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# PIXE analysis of ancient Indian coins

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## Abstract

A number of coins of Hindu Shahis Dynasty of Kabul (990–1015 A.D.) have been analysed using proton induced X-ray emission (PIXE) technique. The 3 MeV proton beam from the Pelletron Accelerator at the Institute of Physics, Bhubaneswar, India was used for the production of X-rays. The X-rays were detected by Si(Li) detector ( FWHM = 180 eV at 5.9 keV) placed at 90° to the beam direction. For the reliable calibration of the analytical system, thin foils of Micromatter standards of Fe, CuS, KCl, and $RbNO_3$ were used. The computer code GUPIX was employed to get concentration of trace elements in these coins. The elements Ca, Ti, Cr, Fe, Ni, Zn, As, Sb, Pb, and Bi were detected in these coins alongwith the major component of Cu and Ag. The coins were classified in two groups, coins no. 3, 9, 10, 11, 13, 14, 15, 16, 18, 19 as copper or billon coins having major component of copper, while coins no. 6, 17, 20, 21, 22 as silver coins having the major component of silver. The first group seems to belong to lower denomination while the other group belongs to higher denomination coins. There is a strong positive correlation between lead and zinc and also a strong negative correlation between copper and silver. The weight of coins varied between 3.05 and 3.39 gram. The comparison of our results with that of the ores of various mines indicates that the source of copper in these coins is from Khetri mine in Rajasthan. Silver seems to come from Afghanistan since it is not reported to occur as a primary mineral in ancient India.

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## 1. Introduction

The study of the composition and the content of the trace elements of ancient objects provides important information concerning technology, provenance and other historical facts. The chemical analysis of old coins provides valuable information about the metallurgy and economy of the time of minting the coins [1]. Little analytical work has been done so far regarding the ancient Indian artefacts. The techniques of the semiquantitative spectrographic analysis, atomic absorption spectroscopy, the electron beam induced X-ray fluo-

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rescence with an energy dispersive detection system (EDAX) and transmission electron microscopy (TEM) have been used in the past to study very few icons and some coins of ancient India [2,3].

The proton induced X-ray emission (PIXE) is non-destructive, multielemental and fast technique, so a large number of objects from archaeological excavations or museum collections can be analysed. It is comparatively universal, i.e. applicable to many materials and objects of any dimension and it is highly sensitive (ppm). Therefore, it is ideally suitable for the analysis of archaeological samples.

Presently a preliminary survey intending to investigate the possibility of classification on the basis of alloy composition has been done on the coins of Hindu Shahis Dynasty of Kabul (990–1015 A.D).

## 2. Experimental set up

The 3 MeV proton beam from the Pelletron Accelerator (9SDH2 from NEC, USA.) at the Institute of Physics, Bhubaneswar was used [4]. A multipurpose scattering chamber with 20 inch diameter is designed to carry out Rutherford backscattering (RBS), channelling, nuclear reaction analysis (NRA), and with a special arrangement for particle induced X-ray emission (PIXE) studies, it is attached to the beam line as shown in Fig. 1.

The vacuum obtained inside the experimental chamber was of the order of $10^{-7}$ Torr. The chamber has two view ports and several other ports for various feed throughs. The detector signal was shaped and amplified and finally through a pulse height analysis the energy spectrum was stored and displayed in a multichannel analyser (CANBERRA-88). The beam size at the target position was ~2 mm diameter. The target was positioned at 45° w.r.t. the beam direction and the characteristic X-rays were detected by Si(Li) detector (FWHM = 180 eV at 5.9 keV ) at 90° to, the beam line as shown in Fig. 1. A 35 μm mylar window was attached to the X-ray detector port. The distance between the target and the detector was 9 cm, out of which 4 cm is in the air (outside the chamber). To reduce high count rate, an aluminised mylar (150 μm) has been used as absorber. This absorber reduces X-ray intensities of low $Z$ elements (Si–Ca) much more as compared to high $Z$ elements ($Z$>25). This enables the use of high beam currents and gives increased sensitivity to heavy elements. The beam current was integrated in the sample (for thick targets) and in a Faraday cup behind the target (thin targets). To get an accurate charge integration at the sample position, a secondary electron suppresser system applying negative ~200 volts was used. For the reliable calibration of the analytical system (viz. X-ray yield observed by the detector per unit charge per unit mass of the element) thin Micromatter standards were used. The reported concentration alongwith experimental ones for Micromatter standards are given in Table 1.

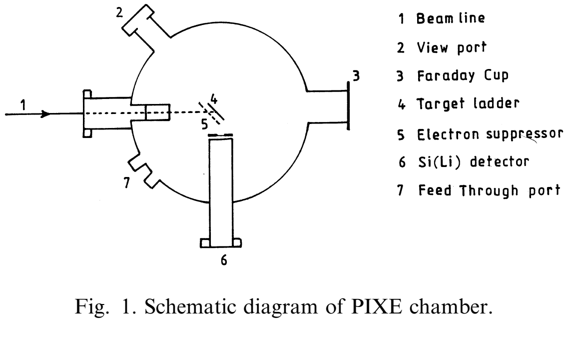


Fig. 1. Schematic diagram of PIXE chamber.

The coins were kept in 10% caustic soda solution for about a fortnight and were scrubbed with tooth brush to remove the corrosion, these were then washed in fresh running water for about 8–10 h. This solution affects the patina only and not the core. Each target was run for a charge of about 3 μC. The beam current was kept lower than 5 nA in order to avoid high counting rates at the detector that would reduce the detection sensitivity due to increase of the background noise. The typical spectra of two copper and silver coins are shown in Fig. 2.

## 3. Data analysis

The Guelph PIXE code GUPIX was employed. The detailed features of this code has been ex-

Table 1
Reported and experimental concentration for Micromatter standards

| Micromatter | Fe | CuS | | KCl | | $RbNO_3$ |
|---|---|---|---|---|---|---|
| Standard | | Cu | S | K | Cl | Rb |
| Reported (μg/cm$^2$) | 216 | 151 | 43 | 88 | 80 | 83 |
| Measured (μg/cm$^2$) | 207 | 155 | 42 | 82 | 74 | 85 |

plained by Maxwell et al. [5]. The quantitative estimation was done using thick target option of GUPIX code. The GUPIX software utilises the fundamental parameter method for the quantitative analysis. For a known experimental geometry the sample composition can be calculated from the measured intensities of the X-ray lines using known physical parameters like X-ray ionisation cross section, mass attenuation coefficient, and fluorescent yields. The calculations consider particle stopping powers and the energy dependence of the ionisation cross sections. The absorption of X-rays leaving the target from different depths in direction to the detector are taken into account. The coins are infinitesimally thick target for 3 MeV protons, therefore, matrix effects with infinitesimally thick target were applied. Since the coins are made of metal and all of their elements are seen in the X-ray spectrum, during the concentration iteration procedure no invisible elements ($Z = 1-16$) concentration had to be provided. Therefore all information to apply matrix correction could be obtained from the elements seen in the spectrum. We normalised the sum of concentrations so obtained assuming that no invisible element is present in the coins. The error in the final concentration values is of the order of 5–10% due to the fundamental parameters and efficiency calibration.

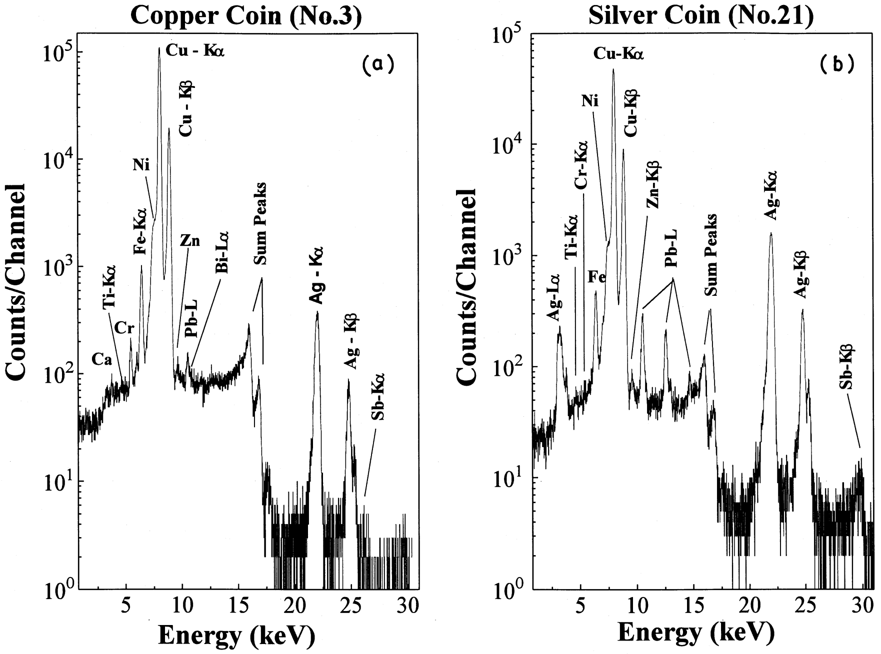
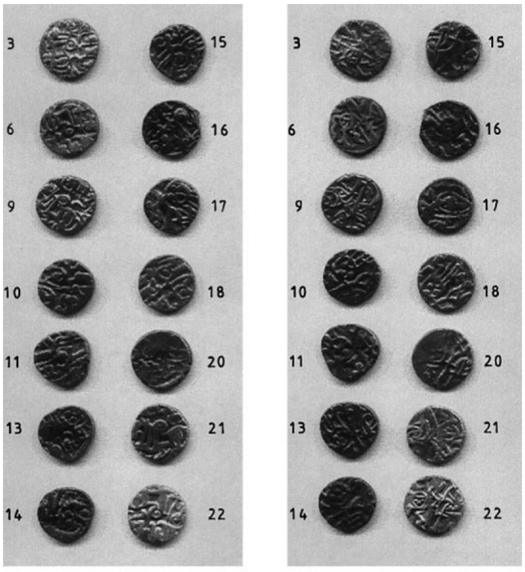


Fig. 2. Typical PIXE spectrum of (a) coin No. 3 (copper); (b) coin No. 21 (silver).

## 4. Results and discussion

The ancient period approximately ends in 1200 A.D. At that time India embraced the whole subcontinent including the present Pakistan, Bangladesh, Afghanistan, Srilanka, Nepal and Tibet. The elemental analysis of fifteen of existing twenty two coins of Hindu Shahis Dynasty of Kabul (990–1015 A.D.) (Fig. 3) was done using proton induced X-ray emission (PIXE) technique and the results are discussed. These coins were found at Sunam and Bhudan in Ludhiana district, Janer in Moga district and Sarainanga in Faridkot district of Panjab state in north-west India. The twelve elements namely Ca, Ti, Cr, Fe, Ni, Cu, Zn, As, Ag, Sb, Pb, and Bi were detected by the present experimental set up. The percentage abundance of these elements are given in Table 2. The weight of these coins are shown in Table 3. These are found to have standard deviation of ±0.112 g.

The coins are mainly either of copper or silver. The variation of copper is from 30.9 to 78.4% and that of silver from 6.95 to 66.2% while the variation for lead is from 0.2 to 21.6%. Also the correlation between different elements has been calculated. There is a strong positive correlation between lead and zinc and also strong negative correlation between copper and silver. Since copper and silver are the main elements, we can divide these coins in two groups; coins no. 3, 9, 10, 11, 13, 14, 15, 16, 18, 19 as group one and the coins no. 6, 17, 20, 21, 22 as group two.



(a) (b)

Fig. 3. The picture of both sides of Hindu Shahis Dynasty coins (a) obverse (bull side); (b) reverse (horse side).

The first group is called copper or billon (alloy of copper and silver with unfixed combination) group and the second group is called silver group. In the latter the percentage of silver is above 40%. The range of variation of copper in the silver coins is found to be from 30.9 to 56.3% which is the principal debasing component. In all the silver coins arsenic is absent but bismuth is present and lead concentration is relatively smaller i.e. less than 2%, whereas in copper coins arsenic is present but bismuth is normally absent and lead concentration in seven coins out of ten is greater than 6% whereas in others it varies between 0.2 and 2%.

Recently Biswas [3] has pointed out that the ore-metal correlation depends upon:

a) The type of the ore, oxide or sulphide or silicate and the nature of impurities.
b) The precise conditions of smelting, such as temperature, nature of fuel, flux etc., and several other factors.

The presence of antimony in all the coins (except one) indicates primitive smelting. Antimony is a common impurity of galena and also some copper ores, its presence can be due to an admixture of antimony mineral such as stibnite i.e. antimony trisulphide ($Sb_2S_3$).

## 5. Silver coins

Earlier results of the analysis of twelve silver coins of Adivaraha type of the Pratihara King Bhoja (833–890 A.D.) have been reported by Prakash and Singh [2]. The content of silver in Adivaraha coins was found between 27.7 to 47% and that of copper was found to be from 51.4 to 70.8% by chemical analysis (Table 4). Although there are some coins with low silver, all of them are called silver coins. The percentage of Cu and Ag in Adivaraha and the present coins is found to be almost of the same order. This shows that the

Table 2
Percentage concentration of present elements in analysed coins

| Coin No. | Ca | Ti | Cr | Fe | Ni | Cu | Zn | As | Ag | Sb | Pb | Bi |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 3 | 0.17 | 0.00 | 0.10 | 0.37 | 0.48 | 78.4 | 0.30 | 0.12 | 19.5 | 0.23 | 0.20 | 0.13 |
| 6 | 0.28 | 0.03 | 0.07 | 0.29 | 0.48 | 51.8 | 0.86 | 0.00 | 43.2 | 0.32 | 2.17 | 0.50 |
| 9 | 0.66 | 0.02 | 0.02 | 0.11 | 1.72 | 71.8 | 0.92 | 0.52 | 16.8 | 1.33 | 6.11 | 0.00 |
| 10 | 0.16 | 0.02 | 0.00 | 1.73 | 0.55 | 56.9 | 2.38 | 0.26 | 19.8 | 1.11 | 17.1 | 0.00 |
| 11 | 1.34 | 0.03 | 0.10 | 0.23 | 1.27 | 74.4 | 3.53 | 0.67 | 6.95 | 0.78 | 10.7 | 0.00 |
| 13 | 2.11 | 0.01 | 0.02 | 0.24 | 0.42 | 66.1 | 3.71 | 0.30 | 8.11 | 1.08 | 17.9 | 0.00 |
| 14 | 0.48 | 0.00 | 0.21 | 1.00 | 0.24 | 67.5 | 1.13 | 0.57 | 17.0 | 0.43 | 11.3 | 0.14 |
| 15 | 1.15 | 0.04 | 0.03 | 0.85 | 0.28 | 54.2 | 2.45 | 0.50 | 24.2 | 0.60 | 15.7 | 0.00 |
| 16 | 1.70 | 0.02 | 0.00 | 1.91 | 0.40 | 60.0 | 4.80 | 0.00 | 8.03 | 1.54 | 21.6 | 0.00 |
| 17 | 0.20 | 0.02 | 0.02 | 0.05 | 0.31 | 44.2 | 0.16 | 0.00 | 53.1 | 0.37 | 1.14 | 0.43 |
| 18 | 0.06 | 0.00 | 0.00 | 0.14 | 0.63 | 70.5 | 0.50 | 0.40 | 24.7 | 0.37 | 2.56 | 0.14 |
| 19 | 0.14 | 0.02 | 0.01 | 0.16 | 0.63 | 67.0 | 0.37 | 0.25 | 27.8 | 1.36 | 2.20 | 0.06 |
| 20 | 0.16 | 0.01 | 0.02 | 0.20 | 0.49 | 45.8 | 0.29 | 0.00 | 52.1 | 0.00 | 0.91 | 0.04 |
| 21 | 0.19 | 0.01 | 0.00 | 0.26 | 0.32 | 30.9 | 0.22 | 0.00 | 66.2 | 0.10 | 1.62 | 0.18 |
| 22 | 0.20 | 0.00 | 0.10 | 0.46 | 0.36 | 56.3 | 0.37 | 0.00 | 40.5 | 0.18 | 1.27 | 0.26 |

source of ore used by Hindu Shahis (990–1015 A.D.) was the same as used by earlier kings.

The presence of bismuth in silver coins may be responsible for embrittlement of these coins. Silver is not reported to occur as a primary mineral in India. The Faranjal mines of Afghanistan, some mines in Armenia and many lead mines of Persia have been reported for obtaining silver in ancient India [2].

Table 3
Weight of analysed coins

| Coin No. | Weight (g) |
|---|---|
| 3 | 3.061 |
| 6 | 3.288 |
| 9 | 3.260 |
| 10 | 3.098 |
| 11 | 3.211 |
| 13 | 3.212 |
| 14 | 3.350 |
| 15 | 3.289 |
| 16 | 3.050 |
| 17 | 3.356 |
| 18 | 3.329 |
| 19 | 3.226 |
| 20 | 3.388 |
| 21 | 3.081 |
| 22 | 3.237 |

## 6. Copper coins

Friedman et al. [6] have claimed that with regard to the copper artefacts, the elements of silver, arsenic, bismuth, iron, antimony and lead were the most important metallic impurities in relating the metal back to the original type of ore. The presence of iron as impurity in our samples could be related to the use of the sulphide ore (chalcopyrite). The Indian sources for copper were Baluchistan, Jaipur area, Ajmer, Mewar, Khetri and Singhana which had been worked upon from early times. These regions could be taken as the source of copper, because of the presence of small quantities of sulphur (in low energy part of spectrum which were selectively absorbed by filter) and the absence of tin point to the use of sulphide ore, which abounds in these mines. Also the presence of nickel and arsenic in these coins indicates that Khetri and Singhana mines might have been the major source of copper. Presence of arsenic in our coins shows that primitive smelting procedures may have been used in minting of these coins. Since the boiling temperature of arsenic is 613°C hence we may conclude that these coins were die-struck and not cast which needs high temperature.

Table 4
Percentage of silver and copper in Adivarah coins

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ag | 34 | 36.9 | 43.6 | 47 | 45.8 | 33.3 | 29.7 | 27.7 | 29.4 | 31.8 | 31.8 | 46.3 |
| Cu | 64.4 | 61.7 | 55.1 | 51.4 | 53.1 | 64.8 | 68.8 | 70.8 | 68.4 | 66.6 | 66.1 | 52.3 |

## 7. Conclusion

From our results we can say that the primary source of ore for copper coins was local, i.e. Khetri and Singhana in Rajasthan, and that of silver from Afghanistan. Also the technology of minting of the coins seems to be primitive i.e. smelting at low temperature. The presence of arsenic in the coins vouches die-striking technique for the specie.

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