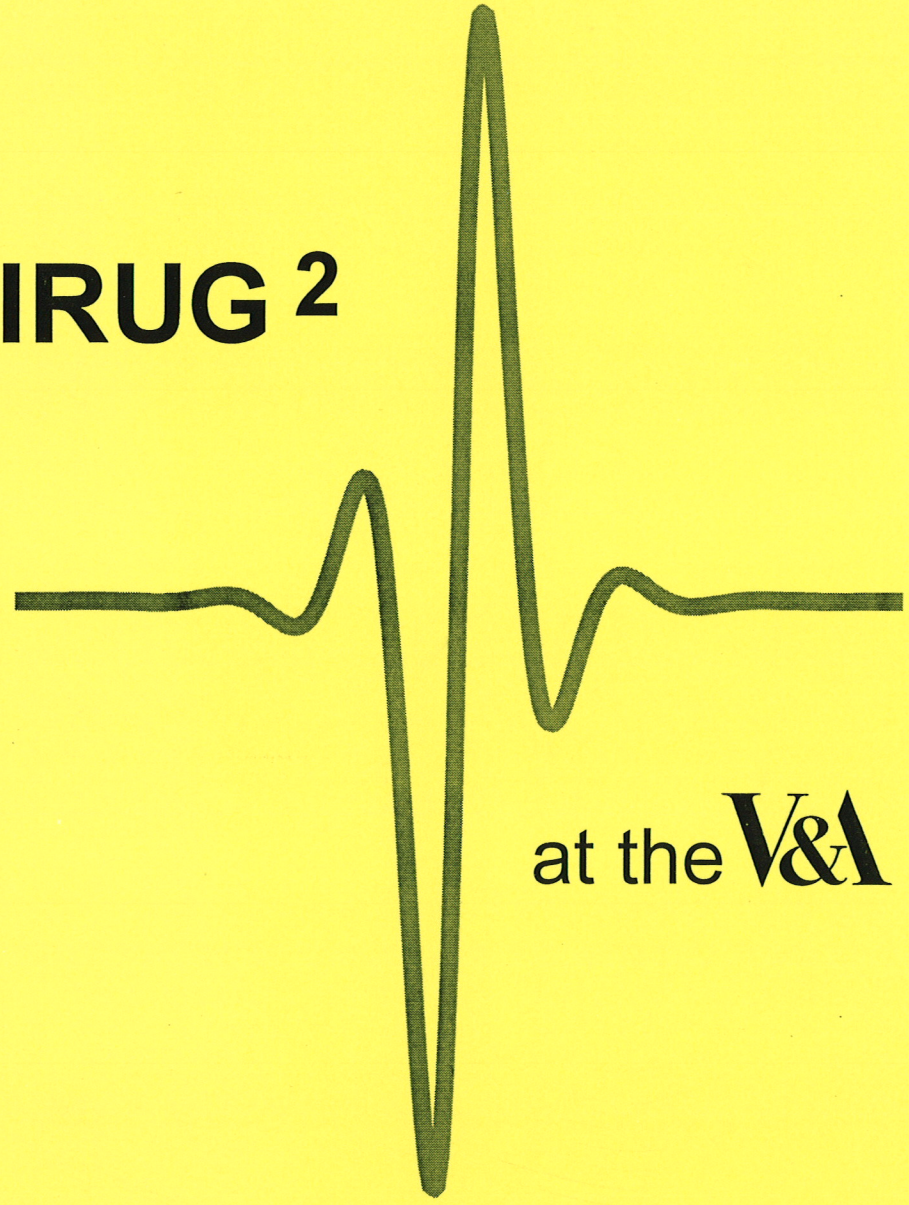
# Postprints:

## IRUG 2

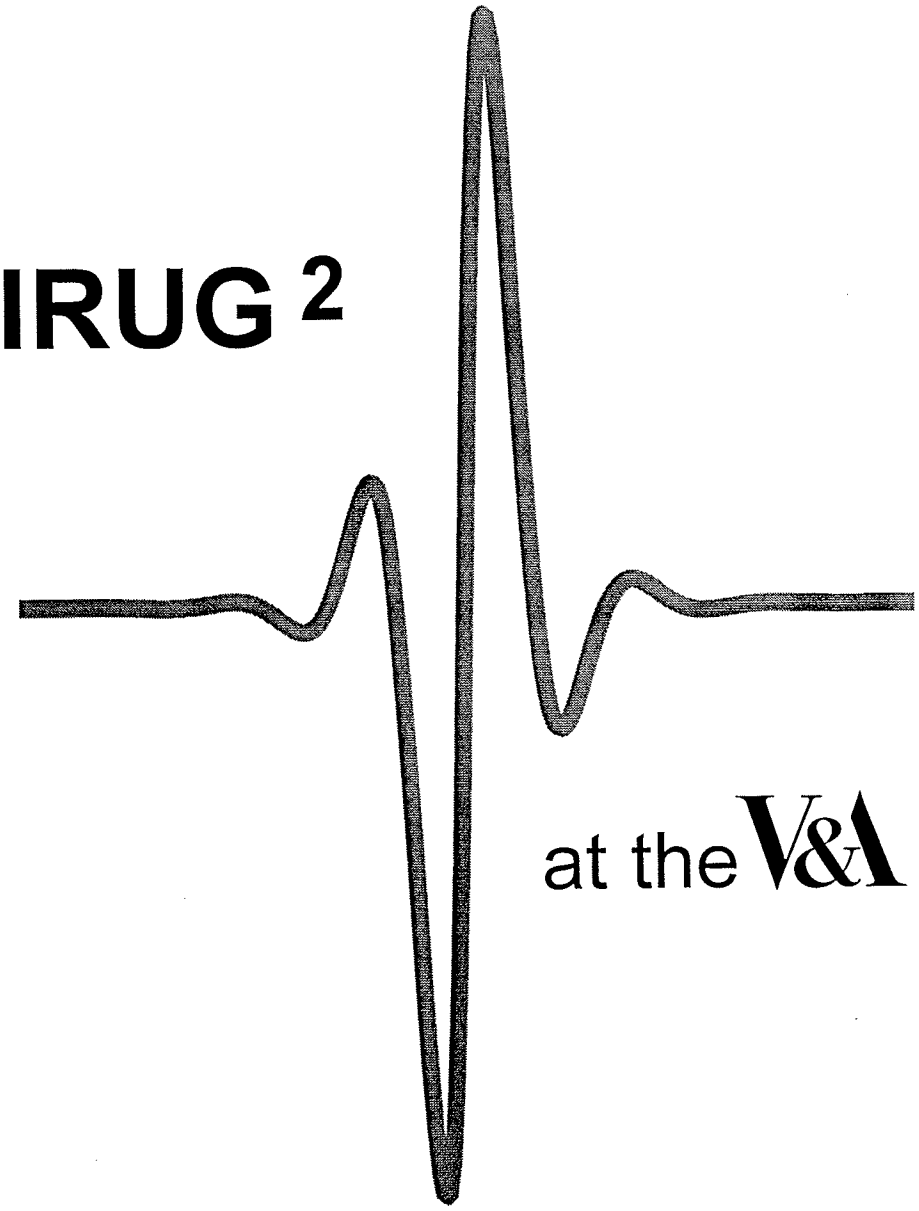


at the V&A

**May 1998**
**(meeting held in September 1995)**

# Postprints:

## IRUG 2



at the V&A

**May 1998**
**(meeting held in September 1995)**

## Contents

Page

## Introduction

This document contains the summaries ( abstracts as included in the preprints issued at the meeting) and papers (submitted after the meeting) of presentations given at the Infrared User's Group (IRUG) meeting held on the 12 and 13 September 1995 at the Victoria & Albert Museum (V&A) in London.

Papers are presented in the order that they were given at the meeting. Apart from small editing changes, corrections and formatting, the text of papers is reproduced as submitted. Figures were supplied in as hard copies or digital images, depending on the author. Only limited adaption of the figures was possible and they are therefore not reproduced in an entirely consistent format. Several authors chose not to submit their paper for inclusion in the postprints. In this case, only the abstract submitted for the preprints is reproduced.

The short biographies of authors and addresses of delegates have not been updated to reflect changes since 1995.

The postprints were prepared in time for the third IRUG meeting (28 - 30 May 1998, Winterthur, USA) and will be sent to contributors to IRUG2.

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## *** Session One ***



## *** Session Two ***



## *** Session Three ***



## *** Session Four ***

# Papers and biographies

# 1. The use of a diamond cell for the FTIR characterisation of paints and varnishes available to twentieth century artists

Tom Learner
Tate Gallery

## 1.1 Summary

FTIR has been widely used in binding medium analysis at several art galleries and museums around the world. Most of this work has concerned the natural materials used as traditional binding media and picture varnishes, such as the drying oils, natural resins, proteins, gums and waxes. To complement the choice of materials available to the artist in the twentieth century, a vast range of synthetic resins has been developed, including the acrylics, poly vinyl acetates (PVAc's), alkyds, cellulose nitrate, polyurethanes and epoxies. Although only some of these have been used in artists' paints and varnishes, many others are present in the commercial decorative and industrial paints and coatings which have been used by certain artists this century. A means of identifying as many of these synthetic products as possible would be of immense benefit to the conservators who oversee their preservation. This paper will consider the use of FTIR in the characterisation of modern binding media and varnishes. The use of a diamond anvil cell and a beam condenser will be discussed as a cheaper alternative to a microscope for achieving good transmission spectra on small paint samples.

## 1.2 Introduction

Fourier Transform infrared (FTIR) spectroscopy has received extensive use in the identification of the various kinds of resin, varnish, coating and adhesive which may be found in works of art (eg: [1-3]). Since many of these different materials exhibit very characteristic absorptions in the infrared region, FTIR can be an excellent way of obtaining information quickly about the basic chemical class of such a material. However, the analysis of multi-component (and multi-layered) samples and the actual sample size have always been major limitations to the use of FTIR in such analysis.

The analysis of the binding medium in a paint by FTIR has therefore always been somewhat problematic, due to the presence of additional components in the formulation, most obviously the pigment(s). In the case of most twentieth century paints this can be further complicated by the presence of large quantities of extenders (also called fillers) in addition to the pigment(s), which are added to improve a paint's consistency and to decrease its cost. Therefore, although the various classes of resin which are used as binding media in twentieth century paints may exhibit extremely characteristic absorptions in their FTIR spectra, in practice many of these are often masked by the strong absorptions from the pigments and extenders. However, from an awareness of the kinds of materials which are used as binding media, pigments and extenders in these paints it can often be possible to assign various absorptions in a paint's FTIR spectrum to the individual components. This means that sometimes not only can an accurate identification of the binding media be made, but the characterisation of the pigment(s) and extender(s) also be achieved all from a single analysis.

The use of an IR microscope is the obvious method for dealing with a very small sample size, especially if more than one layer is present. However, these microscopes are still very expensive and usually a great deal of sample preparation is required, especially

if transmission spectra are desired. For example, it would not be unusual for this to involve embedding the sample in a resin, grinding the resin down, taking a thin section with a microtome and finally flattening the sample. There is also a problem with the choice of embedding resin, as many of the standard materials (eg: polyesters, waxes and epoxies) exhibit strong absorptions of their own in the infrared region and therefore cannot be used.

An alternative sampling method is the use of a diamond anvil cell, placed in a beam condenser in the spectrometer. The use of such a cell has previously been described for obtaining good FTIR spectra from small samples at a fraction of the cost of an IR microscope [4]. The main drawback with the diamond cell (compared to the microscope) appears to be its inability to deal with multi-layered samples, and so for its full analytical ability to be realised single paint layers are favourable. However, in twentieth century paintings it is not unusual to find either very thick layers of paint or paint which has been applied straight from the tube, both of which can often extend around the tacking margins or even the reverse of the painting. This, taken with the fact that many such works have not been varnished, often makes the sampling of single paint layers much more straightforward than in pre-twentieth century paintings.

This paper will briefly outline the salient features of some of the materials found in typical twentieth century paints, discuss the use of the diamond cell and beam condenser for their analyses and demonstrate how the binding media, pigments and extenders can be identified from the resulting FTIR spectra. Although emphasis will be placed on the analysis of paints, this method is clearly just as applicable to varnishes and other types of coating.

### 1.3 Components of twentieth century paints

Essentially there are three components of interest here; the binding medium, the pigment(s) and the extender(s). Although there will also be numerous additives in these formulations, such as dispersants, thickeners, surfactants and antifoaming agents (in emulsions) or stabilisers and driers (in oil based paints), these are only present in very small quantities and would require special extraction techniques for their identification.

The four main classes of binding media found in twentieth century paints are the oils, alkyds, acrylics and polyvinyl acetates (PVAc's). Generally, the oils and acrylics are found in paints which have been manufactured specifically for artists' use, whereas the alkyds and PVAc's tend to be used more in commercial products, especially household paints. Other types of resin (such as nitrocellulose, chlorinated rubber, polyurethanes and epoxies) can also be utilized, but their use tends to be restricted to highly specialised coatings and they are not discussed any further here.

*Oils* consist of mixtures of mixed triacyl glycerols (the tri-esters of glycerol and fatty acids, normally those between $C_{16}$ and $C_{18:3}$. Linseed oil is still the most commonly used drying oil, although others such as soya and safflower are more commonly used in whites and other light colours, where the yellowing tendencies of linseed oil would be

more noticeable.

*Alkyds* require three components; a polyhydric alcohol (usually glycerol or pentaerythritol), a polybasic acid (normally phthalic anhydride) and an unsaturated mono acid (normally added in the form of a drying oil). They are therefore often described as oil-modified polyester paints. Further modification to the alkyd resins can be achieved by adding compounds such as styrene or vinyl toluene to improve drying time. Alkyd resins have remained the binding media in the vast majority of all solvent-borne commercial paints since about the mid 1930's.

*Acrylics* are high molecular weight (HMW) polymers of the esters of acrylic and methacrylic acids. They are available either as dispersions or in solution, but the dispersion (or emulsion) form is by far the most important. The use of emulsions in works of art has increased steadily since their introduction in the mid 1950's in the USA and in the early 1960's in the UK. The early acrylic emulsions were mostly based on a copolymer of ethyl acrylate (EA) and methyl methacrylate (MMA). More recently, however, these emulsions have largely been replaced by copolymers of n-butyl acrylate / methyl methacrylate (nBA/MMA). Sometimes styrene is used instead of MMA in the copolymer (i.e. a styrenated acrylic) which will reduce the cost of a formulation, but will render the film more prone to yellowing. The solution form of acrylic paints have all been based on poly n-butyl methacrylate (pnBMA).

*Polyvinyl acetates (PVAc's)* are HMW polymers of vinyl acetate. As with the acrylics they are available in dispersion or solution form and again the dispersion form is far more important. They first appeared in the 1940s, i.e. slightly earlier than the acrylics. Although a few artists' colourmen have marketed paints based on PVAc, most have now been discontinued. However, PVAc remains to be the most commonly used resin in UK household emulsion paints, and it is in this form that they are most often encountered on works of art. PVAc homopolymers are slightly too hard to form coherent films from an emulsion and so are usually plasticised. In early formulations this was achieved with standard plasticisers such as the phthalates, although since the 1960s it has been accomplished by copolymerising vinyl acetate with a softer vinyl resin, such as the vinyl versatate (VeoVa) resins.

*Pigments* can be inorganic or (increasingly so) organic solids. A vast range is now available to the manufacturers of paints and there is insufficient space here to describe their chemical structures in any detail. However, important classes of 20th century pigments include the cadmium reds, oranges and yellows, iron oxide reds and ochres, naphthol (azo) reds and yellows (Hansa), quinacridone reds and violets, phthalocyanine greens and blues, prussian blue, ultramarine blue, cobalt blue, the earth colours (natural and synthetic iron oxides), titanium white, carbon black and iron oxide blacks.

*Extenders* which are commonly found in modern paints are calcium carbonate (chalk or marble dust), barium sulphate (blanc fixe or barytes), hydrated aluminium silicate (china clay or kaolin), magnesium carbonate (magnesite), calcium sulphate (gypsum or

terra alba) and hydrated magnesium silicate (talc).

### 1.4 Diamond cell and beam condenser

The diamond cell and beam condenser used here are made by Spectra Tech. The cell itself consists of two type IIA diamonds, 1 mm in thickness and 1.8 mm in width, between which the sample is compressed. The beam condenser reduces the diameter of the IR beam by approximately four times to a diameter of about 1 mm. Providing the sample is sufficiently malleable (as the majority of modern paints are), it is readily compressed to a film thin enough to obtain a decent transmission spectrum usually with only 64 scans. Diamond is a largely transparent material in the infrared region apart from lattice absorption bands at approximately 2200 $cm^{-1}$. However, few other absorptions occur in this region and they are easily eliminated by running a background. The sample size required for this technique is extremely small and quite comparable to that often associated with using an IR microscope. A sample weight in the region of micrograms is normally quite sufficient.

The main advantages of using a diamond cell and beam condenser over a microscope are:

- it is a completely non-destructive technique (after each measurement the sample can be peeled off one of the diamond faces and used for additional analysis)
- there is minimal sample preparation (it is therefore an extremely rapid technique)
- it is of relatively low cost (approximately 10 times less expensive than a microscope).

The main disadvantages are:

- it is a non-specific technique, so a certain area (or layer) of a sample cannot be analysed in isolation (as is possible with a microscope)
- it is not appropriate for hard or brittle materials where a thin film is not readily achieved (this is not a problem with modern paints)
- IR spectra can be affected (for example by frequency shifts or relative intensity changes) by pressure effects. Although these only tend to become apparent at much higher pressures than those experienced in this cell, a uniform pressure was attempted for every sample by tightening the cell by a set amount.

Spectra were collected on a Perkin Elmer series 2000 FTIR spectrometer at 4 $cm^{-1}$ resolution running IRDM software. Data was processed with GRAMS 386 (Galactic) software.

### 1.5 FTIR spectra

1.5.1 Binding media

Figure 1 shows the FTIR spectra of two unpigmented acrylic media based on p(EA/MMA) and p(nBA/MMA) copolymers and an unpigmented styrene-acrylic emulsion. In the C-H stretching region, the p(EA/MMA) resin has peaks at 2986 $cm^{-1}$ and 2954 $cm^{-1}$, which are of similar strength and often badly resolved. There are two additional peaks observed as shoulders at 2912 $cm^{-1}$ and 2878 $cm^{-1}$. In contrast the

p(nBA/MMA) acrylic resin shows absorptions at 2961 $cm^{-1}$ and 2878 $cm^{-1}$ (with the former always significantly stronger), with a shoulder at 2940 $cm^{-1}$. The styrenated acrylic medium is identified by the presence of aromatic C-H stretching frequencies at 3030 $cm^{-1}$, 3063 $cm^{-1}$, 3086 $cm^{-1}$ and 3104 $cm^{-1}$. The values for the carbonyl stretching frequency in all three emulsions are very similar at 1732/3 $cm^{-1}$. The strongest peak in the fingerprint region for the p(EA/MMA) acrylic resin is a doublet at 1177 $cm^{-1}$ and 1162 $cm^{-1}$, with a peak of medium intensity at 1239 $cm^{-1}$. With the p(nBA/MMA) acrylic this becomes a single peak centred at 1170 $cm^{-1}$ with a shoulder at 1153 $cm^{-1}$, although the peak at 1240 $cm^{-1}$ is also present. The presence of styrene is confirmed by the strong aromatic C-H out-of-plane bending absorptions at 761 $cm^{-1}$ and 702 $cm^{-1}$ (indicative of a mono-substituted aromatic compound) and also the sharp aromatic skeletal ring breathing absorptions at 1456 $cm^{-1}$, 1496 $cm^{-1}$, 1585 $cm^{-1}$ and 1604 $cm^{-1}$.

Figure 2 shows the FTIR spectra for a PVAc/VeoVa emulsion, a drying oil (linseed) and an alkyd resin. The PVAc/VeoVa copolymer exhibits C-H stretching at frequencies similar to those for the p(nBA/MMA) acrylic at 2966 $cm^{-1}$, 2940 $cm^{-1}$ and 2877 $cm^{-1}$. The values for an unplasticised PVAc (not shown here) are very different, with one main peak at 2941 $cm^{-1}$ and a shoulder at 2966 $cm^{-1}$. This spectral region in the oils and alkyds, however, is very different and is usually characterised by two sharp and well resolved peaks at 2933-4 $cm^{-1}$ and 2858-60 $cm^{-1}$. The PVAc/VeoVa carbonyl peak appears at around 1740 $cm^{-1}$, which is also where the carbonyl peak appears in drying oils. The alkyds, however, absorb at a slightly lower wavenumber (about 1732 $cm^{-1}$). The fingerprint region is not particularly diagnostic for the drying oils, but it contains very important peaks for both the PVAc's and alkyds. With all PVAc's (i.e. not just the PVAc/VeoVa emulsions) the strongest peak in this region is around 1244 $cm^{-1}$ and is usually characteristically rounded in profile, but there is also another strong absorption at 1112 $cm^{-1}$. With alkyds there is also a rather broad and rounded dominant peak centred at a higher wavenumber (about 1273 $cm^{-1}$ ), as well as two other sharp peaks at 1139 $cm^{-1}$ and 1073 $cm^{-1}$. For styrene-modified alkyd resins, the characteristic absorptions for styrene (as listed above with the acrylics) also become apparent.

### 1.5.2 Extenders

Figure 3 shows the FTIR spectra of three commonly used extenders in modern paints, namely chalk (calcium carbonate), Blanc fixe (barium sulphate) and china clay (hydrated aluminium silicate). Chalk has a strong and very broad absorption between 1390 $cm^{-1}$ and 1490 $cm^{-1}$ and is further characterised by a strong and sharp absorption at 877 $cm^{-1}$, and less strong, but still sharp peaks at 713 $cm^{-1}$, 1796 $cm^{-1}$ and 2514 $cm^{-1}$. These latter two peaks have proved extremely useful for the identification of chalk, as no other materials appear to absorb there. In contrast, blanc fixe displays a high absorption at between 1070 $cm^{-1}$ and 1200 $cm^{-1}$, consisting of three distinct peaks at 1075 $cm^{-1}$, 1121 $cm^{-1}$ and 1196 $cm^{-1}$. There are also sharp but less intense absorptions at 611 $cm^{-1}$ and 640 $cm^{-1}$. China clay absorbs strongly in the region between 900 $cm^{-1}$ and 1150 $cm^{-1}$, with peaks observed at 1118 $cm^{-1}$, 1034 $cm^{-1}$ and 1016 $cm^{-1}$, with an additional peak at 917 $cm^{-1}$. However, the most characteristic area in its FTIR spectrum is between 3620 $cm^{-1}$ and 3700 $cm^{-1}$, where the O-H stretching frequency occurs. Up to four very sharp

peaks are present, the two most prominent at 3621 $cm^{-1}$ and 3695 $cm^{-1}$.

1.5.3 Pigments

There are clearly far too many pigments available to discuss their FTIR spectra in any detail here. However, as a broad generalisation, organic pigments are usually characterised by several very sharp and strong peaks in the fingerprint region of the spectra. The spectra of inorganic pigments, however, are typically more simple and contain only a few rather broad peaks. There are plenty of examples of these in the IRUG Infrared Spectral Library.

1.5.4 Paints

Figures 4 and 5 show the FTIR spectra of two dried tube paints and in each case they are shown with the spectra of the respective binding medium, main pigment and extender.

Paint 1 (yellow), figure 4

- Binding medium: C-H stretching bands at 2985 $cm^{-1}$ and 2955 $cm^{-1}$, C=O stretching at 1732 $cm^{-1}$ and skeletal vibrations at 1179 $cm^{-1}$ are all indicative of a poly (ethyl acrylate / methyl methacrylate) acrylic emulsion.
- Extender: The four sharp absorptions at 2520 $cm^{-1}$, 1799 $cm^{-1}$, 877 $cm^{-1}$ and 713 $cm^{-1}$ and the strong but broad absorption between 1400 $cm^{-1}$ and 1500 $cm^{-1}$ are characteristic of chalk.

- Pigment: The sharp peaks at 1667 $cm^{-1}$, 1562 $cm^{-1}$, 1508 $cm^{-1}$, 1296 $cm^{-1}$, 1140 $cm^{-1}$, 953 $cm^{-1}$ and 774 $cm^{-1}$ are diagnostic of the presence of the organic azo (or Hansa) yellow pigment, PY1.

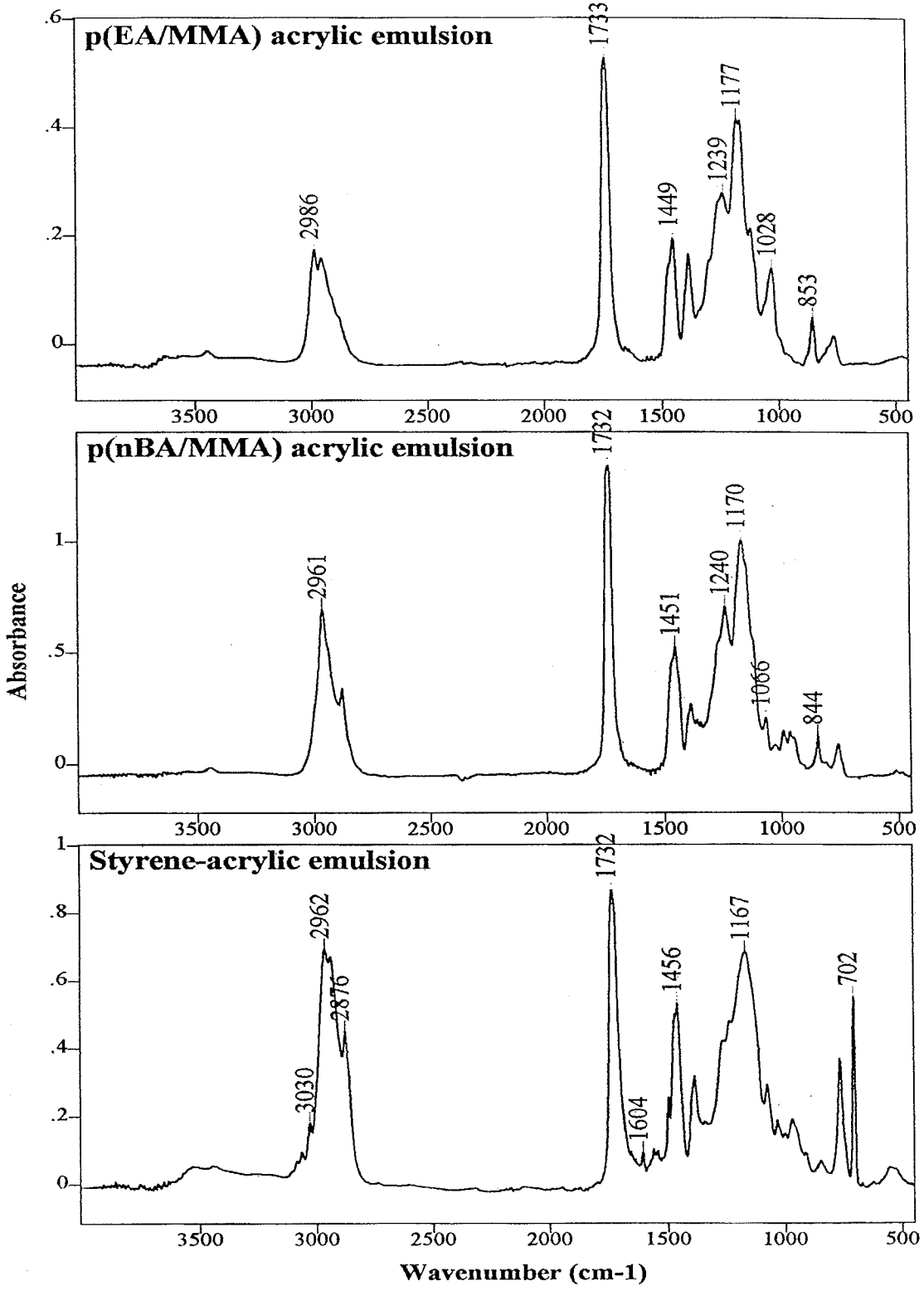
p(EA/MMA) acrylic emulsion
1733
1177
1239
1449
2986
1028
853
p(nBA/MMA) acrylic emulsion
1732
1170
1240
2961
1451
1066
844
Styrene-acrylic emulsion
1732
2962
1167
1456
2876
3030
1604
702
Absorbance
Wavenumber (cm-1)
3500
3000
2500
2000
1500
1000
500

Figure 1

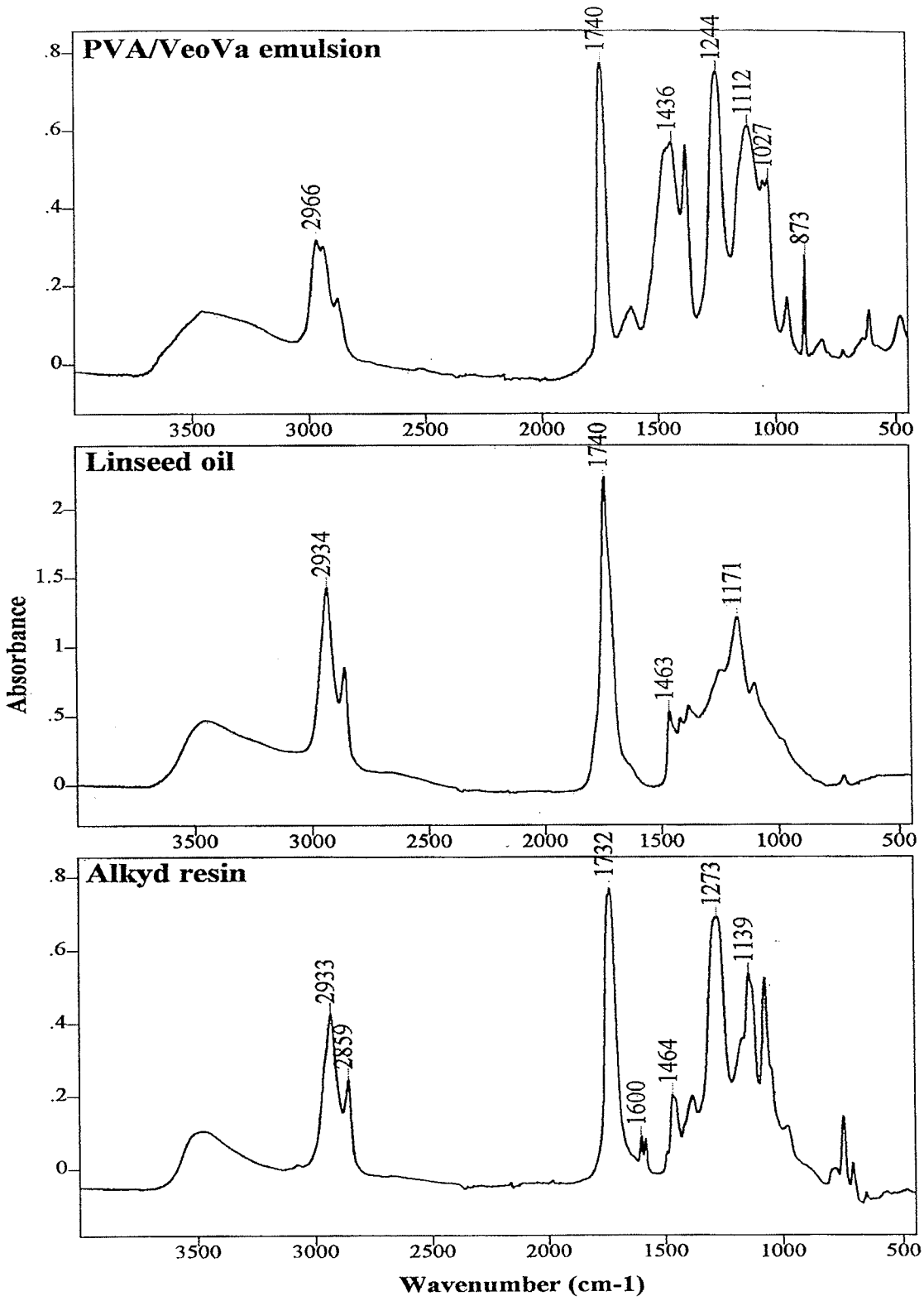
PVA/VeoVa emulsion
1740
1244
1436
1112
1027
2966
873
Linseed oil
1740
2934
1171
1463
Alkyd resin
1732
1273
2933
1139
2859
1464
1600
Absorbance
Wavenumber (cm-1)

Figure 2

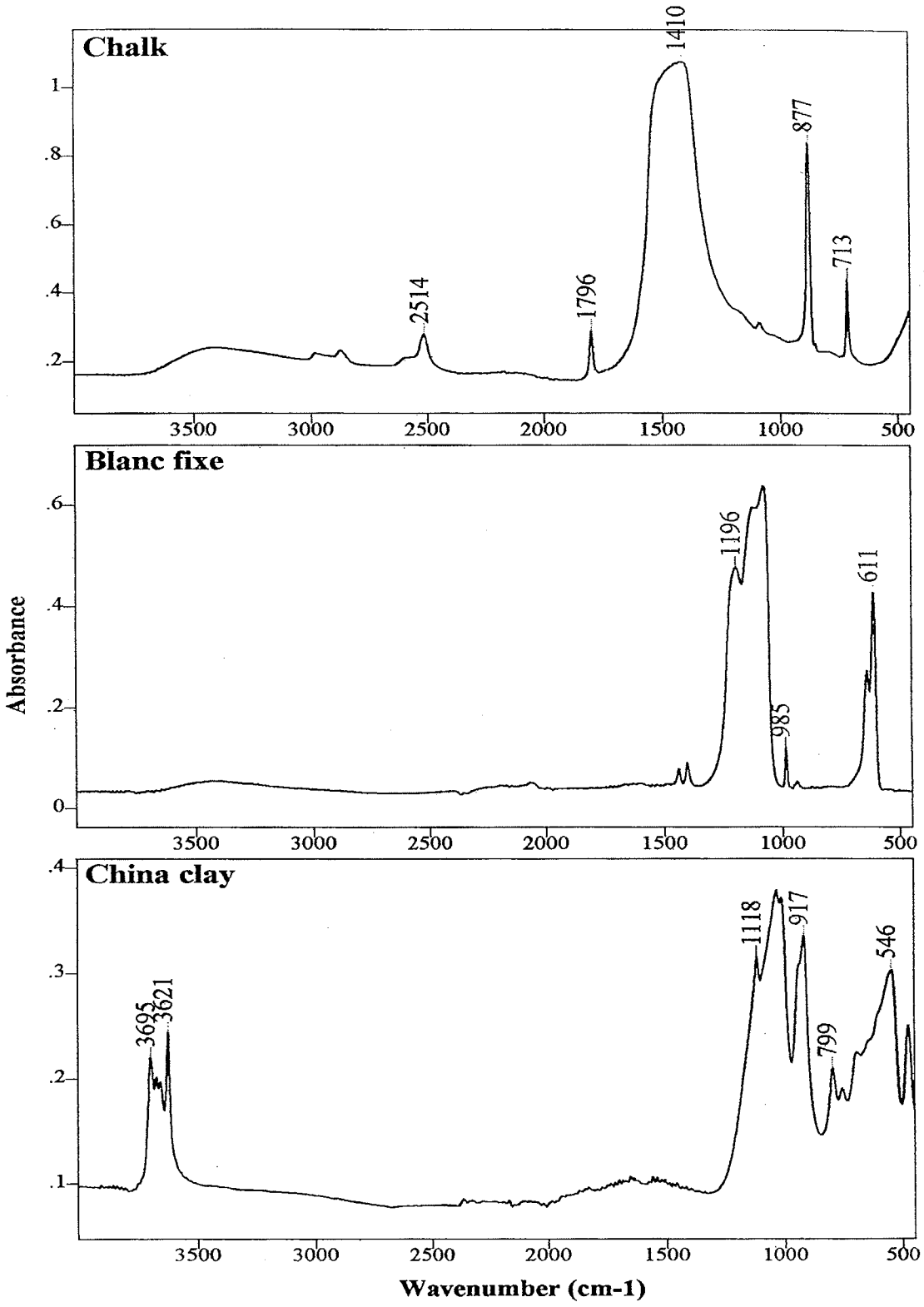
Chalk
1410
877
713
2514
1796
Blanc fixe
1196
611
985
China clay
1118
917
546
799
3695
3621
Absorbance
Wavenumber (cm-1)
3500
3000
2500
2000
1500
1000
500

Figure 3

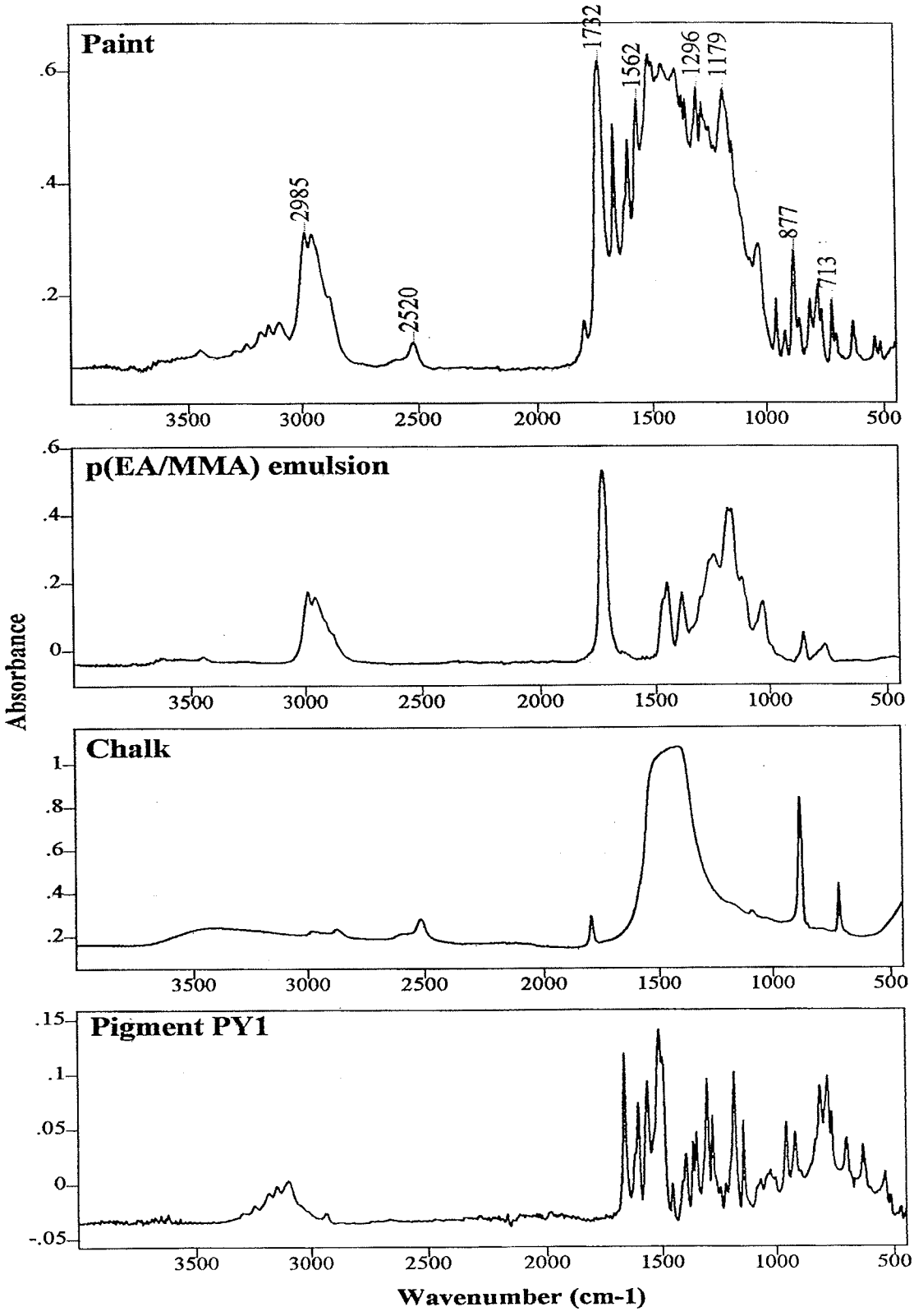
Paint
2985
2520
1732
1562
1296
1179
877
713
p(EA/MMA) emulsion
Chalk
Pigment PY1
Absorbance
Wavenumber (cm-1)
3500
3000
2500
2000
1500
1000
500

Figure 4

Paint 2 (yellow ochre), figure 5

- Binding medium: C-H stretching at 2960 $cm^{-1}$ and 2877 $cm^{-1}$ and the C=O stretching at 1733 $cm^{-1}$ suggest a poly (n-butyl acrylate / methyl methacrylate) acrylic emulsion. Much more of the fingerprint region of the medium is masked by the pigments/extender here.
- Extender: Strong absorptions at 640 $cm^{-1}$ and 609 $cm^{-1}$, and a strong but broad absorption between 1050 $cm^{-1}$ and 1250 $cm^{-1}$ is indicative of barium sulphate.
- Pigment: The broad area of absorption peaking at 3121 $cm^{-1}$, and the two peaks at 801 $cm^{-1}$, and 904 $cm^{-1}$ are characteristic of a synthetic yellow ochre (PY42).

Figure 6 shows the FTIR spectrum of the blue paint sampled from Hyena Stomp (1962) by Frank Stella ( Tate Gallery T00730).

- The binding medium is an alkyd resin, identified by the C-H stretching frequency 2929 $cm^{-1}$ and carbonyl absorption at 1730 $cm^{-1}$. The characteristic C-O stretching peak for alkyds is just visible at 1283 $cm^{-1}$.
- The pigment is prussian blue ($KFe^{III}Fe^{II}(CN)_6.xH_2O$), which is rarely missed with FTIR due to its very strong absorption at 2094 $cm^{-1}$, an area where virtually no other painting materials absorb. In addition, EDX analysis identified the presence of a small amount of titanium (dioxide) which accounts for the overall absorption at under 700 $cm^{-1}$.
- The main extender is chalk, which is present in much higher concentrations than in paint 1 (figure 4). The peaks at 1800 $cm^{-1}$, 2520 $cm^{-1}$, 878 $cm^{-1}$ and 713 $cm^{-1}$ are all very clear and the broad absorption between 1400 $cm^{-1}$ and 1450 $cm^{-1}$ has masked all other details in that region. In addition, the overall absorption between 1000 $cm^{-1}$ and 1150 $cm^{-1}$ is characteristic of a silica extender. The presence of silicon was confirmed with EDX.

The presence of an alkyd resin and the large amounts of extender are indicative of a commercial housepaint.

### 1.6 Conclusions

The use of FTIR has proved to be a very useful method for the rapid differentiation between the main types of twentieth century paint media. The presence of pigments and extenders significantly changes the FTIR spectrum from that of the pure binding medium, but often there is sufficient information from each of these components to permit the detailed characterisation of a paint film.

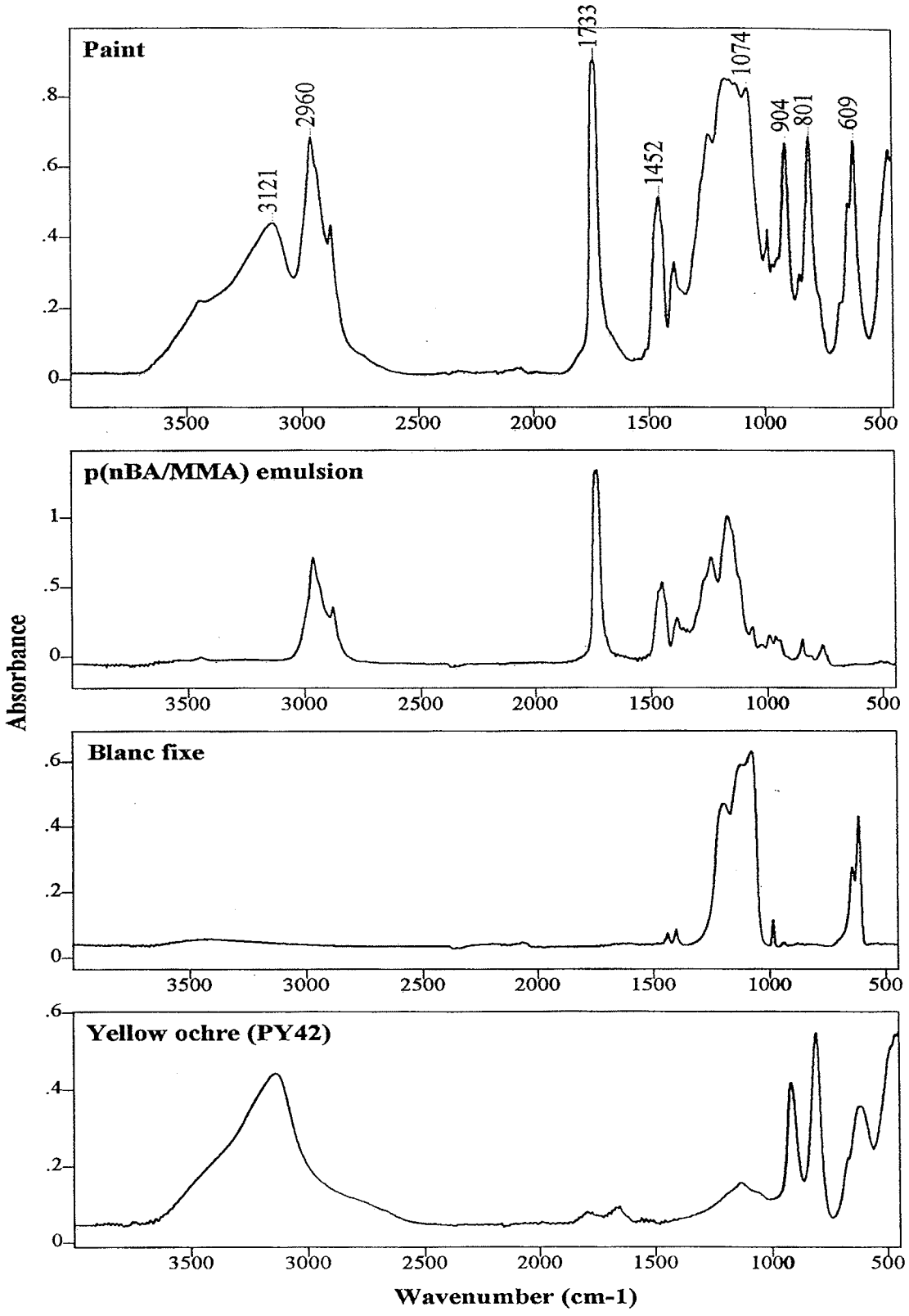
Paint
3121
2960
1733
1452
1074
904
801
609
p(nBA/MMA) emulsion
Blanc fixe
Yellow ochre (PY42)
Absorbance
Wavenumber (cm-1)
3500
3000
2500
2000
1500
1000
500

Figure 5

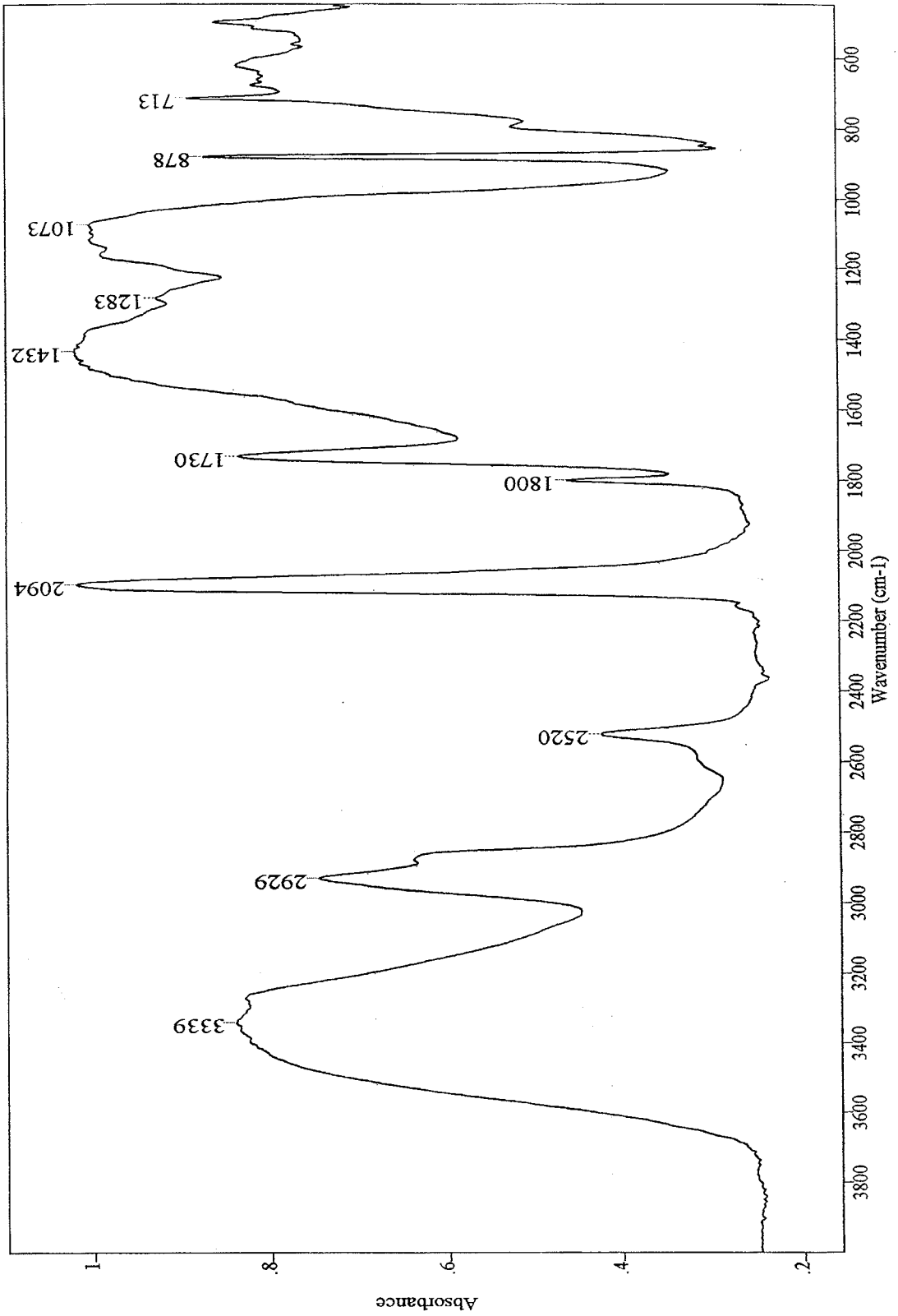
713
878
1073
1283
1432
1730
1800
2094
2520
2929
3339
Absorbance
1
.8
.6
.4
.2
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
Wavenumber (cm-1)

Figure 6

## 1.7 Acknowledgments
This research is made possible by The Leverhulme Trust which is generously funding a four-year research post at the Tate Gallery into the analysis of 20th century paint media. The FTIR spectrometer is located at Birkbeck College, University of London.

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# 2. Assessing plastic collections in museums by FTIR spectroscopy

Brenda Keneghan
V&A

## 2.1 Summary

Many people are surprised to learn that there are plastic objects amongst museum collections, as most peoples experience of plastic is limited to cheap, disposable everyday objects. The Victoria & Albert Museum, as the national museum of art and design, contains within its collections very many objects made entirely from plastic, or with plastic components. These objects date from the earliest usage of these materials, for example compressed horn, to the latest carrier bag from Tescos. Plastics are dispersed throughout the collections. A common misconception is that plastic lasts forever. Environmentalists complain about the non-degradability of these new materials. People can, therefore, be forgiven for assuming that plastic objects in museums are completely stable and no cause for concern. This, unfortunately, is not the case. Plastics do degrade and several costly examples have made most museums and galleries take notice. It was this concern that prompted the V&A to undertake a survey of their plastic objects. The term "plastic" is commonly used to describe an ever-growing range of organic materials. Due to its lack of specificity the term has no meaning to a materials scientist or plastics conservator. As different plastics will degrade in manners characteristic of their chemical composition it is essential that this composition is known. The identification of the plastics involved forms an integral part of our survey. The major technique which we use is Fourier Transform Infrared Spectroscopy. Of particular interest is the sampling technique known as "diffuse reflectance", which requires ~2 mg sample which is acceptable by museum standards. This presentation will illustrate how FTIR has been used in the V&A to:

i) identify particular materials within collections. ii) assist conservators in other areas make informed decisions on particular treatments.
iii) assist conservation students and members of the public with "problem" objects.

## 2.2 Abstract

This paper describes briefly the applications of Fourier Transform Infrared spectroscopy in the survey and analysis of polymeric materials amongst the collections of the Victoria and Albert Museum.

## 2.3 Introduction to plastics in collections

Many people are surprised to learn that there are plastic objects among museum collections, as most peoples experience of plastic is limited to cheap, disposable, everyday objects. The Victoria and Albert Museum, as the national museum of art and design, contains within its collections very many objects made entirely from plastic, or with considerable plastic components. Plastics are dispersed throughout the collections. The objects date from the earliest usage of natural materials, for example compressed horn, to the latest supermarket carrier bag.

A common misconception is that plastic lasts forever and environmentalists complain about the non-degradability of these new materials. When it is realised that there are plastics in museums one can be forgiven for assuming that they are completely stable and no cause for concern. This, unfortunately, is not the case. Plastics do degrade and several costly examples have made most museums and galleries take notice. It was this concern that prompted the V&A to undertake a survey of their plastic objects.

## 2.4 Aims of survey

There were several objectives in mind when the plastics survey was being considered. It was hoped that the results would provide the following information:-

i) the number and location of objects within the various collections of the museum made entirely from plastic or containing substantial plastic components

ii) the condition of these objects

iii) the identification of the plastics involved.

Practically, what is done is the collections are visited and those objects made completely from plastic or with a high plastic content are examined. A survey form is filled in on the spot and the results are later transferred to a computer database. On the survey form there is a section describing the material from which the object is made. This is where the method of analysis is important.

## 2.5 Analysis of plastics

Although an indication of the composition of artefacts may be made by eye, since the earliest plastics were developed to imitate highly valued, natural polymers like tortoiseshell for example, a more definitive technique is required. Some people talk about the smell or even taste of polymers as methods of identification, but unambiguous identification cannot be made by these procedures. The term "plastic" is commonly used to describe an ever-growing range of organic materials. Due to its lack of specificity the term has no meaning for a materials scientist. As different plastics will degrade in manners characteristic of their chemical composition it is essential that this composition is known. From our analysis of plastics it is hoped that we will be able to identify the components of a formulation and also assess deterioration. To date, unfortunately , deterioration assessment has had to take a back seat to identification.

The tool which we use most frequently for identification of plastics is Fourier Transform Infrared spectroscopy. Sampling methods vary depending on the nature and condition of the object. NaCl cells have been used for plasticiser analysis and a diamond cell (courtesy of the British Museum) has proved invaluable for "rubbery" samples. The most common sampling technique which we use however, is diffuse reflectance. Although "technically" a destructive technique, the minimal amount of sample required (~2 mg) is acceptable by museum standards especially when we consider that an unambiguous identification can influence storage conditions which may result in the difference between life or death of an object.

## 2.6 Examples

There are three common situations where the identification of plastics by FTIR is routinely used:

- to survey the collections, identify materials at risk and recommend suitable

storage conditions- eg: in the Bethnal Green Museum of Childhood an outstation of the V&A, over six thousand plastic objects have been examined and several groups of materials have been identified.

- To assist conservators from other areas of conservation in the identification of materials so that more informed decisions on particular treatments may be made.
- To assist students on conservation courses and members of the public with "problem" objects.

Examples which illustrate how useful FTIR is for distinguishing between similar materials among the collections are given below.

Toys made from natural rubber versus toy figures made from polyurethane foam. Both these materials are physically similar but chemically quite different. Although they may have degradation reactions in common for example *oxidation*, there may be some mechanisms specific to one material alone.

Photographic negative materials - acetates versus nitrates. This is a very important area in which good use of FTIR has been made to differentiate between two materials which are physically identical but chemically quite different, and whose degradation products may cause severe problems if they are not separated. Using the diffuse reflectance sampling technique a minute sample is taken from along the edge of the negative and analysed.

Figure 1 demonstrates the use of FTIR for the identification of photographic negative materials. Nitrate has strong $NO_2$ stretching vibration at ~ 1650 $cm^{-1}$. Acetate has strong C=O stretch at ~1730 $cm^{-1}$. It is possible to differentiate between the two materials at a glance.

Author

Brenda Keneghan received a Masters Degree in organic chemistry from the National University of Ireland in 1986. She then joined the Polymer Physics group at Queen Mary & Westfield College (University of London), where she was part of a research team. She carried out her research work towards a PhD in the Materials Department at Queen Mary & Westfield in the area of polyurethane synthesis and degradation. She is currently completing the writing up of her thesis and hopes to submit before the end of the year. She has been working as Plastics Conservator at the Victoria & Albert Museum since November 1993.

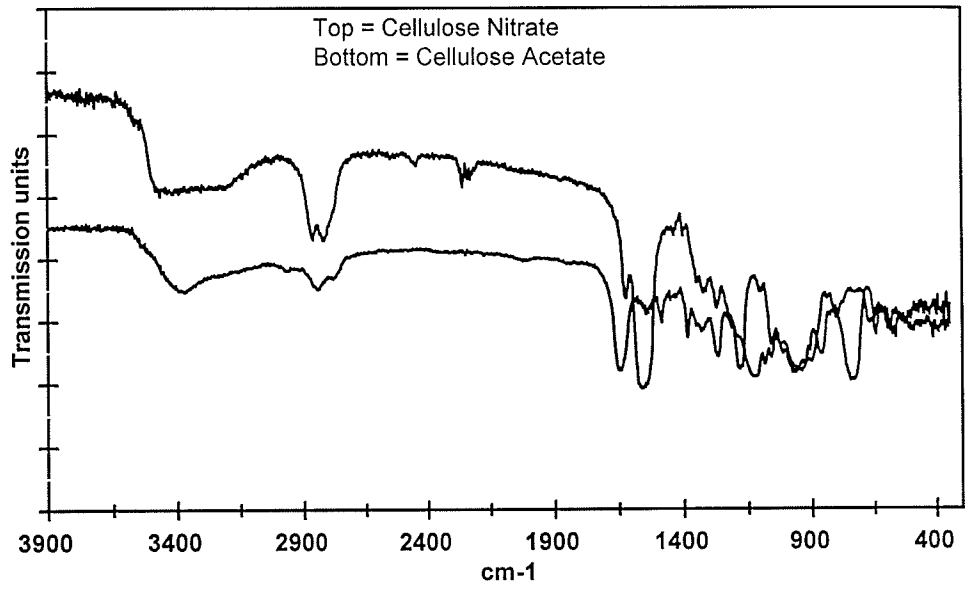


Figure 1: superimposed spectra of samples from cellulose acetate and cellulose nitrate negatives

# 3. Identification of calcium carbonate contained as body in modern paints by FTIR spectroscopy

Yasunori MATSUDA and Masahiko TSUKADA
Tohoku University of Art & Design

## 3.1 Summary

Since the industrial production of the paints for the coatings of architecture and the colours for fine arts had begun, some kinds of colourless or white pigments have been contained in the paint materials as a body pigment. Usually X-ray diffraction or X-ray fluorescence analysis is adopted to the identification of these pigments. However, we found that we can identify them, especially calcium carbonate, by FTIR spectroscopy rapidly, simply and accurately. This method depends on the fact that the calcium carbonate shows strong absorption peaks in IR spectrum at 1430, 875 and 712 $cm^{-1}$ (attributable to the vibration of C=O in the carbonate ion), which characterize the pigment.

We have examined the samples of the paint layers taken from two different types of artifacts. One is a Chinese architecture in Yokohama, which is called "JIZO-O-BYO" (the tomb of Jizo Emperor). From the documents we found that it was restored and retouched several times. The other is the modern picture painted with oil, acrylic and gouache colours. The measurement of IR spectra was carried out using Perkin Elmer 1600 Series FTIR spectrometer and samples were prepared with the KBr pellet method.

In the former case, the vehicle of most coloured layers was considered to be some kind of alkyd resin. Therefore, in both cases, the binding mediums interfered the clear attribution of the peak at 1430 $cm^{-1}$ of calcium carbonate because they have absorption around 1450 $cm^{-1}$ (attributable to the variation of C-H of methylene or methane group). However, the sharp absorption peaks at 875 and 712 $cm^{-1}$ were detected clearly, which suggests that calcium carbonate is contained as a body pigment. In the paints of former case it would have been used for the purpose of fixing organic dyes on, as we could extract them with acetone.

## 3.2 Abstract

Calcium carbonate contained as a body pigment in modern paints can be detected accurately by FTIR, paying attention to the absorption peaks at 1430, 875, and 712 $cm^{-1}$. But its strong absorption at 1430 $cm^{-1}$ sometimes interferes the detection of remaining components such as binding media or organic colorants. Examples of the analyses of modern paint samples from an architecture and a painting were described, and the attempt to identify organic colorants by extracting them with organic solvents were discussed.

## 3.3 Introduction

Since developments in technology made it possible to produce paints for architectural elements and colours for fine arts industrially, many unfamiliar substances have been introduced as components of paint materials. One of them is the body pigment, which is contained in the paint for many purposes: as the filler; as the base to absorb dyestuffs; to control properties of the paint (eg: hue, viscosity, velocity of drying). It consists of some kinds of transparent or white mineral pigments, such as calcium carbonate, barium sulfate, or aluminium hydroxide. Commonly their identification is carried out by X-ray diffraction or X-ray fluorescence analysis.

Recently we had the opportunity to analyse samples of paint layers taken from the artifacts of two different types: an architecture and a painting. After X-ray fluorescence

analysis of the pigments using SEM-EDX, we tried to obtain information on the organic substances contained in them by FTIR. Contrary to our purpose, however, we had IR spectra which only suggested that samples from the both artifacts contained calcium carbonate as a body pigment. Below, we describe the result of these analyses and the fact that we can detect calcium carbonate by FTIR spectroscopy rapidly, simply and accurately. We also discuss using the method to identify the remaining components contained in the samples and the limitation of this method.

### 3.4 IR spectrum of calcium carbonate

Figure 1 shows the IR spectrum of calcium carbonate from analytical grade chemicals, measured by KBr pellet method (see Appendix for details about the instrument and the measurement of spectra). It is well known that calcium carbonate has two different crystal forms, calcite and aragonite, and that calcite shows strong absorption peaks at 1430, 875, and 712 $cm^{-1}$ in its IR spectrum. These peaks are attributable to the vibration of carbon-oxygen double bond in the carbonate ion [1]. Details about this pigment are written in many books (eg: [2]).

### 3.5 Analysis of paint samples from a Chinese architectural element

The first example is of samples from a Chinese architecture at Yokohama. Its name is "JIZO-O-BYO," which means the tomb of Jizo Bosatsu (Ksitigarbha). It was constructed in 1892 as the temple of the cemetery for the Chinese immigrants at Yokohama. Its internal construction is mainly made of wood with painted surfaces (figure 2). From the documents we found that it had been restored and retouched several times already. Recently, taking occasion to restore it, we were asked by the restorers to analyse the chemical composition of paint layers. The samples were taken by the restorers from the ceiling and the columns of its main gate. Their colours were white, red, brown, and green.

From the observation of the cross section, we noticed these samples had multi-layered paint structures. As the result of the elemental analysis by SEM-EDX, calcium was detected as the principal element not only in the white but also in some other colour layers. It seemed that the samples contained organic pigments, such as lake pigments. To analyse organic components, we scraped off each layers with a fine scalpel as carefully as possible, and measured their FTIR spectra.

Figure 3 shows the spectra of the red paint in the surface layer of the ceiling and of the brown paint in the surface layer of a column. They both have very distinctive sharp peaks around 1430, 875, and 712 $cm^{-1}$. It is well known that many binding media, such as oil, animal glue, or some kinds of synthetic resin, have absorption around 1450 $cm^{-1}$, which is attributable to the vibration of carbon-hydrogen bond of methyl or vinyl group. The peak 1430 $cm^{-1}$ could therefore be attributed either to absorption of binding medium or to the calcium carbonate. The clearly detectable peaks at 875 and 712 $cm^{-1}$, however, suggest the presence of calcium carbonate as a body pigment.

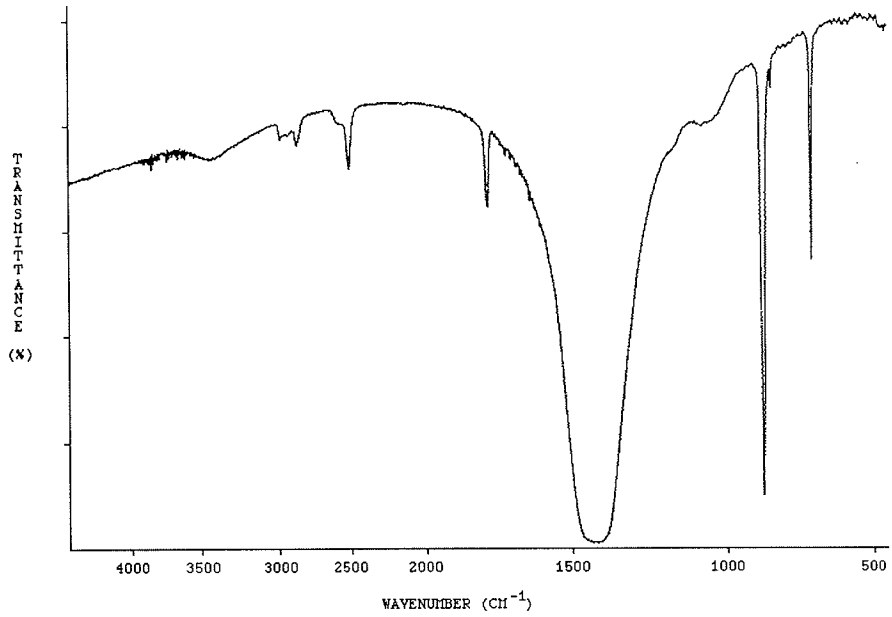


Figure 1: IR spectrum of calcium carbonate from analytical grade chemicals

Figure 2: Interior of the main gate of JIZO-O-BYO

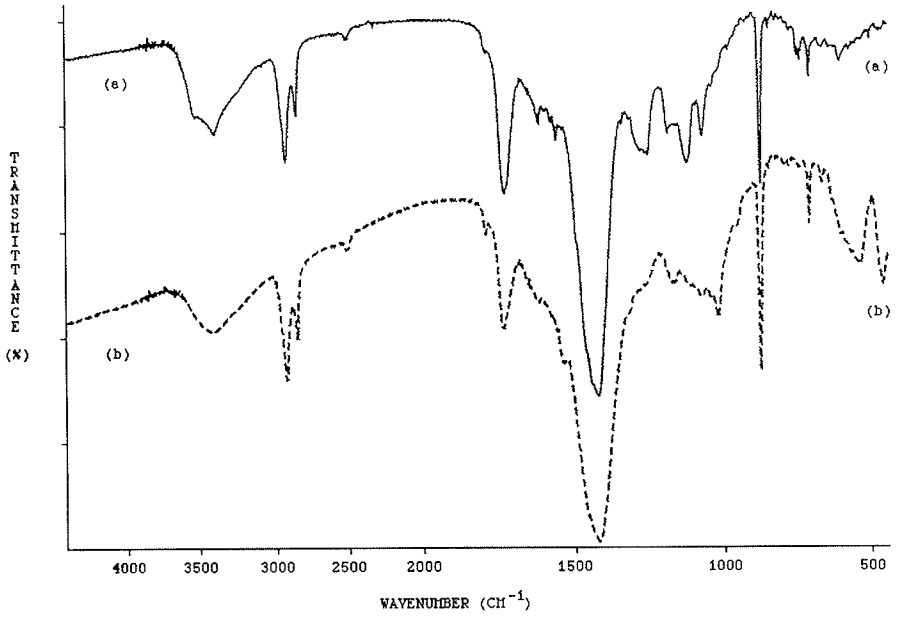


Figure 3: IR spectra of the red paint from the ceiling (a) and the brown paint from a column (b) of JIZO-O-BYO

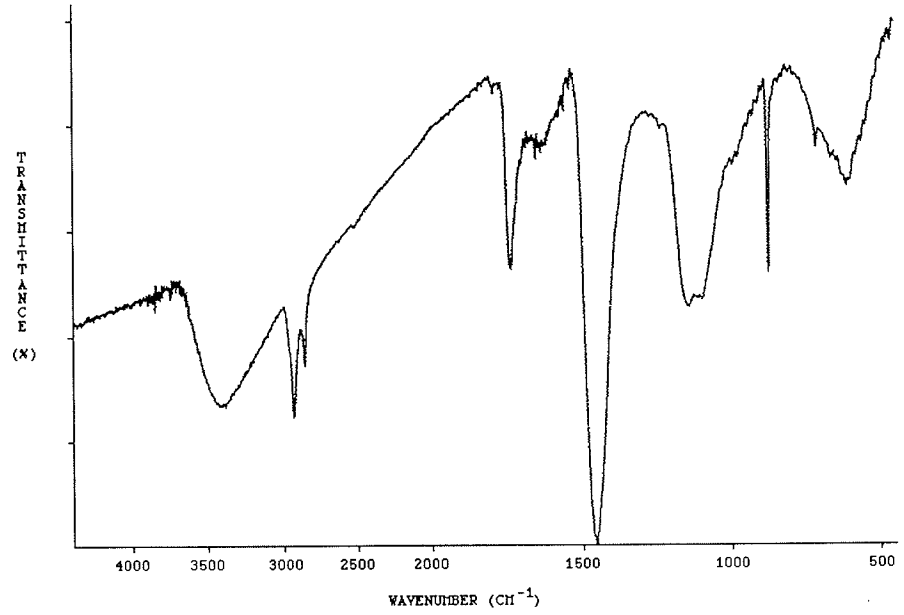


Figure 4: IR spectrum of the oil colour of vermilion from our student's picture

### 3.6 Analysis of paint samples from a painting

The second case of the analysis is on samples from a very modern picture, painted with commercial artistic oil, acrylic, and gouache colours. This picture is painted by students of our course. They draw pictures in order to study the structure of paintings and we use these pictures to teach the methods of scientific investigation of paintings. For example, a picture has another picture under the surface and students learn the techniques of X-ray radiography, IR reflectography, cross section, and so on. Of course the colours they used were fully documented.

We analysed the samples of some colours taken from a picture by FTIR. Figure 4 shows the spectrum of the oil colour of vermilion. The pigment of vermilion itself does not show a good infrared spectrum by the KBr pellet method [3], but the spectrum of this oil colour shows apparent absorption peaks at 1430, 875, and 712 $cm^{-1}$. We can attribute them to calcium carbonate.

Figure 5 shows the spectra of the oil and the gouache colours of cerulean blue. The oil colour sample has the very strong absorption peaks of the pigment of cerulean blue at 646 and 596 $cm^{-1}$, and also the peaks of calcium carbonate. The gouache colour sample, however, does not have the peak of the pigment of cerulean blue, but of the calcium carbonate. This fact suggests that the gouache colour in this case contains some other blue colorants. We will discuss about it in the next section.

### 3.7 Method to identify remaining components

As we have described so far, calcium carbonate used as a body pigment can be detected very rapidly and easily by FTIR, paying attention to the absorption peaks at 1430, 875, and 712 $cm^{-1}$. Especially the peak at 875 $cm^{-1}$ is not overlapped with the peaks of other components, so it can be detected very accurately.

However, our main purpose to use FTIR in the both cases mentioned above was to identify the remaining organic components such as organic colorants contained in the samples. As figures 2 and 4 show, the absorption peak of calcium carbonate at 1430 $cm^{-1}$, which possibly overlapped with the absorption peaks of binding media or of some organic colorants, was very strong and wide in some spectra, and it interfered the detection of minute absorption of other components in this region. Therefore we planned a method to identify the components contained in low concentration like organic colorants. Initially, we record the FTIR spectrum of the sample as we mentioned so far. After that, if calcium carbonate is detected and if it is evident that the sample also contains some organic colorants, we try to separate them by extraction with appropriate organic solvents. Then we measure the FTIR spectra of the separated components. With some samples of the cases mentioned above, we tried to apply this method. Figure 6 shows the spectrum of the red substance extracted with acetone from the red paint in the surface layer of the ceiling of JIZO-O-BYO. This spectrum corresponded closely to that of a kind of diazo type red pigment in a commercial reference spectral library [4].

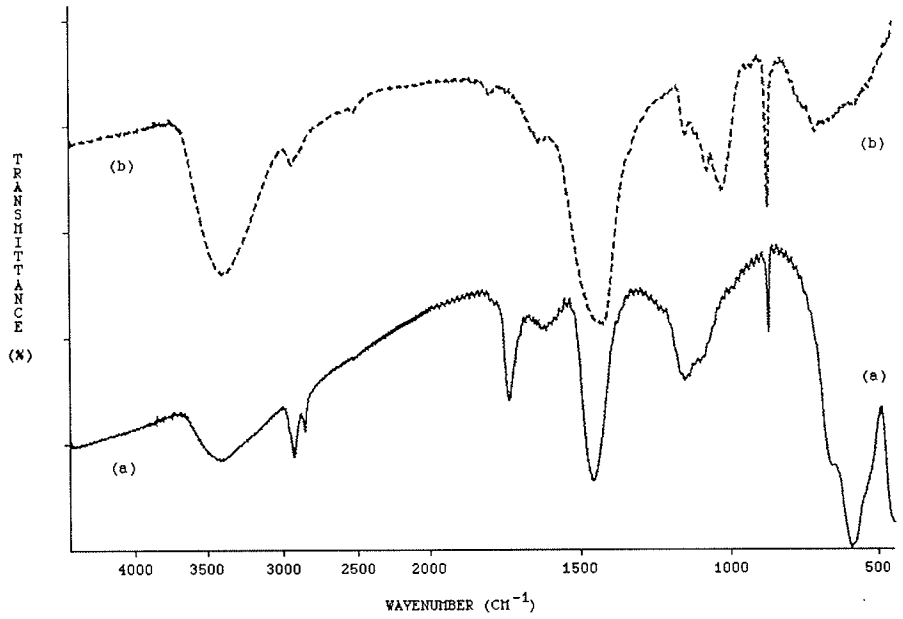


Figure 5: IR spectra of the oil (a) and the gouache (b) colours of cerulean blue from our student's picture

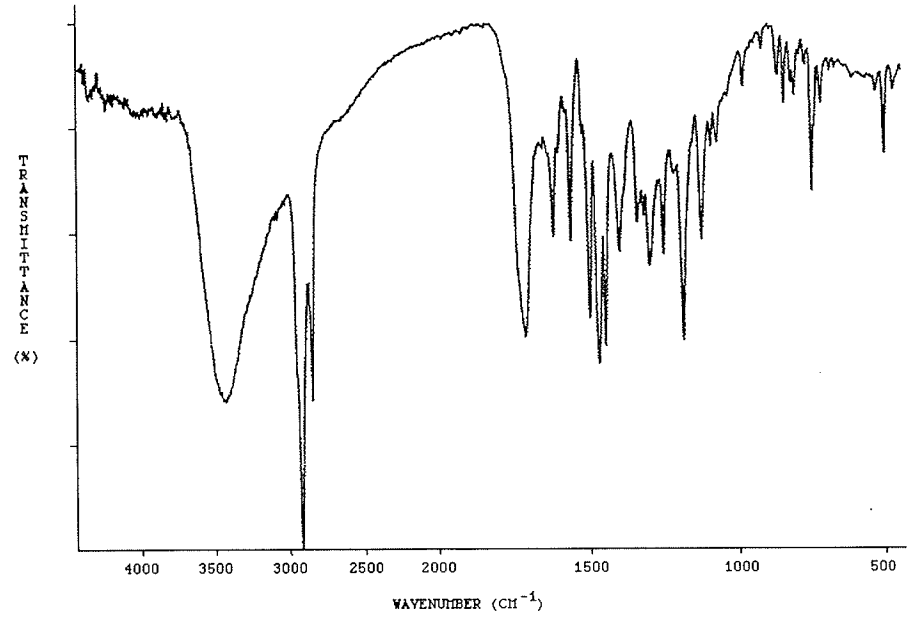


Figure 6: IR spectrum of the red substance extracted with acetone from the red paint of the ceiling of JIZO-O-BYO

Figure 7 shows the spectrum of the brown substance extracted with toluene from the brown paint in the surface layer of the column of JIZO-O-BYO. Contrary to the red paint, we could not find any reference spectrum which corresponds to this. From this result, we can guess that multiple components were extracted with toluene in this case. However, the chemical structure of organic colorants in general is complicated. They show many absorption peaks in IR region, and the attribution of each peak in the spectra of their mixture is very difficult. Therefore we could not identify this brown organic colorant.

Finally, we consider the gouache colour of cerulean blue of our student's picture. As we detected the trace amount of copper in this sample by the SEM-EDX analysis, we thought that this gouache colour contained some kinds of phthalocyanine blue pigments. It is known that phthalocyanine pigments do not dissolve in normal organic solvents but do in concentrated sulfuric acid, and that when this solution is diluted with water, the pigments precipitate without any chemical change. Following this procedure, we added a little amount of concentrated sulfuric acid to this sample, then diluted with water in order to separate phthalocyanine pigment. This caused a problem. Calcium carbonate reacted with sulfuric acid to produce calcium sulfate. A mixture of phthalocyanine pigment and calcium sulfate precipitate resulted from this chemical reaction. Figure 8 shows its spectrum. Because the absorption peaks of calcium sulfate at 1140 $cm^{-1}$ are very strong, we can hardly find the peaks of phthalocyanine at 1334, 1287, and 1006 $cm^{-1}$. In this case, we could not separate the organic pigment from the remaining components.

From the result of the analysis of the three samples we guess that the extraction of organic colorants can be a solution for our purpose. However, in some case the solvent extracts multiple components and their identification can be very difficult. And when the sample contains phthalocyanine, and calcium carbonate is its body pigment, we have to think of another way to detect the phthalocyanine positively.

### 3.8 Conclusion

As the conclusion, we would like to mention again the following two points:

- calcium carbonate can be detected very rapidly and easily by FTIR, paying attention to the absorption peaks at 1430, 875, and 712 $cm^{-1}$. Especially the peak at 875 $cm^{-1}$ can be detected very accurately.

- To analyse organic colorants of the sample in which calcium carbonate is contained as a body pigment, the extraction with organic solvents can be a solution. But it is not always adoptable, and the choice of the appropriate solvent is important.

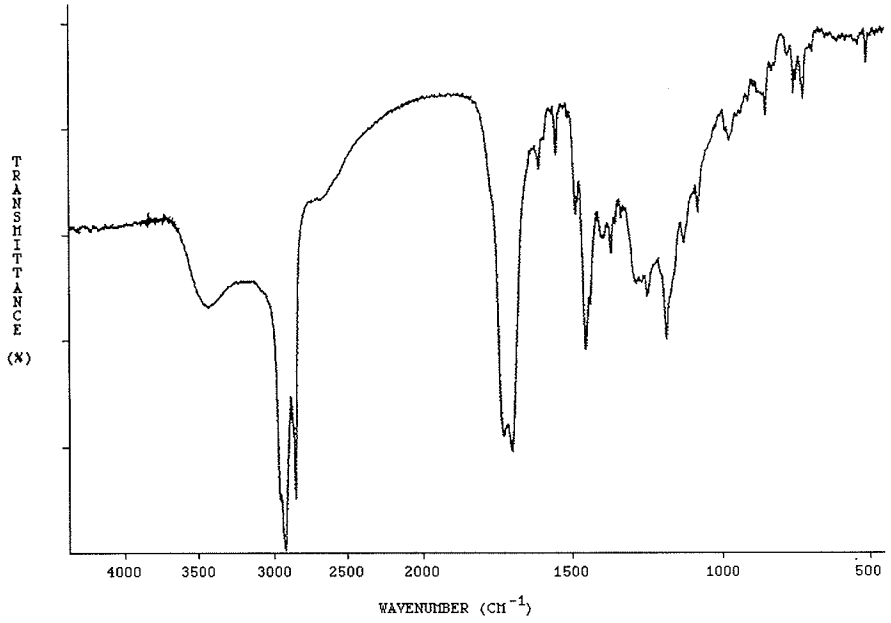


Figure 7: IR spectrum of the brown substance extracted with toluene from the brown paint of a column of JIZO-O-BYO

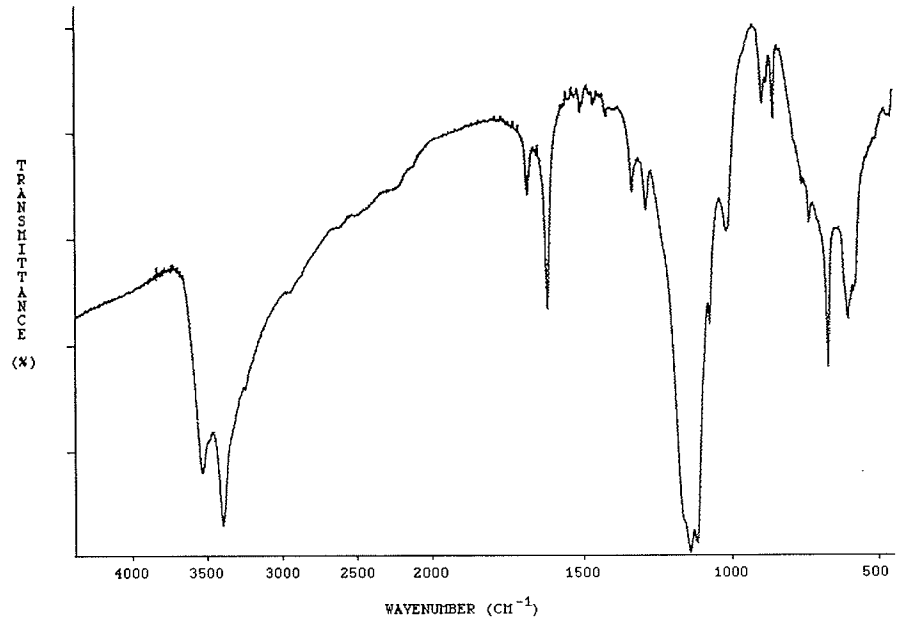


Figure 8: IR spectrum of the precipitant in the diluted sulfuric acid solution of the gouache colour of cerulean blue from our student's picture

## 3.9 Reference

1 WB White, "The carbonate minerals". In *The Infrared Spectra of Minerals* (VC Farmer, ed), 1974, pp 227-284, Mineralogical Society, London

2 RJ Gettens, EW Fitzhugh, and RL Feller, "Calcium carbonate whites". In *Artist' Pigments* vol.2 (A Roy, ed), 1993, pp 203-226, National Gallery of Art, Washington

3 RJ Gettens, RL Feller, and WT Chase, "Vermilion and cinnabar". In *Artist' Pigments* vol.2 (A Roy, ed), 1993, pp 159-182, National Gallery of Art, Washington

4 The reference spectral library was supplied together with the FTIR spectrometer by Perkin Elmer

## Appendix. Instrument and measurement of spectra

Spectra were recorded using Perkin Elmer 1600 Series FTIR spectrometer. Samples were prepared with the KBr pellet method and spectra were collected as the sum of 64 scans at a resolution of 4 $cm^{-1}$ in the spectrometer purged with dry $N_2$ gas.

Authors

Yasunori MATSUDA, born in 1955, is an Associate Professor in the Department of conservation at Tohoku University of Art and Design, established in 1992, Yamagata, Japan. After he obtained his MA degree from Tokyo National University of Fine Arts and Music in 1981, he joined the Pearl Research Laboratory of K. Mikimoto Co., Ltd. where he mainly studied on analytical chemistry of natural materials, especially pearls and dye stuffs. He is currently interested in the identification and/or characterization of fresh and deteriorated materials of art objects using FTIR and 3-D fluorescence spectroscopy.

Masahiko TSUKADA, born in 1966, is a Research Assistant in the Department of conservation at the Tohoku University of Art & Design. He obtained a BSc in chemistry from the Jochi University in 1990. In the following two years he studied the restoration of paintings and the analysis of materials applied for the paintings in Florence, obtaining a Diploma from the Università Internazionale dell'Arte. In 1993 he obtained a MA in conservation science from the Tokyo National University of Fine Arts and Music. He is interested in the identification and characterization of organic materials.

# 4. Infrared spectroscopy - An analytical tool for conservators

Edward Then
National Museum of Science and Industry

## 4.1 Summary

Infrared spectroscopy is no doubt one of the most useful analytical tools available to conservators today. The popularity of the technique is reflected by the presence of the infrared users group (IRUG). One reason why it is becoming popular is because of its (nearly) nondestructive sampling techniques. With the advent of Fourier transform infrared (FTIR) spectrometers and improved sampling techniques, the scan speed and quality of the spectra have been improved tremendously. It is also one of the cheaper and more versatile techniques available for analysis.

Infrared spectroscopy is used by researchers working on conservation projects funded by the museum at Bristol University and London University. Among the materials identified with varying degrees of success using infrared techniques are organic components such as plastics and inorganic fillers.

This paper highlights some of the ways infrared spectroscopy can be used to help in the conservation of artefacts.

Paper not submitted for inclusion in the postprints.

Author

Edward Then graduated from the University of London in 1985 with a BSc (Eng) degree in Materials Science and Engineering. He was awarded his DPhil degree at Sussex University (School of Molecular Sciences) in 1989, where he also worked as a research fellow for two years. In 1992 he joined the conservation department at the Victoria and Albert Museum, London, as a Plastics Conservator. He joined the newly formed conservation section at the Science Museum in 1993 as the Senior Conservator for New Materials. Dr Then is also corporate member of the Institute of Materials (MIM).

# 5. Identifying archaeological jet and jet-like artifacts using FTIR

Siobhan Watts and A Mark Pollard
Department of Archaeological Sciences, University of Bradford

## 5.1 Summary

Recent work has illustrated the problems with identifying the various materials that were used to make black lithic ornaments in the past. The different materials that were worked include jet, cannel coal, oil shale, lignite and solidified bitumens - all of these originate from sedimentary deposits rich in organic material. Fourier Transform Infrared Spectroscopy (FTIR) has shown potential as a technique for identifying the materials; the analysis of geological samples from different material types produces distinctive spectra which can be related to their geological depositional environment, based on their chemical composition.

This paper will discuss the problems encountered when the method is applied to archaeological material; the artifacts are often small and intricately carved, so that they are difficult to sample. Where artifacts have been conserved, the resins used for conservation produce an infrared spectrum which can mask the spectrum from the original material. This problem is lessened when the resin is identified and spectral subtraction methods are used to remove its IR spectrum from that of the jet or jet-like material. Oxidation of jet and coals in the archaeological burial environment can also alter their characteristic infrared spectra, and affect the success of FTIR as a discriminating technique. The results of FTIR analyses from two archaeological assemblages - from York and Verulamium - will be discussed to illustrate these points.

## 5.2 Abstract

Recent work has illustrated the difficulty of identifying the various materials that were used to make black lithic ornaments in the past. The materials which were worked all originate from sedimentary deposits rich in organic material. Fourier transform infrared spectroscopy has shown potential as a technique for identifying the different materials. The analysis of geological samples from the various sources produces distinctive spectra, which can be related to their geological depositional environment, based on their chemical composition. The IR spectra of the various raw materials are discussed in this paper, together with the problems encountered in analysing archaeological artefacts using FTIR. The results of FTIR analyses of artefacts from Verulamium and York are used to illustrate some of these problems.

## 5.3 Introduction

Jet is one of a range of different black lithic materials that were used to make jewellery and ornaments in the past. Other materials that were worked include cannel coal, oil shale, lignite, and solidified bitumens - all of which originate from sedimentary deposits that are rich in organic material. When polished, the various materials are difficult to distinguish, and in recent years there has been considerable interest in finding reliable methods to identify and provenance them [1,2,3,4,5,6,7,8]. Fourier transform infrared spectroscopy (FTIR) showed promising results in a recent pilot study [6] - geological samples of the different materials produced distinctive spectra. Our investigation of FTIR as an identification method is part of broader research into reliable techniques for analysing archaeological jet and jet-like materials. The aims were to try and understand the infrared spectra produced by the different materials in terms of their geological depositional environment, and to apply the method to archaeological artefacts.

### 5.4 Approaches to identifying archaeological jet-like materials

Previous research into identifying these black lithic materials has approached the problem in three different ways. Much of the work has concentrated on studying the inorganic elemental characteristics of jet and the other organic-rich rocks [1,6,7]. X-ray fluorescence, often in conjunction with X-radiography, has been used to discriminate between the different materials. This approach has many advantages, in that it is an inexpensive, quick, accessible and non-destructive method for studying archaeological assemblages. Iron is the main discriminant, since jet is almost pure organic material, whereas cannel coals and oil shales contain some minerals, so tend to have much higher iron levels than jet. However, the mineral contents of the different materials can be variable, so that the technique is often limited to identifying broad categories of material, such as 'jet', 'shale' and 'intermediate' [6].

Petrological and palynological methods have also been applied, to identify the material type microscopically, and to extract the spores from the rock, and find out which geological horizon it belongs to [5,8,9]. In certain specific cases this approach has proved extremely informative, and has provided precise provenances for individual artefacts. The disadvantages with these methods are that they require access to specialist equipment and expertise which is expensive for analysing whole assemblages, as well as needing large samples which are too destructive for many of the small, delicate ornaments that were made from jet-like materials.

Organic chemical methods have been used to characterise the organic components of the different materials. The methods applied include electron spin resonance 6,10 nuclear magnetic resonance [11], pyrolysis-gas chromatography/mass spectrometry [12], and Fourier Transform infrared spectrometry [6,13]. Chemical differences between the organic matter in these materials should prove more reliable for identifying them, since the nature of the organic matter is directly related to the original precursor organisms, and their environment of deposition. Apart from electron spin resonance, which produced disappointing results [6], the initial research has proved promising. Until now, this approach has been limited to pilot studies which analysed geological samples. This is the first time FTIR has been used to identify assemblages of archaeological jet-like artefacts.

### 5.5 Geology and geochemistry of organic sedimentary deposits

An understanding of the geochemistry of the various sources of black lithic materials is essential for interpreting their infrared spectra. These materials were selected for creating ornaments because they are rich in organic carbon - usually in a waxy or oily form - which makes them easy to carve, and gives them a good polish. Coals and other organic-rich rocks can be studied microscopically, and the different components identified provide information on the original type of organic matter deposited, the environment of its deposition, and the maturity of the sediment. All these factors affect the chemical composition of the resultant material, so that petrological characterisation is an important technique for coal and fuel scientists.

The geological samples used in this study were selected from a reference collection of over 100 samples, held at the University of Bradford for research on jet and similar materials. Organic petrological methods were used to study the nature of the organic material in the different geological sources, and this information was applied to the interpretation of the infrared spectra.

The microscopic constituents of coals, and other organic-rich rocks, can be distinguished by their shape and colour. The different constituents are known as coal macerals, and they are analogous to minerals in inorganic rocks. Coal macerals can be divided into three groups, each of which share some broad similarities in terms of their chemical composition [14].

Vitrinite originates from plant cell walls, and woody tissues. It tends to have a high oxygen content, and is composed of humins with aromatic nuclei surrounded by aliphatic functional groups.

Inertinite often originates from similar plant material to vitrinite, but has been oxidised at an early stage - either by increased oxidative degradation, or possibly sometimes by fire. It is rich in carbon, in the form of concentrated aromatic structures.

Liptinite which encompasses all the waxy and fatty components of plants - spores, leaf cuticles, resins and algal material. Liptinites have a high hydrogen content and are rich in aliphatic carbon. The rocks selected for carbon often contain concentrations of liptinites, since their waxy nature results in a good polish. Liptinites usually fluoresce when illuminated with ultra violet or blue light, so that fluorescence microscopy has become a standard technique for examining coals and oil shales [15].

The infrared spectra produced by the different jet-like materials should be a function of their component macerals. Coals and oil-shales also contain variable amounts of mineral matter, and some of these minerals also produce characteristic absorption peaks in the infrared spectra. By comparing the results of the petrological work on geological samples, to the infrared spectra from the same samples, we should obtain some information on how to interpret the infrared spectra produced by archaeological artefacts to identify the material from which they are made.

**5.6 Experimental**

The geological samples were ground in a ball mill to a particle size of 75 mm or less. 0.4 mg of the pulverised sample was mixed with 15 mg of KBr, and compressed to form a disc. The KBr discs were analysed on a Perkin Elmer 1720-X Infrared Fourier Transform Spectrometer, using Perkin Elmer IRDM software. Samples were scanned 20 times over wavenumbers 4000 $cm^{-1}$ to 400 $cm^{-1}$, at a resolution of 4 $cm^{-1}$.

The constraints on sampling the archaeological artefacts meant that the samples taken were too small to pulverise in a ball mill, before mixing with the KBr. This is discussed below, section 5.8.1

## 5.7 Characterisation of geological samples

Infrared spectroscopy has a long history in the study of the chemical composition of coals and other organic-rich rocks [16,17]. FTIR spectroscopy has been widely applied to study the chemical changes that occur with increasing rank, and the variations in aromatic:aliphatic ratios and the functional groups present between different coal macerals [18,19,20,21,22,23]. The assignment of absorption bands to particular structures given here are based on this work, and are summarised in table 1.

### 5.7.1 Whitby jet

Jet is formed from discrete pieces of wood which have been washed into the sea, and have settled in the sea bed. As the sediment accumulated, marine planktonic material deteriorated to produce fluid hydrocarbons, which impregnated the degraded wood structure. Whitby, in North Yorkshire, is the most well-known, and certainly the most abundant source of British jet. Under the microscope, the woody structure of this jet is still visible, in a highly compressed form, so the jet appears to be almost pure vitrinite. However, under blue light excitation, the whole jet structure fluoresces, showing the presence of this oily material.

The infrared spectrum of Whitby jet shows a combination of aliphatic and aromatic structures (figure 1). The aromatic groups are indicated by the aromatic C-H stretch at 3030 $cm^{-1}$, a shoulder at 1500 $cm^{-1}$ which is the aromatic C=C stretch, and the C-H deformations between 900 and 700 $cm^{-1}$, which are due to the different substitutions on the aromatic ring. The band at 1600 $cm^{-1}$ is very characteristic of coals and is usually thought to an aromatic ring stretch, possibly enhanced by the presence of phenolic groups [23].

Aliphatic C-H stretches occur as strong bands just below 3000 $cm^{-1}$ with the aliphatic C-H deformation at about 1430 $cm^{-1}$. Other absorptions that can be seen are the O-H stretch between 3700 and 3100 $cm^{-1}$, and the complex bands arising from the C-O stretch between about 1300 and 1000 $cm^{-1}$.

### 5.7.2 Lignite

Lignite is an immature coal which has passed through the peat stage in the coal series, but has not yet developed into bituminous coal. It has a high water and volatile content, so that the lower rank lignites tend to dry out and crack when exposed to the atmosphere. It is the black lignites, which are closer to the sub-bituminous coals, that are thought to have been worked in the past. Its microscopic structure is similar to jet, although the wood tissues appear less compressed.

The infrared spectrum of lignite is similar to the Whitby jet spectrum, but lignite shows a broader and more pronounced O-H stretching band between 3700 and 3100 $cm^{-1}$, as well as a band at 1700 $cm^{-1}$ from C=O bonds in carbonyl and carboxylic groups (figure 2). These bands are evidence of the lower rank of the lignite; as coals mature, the O-H and C=O groups are eliminated [24].

These results were initially encouraging; it is difficult to distinguish between jet and lignite based on their elemental characteristics [7], so if the 1700 $cm^{-1}$ absorption in the FTIR spectra of lignites could be used differentiate them from jet, then the technique would be an improvement on identification methods based on inorganic elemental analysis.

5.7.3 Cannel coal

Cannel coals have a very different micro-structure to jet and lignite. They are formed from finely comminuted organic debris, which settles in stagnant pools on the edge of coal swamps [25]. In these conditions the liptinites are preserved, as they are more resistant to decay. The remains of spores, leaf cuticles and algal bodies can be clearly observed with the petrological microscope, and they are usually embedded in a groundmass of micrinite - a granular inertinite maceral which is described as polymerised resin [8].

The FTIR spectrum from cannel coal (figure 3) shows a less aromatic character than the jet - presumably because it lacks the concentrated wood-derived structures that are found in jet and lignite. The 1500 $cm^{-1}$ band is absent, the aromatic C-H deformations between 700 and 900 $cm^{-1}$ are less well defined, and mineral absorptions from alumino-silicates are sometimes present at 1030 $cm^{-1}$ below 600 $cm^{-1}$.

5.7.4 Oil shale

The term 'oil shale' can include any sedimentary rock with over 10% organic carbon, but those selected for carving and making ornaments would have been extremely rich in organic material, otherwise they would have disintegrated when they were worked. In Britain, there is one particular organic-rich seam that outcrops in the cliffs at Kimmeridge in Dorset - known as the Kimmeridge shale, or Blackstone. This seam was worked extensively in the past, and concentrations of the working debris are found on Iron Age and Roman sites in the area [26,27].

The Kimmeridge oil shale was formed in anaerobic sediments at the bottom of a shallow marine environment. The organic material is probably derived from marine planktonic organisms which are so degraded that they cannot be distinguished microscopically [5,28]. The Kimmeridge shale appears under the microscope as a groundmass of intermixed clay mineral and organic material together with grains of quartz, calcite and other minerals. The groundmass shows strong fluorescence when illuminated with blue or ultra-violet light, and this fluorescing organic matrix is termed bituminite, and is classified as a liptinite maceral [15].

The infrared spectrum from Kimmeridge shale shows absorptions from aliphatic structures, and sharp absorptions in the free O-H stretching region (figure 4). It also has very strong mineral absorptions at 1420 $cm^{-1}$ from carbonate, and at 1030 $cm^{-1}$ and below 600 $cm^{-1}$ from silicates and alumino-silicates.

The oil shale at Kimmeridge has also been the source of occasional seams of jet.

Although the jet does not occur in anything approaching the quantities of the jet at Whitby, it is likely that any jet found at Kimmeridge whilst the surrounding shale was worked would also have been used for making ornaments.

5.7.5 Kimmeridge jet

Kimmeridge jet has a similar microscopic structure to the Whitby jet - although it does not show the same fluorescence intensity when illuminated with ultra-violet or blue light. The infrared spectrum of the Kimmeridge jet is similar to the spectrum from Whitby jet, except for a sharp absorption at about 1500 $cm^{-1}$ (figure 5). This absorption is assigned to an aromatic C=C stretch, and is present as a characteristic shoulder in the Whitby jet, but it is rarely seen on other coals. A comparison of the IR spectra of Whitby jet, cannel coal, and Kimmeridge jet (figure 6) illustrates the variation in the 1500 $cm^{-1}$ absorption.

FTIR studies comparing jet and other high volatile vitrinites from Spain has demonstrated that the absorption band at 1500 $cm^{-1}$ is an unusual feature of the infrared spectra of these types of coal [19,29]. A sharp absorption at 1500 $cm^{-1}$ was also observed in the spectrum of jet from Utah in the USA.13 Iglesias et al [19] explain this absorption in terms of a different type of substitution on the aromatic ring structures in hydrogen-rich coals such as jet. The intensity and the exact position of the aromatic C=C stretch is dependant on the substitution patterns and the degree of condensation of the aromatic ring. The aromatic structures in these hydrogen-rich coals are thought to have different substitution patterns to other coals, which produces the sharper absorption at 1500 $cm^{-1}$.

The Whitby jet originates from more mature sediments than the Kimmeridgian sediments, so that the wood structure of Whitby jet has been impregnated by fluid hydrocarbons from the parent shales. A detailed comparison of the organic geochemistry of these two sources of British jet has shown the different chemical nature of the mature Whitby jet using py-GCMS [12]. The variation in the absorption intensity of the 1500 $cm^{-1}$ band presumably reflects this difference in maturity; the immature hydrogen-rich vitrinite analysed by Suárez-Ruiz et al [29] likewise produced a more intense, sharper absorption in the 1500 $cm^{-1}$ region (similar to the spectrum from Kimmeridge jet) than the more mature Spanish jet.

This work on FTIR analyses of geological samples was promising. As in the earlier pilot study by Hunter et al [6], the different materials produced spectra which were distinct from each other, and the differences noted in the IR spectra could be explained by the various organic precursors and depositional environments that were inferred from the microscopic examination. The next stage was to find out whether this information could be usefully applied to identifying the archaeological artefacts from their infrared spectra.

## ABSORPTION BANDS IN THE IR SPECTRA OF COALS

| Wavenumber ($cm^{-1}$) | Assignment |
|---|---|
| 3300 | hydrogen-bonded OH |
| 3030 | aromatic C-H stretching |
| 3000-2700 | aliphatic C-H stretching |
| 1700, 1650 | C=0 stretch |
| 1600 | aromatic C=C<br>- poss. enhanced by phenolic groups |
| 1500 | aromatic C=C |
| 1450 | $CH_2$ and $CH_3$ bending |
| 1420 | carbonates |
| 1375 | $CH_3$ groups |
| 1030 | silicates |
| 900-700 | aromatic C-H out-of-plane bending |
| 400-600 | silicates |

Table 1: band assignments

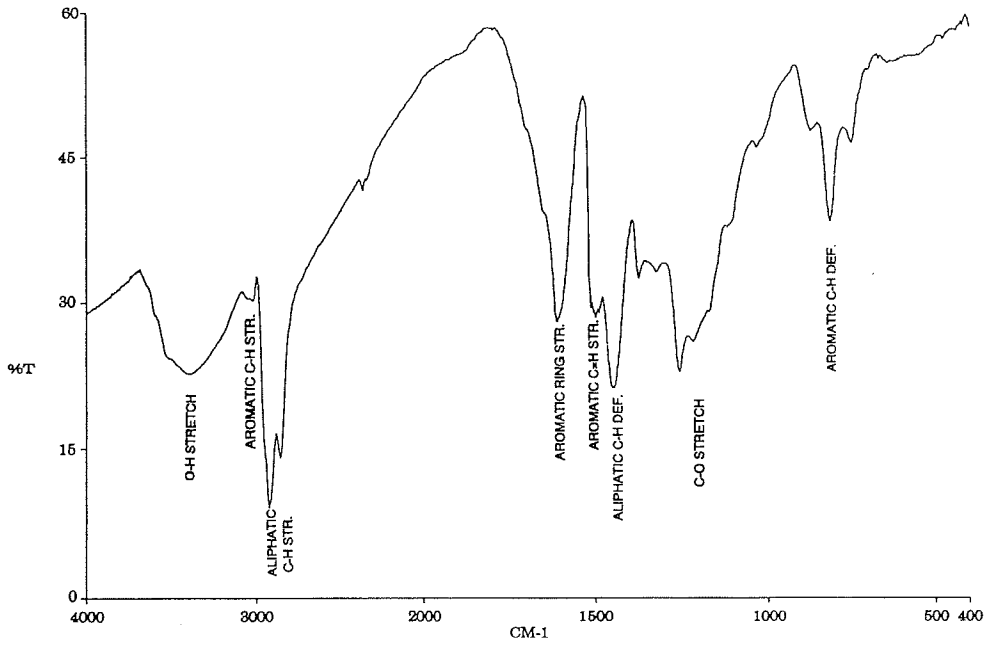


Figure 1: FTIR spectrum of Whitby jet

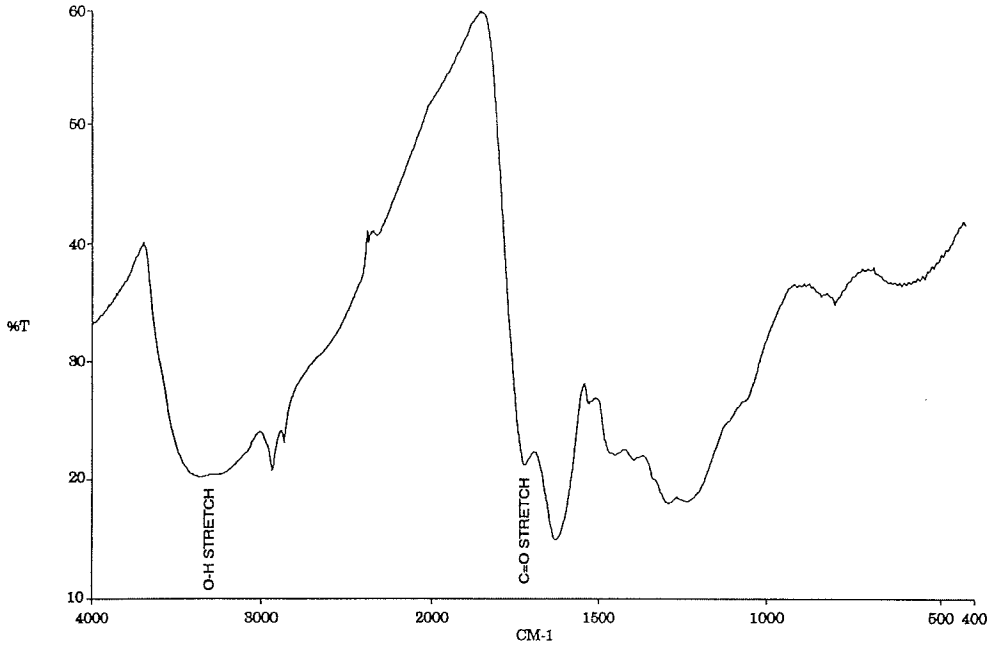


Figure 2: FTIR spectrum of lignite

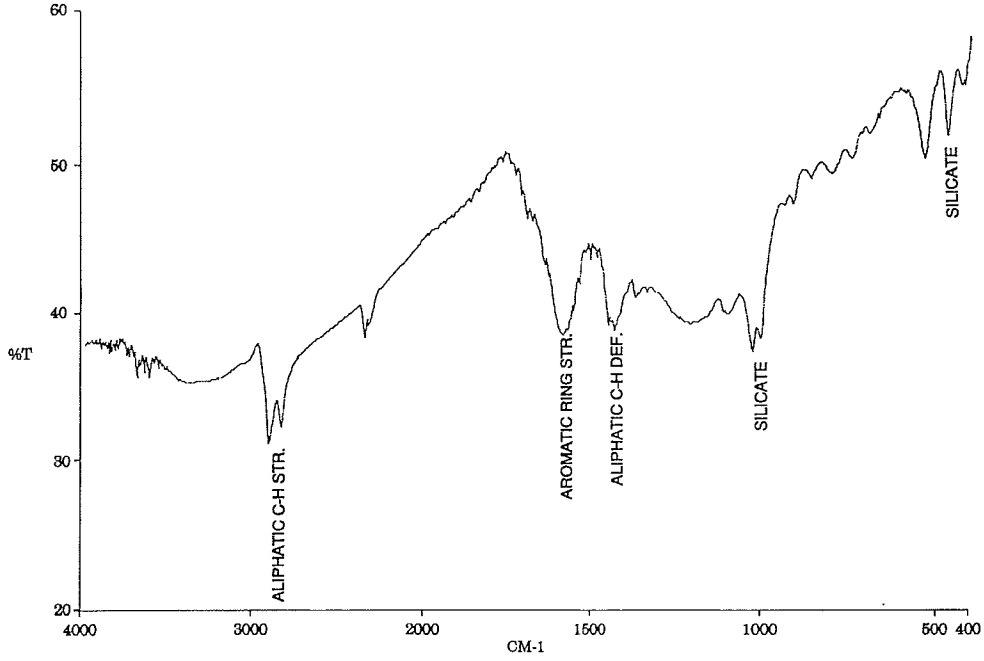


Figure 3: FTIR spectrum of cannel coal

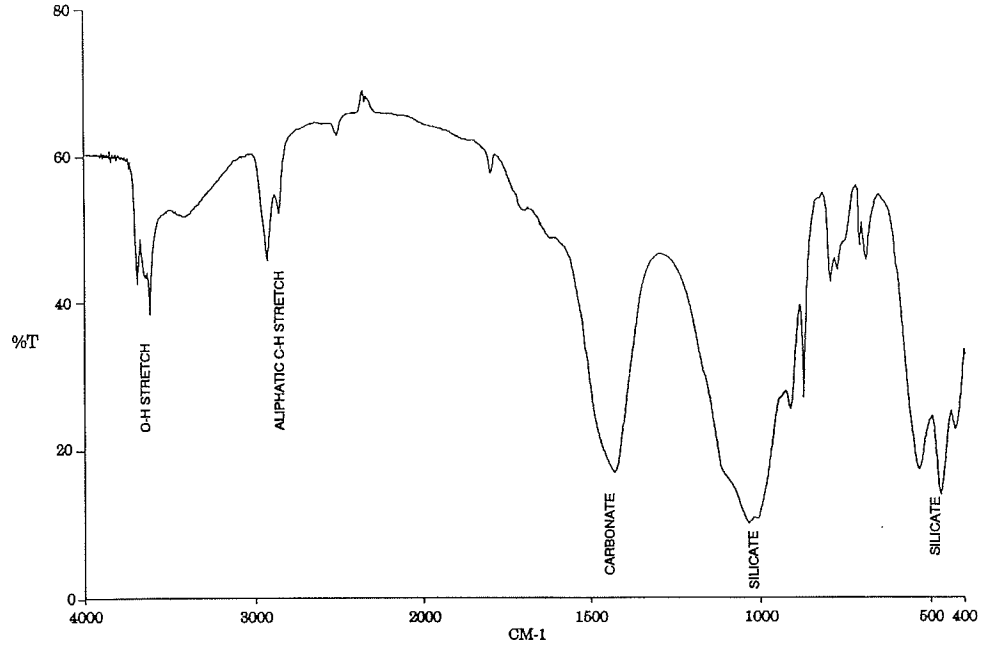


Figure 4: FTIR spectrum of Kimmeridge shale

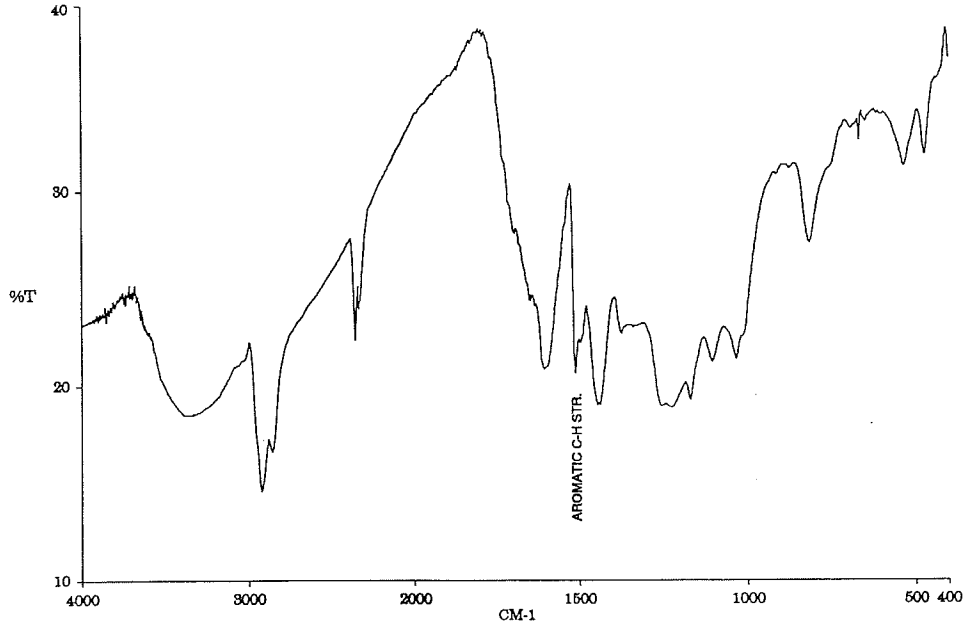


Figure 5: FTIR spectrum of Kimmeridge jet

## 5.8 FTIR analyses of archaeological assemblages

The artefacts analysed were from sites in two major military and civilian centres during the Roman period: Verulamium and York. It was hoped that results from the two different centres of Roman activity would provide a useful contrast for understanding the use of the various black lithic materials. York is close to the major British source of jet at Whitby, and the discovery of partly worked fragments of jet or similar materials has led to the suggestion that it was an important centre for the manufacture of these ornaments [30].

In total, 107 archaeological examples of black lithic materials were analysed using FTIR: 29 from York and 78 from Verulamium. There were several factors to be taken into account when analysing the artefacts, so that interpreting the infrared spectra to identify the different materials proved to be more difficult than the results from geological material had suggested.

### 5.8.1 Sampling methods

The archaeological material analysed ranged from large unworked and semi-worked fragments, to broken armlets, and small, complete, intricately carved beads. It was not possible to follow the same procedure that had been used for analysing geological samples (i.e. carefully quantified KBr discs prepared from homogenised samples of the raw material). Where possible, a small sample was removed with a scalpel from a broken edge, and ground by hand together with the KBr. Even this method would have been too destructive for many of the complete beads and pins. Some of the smaller artefacts from Verulamium were analysed using an infrared microscope, at the School of Chemistry and Applied Chemistry, University of Wales College of Cardiff. The constraints imposed on the sample preparation by the nature of the artefacts often resulted in spectra with much poorer resolution.

### 5.8.2 Effect of conservation resins on the IR spectra

Many of the artefacts analysed had been conserved, and impregnated with various consolidants. The conservation materials produce their own characteristic absorption peaks in the IR spectra from the artefacts. One of the consolidants frequently used was easily identified as polyethylene glycol 4000 (figure 7), which is one of the published methods for the treatment of deteriorating shale artefacts [31]. When the consolidant can be identified, it is possible to use spectral subtraction methods to remove the absorption peaks from an artefact's IR spectrum. Figure 8 shows the same spectrum as in figure 7 but with the PEG 4000 spectrum subtracted, leaving an absorption pattern which is much closer to that of an oil shale (figure 4).

Several artefacts showed unusual peaks which were not attributable to any of the conservation materials that are commonly used to treat jet and jet-like artefacts. In particular, many of the Verulamium artefacts had been excavated in the 1930's, 1940's and 1950's, so there was no record of the conservation treatment applied. A search of the library compiled by the Infrared Users Group may help to solve this problem, and identify the more elusive conservation resins.

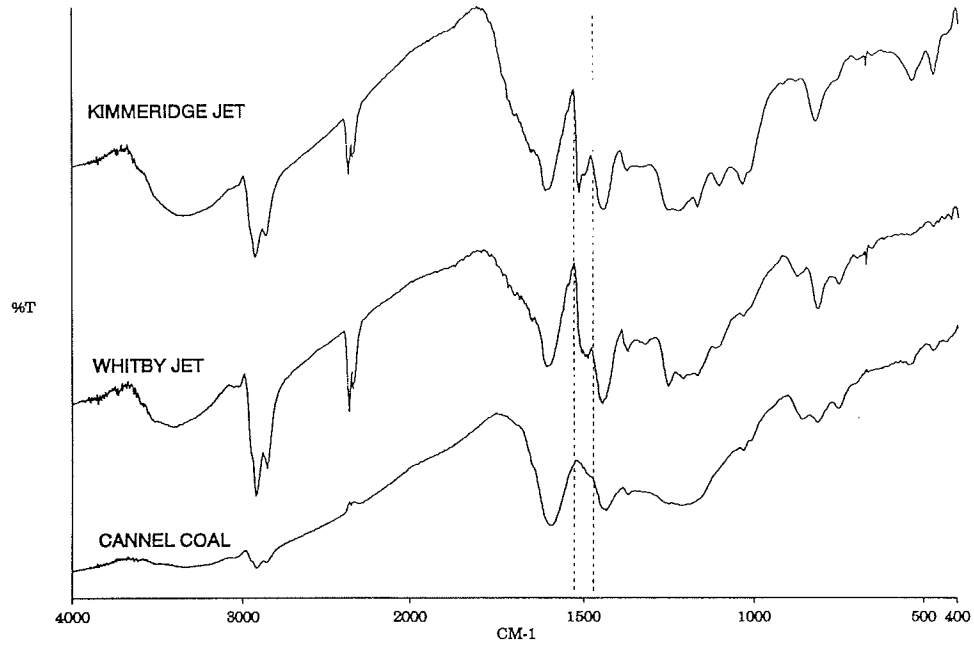


Figure 6: Comparison of the FTIR spectra of Kimmeridge jet, Whitby jet and cannel coal, showing the differences in the 1500 $cm^{-1}$ absorption

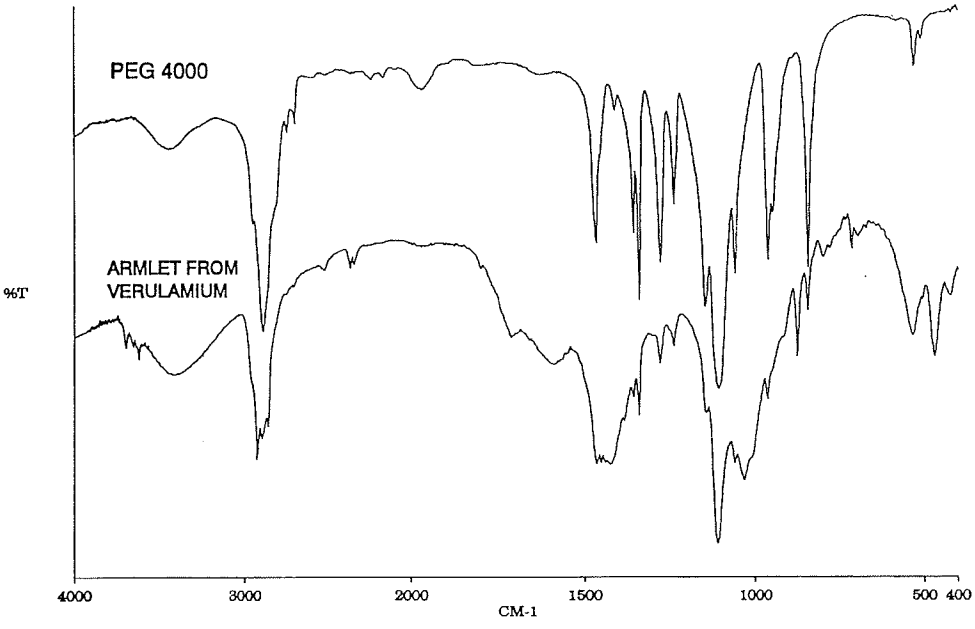


Figure 7: FTIR spectrum of a shale armlet which has been consolidated with PEG 4000

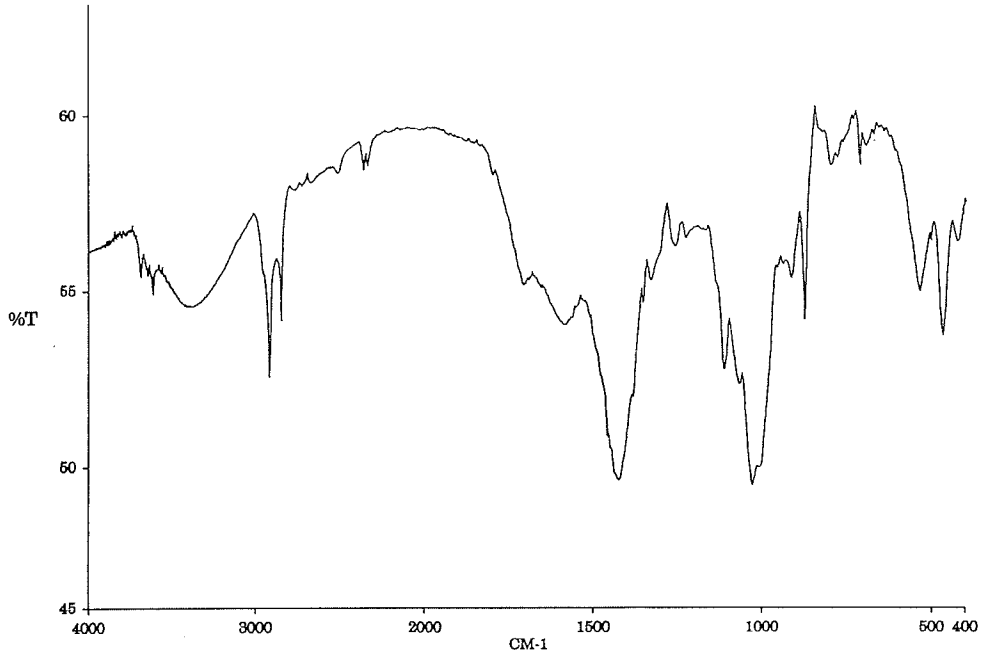


Figure 8: The same spectrum as in figure 7, with the PEG 4000 spectrum subtracted. The spectrum is now almost identical to the FTIR spectrum of an oil shale, shown in figure 4

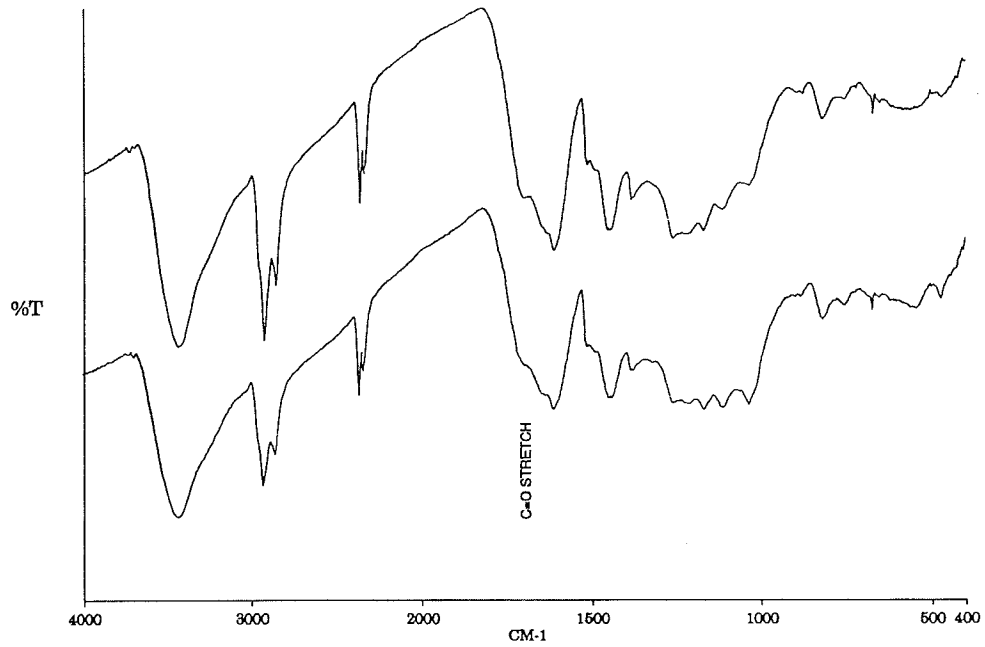


Figure 9: FTIR spectra of two artefacts from Verulamium, showing a C=O stretch at 1700 $cm^{-1}$, which is probably the result of oxidation of the jet

5.8.3 Oxidation of jet in the burial environment

One problem encountered in analysing archaeological jet-like artefacts has proven more difficult to monitor - and that is the changes to their chemical structure that take place in the burial environment. All the geological samples of Whitby jet analysed produced virtually identical, characteristic infrared spectra. None of the spectra from either the Verulamium or the York artefacts matched the Whitby jet spectra. Some were extremely close - such as the two illustrated in figure 9, which show the same combination of aromatic and aliphatic absorptions, and the characteristic shoulder at 1500 $cm^{-1}$. However, both spectra also show a marked absorption at 1700 $cm^{-1}$ - a peak which usually appears in the spectra of lower rank coals, and is one of the discriminants used to identify lignite. Carbonyl peaks at around 1700 $cm^{-1}$ also occur in the spectra of more mature coals that have oxidised. Detailed studies of oxidised coals have noted absorptions from carbonyl groups in the spectra of coal samples from near the mouth of a coal adit, as well as in the spectra of coals oxidised in the laboratory [32,33].

The samples taken from archaeological artefacts are necessarily very small, and from the surface of the artefact - which is the area most likely to have oxidised and to show the absorption from carbonyl peaks. These changes have made it difficult to distinguish jet from lignite amongst the archaeological assemblages; this is disappointing, since these two materials are also difficult to distinguish using X-ray fluorescence [7]. It is clear that more work is needed to monitor the changes in the IR spectra of the different materials that occur during burial. Low temperature air oxidation of samples in the laboratory may be one method of determining whether it is possible to distinguish between materials such as jet and lignite amongst the archaeological assemblages.

## 5.9 Conclusions

The initial FTIR characterisation of the geological reference material was promising, since the spectra could be interpreted in terms of the different geological depositional environments.

FTIR analyses of archaeological assemblages from Verulamium and York has enabled the artefacts to be classified into three groups: jet/lignite, cannel coal and oil shale. Distinguishing between jet and lignite proved to be difficult, partly because limitations in the sample size and preparation methods led to poor resolution, and partly because the jet appears to have oxidised, producing absorptions in the 1700 $cm^{-1}$ region, which are usually characteristic of lignite.

A better understanding of the chemical changes taking place during burial in an archaeological environment may enable us to identify the material types more precisely using FTIR. The problems of poor resolution were improved by using the FTIR microscope; it seems that infrared microscopy is a more suitable technique for the analysis of archaeological artefacts, since the sample size required to obtain good spectra is minimal.

**5.10 Acknowledgements**
Thanks are due to the Museum of Natural History and Archaeology, Trondheim, for a travel grant to attend the IRUG seminar. The archaeological artefacts analysed were from Verumlamium Museum and the York Archaeological Trust for Excavation and Research, and we are grateful to Vivienne Holgate of Verulamium Museum, and Dr H. Cool (formerly of Y.A.T.) for organising access to the collections. We are also grateful to Neil Tyers and the IRC polymer science research group at Bradford University, for use of the FTIR; to Dr S Hardman and the School of Chemistry and Applied Chemistry, University of Wales College of Cardiff, for access to and help with the IR microscopy; to Dr C Heron for discussions of the interpretation of the IR spectra; to Dr RV Tyson (Postgraduate Institute of Fossil Fuels and Organic Geochemistry University of Newcastle-upon Tyne), Dr R Clements (Department of Earth Sciences, University of Leicester) and Mr G Mulholland (Department of Earth Sciences, University of Sheffield) for providing geological samples, and also to Dr JM Jones, Dr AHV Smith and Dr RV Tyson for help and advice with the organic petrology; to Dr M Teichmüller for access to her work on jet-like artefacts from Germany, and to Mr M Nutbrown (Department of Biomedical Sciences, University of Bradford) for help with the fluorescence microscopy. SW acknowledges the support of a studentship provided by the Science and Engineering Research Council and now the Natural Environment Research Council.

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Siobhan Watts obtained her BA (Hons) in Classics from New Hall, Cambridge in 1989. She received an MA in the Conservation of Historic Objects (Archaeology) from Durham in 1992 (including a one year placement at the Ancient Monuments Laboratory, English Heritage). She then became a research student at Bradford University, Department of Archaeological Sciences, researching analytical methods for identifying archaeological jet and jet-like materials since 1993. During this time she has also spent a year working as an archaeological conservator for the Museum of Natural History and Archaeology in Trondheim, Norway.

# 6. FTIR microscopic studies on organic materials used for cultural properties

Masanori SATO and Masaaki SAWADA
Nara National Cultural Properties Research Institute

## 6.1 Summary

The identification of several kinds of ancient organic materials is one of the important subjects in the field of conservation study as well as archaeology. Specimens usually decompose under several conditions of preservation. Also, the quantity of samples that can be examined is minimal. As a result of recent improvements in instruments, FTIR microscopy has become a promising method of analysis having a sufficient sensitivity for the investigation of organic materials in the above-mentioned situations.

This paper describes several aspects of investigations of textile materials (wool, silk, hemp, ramie), leather, natural dyestuff and Japanese lacquer ("Urushi").

Under good conditions of preservation, silk fibres used for clothes (6th C) showed distinct spectrum corresponding to amide I and II. On the contrary, fibres attached to the surface of iron or copper articles completely lost organic characteristics and were estimated to be substituted with metallic oxide, though they still showed fibre-like appearance. A very small sample collected from a part of iron armour (6th C), showing a completely rusted appearance, had a spectrum corresponding to an animal component (amide I and II).

A large amount of textiles found at the 12th C site were covered with black material. FTIR investigation confirmed that the fibre material was of ramie and the black material at the surface of the fibre was of Japanese lacquer.

The fibre quality of wool carpet ("Kasen") having been stored in Shoso-in (8th C) was compared with that of modern animal hairs of several species. Though the results using an electron scanning microscope showed that the quality of ancient fibre was very good and comparable to that of modern production, FTIR investigation revealed distinct difference between spectra of ancient wool and modern ones.

Paper not submitted for inclusion in postprints.

Presenting author

Masanori SATO graduated from Kyoto University Faculty of Science in 1954. He was awarded his Doctor of Science (Kyoto University) in 1959. In 1978, he became Professor of Kyoto Institute of Technology, Faculty of Textile Science. He is currently a guest researcher at the Conservation Science Laboratory, Nasa National Cultural Property Research Institute.

# 7. IR reflectance spectra of weathered medieval stained glass

Manfred Schreiner
Institute of Chemistry, Academy of Fine Arts, Vienna

## 7.1 Summary

In medieval glass paintings stained window panes of potash-lime-silica glasses with low silica contents and high amounts of $K_2O$ and CaO were used. During the natural weathering of that type of glass water and/or aqueous solutions of air pollutants are present on the glass surfaces due to condensation or precipitation. An ion exchange mechanism takes place, where the alkaline and earth alkaline glass components are leached and hydrogen bearing species are incorporated into the silicate structure according the chemical reaction

$$Si\text{-}O^-M^+ + H^+_{aq} \leftrightarrow Si\text{-}OH_{aq} + M^+$$

As a consequence, a surface layer is formed: The structural changes in this layer can be analysed by using Infrared Reflectance Spectroscopy (IRRS) in the range 1300 - 700 $cm^{-1}$. The shift and the variations in intensity of the silicon-nonbridging oxygen vibrations and the silicon-bridging oxygen stretching bands at approximately 950 $cm^{-1}$ and 1050 $cm^{-1}$, respectively, can be detected.

Leaching experiments in various acidic solutions were carried out on several sample glasses with a chemical composition similar to medieval stained glass. The freshly polished and corroded glass specimens were measured in a single-beam FTIR spectrometer of Bruker, type IFS 113v. The measurements were performed at a grazing angle of 20° using a Perkin Elmer IRRS unit. The spectra were obtained using an aluminum mirror as a reference material and calculating the absorbance by Greenler's algorithm.

The IR measurements carried out on untreated glass specimens and samples treated in $10^{-4}$ and $10^{-2}$N $HNO_3$, HCl, $H_2SO_4$ and oxalic acid reveal an increase of the peak intensity at 1050 $cm^{-1}$ and a shift of the peak maximum to a higher wavenumbers during the leaching process. On the other hand the silicon-nonbridging oxygen vibrations at approximately 950 $cm^{-1}$ decrease in intensity and wavenumber. These results indicate the formation of a vitreous silicon and a greater amount of Si-bridging oxygens on the glass surfaces than in the bulk due to the condensation reaction.

$$Si\text{-}OH + HO\text{-}Si\text{-} \leftrightarrow \text{-}Si\text{-}O\text{-}Si\text{-} + H_2O$$

Paper not submitted for inclusion in postprints.

Author

Manfred R. Schreiner studied chemistry at the University of Technology in Vienna. In 1975 he obtained an engineering degree in chemistry. He was awarded a PhD in material science (hard metals, cemented carbides) in 1980 and went on to do a post doc at the University of California San Diego, researching on hydrogen storage in metals and intermetallic compounds. In 1981 he became assistant professor at the Institute of Chemistry at the Academy of Fine Arts in Vienna. In 1985 he went to the Fraunhofer Institute of Silicate Chemistry in Wuerzburg/FRG, researching in to deterioration of glass and other silicate materials. He was awarded a 2nd PhD (Habilitation) in analytical chemistry in art (application of surface analytical techniques for studying the deterioration process of medieval stained glass) in 1989 and is now Professor at the Institute of Chemistry at the Academy of Fine Arts. He is a member of IIC and ICOM

# 8. The use of a beam-condenser for micro analysis

David Thickett
British Museum

## 8.1 Summary

Infra-red spectroscopy is a powerful method of analysis and has found widespread use in the field of conservation research. By concentrating the energy of the infra-red beam through a small area, a beam-condenser allows very small samples to be analysed using infra-red spectroscopy without the expense of an infra-red microscope. When dealing with antiquities and objects of art, it is obviously desirable to remove as small a sample as possible. Also certain degradation processes produce only microscopic amounts of material, for example, efflorescences of soluble salts.

A diamond compression cell provides a convenient way to prepare micro samples for a beam-condenser. Also this is non-destructive to the sample and it can be used for further analysis. The diamond windows of the cell are inert and undergo no reaction with the sample. This can be advantageous with certain hydrated materials such as iron corrosion products which may become dehydrated when pressed into a potassium bromide disc, a common sample preparation method.

Various examples of successful and unsuccessful applications are presented.

## 8.2 Abstract

Infra-red spectroscopy is a powerful method of analysis and has found widespread use in the field of conservation research. When dealing with antiquities and objects of art, it is obviously desirable to remove as small a sample as possible. Furthermore, certain degradation processes produce only microscopic amounts of material. Concentrating the energy of the infra-red beam through a small area, using a beam-condenser allows very small samples to be analysed without the expense of an infra-red microscope.

A diamond compression cell provides a convenient way to prepare micro samples for a beam-condenser. This technique of sample preparation is non-destructive to the sample which can be used for further analysis. The diamond windows of the cell are inert and undergo no reaction with the sample. This can be advantageous with certain hydrated materials such as iron corrosion products which may become dehydrated when pressed into a potassium bromide disc, a common method of sample preparation.

The scope of the beam-condenser and diamond cell will be illustrated with several examples of analyses from objects in the British Museum collections.

## 8.3 Introduction

Infra-red (IR) spectrometry is a powerful and versatile method of analysis, and has been applied to a wide range of problems in both conservation research and art history [1,2]. At the British Museum it has been applied mainly to the analysis of organic materials.

When dealing with historic artefacts, non-interventive methods are obviously desirable. Although non-interventive techniques such as specular reflectance; diffuse reflectance Fourier transform IR spectrometry (DRIFTS) and IR reflectance spectrometry are available, their application has been limited due to constraints on the sample type for

the technique to be viable. Specular reflectance requires a thin layer on a shiny surface and has been used in the British Museum to analyse coatings on metal artefacts. The geometry of the DRIFTS accessory limits maximum sample sizes to a disk approximately 5 cm in diameter but has been successfully used to analyse coatings on oriental coins. IR reflectance spectrometry requires a flat reflective surface and has been applied to studies of glass deterioration [3]. However, the majority of analytical methods require the removal of a sample from the object. Such sampling should be as discrete as possible and the sample size should always be minimised. The introduction of interferometric Fourier transform spectrometers has reduced both the energy lost through the use of diffraction gratings (Jacquinot's advantage [4]) and the time required to collect a spectrum (Fellgett's advantage [4]). Hence several spectra can be collected and averaged, increasing the signal to noise ratio and significantly reducing the sample size required for IR spectrometry. The size of sample required to produce a useful spectrum depends on the extinction coefficient of the sample, but Table 1 gives a guide to the approximate sample sizes required for the techniques presently used in the British Museum.

| **Technique** | **Sample type suitable** | **Approximate sample size** |
|---|---|---|
| Potassium Bromide (KBr) Disc | most solids | 100$\mu$g |
| DRIFTS | brittle materials, coatings, inorganic powders | 100$\mu$g |
| Silicon Carbide on DRIFTS | brittle materials, coatings | 20$\mu$g |
| Specular Reflectance | coatings | 3 mm diameter |
| ATR | elastic materials, strongly absorbing liquids and powders | 7 cm |
| Beam-Condenser + KBr Disc | most solids | 12$\mu$g |
| Beam-Condenser + Diamond Cell | most solids | 5$\mu$g |

Table 1: IR sampling techniques

Table 1 shows that the use of a beam-condenser can significantly reduce the sample size required for transmission techniques such as the KBr disc method.

## 8.4 The apparatus

### 8.4.1 Beam-condenser

The beam-condenser (figure 1) consists of two sets of plane mirrors (A, B, E and F) to direct the IR beam onto the focussing mirrors (C and D) and back to the IR detector. The focussing mirrors are concave and elliptical and focus the IR beam from an approximately 8 mm diameter circle to a 2 mm diameter circle. This increases the energy density in the beam at focus by a factor of sixteen. However due to some attenuation from the mirrors, the beam has a resultant amplification of approximately ten.

The beam-condenser can be used with "micro" potassium bromide discs. These are 5 mm in, diameter as opposed to 13 mm for a normal KBr disc. The sample is ground with KBr and, pressed in a die to 2 tonnes pressure to produce the disc. Some care is required to ensure that, all of the sample is placed in the centre 2 mm of the disc, the area sampled by the IR beam. The disc is placed into a holder, which can be aligned in the IR beam using an x-y-z stage to accurately place the sample in the beam. A spectrum of Baltic amber produced by this method is shown as figure 2. A 15 mg sample was used, and the spectrum shows all of the characteristic absorptions of amber, with good definition in the 1100-1250 $cm^{-1}$ region, showing the shoulder at 1250 $cm^{-1}$, characteristic of amber from the areas around the Baltic sea.

One problem commonly encountered with the use of IR spectroscopy in conservation research is that many materials are mixtures of both organic and inorganic components. Techniques such as x-ray diffraction and scanning electron microscopy with energy dispersive x-ray analysis can be used to characterise the inorganic components. Organic components do not significantly interfere with these methods. However, it is often impossible to identify the organic component in such mixtures using IR, as the inorganic components absorption bands are stronger and very broad. It is therefore necessary to separate the components and this is usually achieved by extracting the organic component in a suitable solvent. This process often results in some loss of sample, and if the original sample size is small, detection limits become extremely important. If the solvent solution is dried onto a potassium bromide pyramid, figure 3, then the geometry of the pyramid causes the organic extract to concentrate at the tip as it dries. The tip can then be broken off, ground and pressed into a micro-disc. This method allows extraction with very little loss of sample.

### 8.4.2 Diamond cell

High pressure diamond anvil cells were first used for geological studies in 1960 [5], and their use was first proposed for conservation in 1975 [6]. Recently, more economically priced finger pressure cells have become available. These cells generate only moderate pressures, but these are sufficient for most of the sample types encountered during investigations for conservation purposes. A sample placed in the diamond cell is deformed to produce a thin film which is the ideal form for IR spectroscopy. Consequently the smaller sample size can be used. The diamond plates are inert; very little sample preparation is required; and samples can be easily manipulated on the

diamond plates.

The "Diasqueeze" diamond cell (figure 4) used at the British Museum consists of two matched, type IIA diamond plates. Each plate is mounted into a circular metal frame. The sample is placed between the two plates, which fit into a holder, with three small guide pins to keep the diamond plates parallel. A rubber "O" ring fits between the plates to regulate the pressure. The top piece of the holder is screwed down using finger pressure to compress the sample between the diamond plates to form a thin film. The diamond cell is placed in the beam condenser and the x-y-z stage aligned to achieve maximum energy throughput.

The diamond plates absorb strongly in the IR region (figure 5). Fortunately the major absorption bands occur between 1750 and 2500 $cm^{-1}$, where there are likely to be very few absorptions of interest when dealing with a sample, although this does slightly overlap into the region for carbonyl stretching absorption bands. The background spectrum of the diamond plates and of atmospheric carbon dioxide and water is first recorded and is then automatically subtracted from any subsequent spectra. This process is not perfect as the path of the IR beam through the diamond plates changes slightly as the plates are moved apart by the sample.

The choice of beam-condenser for use with a diamond cell is a compromise. A high factor condenser produces finer focus and higher energy density through the sample and therefore allows a smaller sample size. However it also increases the pathlength through the diamond plates, losing more of the energy in the process. A three times beam-condenser is reported to be the ideal for this application. Since this piece of equipment is not commercially available, a four times beam-condenser is used at the British Museum.

As with all micro-analytical techniques, contamination of the apparatus from previous samples is of concern. The diamond plates can be cleaned with a wooden spatula, viewed under magnification. Since in The British Museum IR is used predominantly for the analysis of organic materials, then residual material on the diamond plates can be detected by the presence of absorption bands around 3000 $cm^{-1}$ which are not normally present in the background spectrum of the diamond cell. If the wooden spatula does not clean the diamond plates fully, solvents can be used but care should be taken as aggressive or chlorinated solvents can remove the adhesive used to hold the diamond plates in place.

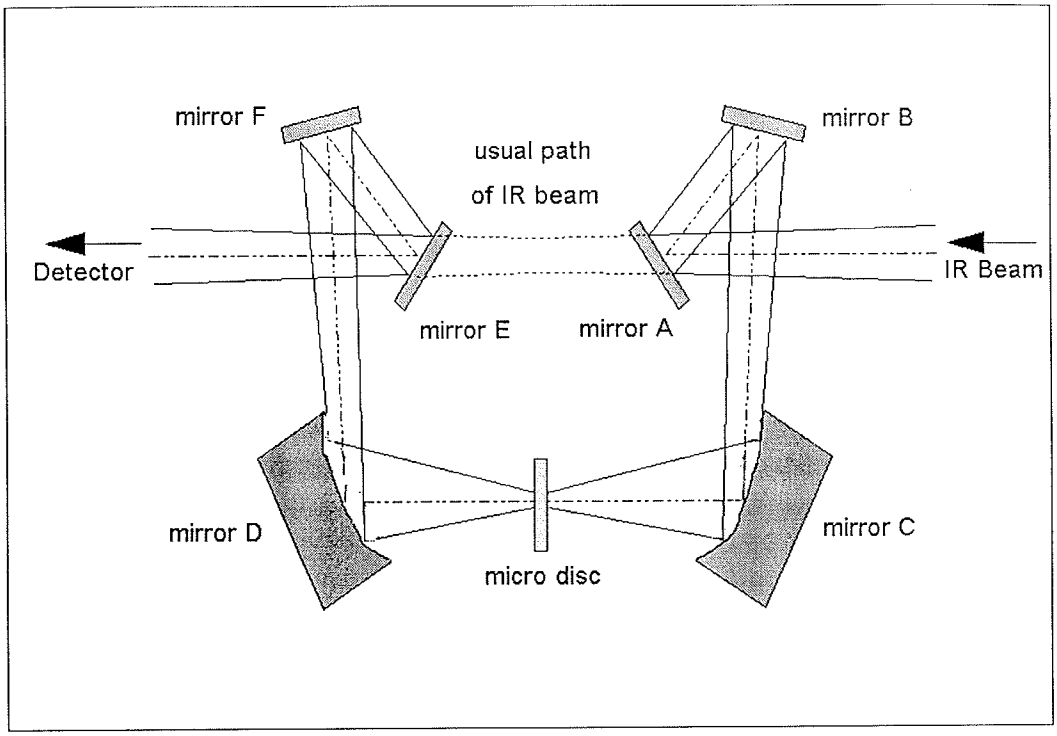


Figure 1: beam-condenser

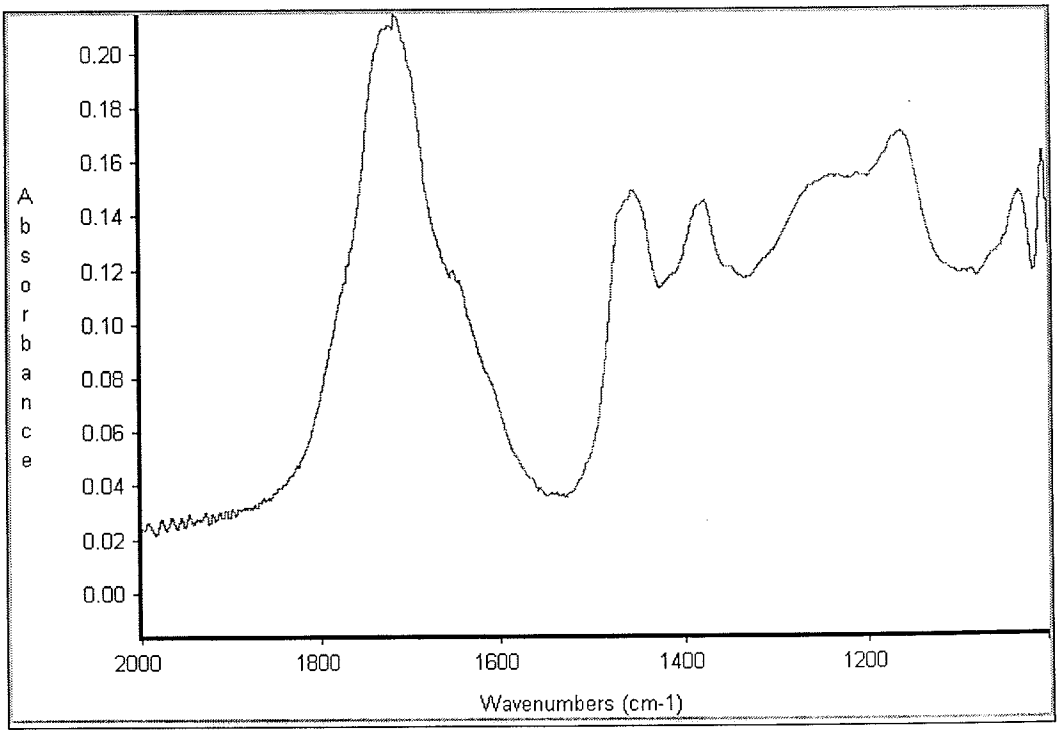


Figure 2: spectrum of Baltic amber produced with beam-condenser

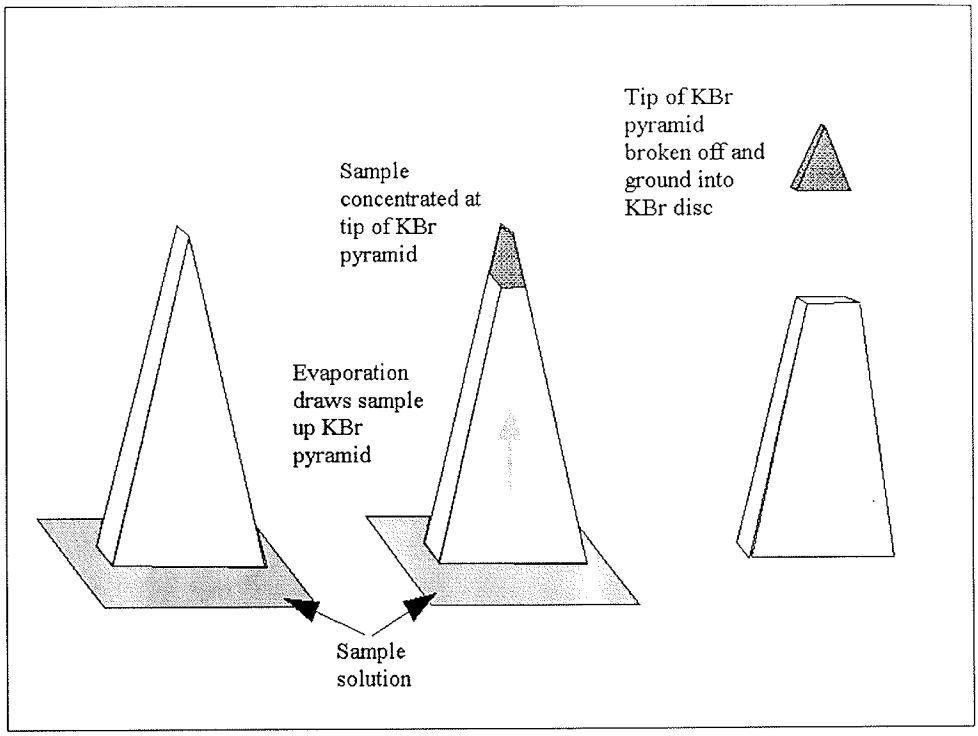


Figure 3: use of KBr pyramid

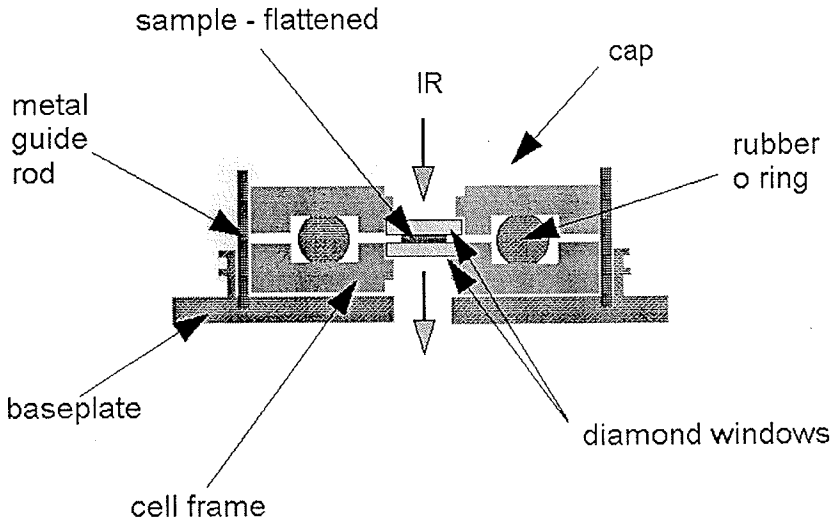


Figure 4: diamond cell

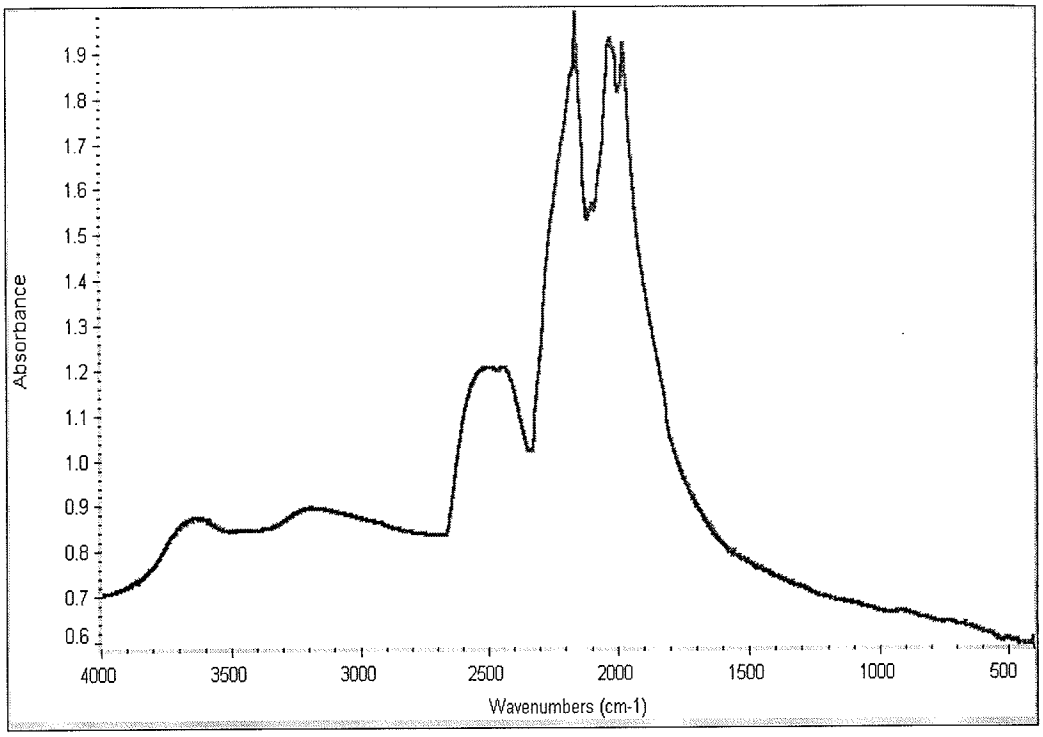


Figure 5: spectrum of diamond plates

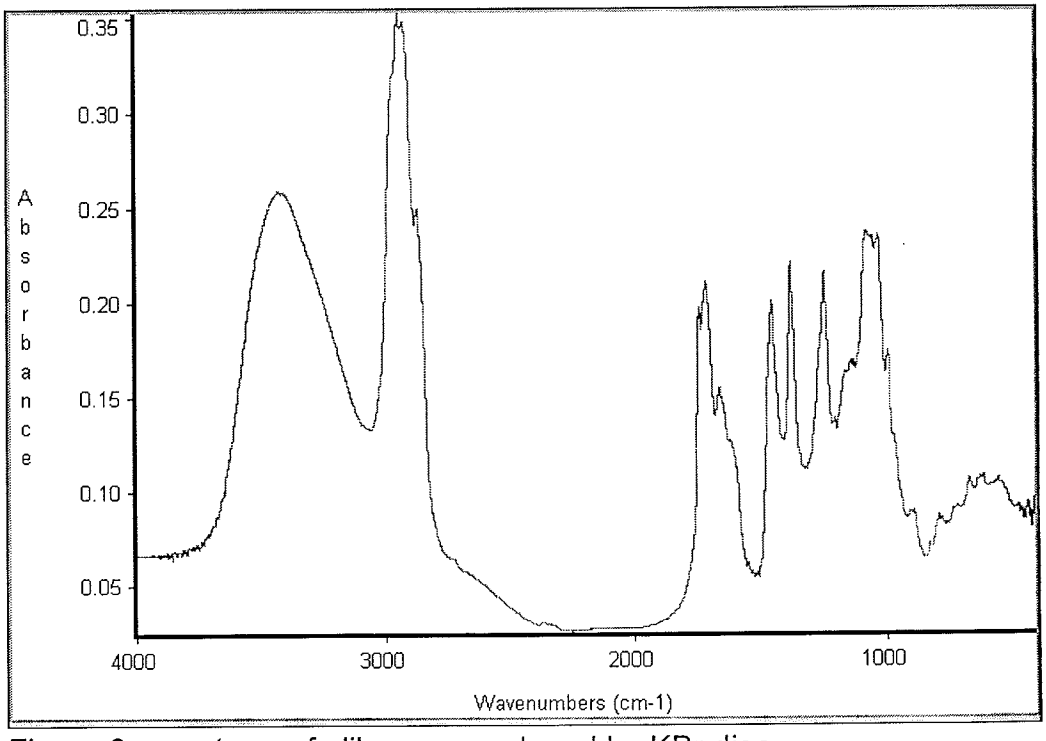


Figure 6: spectrum of olibanum produced by KBr disc

### 8.5 Sampling considerations

A sample must be able to be deformed under moderate pressure to produce a good spectrum using a diamond cell. In practice, most materials, including many inorganic fillers and metal corrosion products has been found to be suitable. If a material has a high compressive strength, it will not deform. This means that not only will the sample probably consist of a single solid piece, a far from an ideal preparation for IR spectroscopy, but that it will also hold the diamond plates apart. This gives rise to the appearance of regular interference bands in the spectrum that can obscure absorption bands from the sample. The interference bands can often be eliminated by removing one of the diamond plates and running a spectrum with the sample on just one plate, although a new background with just a single diamond plate will need to be run and subtracted from the spectrum. When dealing with particularly hard materials, such as amber or shellac, some grinding may be necessary to provide an adequate dispersion of material between the diamond plates.

A comparison was carried out between the KBr disc method, which is the standard sample preparation technique used at the British Museum, and the diamond cell with beam- condenser, using a sample of olibanum, a gum-resin typical of the type of samples routinely encountered. Spectra were collected using both techniques, reducing the sample size each time, until the absorption bands could not be distinguished from the background noise.

Spectra obtained from 100 mg of olibanum by KBr disc and from 5 mg by diamond cell are shown as figures 6 and 7. As can be seen, the diamond cell spectrum is not as well defined as that produced by the KBr disc, but all of the absorption bands are present and it is of sufficient quality for identification.

### 8.6 Analytical examples

The diamond cell is particularly useful when dealing with rubbery samples such as many modern adhesives and consolidants. These materials can be very difficult to prepare by other IR sampling techniques. ATR is suited for such materials, but the large sample size required is often not available. Natural rubber is amongst the most difficult of materials to sample and the traditional technique of preparation is time consuming and involves freezing in liquid nitrogen and then grinding into a KBr disc. The British Museum has a large and growing collection of rubber-containing objects, and work has been carried out to develop a conservation strategy for this material [7].

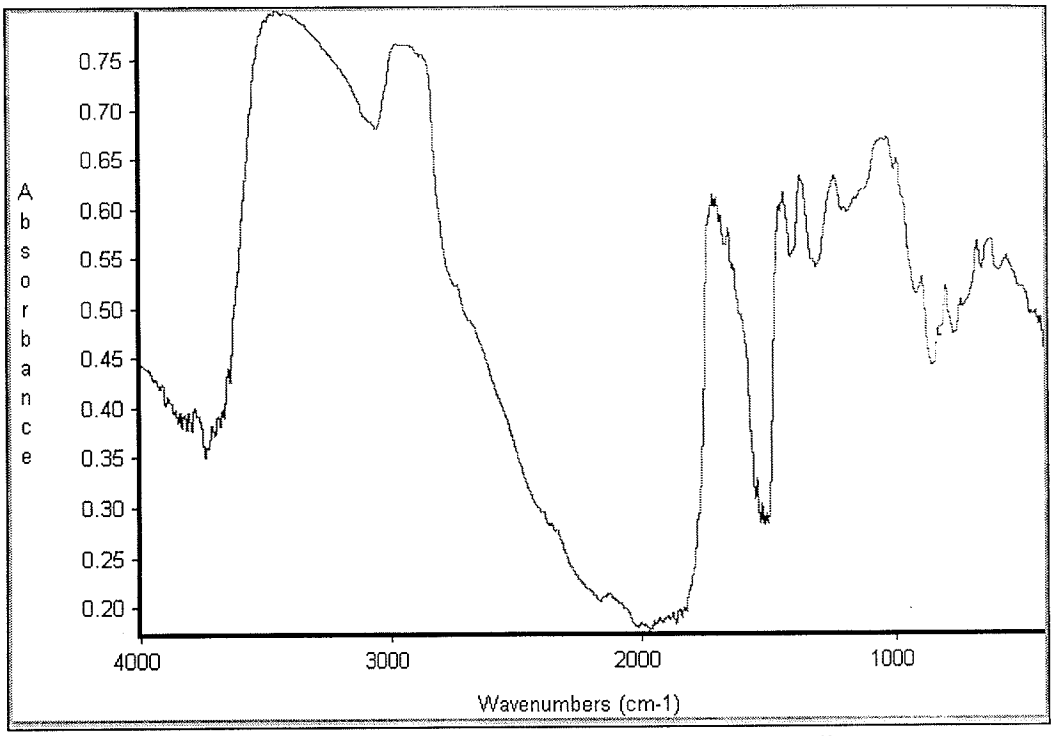


Figure 7: spectrum of olibanum produced by diamond cell

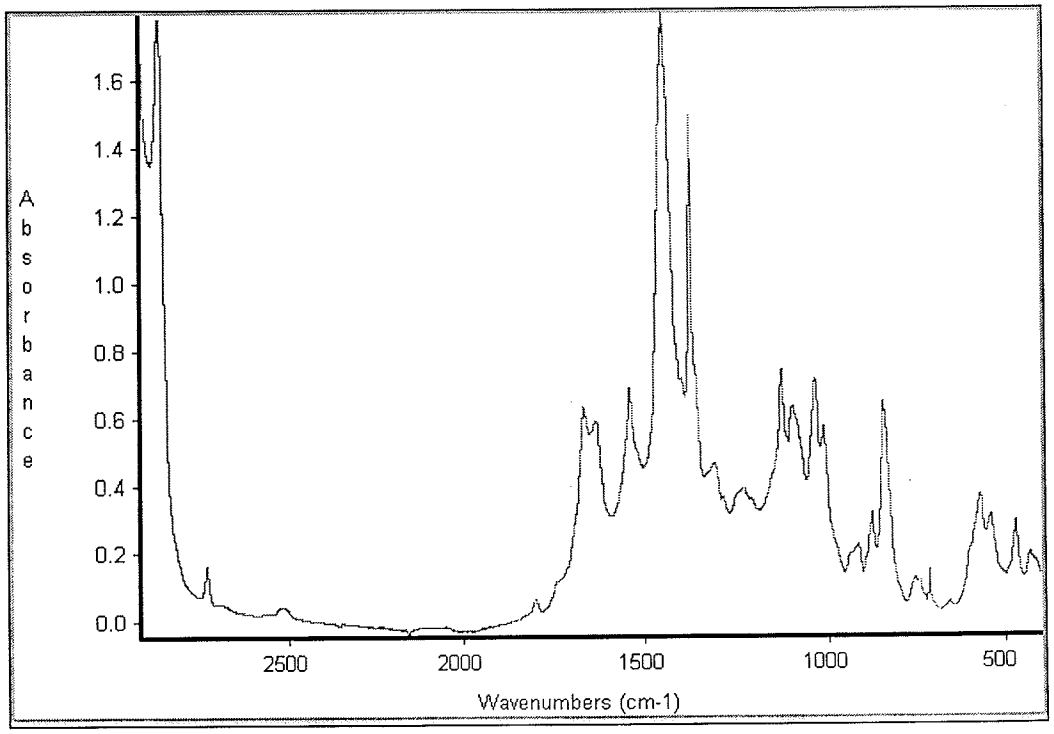


Figure 8: spectrum of undeteriorated rubber

Rubber degrades via oxidation of the carbon-carbon double bond. This can lead to the formation of a white powder on the surface or cracking of the surface, especially when under tension. The scission of carbon-carbon double bonds produces carbonyl groups; this reaction can be observed in the IR spectrum by the appearance of a absorption band at 1710 $cm^{-1}$. It is possible to use the spectrum to estimate the extent of degradation, but to use the absorption band quantitatively one needs to know the pathlength. Since the pathlength through the sample in a diamond cell cannot be controlled or measured, it is necessary to use one of the stable absorption bands as an internal standard against which the carbonyl stretching absorption is ratioed. The carbon-hydrogen stretching absorption at 2960 $cm^{-1}$ was used as this bond is inert to oxidation and hence the intensity of this absorption band would not be affected by the degradation process. Figure 8 shows the spectrum of unaged rubber and figure 9 shows that of degraded rubber with the carbonyl absorption at 1710 $cm^{-1}$ clearly visible. This quantitative technique can be used both to determine the efficiency of conservation treatments on experimental samples of rubber and to monitor the extent of degradation of artefacts.

Many of the phenomena that are of interest to conservation researchers occur on a microscopic scale and produce limited amounts of sample. The small sample size required for the diamond cell has allowed IR analysis to be applied to new areas of research.

Glass that contains no calcium or lead can form droplets of moisture on its surface when exposed to high relative humidities due to migration of the alkali. This condition is known as "weeping glass". If the relative humidity drops, a dried deposit is left on the glass surface. A Venetian glass vessel from the collections of the Department of Medieval and Later Antiquities had a white bloom over its inside surface. The composition of this material was important since if the glass was indeed weeping then it would have to be stored at a controlled relative humidity to ensure its continued preservation. However the deposit may have been the result of usage, or contamination acquired during storage. X-ray diffraction of the deposit was inconclusive. A small sample of the deposit was removed and its IR spectrum collected using the diamond cell, figure 10. This indicated the material to be a sulphate or possibly a hydrogen sulphate. Since the deposit was not an alkali, as would normally be associated with the occurrence of weeping, the glass was deemed to be stable. This example highlighted the requirement for expanding the collection of IR standard spectra to gain the full benefit from the technique when applied to new fields. The sample was easily retrieved from the diamond cell and submitted to ion chromatography analysis, which confirmed the presence of sulphate and chloride ions. The ease of retrieval of the sample and its possible use for other techniques is of great importance as several techniques are often required to perform a full identification of an unknown material.

The occurrence of both metal corrosion and salt efflorescence on objects can be very localised, resulting in limited sampling opportunities. Samples may contain more than one phase. Although x-ray diffraction can be used for small samples, the relatively long

exposure times required (about six hours) gives such samples the opportunity to change due to the absorption or loss of water. Since IR spectroscopy takes only a few minutes, sample alteration is less likely to occur. The inertness of the diamond plates also removes the possibility of ion exchange and hydration/desiccation encountered with the KBr methods. A large copper alloy coin from the Xianjeng tang bao period, minted in 1854, was showing spots of green corrosion. The corrosion was found to be hygroscopic and unsuitable for x-ray diffraction analysis. It was sampled and the IR spectrum, figure 11, found to be a good match for basic copper acetate, figure 12 [8]. It is thought that the formation of this corrosion product was due to a previous conservation treatment with acetic acid. The presence of extra absorption bands at 1146 and 924 $cm^{-1}$ indicates that some other material is mixed in with the copper acetate. It may be possible under magnification to separate mixed corrosion products, by their different morphologies or colours and produce spectra of each component.

### 8.7 Conclusions

A beam-condenser can allow much smaller samples to be analysed using IR spectroscopy. When combined with a diamond cell it provides a fast and convenient method of analysis. It deals easily with the types of organic samples that have been the primary use of IR spectroscopy in the Conservation Research Group of the British Museum in the past. It also allows the application of IR to types of sample, previously not analysable due to limited sample size or other properties. Rubber, deposits on glass, and metal corrosion products have been analysed. Other applications of the technique are pigments and salt efflorescences, especially those containing organic components.

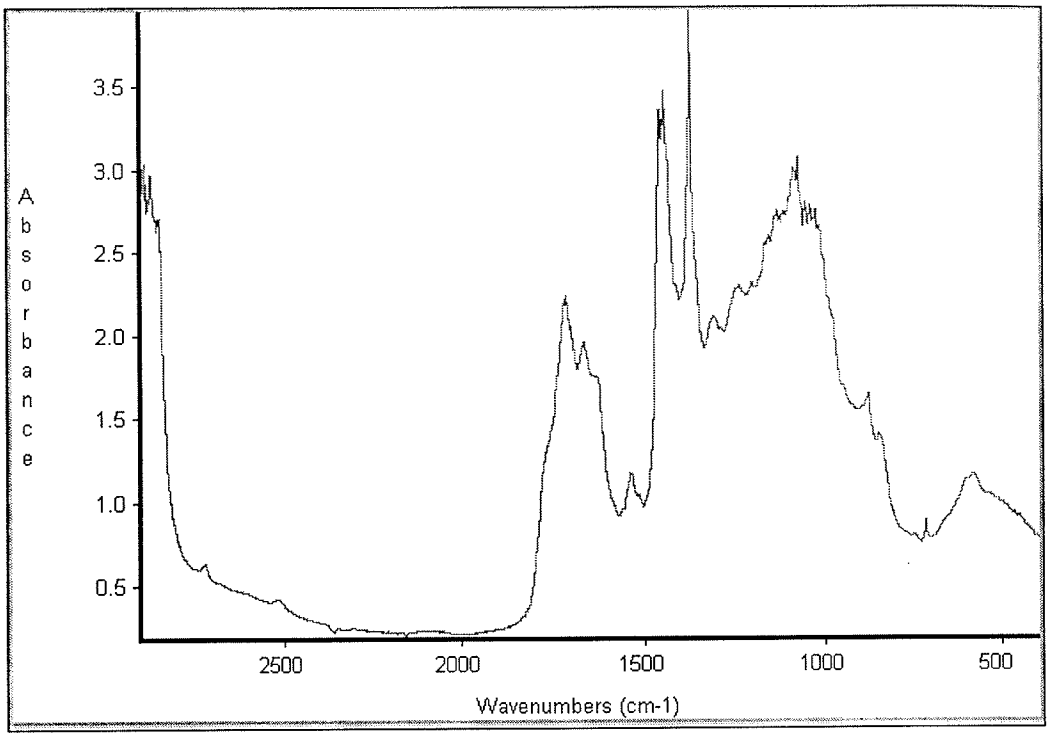


Figure 9: spectrum of deteriorated rubber

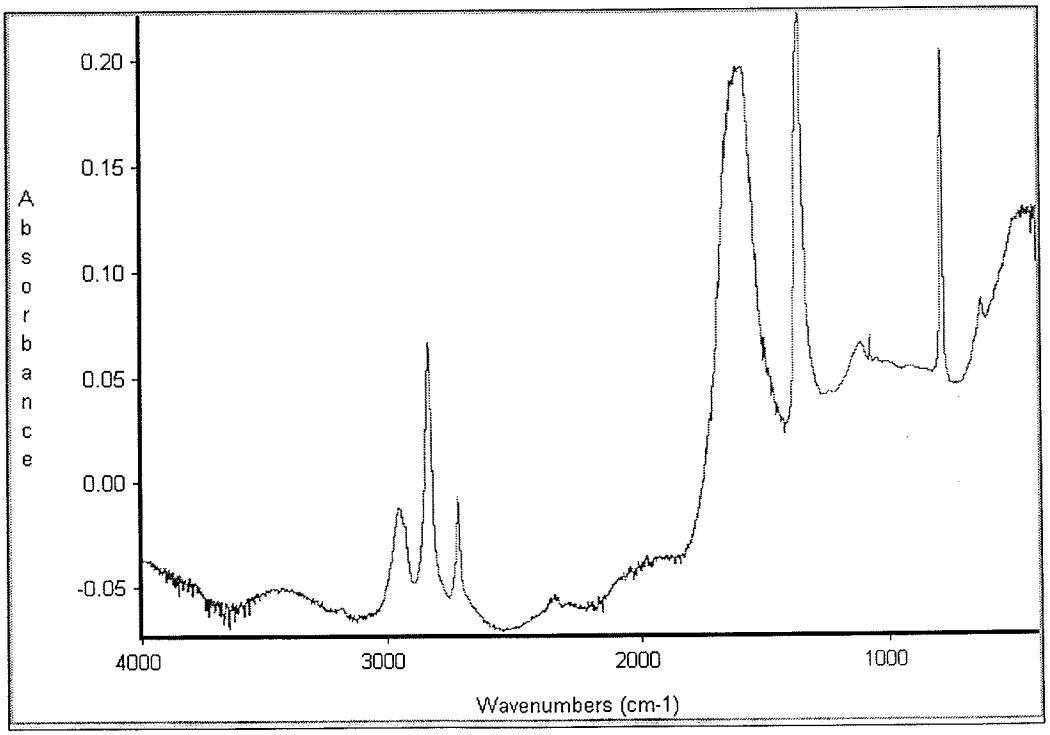


Figure 10: spectrum of deposit from glass vessel

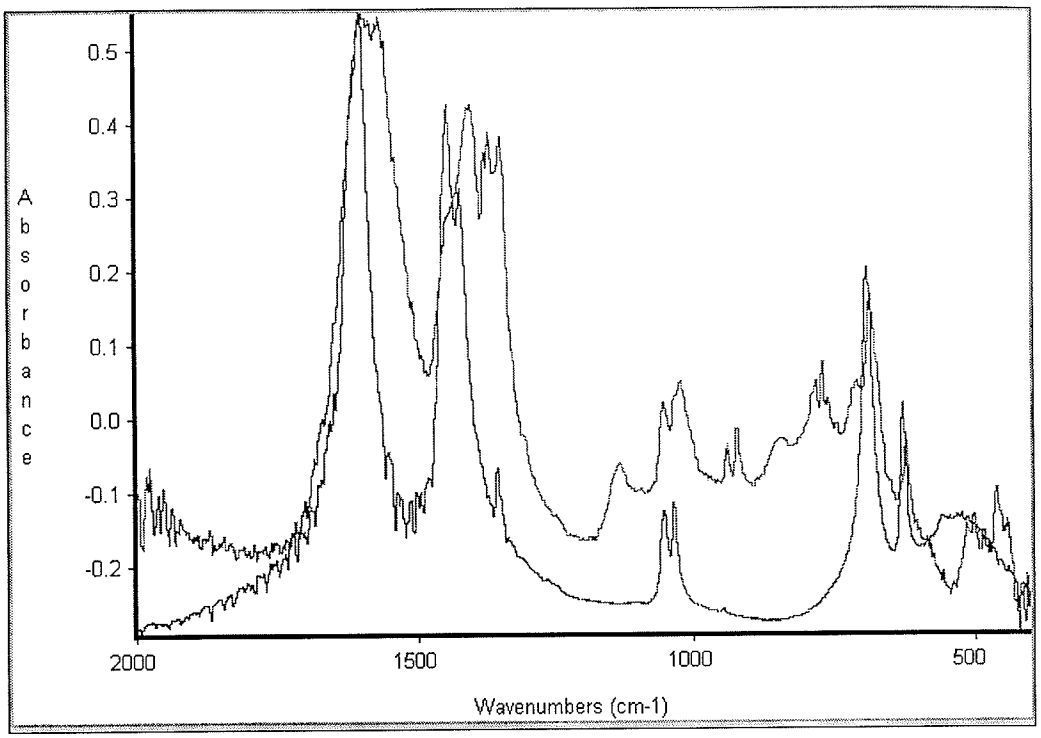


Figure 11: spectrum of corrosion from Chinese coin

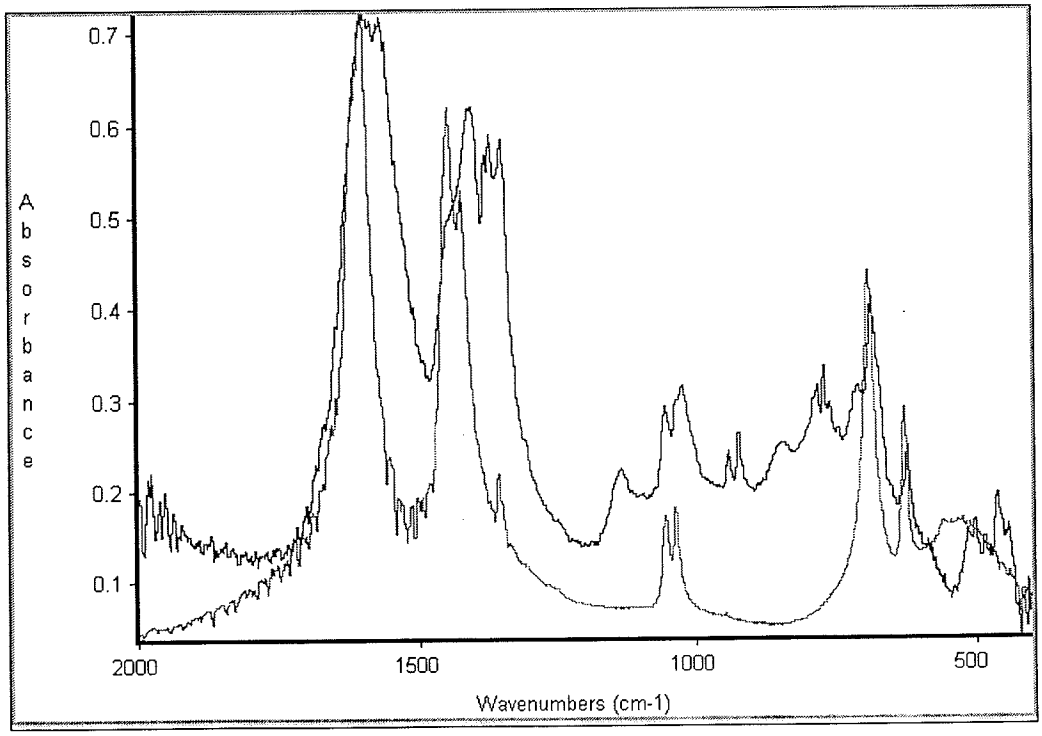


Figure 12: standard spectrum of basic copper acetate

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# 9. Improving the resolution of IR spectra

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National Gallery, London

## 9.1 Summary

The problems we have in interpreting binding media from IR spectra are increased by natural products being rarely pure and having similar functional groups. Furthermore, with ageing. they are susceptible to oxidation, polymerisation and reaction with the pigment. Certain types of paint artists used continually give us headaches: mixtures of oils and protein, the possibility of a touch of resin added and lake pigments frequently produce spectra with high baselines and overlapping features. Often, collecting data at a higher resolution cannot yield more accurate information.

Derivatives are used to enhance a spectrum; the second order is the most common but analysis of multiple derivatives can further enhance the spectrum. We now use Nicolet OMNIC software which uses Fourier Self-Deconvolution. The FSD trace is able to resolve the overlapping bands and improve resolution.

## 9.2 Introduction

The task of the organic conservation scientist in interpreting binding media from IR spectra is complicated by natural products being rarely pure and having similar functional groups. Then with ageing, they are susceptible to oxidation, polymerisation and perhaps reaction with the pigment. Certain types of paint used by artists continually give us headaches. For example, emulsions of oil and protein, the possibility of a touch of resin having been added or the lake pigments which frequently produce spectra with high baselines and overlapping features. Collecting data at a higher resolution or a different method of sample preparation cannot often yield more accurate information.

A spectrum can be enhanced by using derivatives, the second order being the most common but analysis of multiple derivatives may further improve the spectrum. We now use Nicolet OMNIC software which contains a Fourier Self-Deconvolution option. The FSD trace is able to resolve the overlapping bands to improve resolution. The final spectrum is still in absorbance and is comparable to the original since it does not look at the minimum of a negative peak of each band as a second order derivative does. Instead, it uses the maximum of a positive peak obtained from the multiple derivative of each band. Put simply, the absorbance bands in a spectrum have a Lorentzian profile of a band with a sinusoidal shape and an exponential envelope. In deconvoluting the spectrum, the broadening is removed and the resulting band width is less than the original and so resolution is improved. The measured absorbance spectrum is transformed into an absorption interferogram through calculating the inverse FT. This new data is multiplied by a function (a parabolic weighting) and the spectrum recovered by computing the forward FT [1]. The noise is constant throughout the spectrum, so where the signal level is low the noise will be most apparent. Thus the best spectra will result if the noise level is as low as possible when using multiple derivatives.

### 9.3 Examples

To begin, an example of the clarity given by a deconvoluted spectra. As part of our French School study, we sampled the painting of *A Sunset in the Auvergne (NG2635)* by the Barbizon painter Henri Theodore Rousseau. A yellow highlight from the sunset appeared to contain largely white paint with flecks of orange-red. The spectrum (figure 1) showed a simple mixture of basic lead carbonate in a drying oil (gas chromatography indicates walnut oil) - the orange-red particles were not active in the mid-IR. After deconvoluting this result (figure 2) the three positions for a carbonyl - lactone, ester and acid are well resolved. The main carbonate band was now seen as its doublet and the lead carboxylate soaps are clearly marked at 1527, 1620 and 1655 $cm^{-1}$. The C-O absorptions at 1242, 1169 and 1088 $cm^{-1}$ plus the various CH stretches between 2958-2858 $cm^{-1}$ were also unmistakable.

The majority of samples give spectra whose inorganic pigments greatly interfere with the organic bands, often masking them. As in the above example, the organic absorbances are comparatively weak. We have found that spectra of certain pigments appear to show no organic bands. The following example is from the sky in the Master of the Aachen Altarpiece *The Crucifixion (NG1049)*. Currently on a long term loan to the Walker Art Gallery displayed with the wings also in Liverpool. Under the IR microscope both blue and white paint can be seen and this produces a typical spectrum (figure 3) of a drying oil with basic lead carbonate and azurite. If an isolated particle of the azurite is analysed, the spectrum is of pure azurite with very little indication of a binding medium - often seen with this mineral. The spectrum shows possible absorbances in the carbonyl, C-H and C-O regions, but they aren't clear. Even after deconvoluting the spectrum, (figure 4) the bands are still very weak but shoulders on the broad mineral absorbance can be resolved and attributed to the binding medium. There is also a hint of protein in the amide region.

Another good example of the difficulty in detecting the medium with leanly bound paint is highlighted in one of the gallery's Tüchleins. *The Entombment (NG644)* was painted in the 1450s by Dieric Bouts in an aqueous medium directly onto canvas. It was examined in 1985 [2] and two samples taken for medium analysis - blue sky and white drapery. They both broke up on warming with water and GC showed the absence of oil and egg fats. A modified Ehrlich test proved positive for the presence of hydroxyproline - the amino acid particular to animal glue and this was the final conclusion. Many years later, the FTIR was purchased and we also began a comprehensive study of the early netherlandish paintings. The Entombement was sampled and we could now confirm the glue. At that time we had only the NICOS software which used the 2nd derivative curves. These gave quite noisy bands in the fingerprint region - figure 5 shows the result of a sample of the sky. Re-analysing the data a few years later with the new OMNIC software we are now able to attribute some bands to the medium.

At the top of the painting is a dull blue sky which was intended to be much bluer. At the very edge it is a much stronger colour where the painting has been protected by the frame. Microscopy shows there to be only azurite present [3] which has worn away to

show more of the brown canvas, this also has darkened. There appears to be no colour change of the pigment and indeed the IR analysis supports this - the azurite is extremely leanly bound and an enhanced spectrum (figure 6) is able to resolve some of the bands on the shoulder of the broad carbonate absorbance. Weak amide I absorbances can be picked out at 1659 and 1628 $cm^{-1}$ - amide II bands are a little more tricky. The one at 1555 $cm^{-1}$ has a larger than expected intensity - probably increased by the proximity of the broad mineral band. Another interesting point about this painting is that the sides have been edged with a brown paper strip. At the right hand edge part of this has been torn and a darker blue-green landscape can be seen. Analysis in 1985 assumed there to be indigo which has faded allowing a yellow inorganic pigment to dominate and we can now confirm this. The spectra (figure 7) largely show polysaccharide bands due to the gummed paper but among these, there are numerous sharp bands due to indigo (plus a little azurite) which cannot be missed.

The analysis of dyes by FTIR in paint samples presents a difficulty. Indigo and synthetic dyes present no problem but the red and yellow insect and vegetable dyes are best analysed by extracting the dyestuff and then separated by chromatography. A lake paint is a complex mixture of the dyestuff, its substrate and the medium. A typical result of such a sample is shown from a study of the gallery's Gustave Moreau picture *St. George and the Dragon (NG6436)*. The medium is oil as shown by a number of bands in the spectrum. However, in spite of the fact that there are still numerous bands remaining to be interpreted, the source of the red dye is impossible to identify by this method. HPLC easily analyses the dye as cochineal. Confusingly, the original absorbance spectrum looks proteinaceous with intense bands centring in the amide I & II regions plus an overtone. After deconvoluting this result (figure 8), they sit at 1667, 1643, 1565 $cm^{-1}$ and together with the carbonyl at 1778, 1736 and 1709 $cm^{-1}$, it immediately suggests that this is an emulsion of a drying oil and protein. The amide bands are relatively intense; if some egg or glue was used as the medium (or a part of it) we might expect the bands to be weaker. Analysis of the fats present by gas chromatography do not indicate any other than those of a heat bodied walnut oil.

Another example of this is was found in an early German painting by Stephan Lochner *Saints Matthew, Catherine of Alexandria and John the Evangelist (NG705)* painted around 1445. The reverse is quite damaged and depicts the Saints Gregory and Jerome with a female martyr in the middle. Saint Jerome's drapery is painted with an opaque red/pink layer over which lies a transparent glaze. Bands appear due to the lake substrate, but any bands relating to the dyestuff (probably extracted from Kermes in this case) are too weak to isolate. Again, the paint sample absorbs intensely in the amide regions and when this result is deconvoluted (figure 9), the bands appear at 1660, 1623 & 1582, 1546 $cm^{-1}$ plus an overtone at 3079 $cm^{-1}$. The GCMS results show a heat bodied linseed oil and a touch of resin only. Therefore these bands are nothing to do with the medium and it is more likely that they are related to the method of preparation of the lake pigment; they appear to be associated particularly with lake pigments, but are not invariably present. Work is still in progress to clarify this.

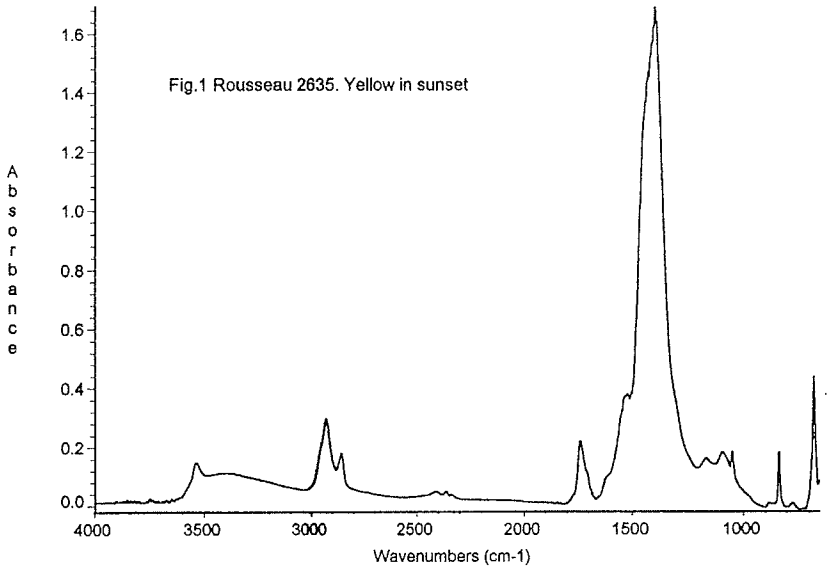
Fig.1 Rousseau 2635. Yellow in sunset
Absorbance
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
4000
3500
3000
2500
2000
1500
1000
Wavenumbers (cm-1)

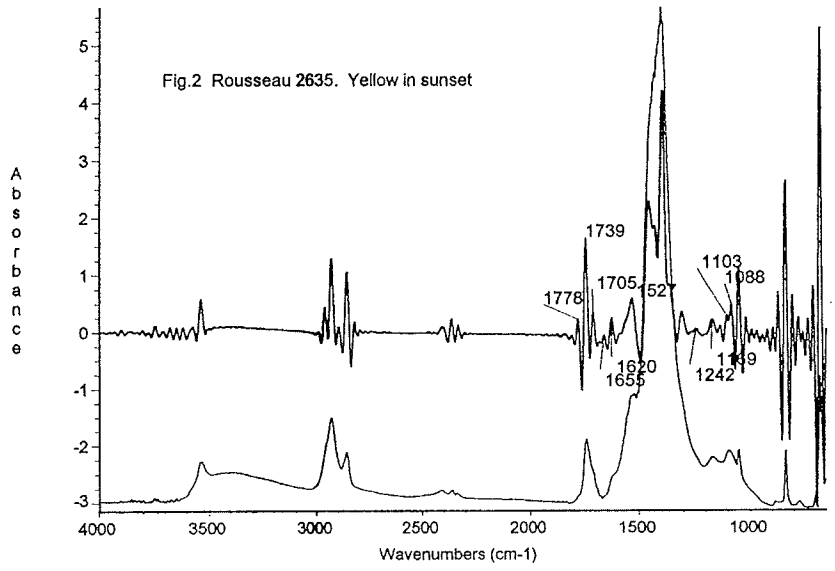
Fig.2 Rousseau 2635. Yellow in sunset
Absorbance
5
4
3
2
1
0
-1
-2
-3
1739
1778
1705
1527
1103
1088
1620
1655
1242
4000
3500
3000
2500
2000
1500
1000
Wavenumbers (cm-1)

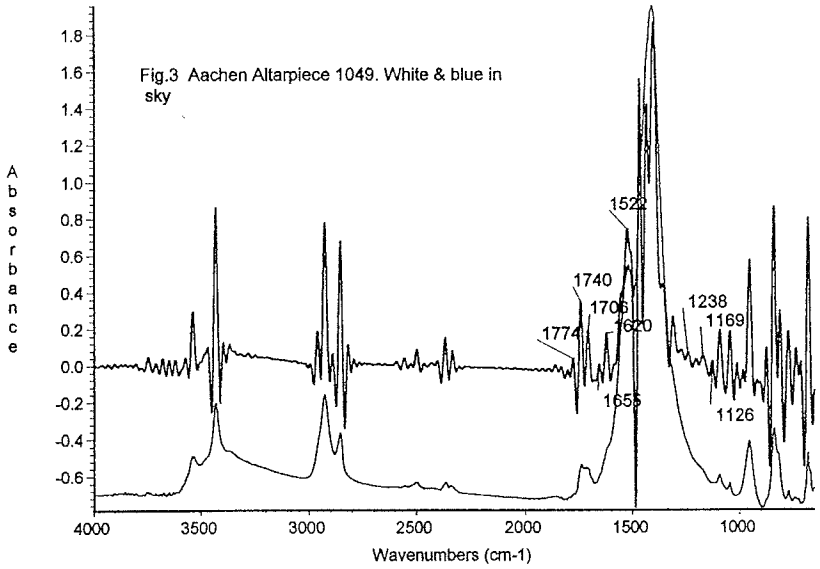
Fig.3 Aachen Altarpiece 1049. White & blue in sky
Absorbance
Wavenumbers (cm-1)
1522
1740
1706
1620
1774
1655
1238
1169
1126

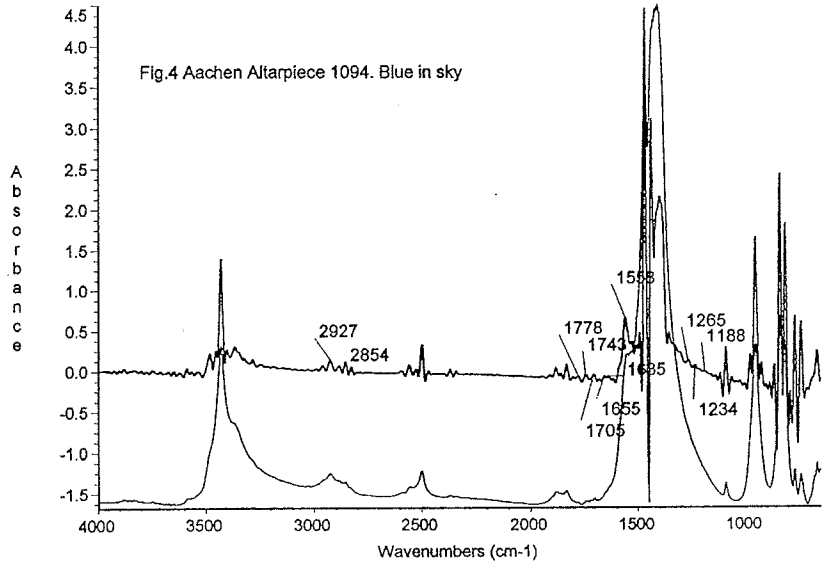
Fig.4 Aachen Altarpiece 1094. Blue in sky
Absorbance
Wavenumbers (cm-1)
2927
2854
1778
1743
1655
1705
1265
1188
1234

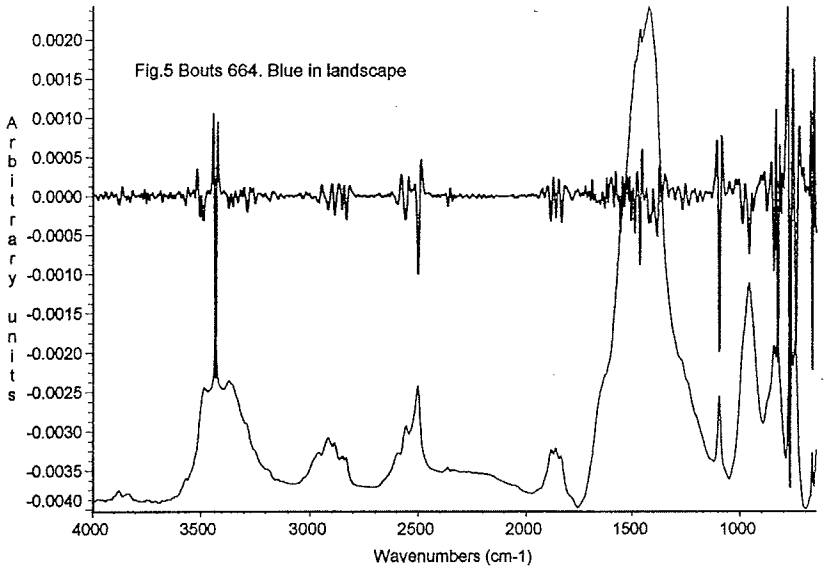
Fig.5 Bouts 664. Blue in landscape
Arbitrary units
0.0020
0.0015
0.0010
0.0005
0.0000
-0.0005
-0.0010
-0.0015
-0.0020
-0.0025
-0.0030
-0.0035
-0.0040
4000
3500
3000
2500
2000
1500
1000
Wavenumbers (cm-1)

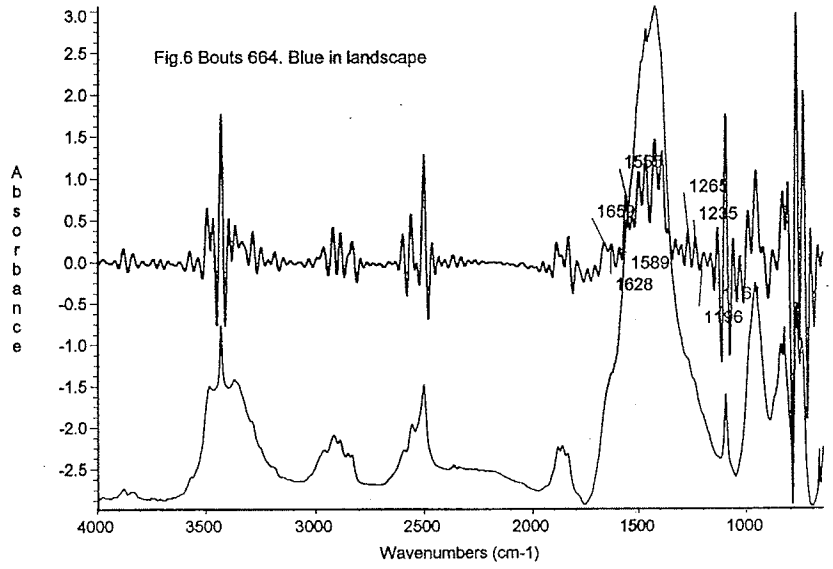
Fig.6 Bouts 664. Blue in landscape
Absorbance
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
1655
1589
1628
1265
1235
1136
4000
3500
3000
2500
2000
1500
1000
Wavenumbers (cm-1)

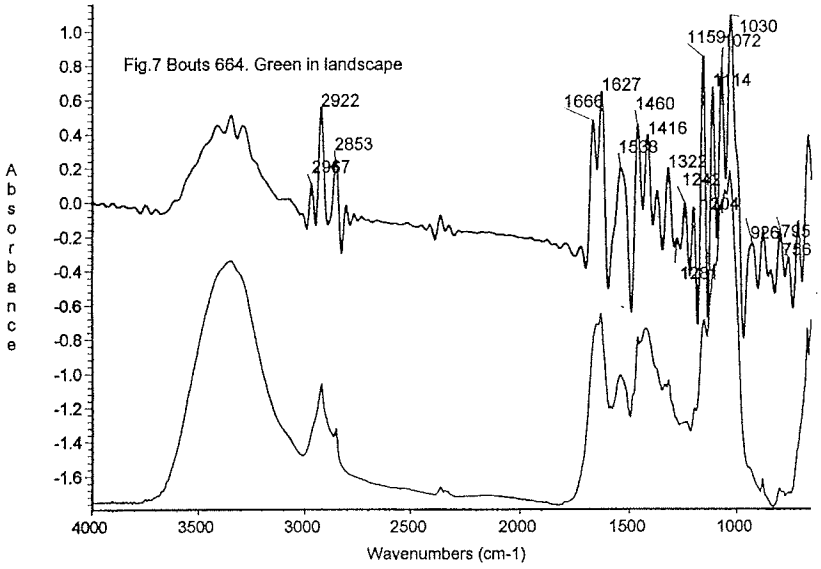
Fig.7 Bouts 664. Green in landscape
2922
2853
2967
1666
1627
1460
1416
1538
1322
1159
1072
1030
1114
1204
926
795
756
1251
Absorbance
Wavenumbers (cm-1)

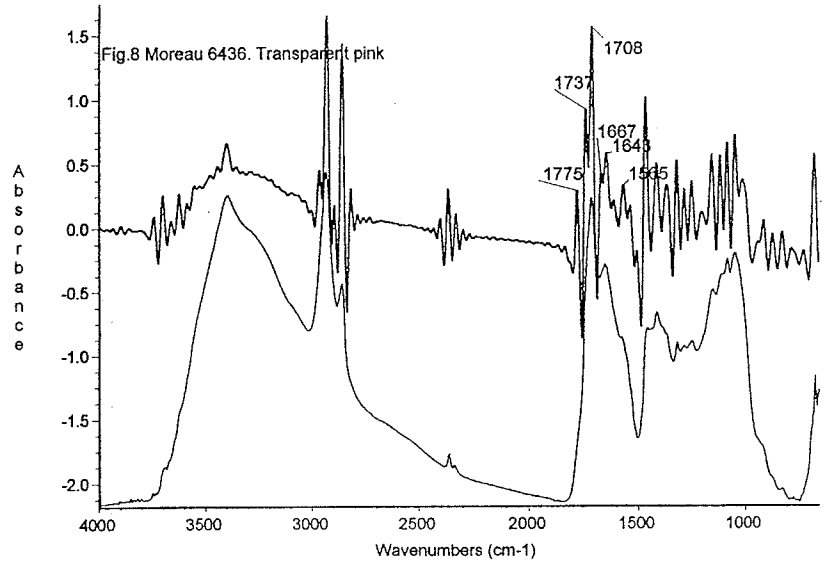
Fig.8 Moreau 6436. Transparent pink
1708
1737
1667
1643
1775
1505
Absorbance
Wavenumbers (cm-1)

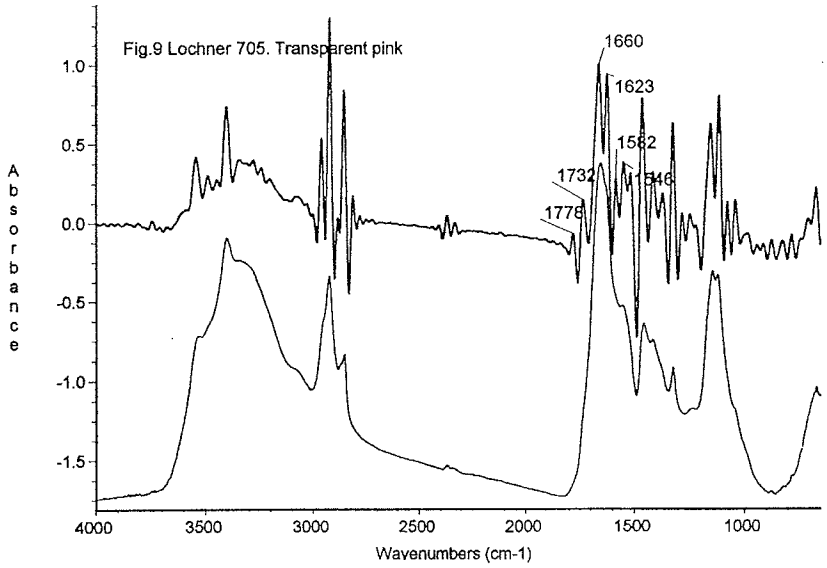
Fig.9 Lochner 705. Transparent pink
1660
1623
1582
1732
1546
1778
Absorbance
1.0
0.5
0.0
-0.5
-1.0
-1.5
4000
3500
3000
2500
2000
1500
1000
Wavenumbers (cm-1)

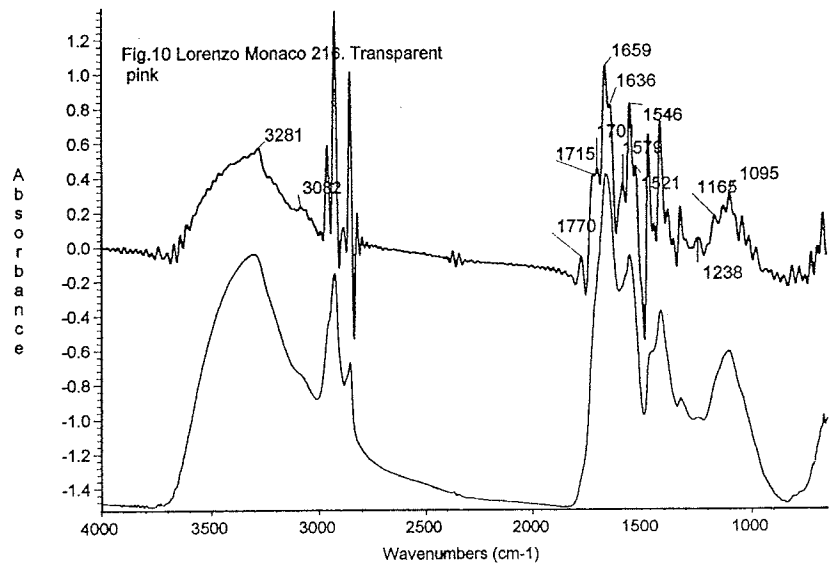
Fig.10 Lorenzo Monaco 216. Transparent pink
1659
1636
1546
3281
1715
1521
1165
1095
1770
1238
Absorbance
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-1.4
4000
3500
3000
2500
2000
1500
1000
Wavenumbers (cm-1)

The results obtained from the Moreau and Lochner compare interestingly with a lake sample in egg, a rather rare occurrence in our collection. The right wing of the altarpiece *The Coronation of the Virgin (NG1897)* by Lorenzo Monaco is titled *Adoring Saints (NG216)* was recently in our conservation studios. Saint John the Evangelist's cherry red robe at the left edge of the panel was sampled and contained a transparent red glaze. The carbonyl and amide regions were not well resolved but after deconvolution (figure 10) we can see amide bands at 1659, 1636 & 1579, 1546 $cm^{-1}$ plus an overtone at 3082 $cm^{-1}$. With a carbonyl at 1770 and 1715 and 1701 $cm^{-1}$ there clearly was some oil present but this type of result needs additional information in order to interpret the results with surety. Subsequent analysis by GC confirmed that this was an egg tempera glaze.

All the samples were analysed in transmission using 256 scans at 8 $cm^{-1}$ on a Nicolet 710 bench with a Nicplan microscope. Nicolet's OMNIC software was used to control the instrument and manipulate the data.

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# 10. Infrared microspectroscopy mapping techniques for the analysis of paint cross sections

Michele Derrick and Tanya Kieslich
Getty Conservation Institute

## 10.1 Summary

Infrared microspectroscopy is useful for characterizing binding media in very small paint cross section samples using both transmission and reflection modes of analysis. In a direct comparison of the two methods, reflection techniques produce poorer quality spectra than the transmission methods. However, many of the problems of reflection spectra can be mitigated by looking at the variation that occur between spectra taken under similar conditions. An excellent venue for such a study is the use of infrared mapping. Mapping studies compare the intensities of absorption bands versus their location in the sample to generate an image of compositional differences in a region.

The method used for a multilayer paint cross section embedded in plastic, is to microtome or polish the sample to produce a level surface for analysis, then it is placed in the infrared microscope for analysis. An analysis grid is selected with an automated X-Y stage then spectra are collected by reflection of an apertured beam of infrared radiation off the sample surface. From the array of spectra, contour maps may be produced by selecting a wavelength of interest, such as a hydrocarbon stretching band, and plotting its intensity versus its collection position in the grid. Because previous extensive analysis is done on the samples, the selected infrared absorption band and corresponding functional group can be related to components in the sample. Several examples will be shown to discuss the advantages and limitations of the technique.

Paper not submitted for inclusion in postprints.

Presenting Author

Tanya Kieslich worked on the infrared microspectrometer at the Getty Conservation Institute with Michele Derrick while studying Chemistry at Loyola Marymount. She is currently training at the Courtauld Institute of Art in London for a post graduate diploma in the conservation of easel paintings.

# 11. The characterisation of iron earth pigments using infrared spectroscopy

Kate Helwig
Canadian Conservation Institute

## 11.1 Summary

Iron earth pigments, coloured by the oxides, oxyhydroxides and hydrated oxides of iron, have a long history of use by many different societies from the palaeolithic to the post-modern.

The geological sources of the iron earths are varied and their chemistry is complex. Depending on the environment which led to their formation, many types of accessory minerals (such as clays, carbonates, sulfates and aluminium hydroxides) may be associated with the iron oxide compounds. As well, the genetic environment will affect properties of the iron oxide minerals such as hydration, structural order and crystal size. The chemistry of these pigments may be complicated further by processing such as heat treatment or the addition of pigments and fillers to achieve a desired colour.

Infrared spectroscopy is a powerful technique for the characterization of these complex materials. When only small quantities of accessory minerals are present, the infrared spectrum provides information about the properties of the iron oxide compounds themselves. Often, however, the infrared spectrum is dominated by absorptions due to accessory minerals. This may be used to advantage by allowing pigments to be grouped depending on the presence of certain materials, and in some cases may indicate a specific type of geological formation as the source of the earth. Heat or chemical treatments may be used to aid in spectral interpretation by resolving overlaps between the iron oxides and the accessory minerals.

Examples of the characterization of iron earth pigments by infrared spectroscopy will be presented, using standards of known origin as well as samples from cultural artifacts.

## 11.2 Introduction

The iron earth pigments, which are coloured by the naturally occurring oxides and oxyhydroxides of iron, have been used in works of art and cultural artifacts since the upper palaeolithic, and long before this, as early as 300,000 BC, there is archaeological evidence that red and yellow ochre was collected and transported for specific purposes [1]. Because these pigments are readily available, can produce a wide range of colours, and are chemically stable, many distributors of artists' materials [2] still employ natural earths in their iron oxide-based paints.

X-ray diffraction, Mossbauer spectroscopy, thermal analysis, x-ray fluorescence and infrared spectroscopy are some of the most important techniques which have been used to characterize iron earth pigments. Although this paper concentrates on the use of infrared spectroscopy, other techniques will be mentioned to illustrate the complementary nature of the different methods.

Before discussing what can be learned from the infrared spectra of the iron earth pigments, it is useful to give a general picture of the composition of these materials. The iron earths can be thought of as containing two main components: the iron oxide minerals and the accessory minerals.

The iron oxide minerals, both oxides and oxyhydroxides, provide the characteristic red,

brown or yellow colouration of the pigment [3]. Various iron oxide minerals exist in geological environments, and, as such, are potential pigmenting materials. In most cases, however, red colouration is linked to the presence of hematite, and yellow colouration to the presence of goethite. Although hematite and goethite are most commonly identified, other iron minerals, such as maghemite, lepidocrocite and akaganeite for example, may sometimes be present in earth pigments.

While it is the iron oxides and oxyhydroxides which produce the colour, minerals such as quartz, clays, carbonates and sulfates are also often present. The type and amount of these accessory minerals will depend on the source of the earth and the degree of processing which the pigment has undergone. Because of the high pigmenting power of the iron oxides, strongly coloured earths which are suitable as pigments may contain a relatively low concentration of iron compared to the concentration of the accessory minerals [4].

## 11.3 Experimental

The earth pigments which were obtained for this study came from a number of manufacturers and represent many geological sources. Pigments from the Forbes collection [5] were also examined. In addition, examples of the characterization of pigments from cultural artifacts are given.

The infrared spectra of the pigments were collected using a Bomem MB-100 spectrometer. The samples were mounted in a low pressure diamond cell, which is positioned in the microbeam sample compartment of the spectrometer. The spectra were collected from 4000 to 400 $cm^{-1}$. It is important to note that although the low energy cut-off of the spectrometer is 400 $cm^{-1}$, there are often bands in the 200 to 400 $cm^{-1}$ region which are useful for mineral characterization.

## 11.4 Discussion of spectra

The following discussion of the infrared spectra of the iron earth pigments illustrates the kind of information which can be obtained in two limiting cases. First, examples of earth pigments for which the infrared spectrum is dominated by absorptions due to hematite or goethite are given. In this case, information about characteristics of the iron oxides such as particle size and shape, or the degree of crystallinity may be obtained. In the second case, which is much more common in pigment samples, the infrared spectrum is dominated by absorptions due to the accessory minerals. Identification of these minerals from their infrared spectra can sometimes provide information about pigment sources.

### 11.4.1 Iron oxides/oxyhydroxides

- Hematite

For certain red earth pigments, which come from deposits of relatively pure iron oxide or have undergone processing to remove the accessory minerals, the infrared spectrum is dominated by absorptions due to hematite.

The infrared spectrum above 400 $cm^{-1}$ of powdered hematite samples has two major bands, attributed to lattice vibrations. Published values for the position of these two bands differ by up to 30 $cm^{-1}$. Several reasons for these variations have been suggested in the literature, but it is generally accepted that variations among the spectra are most often caused by differences in the size, and more importantly the shape, of the hematite particles [6].

Work which has been done in the study of soils and clays has shown that hematite in which the particles have a fairly equant shape, the most common morphology, produces an infrared spectrum with bands at approximately 560 and 480 $cm^{-1}$, with the more intense band at 560 $cm^{-1}$. On the other hand, when the hematite particles are platy or elongated, these bands are both shifted to lower energy by approximately 30 $cm^{-1}$ and the band at 450 $cm^{-1}$ is more intense. Samples with a range of morphologies produce broader bands with maxima between these two extremes [7,8]. It is important to be aware of these possible variations in the study of hematite-based pigments, since pigments which are from different sources, or were processed in different ways can sometimes be distinguished by their particle morphology.

Figure 1 shows the infrared spectra of two red earth pigments which show significant differences in the position of the hematite absorptions. The upper spectrum, of a red ochre pigment, is similar to that reported for hematite with an equant shape. The bands in the lower spectrum, of an Indian red pigment, have been shifted to lower energies by approximately 20 $cm^{-1}$ and the spectrum is closer to that reported for hematite with a platy or elongated morphology. The calcium carbonate present in the Indian red pigment sample does not have an effect on the hematite absorptions; treatment of the pigment with dilute hydrochloric acid removed the carbonate but did not change the position of the hematite bands.

An examination of these samples using scanning electron microscopy shows that the differences in the infrared spectra do indeed reflect variations in the hematite particle size and shape. The hematite particles in the red ochre sample have an irregular, but generally equant shape. These particles vary in size from approximately 0.04 to 0.25 micrometers. The majority of the hematite particles in the Indian red pigment, on the other hand, have an elongated, rod-like morphology. The rods are between 0.5 and 1 micrometer in length and about 0.2 micrometers wide.

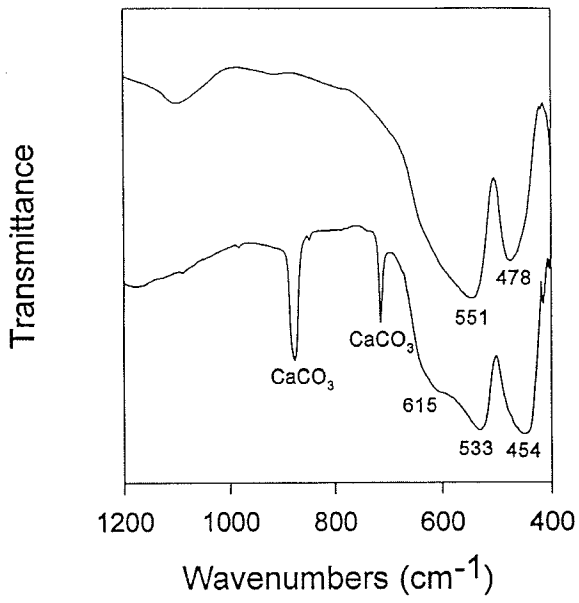


Figure 1: infrared spectra of two hematite-based pigments showing variations in the position of the hematite bands due to differences in particle size and shape

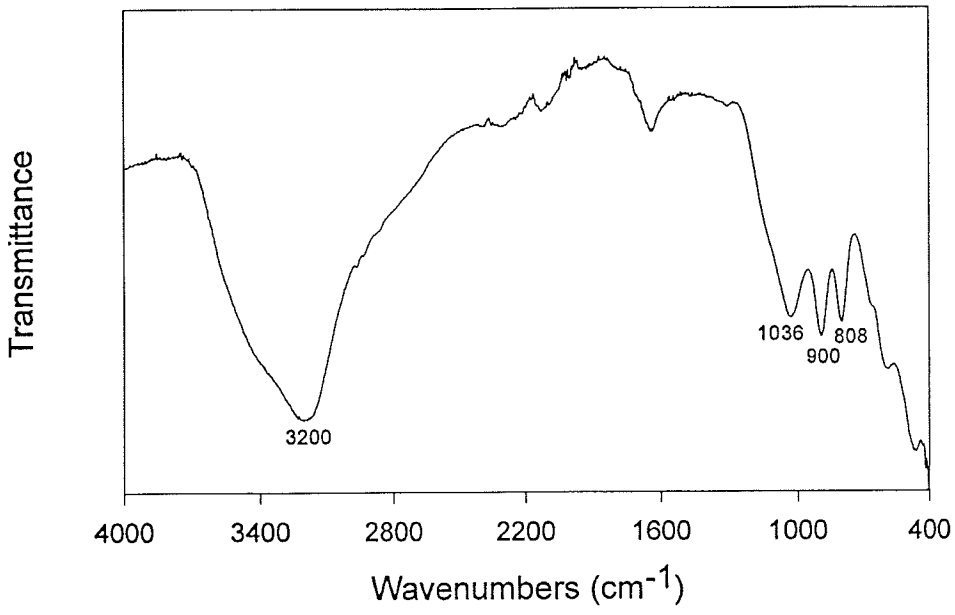


Figure 2: infrared spectrum of a raw sienna pigment from Mount Amiata

- Goethite

While red earth pigments are generally coloured by hematite, most of the yellow or yellow-brown earths are coloured primarily by goethite. The infrared spectrum of goethite has a characteristic hydroxyl stretch at approximately 3150 $cm^{-1}$ and hydroxyl deformation bands near 900 and 800 $cm^{-1}$. The lower energy bands are attributed to lattice vibrations [9].

Studies of synthetically prepared goethites have shown that factors such as crystallinity, adsorbed water, and isomorphous substitution of iron by aluminum will influence the position of these bands. For example, in a series of synthetic goethites of varying crystallinity, the hydroxyl stretch shifted from 3130 $cm^{-1}$ in the most crystalline sample to 3170 $cm^{-1}$ in the sample with the least amount of structural order [10].

This kind of work, however, has a limited application in the study of earth pigments because it is very rare that goethite dominates the infrared spectrum. In fact, in an examination of over 70 standard pigment samples of yellow and yellow-brown earths from various sources (including raw umbers and siennas as well as yellow ochres), in only two cases did absorptions due to goethite dominate the infrared spectrum; these pigments were both from Siena.

Siennas have been quarried for centuries in Italy at the foot of Mount Amiata. These iron earth deposits, which were formed as a result of volcanic activity in the Tuscan region, have a high iron content and little clay [11]. However, even in the case of the siennas, which contain more goethite than many other earths, the presence of small amounts of silicates makes a precise interpretation of the infrared spectrum difficult.

The spectrum of a raw sienna pigment, shown in figure 2, indicates that the goethite hydroxyl stretch is partially obscured by the presence of water, adsorbed either on the goethite or the silicate. The bands at 900 and 808 $cm^{-1}$ can certainly be attributed to goethite, but because of possible overlaps, it is difficult to assign exact peak positions. Quartz has a strong absorption around 800 $cm^{-1}$ and many clays absorb in the region of 900 $cm^{-1}$ [6].

### 11.4.2 Accessory Minerals

Although the accessory minerals can make characterization of the iron oxide component difficult using infrared spectroscopy, in some cases, their presence can be used to advantage. An examination of the accessory minerals present in the earth pigments is important for several reasons. First, the presence of certain minerals may sometimes indicate a type of geological source for the pigment or allow pigments from different sources to be distinguished. Secondly, documenting accessory minerals which are present in large numbers of samples from different artifacts may allow patterns of use for specific mineral mixtures to be recognized.

- kaolin minerals

Clays, generally of the kaolin group, and quartz are by far the most commonly found accessory minerals in the yellow earths and are also often found in red earth pigments. Many types of rock weathering will lead to the formation of these minerals. For example, the yellow ochre from the Apt basin in the south of France, which contains goethite and kaolinite together with detrital quartz, is produced by the weathering of glauconitic sands [12].

The strong hydroxyl bands at 3700 $cm^{-1}$ and 3620 $cm^{-1}$ are characteristic of kaolin-group clays [6]. Because few other minerals absorb in this region, infrared spectroscopy is a sensitive technique for the identification of kaolin. Even when kaolin is not detected in an earth pigment by x-ray diffraction, due to low crystallinity or concentration, its presence can often be determined from the infrared spectrum of the earth.

Because kaolin occurs in earth pigments from many geological environments, its presence does not indicate a specific source. However, the hydroxyl band intensities and positions are very sensitive to the order and crystallinity of the kaolin [6,13] and it is possible that changes in the hydroxyl absorptions could be used to differentiate pigment sources.

Figure 3 shows the infrared spectra for yellow earth pigments from three geological sources: Argentina, Italy and France. The kaolin hydroxyl absorptions in the yellow earth from Argentina are different from the other two samples and the broader bands suggest that the kaolin is relatively disordered. The samples from Italy and France, on the other hand, are very similar to one another and contain well-crystallized kaolinite. This illustrates that while differences in the kaolin hydroxyl bands may indicate different pigment sources, the converse is not the case, since kaolin from different sources may produce very similar spectra.

- other minerals

While kaolin is widespread and does not indicate a specific type of pigment source, some of the less commonly encountered accessory minerals can point to a particular type of geological formation as the source of the iron earth.

This is illustrated in the analysis of one of the red earth pigments in the Forbes collection (6.02.78). The infrared spectrum of this pigment, shown in figure 4, allows the identification of two aluminum hydroxide minerals: gibbsite and boehmite. The presence of these minerals together with hematite indicates that the source of this pigment is a bauxite deposit; they do not occur together in any other type of geological formation [14]. Bauxite, which is produced by rock weathering under tropical conditions, occurs in Europe as well as in North and South America. The fact that gibbsite is the dominant mineral in this sample suggests that the source is a deposit outside Europe, since the European deposits are dominated by either boehmite or another aluminum hydroxide, diaspore [15].

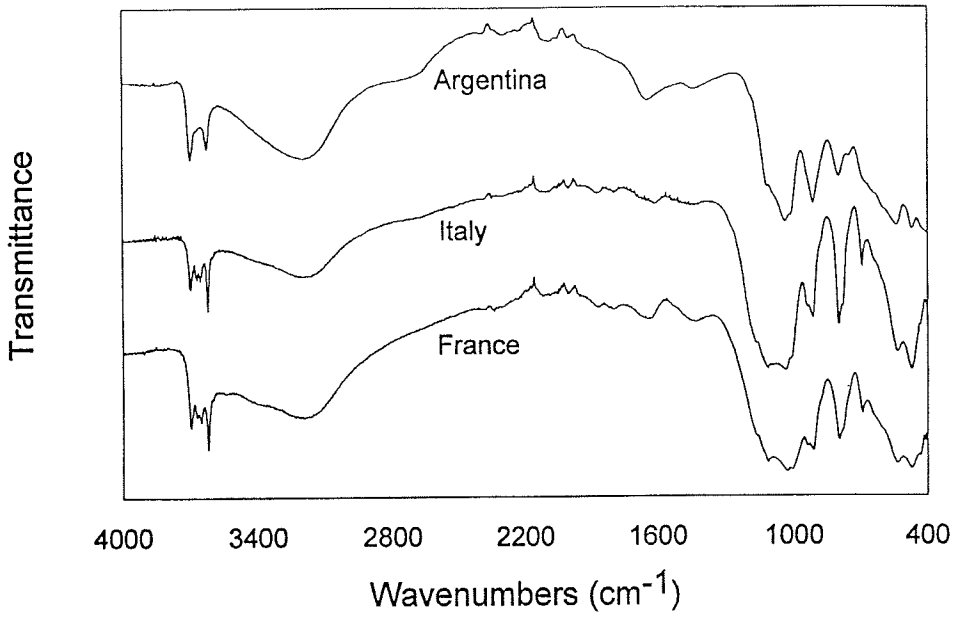


Figure 3: infrared spectra of yellow earth pigments from three geological sources

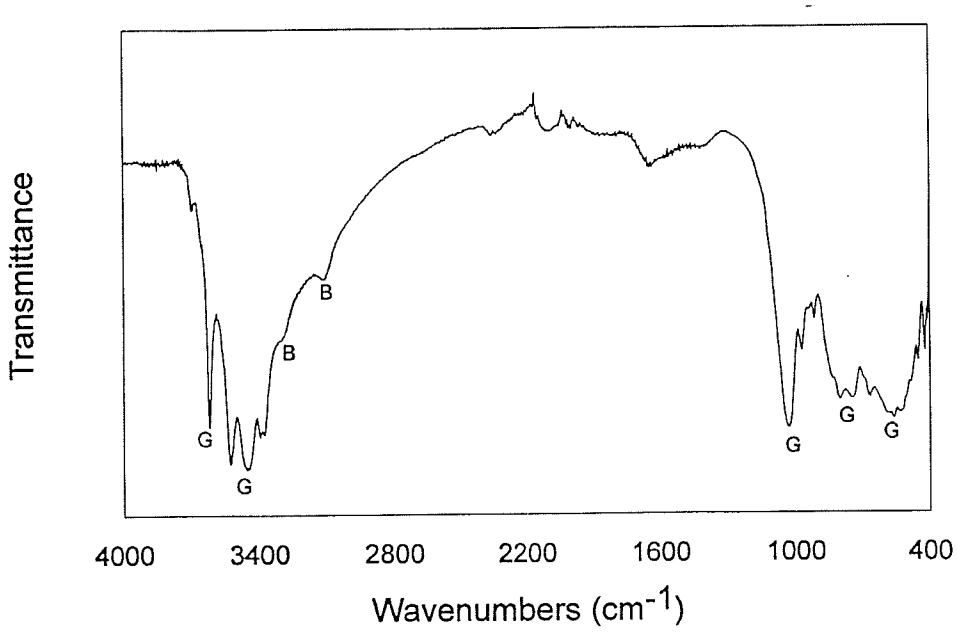


Figure 4: infrared spectrum of a red earth pigment from the Forbes collection indicating the presence of gibbsite and boehmite. G=gibbsite bands; B=boehmite bands

While infrared spectroscopy can be very useful in characterizing accessory minerals, it is important to realize the limitations of using mineral identification techniques to determine information about geological sources. This is illustrated in the analysis of a group of coloured rocks, excavated close to an important pictograph site, Cerro de los Indios, in Argentina [16]. These rocks are thought to have been brought to the site as potential pigments. Both red and yellow rock fragments, as well as rocks to which pigment had been applied were found during the excavation. By analysing these materials, we hoped to provide a comparison for the pigments in the pictographs themselves and also possibly determine a geological source for the material. The infrared spectrum, of a powdered sample from the interior of one of the red rock fragments, indicated the presence of quartz and a feldspar mineral as well as a small amount of carbonate. X-ray diffraction verified that the red colouration was produced by hematite. This type of information is useful as a comparison for the pictograph pigments, but it does not help to determine a geological source for the hematite. Unlike the aluminum hydroxides discussed in the previous example, quartz and feldspars occur in a wide range of igneous and metamorphic rocks as well as in sediments under some conditions [17].

Petrographic examination of a fragment of the sample in a thin section, on the other hand, showed that the quartz and feldspar occur as phenocrysts, visible as large crystals embedded in the fine-grained hematite-rich groundmass. These quartz and feldspar phenocrysts are remnants of the volcanic texture of the source rock which produced the hematite. This examination allowed a much more specific characterization to be made than had been obtained by infrared spectroscopy. From the petrographic analysis, it could be concluded that the hematite was formed by the weathering of a volcanic rock of the dacite type [18].

## 11.5 Conclusions

Infrared spectroscopy can provide useful information for the characterization of the iron earth pigments. However, one must also be aware of the inherent limitations of this technique. The variability in chemical composition and the occurrence of multi-component mixtures makes the analysis the iron earths challenging. In many cases, it is only with the use of several complementary methods of analysis that these interesting and complex pigments can be fully understood.

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# 12. Analysis of mineral salts from monuments by infrared spectroscopy

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Det Kongelige Danske Kunstakademi

## 12.1 Summary

Identification of salt efflorescence from monuments, such as wall paintings, masonry and stone sculpture, is important in determining courses of deterioration and in finding the proper preventive and conserving methods. Normally identification has been done by a combination of optical microscopy and microchemical tests or X-ray diffraction. Infrared spectroscopy can be a convenient supplement or an alternative to these often time consuming techniques which require considerable skill and experience. Most salt efflorescence (except alkali metal halides) can easily and quickly be identified by Infrared spectroscopy and mixtures or X-ray amorphous salts are also recognised by the often simple spectra of these inorganic products. Illustrated with case histories, the presentation will discuss strategies for salt analysis by combining FT-IR spectroscopy with microchemical tests and optical microscopy. Different sample preparation techniques such as nujol mull, potassium bromide pellets and disposable IR cards from 3M will be reviewed. Also diffuse reflectance techniques for salt analysis will be discussed. Finally a collection of spectra from salts that are common in monuments will be presented.

## 12.2 Introduction

Salt efflorescence is the single most important deteriorating factor on porous monuments such as wall paintings and stone sculpture. An important factor in solving a salt problem is to identify the damaging specimen. This is often done by X-ray diffraction or by optical microscopy in combination with microchemical slide tests [1, 2].

Infrared spectroscopy has several advantages as a means for identifying salt efflorescence. The spectra of most of the common salts are simple but still distinctly different. This means that they function as good fingerprints even for mixtures. Another advantage is that amorphous salts can also be identified with IR, which is not possible with XRD. Important damaging compounds that do not absorb in the mid IR are the alkali metal chlorides but they can easily be identified by other means.

## 12.3 Spectra of salts common in monuments

Common anions in efflorescing salts are nitrates, sulfates and carbonates. Nitrates have bands in two characteristic intervals from 800 to 840 $cm^{-1}$ and from 1340 to 1380 $cm^{-1}$. The individual frequencies of the sharp nitrate bands around 820 $cm^{-1}$ allow an identification of them. For example sodium and potassium nitrates have the sharp band at 836 and 825 $cm^{-1}$ respectively. This difference is enough to recognise them (figure 1).

Sulfates have strong bands in the region 1080 to 1150 $cm^{-1}$ and also a medium strong band between 580 and 670. The presence of hydroxyl bands in the area 3700 to 3100 $cm^{-1}$ is convenient for distinguishing the different hydrates. For example in the system $CaSO_4$ - $H_2O$. The three types of $CaSO_4$: gypsum, hemihydrate and anhydrite, are easily identified just by the differences around 3500 $cm^{-1}$ and by the different splitting of the peak around 1620 $cm^{-1}$ (figure 2).

Carbonates all have the strong band around 1410-1450 $cm^{-1}$. They also have a medium strong band in the 840-880 $cm^{-1}$ range; a band which normally goes to lower frequency as the cations become heavier. Salts of organic acids (figure 3) can result from conservation treatment of the monuments. They can be formed from acids liberated from wood or be caused by fungal activity. Calcium and magnesium formates found in sandstone buildings have been attributed to cleaning with formic acid [3].

Oxalates can also be ascribed to treatments. In 1899 a method for consolidating porous lime bound colours with oxalic acid or ammonium oxalate was patented in Denmark [4].

More often oxalates are caused by fungi. Especially the dry rot fungus Serpula lacrymans produces large amounts of calcium oxalates. It actually needs to have access to calcium carbonate in order to neutralise the oxalic acid which it utilises to degrade the wood [5].

Calcium formate and acetate efflorescences have been identified on mollusc shells by IR- spectroscopy [6]. The formation was caused by the formic- and acetic acid vapours produced in the wooden drawers in which the shells were kept.

### 12.4 Sampling and sample preparation

The salt samples should be taken with proper tools such as scalpel and brush and if possible under the binocular in order to get the pure salts without contamination. The sample should be transported to the lab in air tight vials so that the salts do not recrystallize. At the lab, preliminary tests for halogenide, sulfate and nitrate can be performed by usual wet chemical tests [7] - chloride: formation of silver chloride with silver nitrate; sulfate: precipitate with acid barium chloride. Nitrates can conveniently be tested for by Merck's merckoquant nitrate sticks. If chlorides are present, it is advantageous to make further investigations as these species might not show up in the IR spectra. By optical microscopy the alkali chlorides are recognised as isotropic cubes and they can be distinguished by their refractive index.

#### 12.4.1 Preparation

Many of the salt-spectra that we have made were obtained on KBr pellets. The salts are ground with KBr (approximately 1% sample) in an agate mortar for only about a minute in order to avoid reaction between the sample and the KBr. In spite of the possible cation exchange reactions and the pressure induced structural transformations that can take place when inorganic samples are prepared as KBr pellets we only faced problems with sodium salts and only when the samples were ground for a very long time. With nujol mull transformations do not take place but the method is a bit inconvenient and the hydrocarbon peaks in some cases obscure important bands. This can be overcome by the so called split mull technique where spectra are recorded in two types of mull: the upper part in mineral oil and the lower part in perfluoro-hydrocarbon.

12.4.2 Diffuse reflectance spectroscopy
Diffuse reflectance simplifies the sample preparation. It is enough to mix the powdery salt with KBr powder, then put the mixture in the sample cup and record the spectrum, ratioed against KBr. With this technique some drawbacks of the KBr pellets technique are avoided but other ones are introduced. If pure sample is used, specular reflectance is a problem but this can be eliminated by admixing the right amount of KBr powder. Intense overtone bands are characteristic in diffuse reflectance spectra of many inorganic compounds. The relative ratio of the spectral bands are not always consistent with transmittance spectra. This can make it difficult to use transmission spectra as reference.

12.4.3 Extracts and polyethylene cards
Extracted salts from a sample can be screened for nitrate, sulfate, chloride by the spot tests mentioned before. After evaporation the IR spectrum can give information about the species present. Here the 3M disposable IR cards have proved versatile. The cards have a zone made of porous polyethylene or Teflon. A drop of sample solution is placed on this zone and the solvent is evaporated with nitrogen. The spectrum can then be recorded ratioed against the empty PE-card. If the particle size of evaporated salt is too big the spectrum becomes distorted. The cards can be too expensive as sample support for routine use, therefore a method using Teflon tape purchased at a local hardware store has been developed [8].

**12.5 Examples of identified samples**
Although a lot of different composite salts species have been found in wall-paintings [9,10] we have only found rather few and simple salts in the efflorescence of the Scandinavian brick buildings and wall paintings we have examined. Most of them are calcium and alkali metal salts.

The only example of a magnesium salt we have is from Italy (figure 4). It comes from a 14th c wall painting and it is magnesium carbonate trihydrate with a little nitrate. What kind of nitrate it is not possible to tell. In several published spectra of pigment samples from wall-paintings a dominant peak at 1384 $cm^{-1}$ is observed. This peak is no doubt due to a nitrate, but the band in the 800 -840 $cm^{-1}$ region is often masked by other heavy bands thus making it impossible to identify the nitrate with certainty.

In other parts of the same Italian wall-painting the efflorescence consists of pure gypsum. Gypsum is one the most common efflorescing salts. In an example from a Danish 13th c. wall-painting (figure 5 ) we found, in addition to the gypsum, calcite and nitrate. Again, it is not possible to tell which nitrate. A bit further down the wall potassium sulfate was dominant (figure 6). In an example from a basement wall, the efflorescence consisted of nitrate and in this case it could be identified as a mixture of potassium and sodium nitrate (figure 7).

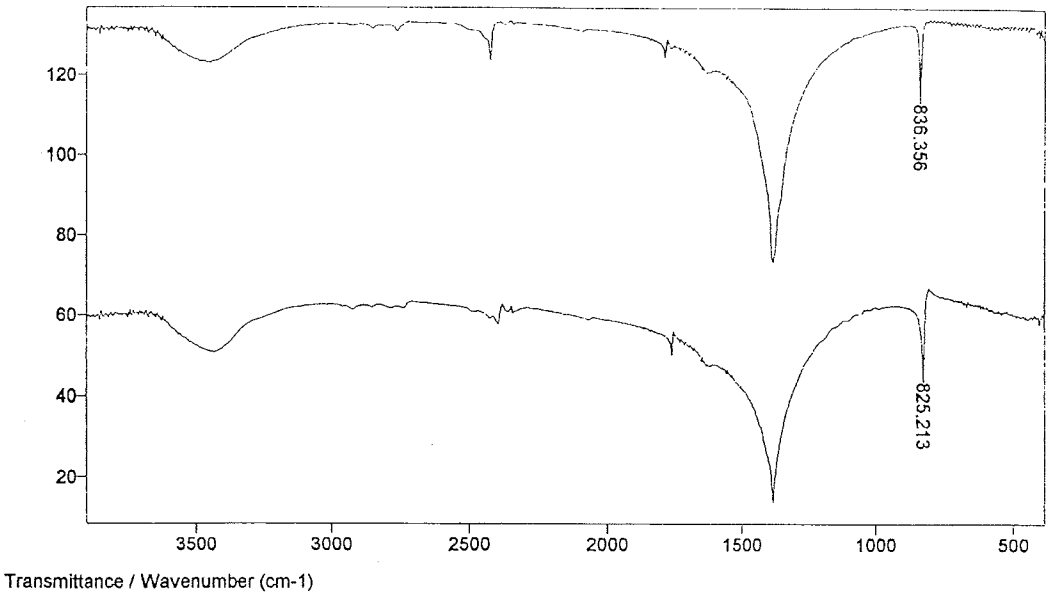


Figure 1: top: sodium nitrate - bottom: potassium nitrate both in KBr

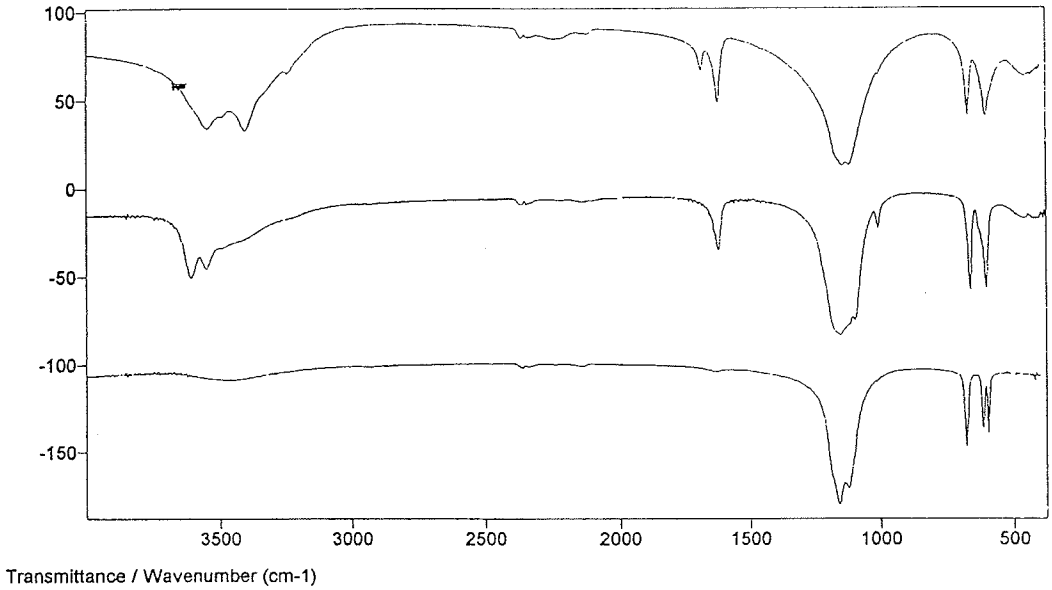


Figure 2: gypsum in its different hydrated forms - top: calcium sulphate dihydrate; middle: calcium sulfate hemihydrate; bottom: anhydrite

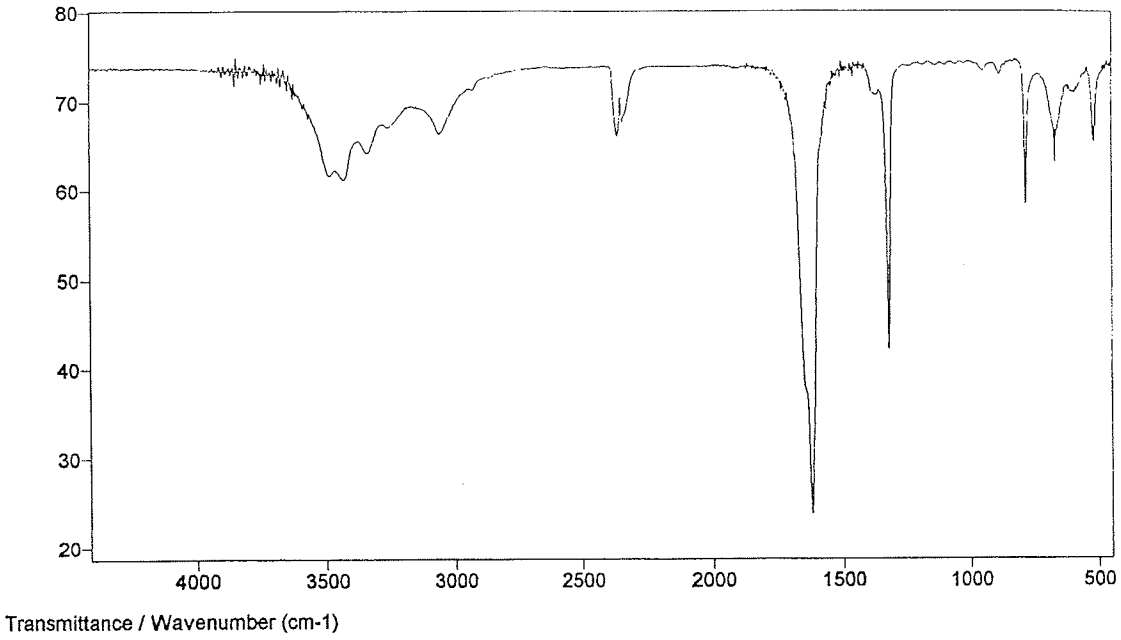


Figure 3: calcium oxalate monohydrate (whewellite),the most stable of the existing hydrates of calcium oxalate

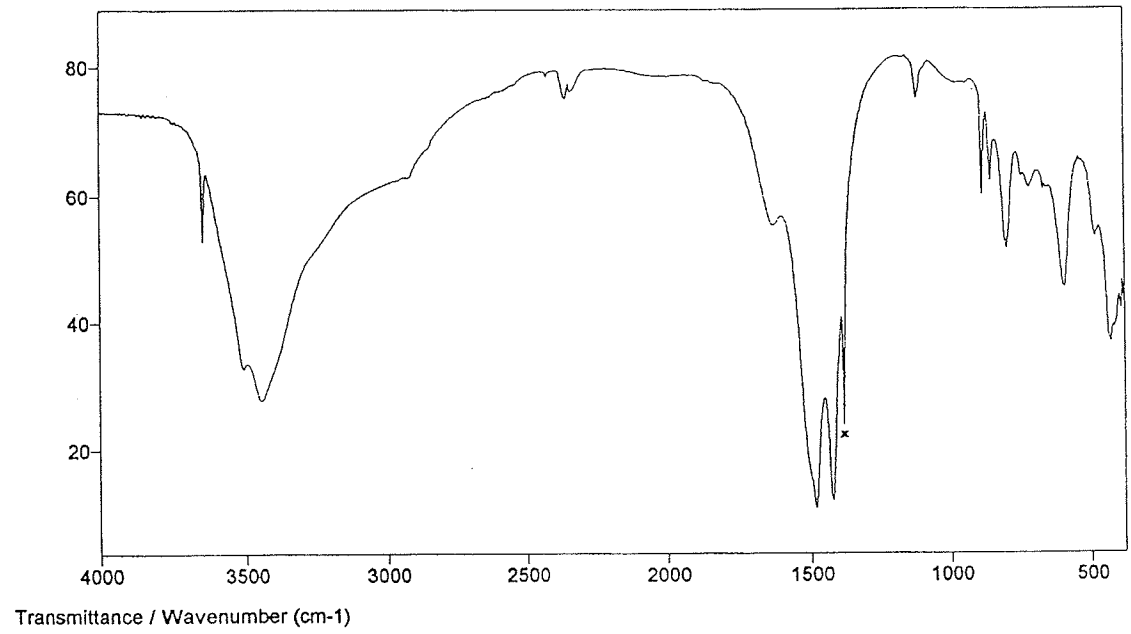


Figure 4: efflorescence from 14th c. wall painting northern Italy consisting of $MgCO_3$, 3 $H_2O$ and nitrate (x)

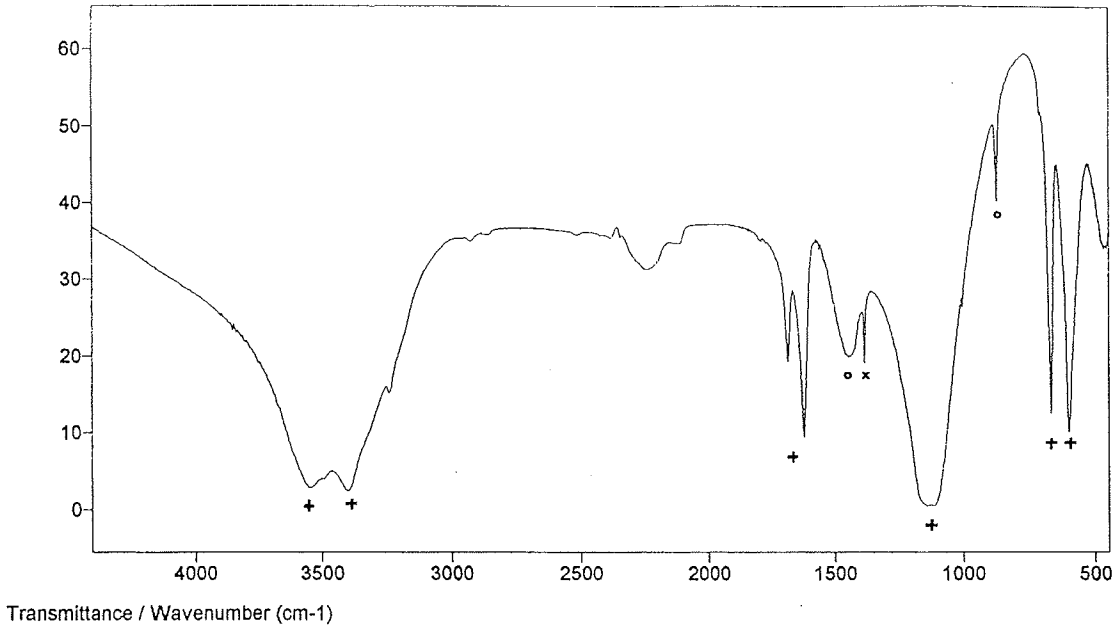


Figure 5: efflorescence from Danish 13th c. wall painting $CaSO_4$, 2 H2O (+), $CaCO_3$ (o) and $NO_3^-$ (x)

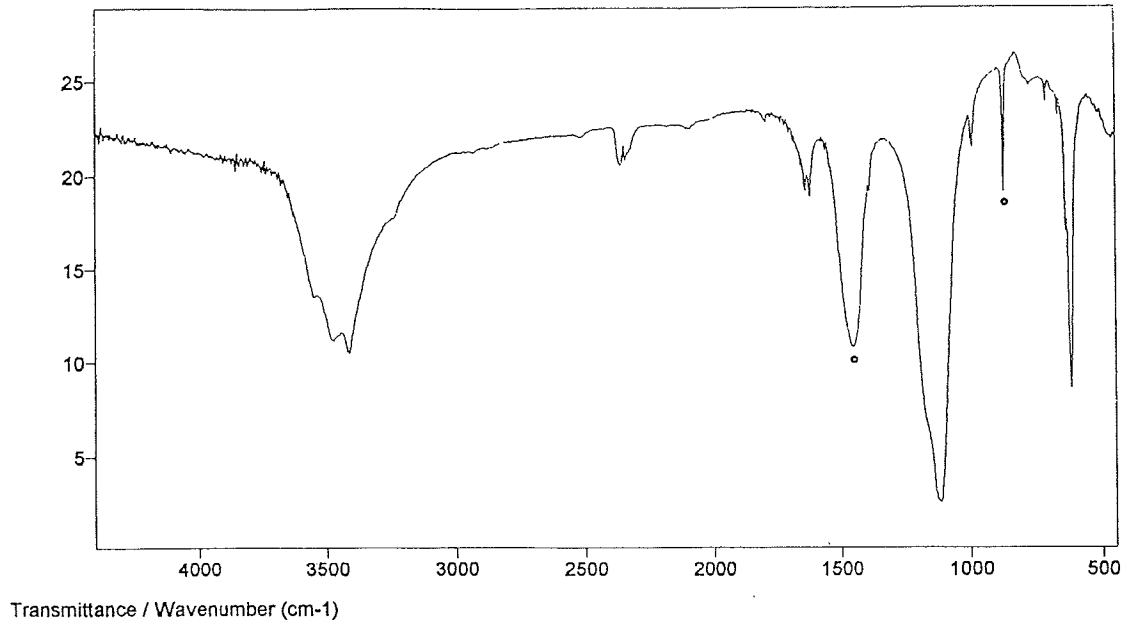


Figure 6: efflorescence from Danish 13th c. wall painting consisting of $Na_2SO_4$ and calcite (o)

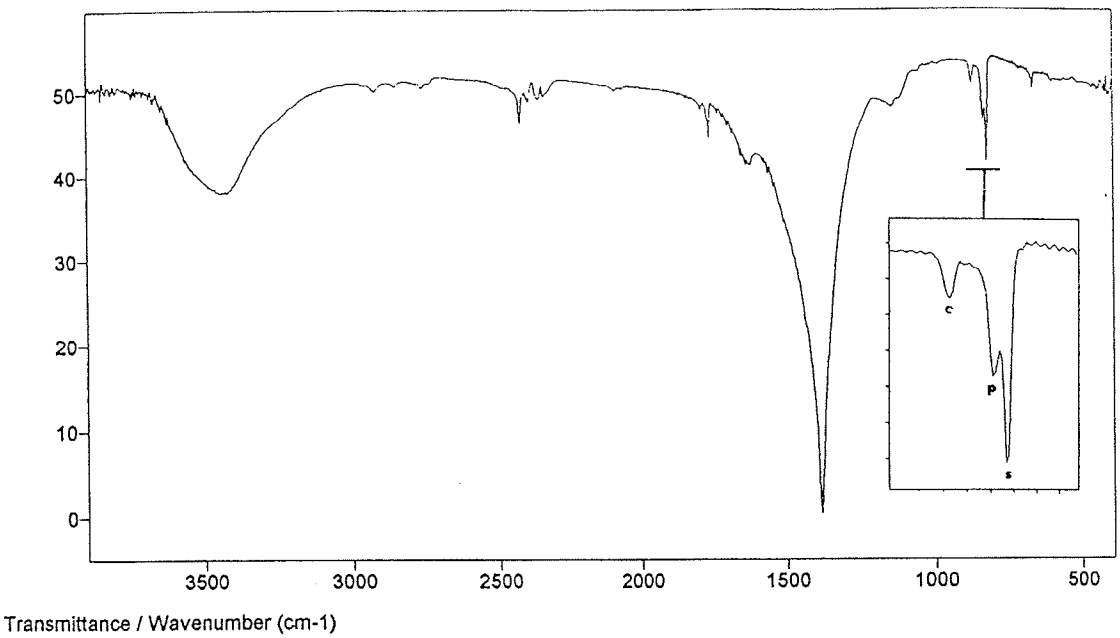


Figure 7: efflorescence from a basement wall: sodium nitrate (s), potassium nitrate (p) and calcite (c)

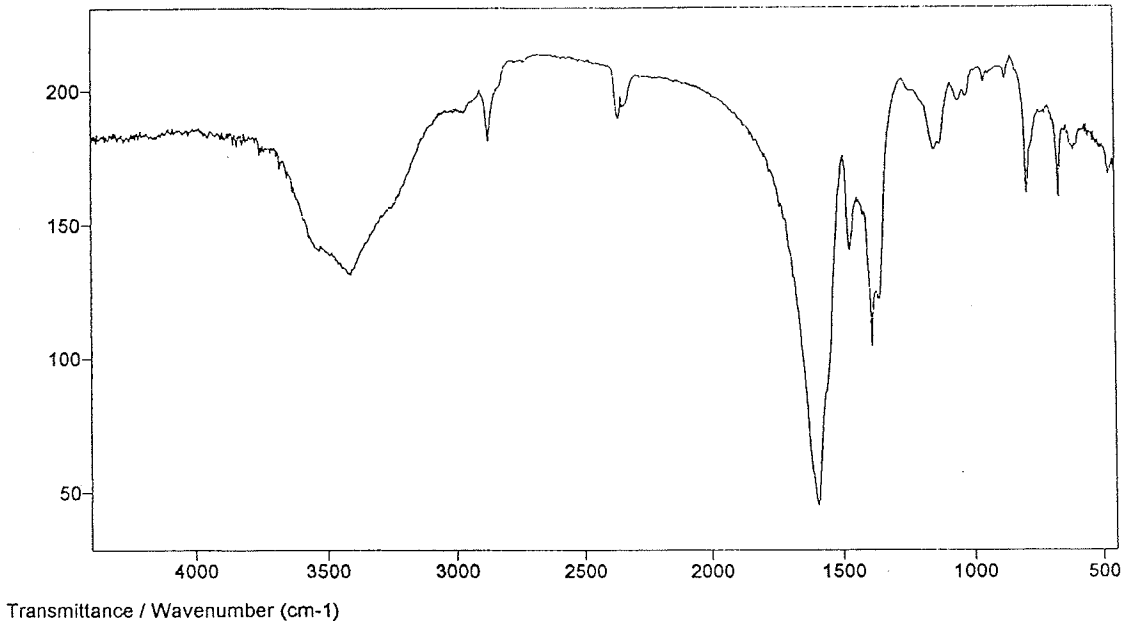


Figure 8: efflorescence on a coral - the spectrum is similar to a spectrum of $3Ca(CH_3CO.O)_2,4Ca(CHO.O)_2,5H_2O$

An efflorescence on corals used as ornament on a baroque cabinet turned out to be a calcium acetate formate (figure 8) with a spectrum similar to spectra of efflorescence found on mollusc shells [6]. The corals had probably been attacked by acids liberated from the wooden cabinet or cellulose or vinyl acetate conservation substance.

## 12.6 Conclusion

It is necessary to have standard spectra to distinguish related compounds. Reference spectra of the different possible salts are not easily available. Some are found in older reference collections [11] or they can be found in the expensive commercial libraries offered by eg: Sadtler. We try to build up a library of spectra from reference material that has either been bought or synthesised and at the moment we are synthesising more rare composite salts that occasionally can be found in monuments. The spectra including the ones mentioned in this paper are available from the author.

## 12.7 References

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3 K Zender, and A Arnold, "Stone damage due to formate salts", *Studies in Conservation* **29** (4) pp 32-34 1984

4 A Nielsen, DK-A-3188 (1900)

5 J Bech-Andersen, "Production, function and neutralisation of oxalic acid produced by the dry rot fungus and other brown rot fungi", The international research group on wood preservation, Document IRG/WP/1330 (1987) 6

6 NH Tennent, and T Baird, "The deterioration of Mollusca collections: identification of shell efflorescence", *Studies in Conservation* **30** (7) pp 73 - 85 1985

7 JM Teutonico, "A laboratory manual for architectural conservators", ICROM Rome (1988) 8

8 KA Oberg, and DR Palleros, "Teflon tape as a sample support for IR spectroscopy", *Journal of Chemical Education* **72** (9) pp 857- 859 1995

9 A Arnold, and K Zehnder, "Monitoring wall paintings affected by soluble salts". In *The Conservation of Wall Paintings*, proceedings of a symposium, London (1987) pp 103 - 135 10

10 MHPC Holtkamp, and WMM Heijnen, "The mineral darapskite in the efflorescence on two Dutch churches", *Studies in Conservation* **36** (11) pp 15-178 1991

11 RP Nyquist, and RO Kagel, "Infrared Spectra of Inorganic Compounds", New York (1971)

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# 13. FTIR techniques at the Building Research Establishment (BRE)

Matthew Murray
Building Research Establishment

## 13.1 Summary

The BRE uses diffuse reflectance and IR microscopy to analyse the surfaces of building materials such as limestone, sandstone, mortars and masonry treatments. Of particular interest is the effect of sulphur dioxide from atmospheric pollution on stone masonry, and the resultant sulphate products. At the BRE we have recorded the location of sulfates and carbonates at 100 micron intervals into the surface of weathered stone masonry using IR microscopy in reflection. Individual mineral crystals can also be identified as either sulphate carbonate or silica under the microscope. Techniques using diffuse reflectance FTIR have also been developed to observe the depth of penetration of stone treatments such as stone consolidants and microcrystalline waxes into masonry surfaces. The BRE will explain the various techniques that it has adapted or developed to analyse masonry surfaces, using results to show their effectiveness.

Paper not submitted for inclusion in postprints.

Author

Matthew J. Murray obtained his BSc in Chemistry from Kings College, University of London. He went on to obtain an MSc (Biosensors) from the University of Newcastle in 1989. He joined the Weathering Science Section, BRE in 1992 and has been involved in the development and use of an ion chromatography for analysing products front the reaction of atmospheric pollution and building materials, He is now responsible for the running of this system which provides a valuable service to the Section. He has also worked on the application of other analytical techniques to determine the composition of the surface of weathered stone and on the protection of natural stone, in particular, the use of FTIR which is being used additionally for research on graffiti removal and consolidants.

# 14. An Infrared Spectral Library of Naturally Occurring Minerals

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## 14.1 Summary

An infrared spectral library of naturally occurring minerals from the collections of Rutgers University (Chester Collection) and the Mineral Sciences Department of the National Museum of Natural History - Smithsonian Institution has been compiled. This paper will discuss the formation of the spectral collection and present several examples from conservation applications illustrating its use.

## 14.2 Introduction

The *Infrared Spectral Database of Naturally Occurring Minerals* is a compilation based on the mineral collections at Rutgers University (The Chester Collection), the University of Delaware, the University of Pennsylvania, Harvard University, and the Smithsonian Institution Department of Mineral Sciences of the National Museum of Natural History. The database is the result of an ongoing collaboration between the Philadelphia Museum of Art, the Winterthur Museum, and the Museum of Fine Arts, Boston. The micro-FTIR analyses were supplemented by x-ray diffraction and x-ray fluorescence. This paper describes the *Infrared Spectral Database of Naturally Occurring Minerals* and illustrates, with several examples, its use conservation applications. An overview of commercial spectral compilations is also presented.

## 14.3 Advantages of the micro-FTIR technique for minerals analysis.

There are several advantages of using the micro-FTIR technique for minerals analysis. Sample preparation is relatively fast and easy. With the IR microscope and the micro compression diamond cell, KBr pellets and Nujol mulls are no longer necessary. Sub-milligram quantities of an unknown are more than sufficient for analysis. IR is extremely sensitive to certain common minerals and it can also detect them as minor impurities. Calcite and quartz are two good examples of such minerals. IR can provide a quick method to distinguish polymorphs; minerals with the same chemical composition but with a different crystal structure. Micro-FTIR is also useful as a complement or alternative to the more traditional methods of x-ray analysis such as XRD, SEM w/EDS, and EPMA. While a mineral specimen may take several hours to analyse by XRD, IR can produce a spectrum unique to a mineral in a few minutes. Kaolinite is often cited in the literature as an example of a mineral which when present as a minor impurity, may be more difficult to detect by x-ray analysis than by IR.

## 14.4 Why a minerals database?

The need for a minerals database specific to the conservation application was first suggested at the 1994 IRUG meeting in Philadelphia. It is well known that minerals are commonly detected in conservation samples. Minerals are found as pigments and fillers in paint films, in soil moulded into earthen artifacts and mudbrick, as corrosion products on metal surfaces, in stone fabricated as sculpture and architectural monuments, and in ceramics. Having a spectral database of minerals available will facilitate spectral searching, and spectral manipulations such as subtractions and additions.

## 14.5 Commercial digitized mineral libraries

Some digitized mineral libraries are commercially available. However they tend to be variable in quality and are relatively expensive for most museum analytical laboratories. Examples of commercial digitized libraries are given below.

- The *Sadtler Library* of Minerals and Clays, is the most extensive compilation with 430 spectra but it is missing some important minerals that are present in artist's materials. There are also some miss-assignments. Furthermore, if one is using Nicolet software, separate Sadtler software is required.
- The *US Geological Survey Library* has 78 chemically analysed spectra, but the library is limited mostly to silicates and the spectra are of variable quality.
- The *Nicolet Painter's Mineral Library* contains 23 filler and extender type minerals..
- The *KVB/Analect Library* contains 53 spectra, however, access to the Analect library is limited to the Analect user.

## 14.6 Mineral spectral reference books

There are excellent mineral spectral reference books available containing numerous original citations. Among these are:

- Gadsen, JA, 1975, *Infrared Spectra of Minerals and Related Compounds*, Butterworths, London.
- Farmer, VC, 1974, *The Infrared Spectra of Minerals*, Mineralogical Society, London
- Jones, GC and Jackson, B, 1993, *Infrared Transmission Spectra of Carbonate Minerals*, Chapman and Hall, London.
- Moenke, H, 1962, *Mineralspecktren,* Akademie-Verlag, Berlin.
- Ferraro, JR, *1882, The Sadtler Infrared Spectra Handbook of Minerals and Clays,* Philadelphia.
- Van der Marel, HW, and Beutelsacher, H, 1976, *Atlas of Infrared Spectroscopy of Clay Minerals and their Admixtures* Elsevier Scientific Publishing Company, Amsterdam.

Gadsden, Jones and Jackson, and Van der Marel were found to be the most useful for confirming the band assignments in the *Naturally Occurring Minerals Database.* Of these references, it was noted that Gadsen lists peak positions and intensities, however, it does not include spectra making it impossible to check the band contours. Jones and Jackson published in 1993, has very high quality spectra and peak tables but is limited to carbonates. Van der Mabel has an excellent review of the clay minerals; includes spectra and good discussion on band assignments.

## 14.7 General inorganic spectral references

The books listed above are specific for minerals. Other spectral compilations of inorganic compounds are available but include only a limited number of minerals:

- RA Nyquist, and RO Kagel, 1971, *Infrared Spectra of Inorganic Compounds*, Academic Press, New York.
- FA Miller, and CH Wilkins, 1952, *Infrared Spectra and Characteristic Frequencies of Inorganic Ions*, Analytical Chemistry, 24, 1253-1294.

### 14.8 General mineral reference books

To classify the minerals in the database the following books were consulted:

- AM Clark, 1993, *Hey's Minerals Index,* Chapman and Hall, London.
- ES Dana, and WE Ford, 1949, *A Textbook of Mineralogy*, John Wiley and Sons, Inc, New York.
- M Fleischer, and JA Mandarino, *1995, Glossary of Mineral Species*, The Mineralogical Record Inc, Tucson.
- Klein and Hurlbut, 1977, *Manual of Mineralogy,* John Wiley and Sons, Inc., New York.
- EH Nickel, and MC Nichols, *1991, Mineral Manual, Van Nostrand Reinhold, New York.*
- Aleph Enterprises, 1989, *The Mineral Database*, Aleph Enterprises, Livermore, California.

Fleischer and Mandarino's *Glossary of Mineral Species,* approved by the International Mineralogical Association, was used as a reference for the mineral names and formulas recorded in the database.

### 14.9 Overview of the database: mineral classification

The database, an on-going compilation, now contains about 75 minerals. Currently, the mineral specimens are from the following sources the Rutgers University Geology Museum, New Brunswick, NJ; The Smithsonian Department of Mineral Sciences, Smithsonian Institution, Washington, DC; the Geology Department, University of Delaware, Newark, DE; the Geology Department, Harvard University, MA; and the Geology Department, University of Pennsylvania, Philadelphia, PA. As no single mineral collection is complete, there are certain minerals we seek to acquire from other sources.

Minerals are generally defined as *naturally occurring* homogenous solids with a definite but not fixed chemical composition and a highly ordered atomic arrangement or crystal structure. The term, "naturally occurring" refers to substances formed by natural processes as distinguished from those made in the laboratory. Any synthetic minerals such as NIST standards, are marked as synthetic or artificial in the database.

Today, there are about 4000 published mineral species. They are classified in a variety of ways. Most are adapted from the Dana system started in 1837 and their classification is based on chemical composition and crystal morphology. This system includes some of the following groups: native elements, sulfides, sulfosalts, oxides (including hydroxides), halides, carbonates, nitrates, borates, phosphates, sulfates, tungstates, and silicates. The last group, the silicates, account for approximately 80% of the

minerals on the Earth's surface and are classified more on a structural rather than chemical basis.

### 14.10 Scope of the database

The carbonates, halides, phosphates, silicates, and sulfates are exemplified in the database. The borates, nitrates, sulfosalts and tungstates are excluded because these minerals are not typically found in conservation samples. The mineral oxides have very limited mid-IR activity and are not in the database. For example, the titanium oxides (anatase, brookite, rutile), copper oxides (cuprite, tenorite), iron oxides (hematite, magnetite), lead oxides (massicot and litharge) and manganese oxide (pyrolusite) show only a single band at or below 700 $cm^{-1}$ with the MCT detector. The mineral sulfides (cinnabar, realgar, orpiment, chalcocite, digentite, djurleite, stromeyerite) have no bands above 400 $cm^{-1}$ so these are also not included in the database.

### 14.11 Sample preparation

The interior of the mineral specimens was sampled to avoid adsorbed organic contaminants and surface water as clay minerals are susceptible to these. The resulting particulate was mounted on a single diamond compression cell and flattened with a metal roller tool to obtain a thin film at least 20 x 20 micrometers in area. This procedure was followed to be consistent with our usual method of sample preparation.

XRF was used to screen specimens. If the IR data was inconsistent with published spectra, the sample was further analyzed by XRD and, when necessary, a replacement specimen obtained.

#### 14.11.1 Instrumental conditions

Samples were run on a NIC-Plan microscope attached to a Nicolet 510P bench with a dry air purge. The data was collected in the transmission mode, at 4 cm-1 resolution, for 200 (or more) scans. The collection range was 4000 - 625 $cm^{-1}$; 625 cm-1 is the lower detection limit of the microscope MCT detector. Although additional bands for minerals occur between 625 and 200 $cm^{-1}$, our collection range reflects the common usage of the IR microscope in conservation analytical laboratories today.

### 14.12 Spectra

The hard copy spectra include a standard plot between 4000 and 625 $cm^{-1}$, and expanded plots in two regions. The first is in the O-H stretching region since the OH group is virtually the only independent vibrator in mineral spectra and important distinguishing information can be gleaned from this region. The second region is occurs below 1500 $cm^{-1}$ where many of the bands tend to be concentrated and overlapped.

All spectra were baseline corrected and normalized, and each is referenced with the mineral name, chemical formula, geographic locality and collection source.

## 14.13 Examples of minerals in the database

14.13.1 Aragonite vs. calcite (figure 1)

Aragonite and calcite are two species from the carbonate group and are trimorphous with vaterite. These minerals consist of the single cation, calcium, and the carbonate anion $(CO_3)^{-2}$. While calcite and aragonite have been detected in conservation analyses, vaterite occurs rarely in nature although it has been reported in Northern Ireland.

Aragonite can be distinguished from its polymorph, calcite, in the mid-IR by the position of the strong asymmetric C-O stretch (1469 vs 1422 $cm^{-1}$), the 1083 $cm^{-1}$ band, the out-of-plane bend (857 vs 878 $cm^{-1}$), and the in-plane bend (712, 700 $cm^{-1}$ doublet vs 712 $cm^{-1}$ singlet).

14.13.2 Carbonates (figure 2)

Figure 2 shows, in expanded detail, five carbonate minerals with different cations: barium, iron, magnesium, calcium and magnesium, and manganese. The radius, mass, and electro negativity of these cations influence the wavelength or frequency of the carbonate ion vibration. It is possible to distinguish these carbonates by the position of the out-of-plane and in-plane bends. Although the asymmetric C-O stretch is not included in this expanded detail, its position also varies with cation substitution.

14.13.3 Polymorphs of silica (figure 3)

Quartz, cristobalite, and tridymite are polymorphs of silicon oxide ($SiO_2$). As with the calcium carbonates, there are notable differences in the spectra, here, the respective Si-O stretches. Quartz often shows up as an impurity in clay minerals, distorting the shape and the position of clay mineral bands.

14.13.4 Impure glauconite spectrum (figure 4)

Glauconite is a phyllosilcate in the mica group. Figure 4 shows a spectrum generated from a "glauconite" specimen which is overwhelmingly quartz. This spectrum illustrates the ubiquity of quartz and also the difficulty in acquiring suitable specimens.

14.13.5 Common clay minerals (figure 5)

Several of the most common clay minerals are shown here. The assignment of the infrared bands in these clay minerals is difficult because of their complex, varying composition and the inclusion of foreign ions which can distort the band shapes and frequencies. In some cases a match with more than one reference spectrum may be required for a definitive identification. Therefore, multiple spectra of certain minerals are necessary in the database.

At first glance, the spectra in figure 5 may not appear very informative but on closer examination of kaolinite, for example, the distinctive shapes of the four O-H stretching bands in the 3668 - 3620 $cm^{-1}$ range, the Si-O stretch at 1032 $cm^{-1}$, and the 938 and 915 $cm^{-1}$ O-H in-plane bends are noted.

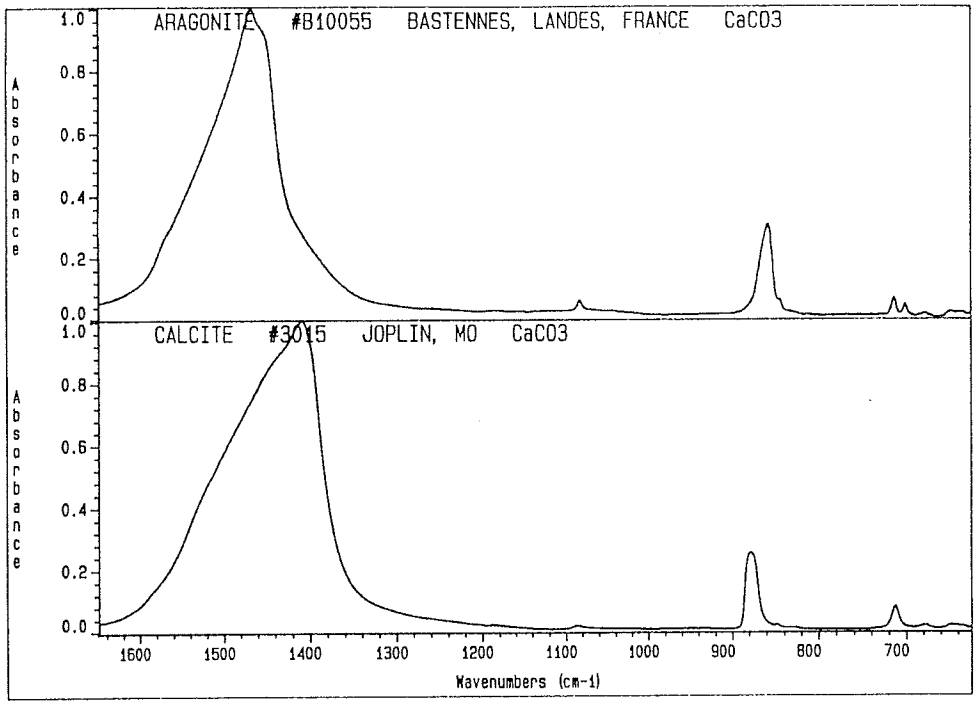



Figure 1: spectra of aragonite and calcite

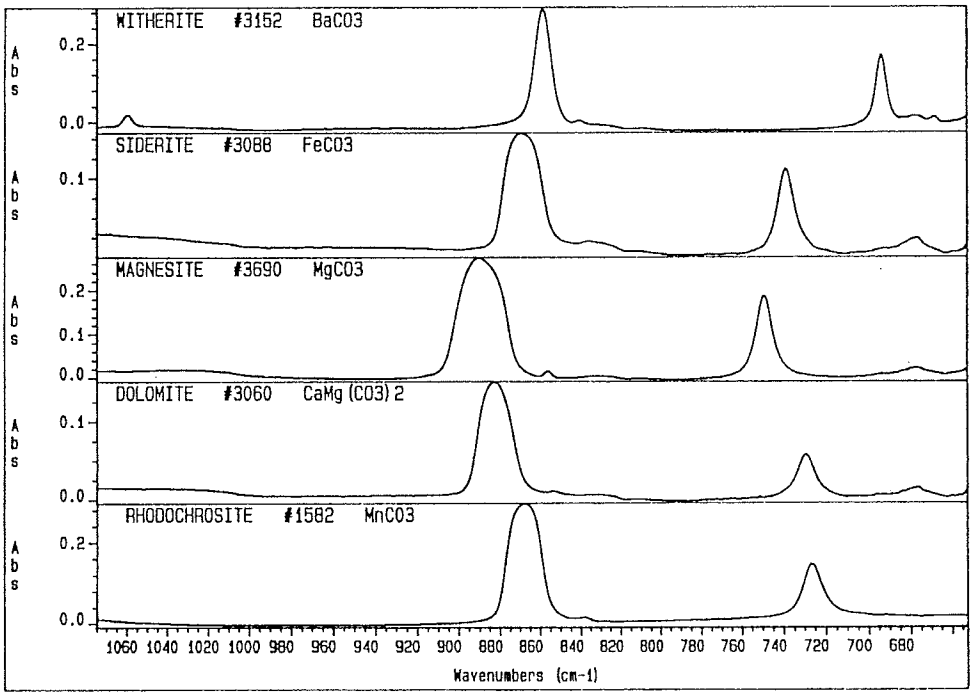



Figure 2: spectra of witherite, siderite, magnesite, dolomite, and rhodochrosite

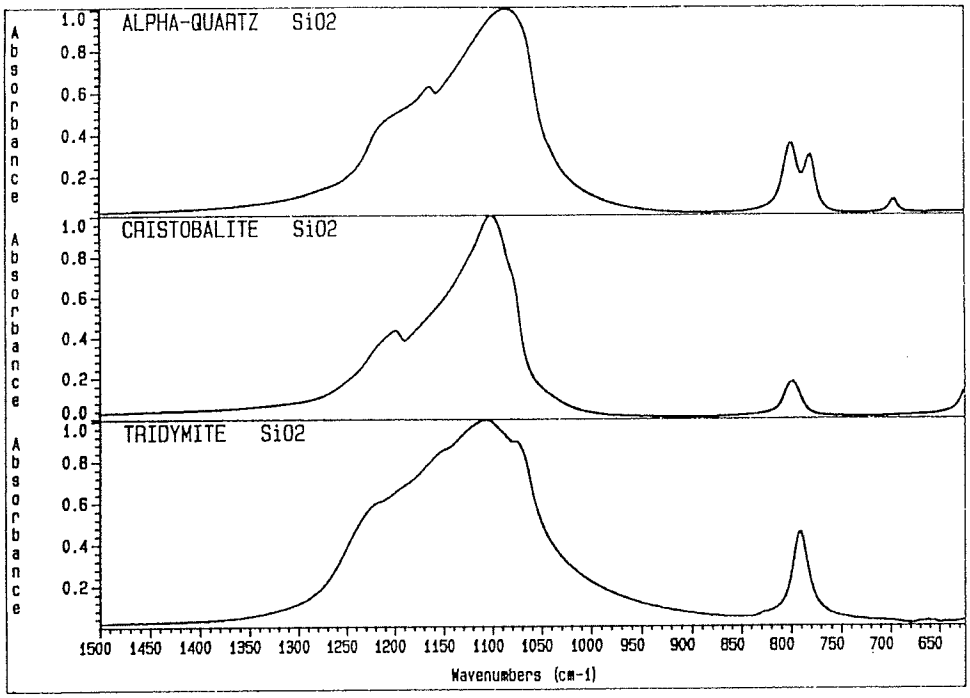



Figure 3: spectra of quartz, cristobalite, and tridymite

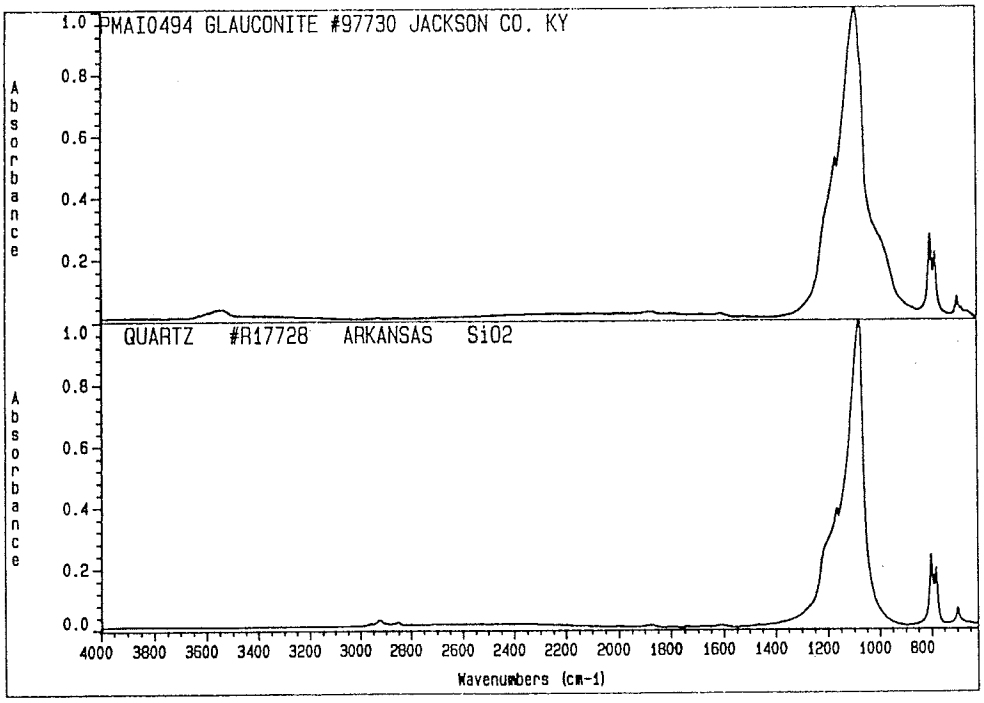



Figure 4: spectra of glauconite and quartz

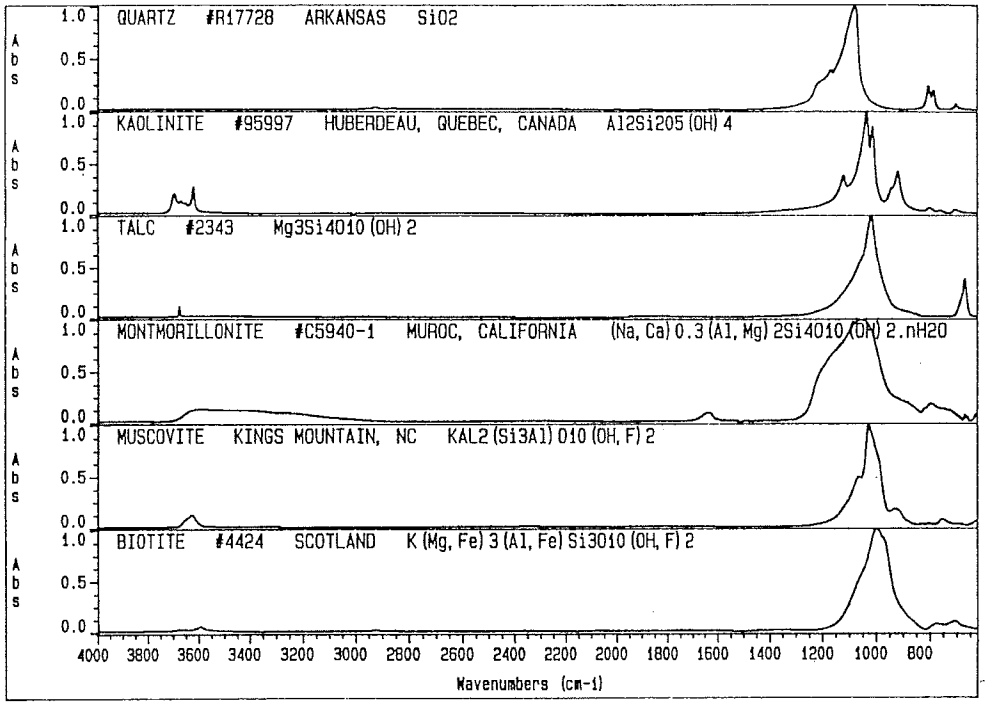



Figure 5: spectra of quartz, kaolinite, talc, montmorillonite, muscovite, andbiotite

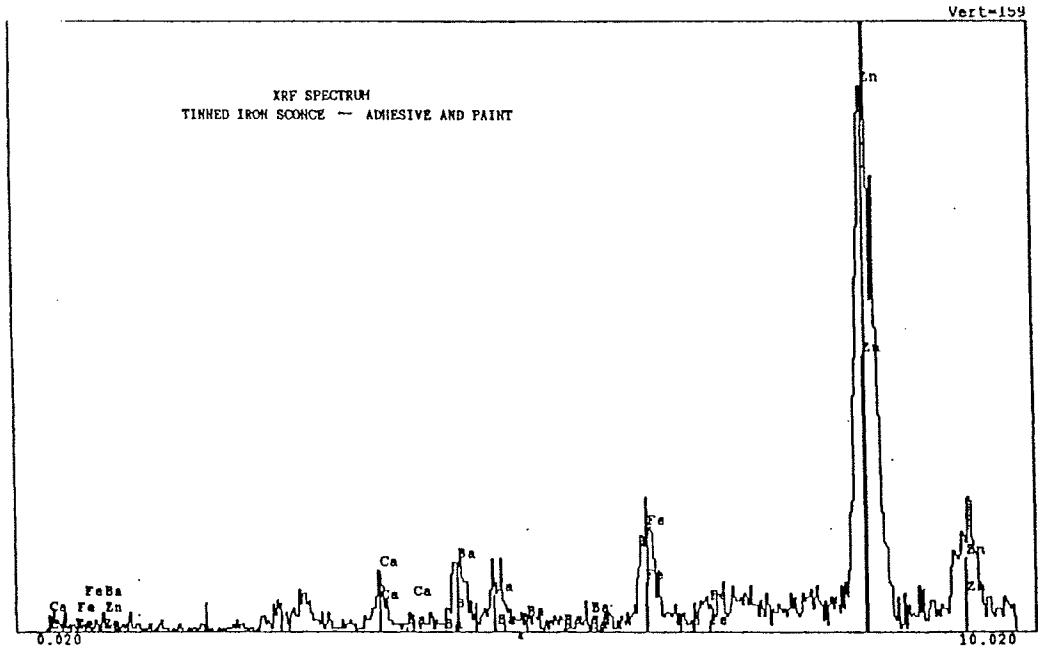



Figure 6A: XRF spectrum of tinned iron sconce

## 14.14 Application of the database to conservation analyses

14.14.1 19th C. American tinned iron sconce (figures 6A-C)

Several losses in an early 19th C. American tinned iron sconce from the Winterthur collection, had been filled with an adhesive. The fills and the sconce were heavily overpainted with a thick white-yellow paint. XRF analysis (figure 6A) showed the paint to contain a high concentration of zinc, together with barium and calcium as well as iron and tin from the base metal material. The detection of zinc and barium indicates the presence of lithopone, a zinc sulfide-barium sulfate pigment. Because lithopone has only been in use since the late 19th century, it clearly is not original to the sconce.

FTIR analysis of the paint was also performed (figure 6B). Bands due to organic components, probably an oil, are seen at 2932, 2861, and 1756 $cm^{-1}$. However, evidence of calcium carbonate is present in the bands at 1435 and 888 $cm^{-1}$; the bands due to lithopone, or more precisely, the barium sulfate component of lithopone at 995, 1090, 1126 and 1185 $cm^{-1}$ are also evident. These bands compare very favourably to the bands of a reference spectrum of the mineral barytes, barium sulfate (figure 6C).

14.14.2 St. Gaudens sculptures (figures 7A-D)

Another mineral sulfate, gypsum (the calcium sulfate dihydrate) was readily identified by micro-FTIR in the surface scrapings from one of two plaster models of St. Gaudens sculptures treated by a Winterthur/University of Delaware student, during a summer work project for the National Park Service. These objects are part of the collection at the St. Gaudens Memorial in Cornish, New Hampshire. The FTIR spectrum (figure 7A) of a sample taken from the surface of the first sculpture shows that the sample was rather thick and consequently, the typical sulfate bands around 1155 $cm^{-1}$ are not well-resolved. However, the characteristic sharp bands due to hydrated water at 3556, 3414 and 1631 $cm^{-1}$ are quite visible and compare well with the reference spectrum of gypsum (figure 7B).

The spectrum of a sample taken from the second sculpture is quite different (figure 7C). Not only are bands due to an organic component (probably shellac) much more evident, but the gypsum does not appear to be present. Instead, bands at 3702, 3663, and 3620 $cm^{-1}$ (hydrated water) and Si-O stretching bands centred around 1048 $cm^{-1}$ suggest the presence of the siliceous clay mineral, illite. Compare this with the reference spectrum of that illite (figure 7D).

14.14.3 8th C Qur'anic fragment (figures 8A-C)

Gypsum was also detected in an 8th century Qur'anic fragment as a surface accretion which (under magnification) appeared to be on top of both ink and vellum. The fragment is part of the Robert Garrett Manuscript Collection, Manuscript Division, Rare Books and Special Collection Department, Princeton University Libraries. The manuscript could not be sampled without gathering some of the vellum fibres. Spectra were recorded of a fibrous area and an area with a relatively high concentration of a particulate material. Both spectra are shown in figure 8A. The spectrum of the fibre is typical of proteinaceous materials. The spectrum of the accretion plus fibre, shows small

additional bands at 1167 and 1131 $cm^{-1}$. Subtraction of the two spectra produced a result (figure 8B) with a broad band centred about 1131 $cm^{-1}$ and two small bands at 3556 and 3426 $cm^{-1}$. Also visible in the spectrum are artifact bands of the subtraction process as well as, some residual proteinaceous bands from the vellum.

A computer spectral search and a comparison with a reference spectrum of gypsum (figure 8C) indicated that the accretion material was probably gypsum. The detection of the calcium sulfate, gypsum, as the primary calcium containing component is interesting because previous work on a similar manuscript showed only calcium carbonate to be present. In this Qur'anic fragment, only trace carbonate (band at 888 $cm^{-1}$) was evident.

14.14.4 Memling copy, *Man of Sorrows* (figure 9A-E)
Calcium sulfate exists in three different forms. As mentioned above there is the dihydrate (gypsum), the mono-hydrate (hemi-hydrate), and the completely dehydrated form (anhydrite). The ground of the painting, *Man of Sorrows*, a Memling copy in the Philadelphia Museum of Art (PMA) collection, was determined by FTIR to be predominately anhydrite. Compare the sample spectrum (figure 9A) to a reference spectrum of anhydrite (figure 9B). Note the near, but not complete, absence of the typical hydrated water bands in the sample, and their complete absence in the anhydrite. The bands are present, of course, in gypsum (figure 9C). Also visible in the sample spectrum are weak bands at 1650 and 1550 $cm^{-1}$, the amide I and II bands, which compare well with the reference spectrum of hide glue (figure 9D). If the reference spectra of anhydrite, gypsum and hide glue are spectrally added together, a very close match to the sample results (figure 9E).

14.14.5 Israels, *The Last Breath* (figures 10A-D)
A commonly encountered clay mineral was detected within a surface coating from the Philadelphia Museum of Art painting by Israels, entitled *The Last Breath*. Visual examination as well examination under UV light indicated the probable presence of two distinct coatings. One was readily characterized by FTIR as a natural resin, probably shellac. The second coating was transparent with a red/brown particulate dispersed throughout. The organic component of this layer was identified by FTIR as polyvinyl acetate (figure 10A) as is evident from the reference spectrum of PVAc (figure 10B) But the group of small but sharp bands, between 3699 and 3620 $cm^{-1}$ are characteristic of kaolinite (figure 10C), a common fill or bole material. The addition of the spectra of PVAc and kaolinite resulted in a spectrum (figure 10D) which closely resembles the Israels sample. The kaolinite appears to have been a contaminant, probably bole, in the PVAc.

14.14.6 Toulouse-Lautrec, *Divan Japonnais* (figures 11A-D)
Kaolinite (figure 11D), most likely a filler in the paper substrate, was also found in a Toulouse-Lautrec poster, entitled *Divan Japonnais*, one of a group of 15 posters by that artist being examined by paper conservators at the Philadelphia Museum of Art. Also visible in the sample spectrum (figure 11A) were bands due to proteinaceous material

(1650 and 1550 $cm^{-1}$) probably from a glue adhesive (figure 11B), as well as evidence at about 1000 $cm^{-1}$ of cellulosic paper fibre (figure 11C).

14.14.7 16th C Spanish colonial Jesuit mission church (figures 12A-C)
Clay minerals were identified in a sample from the wall of a historic 16th century Spanish colonial Jesuit mission church in Brazil. Much of the church was built of earthen materials and infrared spectroscopy was one of a group of instrumental methods used to identify the constituents. The residue remaining from a chloroform treatment was compressed on a diamond cell for transmission analysis (figure 12A). The silicate region is rather broad and poorly resolved. However, close examination of the O-H stretching and bending regions is informative. Comparison of this region (figure 12B) with a reference spectrum created by spectral addition of illite (figure 12C) and dickite (or nacrite, its spectrum is essentially identical since they are all hydrated aluminum silicates), suggests that these minerals are present in the sample. At least one other unidentified similar clay mineral is also evident, in the expanded sample spectrum (figure 12B), with the band at 3449 $cm^{-1}$.

14.14.8 Sri Lankan mural painting (figures 13A, B)
The work of BD Nandadeva, PhD candidate in the University of Delaware Art Conservation Department, involves the study of materials used in Kandian period mural paintings in south central Sri Lanka from the mid 18th to late 19th c. Many of these are in cave or rock shelter shrines; others are in Buddhist temples. The paintings are generally executed, as one would expect, in several layers. The first is a preparatory layer of clay, sand and sometimes fibre together with gum or oil medium. The second or priming layer has in some cases been identified by XRD as hydrous magnesite, a basic magnesium carbonate. Mr Nandadeva 's work confirmed the use of hydrous magnesite in some areas but in others he found something quite different. The spectrum of the residue left after chloroform and water extractions of a red pigment (vermilion) together with the priming layer from one site is shown in figure 13A. The spectrum is virtually identical, not to hydrous magnesite, but to huntite (figure 13B), a mixed magnesium-calcium carbonate, $CaMg_3(CO_3)$. Huntite is characterized by the doublet at 876 and 900 $cm^{-1}$, and by the two pairs of bands centred around 1530 and 1450 $cm^{-1}$. Huntite is probably the most easily distinguished carbonate mineral by the IR technique.

14.14.9 Chinese 18th century painted silk dress (figures 14A-D)
A coloured carbonate material, the green pigment malachite, was identified in the paint used to decorate a Chinese 18th century painted silk dress at the Philadelphia Museum. The green pigment (figure 14A) had been found by XRF to contain copper, and was thought to be malachite. However, further analysis was required to confirm that the pigment is indeed malachite, a basic copper carbonate. A comparison of the sample spectrum (figure 14A) with a reference spectrum of malachite (figure 14B) is convincing. The reference spectrum of azurite (figure 14D) matches with a blue inclusion (figure 14C) in the green pigment. Significantly less sample was required for the micro-FTIR analysis than would have been needed for an XRD analysis.

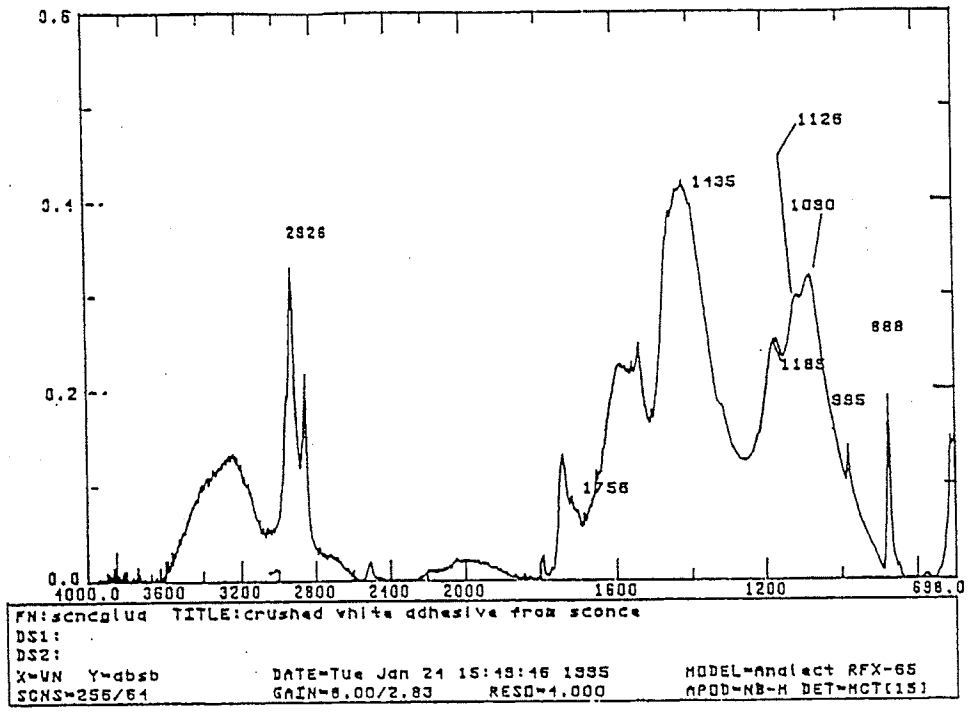



Figure 6B: spectrum from crushed white adhesive

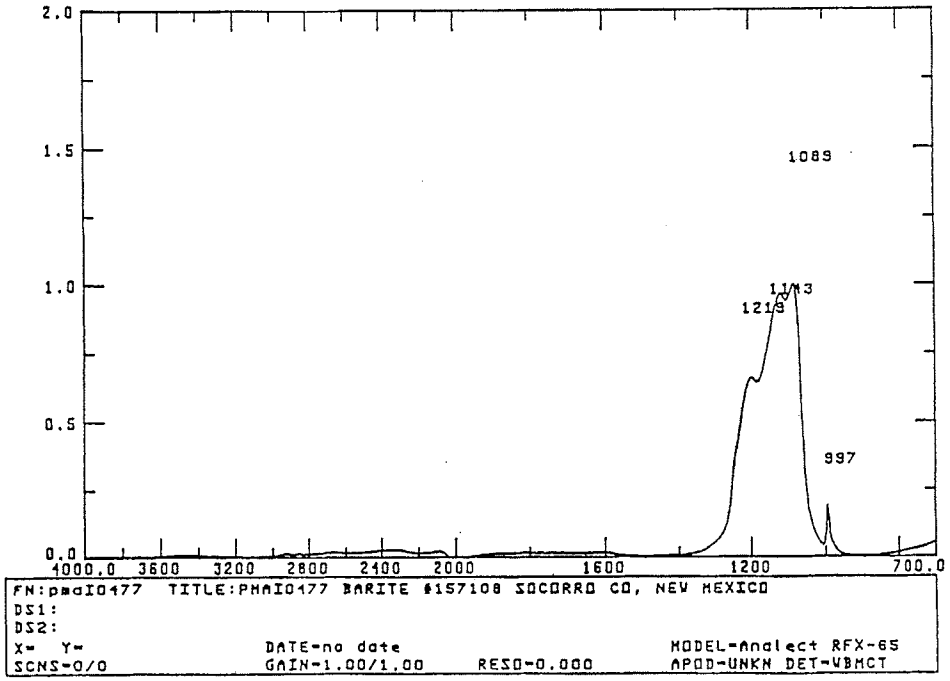



Figure 6C: spectrum of barite

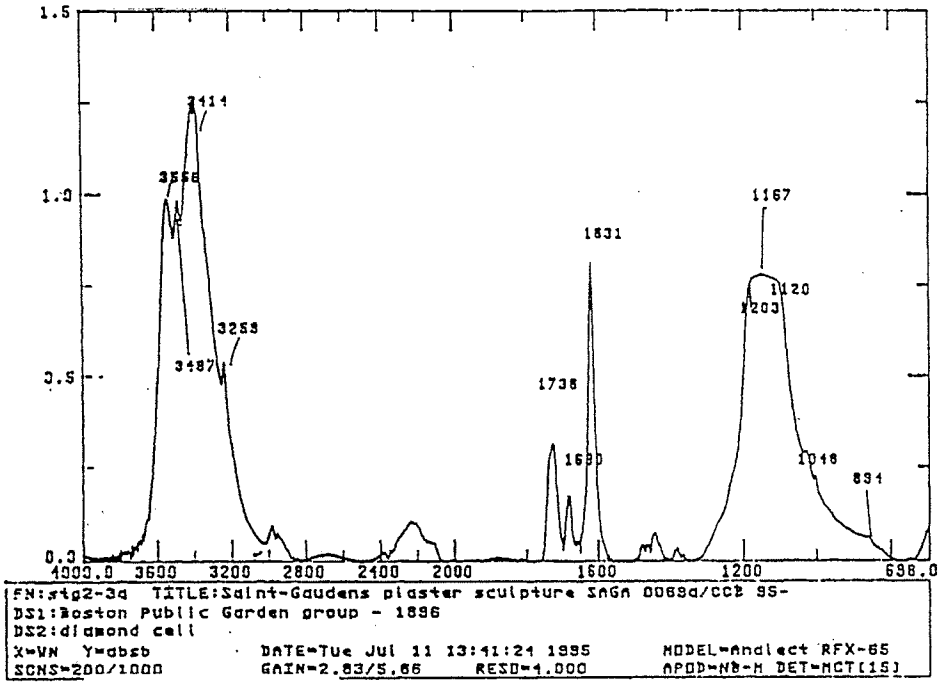



Figure 7A: spectrum of plaster from sculpture

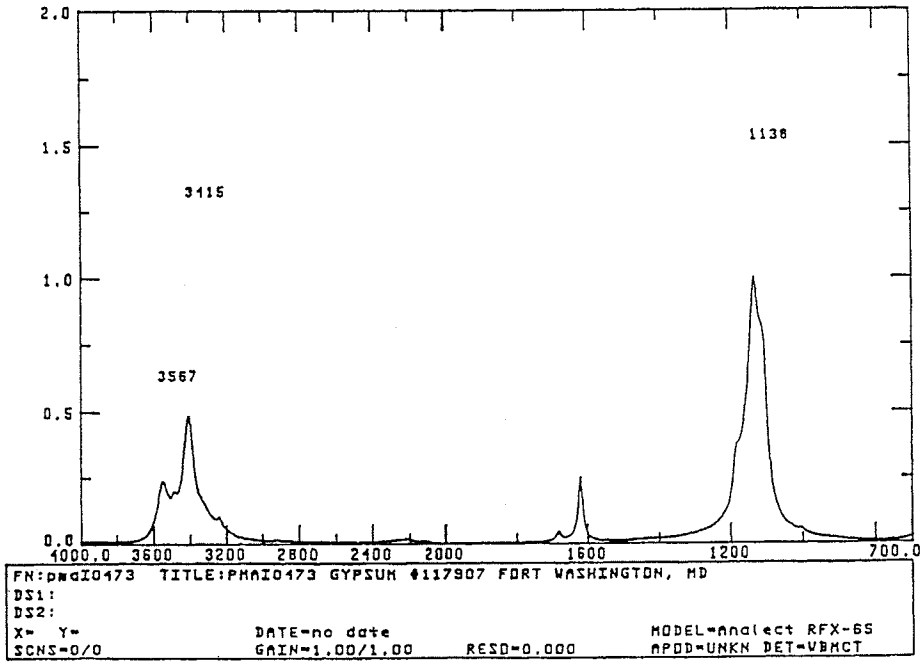



Figure 7B: gypsum

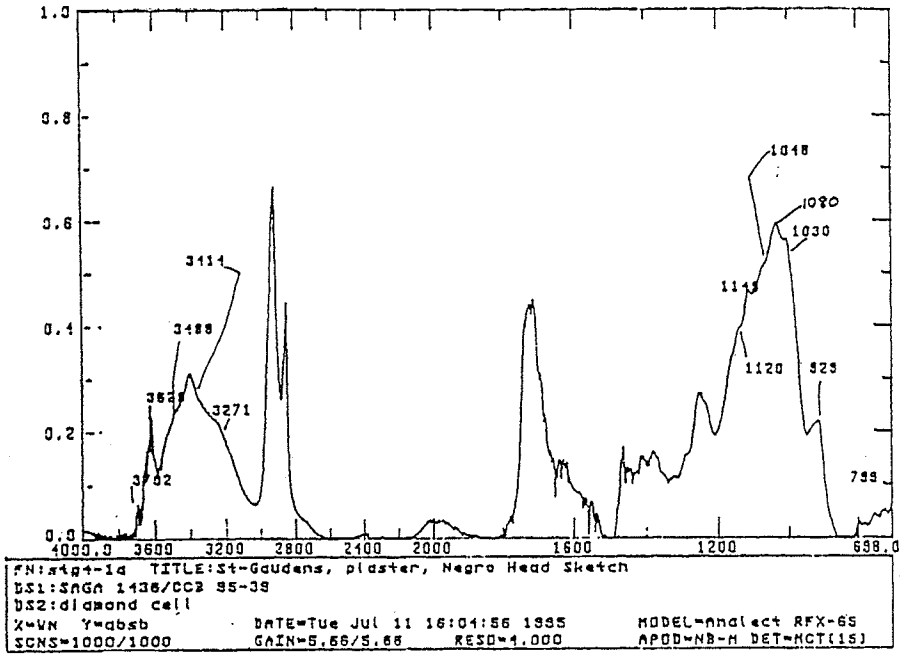



Figure 7C: plaster from sculpture

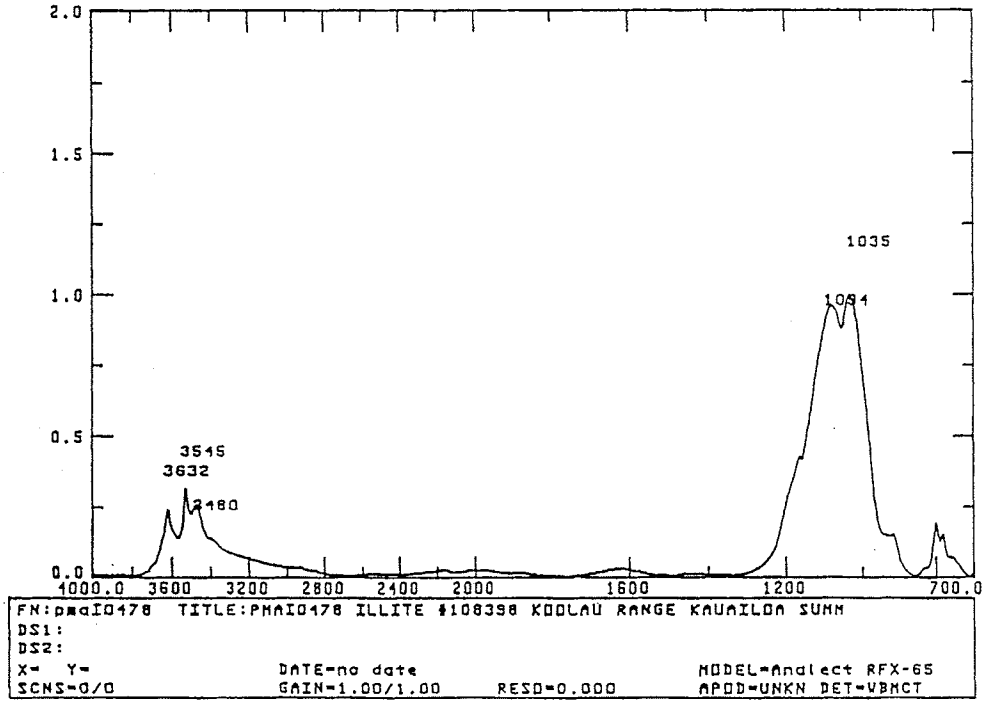



Figure 7D: illite

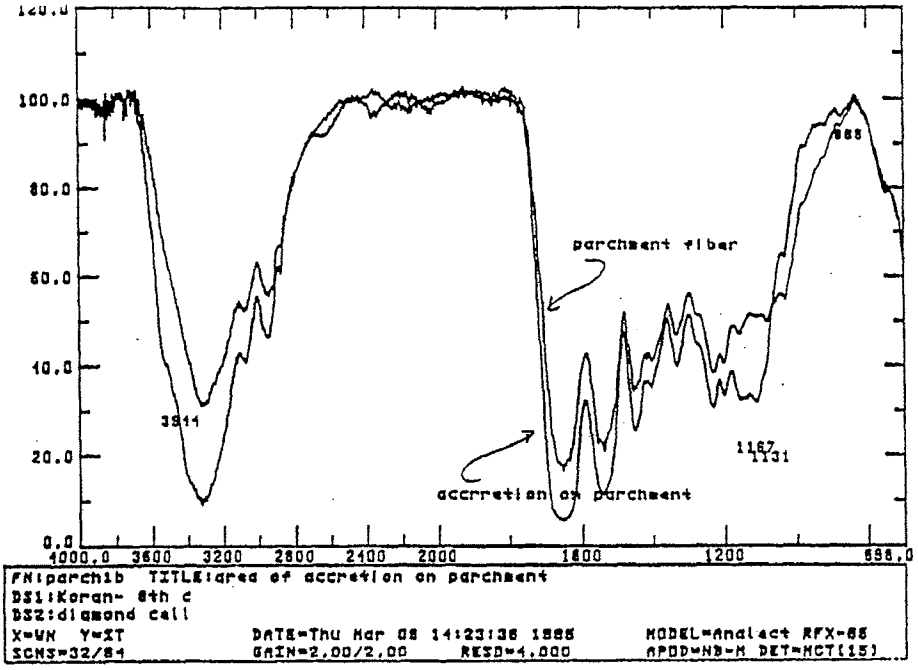



Figure 8A: spectra from parchment

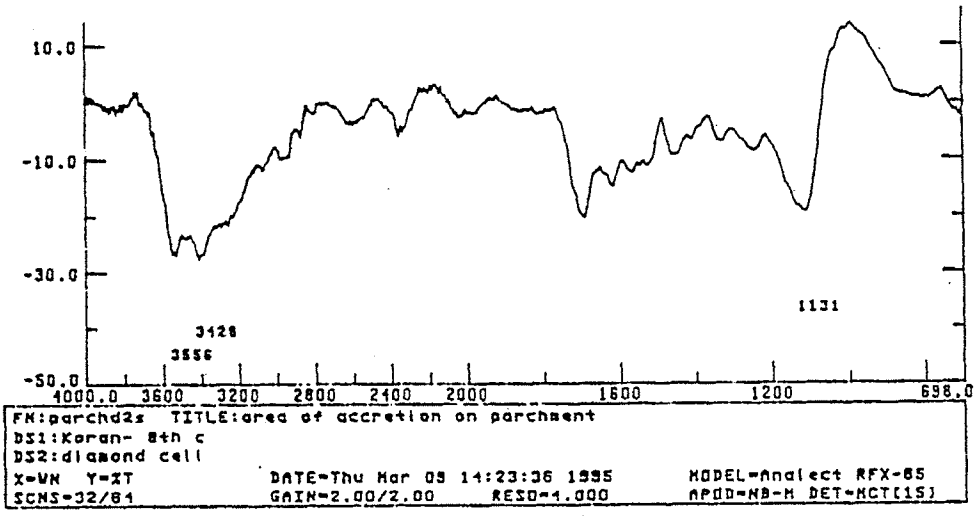



Figure 8B: spectra from parchment

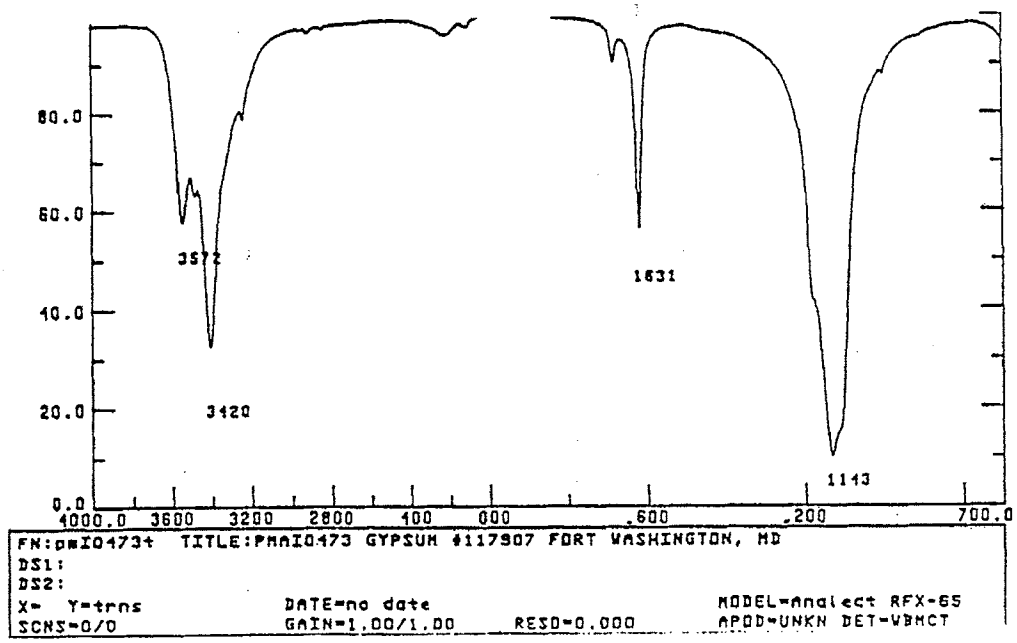
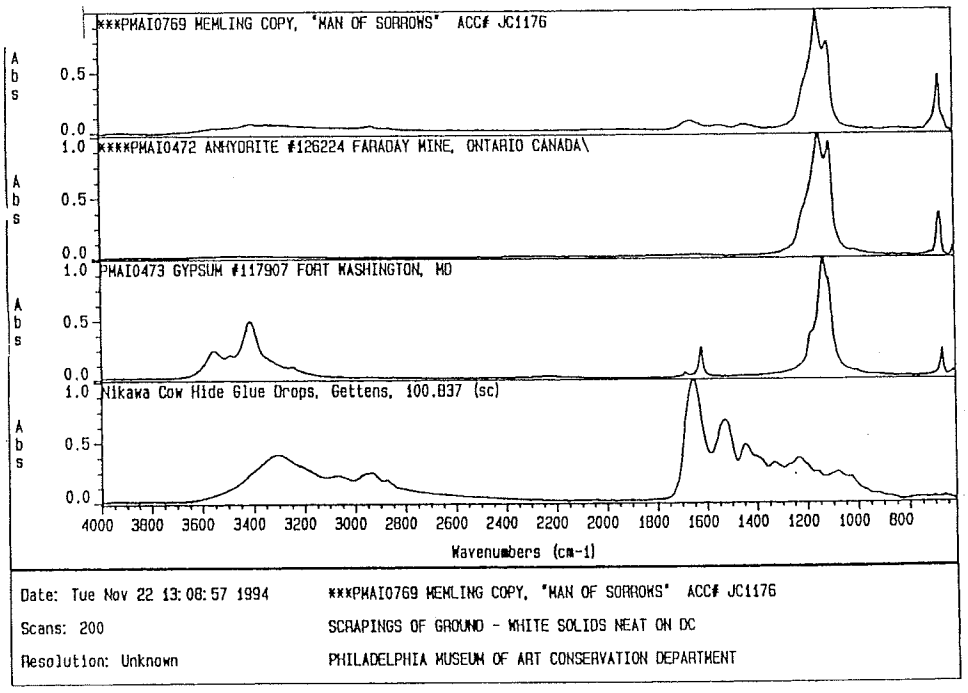



Figure 8C: gypsum




Figures 9A-D: spectrum of *Man of Sorrows* (top) and spectra of possible components (anhydrite, gypsum, cow hide glue)

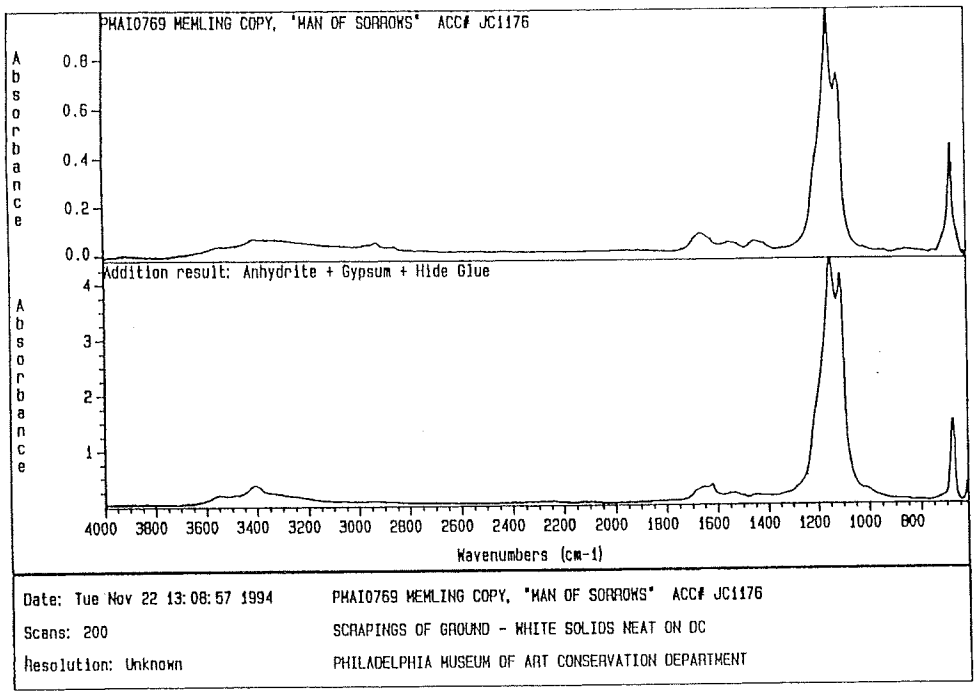
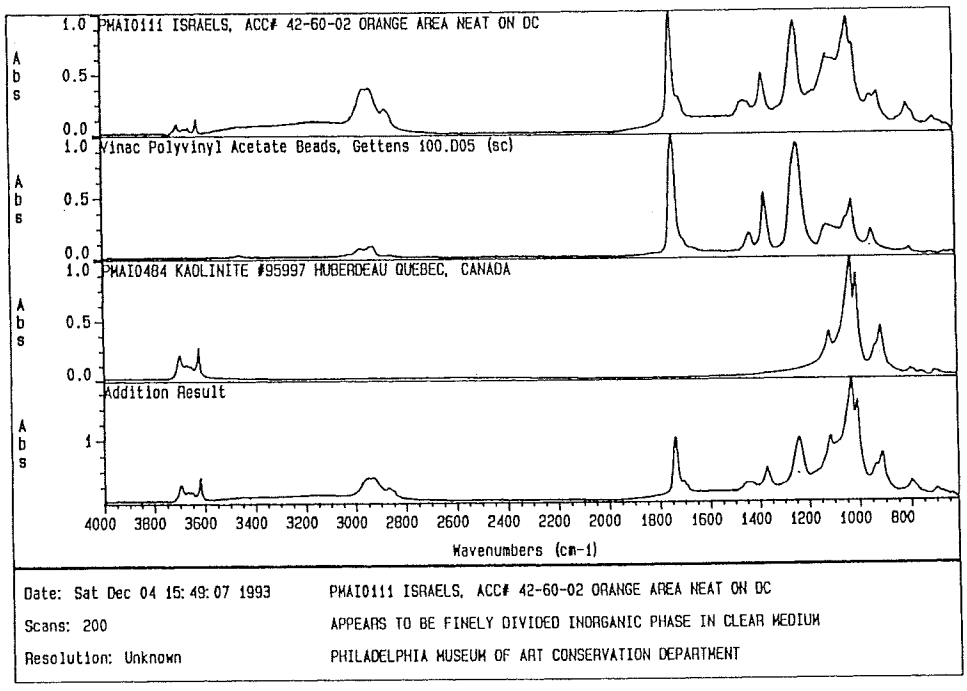
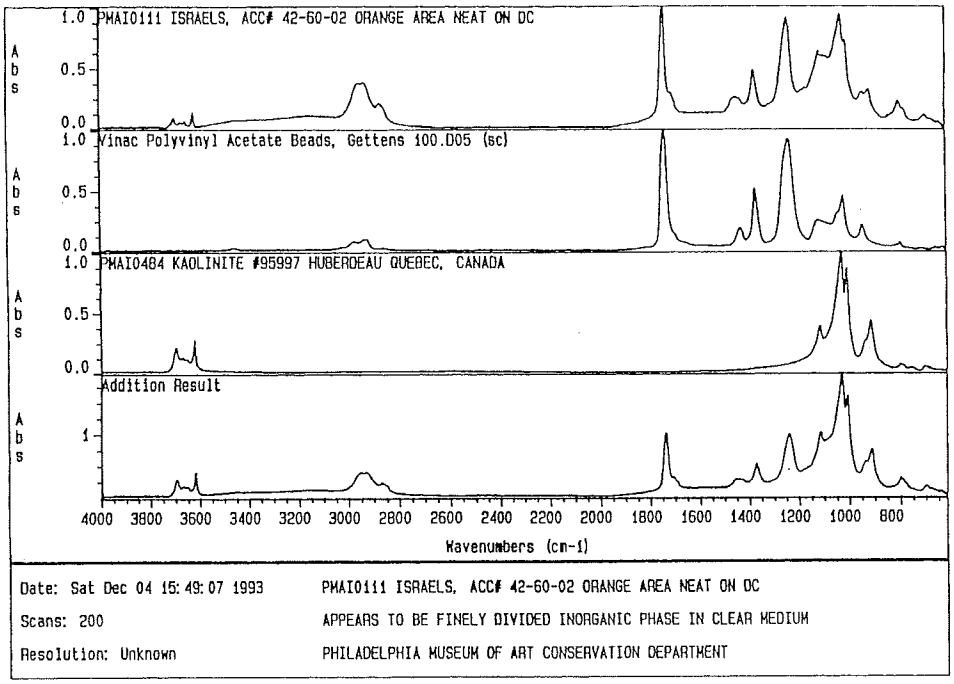



Figure 9E: spectrum from *Man of Sorrows* (top) and addition spectrum of components in figures 9B-D (bottom)




Figures 10A-D: spectrum from Israels (top), spectra of possible constituents (PVAc, kaolinite) and resulting addition spectrum (bottom)




Figures 11A-D: spectrum from Toulouse Lautrec (top); spectrum of cow hide glue; subtracted spectrum (A-B); and spectrum of kaolinite

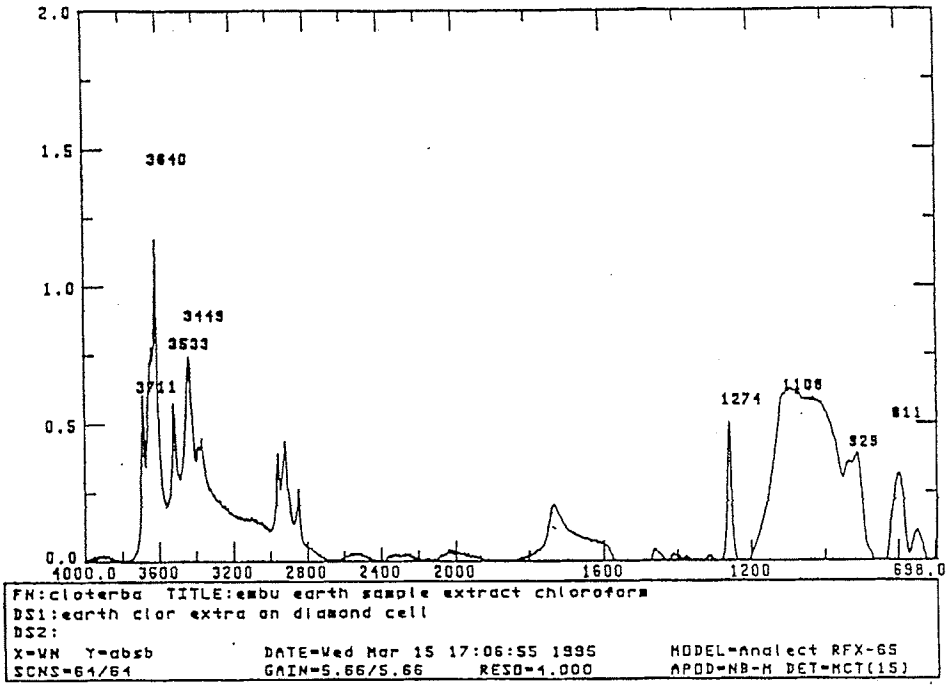



Figure 12A: earth residue

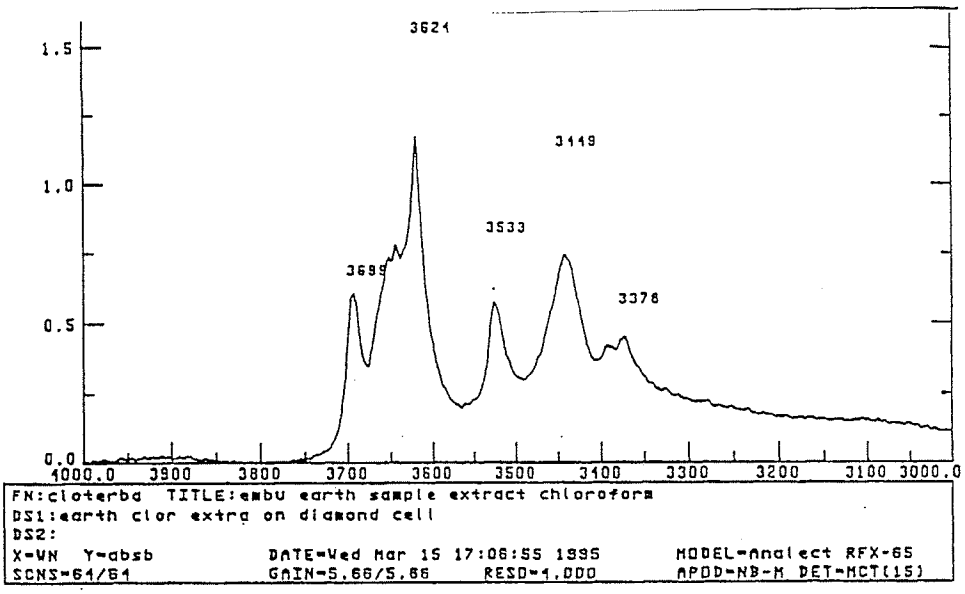



Figure 12B: earth residue (close-up)

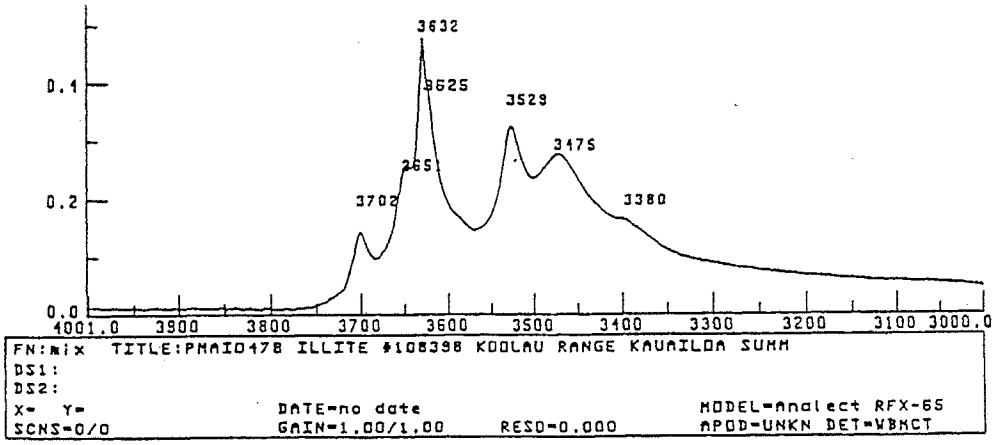



Figure 12C: spectrum of illite

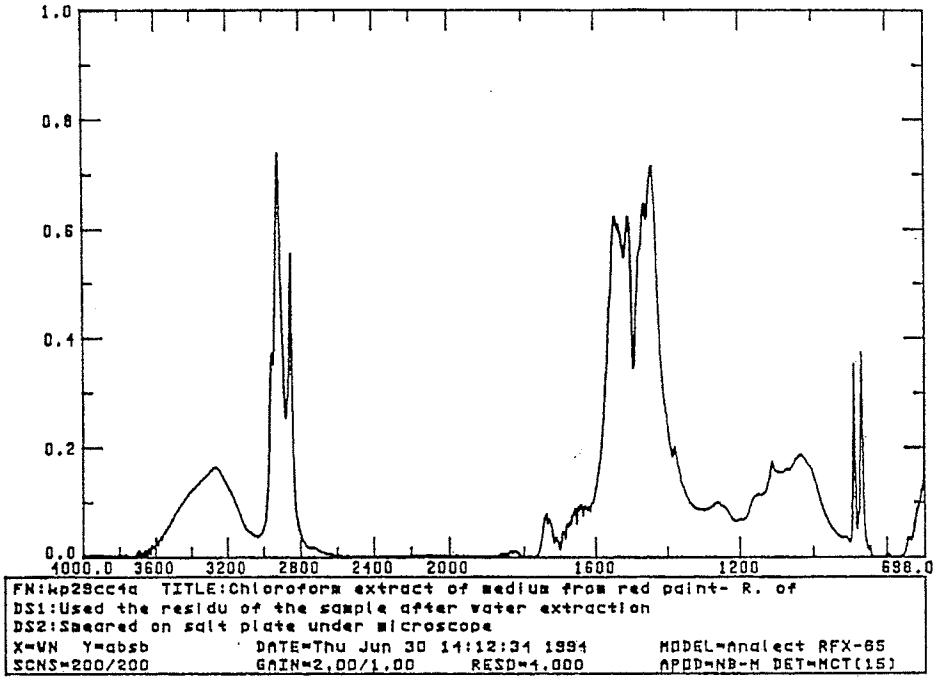



Figure 13A: spectrum of extract from red paint

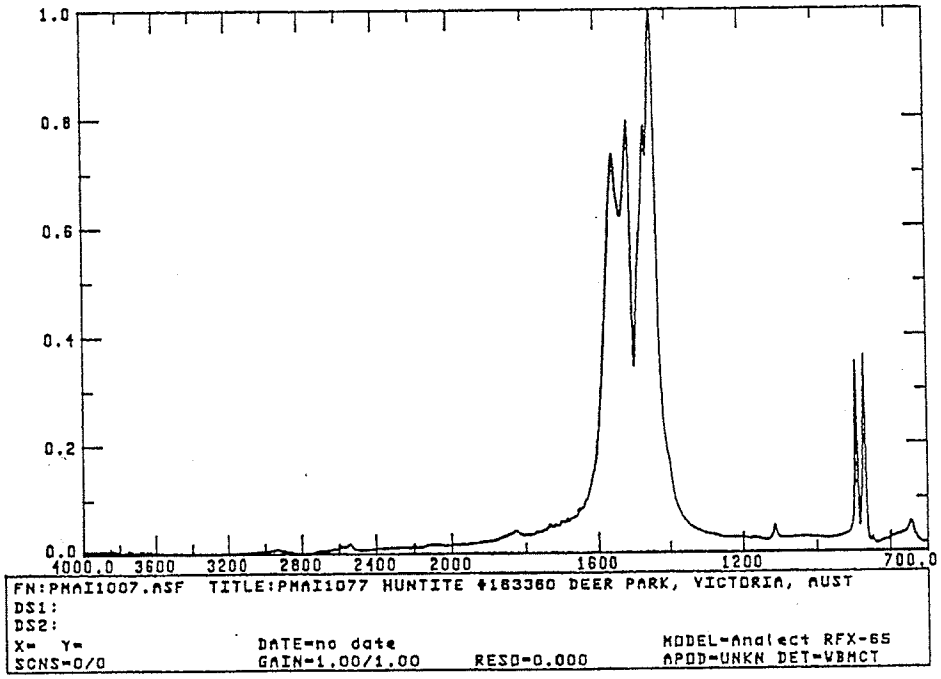
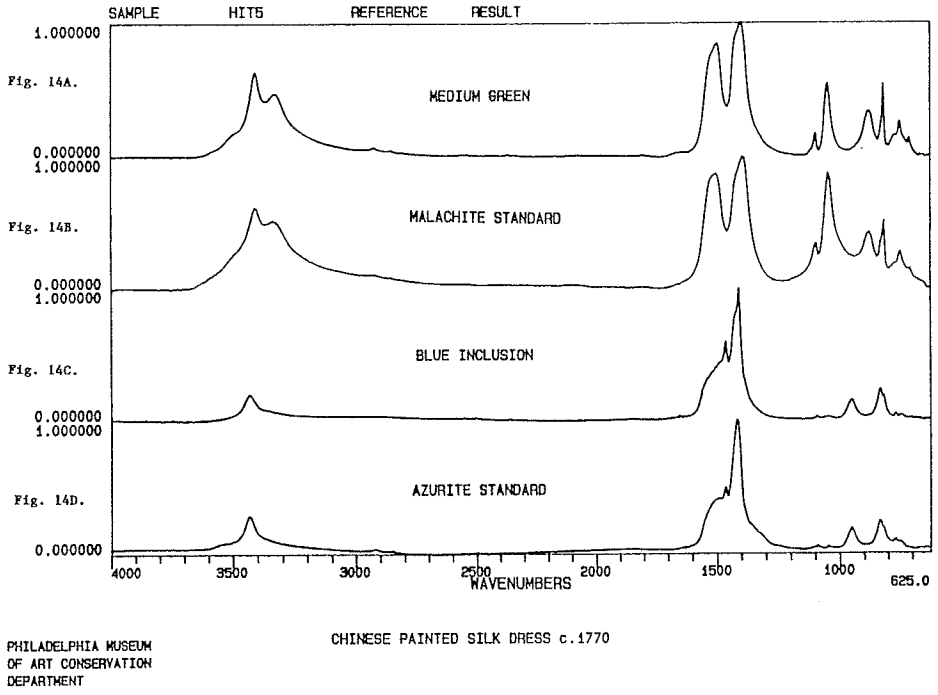
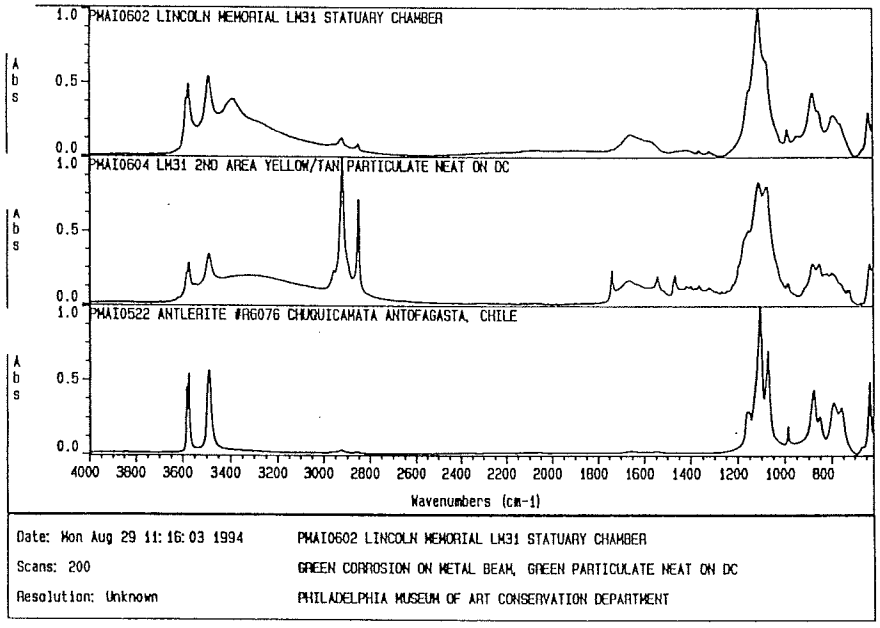



Figure 13B: huntite




Figures 14A-D: spectra from painted silk dress and standards: green (top); malachite; blue inclusion; and azurite (bottom)




Figures 15A-C: spectra from Lincoln Memorial (top, middle) and antlerite (bottom)

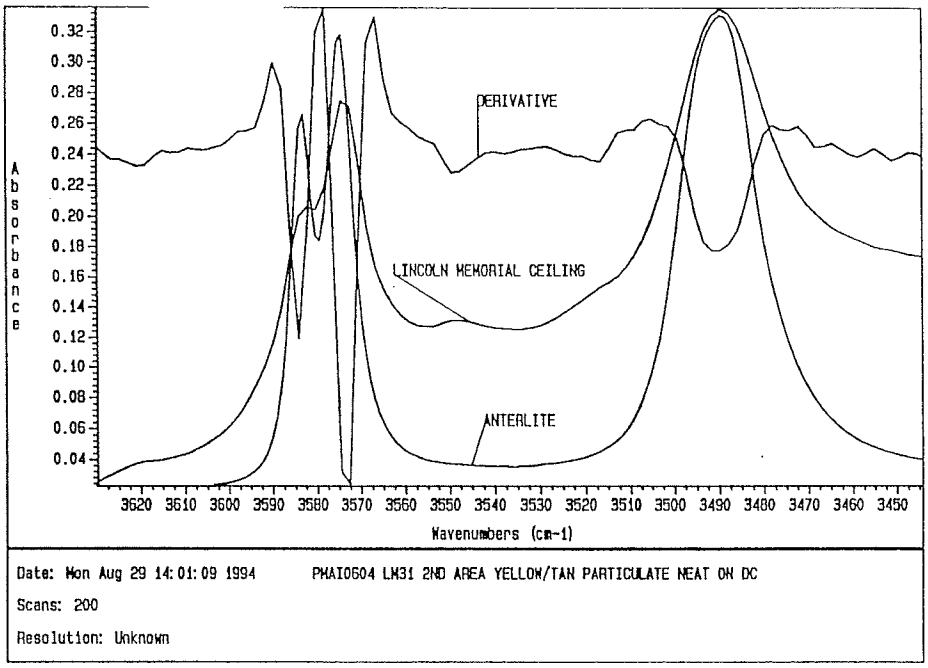
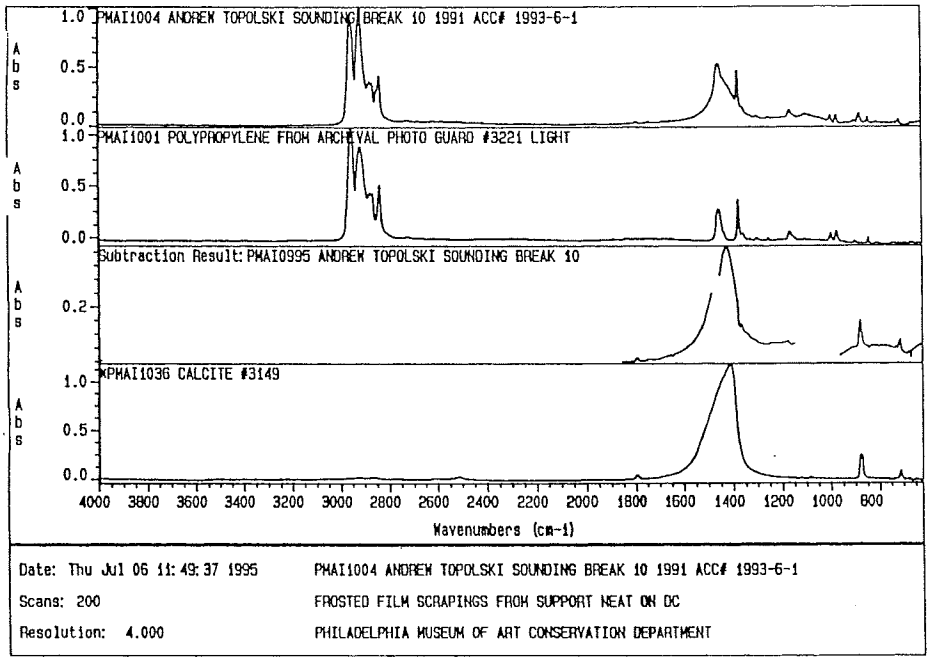



Figure 15D: spectra from Lincoln Memorial and antlerite (close-up)




Figures 16A-D: Spectra form Andrew Topolski (top), polypropylene, subtraction. and calcite (bottom)

14.14.10 Lincoln Memorial ceiling (figure 15A-D)
The ceiling of the Lincoln Memorial, in Washington DC, is composed of ornamental sand-cast copper alloy beams with marble infill panels which filter and diffuse the sunlight. The beams are filled with a cement, sand and cinder matrix. Over the years, the ornamental beams had developed a greenish-brown patina. In a technical study performed at the Philadelphia Museum in support of the National Park Service, FTIR analysis was used. Spectra of two different corrosion samples, green and yellow-tan are shown in figures 15A and 15B. The spectra of these materials contain bands which match closely with those in the antlerite spectrum, a hydrated copper sulfate (figure 15C). The second derivative taken of the 3400-3600 $cm^{-1}$ region (together with the normal absorbance and reference spectra in figure 15D) provides additional confirmation of the antlerite. The presence of antlerite on these copper alloy beams results from exposure to the polluted urban environment.

14.14.11 Topolski, *Sounding Break 10* (figure16A-D)
A final example of the application of micro-FTIR to the identification of naturally occurring minerals involved the support from Topolski's *Sounding Break 10*, in the PMA collection. The drawing was executed with graphite, pigment and transfer type on a translucent "frosted film". The film was originally thought to be a polyester. However, FTIR analysis showed the polymer film to be primarily an aliphatic hydrocarbon based polymer (figure 16A). A computer spectral search confirmed it to be polypropylene (figure 16B). When polypropylene was subtracted from the sample spectrum a result (figure 16C) was obtained which compares very favourably with calcium carbonate type materials. More specifically, the sample appears to be calcite because of the bands a 878, 848 and 713 $cm^{-1}$ (figure 16D). Vaterite, a calcium carbonate polymorph, has an additional band at 1089 $cm^{-1}$ which is absent in this sample and aragonite, a third polymorph, has a doublet at 713 and 700 $cm^{-1}$, as well as, the 1083 $cm^{-1}$ band.

## 14.15 Conclusion

These examples, taken from routine analyses illustrate of the utility of the *Infrared Spectral Database of Naturally Occurring Minerals* for the conservation application.

Many materials analysed in conservation technical studies contain minerals as a major, minor or even trace components. If the mineral is a major component, other techniques, particularly XRD, may provide a more definitive identification, particularly for oxides and sulfides but substantially more sample and time may be required. For minor and trace mineral components, FTIR is especially well suited. While the organic matrix in which the mineral is situated may interfere with assignment of the carbonate, sulfate, phosphate or silicate bands, spectral subtraction or derivitization often compensates for this difficulty. The sharp bands due to hydrated water present in many mineral spectra (especially silicates and sulfates) are less likely to be obscured by the matrix bands. This makes the identification or at least classification of even trace mineral components possible. Finally, polymorphs of minerals can also be detected.

## 14.16 Acknowledgements

We would like to thank Bill Seldon of Rutgers University, Jeff Post and Russell Feather of the Smithsonian Institution and Sari Uricheck, a volunteer at the Philadelphia Museum of Art who collected many of the spectra in the database, for their generous assistance and would also like to acknowledge the Philadelphia Museum of Art and the Henry Francis duPont Winterthur Museum.

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Janice H. Carlson received her BA in chemistry from the College of Wooster and her MS in Analytical Chemistry from the University of Michigan. After working for several years in industry, she joined the staff of The Henry Francis DuPont Winterthur Museum near Wilmington, Delaware where she is Museum Scientist. She also serves as Adjunct Associate Professor of Conservation Science in the University of Delaware/Art Conservation Program in the Conservation of Artistic Historic Works.

# 15. The identification of nitrates on carbonate substrates using diffuse reflectance infrared Fourier Transform DRIFTs in $CaF_2$ Matrix

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## 15.1 Summary

Marcello Picollo had to withdraw from the conference and could not present the paper. The full paper is reproduced her for information by kind permission of the authors.

## 15.2 Abstract

It is well known that both pollution and other alteration factors produce the growth of authigenetic minerals which previously were not present in the original composition. For the conservation of works of art it is necessary to be able to recognize these products. The most common substances found on carbonate substrates are: sulfates, oxalates, nitrates and chlorides. The main focus of the present work is the detection of $NO_3^-$ ions and, in particular, their spectroscopic characterization.

Among the various techniques of analysis, FTIR is one of the fastest and most commonly used. However, when the analysis is performed using KBr pellets without any specific sampling procedures, FTIR only provides information about the presence of the $NO_3^-$ ion without giving information about the associate cation. In fact, the presence of inorganic nitrates is commonly related to a strong absorption band around 1385 $cm^{-1}$ without the characterization of the associated cation. This non-characterization could be partially due to the cation exchange between $NO_3^-$ and KBr facilitated by the high mechanical pressure used in the pelletting process.

To verify this, spectra of $KNO_3$ and $NaNO_3$ in both transmittance (KBr pellets) and diffuse reflectance (KBr and $CaF_2$ matrix) modes were performed. The diffuse reflectance measurements (DRIFT) were collected after grinding each sample without the matrix and then mixing the sample together with the matrix without any pressure.

Both transmittance and DRIFT in KBr matrix present the same absorbance band around 1385 $cm^{-1}$ for the two nitrates, even if the DRIFT spectra also show different bands in this part of the spectrum. On the other hand, the DRIFT spectra in $CaF_2$ matrix show different absorption bands in the same part of the spectrum, so that DRIFT measurements in $CaF_2$ matrix can be proposed in the characterization of inorganic nitrates.

## 15.3 Introduction

Large amounts of inorganic materials derived from decomposition of stone as well as from authigenetic minerals are present nowadays on several monuments and works of art in general [1]. Most of these compounds are identified as sulfates, chlorides, oxalates, and nitrates [2,3]. The perception of their presence and concentration is very important for conservation purposes. In fact, hygroscopic salts, such as chlorides and

nitrates, are able to condense a great amount of water on the surface of stones, walls, frescoes, etc. so that the presence of nitrates on frescoes might be the cause for the decrease of the dew point [4].

The most commonly used techniques in the identification of these inorganic compounds are XRD and FTIR spectroscopy. However, these two techniques sometimes are not able to identify nitrates ($NaNO_3$ and $KNO_3$) when they are found in low concentration mixed with the substrate as well as with other alteration compounds, such as gypsum. Various sample mixtures were prepared for verifying the sensibility of these techniques.

XRD has a low sensibility when nitrates are mixed with calcite ($CaCO_3$) and gypsum ($CaSO_4 \cdot 2H_2O$). This low sensibility is caused by the superimposition of the main diffraction peaks of $CaCO_3$ and $CaSO_4 \cdot 2H_2O$ on those belonging to $NaNO_3$ and $KNO_3$. On the other hand, using FTIR the presence of the nitrates is clearly detected. However, the spectra performed in KBr pellets show the most intense absorption band (the double degenerate anti-symmetric N-O stretching mode [$\nu_3$]) around 1385 $cm^{-1}$ without giving any information about the associated cation.

Bearing these facts in mind, it was decided to perform diffuse reflectance measurements (DRIFT) with KBr and $CaF_2$ matrix in order to find a new FTIR methodology for identifying $NaNO_3$ and $KNO_3$.

### 15.4 Experimental

The FTIR measurements were performed in transmittance (KBr pellets) and in reflectance (KBr and $CaF_2$ matrix) using a Perkin-Elmer Sys 2000 spectrophotometer. In particular, the diffuse reflectance infrared Fourier Transform (DRIFT) measurements were made in KBr and $CaF_2$ matrix. Both the diluents (chemical reagent grade) were purchased from Aldrich. The spectra in transmittance and in DRIFT were collected for pure nitrates and mixtures of the same nitrates with $CaCO_3$ (calcite) and with $CaCO_3$ plus $CaSO_4 \cdot 2H_2O$ (gypsum). The concentration of these mixtures is reported in table 1. Their homogenization was made by stirring the solid in presence of non-polar solvent (n-hexane) for half an hour before evaporating the solvent in vacuum. The same mixtures as well as the pure nitrates were also used for XRD analysis.

| sample | $KNO_3$ (w%)[a] | $NaNO_3$ (w%)[b] | $CaCO_3$ (w%)[c] | $CaSO_4 \cdot 2H_2O$ (w%)[d] |
|---|---|---|---|---|
| mix110 | 10 | - | 50 | 40 |
| mix130 | 30 | - | 30 | 40 |
| mix150 | 50 | - | 50 | - |
| mix165 | 35 | - | 65 | - |
| mix175 | 25 | - | 75 | - |
| mix190 | 10 | - | 90 | - |
| mix210 | - | 10 | 50 | 40 |
| mix230 | - | 30 | 30 | 40 |

| sample | $KNO_3$ (w%)[a] | $NaNO_3$ (w%)[b] | $CaCO_3$ (w%)[c] | $CaSO_4 \cdot 2H_2O$ (w%)[d] |
|---|---|---|---|---|
| mix250 | - | 50 | 50 | - |
| mix265 | - | 35 | 65 | - |
| mix275 | - | 25 | 75 | - |
| mix290 | - | 10 | 90 | - |

Table 1: concentration in weight % of the analysed mixtures: a) from BDH; b) from Merk; c) from Carlo Erba; d) prepared in our laboratory

## 15.5 Results and discussion

The FTIR transmittance spectra in KBr pellets of $NaNO_3$ and $KNO_3$ are reported in figure 1. Following this method, in general only the absorption band at 1385 $cm^{-1}$ gives the presence of both these nitrates and, therefore, it cannot be used for their discrimination. Nevertheless, their identification could be performed by looking at the less intense band around 820-840 $cm^{-1}$ (the out-of-plane bending mode [$\nu_2$]) which, however, is difficult to detect working on actual samples.

Some authors suggested that the band at 1385 $cm^{-1}$ may be due to the cation exchange from nitrates and KBr used to prepare the pellets and that this exchange could be facilitated by the high mechanical pressure used in the pelletting process [5,6].

Bearing this fact in mind, it was decided to perform the analysis in DRIFT in KBr matrix. Both pure nitrates and mixtures as well as the matrix were individually ground and then they were softly mixed together. The diffuse reflectance spectra of two mixtures are reported in figure 2. Here, the two nitrates show the same absorption band at 1385 $cm^{-1}$, thus giving us no specific information for their discrimination. Moreover, this measurement highlights that the KBr may induce the cation exchange even if the pressure applied for the preparation of the reflectance samples was much lower than that used for the pellets.

Finally the $CaF_2$ matrix was used for performing DRIFT analysis. The same procedure used in the previous measurements for the preparation of the DRIFT samples was followed. The recorded spectra (figure 3) show small difference for the two nitrates, since $KNO_3$ presents its main peak at 1400 $cm^{-1}$ and $NaNO_3$ around 1390 $cm^{-1}$. This small shift between the two peaks, which was shown for the pure nitrates, was also present in the spectra of the sample mixtures (figures 4, 5). Moreover, the main absorption band of the $CaCO_3$ does not affect the position of the nitrate peak around 1400-1390 $cm^{-1}$. The $\nu_3$ peak position for both the pure nitrates and the sample mixtures (nitrates and $CaCO_3$ plus $CaSO_4 \cdot 2H_2O$) in $CaF_2$ matrix are reported in table 2.

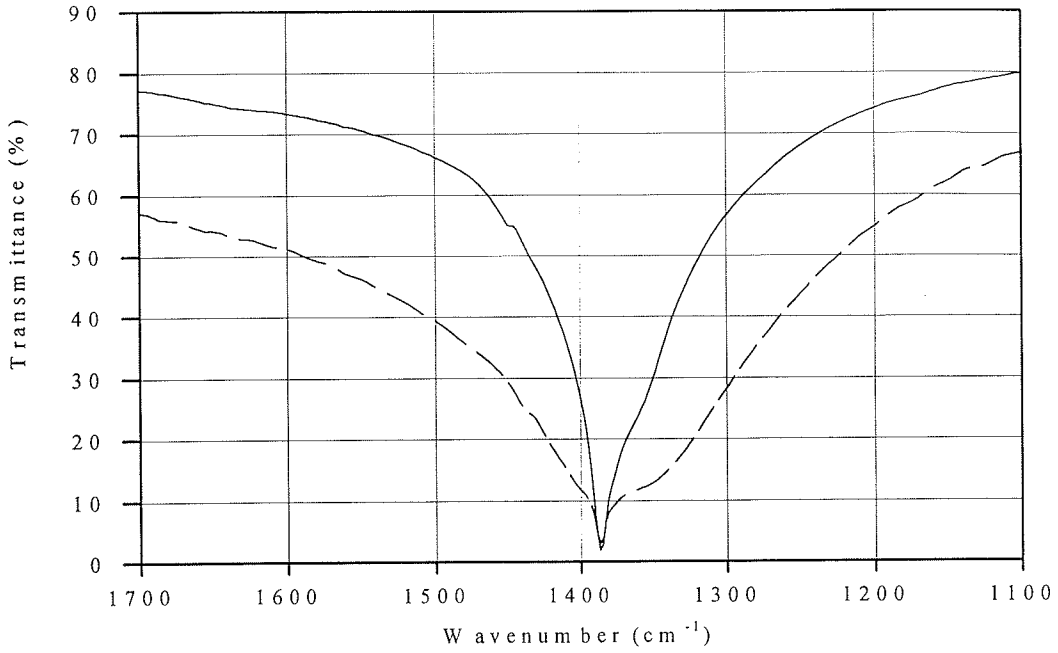


Figure 1: transmittance spectra of pure $NaNO_3$ (solid line) and $KNO_3$ (dashed line)

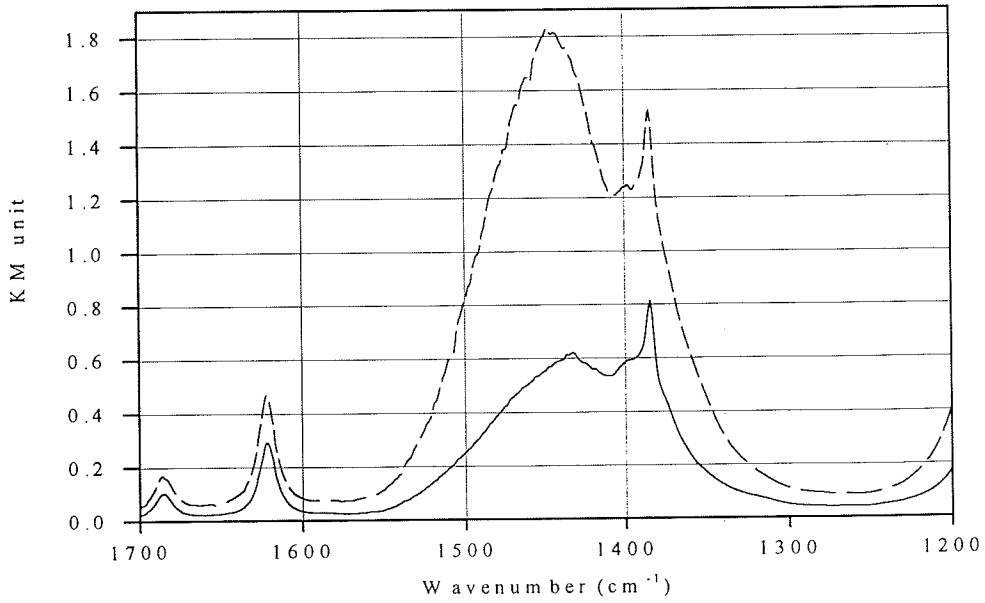


Figure 2: DRIFT spectra in KBr matrix of the $NaNO_3$ (10%$NaNO_3$ 50%$CaCO_3$ 40%$CaSO^4x2H_2O$ solid line) and KNO3 (10%$KNO_3$ 50%$CaCO_3$ 40%$CaSO_4x2H2O$ dashed line) mixtures

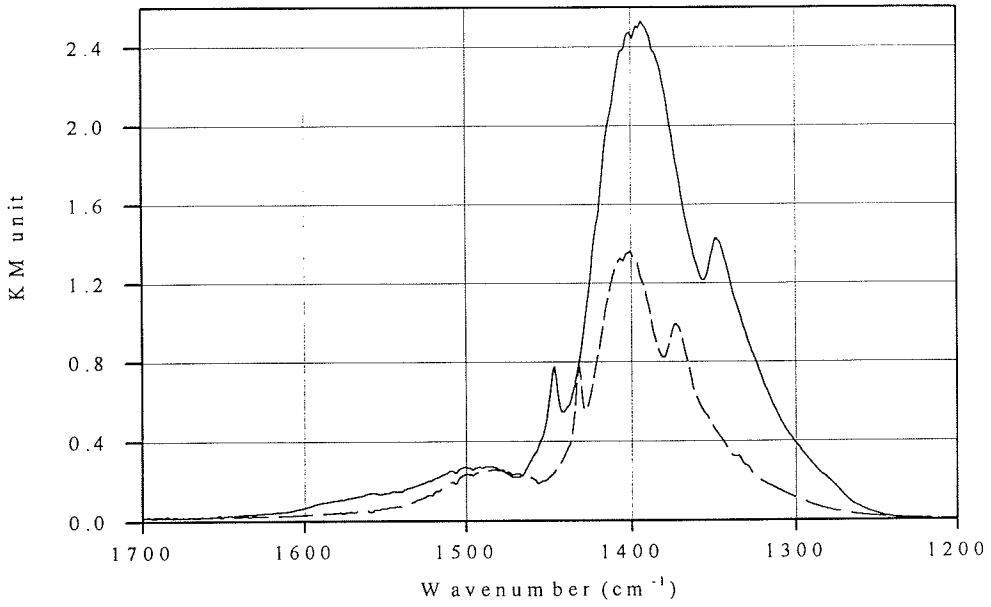


Figure 3: DRIFT spectra in CaF2 matrix of the pure $NaNO_3$ (solid line) and $KNO_3$ (dashed line)

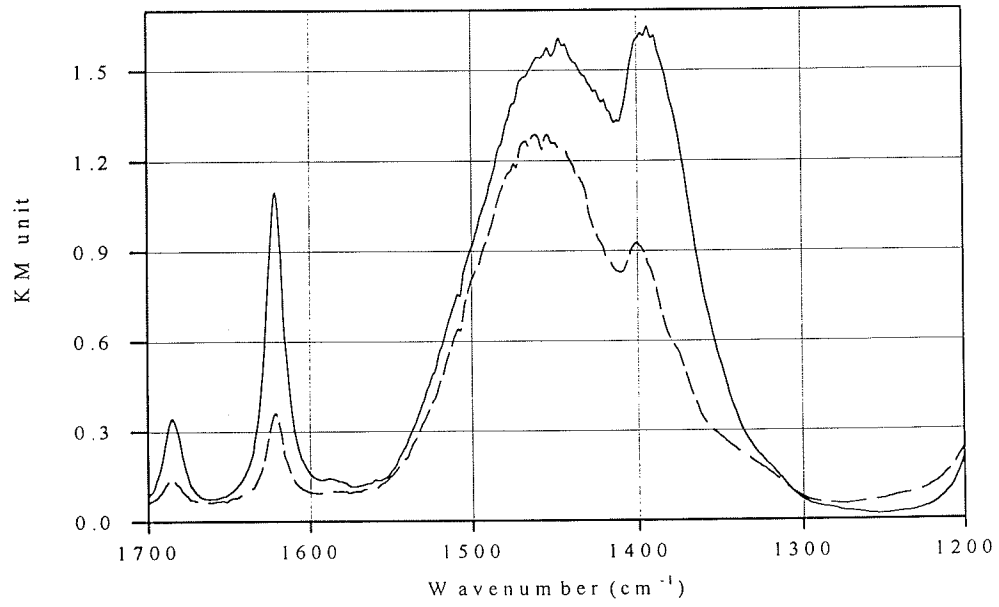


Figure 4: DRIFT spectra in $CaF_2$ matrix of the $NaNO_3$ (10%$NaNO_3$ 50%$CaCO_3$ 40%$CaSO_4x2H_2O$ solid line) and $KNO_3$ (10%$KNO_3$ 50%$CaCO_3$ 40%$CaSO_4x2H_2O$ dashed line) mixtures

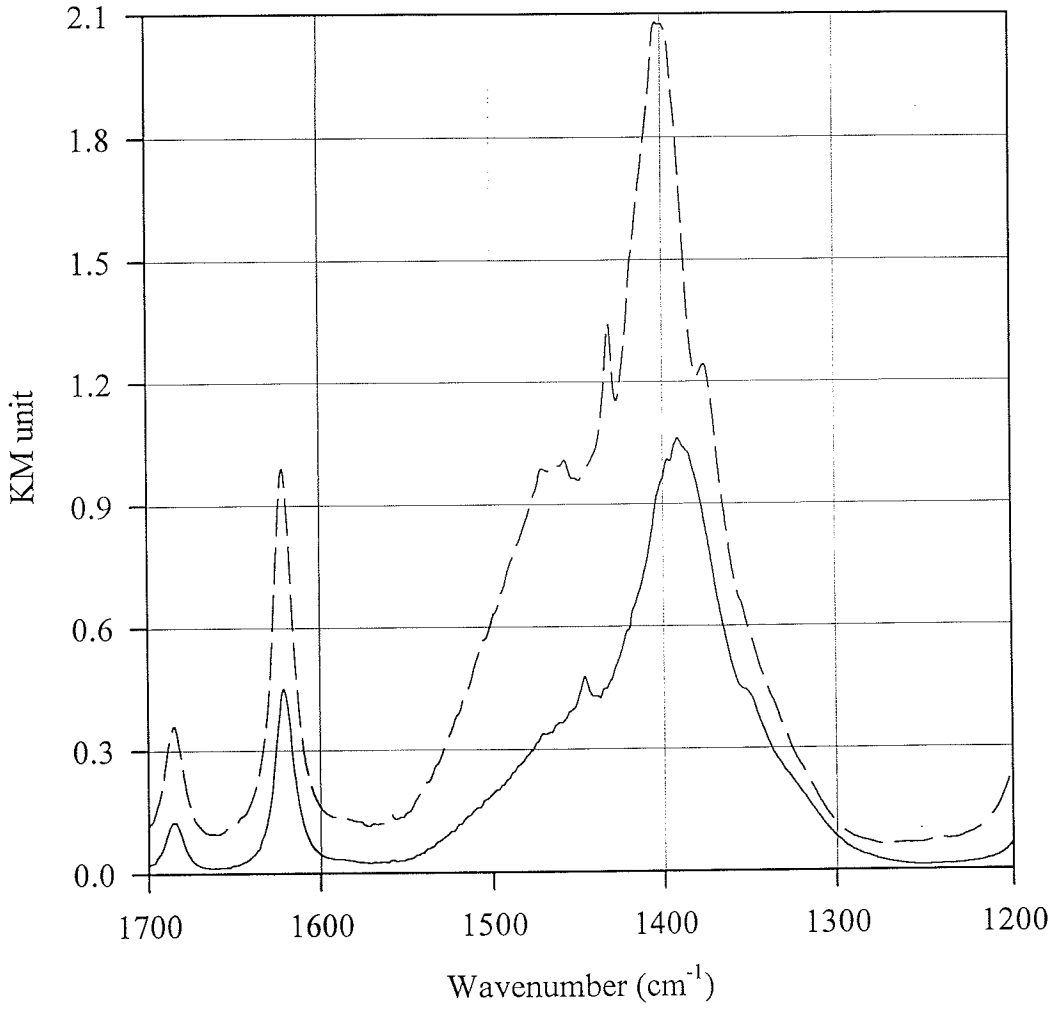


Figure 5: DRIFT spectra in $CaF_2$ matrix of the $NaNO_3$ (30%$NaNO_3$ 30%$CaCO_3$ 40%$CaSO_4x2H_2O$ solid line) and $KNO_3$ (30%$KNO_3$ 30%$CaCO_3$ 40%$CaSO_4x2H_2O$ dashed line) mixtures

| sample | $\nu_3$ frequency ($cm^{-1}$) |
|---|---|
| pure $KNO_3$ | 1400 |
| mix110 | 1400 |
| mix130 | 1403 |
| pure $NaNO_3$ | 1393 |
| mix210 | 1389 |
| mix230 | 1390 |

Table 2: infrared frequencies for the double degenerate anti-symmetric N-O stretching mode ($\nu_3$)

## 15.6 Conclusions

The DRIFT measurements in $CaF_2$ matrix may be considered a suitable method to detect nitrates when they are mixed, even in low concentration, with $CaCO_3$ (substrate) and $CaSO_4 \cdot 2H_2O$, (one of the most common alteration compounds). This DRIFT technique allows the observation of a small shift between the frequencies for the N-O stretching mode ($\nu_3$) of $KNO_3$ and $NaNO_3$. On the contrary, the FTIR methods in KBr pellets (transmittance) as well as in KBr matrix (reflectance) indicate the presence of nitrates, but is not able to characterize the cation regarding the most intense absorption N-O stretching mode ($\nu_3$).

## 15.7 References

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## 17. Presentations (alphabetical by speaker)

| NAME | ADDRESS | TITLE |
|---|---|---|
| Mads Chr. Christensen | Det Kongelige Danske Kunstakademi, Denmark | Analysis of Mineral Salts from Monuments by IR Spectroscopy |
| Kate Helwig | CCI, Canada | The characterization of iron earth pigments using infrared spectroscopy |
| Brenda Keneghan | V&A | FTIR Spectroscopy as a Tool when Assessing Plastics Collections in Museums |
| Michele Derrick<br>Tanya Kieslich | Getty Conservation Institute USA | Infrared Microspectroscopy Mapping Techniques for the Analysis of Paint Cross-sections |
| Tom Learner | Tate Gallery | The use of a Diamond Cell for the FTIR Characterization of Paints and Varnishes Available to 20thC Artists |
| Yasunori MATSUDA<br>Masahiko TSUKADA | Tohoku University of Art & Design | Identification of Calcium Carbonate contained as Body in Modern Paints... |
| Matthew Murray | Building Research Establishment | FTIR Techniques at the Building Research Establishment |
| ~~Marcello Picollo~~ | ~~Consiglio Nazionale Delle Ricerche...~~ | ~~The identification of nitrates on carbonate substrates using DRIFTs in CaF2 Matrix~~ |
| Jenny Pilc | National Gallery | Improving the Resolution of IR Spectra |
| Beth Price<br>Janice Carlson | Philadelphia Museum of Art<br>Winterthur Museum | An Infrared Spectral Library of Naturally Occurring Minerals |
| Masanori SATO<br>Masaaki SAWADA | Nara National Cultural Properties<br>Research Center,<br>Nara, Japan | FTIR Microscopic studies on Organic Material used for Cultural Properties |
| Manfred Schreiner | Institute of Chemistry<br>Academy of Fine Arts<br>Schillerplatz 3<br>A 1010 Vienna, Austria | IR Reflectance Spectra of Weathered Medieval Stained Glass |
| Edward Then | Science Museum | Infrared spectroscopy - An analytical tool for conservators |
| David Thickett | British Museum | The use of a Beam-condenser for Micro Analysis |
| Siobhan Watts | FakArk<br>Vitenskapsmuseet<br>Universitet I Trondheim<br>Trondheim; N-7004 Norway | Identifying Archaeological Jet & Jet-Like Artefacts using FTIR |