

SPECTRAL ANALYSIS OF ORIGINAL AND RESTAURATED ANCIENT PAPER FROM ROMANIAN GOSPEL

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A complete characterization of Romanian Gospel from 1740, has been carried out including X-ray fluorescence (EDXRF), induced coupled plasma-atomic emission spectroscopy (ICP-AES), Fourier transformed infrared spectroscopy (FTIR) and thermal analysis (DTA-TGA-DSC). The analysis of the paper showed the presence of Fe₂O₃, CaCO₃, ZnO, BaSO₄, SrCrO₄, K₂O, Na₂O, Al₂O₃, Ca₃(PO₄)₃ and also some organic trace due to.

Key words: Romanian Gospel, including X-ray fluorescence, ICP-AES, FTIR.

1. INTRODUCTION

Artefacts are examined in order to answer art historical questions about the origin of a work, and by whom a work was created. Non-destructive tools, particularly optical spectroscopic or imaging techniques, are more widely used to study these objects. It should be pointed out that artworks are almost always analysed by XRF technique, and this kind of study is complemented with other atomic techniques (XRD, etc.) or other molecular techniques (Raman, FTIR, ATR, etc.). Identificating pigments and inks are more difficult because of the lack of pronounced chemical differentiation between the ink types and because of possible interferences in the analysis from the paper substrate [1–7].

The manufacture of the paper in Europe was first established in Islamic Spain in the middle of the 11th century. In the second half of the 14th century, the use of paper had become well accepted in Western Europe. Prior to 1850, paper was made from cellulose and water by using hemp, flax and cotton fibres. Historical paper differs in many ways from contemporary paper. Antique paper was made entirely from rags, *i.e.*, from linear long cellulose fibres, only with the addition of sizing compound, whilst contemporary paper can be manufactured from short fibres, hemicellulose and lignin, and may contain nonfibrous compo-

nents including various colouring agents, fillers, and coatings. Originally animal glue was used for sizing. It was substituted in the 19th century by rosin and alum, and more recently by other synthetic products. Causes of deterioration may be either internal (endogenous) or external (exogenous). In the first case, if the component elements of a paper are relatively pure, it has good durability and quite long life expectancy. This is the case of most of the papers made up until the 19th century. Unfortunately, the appearance of wood pulp in the 19th century led to a reduction in the quality. Paper made with wood pulp was well purified more or less according to the process applied-mechanical or chemical. The wood pulp was then sized with rosin (pine resin) in an acidic medium stands up much less to ageing than most of the papers made previously. It becomes yellow and rapidly loses its original flexibility. Moreover, the presence of transition metals (iron and manganese) catalyses the oxidation processes including the sulphur oxide, which forms sulphuric acid. Lignin and rosin may combine to form peroxides even at ambient temperature. These are very powerful oxidation agents reacting directly on the different chemical groups of the cellulose. External factors may also be added to the internal causes of deterioration such as air pollution, unfavourable climate, lighting conditions and biological agents.

In this paper, we report the elemental composition of paper and ink belonging to Romanian Gospel from 1740. A complete characterization has been carried out including X-ray fluorescence (EDXRF), induced coupled plasma-atomic emission spectroscopy (ICP-EAS), Fourier Transformed infrared spectroscopy (FTIR) and thermal analysis (DTA-TGA-DSC).

2. EXPERIMENTAL

2.1. APARATUS AND METHODS

A Varian Liberty 110 Series spectrometer was used for the ICP-AES analysis. Multielement, matrix matched standards were used for the quantitative determinations. Microwave assisted digestions were performed in a Berghof microwave oven with the use of high-pressure closed Teflon PFA vessels and online pressure and temperature control. In particular, 0.1 g of each sample was placed in the Teflon PFA digestion vessels and a mixture of 5 ml HF 40% and 5 ml HNO₃ 69.5% was added.

Fourier transform IR spectroscopy, FT-IR were collected by using a Perkin Elmer Spectrum GX spectrometer. A range of 400–4000 scans were accumulated for each spectrum at a spectral resolution of 4 cm⁻¹. It was possible to use the drift accessory with the powdered pure substance, thereby allowing for a better and easier analysis.

A spectrometer EDXRF PW4025 – MiniPal – Panalytical was used for semi-quantitative compositional analysis of these pigments.

Thermogravimetric analysis of the paper was carried out simultaneously on a Du Pont TG -DTA analyzer. A sample of 12 mg was used initially and thermal analysis was carried out from room temperature to 800°C at a heating rate of 5°C/minute in the atmosphere of oxygen gas with open sample holder and small platinum boat in static air.

2.2. ARCHAEOLOGICAL MATERIAL

The Romanian Gospel from 1740, has been offered for investigations by a private collectionar, and all the investigations did not damaged this piece of art.



Fig. 1 – The picture of Romanian Gospel from 1740.

3. RESULTS AND DISCUSSION

The manufacture of paper in Europe was first established in Islamic Spain in the middle of the eleventh century [8]. The art of paper-making gradually spread. By the twelfth century, it had become the most common writing material in Western Europe, since Europeans learned this art from the Arabs. In the second half of the fourteenth century, the use of paper had become well accepted in Western Europe [9]. Between the fifteenth and eighteenth centuries paper samples were made of rags and were of higher quality compared to modern paper made of wood pulp [10]. Paper documents are fragile and delicate art objects that need for its examination a suitable non-destructive technique for *in situ* analyses. It is important that ICP-AES analysis has been achieved both for original sample and for ash paper.

ICP-AES in standard configuration, is a destructive method, involving the samples deaggregation. The coupled induced plasma is an atomic source which could be used for all elements, but with argon exception. This source is used for sample dissociation into atoms or ions, by exciting on a high energetic level. They will recome on the ground state by emission of a photon with characteristic energy. This emission is registered by an optical spectrometer. The intensity is

Table 1

ICP-AES determination of trace elements

Element	Gospel paper	Ash paper
Ag	8.9 mg/kg	808 mg/kg
Ti	109.5 mg/kg	427 mg/kg
Al	0.6%	6.43%
Sr	98.4 mg/kg	664.9 mg/kg
Ca	646 mg/kg	1.84%
Ba	0.24%	1.99%
Si	1.79%	10.52%
Mn	6.63 mg/kg	143 mg/kg
Fe	458 mg/kg	0.88%
Cr	32.7 mg/kg	519 mg/kg
Mg	133 mg/kg	0.22%
Na	334.5 mg/kg	0.31%
B	282 mg/kg	7.74%
Sn	660 mg/kg	4.45%
Zn	37.7 mg/kg	719.8 mg/kg
P	587 mg/kg	–
Cu	43.3 mg/kg	270 mg/kg
K	300.9 mg/kg	0.81%

proportional with the concentration of each sample element and is calculated from a calibration curves set in order to obtain the measured concentrations.

This method has a linearity area for 5–6 size ordins and the detection limits are 1–100 $\mu\text{g/mL}$, for the conventional methods.

Energy dispersion X-ray fluorescence spectroscopy (EDXRF) is a technique that can be used for direct analysis of solid metal samples, from beryllium ($Z = 4$) to uranium (U), and very popular instruments. Compared to other competitive laboratory techniques, EDXRF has the advantage of being non-destructive, multi-elemental, fast and cost-effective. Its main disadvantage is that analyses are generally restricted to elements heavier than sulfur for isotope based instruments or titanium for tube based instruments. XRF has developed over the last few decades from the first commercial instruments into a powerful, affordable, fast, non-destructive, and relatively accurate technique for qualitative as well as semi-quantitative chemical analysis.

EDXRF analysis of the Romanian Gospel paper corroborated with ICP-AES, data showed the presence of Fe, Ca, Mn, Zn, Ba, Si, Al, Na, K, Fe_2O_3 , CaCO_3 , ZnO, BaSO_4 , SrCrO_4 , K_2O , Na_2O , Al_2O_3 , $\text{Ca}_3(\text{PO}_4)_3$.

Fig. 2 summarises the relationships (peak area) among all determined elements in the paper composition.

Many traditional inorganic pigments contain polyatomic ions. These ions frequently encountered include carbonate (malachite, azurite, calcite, cerussite, hydrocerussite), sulfate (gypsum, barite, anhydrite) and carbonate (chrome yellows, chrome orange, chrome greens). Infrared spectroscopy is most widely used with organic materials, since C-H, C-O and other types of bonds which are found in compounds of this category have fundamental vibration frequencies in the infrared region, particularly in the “mid-infrared” which extends from about 2.5 to 25 microns (4000 to 400 cm^{-1}). The Fourier transform instrument was

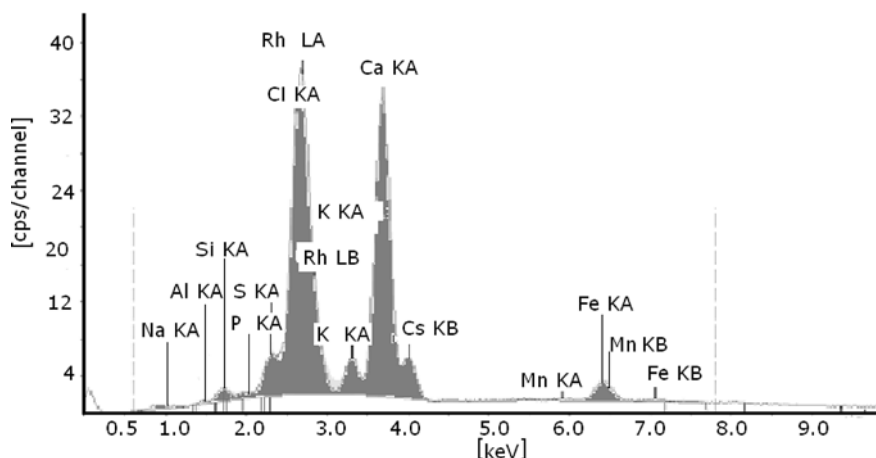


Fig. 2 – The EDXRF spectrum of paper.

found to give the highest quality spectra with the sample sizes here used. FTIR spectra acquired in different locations confirm that the sample is a complex mixture of both mineral and organic phases.

The broad peak at around 3300 cm^{-1} can be attributed to O–H stretching of hydrogen-bonded hydroxyl groups. The additional presence of a fine O–H stretching band at 3535 cm^{-1} is in favor of the identification of hydrocerussite $((\text{PbCO}_3)_2 \cdot \text{Pb}(\text{OH})_2)$, a compound currently used in painting when associated with cerussite $(\text{PbCO}_3)_2$ and called lead white [11–13]. The broad band centered at approximately 3400 cm^{-1} and the sharp peak(s) around 1600 cm^{-1} are due to the water of hydration in its structure.

Another very interesting feature is the presence of the peak at 2900 cm^{-1} associated with the C–H stretching of non-aromatic compounds. The FTIR spectra present the characteristic bands of Prussian blue $(\text{Fe}_4[\text{Fe}(\text{CN})_6]_3)$, and calcium carbonate. Prussian blue may be identified in all three by the band at $2070\text{--}2080\text{ cm}^{-1}$, which is due to vibration of C N, in the ferrocyanide ion [14].

We presume that in this paper exists an organic pigment which contains a carbohydrate binding medium. This accounts for the broad hydroxyl band centered at about 3400 cm^{-1} , the C–H absorption between $2800\text{--}2900\text{ cm}^{-1}$, and the carboxylate group absorptions at 1622 and 1419 cm^{-1} . From all the results we can also observe that Ba is the predominant element in the paper. This can be explained considering that this element is usually used as filler in papermaking [1, 2].

The bands from 1805 to 1672 cm^{-1} , which covers the contribution of both ester and acid groups. These two forms exhibit characteristic C=O stretching at around 1737 and 1712 cm^{-1} . In addition, the spectrum presents two broad bands at 1600 and 1315 cm^{-1} that are consistent with the presence of carbon black (amorphous C). These results are also confirmed by FTIR ATR analysis. In all spectra (Fig. 3), two peaks appear at 1723 and 1236 cm^{-1} . These two peaks are associated with the C=O and the C–O stretching of the carboxyl group, respectively. The appearance of these two peaks indicates the presence of the acetyl groups [15].

The CH_2 groups give a scissoring vibration band at $1480\text{--}1440\text{ cm}^{-1}$. With an adjacent carbonyl group, this band occurs at $1450\text{--}1405\text{ cm}^{-1}$. Some carbonates, are also identified thanks to the large band around 1405 cm^{-1} .

A weak peak centred at 1085 cm^{-1} that is due to calcium carbonate (CaCO_3) , Fig. 3. A little amount of red iron oxide would be present, as determined by the EDXRF analysis. This metal probably comes from lead white. Iron oxide $(\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O})$ according to the peaks at 397 and 300 cm^{-1} that are present in the FTIR spectra. Unfortunately, XRF cannot identify amorphous carbon detected by FTIR spectroscopy in the dark yellow colour, which according to FTIR analysis is a mixture of yellow iron oxide, calcium carbonate.

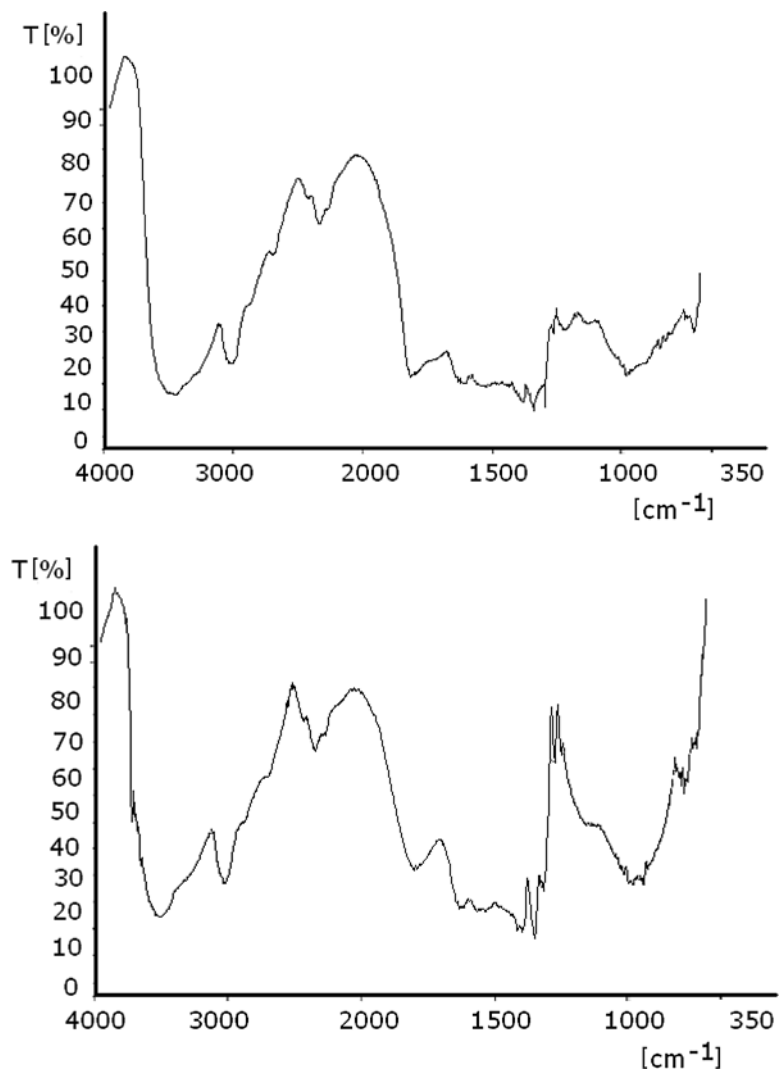


Fig. 3 – The FTIR spectra of non-restaured (up) and restaured Gospel (down).

A very weak band at 962 cm^{-1} , due to the presence of the calcium phosphate $[\text{Ca}_3(\text{PO}_4)_2]$. This compound is usually related to the presence of carbon black of animal origin, thus, the carbon black is in fact bone black. EDXRF analysis shows the presence of iron and calcium, coming probably from Prussian blue and calcium carbonate [16–18].

The absorptions of the SO_4^{2-} ion in the BaSO_4 found in the pigments, with the corresponding absorptions found by other authors for mineral BaSO_4 (barite). Such results could be corroborated with the thermogravimetric analysis of Gospel paper, which indicated that the paper is strongly degrading starting at

294°C at which the weight loss exceeds 58%. Under heating, the studied compounds undergo three main processes: dehydration, thermal degradation and oxide formation, all these indicating that the residue is due to BaSO₄.

Also, the paper appear to contain α -quartz, two of whose transverse lattice vibrations produce the pair of absorptions at 794–797 and 780 cm⁻¹ in the samples. The 1033 and 1008 cm⁻¹ bands in pigment occur in positions in which certain silicate minerals (particularly clays) absorb and may be due to such a component [19], probably celadonite and glauconite which may be regarded as derivatives of muscovite, KAl₂(AlSi₃)O₁₀(OH)₂. The most important differences are that in both of the green earth minerals the two octahedrally-coordinated Al³⁺ ions of muscovite are partially or totally replaced by Mg²⁺ or Fe³⁺, and the tetrahedral Al is at least partially replaced by Si [20].

The other absorption bands of interest in identifying these minerals occur below 500 cm⁻¹ and are known to be very sensitive to variations in the octahedrally-coordinated ions in these structures, and particularly to Fe³⁺. The triplet of bands at 494, 457, and 442 cm⁻¹ occurs in virtually the same position in the two dry green earth pigments (celadonite) and in the glauconite sample, which indicates a similarity in octahedral ion compositions.

The Cr₂O₃ dry pigment whose spectrum is given here was not further ground, in which sample preparation included careful grinding. In Cr₂O₃, each O₂⁻ is coordinated by four Cr³⁺ in a distorted tetrahedron [21]. The strongest bands, at 632 and 566 cm⁻¹ in Cr₂O₃, do not correspond to specific O₂⁻ displacements and are probably due to various combinations of O₂⁻ and Cr³⁺ displacements in the lattice. The pair of sharp bands at 443 and 416 cm⁻¹ corresponds to two specific O₂⁻ displacements in the lattice. The hydrated oxide (viridian) has not been studied, but the absorptions are probably due to similar types of displacements, whose frequencies have been shifted due to the presence of water in the structure [22–30].

In the ancient times usually a very stable carbon black inks were used for writing, so the colour remain unchanged over many centuries [1–3, 16, 17]. Knowledge about inks composition was crucial as it implied the eventual choice of chemicals which could be applied without destroying the document. In the case of the Romanian Gospel letters were whitish, therefore it was important to analyse elemental composition of the ink. The decision concerning conservation treatment should always be preceded by a careful analysis of the object. K and Na were found in investigated ink samples, but lead was the main element of both: white and black inks. We presume that the pigment is a phthalocyanine one. Phthalocyanine blue, C₃₂H₁₆N₈Cu, exists in polymorphic forms, the two most common of which are designated α and β [31–33].

In the mid-infrared region, the phthalocyanines give very distinctive spectra which (particularly below about 1700 cm^{-1}) contain many sharp bands due to stretching deformations of the aromatic ring system carbon-carbon bonds, and in-plane and out-of-plane bends of the carbon-hydrogen bonds in the ring system. Fig. 4 shows the full spectrum of a dry copper phthalocyanine pigment and an expanded portion of its spectrum. This paper is also extended with BaSO_4 , which is often the case with the strongly tinting phthalocyanines; the bands at 1186 , 1120 , 1082 , 983 , 638 , and 610 cm^{-1} are due to this sulfate compound. In spite of these interferences, the pigment is readily identifiable, and the polymorph may be definitely established as α on the basis of the sharp band at 723 cm^{-1} , due to out-of-plane bending of C-H bonds. This band is located at 730 cm^{-1} in the β modification. The dry pigment is also the α polymorph.

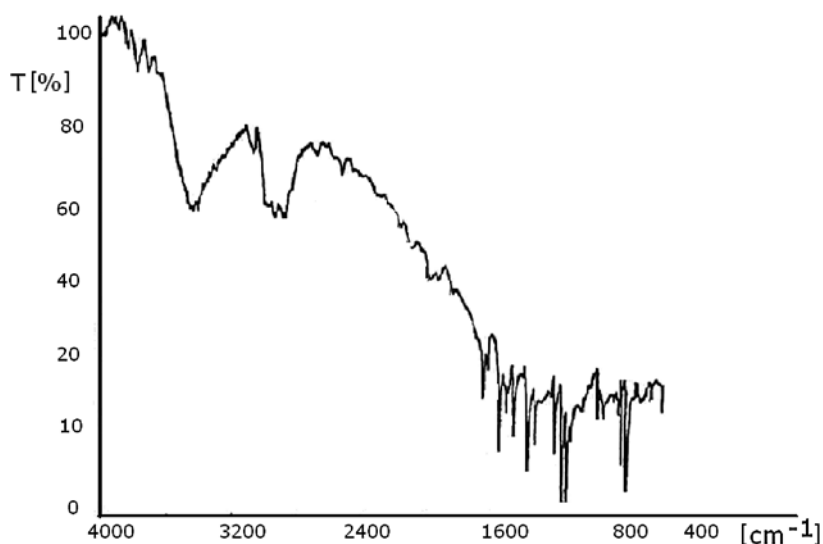


Fig. 4 – FTIR spectrum of Cu-Phthalocyanine.

4. CONCLUSION

From this work we can conclude that EDXRF is a good elemental technique to identify and to distinguish different kinds of paper with the advantage of being non-destructive, which is quite important since we are analysing ancient documents with historical value. Since old documents generally present a bigger number of trace elements, we can say that this technique permits the distinction between old and modern documents. As final remark we can say that this work is a contribution to enlarge the applications of EDXRF, FTIR, ICP-AES, DSC, DTA, TG as some easy tools for identifying and characterizing different paper manufacturing and ink composition.

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