

INFRARED MAPPING MICROSPECTROSCOPY FOR IDENTIFICATION OF FURNITURE FINISH LAYERS

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Infrared mapping microspectroscopy is a new technique which is able to give information about the composition, position, and size of individual layers in a multilayered sample. Multilayered facsimile samples as well as cross-sections taken from furniture were microtomed with and without the use of embedding media. Infrared spectral maps were systematically collected from areas of 20 x 400 μm across the sample in 20 μm steps. The resulting chemical profiles were used for identification of individual layers even when these layers were not distinguishable under an optical microscope. The technique provides means to analyze multilayered samples found in many furniture finishes and other surface coatings.

INTRODUCTION

Identification of resins used for furniture finishes is important for art historical analysis of an artifact as well as for an initial material survey in restoration or conservation treatments. A detailed chemical analysis of surface finishes can also provide important information on previous surface treatment procedures and craftsmen techniques.

The materials and techniques available to the craftsmen dealing with furniture surface treatment had been developed, for most part, empirically throughout the ages. The craft was industrialized in the second half of the nineteenth century, yet many craft procedures were retained until the start of the twentieth century. Collections of old recipes provide some insight into the chemistry of varnishes used for furniture surface treatment [1,2,3]. However, the natural resins used to a great extent for these surface finishes are very difficult to analyze due to their complex composition, their natural variability, and their susceptibility to polymerization and oxidation.

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A review on the chemistry of natural resins important for research in art and archaeology was published by Mills and White [4]. Analytical methods used for natural resin identification were reviewed several years ago by Masschelein-Kleiner [5]. The advantages of infrared spectrometry for the analysis of varnishes and surface finishes was recognized relatively early [6,7]. Since then infrared spectroscopy has found a widespread application in art conservation laboratories and laboratories which deal with

analysis of natural resins [8-12]. More recently, a paper was published on the capabilities and limitations of Fourier Transform Infrared (FT-IR) spectrometry for the identification of natural resins used in historic furniture finishes [13].

Evaluating the role of infrared spectrometry in identification of natural resins, Masschelein-Kleiner wrote [5]: “the method (IR) needs previous purification of the sample to ensure as far as possible that only one layer (of varnish) has been taken...”. This is difficult to do because some varnish layers are very thin and some surface finishes represent complex multilayer structures. However, the recent advance of infrared microspectroscopy allows for analysis of small sample areas through the coupling of an optical microscope to a FT-IR spectrometer. This paper describes a method for the analysis of multilayer structures of surface finishes using infrared microspectroscopy which can identify individual varnish layers in a multilayer cross-section.

EXPERIMENTAL

The resins examined in this study were: shellac, copal, mastic, rosin, and sandarac. Solutions of the resins in ethanol (40% weight/volume) were prepared to represent typical spirit varnish formulations [14,15]. Facsimile samples were prepared by application of varnish layers to mahogany veneer, Teflon, or polyethylene surfaces. For the first set of samples, small portions (e.g. 5 x 2 mm) of the veneer/resin composite were removed by means of a razor blade from the remainder of the plywood support. The resulting sample section was of sufficient strength to allow for direct mounting and slicing on a Reichert-Jung Model 2040 Autocut microtome with a stainless steel blade. Cross-sections were typically cut at 15-25 μm .

The second approach of cross-section preparation involved removing small portions (e.g. 1 x 3 mm) of the multilayer resin coat from either the Teflon or polyethylene support. This sample was then embedded into paraffin wax. The resulting wax mold was cooled to -10°C . While the wax mold was still at sub-ambient temperature, the sample was microtomed as described above.

The wax embedding media worked well for slicing, however the opacity of the wax caused some difficulties. Despite careful positioning, the exact placement and orientation of the sample during the microtoming was difficult to determine until the sample was reached. Since small samples could inadvertently be lost, several other clearer embedding media were tested. A polyester resin (sold under the trade names of Bioplast and Caroplast) was used successfully. Thus, all sample finishes obtained from objects were embedded in the polyester then microtomed as described above.

Once sliced, the cross-sections were placed on a BaF_2 window and transferred to the sample stage of the infrared microscope for analysis. The infrared microscope used in this study was the Spectra-Tech IR-Plan II research infrared microscope positioned in the sample beam of a Perkin-Elmer Model 1760 Fourier Transform infrared spectrometer equipped with a narrow-band, cryogenically cooled Mercury Cadmium Telluride (MCT) detector. The spectrometer was interfaced to a Perkin-Elmer Model 7700 Data Station. Spectra were collected from $4000 - 700 \text{ cm}^{-1}$ using 120 scans with a resolution of 4 cm^{-1} .

RESULTS AND DISCUSSION

Multilayer Sample on Mahogany Veneer

One cross-section of a facsimile binary resin layer, made by coating a mahogany surface with three coats of shellac followed by two coats of copal, is shown in figure 1. The infrared mapping

experiment was initiated at the outermost region of the copal layer isolating a 20 x 400 μm area for study. Subsequent regions were examined by a 20 μm movement across the sample to reveal the adjacent area. This mapping process was continued until spectra were observed characteristic of the mahogany wood. Infrared spectra were collected for each step of the mapping experiment from 4000 - 700 cm^{-1} , but the region from 1000 - 700 cm^{-1} proved most convenient for characterization of the layers (see fig. 2). Reference spectra of each resin as well as the mahogany in the 1000 - 700 cm^{-1} region are also presented (see fig. 3). The characteristic bands for copal present at 890 cm^{-1} and 793 cm^{-1} can be observed in steps 1 - 3 of the map and to a small degree in step 4. Study of step 5, however, reveals that these bands have disappeared from the spectrum. Bands characteristic of shellac occur at 945, 930, and 724 cm^{-1} . These bands are not present in the early steps of the map, but begin to appear in steps 3 and 4. By step 5, the spectrum observed is characteristic of shellac. Additional mapping reveals that at step 8 the spectrum obtained is that of mahogany.

The results indicate that the transition from the copal to shellac layer occurs in the area sampled by steps 3 - 4. Due to the fact that the boundary between the layers is not necessarily uniform in its linearity across the sample and the fact that the size of the aperture in the dimension perpendicular to the mapping axis is relatively large (400 μm), the boundary between the layers is not expected to be sharp. In addition, the mapping experiment was conducted using manual movement of the sample which most likely provided a degree of uncertainty with respect to absolute position. But by using the evidence supplied by relative intensities of the pertinent bands, the boundary is estimated to occur three-fourths of the way through step 3. Because each step of the map corresponds to a 20 μm increment, the thickness of the layers predicted using the infrared data are: 55 μm for the copal layer and 85 μm for the shellac layer. The thickness of the layers observed visually calibrated to a sample stage micrometer were recorded to be 52 μm for copal and 96 μm for shellac.

Multilayer Sample Embedded in Paraffin Wax

Small or fragile samples need the additional support of an embedding media before they can be microtomed. In our initial experiment, some cross-sections of the multilayer resin samples were embedded in paraffin wax, microtomed and analyzed using the same mapping techniques as previously described. An example of this approach involved the study of a cross-section taken from a sample made by applying three coats of shellac onto a Teflon surface followed by the addition of three coats of mastic (see fig. 4). Due to the thickness of the sample, mapping steps were increased to 40 μm increments (see fig. 5). In the 1000 - 700 cm^{-1} region, the band at 841 cm^{-1} is useful in the identification of the presence of mastic. This band is clearly present in steps 1 - 4, but disappears in step 5. As previously discussed, the bands characteristic of shellac are located at 945, 930, and 724 cm^{-1} . Although not initially present, these bands appear in steps 5 and 6 of the map. The final step of the map shows spectral features attributable to the paraffin wax. Although the same number of coats of each resin was used, it appears that the mastic was applied in much thicker coats.

Furniture Finish Sample Embedded in Polyester

Several embedding media (wax, epoxy, acrylic, silicone and polyester) were tested for their ease of sample preparation, clarity and microtoming qualities. Of these, the polyesters (Bioplast[16] and Caroplast[17]) worked well and were selected for the analysis of several furniture finish samples. A microtomed cross-section from one sample taken from the Paris Peace Treaty desk (British, circa 1780, from the United States Department of State collection, acquisition # 64.010) is presented in figure 6. Through an optical microscope with polarized transmitted light, the thin section appeared to have

distinct layers: wood, a clear layer, and a darker layer with a dirty surface. Infrared analysis of the sample, however, indicated that the entire coating was shellac (see fig.7). The full infrared spectra, 4000 - 700 cm^{-1} , presented in figure 7 showed the transition from the embedding media in step 1 (Caroplast) to the wood in step 6. The coating on the wood, represented by steps 2-5, corresponds to shellac. There are some minor differences in the step 2 spectrum from the outer surface of the coating. The sharp bands at 3010, and 1500 cm^{-1} , along with the change in the band at 14 cm^{-1} , are due to the Caroplast. Other small changes may be due to a thin layer of dirt, oil or wax or to surface oxidation, but none of these possible causes can clearly be determined from these spectra.

CONCLUSION

Infrared mapping microspectroscopy has been found to be a useful technique in the identification of individual layers present in a multilayered varnish sample. Cross-sections of multilayered resin samples were obtained suitable for infrared microscopic analysis by the use of three microtoming strategies. One approach involved examination of cross-sections cut from varnish layers applied to and still adhering to mahogany surfaces. The second used paraffin wax as an embedding medium to support samples of resin layers removed from Teflon and polyethylene substrates. The third method, which worked the best and was used on actual finish samples, was to embed the multilayer sample in a polyester media for support during microtoming. In each case, infrared spectra were obtained from analysis of 20 x 400 μm regions of the samples. Systematic stepping through the cross-section with subsequent collection of infrared spectra allowed for the mapping of the multilayer resin sample providing information about composition, position, and size of each layer present.

Future work will be done to examine the effects of ageing and refinishing on the resin boundaries and surface oxidation. Using the current method, it is likely that thin layers, such as a wax or oil may be missed. Additionally, while the polyester resin works well for embedding and slicing, it may cause some problems due to resin dissolution on the surface.

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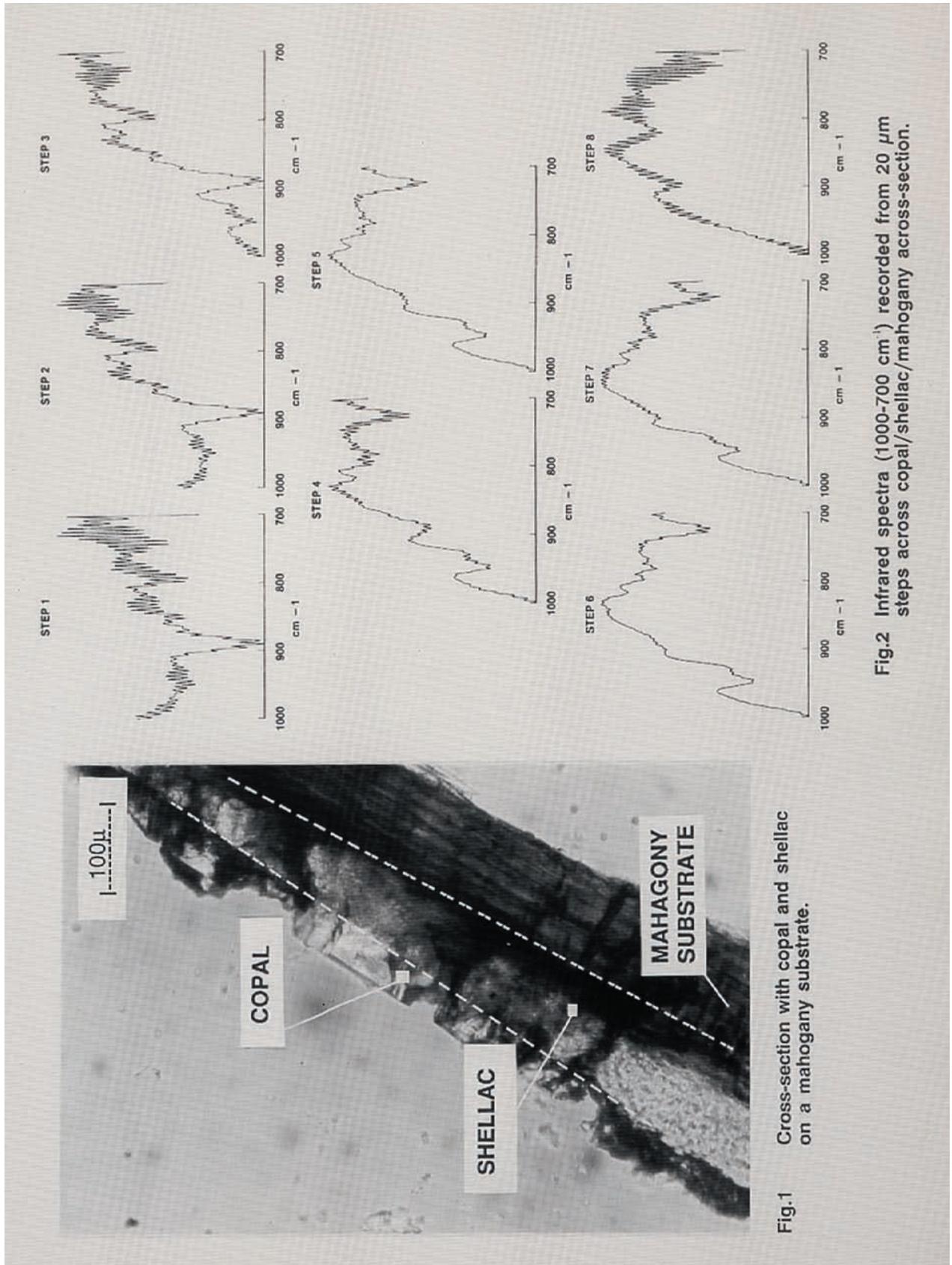


Fig.1 Cross-section with copal and shellac on a mahogany substrate.

Fig.2 Infrared spectra (1000-700 cm^{-1}) recorded from 20 μm steps across copal/shellac/mahogany cross-section.

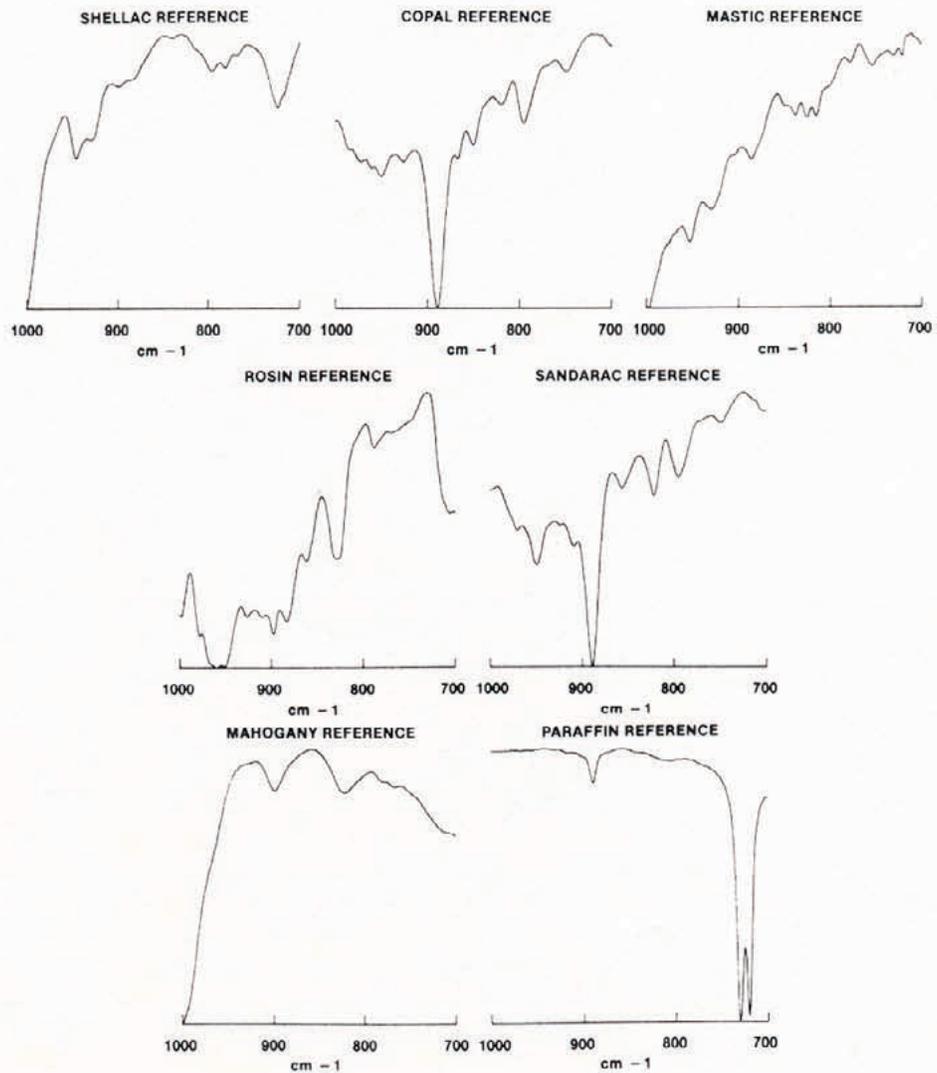


Fig.3 Infrared reference spectra (1000-700 cm⁻¹) of selected natural resins and embedding and support media.

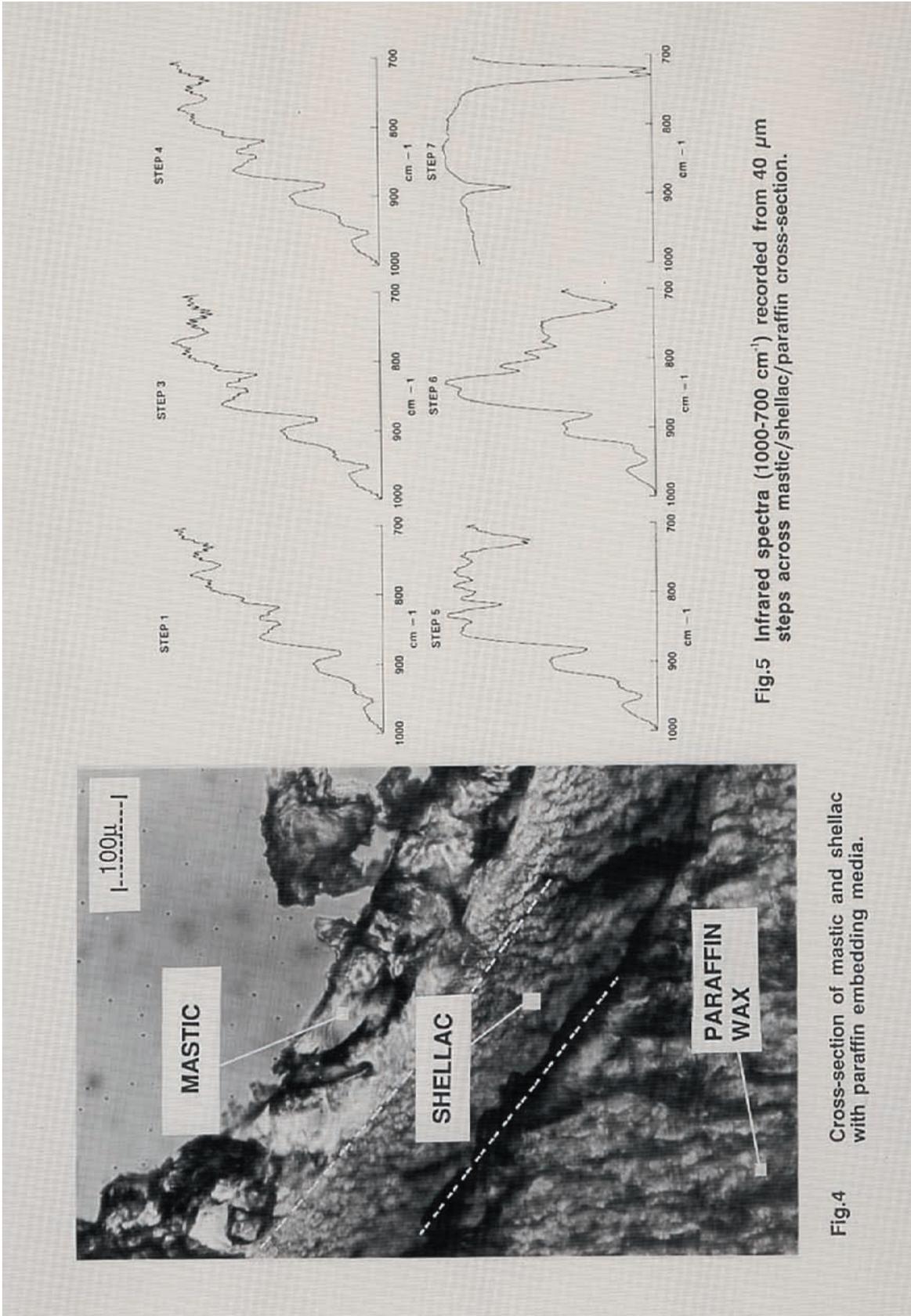


Fig.5 Infrared spectra (1000-700 cm^{-1}) recorded from 40 μm steps across mastic/shellac/paraffin cross-section.

Fig.4 Cross-section of mastic and shellac with paraffin embedding media.

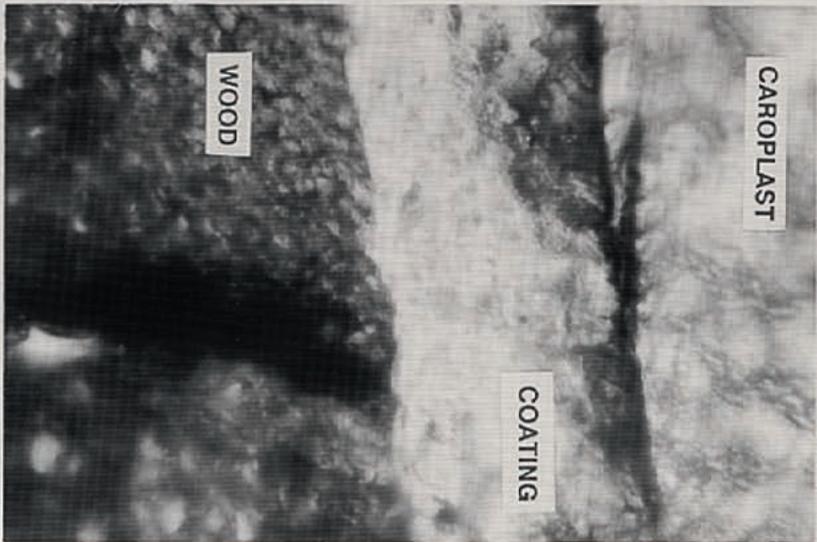


Fig.6 Cross-section of sample from Paris Peace Treaty desk (British, circa 1780, from the collection of the U.S. Department of State, Acq # 64.010)

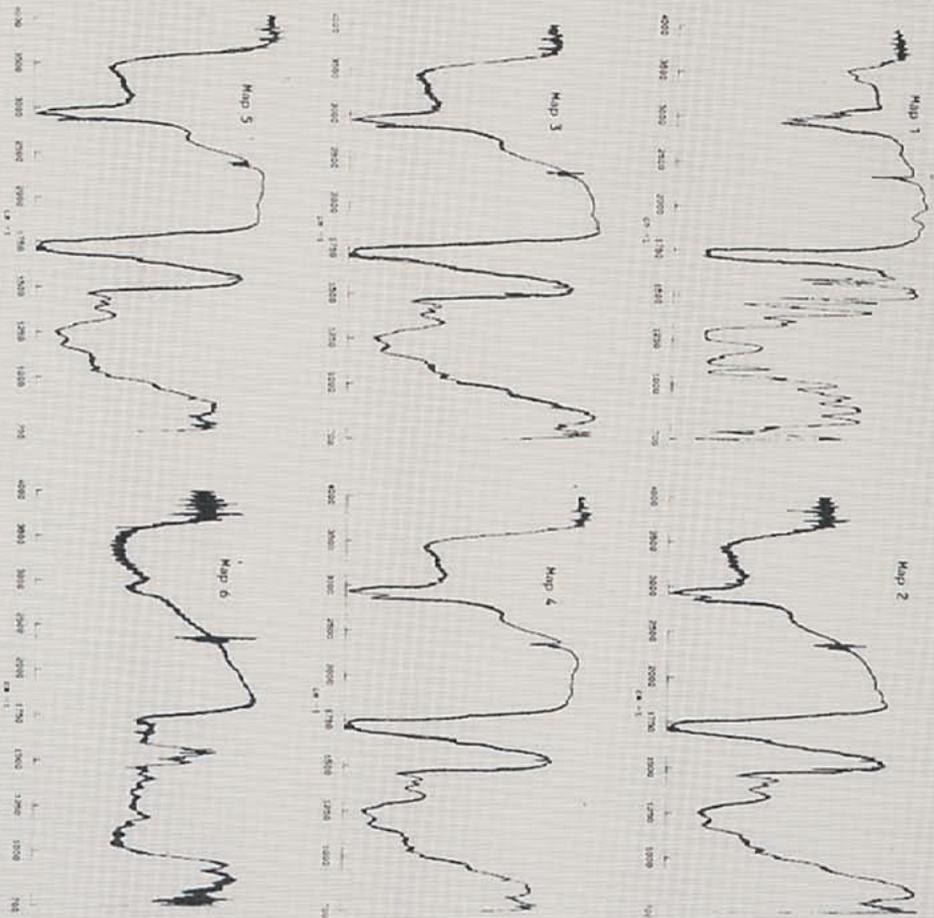


Fig.7 Infrared spectra (4000-700 cm^{-1}) recorded from 40 μm steps across sample shown in figure 6.

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