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ANALYTICAL METHODS HELPING THE ARCHAEOLOGISTS: ARCHAEOMETRY

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ABSTRACT

Very important objects of cultural heritage are material objects and objects of art produced by all communities. The physical and mechanical properties of material culture are always of prime concern to archaeometry and science-based archaeology. The preservation of material culture for future generations with the best possible fidelity requires in-depth knowledge, to aid the most suitable restoration, conservation, storage, and eventual museum display. A wise utilization of modern methods of chemical analysis is a significant element of research studies into such objects providing information on the most suitable methods of their restoration and conservation. There is wide enthusiasm among conservators and curators for the application of analytical tools to enhance the management of collections.

Modern chemical analysis offers numerous methods and measuring techniques which can be employed for archaeometric purposes. This paper is a short overlook to the analytical methods currently applied in archaeometry, as well as our own group experience concerning this subject.

KEYWORDS: archaeometry, analytical methods

1. Introduction

All communities, in diverse ways, attempt to preserve their cultural heritage, as it is the main element of their identity within modern civilization. The different directions and ways in which these processes are realized depend on the particular stage of development of science and technology, welfare of society, and encountered dangers of this identity.

A wide availability of modern analytical instrumentation and methods for thorough quantitative and qualitative analysis of various materials are increasingly employed in recent decades in archaeometry. In fact, physico-chemical characterization of archaeological objects has essentially contributed to the progress in studies of culture heritage. This also has broadened the knowledge of technologies used and of the materials employed in the past, and have led to significant historical conclusions, and has provided new information about trade, human migration, and penetration of various cultures and technological trends. Some of those methods give also a way for dating historical objects, which is an important contribution in identification of archaeological objects. Knowledge of detailed chemical composition of materials used in the past may significantly affect methods of restoration and conservation. Information about possible routes of chemical degradation of various materials is often helpful when identifying materials employed in the past, and also may result in the development of effective methods to preserve particular objects to be protected from further deterioration.

Literature about archaeometric applications of chemical analytical methods is abundant, albeit dispersed between journals dedicated to archaeology, history of art, art conservation and analytical chemistry. Modern chemical analysis offers numerous methods and measuring techniques which can be employed for archaeometric purposes. Advances in their use have already been the subject of several books [1–4], review papers [5–7], and even recent special issues of analytical international journals, e.g., X-Ray Spectrometry in 2000, Journal of Separation Science in 2004, or Microchimica Acta in 2007. From the point of view of application to an investigation of archeological and art objects, it is often important to use both nondestructive (which can be in some cases fully noninvasive) methods as well as destructive methods of modern microanalysis for analysis of small samples. As information about given objects or artistic techniques based only on historical sources may often lead to serious misinterpretations, there are numerous different purposes for the application of chemical analysis in archaeometric studies. They may be extremely valuable in the investigation of the provenance of an object and the origin of the materials used for its manufacture, and in addition in determining its degradation state and monitoring the transformations that happen during the ageing process. They are also useful when choosing the most suitable methods of restoration and conservation, the type of materials for conservation, and also in monitoring the progress of conservation processes. Various analytical methods can also be employed for dating of material objects and identification of fake art objects. Earlier works in this field concentrated mainly on analysis of inorganic materials [1]; however, in the last two decades substantial progress in high-performance separation techniques has allowed detailed determinations of various groups of organic compounds essential for materials studies (dyes, resins, oils, waxes, carbohydrates, and proteins). Nondestructive 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. These methods are most commonly employed for elemental analysis, but in recent decades they have also been used for determination of various groups of compounds.

2. Analytical methods in archaeometry

The first applications of chemical analysis in the examination of historical objects appeared at the beginning of the twentieth century with the use of microchemical techniques and numerous spot tests providing information about particular inorganic and organic constituents. They are typical destructive methods of analysis, requiring material sampling and usually its dissolution. Despite significant progress in analytical instrumentation, these methods nowadays still play an essential role in investigation of historical objects. FTIR (Fourier Transform – Infrared Spectroscopy) provides specific information about chemical bonding and molecular structure. The mineralogical composition was determined on the basis of FTIR spectra and pigments, too.

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 ^{o}C and data regarding the content of CO_2 released during the decomposition of the carbonate phases, which is the weight loss >600 ^{o}C.

In addition to microscopical 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.

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.

Many examples of EDXRF applications can be found in the literature for the analysis of pigments of works of arts, e.g., pigment identification in manuscripts [8], in polychrome sculpture [9], etc. EDXRF has also been employed in studying the weathering products of historic glasses [10] and coins [11] as well as the provenance and dating of ancient Chinese porcelain [12]. Furthermore, the portable EDXRF spectrometer and new forms of XRF, such as micro X-ray fluorescence (μ-XRF) and total reflection X-ray fluorescence (TRXRF) have been introduced and applied to the analysis of works of art.

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). The advantages and limitations of SEM/EDX are presented in a few case studies: analysis of pigments in cross-sections of paint layers, quantitative analysis of archaeological glass from the Roman period, and investigations on glasses with medieval composition concerning their weathering stability and degradation phenomena.

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.

3. Archaeometric studies

3.1 Metal artefacts

The analysed materials were a part of roman mirror, from the castrum of cohorta I Britannica Milliovia, from Caseiu, which was dated as a II century artifact, provided by National History Museum of Transylvania – Cluj-Napoca, and a private coin collection (dating from 1867 to 1945)

For the first material studied, some literature data have been found for bronze roman mirrors (speculum); their compositions indicate a high content of tin (20%), and lead (max. 17%). Romans did not use only bronze. They produced alloys with different composition. Thus, the best quality is in the military artefacts or bronze chains. In the investigated sample, copper is the main element in the alloy, and the lead is present less than 10%. Tin is present on a concentration of around. 20%. The XRD analysis (figure 1) revealed the intermetallic alloys such as $Cu_{81}Sn_{22}$ and $Cu_{5,6}Sn$ and also the presence of lead.

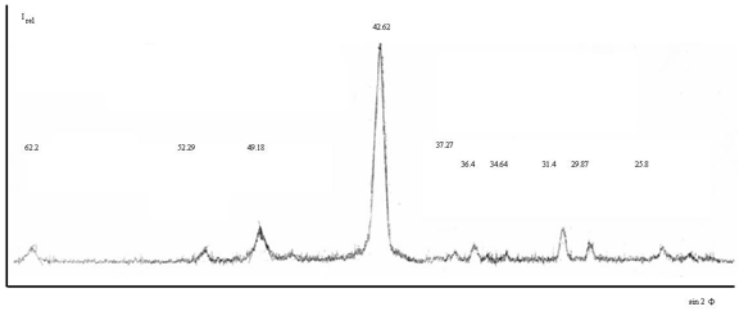

Fig. 1. *XRD results for the roman mirror*

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 [13, 14]. 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 economical crisis, from the middle of the III century, known as military anarchy.

It must be said that this evolution should not be assigned only to the economical crisis.

The second materials analysed were some Romanian coins [11].

For the Romanian coins study, was followed the chemical composition of the alloys, the corrosion products that appear, as well as the correlation chemical composition-historical age.

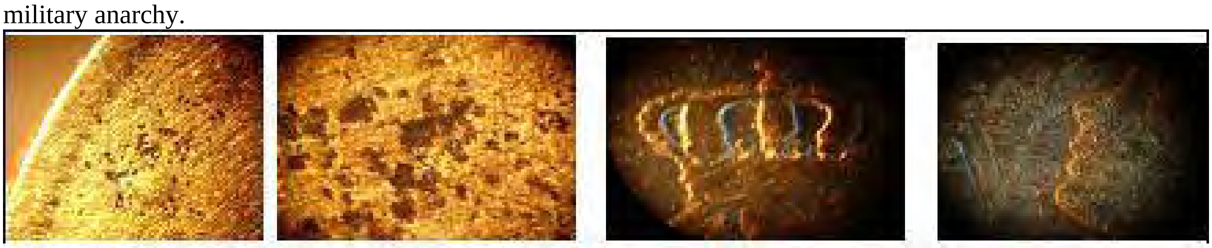

Fig. 2. *The surface morphological features observed via optical microscopy for some of the coins analyzed*

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)

-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 (figure 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.

3.2 Ceramic artefacts

The ceramic material analysed was a stowe ornament from the XVII th – XVIIIth century from the Medieval Custom, Brasov, provided by the Regional History Museum Brasov. The high content in Zr, Sc and Sn could be explained by erosion phenomenon, causing saprolit, confirmed by the decrease in Cl, Co, Cu, V, Mn and rare heavy earth elements Sm, Gd, Dy, Ho, Er, Yb and Lu. The analysis performed manages to identify the components of the ceramic support material, as well as the pigment composition [15]. The ceramic pigments offer a large variety of colours. In figure 3 is presented the FTIR spectrum of the blue pigment.

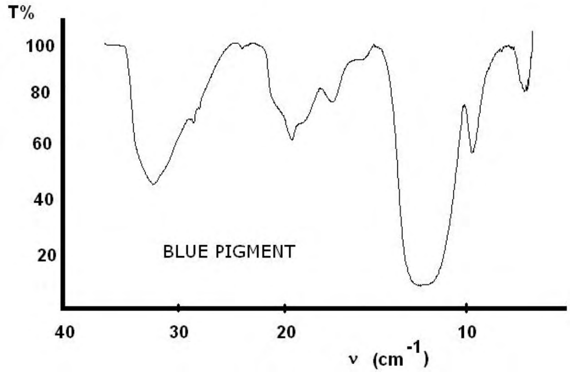

Fig. 3. *FT-IR spectrum obtained for the blue pigment*

3.3 Glass artefacts

To analyse the ancient glass, we have used small pieces of broken glass without any possibility to be included in other pieces, provided by the Regional History Museum Brasov (figure 4) [10]. Different coloured glass (brown, green, uncoloured) were quantitatively analysed by EDXRF. Assuming that each kind of glass can be characterized by a specific composition of major, minor and trace elements, the selection of appropriate analytical methods is essential. In this work, ICP-AES was used complementary to EDXRF which gives an overall view of the samples’ composition. By applying ICP-AES, it was possible to determine a number of elements which are present bellow the detection limit of EDXRF and to evaluate the homogeneity of investigated material. It was possible to determine new elements which could not be determined by others techniques.

Fig. 4. *The pieces of glass analyzed*

3.4 Hystorical paper artefacts

The Romanian Gospel from 1740 (figure 5), is from private collection, and all the investigations did not damaged this piece of art [8].

Fig. 5. *The picture of Romanian Gospel from 1740.*

EDXRF analysis of the Romanian Gospel paper corroborated with ICP-AES, data showed the presence of Pb, 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, $Ca_3(PO_4)_3$. The FTIR spectrum 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 ($(PbCO_3)_2 \cdot Pb(OH)_2$), a compound currently used in painting when associated with cerussite ($(PbCO_3)_2$) 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 SO_4^{2-} ion in the $BaSO_4$ found in the sample, 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 $BaSO_4$.

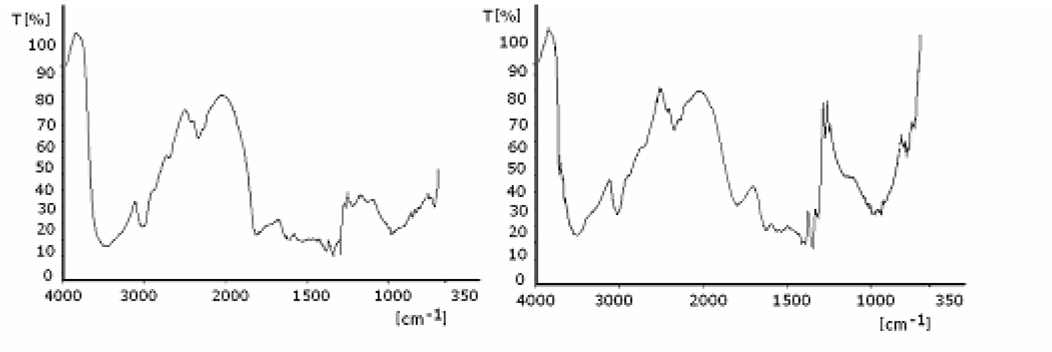

Fig. 6. *The FTIR spectra of non-restaurated (left) and restaurated Gospel (right).*

From the work done on the Romanian Gospel, we concluded 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.

4. 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.

There is no doubt that current research has strengthened the multidisciplinary community in this field. It has enhanced the capability for answering questions related to museum objects, which could not readily be solved, and the exchange of knowledge in both directions. 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.

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