Studii şi Cercetări Ştiinţifice 2011, **12** (1), pp. 017 – 024
Chimie şi Inginerie Chimică, Biotehnologii, Industrie Alimentară

Scientific Study & Research
Chemistry & Chemical Engineering, Biotechnology, Food Industry **ISSN 1582-540X**

ORIGINAL RESEARCH PAPER

ANALYTICAL METHODS IN ARCHAEOMETRY: STUDY OF SUPPORT MATERIAL[♦]

Irina Dumitriu[1,2*], Radu Claudiu Fierascu[1,2], Rodica Mariana Ion[1,2]

[1] "Valahia" University, Mechanical Engineering, Mechatronics and Robotics Department, 18-20 Unirii Blvd., 130082, Targoviste, Romania
[2]National Research & Development Institute for Chemistry and Petrochemistry - ICECHIM, Analysis Department, 202 Spl. Independentei, 060021, Bucharest, Romania

*Corresponding author: dumitriu.irina@yahoo.com

Received: July 21, 2010
Accepted: December 20, 2010

Abstract: The application of some analytical techniques developed initially in materials science (techniques based on physical-chemical phenomena) in the study of art and archaeological objects offers the historian and archaeologist quantitative information that can prove useful in order to better understanding of ancient society. 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. The use of analytical techniques often proves useful for the specialists in conservation and/or restoration due to the valuable information given (composition, state of degradation, and so on). This paper describes the use of some analytical techniques (X-ray fluorescence - XRF, inductively coupled plasma - atomic emission spectrometry - ICP-AES, Fourier transformed - infrared spectroscopy - FTIR) for analyzing compositions of artifacts.

Keywords: *archaeometry, analytical techniques, artifacts, FTIR, ICP-AES, XRF*

♦ Paper presented at the 6th edition of *Colloque Franco-Roumain de Chimie Appliquée*, **COFrRoCA 2010**, 7-10 July 2010, Orléans, France

INTRODUCTION

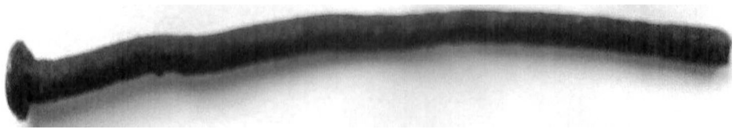
The physical and mechanical properties of material culture are always of prime concern to archaeometry and science-based archaeology. The preservation of material culture for future generations with the best possible fidelity requires in-depth knowledge, to aid the most suitable restoration, conservation, storage, and eventual museum display [1 – 3]. Modern chemical analysis offers numerous methods and measuring techniques which can be employed for archaeometric purposes. This paper describes the use of some analytical techniques (X-ray fluorescence - XRF, inductively coupled plasma - atomic emission spectrometry - ICP-AES, Fourier transformed - infrared spectroscopy - FTIR) for analyzing compositions of artifacts in connection with their origin [4].

EXPERIMENTAL

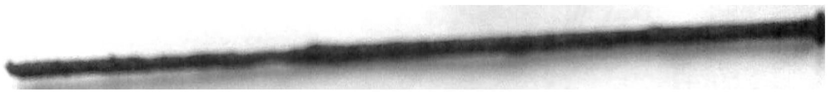
Archaeometric studies

Metallic objects

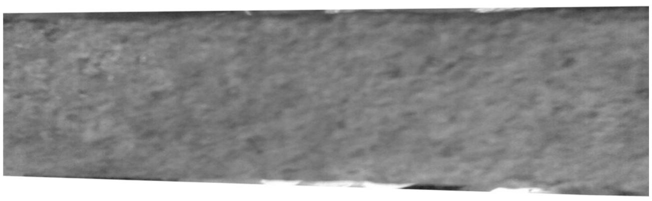
The samples consisted of three iron artifacts obtained from personal collection, with provenience in the southern Romania (Figure 1), all samples being at least 200 years old, clearly manufactured. Two of the samples represents iron nails (Figures 1a and 1b) with dimensions of 19 cm in length and a diameter of 0.7 cm (sample 1 – Figure 1a) and respectively 16 cm in length and a diameter of 0.15 cm for sample 2 (Figure 1b) and one iron plate, sample 3 (Figure 1c) with length of 21 cm, width 5 cm and thickness 0.4 cm.



a



b



c

Figure 1. *Iron artifacts used for the study: 1a – iron nail sample 1, 1b – iron nail sample 2, 1c – iron plate – sample 3*

Historical papers

The Romanian Gospel from 1740 (Figure 2), is from a private collection. 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, $Ca_3(PO_4)_2$ [5, 6].

Figure 2. *The picture of the Romanian Gospel from 1740*

Apparatus

The EDXRF analysis were conducted on a MiniPal PW4025 EDXRF spectrometer (PanAnalytical) equipped with a Si(PIN) detector. The determinations have been carried out in Helium atmosphere, for a period of 300 seconds, without any filter, by the use of a 3.6 μm Mylar tissue. The concentrations were calculated automatic by the spectrometer's software. For the ICP-AES determinations, we used an ICP-AES spectrometer Varian, Liberty 110. The thermogravimetric determinations were carried out on a TGA/SDTA 851e (Mettler Toledo), from 25 to 1000 °C, at a heating rate of 20 C°/min., nitrogen atmosphere, in alumina crucible.
The FT-IR spectra were recorded on a FT-IR GX Perkin Elmer, working domain 4000 – 400 cm^{-1}, Dynascan interferometer, DTGS detector, equipped with ATR (Attenuated Total Reflectance) device.

RESULTS AND DISCUSSION

The results obtained by EDXRF on the samples revealed the presence of Fe, as a major constituent in all three samples, in different concentrations (for the metallic objects). The presence of other trace elements (Mn, Cu, Pb, Si, Na, Mg, Al, Cr) and also the presence of the very high amount of chlorine in the sample could be explained due to the corrosion system on the iron pieces or from the leaching of those elements from soil during its burial (Figures 3 – 5) [7].

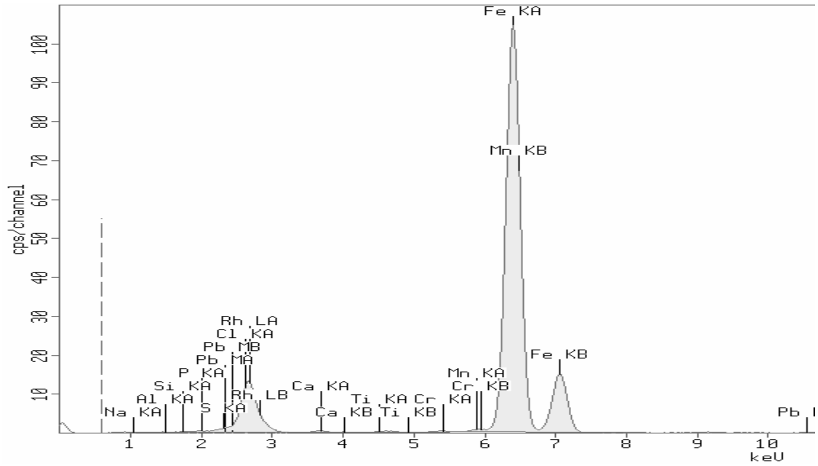


Figure 3. *The EDXRF spectrum of sample 1*

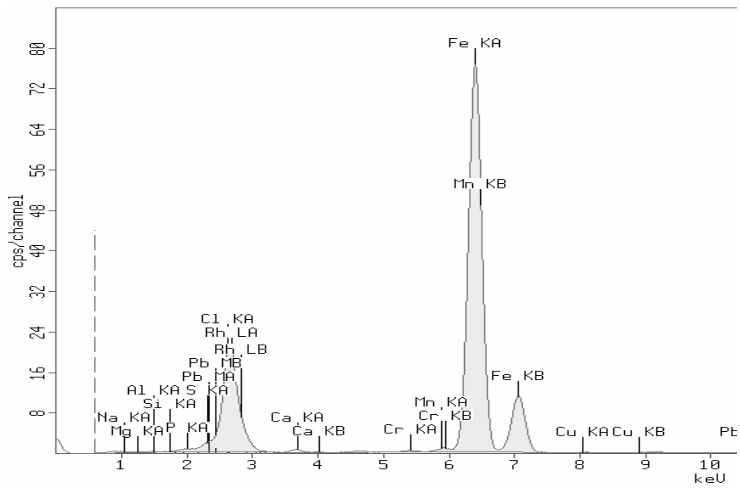


Figure 4. *The EDXRF spectrum of sample 2*

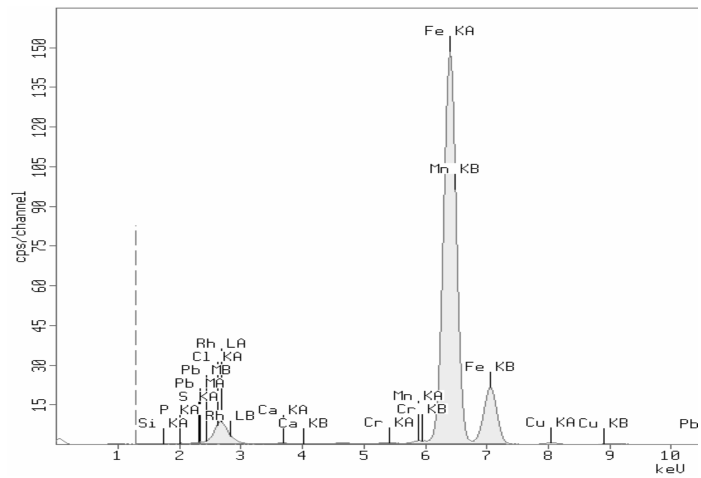


Figure 5. *The EDXRF spectrum of sample 3*

As a second step of analysis, from all the iron artifacts corrosion samples were collected and analyzed the corrosion products (named sample 4 – corrosion sample from artifact

#1, sample 5 – corrosion sample from artifact #2, sample 6 – corrosion sample from artifact #3). The results obtained by EDXRF analysis are presented in Figures 6 – 8, as spectra.

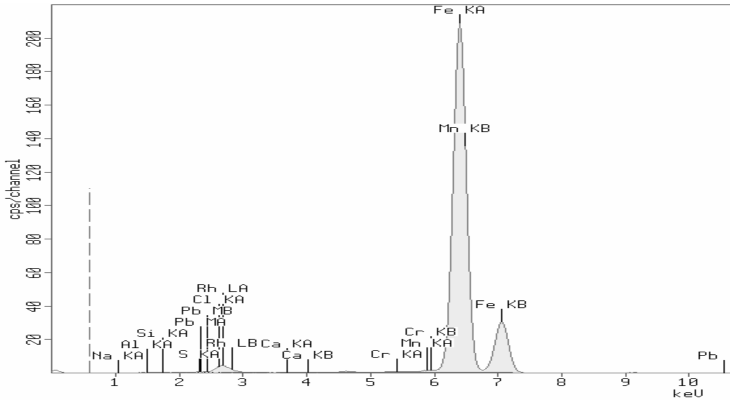


Figure 6. *The EDXRF spectrum of sample 4*

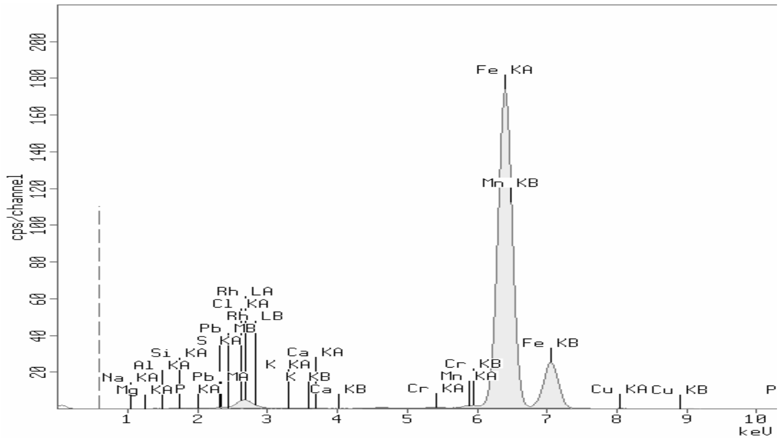


Figure 7. *The EDXRF spectrum of sample 5*

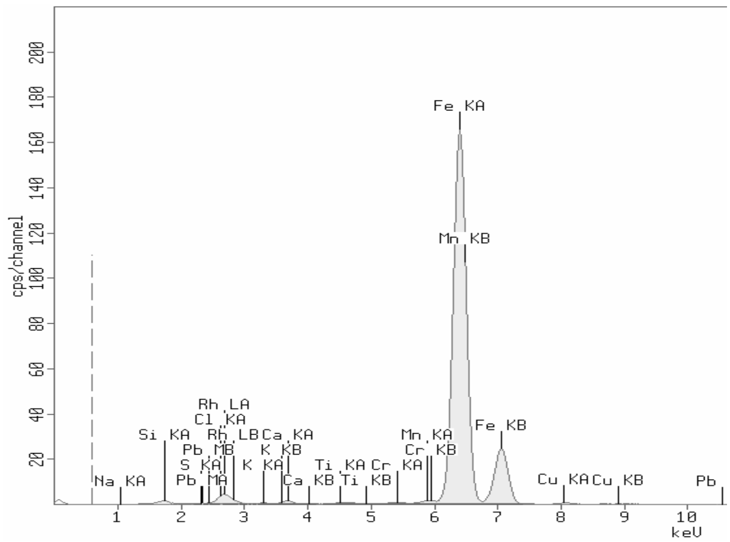


Figure 8. *The EDXRF spectrum of sample 6*

The differences between the corrosion samples and the original samples are obvious, and denote the presence of multiple corrosion products, confirmed by ICP-AES and EDXRF analysis.

Table 1. *ICP-AES results for the analyzed samples*

Element	**Concentration of element [%] in sample:**					
	#1	**#2**	**#3**	**#4**	**#5**	**#6**
Ti	0.0002	0.0016	0.0005	0.0026	0.0022	0.0070
Al	0.0060	0.0568	0.0112	0.0481	0.0578	0.3610
Sr	0.0028	0.0072	0.0058	0.0107	0.0044	0.0064
Ca	0.0037	0.0091	0.0072	0.0063	0.0067	0.0073
Co	0.0317	0.0076	0.0181	0.0158	0.0058	0.0111
Ni	0.0685	0.0582	0.0569	0.0219	0.2257	0.0677
Si	0.0258	0.6301	0.0256	0.1807	0.2717	0.2547
Mn	0.7533	1.0599	0.9106	0.3382	0.7313	0.3773
Cr	0.0253	0.0818	0.0242	0.0135	0.0495	0.0419
Mg	0.0472	0.1233	0.0923	0.0954	0.1234	0.3391
Na	1.0734	2.9400	2.0780	1.5850	1.8628	0.8312
Sn	0.0378	< 0.00005	0.0112	0.0540	< 0.00005	0.0044
Zn	0.0199	0.0223	0.0223	0.0173	0.0245	0.0173
P	0.0205	0.2498	0.0227	0.0186	0.1632	0.0214
Cu	< 0.00005	0.1307	0.7908	< 0.00005	0.1736	0.3329
K	0.0158	0.0739	0.0249	< 0.00005	0.1957	< 0.00005

The ICP-AES results for the three samples and their corrosion products, presented in Table 1, confirm the EDXRF determination. It is worth mentioning that the EDXRF analysis showed the presence of sulfur (concentrations varying from traces to 1%), element that cannot be determined by ICP-AES, in our working conditions.

In the case of historical paper of the Romanian Gospel, the complex characterization was performed by EDXRF, ICP-AES, FTIR, analysis and thermogravimetric determinations [5]. EDXRF analysis for the paper indicates a small quantity of iron (Figure 9).

The spectral analysis corroborate with FTIR analysis (Figure 10) indicate the presence of calcium carbonate, calcium phosphate, Prussian Blue and magnesium carbonate.

The absorptions of the SO_4^{2-} ion in the $BaSO_4$ found in the sample match 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 $BaSO_4$ [5]. From the results obtained, we can explain the presence of barium as a predominant element in the filling of paper. Its presence can be explained by the use of barium sulfate as filler and bleaching agent in the manufacturing process of paper.

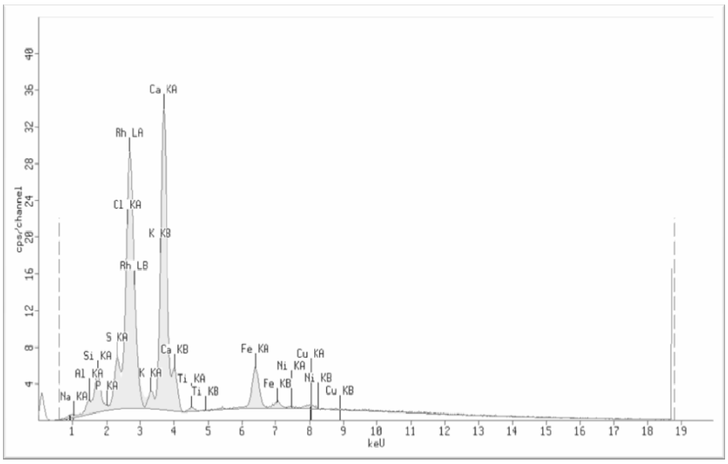


Figure 9. *EDXRF spectrum of the paper sample*

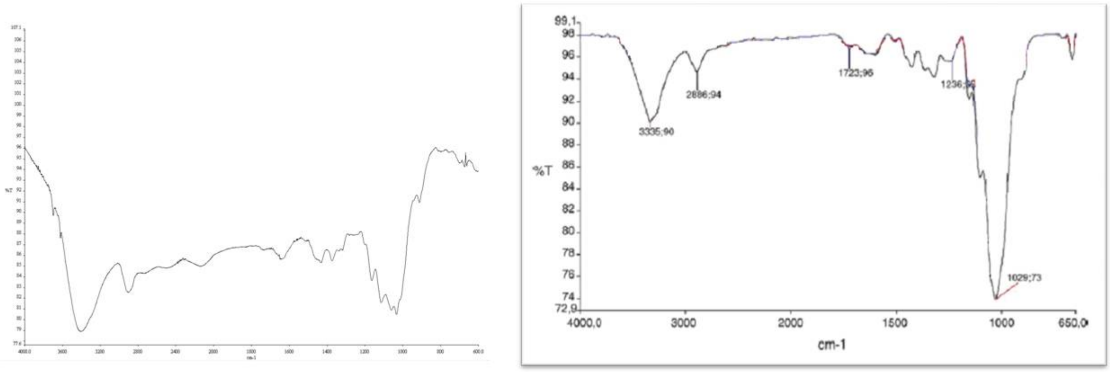


Figure 10. *FTIR spectrum for paper sample*

CONCLUSIONS

The scientific study of art and archaeological objects is an area that is growing rapidly and many new research groups are becoming established there. A large number of interesting new avenues will probably open in the future as the artificial separation between the arts and sciences is reduced, largely through the efforts of researchers around the world.

Considering the world trends regarding the application of modern analytical techniques in the study of the artifacts in order to obtain complex information, we have presented our own experience in the field of archaeometry. In our study, the use of a series of analytical methods led to information about:

- composition / chemical nature of selected parts of cultural artifacts and materials in order to elucidate their origin;
- state of degradation (on surface and / or internal) of the objects as a result of exposure to environmental conditions over a long period;

There is no doubt that current research has strengthened the community in this multidisciplinary field. It has improved the ability to answer questions related to museum objects, which could not be easily resolved, and the exchange of knowledge in both directions.

ACKNOWLEDGEMENTS

The present study was partially supported by CNCSIS trough the BD program.

REFERENCES

1. Ion, R.M., Dumitriu, I., Boros, D., Isac, D., Ion, M.L., Fierascu, R.C., Catangiu, A.: Characterization of Corrosion Products on Roman Mirror, *Metalurgia International,* **2008, 13** (8), 43-46;
2. Fierascu, R.C., Dumitriu, I., Ion, M.L., Catangiu, A., Ion, R.M.: Combined Use of Surface and Micro-analytical Techniques for Archaeometallurgy, *Analele Universitatii din Bucuresti – Chimie,* **2008, 17** (1), 9-14;
3. Ion, R.M., Boros, D., Ion, M.L., Dumitriu, I., Fierascu, R.C., Radovici, C., Florea, G., Bercu, C.: Combined Spectral Analysis (EDXRF, ICP-AES, XRD, FTIR) for Caracterization of Bronze Roman Mirror, *Metalurgia International,* **2008, 13** (5), 61-65;
4. Fierascu, R.C., Dumitriu, I., Ion, M.L., Catangiu, A., Ion, R.M.: Surface and Analytical Techniques Study of Romanian Coins, *European Journal of Science and Theology,* **2009, 5** (1), 17-28;
5. Ion, R.M., Ion, M.L., Niculescu, V.I.R., Dumitriu, I., Fierascu, R.C., Florea, G., Bercu, C., Serban, S.: Spectral Analysis of Original and Restaurated Ancient Paper from Romanian Gospel, *Romanian Journal of Physics,* **2008, 53** (5-6), 781-791;
6. Doncea, S.M., Ion, R.M., Fierascu, R.C., Bacalum, E., Bunaciu, A.A., Aboul-Enein, H.Y.: Spectral Methods for Historical Paper Analysis: Composition and Age Approximation, *Instrumentation Science & Technology*, **2010, 38** (1), 96-106;
7. Ion, R.-M., Boros, D., Ion, M.-L., Dumitriu, I., Fierascu, R.C., Radovici, C., Bercu, C., Aksahin, I.: Compositional Analysis of the Iron Ores from Ancient Archaeological Site Covasna, *The scientific Bulletin of VALAHIA University – Materials and Mechanics*, **2009, 6** (1), 79-84.