X-RAY
SPECTROMETRY

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Analysis of mural paintings using *in situ* non-invasive XRF, FTIR spectroscopy and optical microscopy

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An analytical protocol consisting of X-ray fluorescence spectroscopy, optical microscopy and Fourier transform infrared spectroscopy was used to study the origin and the nature of the materials (pigments, binders and coating preparation) of the Fundenii Doamnei church mural paint from Bucharest. The main interest of the present study consisted in the original votive paint from narthex, painted in 1757 in *a secco* technique.

During analysis, an unexpected pigment in the votive paint could be detected by the combined analytical techniques: ultramarine blue. Along with this pigment, the presence of gypsum binder based on egg and flax seed oil could also be evidenced. These results demonstrated *a secco* execution technique of the votive paint and also the presence of a restoration treatment. Moreover, during the present study, the components of the preparation layer and the constitutive pigments from both 1699 and 1757 years mural paints have been analyzed. Hence, the following pigments could be identified: vermilion, azurite, cinnabar, lead white, ochre, natural umber and gold, by using the combination of the analytical techniques.

The novelty of our results consists in detecting the composition of the materials used in this church painting (*fresco* and *a secco*) during these 254 years since its first restoration.

The results of these investigations pointed to the suitability of the non-destructive and semi-destructive analytical techniques in the complex characterization of the paints realized in different techniques, at different periods.

Introduction

The conservation of heritage values – preservation and restoration – represents a complex research field, involving multiple disciplines. Knowledge of material composition from a mural's paint structure is essential in understanding the degradation mechanisms and their most appropriate restoration. In addition to the directly important information contained in the analyzed artwork surfaces, this knowledge contributes to a better understanding of the traditional painting techniques, to determine their age and authenticity. Moreover, knowledge of the original pigments provides important information regarding the composition of the materials recommended in the conservation treatments.

X-ray fluorescence (XRF) analysis represents the most accurate and fastest method in the inorganic material analysis of the analytical methods used for non-destructive determination of the elemental composition.[1,2] In recent years, portable XRF spectrometers have been developed for the *in situ* elemental analysis;[3–5] they increased the efficiency of the method. However, XRF is known to be useful only in the analysis of inorganic materials (pigments in paints), but organic components in mural paint (from binders, coating formulation) undergo physical and chemical modifications as well under the environment influence (light, oxygen, humidity).[6,7]

To answer all questions related to the complex structural composition of the paint layers or to the chemical nature of their components, sampling is inevitable. Therefore, the identification of the organic materials in pictorial layer is realized with micro-destructive methods as Fourier transform infrared (FTIR) spectroscopy, which, besides other analytical methods as stratigraphy, microscopy and analysis of the images obtained with different types of light sources,[8–11] provides reliable and detailed information about the analyzed painted surfaces. Recent studies realized in this regard on a variety of painted supports confirm the necessity of these methods.[12–18]

Our research study is focusing on the paints in "Saint Eftimie" church and "Fundenii Doamnei" church, built in 1699, by the high steward Mihail Cantacuzino. This monument is remarkable by the exotically delicate beauty of the decoration of the facades, delightful and skillful, in the oriental stucco style with Persian influence. Stone column ornamentation from narthex, the door and window frames, as well as the other artistic components, is adding value to the monument.

The painting was realized by Parvu Mutu, the court painter of the Cantacuzino family. During 1756–1757 the original paint from 1699 was almost removed and the church was repainted (Fig. 1).

The present study represents the first scientific investigations of the materials that were contained in the mural painting with modern non-destructive and micro-destructive analytical methods

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Figure 1. Technique of fresco painting in the 18th century.

and have been obtained during restoration work of this church, begun in 2011.

As a result of the cleaning *a fresco* mural paint from the 18th century, the restorer concluded that the paints from the altar, nave, narthex and porch presented the same technical, stylistic and graphological features. Moreover, the narthex painting was better preserved, as it had been less submitted to unprofessional cleaning.

A secco technique unlike the *fresco* church painting was noticed in the case of votive paint from the narthex that resulted in a detailed analysis of the corresponding pigments, binder and preparation layer.

On the other hand, the analysis of the 18th-century degraded painted areas in the sanctuary, nave, narthex and porch revealed the original painting (from 1699). The *a fresco* technique used here is extremely resistant as it was executed on a wet lime plaster that includes the pigment through a carbonation reaction, whereas for *a seco* technique the painting is applied on a dry plaster using different binders or emulsions.[19]

In the votive paint on the western wall (Fig. 2(b)) of the narthex is painted the founder of the second stage (1756–1757), the great chancellor Dumitrascu Racovita with his wife Despa and their children Dumitrascu and Soltana alongside the high steward Mihail Cantanuzino. Continuing, on the southern wall are represented Ilinca Cantacuzino and her husbend and on the south-eastern side of the narthex (Fig. 2(a)) is depicted the family of the ruler Constantin Mavrocordat and his wife Ecaterina.

The chemical composition of the painting layer and the mural preparation layer of the 17th and 18th centuries in this work was determined using an analytical protocol based on XRF, FTIR and optical microscopy (OM). This combined analytical methodology revealed surprising information about the nature of the materials and painting techniques.

We ascertained that the original painting and the one of the 18th century have the same mortar composition (lime, sand), same pigments (natural umber, ocher, cinnabar/vermilion, ivory black, gold), using portable XRF spectrometer.

As regards the votive paint, we discovered that the painting is realized in fat tempera with egg emulsion and on some areas with oil supplement. The preparation layer of the votive paint had the same lime and sand composition as the main painting.

Materials and methods

Non-invasive techniques: X-ray fluorescence

X-ray fluorescence is a non-destructive investigation technique that allows the analysis of the chemical elements in a surface. These features make is useful in the study of the polychrome surfaces in general and particularly in painted surfaces. The first applications in this domain were reported in the early seventies. The analysis method was widely applied in cultural heritage field (paint, stone, metal, ceramic, pigments, inks, etc.) and continues

Figure 2. Votive *a secco* painting technique, 1757. (a) Prince Constantin Mavrocordat and his wife Catherine. (b) Racovita Dumitrascu great chancellor, Despa wife and their children, with the analyzed points indicated.

to be applied in museums, universities and research laboratories, in the whole world.[20]

Non-destructive XRF spectrometry with portable instruments is used for the *in situ* measurements in works of art, and this represents one of the newest branches of XRF. The development of the portable devices had, as a consequence, the development of the scientific investigation applications in cultural heritage as, in some cases the sampling is impossible, even at micrometer scale. A small X-ray beam allows the analysis of an object, for example, to verify if all parts are made of the same material or to investigate the homogeneity of the material.

An element is generally identified according to the wavelength (λ) or the energy (E) of the characteristic X-ray emission. The concentration in a certain element is quantified according to the intensity of the characteristic band. Therefore XRF spectrometry determines the elemental composition of a material. Qualitative analysis is realized by determining the position of the fluorescence peaks in the spectrum, whereas quantitative analysis can be achieved by measuring the intensity of the characteristic radiations emitted.

X-ray fluorescence spectrometry easily and rapidly identifies and quantifies the elements at a dynamic concentration level, from p.p.m. to 100% in weight. As the chronological utilization of the majority of the pigments is well known, in some cases, the method allows the authentication of the painting in study. However, some problems related to pigments identification can arise; for instance, the presence of Cu in the X-ray spectrum may indicate the presence of either green or blue pigment.[20] Even so, XRF is a precisely method of analysis. The precision is at the same order of magnitude compared with the chemical method for the components at high concentration. Generally,

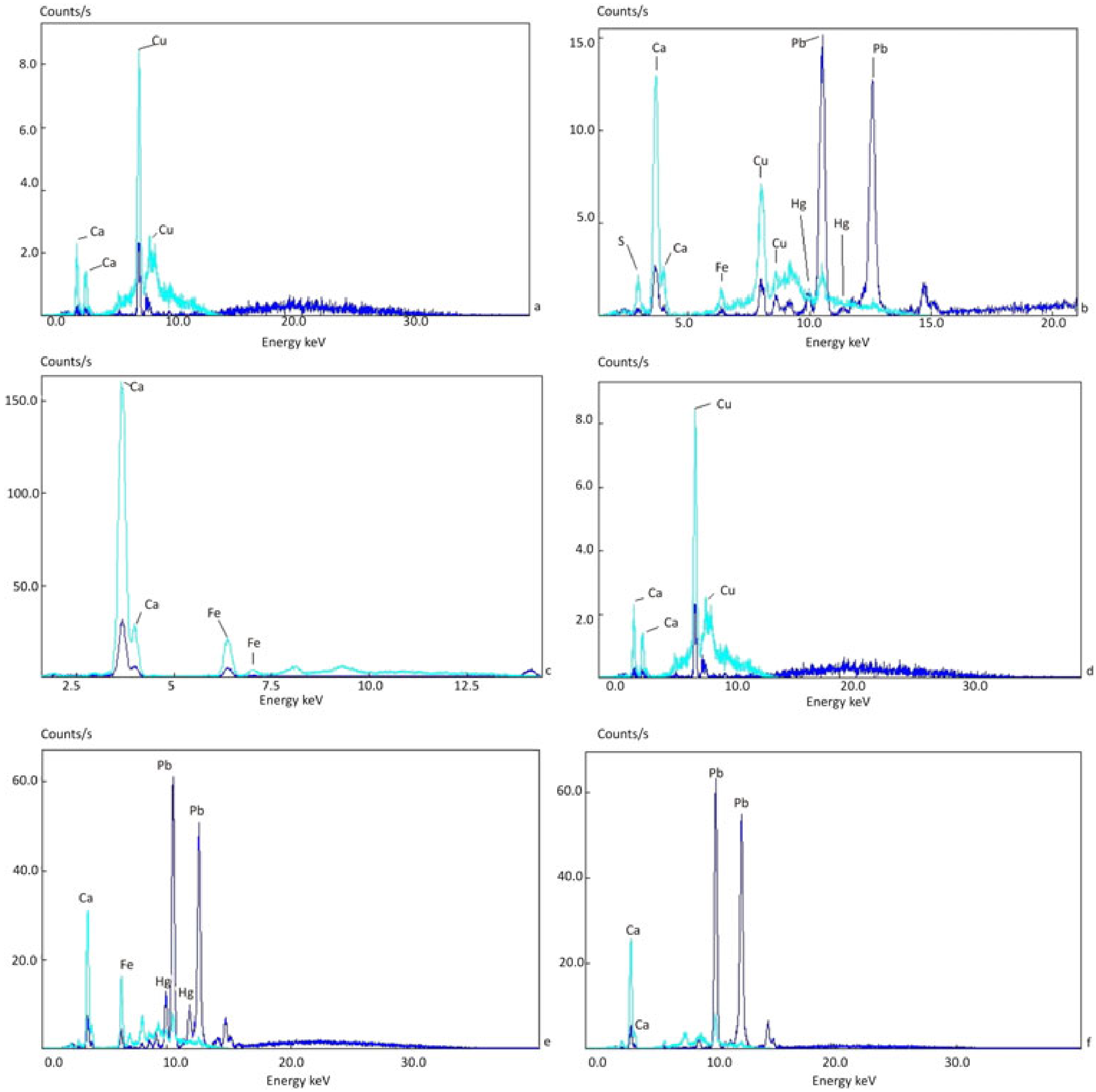

Figure 3. XRF spectra: (a) layer coating of lime in the P1 element as indicated by the signal; the measurement was made on the white background of the church; (b) brown ocher pigment, Michael Catacuzino's hand, P2; (c) preparation and sienna pigment layer of the image, Dumitrascu Racovita ocher background, P3; (d) carbon black pigment identified, P4, edge Dumitrascu Racovita coat; (e) Indicative for the red pigment vermilion (Hg signal), P5, Michael Catacuzino backrest; (f) white pigment with strong Pb signal, garment Ilinca Cantacuzino P6.

the concentration in an element should be over 0.01–0.1% to be detected by this method. Absolute limit for detection is considered to be 10^{-8} g.[20]

In the present study, determinations *in situ* in 13 points of different areas of the surface layer from votive paintings and 40 points, in different areas of the original and later (1757) painting, from both nave and narthex, were carried out.

The experimental measurements were realized for the organic components of the pigments and preparation layer, using an XRF spectrometer, type *Innov X* Systems Alpha Series. This device is equipped with an X-ray tube with W anode, working at the maxim parameters of 35 kV and 40 μA, the fluorescence radiation being detected and analyzed with a Si detector (PIN), with thermoelectrical cooling, controlled by a minicomputer. For specra aquisition and semiquantitative analysis of a heavy matrix, the Analytical mode software has been used for a selected 30-s excitation duration, and for a light matrix (60-s excitation), the Soil mode software was used. The equipment is very light (about 1.5 kg), compact and easy to manipulate; therefore, it is very well adapted to *in situ* XRF analysis. The corresponding spectra presented here are illustrative for the identified pigments.

A digital portable microscope VT 300 was used for the selection of the painted surface areas taken into study.

Infrared spectroscopy

A large variety of natural and synthetic materials from polysaccharides to acrylics and from carbonates to oxides have been used in the creation of the works of art.

Fourier transform infrared spectroscopy is a recent technique applied in analyzing the organic materials used in the works of art. An important application of IR spectroscopy consists in analyzing the organic components in painting samples. Therefore, we selected this method to identify the binders used in mural paintings to provide important indications regarding their realization techniques.

Ten tiny specimens have been sampled from different areas of the votive paint; they have been further prepared according to the standard methodology by KBr pelletizing.

Vegetable and animal oils are composed of glycerine fatty acid esters with a large number of carbon atoms. IR spectroscopy is an ideal method to identify the oils and proteins used in preparation of the binders in painting. For analyzing the binders in the selected samples, a Vertex 70 Bruker FTIR spectrometer was used in the 5000–400 cm^{-1} domain. The IR identification is realized either by assigning the characteristic chemical groups to the peaks of the spectra, or by comparison of the spectra with the ones of already known compounds that fitted best.[21] Practically, both methods were used for each of the ten samples. First, we obtained the spectra that presented peaks characteristic to the known chemical groups in certain ratios, and then, we compared the obtained spectra with the corresponding ones from the databases for validation of the supposed compound.

Optical analysis of samples

Paint analysis usually begins with the visual investigation of the surface of the object, primarily with the purpose of locating intact and representative areas for further analysis. Taking even a tiny sample for a cross section means removing and destroying a part of the artifact's original structure. Thus, samples are best taken from areas with flaking paint, so that still intact paint layer will not be damaged. The size of the particle should be as large as necessary but as tiny as possible. Usually, a particle with a size of 1 mm × 2 mm is absolutely sufficient, and attention should be given to the sampling procedure to collect from all the paint layers.[22] The morphology of the pigment particle, including homogeneity, shape, size, surface character and crystal form, is among the first in the sequence of observations that should be made in an investigation and that can help to determine the source of a pigment and to decipher subtle differences between natural and synthetic versions of a pigment. OM can provide information such as the sequence of paint layers, color and texture of those layers, and layer thickness.[23] The pigments analyzed in this study consist of natural minerals or inorganic synthetic analogues.

For the stratigraphic study, five samples were collected from the votive painting and two from the mural painting from 1757. This analysis was realized with an Olympus SZX 160 microscope with epi-fluorescence illuminator and an RFA16 SZX2-SET E-330 professional digital SLR camera. To get the best explanation of the obtained images, we considered for comparison the international data base.[24,25] The samples were processed according to the stratigraphy analysis technique methodology (involving the use of the resins for impregnation or of the balsam of Canada) and immobilization the micro sample in thin sections. Thin sections are normally 3–30 μm thick.

Results

X-ray fluorescence analysis

X-ray fluorescence analysis (Figs 3–5) indicated for the preparation layer of the paintings from 1699 and 1757 (church painting and votive paint) a strong peak corresponding to Ca, suggesting the presence of $CaCO_3$ (Table 1). On the other hand, no matter what technique was used, the main component of the preparation layer for the mural paint is lime, so this supports the hypothesis.

X-ray fluorescence analyzes and interpretations of results are listed in Table 1.

Table 1. Pigments and their identification key based on XRF analysis

Color	Samples	Chemical composition	Key elements(s)	Pigment name
White	1, 3, 4, 5, 6, 7, 9, 10, 11, 12, 13, 14	$CaCO_3$	Ca	Chalk
	2, 8	$CaSO_4 \times 2H_2O$	Ca, S	Gypsum
	4, 5, 6, 8, 13	$2PbCO_3 \times Pb(OH)_2$	Pb	White lead
Red	5	HgS	Hg, S	Vermilion
	8	Fe_2O_3	Fe	Red ochre
Black	4	C (95%)	−(K)	Carbon black
Blue	14	$2CuCO_3 \times Cu(OH)_2$	Cu	Azurite
	8	$Na_{8-10}Al_6Si_6O_{24}S_{2-4}$	S	Ultramarine ?
Yellow–brown	2, 3, 10, 11	$Fe_2O_3 \times nH_2O$	Fe	Ochre

After detection of the signals for Ca, S ($CaSO_4$) in P2 and P8 samples from the votive paint, we had to answer the question whether this is from gypsum added during previous restoration or it is the consequence of chemical reaction due to the temperature and relative humidity fluctuation. For this purpose, ten other samples from the votive paint surface have been analyzed, but no similar result could be achieved. We deliberately avoided the red pigment that could contain S and affect the final result. We can conclude that in the two areas, gypsum was used for restoration.

Using the XRF method, we could establish also the pigments palette used in the original painting, in the one from 1757 and in restoration late procedure:

1. Pigments in *a fresco* 1757: vermilion, azurite, gold, white lead.
2. Pigments in the fragments from *a fresco* paint 1699: cinnabar azurit, gold, umber.
3. Pigments in *a secco* painting from votive paint from 1757: white lead, gold, ochre, vermilion, umber, carbon black, azurite.
4. Pigments used in votive paint restoration: ochre, ultramarine, white lead.

The hypothesis of ultramarine pigment existence in restoration area P8 could not be confirmed by XRF data. Therefore, we chose the FTIR analysis of a sample from that area. The obtained corresponding spectrum (ultramarine-signal at 2340 cm^{-1}) was compared with the one from databases, and the hypothesis

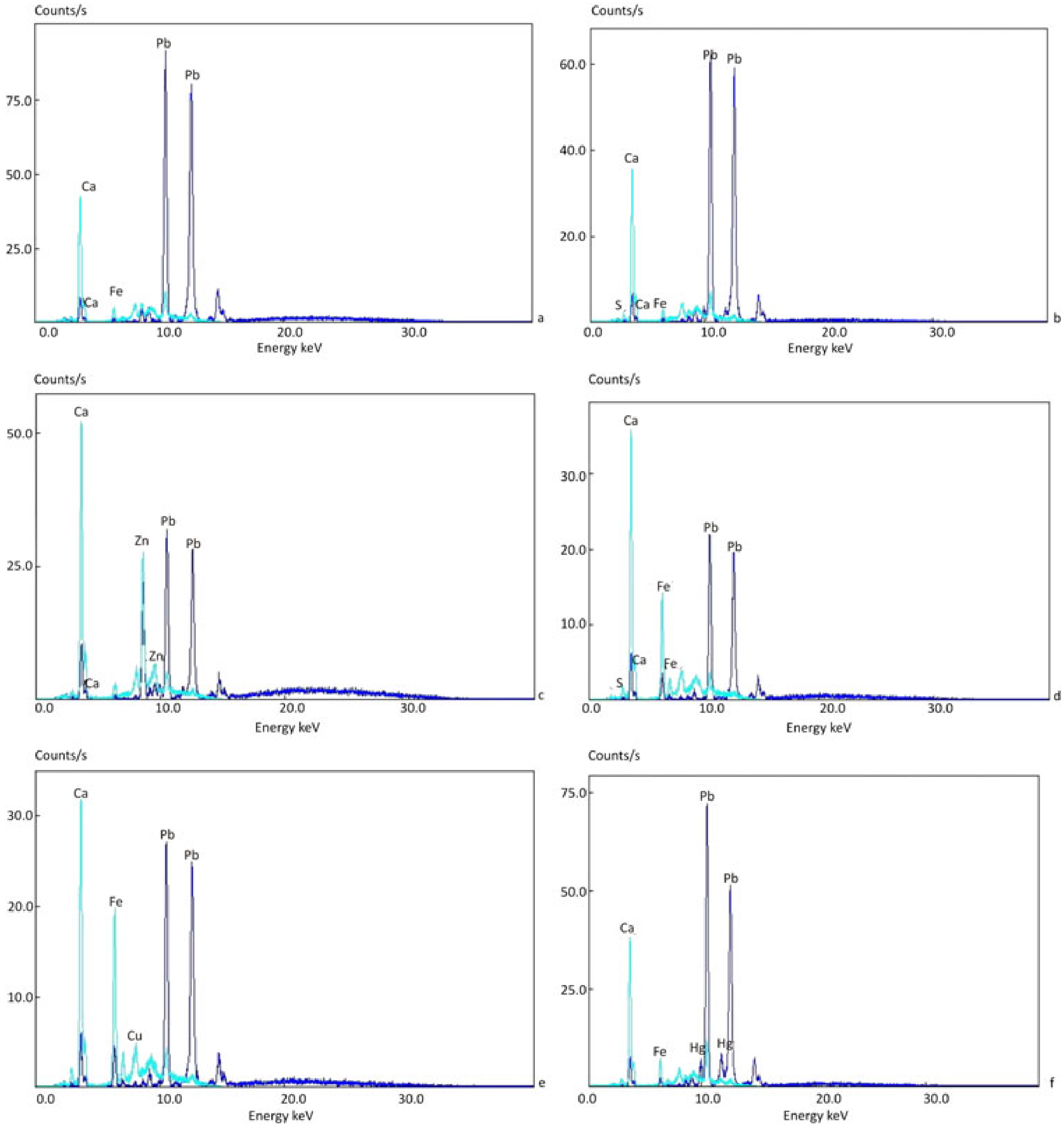

Figure 4. XRF spectra : (a) lime coating Ca, votive painting background, the P7; (b) strong Ca and S signals corresponding to gypsum, Ilinca Cantacuzino's eyes, P8; (c) layer coating of lime indicated by the image signal component Ca, Soltana, P9; (d) brown pigment, P10, fur coat, Dumitrascu Racovita; (e) ocher pigment, P11, roof church votive painting; (f) preparative layer, Michael Cantacuzino's hand P12.

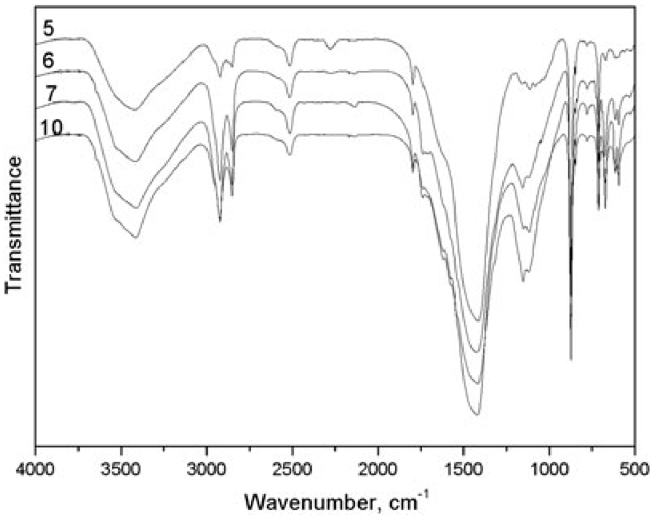

Figure 5. XRF spectra: (a) P 13, lead white pigment, showing a strong signal of Pb and a preparative layer of lime indicated by the colored signal (Ca) in the fur coat of lady Soltana; (b) layer coating of lime (Ca) and pigments, gold (Au) and blue azurite (Cu), the P14 from the original painting in north apse.

was confirmed. The natural or synthetic nature of the pigment will be discussed in another research stage.

Infrared spectroscopy

To assess the technique used in votive paint realization and the corresponding organic components, the samples previously prepared were analyzed by FTIR.

In spectra 5, 6, 7 and10, we could observe strong vibration bands attributed to calcium carbonate (calcite) at 1424, 1422, 1420 and 1419 cm^{-1} (symmetric stretch, ν_1), respectively, for the frequency band of CO_3^{2-} anions and the stretching band at 873 and 872 cm^{-1} assigned to the O–C–O bending band (Fig. 6). Amorphous silicon Si–O stretching produces a strong band at about 1050 cm^{-1} and crystalline quartz (silica minerals) has a primary absorption band nearby 1100 cm^{-1}.[21] The signals at 1051, 847 and 839 cm^{-1} are assigned to vibrations of the absorption bands for silica (Si–O). These data confirm the composition of the coating layer of lime, sand and hemp.

It is known that vegetable and animal oils consist of glycerol esters of fatty acids with large number of carbon atoms. Their diversity consists in the type and composition of the fatty acids. Spectra corresponding to the flex seed oil present a strong sharp signal, corresponding to the carbonyl ester group, at 1750–1740 cm^{-1}. This is the clear proof of the oil presence. However, mixed with some pigments, the carbonyl group signal can be shifted to slightly lower wave numbers.[21]

Therefore, in our samples (Fig. 7(a) and (b)), the signals at 1734 and 1739 cm^{-1} are attributed to ester C = O stretching bands specific to the oil. Other characteristic bands of flax seed oil are stretching bands allocated to aliphatic C–H groups at 2923, 2922 and 2850 cm^{-1} and attributed to C–O bonds at 1154, 1152, 1117 and 1113 cm^{-1} (Fig. 6).

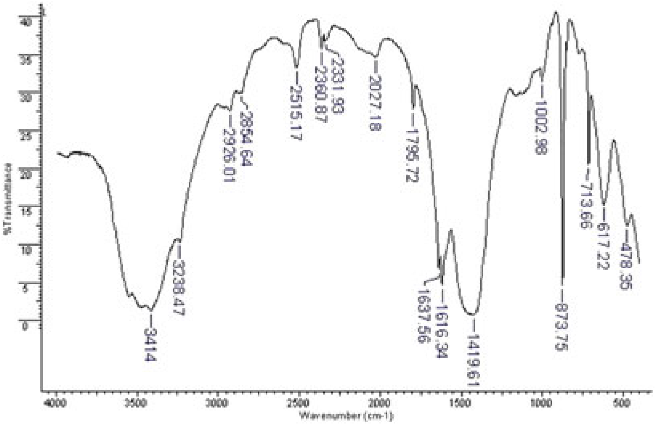

Figure 6. FTIR spectra for identification of binder and setting the votive painting technique: Mihail Catacuzino back of sample 5; sample 6 Ilinca Cantacuzino garment; sample 7 votive painting background, maybe sample 10 coat, Dumitrascu Racovita.

Characteristic signals of protein from egg in FTIR spectra are assigned as follows: at 3238 cm^{-1} to N–H groups asymmetric vibration, at 1585 cm^{-1} to the C–N–H group bending band, at 2926 and 2872 cm^{-1} to aliphatic C–H stretching groups, and at 1616 cm^{-1} to the carbonyl group (C = O) stretching (Fig. 7(a) and (b)). The vibration bands corresponding to 873, 1793, 1795 and 1153 cm^{-1} wave numbers are assigned to group linoxyn (R–OO–R) from flax seed oil, and the signal at 1122 cm^{-1} is attributed to SO_4^{2-} anion. The low intensity band is assigned to the same ion at 617 cm^{-1}. The presence of the SO_4^{2-} ion bands in the FTIR spectra of samples 2, 3 and 8 is due to the use of gypsum in restoration work. In this case also appears the signal corresponding to the CO_3^{2-} anion stretching band attributed to limestone. Accumulating information provided by FTIR analysis, we can conclude that the votive painting was realized in *a secco* technique based on fat emulsion based on flax seed oil and egg yolk.

Optical analysis of samples

Stratigraphy analysis completed the information regarding the painting technique used in votive paint.

Optical analysis of a cross section of the red pigment sample, which is cinnabar according to XRF analysis, shows that the color layer was applied directly to the substrate that contains voids, quartz particles and blue pigment migrated granules (Figs 8 and 9).

As for azurite blue pigment, granules penetration in lime mortar indicated that the paint must have been applied on a wet mortar (Fig. 7). In thin sections, the pigment particles are often randomly oriented in the paint layer (Fig. 10).

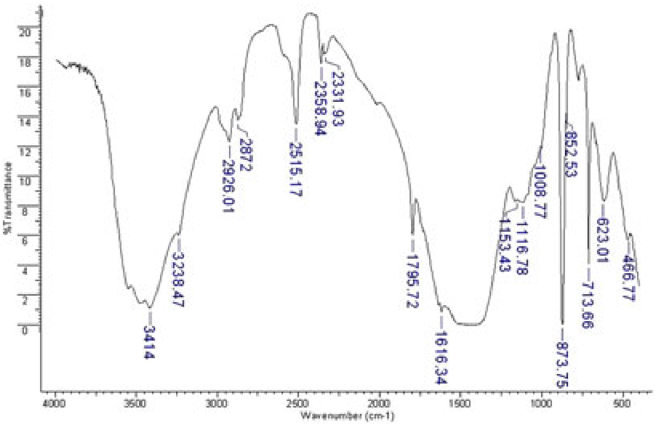

Figure 7. FTIR spectra for identification of binder and setting in the oil votive painting technique: (a) sample 2 from the intervention of Michael Catacuzino hand, P2; (b) sample 3 layer preparation in the area of intervention in the eyes of Ilinca Cantacuzino, P8.

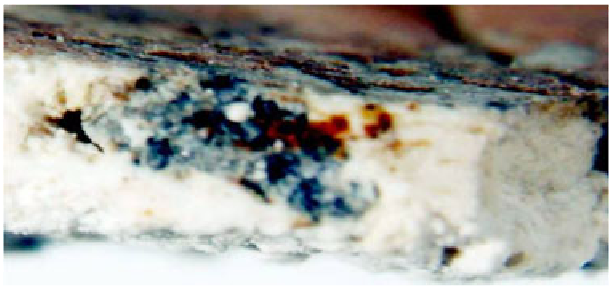

Figure 8. Microphotograph of a polished cross section of sample 5 under reflected visible light: cinnabar, calcium carbonate and azurite (white and blue layer),160×.

When rotating the angle of the polarized light falling on the sample, finely dispersed quartz crystals are highlighted in the masonry layer and the pigment appears as an amorphous or poorly crystalline mass, demonstrating the presence of mortars based on lime and sand (Fig. 8); the gaseous inclusions resulted during chemical and microbiological *in situ* processes.

The seven samples revealed the existence of a single color layer and, in the protective film area, deposits with an uneven structure and with a thickness that, in some areas exceeded color layer size, could be observed. The structure of these deposits consisting of soot/ tar, dust, degradation products, aerosols and so forth showed the absence of any protective films. These allowed the deep diffusion into the color layer by reactive effects (chemical attack) that destroyed some areas of painting on large surfaces (at some samples, the alterations of the pigment structure under the chemical action of surface deposits could be observed). These deposits are adherent (strongly attached to the color layer) or partially adherent.

All the non-destructive and semi-destructive analytical methods used in this work for characterization of the pigments and preparative layer of votive paint unanimously showed that the painting techniques consisted in fat tempera, with egg and oil emulsion, unlike the rest of mural painting from 1757, which is done in *fresco* technique. This argument is supported by FTIR identification of egg protein only in votive painting, used as a binder along flex seed oil. The presence of gypsum in two areas of the votive paint makes us sure that it was added as a subsequent conservation treatment, but this was not documented. At no other places of the painting layer from the church, it could be identified.

Another indication for the restorers in determining the areas where conservation treatments have been made at the votive painting is the identification at Soltana eye, in the restoration area P8, of a purple pigment based on ultramarine blue.

Figure 9. Microphotograph of a polished cross section of sample 9 under reflected visible light: azurite, calcium carbonate and ochre grains (white and ochre layer),160×.

Figure 10. Microphotograph of a polished cross section of sample original painting age 1699: cinnabar, calcium carbonate and quartz crystals,160×.

Conclusions

Following the current restoration interventions, it was found that the painting attributed to Parvu Mutu in 1699, is no longer preserved but fragmentary, and it was almost completely removed.

In 1756–1757, when the church was repainted, the votive painting was removed and the present votive picture was painted, in fat tempera with flex seed oil and egg yolk using *a secco* technique.

This finding was supported by e-analytical results (XRF, FTIR, OM) obtained by analysis of pigments, preparation layer and binder, demonstrating the painting technique and materials composition. Pigments were found degraded by chemical attack, presenting chromatic modifications (discoloration, shifting to gray, etc.). Erosion of the color layer in some areas demonstrated some cleaning/dust removal interventions by wiping.

So after many years (254), this valuable, historic and artistic mural painting is known under its technical aspects.

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References

[1] B. Beckhoff, B. Kanngießer, N. Langhoff, R. Wedell, H. Wolff (Eds), Handbook of Practical X-ray Fluorescence Analysis, Springer-Verlag, Berlin, **2006**.
[2] K. Janssens, R. Van Grieken (Eds), Comprehensive Analytical Chemistry, Volume XLII Non-Destructive Micro Analysis of Cultural Heritage Materials, Elsevier B.V., Amsterdam, **2004**.
[3] J. Bredal-Jørgensen, J. Sanyova, M. L. Sargent, R. H. Therkildsen. *Anal. Bioanal. Chem.* **2011**, *401*, 1433–1439.
[4] M. Mantler, M. Schreiner. *X-Ray Spectrom.* **2000**, *29*, 3–17.
[5] S. Lorusso, A. Natali, C. Matteucci, R. Bertolino. *Conserv. Sci. Cult. Herit.* **2007**, *7*, 351–378.
[6] D. Camuffo, A. Bernardi. *Stud. Conserv.* **1995**, *40*, 237–249.
[7] F. J. García-Diego, M. Zarzo. *J. Cult. Herit.* **2010**, *11*, 339–344.
[8] G. A. Mazzocchin, F. Agnoli, S. Mazzocchin. *Talanta* **2003**, *61*, 565–572.
[9] I. Liritzis, E. Polychroniadou. *ArchéoSciences* **2007**, *31*, 97–112.
[10] F. Agnoli, I. Calliari, G. A. Mazzocchi. *Ann. Chim.* **2007**, *97*, 1–7.
[11] F. Govaert, G. Roy, B. Decruyenaere, D. Ziernicki. *Prob.Forensic Sci.* **2001**, *XLVII*, 333–339.
[12] C. Genestar, C. Pons. *Anal. Bioanal. Chem.* **2005**, *382*, 269–274.

[13] L. Bonizzoni, A. Galli, M. Milazzo. *X-Ray Spectrom.* **2010**, *39*, 346.
[14] C. Duce, L. Ghezzi, M. Onor, I. Bonaduce, M. P. Colombini, M. R. Tine, E. Bramanti. *Anal. Bioanal. Chem.* **2012**, *402*, 2183–2193.
[15] N. Civici. *X-Ray Spectrom.* **2007**, *36*, 92.
[16] T. Grygar, J. Hradilová, D. Hradil, P. Bezdička, S. Bakardjieva. *Anal. Bioanal. Chem.* **2003**, *375*, 1154–1160.
[17] M. F. Guerra. *X-Ray Spectrom.* **2008**, *37*, 317–327.
[18] H. H. Marey Mahmoud, *MAA* **2011**, *11*, 99–106.
[19] P. Mora, L. Mora, P. Philippot, Conservation of Wall Paintings, Butterworths, London, **1984**.
[20] C. Seccaroni, P. Moioli, Fluorescenza X. Prontuario per l'analisi XRF portatile applicata a superfici policrome, Nardini Editore: Firenze, Italy, **2002**.
[21] R. M. Derrik, D. Stulik, M. J. Landry, Infrared Spectroscopy in Conservation Science, Scientific Tools for Conservation, Getty Conservation Institute, Los Angeles, **1999**.
[22] M. L. Gil, A. Carvalho, I. Seruya, P. Ribeiro, A. Alves, A. Guilherme, J. Cavaco, A. Candeias. *X-Ray Spectrom.* **2008**, *37*, 328–337.
[23] A. Kriznar, A. Ruiz-Conde, P. J. Sánchez-Soto. *X-Ray Spectrom.* **2008**, *37*, 360–369.
[24] N. Eastaugh, V. Walsh, T. Chaplin, R. Siddall, Pigment Compendium Set: Pigment Compendium: a Dictionary of Historical Pigments, Butterworth-Heinemann, Oxford, **2004**.
[25] N. Eastaugh, V. Walsh, T. Chaplin, R. Siddall, Pigment Compendium: Optical Microscopy of Historical Pigments, Butterworth-Heinemann, Oxford, **2004**.