

**MULTI-ELEMENTAL ANALYSIS OF COLONIAL AND POST-COLONIAL
NIGERIAN COINS BY PROTON INDUCED X-RAY EMISSION (PIXE)
SPECTROMETRY**

G. C. Ezeh* and E. I. Obiajunwa

Centre for Energy Research and Development, Obafemi Awolowo University, Ile-Ife, Nigeria

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ABSTRACT

The investigation of old and new coins from different countries in the world has generated a growing interest among numismatic and archaeological researchers. The challenge is to explain the large diversification of these coins, to determine the differences in composition, weight and physical aspects. A non-destructive physical method of ion beam analysis; PIXE was employed to investigate elemental properties of colonial and post-colonial Nigerian coins. The weights of the coins varied between 1.89 and 11.46 g while their thicknesses ranged from 0.10 to 0.40 mm. The elements; Al, Si, Mn, Fe and Zn were detected along with the major components of Ni and Cu. The elements displayed both positive and negative correlations. The study could aid in solving some scientifically questions of conservators and tourists on “what” material is it especially now that coins have long been demonetized in Nigeria.

Keywords: archaeology, coins, composition, numismatic, PIXE.

Author Correspondence, e-mail: goddyich@yahoo.com

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1. INTRODUCTION

Elemental composition studies of ancient objects (such as ancient glasses, coins, ceramics, metal alloys, ornaments, wooden wares and so on) are necessary in archaeology as



information regarding technology, provenance and other historical facts could be revealed. Again, the elemental analyses of artefacts such as ancient coins could provide valuable information regarding metallurgy and economy at the time of minting. The problem arises from the necessity to explain large diversifications of these coins as well as the differences in compositions, weights and physical aspects. Coins usually have a roughly homogenous core and mostly thin surface layer with different compositions and varying thickness. The layers can be enriched, oxidized, corroded or soiled during usage or storage.

Several spectroscopic techniques such as atomic absorption spectroscopy (AAS), x-ray fluorescence with an energy dispersive detection system (EDXRF) spectroscopy and transmission electron microscopy have been used in the past to study the chemical compositions of Indian ancient coins (Hajivaliei *et al.*, 1999). Proton Induced X-ray Emission (PIXE) experiment, an accelerator-based ion beam analysis (IBA) technique has been applied to the studies of archaeological objects for many years (Cohen *et al.*, 2004). PIXE is well suited for such studies because of its unique advantages; it is non-destructive, multi-elemental, fast, low minimum detection limits (MDLs) for a very broad range of elements in the Periodic Table and can quantitatively detect picograms of materials in micrograms of samples. It is comparatively universal, i.e. applicable to many materials and objects of any dimension. Therefore, large number of objects from archaeological excavations or museum collections could be studied.

A preliminary survey to investigate the chemical compositions of Hindu Shahis Dynasty of Kabul coins have been reported (Hajivaliei *et al.*, 1999). In Nigeria, little or no analytical work has been reported on ancient pre or post-colonial coins, thus information on elemental compositions is grossly dearth. Hence, in this work PIXE was applied for the elemental characterization of colonial and pre-colonial Nigerian coins.

1.2 Brief history of Nigerian currency

The West African Currency Board was responsible for issuing currency notes and coins in Nigeria from 1912 to 1959. Prior to the establishment of West African Currency Board, Nigeria had used various forms of money including cowries and manilas. On 1st July, 1959 the Central Bank of Nigeria issued Nigerian currency notes and coins while the West African Currency Board notes and coins were withdrawn. It was not until 1st July, 1962 that legal tender status

was changed to reflect the country's new independent status. Nigerian government changed to decimal currency in 1st January, 1973 with major currency unit called Naira which was equivalent to ten shillings while the minor unit was kobo; 100 of which would make one Naira. In 1973, coins were introduced in denominations of ½, 1, 5, 10 and 25 kobo while in 1991, 50 kobo, 1 and 2 naira coins came on board. However, it is sad to note that due to bad economic policies, Nigerian coins are now only visible in the archives as they have long been demonetized.

2. RESULTS AND DISCUSSION

2.2 Physical characteristics of the samples

Table 1 displayed the physical characteristics (weight, thickness and diameter) of the coins. The weights ranged from 1.89 to 11.46 g with average mean weights of 4.71 g. Again, the thickness and diameter were in the range of 0.10 to 0.40 mm and 17.70 to 27.60 mm respectively. The standard variance of the physical parameters showed no significant variation in the thickness ($S^2 = 0.01$) while the weights ($S^2 = 8.52$) and diameter ($S^2 = 10.12$) varied significantly.

Table 1: Physical characteristics of the coins

Coins	Weight (g)	Thickness (mm)	Diameter (mm)
1	7.48	0.20	26.00
2	3.40	0.13	21.60
3	5.65	0.14	25.00
4	4.40	0.16	22.40
5	2.67	0.12	20.00
6	11.46	0.40	27.60
7	2.94	0.13	19.00
8	2.37	0.13	17.70
9	1.89	0.10	20.30
10	4.84	0.16	22.80
Variance (S^2)	8.52	0.01	10.12

2.3 Calibration of PIXE set-up

The results of the Certified Standard reference for six thin-film samples are presented in Table 2 alongside with their corresponding laboratory observed values and PIXE efficiency values. This was to validate the outcome of PIXE data as well as to determine its efficiency. The geometry of samples plays a decisive role in the quantitative PIXE experiment, therefore the

ionized layers were within the flat surface so that self-absorption effects of the X-ray emission are negligible. The laboratory observed values of Si, K, Ca, Fe, Ru and Pb reference thin-films standards recorded at least 94 % efficiency in each sample. Results were in agreement with the certified values, which indicate the reliability and reproducibility of PIXE facility employed for elemental analysis.

Table 2: PIXE set-up efficiency measurement with reference standard

Thin Film Labels	IAEA certified reference values ($\mu\text{g cm}^{-2}$)	Observed experimental values ($\mu\text{g cm}^{-2}$)	PIXE efficiency (%)
Si	43.1	41.7	96.8
K	53.0	50.1	94.5
Ca	47.4	46.5	98.1
Fe	46.3	46.4	100.2
Ru	46.1	44.1	95.7
Pb	52.8	50.9	96.4

2.4. Elemental composition of the samples

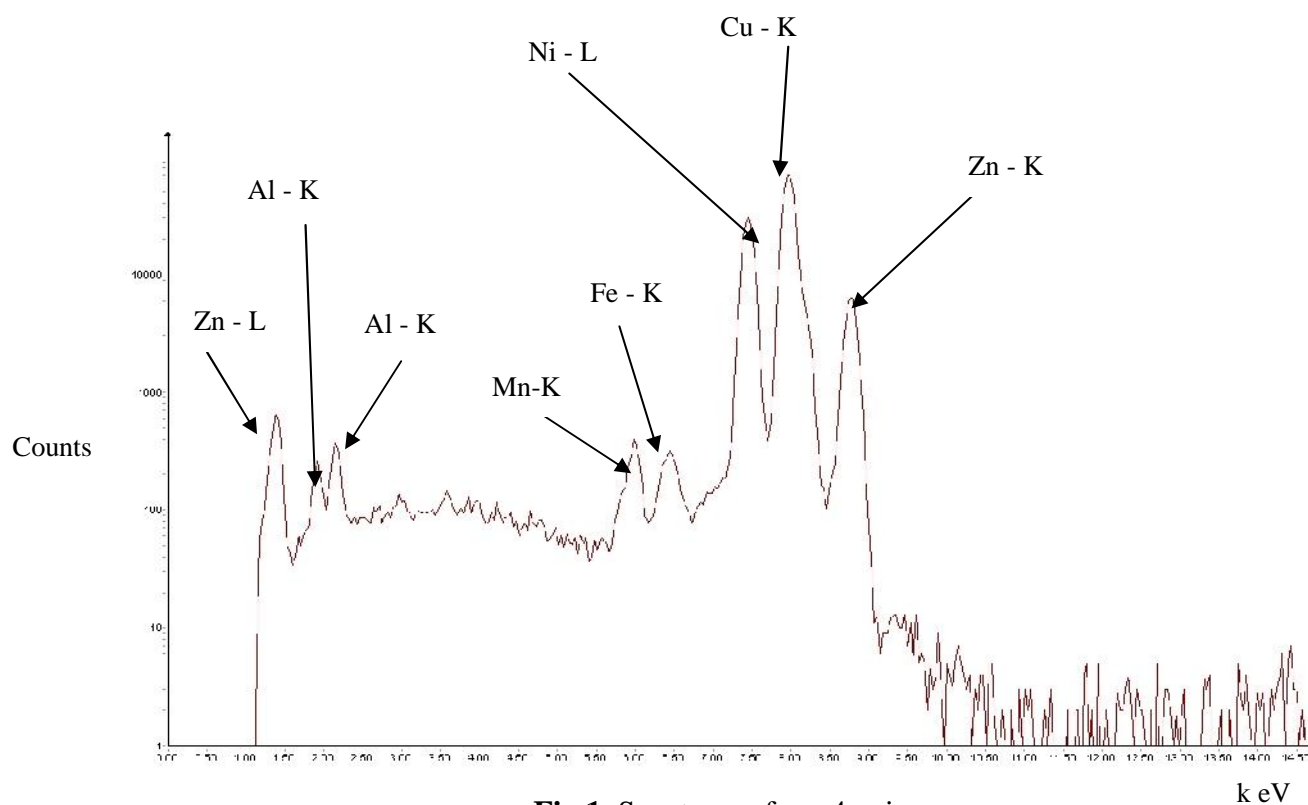
In general, the concentrations of Al, Si, Mn, Fe, Zn alongside the major elements Ni and Cu were detected (Table 3) in the coin samples. Measurement errors were typically of the order ± 1 to ± 10 % for most species due to fundamental parameters and efficiency calibrations. Fig. 1 displayed the spectrum of coin no 4.

The coins were mainly either of Cu or Ni unlike the ancient coins of India which were made up of Cu and Ag (Hajivaliei *et al.*, 1999). The variations for Cu ranged from 33400 to 57900 ng cm^{-2} while Ni is from 10 to 47900 ng cm^{-2} . Samples labelled 2, 3, 4, 5, 7, 8 and 9 were in “Cu” group while 1, 6 and 10 belong to “Ni” group simply because the concentrations of Cu and Ni were more pronounced than other elements. The concentration of Cu (46800 ng cm^{-2}) in sample no. 2 is nearly ten times Zn concentration (600 ng cm^{-2}) thus indicate that the bulk of the sample is Cu based. Similarly, sample 3 to 8 followed similar pattern.

Table 3: Elemental concentrations (ng cm^{-2}) of the coins

Coins	Al	Si	Mn	Fe	Ni	Cu	Zn
1	0.63 (0.04)	1.42 (0.08)	33.92 (1.73)	62.35 (2.46)	47943.30 (76.71)	nd	nd
2	0.75 (0.04)	3.04 (0.11)	0.78 (0.70)	15.53 (1.71)	Nd	46814.27 (55.95)	586.20 (25.97)
3	0.55 (0.04)	1.32 (0.07)	nd	35.71 (2.07)	Nd	57909.14 (110.03)	nd
4	1.29 (0.06)	6.61 (0.18)	1.87 (0.81)	384.00 (4.65)	9.49 (3.81)	51443.27 (92.60)	634.70 (27.36)
5	0.72 (0.08)	2.56 (0.13)	44.52 (1.87)	35.32 (2.53)	9879.13 (39.52)	39746.62 (103.34)	259.20 (14.02)
6	0.69 (0.04)	1.03(0.06)	nd	1534.00 (9.36)	37515.13 (67.53)	nd	nd
7	0.30 (0.06)	1.78 (0.09)	55.55 (1.78)	57.68 (2.55)	7495.39 (38.22)	33441.21 (123.73)	237.60 (12.55)
8	0.29 (0.07)	2.65 (0.11)	12.71 (1.17)	34.24 (2.17)	8435.29 (33.74)	34101.41 (78.43)	241.90 (12.82)
9	0.74 (0.04)	1.28 (0.07)	nd	9.22 (1.70)	562.80 (8.78)	45936.08 (87.28)	8981.11 (52.99)
10	0.64 (0.07)	1.82 (0.10)	42.36 (1.69)	27.90 (2.29)	11525.14 (39.19)	37641.57 (82.81)	368.60 (13.68)

“nd” means not “detected”

**Fig.1.** Spectrum of no. 4 coin

However, sample 3 was exceptionally different as it recorded the highest concentration of Cu (57900 ng cm^{-2}) while other associated major elements (Ni or Zn) were not detected. Contrary, the concentrations of Ni in coin nos. 1, 6 and 10 were higher than other associated elements. For instance, coins labeled 1 and 2 registered Ni concentrations of 47900 ng cm^{-2} and 37510 ng cm^{-2} respectively as the only major element. However, we observed that Ni/Cu ratios were

nearly the same from 0 to 0.31 which is the principal debasing components. The presence of Al, Si, Mn and Fe as an artifact could be related to the use of sulphide ore (chalcopyrite). The absence of arsenic and antimony in all the coins indicate modern smelting procedures and that these coins were not die-struck (Hajivaliei *et al.*, 1999).

2.5. Statistical analysis

The regression plot (Fig. 2) clearly revealed a linear regression of $r^2 = 0.031$ which indicates weak or no correlation for Cu and Ni. However, two points in the scatter plot were outliers due to non-detection of corresponding Ni concentration.

Pearson correlation matrices for the elements are presented in Table 4. The elements displayed positive and negative correlations. The elements displayed both negative and positive correlations. For instance, Cu correlated with Zn ($r^2 = 0.24$) but showed negative correlation with Mn ($r^2 = -0.31$) and Fe ($r^2 = -0.18$). Thus, strong correlations found between the elements could indicate a common source or chemical similarity, whilst weak correlations could imply different source origin or non-chemical similarity (Adebiyi *et al.*, 2006). However, 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 (Biswas, 1996).

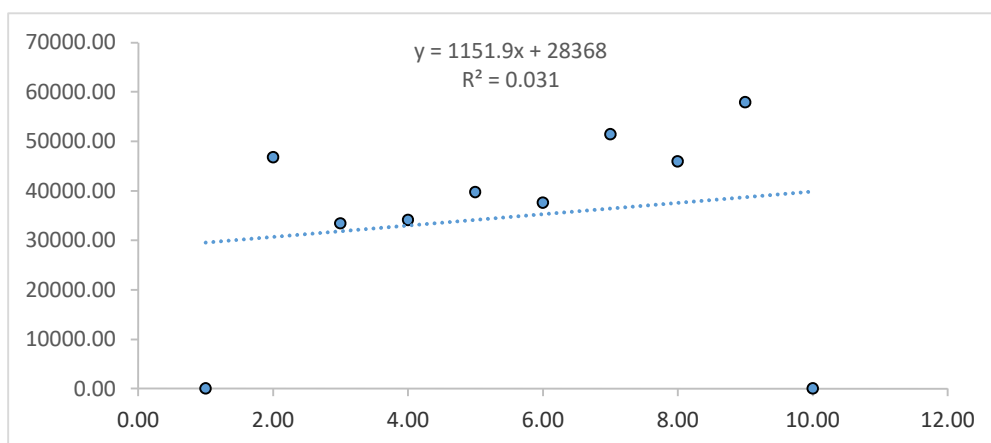


Fig.2. Regression analysis of Cu and Ni

Table 4: Pearson correlation matrices

	Al	Si	Mn	Fe	Ni	Cu	Zn
Al	1.00						
Si	0.70	1.00					
Mn	-0.40	-0.19	1.00				
Fe	0.21	-0.07	-0.34	1.00			
Ni	-0.14	-0.41	0.21	0.49	1.00		
Cu	0.22	0.42	-0.22	-0.56	-0.964	1.00	
Zn	0.15	-0.16	-0.31	-0.18	-0.30	0.24	1.00

3. EXPERIMENTAL

3.1 Sample descriptions

Ten coins (Fig. 3) sourced from local antiquity markets in Enugu, Nigeria were used for the study. The coins were grouped into two; colonial (coins number 7, 8, 9, 10) and post-colonial (coins number 1, 2, 3, 4, 5, 6) types. The identities of the coins were one naira (1), half-kobo (2), one kobo (3), twenty-five kobo (4), five kobo (5), one naira (6), three pence (7), six pence (8), one-tenth of a penny (9) and one shilling (10).

3.2 Sample preparation

Although PIXE requires little or minimal sample preparations, care must be taken in handling the material to be analyzed. The samples (coins) were kept in 10 % caustic soda solution for 28 days and were scrubbed with tooth brush to remove corrosion. The basic solution affects the patina only and not the core of the coins. These were then soaked inside deionized water for 3 hrs, washed thoroughly, dried and were kept inside a desiccator prior to PIXE elemental analysis.

3.3 PIXE set-up and analysis

Fig. 4 displayed the schematic diagram of 1.7 MV Tandem accelerator (a facility of Centre for Energy Research and Development, Obafemi Awolowo University, Ile-Ife, Osun State Nigeria) used for the study. It has a general purpose scattering chamber designed to carry out Rutherford Back Scattering (RBS), Proton Induced Gamma Ray Emission (PIGE) and a special arrangement for Particle Induced X-ray Emission (PIXE) studies. The vacuum obtained inside the experimental chamber was of the order of 10^{-7} Torr.

The chamber has one view port for monitoring the beam and also equipped with a variable collimator for beam size selection of 1, 2, 4, and 8 mm. The detector signals were shaped,

amplified and through a pulse height analysis the energy spectrum was stored and displayed in a multi-channel analyzer (Canberra-88). In this work, a beam size (8 mm), energy (2.5 MeV) and charge ($3.0 \mu\text{C}$) were used for sample irradiation. The target was positioned at 45° with respect to the beam direction and the characteristic X-rays were detected by a Si-Li detector (model ESLX 30 - 50, - 500 V) equipped with a $90 \mu\text{m}$ Kapton filter attached to the X-ray detector port. The filter was used as an absorber to reduce high count rate. The absorber also reduces X-ray intensities of low Z elements (Na to Ca) much more as compared to high Z elements in order to enable the use of high beam currents for increased sensitivity of heavy metals.



Fig.3. Pictures of the coins under study

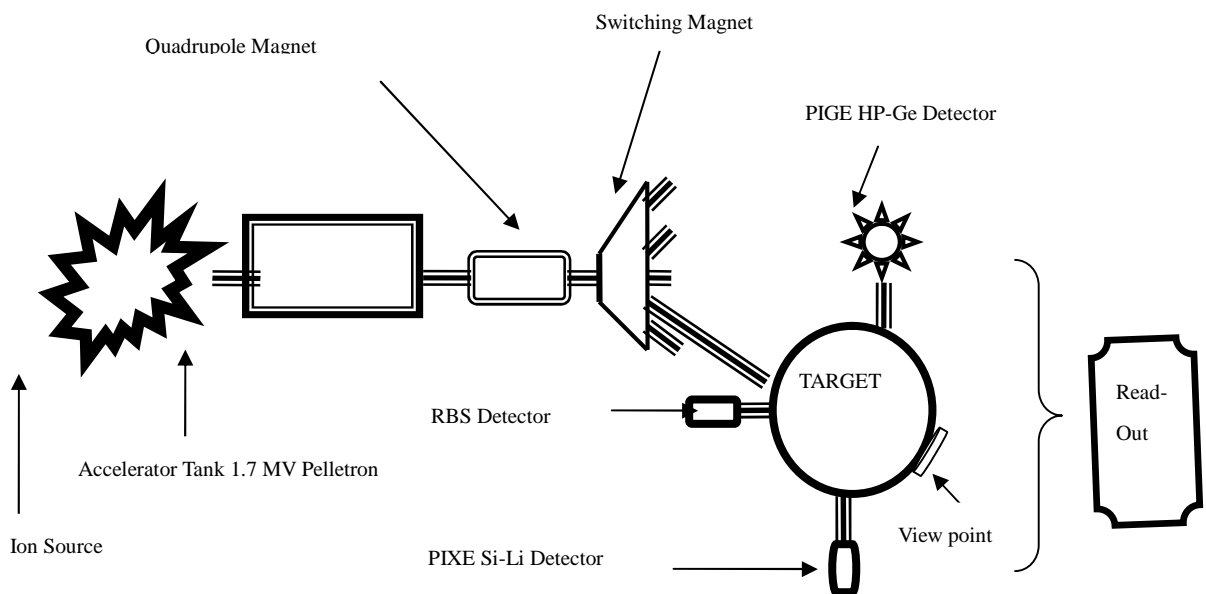


Fig.4 Schematic diagram of CERD ion beam analysis set-up

The distance between the target and the detector was 9 cm, out of which 4 cm was in the air

(outside the chamber). The beam current was integrated in the sample (for thick targets) and in a Faraday cup behind the target (for thin targets). To get accurate charge integration at the sample position, a secondary electron suppresser system applying negative 200 volts was used. Again the beam current was kept lower than 5 nA in order to avoid high counting rates. For 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. X-ray spectra obtained from PIXE measurements were analyzed using thick target option of computer-coded GUPIXWIN. Detailed features of the code have been explained (Cambell *et al.*, 2010).

The choice to use GUPIX was based on several considerations; the main advantages were the good status of the databases (cross sections, fluorescence and Coster-Kronig probabilities, stopping powers, and attenuation coefficients) involved (Cambell *et al.*, 2010). GUPIXWIN has also some useful options, such as matrix iteration, adding invisible element to the fit and analyzing spectra in batches. Calibration of the PIXE system was performed by irradiating suitable micrometer thin-film targets (Ezeh *et al.*, 2014).

3.4 Statistical analyses

The elemental concentrations of the analyzed samples were subjected to statistical analysis to determine the variances, Pearson distance correlation and regression matrices of the elements. This was calculated using Statistical Package for Social Scientist (SPSS) software.

4. CONCLUSION

The elemental compositions of pre-colonial and post-colonial Nigerian coins were determined using proton induced x-ray emission technique (PIXE). Seven elements (Al, Si, Mn, Fe, Ni, Cu and Zn) were detected and their concentrations established. From our results, the coins were majorly either Cu or Ni based with no significant correlation among the elements. The data obtained from this study could provide insight into some of the scientific questions of conservators and tourists on “what” material is it especially now that the coins have long been demonetized in Nigeria.

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