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Analytical methods for the determination of the chemical composition of ancient coins

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Introduction

The determination of the chemical composition of ancient coins may offer valuable information to archeologists, historians and numismatists, mainly regarding their manufacturing technology, age, minting places, and authenticity. The composition of the major elements can provide useful information about the history and the economy of a city, a kingdom or an empire, for a specific period of time, and also about the materials technology applied for the production of metal alloys. In the case of trace elements, their detection or not in the coins under examination may provide indications about the source of the ores (determination of the metal’s provenance) and the manufacturing procedure. Moreover, the composition of ancient coins can assist the discrimination between genuine and forged coins. Even though the analytical studies of coins have been already carried out for more than 50 years, the relatively recent development of non-destructive analytical techniques has opened new potentials for the analysis of coins with no or minimal damage caused, since museum curators and collectors do not allow any permanent damage to the coins, even of those in poor condition.

In this paper, the most common techniques which are used or have been used for the analysis and the determination of the chemical composition of ancient coins, along with their advantages and limitations, will be presented, without providing much information about the methodological aspects of the techniques.

Methods of analysis

The analytical methods can be divided into two major categories: destructive and non-destructive. Nowadays, almost all techniques which are frequently used for the chemical analysis of ancient coins are totally non-destructive or demand a very small sample of the coin under study, thus causing very limited damage to the coin, non-visible to the naked eye.

Starting with the non-destructive methods, one of the first techniques applied for the
determination of the composition of coins, especially gold ones, is the specific gravity method.¹ This method of analysis has the advantages of being non-destructive, inexpensive and uses the whole coin, eliminating in this way sampling errors that may arise with other analytical methods (i.e. very small or non-homogenous samples). Despite its advantages, the gravity method has serious limitations.² The most important one is that this method can only be applied to and be highly accurate for coins made with binary alloys, in particular when both components of the alloy are precisely known. Furthermore, since the specific method is based on the mass and the volume of the coin being studied, any parameter that may affect its gravity, like corrosion products on its surface or gas bubbles inside it, may lead to misleading results. The presence of corrosion products lowers the measured specific gravity and increases the estimated gold content, which is lower than its true value. In coin analysis, the error is bigger since the ratio of the surface area to the volume is very large. The best way to overcome this limitation is the removal of corrosion products.³ The presence of gas bubbles in the metal used for the production of the coins also lowers the measured specific gravity and consequently the estimated metal content. However, the fact that the majority of the coins were made by striking and that their surface was additionally treated, eliminates the presence of gas bubbles.⁴

Neutron Activation Analysis (NAA) is a fast, non-destructive method which can be employed for the determination of the major, minor, and trace elements content of ancient coins.⁵ This specific technique is non-destructive for the analysis of coins due to their small size that allows them to be placed in the irradiation container and enter the reactor without the need of sampling. More commonly, over the past decades, a very small sample was taken from the coins (50 mg was a sufficient quantity for analysis), usually by drilling; but nowadays, in almost all cases, sampling is forbidden. In most cases, irradiations take place in a high neutron flux of a nuclear reaction, but even the use of an isotopic neutron source can produce lower neutron fluxes which are capable to determine, with a sufficient precision, the silver and gold content of ancient coins.⁶ Such small neutron sources are relatively inexpensive and provide fast analysis without causing any long-term radioactivity to the coins being studied; however, the limited irradiation does not allow the measurement of the concentration of all major, minor and trace elements.⁷ In some cases of silver coins when the technique of Neutron Activation Analysis doesn’t ensure sufficient penetration depth, this method can be used only for the study of the surface composition.⁸ On the contrary, the use of the Fast Neutron Activation Analysis (FNAA) allows the bulk analysis of the coinage without damaging the samples, as it achieves greater penetration depth. In this method, neutrons are produced by nuclear reactions performed in cyclotrons.⁹
Another method of activation analysis used for the determination of coin composition is the Proton Activation Analysis (PAA). The proton beam which is used for the bombardment of the coins is produced by a cyclotron. In the case of gold coins, the penetration depth of the proton beam is around 240 μm, and therefore the measurement is not affected by the gold surface enrichment or the reduction of the copper content due to oxidation. Moreover, Photon Activation Analysis (PAA) has been also applied on the study of ancient coins. This method uses high energy photons (bremsstrahlung) with higher irradiation times than the most commonly used fast neutrons, which allow better penetration depth than Neutron Activation Analysis (NAA).

X-ray fluorescence (XRF, both wave length-dispersive [WD] and energy-dispersive [ED]) [Fig. 1], Proton induced X-ray emission (PIXE) and Electron probe microanalysis (EPMA) are recognized as surface methods for the chemical analysis of coins, since only a surface layer of limited depth (from a few micrometers up to a few tens of micrometers) is analyzed.

The energy-dispersive X-ray fluorescence (EDXRF) method is rapid, multi-elemental (allows the qualitative and quantitative analysis of a great number of elements in a wide concentration range) and totally non-destructive, as it does not require any sample preparation. The limit of detection can be as low as some hundreds of ppm (parts per million), depending on the element, the composition of the coin (matrix) and the time of analysis (count time). The X-rays are usually produced from an X-ray tube (XRF), a radioactive source (γXRF) or a synchrotron (SRXRF). The main disadvantage of the method is the surface nature of the analysis, as the X-ray beam cannot penetrate the sample more than some tens of micrometers. Consequently, the results of the analysis are not very quantitatively reliable, especially in the presence of surface enrichment or depletion phenomena (ion migration processes, patina and so on), which are very common in ancient coins. In the case of the analysis of copper or bronze coins where a thick layer of corrosion products usually covers the surface of the coins, an area or some areas must be cleaned, otherwise the X-ray beam cannot penetrate the corrosion layer to reach the original surface and thus the results of the analysis will only describe the composition of the surface corrosion layer, usually enriched in copper, and not the body of the coin. The dimensions of the surface area to be cleaned depend on the diameter of the X-ray beam. Moreover, in cases where the corrosion layer is thin enough or there is no alteration on the surface of the coins, EDXRF can be used directly for the analysis without any polishing or surface treatment. Another limitation of the method is the need for calibration with the use of reference materials or standards of similar composition to that of the analyzed coins in
order for quantitative results to be provided, as the specific technique is considered semi-quantitative.\textsuperscript{20}

On the other hand, the use of wavelength-dispersive X-ray fluorescence (\textbf{WDXRF}) offers better sensitivity and resolution, plus higher penetration when compared to energy-dispersive X-ray fluorescence (\textbf{EDXRF}),\textsuperscript{21} but is not as popular as EDXRF when it comes to ancient coin analyses.

The proton induced X-ray emission (\textbf{PIXE}) is a fast, multi-elemental, totally non-destructive method with good accuracy, high analytical sensitivity and no need for standards in order to provide quantitative results.\textsuperscript{22} Also, it permits lower detection limits for the elements (very low bremsstrahlung radiation is induced by the protons) compared with EDXRF.\textsuperscript{23} Also, PIXE uses $\mu$m-sized beams and thus allows the analysis of very small details.\textsuperscript{24} Its major disadvantage, as in the case of X-ray fluorescence method, is the surface analysis,\textsuperscript{25} which can be affected by the presence of corrosion products, especially in the case of copper or bronze coins.\textsuperscript{26} For PIXE analysis with proton energies between 1 and 3 MeV the reachable analytical depth is about 70 $\mu$m, depending always on the composition of the coin and the atomic number of the detected elements, and is lower compared with that of XRF (up to $\sim$100 $\mu$m). The use of high-energy PIXE results to a greater analyzable depth of several millimeters.\textsuperscript{27}

The electron probe microanalysis (\textbf{EPMA}) [Fig. 2], usually coupled with an energy-dispersive X-ray detector, is a near-surface (the depth of analysis is some $\mu$m),\textsuperscript{28} completely non-destructive technique. The compositional analysis is based on the impact of a very small in diameter electron beam on the surface of the coin and the production of X-rays. This technique is semi-quantitative; the chemical composition of the coin is determined by comparing the X-ray intensities from the coin’s material with intensities from known composition of reference materials. The limits of detection depend on the coins’ element and matrix, and range from 100 ppm to 0.2%.\textsuperscript{29}

Inductively coupled plasma mass spectrometry (\textbf{ICP-MS}) is a destructive method of analysis\textsuperscript{30} and is used for the determination of a wide range of trace elements in ancient coins at very low concentration levels. The sample can be introduced in liquid or solid form with the use of laser ablation (\textbf{LA-ICP-MS}).\textsuperscript{31} Laser ablation, as a sampling method (some $\mu$g needed, depending of the number of measurements), creates very small craters on the surface of the coins,\textsuperscript{32} non-detectable to the naked eye. The use of ICP-MS offers much lower detection limits, compared to LA-ICP-MS, but needs a higher quantity of sample (mg), in liquid form.
Inductively coupled plasma atomic emission spectrometry (ICP-AES) and atomic absorption spectrometry (AAS) are totally destructive methods, as the analyzed coin sample must be in liquid form. This is the main reason why these methods are rarely used nowadays in ancient coin chemical analyses, although they provide very low detection limits, especially for trace elements (ppb level for some elements).

In some limited case studies, where sampling or even sectioning of the coins is permitted, the energy-dispersive X-ray microanalysis in a scanning electron microscope (SEM/EDX) can be applied in order to investigate the microstructure and homogeneity/heterogeneity of the coins' chemical composition, especially of their core, by using their cross-sections. With this method, the coins' stage of corrosion can also be determined. The chemical composition of the coins' surface may be changed by corrosion processes and thus reveal great divergence from the composition of the core. The high magnification provided by the scanning electron microscope allows the detection and quantitative analyses on areas of the coins' core that are not affected by corrosion.

Conclusions

Since the 1960s, many techniques, both destructive and non-destructive, have been applied for the analysis of ancient coins, mainly for the determination of their chemical composition. Nowadays, the majority of analytical techniques used are non-destructive, mostly because museum curators and collectors do not permit sampling or any other method that may destroy the coins. In the case of some very valuable coins, it is not even allowed that they are moved out of the museum for analysis; for this reason, portable techniques, such as portable EDXRF, are becoming more and more popular. The presented analytical methods have both advantages and disadvantages and some of them are not used anymore in the analysis of ancient coins for practical reasons. Each method has certain detection limits along with some limitations, namely elements which cannot be specified or which may be determined with relatively poor precision. Nevertheless, the cautious use of a technique or the combination of techniques can provide coin experts with valuable information about the chemical composition of ancient coins, which can answer very important archaeological queries.
List of illustrations

The images that follow are available in the digital version of the present article in the website Kyprios Character. You can view the images by following the link: kyprioscharacter.eie.gr/en/t/AQ

Fig. 1: pXRF instrument (image: A. Charalambous)

Fig. 2: EPMA instrument (image: courtesy of Olivier Bonnerot)

Fig. 3: SEM/EDX instrument (image: A. Charalambous)
Endnotes

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