

Comparison of EDXRF and PIXE in the analysis of ancient gold coins

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The metal contents of several ancient uncleaned gold coins, with compositions ranging from about 35% to 99% Au, were determined and compared by using two techniques: EDXRF and PIXE. These techniques have proved to be a powerful tool in numismatic investigations, due to their ability of rapid, simultaneous and nondestructive multielement analysis. The results obtained with the two techniques for coins where gold is present in concentrations above 94% showed to be in good agreement. However, they appeared to diverge for coins with a lower standard of fineness. In this case, the Au contents determined by PIXE are higher than those obtained by EDXRF. This may be due to the well known surface enrichment effect and to the circumstance that the protons used as incident beam in PIXE analysis have a shorter penetration depth than the primary X-rays generated by the XRF tube.

1. Introduction

Several studies of the Suevic and Visigothic gold coinages have been and are still being carried out in the "Instituto de Ciências e Engenharia Nucleares, LNETI", at Sacavém, Portugal, in collaboration with some numismatists, concerning the analysis of the coin weights and of their metal contents [1].

Most of those coins are very scarce. There are probably fewer than two hundred Suevic specimens in existence, above ground, today. One can understand, therefore, that even minimal damage to these specimens, such as the one caused by the removal of a layer from the surface of a small area of the coins, had not been accepted by their proprietors. Thus, it was decided to apply in the studies referred to above two analytical nondestructive techniques – energy dispersive X-ray fluorescence spectrometry (EDXRF) and particle induced X-ray emission (PIXE) – without removing any surface materials from the coins.

The nondestructive character of these powerful techniques is very convenient for the analysis of valuable artifacts. However, they are limited, since only results from a thin surface layer can be obtained. Furthermore, it has been widely proved that ancient metal alloys usually present a distinct surface layer, due to the well known surface enrichment effect [2,3]. Consequently, the results obtained without cleaning the surface can only be regarded as approximate and they are expected to deviate from one technique to the other due to differences in the properties of the excitation beams.

The aim of this work is to compare PIXE and EDXRF methods in the determination of the composition of 32 uncleaned gold coins, with gold contents ranging from about 35% to 99%. It is hoped that this comparison may contribute to a better interpretation of the results obtained in those studies.

2. Experimental techniques

2.1. EDXRF

A commercially available energy-dispersive X-ray spectrometer, a Kevex Delta XRF Analyst System, was used. The primary photon beam is produced by a high power rhodium anode X-ray tube with appropriate secondary targets and filters. The characteristic X-rays emitted by the samples were collimated at 90° and measured by a Si(Li) detector with a resolution of 165 eV and an active area of 30 mm². Coins were irradiated using a monochromatic X-ray beam generated by a Gd secondary target and filter, with a high voltage of 57 kV and a current intensity of 1 mA during 300 s, under low vacuum conditions. X-ray intensities were processed using a DEC LSI 11/73 computer system, that provides programmed control of the X-ray generator, detection system and multichannel analyser.

Spectra were processed using a Gaussian deconvolution that assumes a theoretical relationship among the intensities of X-ray lines within each elemental line series [4]. Elemental concentrations were determined through the EXACT computer program, based upon a

fundamental parameter method [5], that uses calibration coefficients and accounts for matrix effects. Standards with the same constituent elements of the unknowns are required.

2.2. PIXE

All samples were irradiated in vacuum with 1.7 MeV protons supplied by a 2 MV Van de Graaff accelerator. Through a 1.5 mm diameter collimator set, a beam of 5–10 nA could be adjusted. A 210 eV resolution Si(Li) detector is placed at 90° relative to the proton beam direction and the face of the coins was tilted to an angle of 45° with the incident beam. A 25 μm Al absorber was used to suppress the Au_M lines.

Spectra analysis were performed by the AXIL-PC V3.1 [6] computer code. Quantitative analysis was carried out through the DATPIXE program that accounts for proton energy loss, X-ray absorption in the sample, energy dependent X-ray production cross sections and does not require comparison with standard samples, as described elsewhere [7].

3. Experimental procedure and results

After degreasing the coins with acetone, a stereomicroscope with a magnification up to 50 \times was used for surface inspection. The deposits still observed on the surface of the coins were carefully removed with a needle and the coins cleaned again with acetone.

For all specimens the obverse and the reverse were analysed by both techniques. While in PIXE irradiation

Table 1
Results obtained for the analysed standards (wt.%)

Standard	Composition ^a [%]	EDXRF ^b	PIXE ^c
Au–Ag 90–10	Au 90.15	90.16 \pm 0.24	90.02 \pm 0.10
Au–Ag 90–10	Ag 9.85	9.84 \pm 0.24	9.98 \pm 0.10
Au–Ag 80–20	Au 80.20	80.28 \pm 0.11	79.96 \pm 0.44
Au–Ag 80–20	Ag 19.80	19.72 \pm 0.11	20.04 \pm 0.44
Au–Ag 70–30	Au 69.97	70.20 \pm 0.20	69.26 \pm 0.44
Au–Ag 70–30	Ag 30.03	29.80 \pm 0.20	30.74 \pm 0.44
Au–Ag 60–40	Au 59.98	60.17 \pm 0.10	59.32 \pm 0.35
Au–Ag 60–40	Ag 40.02	39.90 \pm 0.10	40.68 \pm 0.35
Au–Cu 90–10	Au 90.02	90.05 \pm 0.25	89.37 \pm 0.10
Au–Cu 90–10	Cu 9.98	9.95 \pm 0.25	10.63 \pm 0.10

^a Composition determined taking as a basis the measured weights of the components.

^b Mean value and standard deviation of three independent measurements.

^c Mean value and standard deviation of results obtained in three different spots.

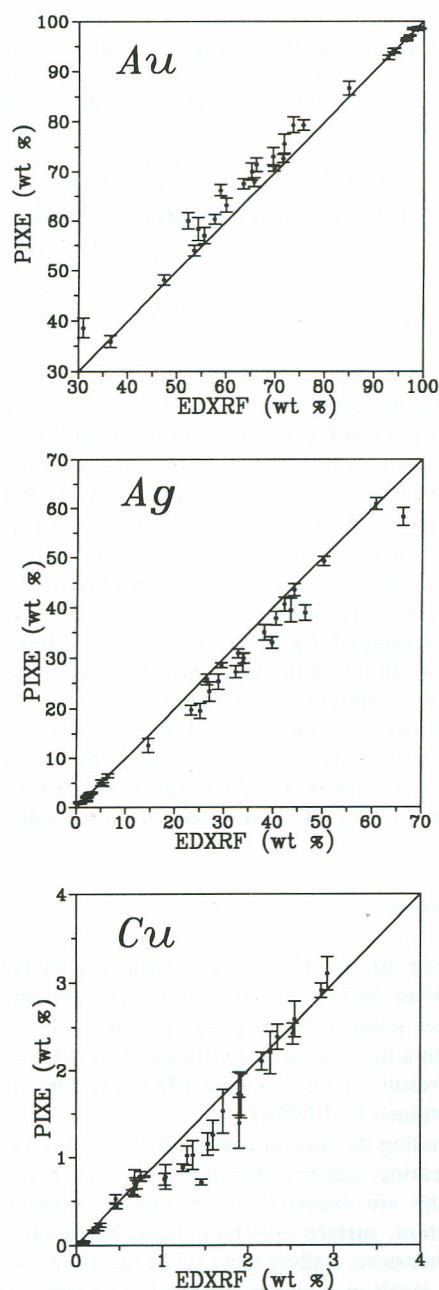


Fig. 1. EDXRF and PIXE results (wt.%), for each of the major components (Au–Ag–Cu) of the analysed coins. The lines drawn represent the lines of equal concentration and are used just to guide the eye.

tion two or more spots on each face could be chosen for analysis, the EDXRF beam cross section permitted only global analysis on each face. Quantitative analyses were carried out assuming that the sum of the detected elements concentrations was 100%.

The accuracy of PIXE and EDXRF methods was ascertained by analysing several binary alloy standards

Table 2

Calculated effective penetration depth of analysis for Au–Ag matrices with different compositions (wt.% values). The given values represent the thickness, in μm , from which 90% of the detected X-rays are produced. Exciting radiation: PIXE – 1.7 MeV protons; EDXRF – X-rays from Gd secondary target. X-ray lines considered: $\text{Cu}_{K\alpha}$; $\text{Ag}_{K\alpha}$; $\text{Au}_{L\alpha}$.

Element	Matrices									
	Au 100		Au–Ag 70–30		Au–Ag 50–50		Au–Ag 30–70		Ag 100	
	EDXRF	PIXE	EDXRF	PIXE	EDXRF	PIXE	EDXRF	PIXE	EDXRF	PIXE
Cu	3.9	3.6	4.4	4.0	4.8	4.3	5.8	4.7	6.6	5.3
Au	6.0	4.5	6.9	4.9	7.6	5.2	8.6	5.6	10.3	6.2
Ag	11.9	4.7	16.8	5.1	22.0	5.5	30.1	5.9	54.5	6.6

of Au–Ag and Au–Cu. The standards were prepared by one of us (J.M.P.C.). The results obtained for these standards with both techniques are presented in table 1, together with their elemental composition. Relative differences less than 1.5% can be found for Au results.

The results obtained in each set of measurements performed on each coin were averaged and their standard deviations calculated. In the case of EDXRF this calculated values for gold are less than 1%, indicating a good overall coin's homogeneity. As concerns PIXE, the relative standard deviation results are larger than in the former case and can be regarded as a measure of local inhomogeneities. The results obtained for the analysed coins are presented in fig. 1, where the error bars represent the PIXE standard deviation values.

4. Discussion

As seen in fig. 1, for coins with a gold content greater than 94%, the results obtained with the two techniques seem to be in good agreement. For specimens with a lower standard of fineness, it is found that the Au results determined by PIXE are higher than those obtained by EDXRF.

Depending on several conditions (e.g. burial conditions, wearing, conservation processes), even coins of gold alloys are expected to present, to a greater or lesser extent, surface enrichment on that noble metal [8]. Furthermore, a silver increase in the alloy composition will result in a higher chemical reactivity with the external environment and consequently will promote the gold surface enrichment process.

Values listed in table 2 show that the effective depth in PIXE analysis is shorter than in EDXRF and does hardly depend either on matrix composition or on the element being determined, which is not true in the case of EDXRF [9]. As a matter of fact, considering a silver content increase from 30% to 50%, the ratio of effective penetration depth between Ag and Au increases only 2% for PIXE analysis but 19% for EDXRF. Consequently in the case of EDXRF analysis, the silver is measured in deeper layers and there-

fore is not so influenced by the silver depleted layer as in the case of PIXE.

The combination of the physical and chemical effects referred to above, explains the worsening of agreement for coins with gold contents ranging from 50% to 80%.

The uncertainty in the results obtained for copper is larger than the uncertainties for gold or silver. The small percentage of copper in the analysed coins and the existence of the spectra interference due to $\text{Cu}_{K\alpha}$ and $\text{Au}_{L\alpha}$ escape peak overlapping cause the copper results to be less precise. This fact does not allow one to extract further information on possible different values obtained by both techniques.

5. Conclusions

As EDXRF results are obtained measuring characteristic X-rays that are produced in deeper layers, for uncleaned gold coins they are more accurate than PIXE results.

For coins with a high standard of fineness ($\text{Au} > 94\%$) no significant differences between the results are found. However, for coins where gold contents are in the range 50–80% of the total matrix composition, relative deviations up to 15% can be observed in Au concentration.

Thus, although each technique alone can be satisfactorily used for classifying uncleaned gold coins by alloy composition, some care should be taken when trying to combine results obtained by both techniques.

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