

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

Maria Cristina TIMAR

Prof.dr.chem. – TRANSILVANIA University in Brasov – Faculty of Wood Engineering
Address: B-dul Eroilor nr. 29, 50036 Brasov, Romania
E-mail: cristinatimar@unitbv.ro

Dana Mihaela POP

MSc – TRANSILVANIA University in Brasov – Faculty of Wood Engineering
Address: B-dul Eroilor nr. 29, 50036 Brasov, Romania

Anca Maria VARODI

Dr.eng – TRANSILVANIA University in Brasov – Faculty of Wood Engineering
Address: B-dul Eroilor nr. 29, 50036 Brasov, Romania
E-mail: anca.varodi@unitbv.ro

Daniela LĂZUREANU

Chem. – CNM ASTRA Sibiu- Centre for Cultural Heritage
Address: Piața Mică, nr. 11, 550182, Sibiu, România
E-mail: dana_canura@yahoo.com

Iov TOLEMEIU

Phys. Chem. – CNM ASTRA Sibiu- Centre for Cultural Heritage
Address: Piața Mică, nr. 11, 550182, Sibiu, România,
E-mail: iovtolomeiu@yahoo.com

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%), below 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 readily 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 ($4000 - 400 \text{ cm}^{-1}$) is specific to the chemical structure features of organic substances. Absorption bands in the group frequency region $4000-1300 \text{ cm}^{-1}$ 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 $1300-500 \text{ cm}^{-1}$, 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















Artefact/ Inventory number <i>Remarks</i>	General view	Sample code	Sample type*	Prelevation place	Sample aspect Weight
Round table top Craiova (21749 AL) <i>No recorded restorations New acquisition</i>		P1	FL/W		 0.172g
Piano (13451 AL) <i>Dated 1903 Restored in 1996, shellac was employed</i>		P2.1	FL		 0.008g
		P2.2	FL		 0.001g
Bed (13703 AL) <i>Dated 20th century Conservation treatments 1997**</i>		P3	FL/W		 0.012g
Clock (12121 AL) <i>Dated around 1900- 1940 No recorded restorations, excepting cleaning Cherry wood</i>		P4	FL/W		 0.022g
Note	*FL/W - Finishing layer on wood substrate ; FL - Finishing layer ** materials employed beeswax, white spirit and linseed oil				

Table 2

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

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

Table 3

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

Type of test (code)	Class of materials	Reagents / Conditions	Features of positive test
Test for fatty materials (GM)	Oils, fats, waxes	Hydrogen peroxide (H ₂ O ₂) 30% Ammonia (NH ₃) 25%.	Formation of a stable foam (for about 10min) (Fig.1b)
Test for oils (O1)	Drying oils	Nitric acid 65 %	Turns oil films reddish-brown (Fig.1d)
Test identification for iron (Fe ³⁺)	Pigments containing Fe	Potassium sulphocyanide (KSCN) /acidic medium	Red colouration (Fig 1e).
Test for animal glue (AG)	Proteins	Dissolution in hot water Acid Fuchsin 1%	Dissolution, red staining with fuchsin (Fig. 1f)

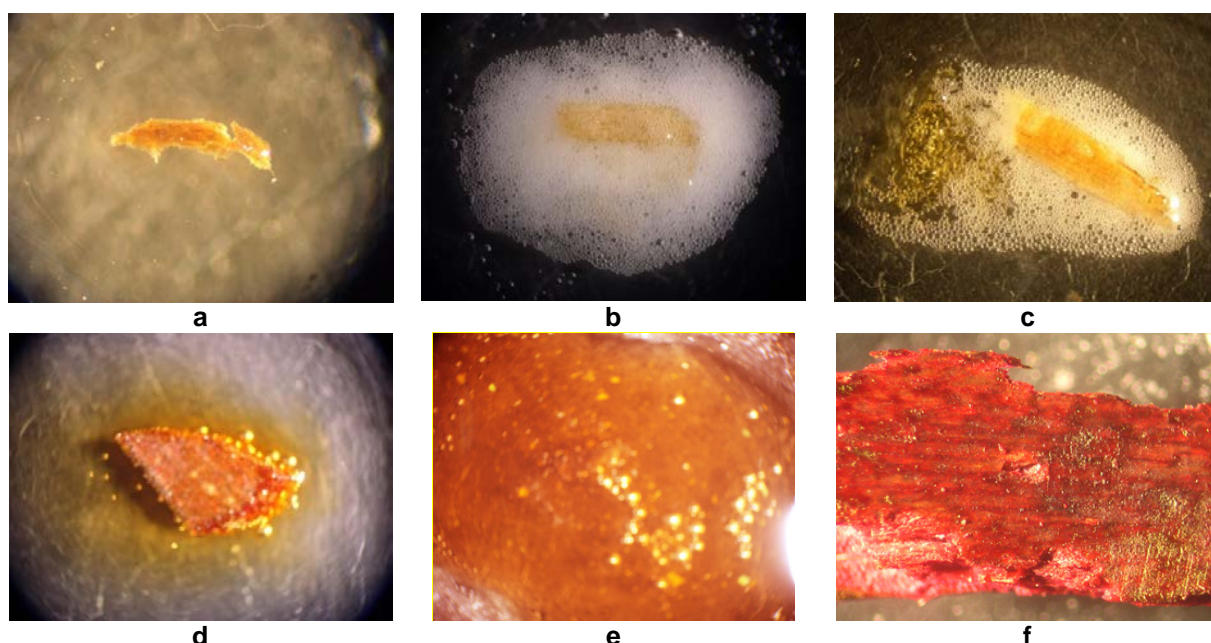


Fig. 1.

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.

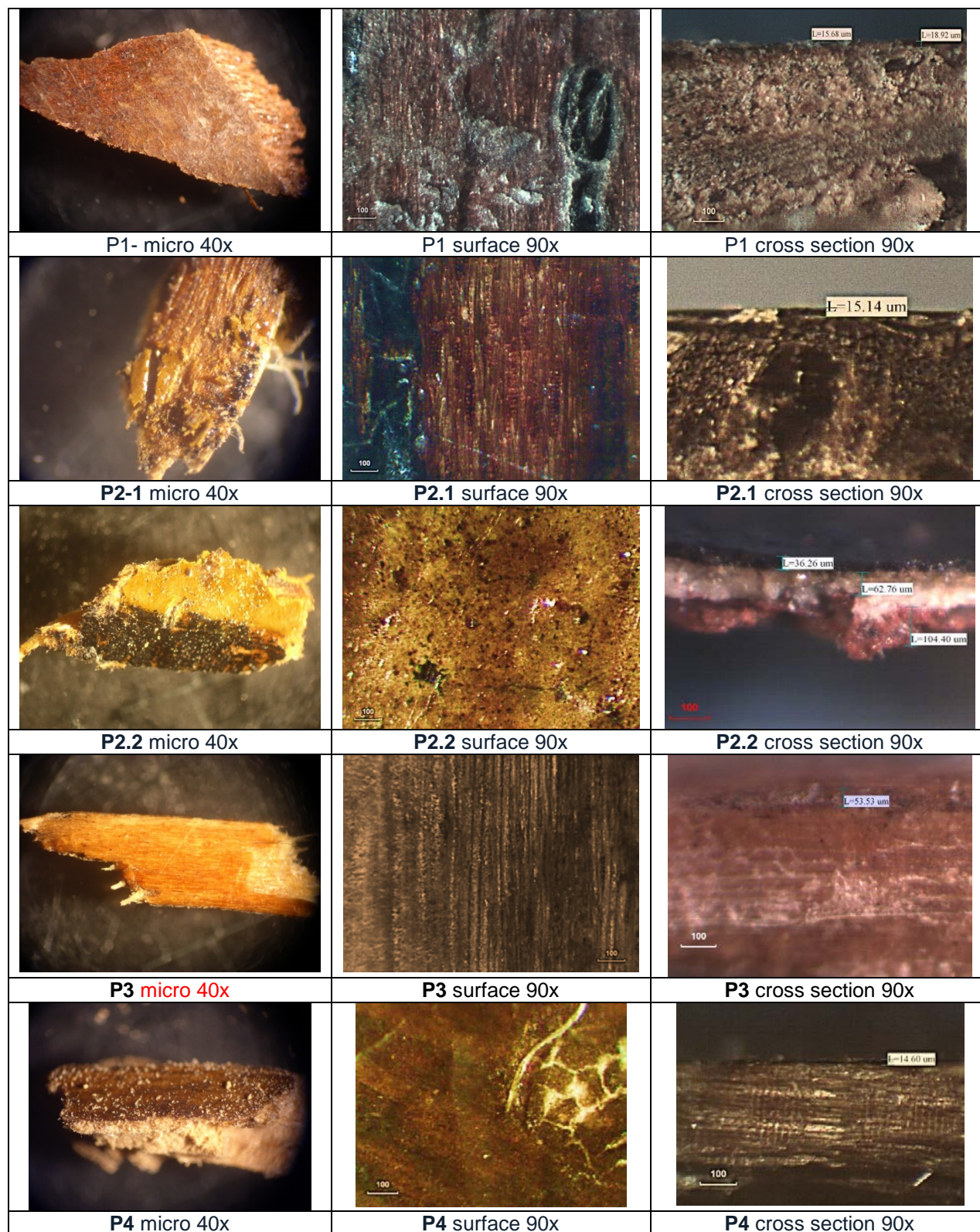


Fig. 2.

Structural features of the investigated samples observed at different magnifications

Table 4.

Results of the physical and micro-chemistry tests at Sibiu

	Solubility tests <i>In situ</i>	Physical tests Laboratory		Micro-chemistry tests			Results Sibiu
		OS-A	HT	GM	O1	Fe AG	
P1	Ethanol \pm i-Propanol \pm Turpentine \pm	+	Burnt oil and aromatic smell Colour change to brown around 190°C	+	+	(0) +	Possibly synthetic lacquer, drying oil present AG possibly present
P2	Ethanol ++ i-Propanol + Turpentine \pm	+	Burnt oil and aromatic smell Melting at 100°C	+	(0)	++ +	Possibly shellac; paraffin oil present Fe based pigment AG possibly present
P3	Very limited in all solvents $-/\pm$	+	Burnt oil and aromatic smell Colour change to brown around 190°C	++	+	(0) (0)	Possibly resin impregnated in wood; paraffin / wax and oil on the surface
P4	Ethanol ++ i-Propanol + Turpentine +	+	Burnt oil and aromatic smell Colour change to brown around 190°C	+	+	(0) +	Possibly shellac as a mixture with other natural resins; oils present AG possibly present
Legend		+ positive, ++ strongly positive; - negative; \pm 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.

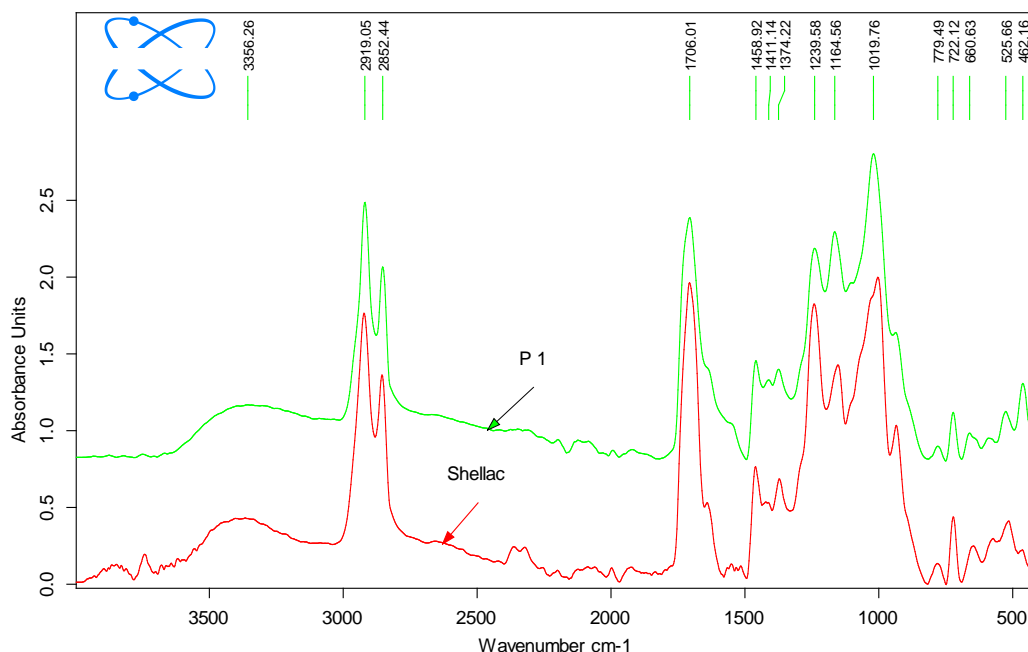


Fig. 3.
FTIR spectra of sample P1 in comparison with shellac reference

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.

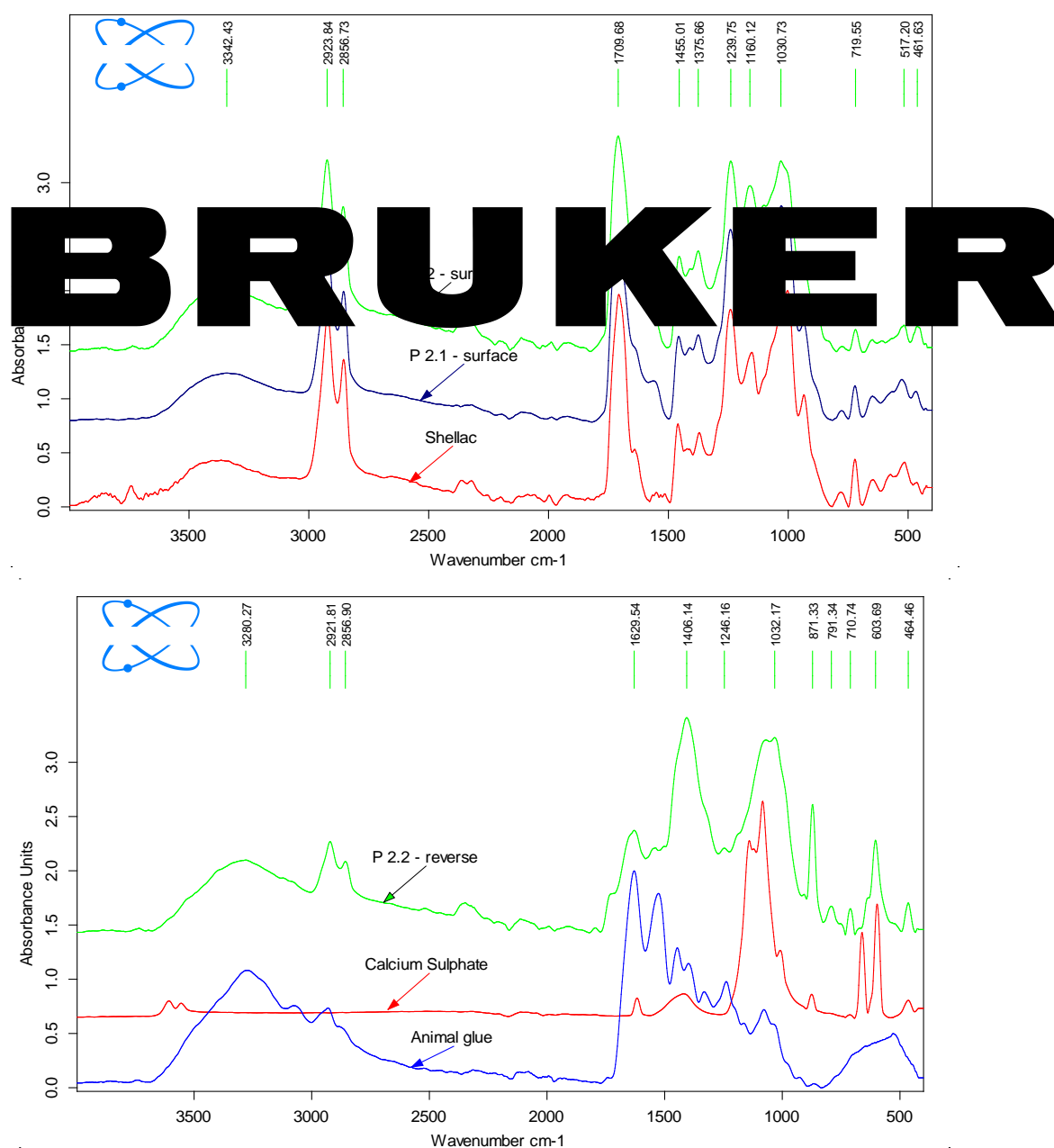


Fig. 4.
FTIR spectra of surfaces of samples P2.1 and P2.2 in comparison with shellac reference (top)
and reverse side of sample P2.2 in comparison with animal glue and calcium sulphate
references (bottom)

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 paraffin 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 $50\mu\text{m}$. The main absorption bands are at around 3300 cm^{-1} (OH, strong), $2920\text{--}2850\text{ cm}^{-1}$ (methylene, methyl, strong), 1720 cm^{-1} (carbonyl, very small), 1644 cm^{-1} (C=O stretch – 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 $1700\text{--}1200\text{ cm}^{-1}$ with that of reference animal glue, presenting clearly evidenced 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 only 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.

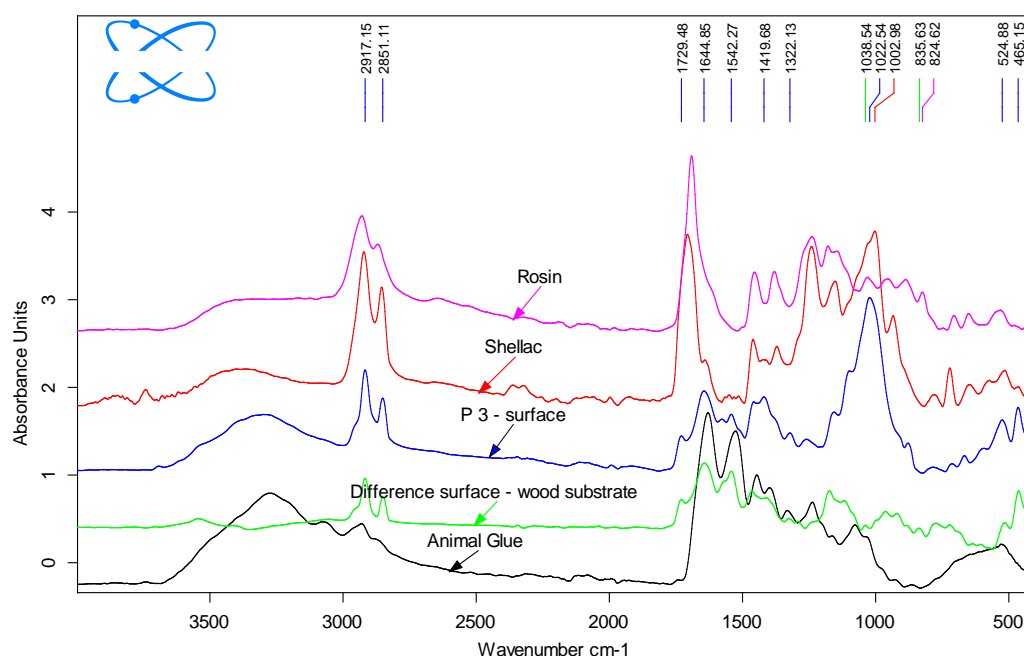


Fig. 5.
FTIR spectra of surface of sample P3 in comparison with shellac, rosin and animal glue references and the difference spectra surface- wood substrate

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 μm) 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.

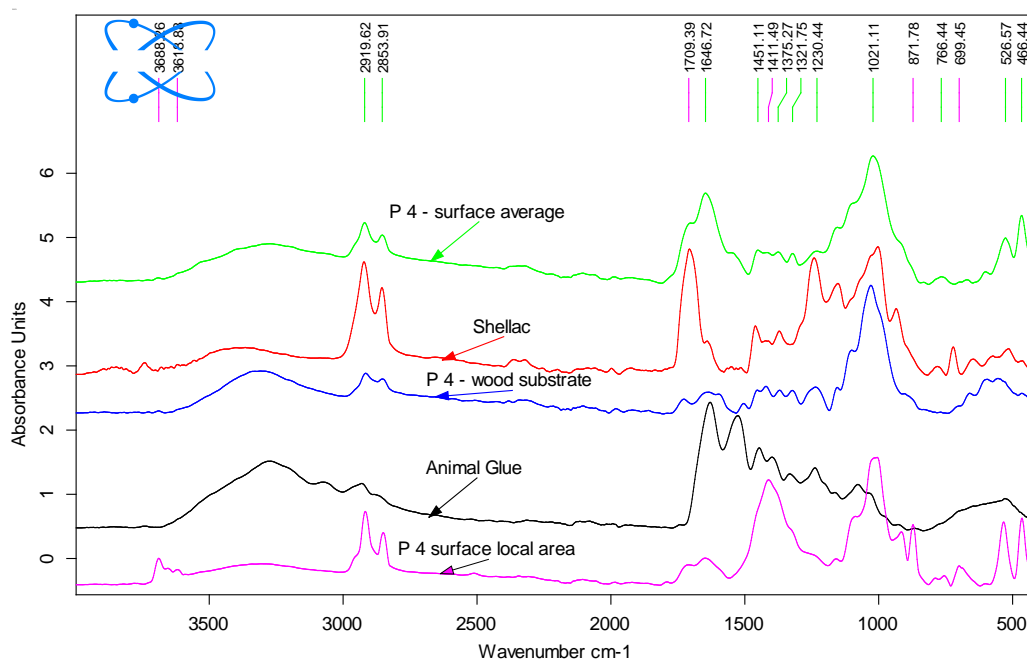


Fig. 6.

FTIR spectra of surface and reverse of sample P4 in comparison with shellac and animal glue references and the spectrum of local areas with different aspect

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%), below 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.

ACKNOWLEDGEMENT

This work is a result of cooperation between *Transilvania* University of Brasov – Faculty of Wood Engineering and CNM ASTRA Sibiu – Centre for Cultural Heritage, which we do appreciate as valuable for both institutions.

The authors acknowledge the structural funds project PRO-DD (POS-CCE, O.2.2.1., ID 123, SMIS 2637, ctr. No 11/2009) for providing the infrastructure used in this work at the CDI Institute of *Transilvania* University of Brasov.

REFERENCES

- Beltran V, Salvado N, Cinque G (2015) Micro infrared spectroscopy discrimination capability of compounds in complex matrices of thin layers in real sample coatings from artworks. *Microchemical Journal* 118:115-123.
- Caruso F, Martino DFC, Saverwyns S, Van Bos M, Burgio L et al. (2014) Micro-analytical identification of the components of varnishes from South Italian historical musical instruments by PLM, ESEM–EDX, microFTIR, GC–MS, and Py–GC–MS, *Microchemical Journal* 116:31–40.
- Chang CW, Lu KT (2013) Linseed-oil-based waterborne UV/air dual-cured wood coating, *Progress in Organic Coatings*, 76:1024-1031.
- Derrick M, Stulik D, Landry JM (1999) *Infrared spectroscopy in conservation science*, the Getty Conservation Institute, Los Angeles.
- Derry J (2012) Investigating Shellac- documenting the process, defining the product, MSc thesis, Oslo University, Norway, <http://www.duo.uio.no/>
- Domenech-Carbo MT (2008) Novel analytical methods for characterizing binding media and protective coats in artworks, *Analytica Chimica Acta* 621:109–139.
- Echard JF, Lavedrine B (2008) Review on the characterisation of ancient stringed musical instruments varnishes and implementation of an analytical strategy, *Journal of Cultural Heritage*, 99:420-429.
- Farag I, Leopold CS (2009) Physicochemical Properties of Various Shellac Types, *Dissolution Technologies*, pp. 33-39.
- Gettens RJ, Stout GL (1966) *Painting Materials: A Short Encyclopedia*, Dover Publications Inc.
- Girtler R (2014) *Die Landler in Rumänien: Eine untergegangene deutschsprachige Kultur*, LIT Verlag GmbH & Co, Wien 2014.
- Istudor I (2011) *Noțiuni de chimia picturii*, Editura ACS, București, ISBN 978-606-92536-5-6.
- Odegaard N, Carroll S, Zimmt WS (2005) *Material Characterization -Tests for Objects of Art and Archaeology*, Second edition, Archetype Publications, 2005.
- Plesters J (1956) Cross-sections and Chemical Anaysis of Paint Samples, in *Studies in conservation*, 2(3).
- Sandu I, Sandu ICA, van Saanen A (1998) *Expertiza stiintifica a operelor de arta, Autentificarea, Stabilirea paternitatii si evaluarea patrimoniala*, volumul 1, Editura universitatii ALL Cuza Iasi, 1998.
- Schonemann A, Edwards HGM (2011) Raman and FTIR microspectroscopic study of the alteration of Chinese tung oil and related drying oils during ageing, *Anal Bioanal Chem* 400:1173-1180.
- Stuart B (2007) *Analytical Techniques in Materials Conservation*, John wiley and Sons, England.
- Sutherland K., del Rio JC (2014) Characterisation and discrimination of various types of lac resin using gas chromatography mass spectrometry techniques with quaternary ammonium reagents, *Journal of Chromatography A*, 1338:149–163.