



ANALYTICAL METHODS FOR ARTEFACTS COMPLEX ANALYSIS

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Knowledge of detailed chemical composition of materials used in the past may significantly affect methods of restoration and conservation. Among the materials composing the art object, organic compounds used as binding media or protective coatings have attracted the attention of the conservation profession given their noticeable ability for undergoing morphological and chemical changes on ageing. Thus, the aim of this paper is to review the most recent advances in our work regarding archaeometry. Spectroscopic techniques, such as UV-Vis, FTIR and thermal analysis (TG, DSC, DTA), ICP-AES, radiation-based analytical methods (EDXRF, XRD) have been coupled with light microscopes for these purposes. Finally, a number of new instrumental techniques have been proposed as a suitable alternative to the conventional microscopy techniques for morphological studies.

INTRODUCTION

Many important objects of cultural heritage are material objects and objects of art produced by communities. The preservation of different artefacts for future generations with the best possible fidelity requires in-depth knowledge, in order to change the most suitable restoration, conservation, storage, and eventual museum display. The modern methods of chemical analysis appear significant data for such objects providing information on the most suitable methods of their restoration and conservation. Modern chemical analysis offers numerous methods and measuring techniques which can be employed for archaeometric purposes. The physico-chemical characterization of archaeological objects has an essential contribution for culture heritage. There is wide enthusiasm among conservators and curators for the application of analytical tools to enhance the management of collections.

In spite of some contrary position regarding the utility of physical techniques, we still believe that the processing process of their results and knowledge/correlation with chemical data is without doubt, essential for correct results and correct recommendation for restoration and conservation process. That's why in this paper will be treated and correlated different results obtained from different analytical techniques, usually non-destructive, applied to different artefacts.

Non-destructive methods find a particular place among analytical methods used for archaeometric purposes because of the unique value of most of the objects analyzed. Their principal advantage is the lack of necessity for sampling from objects, and in the case of modern portable instrumentation there is also the possibility of performing measurements on-site. Most commonly these methods are employed for elemental analysis, but in recent decades they have also been used for determination of different groups of compounds.

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The most useful technique is XRF (X-ray Fluorescence) which is an analytical technique, which is widely employed for the analysis of elemental composition in materials. When an object is irradiated with a beam of X-rays, it causes the atoms of each element present to fluoresce at characteristic wavelengths. Utilizing a spectrometer, it is possible to separate the resulting wavelengths and identify the elements present in the sample site. The amount of each element in the sample can be determined by measuring the intensity of the fluorescence.

Scanning electron microscopy has been extensively used for the material characterization of objects of artistic and archaeological importance, especially in combination with energy dispersive X-ray microanalysis (SEM/EDX).

In addition to microscopy and chemical analyses, X-ray diffraction (XRD) analysis is suitable for the identification and differentiation of binders.

The basic principle of XRD is that each crystalline substance has a characteristic arrangement of atoms which diffracts X-rays in a unique pattern. X-ray reflection on lattice planes occurs according to Bragg's Law.

Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) can also be used, due to the very small amount of sample needed. In this technique, flame represents the source, in that its heat is used to promote atoms into an excited state where they undergo subsequent emission of photons.

FTIR (Fourier Transform – Infrared Spectroscopy) provides specific information about chemical bonding and molecular structure.

Thermogravimetric analyses involve measuring the thermal variations associated with the physical and chemical reactions which occur due to heating of the specimen. TG analysis allows to obtain data regarding the content of bound water, which is the weight loss in the temperature range 200-600 °C and data regarding the content of CO₂ released during the decomposition of the carbonate phases, which is the weight loss >600 °C.

ARCHAEOMETRIC STUDIES

Metal artefacts

For metallic objects, radiation based techniques (XRD, EDXRF) proved to be the most useful techniques. For example, let's take the results obtained for a Roman mirror, from the Castrum of Cohort I Britannica milliaria, from Caseiu, which was dated as a II century artefact, provided by National History Museum of Transylvania – Cluj-Napoca, and a private coin collection (dating from 1867 to 1945). The main element in this piece was copper, and lead is present less than 10% (the literature data offering the value of lead around 17%). Tin is present on a concentration of around 20%. The XRD analysis (Fig. 1) revealed the intermetallic alloys such as Cu₈₁Sn₂₂ and Cu_{5,6}Sn and also the presence of lead.¹⁻⁴

A second aspect of the analysis, beside the optimization of the alloy to the final product, would be progressive decay of the metal alloys, with the military, political and economic crisis, from the middle of the IIIrd century, known as military anarchy.¹ By means of optical microscopy, the corrosion products present at the surface of the mirror were analysed, confirming the presence of cuprit and cuprous chlorides.

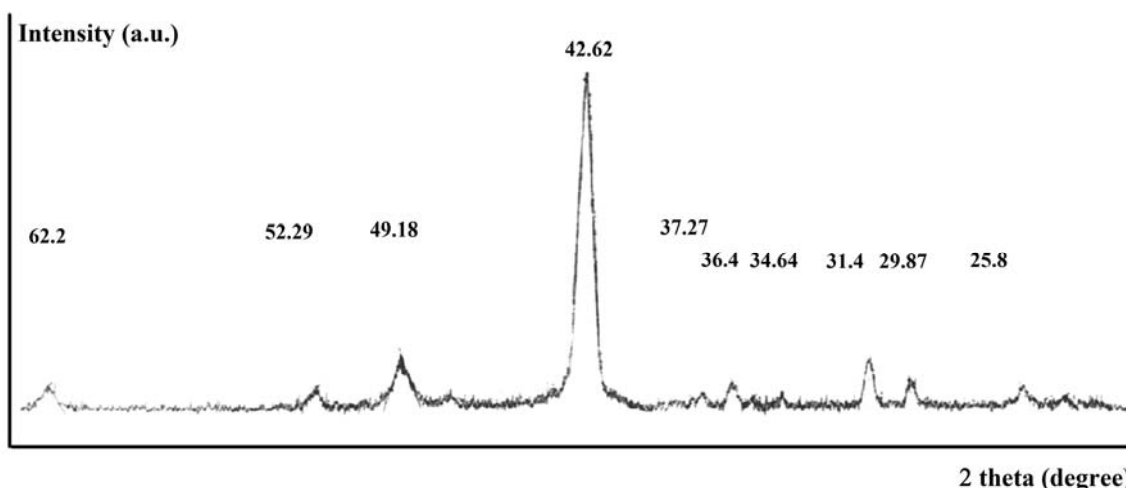


Fig. 1 – XRD results for the Roman mirror.

Other materials analysed were some Roumanian coins. For the Roumanian coins study, was followed the chemical composition of the alloys, the corrosion products that appear, as well as the correlation chemical composition-historical age. By means of XRF, the coins studied could be divided in to three categories: Ag/Cu alloys (coin from 1900 and coin from 1944 of great value), Cu/Zn alloys (coins from 1930 and 1945) and

Cu/Sn alloys, where Zn is present (coin from 1867 of small value).

The correlation of the alloys used with the historic age was made considering the historic realities of the time. Optical microscopy (Fig. 2) and classic chemical analysis helped to identify the corrosion products as cuprit and cuprous chlorides, as well as in the case of the Roman mirror.

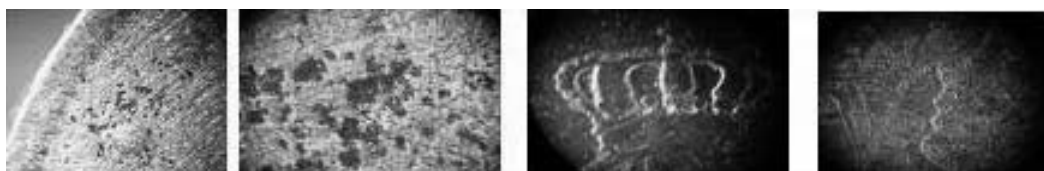


Fig. 2 – The surface morphological features observed via optical microscopy for some of the coins analyzed.

Hystorical paper artefacts

The Roumanian Gospel from 1740 (Fig. 3) is from a private collection.⁵

EDXRF analysis (Fig. 4) of the Roumanian Gospel paper corroborated with ICP-AES, data showed the presence of Pb, Ca, Mn, Zn, Ba, Si, Al, Na, K, Fe₂O₃, CaCO₃, ZnO, BaSO₄, SrCrO₄, K₂O, Na₂O, Al₂O₃, Ca₃(PO₄)₃.



Fig. 3 – Roumanian Gospel from 1740.

The FTIR spectrum (Fig. 5) shows a 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 favour of the identification of hydrocerussite ((PbCO₃)₂·Pb(OH)₂), a compound currently used in painting when associated with cerussite ((PbCO₃)₂) and called lead white. 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.

The absorptions of the SO₄²⁻ ion in the BaSO₄ found in the sample is similar with the corresponding absorptions found by other authors for mineral BaSO₄ (barite).⁶ 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.

Eight different types of papers from books of the XIXth and XXth centuries were also studied.^{6, 7} The FT-IR analysis of the samples from the ancient manuscript clearly shows the cellulose being the major component of the sample. Despite the main goal of the IR characterization was achieved, few vibrations are identified rather approximately. Therefore, some comments regarding interpretation of IR spectrum presented are fairly speculative. Consequently, the exact origin or history of some grouping is not exactly known. Though an exact identification of an artifact paper cannot be entirely possible, due to the similarity of spectra of different compounds, the general classification still remains the principal topic for the conservation. The next goal is to identify as many types of filler as possible, for historical paper, to establish a reliable method of preservation and to evaluate the age of the paper. The papers were delivered from private collections. The eight samples were codified from M1 to M8, each representing a different book (M1 sample from a French book, Paris, 1871, M2 sample from a French book, Paris, 1913, M3 sample from a Roumanian book, Bucharest, 1914,

M4 sample from a French book, Paris, 1929, M5 sample from a German book, Berlin, 1931, M6 sample from a French book, Paris, 1935, M7

sample from a Roumanian book, Bucharest, 1888 and M8 sample from a Roumanian book, Bucharest, 1889).

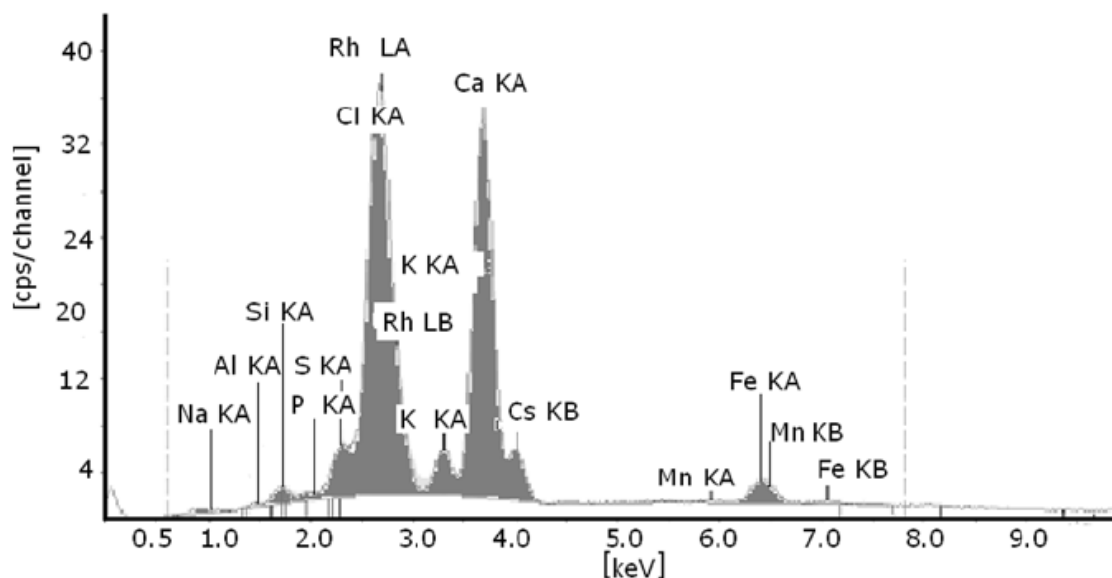


Fig. 4 – EDXRF spectrum of paper.

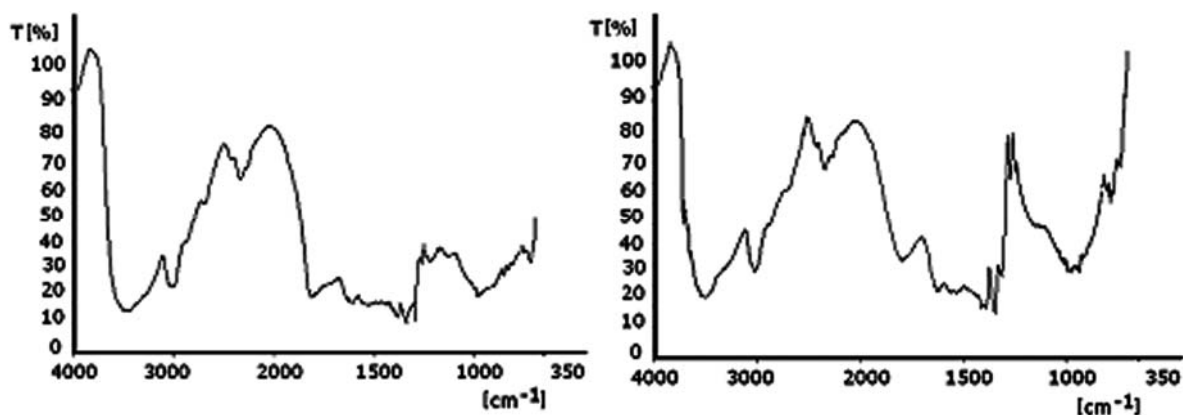


Fig. 5 – The FTIR spectra of non-restaurated (left) and restaurated Gospel (right).

The samples were from the edges of the sheets, unwritten and uncolored.

Different fillers were used for comparison: calcium sulfate dihydrate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, anhydrous calcium carbonate, CaCO_3 , anhydrous barium sulfate, BaSO_4 , kaolin, $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, aluminum sulfate, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, zinc oxide, ZnO , titanium dioxide, TiO_2 , talcum, $3\text{MgO} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$. All the reagents were reactive grade (Merck, Germany).

FTIR analysis is considered “non-destructive” since the procedure does not alter the sample, allowing it to be used for subsequent analysis. In reality, very small quantity of sample (0.5 up to 1.0 mg) was scratched out from the edge of the papers.

Furthermore, in order to better define the elemental composition of the papers EDXRF has been used.

Figs. 6-10 are presented the FTIR spectra of standard microcrystalline cellulose (Fig. 6), the eight paper samples (M1- M8, in Figs. 7 and 8) and 9 inorganic substances used as fillers’ (Figs. 9 and 10), while Fig. 11 presents an EDXRF spectra for M3 paper.

In direct connection with the elemental analysis, the FTIR technique has been applied to some possible fillers’ (kaolin, calcium carbonate, calcium sulfate, barium sulfate, zinc oxide, titanium dioxide, talcum, aluminum sulfate) already mentioned in the literature’s recipes for historical paper.⁶

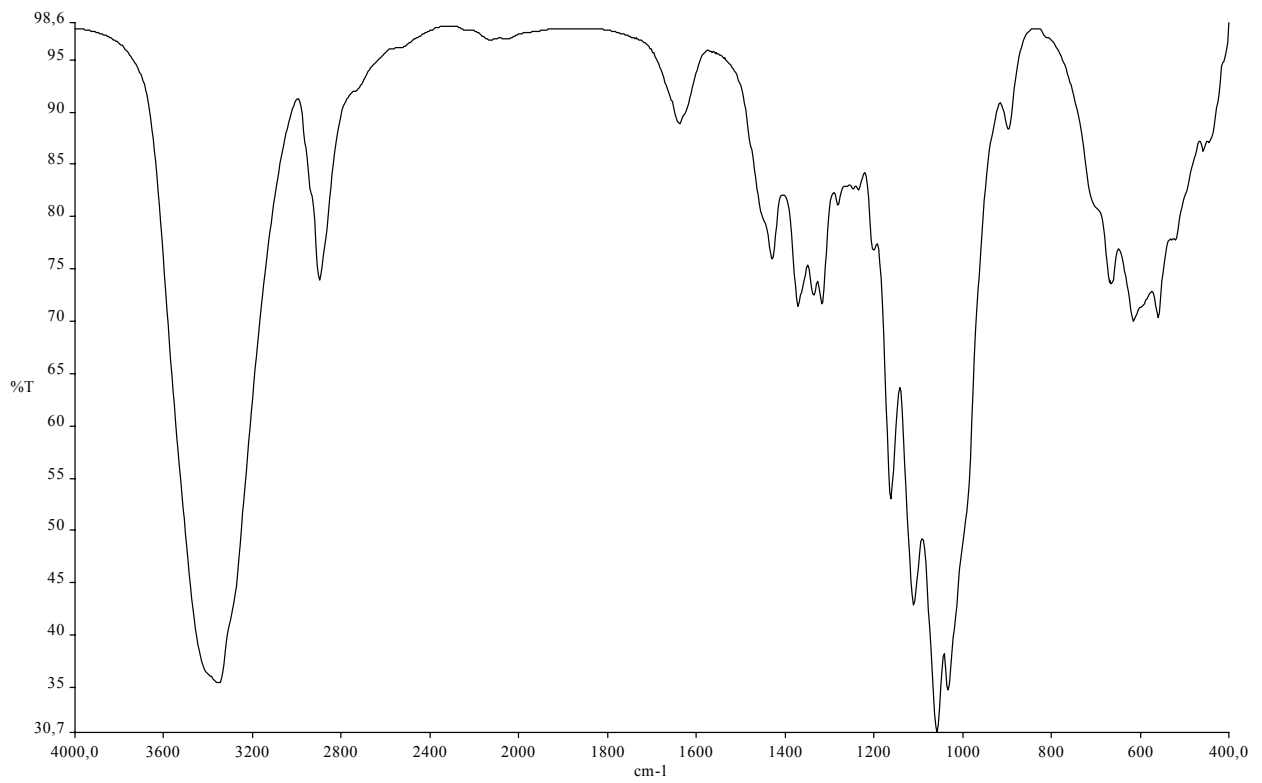


Fig. 6 – FTIR spectra of microcrystalline cellulose in KBr pellets.

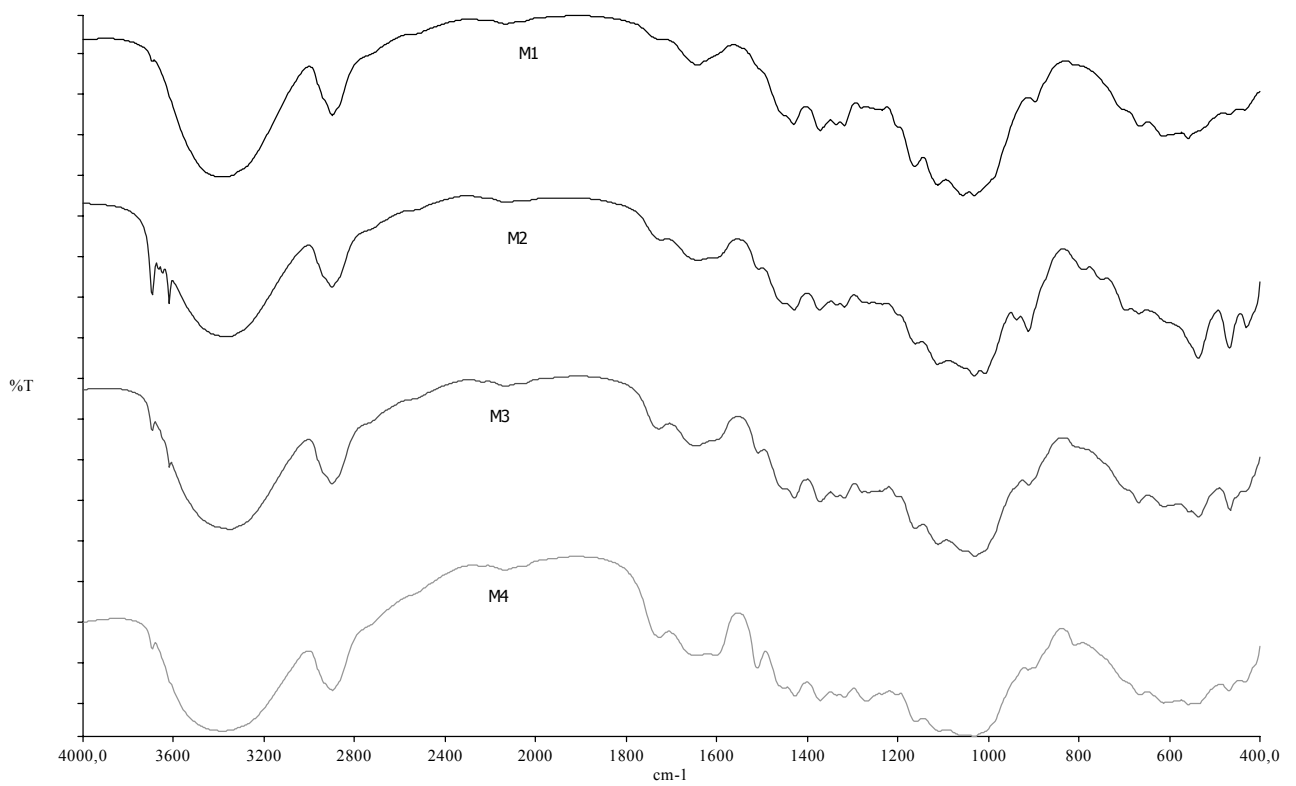


Fig. 7 – FTIR spectra of different types of papers in KBr pellets.

M1 – M1 paper, M2 – M2 paper
M3 – M3 paper, M4 – M4 paper

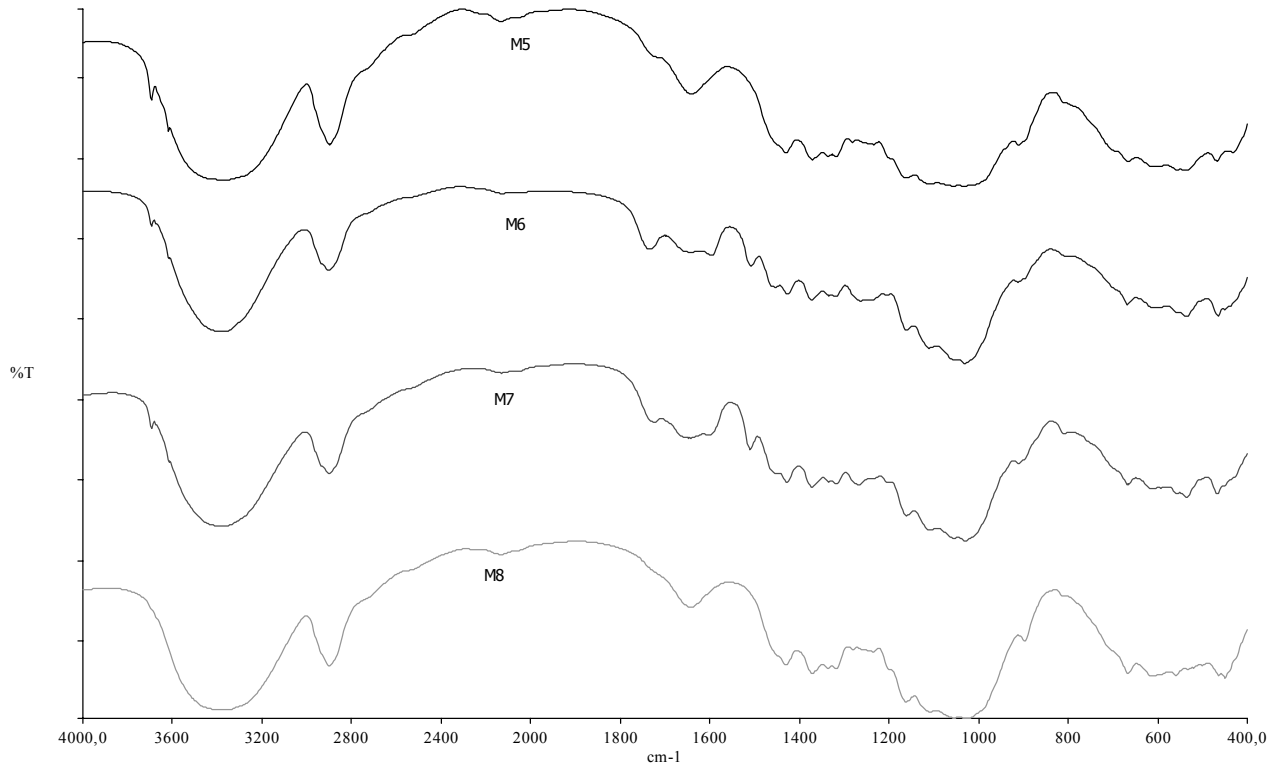


Fig. 8 – FTIR spectra of different types of papers in KBr pellets.

M5 – M5 paper, M6 – M6 paper
M7 – M7 paper, M8 – M8 paper

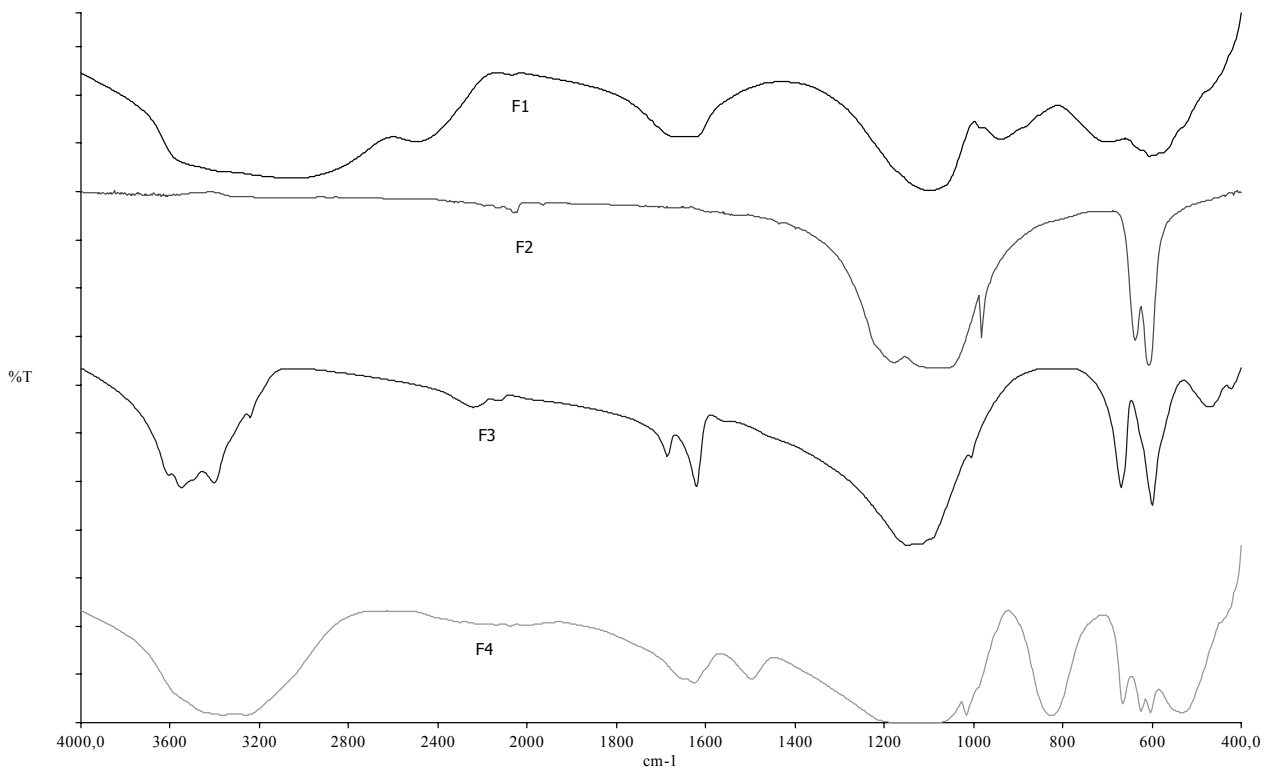


Fig. 9 – FTIR spectra of different types of sulfate fillers in KBr disk.

F1 – Aluminium, F2 – Barium
F3 – Calcium F4 – Ferrum

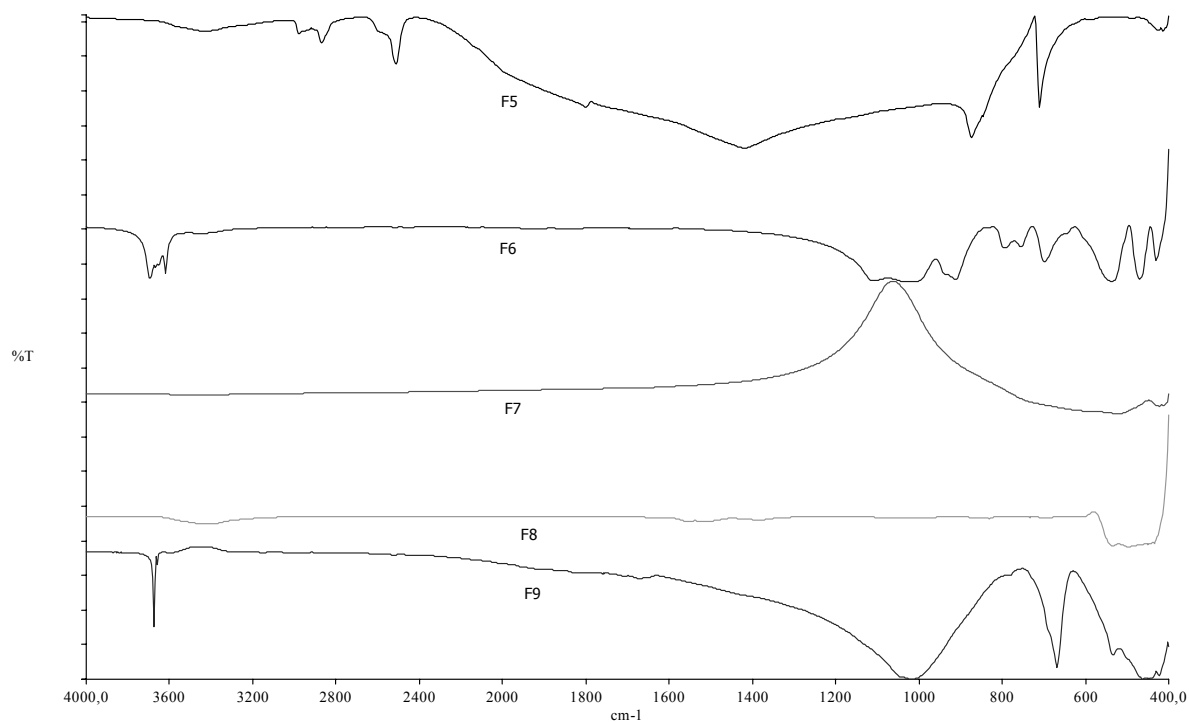


Fig. 10 – FTIR spectra of different types of fillers in KBr disk.

F5 – CaCO₃, F6 – Kaolin
 F7 – TiO₂, F8 – ZnO
 F9 – Talc

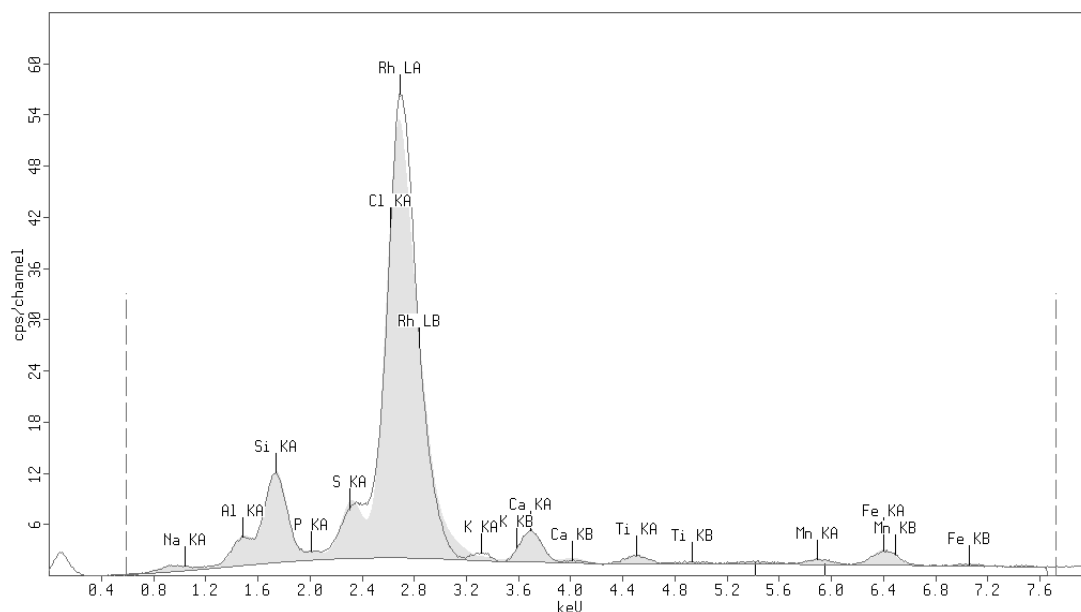


Fig. 11 – EDXRF spectra for M7 paper (similar results were obtained for all the samples).

Ceramic artefacts

Sampling, reported in Table 1, was performed at the ruins of the Schneckenberg culture, Dealul Melcilor, Braşov, Roumania. It is interesting that in this region concerved many cultures (Vatina, Gârla Mare, Luciu de Sus, Wietenberg and

Otomani). The ceramic samples were dated back to the XVIth century. Other samples of ceramics were from stove ornaments (Medieval Customs, Bran, Braşov) and from Tropaeum Traiani (Adamclisi, Constanţa). All the ceramic samples contain as degreasing agent limestone shell.⁸⁻¹⁰

Table 1
Pottery samples used for the study

No.	Sample	Observation
1	Ceramic	Black
2	Ceramic	Grey
3	Ceramic	Red
4	Ceramic	White
5	Ceramic	Green
6	Ceramic	Brown
7	Ceramic	Braşov
8	Ceramic	Teracota Braşov site
9	Ceramic pot	Braşov
10	Ceramic pot	Tropaeum Traiani site

Thermal analysis (Fig. 12) – a powerful tool for the characterization of pottery – allows us to conclude that the chemical and phase composition, as well as the history of manufacture of these two Bronze Age pottery samples found in different archaeological complexes are also very similar. This allows us to conclude that the archaeological pottery was fired at relatively high temperatures. The thermal behavior of such samples is coherent with their chemical and mineralogical composition.

Few weight loss events are seen in the TG and DTG curves. The first one at 50-70 °C is related to the evolution of the physically adsorbed water by

the particles, The second loss is at 300-400 °C, with a large exothermic peak around 325 °C due the organic matter decomposition, was observed for all studied samples. The last one appears at 400-450 °C, whose total weight loss is in the 1-3 % range. This peak could be responsible for Kaolinite whose dehydroxylation is seen at 400-450 °C where metakaolinite is generated. By losing the hydroxyl groups, metakaolinite transforms into three phases – mullite, a transition alumina phase and silica.

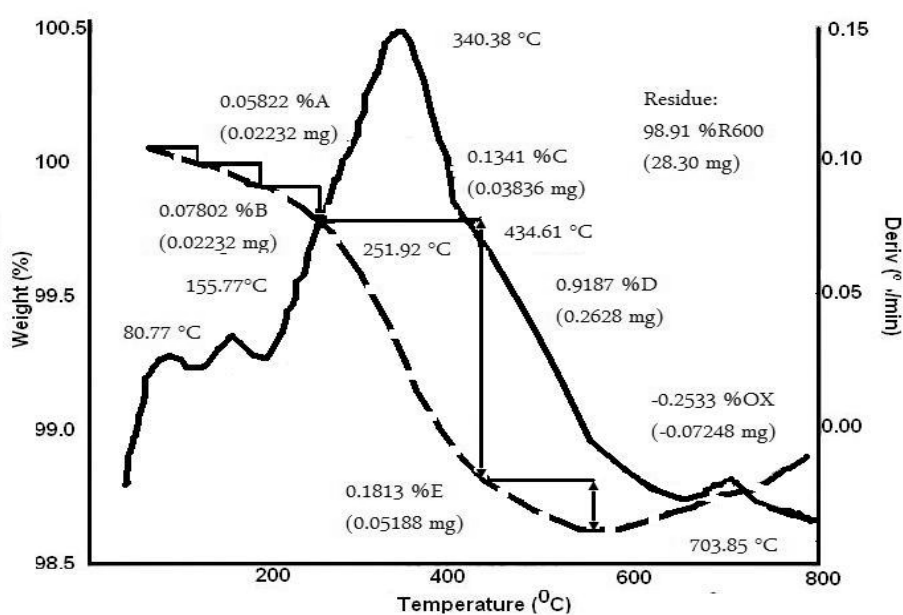


Fig. 12 – DTA diagram for the white ceramic sample.

The most common clay minerals (kaolinite, illite and smectite) could be responsible for the strong endothermic effects within the range 550-650 °C (somewhat higher for chlorite) in the ceramic samples from Brasov not colored, but glazed. These results confirm the predominance of the kaolinite clay mineral in the studied samples, and are consistent with X-ray diffraction (Fig. 13).

An important factor is the carbonate content (Ca-rich – Fig. 14 – or Ca-poor – Fig. 15 – raw clays). Quartz, feldspars are mainly preserved in

Ca-poor ceramics. The decomposition of calcite (in an oxidizing atmosphere) occurs at a lower temperature than for illite. As a consequence, there is free CaO until about 800°C and it can react at higher temperature with clays and SiO₂, forming new silicate phases. In a reducing atmosphere the breakdown of illite and calcite runs almost parallel, and due to increased CO₂ partial pressure, the dissociation of calcite is shifted to higher temperatures (as well as the formation of CaO).

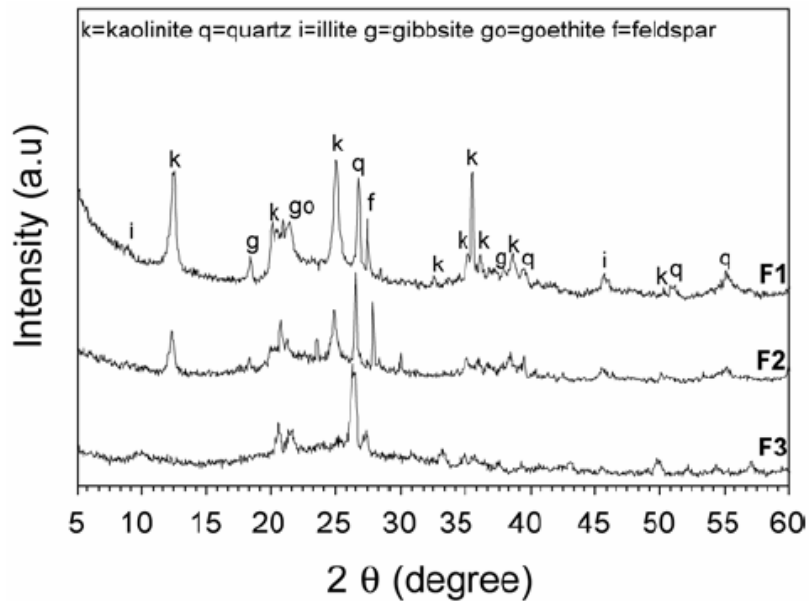


Fig. 13 – XRD spectrum of different clay minerals.

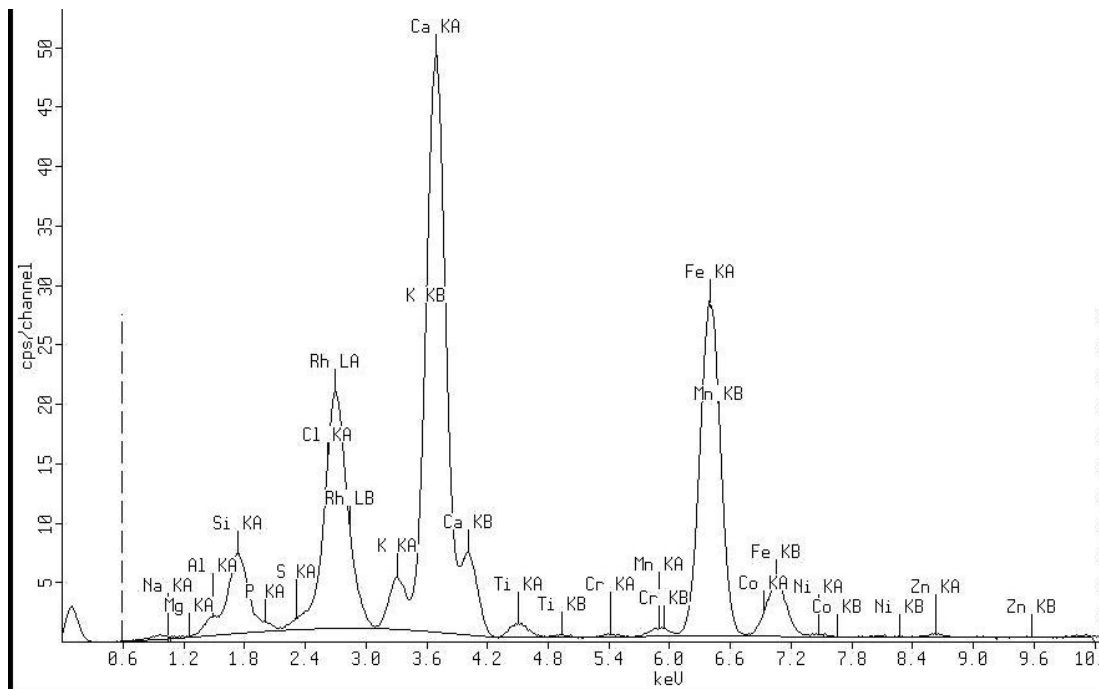


Fig. 14 – EDXRF spectrum of Ca-rich ceramic.

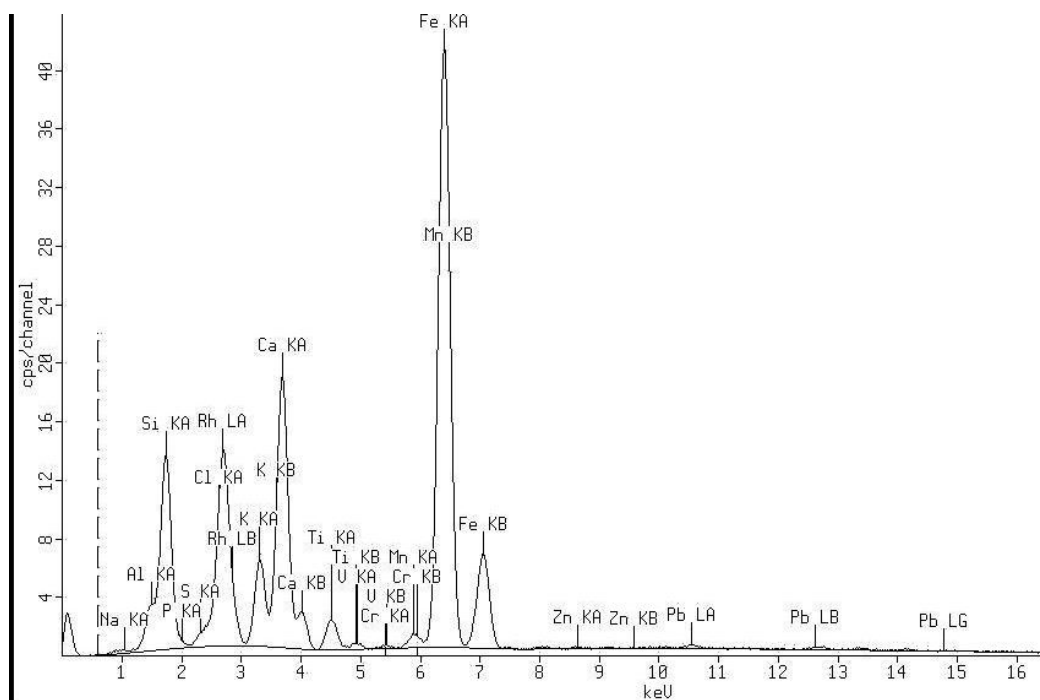


Fig. 15 – EDXRF spectrum of Ca-poor ceramic.

CONCLUSIONS

The scientific study of artwork and archaeological artefacts is an area which is expanding rapidly, and many new research groups are becoming established therein. A very large number of exciting new avenues will undoubtedly open up in the future as the artificial separation of the arts and the sciences is reduced, largely by the efforts of scientists throughout the world.

This review does not aim to be an exhaustive summary of all the techniques which can be applied in the field of cultural heritage research, but a short overlook of our own experience.

The results have demonstrated that spectroscopic analyses are indispensable tools in discovering some special technological features of artifacts.

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