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GC-MS BINDING MEDIA STUDY OF TRANSYLVANIAN PAINTED CEILINGS

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ABSTRACT. Gas chromatography coupled with mass spectrometry (GC-MS) was used to investigate the organic materials of painted coffered ceilings of five medieval churches in different regions of Transylvania, applying a methodology designed to identify organic binding medium in the same microsample. Results showed a very restrained use of organic materials since only animal glue was identified in most of the samples. The study provided a better understanding of the painting technique and of the decay processes of this specific local heritage, and proved helpful in the planning of suitable conservation strategies.

Keywords: *GC-MS analyses, organic binders, animal glue, painted ceilings, Transylvanian heritage*

INTRODUCTION

Cultural heritage objects are often decorated with painted surfaces. Paint layers are complex structures consisting of colored material, the pigment, embedded in an organic matrix which enables the application of the pigment on the surface and which is responsible for the cohesion of the resulting layer and its adhesion to the surface. The type of organic materials in the painted surfaces have major contribution to the aspect of the paint; actually they define the painting technique [1,2]. The degree of degradation of these organic materials is mainly responsible for the condition of the paint layers. A flaking or powdery paint has usually an organic binder affected by ageing, complex chemical alteration of the material in time, mainly due to free radical auto-oxidations, ionic or enzymatic hydrolyses and cross-linking reactions [3-5]. Consequently, it is very important to identify by analytical methods the organic constituents of paint layers in order to understand their painting technique, their degradation processes and to properly plan their conservation.

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Up to now, a comprehensive study of the organic materials in paint layers was not performed on Romanian heritage objects. Staining tests [6] were reported to check the protein content of wall painting samples [7]; Fourier Transformed Infrared spectroscopy (FTIR) and direct infusion mass spectrometry (DI-MS) were used to identify classes of organic materials used in some icons [8].

Painted woodworks were chosen as subject of the present study since they are widespread in Transylvania giving a specific character to the built heritage of the region (Figure 1.). In fact, painted ceilings are encountered in about 150 medieval churches [9]. The interior of these churches was decorated with painted woodworks mainly during the 17th, 18th century by painter-carpenter workshops. A famous painter-carpenter family of the 18th century was the Umling family, Umling Lőrinc the elder, together with his sons, Lőrinc the younger and János. They were active in Călata (Kalotaszeg), the region around Cluj, living behind a corpus of work that can be found in over 40 churches of the region. Most of the samples studied originate from their works (Figure 2).

The study was carried out using gas chromatography coupled with mass spectrometry (GC-MS), applying a procedure which permits the quantitative characterization of the organic binders encountered in painted surfaces in a single sample [10].

The aim of the research was to characterize the painting technique of the ceilings and woodworks, to evaluate the use of binders on the basis of the pigments applied, and to compare the techniques used by different workshops. Finally, the scientific data could improve understanding of the observed decay processes in the paint layers and help choosing a proper conservation strategy.

RESULTS AND DISCUSSION

Samples analyzed were collected by the restorer Ferenc Mihály from the painted ceilings of five medieval churches from different regions of Transylvania. Their interior painted woodwork decoration dated from 17th and 18th century. Three of the churches were decorated by the Umling workshop mentioned above. Five samples were taken from different colors of the same ceiling coffer in order to compare their binders. One of the samples belonged to a pew parapet (L7) most probably painted by the same workshop performing the ceiling. This permitted to check if the apparently similar paintings of the ceiling and of the pew were realized with the same technique. Samples from ceilings painted by other workshops, in other periods, were also provided in order to obtain and compare information connected to different workshops and historic periods.

A number of 13 samples were analyzed. Before analyses samples were observed and documented with low magnification optical microscope (Figure 3). Detailed sample description is reported in Table 1.

Figure 1. Detail from the painted ceiling of the Reformed church in Crasna (Kraszna, SJ), 1736, painted by Pataki Asztalos János (sample K1)

Figure 2. Coffer G13 from the painted ceiling of the Reformed church in Luna de Sus (Magyarlóna, CJ), 1752, Umling Lőrinc, the elder, showing the sampling places for samples L1 to L5

Working methodology

Ethical aspects of sampling from heritage objects impose minimum sample size which should be used to provide as many information as possible. Thus, the adopted working methodology enabled the identification of all usual organic binders from the same microsample avoiding interferences from inorganic media [10].

The method is based on a multi-step chemical pretreatment of the sample. First proteins and polysaccharide materials were subjected to ammonia extraction in order to separate them from lipid and resinous materials. Proteins

and sugars were separated afterwards by monolithic sorbent tip technology with a C4 stationary phase and purified before hydrolysis. Three fractions were generated analyzed separately by GC-MS. Lipids and resins were subjected to saponification assisted by microwaves and the three fractions were separately derivatised. A detailed description of the procedure has been published elsewhere [10].

Table 1. Detailed sample description

Sample code	Sampled painted ceiling	Weight (mg)	Sample description
A1	Reformed church in Alunişu (Magyarókereke, CJ), 1746, Umling Lőrinc, the elder	0.1	Blue paint layer with white ground layer, possibly with wood fibers
A2	Reformed church in Alunişu (Magyarókereke, CJ) 1786, Umling Lőrinc, the younger	0.6	Grayish-blue paint layer fragments with white ground layer
L1	Reformed church in Luna de Sus (Magyarlóna, CJ), 1752, coffer G13, Umling Lőrinc, the elder	0.1	White paint layer fragments
L2	Reformed church in Luna de Sus (Magyarlóna, CJ), 1752, coffer G13, Umling Lőrinc, the elder	0.9	Black paint layer fragments with white ground layer
L3	Reformed church in Luna de Sus (Magyarlóna, CJ), 1752, coffer G13, Umling Lőrinc, the elder	0.5	Light green paint layer fragments with white ground layer
L4	Reformed church in Luna de Sus (Magyarlóna, CJ), 1752, coffer G13, Umling Lőrinc, the elder	0.8	Red paint layer fragments
L5	Reformed church in Luna de Sus (Magyarlóna, CJ), 1752, coffer G13, Umling Lőrinc, the elder	0.2	Ochre paint layer fragments
L6	Reformed church in Luna de Sus (Magyarlóna, CJ), 1752, Umling Lőrinc, the elder, another coffer	0.4	Blue paint layer fragments with white ground layer
L7	Pew parapet, Reformed church in Luna de Sus (Magyarlóna, CJ), 1768, Umling Lőrinc, the younger	0.4	Blue and black paint layer fragments with white ground layer
G1	Catholic church in Ghelinţa (Gelence, CV), 1628	0.7	Green paint layer fragments with wood fibers
P1	Reformed church in Petrindu (Nagypetri, SJ),), 1713, Zilahi Asztalos János	0.3	Red paint layer fragments with white ground layer
K1	Reformed church in Crasna (Kraszna, SJ),1736, Pataki Asztalos János	0.1	Green paint layer fragments with white ground layer
K2	Reformed church in Crasna (Kraszna, SJ),1736, Pataki Asztalos János	1.1	Red paint layer fragments with traces of white ground layer

Figure 3. Optical microscope image of samples A2, L6 and P1 (40x)

Data interpretation

Chromatograms were acquired in Synchronous SIM/Scan mode that enabled collection of both SIM (Selected Ion Monitoring) data and full scan data TIC (total ion chromatogram) in a single run. Quantitative determinations of the compounds in each fraction were based on the corresponding SIM chromatograms. Calculations were performed using calibration curves based on standard solutions of amino acids, aldoses and uronic acids or aliphatic mono- and dicarboxylic acids. The individual response of each analyte was evaluated by daily recoveries. Individual derivatizations and injections were controlled by adding internal standards (norleucine, mannitol or tridecanoic acid respectively, and hexadecane). Running blanks of the procedure revealed low levels of contamination. Limit of detection (LOD) and quantification (LOQ) were evaluated for each analyte.

Proteins

Figure 5 reports the SIM chromatogram of the aminoacidic fraction of sample L4.

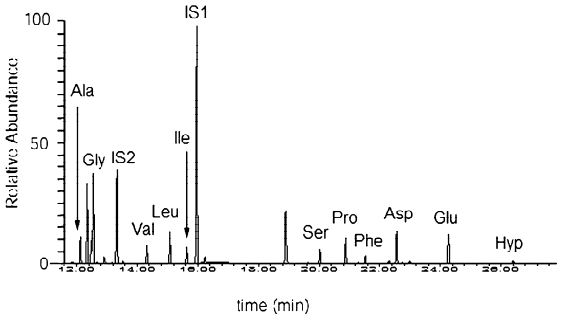

Figure 5. SIM chromatogram of the amino acid fraction of sample L4.

The corresponding m/z values for each monitored amino acid are given in parentheses. Ala – alanine (158, 232); Gly – (147, 218, 246, 261); Val – valine (186, 260); Leu – leucine/ Ile – isoleucine/ IS (internal standard: norleucine) (200, 302); Ser – serine (362, 390); Pro – proline (258, 330); Phe – phenylalanine (302, 336); Asp – aspartic acid (302, 418); Glu – glutamic acid (330, 432); Hyp -hydroxiproline (460, 462); IS2 – injection standard (hexadecane)

Proteinaceous materials were identified based on the percentage amino acid content of the corresponding amino acid fraction, reported in Table 2.

The main proteinaceous materials encountered in paint layers - egg, animal glue, and casein - have characteristic amino acid compositions [3, 5]. If used as mixtures, it is more difficult to distinguish between them on the basis of amino acid percentage content. Statistical data treatment by Principal Component Analysis (PCA) enabled an easier and more unambiguous interpretation. Introducing as variables the percentage amino acid content of the 11 amino acids monitored in SIM, two principal components of the correlation matrix have been taken into account. The corresponding score plot position of the samples was checked against 121 protein reference samples (egg, casein and animal glue) analysed in the laboratory in Pisa [11]. Unmixed proteins would integrate in the corresponding cluster; mixtures will be located between the clusters. The score plot of the historical samples compared to the references is presented in Figure 6.

Table 2. Percentage amino acid content and protein content of the samples

Sample	Ala	Gly	Val	Leu	Ile	Ser	Pro	Phe	Asp	Glu	Hyp	Protein content (µg)
A1	8.2	22.8	4.6	7.4	4.0	9.7	11.0	3.1	12.4	15.9	0.9	0.4
A2	9.3	23.3	4.0	5.7	3.1	5.1	15.7	3.3	9.0	12.5	8.9	1.4
L1	10.8	19.3	6.8	8.5	4.7	2.9	10.9	4.1	13.3	16.7	2.0	0.3
L2	11.9	33.0	4.2	5.1	2.7	2.6	14.6	2.9	10.2	10.9	1.9	3.8
L3	11.3	22.5	5.5	5.5	2.9	6.2	10.9	3.1	9.0	10.0	13.2	3.9
L4	10.1	24.2	3.1	4.5	2.0	3.5	15.4	2.7	8.5	15.6	10.3	13.8
L5	14.3	35.7	3.7	3.3	1.8	3.9	6.6	1.9	12.2	14.8	1.9	46,0
L6	11.2	21.4	6.8	8.5	4.4	3.5	14.2	4.4	13.3	11.5	0.9	1.3
L7	10.3	25.4	3.4	4.1	1.9	3.2	13.5	2.6	10.1	16.2	9.4	12,9
G1	9.8	29.5	3.9	4.6	2.2	2.9	18.5	2.5	6.7	14.9	4.5	6,8
P1	9.8	26.1	2.9	4.1	2.0	3.4	14.5	2.6	8.4	14.8	11.5	1.8
K1	9.2	26.3	4.2	7.4	3.6	6.1	11.6	2.7	10.1	12.3	6.5	0.6
K2	10.6	27.1	4.0	5.5	2.4	3.7	16.5	3.2	8.0	12.1	6.9	14,9

The statistical data treatment highlights that animal glue is present in almost all the samples. Three samples, A1, L1 and L6, are positioned between the egg and animal cluster, meaning that they could be a mixture of the two. Crosschecking with the sample description (Table 1) it can be noticed that these three samples are from paint layers of Umling the elder; L1 from a white layer, the other two samples from blue layers, suggesting that the elder master would prefer to use egg (if animal glue was the binder of the ground layer of the samples) or egg mixed with animal glue for some colors. From his biography, we know that he was formed in a panel painting workshop, where egg was a usual binder[1]. He might have preserved this usage for some of his colors in his painter-carpenter activity.

[1] Personal communication of Ferenc Mihály, May, 2011.

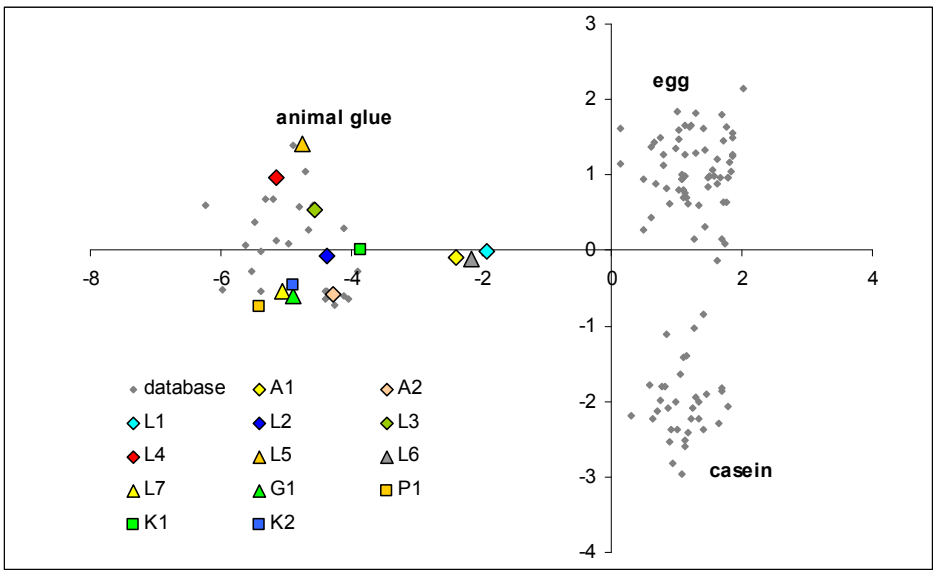

Figure 6. PCA score plot of the percentage amino acid content of the samples compared to a database established in Pisa laboratory on reference protein materials

Samples coming from painted ceilings of other masters, working in different periods, contain only animal glue as proteinaceous material, showing that the use of this material was a specific feature of the painter-carpenter painting technique of the 17th and 18th century. Sample L7, coming from a pew parapet has also animal glue in its composition, suggesting that the same decorative technique has been used both for painted ceilings and other painted woodwork in the interior of the church.

Polysaccarides

Saccharide fractions were analysed for six samples. The sugar content of sample K2 was below detection limit; the sugar content of all other analysed samples is reported in Table 3. The saccharide profile was compared with that reported in the literature [12]. Two samples taken from the wooden support of the ceiling in Alunişu (Magyarókereke, CJ) were also analyzed according to the same procedure to be used as environmental blanks. The obtained average saccharide profile is also reported in Table 3.

Samples A1, A2 and P1 showed a qualitative and quantitative profile that it is not in agreement with any of the reference materials in the literature. The high content of xylose seems to point to a contamination probably due to migration from the wood support. Samples G1 and K1 show the same qualitative and similar quantitative saccharide profiles. The presence of methylpentoses

and uronic acids in significant amounts (>1%) points to the presence of a polysaccharide material which cannot be identified, since the saccharide profile is not in agreement with the references in the literature.

Table 3. Saccharide profile (percentage relative monoglucide and uronic acid content) of some of the samples and of the wood from the support (Xyl – xylose; Ara – arabinose; Ram – ramnose; Fuc – fucose; Gal ac – galacturonic acid; Glu ac – glucuronic acid; Glu – glucose; Man – mannose; Gal – galactose)

Sample	Xyl	Ara	Ram	Fuc	Gal ac	Glu ac	Glu	Man	Gal	Sugar content (µg)
A1	59.1	14.3	0.0	0.0	0.0	0.0	0.0	18.6	8.0	0.7
A2	51.5	5.5	0.0	0.0	0.0	0.0	0.0	25.5	17.5	1.6
G1	28.7	8.0	8.6	2.3	1.0	4.8	0.0	26.2	20.4	3.1
P1	51.4	8.9	0.0	0.0	0.0	0.0	0.0	12.5	27.2	1.2
K1	20.0	10.6	5.0	9.2	1.0	10.0	0.0	21.9	22.3	2.0
wood	25.7	16.2	1,7	1	0.0	0.0	32.0	17.5	6.4	2.5

Lipid-resinous materials

Glycerolipid identification was based on the mono- and dicarboxylic aliphatic acid content resulting from the lipid-resinous fraction. Waxes and natural resins were checked from the same fraction looking at specific molecular patterns and/or stable degradation markers [4].

The evaluation of the SIM chromatograms acquired from the lipid-resinous fraction of these samples showed that the lipid content of all samples was below detection limit, chromatograms presenting a typical blank profile. Peaks corresponding to the markers of wax and terpenoid resins could not be identified in the TIC chromatogram.

Moreover, the lack of lipid content in samples A1, L1 and L6, containing egg in their protein fraction suggested that egg could be used as a glair.

CONCLUSIONS

The study focused on the analysis of the organic materials in painted surfaces, mainly wooden ceilings from different Transylvanian churches. Thirteen samples were analyzed by GC-MS applying a methodology that enables the identification of the natural organic binders from the same microsample avoiding interferences due to inorganic media. The analyses revealed that the paint layers on painted woodwork were mainly applied with animal glue as binder. No lipid or resinous materials were identified in the samples, which is in good agreement with the matte aspect of the paintings. A polysaccharide material could be detected also in some samples though its identification was not straightforward. Painting technique proved to be similar for the studied ceilings

painted by different workshops in the 17th and 18th century. Other painted woodwork in the churches, such as the pew parapet studied also here, seems to be painted in the same manner. Therefore, macroscopic decay of the painted surfaces could not be related to the use of a particular binding media. However, an interesting specific feature was revealed for the binding media used by Umling, the elder, who mixed egg and animal glue to apply some of his colors (white and blue in the present study).

The results give a preliminary view on the painting technique of Transylvanian painted woodwork and its decays, and may help in planning suitable conservation strategies.

EXPERIMENTAL SECTION

Analyses were performed in the laboratories of the research group "Chemical Science for the Safeguard of Cultural Heritage", within University of Pisa, Department of Chemistry and Industrial Chemistry.

Microphotographs were taken by a Nikon SMZ800 microscope, equipped with Nikon digital camera.

A microwave oven model MLS-1200 MEGA Milestone (FKV, Sorisole, Bergamo, Italy) was used for the hydrolysis of proteins and polysaccharide materials.

The OMIX C4 pipette tips were purchased from Varian (Milan, Italy). Zerolit DMF cation/anion exchange resin was supplied by BDH Chemicals Ltd. (UK).

GC-MS analyses of the samples were performed on a 6890N GC System Gas Chromatograph (Agilent Technologies), coupled with a 5975 Mass Selective Detector (Agilent Technologies) single quadrupole mass spectrometer, equipped with a PTV injector. MS was operating in the electron impact (EI) positive mode (70 eV). The MS transfer line temperature was 280°C; the MS ion source temperature was kept at 230°C; the MS quadrupole temperature was at 150°C. Chromatographic separations were performed on an HP-5MS fused silica capillary column (5% diphen-yl-95% dimethylpolysiloxane, 30 m × 0.25 mm i.d., 0.25 μm film thickness, J&W Scientific, Agilent Technologies, Palo Alto, CA) coupled with a deactivated silica precolumn (2 m × 0.32 mm i.d) using a quartz press fit. Detailed working conditions are reported in the literature [10].

Principal Component Analysis was performed using SCAN Release 1.1 (Minitab Inc., USA)

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