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INVESTIGATION OF VARNISH LAYERS FROM MANCHESTER TOWN HALL

FOR

HIRST CONSERVATION

Distribution:

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y 2004

SGS UKAS QUALITY MANAGEMENT 005

Director of External Relations
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Investigation of Varnish layers from Manchester town Hall For Hirst Conservation

Description of sample

Sample 3, from Manchester Town Hall, three layers of varnish, two brown and one colourless on wood.

Experimental

Fourier Transform Infra-red (FTIR) Analysis

Layers from the small sample were separated as best as possible and placed onto the diamond window of a Durascope diamond ATR attachment linked to a Perkin Elmer 1000 Fourier transform Infra red spectrometer. The separated layers were pressed against the window using a metal anvil and scanned sixteen times. The background scan was automatically subtracted and the scans averaged to produce a spectrum. The layers were thus analysed by reflectance FTIR.

Cross Section

A sample of the varnish on wood, provided, was mounted in Beuhler's *Sample Quick*® resin and ground and polished to produce a cross section.

Fluorescrence microscopy

The cross section was observed and photographed at 100X magnification using a visible, incident 'cold light' source fitted to a Nickon microscope, and also with UV light from a mercury vapour lamp filtered to allow only visible light back up to the camera.

GC-MS analysis of Oils/resins

A sample was separated into two one portion contained the top brown layer and gthe transparentlayer while the other contained the lower brown layer and thw wood. This is the best separation which could be made on a scale big enough for GC-MS analysis on such a small sample. Sometimes it is easier to separate layers in situ by careful scraping. A portion of each of the two layers from the sample were transferred to a Reactivial and was derivatised and subjected to chromatographic analysis by gas chromatography and mass spectroscopy (GC-MS). The Samples of the varnish layers were heated with a 5% methanolic solution of 3-trifluoromethylphenyltrimethylammonium hydroxide to 60°C for 5 hours and subjected to thermal decomposition at 250°C, before analysis by GC-MS in order to look for evidence of drying oils, drying alkyds and resins in the varnish. The GC-MS instrument used was a "Hewlett Packard 5890 series III gas chromatograph" fitted with a "H.P. 5971A mass selective detector".

Results and Discussion

Cross section and fluorescence microscopy

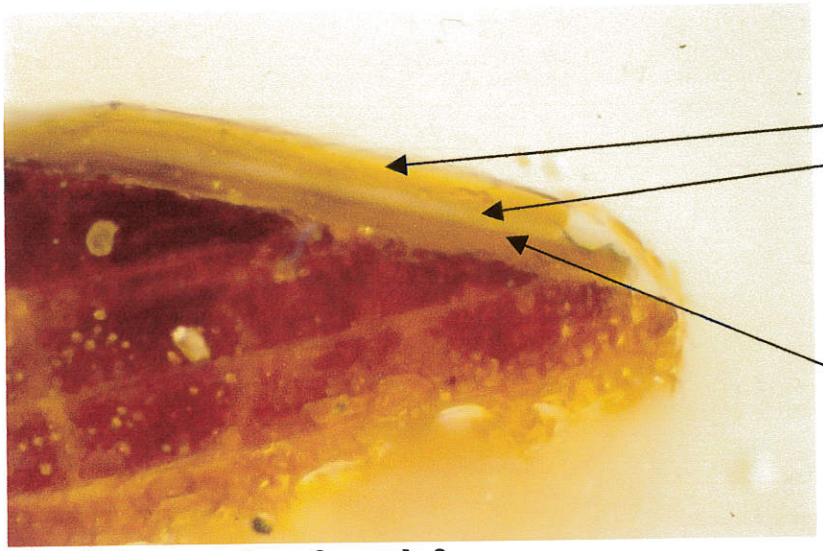


Plate 1 Cross section of sample 3

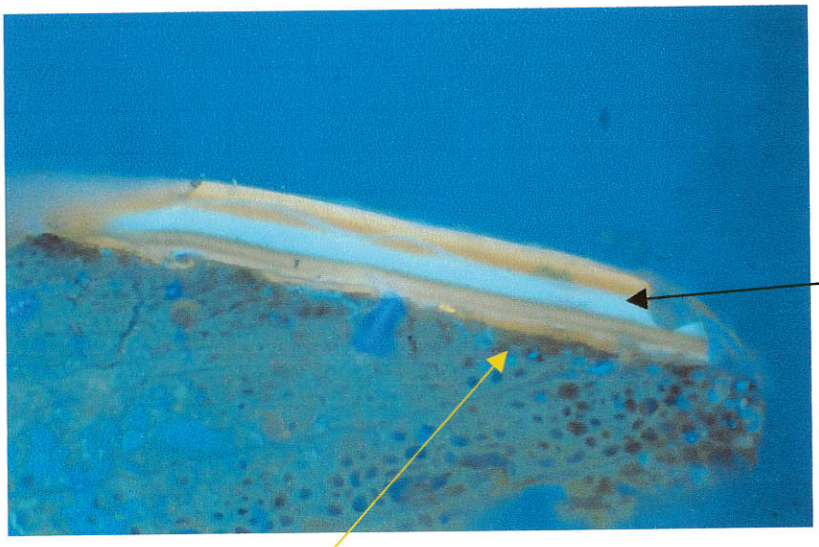




Plate 2 Cross section of sample 3 illuminated with Ultra Violet light + detail

The cross section (Plate1) seemed to reveal three layers of varnish ; yellow, colourless and brown. However, under UV light (Plate 2) the upper yellow layer seemed to be composed of two layers, the very top fluorescing yellow and the second non-fluorescent. The colourless layer fluoresced bright blue-white and the lower brown layer (Plate 2 – detail) seemed to be composed of three layers; the upper non-

fluorescent, the middle slightly fluorescing white, which may indicate a thin oil-resin layer, and the lowest showed a yellowish-orange fluorescence which may indicate shellac[1].

Infrared Spectroscopy

The layers were separated as best as possible. The top yellow and transparent layer easily separated from the lower brown layer(s). Thus the top yellow (Figure 1) and transparent layer (figure 2) could be investigated by taking a Fourier Transform Infrared spectrum of each side of this separated sample. As much of the lower brown layer as possible was scrapped from the wood to leave the oldest layer possible and an infrared spectrum was also recovered from the varnish left on the wood surface (Figure 3) thus given a spectrum of the lowest part of the brown layer.

The top layer, it was thought, might be shellac since it had fluoresced yellow under UV light but the infrared spectrum (Figure 1) suggested that it is an alkyd resin based on a drying oil treated with phthalic anhydride and terephthalic acid and modified with styrene. The colourless middle layer gave an infrared spectrum (Figure 2) which identified it as a drying alkyd based on a drying oil treated with phthalic anhydride. The layer closest to the wood gave an infrared spectrum (Figure 3) identical to that of our reference sample of shellac (Figure 4) thus identifying the lowest layer in the cross section as shellac.

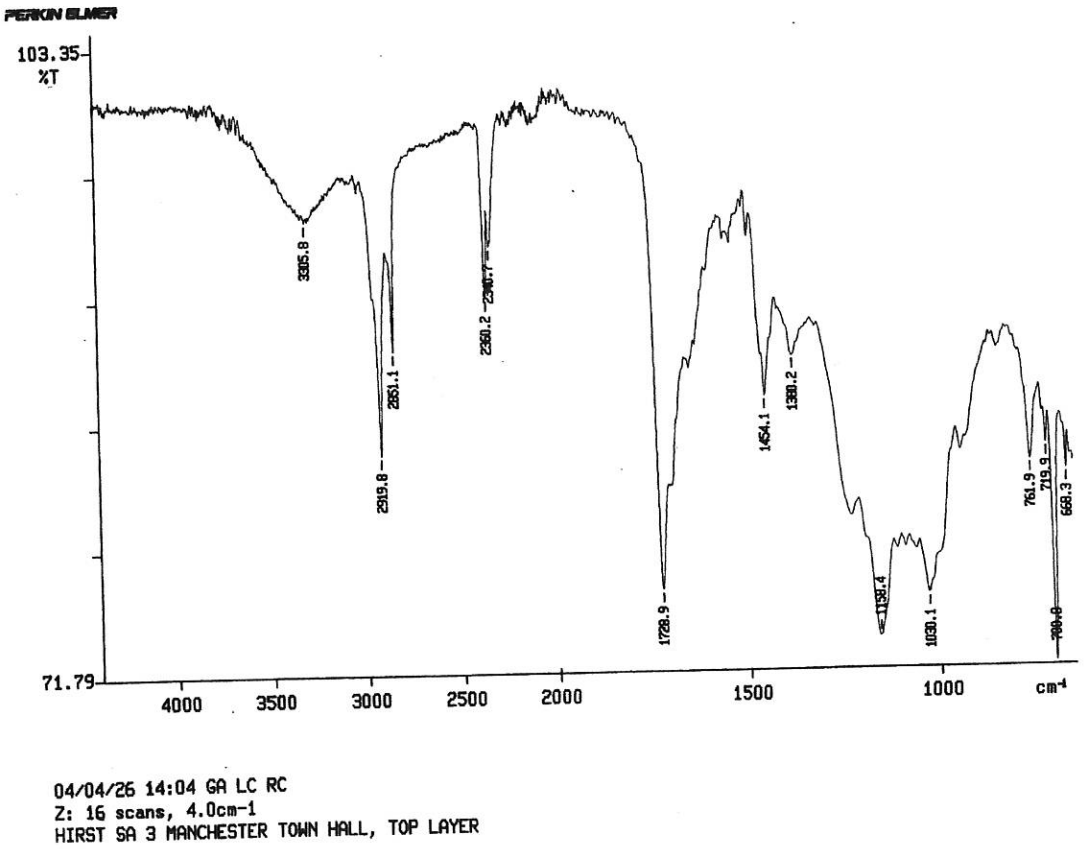
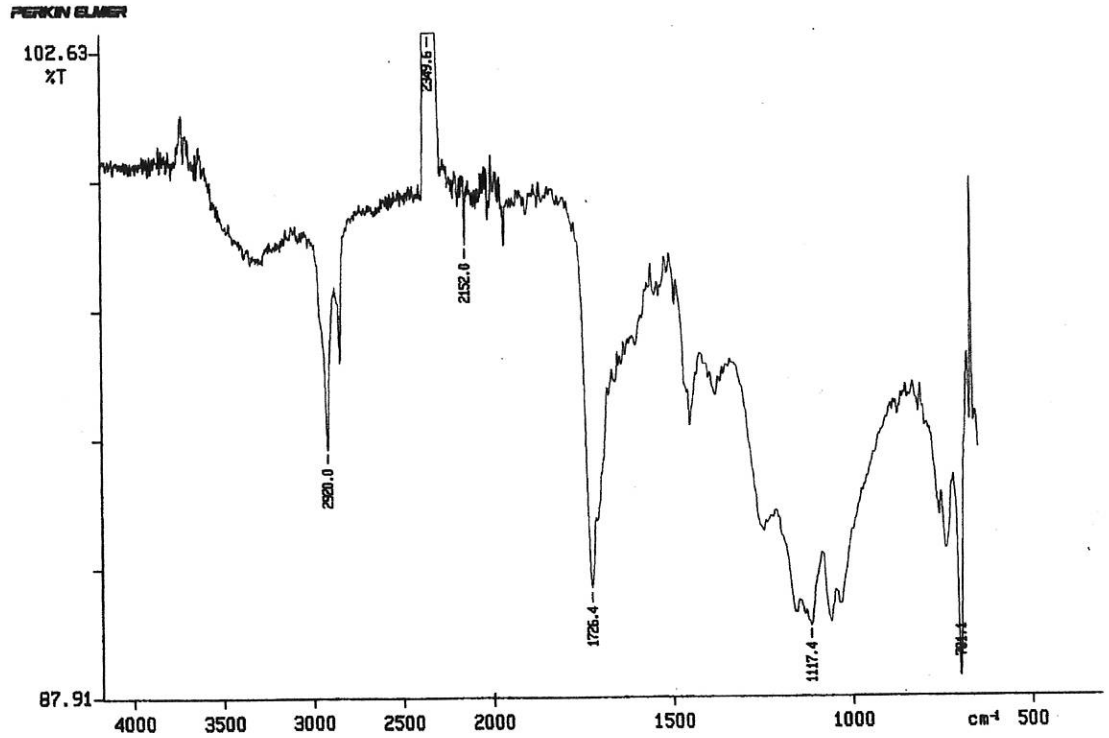


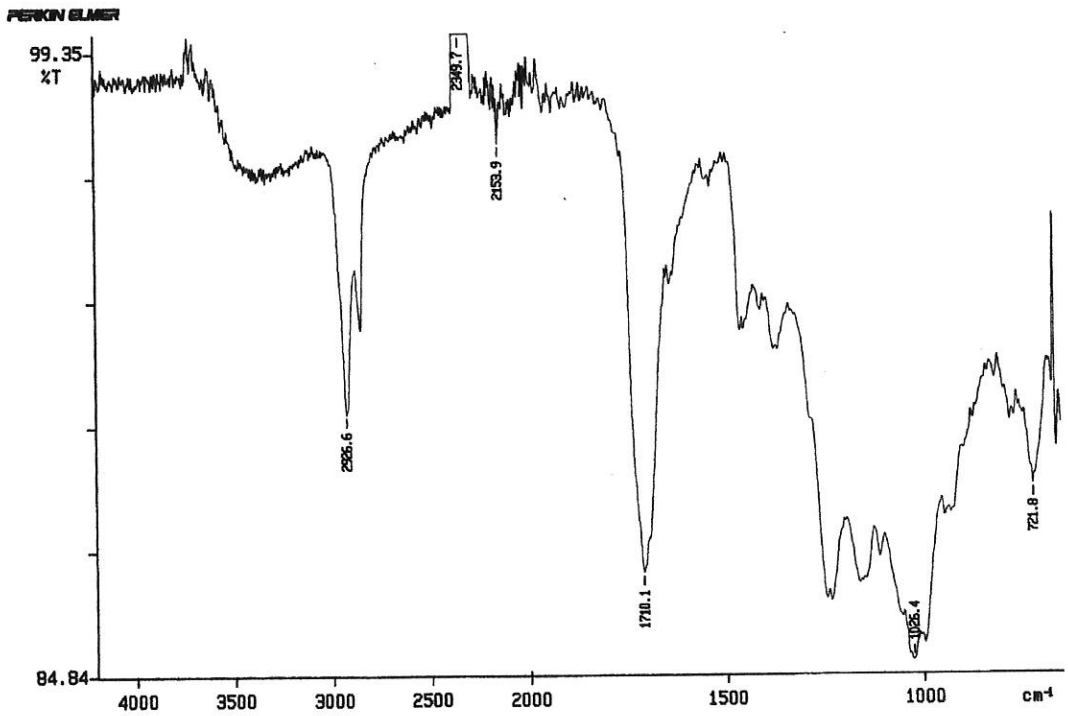
Figure 1 FTIR spectrum of sample 2,top yellow layer

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04/05/07 13:14 maria rubio
Z: 16 scans, 4.0cm-1
hirst sample 3 transparent colourless layer

Figure 2FTIR spectrum of colourless layer



04/05/07 13:03 maria rubio
X: 16 scans, 4.0cm-1
hirst sample 3 lower layer

Figure 3 Infra red spectrum of lowest layer nearest the wood

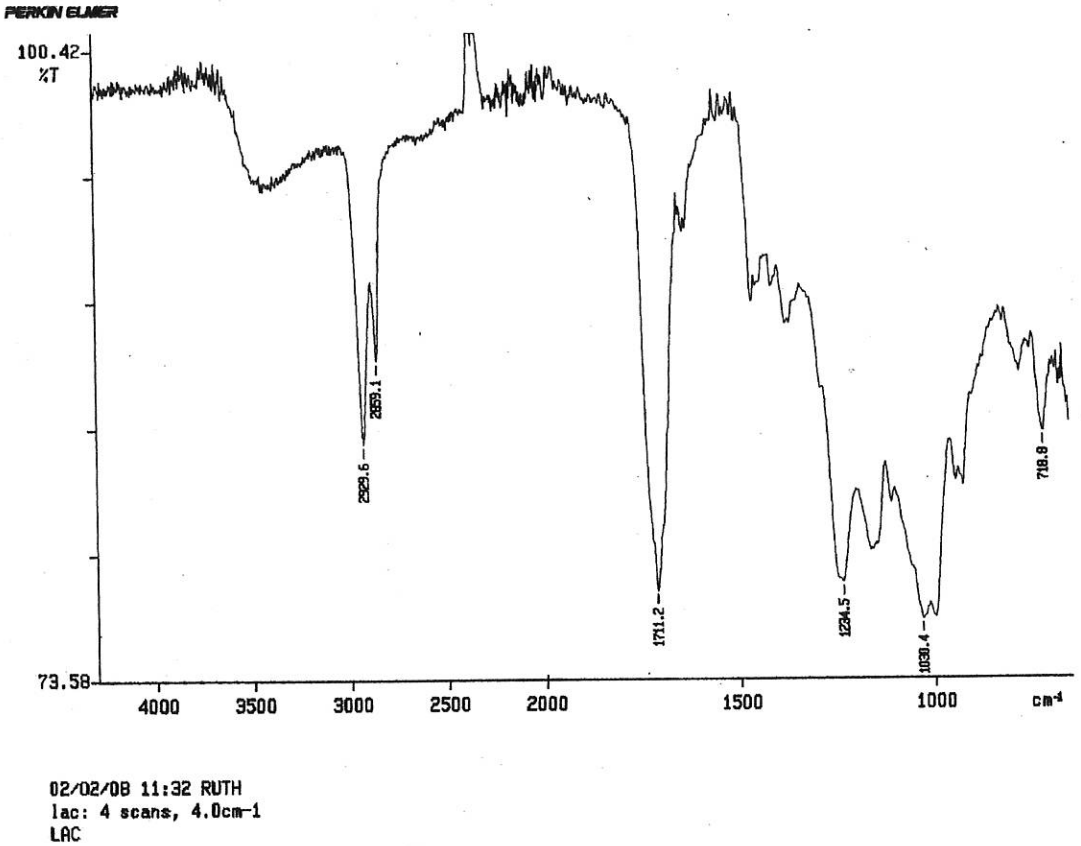


Figure 4 FTIR spectrum of Shellac

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GC-MS analysis
Upper layers

```
File       : C:\HPCHEM\1\DATA\HIRST3.D
Operator   : brian singer
Acquired   : 14 Jul 100  10:36 pm using AcqMethod PAINT
Instrument :   5971 - In
Sample Name: Hirst sample 3
Misc Info  : varnish top layer
Vial Number: 1
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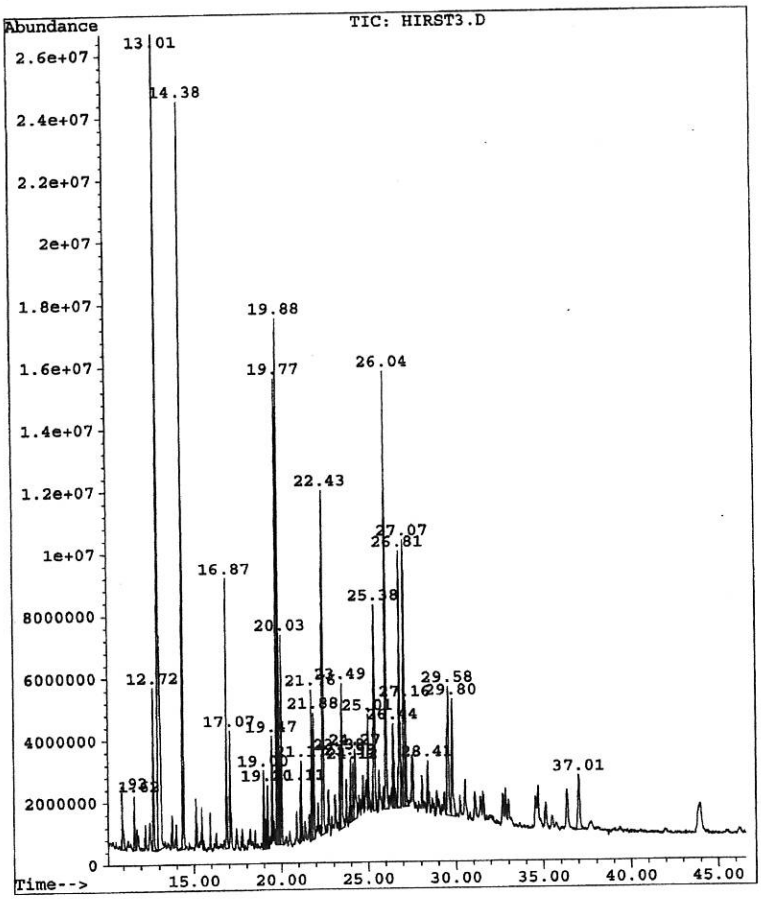


Figure 5 GC-MS chromatograph of upper two layers

The samples of yellow top layer and colourless layer were difficult to separate and were derivatised together to give a chromatogram (Figure 5) (appendix 1) which showed: a strong peak for nonandioic acid (azelic acid) together with palmitic acid (hexadecanoic acid) indicating that a drying oil or drying alkyd was present[2]. There is a very large peak at 13.01 minutes due to dimethyl phthalate which confirms that a drying alkyd based on phthalic anhydride is present. A small peak at 13.74 minutes is due to dimethyl terephthalate and shows that a drying alkyd based on terephthalic acid may also be present. The palmitic acid to stearic acid ratio was difficult to work out since the peak due to stearic acid is masked by that of another compound which has co-eluted with it, but many different seed oils can be used to prepare alkyds. There is a tiny trace of compounds found in shellac in this sample and also a tiny trace of 7-oxodehydroabietic acid which can indicate pine resin, but these may be contaminants from the lower layers (see below). There is also a large amount of unidentified material which may be modern oligomers used as paint/varnish additives used to increase gloss.

Lower Layers

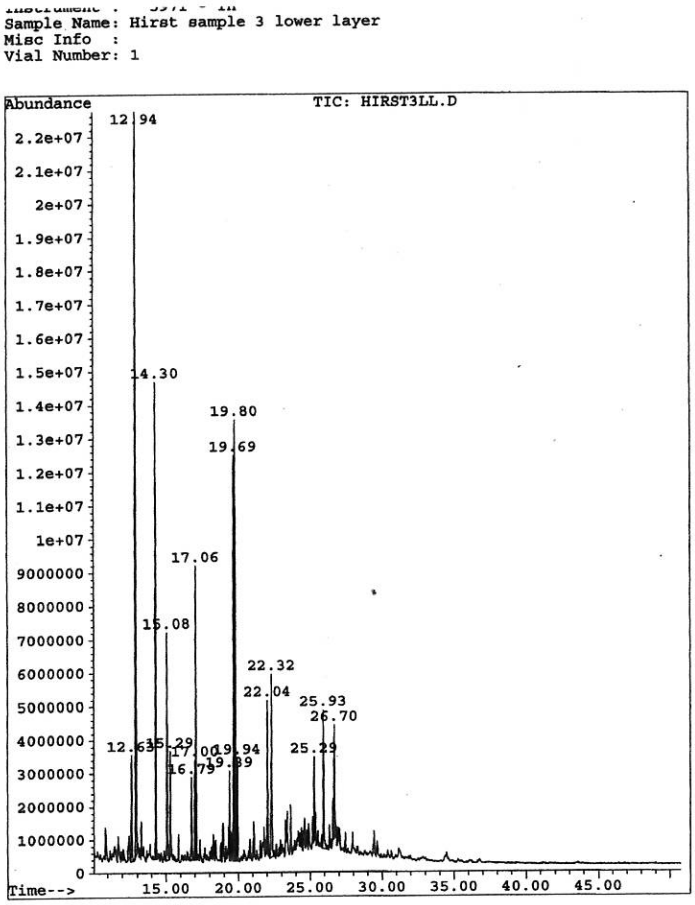


Figure 6 GC-MS chromatograph of lower layers

The remaining lower layers were derivatised together to give a chromatogram (Figure 6) (appendix 2) which showed: a strong peak for nonandioic acid (azelic acid) together with palmitic acid (hexadecanoic acid), stearic acid (octadecanoic acid) oleic acid indicating that a drying oil or drying alkyd was present[2]. There is a very large peak at 12.94 minutes due to dimethyl phthalate which confirms that a drying alkyd based on phthalic anhydride is present. The palmitic acid to stearic acid ratio was 1.74 (Table 1), which indicates that linseed oil was possibly the oil used to make this alkyd but many different seed oils can be used to make alkyds some of which have similar ratios. There are also compounds found in shellac in this sample; these are easily found by looking for compounds with 155 and 276 and 308 ions in their mass spectra. The pattern produced by selecting these ions (Figure 7) was similar to that obtained in our reference sample of shellac (Figure 8) and also agrees with the literature[3]. In particular, The peak at 23 minutes showed a mass spectrum (Figure 9) typical of an unknown compound in shellac[3]. There are also traces of dehydroabietic acid, 7-oxodehydroabietic acid and pimaric acid all of which may indicate traces of a coniferous resin, perhaps in the thin layer above the shellac layer which had fluoresced slightly. Alternatively these may be due to the alkyd layer having 'Tall oil', an oil derived from pine trees, incorporated in its manufacture.
Also present in the chromatogram (Figure 6) (appendix 2) were methyl esters of 3,4-dimethoxy benzoic acid and 3,4,5-trimethoxybenzoic acid and also 3,4,5-trimethoxybenzaldehyde. These compounds are reported to have been found in Kassel

Earth pigment when using a similar methylation / GC-MS technique[4]. Kassel earth is a ground lignite also known as Van-Dyke brown, Cassel Earth and Cologne Earth. Hence, it seems probable that this brown pigment has been used in these lower layers; either in the shellac layer or the brown layer directly above it or in both perhaps.

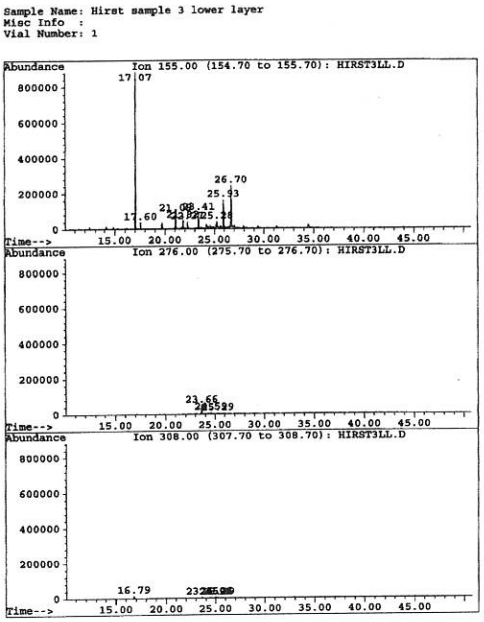


Figure 7 Sample 3 lower layers

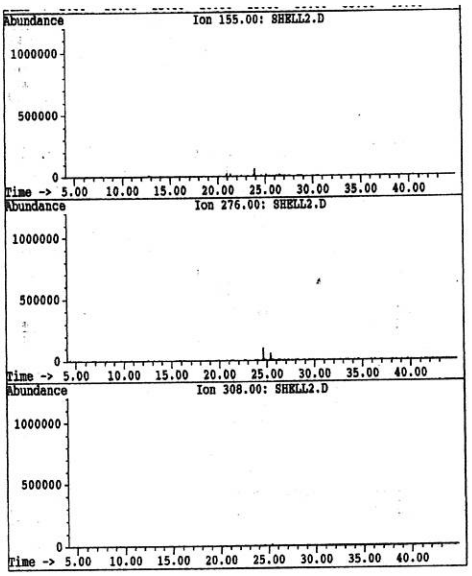


Figure 8 Reference shellac sample

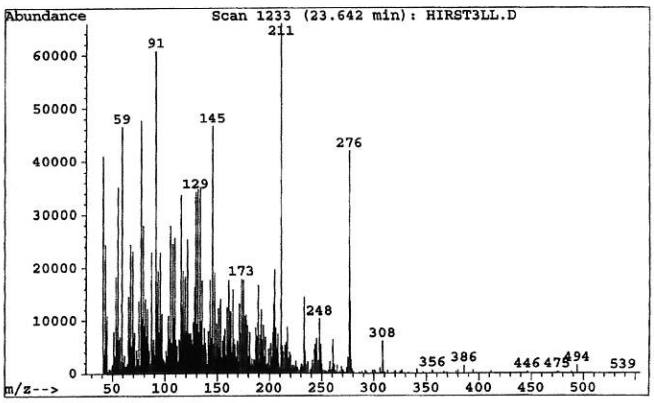


Figure 9 Mass spectrum of peak at 23.642 minutes

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Conclusions

- The upper yellow layer in varnish sample 3 is a modern drying alkyd manufactured from a seed oil and terephthalic acid. It may be modified with styrene resins.
- The transparent layer is also a modern drying alkyd manufactured from a seed oil and phthalic anhydride. It may be modified with oligomers.
- The upper part of the brown layer is a modern alkyd based on linseed oil or another seed oil and phthalic anhydride.
- There are also traces of coniferous resin in the lower layers, perhaps in the thin layer between the shellac layer and the upper part of this brown layer. This thin layer fluoresces slightly white and may be an oil-resin layer.
- The layer nearest to the wood is shellac, since it fluoresces orange-yellow and gives an infrared spectrum identical to shellac and yields compounds detected by GC-MS, which are associated with shellac.
- Kassel Earth, also known as Van Dyke brown or Cologne Earth is a pigment present in the lower layers.

References

1. UV light photography as an aid in the Conservation of 18th century furniture http://www.wag-aic.org/1997/WAG_97_philp.pdf
2. John S. Mills and Raymond White, *The Organic Chemistry of Museum Objects*, Second Edition, 1994, Butterworth - Heinemann, Oxford, pp 170 - 172.
3. John S. Mills and Raymond White, *The Organic Chemistry of Museum Objects*, Second Edition, 1994, Butterworth - Heinemann, Oxford, pp 180 – 183
4. Georgiana M. Languri, *Molecular studies of Asphalt, Mummy and Kassel earth pigments,* **AMOLF**, Molart reports, Archetype Publications, London, 2004 pp 96-102