THESES OF PH. D. DISSERTATION

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APPLICATION OF X-RAY FLUORESCENCE ANALYTICAL METHODS TO DETERMINE THE COMPOSITION OF ARCHAEOLOGICAL AND ENVIRONMENTAL SAMPLES

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INTRODUCTION

In research field where non-destructive methods are needed for multielement analyses, the X-ray fluorescence spectroscopy is a most-widely applicable analytical method.

The quantitative and qualitative analyses of the alloying components in the museum-piece coins and jewellery demands a non-destructive method of measurement where neither the surface nor the images and inscriptions get damaged. All that is ensured by the X-ray fluorescence analytical method. Further advantages of the isotope excited EDXRF technique are that information can be obtained from the complete surface of the sample, the object under investigation is in normal atmospheric surroundings, the material studied does not become radioactive (as opposed to the neutron activation analytical method), while the radiation-protection regulations accompanying the use of the appliance are minimal.

In the opinion of historians, the possibilities of archaeological research into the early middle ages have, in effect, expired, whereas the investigation of the composition of coins and jewellery may provide new information. Analysing the elements making up the archaeological artefacts makes it possible to compare the objects originating from different ages, and in that way may promote the determination of the place of origin and time of production. Knowing the exact concentration of the main components is generally important, and the identification of trace elements may also help answering archaeological queries. The chosen research theme is closely connected with other branches of science, it asks for an interdisciplinary study.

Perhaps the two most prominent numismatic collections in Hungary are possessed by the Hungarian National Museum and the Hungarian National Bank. During the research work summed up in this Ph.D. dissertation, non-destructive analyses were carried out in the collections of the above institutions at the request of historians. Measurements at the time of beginning this Ph.D. work covered the following major areas:

a) clarifying, through determining the silver content, the circumstances of how the early Hungarian silver coins were minted,

b) the determination of the components and the impurities of gold coins and jewellery from the 10^{th} – 11^{th} century in order to identify the place of manufacture,

c) assistance in recognising forgeries - for example, when adding new items to the collection - through determining the composition and accompanying minerals characteristic of the mine in gold and silver coins.

The analytical study of the elements that make up biological and environmental samples is an important task in many an area. The enrichment of toxic trace elements - e.g. lead, cadmium, arsenic, mercuryr - represent the most

dangerous form of environmental pollution, which has a fundamental health, economic, and ecological significance. The microelements generally have an extremely long biological half-life and inactivation period, while the level of these microelements accumulating at higher levels of the food chain will or might reach a concentration that make the meat product unfit for consumption. In my Ph. D. thesis the study of the microelement content of different fish-meat and fish-liver samples is discussed, while the determination of heavy metals amassed in the sediments but also getting back into the food chain is touched upon as well.

AIMS OF THE STUDY, FORMULATION OF THE PROBLEM

In the first part of thesis, the aim set for the research was to work out an analytical method utilising XRF for the quantification of the alloying components of gold and silver coins and jewellery as well as the qualitative identification of the accompanying minerals characteristic of the mine. The X-ray fluorescence analysis is perhaps one of the most matrix sensitive analytical procedures. The intensity of the characteristic X-ray photons originating from the sample and reaching the detector depends not only on the quantity of the components present in the sample but also on numerous other parameters. For that reason, when using this method of analysis, one needs to work out a separate procedure for the quantitative spectrum evaluation for almost each type of matrix, which requires independent research and developmental work.

The non-destructive analyses of coins and jewellery as precious metal alloys especially presents several problems of measuring technology whose effects must be considered together when working out a method for the quantitative analysis.

- The main components in silver coins are Ag and Cu, those in gold coins Au, Ag, and Cu, beside which other impurities will occur but in trace-like quantities. A strong matrix effect must be expected because of the high atomic numbers of the main components.
- Considering the high museological value of the specimens, the chemical or physical preparation of the objects is impossible, so the standardisation of the size or structure of the specimen for serial measurements is out of the question. The shape and thickness of the coins and jewellery under investigation are naturally different from each other and also from such coins as have a known composition, and which might be used as certified materials.

- The X-ray fluorescence method for quantitative analysis can be used when the composition of the coin's surface is representative of the whole of the coin. Furthermore, in the investigation of coins, the proportion of the alloy-forming components must be taken into consideration as the homogeneity of the coins may be influenced by the technological processes of minting, and also by the circumstances at storing and restoration.

In the second half of the thesis, research work was concerned with the matrix effect, and with solving the technical problems of measurement arising from the different sizes of the particles, when studying biological and environmental samples. It was necessary to work out a process to prepare the fish and sediment samples for study; further scientific research work was needed in choosing the suitable standards when evaluating the spectra, in determining the duration of measurements, and in the quantitative calibration of the experiment.

MATERIALS AND METHODS

The measurements were made with an Iodine-125 isotope excited X-ray fluorescence analysis system. The advantage of using ^{125}I for the analyses of silver, gold and copper alloys is that its 27.6 keV-emitted line excites the 22.16 keV K_α line of silver with a very high efficiency. At the same time it excites the 8.04 keV K_α line of copper constantly occurring in the alloys on an acceptable level. The determination of gold content is carried out by exciting the 9.7 keV L_α and the 11.4 keV L_β lines. The length of time, the duration of the measurement is determined by the isotope's activity at the moment; with silver coins a duration of 300 s, with gold coins 120 s were used whereas in the case of the environmental samples, and in the determination of the trace elements in the coins a measuring time of twenty-four hours was employed.

In working out the quantitative methods, a set of standards with a known composition and put at our disposal by the Institute for Testing and Standardisation of Nobel Metals were used. The reliability and accuracy of the developed methods was checked using different gold and silver certified coins, and gold sheets obtained from the Hungarian National Bank and the Institute for Testing and Standardisation of Nobel Metals. The results of the measurements were, in a few cases, also compared with those obtained by prompt-gamma activation analysis.

In the quantitative analyses of fish and sediment samples, the Canberra AXIL softwer was employed, namely the method for determining concentrations through direct comparation of count rates. To test this method, international reference materials were used (sediment IAEA-SL-1; IAEA-SOIL-7dogfish muscle NRC-DORM-2; dogfish liver NRC-DOLT-2). Comparative studies were carried out with GFAAS and FAAS techniques, where the sample decomposition was done by microwave-assisted acid digestion procedure.

With the methods developed for the evaluation of spectra, the composition of several hundreds of gold and silver pieces as well as that of old jewellery was determined, just as the composition of different sediment and fish samples.

NEW SCIENTIFIC RESULTS, THESES

The new scientific results achieved in the field of the qualitative and quantitative analysis of archaelogical and environmental samples using x-ray fluorescence are summarized as follows:

- An individual matrix and geometrical correction procedure was developed, which is suitable for evaluating the spectra of both the two-component silver and the three-component gold coins. Mathematical connections were established between the concentrations of the components in an alloy and the intensity of the characteristic X-ray photons. The calibration curves belonging to the alloying components were determined, and the validity range of linear approximation was also ascertained.
- Through the element analysis of certified bi- and multi-component, homogeneous silver and gold samples it was found that:
  1. The calibration function worked out with the help of the X-ray fluorescence intensity ratios and the concentration ratios diminishes the measurement errors caused by the geometrical differences.
  2. The accuracy of the concentration measurements can be improved by doing the calibration within a narrow concentration range in order to keep the matrix effect in check. This can be done on condition that one has, at one's disposal, a wide array of standards similar in composition to the sample under investigation at the time of the calibration.
- Using the spectrum evaluation method based on the proportion of peaks it was found that the parameters of the calibration straight obtained from different instruments and at different points in time did not change with time. So this method makes it possible to use a calibration straight during the whole of the investigation process.
- It was shown for the first time that the matrix correction procedure based on the ratio between the intensities of scattered radiation and characteristic X-ray radiation can be applied to correct the geometrical diversity. In the case of gold pieces, the method can only be used to check the silver content as only in this case does a linear connection exist between the intensity ratios and concentrations.
- A sample preparation process was worked out for the X-ray fluorescence analysis of fish-meat and fish-liver, and sediment and soil samples, and the quantitative spectrum analysis of the samples was standardized.

- Through the determination, by XRF, of the trace-element content in fish and sediment samples, the following new, (bio)chemical observations were made:
    1. lead accumulates in the flesh of bream as the animal advances in age,
    2. in the flesh of crucian carp the trace elements zinc and copper show a significantly higher enrichment than in other fish species living under identical conditions,
    3. at locations where the surface waters contain more arsenic than at other places, the arsenic concentration in the fish meat is also higher,
    4. after the heavy-metal pollution originating in Romania, the heavy-metal content of the livers of the fish in the River Tisza shows a great variety and high values,
    5. the heavy-metal content of the sediment measured at various locations along the River Tisza is higher than in the sediments of different fishponds or in the Oxbow lake of the River Körös.

THE APPLICATION OF THE RESULTS

Using the method developed, the analysis of a substantial number of gold and silver coins that belonged to different ages, and which came from the numismatic collections of the Hungarian National Museum and the Hungarian National Bank, was done.

Among the coins, analysis was done on the first Hungarian silver pieces stamped in the time of King Stefan I (997-1038), and on Hungarian and European silver coins from the 10^{th} century (Bavarian, Czech, of Salzburg, and Dresden). Investigation was also carried out on Hungarian and Byzantine gold pieces and jewellery from the 10^{th} century, the silver pieces of Hungarian King Matthias I (1458-1490) and his contemporaries, the gold forints of Hungarian King Karol (Robert) I (1308-1342), King Louis I (the Great, 1342-1382), and Queen Maria (1382-1385). Altogether approximately 600 museum-piece coins were analysed.

The results of these investigations can help museologists to better judge the coins and artefacts that form part of the national wealth, indeed, they have already been used in the course of their historical work. In the opinion of some numismatists, the trace element spectrum of the alloy -like a human fingerprint - could help identify the location of the ore mine. Based on the present measurements, metallurgical and geological experts were able to say that the gold used in the coins of King Stephan I was washed out from the sands of the River Danube in Hungary. Then, the analysis of the coins from the time of King Matthias I made it possible for the numismatists to better understand the contemporary monetary reform and to lay the foundation of a new concept**.**

With the help of the analytical method developed for the investigation of environmental samples, as part of different projects, samples of carp flesh coming from diverse waters, along with different species and fish of varying sizes were studied. In connection with the heavy-metal pollution of the River Tisza, bits of flesh and liver from different fishes were compared as well as the heavy-metal concentrations in the sediments at the different sampling locations.

All in all, the result of our work summed up in this dissertation is that our measurement data provide new, valuable information, all practically applicable. I have given an account of the result of my scientific work in numerous publications and at talks (Sándor, 1997, 1998, 2002, 2002, 2003, 2004), which have since then been referred to on several occasions.(J. Anal. At. Spectrometry; J. Radioanal. Chem. Etc.)

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