental techniques used in this study to investigate the causation of discolouration under a fluctuating test environment simulating ambient conditions.

A further assessment of the chemical interaction of air, water and cellulose was motivated for inclusion in the experimental methodology, in the investigation of the crystalline/amorphous ratio of the cellulose structure.

The modification of the fine structure of the cellulose in response to the fluctuating moisture content of the material was proposed as a measure of paper permanence, in the determination of a chemical mechanism of oxidative degradation in relationship between storage environment and paper substrate.

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CHAPTER THREE

BACKGROUND TO THE STUDY OF THE RELATIONSHIP BETWEEN ENVIRONMENTAL CONDITIONS AND CHEMICAL DEGRADATION

3.1 INTRODUCTION

Paper is an organic product manufactured from the cellulose polymer, and is subject to a natural process of deterioration from the moment of its production. The rate of deterioration is controlled largely by the manner in which it is handled, and by its storage environment. The present study serves the field of library and archival preservation in the application of conservation science to the development of an understanding of the relationship between environmental conditions and the specific mechanism of chemical degradation in the oxidation at the wet/dry interface identified in tideline staining.

The extreme humidity experienced in a sub-tropical climate, and the annual fluctuation caused by a sharp drop in humidity in the short winter months gave rise to the research objectives to study the interaction of environmental conditions and paper permanence. In this chapter, the psychrometric properties of moist air are examined in terms of the chemical reactivity of paper in the causation of cellulosic discolouration. Current preservation

strategies of environmental control can thus be evaluated, based on the findings of this investigation, and are presented in Chapter 6.

The evaluation of accepted strategies for environmental control in the context of humid climatic conditions was considered appropriate at a time when recommended standards have been called into doubt, addressing issues of preservation management that relate to a lack of adequate resources for archival storage in developing countries, many of which fall in tropical and sub-tropical climatic regions.

The acceptance of the recommendation of airconditioning as the ultimate solution to environmental control, without critical independent consideration given to humidity control, may contribute to an accelerated rate of deterioration in these regions. Excursions to dewpoint may result in the absorption of excessive amounts of atmospheric water vapour by capillary condensation in the hygroscopic paper substrate.

The relationship between EMC and fine structure of the cellulose was investigated in the increased chemical reactivity of paper exposed to humid conditions. The influence of crystallinity on paper ageing is presented in 3.3.1 below. The relationship was measured in an accelerated ageing process, including a dynamic simulated climate ageing programme, reliant upon the psychrometric properties of the ambient climate. The validity of the accelerated ageing programme employed in this study to monitor the

response of the equilibrium moisture content (EMC) to fluctuating environmental conditions is examined and the findings presented in 3.3.2 below.

The theoretical model of the proposed oxidative mechanism of deterioration, based on the response of the EMC, was found to be applicable to a wider range of climatic conditions:

- 1 in the macro-environment of a hot humid climate;
- 2 in the forced evaporation of artificial heating of a cold climate;
- 3 in regions of strong diurnal and season fluctuations;
- 4 in the microclimate of a storage context in a library or archive situated in a moderate climate.

The characterisation of environmental conditions for the application of the theoretical model of oxidative degradation is presented in 3.4 below.

3.2 ENVIRONMENTAL FACTORS IN CHEMICAL MECHANISMS OF DEGRADATION

Environmental factors which affect the deterioration of library and archival materials include temperature, humidity, light, particulate and gaseous atmospheric pollution, vibration and insect pests, all of which have been treated extensively in the conservation literature. (BROMELLE, 1967;

PREUSSER & DRUZYK, 1989; REILLY, 1996; WESSEL, 1970; WESSEL & THOM, 1954)

The effect of temperature and humidity on the permanence of paper has been studied independently, in relation to the accelerated ageing of paper, (GRAMINSKI, PARKS, & TOTH, 1979) to the fading rate of watercolours, (KÜHN, 1967) to infection by certain fungi, (ALLSOPP, 1984; VALENTIN, LIDSTROM, & PREUSSER, 1990) and to environmentally induced physical stress in materials. (MECKLENBURG & TUMOSA, 1996)

While acid hydrolysis appears to be the dominant mechanism under ambient conditions, oxidation contributes significantly to paper degradation. Hydroxyl groups in the cellulose macromolecule are oxidised to carbonyl and carboxyl groups. This oxidation leads to the discolouration of paper, and a decline in the physical properties indicating strength. Oxidative degradation can occur during manufacture in pulping and bleaching processes, or in the introduction of trace metals, which act as oxidation catalysts. Lignin residues, sunlight, UV light, atmospheric pollutants, as well as heat and humidity, facilitate the oxidation of cellulose in paper fibres. (TANG, 1986)

Photochemical degradation, gaseous and particulate pollutants, while relevant to the study of oxidative mechanisms of degradation, are readily excluded from the library or archive environment and are not included in the present study. Both these factors are acknowledged as capable of

initiating similar or concurrent oxidative reactions in paper, and respectively, have been extensively researched. (BISHOP, 1956; DESAI, 1970; FELLER, 1964; FELLER, 1973; HON, 1979; LAUNER & WILSON, 1949; LEE, BOGAARD, & FELLER, 1989; LEE, 1989; MASON, 1967; PADFIELD, 1969; SILVY & LE NEST, 1973; WHITMORE & BOGAARD, 1994) (HACKNEY, 1984; HERRERA, 1990; PREUSSER & DRUZIK, 1989; THOMSON, 1965)

Temperature and humidity cannot be eliminated, and the determination of suitable values for environmental control, based on their synergistic effect on paper ageing, is fundamental to the preservation of library and archival collections. This study will show the effects of temperature, and particularly of humidity, to be more varied and more complex than was previously perceived.

The established relationship between the effect of an increased storage temperature and relative humidity on the increased rate of deterioration, as described by the Arrhenius equation, was presented in 2.1. However, the recommended environmental levels for the storage of library and archival material, at 20°C and 50%RH, were adopted from museum-based studies and are limited to considerations of the physical stress on composite artefacts experienced under fluctuating environmental conditions.

The research work of Thomson is considered as the basis of modern environmental control. Thomson points, however, to his selection of

55%RH simply as a point midway between an upper limit of 65-70%RH to prevent mould growth, and a lower limit of 40-45% RH to prevent the cracking and distortion of museum materials, such as wood and ivory, and the increased brittleness of paper. (THOMSON, 1986) Stefan Michalski reported that, in tracing the derivation of these generally accepted values, there seemed more justification for their recommendation in their mechanical feasibility in the temperate climate zone than by any research designed to determine the values that minimised damage. (MICHALSKI, 1993b)

A limitation of the current understanding of RH control is expressed thus:

“The necessity for RH control to avoid mechanical damage or mold (sic) growth is fairly well understood...the magnitude of the effect of temperature and humidity on the rate of *purely chemical forms of deterioration* are not widely known or appreciated...” (REILLY, NISHIMURA, & ZINN, 1995 p.3)

Despite this limitation, the storage life span of papers for the preservation of library and archival material, attained at the recommended levels of environmental control at 20°C and 50%RH, have been quantified in terms of the acknowledged chemical degradation process in acid-catalysed hydrolysis. The storage life span of both acid and alkaline papers was measured as increased sixfold when these values are reduced to 15°C and 30% RH, demonstrating the influence of temperature and humidity on the ageing rate of paper. (DU PLOOY, 1981)

The maximum storage life values attained by minimising acid-catalysed hydrolysis is therefore equated with an environmental control strategy aimed at storage as cool and as dry as possible. However, two aspects of degradation have been identified: the oxidative and the purely thermal. (ARNEY & JACOBS, 1979) The risk of a fluctuating moisture content, resultant upon excursions to extreme values of humidity, is considered in this study in the causation of oxidative degradation of paper, by the phenomenon of the brown line at the wet / dry interface. The implications of the role of the psychrometric properties of the atmosphere in the oxidative mechanism of degradation are added, in this study, to the equation.

3.2.1 PSYCHROMETRIC PROPERTIES IN ENVIRONMENTAL CONTROL FOR ARCHIVAL STORAGE

“Psychrometrics is the science involving thermodynamic properties of moist air, the definition must be broadened to include the effect of atmospheric moisture on human comfort and materials, and the method of controlling the thermal properties of moist air.” (GOSLING, 1980 p.1)

The basis for the measurement of air properties is the psychrometric chart, from which is determined the dry bulb temperature; wet bulb temperature or dew point temperature; percentage saturation or relative humidity (RH); moisture content of the air by mass per kilogram of dry air, as well as specific volume and specific enthalpy. Any two of these independent properties locate the point of intersection representing the state of the air at

the given time. Once this point is located, the remaining properties can be read from the chart. The interrelationship of psychrometric properties governs the relationship between the storage environment and its effect on the collections. (CONRAD, 1996; THOMSON, 1986) (See Figure 3.1)

The psychrometric relationship between temperature and humidity is well known to research workers in the determination of storage life values to minimise acid-catalysed hydrolysis. Defined in terms of the difference between dry and wet bulb temperatures, the values of temperature and humidity are routinely monitored in libraries and archives by means of a hygrometric table utilised in conjunction with a sling psychrometer, or by thermohygrograph, or by digital datalogger with software interface. The monitoring of temperature and humidity in the library and archival environment serves as a tool in the identification of specific environmental conditions or of possible risk which requires psychrometric analysis to determine the other properties representing the state of the air at that time. (BROWN, 1994; CONRAD, 1996; PITA, 1981) The critical relevance for this study of the psychrometric properties of the air lies in the absolute humidity, or volume of water vapour present in a warm, humid climate. RH is merely an expression of that amount of water vapour as a percentage of the maximum amount which that same volume of air can hold at that temperature.

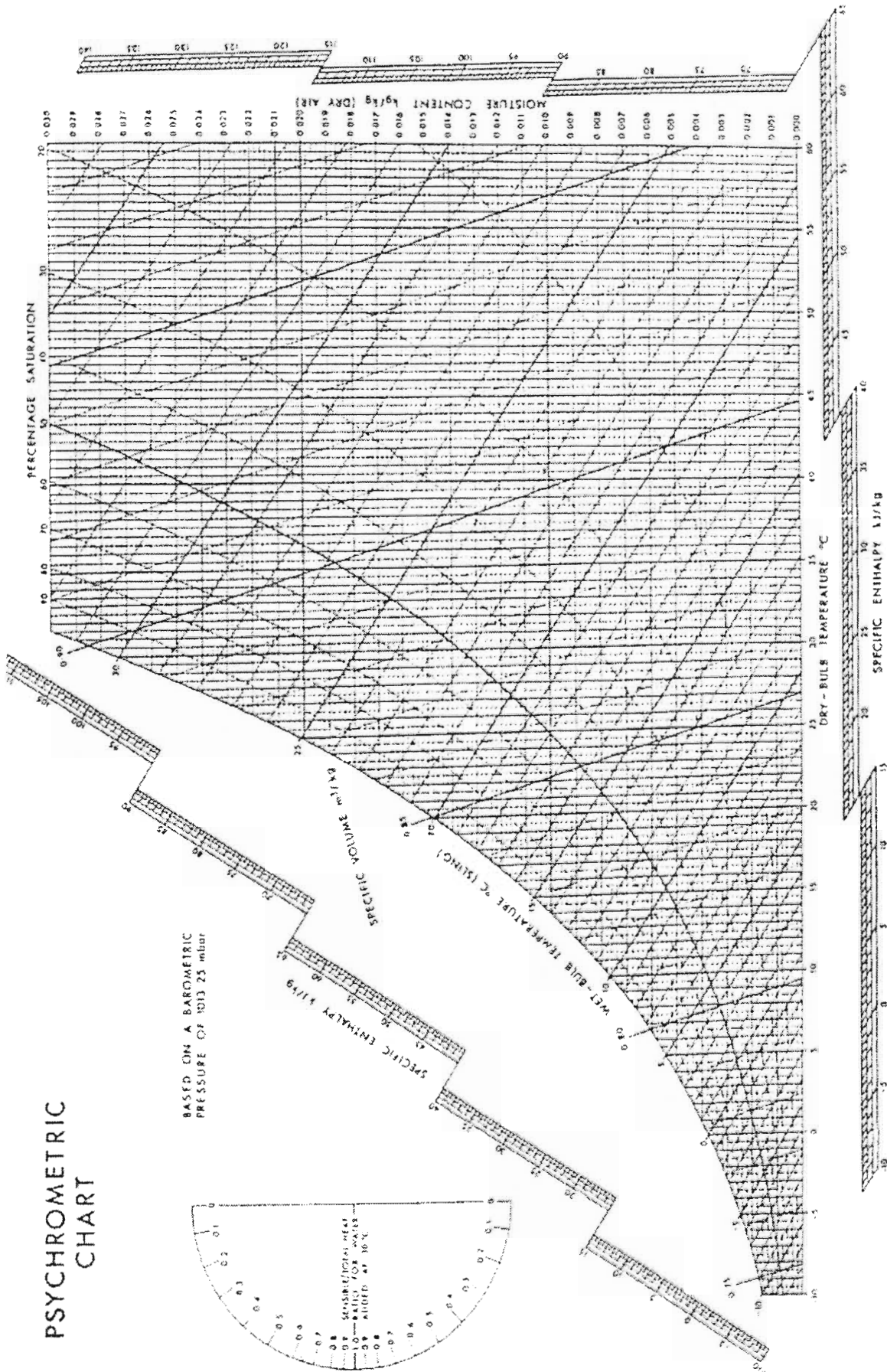


Figure 3.1 Psychrometric chart (THOMSON, 1986 p.211)

Thomson defines the concept thus:

$$\text{RH} = \frac{\text{amount of water in given quantity of air}}{\text{maximum amount of water which the air can hold at that temperature}} \times 100\%$$

"Air at 50%RH, whatever the temperature, is therefore holding half the water it can." (THOMSON, 1986 p.68)

The concept of dewpoint is fundamental to an appreciation the importance of psychrometric properties of the air. Dewpoint is the maximum amount of humidity, or water vapour a volume of air can hold, before the air is saturated at that temperature. When cooled further, the given volume can hold no more water vapour, and the excess is condensed out in liquid form.

"The dewpoint specifies the absolute water vapour concentration in the air. Relative humidity is the ratio of this absolute water vapour concentration to the maximum water vapour concentration possible at that temperature. This maximum increases with temperature. Air with a specific water vapour concentration (dew point) has a lower relative humidity at a higher temperature." (VITALE & ERHARDT, 1993 p.507)

Conversely, under conditions of high RH, the dewpoint is quickly reached with a small decrease in temperature.

Meteorological measurements of the subtropical coastal region of southeast Africa, recorded over an acceptably long period of thirty years to be considered accurate, reflect the highest humidity reading at 92% at 20h00 in the month of March. (Climate..., 1986) The equivalent dry bulb

temperature measured at that time was 23,5°C. From these two independent properties, the point of intersection representing the state of the air at that time can be located on the psychrometric chart. It is noted that the dewpoint temperature in that environment was 21,6°C. A drop in temperature exceeding 1,9°C in the course of the night would therefore result in dewpoint condensation on cold and impervious surfaces in the library or archive, such as metal shelving and cabinets, and the glazing of framed artworks. The phase transfer from atmospheric vapour to the liquid condensate, however, is seldom apparent in library and archival repositories. The effect of such fluctuations is buffered by the building envelope, and the excess atmospheric moisture is taken up directly by the porous substrate of the paper in books and documents. The porous nature of the paper substrate allows for the absorption of the increased atmospheric vapour, or absolute humidity, well before dewpoint is actually reached. (KARP, 1983; MEI & WOOLRICH, 1965; ROSE, 1994)

Ventilation plays an important role in deferring the dewpoint by mixing the air in the surface boundary layer. The amount of water adsorbed by the porous substrate is limited by the diminished the water vapour concentration at the surface. (KING & PEARSON, 1992; PADFIELD & JENSEN, 1990; VERRALL, 1962)

In a previous investigation of the relationship of paper discolouration and deterioration reactions, accelerated ageing tests were conducted under

conditions, ranging from 50-90°C and 30-80%RH at three specific dewpoints. An increased dewpoint resulted in increased colour production. Dewpoint is considered the best predictor of chemical stability in storage. (VITALE & ERHARDT, 1993) The current study has developed the theory of chemical deterioration resulting in increased discolouration as a consequence of the sorption and desorption kinetic of materials exposed to excessive absolute humidity in periodic excursions to dewpoint in a humid climate.

The application of the psychrometric chart to meteorological data for the region confirmed the prevalent problem in the risk of frequent excursions to dewpoint. Acting as a natural moisture reservoir, the equilibrium moisture content of paper responds to fluctuations in RH. Separate research is underway to analyse the effect of the potential moisture reservoir of paper-based collections in buffering fluctuations in the storage environment. (MONTORI, MORROW, & SEBERA, 1994) The concept of porous materials applied in buffering RH is adopted from museum studies, and is applicable to the library and archival environment in the use of protective storage enclosures. (BRIMBLECOMBE & RAMER, 1983; KAMBA, 1987; KENJO, 1982; MIURA, 1981; PADFIELD, ERHARDT, & HOPWOOD, 1982; STOLOW, 1966; THOMSON, 1977; TOISHI, 1959; TOISHI, 1961)

This study is aimed at developing an understanding of the risk of the degradation mechanism at the wet/dry interface, driven by the sorption and

desorption kinetics of the moisture reservoir of collections in relationship with the storage environment.

3.3 RESPONSE OF THE EQUILIBRIUM MOISTURE CONTENT OF PAPER TO ENVIRONMENTAL CONDITIONS

The role of environmental control has been the subject of recent investigation based, however, on the chemical mechanism of acid hydrolysis and stress mechanisms induced by fluctuations in RH. (McCORMICK-GOODHART, 1995; McCORMICK-GOODHART, 1996; SEBERA, 1994) Fundamental research has indicated that since chemical reactions in unstable materials are mediated by moisture, any level of RH above 0% is potentially destructive. (GRAMINSKI, et al., 1979; MICHALSKI, 1993a; WILSON, 1993; WINK, 1961)

Cellulosic materials have a known equilibrium moisture content which can be measured as the amount of water vapour held by a material when it has reached equilibrium with the environment, expressed as a percentage of its dry weight. (STOLOW, 1966) As the RH drops, moisture is released, and as the RH increases again, moisture is re-adsorbed, until equilibrium with the surrounding atmosphere is re-established.

The transport of water vapour through paper is therefore of intrinsic interest in the application of the phenomenon of the formation of a brown line at the

wet/dry interface to the environmental conditions in the library or archive. The force of capillary rise, used in the previous study of the brown line formation, is replaced in the theoretical model by the absorption and desorption by condensation of water vapour on the porous cellulose cellulose in a humid climate. The response to fluctuating environmental conditions acting as the controlling mechanism in the transport of water vapour through paper.

The increased rate of absorption and desorption of water vapour in the paper fibres, the water vapour permeability, determined by vapour pressure, is associated with high humidity. Absorption of water vapour from the air is dependent on the amount of water available, and its temperature. The flow rate of water vapour through paper by the surface concentration of water vapour (absolute humidity) on surface diffusion. Surface diffusion is said to start at 25% RH (at 20°C), the absorption isotherm rising steeply at high humidity, when surface diffusion becomes proportional to the surface concentration of atmospheric moisture. (CORTE, 1982) The effect of high humidity therefore enhances the water vapour permeability of materials. Where condensation, or the localised application of liquid occurs, the permeability is further increased in that area accordingly, forming a site of moisture accumulation. (JOY & WILSON, 1965)

In conditions of high humidity, or following an excursion to dewpoint, a difference in behaviour can be anticipated between a general rate of

adsorbed water vapour and that which is condensed in the liquid phase at points of moisture accumulation, exhibiting an increased water vapour permeability. Points of moisture accumulation have been previously associated with foxing stains and discolouration, (LIGTERINK, PORCK, & SMIT, 1991) The manifestation of cellulosic discolouration, identified in 1.2.2, correlates well with potential sites of moisture accumulation, i.e. at the margins of books, dog-eared corners, in the leaves adjacent to less pervious coated paper and in the airspaces of uneven glue applications in the lamination of works of art on paper. The response of the EMC to changes in the ambient environment is therefore more immediate at points of moisture accumulation than in the surrounding paper, constituting a localised wet/dry interface at which oxidation is initiated.

The transfer of water from the material to the surrounding air, in the process of desorption, is of particular interest in applying the theoretical model of the brown line formation in the evaporation of water at the wet / dry interface to the library and archive environment.

Materials housed in a humid climate can be said to adsorb excessive water vapour by surface diffusion proportional to the surface concentration of atmospheric moisture. Equilibrium of these materials with the environment is maintained as long as the available amount of atmospheric moisture (absolute humidity) and its temperature, and the moisture content of the material and its respective temperature, remain constant. When the relative

humidity falls sharply during the short winter months, the hygroscopic material is no longer in equilibrium. A higher vapour pressure exists in the material than in the air. The rate of desorption is dependent on the moisture content of the paper, and its temperature. In order to evaporate, latent heat is required, a temperature change in which moisture content is adjusted. Latent heat is drawn first from the material, and, following a small drop in surface temperature, from the surrounding air. The potential risk of capillary condensation is related to the transfer of water from the material and the equivalent energy transfer to the material, as the surface temperature of the material approaches the wet bulb temperature of the air. Consequently, the air adjacent to the paper surface is cooler and more saturated than the surrounding air. The rate of evaporation is dependent on the vapour pressure in the boundary layer, and convective currents in the ventilation of the boundary layer above the surface. (ERIKSON, 1965; POLLACK, 1961)

Desorption takes place in two processes, in the diffusion of water through the pores of the fibrous structure to the surface, and in surface evaporation of vapour to the atmosphere. (FUZEK, 1985) The rate of evaporation is increased with the speed of circulation, and when it is sufficiently high, evaporation takes place in the pores and not on the surface of the material. This was confirmed in the increased methylene blue absorption evidenced in the bulk of materials aged in the forced ventilation of the climate cupboard. The slow rate of circulation in an enclosed library shelf is expected to reduce surface evaporation from a bound volume below the rate

of diffusion in the moisture migration through the volume. The disruption of internal flow creates an accumulation of moisture at permeable points as described in the manifestation of discolouration noted above. The difference in partial pressure of water vapour in one direction, and of latent heat in the other direction meet in the wet/dry interface created at points of moisture accumulation in the evaporative process of desorption.

Desorption is graphically represented in the lateral flow of moisture, determined by the capillary action induced by parallel fibres lying on the paper surface. Surface morphology is commonly evidenced in the feathering of ink, and its role in the nature of cellulosic staining is evidenced in Figure 1.2. Lateral migration has been measured towards the outer edges during slow drying, at elevated RH in excess of 55%, consistently proceeding towards the area where the most rapid evaporation is occurring. Lateral migration was not found in rapid drying at high temperatures, or where the draft-free chamber was large in relation to the size of the sample. (BERTONIERE, KING, & ROWLAND, 1984) (See Figure 3.2)

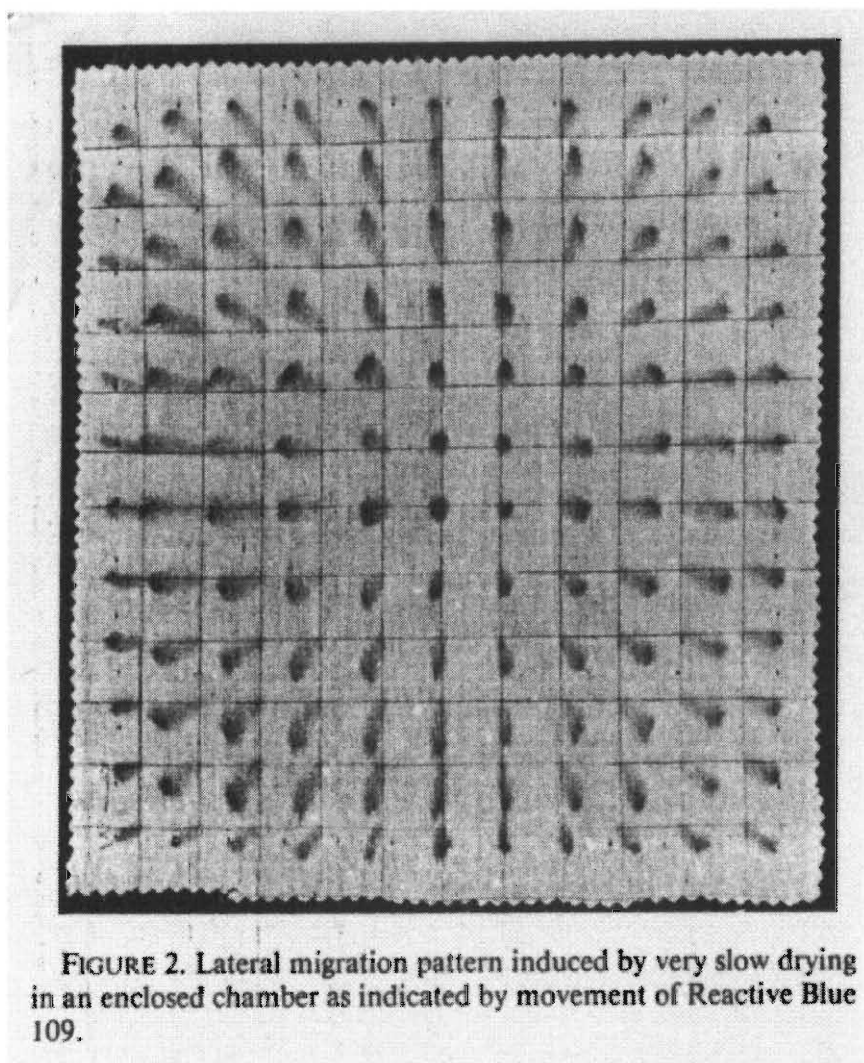


Figure 3.2 Lateral migration (BERTONIERE, et al., 1984 p.52)

Moisture also moves transversely penetrating through the leaves of a book by the capillary action of the porous structure in the pores and spaces between the fibres, in the process known as transudation. The surface characteristics of paper were therefore also considered in the investigation of the localised nature of a wet/dry interface in the form of cellulosic discolouration in the causation of foxing.

Paper fibres have a small diameter and enclose small pockets of air, presenting a large surface area per unit mass. Their hygroscopic nature, combined with the large accessible surface for diffusion, allows the rapid sorption and desorption of water vapour, accompanied by the simultaneous evolution or absorption of heat on the respective cycles. (KING, 1959; LAUER & CHAO-WU, 1961) Coated papers pick up moisture at a lower rate than cellulose papers, as diffusion through the coating must take place before sorption on the fibres can take place. The reduced rate of permeability of coated papers creates a point of moisture accumulation in the adjacent sheet, as the transport of water vapour is blocked. (BROOKS, 1967)

The swelling caused by water vapour interacts with the roughness of the sheet, penetration facilitated by the contact angle of fibres of adjacent sheets. (DAVISON, 1975; HOYLAND, HOWARTH, & FIELD, 1976; OLIVER & MASON, 1976) The important role of surface roughness and porosity and fibre morphology of the paper accounts for both the transudational flow

penetrating adjacent sheets and the resultant localisation of cellulosic discolouration at points of contact between the compacted pages of a bound volume, with the resultant three dimensional staining, unsatisfactorily explained by fungal causation. (LIGTERINK, et al., 1991; SZCZEPANOWSKA, 1986)

Important confirmation of chemical reactivity in transudational vapour penetration was provided in related research of a dry deacidification method by electrochemical migration. Books were pre-conditioned to a high humidity of 97%RH, the pages interleaved with paper containing calcium carbonate and placed under pressure. The migration of ions across the interface between adjacent leaves was achieved in the formation of continuous pathways resulting from the condensation of water in capillaries in the region of contact. The role of high humidity was demonstrated in the failure of transfer to take place at lower humidities. (McCRADY, 1995) Further evidence of increased reactivity related to moisture content was recently reported in the development of a device for locally confined ion migration, designed to remove copper ions by electrochemical transfer. It was revealed that even minimally raising the moisture content of the cellulose fibre was sufficient to trigger ion migration in an electrical field. (GOTTSCHALK, 1997) The association of a chemical mechanism of oxidative degradation with both the lateral and transudational migration of water vapour of an unstable moisture content was confirmed in this study, and is presented in 5.3.1.

Cellulose-water interactions are the subject of debate wider than the scope of this study. (ANT-WUORINEN & VISAPAA, 1960a; BROOKS, 1967; CAULFIELD & STEFFES, 1959; CORTE, 1982; HATAKEYAMA, Y, & HATAKEYAMA, 1987; JEFFRIES, 1963; JEFFRIES, 1964; NEVELL & ZERONIAN, 1985; ROBERTS, 1996; ROWLAND, 1977; SHEPPARD & NEWSOME, 1934; VALKO, 1943) For the purposes of this study, cellulose-water interactions were investigated in the response of the equilibrium moisture content to the environment. The equilibrium conditions of the volume of sorption and desorption, the moisture loss and regain, are determined by the psychrometric properties of the environment and the phenomenon of hysteresis.

The phenomenon of hysteresis is defined as the sorption or desorption of water vapour by cellulose until equilibrium is reached. The volume of water vapour transported through the cellulose differs on absorption from that on desorption, and is not constant in repeated cycles. The volume is dependent not only on the relative vapour pressure (absolute humidity) , but also on the direction from which equilibrium is approached, and is smaller on sorption than on desorption. Significantly, the first desorption curve lies above all subsequent and is irreversible, indicating a modification of the cellulose structure. A popular explanation being that the strength of hydrogen bonds formed during the initial drying cannot be broken in subsequent swelling. (BROOKS, 1967; CROOK & BENNETT, 1962; JEFFRIES, 1963; MICHALSKI, 1993a; STOLOW, 1966; VALKO, 1943) Hysteresis can be

therefore be associated with the stress relaxation of the cohesive forces opposing swelling, indicating differences in the structural conformation between the absorption and desorption states. (ZERONIAN, 1985) The association of hysteresis with moisture regain, and with structural changes of the cellulose is of relevance to this study in the changing capacity of the sample to participate in chemical reactions in response to fluctuating conditions of relative humidity.

“After sorption, paper samples appeared rougher, less glossy, more limp and less crinkly. This indicates that some physical change in sheet structure is irrecoverable even after one exposure cycle to moisture.” (BROOKS, 1967 p.108A)

The absorbent capacity of cellulose in the paper substrate depends on the number and nature of previous absorption and desorption cycles to which it is exposed. Repeated sorption experienced under fluctuating environmental conditions, and the strong kinetic of capillary condensation driven by the psychrometric properties of a humid climate, progressively reduces sorptivity towards a constant value over subsequent cycles. (EKLUND & LINDSTRÖM, 1991; JEFFRIES, 1963) The relevance of the concept of hysteresis was acknowledged in the development of an experimental model for this study as twofold:

- 1 The phenomenon of hysteresis affects the result of the experimental procedure according to the previous history of the sample. Standard paper testing procedures are preceded by a period of conditioning at

20°C and 50%RH to control the direction of hysteresis.(CROOK & BENNETT, 1962)

It was therefore decided to use a control sample of known previous history, in a Whatman's filter paper of recent manufacture to overcome the effect of a previous sorption history.

- 2 The hysteresis phenomenon was considered to be relevant to the research hypothesis in the role of a diminishing moisture regain, as an indicator of the variable level crystallinity in determining chemical reactivity. (HEDGES, 1928) Hon established the swelling effect on bound water in amorphous regions, enhancing free radical formation at a moisture content greater than 5-7%, but a significant decrease in free radical formation in the range of 5-7%. It is the belief of the researcher that, in repeated environmental fluctuations, the equilibrium moisture content (EMC) of the substrate, i.e. the amount of water vapour contained by the material at equilibrium expressed as a percentage of its dry weight, is reduced by the hysteresis effect to the stabilising range, and is equated with an diminishing moisture regain. The relationship between moisture regain and crystallinity is investigated further in 3.3.1 below.

3.3.1 THE CRYSTALLINE/AMORPHOUS RATIO OF THE CELLULOSE STRUCTURE IN THE DETERMINATION OF A RELATIONSHIP BETWEEN ENVIRONMENTAL CONDITIONS AND CHEMICAL DEGRADATION.

The measurement of the relationship between environmental conditions and chemical reactivity of the paper was achieved by monitoring the change in crystalline structure of the cellulose molecule in response to changes in the equilibrium moisture content under fluctuating climatic conditions. An assessment of the influence of crystallinity on paper properties and ageing has been reported, without specific evidence of a relationship to oxidative mechanisms of degradation, which this study set out to determine. (ATALLA, 1979; DANIELS, 1986)

The role of amorphous/crystalline ratio was considered to be relevant in terms of the effect of accessibility on the structure of the cellulose. This is expressed in the relationship between the chemical modification of cellulose, evidenced in the formation of functional groups, and the moisture regain, or the sorption behaviour of the cellulose molecule in response to humid environmental conditions.

The crystallinity of cellulose is defined as that fraction of OH (hydroxyl) groups comprising the anhydro-D-glucopyranose units of the polysaccharide cellulose molecule which are hydrogen bonded in a crystalline, or ordered

manner, as distinct from the amorphous or disordered fraction. (MANN & MARRINAN, 1956) Chemical reactivity is limited to those accessible hydroxyl groups in the amorphous fraction, accessibility thus being a function of the degree of crystallinity of the cellulose structure. (ANGIBEAUD, DEFAYE, & GADELLE, 1985 ; BERTONIERE & ZERONIAN, 1987; TASKER, BADYAL, BACKSON, & RICHARDS, 1994)

The disordered fraction of the cellulose, the amorphous fraction, is readily accessible to chemical reaction as chemical reagents readily penetrate non-crystalline regions. It is reported that crystallites, resisting entry of external reagents, limit the transport of water vapour or air to the accessible hydroxyl groups, and of degradation products away from them. (GILES, SHAH, JOHARI, & SINCLAIR, 1972 ; LAUER, 1961; WHITMORE & BOGAARD, 1994) About one-third of the hydroxyl groups in cellulose are accessible to the atmospheric water vapour available under conditions of high relative humidity, but not to aqueous solutions. (JEFFRIES, ROBERTS, & ROBINSON, 1968) A proportional relationship exists therefore between moisture sorption capacity of a fibre and its structural content of accessible material. Indeed, the measurement of moisture regain has been determined as a linear function of the amorphous fraction and provides an approximate measure of crystallinity. (JEFFRIES, 1964; MANN, 1963)

Chemical reactions of cellulose are limited to OH groups that are accessible to the reagent, a determining factor in the rate of vapour diffusion in the

paper substrate. The chemical modification of cellulose resulting from oxidative degradation results in the alteration of its fine structure. These changes are caused by the replacement of alcoholic groups by carbonyl or carboxyl groups. A linear relationship is reported between the increasing content of carbonyl groups at C2 and C3, together with the content of carboxyl groups at C6, and the increasing values of the functions of accessibility - reactivity and sorption behaviour. (KUNIAK, ALINCE, MASURA, & ALFOLDI, 1969) The rate of chemical degradation of cellulose, which results in a change in the functional group content, i.e. the formation of carboxyl and carbonyl groups, is determined by a change in the state of accessibility, during which the crystallinity of cellulose decreases. (ANT-WUORINEN & VISAPAA, 1960a; CHATTERJEE & SCHWENKER, 1972). Accessibility thus provides a link between the investigation of the moisture sorption of the fibre and the analysis, by chemical means, of the functional groups associated with oxidative degradation. This relationship may be expressed as the rate determining factor of chemical reactions, by which the rate of diffusion inside the fibres is determined by the degree of crystallinity. The lower rate of diffusion associated with a higher degree of crystallinity is termed the diffusion-restriction (DR) effect. It is therefore deduced that oxidative reactions will proceed more rapidly in paper samples of a lower degree of crystallinity.

However, a further factor relating to accessibility is pertinent to this study. It is reported that increasing relative humidity lowers the crystallinity index

and is partially reversible. (ANT-WUORINEN & VISAPAA, 1960b) The crystallinity index reflects the general degree of order, and is not an estimate of the proportion of crystalline to amorphous fractions present. The crystallinity index is therefore an indicator of the changing capacity of the sample to participate in chemical reactions in response to fluctuating conditions of relative humidity. Vapour diffusion to the paper substrate is not fixed, but varies in response to the availability of water vapour, and the hysteresis effect, which is reflected in the diminishing accessibility of the cellulose structure on repeated sorption and desorption.

The response of library and archival materials to cycling RH is not readily visible in the unstable equilibrium moisture content. However, the rate of chemical reactivity is shown to increase on each sorption cycle, in the increased accessibility of the cellulose structure. The production of free radicals, limited to the amorphous region, is reported to increase when moisture content exceeds the range of 5-7%. (HON, 1975) Chemical reactivity peaks therefore, with the maximum number of hydroxyl groups accessible in the amorphous fraction at the onset of the desorption cycle. The mechanism of oxidative degradation subsequently takes place on desorption, as in the evaporation of water at the brown line, at points of moisture accumulation constituting a wet/ dry interface.

A diminishing fluctuation of the crystalline/amorphous ratio of the hydroxyl groups in the cellulose molecule, but progressing towards an irreversible

increase in crystallinity is thus indicative of a relationship between environmental conditions and chemical degradation. The effect of cycling environmental conditions on the fine structure of cellulose was investigated in the experimental design, presented in Chapter 4. The infrared spectroscopic analysis of the samples measured on completion of the cycling programme afforded a crystallinity index of the sample material, presented in 5.2.2. An interpretation of the analytical data confirms the reported relationship of the crystalline/amorphous ratio to the oxidative mechanism of degradation, in the linear relationship between accessibility and moisture regain, presented in 5.3.2.

3.3.2 THE RESPONSE OF THE EQUILIBRIUM MOISTURE CONTENT IN ACCELERATED AGEING

The ageing chemistry of paper has been studied in depth, primarily in the application of accelerated ageing to the effects of acid hydrolysis. This has led to a better understanding of the importance of the pH value for paper permanence, and has contributed to the conservation practice of deacidification to improve paper permanence. The chemical basis for and the practical application of aqueous, non-aqueous and mass deacidification techniques forms an important area of research beyond the scope of this study. (ARNEY, JACOBS, & NEWMAN, 1979; ARNEY, JACOBS, & NEWMAN, 1980; DANIELS, 1980; FELLERS, IVERSEN, LINDSTROM, NILSSON, & RIGDAHL, 1989; HUDSON, 1976; SMITH, 1970; WILSON, GOLDING, MacLAREN, & GEAR, 1981) The implications of this study for the conservation practice of deacidification will be presented in 6.5.2.

In the establishment of international standards,¹ the criteria for paper permanence and durability are based on the evaluation of requirements concerning pH value and alkaline reserve, as well as physical requirements for tear resistance and resistance to oxidation paper deterioration by accelerated ageing test methods. The concept of paper permanence refers to the property or properties a material which resist change during ageing.

1

ISO 9706: Information and documentation - Paper for documents - Requirements for permanence. (standard..., 1993)

Durability refers to the degree to which physical properties are retained under continued usage. (BROWNING & WINK, 1968) Accelerated ageing, measured by a series of standard or normed procedures, relies on a manipulation of temperature and humidity to predict the permanence of paper by measuring the decline in physical properties, such as folding endurance and tensile strength. (ARNEY & NOVAK, 1982; AUBEY, 1990; CROOK & BENNETT, 1962; ERHARDT & MECKLENBERG, 1994; FELLER, 1994; VENTER, 1966)

Contentious in the correlation to natural ageing, accelerated ageing data recorded at 90°C, and even as high as 150°C, cannot accurately predict the predominant degradation process at room temperature, as would be experienced during natural ageing in the library or archival context. For lack of alternative standards, the study of ageing processes continues to rely on accelerated ageing to predict the effects of natural ageing and in the determination of the long term behaviour of conservation materials, as well as the effects of conservation treatments. (ERHARDT & MECKLENBERG, 1994) Until the life expectancy of paper artefacts can be satisfactorily predicted on the basis of a measured response to environmental conditions simulating natural ageing, standard recommendations for environmental control have limited application.

The validity of the accelerated ageing procedure, applied to this study in the determination of an oxidative reaction in the response of the equilibrium

moisture content to fluctuating environmental conditions, was investigated.

Experimental techniques developed to allow the quantitative evaluation of the ratio of atmospheric oxidation to the total rate of deterioration of paper suggests that atmospheric oxidation, and not hydrolysis may play a major role in paper ageing. (ARNEY & JACOBS, 1978) Moisture hysteresis, oxidation, humidity excursions and stress relaxation have a significant and permanent effect on paper properties, but their description is beyond the parameters of current standard accelerated ageing procedures. (DU PLOOY, 1981; ERHARDT, 1990; FELLER, 1994; SEBERA, 1994; SHAHANI, HENGEMIHLE, & WEBER, 1989)

Accelerated ageing is accepted as providing an indication of the life expectancy of different papers, based on environmental factors, but is acknowledged as a limited tool. Dry oven ageing reflects only the degradation associated with the mechanism of acid hydrolysis, while moist oven ageing will find both acid degradation and the oxidative degradation monitored in this study. (PHILLIP, BAUDISCH, & RUSCHER, 1969) It was therefore imperative that the moist oven ageing procedure described in ISO 5630-3 be employed in this study, in the pre-treatment of the Whatman's filter paper described in 4.2.1, to provide an equivalent age comparison with naturally aged samples. Ambient climatic conditions were selected as the environmental parameters in the subsequent dynamic accelerated ageing programme, to simulate the natural ageing process in a humid climate. The

experimental objective of induced oxidative damage was achieved within a reasonable space of time by means of the short duration and the repeated of the programmed cycles to which samples were exposed. Details of the analytical procedure adopted are presented in 4.2 below.

Permanence assumes a direct relationship between the chemical changes in the cellulose and the physical properties in the paper. However, this is not always the case. The complexity of the degradation processes involved - ultimately measurable in acid hydrolysis, but initially also in oxidation and cross-linking - make this assumption questionable. The rate of change of a physical property depends on the rate at which any one of these reactions proceeds in relation to the others. (GRAMINSKI, PARKS, & TOTH, 1978; GRAMINSKI, et al., 1979)

It is therefore significant that previous accelerated ageing studies have noted alternative degradation processes that may be sequential, such as oxidation, hydrolysis, cross-linking, photochemical degradation and biodeterioration. (WHITMORE & BOGAARD, 1994; WHITMORE & BOGAARD, 1995)

The complexity and interchangeable sequence of the various degradation processes are also inadequately reflected in the monitoring of the resultant change in property, such as tensile strength, which may be dependent on more than one degradation process. The sequence of degradative reactions

is an area of potential further research. The experimental project developed in this project was designed to monitor instead, the progression of the oxidative reaction under fluctuating climatic conditions, simulating the ambient conditions of a humid climate. The role of the oxidative degradation process has not previously been considered in the standard accelerated ageing procedure to monitor the relationship between chemical changes and paper permanence.

The effect of variations in RH on the accelerated ageing of paper has been the subject of previous study, and was investigated in the development of an experimental model, designed to measure the response of the equilibrium moisture content in accelerated ageing. (ARNEY & JACOBS, 1979; WHITMORE & BOGAARD, 1994; WHITMORE & BOGAARD, 1995; WILSON, 1997)

An increased rate of accelerated ageing is reported for bound records, found to be generally weaker and having a higher acid content than loose papers in boxes, even those stored in highly acid enclosures. Possible explanations offered include that of a more stable microclimate, as a barrier to atmospheric pollutants. (ROBERSON, 1976; SHAHANI, et al., 1989) The increased rate of deterioration noted in accelerated ageing of sheets compressed to simulate a book, over that of single sheets allowed to interact freely with the environment, is confirmed in later studies, and ascribed to the autocatalytic effect of trapped degradation products in the

larger mass. (DESSAUER, 1989; SHAHANI, 1996; SHAHANI, HENGEMILE, & WEBERG, 1993)

A suggested combination of increased moisture content and autocatalysis was proposed in the increased rate of deterioration found on accelerated ageing of material enclosed in shrink-wrapping. (McCRADY, 1984) The association of a fluctuating moisture content with an increased rate of deterioration, measured by accelerated ageing, was made in the study of the implications of moisture-content isolines for accelerated ageing and long-term storage of photographic materials. In testing the assumption of constant moisture content at constant RH, the difference in experimental results between free-hanging samples and enclosed samples was identified in the change in moisture content of enclosed samples, which changes as temperature changes, in response to psychrometric properties of the enclosed space. (McCORMICK-GOODHART, 1995; McCORMICK-GOODHART, 1998)

The hypothesis held by this researcher develops this theory of an increased rate of deterioration of enclosed materials. The evolution of chemical reactants in the kinetics of sorption and desorption in an unstable equilibrium moisture content contributes to the autocatalytic degradation in the enclosed spaces that comprise library and archival storage - in bound volumes, on shelves, in drawers and boxes, in polyester enclosures and in picture frames. The consideration of the response of the moisture content of library

and archival materials, routinely stored in various forms of enclosure, gave rise to the further consideration of the application of the theoretical model of oxidative degradation to a similar environmental context beyond the humid climate. The environmental characterisation for the application of the theoretical model is presented in 3.4 below.

The increase in the uptake of moisture noted in books, over that in single sheets, confirms the increased capillary force of a greater moisture reservoir in a bound volume. The significant inference of the previous body of research is that, if the rate of deterioration is very different for free-hanging samples than for enclosed samples, the standard accelerated ageing tests using single sheets cannot be considered valid for monitoring the ageing processes of bound volumes. The decision to employ sample stacks in the experimental design, to simulate bound volumes, was therefore taken on the basis of previous research.

The validity of this decision is confirmed in ongoing research into the ageing process of bound volumes. Since the completion of the experimental project for this study, the Library of Congress has published the current development of a new accelerated ageing test for paper to more accurately predict the rate of degradation in bound volumes. Comparative testing of loose sheets, of paper in stacks to simulate books and of paper strips within capped glass tubes to trap degradation products, has shown by degradation product analysis, that the latter method most closely simulates natural

ageing. The advantage of this procedure is that ageing can be conducted in a dry oven, not necessarily in a sophisticated ageing chamber, with controlled relative humidity and temperature conditions. Also, the duration of the accelerated ageing test is reduced from the standard period of thirty days, and is now conducted within a week. This test reportedly corresponds to dark ageing - the chemical effects from exposure to light or from interaction with pollutants are not addressed. Since the rate of degradation in glass tubes is equated with natural ageing in terms only of trapped degradation products, the role of a changing moisture content in the enclosed glass tube has apparently yet to be addressed. (SHAHANI, 1998)

A recent study reports the development of a dynamic ageing programme with constant temperature and cycled RH delivered in a climate cabinet, in a manner similar to that applied in this study. The test procedure resulted in the initial development of foxing spots, which were not successfully induced in the present study. (KAESSBERGER, DESSAUER, & STARK, 1998)

The re-evaluation of this research hypothesis under the ageing procedures currently in development forms an area of subsequent study.

3.4 ENVIRONMENTAL CHARACTERISATION IN THE APPLICATION OF THE THEORETICAL MODEL OF CHEMICAL DEGRADATION

The effects of sorption and desorption of water vapour were readily apparent to this researcher, in the abundant evidence of cellulosic discolouration, in paper artefacts stored at high ambient humidity. However, the theoretical model of oxidative degradation, based on an unstable equilibrium moisture content of materials, is applicable to a range of environmental conditions, as indicated in 3.1 above.

Many libraries and archives in developing countries are unable to maintain environmental control by full air-conditioning. Others, housed in non-specific buildings, experience intermittent control during office hours only. The cycling effect of the moisture content of materials under these fluctuating conditions has an irreversible effect in the structural modification of the cellulose, the rapid response to intermittent environmental control being far more detrimental than the slow seasonal changes effected by no air-conditioning at all. (KING & PEARSON, 1992)

The winter heating required in a cold climate also imposes a strong influence on fluctuating levels of RH. The effect of forced evaporation of artificial heating has led to the current re-evaluation of environmental conditions in relation to the resultant mechanical stress. (MECKLENBURG & TUMOSA, 1996; MICHALSKI, 1996) The effect of chemical oxidation in the recommendation of relaxed environmental control needs to be considered

in further study, in the relationship of rate of deterioration to the rate of seasonal change.

Evidence of cellulosic discolouration, similar to that commonly found in a humid climate, was also noted by this researcher in the storage of archival material in a dry arid climate.² Dry arid regions are characterised by significant diurnal ranges of temperature of 20 - 30°C recorded in the interior regions of southern Africa. The effect of this wide diurnal range in temperature on paper-based collections is twofold:

- 1 Nocturnal excursions to dewpoint increase the moisture content of materials by absorption, subsequently desorbed in daily fluctuations. The high levels of particulate dust in arid regions provide points of moisture accumulation, at which the oxidative mechanism is precipitated.
- 2 The influence of wide temperature variations on an unstable moisture content is associated with an increased rate of deterioration in storage enclosures, as presented in 3.3.2 above.

2

George Mervyn Lawson (c1865-1945). Graphic art collection in William Humphreys Art Gallery, Kimberley. Cellulosic staining on prints and drawings assembled in albums. Anecdotal evidence of microclimate storage environment.

The thermodynamics of storage enclosures was investigated in terms of the wet/dry interface as the cause of browning of mounted paper artefacts stored in archival enclosures. The limited volume of air within a microclimate was found to respond in reverse to the psychrometric properties of the macroclimate. Instead of the decrease in RH following an increase in temperature, the reverse phenomenon of increased humidity driven by a rise in temperature was experimentally measured in the microclimate of a storage enclosure. (HOFENK DE GRAAFF, 1994; McCORMICK-GOODHART, 1995) The degree of browning was found by Hofenk de Graff to increase with the frequency of these fluctuations. Heat had caused unbound water to evaporate from the paper surface, and a fall in temperature resulted in the re-absorption from the vapour phase of dewpoint condensation. (HOFENK DE GRAAFF, 1994; HOFENK DE GRAAFF, VAN BOMMEL, & PORCK, 1993)

The implications of an unstable moisture content equilibrium in storage enclosures, resulting in an oxidative degradation of materials, are compounded by the autocatalytic effect of the degradation products trapped therein. (McCRADY, 1984; SHAHANI, 1996; SHAHANI, et al., 1989; SHAHANI, et al., 1993)

The evidence of similar discolouration found in a range of climatic conditions validates the theoretical model of an oxidative mechanism of deterioration. The response of the equilibrium moisture content to the rate of evaporation

from the surface resembles the phenomenon of the tidemark effect at the wet/dry interface. The evidence indicates significant implications for the preservation of library and archival collections materials, in the environmental characterisation for an oxidative mechanism of degradation in environmental conditions far wider than humid geographical regions.

3.5 SUMMARY

The study of the relationship between environmental conditions and chemical degradation has sought to develop an understanding of the relationship between environmental conditions and a specific mechanism of chemical degradation, in the oxidation at the wet/dry interface identified in tideline staining.

The manifestation of damage, attributed by this researcher to the oxidative mechanism of degradation, was believed to be of direct environmental causation. The increased chemical reactivity of cellulosic materials in a humid climate, generated in the relatively high equilibrium moisture content, is coupled with the seasonal fluctuation in the sharp drop in humidity in the short winter months.

Other environmental factors capable of initiating similar or concurrent oxidative reactions are acknowledged, but have been adequately treated elsewhere in the conservation literature. The psychrometric properties of atmospheric moisture reveal rather, the role of temperature and humidity in the causation of the oxidative mechanism. An excessive volume of water vapour present in a warm humid climate is adsorbed by the porous substrate, added to which is the periodic and localised capillary condensation of water following the excursions to dewpoint on a slight decrease in temperature. Dewpoint is associated with the formation of

cellulosic discolouration and is considered a predictor of chemical stability in storage.

The transport of water vapour through the porous substrate in the increased rate of sorption and desorption by an increased water vapour permeability is associated with the formation of a brown line at the wet dry interface. The difference in the rate of desorption processes in surface evaporation and the diffusion of water vapour through the pores is explained in terms of the slow rate of circulation. The disruption in transudational and lateral flow resulting from environmental fluctuations create points of moisture accumulation in the fibrous moisture reservoir of a bound volume. Such points of moisture accumulation have been ascribed to the formation of localised areas of cellulosic discolouration, known as foxing.

The absorbent capacity of cellulose in the paper substrate was found to be related to the effect of psychrometric properties on the equilibrium moisture content. The response in moisture regain varied on subsequent cycles of sorption and desorption, governed by the phenomenon of hysteresis, and measured in the change ratio of the crystalline/amorphous fraction. The limitation of chemical reactions in cellulose to the OH groups that are accessible to vapour diffusion provides a measure of the structural modification undergone in the formation of functional groups associated with oxidative degradation.

The determination of an oxidative reaction by means of standard accelerated ageing procedures was investigated, and adapted on the basis of previous research, in the development of an experimental model for the induced degradation of cellulosic staining under fluctuating environmental conditions.

The theoretical model of oxidative degradation was found to be applicable to a range of environmental conditions, and the implications of an unstable moisture content equilibrium found to be profound in the use of microclimates for the protective enclosure of library and archival collections.

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CHAPTER FOUR

RESEARCH DESIGN FOR INDUCED OXIDATION

4.1 INTRODUCTION

In order to test the hypotheses of the causation of cellulosic staining in the formation of a wet/dry interface in response to humid environmental conditions, an analytical procedure was developed to induce such staining. It was expected that a comparison of the oxidative degradation products found in stained areas of naturally aged samples with those formed during the induced staining procedure would give evidence of a relationship between the degradative mechanism and the unfavourable environmental conditions experienced in a humid climate.

Two sample groups were thus established. Sample Group 1 comprised a collection of seven book papers with evidence of typical cellulosic discolouration. The study sample of books was assembled in the late nineteenth and early twentieth century in the Verulam Library, on the North Coast of KwaZuluNatal. The collection was subsequently discarded and relocated to the Campbell Collections and stored in the attic of the house at Muckleneuk on the Berea, a suburb of Durban, also on the southeast African coast. Extreme climatic conditions experienced in the untempered attic space over a period of 30 years had given rise to marked cellulosic staining,

as was also sporadically evidenced in volumes in the rare collection of the Campbell Collections of the University of Natal. Since the Verulam collection did not comprise part of the rare Africana book collection, it provided an suitable experimental sample stock.

Sample Group 2 of artificially aged papers comprised two stacks of Whatman 5 filter paper. This choice of filter paper for the induced deterioration by artificial ageing was made in compliance with its previous use as a representative paper sample for wet/dry interface investigations. (DUPONT, 1996a; EUSMAN, 1995)

To provide a realistic comparison between the two sample groups, the two stacks of filter paper were aged according to ISO 5630-3.¹ Moist oven ageing is reported to measure the effect of both acid hydrolysis and oxidation. (PHILLIP, BAUDISCH, & RUSCHER, 1969) These were transferred to the climate cupboard, to which were added further comparable samples representing a variety of fibre furnish, pH value, deacidification and history of previous ageing. The value of extending the representative analytical sample was felt to lie in determining possible recommendations for conservation treatment of oxidised material.

1

ISO 5630-3 specifies the procedure for moist oven ageing at 80°C and 65%RH for 30 days. (CASEY, 1967; KRAUSE, 1991)

A simulation of natural local climatic conditions was followed in a dynamic climate ageing procedure, in an attempt to achieve the desired result of induced staining within a reasonable period of time. The selection of simulated environmental conditions was based on representative meteorological records. The analytical techniques applied in the identification of an oxidative reaction in the two sample groups and their comparison are presented in this Chapter, while the assembled data are presented in Chapter 5, with an interpretation thereof.

4.2 ANALYTICAL PROCEDURE

The analytical procedure was developed to enable a comparison of evidence of oxidative degradation in naturally aged samples with that found in samples subjected to dynamic artificial ageing simulating the natural ambient conditions.

Sample Group 1 comprised a selection of naturally aged archival papers of known provenance. This series was labelled NA001-NA007.

Sample Group 2 comprised a series of artificially aged papers of simulated deterioration, labelled AA001-AA004.

4.2.1 PRE-CONDITIONING IN SIMULATION OF NATURAL DETERIORATION

Naturally aged samples were selected on the basis of evidence of cellulosic staining. Simulation of natural deterioration was achieved using a second comparative Sample Group prepared in the following manner:

- 1 Whatman 5 filter paper was selected as a representative sample for Group 2, based on its reported previous use in similar experimentation.
- 2 Two 500 g sample stacks were prepared to represent pages of a heavy volume, one as a gravimetric control, the other for analytical investigation of simulated deterioration, designated Sample AA001. Testing in stacks rather than free-hanging single sheets was employed to induce the capillary force of a substantial moisture reservoir, based on the findings of previous research, presented in 3.3.2 below. (DESSAUER, 1989; SHAHANI, 1996; SHAHANI, HENGEMILE, & WEBERG, 1993)
- 3 The simulated deterioration sample stack, Sample AA001, was made up of five bundles of 100 g each, prepared to simulate damage that might constitute a wet/dry interface at sites of moisture accumulation occurring under normal storage conditions. Water staining, uneven

paste and glue application, dog-ear folds and tears were separately introduced to each of separate bundles. Representation of particulate nuclei for moisture condensation in marine climate was achieved by sprinkling the fifth bundle with a saturated solution of sodium chloride (NaCl).

- 4 Accelerated ageing of both the sample stack and control stack was conducted according to ISO 5630-3.

4.2.2 SORPTION CABINET PROCEDURES

Sample Group 2 was subsequently submitted to an additional dynamic simulated ageing programme:

- 1 Sample Group 2 was extended to include further samples, as indicated above, designated Samples AA002-AA004, stacked separately on 6mm plate glass tiles within the climate cabinet, each weighted down with plate glass strips.
- 2 Values of 10°C / 90%RH and 30°C / 40%RH were initially programmed into the climate cupboard as reflecting the extremities of environmental conditions likely to be encountered in the natural ageing process. These were then adjusted to a constant 30°C and a

fluctuation between 30%RH and 90%RH, to increase the rate of induced degradation for experimental purposes.

- 3 The values were programmed into the climate cabinet to fluctuate for thirty days, initially in 24 hour cycles, and then in 8 hourly cycles for 30 days. The cyclical duration was shortened to increase the effect of a dynamic simulated climate ageing programme.
- 4 The change in equilibrium moisture content was monitored by recording the mass of the control sample at the end of each cycle change during of the climate cupboard procedures. The slope of EMC for the control sample was derived from the data log of temperature, relative humidity (RH) and gravimetric mass.

4.2.3 THE COMPARISON OF NATURALLY AND ARTIFICIALLY AGED SAMPLES

A comparative analysis of the two sample groups was conducted by the following analytical techniques to determine the existence of a relationship between the oxidative degradation mechanism and the unfavourable environmental conditions experienced in a humid climate:

- 1 Fourier Transform Infrared (FTIR) analysis
Measurement of both sample groups to follow oxidative changes in

the cellulose molecule by increase in absorbance due to carbonyl and carboxyl groups. The absorption band at 1720 cm^{-1} is characteristic of the carbonyl function of the carboxyl groups.

2 Methylene Blue Reagent Staining

Determination of the concentration of carboxylic groups at the wet/dry interface by increased methylene blue absorption.

3 Hydrogen Peroxide Reagent Staining

Determination of hydrogen peroxide formation as an indication of oxidation at the paper surface by peroxide reagent, Naphtorin.

The data supporting the comparative analysis of the two sample groups is presented in Chapter 5.

4.3 THE SIMULATION OF NATURAL AGEING CONDITIONS UNDER AN EXPERIMENTAL TEST ENVIRONMENT

For the experimental test environment accurately to simulate natural ageing conditions, the aim of the analytical procedure was to speed up the reactions produced in that environment without producing potentially new reactions. It was the intention of the author to monitor the development of the oxidative reaction under experimental test conditions comparable with natural conditions. No attempt was made to determine the change in physical

properties, such as tear resistance or tensile strength, which, although commonly used in the study of paper deterioration, may be dependent on more than one reaction, primarily acid hydrolysis. (ERHARDT & MECKLENBERG, 1994)

Ageing below 60°C is thought to be too slow for experimental work, (LUNER, 1976) and little evidence of low temperature ageing could be found, with a notable exception. (CARDAMONE, 1989) In order to simulate an environment that would speed up the reaction in promoting molecular mobility, the sample was therefore pre-conditioned by moist oven ageing, according to ISO 5630-3, in order to relate the sample material to the general condition of the book stock. Accelerated ageing, normally conducted at a minimum of 80°C, was applied in the preliminary ageing procedure. In selecting a low temperature value for the dynamic ageing procedure, the effect of temperature on the sample was effectively excluded, clearly indicating the humidity dependence of the induced reaction.

Consequently, a realistic comparison between Sample Groups 1 & 2 was envisaged. The oxidative degradation process was then induced by fluctuating the environmental conditions to the extremities of average climatic conditions as recorded in the meteorological records in a dynamic ageing cycle, rather than by the conventional static standard accelerated ageing procedure. The intention was to induce the oxidative degradation

mechanism under the same conditions to which the results of the investigation could be applied.

4.3.1 PREPARATION OF NATURAL AND ARTIFICIALLY AGED SAMPLE GROUPS

For the purposes of this study, Sample Group 2 was subjected to two types of ageing process, to best relate the simulated deterioration with that found in naturally aged Sample Group 1. The ISO moist oven accelerated ageing process was first employed to provide an appropriate age comparison between the two sample groups. This comprised a 30 day cycle at 80°C and 65%RH. Sample Group 2 was then further subjected to the dynamic artificial ageing process designed for this project to induce the degradation noted in naturally aged samples.

All samples were measured for pH and lignin content, commonly accepted indicators of paper permanence. The pH was measured using a Knick 761 Calimatic pH meter and an Ingold 453-S7 flat electrode. The average of three consecutive readings was recorded. The detection of lignin was conducted using the phloroglucinol method according to Browning. (BROWNING, 1969) It is acknowledged that both these methods provide an approximation of the respective values. They were selected for the purpose of this study as being widely applicable, and generally available in conservation facilities of libraries and archives.

The antioxidant effect of lignin was considered to be of interest, and the measurement of lignin as a possible variable in oxidative degradation was recorded in the preparation of samples for this analysis. The solution of phloroglucinol stained only the artificially aged sample AA003 positively for lignin. The phloroglucinol stain on naturally aged sample NA005, was inconclusive, and the presence of lignin was confirmed microscopically, with an iodine stain. The Herzberg stain confirmed the presence of lignin in an unbleached softwood chemical pulp. (BROWNING, 1969) The previous history of each sample was recorded. The naturally aged sample group was described by the following tabulation:

NO	DESCRIPTION	LIGNIN	pH	NOTES
NA 001	B. D. W. RAMSAY (1882). <i>Rough recollections of military service and society</i> . Edinburgh: William Blackwood and Sons.	no	4.87	stained at dog-eared corner
NA 002	E. B. BROWN (1884). <i>In memoriam: James Baldwin Brown</i> . London: Clarke.	no	4.45	frontispiece stained. decorated edge.
NA 003	S. L. HINDE (1897). <i>The fall of the Congo Arabs</i> . London: Methuen.	no	4.64	lacks size
NA 004	- (1822). <i>The state of the nation as at the commencement of the year 1822...</i> London: Hatchard.	no	5.50	rag, soft handle
NA 005	J. ASHTON (1886). <i>The dawn of the XIXth century in England</i> . London: Fisher Unwin.	yes	4.92	unbleached softwood, brittle
NA 006	G. HOOPER (1887). <i>The campaign of Sedan</i> . London: George Bell.	no	4.56	
NA 007	G. BANCROFT (1864). <i>History of the United States from the discovery of the American continent</i> . Boston: Little Brown.	no	5.00	rag, soft handle

Table 4.1 Naturally aged Sample Group 1

Preconditioning of the comparative Sample Group 2 was achieved by accelerated ageing conducted using the following sample material:

Control: 500 sheets Whatman 5 125 mm diameter, as a gravimetric control.

Sample 1: 500 sheets Whatman 5 125 mm diameter simulated deterioration, comprising a stack of five separate bundles:

100 sheets water stained. Direct water staining was induced to represent localised conservation treatment, by applying a drop of water at four points on alternate sheets. The bundle was marked "1/W".

100 sheets folded and torn, to represent physical damage commonly encountered in the bookstock, and generally associated with evidence of cellulosic staining. Folded sheets at intervals throughout the bundle represented physical deterioration, tears, dog-eared corners, etc. and were marked "1/F".

100 sheets partially pasted with Carboxymethyl cellulose (CMC), a cellulose derivative paste. Conservation treatment was represented in the application to alternate sheets of CMC

in two parallel lines, as in an uneven paste application, where airpockets are formed when works of art on paper are improperly laid down on a support sheet. The discolouration that becomes evident in the area of such airpockets was felt to be a result of the wet/dry interface created in the uneven paste application. The bundle was marked "1/CMC".

100 sheets partially glued with polyvinyl acrylate, an acrylic glue commonly applied in bookbinding. The application of polyvinyl acrylate glue in a square formation was intended to represent similar use to that of CMC. Uneven discolouration has frequently been noted on the pastedown of unevenly glued endpapers. This bundle was marked "1/PVAC".

100 sheets in simulation of a marine climate. Representation of particulate nuclei for moisture condensation in marine climate was achieved by sprinkling the fifth bundle with a saturated solution of sodium chloride, marked "1/NaCl".

An additional three samples were added to Sample Group 2, to increase the variety of fibre furnish included in the dynamic simulated ageing programme. Sample Group 2 was tabulated as follows:

NO.	DESCRIPTION	LIGNIN	pH	NOTES
Control	Whatman 5 filter paper 125 mm \varnothing (500 sheet stack)	no	7.16	cellulose
AA01	Whatman 5 filter paper 125 mm \varnothing (500 sheet stack)	no	7.16	cellulose
AA02	Filter paper U/S	no	7.30	cellulose
AA03	Bundeshaushaltsplan 1959	yes	4.05	brittle
AA04	Zanders bond 53.5 g (70% longfibre: (50/50 pine/spruce) and 30% short fibre: beech/ eucalyptus)	no	5.40	acid sized wood-free sulfate

Table 4.2 Sample Group 2 for inclusion in dynamic simulated ageing programme

Samples were selected that had been exposed to either, or both accelerated ageing and non-aqueous deacidification, to enable a comparison between the effects of these treatments and to provide a realistic sample of the previous history of a library or archival collection. Care was taken in the selection samples deacidified by the Batelle process, which was unlikely to cause tidelines or possibly result in a previous aqueous extraction of degradation products. The previous history of samples was recorded and samples labelled A-D according to the following tabulation:

TYPE	ACCELERATED AGEING AT 80°C AND 65%RH (30 DAYS)	DEACIDIFICATION BY BATELLE
A	YES	NO
B	NO	NO
C	YES	YES
D	NO	YES

Table 4.3 Previous history of dynamic aged samples

The stack of filter papers comprising Sample AA001 was given preparatory treatments in simulation of the nature of damage associated by empirical evidence with cellulosic staining. Samples were marked as follows:

- /W application of water to induce staining
- /F folds and tears to represent areas of physical damage
- /C partial pasting with CMC (carboxymethylcellulose paste)
- /PVAC partial pasting with polyvinyl acrylic glue
- /NaCl sodium chloride to represent marine climate

Further samples selected for dynamic climate cabinet ageing, (AA02-AA04) were treated in a similar manner and labelled accordingly. The range of samples included in the climate cabinet therefore represented a variety of previous histories and preconditioning treatments, as might be commonly encountered in the holdings of the library or archive. The five sample stacks were each grouped on a plate glass tile, and subdivided with sheets of Melinex Type O polyester. Each stack was weighted against the air turbulence in the climate cabinet with a 4-mm wide strip of plate glass. The previous history of the samples comprising each stack were marked as tabulated below:

SAMPLE	HISTORY	/WATER	/CMC	/FOLDS	/NaCl
Control	A
AA01	A	x	x	x	x
AA02	A
AA02	B	x	x	x	x
AA02	C	x	x	x	x
AA02	D	x	x	x	x
AA03	A	x	x	x	x
AA03	B	x	x	x	x
AA03	C	x	x	x	x
AA03	D
AA04	A	x	x	x	x
AA04	B	x	x	x	x
AA04	C	x	x	x	x
AA04	D

Table 4.4 Climate cabinet sample table

4.3.2 SIMULATION OF AMBIENT ENVIRONMENTAL CONDITIONS

In furthering an understanding of the interactions taking place in the atmosphere and in the analysis thereof in their effect on problems posed in the conservation of library and archival materials, this study relies on statistical meteorological data in deriving information about the local climate. A tabulation of meteorological data was used as the basis for the selection of environmental parameters in the dynamic ageing process by fluctuating relative humidity. The data presented in Appendix B is a collation of statistical meteorological data for Durban from 1950-1984, based on detailed data prepared by the Weather Bureau. (Climate..., 1986)

Southern Tropical Africa is considered to extend from the equator to about 25°S in the south east, with variations caused by seasonal movements of the Inter Tropical Convergence Zone (ITCZ) extending the limit closer to 20°S in the summer. The coastal city of Durban lies at the co-ordinate 29°58'S and 30°57'E. It is therefore to be expected that weather in the region is characterised by a number of features associated primarily with tropical climates as a result of the general circulation of the southern hemisphere. (PRESTON-WHYTE & TYSON, 1988; VAN HEERDEN & HURRY, 1987)

Features of ambient climatic conditions were described in 1.3.1 above. Of specific interest are the minimal annual range in temperature from 10°C to

30°C, and a general high humidity, with a recorded value of 90%RH in the summer, accompanied by an abrupt seasonal drop in humidity in the short winter months, to a recorded low of 40%RH.

Consideration was given to the psychrometric relations of environmental conditions indicated in the meteorological data. Values of 10°C / 90%RH and 30°C / 40%RH were tested in the climate cupboard as reflecting the extremities of environmental conditions likely to be encountered in the natural ageing process. These conditions were allowed to run for five days, and the equilibrium moisture content measured at each cycle. The resulting difference indicated a minimal transport of 0.004 g moisture through the paper samples. It was decided therefore to increase the variation in absolute humidity within the climate cupboard between 0.003 kg and 0.023 kg moisture/kg of dry air. The temperature was thus fixed at 30°C and the relative humidity set to fluctuate from 90-30%RH over a 24 hour cycle, to allow adequate time for the samples to reach an equilibrium at each of the extreme values. While these values exceed the natural conditions slightly in respect of average temperature, which is recorded as 25.2°C, they are considered representative of the ambient conditions experienced in libraries and archives in subtropical climatic regions.

The values of temperature and humidity selected were programmed into the climate cabinet to represent the extreme ambient at a constant 30°C and a fluctuation between 30%RH and 90%RH for maximum measurable change

in equilibrium moisture content (EMC) under controlled conditions within the limited experimental time frame. In natural ageing, the effects of moisture transportation through the sample material would be considerably slower within the constraints of the psychrometric relationship between temperature and humidity. By maintaining a constant temperature level and fluctuating the relative humidity, the experimental procedure was specifically recording the effect of the fluctuating moisture content of the paper samples.

The cycle was reduced to eight hours to speed up the possible reaction, while continuing to monitor equilibrium moisture content. The selected values were changed abruptly over a fifteen minute period, as a slow change was considered to induce little effect, as noted in the practical experience of brown line formation during drying of material subjected to conservation treatment. (BANIK, 1998) The shorter cycle also conformed with the research findings of the Conservation Research Laboratory, in that minimal degradation was noted over slow seasonal changes in environment. (McCORMICK-GOODHART, 1996; MICHALSKI, 1996)

4.3.2.1 THE ENVIRONMENTAL CONTROL CHAMBER

The environmental cabinet used in the experimental investigation was of the model Heraeus Vötsch HC0020. The environmental limits attainable in the cabinet are 10 - 90°C and 30 - 95 % RH, with a dewpoint range of 5 - 88.7°C. The chamber comprised an area of 1 m³, with an internal height of

1000 mm, wall sensors 100 mm apart, and three adjustable wire shelves.

(See Figure 4.1) The environmental control feature of this cabinet is either electronically programmable or manually set. (Hereaus, 1992)

The programmes devised for the experimental procedure were applied in the sequence E1.1 followed by E1.2.



Figure 4.1 The environmental control chamber

Level	Time/ min	Sensor	Value	Loop	Wait	Notes
0	0	0	30°C	0	1	Level held until cabinet has reached value
1	0	1	75%RH	0	1	Level held until cabinet has reached value
2	-	-	-	40	-	Number of cycles
3	15	1	90%RH	0	0	Level changed within stated time
4	1425	-	-	-	1	Level held for stated time
5	15	1	30%RH	0	0	Level changed within stated time
6	1425	-	-	-	1	Level held for stated time
7	-	-	-	-1	-	Cycle ends

Table 4.5 Environmental control chamber programme E1.1: Duration: 5 days

Level	Time/ min	Sensor	Value	Loop	Wait	Notes
0	0	0	30°C	0	1	Level held until cabinet has reached value
1	0	1	75%RH	0	1	Level held until cabinet has reached value
2	-	-	-	120	-	Number of cycles
3	15	1	90%RH	0	0	Level changed within stated time
4	465	-	-	-	1	Level held for stated time
5	15	1	30%RH	0	0	Level changed within stated time
6	465	-	-	-	1	Level held for stated time
7	-	-	-	-1	-	Cycle ends

Table 4.6 Environmental control chamber programme E1.2 : Duration: 50 days

4.3.3 DYNAMIC SIMULATED CLIMATE AGEING PROGRAMME

The preliminary masses of the equivalent Sample Group 2 stacks were recorded as :

Control stack: 653.18 g

Sample 1 (simulated deterioration stack): 664.57 g

Both sample stacks were subjected to moist oven ageing at 80°C and 65%RH, for a period of 30 days, before being transferred to the climate cabinet, for subsequent dynamic ageing under fluctuating environmental conditions. The mass of the control stack was used in the gravimetric record of moisture content, measured at each value change during the climate cupboard operating procedure.

The equilibrium moisture content measured at the extent of each cycle is presented in 4.6.3 below. The measure of the mass of water absorbed by the paper sample under repeated fluctuating environmental conditions, the moisture regain, was calculated as the difference between the sample mass and the mass of dry specimen of the control sample at the end of each climate cabinet cycle.

The resultant moisture regain is defined as:

$$\text{Moisture regain} = \frac{\text{mass of absorbed water in specimen}}{\text{mass of dry specimen}}$$

The mass of the dry specimen was determined by placing a stack of Whatman 5 similar in mass to the control stack in the drying oven for 24 hours. The resultant mass of 551 g was assumed to contain a residual moisture content of 0.5%. (CORTE, 1982) Since the dry mass and previous history of other samples was not available, the %EMC for the control sample was calculated as a representative indication of moisture regain for all samples. (See Table 4.7)

Sample	C	AA001	AA002	AA003	AA004
Mass of dry sample stack (105°C/24 h)/g	551.0				
Cycle 1%EMC	0.5%				
Mass at 0.0%EMC/g	548.2				
Cycle 2 Ambient: 25°/75%RH					
Board/g	47.5	47.5			
Sample& board/g	653.2	664.6			
Sample mass/g	605.7	617.1			
%EMC	10.48%				
Cycle 3 Accelerated ageing 80°C/ 65%RH (30 days)					
Glass/g	482.9	467.8	450.3	483.1	497.2
Sample & glass /g	1068.5	1057.1	520.5	606.2	697.5
Sample mass/g	585.2	589.4	70.2	123.1	200.3
%EMC	6.75%				
Cycle 4 Climate cabinet: 30°C/ 90%RH (24 h)					
Sample & glass/g	1093,1	1073,8	524,4	611,9	706,1
Sample mass/g	610,2	606,0	74,1	128,8	208,9
%EMC	11.31%				
Cycle 5 Climate cabinet: 30°C/ 30%RH (24 h)					

Sample & glass/g	1074.1	1055.1	519.9	606.2	697.4
Sample mass/g	591.2	587.3	69.6	123.1	200.2
%EMC	7.81%
Cycle 6					
Climate cabinet: 30° / 90%RH (8 h)					
Sample & glass/g	1093.3	1074.6	523.9	611.5	705.6
Sample mass/g	610.4	606.8	73.6	128.4	208.4
%EMC	11.35%
Cycle 7					
Climate cabinet: 30°C / 30%RH(8 h)					
Sample & glass/g	1079.7	1061.1	520.3	607.0	699.1
Sample mass/g	596.8	593.3	70.0	123.9	201.9
%EMC	8.87%
Cycle 8					
Climate cabinet: 30°C / 90%RH(16 h)					
Sample & glass/g	1089.4	1070.6	523.4	611.0	704.6
Glass/g	482.9	467.8	450.3	483.1	497.2
Sample mass/g	606.5	602.8	73.1	127.9	207.4
% EMC	10.63%
Cycle 9					
Climate cabinet: 30°C / 30% RH (8 h)					
Sample & glass/g	1078.3	1059.8	520.3	606.9	698.8
Sample mass/g	595.4	592.0	70.0	123.8	201.6
% EMC	8.61%

Cycle 10 Climate cabinet: 30° / 30%RH(8 h)					
Sample & glass/g	1078.1	1059.5	520.3	606.9	698.6
Sample mass/g	595.2	591.7	70.0	123.8	201.4
% EMC	8.57%
Cycle 11 Climate cabinet: 30°C / 30%RH (8 h)					
Sample & glass/g	1076.9	1057.0	520.2	606.8	698.5
Sample mass/g	594	589.2	69.9	123.7	201.3
% EMC	8.35%

Table 4.7 Gravimetric record of equilibrium moisture content

The plot of moisture regain was prepared from the following data compiled from the gravimetric record of equilibrium moisture content. Cycles of even number recording absorption and cycles of odd number recording desorption:

	Temp/°C	RH%	% EMC
Cycle 1	105	0	0.5
Cycle 2	25	75	10.48
Cycle 3	80	65	6.75
Cycle 4	30	90	11.31
Cycle 5	30	30	7.81
Cycle 6	30	90	11.35
Cycle 7	30	30	8.87
Cycle 8	30	90	10.63
Cycle 9	30	30	8.61
Cycle 10	30	30	8.57
Cycle 11	30	30	8.35

Table 4.8 Summary of moisture regain

Important research by Hon established two significant factors with regard to moisture content. Firstly, that a moisture content in the region of 5-7% leads to a decrease in radical formation, but when the moisture content is higher or lower, radical formation is enhanced. The inhibitory effect of the 5-7% range is believed to be related to the second factor, the almost exclusive radical formation within the amorphous region, and since 5-7% EMC

represents the quasi-crystalline region of chemically bound water, free radical formation is restricted in this region. At a higher EMC, free water may contribute to a swelling effect, opening up the amorphous regions which enhances free radical formation. (HON, 1975) The moisture regain data, given in Table 4.8, reveal a consistently excessive moisture content in the range of 8-11.5 % under the environmental conditions representing ambient conditions, thus fulfilling the requirement for enhanced free radical formation.

The typical hysteresis effect was noted in the resultant chart (Figure 4.2), with diminishing absorption and desorption values, with the desorption values decreasing at a faster rate. It is in the desorption cycle that evaporation of water vapour takes place, and the wet/dry interface is formed. In effect, the EMC value did not tail off in cycles 9-11, but reflects the gravimetric record measured at dry cycles only. From that point samples were periodically removed from the climate cabinet at the end of the dry cycle for analytical investigation. Cycles 9-11 nonetheless reflect the continuing decrease in EMC with ongoing fluctuations. The table of moisture regain provided the basis for investigation of the change in cellulose structure under fluctuating environmental conditions, reflected in the crystallinity of the control sample throughout the experimental test procedure. The result of this investigation will be presented in Chapter 5.

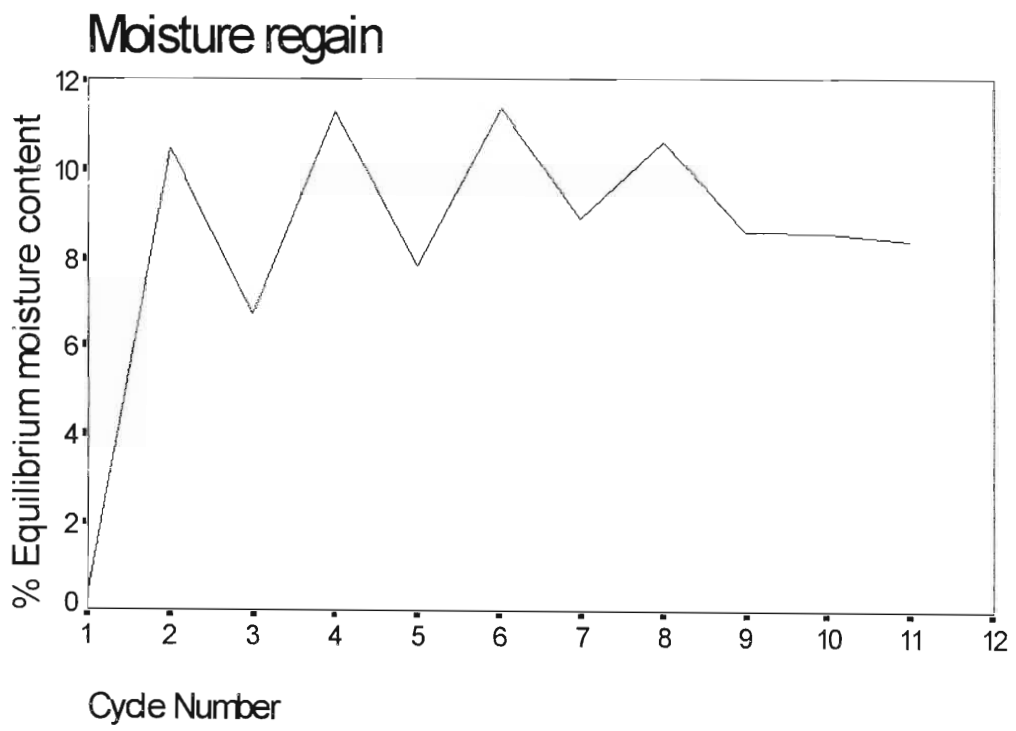


Figure 4.2 Moisture regain

4.4 ANALYTICAL TECHNIQUES APPLIED IN THE IDENTIFICATION OF AN OXIDATIVE REACTION UNDER EXPERIMENTAL CONDITIONS

A comparison of the two sample groups was conducted by various analytical and reagent staining techniques to determine the relationship between oxidation at the wet/dry interface and the climatic conditions selected in the dynamic simulated climate ageing programme. In the Fourier transform infrared (FTIR) analysis various spectroscopic methods were utilised, including attenuated total reflectance (ATR), FTIR microscopy and diffuse reflectance (DRIFT). In addition Raman spectroscopy was also used.

Methylene blue reagent staining and hydrogen peroxide reagent staining provided confirmation of these analytical findings. Further analytical techniques of mass spectrometry by fast atomic bombardment and ultraviolet fluorescence were also investigated.

4.4.1 COMPARISON BY FOURIER TRANSFORM INFRARED (FTIR) SPECTROSCOPY OF NATURALLY AND ARTIFICIALLY AGED SAMPLES

The spectra of naturally and artificially aged samples were measured and compared to follow the progression of oxidative degradation, noting the

development of the absorption band at 1720 cm^{-1} characteristic of the carbonyl function of the carboxyl groups.

The naturally aged samples comprised seven papers selected on the basis of discolouration from a variety of fibre furnish types, in order to determine the susceptibility of chemical degradation in specific papers, both rag and groundwood.

The artificially aged samples comprised two pre-conditioned sample stacks of Whatman 5 filter paper, to which were added a further four papers of various fibre furnish, samples of which had been previously deacidified and/or previously subjected to heat ageing. The control and five samples were subjected to the dynamic simulated climate ageing programme.

4.4.1.1 FTIR - ATR SPECTRAL ANALYSIS OF NATURALLY AGED SAMPLES

Initial attempts to identify oxidative degradation determined by the carbonyl function of the carboxyl groups were conducted by FTIR, using internal reflection. A Spectra-Tech FTIR spectrometer was used with a Baseline HATR (Horizontal Attenuated Total Reflectance) accessory. Use of the internal reflection technique is a standard method in the collection of infrared spectra of solid material, is well documented in conservation studies, and is

recommended for the study of surface reactions such as oxidation or water absorption. (BAKER, VON ENDT, HOPWOOD, & ERHARDT, 1988; CAIN & KALASINSKY, 1983; CARDAMONE, 1991; HON, 1986)

The sample of paper was placed in contact with a zinc selenide (ZnSe) crystal of high refractive index and infrared radiation reflected in a zig-zag pattern between sample and crystal. An evanescent wave of the internally reflected radiation penetrated the sample surface, and the intensity of the signal produced by such multiple reflections was much stronger than that produced by a single reflection. (HATR, n.d.)

The ATR spectra of naturally aged samples compared stained and unstained areas of the same page, labelled SP (stained paper) and CP (clear paper) respectively. The same group of peaks were evident in the 1700-1600 cm^{-1} (C=O stretching) region, which may easily be confused with water vapour. A negative peak was often noted at 2365 cm^{-1} , typically indicating the presence of CO_2 , as the sampling chamber had not been purged with dry air. This inconclusive result indicated only that samples were indeed of deteriorated cellulose, with the only identifiable end products being H_2O and CO_2 , as was to be expected. Cardamone had reported that during low temperature degradation of cellulose the glycosyl units, C(1) -O-C(4'), decompose, with the formation of water, carbon monoxide and carbon dioxide. (CARDAMONE, 1989)

The ATR spectra indicate that the technique is not sensitive enough to distinguish between stained and unstained paper samples, nor between aged and new paper. Only a slight change in intensity of peaks was detected, indicating the quality of detection of reflected light, as no quantitative dependence can be attributed to intensity. This poor differentiation between stained and unstained paper could be due to the fibrous nature of the sample, and consequent poor surface contact with the ATR crystal. Furthermore, the sample was not homogenous throughout. The sample size was determined by the relatively large size of the crystal, measuring 6.5 x 1.5 cm. Because of the nature of the isolated areas of staining, the sample included staining of different degrees, with a relatively small area of dark discolouration, less than 1 cm² of the total sample surface area. Previous attempts at FTIR analysis reported in the literature for identification of degradation products had used ground samples in KBr pellets, possibly to overcome this problem, but had reported difficulty in sampling. (DUPONT, 1996a; HOFENK DE GRAAFF, 1994) Reports of similar analysis had indicated that this result was to be expected, as spectroscopic characterisation of cellulose in the solid state is complicated by problems associated with surface irregularity, which must be balanced against the destruction of the sample in the preparation of KBr pellets, incorporating the bulk of the material and not just the surface species. (CARDAMONE, GOULD, & GORDON, 1987) The FTIR-ATR spectra were therefore not considered for analytical interpretation.

On the basis of this result it was decided to extend the range of scale to 4000 cm^{-1} , to include the OH stretching bands at $3800\text{ -}3200\text{ cm}^{-1}$. In that region it would be possible to evaluate the ratio of amorphous/crystalline regions, by exposing the sample to deuterium oxide, D_2O (heavy water), before spectral analysis, thus displacing bands associated with water absorption, which occur in the same critical region from $1800\text{ -}1500\text{ cm}^{-1}$ as the oxidative degradation products are expected to occur. The method of deuteration, as described by Mann and Marrinan, was conducted in the vapour phase by bubbling dry nitrogen over D_2O , then passing the moist gas over the sample for one hour. (MANN & MARRINAN, 1956)

Infrared microscopy is described in 4.4.1.3 below. The infrared spectra of deuterated samples show a dramatic shift of the OD band at 2500 cm^{-1} , evident in all IR microscope spectra, relative to the OH band at 3400 cm^{-1} , demonstrating the process by which bound water was eliminated. The use of deuteration in the determination of the crystalline/amorphous ratio was not applied in this study, a crystallinity index was derived rather from the peak integration of selected band areas, described in 5.2.2 below.

4.4.1.2 RAMAN SPECTROSCOPY

Raman microscopy was conducted by Professor Sylvia Paul, of the Department of Chemistry, at the University of South Africa (Unisa) in March 1998. The naturally aged sample papers were submitted for comparison

with the results of FTIR-ATR spectroscopy.

Laser excited Raman spectroscopy was felt to offer some important advantages over infrared spectroscopy for structural interpretation of cellulose spectra. Firstly, the Raman microprobe allows spectra to be recorded from areas smaller than 1 mm², the structural homogeneity of the sample being markedly increased. Secondly, the highly polar bonds present in cellulose, which result in intense IR spectra, have weak Raman intensities. The weak Raman bands of water, therefore were not expected to interfere with the cellulose spectrum. (BLACKWELL, 1977; WILEY & ATALLA, 1987)

Raman spectra of areas of discolouration on the seven naturally aged papers uniformly indicated various CH stretching bands at 3000 cm⁻¹ and CO stretching bands at 1200 cm⁻¹. The most significant result was obtained from an area of discolouration on the naturally aged sample paper no. 2, which appeared microscopically to be an accretion, a speck of dust or pigment from the facing frontispiece, functioning as a point of moisture accumulation and therefore creating a wet/dry interface. An apparent relationship was noted between the peak at 1650 cm⁻¹ and the greater intensity in the 3250-3000 cm⁻¹ region. The concurrence of peaks in both these regions probably indicates the oxidation of some OH groups to acid groups in the formation of carboxylic acids at 3200 cm⁻¹ and possibly subsequent ionisation of the carboxylic acid to carboxylate ions, as

reflected in the regions 1610-1515 cm^{-1} and 1420-1300 cm^{-1} .

The limited available wavenumber range from 3500 to 50 cm^{-1} did not allow for the investigation of the OH stretching bond in the 3800- 3600 cm^{-1} range. No definitive conclusions could be drawn from the 1800-1600 cm^{-1} region.

4.4.1.3 FTIR MICROSCOPY

The measurement of naturally aged spectra was repeated using a Bruker IFS28 FTIR spectrometer with microscope attachment in transmission mode. The spectra were thus again acquired from a small, morphologically homogeneous domain.

A sample background was prepared using a watch glass of distilled water placed in proximity to eliminate ambient relative humidity by subtraction from subsequent measurements. Relative humidity in excess of 45% had presented the problem of rapid re-hydrogenation of deuterated samples on exposure, since these had been stored under nitrogen atmosphere until measurement. Comparative spectra were prepared of unstained areas, plotted in red and denoted as "clear"; stained areas, plotted in blue and deuterated samples in black, from the same paper. The IR microscope spectra indicate the consistent presence of albeit weak peaks in the 1725 cm^{-1} region.

A series of comparative spectra was measured on Sample 1 of the second sample group comprising Whatman filter paper, which had been aged at 80°C and 65%RH for 30 days, with subsequent dynamic ageing in the climate cabinet for a further 30 days. Despite visual evidence of discolouration, this series of spectra did not show evidence of similar peaks in the 1800-1600 cm⁻¹ region, except in the case of the deuterated sample.

Results of the preliminary FTIR analysis by ATR, and FTIR microscopy and by Raman microscopy are therefore not conclusive to this study, and were not considered for analytical interpretation.

4.4.1.4 DRIFT SPECTROSCOPY

The difficulty of overlapping water bands, which might obscure the formation of the carbonyl function of the carboxyl group in the critical region was overcome by repeating the measurements using a DRIFT cell attachment. The background was measured using a pan of KBr powder, upon which the paper samples were laid for measurement. The exclusion of water vapour was achieved by thoroughly flushing the chamber for five minutes prior to each measurement, using a stream of nitrogen passed over silica gel.

The problem of overlapping bands was addressed further in applying deconvolution to the spectra, using the second derivate. In the application of FTIR to paper analysis, Calvini had reported a similar difficulty that, while

heterogeneous substances can be easily detected, the investigation of the damage suffered by cellulose is often indicated by only slight modification of the spectrum. With the relevant information of the absorption bands of oxidised and unsaturated groups crowded in a small range of frequency 1800-1500 cm^{-1} , the strong absorption of water near 1630 cm^{-1} often masks the underlying structure of these bands . (CALVINI & MARTINELLI, 1990)

The second derivate evaluation was obtained by digital computation afforded by the peak editor in the sophisticated FTIR Opus software, based on the complex mathematical theory of Savitzky and Golay, allowing the automatic smoothing and differentiation of data. (SAVITZKY & GOLAY, 1964) A 9-point smoothing procedure was selected, and peaks identified by the second derivative. The selection thus attained was indicated on the enlarged spectrum of each sample, and is presented in Chapter 5.

4.4.2 COMPARATIVE IDENTIFICATION OF OXIDATIVE DEGRADATION BY CHEMICAL REAGENT

The spectroscopic measurement of paper samples was supported analytically in the use of chemical reagent staining to compare naturally and artificially aged sample groups.

4.4.2.1 DETERMINATION OF AN INCREASED CONCENTRATION OF CARBOXYLIC GROUPS.

The reagent staining procedure consistently reported in the literature on the investigation of the wet/dry interface is that of employing methylene blue in the determination of an increased concentration of carboxylic groups.

(BOGARTY, CAMPBELL, & APPEL, 1952; BONE, 1934; BONE & TURNER, 1950; DUPONT, 1996b; EUSMAN, 1995; FOX, 1965; HOFENK DE GRAAFF, VAN BOMMEL, & PORCK, 1993; KRAUSE, 1991; LIGTERINK, PORCK, & SMIT, 1991; MADARAS & TURNER, 1953; SCHAFFER, APPEL, & FORZIATI, 1955; WILLIAMS & SHAW, 1991)

Methylene blue was therefore utilised in this study to test the hypothesis of oxidation at the wet/dry interface, resulting from fluctuating climatic conditions, against a reproducible standard. The method described in detail by Eusman was employed, whereby paper samples were immersed for two minutes in a 0.1% solution of methylene blue and rinsed for two hours. The staining was noted to diminish over time, and the presence of oxidative degradation products thus indicated was recorded photographically. The results indicated the concentration of carboxylic groups at areas of moisture accumulation, constituting a wet/dry interface. The reliance of the procedure on colour fidelity was cause for concern, and the most revealing samples were digitally scanned and these images are presented in Chapter 5 below.

4.4.2.2 DETERMINATION OF HYDROGEN PEROXIDE FORMATION

A final analytical procedure employed entailed the determination of the formation of hydrogen peroxide as an oxidation initiator at the wet/dry interface induced by climatic fluctuations. The monitoring of autoxidative degradation of paper was reported in the literature as being accomplished in the recording of the formation of hydrogen peroxide. The photographic technique, known as the Russell effect is recommended. (DANIELS, 1984; EUSMAN, 1994; LECKIE & WILLIAMS, 1994) The use of the technique was considered, but not adopted in this study because of the unavailability of supply of the unstabilised grade of photographic film required. The difficulty in applying the Russell effect was exacerbated by the transient nature of the formation and decomposition of hydrogen peroxide.

Previous research had also reported the use of the related Tollens' reagent, Naphthoresorincol, in the identification of glyconic acid as an oxidation product, as proof that the reaction had taken place. (HOFENK DE GRAAFF, 1994). It was decided to use the more direct chromatographic staining reagent as an indicator of hydrogen peroxide formation.

The selected peroxide reagent, Naphtorin (1-naphthol-N⁴-ethyl-N⁴-(2-ethylsulphonamidomethyl)-2-methyl-1,4-phenylenediamine) was prepared according to the literature. (See Figure 4.3)

The reagent was applied to the paper samples by spraying, so as not to create further possible tidelines, or to diffuse the concentration of hydrogen peroxide in an aqueous immersion, which might compromise the result of interpreting the formation of a wet/dry interface. The samples were dried under nitrogen flow. The resultant blue chromatographic reaction was immediately visible against a light pink background, providing supporting evidence of the reaction. The results were recorded photographically, and are presented for interpretation in Chapter 5.

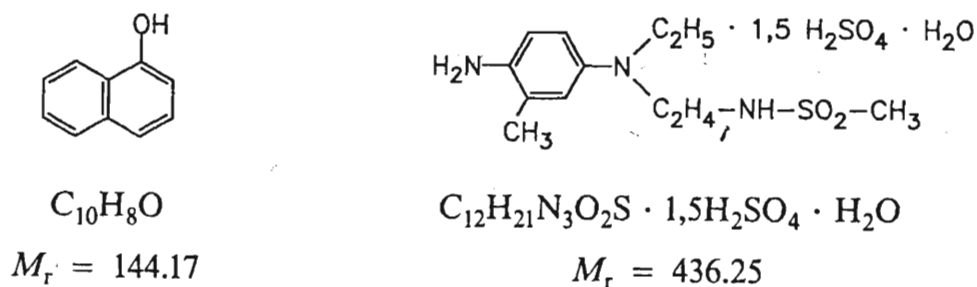


Figure 4.3 Naphtorin reagent (JORK, FUNK, FISCHER, & WIMMER, 1993 p.363)

4.4.3 FURTHER ANALYTICAL TECHNIQUES INVESTIGATED

A major concern of the researcher was the establishment of an analytical procedure that would accurately measure the oxidative degradation process, despite reported difficulty. Further analytical techniques applied with limited success in the course of this study are recorded in support of the investigation in the research process.

4.4.3.1 MASS SPECTROMETRY BY FAST ATOMIC BOMBARDMENT

Mass spectrometry by fast atomic bombardment was employed to identify the oxidative degradation products in an aqueous extraction of 1g in 10ml. Although the discolouration of the resulting extract was clearly visible, the concentration of degradation products in the given solution was apparently too low to be identified by the technique. While the decomposition of hydrogen peroxides is expected to lead to the formation of secondary oxidation products such as ketones, aldehydes, acids, alcohols, water and carbon dioxide, (MESROBIAN & TOBOLSKY, 1961; TOBOLSKY, METZ, & MESROBIAN, 1950) the inconclusive result of this analysis thus resembled that of the FTIR-ATR investigation of the same samples.

4.4.3.2 ULTRAVIOLET (UV) FLUORESCENCE

The use of UV fluorescence is reported in the investigation of cellulosic discolouration in the form of both fungal foxing and the chemical

modification of cellulose at the brown line at the wet/dry interface. It was a consideration that the reactivity resulting in UV fluorescence may link fungal foxing and chemical oxidation, and this technique was employed in this study in terms of that relationship.

Bone and Turner reported evidence that brown lines contain acid and carbonyl groups, fluoresce under UV and cause a localised drop in the degree of polymerisation of cellulose. They identified two types of degradation products at the wet/dry interface, the soluble, transportable, brown product fluorescent in UV, and the solid, non-transportable product with a higher methylene blue absorption than the original cellulose. Thus, while the brown discolouration and its fluorescence could be washed out, the degree of methylene blue absorption remained constant in washed samples. (BONE & TURNER, 1950)

Bogarty and Campbell drew the relationship between the microbiological and the chemical degradation processes in describing the preferential growth of the fungus *Aspergillus niger* along the brown line, indicating a chemical reaction preceding biological degradation. The generation of fluorescent material at the brown line was noted. (BOGARTY, et al., 1952)

An investigation of the inorganic components of foxing, conducted by Daniels and Meeks employed fluorescence in the near UV to aid in differentiation between organic (fungal) and inorganic (ferrous) causation.

(DANIELS & MEEKS, 1992) According to the classification devised by Cain & Miller, the ferrous “bullseye” staining fluoresces dark brown, and fungal “snowflake” staining fluoresces a uniform white or pale yellow. Those areas that are only visible in fluorescence were included in the latter group. (CAIN & MILLER, 1982) Eusman also employed both methylene blue absorption and fluorescence in the investigation of cellulose degradation at the wet/dry interface. (EUSMAN, 1995)

An explanation for the cause of fluorescence in the brown areas is offered by Angrick and Rewicki in the chemistry of browning reactions involving glucose and amino acids reacted together in the Maillard reaction. (ANGRICK & REWICKI, 1980) Browning is produced by the formation of unsaturated compounds with the presence of conjugated double bonds indicated by the fluorescence. Most chemical systems in which browning occurs contain carbonyl or potential carbonyl groups as the reducing sugars (sugars in their linear form), which are further transformed into unsaturated coloured compounds, including furan derivatives. (ANDERS, 1998 ; HODGE, 1953) This relationship to the Maillard reaction was also noted in connection with the formation mechanisms of foxing, and determined by the characteristic components of foxed areas, including reducing sugars in the form of L-malic acid, cello-oligosaccharides, γ -aminobutyric acid, aspartic acid, glutamic acid and ornithine. (ARAI, MATSUI, & MURAKITA, 1988)

This relationship indicated the necessity to apply the technique to the analytical process of this study. An investigation of UV fluorescence of naturally aged samples at the wavelengths of 254 nm and 360 nm revealed no fluorescence. Previous empirical experience of UV fluorescence in foxed areas indicated that the phenomenon might be transitory in nature, as in the case of chemiluminescence, applied in similar degradation studies. (GRATTAN, 1978; KELLY, WILLIAMS, MENDENHALL, & OGLE, 1979; MENDENHALL, 1977)

The examination of artificially aged samples under UV light revealed fluorescence leading to four observations:

- 1 Cloud-like areas of fluorescence were noted in areas corresponding to the position of the plate glass strip weighing down each sample stack against the turbulent airflow within the environmental control chamber. The point of capillary condensation at which the transport of moisture was blocked would thus appear to constitute a wet/dry interface.
- 2 Fluorescence was noted in a tideline formation at the edge of interleaving strips of 75 μm polyester (polyethylene terephthalate) film, supporting the above observation of chemical reactivity at sites of moisture accumulation. This led to the conclusion that the formation of a wet/dry interface in an archival storage situation is a potential hazard where non-porous storage materials are employed.

- 3 Strong fluorescence was evident at the tideline created at the point of evaporation at the edge of pasted areas and encircling the point of application of a sodium chloride solution. This observation was in keeping with those of Eusman in revealing cellulose degradation at the wet/dry interface.
- 4 No evidence of circular spotted areas of fluorescence was found that might correspond to the possible later formation of fungal foxing.

The evidence on which these observations were based was captured on Ektachrome Infrared film sensitive to UV. Unfortunately, due to technical inexperience in the utilisation of the unstable product, the result was unsuccessful. The fluorescence diminished and disappeared within thirty minutes, and these observations could not be considered as conclusive evidence. Confirmation thereof had to be sought in the conclusions based on other successful analytical techniques.

4.5 SUMMARY

An analytical procedure was developed to induce evidence of brown staining that might conform to the development of a wet/dry interface in response to humid environmental conditions. The investigation comprised three stages, the pre-conditioning of paper samples in simulation evidence of damage of ambient environmental conditions in an experimental test environment, followed by a comparison of the formation of oxidative degradation products found in stained areas of naturally aged samples with those resulting from the induced staining procedure. The aim of the analytical research project was to gather evidence in support of the hypothesis of relationship between the oxidative degradation mechanism and the unfavourable environmental conditions experienced in a humid climate.

The selection of environmental conditions for the dynamic simulated climatic ageing programme were therefore made on the basis of representative meteorological data on the region gathered over a thirty year period. The data revealed a small annual and diurnal temperature range, but extended excursions to high humidity with an abrupt annual fall in humidity in the short winter months. Values of temperature and humidity were programmed into the environmental control chamber to represent the fluctuations in the ambient conditions experienced in libraries and archives in subtropical climatic conditions. Similar effects might be extrapolated for paper-based

collections stored in other climatic regions where strong fluctuations in environmental conditions are expected.

Naturally aged samples with evidence of typical cellulosic staining were selected for comparison with samples prepared for artificial ageing and subsequent dynamic climate ageing in simulation of common physical features that might form sites of moisture accumulation and under fluctuating environmental conditions thus constituting a wet/dry interface. Such defects were considered to include the previous tideline formation resulting from water staining that might be accidental or as a result of localised conservation treatment. The application of paste and glue, representing the intentional introduction of moisture, was included as a potential source of damage as confirmation of the empirical evidence of uneven staining of artworks laid down unevenly to a backing board. Physical defects in the form of tears and dog-eared corners were introduced to the sample to represent areas that might hinder the transudational capillary flow. Such defects were noted to have an empirical relationship to areas of staining in the bookstock.

Following the dynamic simulated climate ageing procedure, comparisons were made between both naturally and artificially aged sample groups to determine the formation of similar oxidative degradation products as a result of the climate ageing process. A range of spectroscopic techniques applied yielded varying degrees of success in the measurement of the paper

samples. The most appropriate spectroscopic techniques for this task proved to be FTIR, using a DRIFT attachment. The acknowledged difficulty of measuring old paper successfully by FTIR spectroscopy, which detects only large changes of order, dictated the supplementary comparison of oxidative degradation by means of chemical reagent, as recommended by experienced researchers. (DANIELS, 1995)

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CHAPTER FIVE

PRESENTATION OF DATA AND ANALYSIS

5.1 INTRODUCTION

The experimental data were gathered in an analytical procedure comprising three stages. The first stage entailed sample preparation, to reproduce evidence of natural deterioration, and the second, the sorption cabinet procedures simulation of ambient environmental conditions experienced in a library and archival collection in a humid climate. The sample preparation and simulation of ambient conditions in a dynamic simulated ageing programme was described in Chapter 4. The third stage, presented in this chapter, comprised an analytical comparison of both naturally and artificially aged sample groups, following the formation of identifiable functional groups as evidence of oxidative degradation resulting from exposure to ambient environmental conditions.

The objectives of this analytical procedure were stated in Chapter 1:

- 1 To test the ambient range of environmental conditions to determine the effect of fluctuations in precipitating oxidative mechanisms of degradation.

- 2 To determine the significance of an oxidative reaction at the wet/dry interface in the manifestation of cellulosic discolouration known as foxing.
- 3 To evaluate the relationship between the fine structure of the cellulose substrate and its potential degradation by an oxidative mechanism.

Techniques employed in this experimental phase had been reported in previous research into the phenomenon of cellulosic discolouration at the wet/dry interface, and were applied here in the interest of providing reproducible results. (BOGARTY, CAMPBELL, & APPEL, 1952; BONE, 1934; EUSMAN, 1994; EUSMAN, 1995; FOX, 1965a; FOX, 1965b; HOFENK DE GRAAFF, 1994; LIGTERINK, PORCK, & SMIT, 1991; MADARAS & TURNER, 1953)

The evidence of this analytical investigation is presented in four data sets pertaining to the techniques applied in the identification of an oxidative reaction :

- 1 the spectroscopic measurement by DRIFT of the development of carbonyl groups of the cellulose molecule, as evidence of an oxidative mechanism of degradation precipitated by environmental conditions;

- 2 a crystallinity index determined from the calculation of the ratios of the band areas of selected absorption bands of the resulting spectra, reflecting the relationship between cellulose structure and its response to environmental conditions in an oxidative reaction;
- 3 supporting qualitative evidence of the formation of oxidative degradation products provided by chemical reagent testing in the increased methylene blue absorption; and
- 4 the determination by the chromatographic indicator, Naphtorin, of hydrogen peroxide formation under fluctuating environmental conditions, as an initiator of the autoxidation reaction.

The interpretation of the data is then presented in terms of :

- 1 evidence of an oxidative mechanism induced by unfavourable environmental conditions; and
- 2 the relationship between the paper morphology as determined by the crystalline / amorphous ratio and the oxidative mechanism of degradation.

The significance of these conclusions for the preservation management of libraries and archives is further discussed in Chapter 6.

5.2 EXPERIMENTAL DATA

Following the preparation of natural and artificially aged sample groups, the experimental data presented was acquired in the course of a ten week research scholarship period at the *Institut für Textil- und Faserchemie* (Textile and Fibre Chemistry) at the University of Stuttgart in Germany, from 15 May - 15 July 1998.

The autoxidation reaction carried by free radicals, initiated in the formation and decomposition of hydrogen peroxide is transitory, in the rate of the progression from initiation, propagation to termination. (HALLIWELL & GUTTERIDGE, 1985; MENDENHALL, 1977; MESROBIAN & TOBOLSKY, 1961) It was therefore important that the facilities available at the University of Stuttgart relevant to the experimentation provided the means both for the induction stage and the immediate analysis of samples thereafter. The environmental control chamber, Heraeus Vötsch HC0020, allowed for the simulation of ambient climatic conditions. The availability of a FTIR microscope (Bruker IFS28) and DRIFT cell, allowed for the subsequent spectrometric measurement of samples exposed to the simulated environment, providing valid data for analytical comparison with naturally aged samples. The abundant research on the topic of oxidation at the wet/dry interface conducted in the textile industry made the co-operation with the University of Stuttgart specifically relevant to this study.

5.2.1 DRIFT SPECTRA

The application of FTIR using reflectance attachments in the study of paper ageing was employed in the analysis of the optical properties of the paper in relation to physical changes in the surface layer of an absorbent substrate, active in a specific interaction. Reflectance measurements have been specifically recommended for the kinetic study of surface reactions such as oxidation or water absorption. (BAKER, VON ENDT, HOPWOOD, & ERHARDT, 1988)

In this project, focussed on the relationship between water absorption and oxidation, diffuse reflectance measurements were found to be the most sensitive of FTIR spectrophotometric techniques.¹ The capability of measuring the reflectance of the rough fibrous surface provided the means of following the surface reaction of oxidation. The chemical modification of the sample was also followed in the changes in its fine structure, caused by the replacement of the alcoholic groups by carbonyl or carboxyl groups resultant upon water absorption and desorption under fluctuating environmental conditions. This was achieved in the compilation of a crystallinity index derived from the ratio of the area of the absorption bands at 1375 and 2900 cm^{-1} . The integration reports of the bands at 1375 and

1

In the DRIFT technique, the input beam from the infrared source is passed through the interferometer onto the sample. Diffuse reflection of light from the surface is scattered in all directions, gathered by a series of mirrors and focussed onto the detector. (GRIFFITHS & DE HASETH, 1986; HARRICK, 1967; KORTÜM, 1969)

2900 cm^{-1} are included in Appendix C. The crystallinity index derived from the integration reports is presented in 5.2.2 below.

As a book and paper conservator rather than a conservation scientist, the relative inexperience of the author in FTIR analysis was a further limitation which led to a reliance on the description of similar cellulose spectra found in the literature, noting common band assignments and using correlation tables in the analytical interpretation. (BLACKWELL, 1977; CAIN & KALASINSKY, 1983; CARDAMONE, 1989; CARDAMONE, GOULD, & GORDON, 1987; FOERST, 1961; HON, 1986; LOW & BAER, 1977; LOW & BAER, 1986; SHEARER, 1987; ZHBANKOV, 1966)

Although readily identifiable oxidation products include aldehyde, ketone or carbonyl groups, it was anticipated that the strong C=O stretching bands associated with these groups would not become evident in the infrared spectra in the region from 1740-1670 to cm^{-1} until excessive oxidation had taken place. (O'CONNOR, DU PRE, & MITCHAM, 1958) Oxidised cotton cellulose is characterised by high ketone content and very low aldehyde and carboxyl group content, and similar spectral characteristics were anticipated for paper samples. (LEWIN & ETTINGER, 1969) The region including the characteristic absorption band for carbonyl groups at 1730-1720 cm^{-1} was therefore monitored for change, bearing in mind the limitation that since the aldehyde groups are not free, the band would be likely to be weak, even when the carbonyl group content was high. (KUNIAK, ALINCE, MASURA,

& ALFOLDI, 1969)

The justification for this weak phenomenon postulated by O'Connor (*et al*), lies in the aldehyde groups, which are hydrated by reaction with water as a intermediate oxidation of adjacent hydroxyl and carbonyl groups. The main attack is aldehyde formation at carbons 2 and 3, shown in Figure 5.1 below, but there is evidence of hydration of these carbonyl groups. The intensity of the primary alcohol band is reduced, indicating the possible formation of hemiacetals. The formation of the aldehyde hydrate does not reflect a C=O stretching band in its infrared spectrum, and only on further oxidation is the aldehyde converted to carboxyl, as oxidative attack progresses to the primary hydroxyl groups of the molecule to produce a carbonyl group, is the characteristic C=O stretching of the carboxyl group detectable. (O'CONNOR, et al., 1958)

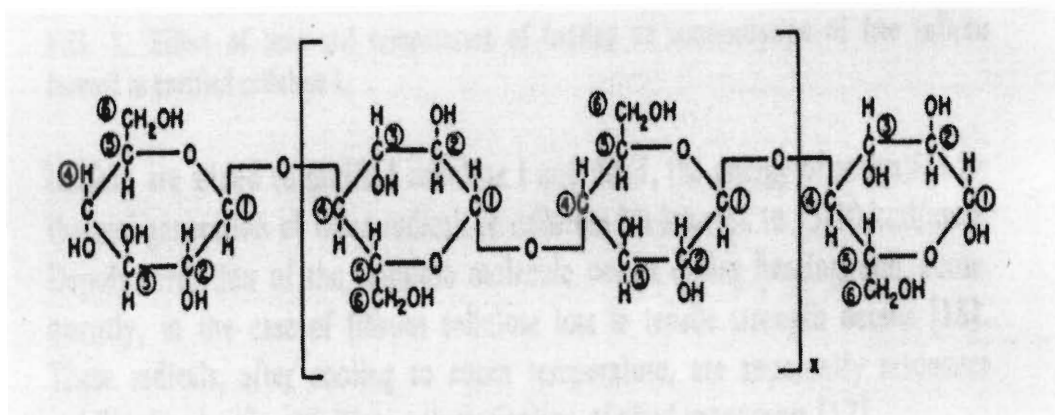


Figure 5.1 Cellulose molecule (ARTHUR & HINOJOSA, 1971)

This concept of progressive attack provides confirmation of the theory of autoxidative reactions, described in Chapter 2.3.1, by which organic peroxides appear among the first products of the reaction, and that the subsequent oxidation of the parent hydrocarbon is initiated by the decomposition of peroxides, which produce free radical carriers for the chain reaction. The decomposition of peroxides thus leads to the propagation stage of the reaction, in the formation of secondary oxidation products such as ketones, aldehydes, acids, alcohols, water and carbon dioxide, etc. (MESROBIAN & TOBOLSKY, 1961; TOBOLSKY, METZ, & MESROBIAN, 1950)

The DRIFT spectra for Sample Group 1, naturally aged, labelled (NA00) and Sample Group 2, artificially aged papers, labelled (AA00) are presented in Figures 5.2 - 5.27, as printed by the software, using the instrument Opus software directly. The spectra for each sample comprise an extended range of wavenumbers from 4000 cm^{-1} to 600 cm^{-1} and an enlarged view of the same spectrum from 2000 cm^{-1} to 600 cm^{-1} , marked on which are the selection of peaks identifying the formation of carbonyl groups in the region 1800 cm^{-1} to 1600 cm^{-1} , as found by the peak editor in the Opus software.

It was noted that the naturally aged samples, Sample Group 1, selected for this study on the basis of the cellulosic staining evidenced therein, all exhibited similar spectral features in the C=O stretching region, with pronounced absorption bands at $1730\text{-}1720\text{ cm}^{-1}$, assigned to carboxylic

acid groups. Strongest peak formation was noted in the rag paper samples, NA004 followed by NA007. (Figures 5.9 & 5.15) The objective was to compare with this evidence with spectra of Sample Group 2, exposed to accelerated ageing and the dynamic simulated climate ageing programme, to determine the effect of environmental fluctuations in precipitating oxidative degradation exhibited in similar spectral features. The formation of similar functional groups exhibited in the absorption bands in the region 1730-1720 cm^{-1} was evidence of oxidative degradation resulting from exposure to fluctuating humid climatic conditions. (See Figures 5.2 - 5.15 NA001-NA007)

Most significant evidence of the limitation of the spectroscopic technique was the measurement of accelerated aged Sample 1 (AA001), the spectra being recorded for comparison prior to ageing and climate exposure (red); following ageing, but prior to the climate programme (blue); and following both accelerated ageing and exposure to the climate programme (green). While the same spectral features were evident throughout, the difference in the structure of the peaks was instructive. The structure observed in the 1800-1600 cm^{-1} of the spectrum of the base control sample, i.e., before accelerated ageing and climate programme, is evidence of water vapour absorbing in the same region.

Confirmation of the suspicion that the presence of functional groups was being obscured by water vapour was seen in the full range of spectra for

Sample 1, subjected to accelerated ageing and to a subsequent dynamic ageing procedure. (See Figures 5.16 & 5.17) The difference between the enlarged spectra of the unaged sample (red), and that of the aged and climate-exposed sample (green), confirms the increase in the amount of bound water between 1650 and 1630 cm^{-1} .

It was concluded, therefore, that while clear evidence of functional groups was exhibited in samples that had been exposed to accelerated ageing and the climate ageing programme, it was not possible to follow the formation of these groups because of the interference resulting from water vapour presence of bound water which had not been adequately compensated.

In Samples 2 - 4 of Sample Group 2, (AA002 - AA004), similar comparison was not possible, as these samples lack a base control sample of recent manufacture, afforded by the Control in Sample 1. The spectra of the Samples AA002 - AA003, despite an unknown previous history of natural ageing, are included nonetheless, as an indication of the consistent exhibition of functional groups in all samples exposed to accelerated ageing and the dynamic climate ageing programme. (See Figures 5.20 - 5.21 : AA002-AA003)

Sample AA04A,B,C represented the comparison of the same sample, before exposure to the climate programme, without previous accelerated ageing (B); following both accelerated ageing and climate programme (A)

and following accelerated ageing, deacidification and climate exposure (C). The strong oxidation of this sample AA04A, though barely evident in the FTIR spectrum, was confirmed in subsequent identification of oxidative degradation by chemical reagent in 5.2.3 and 5.2.4 below. (See Figures 5.24 - 5.25 : AA004A,B,C)

The final investigation was conducted by FTIR measurement into the role of oxidation at the wet/dry interface in the cellulosic staining of samples, commonly known as foxing, and thought to be a result of biological infestation. An alternative explanation was sought in this study for the causation of cellulosic discolouration in the increased chemical reactivity at the wet/dry interface at the paper surface under humid climatic conditions.

In order to test the relationship between cellulosic discolouration and oxidation, three measurements were made from Sample AA04A, in which discolouration was noted following exposure to accelerated ageing and climate ageing programme. The first was taken from a diffuse stained area of the sample (dark), the second from an unstained area (light) and the third from a tideline region. Previous investigations of the wet/dry interface had sampled exclusively from the tideline region in the determination of an oxidative reaction. (DUPONT, 1996b; EUSMAN, 1995) It was anticipated again, that the formation of functional groups would be exhibited in the tideline sample, and perhaps in the dark sample, but the spectra revealed clear evidence that functional group formation had taken place in all three

samples that had been exposed to accelerated ageing and the climate ageing programme. It was not possible therefore to correlate the formation of functional groups with the degree of discolouration. (See Figures 5.26 -5.27 : AA04A)

It was concluded that since the reaction was not limited to the areas of discolouration, chemical modification had occurred throughout the paper substrate as a consequence of exposure to the ageing and climate programme. The localised formation of areas of discolouration, known as foxing, could not be determined by spectrophotometric analysis. The degree of staining could not be evaluated in the measurement of the formation of functional groups, as evidence of oxidative degradation.

Further investigation of the relationship between cellulosic discolouration and oxidation was conducted by reagent staining procedures reported in 5.2.3 and 5.2.4 below.

- 5.2 Naturally aged sample 1: NA001
- 5.3 Naturally aged sample 1: NA001 - enlarged
- 5.4 Naturally aged sample 2: NA002
- 5.5 Naturally aged sample 2: NA002 - enlarged
- 5.6 Naturally aged sample 3: NA003
- 5.7 Naturally aged sample 3: NA003 - enlarged
- 5.8 Naturally aged sample 4: NA004
- 5.9 Naturally aged sample 4: NA004 - enlarged
- 5.10 Naturally aged sample 5: NA005
- 5.11 Naturally aged sample 5: NA005 - enlarged
- 5.12 Naturally aged sample 6: NA006
- 5.13 Naturally aged sample 6: NA006 - enlarged
- 5.14 Naturally aged sample 7: NA007
- 5.15 Naturally aged sample 7 :NA007 - enlarged
- 5.16 Artificially aged sample 1: AA001
- 5.17 Artificially aged sample 1: AA001 - enlarged
- 5.18 Artificially aged sample 1: AA001 - treatments
- 5.19 Artificially aged sample 1: AA001-treatments-enlarged
- 5.20 Artificially aged sample 2: AA002
- 5.21 Artificially aged sample 2: AA002 - enlarged
- 5.22 Artificially aged sample 3: AA003
- 5.23 Artificially aged sample 3: AA003 - enlarged
- 5.24 Artificially aged sample 4 : AA004A,B,C
A- Aged B- Unaged C- Aged and deacidified
- 5.25 Artificially aged sample 4: AA004A,B,C - enlarged
A- Aged B- Unaged C- Aged and deacidified
- 5.26 Artificially aged sample 4 :AA004A
- 5.27 Artificially aged sample 4: AA004A - enlarged

Table 5.1 List of DRIFT spectra

DRIFT Sample1: Naturally aged shierite

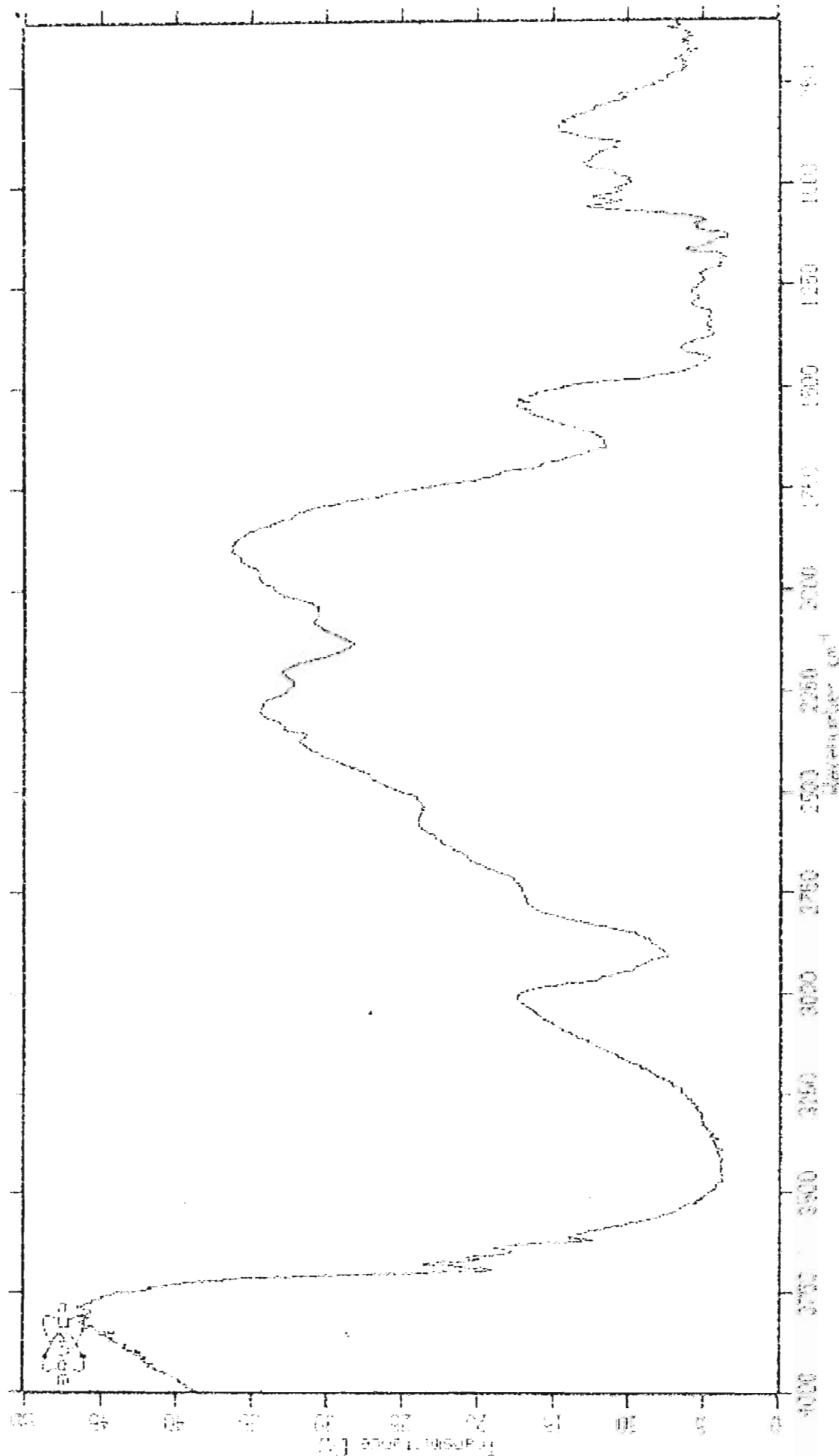


Figure 5.2 DRIFT spectrum: Sample NA001
241

Sample Name: NA001	Operator: M. J. ...
Resolution: 4.0	Sample Name: NA001
Resolution: 4.0	Sample Score: 100
Resolution: 4.0	File Name: NA001.D
Resolution: 4.0	File Path: ...

DRIFT Sample: Naturally aged series - Enlarged

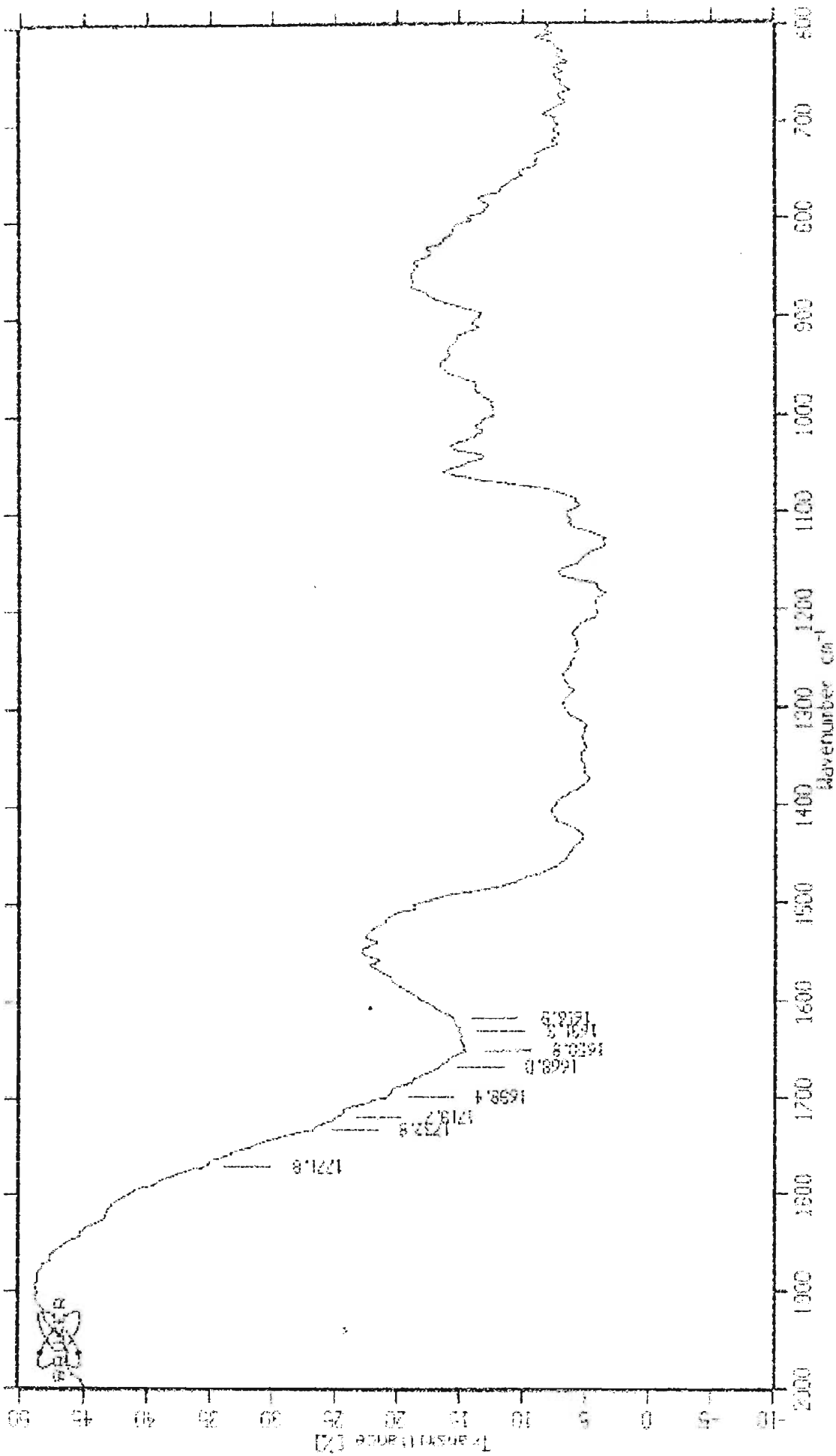


Figure 5.3 DRIFT spectrum: Sample NA001 - enlarged
242

sample: DRIFT series	area range: 259.2255 - 1849.8000	measured: 14.2.1998
technique: DRIFT	resolution: 4.0	Instrument: IF328 sample scans: 100
customer: Date	zencollino p.2	anal. by: Double Subst Forward Backward
name: Subst001		

DRIFT Sample 2: Naturally aged series - Stained area - Enlarged

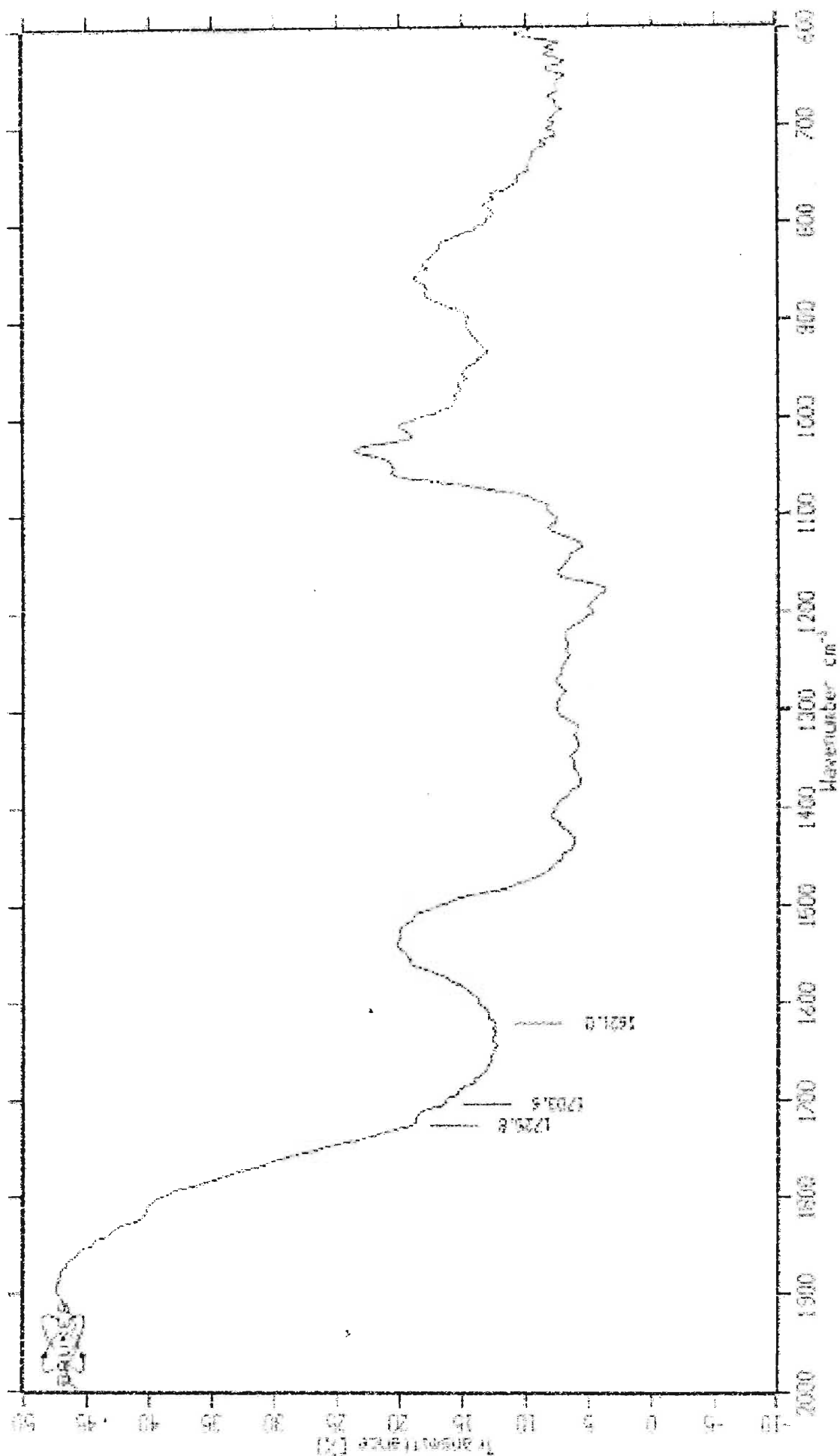


Figure 5.5 DRIFT spectrum: Sample NA002 - enlarged
244

measured: 14.2.1998

area range: 380.2755 - 1991.5465

sample: DRIFT: series

Instrument: IFS28

resolution: 4.0

technician: J.

sample scans: 100

scan rate: 2

customer: Date

comments:

DRIFT Sampling: Naturally aged series - Stained area

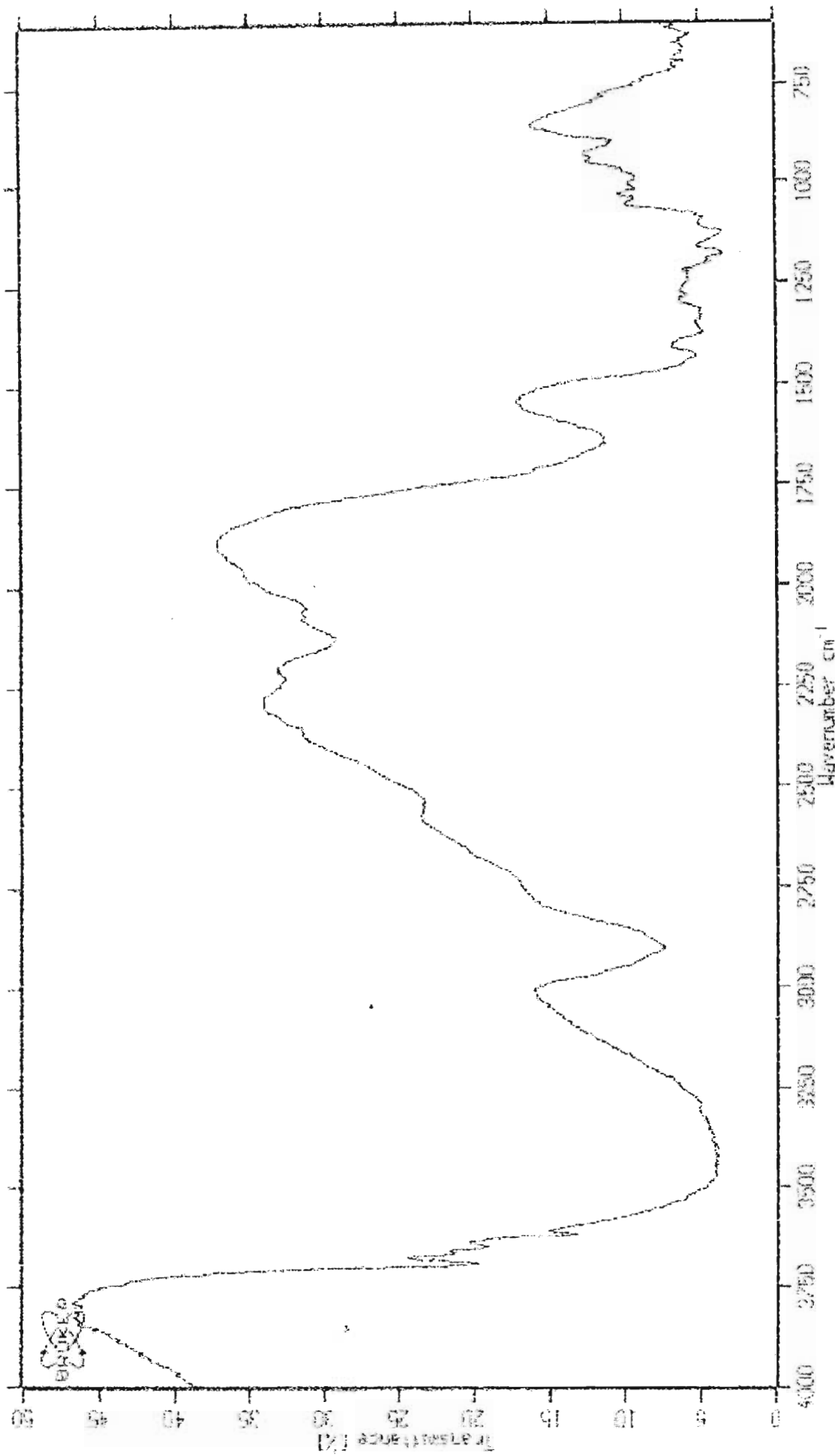


Figure 5.6 DRIFT spectrum: NA003
245

sample: DRIFT series	area range: 309.7205 - 3099.5895	measured: 14. 7. 1998
substance:	resolution: 4.0	Instrument: FTS20B sample scans: 100
collector: Dale	perfillum: 2	anal. by: Bobbe Zedel, Frank Baur
CO number: 7		

DRIFT Sample: Naturally aged series - Stained area - Enlarged

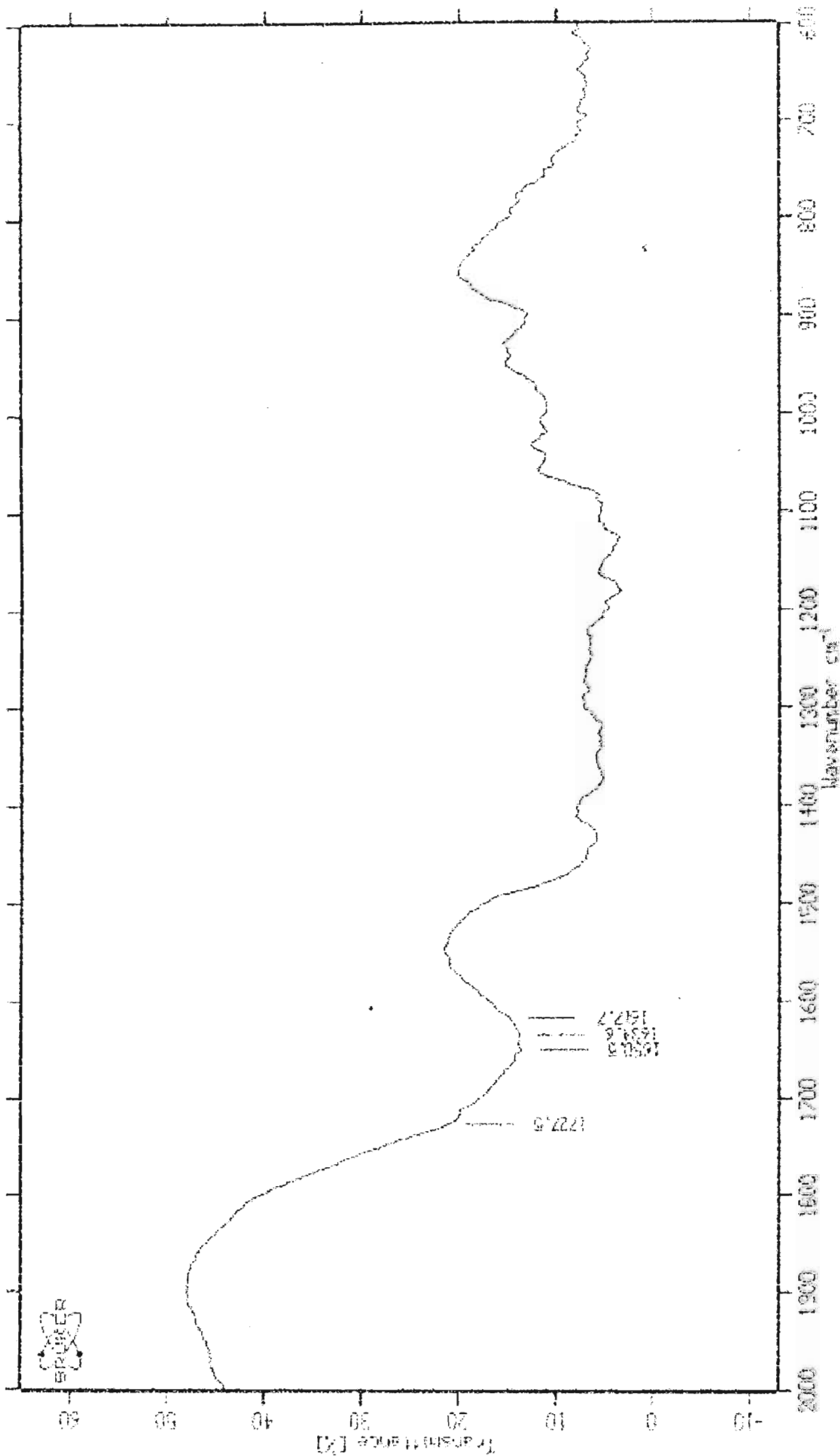


Figure 5.7 DRIFT spectrum: Sample NA003 - enlarged
246

Sample: DRIFT series	Area range: 389.2435 - 3993.9695	measured: 11/2/2009
Technique: DRIFT	Resolution: 4.0	Instrument: FT/20B
Customer: Dale	Resolution: 2	Sample Scans: 100
Comments:	File: Double Stain Forward-Redward	

DRIFT Sampled: Naturally aged series - Stained area

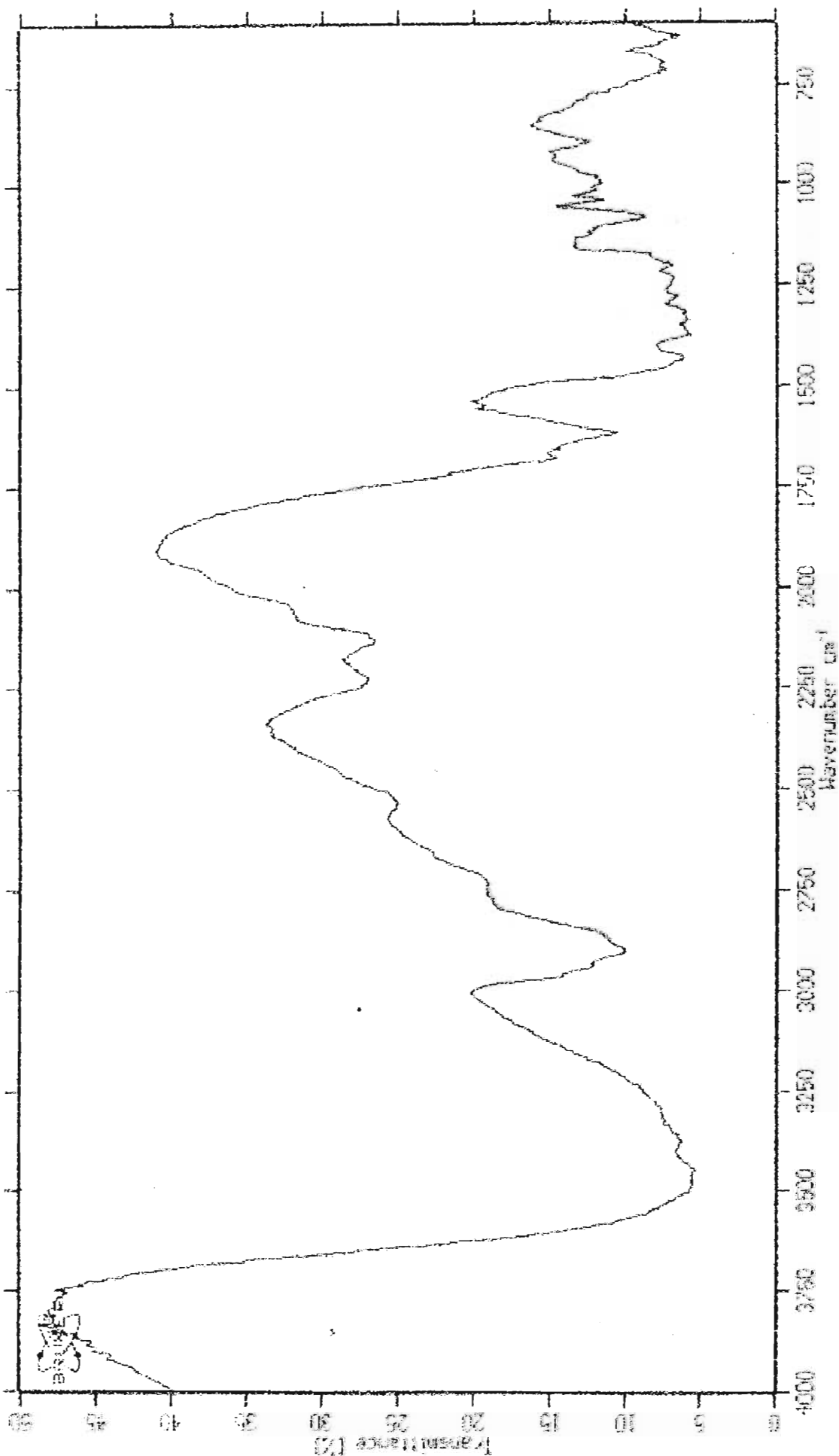


Figure 5.8 DRIFT spectrum: Sample NA004

sample : DRIFT series

meas range : 399.2255 - 1999.9452

measured : 19.7.1998

Instrument : IFS38

resolution : 4.0

customer : Dale

sample scans : 100

resolution : 2

customer : Dale

customer : Dale

DRIFT Sample1: Naturally aged series - Stained area - Enlarged

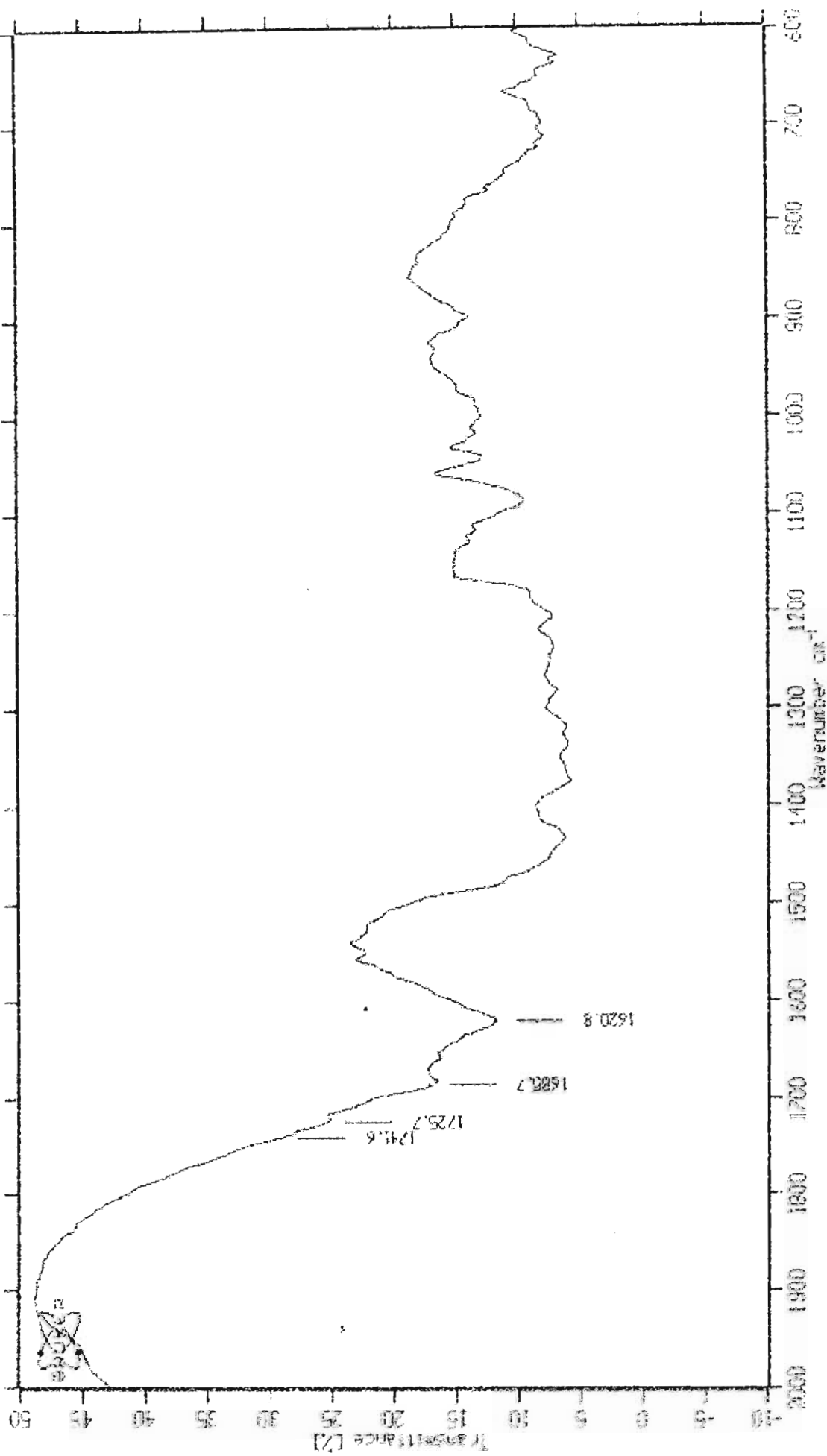


Figure 5.9 DRIFT spectrum: Sample NA004 - enlarged

Sample 1: DRIFT Series	Area: 389.2256 - 3894.5645	Resolved: 14/2/2008
Resolution: 1.410	Instrument: IFS26	Sample Scans: 100
Customer: L. Dale	zephiran@i2	anal. R. J. Smith, St. John's University
Comments 1		

DRIFT Sample 5x Naturally aged series - Stained area

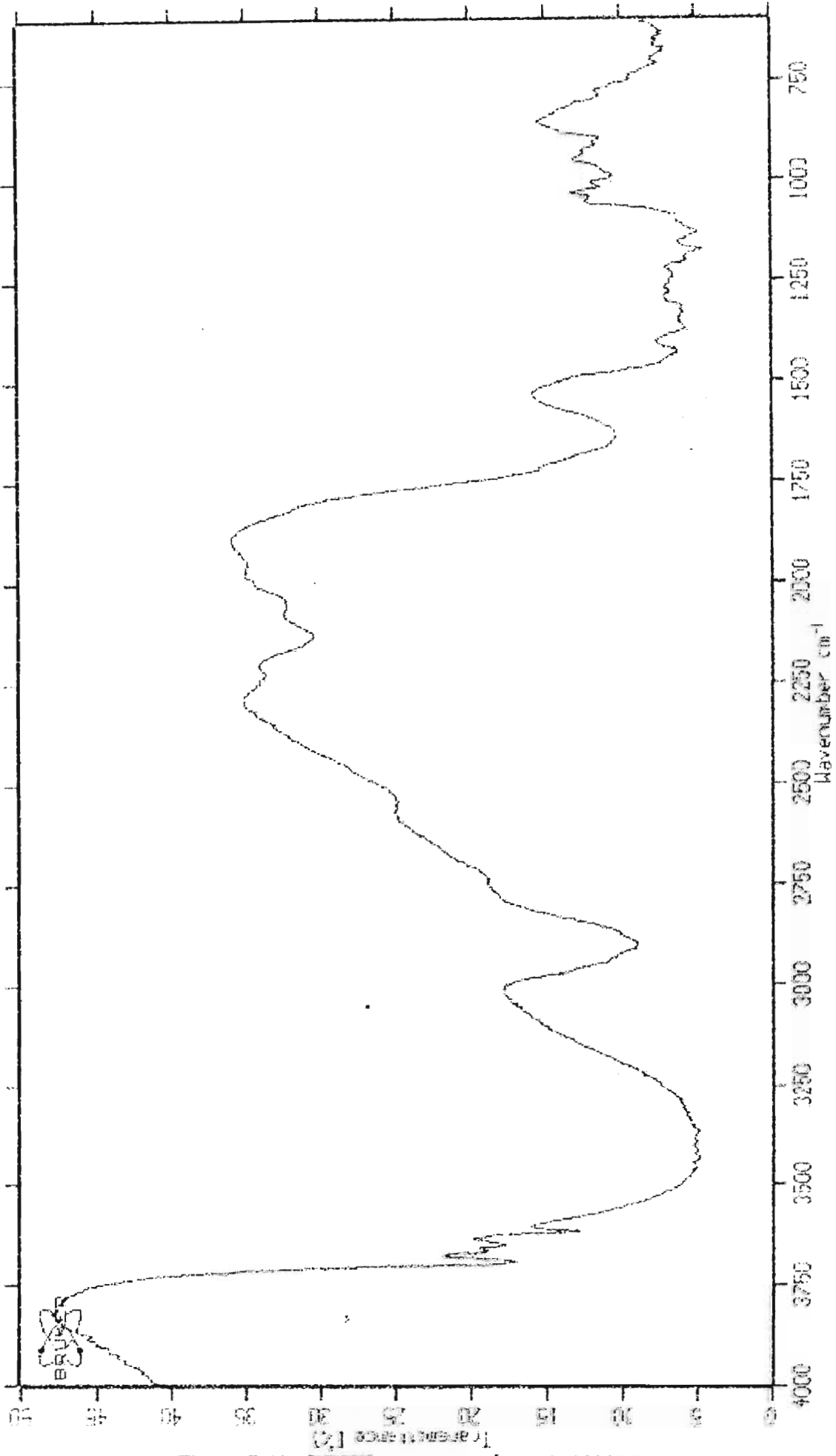


Figure 5.10 DRIFT spectrum: Sample NA005
249

Sample: DRIFT series	freq. range: 3812.45 - 1999.904	measured: 14. 2.1998
Technique: DRIFT	resolution: 4.0	Instrument: FT/20B
Customer: Data	resolution: 2	Operator: Bobbie Sidel Forward Backward
CONSOLE		

DRIFT Sample 5: Naturally aged series - Stained area - Enlarged

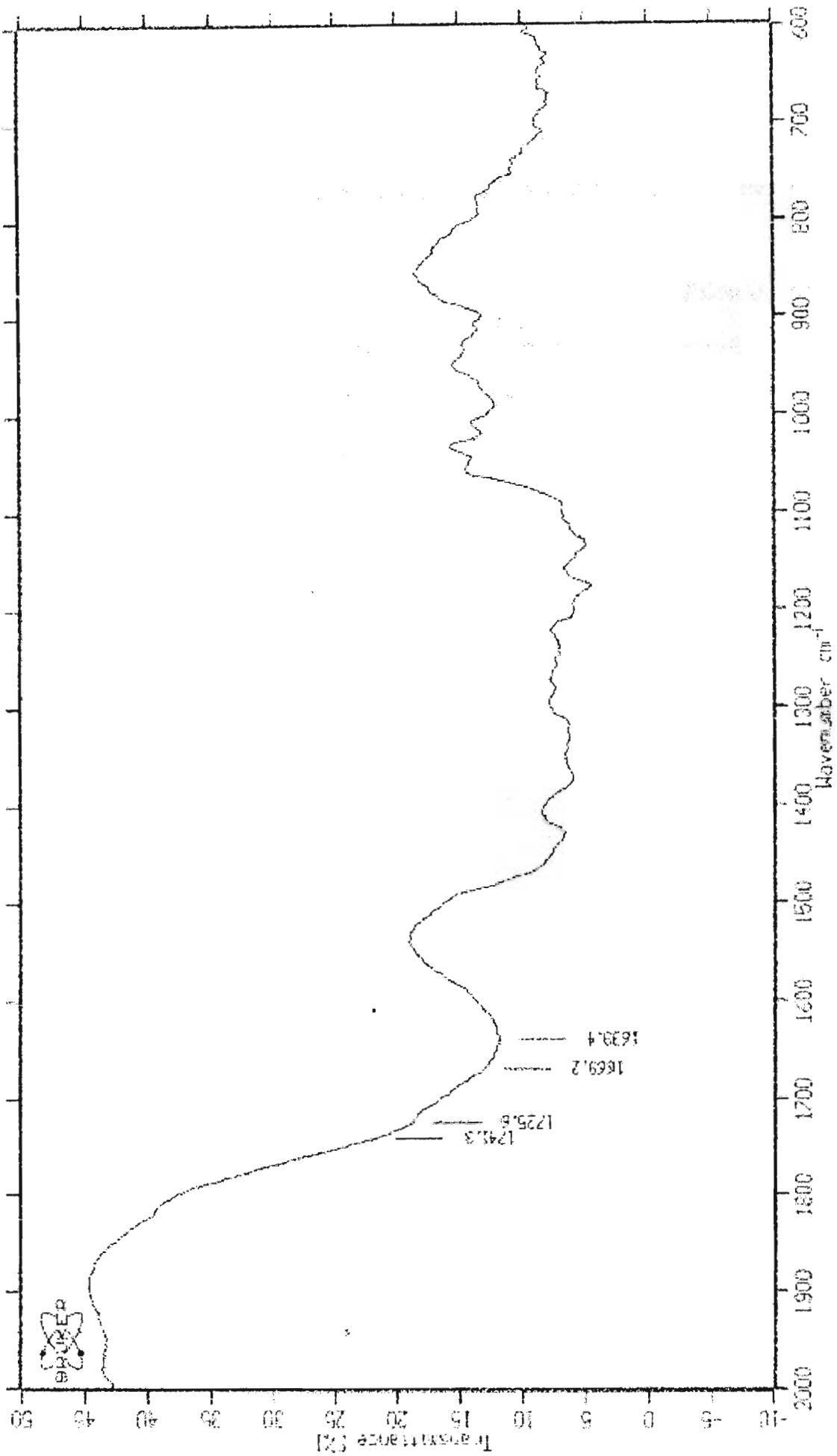


Figure 5.11 DRIFT spectrum: SAmpLe NA005 - enlarged
250

measured: 14/2/1998

area range: 339.2755 - 399.9655

Instrument: IFS28 sample scans: 100

cell: Double Sided Forward Backward

resolution: 4.0

scans: 1.2

Sample: DRIFT series

Technique: 1

Operator: J. Dale

13/06/1998

DRIFT Sample 6: Naturally aged series - Stained area - Enlarged

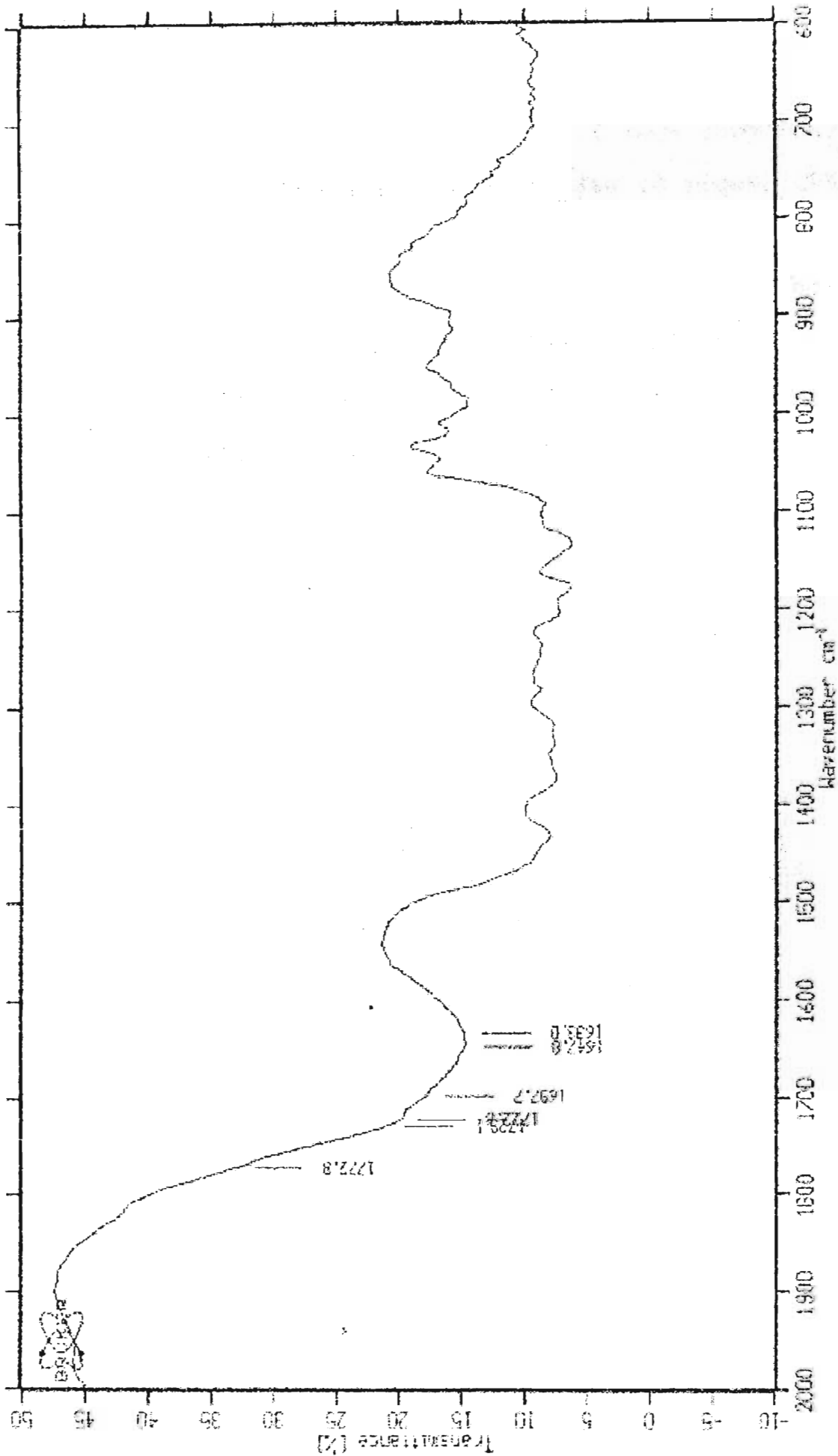


Figure 5.12 DRIFT spectrum : Sample NA006
251

sample : DRIFT series	Wavenumber range : 2000.0000 - 3999.9999	measured : 14.7.8988
technique : DRIFT	resolution : 4.0	Instrument : IFS28
customer : Data	operator : no. 1.2	sample scans : 100
BRUKER		

DRIFT Sample 6: Naturally aged series - Stained area

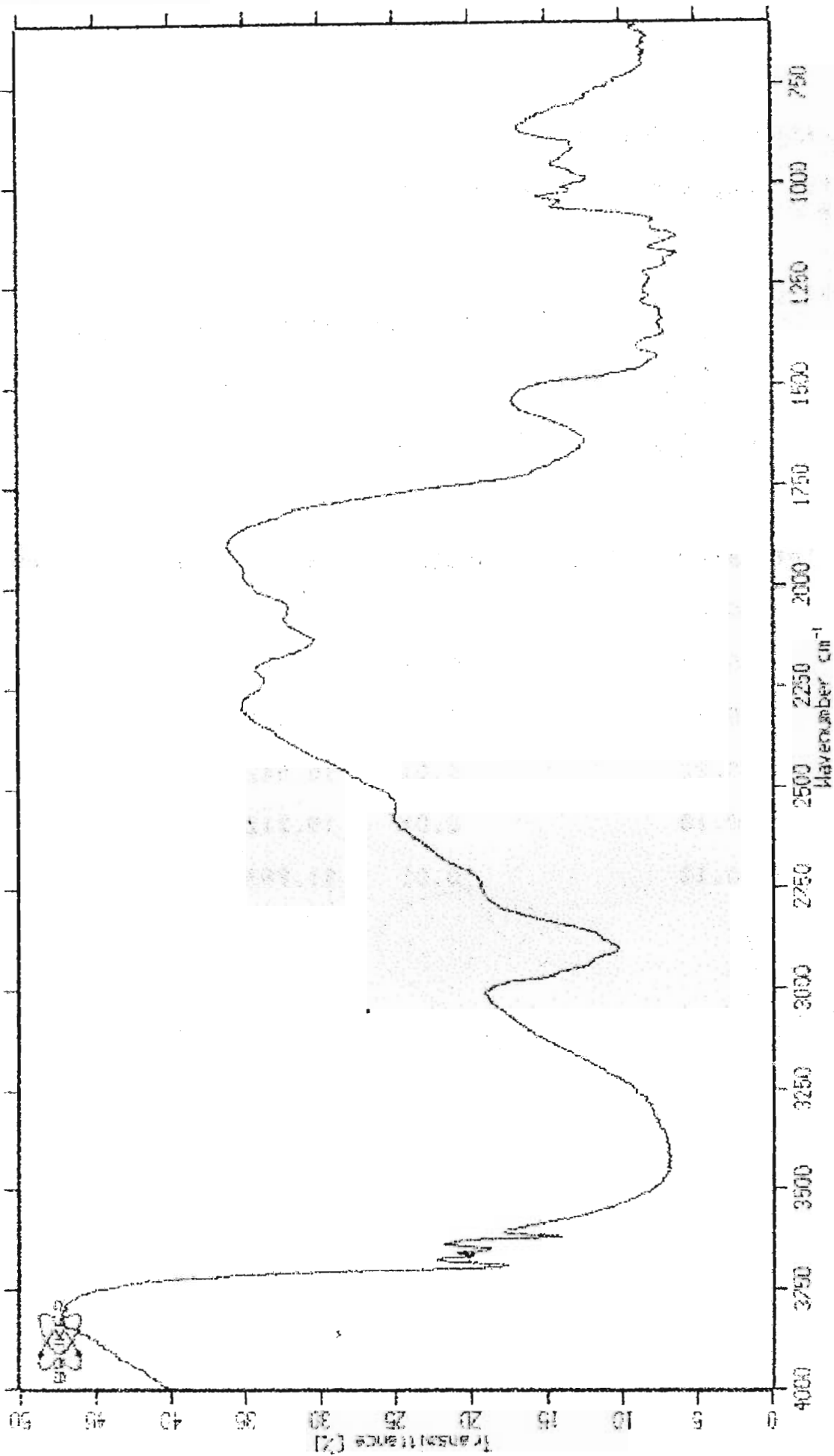


Figure 5.13 DRIFT spectrum: Sample NA006 - enlarged
252

sample: DRIFT series	IR no. 0002 : 0812255 - 1999.9696	measured: 14/7/1998
technique: DRIFT	resolution: 4.0	sample scans: 100
customer: Dale	zerofilling: 2	anal. by: Double Scan Forward Backward
comments:		

DRIFT Sample 7: Naturally aged series - Stained area

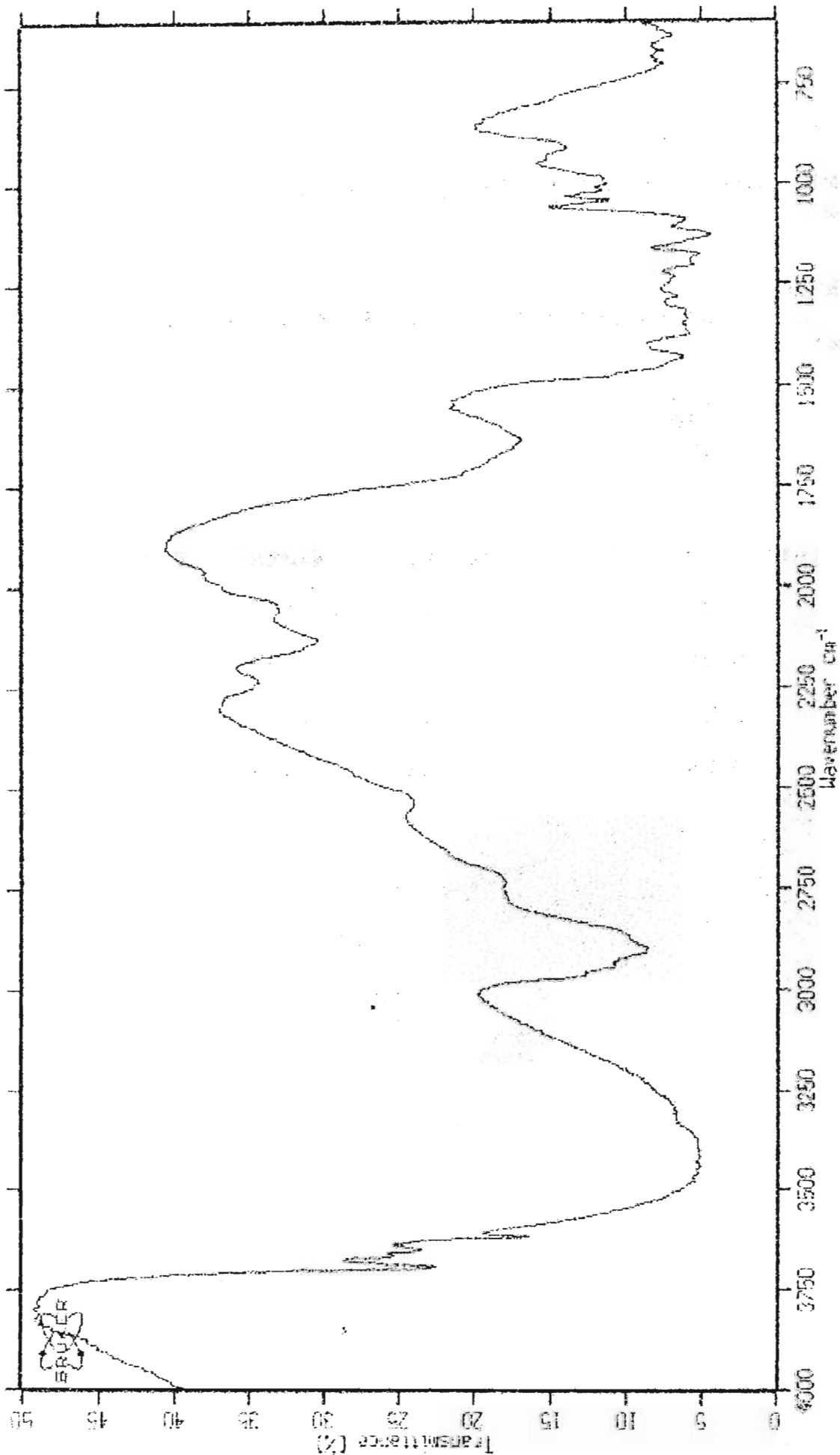


Figure 5.14 DRIFT spectrum: Sample NA007
253

sample: DRIFT series	measured: 14/7/1998
scan rate: 330.2255 - 1998.8665	Instrument: IFS20
resolution: 4.0	sample scans: 100
customer: Date	zero filling: 2
	auth. n.: Sample Stored forward-Badlard
	Comments: 1

DRIFT Sample 7: Naturally aged series - Stained area - Enlarged

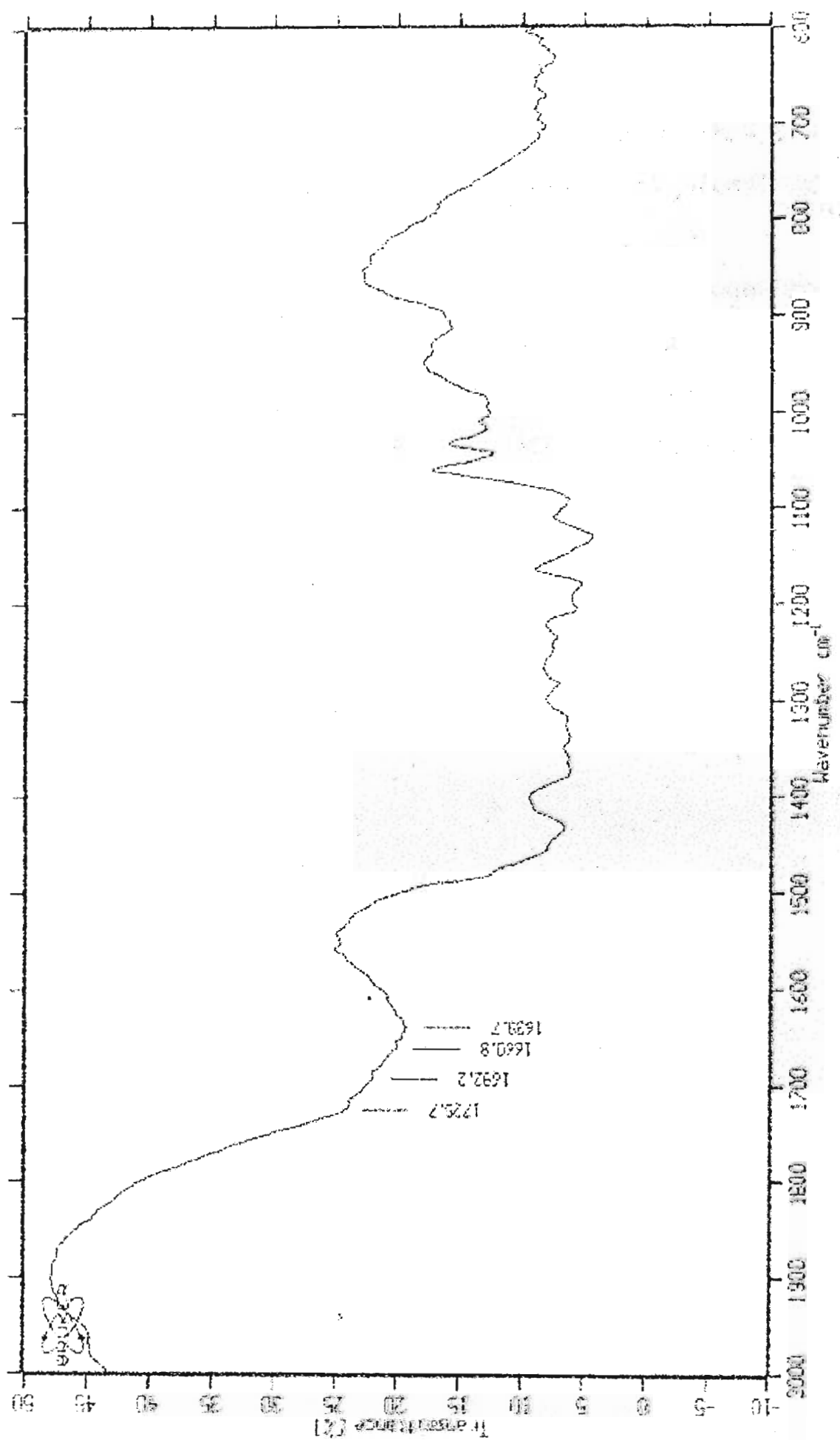


Figure 5.15 DRIFT spectrum : Sample NA007 - enlarged
254

sample : DRIFT series	measured : 14/2/1998
area range : 201.2026 - 2189.8005	sample scans : 100
resolution : 4.0	Instrument : IFS20
scattering : None	path : Double Side Forward Backscat
scattering : 2	
scattering : 2	

DRIFT Sample1: Climate cupboard series

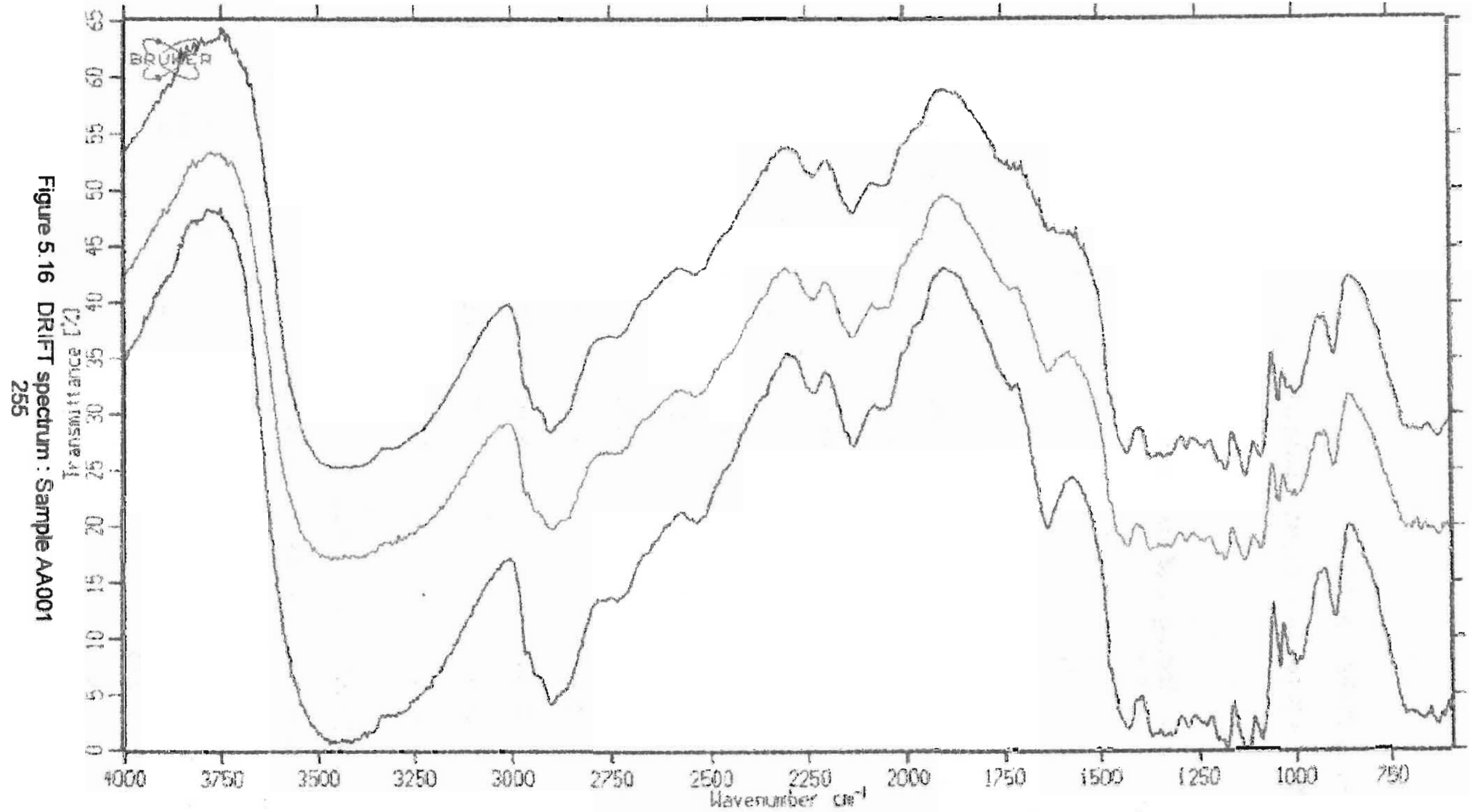


Figure 5.16 DRIFT spectrum : Sample AA001
255

sample : DRIFT series	freq. range : 399.2255 - 1999.9695	measured : 17. 7/1998
technique :	resolution : 4.0	Instrument : IFS28 sample scans : 100
customer : Dale	zero filling : 2	scan. m. : Double Sided Forward-Backward
comments :	Red - 1: Unaged, no climate / Blue - 1: Aged, no climate, Green - 16: Aged, climate	

DRIFT Sample: Climate cupboard series - Enlarged

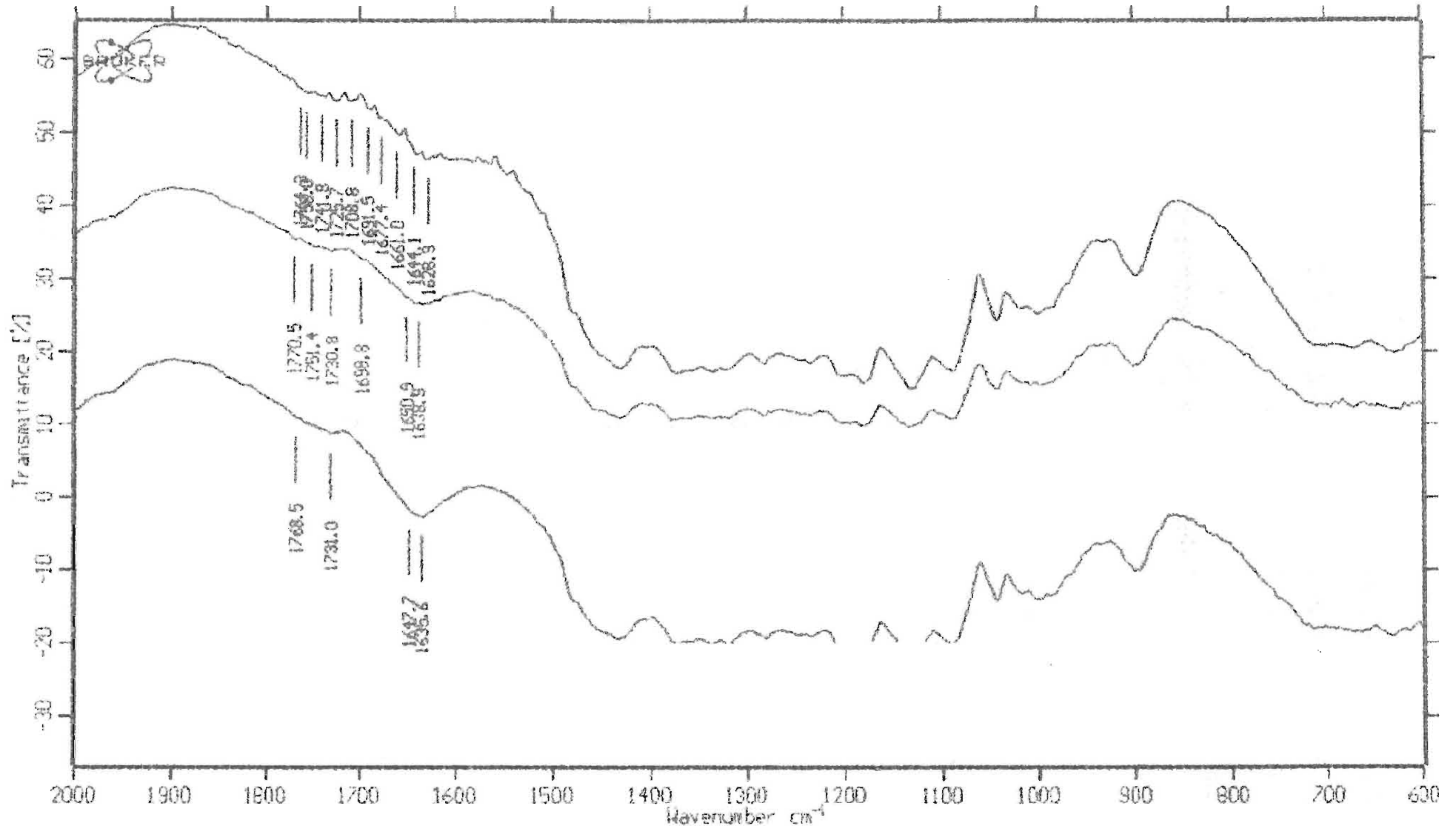


Figure 5.17 DRIFT spectrum: Sample A4001 - enlarged
256

sample : DRIFT series	freq. range : 399.7255 - 3999.9605	measured : 14/ 7/1998
technique :	resolution : 4.0	Instrument : IFS28 sample scans : 100
customer : Dale	zerofilling : 2	acc. n. : Double Sided Forward-Backward
comments : Red - 1: Unaged, no climate / Blue - 1: Aged, no climate, Green - 1A: Aged, climate		

DRIFT Sample1: Climate-coubeard series - treatments

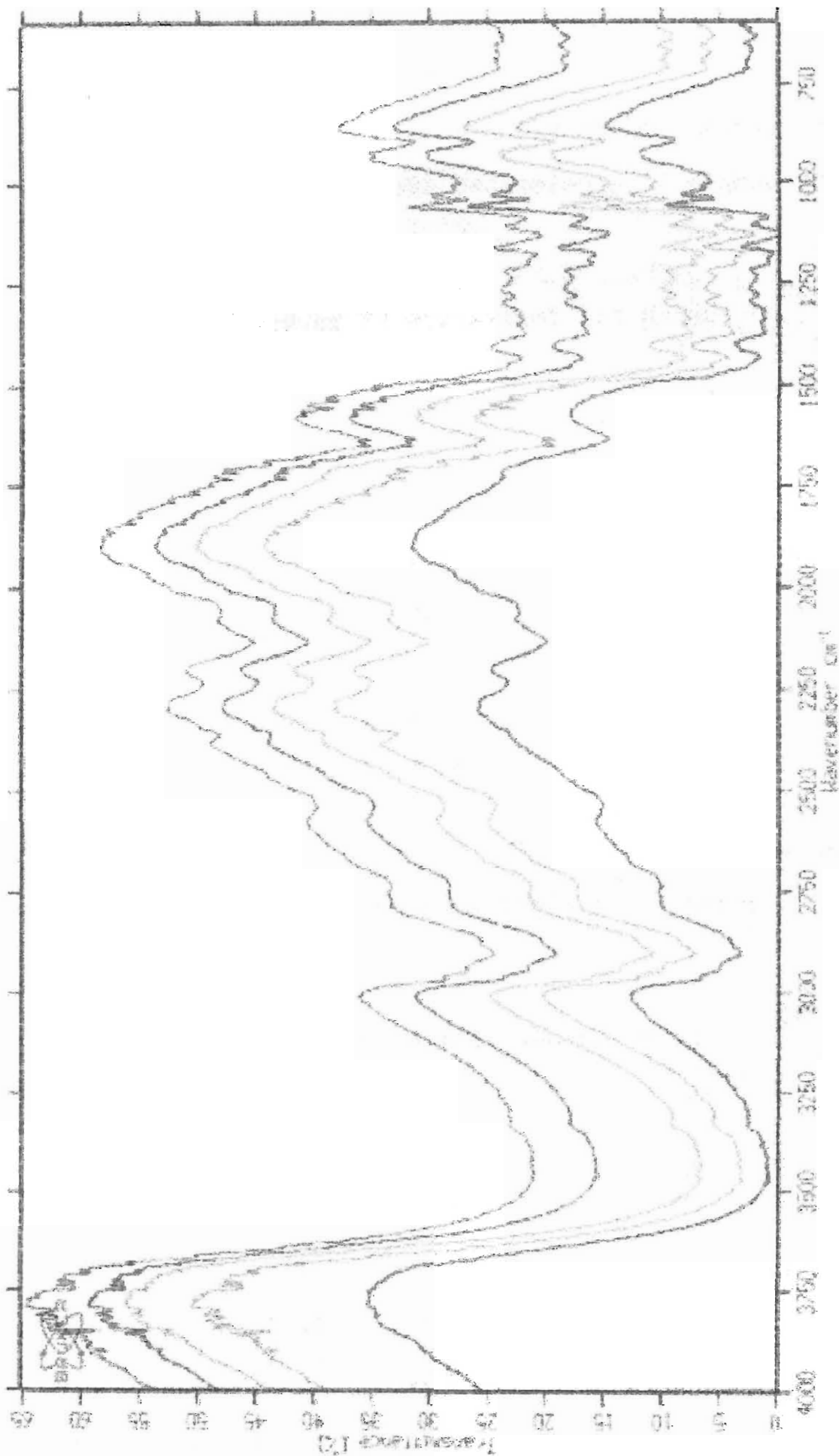


Figure 5.18 DRIFT spectrum : Sample AA(00) - treatments
257

sample : DRIFT series	res. name : 204.2256 - 2008.965	measured : 19/7/1998
technique : DRIFT	resolution : 4.0	Instrument : IFS28
customer : Balle	zero filling : 2	sample scans : 100
comments : green - life hood. climate / purpose for water / people - life time / ground-life / dial / ground-life / salt		

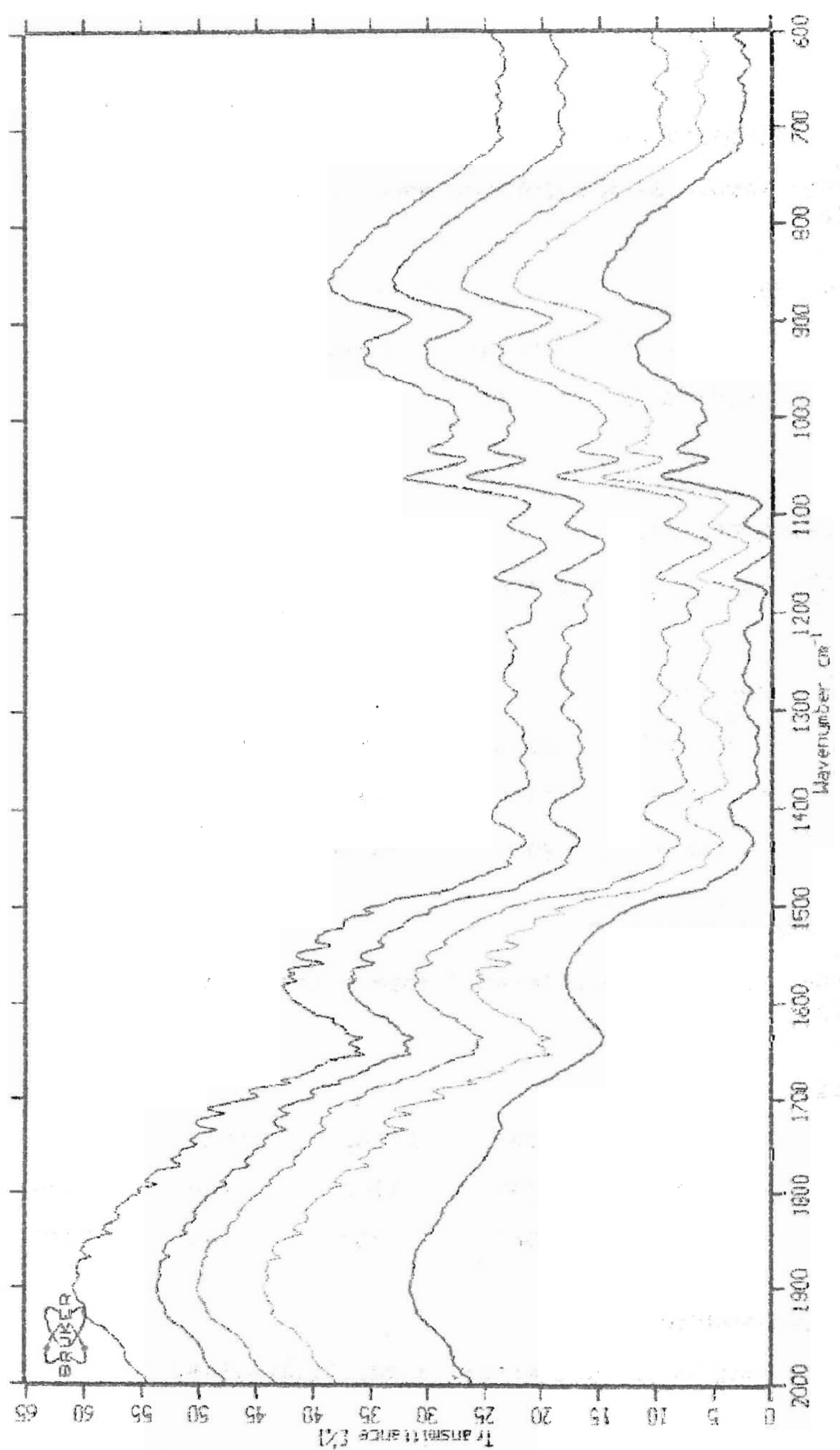


Figure 5.19 DRIFT spectrum : Sample AA001 - treatments - enlarged
258

sample : DRIFT series	freq. range : 2000.7255 - 1999.5695	measured : 14/7/1998
technique :	resolution : 4.0	Instrument : IFS29 sample scans : 100
customer : Dale	zerofilling : 2	anal. M.: Double Sided Forward Backward
comments : Green - 1% food, climate / turquoise-1% water, Purple-1% CNC, Brown-1% PVAC / Grey-1% salt		

DRIFT Sample 2: Climate cupboard series

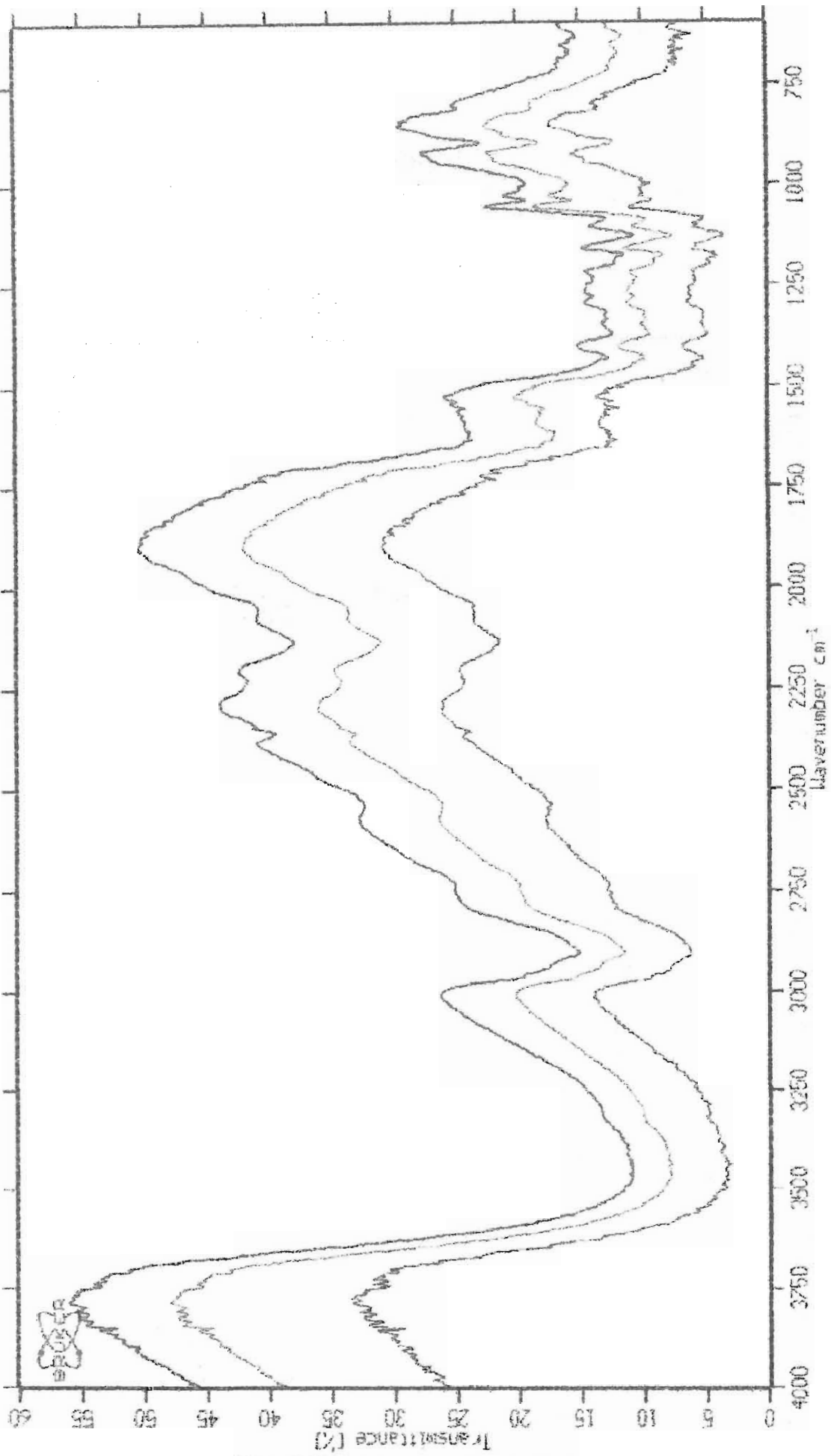


Figure 5.20 DRIFT spectrum : Sample AA002

Sample: DRIFT: Sample 2: unaged, climate	Wavenumber range: 399.2755 - 3999.9695	measured: 17/7/1998
Technique: DRIFT	Resolution: 4.0	Instrument: IFS28
Customer: Dale	Zerocilling: 2	sample scans: 100
Comments: Black-2B: unaged, climate / purple-2C: accelerated ageing, climate / brown-2D/E: unaged, deacidified, water, climate		appt. n.: Double blind, forward-looking

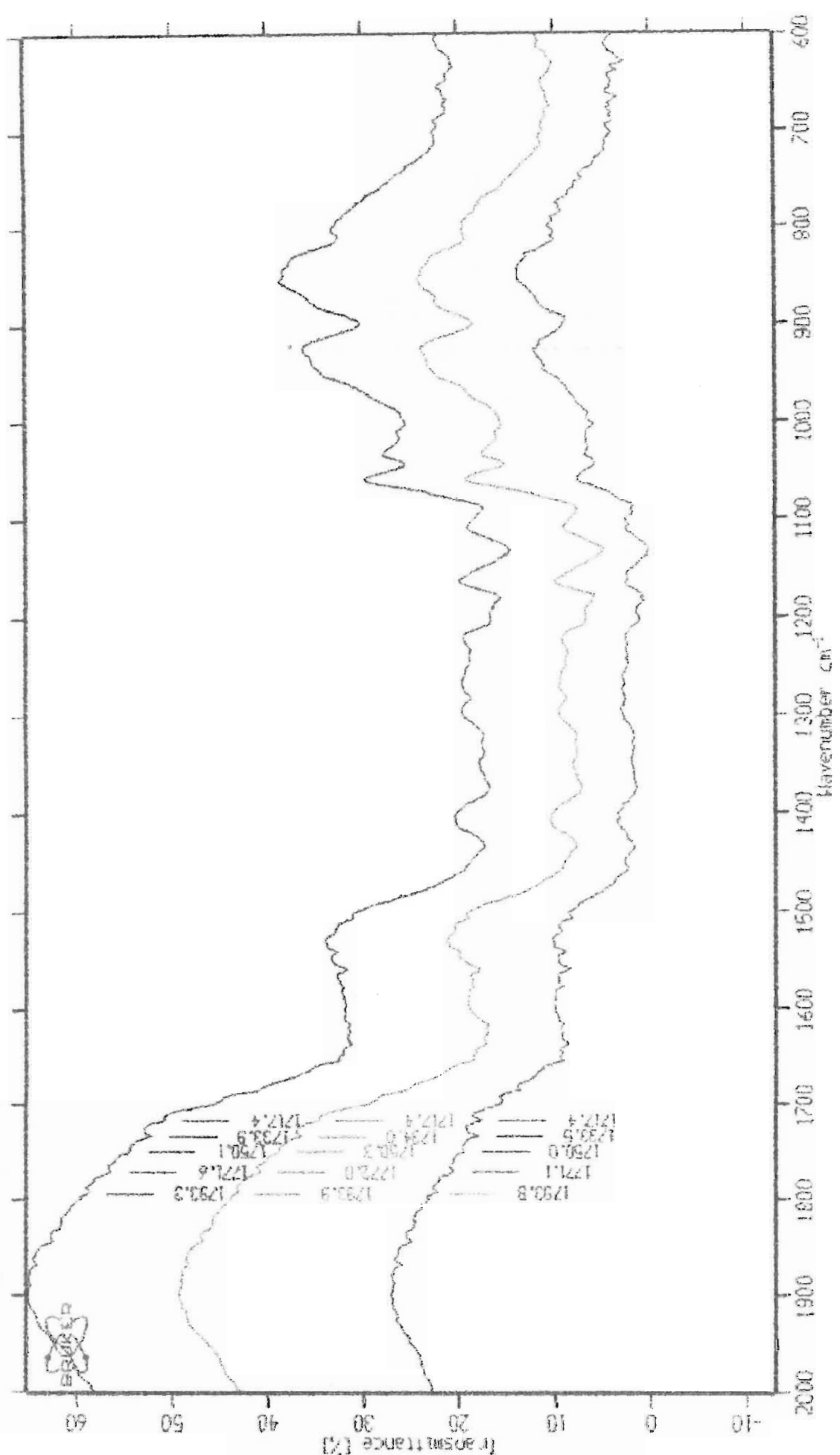


Figure 5.21 DRIFT spectrum : Sample AA002 - enlarged
260

sample: DRIFT: Sample 2: accelerated ageing and climate	freq. range : 399.2755 - 1999.5695	measured : 14. 7.1996
technique :	resolution : 4.0	Instrument : IFS28 sample scans : 100
customer : Dale	zerofilling : 2	ant. n. : Double Sided, Forward-Backward
Comments : Black-26: unaged, climate / purple-20: accelerated ageing, climate / brown-20/k: unaged, deacidified, water, climate		

DRIFT Sample 3: Climate cupboard series

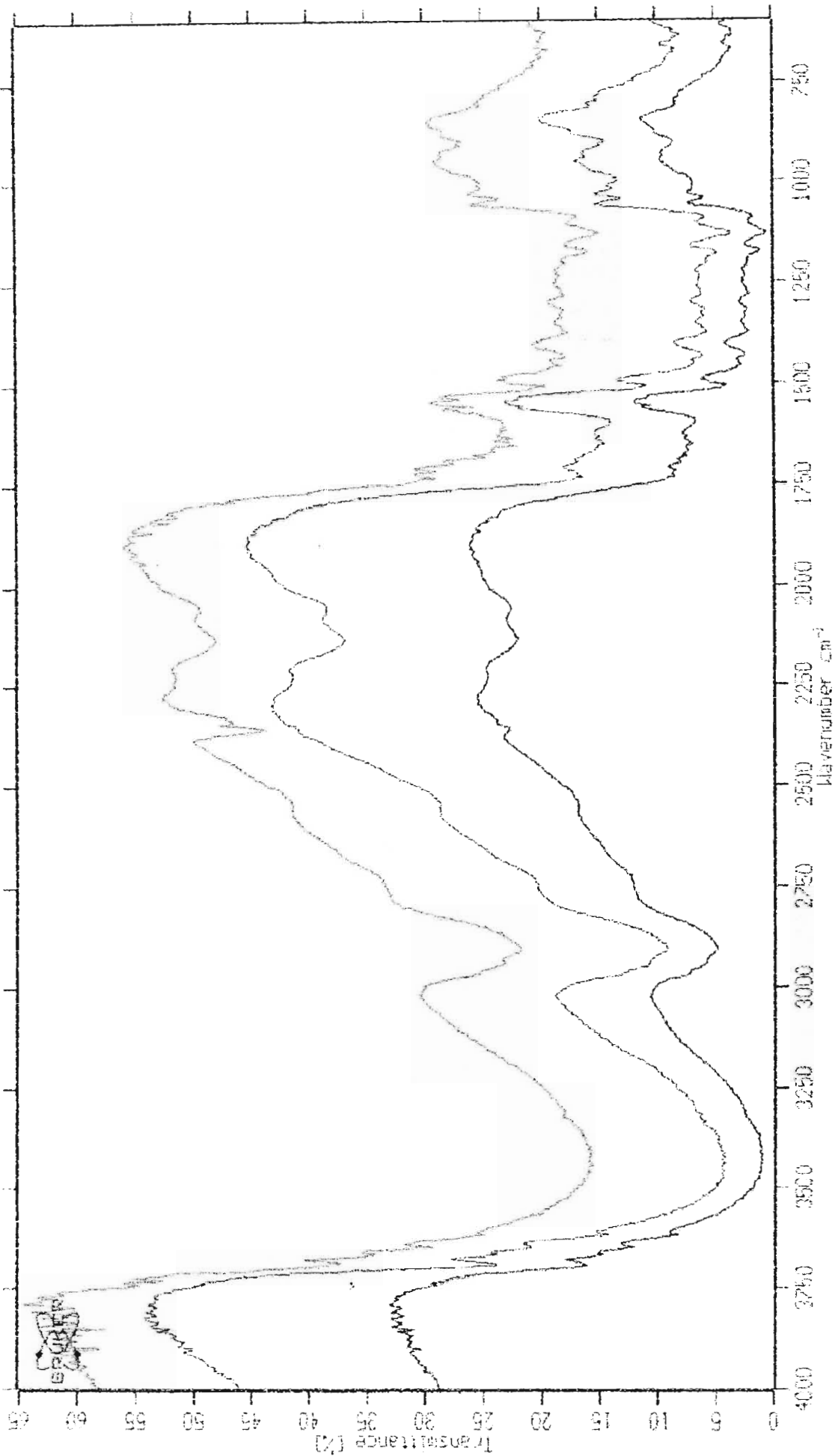


Figure 5.22 DRIFT spectrum: Sample AA003

sample : DRIFT Sample 3: accelerated ageing, climate	freq. range : 399.2255 - 3999.9685	Instrument : IFS28	sample scans : 100	measured : 15/7/1996
resolution : 4.0	zerofilling : 2	scan # : Double Side, Forward-Backward		
customer : Dale	comments : Green-36: aged, climate / Black-38: unaged, climate / Purple-30: accelerated ageing, climate			

DRIFT Sample 3: Climate cupboard series - Enlarged

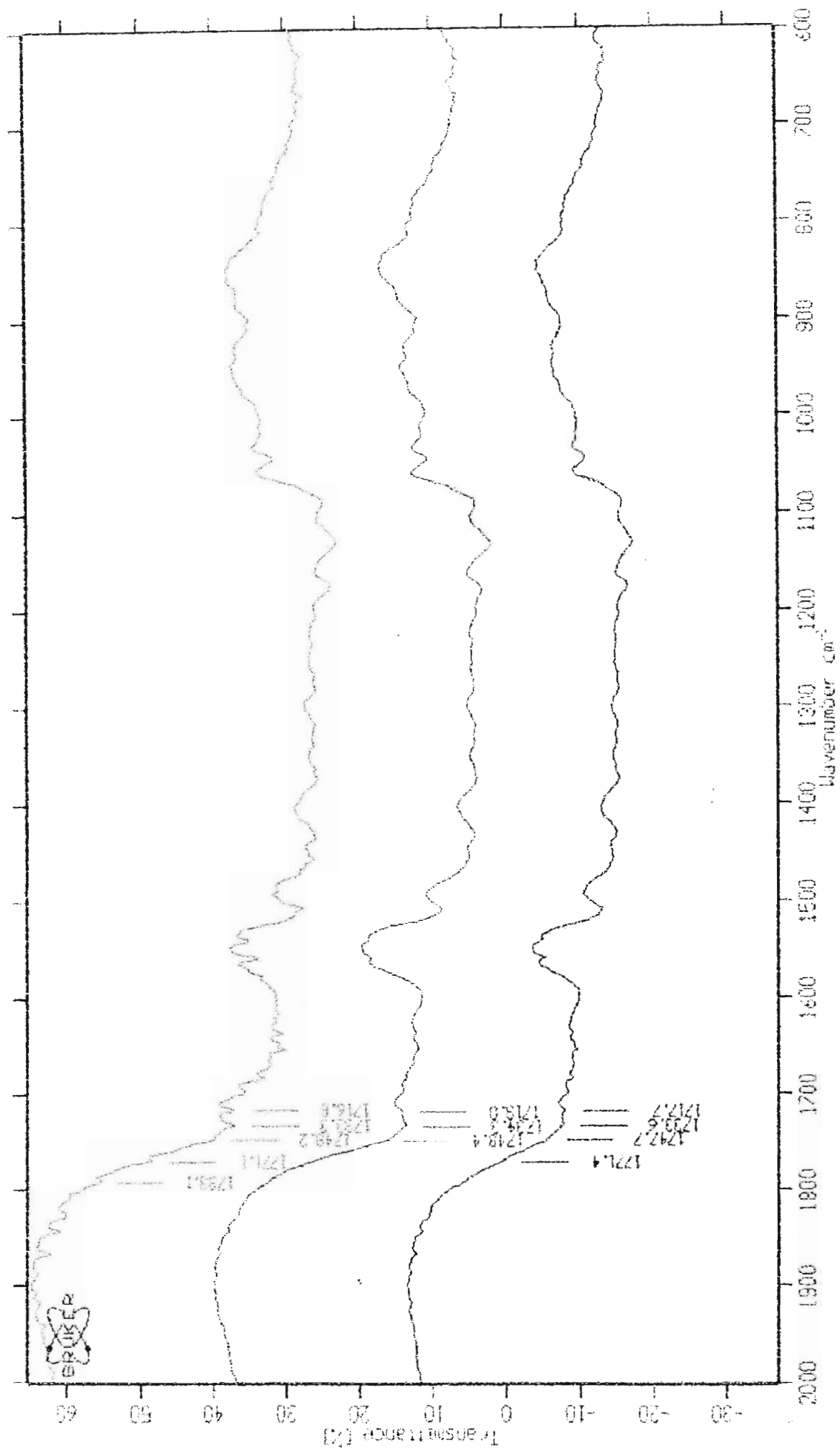


Figure 5.23 DRIFT spectrum : Sample AA003 - enlarged

sample : 003: Sample 3: accelerated ageing, climate	freq. range : 399.2255 - 3999.5655	measured : 15: 7/1988
technician :	resolution : 4.0	Instrument : IFS28 sample scans : 100
customer : Date	zerofilling : 2	app. n. : Double Sided, Forward-Backward
comments : Green-3A: aged, climate / Black-3B: unaged, climate / Purple-3C: accelerated ageing, climate - <i>deacidified</i>		

DRIFT Sample 4A, 4B & 4C: Climate cupboard series

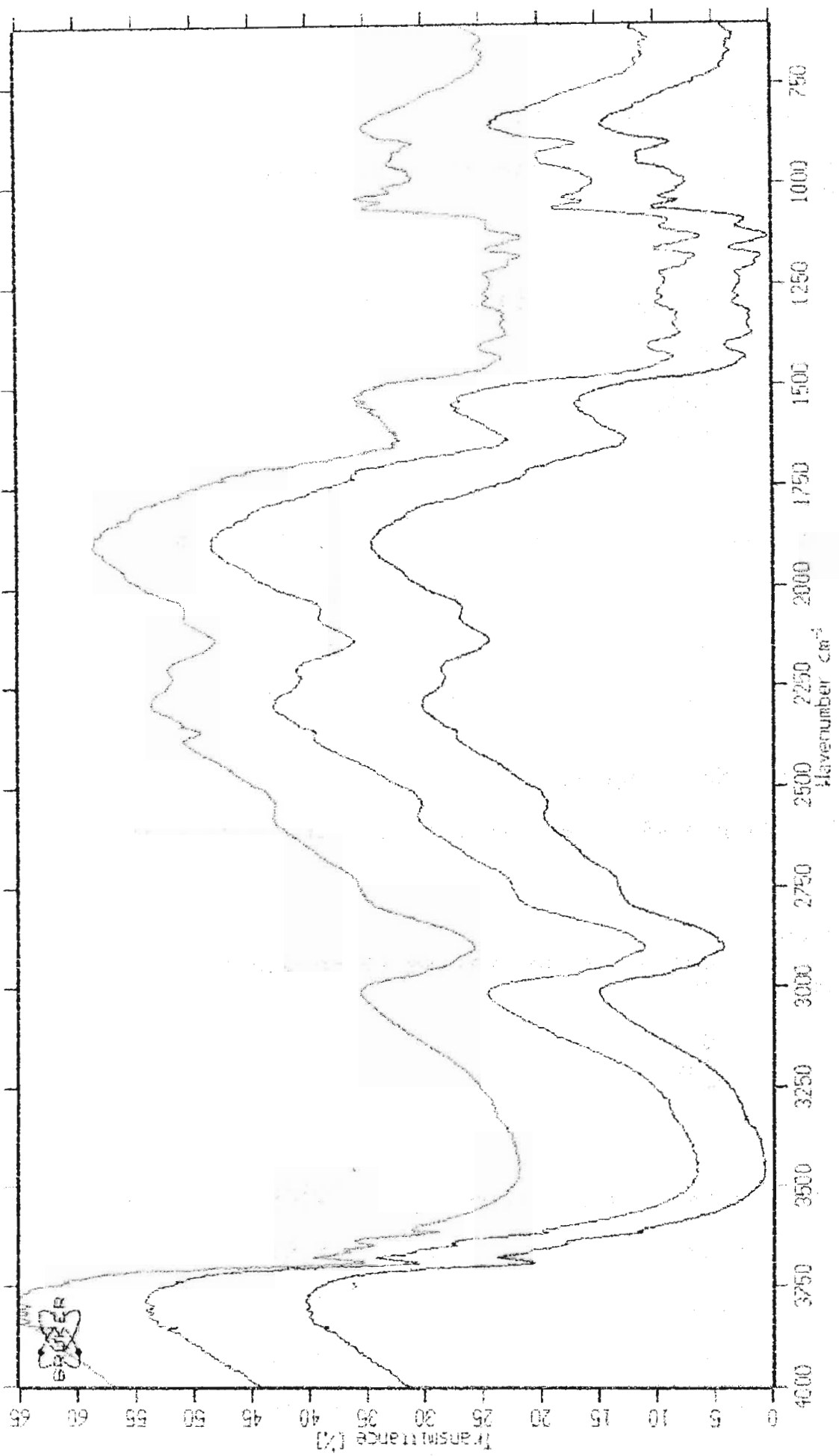


Figure 5.24 DRIFT spectrum: Sample AA004 A,B,C
263

sample : DRIFT series	freq. range : 399.2255 - 3999.9685	measured : 11/7/1988
technique :	resolution : 4.0	Instrument : IFS28
customer : Dale	zerofilling : 2	sample scans : 100
comments : Green- 4H: seed, climate, dark area / Black - unseed, climate, dark area / Purple - seed & deacidified, dark area	anal. n. : Double Sided, Forward Scatter	

DRIFT Sample 4A, 4B & 4C: Climate cupboard series - Enlarged

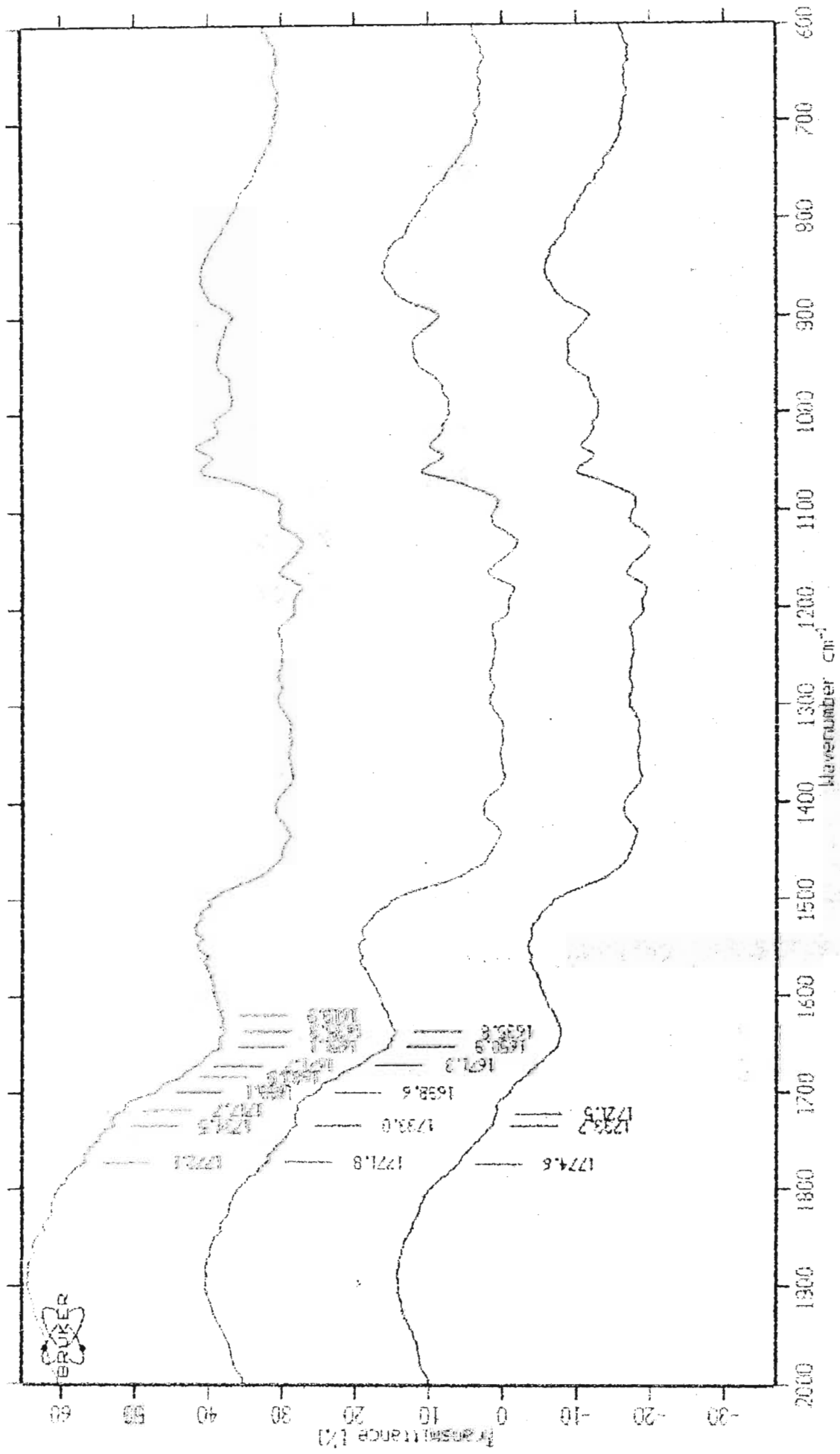


Figure 5.25 DRIFT spectrum : Sample AA004 A,B,C - enlarged

sample : DRIFT series	freq. range : 399.2255 - 3999.9695	measured : 14/7/1990
technique :	resolution : 4.0	Instrument : FT528
Customer : Dale	zerofilling : 2	sample scans : 100
Comments : Green 4ft 2000, climate, dark area / Black - unaged, climate, dark area / Purple - aged & acidified, dark area		anal. #: Double Sided Forward-Biased

DRIFT Sample 14: Climate cupboard series

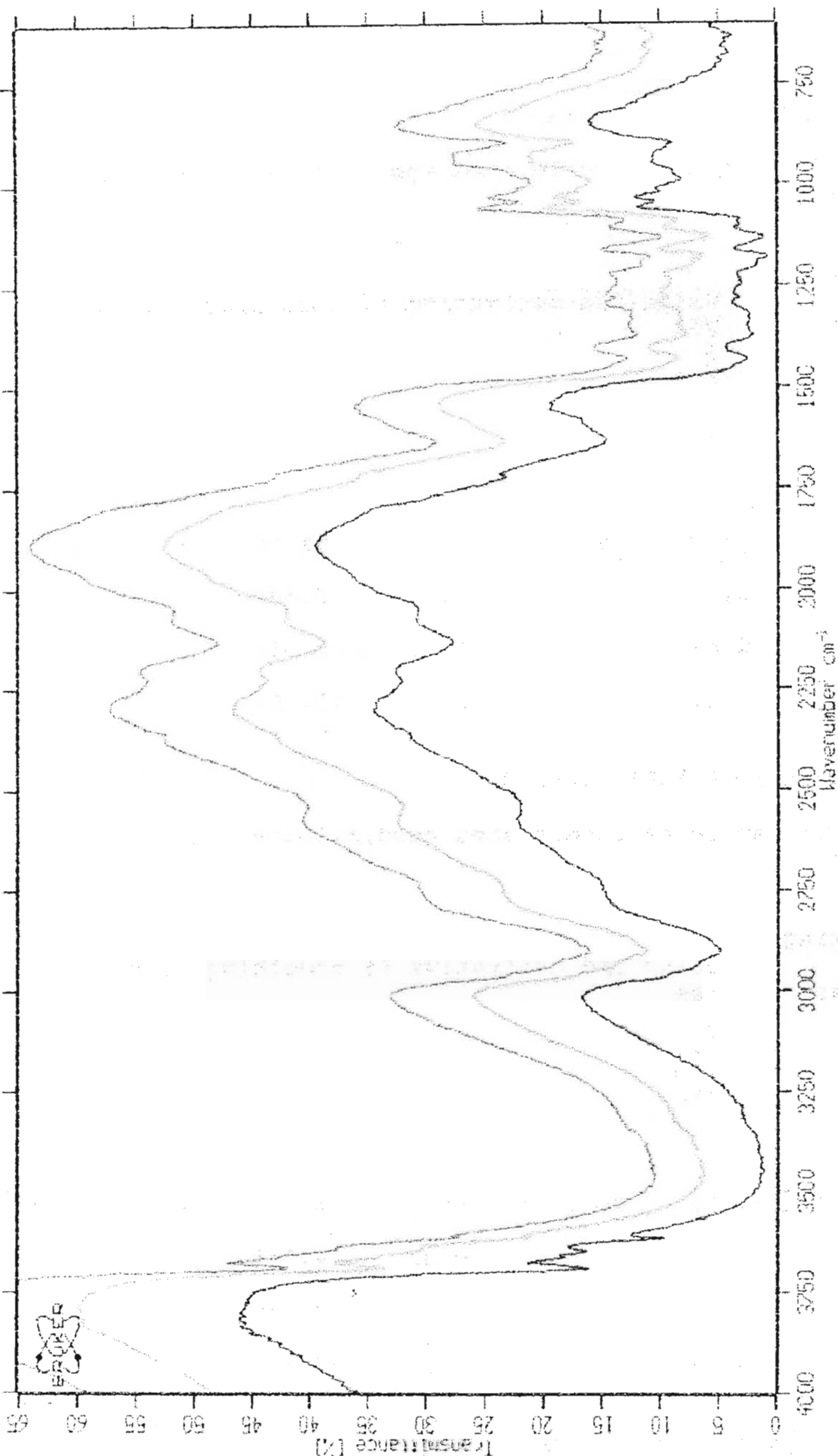


Figure 5.26 DRIFT spectrum : Sample AA004A
265

Sample Name: Sample AA004A	Area range: 399.2295 - 3998.9695	measured: 14/7/1998
Technique:	resolution: 4.0	Instrument: IFS28
Customer: Dale	zerofilling: 2	sample scans: 100
Comments: green-4h: acid, climate, water tideline / fan-4h: acid, climate, light area / Lilac-4h: acid, climate, dark area		anal. n.: Double Sided Forward-Backward

DRIFT Sample 4h Climate cupboard series - Enlarged

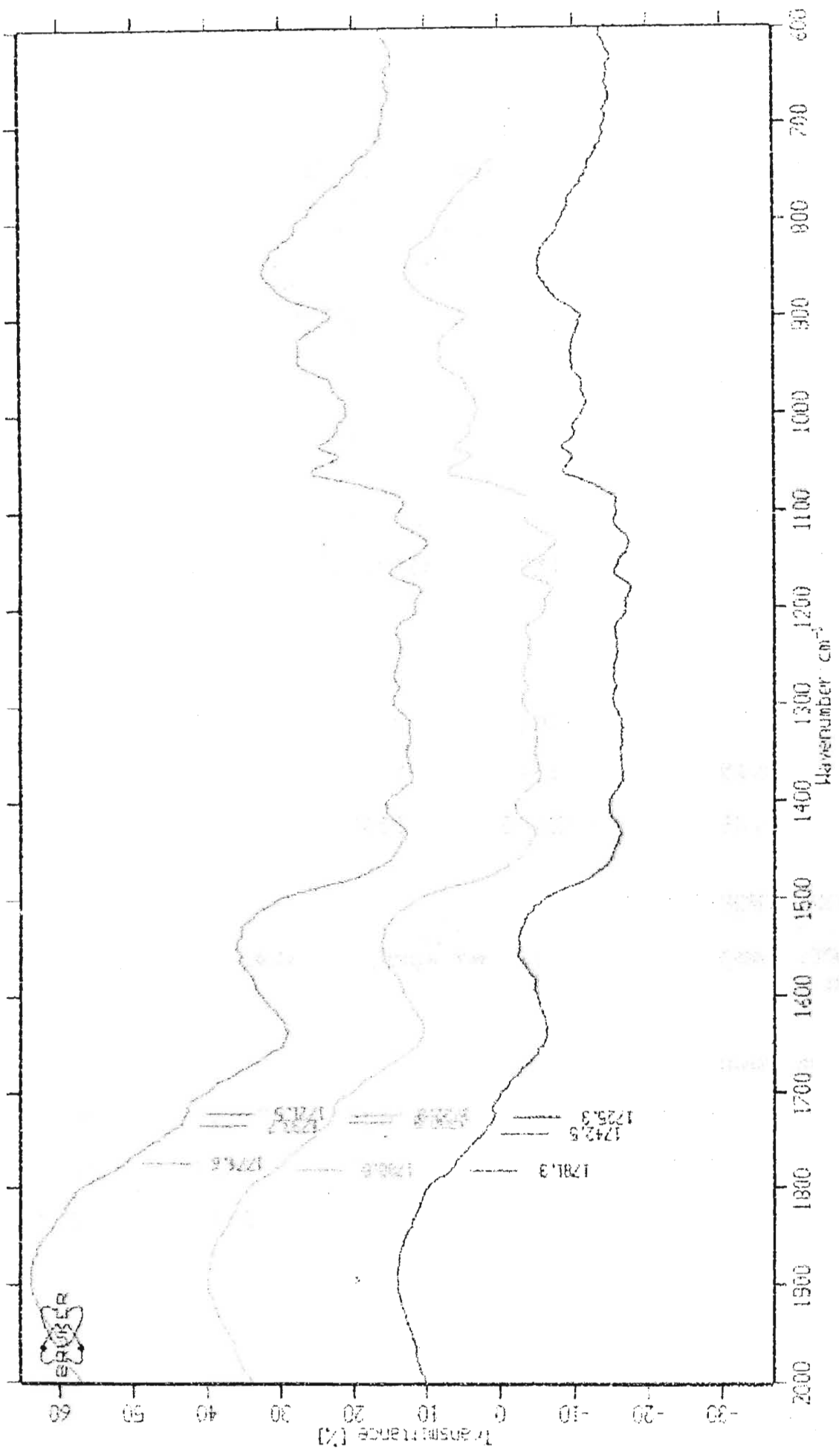


Figure 5.27 DRIFT spectrum : Sample AA004A - enlarged
266

Sample: DRIFT Sample 4h climate cupboard series	measured: 19/7/1996
Technique: DRIFT	Instrument: IFS28
Customer: Dale	scan. n.: Double Sided, Forward-Backward
Comments: Green-4h: aged, climate, water tideline / Tan-4h: aged, climate, light area / Lilac-4h: aged, climate, dark area	sample scans: 100
	Resolution: 4.0
	Zerofilling: 2
	Wavenumber range: 399.2255 - 3999.9695

5.2.2 CRYSTALLINITY INDEX

The restriction of chemical reactivity to the accessible hydroxyl groups in the amorphous fraction provides a useful tool in the study of the oxidative reaction in the quantitative measurement of the degree of crystallinity as an indicator of cellulose degradation. The structural modification of the cellulose was followed in this study, however, in evidence of an oxidative reaction, rather than a quantitative measurement of the degree of the resultant degradation. The bands and intensity variations assigned to the crystalline and amorphous fractions were used, therefore, to detect these structural changes in response to environmental conditions, the ratio of the bands at 1375 cm^{-1} and 2900 cm^{-1} being considered a suitable crystallinity index. (BLACKWELL, 1971; NELSON & O'CONNOR, 1964a; NELSON & O'CONNOR, 1964b; O'CONNOR, et al., 1958)

The crystallinity index derived is an indication of the progress of an oxidative reaction, it does not reflect the estimate percentage ratio of crystalline to amorphous regions of the respective samples. The crystallinity index therefore reflects the relationship described in 3.3.2 above, between changes in the fine structure of the cellulose and its chemical reactivity on the one hand, and changes in its moisture sorption capacity in response to fluctuating environmental conditions on the other.

The initial lack of definitive spectrophotometric results by FTIR-ATR led to the decision to extend the range of scale of the spectra to 4000 cm^{-1} , to include the OH stretching bands between 3800 and 3400 cm^{-1} . In that region it is possible to determine the accessibility of hydrogen linked hydroxyl (OH) groups by deuterium exchange combined with infrared analysis. The hydroxyl groups in the more accessible amorphous regions are thereby converted into OD groups with deuterium oxide, D_2O (heavy water). (BARKER, 1963; HERITAGE, MANN, & ROLDAN - GONZALES, 1963; MARRINAN & MANN, 1954) The basis for this decision was twofold:

- 1 It was anticipated that the structural changes evidenced in the crystalline / amorphous ratio would reveal the progression of the oxidative reaction that was not captured with sufficient sensitivity by spectrophotometric analysis of the functional groups.
- 2 In exchanging the hydroxyl groups with deuterium oxide, it was anticipated that the spectra of the critical region of $1800\text{-}1600\text{cm}^{-1}$, might more readily reveal the formation of functional groups as evidence of oxidative degradation. The family of absorption bands in the C=O stretching region of the infrared spectrum ($1750\text{-}1600\text{ cm}^{-1}$), assigned to the carbonyl function of carboxylic acid, and considered the prime indicator of oxidation, might otherwise be obscured by bound water, the HOH bending band normally being found in the same region. (LIANG, 1972)

Deuteration was conducted according to the qualitative technique given by Mann & Marrinan (MANN & MARRINAN, 1956), in the comparison of naturally and artificially aged samples by FTIR microscope spectroscopy, outlined in 4.4.1.3 above. The reported method of deuteration in the vapour phase was employed by bubbling nitrogen, dried in a column of phosphorus pentoxide (P_2O_5), through 99% deuterium oxide, before passing the moist gas over the sample. (See Figure 5.27)

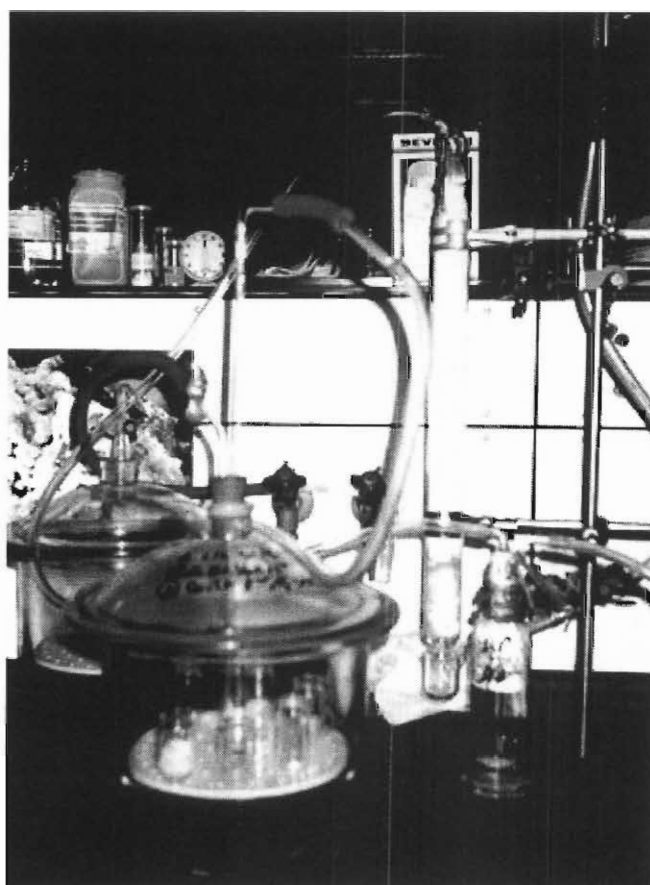


Figure 5. 28 Deuterium oxide exchange

The degree of crystallinity is measured as the ratio of band areas in the region 3600-3000 cm^{-1} after deuteration to that before deuteration. (BARKER, 1963) However, considerable difficulty was experienced in conducting the procedure under the FTIR microscope. The deuteration of the naturally aged samples was clearly evident in the major OH bands, a dramatic exchange noted at 2500 cm^{-1} . The rapid rehydrogenation of the sample, exposed to the water vapour in the air under the microscope, however, resulted in spectra which, despite peak formation at 1800-1600 cm^{-1} , did not exclude the possibility of water overlaid in the 1750-1600 cm^{-1} region. An attempt was made to overcome the problem by increasing the signal intensity of the background measurement to the same fourfold level of the sample measurements, using potassium bromide (KBr) powder under the microscope. The increased intensity allowed for the subtraction of much of the water vapour, previously intensified by the difference in the signal level between background and sample measurement, but the compensation was inadequate. After consultation with Bruker, manufacturers of the spectrometer, a background measurement including water vapour, in the form of a drop of water in a watch glass alongside the microscope platform, was employed in a final attempt, with equivocal success.

A more suitable analytical technique was then devised using the DRIFT cell attachment. The enclosed sampling compartment allowed for the exclusion of water vapour by thoroughly flushing the chamber with nitrogen passed

through silica gel. The absorbed water in each sample was dried in the sampling chamber for five minutes prior to measurement. The improved method of water vapour exclusion allowed for more accurate measurement of the spectra, and the simultaneous compilation of a crystallinity index. The degradation produced by oxidation was followed in the crystallinity index compiled from the ratio of selected band areas calculated in the peak integration reports of the associated spectra, according to the method described by Nelson and O'Connor. (NELSON & O'CONNOR, 1964a; NELSON & O'CONNOR, 1964b; O'CONNOR, et al., 1958) The degree of crystallinity is measured by the use of the ratio of the band areas of selected absorption bands :

$$A_{1372 \text{ cm}^{-1}} / A_{2900 \text{ cm}^{-1}}$$

The ratio of these areas is reported to give a crystallinity index that correlates well with accessibility derived from moisture regain, and was therefore selected for the purposes of this study. (NELSON & O'CONNOR, 1964b) It should be noted that to limit the problem of water vapour, all spectroscopic measurements were recorded from samples removed from the environmental control chamber on completion of the dry cycle, i.e. at 30°C and 30%RH. The values recorded in Table 5.1 and represented in Figure 5.29 below provide a comparative crystallinity index, as an indicator of the degree of degradation, rather than a percentage of the ratio of crystalline / amorphous groups.

The infrared (IR) peak integration of intensities at wavenumbers 1372 cm^{-1} / 2900 cm^{-1} was calculated using the Opus 2.0 software serving the Bruker IFS28 spectrometer. The transmission spectra were converted to absorbance spectra, for the software computation of peak values. Using Integration Method Type L, the peak height was determined in relation to a consistent baseline. For the peak at 1372 cm^{-1} , the left edge was set at 1390 cm^{-1} , the right edge at 1360 cm^{-1} , and the baseline from 1410 cm^{-1} to 1300 cm^{-1} . For the peak at 2900 cm^{-1} , the left edge was set at 2960 cm^{-1} , the right edge at 2800 cm^{-1} , and the baseline from 2740 cm^{-1} to 3010 cm^{-1} . The integration reports are included in Appendix C.

A crystallinity index was prepared from the measurement of the ratio of the selected infrared band areas calculated from the peak integration reports.

The ratio values presented in Tables 5.1 and 5.2 below correspond with those in the peak integration reports in Appendix C. It is not claimed that all digits are significant. A comparison of the chemical modification of the fine structure of the cellulose is thus enabled by means of the DRIFT spectra between Group 1: naturally aged samples with evidence of cellulosic staining, for comparison with Group 2: the artificially aged samples, which had been further subjected to the dynamic simulated climate ageing programme to induce oxidative degradation. (See Figure 5.29)

SAMPLE GROUP 1	1372 cm⁻¹	2900 cm⁻¹	Ratio
DRNA001.0 Sample 1: naturally aged, stained	0.15	0.37	0.41
DRNA002.0 Sample 2: naturally aged, stained	0.11	0.29	0.38
DRNA003.0 Sample 3: naturally aged, stained	0.16	0.36	0.44
DRNA004.0 Sample 4: naturally aged, stained	0.15	0.31	0.48
DRNA005.0 Sample 5: naturally aged, stained	0.14	0.34	0.41
DRNA006.0 Sample 6: naturally aged, stained	0.15	0.35	0.43
DRNA007.0 Sample 7: naturally aged, stained	0.18	0.39	0.46
SAMPLE GROUP 2			
DRAA001F.0 Sample 1A: Accelerated aged, climate, fold	0.07	0.21	0.33
DRAA002 Sample 2A: Accelerated aged, climate	0.14	0.32	0.44
DRAA003 Sample 3A: Accelerated aged, climate	0.11	0.24	0.46
DRAA004: Sample 4A Accelerated aged, climate	0.15	0.37	0.41

Table 5.1 Ratio of band areas at 1372cm⁻¹ and 2900 cm⁻¹

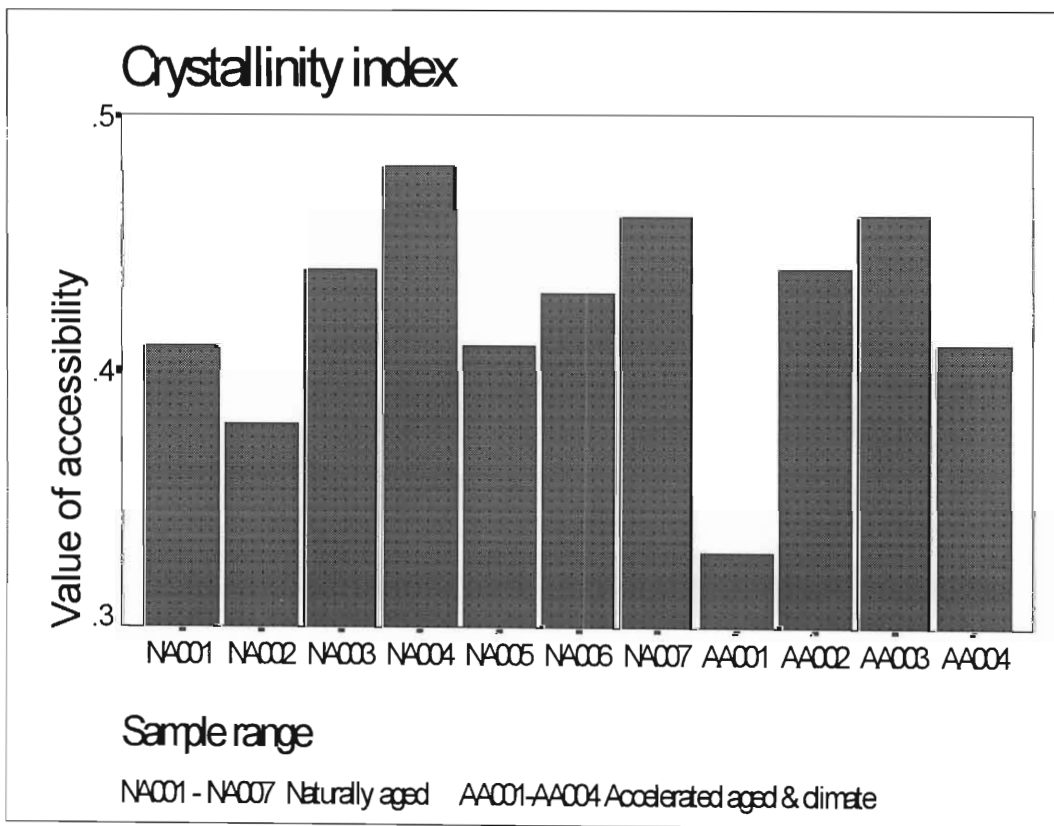


Figure 5.29 FTIR peak integration crystallinity index

The crystallinity index indicated the level of degradation of the various samples in terms of their accessibility to chemical reaction. The dynamic simulated ageing programme devised for this project appeared to have induced a degree of degradation similar to that suffered in natural ageing under ambient conditions, as reflected in the crystallinity index.

Apart from the Whatman filter paper (Sample AA001) of recent manufacture, the artificially aged samples appeared to have suffered a higher degree of degradation than the majority of naturally aged samples. The outliers demanded some qualification, however. The artificially aged sample 1 (AA001) reflected a low level of accessibility and therefore the lowest degree of degradation, while the highest degree of degradation was evident in the two naturally aged rag papers, represented by samples NA004 and NA007. This can be attributed in the case of Sample AA001 to the use of a new, meaning recently manufactured, Whatman filter paper. This is supported by the successive level of accessibility displayed in the recently manufactured Zanders bond paper (Sample AA004). The choice of Whatman filter paper is acknowledged as a poor representation of the average fibre furnish of the general bookstock of library collections. In anticipation of this problem, the sample was therefore enlarged to include a variety of papers, albeit of unknown previous history in samples AA002 - AA004. The choice of Whatman filter paper was made deliberately for reasons of reproducibility with previous studies of the phenomenon of

oxidation at the wet/dry interface. (DUPONT, 1996a; DUPONT, 1996b; EUSMAN, 1995)

An interesting conclusion drawn from the compilation of an infrared crystallinity ratio was the ranking of accessibility of naturally aged samples.

A high crystallinity ratio for the cotton furnish was anticipated in the rag samples NA004 and NA007, (CARDAMONE, et al., 1987), but in fact, the rag paper samples indicated the highest levels of accessibility, and thus, the lowest crystallinity. The peak formation noted in the FTIR spectrum of Sample NA004 in the region 1670 to 1740 cm^{-1} similarly indicated excessive oxidation. (Figure 5.9) The emergent pattern indicated a causative factor of oxidative degradation under humid climatic conditions. The ranking revealed a dependence, not only on the crystalline / amorphous ratio of the cellulose structure as a characteristic of the fibre furnish, but on the capacity of cellulose to undergo structural modification at the molecular level of organisation in response to climatic conditions. Crystallinity is revealed as a variable characteristic, changing in response to environmental conditions, and the index reflected in Figure 5.29 therefore indicates the value of accessibility of the sample range under the given environment at the time of measurement.

A close inspection of the surface characteristics of the naturally aged samples revealed a correlation between the accessibility value and the density of the paper sample and its surface roughness. The soft, limp

surface of the rag papers used in this experiment recorded the highest levels of accessibility. An immediate conclusion is that the increased accessibility is a result of the lack of surface sizing in these samples. In addition, a reported effect of oxidation on morphology is the swelling, or ballooning effect on fibres, which tend to rupture on swelling, which is also related to the soft handle of the samples. (ARTHUR & HINOJOSA, 1971) The smooth surfaced samples of high density recorded the lowest levels of accessibility. This conclusion is supported in the reported relationship between accessibility and moisture regain. (JEFFRIES, 1964; ROBERTS, 1996)

A comparison of the crystallinity index of naturally aged samples (NA001-NA007) , with that of the artificially aged samples (AA001-AA004), further enabled an evaluation of the success of the experimental design in the simulation of ambient environmental conditions for induced oxidation. The use of accelerated ageing in predicting paper permanence, presented in 3.4, was a point of contention in the conceptual design of this project. However, the similarity in the range of accessibility values for both naturally aged samples and those subjected to the simulated ageing procedure was taken as validation of the research design for induced oxidation.

5.2.2.1 MOISTURE REGAIN

As the dry mass of only the control sample Whatman filter paper (Sample AA001) was known, the moisture regain of this sample was traced during the climate cupboard procedure to demonstrate the reported relationship between accessibility and moisture regain under fluctuating environmental conditions. In addition, the structural modification of this sample, reflected in the crystallinity index, is followed as evidence of an oxidative reaction.

The sample was measured spectroscopically using the DRIFT cell, before and after ageing, and following exposure to fluctuating environmental conditions in the environmental control chamber. The index derived from the infrared crystallinity ratios, presented in Table 5.2 and represented in Figure 5.30, indicate the anticipated increase in crystallinity on ageing, and, pertinent to this study, a dramatic drop in crystallinity on further exposure to a fluctuating climate.

Sample	1372 cm ⁻¹	2900 cm ⁻¹	Ratio
Sample 1 Unaged	0.186319	0.40359	0.461654153
Sample 1 Aged	0.20117	0.407672	0.4934604
Sample 1 Aged & climate	0.0754372	0.21954	0.343614831

Table 5.2. Ratio of band areas at 1372 cm⁻¹ and 2900 cm⁻¹: Sample 1 (AA001)

The variation reflected in the crystallinity index of Sample AA001 is evidence of the dynamic response of the fine structure of cellulose to the fluctuations in environmental conditions. Chemical modification of the fine structure of the cellulose had occurred as a result of the experimental procedure, shown to occur in multiple cycles of drying and wetting and equated, in the reduced ability to re-swell, with wet hornification.²

Crystallinity measurements were not made at successive cycle changes in the dynamic simulated climate ageing programme, to minimise disruption of the transudational movement of moisture through the sample stack, which the researcher believed might lead to evidence of cellulosic staining. From the limited data collected a relationship between moisture regain and crystallinity is indicated, as described in 3.3.1. The changes in the fine structure of the cellulose, and its potential for chemical reactivity, clearly mirror the changes in its decreasing moisture sorption capacity in response to fluctuating environmental conditions.

2

Wet hornification is the change affected in fibres by water removal, in contrast to dry hornification resultant upon dry oven ageing. Hornification, defined as a decrease in water retention value, is understood as a crystallisation process. Crystallisation is shown to occur on the drying cycle, mainly in the fines fraction, indicated in a reduced ability to re-swell. (WEISE, 1998)

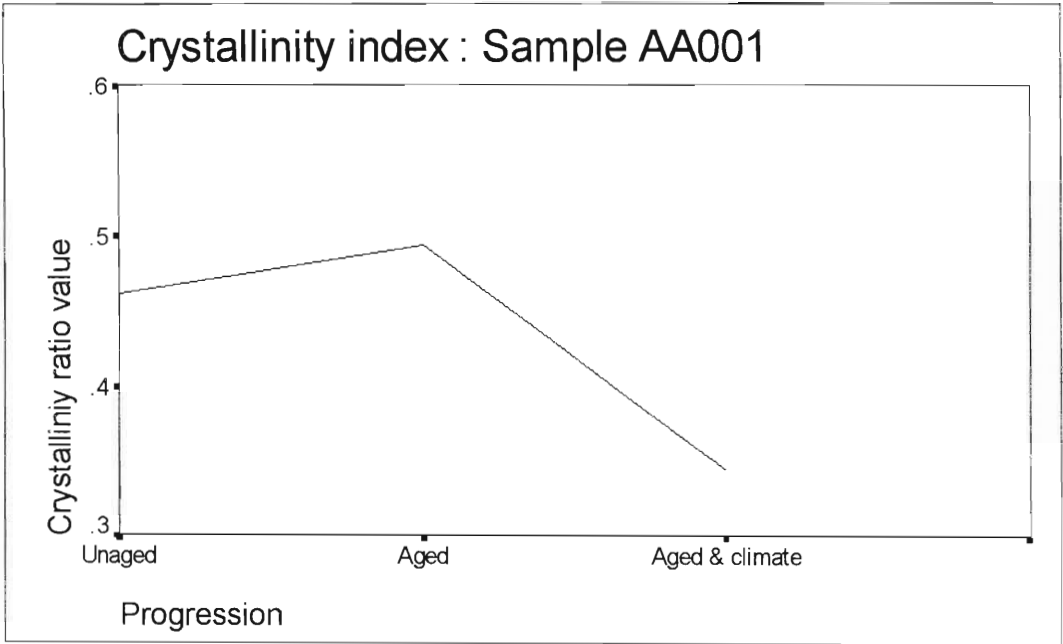


Figure 5.30 Crystallinity index of Sample AA001

5.2.3 METHYLENE BLUE ABSORPTION

The first published observation of the development of a brown line at the wet/dry interface noted the increased methylene blue absorption at the boundary region between wet and dry regions. (BONE, 1934) Methods of quantitative determination of carbonyl groups by ionic exchange with cationic dyes, including methylene blue are described by TAPPI norm: T237 su-63 (KRAUSE, 1991) , and the use of methylene blue as a redox indicator dye is well documented in the literature, and was presented in 2.5.2 and 4.4.2.1 above.

The method employed in this study was reported by Eusman. (EUSMAN, 1995) Paper samples were immersed for two minutes in a 0.1% solution of methylene blue and rinsed for two hours. The results presented here are a qualitative indication of the concentration of carboxylic groups at areas of moisture accumulation, constituting a wet/dry interface.

Naturally aged samples (NA001-NA007) were stained with an even absorption of methylene blue, indicating a general level of oxidative degradation. A representative example of Sample NA001, before and after immersion in the methylene blue solution, is included in Figure 5.31. A comparison of the sample page indicated:

- 1 that the even absorption of methylene blue dispelled any direct correlation between the oxidative degradation and the localised areas of cellulosic staining, traditionally known as foxing; but
- 2 that the increased absorption of methylene blue was noted at the fore-edge and page margin area, in the same general area as water transport might be anticipated, and that the specific foxing spots tended to be similarly located;
- 3 the areas of stronger methylene blue absorption indicated a strip down the centre of the page from top to bottom. The nature of this central stain indicated a distortion of the planar dimension of the volume, permitting the incursion of air, and in a humid climate, of water vapour into the volume in that area.

An exception to the general staining was exhibited in naturally aged Sample NA004, included in Figure 5.32. This sample clearly absorbed methylene blue most strongly, which confirmed the measurement of the greatest accessibility value recorded for this sample in the crystallinity index. (See Fig 5.28) This rag paper, reputedly of the highest quality by traditional permanence standards, had undergone the greatest oxidative degradation exhibited by the test series, as a result of the porous nature of the fibre furnish. The point of particular interest in Sample NA004 was that, while strong methylene blue absorption was noted in the page margins, spotted

areas of discolouration within the margin and encompassing the text block, exhibited notably less absorption. Again, the increased methylene blue absorption revealed:

- 1 that no direct correlation was evident between the oxidative degradation, and the localised areas of cellulosic staining, known as foxing; but
- 2 that increased absorption of methylene blue was noted in the same general area of water transport in which the specific foxing spots were also located.

The lack of methylene blue absorption in the text block area of Sample NA004 indicated a possible previous phenomenon, such as the diffusion of the oil base of the printing ink into the surrounding paper fibres, which would have hindered the transport of moisture vapour in that area. The similar lack of absorption in the spotted areas within the margins leads to the conclusion that a previous reaction has taken place which prevents methylene blue absorption in these areas. Areas of cellulosic discolouration had been removed from the margin for FTIR spectroscopy. The well defined circular forms of marginal spotting are noted as different from the diffuse blotched staining commonly noted, and warrants further investigation of this sample in the classification of foxing in a subsequent study.

Reagent staining of the samples exposed to the dynamic simulated ageing programme revealed interesting results in Sample AA004 . Sample AA004A, i.e. exposed to accelerated ageing and dynamic climate ageing programme, indicated strong general methylene blue absorption in the lowest sheet in the stack, adjacent to the glass plate in the climate cupboard. (See Figure 5.33) The evidence provides justification for the increased cellulosic discolouration noted by this researcher at the endpapers and outer sections of a closed volume, or adjacent to coated illustration pages, where the transport of water vapour is hindered by a less porous surface.

Similar evidence is seen in the same sample, Sample AA004C where the uppermost sheet revealed increased methylene absorption in the area adjacent to the glass weight strip in the centre. General increase in methylene blue absorption was noted in the top and right sides, and particularly in the bottom right-hand corner, exposed to the atmosphere by a fold in the adjacent page. The association of cellulosic staining with dog-eared corners is confirmed by this evidence of oxidative degradation at folded corners. (See Figure 5.34) It was interesting to note that the clear evidence of increased methylene blue absorption seen at the folded corner was not evident in the Whatman filter paper sample (AA001), which absorbed evenly throughout all samples, although at a lower intensity in the non-aged control.

Sample AA001 showed some cellulosic discolouration at the edge of the sample stack, indicating the lateral migration of water introduced in pre-treatment to simulate conservation treatment. The amount of water applied was evidently insufficient, as evidence of oxidation at the edge of the stack was not confirmed in the methylene blue reagent staining. Increased methylene blue absorption was however, noted at the periphery of those samples treated with paste and glue, and in the interstices of the application thereof.

Evidence of oxidative degradation was also revealed in the increased methylene blue absorption noted in the sample prepared to simulate the brush strokes of laminate adhesive on artworks laid down unevenly. In sample AA004/CMC, two sheets were attached at marked strips of carboxymethylcellulose paste spaced equidistant from the centre. A strong methylene blue absorption in the central airspace between the two pasted strips provides clear evidence of a correlation with discolouration noted at air bubbles in laminated works. A tideline was formed in the bottom left of sample at the edge of an interleaving film of Melinex polyester, in the same position at which fluorescence was noted, supporting the observation of chemical reactivity at sites of moisture accumulation. This affirms the major conclusion of the methylene blue reagent staining procedure, that the formation of a wet/dry interface is a potential hazard where non-porous materials are employed for archival storage. (See Figure 5.35)

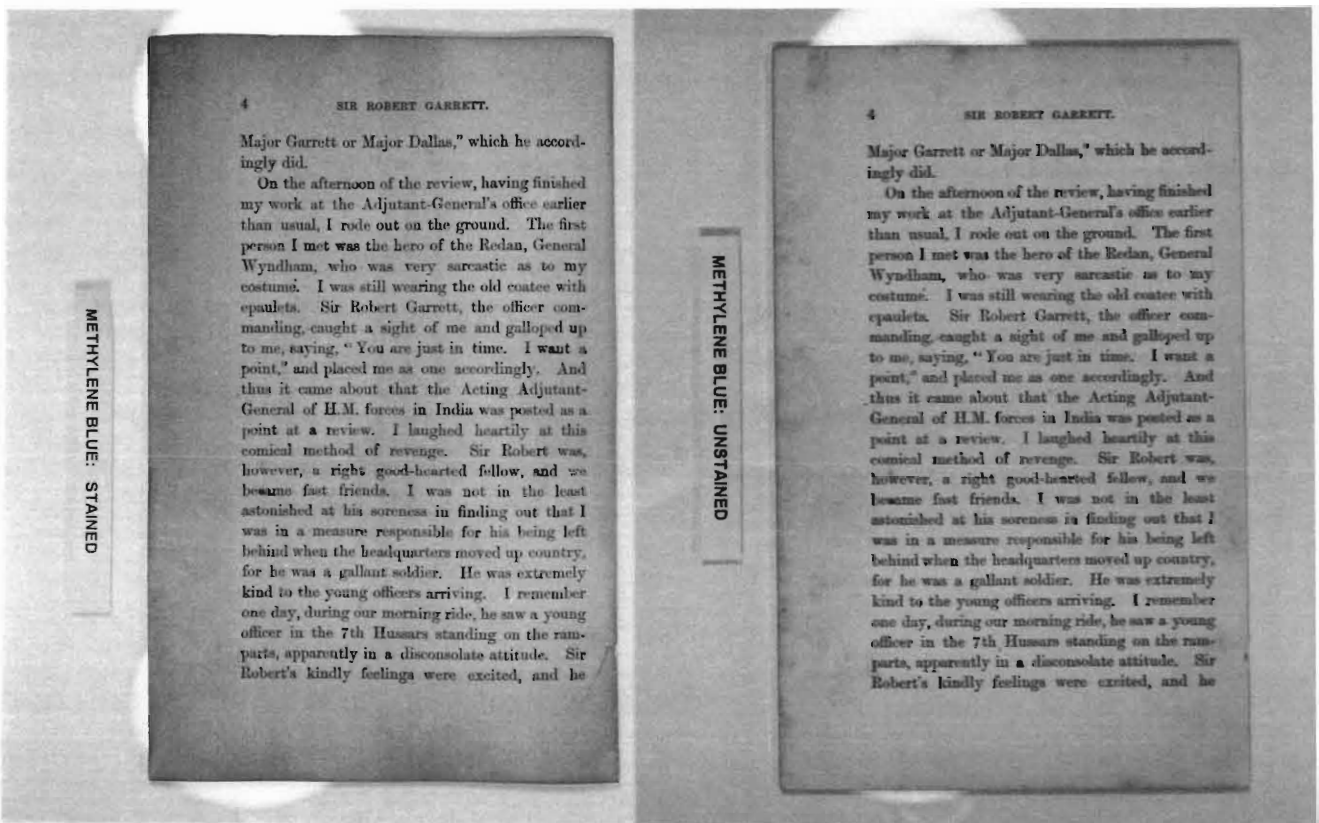


Figure 5.31 Methylene blue absorption : Sample NA001

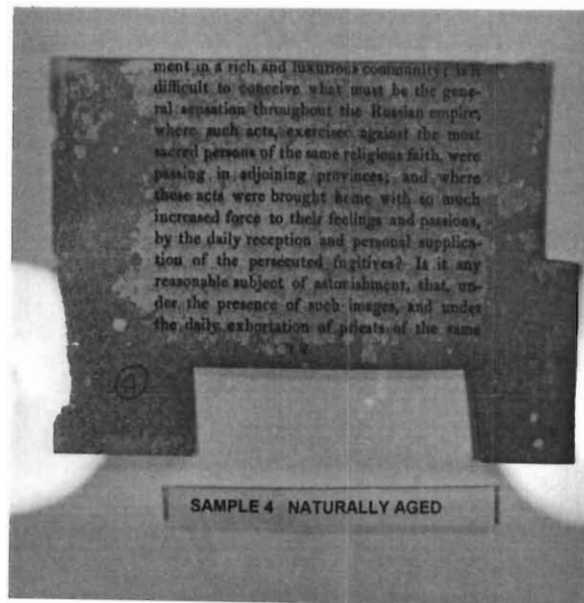


Figure 5.32 Methylene blue absorption : Sample NA004

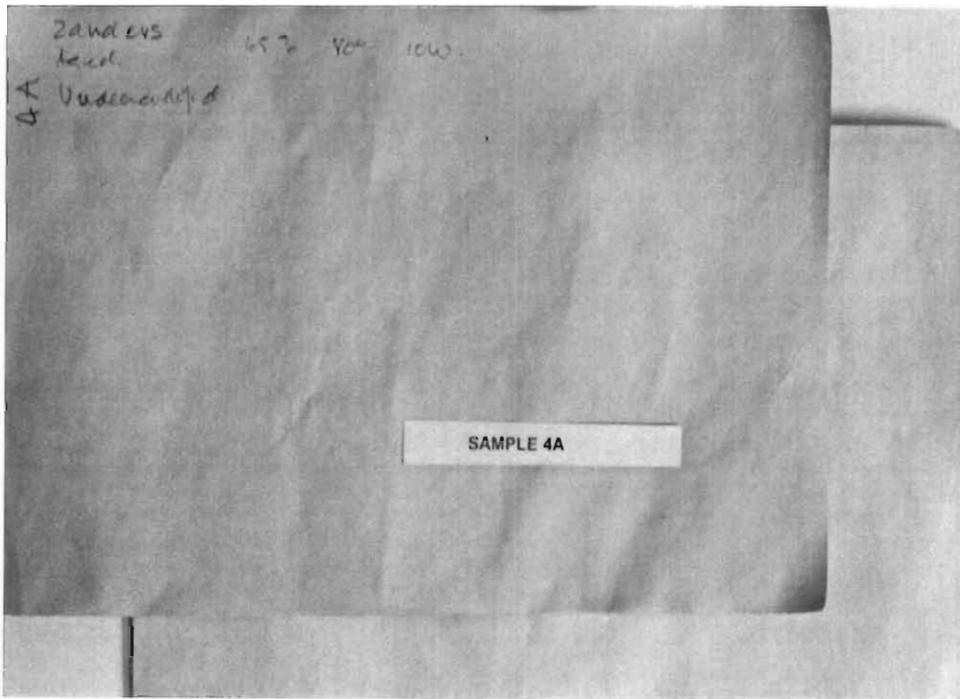


Figure 5.33 Methylene blue absorption : Sample AA004A

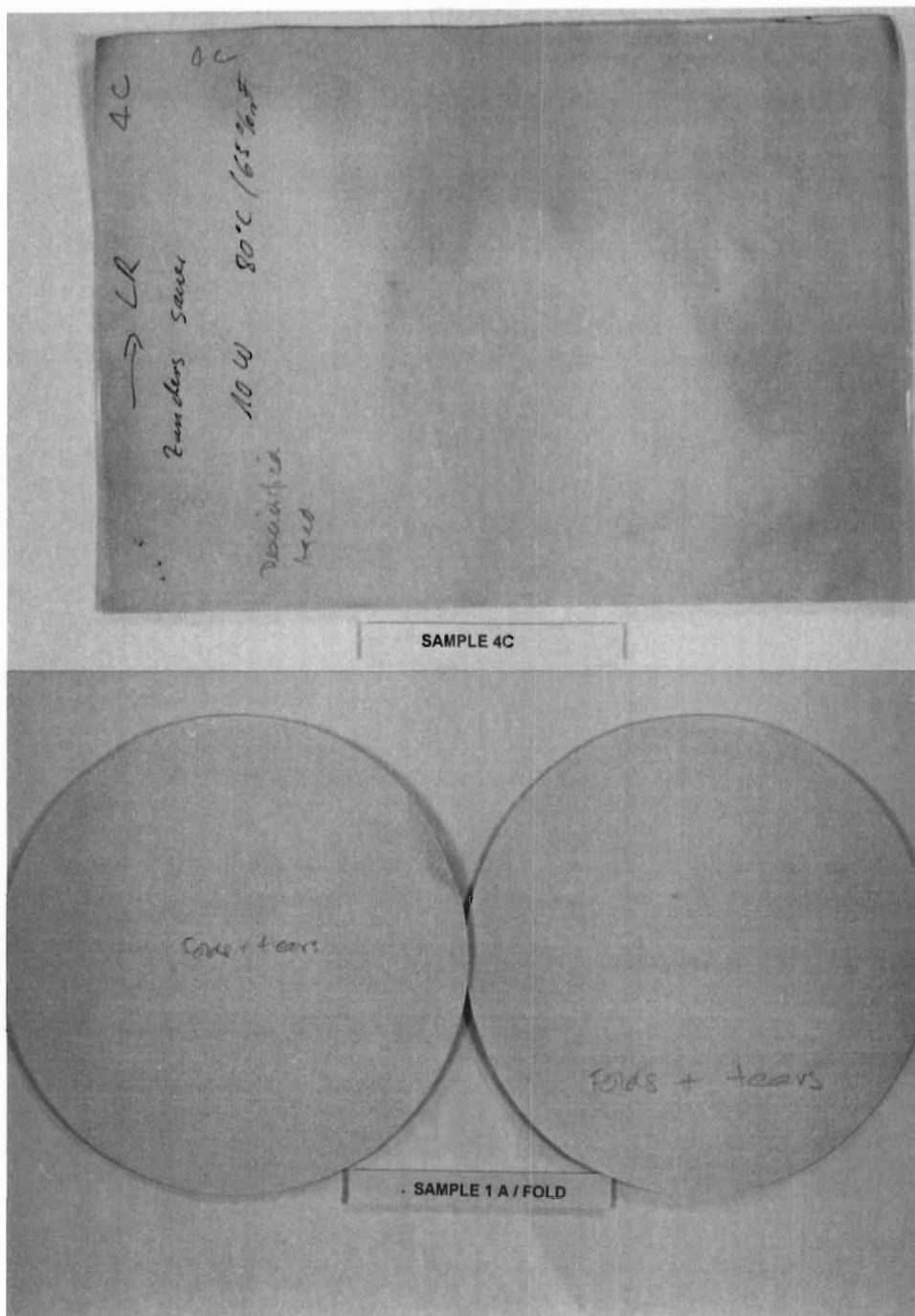


Figure 5.34 Methylene blue absorption : Sample AA004C/AA001AF

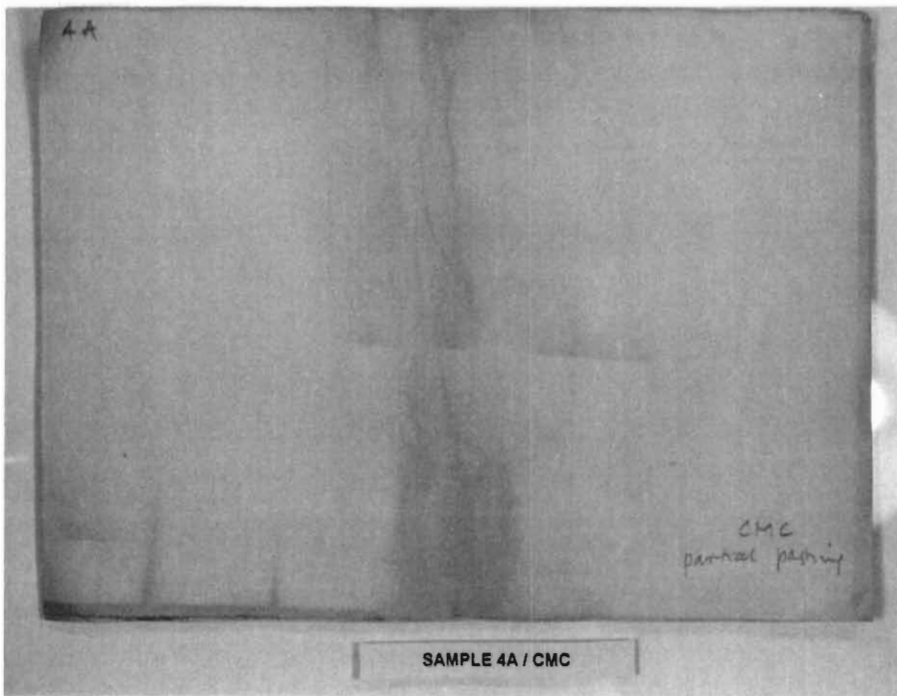


Figure 5.35 Methylene blue absorption : Sample AA004/CMC

5.2.4 HYDROGEN PEROXIDE FORMATION

The oxidative reaction at the wet/dry interface was investigated in 2.3.1, in which organic peroxides are formed by the evaporation of water in the desorption cycle. (DIXON, 1886; LAIDLER, 1993) The subsequent decomposition of the peroxide initiates the oxidation of the parent hydrocarbon, producing free radical carriers for the chain reaction, which results in the formation of secondary oxidation products such as ketones, aldehydes, acids, alcohols, water and carbon dioxide, etc. (MESROBIAN & TOBOLSKY, 1961; TOBOLSKY, et al., 1950) The final analytical procedure applied in this study was the determination of the formation of hydrogen peroxide in response to environmental fluctuations as an initiator of an autoxidative reaction.

The chemical reagent staining technique, employed in the use of methylene blue as an indicator of the formation of carbonyl groups, was therefore extended to the determination of the formation of hydrogen peroxide, as suggested by previous research. (HOFENK DE GRAAFF, 1994) The extraction of degradation products from the area of discolouration had previously yielded poor results, and the direct application of a chromatographic indicator was preferred.

The peroxide reagent selected, Naphtorin, described in 4.4.2.2, was prepared according to the method for thin layer chromatography. In the

presence of peroxides, the aromatic amine of the phenolic indicator is converted to a blue-coloured chinoline pigment. (JORK, FUNK, FISCHER, & WIMMER, 1993)

A control sample was prepared by dropping a 30% hydrogen peroxide solution onto sample AA004. The Naphtorin reagent was then applied to the full range of sample papers (NA001-7) and (AA001-4) in a spray application, to avoid the inadvertent formation of tidelines following immersion, that might be confused with tidelines formed in the dynamic accelerated ageing process. The control sample indicated strong blue pigmentation in the areas spotted with hydrogen peroxide. (See Figure 5.36)

As was anticipated, the transient nature of the formation and decomposition of hydrogen peroxide in the oxidative mechanism of paper degradation precluded the indication of peroxide in the naturally aged samples.

Strong pigmentation was evident in the tideline exhibited in the pasted sample of Whatman filter paper (AA001/CMC), prepared with carboxymethylcellulose paste in simulation of conservation treatment. (See Figure 5.37) Two points of interest arise from the evidence of hydrogen peroxide formation:

- 1 the well defined tideline at the edge of the paste application, indicating the formation of a wet/dry interface at the edge of the

pasted area, can be similarly anticipated in local aqueous conservation treatment; and

- 2 an uneven, cloudy reagent staining in the surrounding area, extending in places to the edge of the sheet, indicating a migration of hydrogen peroxide by capillary action in response to fluctuations in environmental conditions.

The result of reagent staining on Sample AA02D revealed evidence of peroxide formation in a central band, correlating with the glass weight that lay on the surface of this sample. (See Figure 5.38) Confirmation is provided of oxidative degradation in the leaf adjacent to a non-porous surface seen in the evidence of methylene blue absorption. Also of interest is the more widely diffuse evidence of peroxide formation on the verso of the same sheet, indicating the transudational movement of water vapour towards the point of moisture accumulation at the glass surface. This sample provides evidence of oxidative degradation in the desorption process of both surface evaporation and in bulk diffusion.

The evidence of the formation of hydrogen peroxide has no direct relationship to the phenomenon of cellulosic discolouration known as foxing, but in the evidence of transudational flow, provides an explanation of the staining evident in consecutive leaves of a book, and particularly in leaves adjacent to non-porous coated paper inserts in the form of illustration pages.

The reported role of lignin in reducing the rate of oxidative reactions was followed in samples NA005 and AA003. (DANIELS, 1986b; ERICSSON, LINDGREN, & THEANDER, 1971) The formation of hydrogen peroxide was not evident, but the general methylene blue absorption in NA005, as in all naturally aged samples, indicated that oxidative degradation had taken place, despite the presence of lignin.

A final conclusion drawn from the reagent staining procedures was the comparison of two samples of Samples 4AA04C, one stained with methylene blue and the other stained with the peroxide reagent Naphtorin. (See Figure 5.39) The methylene blue stain shows carbonyl formation at the central band corresponding with the glass weight, at the fold in the lower right hand corner, and a general stain in the area demarcated diagonally from top left to bottom right. The peroxide reagent staining of the same sample reveals light discolouration in the corresponding area from top left to bottom right. This phenomenon supports the hypothesis that oxidative degradation, evidenced in the methylene blue stain, is a result of free radical formation by hydrogen peroxide formation and decomposition under environmental fluctuations. The sorption and desorption of water vapour in the response of an unstable equilibrium moisture content of the paper to the ambient environment was seen in this sample to result in an oxidative reaction.

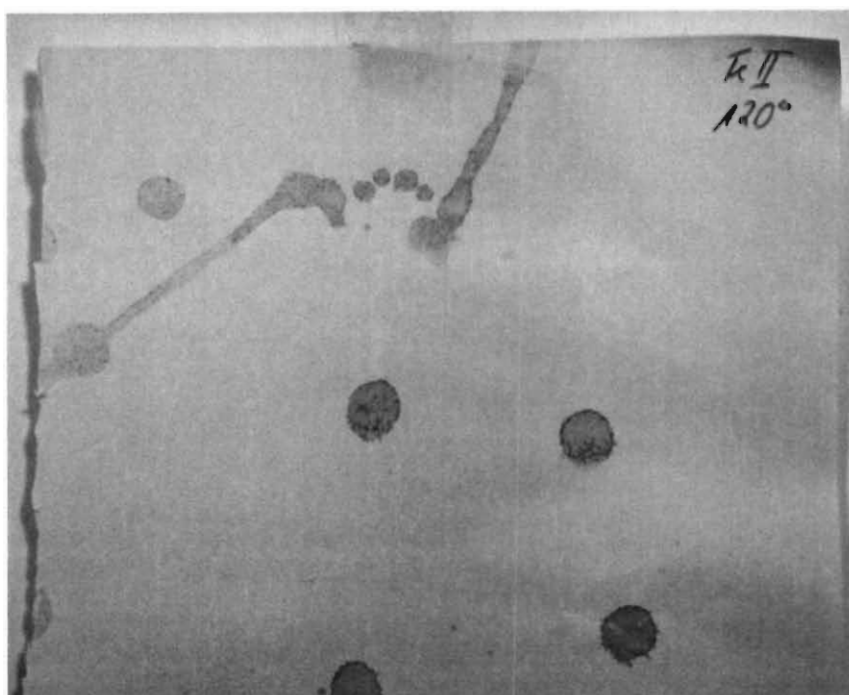


Figure 5.36 Naphtorin staining reagent: control sample

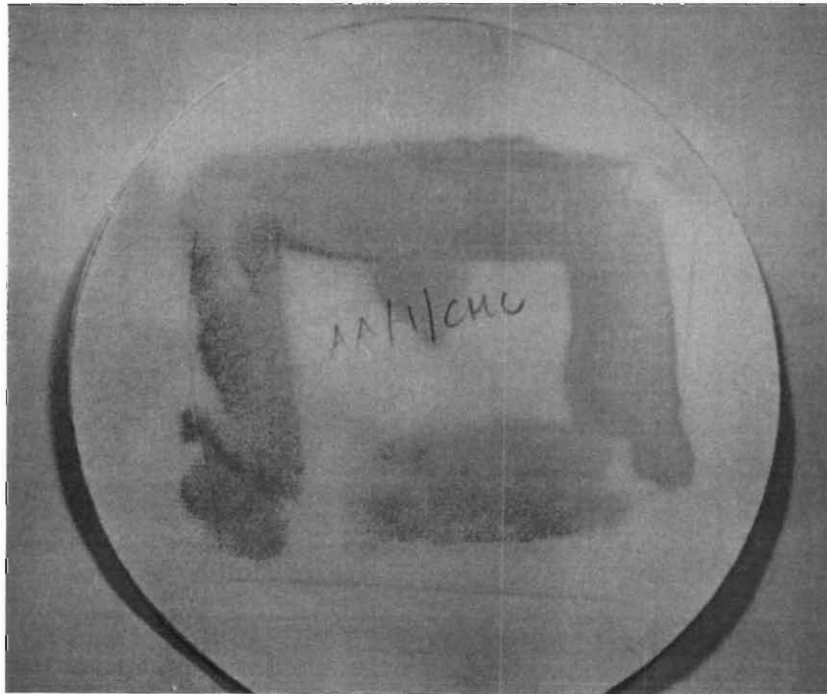


Figure 5.37 Hydrogen peroxide formation - Sample AA001/CMC

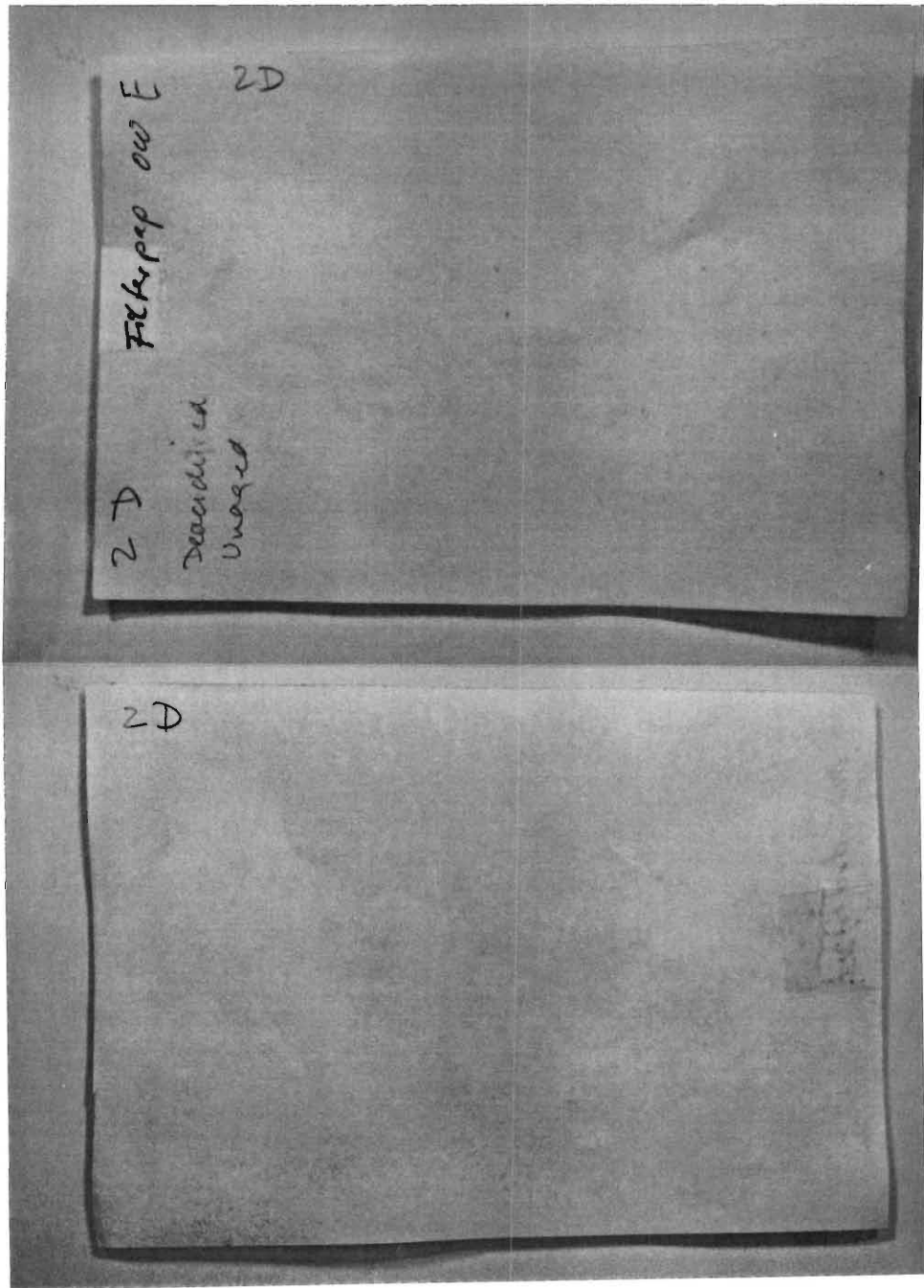


Figure 5.38 Hydrogen peroxide formation - Sample AA002D

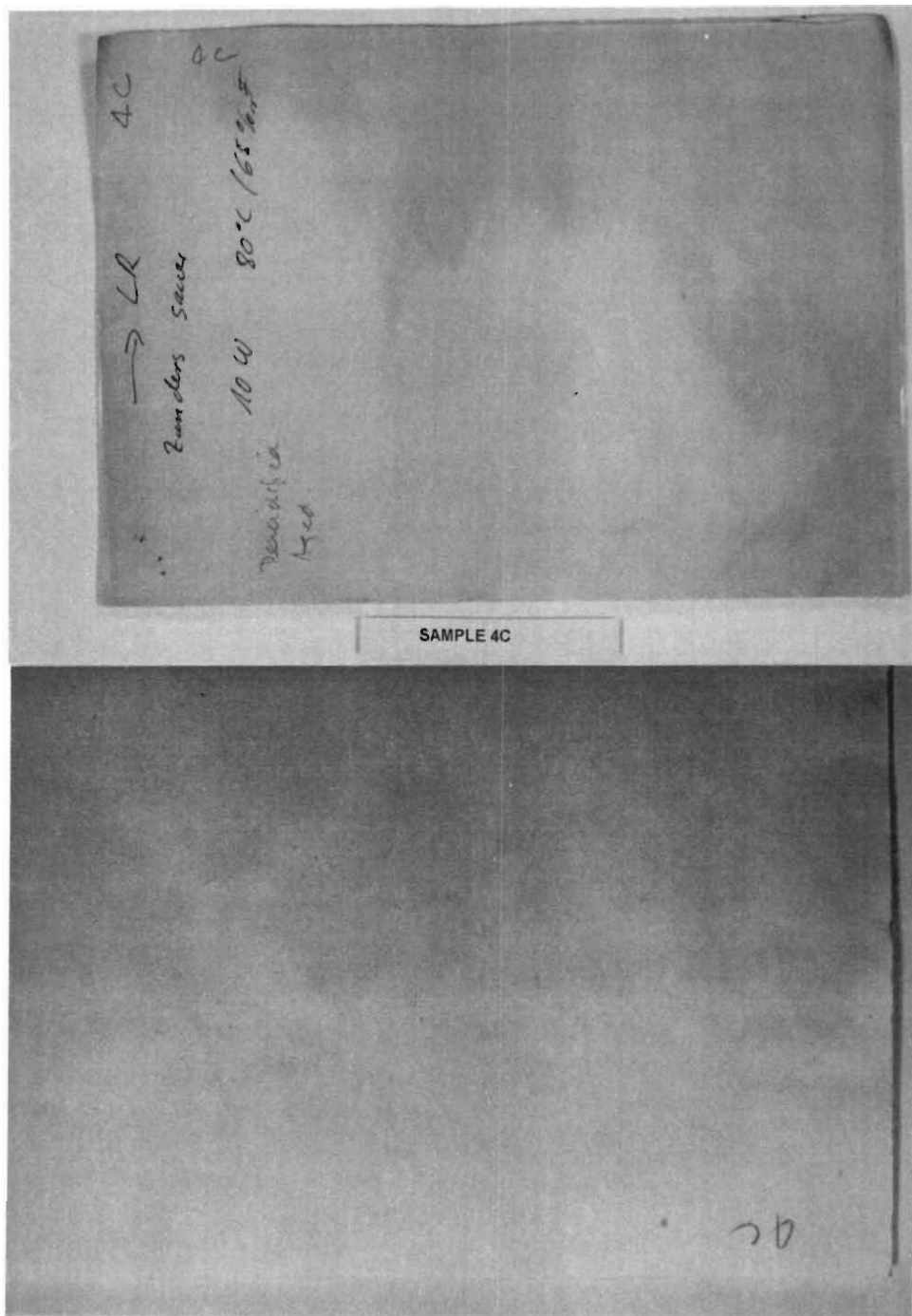


Figure 5.39 Hydrogen peroxide formation / Methylene blue absorption - Sample AA004C

5.3 ANALYTICAL INTERPRETATION

The analytical data compiled in this project served to develop a theory of paper deterioration in the cellulosic discolouration manifest in humid conditions in the phenomenon of oxidation at the wet/dry interface. The objectives of the analysis conducted were formulated as being:

- 1 To test the ambient range of environmental conditions to determine the effect of fluctuations in precipitating oxidative mechanisms of degradation.
- 2 To determine the significance of an oxidative reaction at the wet/dry interface in the manifestation of cellulosic discolouration known as foxing.
- 3 To evaluate the relationship between the fine structure of the cellulose substrate and its potential degradation by an oxidative mechanism.

The study of cellulosic discolouration has focussed in the past on the evidence of foxing as a result of microbiological infestation or of metal-induced catalysis. The role of oxidation reactions has been investigated in the conservation context as the yellowing of paper, and most commonly attributed to factors of light, heat, moisture, the presence of metal cations

and pollutant gases. (CARTER, 1996) Colour reversion is investigated in the paper manufacturing industry, in terms of peroxide formation and the role of free radicals. (BURGESS, 1987; KLEINERT & MARRACCINI, 1963; KLEINERT & MARRACCINI, 1966; MARRACCINI & KLEINERT, 1962; REICHE, 1938) A recent study of the relationship between colour reversion and paper permanence in a radical-containing atmosphere analyses the effect of pollutant exposure. (WAN & DEPOW, 1995)

Previous studies by Hon using FTIR in the chemical analysis of the naturally aged paper degradation products reflect the presence of chromophoric groups - carbonyl, carboxyl and hydroperoxide groups which contribute to the discolouration of the cellulose. (HON, 1979) Carboxylic groups were consistently exhibited in the carbonyl function of carboxylic groups by the absorption band at 1720 cm^{-1} . (HON, 1986) Of particular interest to this study was the fact that the same chemical degradation products were also found in foxed spots. (CAIN, 1983)

The aim of this study in contributing to the field of investigation was the determination of the role of environmental conditions in initiating the oxidative reaction as an alternate explanation for the causation of cellulosic discolouration. The increased chemical reactivity at the wet/dry interface on the paper surface under humid conditions was investigated, firstly, in terms of the relationship between the mechanism of oxidative degradation and the condensation and evaporation kinetics induced by fluctuating environmental

conditions; and secondly, in the relationship of the crystalline / amorphous ratio to the oxidative mechanism of degradation.

5.3.1 EVIDENCE OF AN OXIDATIVE REACTION IN RESPONSE TO ENVIRONMENTAL CONDITIONS

In testing the relationship between ambient environmental conditions and the observed evidence of damage in the form of cellulosic discolouration, the dynamic simulated climate ageing programme was devised to monitor the initiation of an oxidative reaction under reproducible laboratory conditions. This was measured by FTIR spectroscopy, in the development of carbonyl groups associated with oxidative degradation.

The difficulty noted by previous researchers of the application of FTIR to the analysis of paper is acknowledged. While the differentiation between different substances is easily achieved, the degradation evidenced in paper ageing often leads to only slight modification of the spectrum, and in such cases the utility of the FTIR technique is more limited. (CALVINI & MARTINELLI, 1990) Daniels also reported his experience of a lack of success in the FTIR measurement of aged paper samples. (DANIELS, 1995)

A basis for the analytical interpretation was the previous comparison of artificial and natural ageing in cotton, in which the naturally aged samples

exhibited the consistent presence of a group of absorption bands in the C=O stretching region of the infrared spectrum, at 1700-1600 cm^{-1} , which were not found in new samples. New fibres artificially aged at 160°C displayed similar features. The presence of C=O bands in the naturally aged samples indicated that substantial oxidation had occurred. (CARDAMONE, et al., 1987)

In monitoring the band assignments in the same region, a comparison between the spectroscopic measurement of areas of cellulosic discolouration in naturally aged paper and that of samples artificially aged and subjected to the dynamic accelerated ageing programme was enabled. The regions of cellulosic staining of naturally aged Sample Group 1 (NA001-NA007) evidenced the consistent presence of weak peaks in the C=O stretching region, indicating oxidative degradation. The same level of consistency was not achieved in position and intensity of the bands exhibited by Sample Group 2 (AA001-AA004). The measurement of Sample AA001 before and after dynamic ageing afforded the opportunity to follow the development of functional groups, obscured however by the presence of water vapour, which interfered in the region of interest. However, while it was not possible to follow the unequivocal formation of carbonyl groups, the similarity of the resultant spectral features of the two sample groups gave reasonable assurance that oxidative degradation had taken place in samples exposed to fluctuating environmental conditions.

It was noted that cellulosic discolouration of the nature exhibited in naturally aged samples was induced in the dynamic simulated climate ageing programme only in the case of Sample AA004, but more extensive evidence of the formation of tidelines was noted. The measurement of the clear, the discoloured and the tideline regions of that sample all revealed similar spectral features to those of naturally aged areas of cellulosic discolouration. It was therefore not possible to conclude the existence of a direct relationship between an oxidative reaction at the wet/dry interface and the manifestation of localised discolouration known as foxing. However, since the evidence indicated that oxidative degradation had occurred throughout the sample exposed to fluctuating environmental conditions, it is possible to make two further conclusions:

- 1 that the effect of the oxidative reaction is not limited to points of moisture accumulation evident in the formation of a brown line at the wet/dry interface, but that the exposed surface responds in a similar manner to environmental fluctuations which result in an unstable equilibrium moisture content. The effect of the oxidative mechanism on the deterioration of library and archival materials thereby assumes far greater proportions than was originally assumed by the researcher.
- 2 that the rate of evaporation in the climate cabinet was increased with the speed of the forced circulation to a point that deferred dewpoint,

and no longer represented the slow circulation on a library shelf. Points of moisture accumulation were found to develop by capillary condensation on the absorption cycle, and when the rate of surface evaporation from a bound volume is less than the rate of diffusion in the moisture migration through the bulk on desorption, as investigated in 3.3. The limitation of the experimental technique in the simulation environmental conditions of the microclimate of a library or archival shelving system warrants further investigation of the development of points of moisture accumulation in a separate study.

However, the findings of Bogarty *et al*, of preferential growth of *Aspergillus niger*, along the brown line resulting from the evaporation of water from cellulose, indicate a chemical reaction preceding, and possibly even precipitating biological degradation. (BOGARTY, et al., 1952) A similar function of oxidation at the wet/dry interface in response to fluctuating environmental conditions is applicable to the evidence of metal-induced catalysis, in the precipitation and acceleration of cellulosic discolouration associated with foxing.

The reagent staining procedures confirmed the findings of spectrophotometric analysis in meeting the stated objectives of determining the effect of environmental fluctuations in the causation of cellulosic staining and the significance thereof in the manifestation of staining known as foxing.

General evidence of oxidative degradation was revealed in the even distribution of methylene blue throughout the naturally aged samples. While no direct correlation was established between the oxidative degradation and the localised areas of cellulosic discolouration known as foxing, increased methylene blue was absorbed in the same general area as the discolouration was noted to occur : at the point of evaporation of lateral migration of water vapour - at the edges and in the margins and corresponding to airspaces at dog-eared corners and uneven laminations; and in the diffusion process of transudational migration, adjacent to impervious surfaces such as coated paper inserts, at endpapers, and in enclosures which form a vapour barrier.

The determination by the chromatographic indicator, Naphtorin, of hydrogen peroxide formation under fluctuating environmental conditions, confirms the previous research on the wet/dry interface on the role of hydrogen peroxide as an initiator of the autoxidation reaction. The formation of hydrogen peroxide was noted at the tidelines created in local aqueous conservation treatment, and in the transudational flow of water vapour through consecutive leaves approaching a non-porous surface, in response to environmental fluctuations. The well defined tideline at the edge of localised pasting and the uneven surrounding indicator staining reveal capillary transport of hydrogen peroxide beyond the tideline to the edge of the sheet. This supports the evidence of a general distribution of methylene blue absorption throughout the sheet, and provides conclusive evidence of the

formation of hydrogen peroxide in response to the sorption and desorption kinetics of the equilibrium moisture content in response to fluctuating environmental conditions.

Eusman noted similar formation of hydrogen peroxide beyond the tideline, using the Russell effect:

“...grey patches in the top part of the washed and stored test strip indicate peroxide formation in the entire strip during storage” (EUSMAN, 1995 p.17)

The role of peroxide formation in the oxidation of aldehyde groups was established by Marracini and Kleinert, indicating an increased oxidative deterioration under humid conditions. (MARRACCINI & KLEINERT, 1962)

The evidence of the formation of hydrogen peroxide corresponds well with that of methylene blue absorption, providing evidence of an oxidative reaction in response to environmental conditions. This was quantified in the sorption and desorption kinetics of the equilibrium moisture content in response to fluctuating environmental conditions is proof of a similar mechanism of oxidative degradation experienced under humid conditions, to that at the tideline at the wet/dry interface.

The analytical data have provided evidence therefore:

- 1 that an oxidative mechanism of degradation is caused by fluctuating environmental conditions, in the peroxide formation at the wet/dry interface of an unstable equilibrium moisture content; and
- 2 that the oxidative reaction is not limited to the immediate manifestation of cellulosic staining, but as preceding reaction, precipitates and accelerates biological and metal-induced staining known as foxing.

The implications of these findings for autocatalytic degradation in microclimate storage options will be further considered in Chapter 6.

5.3.2 RELATIONSHIP OF THE CRYSTALLINE/ AMORPHOUS RATIO TO THE OXIDATIVE MECHANISM OF DEGRADATION

An early study by Hon had established that moisture content in the range of 5-7% leads to a significant decrease in free radical formation in photoirradiated cellulose, and alternatively, when moisture content is lower or higher, radical formation is increased. It is known that light in the presence of air and moisture causes yellowing of paper fibres; Hon also suggested that water vapour, not oxygen, was necessary for the degradation of cellulose, based on the production of free radicals limited almost exclusively to the amorphous region. (HON, 1975) Thus the

relationship of the moisture content to free radical production provides a causative factor in the oxidative mechanism of paper degradation.

Although Vincent Daniels acknowledged that he had never been able to prove a relationship between the amorphous/crystalline ratio and oxidation, in that there appeared to be no evidence that routine conservation treatments cause crystallinity changes, he suggested that paper cellulose might become more crystalline with ageing if there were more water in the air. (DANIELS, 1986a) Banik noted in similar investigation, a marked concentration of the energy of evaporation in the amorphous region. (BANIK, 1998) The relationship of the crystalline /amorphous ratio to the oxidative mechanism of degradation in the phenomenon of brown line formation in the evaporation of water warranted further investigation.

The increased accessibility to water vapour reported by Jeffries, (JEFFRIES, ROBERTS, & ROBINSON, 1968) could possibly account for Daniels' findings, in that paper conservation treatments were, in the mid-1980's, conducted primarily in the aqueous phase. The increased application of vapour phase treatment, as in the less invasive humidification process, presents new concerns for the ability of conservation treatment to cause crystallinity changes, as indicated in the data presented in 5.2.3 above.

The role of lignin in affording protection against oxidative degradation was examined, the presence of lignin having been determined only in naturally aged sample NA005 and accelerated aged sample AA003, both of which ranked inconclusively. Specific investigation of the role of lignin is warranted in further study.

While exposure to increasing RH was shown to increase accessibility and lower the crystallinity index value, repeated drying cycles are reported progressively to diminish the accessibility. (ANT-WUORINEN & VISAPAA, 1960). The effect of wetting and drying cycles was further investigated in the stabilisation of viscose cellulose, and the reduced moisture regain ascribed to a change in the character of the amorphous regions, rather than a variation of the crystalline / amorphous ratio. (BLACKWELL, 1971) The lower rate of diffusion associated with the progressive increase in crystallinity, the diffusion-restriction (DR) effect, may provide an explanation for the transient nature of the autoxidation reaction as described in 2.3.1, and the self-limiting mechanism thereof related to the degree of crystallinity and the moisture content of the material.

The study of the degree of crystallinity, measured quantitatively by the use of ratios of areas of selected absorption bands, provided the means to follow the degradation produced by oxidation in the changes in fine structure caused by the replacement of alcoholic groups by carbonyl, or carboxylic groups. This study confirmed the hypothesis of irreversible chemical

modification of the molecular structure of paper in an oxidative reaction following exposure to fluctuating environmental conditions, and is similar to the irreversible hornification recognised in the paper manufacturing industry. (CAULFIELD & STEFFES, 1959; KLUNGNESS & CAULFIELD, 1982)

5.4 SUMMARY

The following research hypotheses set out in Chapter I were tested under reproducible laboratory conditions:

- 1 that a fluctuating equilibrium moisture content causes cellulosic staining;
- 2 that the nature and degree of staining can be evaluated by the measurement of the formation of oxidative degradation products, and
- 3 that stringent environmental control can reduce the rate of autoxidative reactions.

Evidence of cellulosic discolouration in the form of spotted blemishes at localised points of moisture accumulation, or foxing, was not induced in this study, due possibly to the limitation of the experimental technique in simulating the slow air circulation in the microclimate of the library and archival shelving system. Cellulosic discolouration in the form of tidelines at the wet/dry interface and general evidence of moisture accumulation

against a non-porous surface was noted. The significant inference made from these findings is that atmospheric oxidation is unequivocally related to cellulosic discolouration in a surface reaction, as suggested by earlier research. (MARRACCINI & KLEINERT, 1962)

The formation of similar functional groups exhibited in the absorption bands in the region $1730\text{-}1720\text{ cm}^{-1}$ in both naturally and artificially aged paper samples is submitted as evidence of a chemical mechanism of oxidative degradation resulting from exposure to fluctuating humid conditions. Supporting evidence is found in the corresponding fluorescence and in reagent staining indicating an oxidative reaction by free radicals resulting from hydrogen peroxide formation and decomposition under fluctuating environmental conditions. Conversely, stable environmental conditions can be expected to reduce the rate of autoxidative reactions in limiting the free radical formation.

The nature of measured degradation was clearly oxidative. The degree of degradation visible as staining was qualitatively evaluated by reagent staining. The correlation of the evidence of the formation of oxidative degradation products with the evidence of cellulosic staining noted in library and archival collections afforded the following conclusions:

- 1 A chemical mechanism of paper degradation is evidenced in the oxidative reaction at the wet/dry interface, following the condensation and evaporation kinetics induced by cycling RH, and driven by temperature fluctuations in diurnal and seasonal ranges.
- 2 The absorption of excessive water vapour is increased in a humid climate by an increased RH or by decreased temperature, where the dewpoint is reached. The vapour concentration rate at the surface, or at the atmospheric interfaces results in chemical deterioration by oxidation similar to that noted at the wet/dry interface, and accounts for the staining evident in paper that has no fungal basis, similar to the tidemark effect noted at the wet/dry interface.
- 3 Sites of moisture accumulation which constitute a wet/dry interface are associated with evidence of cellulosic discolouration by the mechanism of the brown line formation as a surface phenomenon, as a vapour barrier to the transudational force of capillary action.
- 4 Sites of moisture accumulation which constitute a wet/dry interface can be identified in physical defects, such as tears and dog-eared corners of books, at areas of uneven adhesive lamination, in local aqueous conservation treatments, and in impervious archival storage containers or adjacent to impervious surfaces.

The aim of this study was to investigate the causation of cellulosic discolouration in the increased chemical reactivity evidenced in the phenomenon of autoxidation at the wet/dry interface at the paper surface under humid conditions. The significance of an autoxidative phenomenon, as a function of the unstable moisture content of materials similar to that of oxidation at the wet/dry interface, has been previously obscured by the accepted explanation of biological deterioration. Analysis of the experimental work indicates an oxidative mechanism of degradation in response to the condensation and evaporation kinetics induced by cycling relative humidity driven by fluctuations in diurnal and seasonal ranges of temperature and humidity.

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CHAPTER SIX

SUMMARY OF FINDINGS, RECOMMENDATIONS AND CONCLUSIONS

6.1 INTRODUCTION

The aim of this study was to investigate the causation of cellulosic discolouration in the increased chemical reactivity evidenced in the phenomenon of autoxidation at the wet/dry interface at the paper surface under humid conditions.

The summary and recommendations set out in this chapter serve therefore to review the research objectives defined in 1.4.1 as follows:

- 1 To study the interaction between those factors affecting paper permanence which relate to conditions during storage and use, focussing on the role of humidity, while acknowledging the role of temperature, air movement, illumination intensity and distribution and atmospheric pollutants in the oxidation reaction.
- 2 To evaluate accepted preservation strategies of environmental control, ventilation, and microclimate storage options, for the long-term maintenance of collections.

- 3 To review conservation treatment procedures applicable to the restorative intervention into the oxidative reaction.

This research was not directed however, at the development of kinetic laws governing the changes exhibited in the physical properties of paper. The application of the phenomenon of oxidation at the wet/dry interface in relation to the deterioration of paper experienced under humid conditions is presented rather, as a contribution towards the further development of a theory of deterioration, and is based on the findings of the analytical investigation reported in 5.3 above.

In advancing the theory of a chemical response of library and archival materials in the fluctuating moisture content as an explanation for the causation of cellulosic staining, presented in 6.2 below, this study redefines the evidence of foxing. In doing so, it serves primarily to permit librarians, archivists and conservators to identify the basic chemical reactions involved in the process of deterioration, and to recognise the role of oxidative degradation in relation to environmental conditions.

The identification of the causes of deterioration enables the development of sound practices of preventive conservation and appropriate conservation treatment for the long-term preservation of paper-based information. The conservator, together with the librarian and archivist, are provided with recommendations in 6.3 below, for the development of effective preservation

strategies for collections management and suggested conservation treatment proposals, based on the identified effects of oxidative degradation.

In drawing together the professional interests of conservators, librarians and archivists, this study has further developed a thesaurus of relevant keywords for greater bibliographic control in the technical fields of preservation and conservation. The research methodology used in this study has led to the development of a bibliographic database organised by means of an original thesaurus of keywords relevant to book and paper preservation and conservation. The dearth of subject headings provided by the Library of Congress in this technical field of librarianship indicated the need for the development of a thesaurus. Each keyword was assigned a numerical value according to the system of arrangement devised for the references gathered in the course of the study. The physical location of the reference was determined by the numerical value of the first keyword. Additional keywords were assigned, depending on the relevance of the subject matter, and provided means for boolean searching. The keywords listed in Appendix D1 are reflected in the list of works consulted.

The development of a thesaurus of keywords for preservation and conservation is presented as evidence of the research process, and serves as an important tool for reference work in the training of librarians in the specialised field of preservation and conservation.

In conclusion, the role of the mechanism of oxidation at the wet/dry interface is reviewed in the context of library and archival preservation, highlighting areas of further research required in the study of this phenomenon.

6.2 SUMMARY OF THE ROLE OF OXIDATION AT THE WET/DRY INTERFACE IN THE DETERIORATION OF PAPER IN LIBRARY AND ARCHIVAL COLLECTIONS

The three primary mechanisms of paper deterioration driven by excessive RH are chemical reactivity, mechanical stress and biological deterioration. The abundant evidence of cellulosic discolouration in library and archival materials housed in a humid climate, commonly known as foxing, and the disparate evidence of minimal associated microbiological infestation, led the researcher to investigate the causation in an increased chemical reactivity at the wet/dry interface.

The predominant factor relating to conditions of storage and use in the ambient environment was that of a generally high level of relative humidity, seldom contained by sophisticated technologies of environmental control within the standard recommended level of 65%RH. The investigation of the relationship between environment and paper substrate has provided evidence of a chemical mechanism of oxidative degradation in the response of an unstable equilibrium moisture content to the kinetic cycle of sorption and desorption, constituting a wet/dry interface at points of moisture

accumulation in library and archival collections. Previous research has indicated that the mechanism is related to the evaporation of water from paper, in localised treatments (EUSMAN, 1995), and in the microclimates of storage containers (HOFENK DE GRAAFF, 1994).

The potential for oxidation involving molecular oxygen is increased by absorption of excessive water vapour under humid summer conditions, and its intermittent evaporation during the short winter months, providing an interface on the fibrous paper substrate with intimate contact between air and liquid with a large surface area for reaction. (TRYON & WALL, 1961)

The oxidative reaction is known to proceed in three steps: initiation, propagation and termination. Under the appropriate conditions, temperature and RH being the focus of examination, the initiation of the reaction might involve light, photosensitive dyes, or free radical-producing compounds, of which oxygen qualifies as a:

“...species capable of independent existence that contains one or more unpaired electrons”. (HALLIWELL & GUTTERIDGE, 1985 p.11)

The free radical mechanism is strongly supported in this study in the formation and decomposition of hydrogen peroxide, exhibited at points of moisture accumulation adjacent to vapour barriers. The action of heat, light or the presence of metallic ions in the paper will undoubtedly hasten the decomposition of peroxides in the autoxidation of the cellulose, and the

production of highly reactive free radical chain carriers. The reaction of radicals with molecules which lead to stable non-reactive products will terminate the reaction, while other reactions will lead to the formation of volatile oxidation products, such as ketones, aldehydes, water and acids, with irreversible consequences for paper permanence. (HORIE, 1987)

Paper-based collections housed in a humid climate can be expected to absorb excessive water vapour by surface diffusion from the atmosphere. Driven by changes in temperature, psychrometric properties of the humid climate result in frequent excursions to dewpoint, with capillary condensation at points of increased water vapour permeability.

The theoretical model of the formation of a brown line at the wet/dry interface is applied specifically to the library and archival environment in absorption and desorption kinetics, resulting in cellulosic staining as a manifestation of damage. The desorption process takes place by diffusion, in lateral and transudational migration through the fibrous substrate, and by surface evaporation. When the rate of surface evaporation is limited by slow ventilation of the surface boundary layer, the disruption of internal moisture migration creates points of moisture accumulation associated with localised blemish formation.

The slow circulation in a humid climate is exacerbated by the enclosure of library and archival materials for storage and protection, in shelving systems, in drawers, cabinets and boxes. This was found to have wider

implications in application of the theoretical model to microclimate storage options, which is generally considered an effective buffer for passive environmental control. The microclimate storage option will be considered further in 6.3.1 below.

The importance of crystallisation as a factor of ageing has been identified. A close inspection of the surface characteristics of the naturally aged samples revealed a correlation between the accessibility value and the density of the paper sample and its surface roughness. The smooth surfaced samples of compact fibre structure recorded the lowest levels of accessibility. This conclusion led to further investigation of the relationship between crystallinity and moisture regain.

The implications of these findings for preservation in libraries and archives lie in the identification of the environmental conditions which could lead to an oxidative reaction, in order to arrest the reaction. The conservation challenge lies in recovering the properties of the paper artefact exposed to fluctuating conditions of high humidity.

The research hypothesis set out in 1.5 was advanced in three points, which are evaluated here:

- 1 A fluctuating equilibrium moisture content of the paper substrate causes cellulosic staining.

In testing the first hypothesis of the causation of cellulosic discolouration in the fluctuating equilibrium moisture content the analytical procedure was designed within the ambient range of environmental conditions to determine the effect of resultant fluctuations in precipitating oxidative mechanisms of degradation. The analytical techniques applied in the identification of an oxidative reaction positively indicated the formation of similar functional groups in samples exposed to the dynamic simulated ageing programme to those found in naturally aged samples.

The first research hypothesis was tested in the experimental design and found to be positive.

2 The nature and degree of staining can be evaluated by measurement of the formation of autoxidative degradation products.

The nature and degree of staining could not be evaluated in the measurement of the formation of oxidative degradation products, as the correlation of functional group formation with the degree of discolouration evidenced in the paper samples was inconclusively reflected in the FTIR spectra, as reported in 5.2.1. It was therefore not possible to conclude the existence of a direct relationship between an oxidative reaction at the wet/dry interface and the manifestation of localised discolouration known as foxing. However, the reagent staining procedures adopted in the increased methylene blue absorption and hydrogen peroxide indicator confirmed a

positive relationship between cellulosic discolouration and oxidative degradation. It is therefore possible to assume that the rate of evaporation in the climate cabinet was increased by forced circulation to a rate that deferred dewpoint, which precluded the formation of points of moisture accumulation in the differential between the rate of surface evaporation from a bound volume and the rate of diffusion in the moisture migration through the bulk by lateral and transudational flow.

- 3 The more stringent the control of environmental conditions, the slower the rate of autoxidative reaction.

The third hypothesis in the relationship of environmental control to the rate of the oxidative reaction was tested in the structural response of the cellulose molecule to the fluctuations of humidity. The evaluation of the change in the fine structure of the cellulose substrate reflected a linear relationship between moisture regain and accessibility, and thus between environmental conditions and the potential degradation of paper by an oxidative mechanism. The study of the degree of crystallinity confirmed a permanent chemical modification of the cellulose structure following exposure to the fluctuating environmental conditions. It was therefore conclusively proved that oxidative degradation is induced in the range of fluctuations of the ambient library and archive environment tested in the experimental design.

6.2.1 CELLULOSIC DISCOLOURATION IN THE EVIDENCE OF FOXING

Oxidative mechanisms of paper deterioration are complex reactions in which the significance of trace metals, and the role of metal catalysis are drawn into consideration. (URI, 1961) The mechanism of paper deterioration by autoxidation was investigated in this study as a causative factor of cellulosic discolouration encompassing the previously unresolved debate on the causation of foxing.

The mechanisms of the formation of foxing have been classified under two principal theories of causation, biological infestation and metal-induced catalysis, presented in 2.4.1. A further category of discolouration has been identified by conservators as being related to the tidemark staining caused by uneven evaporation noted during localised treatment procedures.

It was not the aim of this study to evaluate the accepted mechanisms of foxing, but rather to investigate an alternative mechanism of oxidative degradation, in recognition of multiple factors in the causation of cellulosic staining, which may operate simultaneously and probably sequentially. In the heightened level of oxidation at points of moisture accumulation, resultant upon the chemical reactivity at the surface exposed to environmental fluctuations, the proposed mechanism provides a common link between the oxidation of metal inclusions, and in the browning by the Maillard reaction, an explanation of preferential fungal growth in the areas

of discolouration.

Research was directed in this study towards the role of oxidation at the wet/dry interface found at the surface boundary layer as a unique phenomenon separate from and preceding the biological deterioration traditionally associated with paper deterioration in a humid climate. The phenomenon was thought to precipitate the causation of foxing.

The significance of an oxidative reaction at the wet/dry interface in the manifestation of cellulosic discolouration known as foxing was found to be inconclusive. Evidence of the general nature planar discolouration did not include localised blemishes, known as foxing, although blemish formation has been reported in similar studies. (KAESSBERGER, DESSAUER, & STARK, 1998) It is believed that the speed of air circulation in the climate cabinet induced a rate of surface evaporation, too high to allow for the development of localised points of moisture accumulation. These would occur under natural conditions, at points of contact between adjacent leaves, either in the surface roughness of the fibre morphology; in particulate nuclei for surface moisture condensation; in dust or salt in a marine climate; or in planar distortions created by physical damage such as dog-eared corners and tears.

Preferential fungal growth at sites which constitute a wet/dry interface have been reported, and can be associated with the resultant chemical reaction in the following manner:

- 1 The chemical modification of the cellulose results in an oxycellulose of the mildly reducing acidic type. The reduced pH of the substrate may break the dormancy of conidial fungi present, the optimum pH range for fungal growth on paper laying between 4.8 and 5.6. (BECKWITH, SWANSON, & IAMS, 1940)

- 2 The increased water vapour permeability of the paper substrate at the point of moisture accumulation at the wet/dry interface is available on absorptive cycles as condensed water for fungal activity.

- 3 The chemical degradation products resulting from the oxidative reaction, such as furfural, may act as activators of specific fungi. (FLORIAN, 1994)

However, most conidial fungi will survive the harshest climatic extremes, reverting to the dormant state as a survival mechanism, until conducive conditions trigger their activation, followed by germination where those conditions are sustained. Fungal proliferation therefore has little to do with biological load, but rather, with the availability of conducive environmental conditions. (FLORIAN, 1994)

The window period of 48 hours noted in a humid climate between activation and germination, when the viability of conidial fungi are vulnerable, provides an effective means of control. A stable environment serves therefore to prevent activation, and as long as RH levels are not consistently high enough to sustain germination, natural control of intermittent activation occurs. Furthermore, the ever diminishing ratio of moisture regain indicated by the increased crystallinity exhibited by the paper substrate may possibly contain the EMC at a level below that required to sustain germination of activated spores. The oxidative mechanism may act in this manner in containing widespread fungal activity that is associated with archival storage in a humid climate.

The role of ventilation in restricting the causation of foxing can be similarly defined in terms of the disruption of surface boundary layers. By increasing the rate of evaporation, the amount of absorbed water in the substrate is reduced below that required for fungal activity, and in promoting desorption in the continuous flow moisture migration through both diffusion and evaporative processes, localised points of moisture accumulation, which constitute a wet/dry interface, are also avoided.

The association of an oxidative chemical reaction with biological activity is therefore mutually inclusive. The exact nature of this relationship is called into question and provides an area of further study to determine the role of local climatic conditions in the causation of cellulosic discolouration.

6.3 RECOMMENDATIONS

The role of environmental control is an acknowledged and well established preventive conservation strategy in collections management programmes, aimed at decreasing the rate of deterioration of entire collections of materials. While the need to provide a storage environment that offers a consistently high level of stability to library and archival materials is indisputable, the rate of paper deterioration has traditionally been measured only in the change of strength properties in the chemical reaction of acid hydrolysis.

The investigation of the phenomenon of oxidation at the wet/dry interface serves to broaden the understanding of the mechanisms of paper deterioration and their function in relation to climatic conditions, in order to identify and develop more effective conservation techniques for the treatment of individual items and to improve preservation strategies for collections management. It is important that custodians in libraries and archives become aware of the interdependent role that the building, the environment and the provision of appropriate storage conditions play in the preservation of collections. This requires a conceptual knowledge of the physical and intellectual nature of paper-based collections, as well as the prevailing environmental factors affecting their life expectancy.

The validation of alternative methods of environmental control by means of appropriate building technology, independent of high maintenance technology, is an important development in the conventional approach of an artificial atmosphere, and has significant implications of financial savings for libraries and archives. A problem of some immediacy in the context of a developing country, this is of contemporary significance with the political demand to secure a growth in the number of community libraries, while budget allocations are steadily diminishing.

The significance of the study is affirmed by the intention to quantify parameters of building technology in terms of scientific evidence of deterioration, rather than on the current basis of a subjective assessment of human comfort. As there are at present no practical guidelines to assist library and archival staff in their interactions with design professionals, this study draws within their sphere of competence, an understanding of the interdependent behaviour of buildings and the environment in the provision of appropriate storage conditions for the preservation of collections.

6.3.1 PREVENTIVE CONSERVATION STRATEGIES OF ENVIRONMENTAL CONTROL AND MICROCLIMATE STORAGE OPTIONS

"There is unfortunately a neurosis that without air-conditioning, museum, gallery and archive collections will rapidly deteriorate. This is not the case. It is more important to have a stable environment than specific levels of temperature and relative humidity, and this can be achieved by careful building design."(KING & PEARSON, 1992) p.65)

King and Pearson point out the problem in developing countries - many of which fall into the tropical and subtropical geographic regions - of a lack of maintenance of high technology mechanical services, coupled with unreliable energy supplies. They advocate alternative building technologies, such as appropriate siting, reduction of environmental "loads" on the building, layout planning to protect vulnerable spaces and the use of appropriate local sun control. In doing so, they pinpoint a weakness in the understanding of conservators, librarians and archivists of the behaviour of buildings and their ability to participate meaningfully in their design.

Recent studies of environmental control have examined the effect of mechanical damage in the dimensional changes associated with sorption and desorption, (ERHARDT & MECKLENBURG, 1994; ERHARDT, MECKLENBURG, TUMOSA, & McCORMICK-GOODHART, 1995; MECKLENBURG & TUMOSA, 1995) or have assessed storage

environments for the risk of mechanical damage and biodeterioration. (REILLY, 1996; REILLY, NISHIMURA, & ZINN, 1995)

The determination of the mechanism of oxidative degradation in response to ambient fluctuations in RH, and the degradative effect on the properties of library and archival materials presented in this study, counterposes the suggested relaxation of environmental control values. The consideration of allowable fluctuations in RH are proven in this study to be limited by the increased chemical reactivity of materials of an unstable equilibrium moisture content of library and archival materials.

Maximum storage life values attained in minimising acid-catalysed hydrolysis is therefore equated with an environmental control strategy aimed at storage as cool and as dry as possible.

The study of the oxidative mechanism of degradation confirms the recent trend in the theory of environmental control that there can be no ideal standard or generally recommended values. The avoidance of extreme values and of rapid or large fluctuations is recommended. The lowest level of RH that can be steadily maintained in a given location can be considered a realistic humidity set point in air-conditioning technology, and provides a strategy that will contain fungal germination and minimise

chemical reactions in the materials.

This study has developed a theory of the mechanisms of deterioration related to the environmental control, enabling effective preservation management in the recommendation to monitor the relevant environmental factors that constitute a possible risk, based on the location and history of the collections, and the evidence of their condition.

The relative humidity level should rather be set as low as can be maintained within the individual parameters of each institution, to which are added the consideration of the building envelope, including its orientation, insulation, natural ventilation, glazing and mechanical systems - factors which contribute to its thermal mass - and the resources of the institution.

Of particular relevance to library and archival application is an aspect of the Smithsonian research into the moisture buffering capacity of the material, testing the assumption of constant moisture content (MC) at constant RH. The implication for accelerated ageing being that Arrhenius-type data, used in the definition of properties of paper permanence by international standards, will project ageing rates along constant MC for such material stored in enclosures, and constant RH for free-hanging samples. (McCORMICK-GOODHART, 1995; McCORMICK-GOODHART, 1996)

Library and archival collections are predominantly enclosed - within bookbindings, on shelves, in folders, boxes, drawers, display cases and in picture frames. A further contribution of this study lies beyond simply monitoring of the RH for effective environmental control - in the identification of the chemical response of the moisture content of library and archival materials .

The thermodynamics of storage enclosures has been investigated in terms of the wet/dry interface as the cause of browning of mounted paper artefacts stored in archival enclosures.(HOFENK DE GRAAFF, 1994) The limited volume of air within a microclimate was found to respond in reverse to the macroclimate, and the reverse phenomenon of increased humidity driven by a rise in temperature was experimentally measured.

The implications of this study in the chemical response of an unstable equilibrium moisture content are momentous to the storage of archival collections. The findings of the experimental procedure presented in 5.3.1 confirm that:

- 1 the occurrence of an oxidative degradation process occurs throughout the sample exposed to conditions which result in a fluctuating moisture content, and;

- 2 the formation of a wet/dry interface occurs at points of moisture accumulation adjacent to impervious surfaces, where the transport of water vapour is hindered by a less porous surface.

The increased rate of deterioration reported in enclosed materials has previously been attributed to the risk of autocatalytic degradation, in the concentration of degradation products trapped within a microclimate.

In a closed book, or a similar mass of paper, the products of any chemical reaction, both polar and non-polar, remain and accumulate over time. Since some of these are acidic, their accumulation within closed books or a stack of papers has an autocatalytic effect on the ageing of paper. (SHAHANI, 1996) Autocatalytic degradation was believed to be accelerated by increasing relative humidity, and to a lesser extent, by increasing temperature. High relative humidity was thought to contribute to the transport and deposition of degradative volatiles present in the chambers. (SLAVIN & HANLAN, 1992)

Both lateral and transudational transport are confirmed in the present study, and the direct formation of oxidative degradation products in an enclosure identified in the process of water vapour desorption, following a decrease in temperature.

The decision to employ protective enclosures for the preservation of collections should therefore be made with great care, and their design

considered so as to allow for atmospheric exchange, by means of ventilation points, so as not to accelerate to the rate of deterioration of the enclosed material. Paper exposed to the air within the enclosure will exchange moisture with the air until equilibrium is reached. When a small amount of paper is exposed to a large airspace, the major change takes place in the paper, as found in the lateral migration of dyestuffs reported in 3.3, but in a limited airspace the major change takes place in the air. (BERTONIERE, KING, & ROWLAND, 1984) The widespread use of protective enclosures for the preservation of archival collections demands careful consideration of their construction.

Protective enclosures should be constructed to fit snugly, the common practice of storing archival material in standard sized boxes can only be recommended in conjunction with the use of additional absorbent buffer material to fill the void in which the moisture exchange would otherwise occur.

The choice of suitable materials and an open design structure serve therefore to support the thermodynamic equilibrium. (McCRADY, 1984; VINE & HOLLINGER, 1993) Current research in the preservation of film has revealed the effective use of molecular sieves as dessicants, which also absorb solvents and pollutant gases. Both water and hydrogen peroxide degradation products are trapped in the crystalline form of sodium aluminosilicate (zeolite) with a pore size of 4 Å. (MANAS, 1994)

The recommendation based on the findings of this study is to provide protective enclosure which does not constitute an impervious microclimate, a vapour barrier to the fluctuations in an unstable equilibrium moisture content. Containers made of paper and board have a similar capacity for heat and humidity exchange as paper, and being inert conductors, are able to stabilise both internal and external climatic conditions in long term storage.

6.3.2 EFFECTIVE CONSERVATION TECHNIQUES IN THE TREATMENT OF OXIDATIVE DEGRADATION

Oxidative degradation and free radical chemistry were introduced to conservation practice in the work of Daniels, who proposed the use of the Russell image in the detection of watermarks, in the comparison of the effects of conservation treatments, in the prevention of autoxidation and in the testing of materials suitable for archival storage. Autoxidation at room temperature was proposed as the most important non-biological cause of degradation. (DANIELS, 1984; GRATTAN, 1978)

Conservators assess their treatment proposals on the visible defects of the object, the human perception of discolouration being one of the strongest factors in the decision to undertake the conservation of paper. In the current

practice of book and paper conservation, numerous treatments are related to the cause and effect of oxidative degradation, particularly aqueous treatments, including washing, deacidification and resizing procedures.

In relating the rate of paper discolouration to the deterioration indicated at dewpoint, Vitale and Erhardt used reflectance spectra of samples to give colour measurement of discolouration induced under various environmental conditions, and removed by washing in deionised water. The results indicate that colour change can be partially reversed by washing. However, the degree of reversal decreases with more severe degradation. (VITALE & ERHARDT, 1993) The early reports of the formation of a brown line at the wet/dry interface report the formation of soluble and insoluble degradation products, the amount of extractable material decreasing in aged samples, or following exposure to high temperature. (BONE & TURNER, 1950)

A general recommendation on the effect of aqueous conservation techniques in the treatment of oxidative degradation can be formulated as follows:

The general efficiency of washing in removing discolouration resulting from oxidative damage can be expected to be limited. The principal conservation benefit is in the removal of acidity rather than the cosmetic effect of stain removal by bleaching procedures, a practice superceded by the ethic of non-invasive

treatment.

Conservators commonly have personal experience of oxidative degradation exhibited in the brown line effect or tidemark resulting from localised aqueous treatments. Preliminary humidification is recommended to equalise the moisture content prior to local treatments, best conducted on a vacuum suction table to prevent the oxidative reaction at the wet/dry interface, visible in the formation of tidelines. (EUSMAN, 1995)

A further recommendation is formulated with regard to localised conservation treatment techniques:

Lateral migration of water vapour was confirmed in this study in the tideline formation found in the samples treated in simulation of conservation treatment. The localised application of moisture in the form of paste or glue is therefore shown to have a similar effect as the tideline formation associated with local treatments, and should therefore be applied following prior humidification.

The antioxidant effect of paper deacidification has been recently challenged in the study of the effect of alkali on the long-term stability of paper fibres containing lignin. While lignin may be a contributory factor to alkaline sensitivity, the three factors identified in the adverse reaction to alkali were the density of the paper; the type and amount of size; and the degree of

oxidative degradation to which the paper was exposed. (BURGESS & BORONYAK-SZAPLONCZAY, 1992; BURGESS & GOLTZ, 1994)

These three factors are shown in this study to be interrelated, the Sample NA004, an unsized rag paper, being a case in point. The potential alkaline sensitivity of oxidised materials is a serious consideration in conservation treatment proposals.

No standard recommendations for the washing and alkalisation of the range of cellulosic fibres could be devised. In most cases, the addition of alkaline magnesium or calcium salts is most beneficial, except for fibres, such as groundwood pulp, which are not stabilised by alkaline processes. It is possible that absorbent or heavily oxidised fibres are more at risk to alkali sensitivity and, as this study has shown, that more absorbent materials are more accessible to chemical reactivity.

It is recommended that soluble acids are removed in washing, without changing the pH to the alkaline range. Results reported elsewhere show that low concentrations of magnesium bicarbonate have a stabilising effect against hydrogen peroxide decomposition and free radical formation. (ASH, 1983; BURGESS, DUFFY, & TSE, 1991; TANG, 1986; WILSON, GOLDING, MacLAREN, & GEAR, 1981)

The presence of transition metal catalysts, compounds of copper, iron or cobalt, increase the rate of oxidation and cause rapid deterioration of paper in a humid climate by the enhanced decomposition of peroxides formed in the oxidative reaction. The use of magnesium carbonate is recommended over calcium carbonate in minimising oxidative degradation by various suggested routes, in stabilising peroxides, or in deactivating transition metal catalysts, or in chelating with oxidative degradation products, or in complexing with hydroxyl groups at C-2 and C-3 of the cellulose ring, thereby stabilising the cellulose against dehydrogenation. (DANIELS, 1996; WILLIAMS, FOWLER, LYON, & MERRILL, 1977)

The final area of conservation practice that is involved in the causation and effect of oxidative degradation by environmental conditions is the procedure of paper sizing.

The practice of sizing is traditionally associated with paper manufacture, alum being introduced to handmade papers in the hardening of gelatin size.

The mechanised process employed alum as a mordant of rosin size and since that time, their combined presence as aluminium salt has provided a major cause of acid deterioration of paper. (BRUECKLE, 1992)

The three factors identified in the adverse reaction to alkali were the density of the paper; the type and amount of size; and the degree of oxidative degradation to which the paper was exposed. Since paper sizing

consolidates the surface topography of the sheet, reducing surface roughness and the related fibre density, it imparts a degree of water repellence to the sheet, limiting wetting before penetration can take place into the accessible regions of the cellulose structure. (DAVISON, 1975; HOYLAND, HOWARTH, & FIELD, 1976) Paper sizing is therefore a recommended conservation technique in the treatment of oxidative degradation.

Sizing provides an important means to protect the surface with a protective barrier against the chemical reaction at the wet/dry interface, in retarding the response of the paper substrate to fluctuations in environmental conditions.

A survey of American practice in this regard, conducted in 1982, suggest that the resizing of artifacts following aqueous treatment is performed infrequently, and with little consensus on its value or function. There was, however, a clear preference for cellulose ethers for both internal and surface sizing. (HENRY, 1986)

Medium to low viscosity grades of cellulose ethers are recommended for increased penetration, the low penetration of high viscosity grades offering useful properties as poultices and in surface cleaning. However, to achieve maximum surface protection, a sequential application of different viscosity grades is recommended. (BAKER, 1982; BAKER, 1984; BAKER, 1992)

The role of coated papers and its physical properties are important to this study. The experience of this researcher has shown the consistent discolouration of the leaves of a book adjacent to clay-coated illustration pages and in the protective tissue adjacent to the frontispiece. The coated papers, however, seem unaffected by the chemical reaction in which they clearly participate.

“...coated papers picked up moisture, but at a lower rate than cellulose fibres of the paper... the coating blocked some of the pores in the paper and reduced kinetic hysteresis...diffusion through the coating must take place before sorption on the fibres can take place, even though there is a higher driving force to equilibrium...coatings can do much to stabilise paper structure on exposure to environments of fluctuating water content. “ (BROOKS, 1967) p.107-108A)

Coated papers are protected from the oxidative mechanism of degradation caused by a fluctuating moisture content. However, in serving as a vapour barrier in the diffusion of moisture through the volume by transudational flow, they create a point of moisture accumulation in adjacent leaves, and therefore constitute a wet/dry interface.

6.4 CONCLUSIONS

A major function of the library and archive is to preserve the documentary evidence of the rich cultural heritage of the nation. At a time of political transformation, the demand for access to educational and informational materials has placed enormous restraint on the resources of libraries and archives. The role of preservation and conservation in ensuring continued access has assumed increasing responsibility in responding to the current user needs, both in preserving the original artefact, and in decontextualising the information from artefact by microfilm or electronic reformatting. The preservation management of libraries and archives requires an appreciation of the nature and value of the documentary heritage, and its interaction with the storage environment, to ensure its preservation for continued access.

It was important to the researcher to reach an understanding of the processes of apparent accelerated deterioration of organic library and archival materials observed in a sub-tropical climate in order to develop a strategy for preventive conservation. The traditional perspective has held that paper-based materials housed in a humid climate are susceptible to microbiological degradation, evidenced in the spotted discolouration known as foxing. It has previously been argued that the general lack of microscopic evidence of biological activity at such sites is related to a change in optimum conditions for sustained growth.

The aim of this study was to investigate the causation of cellulosic discolouration in the increased chemical reactivity evidenced in the phenomenon of autoxidation at the wet/dry interface at the paper surface under humid conditions. Reproducible laboratory experimental work has been presented to indicate a relationship between the process of oxidation, and the condensation and evaporation kinetics induced by cycling relative humidity driven by fluctuations in diurnal and seasonal ranges of temperature and humidity.

The theoretical model of the proposed mechanism of deterioration was shown to be applicable to a wider range to extremities of various climatic conditions, in the macro environment of a hot humid climate or the artificial heating of a cold climate, or in the microclimate of a storage context in a library or archive situated in a moderate climate with strong seasonal and diurnal variations. The research thus forms the basis for the re-evaluation of accepted recommendations for environmental control in terms of the restraints of ambient climatic conditions at an appropriate juncture, when recommended standards have been called into doubt in addressing urgent questions that relate to the storage of collections.

The degradation processes of paper are dominated by hydrolysis and oxidative attack. (BLAZEJ & KOSÍK, 1985; FELLERS, IVERSEN, LINDSTROM, NILSSON, & RIGDAHL, 1989) Recently called into doubt on the grounds of mechanical stress factors, recommended environmental

conditions can only be described once the oxidative mechanism of the formation of cellulosic staining is also well understood. It is in the understanding of the intermediate process of oxidative degradation that the preventive conservation strategy of environmental control is most effective, in the control of a direct chemical interaction of materials with the environment of the given location.

The results of an independent analytical procedure conducted in this study indicate the following conclusions, which serve to develop the theory of paper deterioration under humid climate :

- 1 A chemical process of degradation is evidenced in the oxidation of paper at the wet/dry interface, following the condensation and evaporation kinetic induced by cycling RH driven by temperature fluctuations in diurnal and seasonal ranges.
- 2 The potential hazard of absorption of excessive water vapour is heightened by capillary condensation in a humid climate by an increased RH or by decreased temperature where dewpoint is reached. Subsequent evaporation, or more specifically, the influence of the high vapour concentration rate at the surface on the rate of evaporation, results in chemical deterioration by oxidation of hydroxyl groups and accounts for the staining evident in paper that has no

fungal basis, similar to the tidemark effect noted at the wet/dry interface.

- 3 Environmental fluctuations result in a change in moisture regain related to the structural change in the amorphous crystalline ratio of the cellulose molecule.
- 4 The growth of mould is a sequential development following upon the oxidative reaction under fluctuating climatic conditions, related to the chemical modification at the wet/dry interface, with increased acidity and initial increase in water vapour permeability. The limitation of fungal growth is attributed to the steady decrease in moisture regain following the hysteresis kinetics of repeated sorption and desorption.
- 5 The rate of capillary action in evaporation at the surface boundary layer is in inverse proportion to the damage perceived in the paper. Where the slow ventilation of the surface boundary layer allows the rate of evaporation to fall below that of capillary diffusion in the bulk, points of moisture accumulation are formed.
- 6 Sites of moisture accumulation at which the oxidative reaction readily takes place, and which constitute a wet/dry interface can be identified at surface areas exposed to atmospheric exchange, in physical defects, in uneven adhesive lamination, local wet treatments, storage

in impervious containers or adjacent to an impervious surface which acts as a vapour barrier to the transudational force of capillary action.

6.5 POTENTIAL AREAS OF FUTURE RESEARCH

The limitation of the experimental design in the simulation environmental conditions warrants further investigation of the development of points of moisture accumulation in a separate study. Intensive laboratory testing is also required to determine the exact point or stage at which the oxidative reaction takes place, a categorising of detailed data capture for the recommendation of specific environmental parameters. The justification for the need to measure the effect of ambient local conditions, and therefore to measure the extremes of environmental fluctuation, precluded the determination of such a point in this study.

The re-evaluation of these and further research hypotheses, according to ageing procedures currently in development, is an area of subsequent study.

The assumption that the rate of evaporation in the climate cabinet was increased by forced circulation to a rate that deferred dewpoint, is such an area of future research. The formation of points of moisture accumulation in the differential between the rate of surface evaporation from a bound volume and the rate of diffusion in the moisture migration through the bulk by lateral and transudational flow is a possible cause of the localised nature

of staining known as foxing.

The role of oxidation at the wet/dry interface was found to be a unique phenomenon separate from and preceding the biological deterioration traditionally associated with paper deterioration in a humid climate. The phenomenon was thought to precipitate the causation of foxing in a progression of interrelated factors, which may operate simultaneously and probably sequentially. The interaction between oxidation at the wet/dry interface and the accelerated decomposition of hydrogen peroxide in the presence of transition metal catalysts has been presented. The sequence of the progression of both the Maillard reaction and the utilisation by some fungi of a hydrogen peroxide and ferrous iron system to attack the cellulose is an area of future research.

The role of lignin has been debated in terms of paper deacidification and the effect of alkali on the long-term stability of paper fibres containing lignin. While lignin may be a contributory factor to alkaline sensitivity, the three factors identified in the adverse reaction to alkali were the density of the paper; the type and amount of size; and the degree of oxidative degradation to which the paper was exposed.

The photochemical reaction of lignin in the causation of cellulosic discolouration has been well established. This study has further examined the role of oxidation in colour reversion. The relationship of colour reversion

and permanence in a radical- containing atmosphere is an area of current research. (WAN & DEPOW, 1995) While no conclusive evidence of the reported role of lignin in reducing the rate of oxidative reactions could be found in this study, the excessive oxidation of the rag paper sample without lignin raises the question of the antioxidant effect of lignin as a further possible area of future research.

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Environmental control

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Ventilation
Preventive conservation

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Oxidation 3.1
Chemistry
Photochemical degradation

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Chemistry 3.1
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Chemistry

Equilibrium moisture content

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Chemistry

Equilibrium moisture content

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Foxing 3.3

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Foxing 3.3

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Foxing 3.3

Equilibrium moisture content

Biodeterioration

Cellulosic discolouration

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Biodeterioration

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Accelerated ageing

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Oxidation 3.1

Accelerated ageing

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Oxidation 3.1

Accelerated ageing

Analysis

Equilibrium moisture content

Evaporation

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Oxidation 3.1

Conservation techniques

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Oxidation 3.1

Deterioration

Accelerated ageing

Conservation techniques

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Oxidation 3.1

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Oxidation

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Preventive conservation 2.0

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Chemistry 3.1

Paper fibres

Conservation techniques

Accelerated ageing

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Permanence standards 1.1

Accelerated ageing

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Conservation techniques 3.0

Sizing

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Sizing 3.6
Conservation techniques

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Analysis 3.1
Chemistry

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Accelerated ageing 3.2
Evaporation
Wet/dry interface

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Preventive conservation 2.0
Environmental control
Oxidation
Climatology - tropics
Acid hydrolysis

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Permanence standards 1.1
Accelerated ageing
Analysis

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Analysis 3.1

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Analysis 3.1

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Climatology 2.3

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Foxing 3.3

Oxidation

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Foxing 3.3

Biodeterioration

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Biodeterioration 2.7

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Equilibrium moisture content 2.3

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Chemistry 3.1

Analysis

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Condensation 3.7

Photochemical degradation

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Analysis 3.1

Oxidation

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Analysis 3.1

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Chemistry 3.1

Oxidation

Biodeterioration

Deterioration

Acid hydrolysis

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Oxidation 3.1

Preventive conservation

Atmospheric pollutants

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Wet/dry interface 3.2

Evaporation

Cellulosic discolouration

Oxidation

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Evaporation 3.7

Cellulosic discolouration

Wet/dry interface

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Wet/dry interface 3.2

Evaporation

Cellulosic discolouration

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Equilibrium moisture content 2.3

Environmental control

Microclimates
Evaporation
Analysis

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Preventive conservation 2.0

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Photochemical degradation 3.2
Environmental control
Biodeterioration

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Preventive conservation 2.0
Photochemical degradation
Environmental control

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Equilibrium moisture content 2.3
Relative humidity
Conservation techniques

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Relative humidity 2.3
Environmental control

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Chemistry 3.1
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Sizing 3.6

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Biodeterioration 2.7

Foxing

Airconditioning

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Deterioration 3.2

Acid hydrolysis

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Cellulosic discolouration 3.3

Conservation techniques

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Oxidation 3.1

Conservation techniques

BURGESS, H. D., DUFFY, S. & TSE, S. (1991). Investigation of the effect of alkali on cellulosic fibre. Part 1: Rag and processed wood pulp paper. In Butterfield, F. & Eaton, L. (Eds.), *Paper and textiles: the common ground*. Glasgow: The Scottish Society for Conservation and Restoration, 29-48.

Conservation techniques 3.0

Oxidation

Analysis

Equilibrium moisture content

BURGESS, H. D. & GOLTZ, D. M. (1994). Effect of alkali on the long-term stability of paper fibres containing lignin. *Archivaria: Journal of the Association of Canadian Archivists.*, **1**, 182-202.

Conservation techniques 3.0

Oxidation

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Analysis 3.1
Chemistry
Cellulosic discolouration
Foxing

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Foxing 3.3
Cellulosic discolouration
Analysis

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Deterioration 3.2
Chemistry
Analysis
Foxing
Cellulosic discolouration

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- Oxidation

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- Temperature
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- Analysis
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Analysis

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Cellulosic discolouration
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Wet/dry interface

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Conservation techniques

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Chemistry
Conservation techniques

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Chemistry
Oxidation

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Oxidation
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Environmental control

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Accelerated ageing

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Analysis

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Acid hydrolysis

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Equilibrium moisture content
Introduction
Analysis
Conservation techniques

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Oxidation
Accelerated ageing

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Oxidation
Introduction

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Analysis

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Deterioration

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Oxidation

Acid hydrolysis

Accelerated ageing

Deterioration

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Analysis 3.1

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Biodeterioration 2.7

Foxing

Equilibrium moisture content

Conservation techniques

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Oxidation

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Oxidation

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Chemistry

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Conservation techniques
Environmental control

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Cellulosic discolouration
Foxing

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Moisture content

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Moisture content

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Equilibrium moisture content 2.3

Analytical techniques

Degradation products

Metal catalysts, chelates

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Environmental control

Equilibrium moisture content

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Accelerated ageing 3.2

Environmental control

Equilibrium moisture content

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Preventive conservation 2.0

Accelerated ageing

Analysis

Conservation techniques

Environmental control

Equilibrium moisture content

Sizing

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Oxidation 3.1

Deterioration

Introduction

Chemistry

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Deterioration 3.2

Biodeterioration

Chemistry

Preventive conservation
Climatology
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Analysis 3.1

Chemistry

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Chemistry 3.1

Oxidation

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Chemistry 3.1

Equilibrium moisture content

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Photochemical degradation 3.2

Equilibrium moisture content

Relative Humidity

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Biodeterioration 2.7

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Analysis 3.1

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Analysis 3.1

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Atmospheric pollutants 2.3

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Foxing 3.3

Analysis

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Chemistry
Wet/dry interface
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Wet/dry interface 3.2
Oxidation
Microclimates
Cellulosic discolouration

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Wet/dry interface 3.2
Cellulosic discolouration
Equilibrium moisture content
Evaporation
Conservation techniques
Sizing

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Photochemical degradation 3.2
Oxidation
Analysis
Chemistry

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Analysis 3.1

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Equilibrium moisture content 2.3
Oxidation
Analysis
Chemistry

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Oxidation 3.1

Conservation techniques

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Equilibrium moisture content 2.3

Analysis

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Wet/dry interface 3.2

Cellulosic discolouration

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Wet/dry interface 3.2

Cellulosic discolouration

Foxing

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Foxing 3.3

Insect control

Biocides

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Foxing 3.3

Equilibrium moisture content

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Analysis 3.1
Relative humidity
Equilibrium moisture content

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Analysis 3.1
Equilibrium moisture content

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Analysis 3.1

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Analysis 3.1

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Analysis 3.1
Equilibrium moisture content
Evaporation

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Accelerated ageing 3.2

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Relative humidity 2.3
Equilibrium moisture content
Microclimates
Analysis
Conservation techniques

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Relative humidity 2.3
Condensation

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Oxidation 3.1
Conservation techniques
Chemistry
Analysis

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Equilibrium moisture content 2.3
Microclimates
Relative Humidity

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Preventive conservation 2.0

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Equilibrium moisture content 2.3
Analysis

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Environmental control 2.3
Building technology
Ventilation
Equilibrium moisture content

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Oxidation 3.1
Cellulosic discolouration
Conservation techniques
Chemistry

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Oxidation 3.1

Accelerated ageing
Cellulosic discolouration
Chemistry
Analysis

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Accelerated ageing 3.2

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Foxing 3.3
Oxidation

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Oxidation

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Chemistry

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Chemistry 3.1

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Preventive conservation 2.0

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Evaporation 3.7
Analysis

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Equilibrium moisture content 2.3

Wet/dry interface

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Photochemical degradation 3.2

Equilibrium moisture content

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Microclimates 2.3

Oxidation

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Analysis 3.1

Oxidation

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Climatology - tropics 2.3

Biodeterioration

Preventive conservation

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Photochemical degradation 3.2

Oxidation

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Photochemical degradation 3.2

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Photochemical degradation 3.2

Cellulosic discolouration

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Oxidation 3.1
Chemistry

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Cellulosic discolouration 3.3
Oxidation
Wet/dry interface
Evaporation

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Deterioration 3.2
Chemistry
Oxidation
Acid hydrolysis
Introduction

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Analysis 3.1

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Analysis 3.1

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Oxidation 3.1

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Accelerated ageing 3.2
Analysis

Permanence standards

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Wet/dry interface 3.2

Evaporation

Cellulosic discolouration

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Accelerated ageing 3.2

Oxidation

Analysis

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Conservation techniques 3.0

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Analysis 3.1

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Analysis 3.1

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Oxidation 3.1

Microclimates

Accelerated ageing

Conservation techniques

Cellulosic discolouration

Chemistry

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Analysis 3.1

Equilibrium moisture content

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Photochemical degradation 3.2
Ventilation

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Oxidation 3.1
Microclimate
Introduction
Foxing
Wet/dry interface
Analysis
Microfilm

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Oxidation 3.1
Microclimates
Cellulosic discolouration
Introduction
Analysis
Ventilation
Microfilm

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Equilibrium moisture content 2.3
Accelerated ageing
Microclimates
Analysis

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Relative humidity
Equilibrium moisture content
Microclimate

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- Relative humidity
- Equilibrium moisture content
- Microclimate

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- Analysis

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- Equilibrium moisture content
- Accelerated ageing
- Conservation techniques

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- Relative humidity

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- Equilibrium moisture content 2.3
- Microclimates
- Conservation techniques
- Accelerated ageing

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- Analysis

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- Deterioration 3.2
- Analysis

Relative humidity

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Environmental control 2.3

Analysis

Relative humidity

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Environmental control 2.3

Analysis

Relative humidity

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Analysis 3.1

Relative humidity

Environmental control

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Building technology 2.6

Condensation

Airconditioning

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Oxidation 3.1

Chemistry

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Oxidation 3.1

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Foxing 3.3

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Foxing 3.3

Conservation techniques

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Relative humidity 2.3

Building technology

Environmental control

Analysis

Condensation

Evaporation

Microclimates

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Relative humidity 2.3

Environmental control

Permanence standards

Biodeterioration

Equilibrium moisture content

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Environmental control 2.3

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Oxidation 3.1

Conservation techniques

Cellulosic discolouration

Chemistry

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Relative humidity 2.3
Microclimates
Equilibrium moisture content
Ventilation
Analysis

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Equilibrium moisture content 2.3
Relative Humidity

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Biodeterioration 2.7
Climatology - tropics

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Research methodology 1.6

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Analysis 3.1

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Analysis 3.1

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Oxidation 3.1
Chemistry
Introduction
Deterioration
Analysis

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Oxidation 3.1
Chemistry
Conservation technique

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Equilibrium moisture content 2.3
Chemistry
Oxidation
Analysis

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Climatology - tropics 2.3

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Foxing 3.3

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Analysis 3.1
Oxidation

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Equilibrium moisture content 2.3

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Oxidation 3.1

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Oxidation 3.1

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Photochemical degradation 3.2

Cellulosic discolouration

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Microclimates 2.3

Ventilation

Equilibrium moisture content

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Equilibrium moisture content 2.3

Evaporation

Environmental control

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Biodeterioration 2.7

Foxing

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Preventive conservation 2.0

Biodeterioration

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Deterioration 3.2
Chemistry
Accelerated ageing

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Airconditioning 2.3
Environmental control
Condensation

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Preservation manuals 2.1
Preservation history

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Relative humidity 2.3
Airconditioning
Ventilation

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Equilibrium moisture content 2.3
Relative humidity
Ventilation
Condensation
Evaporation

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Oxidation 3.1
Analysis

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Cellulosic discolouration 3.3
Foxing
Wet/dry interface

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Foxing 3.3
Biodeterioration
Analysis

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Climatology 2.3

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Environmental control 2.3
Microclimates
Atmospheric pollutants
Relative humidity
Biodeterioration

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Oxidation 3.1
Chemistry

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Environmental control 2.3
Accelerated ageing
Deterioration
Introduction
Analysis

REILLY, J. M., NISHIMURA, D. W. & ZINN, E. (1995). *New tools for preservation: assessing long-term environmental effects on library and archives collections*. Washington, DC: Commission on Preservation and Access.

Environmental control 2.3

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Accelerated ageing 3.2
Equilibrium moisture content
Microclimates

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Chemistry 3.1

Equilibrium moisture content

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Cellulosic discolouration 3.3

Oxidation

ROSE, W. (1994). Effects of climate control on the museum building envelope. *Journal of the American Institute of Conservation*, **33**, 199-210.

Equilibrium moisture content 2.3

Relative humidity

Environmental control

Building technology

Airconditioning

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Chemistry 3.1

Equilibrium moisture content

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Analysis 3.1

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Wet/dry interface 3.2

Oxidation

Chemistry

Analysis

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Environmental control 2.3
Introduction

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Equilibrium moisture content 2.3
Ventilation
Relative humidity
Biodeterioration
Building technology
Climatology - tropics

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Equilibrium moisture content 2.3
Chemistry
Accelerated ageing
Environmental control

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Microclimates 2.3
Accelerated ageing
Cellulosic discolouration

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Accelerated ageing 3.2

SHAHANI, C. J., HENGEMIHLE, F. H. & WEBERG, N. (1989). The effect of variations in relative humidity on the accelerated ageing of paper. In Zeronian, S. H. & Needles, H. L. (Eds.), *Historic textile and paper materials II: conservation and characterization*. Washington D C: American Chemical Society, 63-80.

Relative humidity 2.3
Accelerated ageing
Microclimates
Equilibrium moisture content

SHAHANI, C. J., HENGEMILE, F. H. & WEBERG, N. (1993). The effect of fluctuations in relative humidity on library and archival materials and their ageing within contained micro-environments. In *Pan African Conference on Preservation and Conservation of Library and Archival Materials.*, Nairobi:

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Relative humidity 2.3
Equilibrium moisture content
Microclimates
Accelerated ageing

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Analysis 3.1

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Analysis 3.1

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Equilibrium moisture content 2.3
Chemistry

SILVY, J. & LE NEST, J. F. (1973). A photochromic effect shown during the ageing of a cellulose material by light and heat. In Bolam, F. (Ed.), *The fundamental properties of paper related to its uses*. London: Benn for the Technical Division of the British Paper and Board Industry, 755-760.

Photochemical degradation 3.2
Cellulosic discolouration
Accelerated ageing
Analysis

SIMS, R. P. A. & HOFFMAN, W. H. (1961). Oxidative polymerisation. In Lundberg, W. O. (Ed.), *Autoxidation and antioxidants*. New York: Interscience, 654-667.

Oxidation 3.1
Chemistry
Analysis

SLAVIN, J. & HANLAN, J. (1992). An investigation of some environmental factors affecting migration-induced degradation in paper. *Restaurator*, **13** (2), 78-94.

Environmental control 2.3
Cellulosic discolouration
Deterioration
Microclimates

- SMITH, G. (1946). Moulds and tropical warfare. *Endeavour*, **5**, 110-115.
 Biodeterioration 2.7
 Equilibrium moisture content
- SMITH, M. (1987). IFLA Core Programme on Preservation and Conservation. *International Preservation News*, **1**, 1.
 Preservation and conservation bodies 1.7
- SMITH, R. D. (1970) *The nonaqueous deacidification of paper and books*. Dissertation submitted to the Faculty of the Graduate Library School in Candidacy for the degree of Doctor of Philosophy, University of Chicago.
 Deacidification 3.5
- standard..., I. (1993). International standard for permanent paper. *Restaurator*, **14** (4), 253-254.
 Permanence standards 1.1
 Accelerated ageing
- STAZICKER, E. (1987). Climatic control: a hopeless bewilderment. *Journal of the Society of Archivists.*, **8** (3), 171-173.
 Environmental control 2.3
- STOLOW, N. (1966). The action of environment on museum objects. Part I: Humidity, temperature and atmospheric pollution. *Curator*, **9** (3), 175-85.
 Environmental control 2.3
 Equilibrium moisture content
 Climatology
 Microclimates
 Condensation
- STRACHAN, J. (1938). Solubility of cellulose in water. *Nature*, **141**, 332-333.
 Chemistry 3.1
 Cellulosic discolouration
 Wet/dry interface
- STUHRKE, R. A. (1977). Development of permanent paper. In Williams, J. C. (Ed.), *Preservation of paper and textiles of historic and artistic value*. Washington DC: American Chemical Society, 24-36.
 Permanence standards 1.1
 Conservation techniques
- SWERN, D. (1961). Primary products of olefinic autoxidations. In Lundberg, W. O. (Ed.), *Autoxidation and antioxidants*. New York: Interscience, 1-54.
 Oxidation 3.1
 Introduction
 Analysis

SZCZEPANOWSKA, H. (1986). Biodeterioration of art objects on paper. *Paper Conservator*, **10**, 31-39.

Foxing 3.3

Biodeterioration

SZCZEPANOWSKA, H. & LOVETT, C. M. (1992). A study of the removal and prevention of fungal stains on paper. *Journal of the American Institute of Conservation*, **31** (2), 147-160.

Foxing 3.3

Biodeterioration

Conservation techniques

TANG, L. & TROYER, M. A. (1981). Flameless atomic absorption spectroscopy: a useful tool for direct determination of elements in library/archival materials. *Technology and Conservation*, **6** (2), 40-45.

Chemistry 3.1

Foxing

Analysis

TANG, L. C. (1978). Determination of iron and copper content in 18th and 19th century books by flameless atomic absorption spectroscopy. *Journal of the American Institute of Conservation*, **17** (2), 19-32.

Foxing 3.3

Analysis

Chemistry

TANG, L. C. (1986). Stabilization of paper through sodium borohydride treatment. In Needles, H. L. & Zeronian, S. H. (Eds.), *Historic textiles and paper materials: conservation and characterisation*. Washington, DC: American Chemical Society, 427-441.

Conservation techniques 3.0

Oxidation

TASKER, S., BADYAL, J. P. S., BACKSON, S. C. E. & RICHARDS, R. W. (1994). Hydroxyl accessibility in celluloses. *Polymer*, **35** (22), 4717- 4721.

Analysis 3.1

THOMSON, G. (1964). Impermanence: some chemical and physical aspects. *Museums Journal*, **64** (1), 16-36.

Photochemical degradation 3.2

Deterioration

Chemistry

Oxidation

Equilibrium moisture content

Microclimates

THOMSON, G. (1965). Air pollution - a review for conservation chemists. *Studies in conservation*, **10** (November), 147-67.

Atmospheric pollutants 2.3

THOMSON, G. (1977). Stabilisation of RH in exhibition cases - hygrometric half-time. *Studies in Conservation*, **22** (2), 85-102.

Equilibrium moisture content 2.3

Relative humidity

Microclimates

Airconditioning

THOMSON, G. (1986). *The museum environment*. (2nd ed.). London: Butterworths.

Environmental control 2.3

Photochemical degradation

Relative humidity

Atmospheric pollutants

TOBOLSKY, A. V., METZ, D. J. & MESROBIAN, R. B. (1950). Low temperature autoxidation of hydrocarbons: the phenomenon of maximum rates. *Journal of the American Chemical Society*, **72**, 1942-52.

Oxidation 3.1

Chemistry

Analysis

Photochemical degradation

TOISHI, K. (1959). Humidity control in a closed package. *Studies in Conservation*, **4** (3), 81-87.

Equilibrium moisture content 2.3

Microclimates

Relative Humidity

Analysis

TOISHI, K. (1961). Relative humidity in a closed package. *Studies in Conservation*, **6** (4), 111-112.

Relative humidity 2.3

Microclimates

Equilibrium moisture content

TONGREN, J. C. (1938). A reflectance method for the study of discoloration of artificially aged paper. *Paper Trade Journal*, **107** (8), 34-42.

Analysis 3.1

Relative humidity

Cellulosic discolouration

TRYON, M. & WALL, L. A. (1961). Oxidation of high polymers. In Lundberg, W. O. (Ed.), *Autoxidation and antioxidants*. New York: Interscience, 919-984.

Oxidation 3.1
Wet/dry interface
Photochemical degradation
Conservation techniques

TUMOSA, C. S., MECKLENBURG, M., ERHARDT, D. & McCORMICK-GOODHART, M. H. (1998). CAL/ NCPTT environmental conference. *Conservation DistList*, **11:59** (Jan 9, 1998), <http://palimpsest.stanford.edu>.
Environmental control 2.3

University of Natal. (1995) *Curriculum reform: a vision for the University of Natal*. Durban: University of Natal.
Research methodology 1.6

URI, N. (1961). Physico-chemical aspects of autoxidation. In Lundberg, W. O. (Ed.), *Autoxidation and antioxidants*. New York: Interscience, 55-104.
Oxidation 3.1
Analysis
Chemistry

VALENTIN, N., LIDSTROM, M. & PREUSSER, F. (1990). Microbial control by low oxygen and low relative humidity environment. *Studies in Conservation*, **35** (4), 222-230.
Biodeterioration 2.7
Environmental control
Analysis

VALKO, E. I. (1943). Sorption of water and other vapours by cellulose. In Ott, E. (Ed.), *Cellulose and cellulose derivatives*. New York: Interscience, 379-423.
Equilibrium moisture content 2.3

VAN HEERDEN, J. & HURRY, L. (1987). *South Africa's weather patterns*. Pretoria: Acacia.
Climatology 2.3

VENTER, J. S. M. (1966). *The ageing and preservation of paper - a development study* (Development Study No. Contract No 5131/95103). Pretoria: Council for Scientific and Industrial Research.
Deterioration 3.2
Acid hydrolysis
Permanence standards
Accelerated ageing

VENTER, J. S. M. (1967). Aging and preservation of paper. *South African Archives Journal*, **9**, 11-16.
Deterioration 3.2

VENTER, J. S. M. (1968). *The chemistry and mechanism of paper deterioration*. (CSIR Contract Progress Report No. 5131/95103). Pretoria: Council for Scientific and Industrial Research. Timber Research Unit.

- Chemistry 3.1
- Deterioration
- Permanence standards
- Accelerated ageing
- Environmental conditions

VENTER, J. S. M. (1978). *Current state of research on the aging and preservation of paper*. (unpub.report No. R/HOUT 114). Pretoria: Council for Scientific and Industrial Research. National Timber Research Institute.

- Accelerated ageing 3.2
- Preventive conservation

VERRALL, A. F. (1962). Condensation in air-cooled buildings. *Forest Products Journal*, **12**, 531-536.

- Environmental control 2.3
- Airconditioning
- Condensation
- Equilibrium moisture content
- Ventilation
- Building technology

VINE, M. G. & HOLLINGER, W. K. (1993). Active archival housing. *Restaurator*, **14** (3), 123-130.

- Microclimates 2.3
- Oxidation

VITALE, T. & ERHARDT, D. (1993). Changes in paper color due to artificial aging and the effects of washing on color (sic) removal. *ICOM Committee for Conservation. Preprints. 10th Triennial meeting, Washington, DC*. Paris: International Council for Museums. 507-515.

- Equilibrium moisture content 2.3
- Conservation techniques
- Cellulosic discolouration
- Introduction
- Analysis
- Environmental control

WAGSTAFF, J. D. (1977). Fungus deterioration of paper. *Antiques Monthly*, 28-30.

- Foxing 3.3
- Conservation techniques

WAN, J. & DEPOW, M. C. (1995). The roles of free-radicals in paper permanence and color reversion: some recent physical and chemical insights. In *CPPA Technical Section Annual Meeting Preprints*. Ottawa: Canadian Pulp and Paper Association, A219-A222.

Cellulosic discolouration 3.3

Chemistry

Permanence standards

Analysis

WESSEL, C. (1978). Deterioration of library materials. In Baker, J. P. & Soraka, M. C. (Eds.), *Library conservation: preservation in perspective*. Stroudsburg: Dowden, Hutchinson and Ross, 93-144.

Deterioration 3.2

Environmental control

WESSEL, C. J. (1970). Environmental factors affecting the permanence of library materials. *Library Quarterly*, **40** (1), 39-84.

Environmental control 2.3

Permanence standards

Deterioration

Atmospheric pollutants

Evaporation

Photochemical degradation

Biodeterioration

Oxidation

WESSEL, C. J. (1972). Deterioration of library materials. In Kent, A. & Lancour, H. (Eds.), *Encyclopaedia of Library and Information Science*, vol 7. New York: Dekker, 69-120.

Deterioration 3.2

Atmospheric pollutants

Relative humidity

Photochemical degradation

Environmental control

Biodeterioration

Cellulosic discolouration

Wet/dry interface

Oxidation

Accelerated ageing

WESSEL, C. J. & THOM, H. C. S. (1954). Climate and deterioration. In Greathouse, G. A. & Wessel, C. J. (Eds.), *Deterioration of materials, causes and preventive techniques*. New York: Reinhold, 3-70.

Climatology 2.3

Biodeterioration

Chemistry

Environmental control

WHITMORE, P. M. & BOGAARD, J. (1994). Determination of the cellulose scission route in the hydrolytic and oxidative degradation of paper. *Restaurator*, **15** (1), 26-45.

Oxidation 3.1
Photochemical degradation
Accelerated ageing
Chemistry

WHITMORE, P. M. & BOGAARD, J. (1995). The effect of oxidation on the subsequent oven aging of filter paper. *Restaurator*, **16** (1), 10-30.

Accelerated ageing 3.2
Oxidation

WILEY, J. H. & ATALLA, R. H. (1987). Raman spectra of celluloses. In Atalla, R. H. (Ed.), *The structures of cellulose: characterization of the solid states*. Washington, D C: American Chemical Society, 151-168.

Analysis 3.1

WILLIAMS, J. C., FOWLER, C. S., LYON, M. S. & MERRILL, T. L. (1977). Metallic catalysts in the oxidative degradation of paper. In Williams, J. C. (Ed.), *Preservation of paper and textiles of historic and artistic value*. Washington D C: American Chemical Society, 37-61.

Oxidation 3.1
Accelerated ageing
Analysis
Chemistry
Conservation techniques
Acid hydrolysis

WILLIAMS, T. M. & SHAW, D. A. (1991). Methods for evaluating pulp and paper slimicides: a review. In Rossmore, H. W. (Ed.), *Biodeterioration and biodegradation 8*. London: Elsevier Applied Science, 367-368.

Biodeterioration 2.7
Chemistry

WILSON, W. K. (1993). Effect of relative humidity on storage and use of records. *Abbey Newsletter*, **17** (7/8), 91-95.

Relative humidity 2.3
Equilibrium moisture content
Atmospheric pollutants

WILSON, W. K. (1997). Variability of the vapour pressure of oxygen on accelerated aging. *Abbey Newsletter*, **21** (2), 8.

Accelerated ageing 3.2
Oxidation

WILSON, W. K., GOLDING, R. A., MacLAREN, R. H. & GEAR, J. L. (1981). The effects of magnesium bicarbonate solutions on various papers. In Williams, J. C. (Ed.), *Preservation of paper and textiles of historic and artistic value II*. Washington: American Chemical Society, 86-107.

Conservation techniques 3.0

WINK, W. A. (1961). Effect of relative humidity and temperature on paper properties. *Tappi*, **44** (June), 171A-180A.

Relative humidity 2.3

Environmental control

Temperature

Permanence standards

Analysis

ZERONIAN, S. H. (1985). Intercrystalline swelling of cellulose. In Nevell, T. P. & Zeronian, S. H. (Eds.), *Cellulose chemistry and its applications*. Chichester: Ellis Horwood, 138-158.

Equilibrium moisture content 2.3

Chemistry

ZHBANKOV, R. G. (1966). *Infrared spectra of cellulose and its derivatives*. New York: Consultants Bureau / N Y U S A.

Analysis 3.1

LIST OF APPENDICES

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 - 2 DR E EUSMAN
 - 3 DR M V NAIR
 - 4 MS M-L FLORIAN
 - 5 DR C PEARSON
 - 6 DR V D DANIELS
 - 7 MR G SCOTT
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- B METEOROLOGICAL DATA (SEE 4.3.2)
- 1 METEOROLOGICAL DATA : MONTHLY
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 - 2 AVERAGE MONTHLY MEAN :
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- C FTIR-DRIFT INTEGRATION REPORTS (SEE
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PERSONAL COMMUNICATION IN THE DEVELOPMENT OF THE
RESEARCH HYPOTHESIS

- 1 DR J HOFENK DE GRAAFF
- 2 DR E EUSMAN
- 3 DR M V NAIR
- 4 MS M-L FLORIAN
- 5 DR C PEARSON
- 6 DR V D DANIELS
- 7 MR G SCOTT
- 8 PROF D HOLM
- 9 MS A-L. DUPONT

Dr Judith Hofenk de Graff
Scientific Department
Centraal Laboratorium voor Onderzoek
van Voorwerpen van Kunst en Wetenschap
8 Gabriël Metsustraat
1071 EA Amsterdam
The Netherlands

18 January 1994

Dear Dr Hofenk de Graff

THE CONSERVATION OF LIBRARY AND ARCHIVAL MATERIAL IN THE SUB-TROPICAL CLIMATIC REGION OF NATAL\KWAZULU

As a participant in the SAAR Paper Conservation Course held in 1992, I was able to report to my funding authorities that a highlight of the course was the short visit to the Centraal Laboratorium where you were currently engaged in research into the suspected oxidation reaction evidenced in the phenomenon of discoloration at the wet\dry interface; similar discolouration being frequently observed in paper artefacts at the Campbell Collections of the University of Natal.

Further to the article which first attracted my attention to this phenomenon: LIGTERINK, FRANK, PORCK, HENK & SMIT, WIM 'Foxing stains and discolouration of leaf margins and paper surrounding printing ink: elements of a complex phenomenon in books', published in Restauro 3 1989 pp.225-233 and in The Paper Conservator 15, 1991, p.45-52; I have seen no further reference to your own research into this discolouration phenomenon which you explained had originated from the observed staining of sequential passepartouts in the Stedelijke Argief.

I am currently engaged in research towards a Master's degree in Information Studies on the above topic, as a means of testing the informal observation of a relationship between climatic variables and manifestations of damage. As a professional paper restorer with twelve years of experience of the effects of the humid climate, I am convinced of the vital importance of the condensation theory in the causation of paper discolouration. I therefore cannot even contemplate an analytical review of the research in this field without consideration of the findings based on your experimental research.

.../I would be

2.

I would be grateful to learn of any recent or imminent publication of the findings of this research project, and take pleasure in utilising this opportunity to thank you for your personal commitment to paper conservation science, a source of personal inspiration in facing the problems on the bench.

Yours sincerely,

Mrs Dale Peters
Paper Restorer

REPLY RECEIVED 11.4.94. Onderzoek naar de oorzaak van verbruining van papier in passpartouts included. Letter of thanks as follows:

Dr J H Hofenk de Graff
Centraal Laboratorium voor Onderzoek
van Voorwerpen van Kunst en Wetenschap
Postbus 75132
1070 AC Amsterdam
The Netherlands

15 April 1994

Dear Dr Hofenk de Graaf

THE CONSERVATION OF LIBRARY AND ARCHIVAL MATERIAL IN THE
SUBTROPICAL CLIMATIC REGION OF NATAL/KWAZULU

Thank you for your letter of 23 March 1994 enclosing a copy of your report Onderzoek naar de oorzaak van verbruining van papier in passepartouts of 1993.

I was delighted to receive so precise a response to my enquiry for information on your research. A obligatory education in the second language of this country is at last of some personal benefit, in that I now find my command of Nederlands to be adequate to follow this vital report.

Your conclusions regarding the results of humidity fluctuations and recommendations for the use of non-porous storage materials directly mirror my own observations; we now resort to lining storage containers and cupboards to absorb excess moisture resulting from our humid climate and exacerbated by condensation on cold surfaces.

I am most grateful to you for your kind assistance,

With best wishes,

Yours sincerely

Mrs Dale Peters
Paper Restorer

Elmer Eusman
Conservation Department
Baltimore Museum of Art
Art Museum Drive
Baltimore MD 21218
United States

10 November 1994

Dear Elmer,

DISCOLOURATION AT THE WET-DRY INTERFACE

Congratulations on the forthcoming publication, awaited now in great anticipation, and thank you for the kind offer to secure a copy.

My own hypothesis is in the effect of local climatic conditions on the discolouration of paper. The causation and development of foxing has been well established, but I have observed copious examples of discolouration that bear no obvious relation to fungal activity - of which there is also ample evidence! Typical is the stain mirroring the brushstroke of glue or an airbubble in laying down works of art onto board - a common practice of uninformed local framers in an attempt to prevent cockling in our humid subtropical climate. The penetration of areas of discolouration at folds and tears in closed volumes is another common example.

It was important for me in working towards a Masters in Information Studies, to pursue the logical explanation provided by the theory of oxidation at the wet-dry interface, in identifying an alternative and a serious cause of paper deterioration in a humid climate. The relationship between oxidation and biodeterioration is certainly climatic, and your observation on the similarity in fluorescence is an area I am planning to investigate, along with the cuprammonium fluidity, in developing this argument. Needless to say, I have secured the support of a co-supervisor in the Department of Chemistry to oversee this work.

The procedure adopted in the Russell-effect photography is of particular interest, and if the description thereof is not reported, please do let me have details. I have a copy of the Centraal Laboratorium report 90/126, *Onderzoek naar de oorzaak van verbruining van papier in passepartouts*, but you mention a reference by Hon, and I would be interested to follow up the other explanation that the swollen open structure of the humid cellulose fibre, '(which is not [?] covered by a protective water layer)', as being more susceptible. You must have gone back to that early reference (1886) by Dixon, which is very interesting.

I am enclosing an extract from my bibliography pertaining directly to the phenomenon at the wet/dry interface, but I have encountered a serious lacuna between the early experimental work in the area of textile degradation, and a few modern commentaries. I am hoping that your report will encompass other recent experimental work, as I have yet to clarify my own experimental parameters in simulating climatic conditions.

WET-DRY INTERFACE

- 1 AMBLER, H. R. & FINNEY, C. F. (1957). Brown stains formed on wet cellulose. *Nature*, **179** (4570), 1141.
- 2 BOGARTY, H., CAMPBELL, K. S. & APPEL, W. D. (1952). Some observations on the evaporation of water from cellulose. *Textile Research Journal*, **22** (2), 75-81.
- 3 BONE, W. A. (1934). Evaporation of water from cellulose. *Journal of the Society of Dyers and Colourists*, **50**, 307-309.
- 4 BONE, W. A. & TURNER, H. A. (1950). Some effects of the evaporation of water from cellulose. *Journal of the Society of Dyers and Colourists*, **66** (June), 315-327.
- 5 EUSMAN, E. (1994). Wet-dry interface in paper in connection with local treatment in paper objects. In Personal communication, 3 November 1994.
- 6 FOX, M. R. (1965). Wet and dry boundaries on cellulosic textiles. *Journal of the Society of Dyers and Colourists*, **81** (Jan), 7-11.
- 7 HUFFMAN, REBERS, SPRIESTERBACH & SMITH (1955). [Paper chromatographic analysis]. *Nature*, **175**, 990.
- 8 HUTCHINS, J. K. (1981) *The water-soluble components of degraded cellulose*. MA, North Carolina State University.
- 9 HUTCHINS, J. K. (1983). Water-stained cellulostics: a literature review. *Journal of the American Institute of Conservation*, **22**, 57-61.
- 10 IIAMS, T. M. & BECKWITH, T. D. (1935). Notes on the causes and prevention of foxing in books. *The Library Quarterly*, 407-418.
- 11 MADARAS, G. W. & TURNER, H. A. (1953). Further observations on the effects of evaporating water from cotton cellulose. *J. Soc. Dyers and Colourists*, **69**, 371-377.

- 12 MEYNELL, G. (1979). Notes on foxing, chlorine dioxide bleaching and pigments. *The Paper Conservator*, **4** , 30-32.
- 13 PADFIELD, T. & ERHARDT, D. (1987). The spontaneous transfer to glass of an image of Joan of Arc. In *IIC Preprints, 8th Triennial Meeting*, Sydney: IIC, 909-913.
- 14 WESSEL, C. J. (1954). Textiles and cordage. In Greathouse, G. A. & Wessel, C. J. (Eds.), *Deterioration of materials: causes and preventive techniques*. New York: Reinhold,

I have been unable to obtain the thesis listed under 8, and wondered, if you have had access to this reference, whether you would recommend it?

Any other comments or suggestions would be most welcome, your assistance has already been of outstanding value to me. Many thanks to both you and your wife!

Regards,

Dale Peters
Paper Conservator

T H E
BALTIMORE
MUSEUM
OF ART
B M A

Mrs. Dale Peters
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Campbell Collections of the University of Natal
220 Marriott Road
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Elmer Husman
Assistant Paper Conservator
Baltimore Museum of Art
Art Museum Drive
Baltimore, MD 21218

3 November 1994

Dear Mrs. Peters,

First let me tell you that I am very excited that you decided to start your research. I am afraid that I will not have much time in the near future to follow up on some of my research results. I just accepted a new position in the Baltimore Museum which will keep me very busy with treatment and exhibitions. Needless to say that I hope someone will pick some of my research results.

Concerning my research in the National Gallery in Washington DC: The good news is that the results of my research will be published shortly (hopefully in December this year). This will be a National Gallery in house publication which will be available through the same institute. The article will appear in the Studies in the History of Art, Conservation Research Monograph Series. I would be more than happy to be of any assistance to help you obtain a copy. The bad news is that for this reason I will be unable to send you a copy of my manuscript. I would like to keep circulating texts other than the article to a minimum. The Gallery is the owner of the research and they are quite strict about these matters. (The article will also be accompanied by color photographs which are instrumental in the understanding of the research.)

However, I will be able to give you a summary and the general conclusions of my research as well as a literature list (and if the articles are hard to obtain I hope to be able to send you some copies). As I write this letter I realize that this information might be a little too much information at once. Please do not hesitate to contact me for more specific questions and let me know what your research will entail precisely.

My research concerns the wet-dry interface in paper (in connection with local treatment

in paper objects). An experiment to obtain clear these clear demarcations is to suspend a strip of paper vertically with the lower end dipped in water. The liquid rises due to capillary action until it reaches a point at which the steady rise is balanced by evaporation. I used Whatman filter paper #1. As soon as two hours, discoloration and fluorescence will occur in this region. Both the fluorescence and discoloration can be washed out. After washing however, the region is still visible when the sample is immersed in a solution of methylene blue. The former tideline region is visible through an increased methylene blue absorption indicating a higher concentration carboxylic groups (the color of the strip is light blue, the tideline region is dark blue). This indicates two cellulose modification processes are present producing fluorescent, discolored water soluble products and colorless insoluble products. More importantly: A specific modification process takes place in tideline region itself (as supposed to the overall wet part of the strip with their concentrate in the tideline region). These observations were made in the textile industry and were the first indications that an oxidative breakdown of paper occurred at the wet-dry interface.

To prove the latter, we decided to determine the presence of peroxides in the tideline. A quantitative measurement was made by taking the discoloration extract (in water) and let the peroxides present react with iodide to form triiodide. The concentration of the triiodide was measured spectrophotometrically at 362 nm. The ultraviolet-visible spectrum consistently showed the peroxide concentration in the tideline to be ten to twelve times as high as in the wet or the dry region. The difference between the wet and the dry region was small and sometimes non-existent. Also difference in amount between peroxides taken from the water extract and peroxides taken directly from the paper was very small, indicating that most of the peroxides were water soluble.

Russell-effect photography consists of sensitizing a photographic black/white film with ammonium hydroxide. Bringing the film in direct contact with the sample for twenty four hours, will modify silver halide into silver metal in those places where radicals (therefor also peroxides) are present. (Let me know if you need a more precise description of the total procedure.) After exposure and development, the tideline region was clearly visible at every wet-dry interface as a dark line on a light background. Two other observations were made:

* There seemed to be more patches of grey in the region above the tideline than beneath, indicating transportation and concentration of peroxides at the wet-dry interface. But as I mentioned before, quantitative measurement showed that the difference in peroxide content between the wet and the dry region was very small. What happens here (we think) is that only a small amount of a higher concentration of peroxides can initiate a chain reaction producing radicals and more peroxides in the tideline region.

* Generation of new peroxides takes place at every wet-dry interface itself. Even if the same sample was washed thoroughly between the experiments.

There are more explanations for paper degradation in the tideline region, given by other people. One of them suggests that the swollen, open structure of the humid cellulose fiber (which is not covered by a protective water layer) is more susceptible to attacks from oxygen in the air. Another explanation was introduced by Hon who suggested the presence of tension radicals, produced by the physical forces accompanying the swelling and shrinking of cellulose in the tideline region. As far as I am concerned all of these theories may apply. Perhaps a combination of them.

The second part of my research explored the relationship between the fluorescence and the discoloration in the tideline and in paper in general. It became evident that in many cases fluorescence proceeds discoloration. In order to absorb visible light (and become colored material) organic molecules must consist of enough conjugated double bonds (sequence of single and double carbon bonds). Shorter structures are capable of absorbing ultra violet and fluorescing. Degradation can cause these structures to get longer which will enable the molecules to absorb visible violet light, thus appearing yellow.

This is what happened when samples with fluorescent regions would be dark aged in a dry or a humid oven. Not only fluorescent tidelines would turn yellow (in Whatman filter paper) but also fluorescent foxing-like spots in old rag paper. This however, is the only connection between tidelines and foxing as far as I could find (I am sorry to say).

Well, how is this for a start. I am pretty sure you'll have some questions about my poor summary here. A note on what I assume will be part of your research: The interfaces I used in my experiments were well defined to make it easier to analyze them. It has been noted in literature that within a pile of paper or book three dimensional tidelines can occur but you can imagine that researching these is more complicated (not impossible, though). I hope you got a copy of Judith's research on environmental changes in and outside art storage boxes. Let me know what kind of experimental model you hope to develop and what you hope to see happen. As for possible oxidation at an absolute wet-dry interface: there seems to be no question in my mind (and several others) that a combination of hydrolysis and oxidation takes place at every new wet-dry interface. Many questions like why cellulose modification only seems to take place at the interface and how big the differences between the humid and the dry region have to be to modify cellulose (RH fluctuations), remain to be answered.

I hope my letter will be helpful and hope to here from you soon. I also hope to send you my article as soon as it comes out in December.

Sincerely,


Elmer Eusman

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Conservation Department
Baltimore Museum of Art
Art Museum Drive
Baltimore, MD 21218
TEL. (410) 396-6341
FAX. (410) 396-6562



Mrs. Dale Peters
 Paper Conservator
 Campbell Collections of the University of Natal
 220 Marriott Road
 Durban 4001
 South Africa

Elmer Eusman
 Assistant Paper Conservator
 Baltimore Museum of Art
 Art Museum Drive
 Baltimore, MD 21218

14 November 1994

Dear Mrs. Peters,

My apologies for this late reply but things are rather hectic at this time. I am afraid I have some bad news. The publication of my research is postponed until March 1995. I am really sorry about this but it seems to be beyond my control. If you have some questions that I can answer sooner than that, please let me know. So although the Russell effect photography procedure is explained in the article I will give you a short description right now.

Vincent Daniels is the main person to consult on Russell-effect photography. He heads the Scientific Research Department in the British Museum and has written a number of articles on the subject: Vincent Daniels, "The Russell Effect," Studies in Conservation 29 (1984), 57-62; "Monitoring the Autoxidation of Paper Using Photographic Materials," Advances in Chemistry Series 212 (Washington, 1986), 318-327; Oxidative Damage and the Preservation of Organic Artifacts, "Free Radical Research Communications 5 (1989), 213-220.

These articles give you a good idea about the mechanism of this procedure. However, the film Dr. Daniels uses is no longer available. Film that is suitable for Russell-effect photography is difficult to obtain. Generally most types of film contain stabilizers that protect the film from fogging, a term used for what is the result of oxidation of the silver halide, resulting in faint grey patches on the film. This process is thought to be similar to the Russell-effect; silver gelatine film containing these stabilizers is therefor unsuitable for our purposes.

After a long search we found a film in France that works quite satisfactory. The film is Guilleminot EG 18. I don't have the address in France but I know it is available through Chicago Albumen Works, P.O.Box 379, Front Street, Housatonic, MA 01236 (let me know if you need my help ordering). If your French is not as

? PLS

rusty as mine you might give the Guilleminot firm itself a call. I am afraid I do not have their number, though.

Here is how I used the film: In a dark room, sensitize the film by immersing it in a bath of 0.05 ammonium hydroxide for 4 minutes. Rinse the film in distilled water for two minutes and an additional two minutes in ethanol. This way the film will dry fast. The dry film is then put in direct contact with the sample. The film and sample are sandwiched between two glass plates and put away in a lightproof box for 24 hours. The whole procedure should take place in the dark (even red light will expose the sensitized film). The 24 hour-exposed film is developed in Kodak developer D76 for 4 minutes and fixed with Kodak RadidFix for six minutes.

You will have to experiment a little bit with different solutions and sensitizing- and exposure times. If all works well, tidelines show up beautifully.

~~I am still trying to get the article written by Hon~~ and I have a list of his publications. I hope to read some of his research in the near future. I will keep you posted.

The "not" that you question is indeed incorrect. I bury my head in shame... I also never heard of this early reference (1886) by ~~Dixon~~. I have little more to add to your literature list pertaining directly to the wet/dry interface phenomenon and I ran into the same lacuna. ~~M.R. Fox~~ wrote two more articles in the JSDC. The second article could be of interest (pages 46-51) but perhaps you already have it. There is an article by Schaffer, Appel and Forziati, "Reactions at Wet-Dry Interfaces on Fibrous Materials," Journal of Research at the National Bureau of Standards 54 (February 1955), 103-106, but this article concerns more organic solvents rather than water. You might want to read Ligterink, Porck and Smit, "Foxing Stains and Discoloration of Leaf Margins and Paper surrounding Printing Ink," The Paper Conservator 15 (1991) 48. I think I have ~~Hutchins'~~ article in one of my many cardboard boxes. I will try to find it for you. There is also a series of articles by ~~Lewin et al~~ and I will also try to find those for you. These articles concern the yellowing of paper if I remember well.

I do not know of any recent experimentation other than my own. Vincent Daniels however has always been interested in this phenomenon and was one of the reviewers of my forthcoming publication. You might want to contact him for advise on designing your experiments.

I hope my late reply will not keep you from keeping contact. I would like it if you could keep me posted on your research and chase me with more questions. I will send the promised literature as soon as possible.

Sincerely,

Elmer Eusman

Elmer Eusman
Conservation Department
Baltimore Museum of Art
Art Museum Drive
Baltimore MD 21218
United States

16 January 1995

Dear Elmer,

DISCOLOURATION AT THE WET-DRY INTERFACE

Thank you for your fax dated 9 December 1994. It is my turn to apologise for the delay in replying, but as you see, we are survivors of yet another festive season. It is a burden coupled with our summer holidays, but we even survived a (harmless) snake in our living room on a recent sultry evening! *Semper quid nova ex Africa.*

The postponement of your research is indeed bad news, I can hardly contain my anticipation, but you have been so helpful already that I can dare not protest.

As you envisaged, I have a few questions:

- 1 I am intrigued by the observation of increased incidence of patches of grey in the region above the tideline. It is not clear whether this is a general observation on the presence of peroxides, or whether it was restricted to certain paper samples. I am determined to apply the Russell-effect photography to a closed book degraded by fifty years of high moisture content and fluctuating RH. I anticipate predominant evidence of similar patches. Is this effect illustrated for comparison in your published article?
- 2 The relationship between the fluorescence and the discolouration is also of interest, particularly the degree of increase in conjugated double bonds in the increased absorption from ultra violet to visible light. That fluorescence precedes discolouration may be useful as an experimental design parameter. Can you confirm that the fluorescence generally persists once discolouration has formed, as in the case of the rag paper samples you examined? I must consider the implication that these areas of degradation visible only under fluorescence are sites of moisture accumulation susceptible to oxygen and biological attack. You mentioned a reference suggesting the susceptibility of the swollen, open fibre structure, that would be relevant to this consideration. Please let me have further details.

A number of other references you mentioned have been very useful. The Ligterink, Porck and Smit article, which appeared in three separate journals, initially triggered my interest, shortly before my participation in the SAAR course in 1992, where I had the opportunity to discuss with Judith Hofenck de Graff, the experiment on fluctuating humidity she was running at the time. There of course, your name was mentioned, I presume you trained or worked there too.

I have been scratching around for the Dixon reference, which I personally did not consult, but it is mentioned by BONE (1934), JSDC 50, 307-309, "...many years ago the late Prof Dixon claimed to have proved the formation of hydrogen peroxide by the evaporation of water. Dixon had repeated the experiment many times, but with indefinite results." Should you be interested, you will find the details in DIXON (1886), Trans.Chem.Soc. 49, 108. The journal, Free Radical Research Communications is not available in this country, I wonder whether you would let me have a copy of that article by Vincent Daniels. I had already discounted the Schäffer, Appel and Forziati article, but the second article by Fox in the JSDC, may be useful in designing my experimental model. That I can obtain without a problem. The Lewin articles however, are unknown to me, please pass on those bibliographic details. I have a copy of the literature review by HUTCHINS (1983) JAIC 22:57-61, I have not seen his MS thesis, HUTCHINS, JK (1981) The water soluble components of degraded cellulose, North Carolina State University. If you have seen it, what is your opinion? I am reluctant to order it and then find it irrelevant.

I have absolutely no ambition to reproduce your efforts, or those of others in this area; as a paper conservator, I need rather to find an application for your research in an explanation for the deterioration evidenced in our collections.

I have followed up your suggestion to locate the Guilleminot EG 18 film, and have taken the liberty of quoting your name. I am interested to hear if, and how you used the Russell effect in conjunction with oven ageing. I will take this up with Vincent Daniels, as you suggest, but I was wondering whether the link between cause and effect could be made using both processes following exposure to RH cycling. Your peroxide formation evident in the grey patches above the tideline suggest that I will have to consider the role of hysteresis.

Other research that I have encountered through Colin Pearson is the work of Dr Graeme Scott at the Australian Museum on the relationship between moisture content and biodeterioration. His paper to the IIC Congress in Ottawa appears in the Preprints, and is of particular interest in the proposal that high ventilation rates in tropical climates may be offered as a reason why mould growth is not as common as might be expected. This supports my own experience, and my research hypothesis in that the disruptive role of ventilation on the stability of surface layers of air (evaporation) may be restricting mould growth, but ventilation is inconsistent, and resultant RH cycling has serious effects on my interface.

Yours sincerely

Elmer Eusman
Conservation Department
Baltimore Museum of Art
Art Museum Drive
Baltimore MD 21218
United States

16 January 1995

Dear Elmer,

DISCOLOURATION AT THE WET-DRY INTERFACE

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The postponement of your research is indeed bad news. As you envisaged, I have a few questions:

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2.

of water. Dixon had repeated the experiment many times, but with indefinite results." Should you be interested, you will find the details in DIXON (1886), Trans.Chem.Soc. 49, 108. The journal, Free Radical Research Communications is not available in this country, I wonder whether you would let me have a copy of that article by Vincent Daniels. I had already discounted the Schaffer, Appel and Forziati article, but the second article by Fox in the JSDC, may be useful in designing my experimental model. That I can obtain without a problem. The Lewin articles however, are unknown to me, please pass on those bibliographic details. I have a copy of the literature review by HUTCHINS (1983) JAIC 22:57-61, I have not seen his MS thesis, HUTCHINS, JK (1981) The water soluble components of degraded cellulose, North Carolina State University. If you have seen it, what is your opinion? I am reluctant to order it and then find it irrelevant.

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Yours sincerely

Dale Peters
Paper Conservator



Mrs. Dale Peters
Paper Conservator
Campbell Collections of the University of Natal
220 Marriott Road
Durban 4001
South Africa

Elmer Eusman
Assistant Paper Conservator
Baltimore Museum of Art
Art Museum Drive
Baltimore, MD 21218

12 June 1995

Dear Mrs. Peters,

Well, I guess I am setting the new record for late replies but I think it is worth the wait. You are one of the lucky recipients of one of the off-prints of the article. The color photographs came out really nice, I think. Enjoy!

I am also sending you a xerox-copy of a Russell-effect image obtained from a sample containing a tideline. The finer details of the grey region will be lost after the image is copied but you should be able to see that the dry region is considerably darker than the former wet region. The darker region is not is not evenly grey but rather consists of different darker patches. The photographs in the article show perhaps better detail.

These observations pertain Whatman filter paper only because this was the paper used in the different experiments. Using the same technique with other types of paper (like in a book) might add different factors to the experiment which have to be considered to interpret the resulting image. To mind come things like ink, fillers or sizing. I did try to do some tests on older paper containing foxing spots or general discoloration but I obtained inconsistent results.

The fluorescence as I observed it in aging tidelines in Whatman filter paper samples, increases, turns yellow and then slowly diminishes as discoloration increases. The only samples in which the fluorescence totally disappears was in tidelines created by hydrogen peroxides. Under ultra violet light these regions had become absorbent and appeared dark brown. However, I am convinced that if aged long enough the tidelines created, in Whatman filter paper by water, will turn dark brown and loose their fluorescence as well. It is a natural progression in which the fluorescing molecules become longer and start absorbing radiation in the visible spectrum.


You actually should have the reference to the open fibered paper structure: Bone and Turner 1950, p.326. I will send you Daniels' and Lewin's articles. I haven't found Jane Hutchins MS thesis but I am still looking. We just bought a house in Baltimore and moved in two weeks ago. A lot of stuff is still in boxes and is not likely to come out immediately, so bear with me.

Frank Ligterink was a fellow student in my class and he also got me enthusiastic about this topic. Our school is separate from the Central Laboratory but we did follow some lectures by Judith Hofenk de Graaff.

I did a few tests combining aging with Russell-effect. My preliminary conclusion is that the amount of peroxide in a tideline does not increase during aging (where as discoloration definitely does). But don't quote me on this since I hope to do some more tests. The last image on the xerox copy of the Russell-effect images shows three circles made by five drops of liquid on paper. The samples were aged differently resulting in distinct difference in color. However, as you can see, there is no difference in the Russell-effect image.

I will be gone to the Netherlands the end of this week and be back the end of the month. I hope you are making progress and to hear from you soon.

Sincerely,

Elmer 

Dr M V Nair
Director
National Research Laboratory for
Conservation of Cultural Property
Sector E/3, Aliganj Scheme
Lucknow 226 020
INDIA

17 January 1994

Dear Dr Nair

**CONSERVATION RESEARCH - THE EFFECT OF ENVIRONMENTAL FACTORS ON
THE DETERIORATION OF PAPER ARTEFACTS**

Further to our correspondence in 1992 regarding your proposed participation in the South African Paper Conservation Group Conference, I am obliged to seek your assistance once more, this time in furtherance of my own research towards a Master's Degree in Information Studies.

As a professional paper conservator with twelve years' experience in the Campbell Collections of the University of Natal, an archival library of rare Africana books, documents and works of art on paper; my concern for conservation management in our local sub-tropical climate has led me to register this thesis as a means of testing my observations of a relationship between climatic variables and manifestations of damage. As you are no doubt aware, the scope of a Master's degree is limited to an analytical review of existing research to prove such an hypothesis, and it is for that reason that I turn to you.

The NRLC must be considered the foremost research facility in this field, and I am unable to contemplate the topic without reference to the research findings and publications of your various divisions: Paper, Biodeterioration, Environmental and Conservation. I was looking forward to the receipt of regular information on your activities and programmes, but the inclusion of my institution on your mailing list appears to have been unsuccessful.

2.

I therefore ask you to submit my request to the Heads of the various Divisions for copies of published research papers in the following areas:

- i) The effect of a sub-tropical climate in compromising the chemical stability and physical strength of paper artefacts;
- ii) The role of environmental control in creating appropriate storage conditions;
- iii) The effect of restoration techniques in diminishing the induced degradation;
- iv) The attitude of personnel as an indispensable precondition to conservation.

My research objective is to reach an understanding of the phenomena involved in the accelerated deterioration of library and archival material in a sub-tropical climate in order to develop a strategy for preventive conservation.

If you are aware of further research being conducted elsewhere in this field, I would appreciate such information. Your co-operation is highly valued.

Yours sincerely

Mrs Dale Peters
Paper Conservator

APPENDIX A 4

Date: Fri, 24 Mar 1995 23:30:00 +0000
From: CAN-DOGWOOD@IMMEDIA.CA
Subject: Paper with Fox Spots Needed for Research

This request is being cross-posted by Barb Dexter of the Dogwood Regional Network on behalf of Mary-Leu Floridan. Our apologies if you receive more than 1 copy.

Mary-Leu Florian requests small disposable samples of paper with fox spots for research. The paper or printing on the paper must be dated or provenanced. If the sample is used for analysis, the data will be sent to the donor. Please mail them to:

Mary-Leu Floridan
Research Associate
Conservation Services Section
Royal British Columbia Museum
675 Belleville Street
Victoria, BC Canada V8V K

Mary-Leu can be reached by phone/fax: 604-385-8263

30 March 1995

Mary-Lou Florian
Research Associate
Conservation Services Section
Royal British Columbia Museum
675 Belleville Street
Victoria, BC Canada V8V k

Dear Ms Florian

FOXED PAPER SAMPLES

I noted with interest your Internet message requesting foxed paper samples. As I have no shortage thereof, it seemed an excellent opportunity to discuss with you a postgraduate research project in which I am currently engaged, on the conservation of library and archival materials under the sub-tropical climatic conditions of this region, KwaZulu/Natal.

I would be grateful to receive a copy of your paper, recommended in the literature as a major contribution:

1 FLORIAN, M-L. E. (1993). *Conidial fungi (mould) activity on artifact materials - a new look at prevention, control and eradication*. In ICOM Committee for Conservation, the Triennial Meeting., Washington: International Council of Museums, 868-874.

My interest is in the role of oxidation as a causative factor in cellulosic discolouration, but the biochemical factor cannot be overlooked in this climate. I am presently contemplating sample selection from these Collections for comparison by FTIR analysis with my own experimentation; samples of known provenance could thus be made available for your analysis, particularly if the resultant data could be made available to me thereafter.

Please let me have further details of your project and sample requirements, to enable a possible co-operation.

Yours sincerely

Mary-Lou E. Florian
129 Simcoe St., Victoria, B.C. V8V 1K5, Canada
Museum Collections Conservation Science
fax/phone 604 385-8263

14 June 1995

Dale Peters
Paper Conservator
Univ. of Natal
The Campbell Collections and Centre for Oral Studies,
220 Marriott Rd. Durban 4001 South Africa
phone 031 2073711
fax 031 291622

Dear Dale Peters

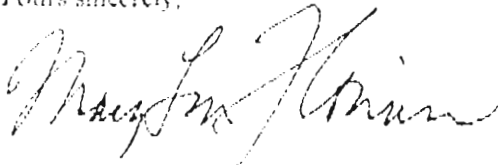
I received your paper samples yesterday, many thanks

Unfortunately I have completed my EDX work for the time being. I am not sure if I will be able to do any more

I will be away until end of July. After which I may be able to do a quick verification of fungi. They way they smell I suspect that most of the spots are fungi!

Again many thanks.

Yours sincerely,



Mary-Lou E. Florian
Conservation Scientist
Emerta-Royal British Columbia Museum

X-cs:
From: Self <LIBD/PETERSD>
To: pearson@science.canberra.edu.au
Subject: Environmental research
Date: Tue, 1 Nov 1994 15:44:15

I have been referred to you by Jim Druzik of GCI, although you need no introduction. Your name is certainly familiar from the ICOM Training Committee...my thanks for your contribution to the Working Group!

I am currently registered for a Master's degree in Information Studies to investigate the phenomenon observed in our Collections, and referred to in conservation literature as the oxidation at the wet/dry interface, although used primarily in relation to textiles.

I am proposing that the subtropical climate of southeast Africa naturally induces the condensation/evaporation cycle in library and archival materials under high absolute humidity and resultant high moisture content, in the exposure to temperature and particularly RH fluctuations. I need to develop an experimental model to simulate these conditions in order to pursue the theory that this form of cellulosic staining has not been previously distinguished from biological causes. To that end I am canvassing possible contacts for suggestions.

I also need to identify other research initiatives in this field, such as the recent work of the Centraal Laboratorium in Amsterdam; the devastating press release from the Smithsonian, and the Science Initiatives of the Commission on Preservation and Access.

Please let me know of any similar research or contact persons of whom you are aware, in Australia and the Pacific Rim. I have one reference to a Regional Seminar on the Conservation of Cultural Materials in Humid Climates, (Unesco, 1980), which looks most interesting, I wondered whether copies are still available. Any assistance would be of great help,

Best wishes
Dale Peters
Paper Conservator

Date: Tue, 13 Dec 1994 16:13:17 +1100 (EDT)
From: Colin PEARSON <pearson@science.canberra.edu.au>
To: PETERSD <PETERSD@lib.und.ac.za>
Subject: Re: Environmental research

Dear Dale

I apologise for not replying to your earlier message but I have been overseas a lot recently. You are studying a topic of which I personally do not have any experience and my teaching staff at the university cannot help either. If you haven't already done so may I suggest that you send your message to the Conservation Distlist at Stanford University. All such messages are collected and then distributed via email to the conservation profession linked to email. To do this simply email your message to: consdist@lindy.stanford.edu

From: Self <LIBD/PETERSD>
To: pearson@science.canberra.edu.au
Subject: Environmental research
Date: Wed, 1 Feb 1995 14:15:37

Many thanks for enabling the contact with Graeme Scott at the Australian Museum, our discussion on water vapour transmission has been most stimulating.

He makes reference to a joint paper by King & Pearson on alternative technologies in environmental control (1992). The conference papers in question are not locally available, may I request a copy? If King is available on e-mail, he may be able to assist in the identification of his local equivalent. The issue is highly relevant in the light of third world realities.

I am dismayed at the dearth of current research in environmental control under tropical and sub-tropical conditions; the National Research Laboratory for Conservation of Cultural Property in Lucknow, India must surely be active, but I elicit no response whatever. Is your experience any different?

I am also eager to contact Stefan Michalski at CCI, you wouldn't also have that Internet address by chance? Please forgive the inconvenience, you are one of few with contacts in this field.

Dale Peters
petersd@lib.und.ac.zaX-cs:

Mon, 6 Feb 95 17:31:52 +1100
Message-Id: <9502060631.AA21676@science>
To: PETERSD@lib.und.ac.za
Reply-To: pearson@science
From: pearson@science (COLIN PEARSON)
Subject: Re: Environmental research
Date: Mon, 06 Feb 95 17:33:03 EST
X-Mailer: Mail-it Version 1.30

Dear Dale

As requested I will send you a copy of the paper by King and Pearson.

Steve King commenced a literature search in the field 2 years ago but has not yet published. I suggest you contact him. Steve King, School of Architecture, University of NSW, PO Box 1, Kensington, NSW 2033. Fax: +61 2 6621378, Email: stevek@keystone.arch.unsw.edu.au
OR
stevek@unsw.edu.au

I am not quite sure of Michalski's email, the address I know but not sure of how to put his name. Suggest you try: stefan.michalski@banyan.dgim.doc.ca If this doesn't work it may be better to fax him at CCI, Fax: 613 998 4721.

I would not expect too much out of India.

Regards

Colin Pearson

6 March 1995

Dr Vincent Daniels
Director
Conservation Research Section
British Museum
London WC1B

Dear Dr Daniels

EXPERIMENTAL DESIGN: OXIDATION AT WET/DRY INTERFACE

I am currently registered for a Master's degree in Information Studies on the general topic of

Conservation of library and archival materials in the sub-tropical climatic region of KwaZulu/Natal

In the course of my professional career as Paper Conservator, my observation of the nature of paper deterioration under humid conditions has led me to differentiate between forms of cellulosic discolouration, and this research is focused on the distinction between biodeterioration, metal catalysed oxidation and chemical processes of degradation, particularly the oxidation of paper at the wet/dry interface.

It has become evident that you have considerable experience in this field, and it is on the advice of Elmer Eusman, of the Baltimore Museum of Art, that I seek to consult with you.

I seek a means of indicating a relationship between humid conditions and the oxidation phenomenon as reflected in the Russell photographic image. I wondered whether you could recommend the technique described by: SIVADJIAN, M. J. (1965). Detection and measurement of humidity and moisture by the hygrophotographic technique. In Wexler, A. (Ed.), *Humidity and moisture: measurement and control in science and industry*. (pp. 656-666). New York: Reinhold.

He describes the detection of humidity in the contact with a photographic plate sensitised by a reversible photochemical reaction accompanied by a change in

colouration which disappears instantly under the action of small quantity of water and of humidity. The emulsion of an ordinary photographic plate is impregnated with a double salt of mercury and silver iodide.

I am concerned that the method may be outdated in a manner similar to the development of the Russell technique as described in: DANIELS, V. D. (1986). Monitoring the autoxidation of paper using photographic materials. In Needles, H. L. & Zeronian, S. H. (Eds.), *Historic textile and paper materials; conservation and characterisation*. Washington D C: American Chemical Society. p.319. Can you comment on the validity of a direct comparison between these two contact images?

Suggestions on an alternate source of an appropriate film for Russell image photography would be appreciated as I understand that the firm Guilleminot, in Paris, suppliers of Guilleminot EG 18 film, is no longer in business.

Of further interest is the research conducted by R M Organ of the British Museum Laboratory some thirty years ago into the relationship between humidity control and moisture content in enclosed spaces. If the data is accessible, I should be grateful to obtain a copy. In studying the interrelationship between the causative factors of cellulosic discolouration, I should also appreciate a copy of:

DANIELS, V., & MEEKS, N. D. (n.d.).

Foxing caused by copper alloy inclusions in paper. (unpub.report) British Museum, Dept. of Conservation.

I am naturally willing to meet any costs involved.

Yours sincerely

(Mrs) Dale Peters
Paper Conservator

THE BRITISH MUSEUM

Department of Conservation

Mrs D Peters
University of Natal
The Campbell Collection
Centre for Oral Studies
220 Marriott Road
Durban 4001
South Africa

Our Ref: CD/VDD/BB

16 March 1995

Dear Mrs Peters

I was interested in your proposed investigations into the distribution between metal catalyst oxidation, biodeterioration and the oxidation at the wet/dry interface.

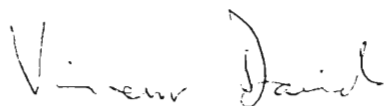
I have now read the article by Sivadjian on hygrophotographic techniques which I found very interesting; I had not seen it before. You ask whether there is a connection between the hygrophotographic and the Russell effects, I don't think there is, as they are caused by separate phenomena. If you suggest that either phenomenon has been attributed to the wrong activating agent then I can tell you that the Russell effect plate cannot develop a latent image from water alone. I tried an experiment similar to Sivadjian's using an almost identical Perspex block containing different concentrations of H_2O_2 in water. Water had no effect.

The chemical basis for hygrophotography is not explained adequately but I can see no reason why the water should not be the activating agent. There is probably too little H_2O_2 to have an effect.

As requested, I enclose a photocopy of Daniels and Meeks on copper alloy inclusions in paper. There is no charge. I also enclose another by the same authors on iron inclusions and a paper on the Russell effect which you probably have seen as it is in a rather obscure non-destructive testing book.

You should try to obtain Kodak LP4 films for your Russell graphs. I would be very interested to hear of your results.

Yours sincerely



Dr V Daniels

enc

29 May 1995

Dr Vincent Daniels
Director
Conservation Research Section
British Museum
London WC1B

Dear Dr Daniels

EXPERIMENTAL DESIGN: OXIDATION AT WET/DRY INTERFACE

I must immediately apologise for the apparent inconsideration in this a tardy reply to your letter dated 16 March 1995. I am somewhat surprised myself to find so much time has passed in the engrossed preparation of an interim thesis submission.

I should like to thank you for the articles so kindly sent together with your letter; these were of particular benefit as I had not encountered them and which have presented further avenues of interest, particularly in the comparative corrosion mechanisms investigated.

My thesis supervisors have recommended that my research project be upgraded from a Masters to Ph.D. I understand that your name, mentioned in my motivation as one of the leading experts in the field, may possibly be selected in the nomination of an independent moderator. I trust that in that event, the evaluation of my proposal may not present an inconvenience.

I hope to test the significance of discolouration resultant upon the evaporation kinetic in phase transformations at the paper surface at high relative humidity, which I maintain has been obscured by the more apparent biochemical deterioration evidenced in foxing.

I seek therefore a means of indicating a relationship between cycling RH and deterioration, or more directly, to measure moisture content in response to phase boundary conditions in relation to the oxidation phenomenon as reflected in the Russell photographic image. My thanks for clarifying the mechanism of the hygrophotography, which obviously can no longer be considered as a possible means to indicate a relationship between environment and deterioration. I hope rather that the function of comparison between induced degradation and naturally aged samples from our Collections will be met by FTIR analysis, in reflecting similar traces of degradation products. If you are able to recommend suitable paper spectra for this purpose, I would be most grateful.

It may interest you to know that I have agreed to exchange information resulting from this analysis with Mary-Lou E Florian, who is engaged in fungal investigation, and will conduct EDX analysis on paper samples which I have submitted from my own experimental sample. One must suppose that your article, *Foxing caused by copper alloy inclusions in paper*, is readily available to her.

My concerns, on which your comment would be valued, are firstly, that if indeed the tideline region, recently researched by Eusman, exists in the surface boundary layer as I surmise, the result of induced degradation by means of manipulation of environmental variables of temperature and humidity may not be sufficiently conclusive. I have considered improving the definition of the phenomenon by introducing to the sample hygroscopic particulate matter which would act as condensation nuclei- sodium chloride being an option as an atmospheric pollutant in a marine climate. A further consideration is to expose a selected sample to UV irradiation, which may however simply add a further variable without enhancing the conclusion. Secondly if the rate of moisture migration through the material itself is not equal to the rate of surface evaporation, which I propose as a major cause of sites of moisture accumulation and resultant discolouration within the material, what accepted method of determination would you suggest to indicate partial pressure gradients in a convective heat transfer?

In conclusion, may I share with you the excitement of the chase in the pursuit of Kodak LP4? The trail led in what seemed an ever widening circle, but through the kind offices of Hoechst Graphics, I am now in contact with George Czekalowski of Kodak, London, (Tel: 0944-181 427 4380), who informs me that the product was discontinued some four years ago, but that I can expect a consignment of a substitute silver-rich film produced once annually for internal use. I gathered that the Russell technique was not unfamiliar; he has recommended revised standards in the use thereof, and I await his further advice in this regard.

With best wishes,
Yours sincerely,

(Mrs) Dale Peters
Paper Conservator

Mail encl.: Experimental design

THE BRITISH MUSEUM

Department of Conservation

Mrs Dale Peters
Paper Conservator
University of Natal
The Campbell Collections and
Centre for Oral Studies
220 Marriott Road
DURBAN 4001
South Africa

Our ref: CD/VD/VT

31 May 1995

Dear Mrs Peters

I am pleased to hear that you now propose to spend more time on the study of paper oxidation at the wet/dry interface; I would be pleased to be involved in the evaluation of your PhD.

I have never met anybody who has used FTIR spectroscopy of old papers usefully. In model systems, using pure cellulose, there is a much better chance of obtaining usable results. I believe one needs quite large changes in order to detect anything happening. FTIR spectroscopy would be good if you could get it to work for you - I don't have suitable spectra I can recommend. The chemical tests, copper number, alkali fluidity, etc, are relatively protracted to do and need large samples, but should not be neglected.

If the wet/dry boundary mechanism was responsible for foxing, hygroscopic nuclei should help to promote the formation of fluorescent spots. Sodium chloride would be worth trying only if your RH cycling exceeds 75%, other more hygroscopic salts may be better. I'm not sure I understand the question about partial pressure gradients in a convective heat transfer.

So, Kodak has discontinued LP4. I last bought some about ten years ago and have kept it in the fridge. The LP4 was recommended by Kodak as a replacement for another film which previous workers at Kodak had used. I hope Kodak are able to supply you with a film that works. If not, there's always the film Elmer Eusman uses. Kodak used to be very secretive about why some films gave a Russell effect and others didn't. I suppose that prevention of the Russell effect is their main objective and understand the process for that reason. Thank you for Mr Czekalowski's telephone number, it may be useful one day.

Yours sincerely



Dr V Daniels

APPENDIX A 7

Date: Thu, 15 Dec 94 12:23:58 AEST
From: DHJ <dhj@amsg.Austmus.oz.au>
Message-ID: <9412151223.A10117@amsg.Austmus.oz.au>
To: petersd@lib.und.ac.za
Subject: RE: Environmental research

Text item: Text_1

15 December 1994

To: Dale Peters,
Campbell Collections of the University of Natal
220 Marriott Road, Durban 4001,
South Africa
email: petersd@lib.und.ac.za

Subject: Environmental Research

Dear Dale,

Colin Pearson sent me a copy of your message regarding oxidation of paper in humid climates since I have been looking at mould growth in similar conditions.

I am sending by post a copy of a paper I wrote for the recent IIC Congress in Canada which gives the background to my work and a list of references, some of which may be of use to you. I am interested in what is happening to moisture in the surface layers of materials in response to variable temperature and RH conditions of surrounding air, thus in the influence of atmospheric vapour pressure on vapour pressure inside materials ('water activity' being the term used by mycologists). Of particular interest in this area is the work done by Cunningham and others at the Building Research Association of New Zealand (BRANZ) which I refer to in the paper. Moisture is moved into and out of materials due to differences in vapour pressure, so temperature, absolute and relative humidity conditions in the immediate vicinity are highly significant.

I have carried out some experiments into mould growth in varying conditions similar to those found in Northern Australia and will be continuing with others as part of my own Masters research. Should you require more information once you have read my paper, I can be contacted via the fax number below or c/o my closest email address:

dhj@amsg.Austmus.oz.au

Good Luck!

Dr Graeme Scott
Materials Conservation Division
The Australian Museum
P O Box A285
Sydney South
NSW 2000
Australia

17-25 January 1995

Dear Dr Scott

MOISTURE, VENTILATION AND MOULD GROWTH

I was very excited to read your paper, it confirms many suppositions for which I had no evidence other than effect. The role of ventilation in the interruption of mould growth by varying water activity in surface layers, is something I have never been able to articulate, but have acknowledged in practise as a response to local conditions, even as an additional measure in airconditioned areas with poor air exchange rates.

I fully endorse the anecdotal evidence for the proposal that high ventilation rates in tropical climates may be offered as a reason why mould growth is not as common as might be expected. This not only supports my experience - my own research hypothesis is based on the direct observation that the damage perceived in library and archival collections housed in a sub-tropical climate, stems not from mould growth alone. I am working towards a Master's degree on the proposal that the evaporation and condensation kinetic induced by cycling RH results in chemical degradation by oxidation at the wet/dry interface. The disruptive role of varied circulation rates on the stability of surface layers of air may well be restricting mould growth, but translated into evaporation, or more specifically, the influence of the vapour concentration rate at the surface on the rate of evaporation, results in chemical deterioration by oxidation of hydroxyl groups at "my interface", and accounts for the staining evident in paper that has no fungal basis, similar to the tidemark effect.

A further factor in this phenomenon is the potential hazard of additional water vapour by increased RH or by decreased temperature where dewpoint is reached. Since I am basing my hypothesis on the hygroscopic nature of paper, in the rate of diffusion of vapour concentration through porous material in a vapour-air mixture, I cannot share your conclusion that changes in temperature and RH are less of a threat to organic materials than previously thought. You, however, must have been a source of satisfaction to those bad guys from the Smithsonian who recently ruined our environment!

Your section on moisture availability is very helpful. However, the physics of phase transformations exceeds my limited intellectual capacity; and the mathematics is heavy going. I would be grateful if you could point me in the direction of further references on response time and moisture transfer, which I would need to translate to a paper model.

Your paper reflects many other aspects of my thesis, from the introduction of climatic conditions, materials science, environmental control, and building technology. With interest I note are an architect by first profession, which accounts for your lucid discussion on the building envelope. I should like to follow up the King references, and would appreciate any assistance or advice in contacting him.

I am including a list of relevant references from my thesis bibliography, please let me know if any are of interest to you.

Bibliography

- 1 ANON (1961). Air conditioning requirements in the tropics. Heating and Ventilating Engineer(Dec 1961), 301-306.
- 2 BLOCK, S. S. (1953). Humidity requirements for mold growth. Applied Microbiology, 1 , 287-293.
- 3 BOGARTY, H., CAMPBELL, K. S. & APPEL, W. D. (1952). Some observations on the evaporation of water from cellulose. Textile Research Journal, 22 (2), 75-81.
- 4 BONE , W. A. (1934). Evaporation of water from cellulose. Journal of the Society of Dyers and Colourists, 50 , 307-309.

PETERSD@lib.und.ac.za

30th January 1995

Dear Dale,

Thanks for your Internet message - the information you sent will be very useful and I am very interested in your further work.

You mentioned that from the point of view of your research you don't agree that changes in temp and RH may be less of a problem than is sometimes thought. I should clarify that when it comes to preventing mould growth in museums in small or remote communities or those with little or no resources, I think that the use of ventilation, air circulation and appropriate building structures to bring variable atmospheric RH to interior spaces may be a more sustainable and reliable option in comparison to trying to maintain stable RH conditions in a building, significantly different from those in the surrounding environment and where air-conditioning equipment can't be relied on. Buildings designed for air-conditioning systems will have relatively high thermal masses and little natural air circulation, so should equipment fail widespread damage may result if RH stabilises at the 'wrong' level.

Of course, other forms of damage may still be a problem but the comparative threat to a collection from variable RH has to be assessed according to individual circumstances - a large institution with reliable funding and able to maintain buildings and equipment ought to be able to control conditions more reliably and closely than a community museum in the back of beyond; a collection of fine, inlaid furniture will be at much greater risk from a daily cycle of RH than one of bark paintings or solid wooden sculptures. If the risk of damage from variable RH is considered unacceptable then special care has to be taken - such as isolation of the sensitive parts of a collection and the use of some form of reliable climate control. Simply put, I believe that potential sources of damage should be prioritised from a local perspective, and variable RH seems to be a cause of relatively minor damage to the types of collection usually found in tropical museums.

Though you don't say what problems you have been having perhaps the Smithsonian didn't understand your local circumstances or priorities fully enough!

On the other points you mentioned:

- I am still trying to gather more on moisture transfer but it has been a bit difficult since much of the work seems to have been done fairly recently in the U.S. and I haven't been able to get copies of relevant papers so far. Malcolm Cunningham of the Building Research Association of New Zealand (BRANZ), Private Bag 50908, Porirua, New Zealand (who wrote the papers I referred to in my paper) sent me the contents page from the Proceedings of the 1992 ASHRAE/DOE/BTECC Conference in Florida - 'Thermal Performance of the Exterior Envelopes of Buildings V'. Pages 531-584 look promising but I haven't been able to track a copy down.

- On response time Stefan Michalski at the CCI has done a lot of work on comparative risks to different types of collections - he reckons (and Cunningham's mathematics confirm it) that a cycles of daily RH change affect materials to about 1-3mm from exposed surfaces, longer cycles such as seasonal changes have a deeper effect. Single sheets of paper will therefore, I imagine, respond within 24 hours but closely packed sheets - in a book for example - will respond more like a solid block - the more exposed areas will be affected first and frequently, deeper regions may remain unchanged.

- Steve King now works at the School of Architecture, University of New South Wales, P.O. Box 1, Kensington, NSW 2033, Australia (fax. 61-2-662 1378), but I have to say that I have had a great deal of difficulty contacting him since he took up his job there - you may have more luck! Colin Pearson should be able to help you with their joint papers.

I will indeed study your bibliography - some references do look useful! - and look out for anything which may be of interest to you. I shall also keep you in touch with my experiments and further research.

Wishing you the best of luck in your endeavours!

Graeme Scott

Dale Peters Paper Conservator
Campbell Collections of the University of Natal
220 Marriott Road Durban 4001
South Africa

Tel: (27) -0- 31- 260-2306 / 207-3711

Fax:(27) -0- 31- 291-622

e-mail: petersd@lib.und.ac.za

fax

to: Prof Dieter Holm
University of Pretoria

fax number: 012 - 346 4168

from: Mrs Dale Peters

date: 21 June 1995

subject: Thesis discussion

pages: 1+1

NOTES: Ich würde mich auf die Gelegenheit freuen, diese
Frage mit dir persönlich besprechen zu können.

THE RELATIONSHIP BETWEEN AIRFLOW AND DEGRADATION OF PAPER OBJECTS.

I am interested in the development of an experimental model to determine the effect of the above relationship in terms of the phenomenon of oxidation at the wet/dry interface in paper. My thesis hypothesis is based on the proposal that the phenomenon is a result of humid ambient conditions and precedes biological infestation in the chemical degradation of the paper substrate by repeated fluctuations in relative humidity.

My concern at present is to establish a means of measuring the rate of evaporation from the surface of the paper, which would be slowed to this critical point if the laminar airflow is insufficient. From discussions with Derek Wang, it would appear that building design is based rather on human comfort than a quantifiable variable such as the chemical or physical deterioration of museum or archival artifacts. It does however provide a parallel body of literature, and he suggested I discuss my application with with you.

From the literature, it would appear that a sorption model has been developed for the movement of moisture through the building envelope. Previously known as the so-called diffusion model, apparently an application of the same theory which gives the concept of the equilibrium condition for objects, but failed to account for moisture carried by air movements. During the period 1980-1984, the so-called convection-model prevailed, emphasising the role of air pressure differences in transmitting water vapour in gaps in construction. Then by 1983, work by Cunningham in New Zealand demonstrated the inadequacy of the convection model, and together with Canadian research established the sorption model.

"Present standards for the measurement and prediction of moisture movement in building materials appear to be in something akin to a pre-Copernican state of tinkering with obsolete models, with dangerous consequences for modern airconditioned museums, archives and libraries." [KING, S. & PEARSON, C. (1992). Environmental control for cultural institutions - appropriate design and the use of alternative technologies. In *La Conservation Préventive*, Paris: ARAAFU, 63-74.]

My question is whether this evaluation of the measurement of airflow is generally supported, I suspect it may be a "conference catch-line". Could you suggest other references on the currently accepted standards for the measurement of moisture movement in the building envelope. I am hoping that such standards may indicate a accepted experimental method to test the relationship between airflow and paper deterioration.

- Refs: 1 CUNNINGHAM, M. J. (1983). A new analytical approach to the long term behaviour of moisture concentrations in building cavities I & II. *Building and Environment*, 18 (3), 109-124.)
- 2 HUNDERMAN, H. J. (1988). Humidity and building materials in the museum setting. In Fisher, C. E. (Eds.), *The interior handbook for historic buildings*. Washington: Historic Preservation Education Foundation, 4.29 -4.34.
- 3 PADFIELD, T. (1987). The dangers of installing air-conditioning in historic buildings. In ICOMOS General Assembly, Washington: ICOMOS.)

HOLM • JORDAAN • HOLM

BR/CC86/04542/23

EKO-ARGITEKTUUR STADSONTWERP ENERGIEBEPLANNING RESTOURASIE / HERGEBRUIK
ECO-ARCHITECTURE URBAN DESIGN ENERGY PLANNING RESTORATION / RECYCLING



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OOK TE / ALSO AT MMABATHO

FAKSNR / FAX NO :

291 622
031 291 622

U Verw / Our Ref :
Ora Verw / Ora Ref :

AAN / TO :

Mrs. Sale Peters

AANDAG / ATTENTION :

Have been away for 1 week.

DATUM / DATE 95-06-02 :

Dear Sale, unfortunately I could not attend the meeting in Durban, having only heard about it when Walter happened to get wind of it.

BOODSKAP / MESSAGE :

Your question: In building technology the standard deviations in the moisture properties of materials (and in the best of placing these materials) is so high that calculations and refined models seldom need go beyond the Copernican concepts. The state of maintenance of air conditioning is no better. I discussed this also with the leading Air Conditioning Engineer who confirms this. If moisture movement is considered at all, the convection model is used.

MANTEL BLADSYE
NUMBER OF PAGES

LEDEMEMBERS

HENNING HOLM B.A.R.C.H. (PRET) DEON VAN ASWEGEN B.A.R.C.H. (PRET) L.I.A.M.I.A. ALBRECHT HOLM B.A.R.C.H. (PRET) L.I.A.M.I.A.
GERIT JORDAAN B.A.R.C.H. (PRET) L.I.A.M.I.A. URBAN DESIGN WATER L.I.A.M.I.A. PROF. DR. DIETER HOLM B.A.R.C.H. (PRET) L.I.A.M.I.A.

This is not to say that the question is not highly relevant vis-a-vis the paper problem where I would tend to use the lastest method model. But when Walter from

Anne-Laurence Dupont
13, rue Denfert-Rochereau
F-69700 Givors
FRANCE

22 May 1997

Dear Madame

DEGRADATION OF CELLULOSE AT THE WET/DRY INTERFACE

I am currently engaged in a postgraduate research project on the role of the oxidative mechanism of paper degradation - as seen at the wet/dry interface - in the deterioration of our library and archival collections housed under humid climatic conditions. Your two articles, published in *Restaurator* 17 (1) & (3), 1996 were of immense interest, and of an exceptional standard, on which I extend warmest congratulations. Since I will need to make extensive reference to your work, there are a number of issues I should like to discuss with you. I do hope you have no objection?

The direction of my own study is in the investigation of the particular micro environment to which you refer, as being necessary at the wet/dry interface for oxidation to occur at that location. The obvious correlation is the staining resultant upon foxing under humid climatic conditions.

Standardised test procedures increase the possibility of reproducible results, and while your suggestion of employing a microcrystalline cellulose is very interesting, the need to simulate the capillary action of evaporation from a book block dictates the use of a sheet form, as provided by the Whatmans filter paper. I am interested in your choice of Whatman filter paper no.5 as the testing substrate., when the sample in the work reported by Eusman and Hofenk de Graf appears to have been Whatman no.1:

EUSMAN, E. (1995). Tideline formation in paper objects: cellulose degradation at the wet-dry boundary. *Conservation Research*, **1995**, 11-27.

HOFENK DE GRAAFF, J. (1994). Research into the cause of browning of paper mounted in mats. In Verschoor, H. & Mosk, J. (Eds.), *Contributions of the Central Research Laboratory to the field of conservation and restoration*. Amsterdam: Central Research Laboratory for Objects of Art and Science., 21-42.)

Were you able to achieve a better result with this slower grade of filter paper? If you are in a position to pursue your own investigation, the improved sample preparation you anticipate in microcrystalline cellulose could be of great promise.

My original intention was to analyse aged samples in order to identify oxidation products, but in view of the findings you have published, there is no need to replicate that methodology. Instead, I propose to conduct artificial ageing procedures in simulation of ambient environmental conditions and compare the resultant degradation products with those found in naturally aged samples from our own archival collection.

Bearing in mind the transient nature of the fluorescent phenomenon at the wet/dry interface, the question is therefore in the choice of analytical procedures by which the degradation products in artificially and naturally aged samples can effectively be compared. Of the analytical techniques you investigated, Fourier transform infrared spectroscopy will certainly be applied in my study, using an FTIR microscope for direct surface investigation, or, alternatively an ATR (attenuated total reflectance) crystal. I wondered whether you had any recommendations in connection with these techniques?

I am also considering the use of fluorescence microscopy to provide a more quantitative definition of oxidative degradation, and because of the comparison afforded with studies of fungal causation. Again, what was the basis for the selection of techniques you have reported, TLC, FTIR (KBr pellet) and GC/MS? My curiosity stems from the absence of techniques such as chemiluminescence and Russell photography, widely reported in connection with this reaction. My personal feeling is that if a choice has to be made between Russell graphs and methylene blue staining, the latter is perhaps less cumbersome in indicating the reaction, while neither is adequate for the identification of the resultant degradation products. Chemiluminescence, on the other hand, has been strongly recommended:

1. GRATTAN, D. W. (1978). The oxidative degradation of organic materials and its importance in deterioration of artifacts. *Journal of the International Institute of Conservation - Canadian Group*, **4** (1), 17-26.
2. KELLY, G. B., WILLIAMS, J. C., MENDENHALL, G. D. & OGLE, C. A. (1979). The use of chemiluminescence in the study of paper permanence. In Eby, R. K. (Eds.), *Durability of macromolecular materials*. Washington DC: American Chemical Society, 117-125.

While intrigued by the analytical capabilities of the technique, I have found little application thereof reported in the literature since, and am discouraged by my thesis supervisors on the grounds of its prohibitive expense. Your opinion on this, and on other matters raised here would be of great interest to me, and yet, perhaps I should apologise for presuming on your time.

Yours sincerely,

Mrs Dale Peters
Paper Conservator
e-mail: petersd@shepfs2.und.ac.za

From: CPR_Temp@pch.gc.ca
To: PETERSD@SHEPFS2.UND.AC.ZA
Date: Thu, 10 Jul 1997 16:13:39 -0400
Subject: Re[2]: wet/dry interface in cellulose <

Dear Mrs Dale Peters

I hope you had a nice trip and interesting talks with Eimer Eusman and Vincent Daniels about wet/dry interfaces. About the Centraal Laboratorium, the supervisor of my research was Dr Johan G. Neevel, Conservation Chemist. You could contact him if you wish to speak to somebody in the Centraal Laboratorium. At that time he was involved in a project on the use of phytic acid for the treatment of iron gall ink corrosion on paper (article published in Restaurator #16:143-160). The Director of the Research Department is Mrs Judith Hofenk de Graaff, who originally was the initiator of the project on wet/dry interfaces, having made preliminary observations on this phenomenon. The Director General of the Centraal Laboratorium is Mrs Agnes Ballestrem. The Centraal Laboratorium has recently merged with the Dutch program in conservation. I am not aware of a possible moving consequently to this merger. As far as I know, the address is still :

Gabriel Metsustraat 8
1071 EA Amsterdam
The Netherlands
tel. 31 20 673 5162
fax 31 20 675 1661

The laboratory carries research in many conservation fields: textiles, paper, natural history collections, paintings, polymers. They have extensive technical scope: XRF microscopy, GC/MS, HPLC, FTIR, aging and pollution chambers, climatic controlled room for paper mechanical testing.... I do specify because my previous e-mail was maybe too ambiguous on this point.

The project on oxidation of cellulose at the wet/dry interface was the subject for my Master thesis for the conservation program in Paris (MST Conservation-restauration des Biens Culturels - La Sorbonne). The methods chosen to study brown line effect on paper were not limited by technical scope, but rather, in addition to the other reasons I already mentioned in my previous e-mail message, by the duration of my internship in the Centraal Laboratorium: only about 7 months. I had to face the deadline for the presentation of my thesis. Rather to

overdiversify in too many directions, it was decided to concentrate on few reliable techniques. Also, some of the instruments were already used for other ongoing projects (that is what I had in mind by saying I had to deal with the instruments I had access to). I am sorry to insist, I just wanted to make clear the Centraal Laboratorium has not indeed limited instrumentation scope, but a very wide variety of research possibilities. I felt guilty to have inadvertently implied the contrary... I really apologize for my insecure English...

I would be glad to be able to help you in your research progress if I can and hope to hear from it.

Sincerely yours,

Anne-Laurence Dupont
Research Fellow
Canadian Conservation Institute

----- Reply Separator

Subject: Re: wet/dry interface in cellulose
Author: PETERSD@SHEPFS2.UND.AC.ZA at PCH
Date: 7/8/97 12:07 PM

Anne-Laurence Dupont:

Many thanks for your supportive response to the continued research into the formation of the brown line at the wet-dry interface. Your reply has indeed answered many questions, but again raises more! I should like to forward a copy to the Institut fuer Textil und Faserchemie, at the University of Stuttgart, who are interested in conducting the analytical techniques for my research in conjunction with a concurrent accelerated ageing project. The technical scope in this country is severely limited, indeed you indicate similar experience. I would be interested to hear more of your connection with the Centraal Laboratorium, the apparent source of much of this research. It is a pity that we cannot meet, as I will be at Cornell University next week. My schedule is very tight, but I hope en route, to meet with Elmer Eusman and Vincent Daniels regarding this

project. I will be in touch again on my return towards the end of the month.

With best wishes,

Dale Peters

----- Dale Peters

Paper Conservator

Campbell Collections of the University of Natal 220 Marriott Road

Durban 4001

South Africa

Tel: 27 31 260-2306

Fax: 27 31 291-622

METEOROLOGICAL DATA

- B1 METEOROLOGICAL DATA OF MONTHLY MEANS RECORDED AT
DURBAN (LOUIS BOTHA) AIRPORT AT ϕ 29° 58' \wedge 30° 57'
FOR THE PERIOD 1956-1984**
- B2 AVERAGE MONTHLY MEAN: TEMPERATURE AND RH**
- B3 AVERAGE MONTHLY RANGE: TEMPERATURE AND HUMIDITY**

Annual average	25,2	16,2	9,0	20,7		75	55,9	33,2	72.7
Annual range	5,3	10,9	6,0	8,5		6	23	24	14

APPENDIX B 1 METEOROLOGICAL DATA : MONTHLY MEANS

APPENDIX B 2

AVERAGE MONTHLY MEAN : TEMPERATURE AND RH

Month	°C	RH ₀
January	24,3	75,5
February	24,5	76,5
March	23,9	75,5
April	21,6	73
May	18,9	71
June	16,5	68,5
July	16,4	65
August	17,4	68,5
September	19,2	74,5
October	20,4	73,5
November	21,8	75,0
December	23,3	79,0

APPENDIX B 3

AVERAGE MONTHLY RANGE : TEMPERATURE AND RH

		T _x	T _H	RH _x	RH _H
January	14h00	27,8			63
January	20h00		20,7	88	
February	14h00	28,0			64
February	20h00		20,9	89	
March	14h00	27,7			59
March	20h00		20,1	92	
April	14h00	26,0			57
April	20h00		17,2	89	
May	14h00	24,4			53
May	20h00		13,4	89	
June	14h00	23,0			46
June	20h00		10,0	91	
July	14h00	22,7			41
July	20h00		10,1	89	
August	14h00	22,8			48
August	20h00		12,1	89	
September	14h00	23,3			59
September	20h00		15,0	90	
October	14h00	24,1			58
October	20h00		16,7	89	
November	14h00	25,3			61
November	20h00		18,3	89	
December	14h00	26,9			62
December	20h00		19,8	86	

DRIFT INTEGRATION REPORTS

File Name: E:\OPUS\WORK\WORK.4
18/07/98, 15:14:19
Sample Name: DRIFT: Sample 4C accelerated aged, climate, dark area
Operator Name: Dale
Sample Form:

Integration Report							
Number of results: 2							
Label	Type	Result	Freq1	Freq2	Freq3	Freq4	Freq5
Freq6							
1372	L	0.139009	1390	1360	1410	1300	
CH2- 2900	L	0.321657	2960	2800	2740	3010	

File Name: E:\OPUS\WORK\WORK.5
18/07/98, 15:14:20
Sample Name: DRIFT: Sample 4B accelerated aged, climate, dark area
Operator Name: Dale
Sample Form:

Integration Report							
Number of results: 2							
Label	Type	Result	Freq1	Freq2	Freq3	Freq4	Freq5
Freq6							
1372	L	0.149495	1390	1360	1410	1300	
CH2- 2900	L	0.373712	2960	2800	2740	3010	

File Name: E:\OPUS\WORK\WORK.6
18/07/98, 15:14:20
Sample Name: DRIFT: Sample 4A accelerated aged, climate, dark area
Operator Name: Dale
Sample Form:

Integration Report							
Number of results: 2							
Label	Type	Result	Freq1	Freq2	Freq3	Freq4	Freq5
Freq6							
1372	L	0.157029	1390	1360	1410	1300	
CH2- 2900	L	0.372557	2960	2800	2740	3010	

File Name: E:\OPUS\WORK\WORK.8
17/07/98, 15:51:14
Sample Name: DRIFT: Sample 4A accelerated aged,climate,dark area
Operator Name: Dale
Sample Form:

Integration Report
Number of results: 2
Label Type Result Freq1 Freq2 Freq3 Freq4 Freq5
Freq6
1372 L 0.157029 1390 1360 1410 1300
CH2- 2900 L 0.372557 2960 2800 2740 3010

File Name: E:\OPUS\WORK\WORK.9
17/07/98, 15:51:14
Sample Name: DRIFT: Sample 4A accelerated aged,climate,light area
Operator Name: Dale
Sample Form:

Integration Report
Number of results: 2
Label Type Result Freq1 Freq2 Freq3 Freq4 Freq5
Freq6
1372 L 0.154247 1390 1360 1410 1300
CH2- 2900 L 0.367766 2960 2800 2740 3010

File Name: E:\OPUS\WORK\WORK.10
17/07/98, 15:51:14
Sample Name: DRIFT: Sample 4A accelerated aged,climate, water tideline
Operator Name: Dale
Sample Form:

Integration Report
Number of results: 2
Label Type Result Freq1 Freq2 Freq3 Freq4 Freq5
Freq6
1372 L 0.150078 1390 1360 1410 1300
CH2- 2900 L 0.588552 2960 2800 2740 3010

File Name: E:\OPUS\WORK\WORK.4
17/07/98, 15:10:50
Sample Name: DRIFT: Sample 3C: accelerated ageing, climate + *deacidified*
Operator Name: Dale
Sample Form:

Integration Report
Number of results: 2
Label Type Result Freq1 Freq2 Freq3 Freq4 Freq5
Freq6
1372 L 0.10395 1390 1360 1410 1300
CH2- 2900 L 0.23739 2960 2800 2740 3010

File Name: E:\OPUS\WORK\WORK.5
17/07/98, 15:10:50
Sample Name: DRIFT: Sample 3B: ~~accelerated ageing~~, climate *Unaged*
Operator Name: Dale
Sample Form:

Integration Report
Number of results: 2
Label Type Result Freq1 Freq2 Freq3 Freq4 Freq5
Freq6
1372 L 0.113434 1390 1360 1410 1300
CH2- 2900 L 0.287143 2960 2800 2740 3010

File Name: E:\OPUS\WORK\WORK.6
17/07/98, 15:10:48
Sample Name: DRIFT: Sample 3A: accelerated ageing, climate, water
Operator Name: Dale
Sample Form:

Integration Report
Number of results: 2
Label Type Result Freq1 Freq2 Freq3 Freq4 Freq5
Freq6
1372 L 0.110831 1390 1360 1410 1300
CH2- 2900 L 0.245181 2960 2800 2740 3010

File Name: E:\OPUS\WORK\WORK.12
17/07/98, 15:13:00
Sample Name: DRIFT: Sample 2D accelerated aged, climate, water
Operator Name: Dale
Sample Form:

Integration Report								
Number of results:		2						
Label	Type	Result	Freq1	Freq2	Freq3	Freq4	Freq5	Freq6
1372	L	0.160787	1390	1360	1410	1300		
CH2- 2900	L	0.349976	2960	2800	2740	3010		

File Name: E:\OPUS\WORK\WORK.10
17/07/98, 15:13:00
Sample Name: DRIFT: Sample 2B Unaged, climate
Operator Name: Dale
Sample Form:

Integration Report							
Number of results:		2					
Label	Type	Result	Freq1	Freq2	Freq3	Freq4	Freq5
	Freq6						
	1372	L	0.169536	1390	1360	1410	1300
CH2-	2900	L	0.365734	2960	2800	2740	3010

File Name: E:\OPUS\WORK\WORK.11
17/07/98, 15:13:00
Sample Name: DRIFT: Sample 2C accelerated aged, climate
Operator Name: Dale
Sample Form:

Integration Report							
Number of results:		2					
Label	Type	Result	Freq1	Freq2	Freq3	Freq4	Freq5
	Freq6						
	1372	L	0.147863	1390	1360	1410	1300
CH2-	2900	L	0.325246	2960	2800	2740	3010

File Name: E:\OPUS\WORK\WORK.10
18/07/98, 16:12:36
Sample Name: DRIFT: Sample 1: accelerated aged,climate,PVAC
Operator Name: Dale
Sample Form:

Integration Report
Number of results: 2

Label	Type	Result	Freq1	Freq2	Freq3	Freq4	Freq5
Freq6 1372	L	0.200203	1390	1360	1410	1300	
CH2- 2900	L	0.395355	2960	2800	2740	3010	

File Name: E:\OPUS\WORK\WORK.11
18/07/98, 16:12:36
Sample Name: DRIFT: Sample 1: accelerated aged,climate,salt
Operator Name: Dale
Sample Form:

Integration Report
Number of results: 2

Label	Type	Result	Freq1	Freq2	Freq3	Freq4	Freq5
Freq6 1372	L	0.215014	1390	1360	1410	1300	
CH2- 2900	L	0.397791	2960	2800	2740	3010	

File Name: E:\OPUS\WORK\WORK.7
18/07/98, 16:12:36
Sample Name: DRIFT: Sample 1: accelerated aged,climate
Operator Name: Dale
Sample Form:

Integration Report
Number of results: 2

Label	Type	Result	Freq1	Freq2	Freq3	Freq4	Freq5
q5	Freq6						
1372	L	0.0754372	1390	1360	1410	1300	
CH2- 2900	L	0.21954	2960	2800	2740	3010	

File Name: E:\OPUS\WORK\WORK.8
18/07/98, 16:12:36
Sample Name: DRIFT: Sample 1: accelerated aged,climate,water
Operator Name: Dale
Sample Form:

Integration Report
Number of results: 2

Label	Type	Result	Freq1	Freq2	Freq3	Freq4	Freq5
	Freq6						
1372	L	0.217105	1390	1360	1410	1300	
CH2- 2900	L	0.39008	2960	2800	2740	3010	

File Name: E:\OPUS\WORK\WORK.9
18/07/98, 16:12:36
Sample Name: DRIFT: Sample 1: accelerated aged,climate,CMC
Operator Name: Dale
Sample Form:

Integration Report
Number of results: 2

Label	Type	Result	Freq1	Freq2	Freq3	Freq4	Freq5
	Freq6						
1372	L	0.200926	1390	1360	1410	1300	
CH2- 2900	L	0.39298	2960	2800	2740	3010	

File Name: E:\OPUS\WORK\WORK.8
18/07/98, 15:54:00
Sample Name: DRIFT: Sample 1- Unaged control
Operator Name: Dale
Sample Form:

Integration Report
Number of results: 2

Label	Type	Result	Freq1	Freq2	Freq3	Freq4	Freq5
Freq6 1372	L	0.186319	1390	1360	1410	1300	
CH2- 2900	L	0.40359	2960	2800	2740	3010	

File Name: E:\OPUS\WORK\WORK.9
18/07/98, 15:54:00
Sample Name: DRIFT: Sample1 - aged, no climate
Operator Name: Dale
Sample Form:

Integration Report
Number of results: 2

Label	Type	Result	Freq1	Freq2	Freq3	Freq4	Freq5
Freq6 1372	L	0.20117	1390	1360	1410	1300	
CH2- 2900	L	0.407672	2960	2800	2740	3010	

File Name: E:\OPUS\WORK\WORK.10
18/07/98, 15:54:02
Sample Name: DRIFT: Sample 1: accelerated aged, climate
Operator Name: Dale
Sample Form:

Integration Report
Number of results: 2

Label	Type	Result	Freq1	Freq2	Freq3	Freq4	Freq5
q5 Freq6 1372	L	0.0754372	1390	1360	1410	1300	
CH2- 2900	L	0.21954	2960	2800	2740	3010	

File Name: E:\OPUS\WORK\WORK.2
18/07/98, 18:11:42
Sample Name: DRIFT: Sample 7: naturally aged, stained
Operator Name: Dale
Sample Form:

Integration Report

Label	Type	Result	Freq1	Freq2	Freq3	Freq4	Freq5
Number of results:		2					
Freq6							
1372	L	0.189516	1390	1360	1410	1300	
CH2- 2900	L	0.39789	2960	2800	2740	3010	

File Name: E:\OPUS\WORK\WORK.2
18/07/98, 17:59:48
Sample Name: DRIFT: Sample 6: naturally aged, stained
Operator Name: Dale
Sample Form:

Integration Report								
Number of results:		2						
Label	Freq6	Type	Result	Freq1	Freq2	Freq3	Freq4	Freq5
	1372	L	0.150495	1390	1360	1410	1300	
CH2-	2900	L	0.352591	2960	2800	2740	3010	

File Name: E:\OPUS\WORK\WORK.2
18/07/98, 17:46:50
Sample Name: DRIFT: Sample 5: naturally aged, stained
Operator Name: Dale
Sample Form:

Integration Report

Number of results: 2

Label	Type	Result	Freq1	Freq2	Freq3	Freq4	Freq5
Freq6 1372	L	0.148709	1390	1360	1410	1300	
CH2- 2900	L	0.344706	2960	2800	2740	3010	

File Name: E:\OPUS\WORK\WORK.2
18/07/98, 17:33:16
Sample Name: DRIFT: Sample 4: naturally aged, stained
Operator Name: Dale
Sample Form:

Integration Report

Label	Type	Result	Freq1	Freq2	Freq3	Freq4	Freq5
Freq6							
1372	L	0.154518	1390	1360	1410	1300	
CH2- 2900	L	0.318402	2960	2800	2740	3010	

File Name: E:\OPUS\WORK\WORK.2
18/07/98, 17:21:02
Sample Name: DRIFT: Sample 3: naturally aged, stained
Operator Name: Dale
Sample Form:

Integration Report
Number of results: 2

Label	Type	Result	Freq1	Freq2	Freq3	Freq4	Freq5
Freq5 1372	L	0.160142	1390	1360	1410	1300	
CH2- 2900	L	0.364712	2960	2800	2740	3010	

File Name: E:\OPUS\WORK\WORK.2
18/07/98, 16:30:02
Sample Name: DRIFT: Sample 1: naturally aged, stained
Operator Name: Dale
Sample Form:

Integration Report								
Number of results:		2						
Label	Freq6	Type	Result	Freq1	Freq2	Freq3	Freq4	Freq5
	1372	L	0.157011	1390	1360	1410	1300	
CH2-	2900	L	0.376794	2960	2800	2740	3010	

THESAURUS FOR BOOK AND PAPER PRESERVATION AND CONSERVATION

D1 KEYWORD LIST

D2 ARRANGEMENT OF PRESERVATION AND CONSERVATION
INFORMATION

KEYWORD LIST

Accelerated ageing	3.2
Acid hydrolysis	3.1
Acid migration	3.2
Adhesives and consolidants	3.6
Airconditioning	2.3
Albums - treatment	3.8
Alkaline paper	3.1
Alkaline sizing	3.6
Analytical techniques	3.1
Archival material - treatment	3.8
Art on paper - treatment	3.8
Artifactual value	1.1
Atmospheric pollutants	2.3
Bibliographies	1.2
Biodeterioration, biocides	2.7
Bleaching	3.4
Book conservation - treatment	3.8
Book cradles and boxes	2.4
Bookbinding - treatment	3.8
Brittle books	2.5
Business administration - finance, correspondence	1.5
Building technology and maintenance	2.6

Case studies, general	3.8
Cellulosic discolouration	3.3
Chemistry	3.1
Climatology	2.3
Coated paper - treatment	3.8
Collections care	2.1
Colour reversion	3.3
Colourants, dyes, inks	3.3
Connoisseurship	1.1
Computers in conservation, software	1.4
Condensation and evaporation	3.7
Condition surveys	1.4
Connoisseurship	1.1
Computers in conservation, software	1.4
Condensation and evaporation	3.7
Condition surveys	1.4
Conference notes and proceedings	1.6
Conservation management - policy, selection	1.5
CoOL - Conservation OnLine Database	1.6
Database management	1.4
Deacidification - aqueous, non-aqueous	3.5
Deacidification - mass treatments	3.5
Degradation products	3.2
Delamination	3.4
Deterioration - causes	3.2
Dictionaries, scientific and technical	1.2
Digital technology	2.5
Disaster response, planning	2.6
Discolouration, staining, yellowing	3.3

Documentation - treatment	1.4
Drying	3.7
Encapsulation	2.4
Environmental control -general	2.3
Environmental monitoring	2.3
Equilibrium moisture content	2.3
Exhibits and loans	2.4
Fibre analysis	3.1
Finance, budgets and grants	1.5
Foxing	3.3
Framing - treatment	3.8
Freeze drying	3.7
Fumigation	2.7
Herbaria - treatment	3.8
Humidity see Relative humidity	
Internet resources	1.6
Lamination, encapsulation	3.6
Leafcasting and splitting	3.6
Lighting	2.3
Lignin, fibres types	3.3
Materials testing	3.1
Materials and equipment, supply	1.5
Metal catalysts, chelates	3.3
Microclimates	2.3
Microforms	2.5
Occupational health and safety	2.6
Organisations, membership	1.7
Oxidation	3.1
Permanence standards and testing	1.1
Personnel - job descriptions	1.5

Pest management	2.7
pH measurement	3.1
Photographic conservation - treatment	3.8
Photochemical degradation	3.2
Photocopying	2.5
Preservation and conservation bodies	1.7
Preservation history	2.2
Preservation manuals	2.1
Preservation in tropics	2.2
Pressure sensitive tapes	3.4
Protective enclosure	2.4
Reformatting	3.5
Regional centres	1.5
Relative humidity	2.3
Research methodology	1.6
Security	2.6
Selection for preservation	1.5
Shelving see Stack maintenance	
Sizing, resizing, alkaline sizing	3.6
Software	1.4
Solvent applications	3.4
Stack maintenance	2.4
Staff training	1.3
Standards, data loggers	2.3
Storage conditions	2.4
Strengthening, mass	3.6
Surface cleaning	3.4
Teaching, courses, certification	1.3
Temperature	2.3
Training see Teaching	

Transparent papers - treatment	3.8
Treatment, general	3.0
Transportation of objects	2.4
Tropical conditions	2.3
User education	1.3
Vacuum and freeze drying	3.7
Ventilation	2.3
Watermarks	3.8
Wet/dry interface	3.2
Wet treatments	3.4
Yellowing see Discolouration	

ARRANGEMENT OF PRESERVATION AND CONSERVATION INFORMATION

1 General works

1.1 Standards, ethics and principles of conservation

Artifactual value, connoisseurship

Permanence standards, tests

1.2 Reference works

Bibliographies

Dictionaries, scientific and technical

1.3 Education

Staff training

Teaching, courses, certification

User education

1.4 Records management

Computers in conservation, software

Condition surveys

Database management

Documentation, treatment

1.5 Administration

Business administration

Finance, correspondence, grant proposals

Personnel, job descriptions

Conservation management, policy formation, selection for preservation

Material and equipment, supply

Regional centres

1.6 Research

CoOL, CHIN, Internet and other resources

Conference notes and proceedings

Research methodology

1.7 Professional affiliation

Organisations, membership

Related national and international bodies

2 Preventive conservation

2.1 Manuals

Collections care

2.2 History of preservation

Preservation in the tropics

2.3 Environmental control

Airconditioning

Atmospheric pollutants, dust, dirt, off gassing

Climatology

Equilibrium moisture content

Light

Microclimates

Relative humidity

Standards, Data loggers

Temperature

Ventilation

2.4 Storage and display

Book cradles and boxes

Exhibits and loans

Encapsulation

Protective enclosure

Stack maintenance

Transportation of objects

2.5 Reformatting

Brittle books

Photocopying

Microforms

Digital technology

2.6 Disaster response

Building technology and maintenance

Disaster planning, supplies, reports

Health and safety regulations

Security

2.7 Biodeterioration

Biocides

Fumigation

Pest management

3 Treatment and materials

3.1 Chemistry

Acid hydrolysis

Alkaline paper

Analytical techniques - pH measurement, fibre analysis

Materials analysis

Oxidation, cross-linking

3.2 Ageing

Accelerated ageing, standards, research and testing

Acid migration

Deterioration - causes

Photochemical degradation, research and testing

Wet/dry interface

3.3 Discolouration

Cellulosic staining

Colour reversion

Colorants, dyes, inks

Foxing

Lignin, fibre type

Metal catalysts, chelates

Tidelines

3.4 Cleaning techniques

Surface cleaning

Bleaching

Pressure sensitive tapes

Wet treatments

Solvents

3.5 Deacidification

Aqueous, non-aqueous methods

Mass deacidification treatment

3.6 Repair and strengthening techniques

Adhesives and consolidants

Leafcasting and splitting

Lamination, encapsulation

Sizing, alkaline sizing

3.7 Drying procedures

Condensation/evaporation

Humidification and drying

Stretch drying, Karibari boards

Vacuum and freeze drying

3.8 Object-specific treatment

Albums

Archival materials

Art on paper

Book conservation

Bookbinding

Case studies, general

Coated paper

Framing

Museum conservation

Herbaria

Photographic conservation

Pressure sensitive tapes

Transparent papers

Treatment, general

Watermarks