

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

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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 C₁₆ 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

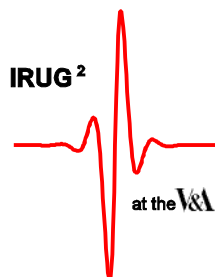
1.5.1 Binding media

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 $1732/3\text{ cm}^{-1}$. 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 $2933\text{--}4\text{ cm}^{-1}$ and $2858\text{--}60\text{ cm}^{-1}$. 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.

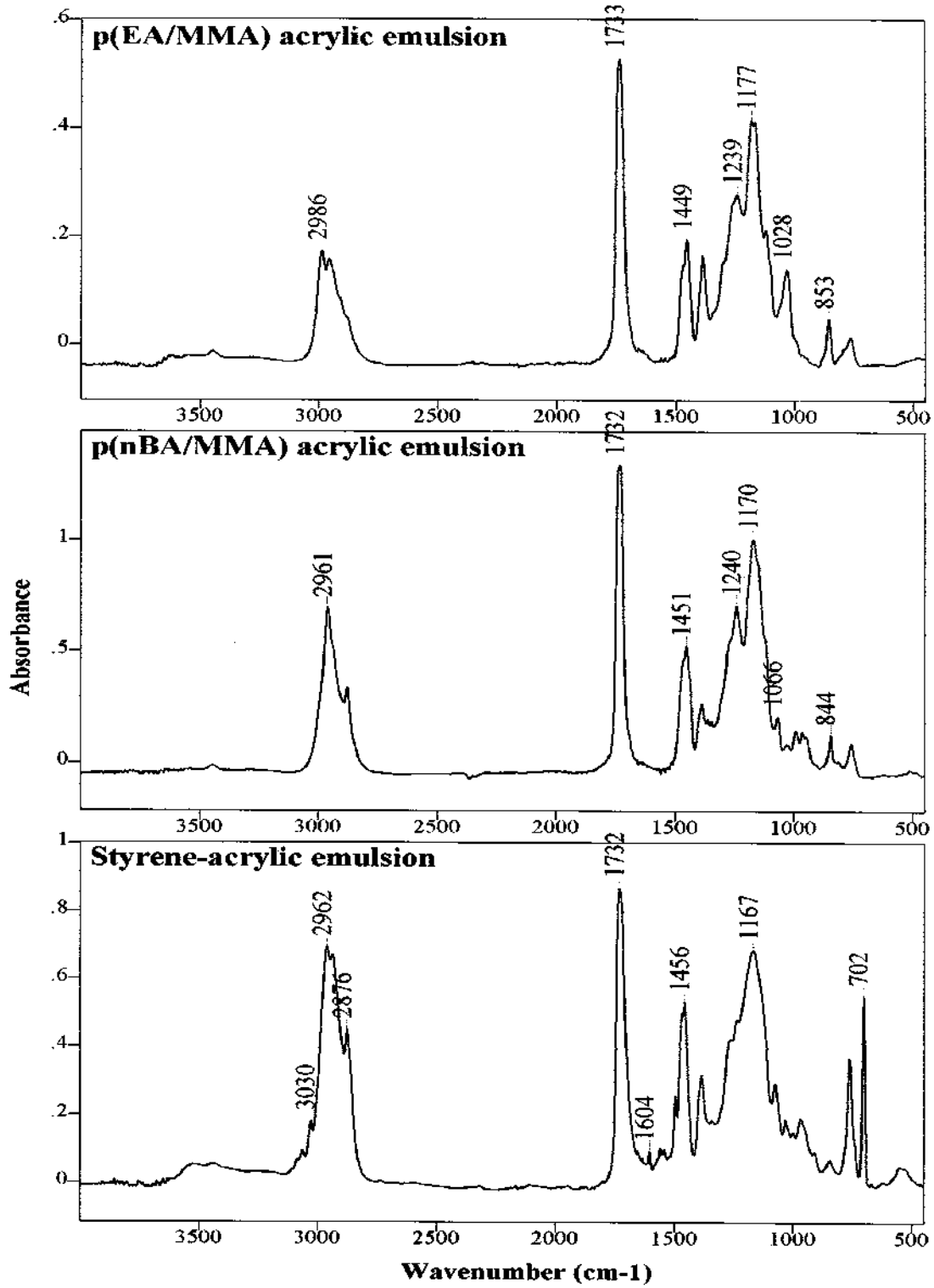


Figure 1

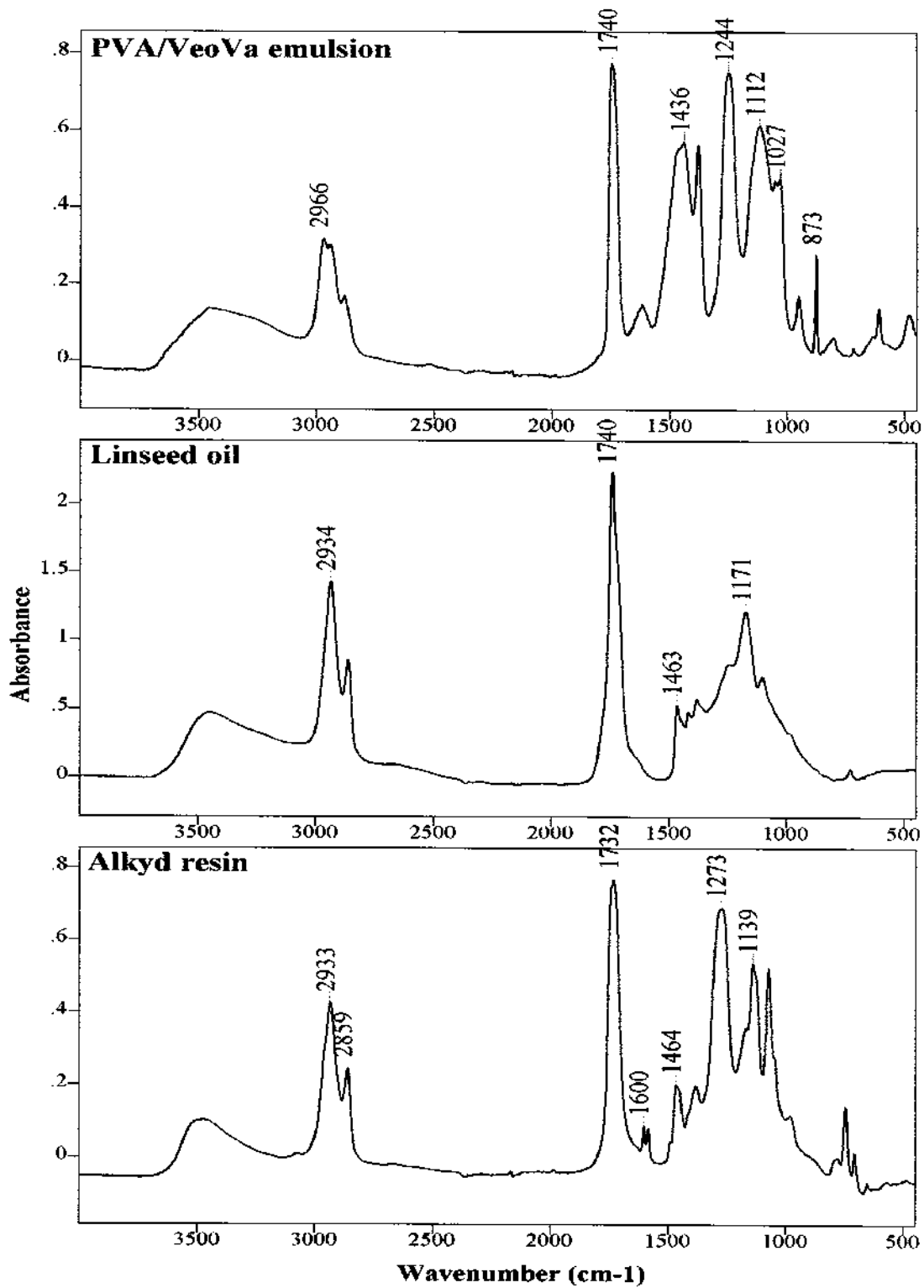


Figure 2

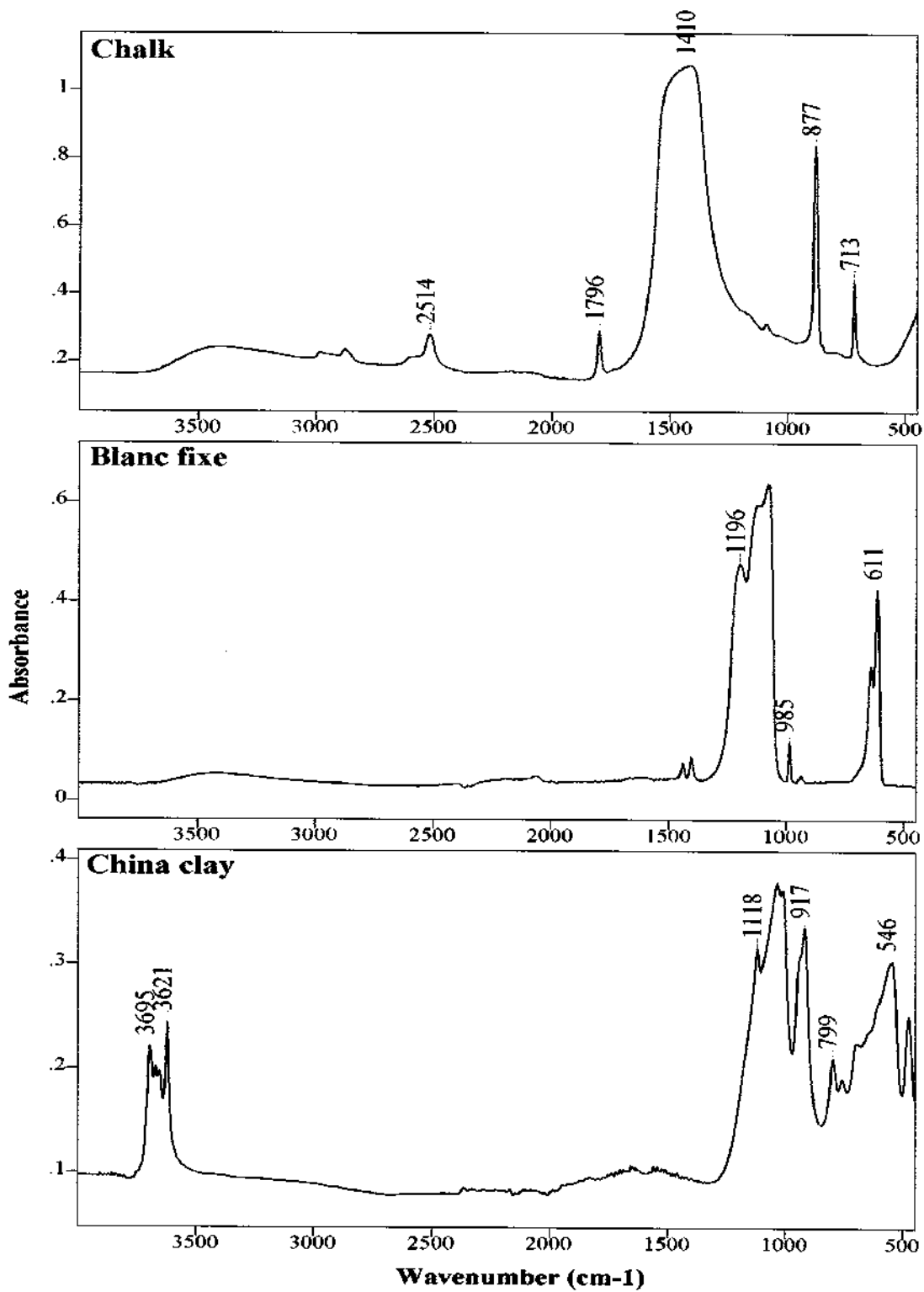


Figure 3

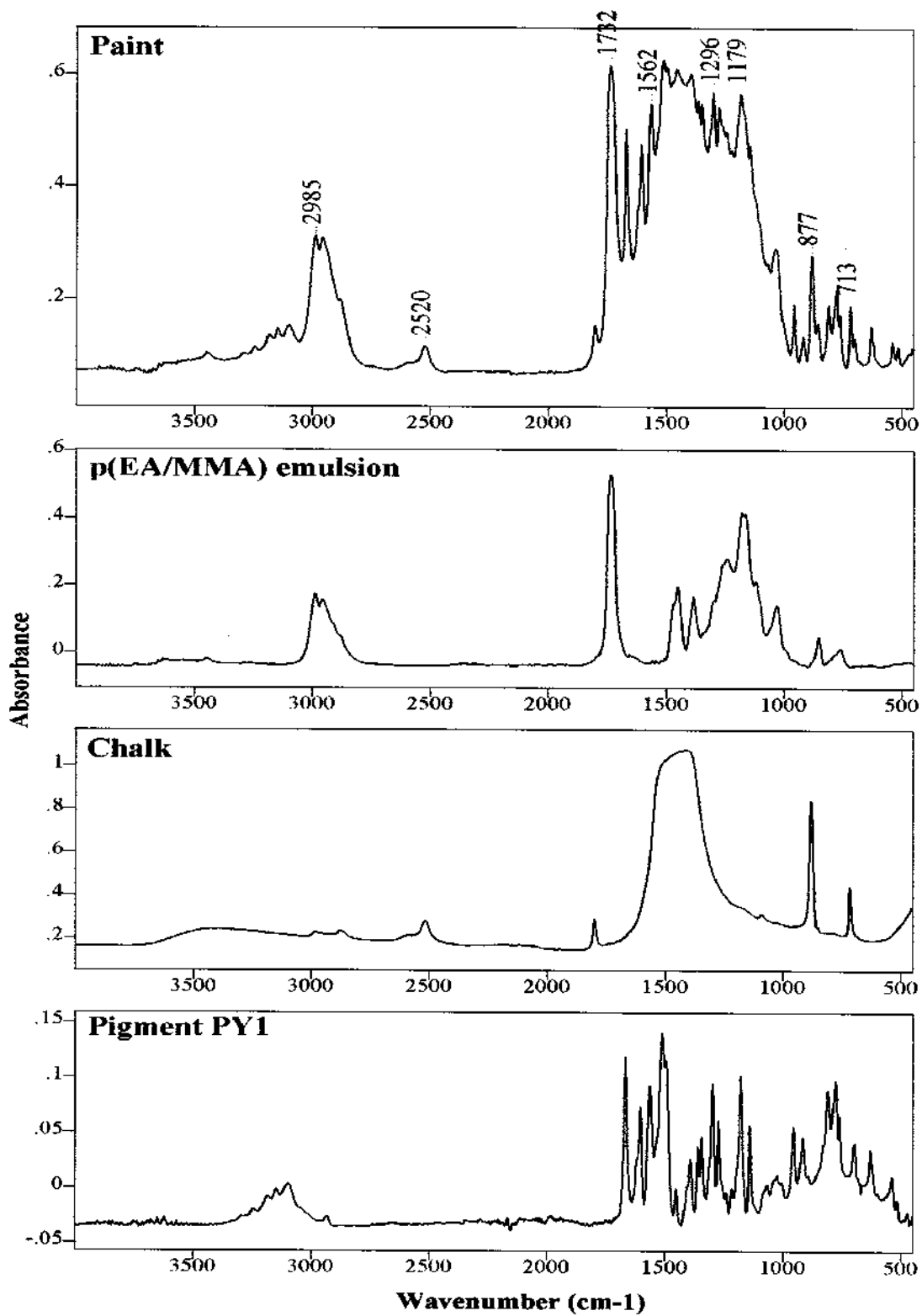


Figure 4



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 ($\text{KFe}^{\text{III}}\text{Fe}^{\text{II}}(\text{CN})_6 \cdot x\text{H}_2\text{O}$), 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.

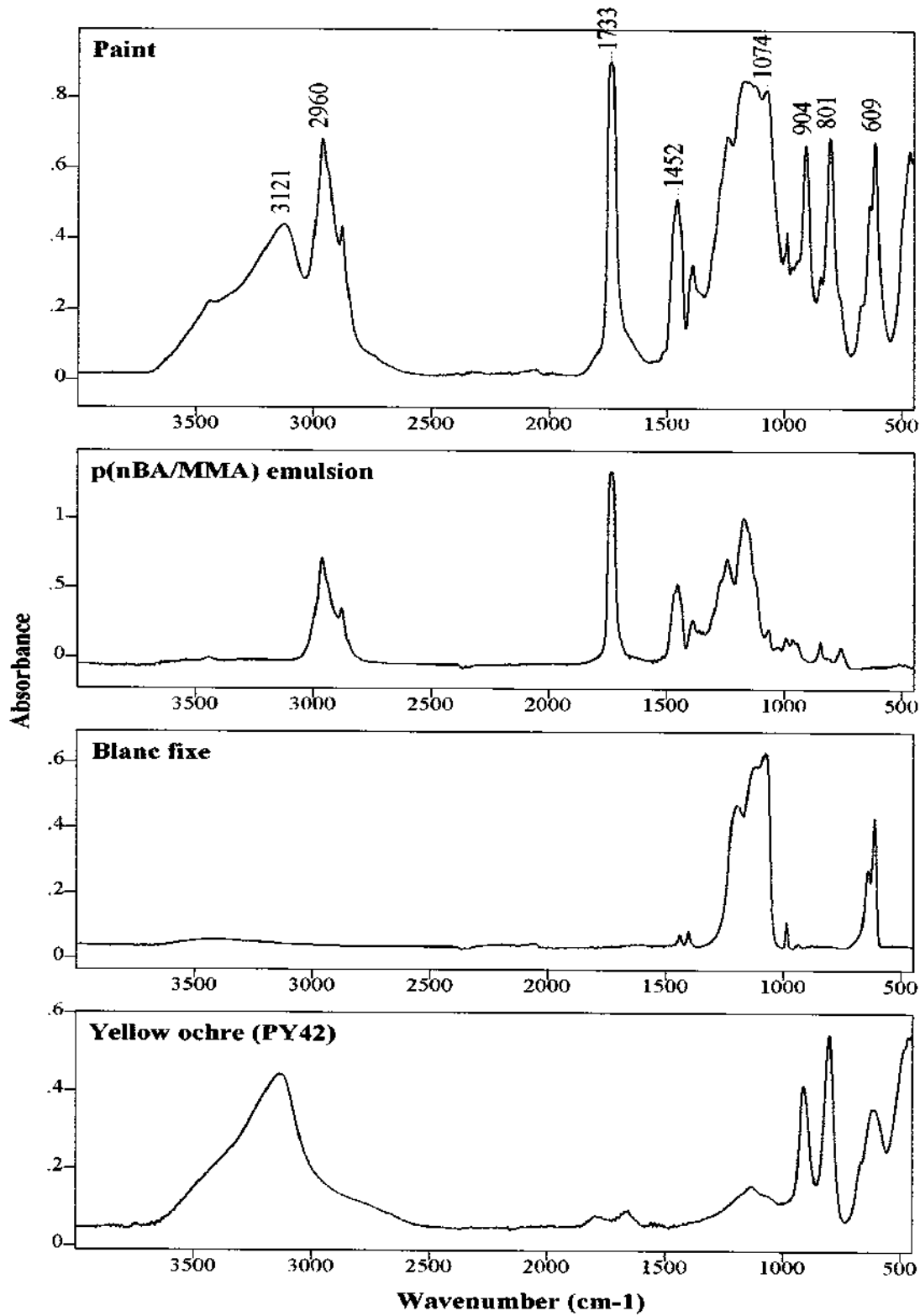


Figure 5

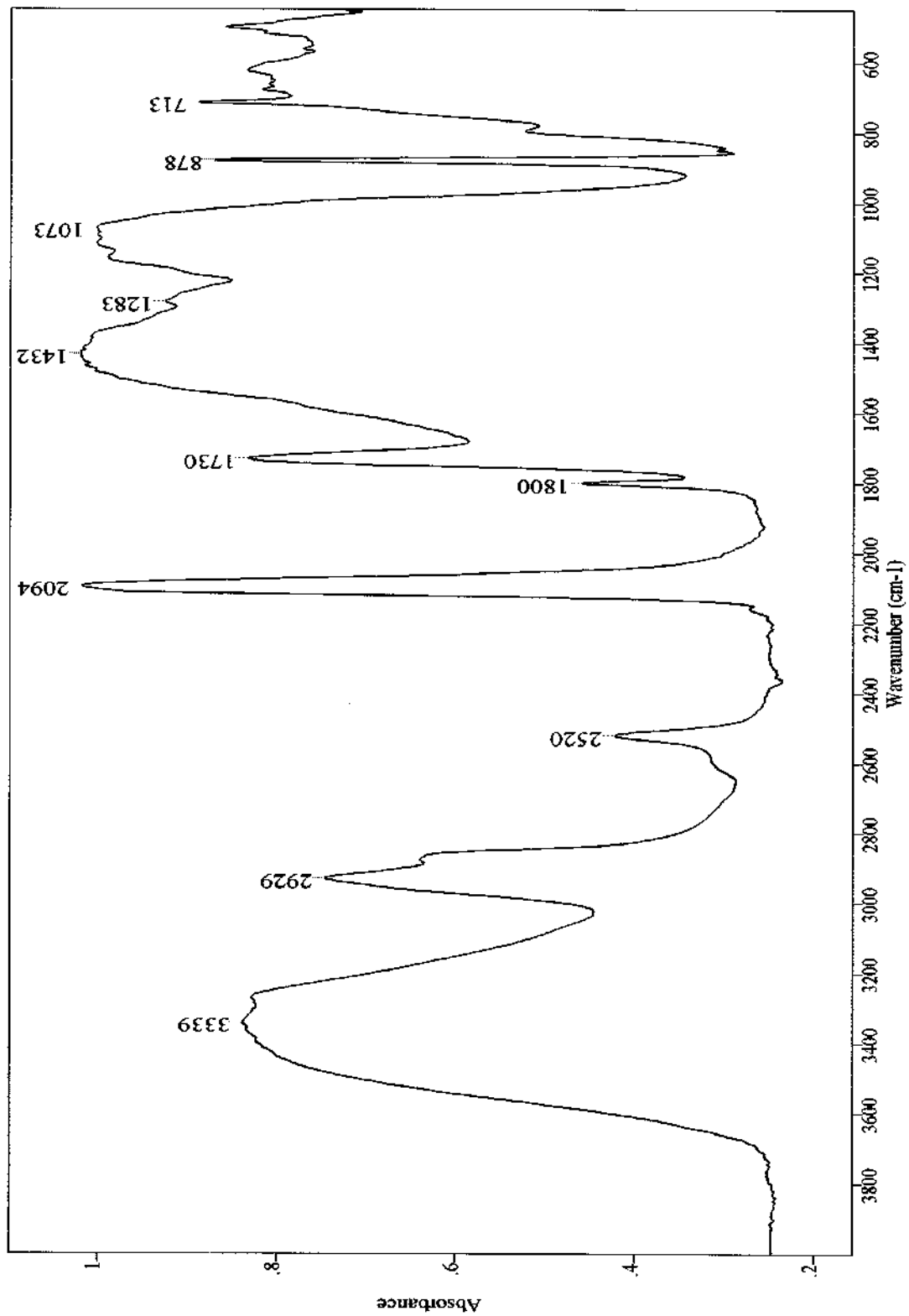


Figure 6



1.7 Acknowledgments

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1.8 References

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