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■Papers■

X-RAY FLUORESCENCE IN RESEARCH ON THE CULTURAL HERITAGE

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Abstract - Radionuclide X-ray fluorescence analysis is a method, which has many advantages for analysing various historic artefacts, as it is relatively cheap, sensitive and non-destructive, and it allows measurements in-situ. However, this analysis has also certain limitations especially concerning sensitivity to chemical elements only, irrespective of the compounds or chemical forms in which these elements have been bonded. In addition, light elements emitting very soft X-rays cannot be measured, and in order to detect a wide range of elements, it is necessary to carry out repeated measurements with different radiation sources. Despite these limitations, valuable information can be obtained about the composition of historic materials and data about the origin and age of these artefacts can be derived. Analyses of wall paintings, ancient metal sculptures or other objects of art provide the basis for historic considerations documented in our results for some objects belonging to the Czech cultural heritage. The results are promising. Thus it is expected that our laboratory will expand its work into more fields of the fine and applied arts.

INTRODUCTION

Analytical methods (where the word "analytical" can be used in a very wide sense) have a wide range of application in many industrial branches, criminology, environmental research as well as in archaeology and in the history of art and architecture. The analysis of materials from which various artefacts are manufactured can bring important information about the origin, production technologies and the authenticity of an archaeological find or a work of art. Especially minor and trace elements, e.g., elements of rare soils or some metals, are usually the most important indicators. In principle, any method for the analysis of the composition can be used, such as activation analysis, all methods based on X-ray emission, atomic absorption spectrometry, Mossbauer spectroscopy, inductively coupled plasma, "classical" chemical methods, etc.

Many various materials were measured and analysed in the effort to contribute to the history of art by recognising the fate of particular pieces of art. We can mention here only a few examples selected from "Archaeometry", one of the leading journals in the branch: Chinese porcelain [1], Italian paintings and enamels [2], brass "Drake Plate" [3, 4], British pewter jugs [5], Celtic glass jewellery [6], pigments on Mexican mural paintings [7], Mediterranean marbles [8], Spanish building stones [9]. Analytical methods, and among them also radioanalytical methods as the very important component, belong nowadays to the standard way of investigation of cultural monuments. A very complex review can be found, e.g., in the recently published book [10].

BASIC FEATURES OF X-RAY FLUORESCENCE ANALYSIS

All modifications of X-ray fluorescence analysis are based on the well-known Moseley's law: The square root of the frequency ν of the characteristic X-rays of a given series is directly proportional to the proton number Z of the element emitting the X-rays. E.g., for the K-series, this rule can be approximately rewritten into the form:

$$E_K = 10{,}25\ (Z - 1)^2$$

where E_k is the photon energy (in eV) and Z the proton number of the element.

Characteristic radiation can be excited by different primary radiations depending on the purpose of measurement and sometimes depending on the equipment of the laboratory:

- gamma rays from radionuclides (RXRFA - radionuclide X-ray fluorescence analysis),
- X-rays from X-ray tubes,
- electrons (electron microprobe),
- protons and other heavy charged particles (PIXE - particle induced X-ray emission).

The idea of analytical use of X-ray emission is simple. Elements contained in the analysed material can be determined from the energies of emitted characteristic photons and concentrations of these elements in the sample can be determined from the intensities of the corresponding spectral lines. However, realisation of each modification of the method brings its specific problems. We will deal here only with the RXRFA, which has been chosen as the basic analytical method for our laboratory. In addition to this method, to broaden our possibilities, we also have links to other laboratories able to provide PIXE and activation analysis.

The main advantages of RXRFA for the purpose of research of various objects of art are:

- RXRFA is a fast and non-destructive method, with relatively simple and cheap instrumentation,
- the equipment is transportable and allows measurements in-situ,
- the method is very sensitive to most elements of the periodic table (measurement of concentrations of the order of magnitude of ppm is possible in some cases),
- the method enables the determination of more elements from one measurement.

On the other hand, there are some problems and sources of error, which exist in RXRFA. They complicate the application of the method and evaluation of measured spectra. The main problems are:

- due to the energy threshold of detection by X-ray spectrometers, light elements cannot be analysed, the lower limit of measurable Z depending on the type of detector,
- the method is insensitive to chemical compounds in which elements are bonded,
- excitation source for K-lines of heavy elements must have an energy of a few tens keV or even more than 100 keV, which results to a substantial Compton background (it complicates quantification of measurements even at excitation energies as low as 59,54 keV of ^{241}Am),
- L-lines of heavy elements can interfere with K-lines of lighter elements, which complicates the processing of spectra (the most important and obvious example - K-lines of arsenic and L-lines of lead),
- matrix effects of various types exist, which need to be corrected and increase the overall error, as e.g.:
  a) absorption of both exciting radiation and characteristic X-rays,
  b) secondary excitation of characteristic X-rays.
- for quantitative analysis the subtraction of the background is needed for determining peak areas; however only an approximation of the real shape of the background can be done by mathematical model,
- variation in surface roughness or grain size of the analysed material can cause an error of measurement,
- only a limited range of chemical elements can be effectively measured with a single

interest measurement needs to be repeated with sources having different excitation energies.

INSTRUMENTATION

Our equipment is relatively simple and cheap. Three ring sources ^{55}Fe, ^{238}Pu and ^{241}Am with the activities of the order of hundreds MBq are used for characteristic X-ray excitation. The ORTEC Si(Li) detector with an effective diameter of 6 mm and thickness of 5 mm (FWHM = 170 eV for the line 5.9 keV of ^{55}Fe) connected to multichannel analyser CANBERRA 35 (laboratory measurements) or ORTEC DART (measurements in situ) are the most commonly used instruments for detection and spectra recording. The AXIL-QXAS computer code developed by L. Markovic in the IAEA laboratory in Seibersdorf (Austria) serves for determining peak areas. And, finally, our own code based on the method of empirical coefficients serves for suppression of matrix effects and calculation of concentrations, when quantitative analysis is needed for the particular measurement.

EXAMPLES OF RESULTS

1. Paintings

The analysis of paints is to some extent difficult because of badly defined layers on the pictures. Therefore this cannot be made quantitatively. Nevertheless, knowledge of presence of some elements in the paint can help to determine non-destructively its type and relate it to the historic period of its use. As an example we can mention the analysis of two icons of unknown origin from a private collection from the Balkans. Plumbeous white and two other colours no longer in use by 19th Century were found in both icons. Yet, Mars's brown, which started to be used about 1857 was found. These findings lead to the conclusion that there is a high probability that both icons were painted in the second half of 19th Century.

Generally, much more detailed results for paintings can be obtained with microbeams, where paint layer structures can be studied, and newer paint layers over the old ones can be recognised. However, important information can be obtained even with the simplest RXRFA measurement described above.

2. Frescoes and wall paintings

Quantitative analyses by RXRFA are impossible also in the case of frescoes and wall-paintings. However, when compared with the above case, frescoes and wall-paintings have better defined areas of single paint layers. This facilitates the interpretation of results. Hence frescoes form one of the main parts of our RXRFA analysis programme.

Recently a great effort of art historians has been devoted to the newly discovered Late Gothic frescoes in the palace and chapel of Zirovnice Castle (Gothic castle from 13th century in SE Bohemia, rebuilt in the second half of 15th Century, then rebuilt again and newly fortified in 16th Century). RXRFA analyses were carried out in three rooms of the castle - the chapel, its antechamber and the so called "Green Room" (Fig.1). These analyses brought to light some interesting findings. The pigments of the same colour in all the three rooms under investigation had the same composition from the point of view of minor elements. This means that all frescoes were probably painted at the same time, although their artistic values differs (the most valuable fresco is in the chapel). A different type of red pigment is used according to the importance of the object painted. Less important objects (elements of architecture or ornaments) are painted with cheap iron containing mineral pigments from local sources, while more important saints and donators with minium. The most important objects (the array of Jesus and one of the three Kings) are painted with vermilion, extremely expensive paint at that time as it was imported from the Mediterranean. Processing the measured spectra allows to determine not only the composition of used paints and their identification, but it also allows testing the procedure during their uncovering, e.g., the missing layer of sulphide shows evidence of removing the surface layer of the fresco during the course of uncovering.

Radionuclide X-ray fluorescence analysis is a method, which has many advantages for analysing various historic artefacts, as it is relatively cheap, sensitive and non-destructive, and it allows measurements in-situ. However, this analysis has also certain limitations especially concerning sensitivity to chemical elements only, irrespective of the compounds or chemical forms in which these elements have been bonded. In addition, light elements emitting very soft X-rays cannot be measured, and in order to detect a wide range of elements, it is necessary to carry out repeated measurements with different radiation sources. Despite these limitations, valuable information can be obtained about the composition of historic materials and data about the origin and age of these artefacts can be derived. Analyses of wall paintings, ancient metal sculptures or other objects of art provide the basis for historic considerations documented in our results for some objects belonging to the Czech cultural heritage. The results are promising. Thus it is expected that our laboratory will expand its work into more fields of the fine and applied arts.

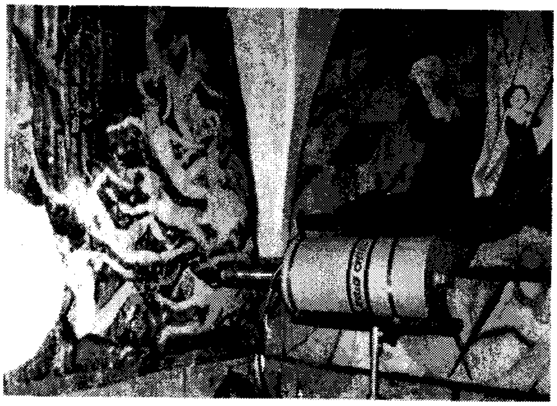

Fig.1. Measurement of the fresco in the chapel of Zirovnice Castle

Probably the most important medieval castle in the whole of the Czech Lands is Karlstejn, Gothic castle built in the 14th Century about 15 miles SW of Prague and substantially restored in the 19th Century. Frescoes in the Chapel of Our Lady in this castle have been analysed, which were also partially restored in the 19th Century. Medieval pigments are rich in lead and the red pigments are also rich in mercury. A remarkable peak of sulphur is also visible in some spectra. Both heavy metals and sulphur are missing in the pigments from the 19th Century restoration. It is thus easily possible to recognise the parts, which have been repaired (Fig. 2).

Similar measurements have also been carried out on the newly uncovered frescoes of St. Hieronymus in the Church of Our Lady before Tyn (a Gothic church from the second half of 14th Century with many Baroque additions, in the Old Town of Prague).

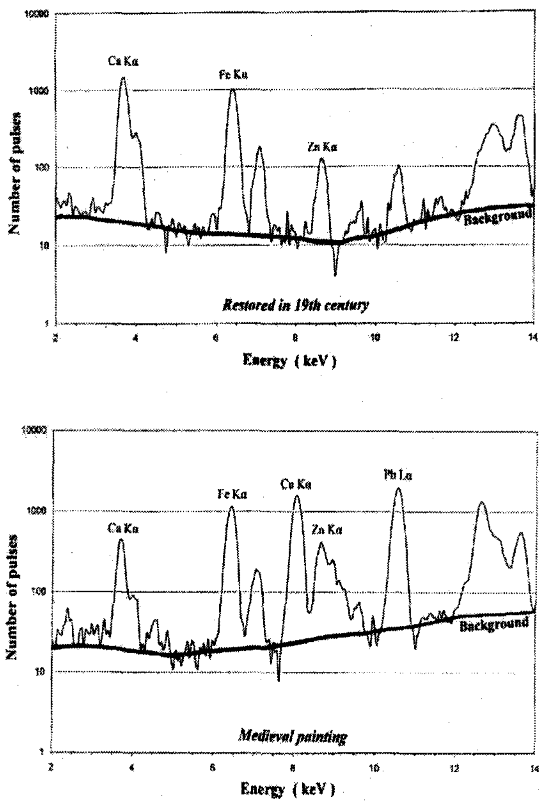

Fig. 2. XRF spectra of black paint in restored and original part of frescoes in the Chapel of Our Lady, Karlstejn Castle.

3. Metal objects

The most valuable metal object investigated up to now has been the Reliquary of St. Maurus, an outstanding example of Romanesque goldsmith work, originating from the abbey at Florennes, Belgium (Fig. 3). Since the end of the World War II it had been hidden in the floor ballast in the Becov Castle in West Bohemia and it was discovered heavily damaged in 1985. Various research and analytical methods were used, including RXRFA, to obtain data for its complete restoration. Following these measurements the sheets made of a silver-copper alloy were divided into five groups according to the ratio of both metals, which leads to the hypothesis that they are of different origin. Mercury traces give evidence about the technology of gold plating used for all metal decoration. Lately, some later additions have been found such as the hand of St. Matthias and the cross.

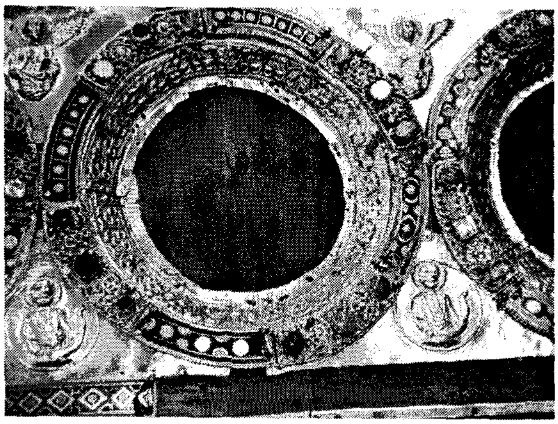

Fig. 3. Detail of decoration of the Reliquary of St. Maurus during restoration works.

Brass statues from the plague column in Olomouc were also measured during their restoration. These statues were damaged during the Prussian bombing of the city in the 18th Century and then repaired. Composition of solders used in the repairs was a matter of interest of art historians and restorers, mainly with the aim to use the material of similar composition for the restoration.

For metal objects the thickness of the layer is usually high enough to be saturated, which allows easy quantification of the measurement.

4. Fired building materials (bricks, roof tiles, etc.):

The research of these materials still needs more work and larger sets of data to be obtained. Concentrations of minor elements differ according to the origin of raw materials. The effect is well-known from building stones (see, e.g., [8]) or ceramics, but less studied for man-made building materials. As in the previous case, the possibility of quantitative measurements is advantageous, usually based on a saturated layer of material. On the other hand, a surface roughness and internal inhomogeneity in the material can influence results, therefore repeated measurements in various points and statistical evaluation are needed.

Our studies are orientated to bricks and roof tiles from the Roman period from various parts of Europe (e.g., Pistiros - Bulgaria, Musov - Czech Republic, Carnuntum - Austria, Trieste - Italy). We have found, e.g., significant differences in iron content in bricks from Musov and Carnuntum. The composition of roof tiles (Ca, Ti, Fe, Zn) from Pistiros is very different from bricks both from Musov and Carnuntum. Bricks from Trieste are different from bricks from England or Musov. Building a larger database of the composition of these materials is needed. The number of samples we have measured is too low up to now to draw more than preliminary conclusions, but it seems that the analyses of minor elements in fired building materials can bring historically and archaeologically significant results.

CONCLUSIONS

Investigations based on the methods of the exact sciences have become an integral part of research in the history of arts. The aim of this paper is only to point out some possibilities of one such method, which is used by ourlaboratory.

Fig. 4. Measurement of parts of statues from the plague Column in Olomouc during restoration.

The results can substantially contribute to our knowledge of measured artefacts. Nevertheless, the conclusions must always be done in an interdisciplinary collaboration of physicists with art historians. It is sometimes difficult to promote such an idea of collaboration, but this is the only way for the results to be relevant and properly interpreted.

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REFERENCES

1. Mazo-Gray, V. - Alvarez, M.: X-ray fluorescence characterization of Ming-Dynasty porcelain rescued from a Spanish shipwreck. Archaeometry 34,(1992).
2. Cesareo, R. et al.: Non-destructive analysis of chemical elements in paintings and enamels. Archaeometry 14,(1972).
3. Michel, H.V. - Asaro, F.: Chemical study of the Plate of Brass. Archaeometry 21,(1979)
4. Hedges, R.E.M.: Analysis of the "Drake Plate": comparison with the composition of Elisabethan brass. Archaeometry 21,(1979).
5. Carlson, J.H.: X-ray fluorescence analysis of pewter: English and Scotish measures. Archaeometry 19,(1977).
6. Frana, J. - Mastalka, A. - Venclova, N.: Neutron activation analysis of some ancient glasses from Bohemia. Archaeometry 29,(1987).
7. Ortega, R.F. - Lee, B.K.: Neutron activation study of ancient pigments from murals of Cholula and Teotihuacan. Archaeometry 12, (1970).
8. Mello, E.-Monna, D. - Oddone, M.: Discriminating sources of Mediterranean marbles: a pattern recognition approach. Archaeometry 30, (1988).
9. Bello, M.A. - Martin, A.: Microchemical characterization of building stone from Seville Cathedral, Spain. Archaeometry, 34,(1992).
10. Radiation in Art and Archeometry (ed. by D.C.Creagh and D.A.Bradley), Amsterdam, Elsevier(2000).