MICROSCOPY, MICRO-CHEMISTRY AND FTIR AS ANALYTICAL TOOLS FOR IDENTIFYING TRANSPARENT FINISHES  
CASE STUDIES FROM ASTRA MUSEUM – SIBIU

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Abstract:  
Conservation of cultural heritage relies on scientific investigation of artefacts, a key point being identification of the original materials. In this context, besides wood species identification, investigation of finishing layers is of ultimate importance for old furniture and any other wooden objects with historic, documentary or artistic value. The present paper refers to a series of micro-destructive investigation methods applied for identification of finishing materials, namely: simple in situ and laboratory physical tests, optical microscopy, micro-chemistry and FTIR – ATR analysis. Small samples of finishing layers were taken from four furniture objects belonging to CNM ASTRA Sibiu and were analysed according to the usual procedures of the laboratories from Sibiu and Brasov. The results showed that physical tests and microscopy are useful to get basic information on the samples' morphology and possible classes of coating materials, while micro-chemistry revealed by some successive tests more specific information on the type of finishing materials. FTIR - ATR is a rapid method of identifying the coating materials based on available reference samples or spectra. However, this is not always straightforward and preliminary physical tests of solubility are useful to select the adequate references, while micro-chemistry tests could complete the FTIR result, especially for those components of the finishing layer present in very small amounts (less than 5%), bellow the FTIR sensitivity. Corroboration of microscopy, physical and micro-chemistry tests with FTIR can provide more reliable results in terms of finishes identification and also valuable information for restoration.

Key words: furniture; conservation; investigation; finishing layer; microscopy; micro-chemistry; FTIR.

INTRODUCTION

It is well acknowledged nowadays that conservation of cultural heritage relies on a comprehensive historic documentation and scientific investigation of artefacts prior any direct intervention. One of the key-point to address is identification of the original materials and techniques. This is equally important for art history studies, authentication and dating of artefacts, as well as for any direct preservation and restoration interventions (Sandu et al. 1998, Odegaard et al. 2005, Stuart 2007, Echard and Lavedrine 2008, Istudor 2011, Beltran et al. 2015).

In this context, besides wood species identification, investigation of finishing layers is of ultimate importance for old furniture and any other wooden objects with historic, documentary or artistic value (Echard and Lavedrine 2008, Domenech 2008, Caruso et al. 2014, Beltran et al. 2015).
Though non-destructive methods would be preferred, a wide range of micro-destructive methods are more ready available and extensively employed. These include *in situ* and laboratory physical tests, especially solubility evaluation, microscopy, micro-chemistry tests and infrared analysis (Odegaard et al. 2005, Stuart 2007).

Microscopy is employed to reveal surface structural patterns as well as the multilayered structure of a coating film (Plesters 1956, Sandu et al. 1998, Istudor 2011) Physical tests consider the different solubility of coating films in specific solvents (ethyl alcohol, white spirit, acetone, diluents, alcoholic ammonia solution, others), directly related to their composition and curing mechanism, but also influenced by ageing, as well as their behaviour when heated (colour modifications, smell, melting point) (Plesters 1956, Gettens and Stout 1966, Istudor 2011).

Micro-chemistry tests are based on specific reactions of the components of a small tested sample with a series of chemical reagents, observed under a microscope. The tests are specific to different classes of materials (e.g. fatty materials, proteins) and a positive test may be related to a colour, foam formation or other specific aspects (Plesters 1956, Sandu et al. 1998, Stuart 2007).

Infrared spectroscopy, especially modern Fourier transform technique known as FTIR, is often considered as a “first choice” investigation method for organic materials identification, including coatings identification. This is because absorption of infrared radiation in the mid IR spectrum (4000 – 400 cm\(^{-1}\)) is specific to the chemical structure features of organic substances. Absorption bands in the group frequency region 4000-1300 cm\(^{-1}\) indicate the presence of different functional groups (e.g. hydroxyl, amino, carbonyl, carboxyl, amide) and carbon chain features (methyl, methylene, double bonds, aromatic rings), while absorption bands in the fingerprint region 1300- 500 cm\(^{-1}\), though difficult to assign individually, form a pattern very characteristic and unique, useful, therefore, for materials identification when it is matched with reference spectra (Derick et al. 1999, Schonemann and Edwards 2011, Chang and Lou 2013, Beltran et al. 2015). Moreover, devices such as ATR (attenuated total reflection) units facilitate and speed up investigation, as almost no preparation of sample is needed. However, the complexity of the spectra of organic coatings, both traditional and modern, their frequent employment as mixtures in different traditional recipes, the ageing phenomena occurring in time, reflected in chemistry changes, restorations or surface re-treatments, as well as wearing of surface layer thinning it to microns, all are reasons for a quite difficult interpretation of spectra (Beltran et al 2015), not always leading straightforward to a conclusive or complete result (Echard and Lavedrine 2008, Caruso et al. 2014). Therefore, preliminary physical and/or micro-chemical tests might help interpretation, or further investigation by more evolved techniques (e.g. pyrolysis combined with chromatography Py-GC or mass spectrometry Py-MS) might be necessary (Sandu, 1998, Domenech-Carbo 2008, Caruso et al. 2014, Sutherland and Rio 2014).

**OBJECTIVE**

The present paper refers to a series of micro-destructive investigation methods applied for identification of finishing materials, with the view of comparing resulting information and highlighting their opportunities and limits. These methods were simple *in situ* and laboratory physical tests, optical microscopy, micro-chemistry and FTIR – ATR analysis. For this purpose, small samples of finishing layers were taken from four furniture objects belonging to CNM ASTRA Sibiu and were analysed according to the usual procedures of the laboratories from Sibiu and Brasov.

**MATERIAL, METHOD, EQUIPMENT**

The finishing samples investigated in this research originate from four artefacts belonging to ASTRA Museum in Sibiu: a table top and a piano, currently in the quarantine area, alongside a bed and a clock from the Vidra household, a monument from Alba County, in the open air museum. Samples were extracted from an area near a defect so that to be minimum destructive but still relevant. Solubility tests with ethyl alcohol, iso-propyl alcohol, acetone and two standard cleaning solutions were performed *in situ*. More info on the artefacts considered in this investigation and on the samples extracted for finishes identification is summarised in Table 1.

Laboratory investigation consisted in microscopic examination under stereo-microscope Optika SZM and Olympus SZ-CTV (fitted with image capturing systems), physical (macro and micro) and micro-chemical tests followed by FTIR analysis. The physical (macro and micro) and micro-chemistry tests employed are briefly presented as principle in Tables 2, 3 and illustrated in Fig.1.
### Table 1

**Summary of artefacts and extracted samples investigated in this research**

<table>
<thead>
<tr>
<th>Artefact/Inventory number</th>
<th>General view</th>
<th>Sample code</th>
<th>Sample type*</th>
<th>Prelevation place</th>
<th>Sample aspect</th>
<th>Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Round table top</strong>&lt;br&gt;Craiova  (21749 AL)  &lt;br&gt;No recorded restorations  New acquisition</td>
<td><img src="image" alt="Round table top" /></td>
<td>P1</td>
<td>FL/W</td>
<td></td>
<td><img src="image" alt="Round table top sample" /></td>
<td>0.172g</td>
</tr>
<tr>
<td><strong>Piano</strong>&lt;br&gt;(13451 AL)  &lt;br&gt;Dated 1903  Restored in 1996, shellac was employed</td>
<td><img src="image" alt="Piano" /></td>
<td>P2.1</td>
<td>FL</td>
<td></td>
<td><img src="image" alt="Piano sample" /></td>
<td>0.008g</td>
</tr>
<tr>
<td></td>
<td></td>
<td>P2.2</td>
<td>FL</td>
<td></td>
<td><img src="image" alt="Piano sample" /></td>
<td>0.001g</td>
</tr>
<tr>
<td><strong>Bed</strong>&lt;br&gt;(13703 AL)  &lt;br&gt;Dated 20th century  Conservation treatments 1997**</td>
<td><img src="image" alt="Bed" /></td>
<td>P3</td>
<td>FL/W</td>
<td></td>
<td><img src="image" alt="Bed sample" /></td>
<td>0.012g</td>
</tr>
<tr>
<td><strong>Clock</strong>&lt;br&gt;(12121 AL)  &lt;br&gt;Dated around 1900-1940  No recorded restorations, excepting cleaning Cherry wood</td>
<td><img src="image" alt="Clock" /></td>
<td>P4</td>
<td>FL/W</td>
<td></td>
<td><img src="image" alt="Clock sample" /></td>
<td>0.022g</td>
</tr>
</tbody>
</table>

**Note**<br> *FL/W - Finishing layer on wood substrate ; FL - Finishing layer<br>** materials employed beeswax, white spirit and linseed oil

### Table 2

**Laboratory micro-physical tests**  
(adapted from Plesters 1956, Gettens and Stout 1966, Istudor 2011)

<table>
<thead>
<tr>
<th>Type of test (code)</th>
<th>Class of materials</th>
<th>Identification elements</th>
<th>Remarks / Specific features</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solubility test with organic solvent – acetone (OS-A)</td>
<td>Resins present</td>
<td>Dissolution – transp. film formation – concentric rings pH - acid</td>
<td>On glass lamella, under microscope (Fig.1a)</td>
</tr>
<tr>
<td>Heating test (on a heated plate, alterations observed under microscope) (HT)</td>
<td>Resins Oils</td>
<td>Specific smell  Colour /aspect changes Melting points</td>
<td>Oils - smell of burnt oil intense; browning at around 190°C  Resins – aromatic smell; contour and colour change 80-150°C</td>
</tr>
<tr>
<td>Solubility test in alcoholic solution of ammonia (S-AA)</td>
<td>Resins - Oils</td>
<td>Dissolution /comparison with references</td>
<td>Resin (e.g. shellac) (Fig.1c) Resin/oil</td>
</tr>
</tbody>
</table>
### Table 3

**Micro-chemistry tests**
(adapted from Plesters 1956, Sandu et al 1998, Stuart 2007)

<table>
<thead>
<tr>
<th>Type of test (code)</th>
<th>Class of materials</th>
<th>Reagents / Conditions</th>
<th>Features of positive test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test for fatty materials (GM)</td>
<td>Oils, fats, waxes</td>
<td>Hydrogen peroxide (H₂O₂) 30% Ammonia (NH₃) 25%</td>
<td>Formation of a stable foam (for about 10min) (Fig.1b)</td>
</tr>
<tr>
<td>Test for oils (O1)</td>
<td>Drying oils</td>
<td>Nitric acid 65%</td>
<td>Turns oil films reddish-brown (Fig.1d)</td>
</tr>
<tr>
<td>Test identification for iron (Fe³⁺)</td>
<td>Pigments containing Fe</td>
<td>Potassium sulphocyanide (KSCN) / acidic medium</td>
<td>Red colouration (Fig.1e)</td>
</tr>
<tr>
<td>Test for animal glue (AG)</td>
<td>Proteins</td>
<td>Dissolution in hot water Acid Fuchsin 1%</td>
<td>Dissolution, red staining with fuchsin (Fig.1f)</td>
</tr>
</tbody>
</table>

**Fig. 1.**
Exemplification of micro-physical and chemical tests observed under stereo-microscope (original magnification 40x): a – positive OS-A test showing formation of concentric rings following resin dissolution in acetone and evaporation (P2); b – positive test for fatty materials – formation of a stable foam with hydrogen peroxide and ammonia (P3); c – dissolution of coating film in alcoholic solution of ammonia – possibly shellac (P4); d – positive test for drying oils – reddish colouration with nitric acid (P1); e - positive test for iron (KSCN) / acidic medium (P2); f - positive test for animal glue with acid fuchsin

FTIR analysis was performed directly on the surface of the samples, in reflectance mode employing an Alpha Bruker spectrometer fitted with ATR unit. Spectra were recorded in the range 4000-400 cm⁻¹ at a resolution of 4cm⁻¹, each spectrum resulting from 24 scans. Spectra were processed with the OPUS software for baseline correction and smoothing before normalisation. Generally, three spectra were recorded for each sample and an average was computed. For some samples, spectra were recorded on both sides, respectively on the finished surface (top layer) and the reverse, representing either the wooden substrate or a preparation layer. Difference between the spectra of those two sides of a sample was calculated for samples P3 and P4 to facilitate interpretation. Recorded spectra were compared with reference spectra from the laboratory collection and literature data.
RESULTS AND DISCUSSION
An overview of the general aspect and structural features of the investigated samples, observed at different magnifications is presented in Fig. 2, while the results of physical and micro-chemistry test are presented in Table 4 and selectively illustrated by the pictures in Fig. 1.

![Structural features of the investigated samples observed at different magnifications](image-url)
**Table 4.** Results of the physical and micro-chemistry tests at Sibiu

<table>
<thead>
<tr>
<th>Solubility tests</th>
<th>Physical tests</th>
<th>Micro-chemistry tests</th>
<th>Results Sibiu</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>In situ</strong></td>
<td>Laboratory</td>
<td>GM O1 Fe AG</td>
<td></td>
</tr>
<tr>
<td><strong>P1</strong></td>
<td>Ethanol ± i-Propanol ± Turpentine ±</td>
<td>+</td>
<td>Burnt oil and aromatic smell Colour change to brown around 190°C</td>
</tr>
<tr>
<td><strong>P2</strong></td>
<td>Ethanol ++ i-Propanol + Turpentine ±</td>
<td>+</td>
<td>Burnt oil and aromatic smell Melting at 100°C</td>
</tr>
<tr>
<td><strong>P3</strong></td>
<td>Very limited in all solvents -/±</td>
<td>+</td>
<td>Burnt oil and aromatic smell Colour change to brown around 190°C</td>
</tr>
<tr>
<td><strong>P4</strong></td>
<td>Ethanol ++ i-Propanol + Turpentine +</td>
<td>+</td>
<td>Burnt oil and aromatic smell Colour change to brown around 190°C</td>
</tr>
</tbody>
</table>

Legend: + positive, ++ strongly positive; - negative; ± partial/limited; (0) – not tested/applicable AG- animal glue

The FTIR spectra recorded for the sample P1 in comparison to shellac reference is presented in Fig. 3. this allows a straightforward identification of the finishing layer as being shellac with a high confidence (95%). The presence of a resin was indicated also by laboratory tests, but its low solubility in alcohol pointed to a possible synthetic resin. However, this contradiction may be explained by the reduction of shellac solubility in alcohols due to ageing when crosslinking reactions occur (Farag and Leopold 2009, Derry 2012). No recent restoration was recorded for the Craiova table, from which this sample originates, and the poor conservation state of the finishing layer supports the assumption of an original, aged finishing layer.

**Fig. 3.** FTIR spectra of sample P1 in comparison with shellac reference
Paraffin oil or another oil may be present in small amounts on the surface of object 1, as it is usually employed in the traditional polishing technique with shellac leading to glossy surfaces, known as French polish (Derry 2012) and also employed in finishes reviving techniques. However, its positive identification on small amounts (less than 5%) by FTIR would be not possible. Anyway it has to be pointed out that oils and shellac have many common group absorption bands (e.g. hydroxyl, methylene, carbonyl) and differences should be thoroughly examined in the fingerprint region (Derrick et al 1999).

The results of FTIR investigation of samples from the piano (2.1, 2.2) are presented in Fig. 4. It can be observed from the spectra (Fig.4 top) that this object was also finished with shellac, at least as top layer, on the whole surface. There are no significant differences between the transparent finish on the top plate and the top layer of finish of the lateral sides of the artefact. However, differences in the aspect of these finishing layers, demonstrating totally different techniques are obvious at both macroscopic and microscopic levels.

![FTIR spectra of surfaces of samples P2.1 and P2.2 in comparison with shellac reference (top) and reverse side of sample P2.2 in comparison with animal glue and calcium sulphate references (bottom)](image)

*Fig. 4.*
The lateral sides present a finish in two colours (yellow and brown) with waved design on an opaque preparation layer, known as flander technique (Girtler 2014). The FTIR of the reverse side of this white opaque layer (Fig.4 bottom) indicate animal glue and calcium sulphate as materials employed in a combination with a pigment with absorption at about 792 cm\(^{-1}\). Micro-chemistry tests also indicated presence of iron containing pigments and of shellac as possible resin for the transparent top coat. This investigation agrees with recorded info on a restoration process in 1996, when shellac was employed. This also explains the possible presence of parafin oil.

FTIR analysis of the sample P3 (Fig.5) could not offer a straightforward answer, the recorded spectrum showing as a result from the contribution of both the wood substrate and the thin finishing layer, of about 50µm. The main absorption bands are at around 3300 cm\(^{-1}\) (OH, strong), 2920-2850 cm\(^{-1}\) (methylene, methyl, strong), 1720 cm\(^{-1}\) (carbonyl, very small), 1644 cm\(^{-1}\) (C=O strect – amide I, strong), 1542 cm\(^{-1}\) (C-N, N-H, amide II, small), 1419 cm\(^{-1}\) (C-H, medium), 1320 cm\(^{-1}\) (very small), 1240 cm\(^{-1}\) (very small), 1155 cm\(^{-1}\) (very small), 1022 cm\(^{-1}\) (C-O-, strong, maximum intensity), 524 cm\(^{-1}\) (medium) and 465 cm\(^{-1}\) (medium). In order to separate the contribution of wood substrate and better highlight the absorption of the top finishing layer, a difference spectrum (green curve in Fig. 5) was calculated by subtracting the spectrum of wood (reverse of the sample) from the spectrum of finished surface (sample P3 consisted in finishing layer on substrate – see also cross section of P3 in Fig.2). This spectrum is very similar in the region of 1700-1200 cm\(^{-1}\) with that of reference animal glue, presenting clearly evidentiated the three amide bands (1644, 1542, 1419 cm\(^{-1}\)). This suggests that very likely a pigment mixed with animal glue was used for colouring in brown the object. The absorption bands at low wavenumbers (524, 465 cm\(^{-1}\)) could be attributed to pigments. Dark brown particles are also visible in a thin base layer of the coating film (see cross section). The quite strong methylene absorption in the difference spectrum should be associated with a long chain molecular compound representing the actual top coating film, but no differentiation between waxes, oils or resins such as shellac or rosin could be made based on it. A small carbonyl absorption (1720 cm\(^{-1}\)), another common chemical feature for shellac, rosin, waxes and oils could be observed. The characteristic peaks of shellac in the fingerprint region (around 1160, 1240 and 1370 cm\(^{-1}\) ) are present, but quite small. Moreover, drying oils present in this region quite similar peaks. Concluding, it can be assumed that a finish made of a colored collagen base coat and a top layer based on oil and shellac was applied. The presence of waxes, probably from maintenance treatments can not be excluded.

![Fig. 5. FTIR spectra of surface of sample P3 in comparison with shellac, rosin and animal glue references and the difference spectra surface- wood substrate](image-url)
The FTIR spectra registered for sample P4 are presented in Fig. 6. The spectrum of surface seems to be very similar with that of the previous sample (P3). The strongest absorption bands are at 1022 and 1643 cm\(^{-1}\), suggesting again a transparency of wood substrate (thin coating film of about 15 \(\mu\)m) and presence of proteins (animal glue), while the bands at around 525 and 455 cm\(^{-1}\) are probably due to a pigment (brown, semi-opaque finish). The peaks of shellac in the fingerprint region (around 1160, 1240 and 1370 cm\(^{-1}\)) are present, though very small. Thus, it is possible to have a similar finish with a colored base coat prepared with animal glue and transparent top layer containing shellac. Again, presence of oils in small amounts can not be excluded, as discrimination between oils and shellac is quite difficult due to IR spectral similarities. These results are in accordance with micro-chemistry tests, but unfortunately not conclusive.

Moreover, for this object there were areas with a slightly different aspect and a significantly different spectrum, in which is evident a strong absorption band at 1411 cm\(^{-1}\). This may be attributed to bitumen (not shown in Fig.6), which presents strong absorption bands at 2920, 2850, 1418 cm\(^{-1}\) and smaller peaks at 871 and 711 cm\(^{-1}\). Probably, in a previous intervention a colouring solution based on bitumen was employed for retouching some areas.

**CONCLUSIONS**

The results showed that physical tests and microscopy are useful to get basic information on the samples’ morphology and possible classes of coating materials, while micro-chemistry revealed by some successive tests more specific information on the type of finishing materials. FTIR - ATR is a rapid method of investigation useful in identifying the coating materials based on available reference samples or spectra, though this identification is not always straightforward. Employing the finishing materials as mixtures, previous interventions of restoration, multi-layered finishes, ageing of materials and thinning of coating films by wearing, are only a few reasons which cause identification problems.

Preliminary physical tests of solubility are useful to select the adequate references for FTIR analysis, while micro-chemistry tests could complete the FTIR results, especially for those components of the finishing layer present in very small amounts (less than 5%), bellow the FTIR sensitivity.

Corroboration of microscopy, physical and micro-chemistry tests with FTIR can provide more reliable results in terms of finishes identification and also valuable information for restoration. Micro-FTIR and more advanced techniques, such as pyrolysis coupled with gas chromatography and mass
spectrometry (Py-GC-MS) would be of great interest in solving complex problems of transparent finishes identification. Cooperation is looked for with this respect for future work.

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