

Research Article

Forensic Elemental Analysis of Five Rupee and One Pound Coin with EDXRF Technique

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Abstract

Energy dispersive X-ray Fluorescence (EDXRF) technique using synchrotron radiation has been employed for elemental analysis of one pound and five rupees coins of two different countries- the UK and India. Total number of 12 coins - 4 one pound and 8 five rupees coin were analysed. A Peltier cooled Vortex solid state detector (SII Nano Technology, USA) having energy resolution of 138 eV at 5.96 keV X-rays was employed for the present analysis. A Peltier cooled Vortex solid state detector (SII Nano Technology, USA) having energy resolution of 138 eV at 5.96 keV X-rays was employed for the present analysis. The investigations were carried out to determine the similarities between the elemental composition and structure of coins. The major elements Cu, Ni, Fe, Cr and traces of two elements Mn and Mo were found during analysis. One of the elements i.e. Cu was found as primary major element in most of the coins. Two other elements Fe and Cr are also found as major element in 2 five rupees coins. Fe was generally considered as cheap metal composition in comparison to Cu. Besides these traces of Mo, S, Ca and Si were also observed whose compositional amount found very low (below 1%). The present study confirms the favorable economic conditions of two countries during their minting time. The XRF spectra and graphical representation of elemental concentration also helps to identify the similarities in structure and composition of coins. Results of present analysis of different types of coins are found in good agreement with standard composition and also with each other. The EDXRF analysis shows its effectiveness in forensic science without alteration of precious samples. Forensic analysis of such coins using Synchrotron radiation is very helpful in archeological study.

Keywords

EDXRF, Si(Li) Detector, Synchrotron Radiation, Coins, Elemental Analysis, Forensic Science

1. Introduction

The Current scenario of any country can be envisioned very easily by currency. From ancient time, currency was playing a vital role in its development. Traditionally, it has

been observed that coins are in frequent use since ancient and medieval time. Much important historical conclusions can be drawn from such type of archaeological samples in

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any form either paper or metallic. However currently, currency in sort of coin with specific secure style and composition are in favour to imprints of earlier era. The coins, as connected with inscription on stone are memorials of historical facts, more certain, because more permanent and unalterable, than writing of the historian. In India, coins of different denomination like Rs 1, 2, 5, 10 are in common use since many decades. The culture, refinement, economy, development of the country easily viewed through currency. Each country has its own currency with precise worth and coins of explicit situation are issued time to time. Many researchers in India and outside India are taking a lot of interest in analyzing coins of ancient, medieval and modern era that helps them to urge info regarding about provenance, minting time and condition. Various types of Egyptian coins, Romanian coins, and gold coins, silver and copper coins of India were analyzed by various researcher and numismatist with different techniques [1-6] like NAA, PIXE and EDXRF etc. One of them, which is fast, sensitive, non destructive and multi elemental in nature is EDXRF i.e. Energy dispersive X-ray Fluorescence. EDXRF [7-13] is a powerful tool to analyze metal compositions of modern and rare ancient coins without any sample preparation. Non destructive nature is the main feature of this method, according to which no loss of sample occurs. Consequently, EDXRF is most favourable to archaeologist and numismatist. In many instances, conventional analytical techniques employed for the examination of metallic samples are unsuitable for the analysis of ancient numismatic artifacts because of their destructive nature. A notable analytical method that facilitates rapid, sensitive, and precise non-destructive micro-analysis is Synchrotron Radiation X-Ray Fluorescence. Recently I. Carlomagno et al. [14] used combining synchrotron radiation techniques for the analysis of gold coins.

In India, Reserve bank of India (RBI) is the authority which decides monetary policy of the country and exchange rate of Indian currency. Each country issues a unique shape, design and composition of coins that differ from other country. Yet there are some similarities in design and compositions of coins of some countries.

Present paper describes here the elemental analysis of coins, One Pound of United Kingdom and Five Rupee, of India; by EDXRF technique. We tend to compare their integrative components to search out facts of matching. First coin of one Pound of the country United Kingdom was issued on 21 April 1983. One Pound has its observe side with a portrait of the Her Majesty the Queen and reverse side showing the United kingdom and its four constituent parts namely (i) Scotland (ii) Wales (iii) Northern Ireland and (iv)

England. The coin edge inscriptions are (i) DECUS ET TUTAMEN (ii) NEMO ME IMPUNE LACESSIT and one coin has decorative pattern symbolizing bridges and pathways. The first old coin of rupee five of Cupro-Nickel alloy was issued in 1992 in India with obverse side bears, lion capital of Ashoka Pillar, with the legend “Satyameva Jayate” in Hindi inscribed below and “INDIA” in English and “BHARAT” in Hindi appearing on either side. The reverse side shows the denominational value “5” in international numeral in center. Below that the word “RUPEES” in English and date in international numerals is shown. A new series of coins of alloy Ferritic Stainless Steel (FSS) and Nickel-brass were issued in years 2007-2008 and 2011. FSS alloy had been introduced only for two years and struck out due to raising cost of copper and nickel and not helping in identification by the visually challenged persons. At present Ni-Brass has been adopted by Indian authority for coin minting.

This analysis would also show effectiveness of synchrotron based EDXRF technique for elemental analysis of coins that reveals the economy and metallurgy of minting time. In ancient and medieval time, precious metals like gold, silver and bronze were most popular for coinage. In modern coinage, metal compositions of Cu, Ni, Zn, Fe etc. are preferred for minting of coins.

2. Materials and Methods

A total of 8 Indian Five rupees coins of India and 4 coins of One Pound of the United Kingdom were put under EDXRF analysis. Obverse and reverse sides of coins are depicted in Figure 1. All coins are personal collection of authors. The characteristic feature and specification of Indian and other coins are shown in Table 1 and also available through various press releases of Reserve Bank of India (RBI) [15] and Royal Mint (Government owned company) U.K. [16]. The RBI is the central banking institution of India, which plays a crucial role in the country's financial and economic stability which also regulate the issue of banknotes, maintain monetary stability in India, and oversee the financial system. Similar role plays by the Royal Mint in UK i.e. to supply coinage for the United Kingdom. Both agencies issued press releases regarding coin mintage. All coins were dipped in Acetone for 24 hours to remove iron enrichment and other corrosion elements presents on the samples. Then coins were cleaned with soft brush and washed with distilled water and finally dried with air drier.



Figure 1. Obverse and Reverse sides of Coin.

Earlier most of the authors used different types of excitation sources like X-ray tubes and radioactive sources. Present experimental work was carried by synchrotron radiation at Raja Ramanna Centre for Advanced Technology (RRCAT), Indore [using Microprobe-XRF beam line (BL-16), Indus-II Synchrotron]. A pictorial view of the synchrotron radiation setup is shown in Figure 2, earlier described by Kumar et al.(2019) [17]. The measurement time for each coin sample analysis was 500 seconds. The elemental compositions of coins were determined by using the formula

$$m_{ij} = \frac{N_{ij}}{I_0 G \varepsilon \sigma_{ij} \beta_i} \quad (1)$$

Where m_j is the concentration of j^{th} element present in the sample, N_{ij} is the net counts per unit time for the i^{th} group of X-rays of j^{th} element, $I_0 G$ is the intensity of the exciting radiation incident on the sample visible to the detector, ε is the detector efficiency for the j^{th} element, σ_{ij} is the theoretical X-ray fluorescence cross section at 20.21KeV excitation energy

and β_i is the self-absorption correlation factor that accounts for absorption of incident and emitted X-rays in the sample.

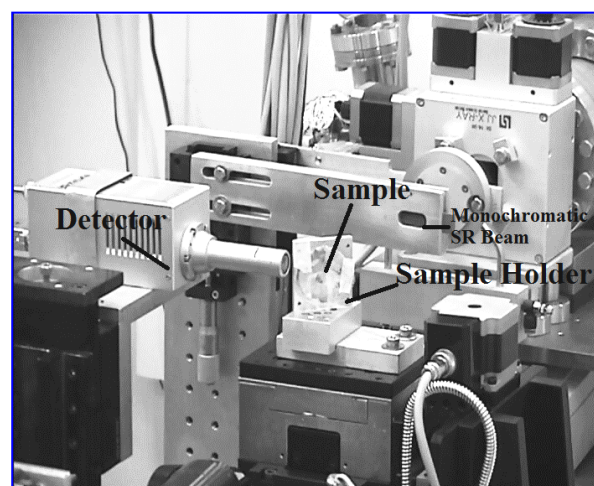


Figure 2. Synchrotron Radiation Setup.

Table 1. Characteristic Features of Coins.

Coin Type	Year of Issue	Country	Weight Standard (in gm)	Weight Measured (in gm)	Diameter	Metal Composition(Standard)
One Pound	1983	United Kingdom	9.5	9.511	22.5mm	Nickle-Brass Cu 70%, Ni 5.5%, Zn 24.5%
One Pound	1989	Scotland	9.5	9.46	22.5mm	Nickle-Brass Cu 70%, Ni 5.5%, Zn 24.5%
One Pound	1996	Northern Ireland	9.5	9.498	22.5mm	Nickle-Brass Cu 70%, Ni 5.5%, Zn 24.5%
One Pound	2005	Wales	9.5	9.426	22.5mm	Nickel-Brass Cu 70%, Ni 5.5%, Zn 24.5%

Coin Type	Year of Issue	Country	Weight Standard (in gm)	Weight Measured (in gm)	Diameter	Metal Composition(Standard)
5 Rupees	1992	India	9	8.868	23mm	Cupro-Nickel Cu 75%, Ni 25%
5 Rupees	1993	India	9	8.828	23mm	Cupro-Nickel Cu 75%, Ni 25%
5 Rupees	1994	India	9	8.995	23mm	Cupro-Nickel Cu 75%, Ni 25%
5 Rupees	1999	India	9	8.957	23mm	Cupro-Nickel Cu 75%, Ni 25%
5 Rupees	2008	India	6	5.926	23mm	FSS Fe 83%, Cr 17%
5 Rupees	2009	India	6	5.946	23mm	FSS Fe 83%, Cr 17%
5 Rupees	2011	India	6	5.972	23mm	Nickle-Brass Cu 75%, Ni 5%, Zn 20%
5 Rupees	2012	India	6	5.987	23mm	Nickle-Brass Cu 75%, Ni 5%, Zn 20%

3. Results and Discussion

The Characteristic features like weight, dimension and composition of coins are depicted in Table 1. Standard and

experimental measurements of weight and diameter show similarity between two types of coins. The result of EDXRF analysis of coins of two countries (U.K. and India) is depicted in Table 2.

Table 2. Elemental Composition of Coins.

Coin No.	Coin Type	Percentage Composition of Elements									
		Cu	Fe	Zn	Ni	Cr	Si	Mn	Mo	S	Ca
1	One Pound	70.191	0	20.449	8.350		0.707	—	0.022	0.084	0.159
2	One Pound	69.111	0	22.529	8.063	—	—	—	0.021	0.097	0.132
3	One Pound	67.560	0	23.617	7.848	—	—	—	0.02	0.148	—
4	One Pound	67.034	0	25.170	6.885	—	0.66	—	—	0.212	—
5	5 Rupees	66.116	0	0	31.263	—	1.516	0.211	—	0.218	—
6	5 Rupees	67.468	0	0	30.066	—	1.015	0.446	—	0.232	—
7	5 Rupees	67.539	0	0	31.143	—	0.956	0.155	—	0.092	—
8	5 Rupees	66.941	0	0	31.558	—	0.668	0.441	—	0.268	—
9	5 Rupees	0	83.573	0	0.338	16.089	—	—	—	—	—
10	5 Rupees	0	84.027	0	0	15.973	—	—	—	—	—
11	5 Rupees	74.570	0	19.127	6.127	—	—	0.123			0.046
12	5 Rupees	73.256	0	20.016	6.425	—	—	0.147	—	—	0.157

Table 3 shows the comparable elemental compositions of major elements of different coins.

In reference to minting alloy of two coins (One pound and five rupee), it is clear that some coins are essentially copper

made rather than their alloy distinction. Two different alloys like Ni-brass and Cupro-Nickel were used for coin minting of these coins. Present investigation also confirms the good economic condition of these countries during their minting

time. One Pound coin of the United Kingdom was found to manufacture with Ni-brass alloy with content of Cu, Ni and Zn as 70%, 5.5% and 24.5%, respectively where five rupee coin of India with Cu and Ni as major elements having composition of 75% and 25% respectively.

Four coins of one Pound of the constituent parts of the United Kingdom of different years were showing here major elements like Cu and Ni having content somewhat lower and higher than as it should be. The content of Copper and Nick-

el were observed in the range of 67.034-70.191% and 6.885-8.350% respectively. Third major element Zn was found in content of 20.449-25.170%. Besides these traces of Mo, S, Ca and Si whose compositional amount were observed very low (below 1%). The harden ability was increased in coins by adding Mo as traces. Other traces are due to earth oxides to be found on coin surfaces. XRF spectrum of one pound coin is shown in Figure 3.

Table 3. Comparable Elemental Compositions of Major Elements.

Coin No.	Coin Type	Cu(in %)		Ni(in %)		Zn(in %)	
		Standard	Experimental	Standard	Experimental	Standard	Experimental
1	One Pound	70	70.191	5.5	8.350	24.5	20.449
2	One Pound	70	69.111	5.5	8.063	24.5	22.529
3	One Pound	70	67.560	5.5	7.848	24.5	23.617
4	One Pound	70	67.034	5.5	6.885	24.5	25.170
5	5 Rupees	75	66.116	25	31.263	25	0
6	5 Rupees	75	67.468	25	30.066	25	0
7	5 Rupees	75	67.539	25	31.143	25	0
8	5 Rupees	75	66.941	25	31.558	25	0
11	5 Rupees	75	74.570	5	6.127	20	19.127
12	5 Rupees	75	73.256	5	6.425	20	20.016
Coin No.	Coin Type	Fe(in %)		Cr(in %)			
		Standard	Experimental	Standard	Experimental		
9	5 Rupees	83	83.573	17	16.089		
10	5 Rupees	83	84.027	17	15.973		

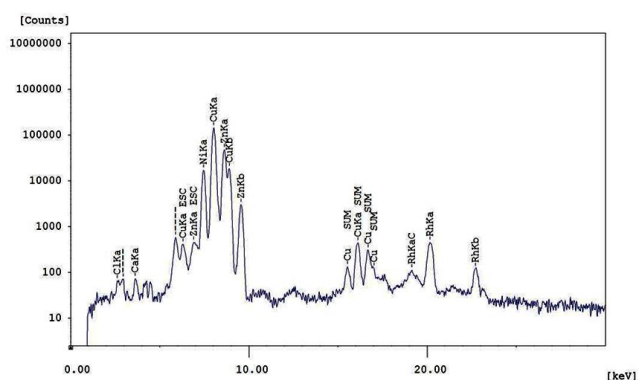


Figure 3. XRF spectrum of One Pound Coin.

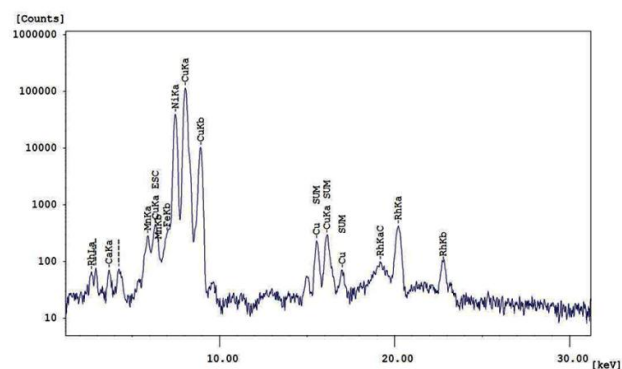


Figure 4. XRF spectrum of Five Rupee Coin.

Similar type of observation has been observed in case of

analysis of five rupee coins of minting years from 1992-1999. Copper and Nickel are found as the major element in the analysis with composition in range 66.116-67.539 % and 30.066-31.558% respectively. Element Zn is found missing here so confirming the coinage of Cupro- Nickel alloy. Traces of Si, Mn and S are also observed in the present analysis with the composition in the range of 0.668-1.516%; 0.211-0.446% and (0.092-0.268%) respectively. XRF spectrum of five rupee coin is depicted in Figure 4.

During analysis of coins of years 2008-2009; two major elements Fe and Cr are found with compositions in the range of 85.573-84.027% and 15.973-16.089% respectively with traces of Ni. The element Fe was generally considered as a cheap metal as compare to high cost metal like Copper and Nickel that was also the reason to put amendment in the composition.

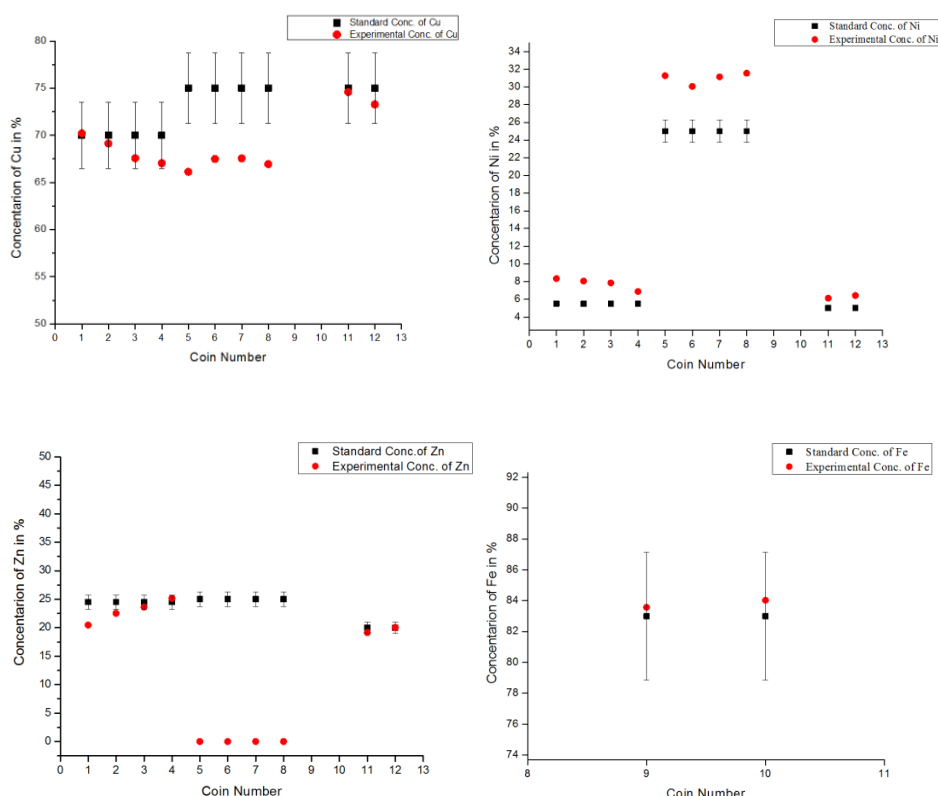
The analysis of coins of year 2011-12 show that Cu, Zn and Ni are the major elements with compositions in the range of 73.256-74.57%, 19.127-20.016% and 6.127-6.425 respectively and also confirmed the amendment preferred in the composition of alloy from FSS to Ni-brass as compare to earlier year's coins. Elemental analysis of coins of two countries provides evidence toward use of copper as the major element in minting except difference of their alloy till 2008. The United Kingdom and their constituent parts most likely preferred Ni-Brass alloy while Indian authority favoured Cupro-Nickel and FSS alloy for coin minting. But now a day in India, Ni-brass alloy are in ordinary use for coin manufacturing with lesser weight.

Present analysis illustrate that the amount of Zn did not

vary much larger than the actual composition in the one pound coin but composition of Ni in the five rupee coins vary somewhat higher than to the actual value. The composition of Ni varies about 26% larger than actual composition in present analysis while that of Cu 6% less than the actual.

Basically these data variation come in to play due to matrix effect during analysis. It may result both in absorption and enhancement of the intensity of characteristic X-ray of interest either due to co-existence of other elemental X-ray or due to addition excitation from the major elemental composition of the sample matrix. This invalidates the direct relationship between the characteristic X-ray intensity and the element amount. Absorption attenuates the secondary X-ray leaving the sample. Enhancement occurs where the secondary X-ray emitted by a heavier element are sufficiently energetic to stimulate additional secondary X-ray from a lighter element. In the present case, Cu emits 8.046 KeV K_{α} X-rays, just above the Ni K-edge. The Cu K_{α} X-rays are absorbed very efficiently by Ni, which then emits additional characteristic X-rays. The Cu line is absorbed while the Ni line is enhanced. Besides this, the primary X-rays from the excitation source are absorbed by the sample. Absorption of primary radiation and absorption and enhancement of characteristic lines are termed as matrix effect.

The major elements Cu, Ni, Zn, Fe and Cr observed in the coins are compared with the standard values and shown Table 3. Figure 5 also depicts the graphically comparison of standard and experimental concentration of major elements of different coins. Comparative analysis is also helpful in forensic analysis and investigation of unknown sample.



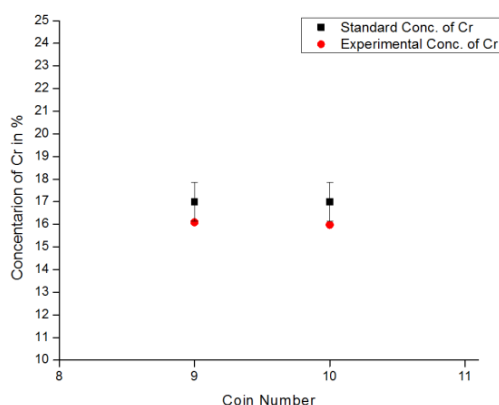


Figure 5. Comparison of Elemental Concentration of major Elements Cu, Ni, Zn, Fe and Cr.

The total uncertainties in the measurements of concentration of element present in the sample are estimated to be 5% (approx.) and are found by the method of propagation of errors in various parameters like area under the L X-ray peaks, mass absorption correction factor, mass per unit area, the geometry factor and detection efficiency used in Eq. (1).

4. Conclusions

Synchrotron radiation based Energy dispersive X-ray fluorescence technique (EDXRF) has been employed for the forensic analysis on one Pound and Five rupee coin of the United Kingdom and India respectively. The investigation clearly demonstrate that two Cu richer alloys i.e. Nickel-brass and Cupro-Nickel were preferred for coin minting which also present good economic policy during that time. Besides this a cheaper FSS alloy are also preferred for coin minting but soon it was struck out. EDXRF is a powerful and very effective analytical tool in the study of elemental composition of metal alloys like coins.

Both coins were successfully analyzed for their elemental compositions with Cu, Ni and Zn as major elements in one Pound coin and Cu, Fe, Cr and Ni in five rupee coins. Traces of two elements Mn and Mo are observed that strengthen the alloy.

One main advantage of this technique that pay special attraction for everyone is its non-destructive nature which means there is no alteration of the sample taken. Some similarities also have been as well found in their shape, size and weight. Forensic analysis of such coins using Synchrotron radiation is very helpful in archaeological study.

Abbreviations

EDXRF	Energy Dispersive X-ray Fluorescence
NAA	Neutron Activation Analysis
PIXE	Particle Induced X-ray Emission

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Author Contributions

Rajive Kumar: Investigation, Software, Supervision, Writing – review & editing

Richa: Methodology, Software, Writing – original

Manoj Kumari: Investigation, Methodology, Visualization, Writing – original

Manoj Kumar Tiwari: Formal Analysis, Resources

Conflicts of Interest

The authors declare no conflicts of interest.

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