EDXRF as a routine tool for numismatic studies

Energy dispersive X-ray fluorescence (EDXRF) technique is a well known analytical tool for the determination of elemental concentrations of various types of samples of archaeological, biological, geological or environmental nature. It is a non-destructive technique capable of detecting elements down to the limit of ppm¹. Compared to the other non-destructive methods, namely particle-induced X-ray emission (PIXE), electron probe micro-analysis (EPMA), etc., EDXRF is a simple and less expensive technique. Hence there is greater demand for analysing precious archaeological items, especially old coins using EDXRF.

The study of old coins in India is not a recent phenomenon. The Indian Institute of Research in Numismatic Studies, Nasik, has been doing this job for quite sometime. But the main technique used, related to the compositional analysis of a coin, is the specific gravity method by which only coins based on the binary alloys could be analysed. Although

Figure 1. Obverse and reverse sides of the analysed coins. No. 1, 1st century BC; No. 2, 4th century AD; No. 3, One rupee Indian coin of 1976; No. 4, One rupee Indian coin of 2000.

EDXRF, PIXE and neutron activation analysis (NAA) have been in use in other advanced countries for a long time, no effort has been made in the past to apply these sophisticated techniques in Indian numismatic studies. Recently, Hajivaliei et al.² and Vijayan et al.³ made attempts to analyse some ancient Indian coins with PIXE. We have now analysed a collection of Indian coins, both ancient (5th century BC-11th century AD) and recent (1975-2000), with our standardless EDXRF system. The obverse and reverse sides of the four coins analysed here are shown in Figure 1. In this communication, we present the results of these four coins (see Table 1) to demonstrate how quickly EDXRF technique can be used in numismatic studies.

The experiment was performed using a system described in Mandal *et al.*^{4,5} A schematic diagram of the present experimental arrangement is shown in Figure 2. A Kevex 60 watt Tungsten X-ray tube at 35 kV with a current of 0.3 mA was the source of primary X-rays. A thick Mo foil was used as a secondary target to get almost monochromatic X-rays. The incident and emergent X-rays make an angle

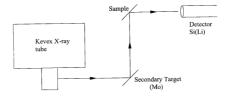


Figure 2. Schematic diagram of the present experimental set-up.

Table 1. Elemental composition (in wt%) of the four coins whose spectra are shown in Figure 3 a-d

Coin no.	Composition
1 (1st century BC)	Zn 1.4%, Pb 98.6%
2 (4th century AD)	Fe 2.4%, Cu 72.0%, Zn 1.1%, Pb 24.5%
3 (1976)	Ni 26.3%, Cu 73.7%
4 (2000)	Cr 16.6%, Fe 83.4%

of 45° with the surface of the sample. The coins were first washed using distilled water and then cleaned with alcohol. They were then irradiated under K X-rays of Mo. Fluorescent X-rays emitted from the coins due to irradiation were detected with an ORTEC LEPS (HPGe) detector having a resolution of 180 eV at 5.89 keV. Figure 3 *a*–*d* shows the spectra obtained from the four coins. The time required for a typical run varied from 30 to 45 min.

Using pure foils of Ti, Fe, Ni, Cu, etc. a good energy calibration curve was obtained. With this curve, the qualitative picture of the coins could be readily ascertained. For quantitative analysis, we used a program used earlier⁶ to determine the composition of alloys. In short, the principle is based on the fundamental parameter method⁷, where physical parameters such as photoelectric crosssections, total mass attenuation crosssections, fluorescence yields, X-ray branching ratio, detector efficiency (calculated theoretically) are given as inputs. The program then theoretically generates fluorescent X-rays and compares the intensities of these fluorescent X-rays with the experimental ones in an iterative manner till the final concentration values converge to a point. The absolute value of the incident flux or the geometrical factor is not required in this calculation, as this program calculates only the relative concentration of elements with the assumption that the sum of concentrations of all the elements (as observed from their X-ray lines) adds up to 100%. In this calculation enhancements produced by the K_{α} , K_{β} , L_{α} and L_{β} lines of higher Z elements has also been considered. Table 1 shows the compositional analyses of the four coins analysed with the present EDXRF system. The advantage of the present technique is that one can calculate the elemental concentration of a coin by exposing it only once under the desired radiation without requiring any idea about the geometry and incident flux. This saves a lot of time compared to the method where different calibration curves are made by exposing different standards.

To an archaeologist, stratigraphy and palaeography of the coins are two main sources of information to reconstruct the

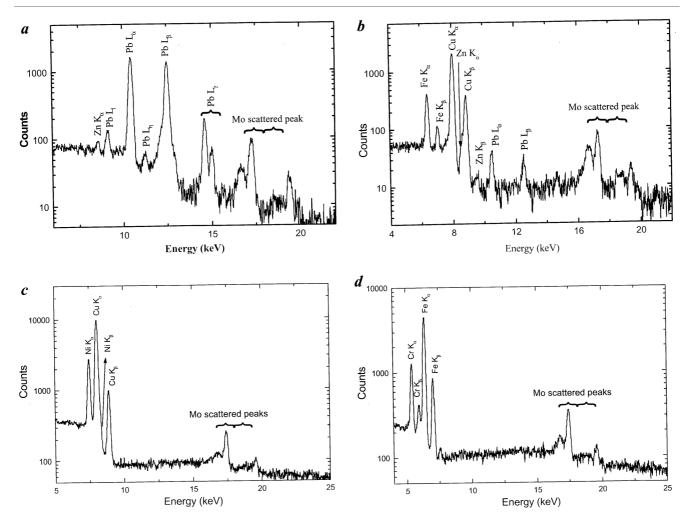


Figure 3. Spectra from a, Coin no. 1 (1st century BC); b, Coin no. 2 (4th century AD); c, Coin no. 3 (1976); and d, Coin no. 4 (2000) excited with Mo K X-rays obtained from a Mo secondary target. The X-ray tube was run at 35 kV with a current of 0.3 mA.

past history. The non-destructive elemental concentration of coins will be an important added information which will enable him to study the economy, availability of different metals and also the metallurgical processes which existed during that period.

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