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RD and ED-XRF study of Indian; Modern, Ancient and Historic Coins

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Abstract: **The This is an innovative study and very few literatures are available on this specific domain as far as Indian coins are concerned. This is the attempt where reasonable number of ancient coins belonging to different periods were analysed by modern non-destructive multi-elemental technique. The six original coins of different time periods are considered for the study. The coins are analyzed by X-ray Diffraction (XRD) and Energy Dispersive X-ray Diffraction Fluorescent (ED-XRF) techniques without any pretreatment. The phase and structural information are obtained by XRD. The elemental composition was analyzed by ED-XRF study. The coins are made from different metallic elements but data of only six common elements are reported here. The archaeological study of spectroscopic techniques is presented. The results are discussed.**

Index Terms: **XRD; XRF; Structural parameters; Historical Background.**

I. INTRODUCTION

The researchers subjected a number of modern, ancient, and historical coins to compositional and structural testing using X-ray fluorescence and X-ray diffraction techniques. X-ray diffraction is the first exact method for the study of the structure of matter. In archaeology, this analysis is used successfully to study stone constructions, ceramics, pigments, etc. These photon excited techniques have become more popular and made major advantages in the past few years for elemental analysis in different interdisciplinary areas especially on archeological samples. The goal was to test the viability of X-ray diffraction as a tool for examining micro-structural characteristics of very old and often corroded coins that could shed light on ancient processes of production. The aim of this study is to explore the potential for the application of XRD to expanding our knowledge of coins.

The six coins discussed here were selected from the original sample because they illustrate the potential and pitfalls encountered during the course of this study. All interpretations related to coin composition and manufactures are preliminary. The issues discussed which relate to the practical aspects of the execution of the XRD scan (mounting techniques, probe and glancing angle settings etc.) are intended to aid those who would engage in similar study in the future. This study seeks the examination of composition and atomic structure investigating the metallic and oxide phases present by x-ray diffraction. In this technique the primary X-rays are made to fall on the sample substance under study. Because of its wave nature, like light waves, it gets diffracted to a certain angle. This angle of diffraction, which differs from that of the incident beam, will give the information regarding the crystal nature of the substance.

The wavelength of the X-rays can be varied for the application by using a grating plate. Scattering of X-rays by the atoms of a crystal that produces an interference effect. The diffraction pattern of a substance is its "fingerprint" allowing us to identify the substance and determine its crystalline structure. Crystalline solids, when exposed to monochromatic X-rays will diffract according to the principles of Bragg's law. The ED-XRF is a non-destructive technique used for chemical analysis of materials. It is a versatile tool in many analytical problems. Major, minor and trace elements can be qualitatively and quantitatively determined in various kinds of samples: metals, alloys, glasses, cements, minerals, rocks, ores, polymers as well as environmental and biological materials. Elements from Na to U are routinely determined using energy-dispersive X-ray fluorescence spectrometry (ED-XRF) (Mandal A. C., 2014). When a sample is placed in a beam of primary X-rays, part of it will be absorbed and the atoms get excited, by the ejection of electrons present in K and L shells. While relaxing they re-emit X-rays of characteristic wavelength. This re-emitted X-rays are called secondary or fluorescent X-rays and hence the name for this technique. Since, the wavelength of the fluorescence is characteristic of the element being excited; measurement of the wavelength and intensity enables to carry out the qualitative and quantitative analyses.

II. HISTORICAL BACKGROUND

The fig.1.shows the photograph of coins manufactured in different

time periods. Coin-1 is Udaipur kingdom/princely state (also called Mewar) is a region of south-central Rajasthan state in western India (1943). Maharana Bhopal Singh as the ruler of Mewar guided its destiny through India's most momentous period, the Independence from British Imperial rule with a vision to lead in an age of turbulence. Coin-2 is Shri Jiwajirao Shinde Gwalier, Pav Ana (1974/1917 Vikram sawant) Maratha ruler. Coin-3.is Queen Victoria Coat of arms of the East India Company two lions, St George's cross on the crest and flags are observed coin 4 is an image of a coin issued by Shivaji Rao, the Maharaja of Indore. One side of the coin depicts a reclining bull along with the Devanagari legend, 'Shrimant Maharaja Holkar Sarkar Indore'. The other side of the coin consists of the value 'PavAnna' and the date in Vikram Savant 1943 within an ornamented circle.5. Crowned head of George VI facing left.

III. XPERIMENTAL METHOD

The following coins are used for study using the of XRD and XRF sophisticated experimental tools. -

Coin No. from right:

1. Coin-1: Cittrakut Udaipur, Dosti Landhan (1943)
2. Coin-2: Shri Jiwajirao Shinde Gwalier, Pav Ana (1974/1917, Vikram sawant)
3. Coin-3: East India Company ½ PICE (1853)
4. Coin-4: Shrimant Maharaj Holaker Indore, Pav Ana (1943)
5. Coin-5: George VI King Emperor,1/2 PICE (1939)
6. Coin-6: Shri Jiwajirao Shinde Gwalier Pav Ana Sawant (1968)

Fig.1. Photograph of Ancient, Modern and historic Indian Coins

A. *X-Ray diffraction study (XRD)*

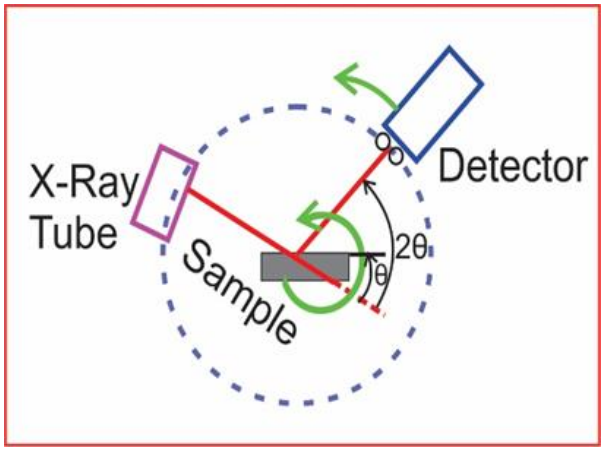

Fig. 2. Diffractometer beam path in θ/2θ mode

When the lattice is illuminated by a collimated beam of X-Ray the lattice reflects the X-rays at angle (θ) specific to the distance spacing of the wavelength of the illuminated X-ray radiation (λ). The Bragg relates (Fig.3) these parameters using equation- $n\lambda = 2d\sin\theta$. An X-ray diffraction pattern is a plot of the intensity of X-rays scattered at different angles by a sample. Every compound has a unique diffraction pattern. In order to identify a substance, the diffraction pattern of the sample is compared to a library database of known patterns International Centre for Diffraction Data (ICDD) (Leng, Y.,2013).

The detector moves in a circle around the sample (Fig.2)

- The detector position is recorded as the angle 2theta (2θ)
- The detector records the number of X-rays observed at each angle 2θ
- The X-ray intensity is usually recorded as "counts" or as "counts per second"

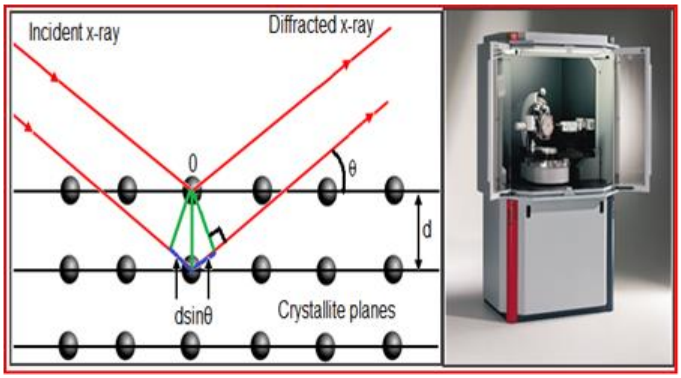

Fig.3. Bruker's X-ray Diffraction D8-Discover instrument

B. *ED X-ray fluorescence study (XRF)*

Currently X-ray fluorescence (XRF) is the most used analysis technique in the study of artifacts with historical-cultural value. XRF works on the atomic level x-rays are produced from the spectrometer and excite the analyzed volume within the specimen. Once this happens it generates the characteristic x-ray equivalent to the energy difference between the inner and outer shell. Each element will have a characteristic x-ray of a specific energy and this is how one can determine what elements are present in the sample (Callister W.D.,2005; Kokatanur R. B.,2015; Marti A.P.,2001).

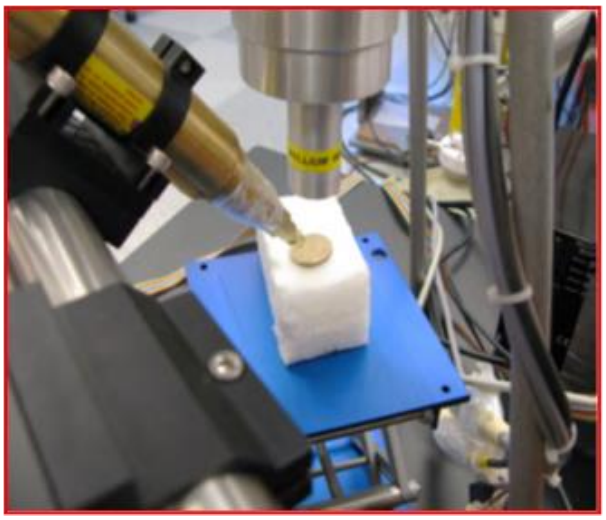

Fig.4. Photograph of XRF machine

IV. RESULTS AND DISCUSSION

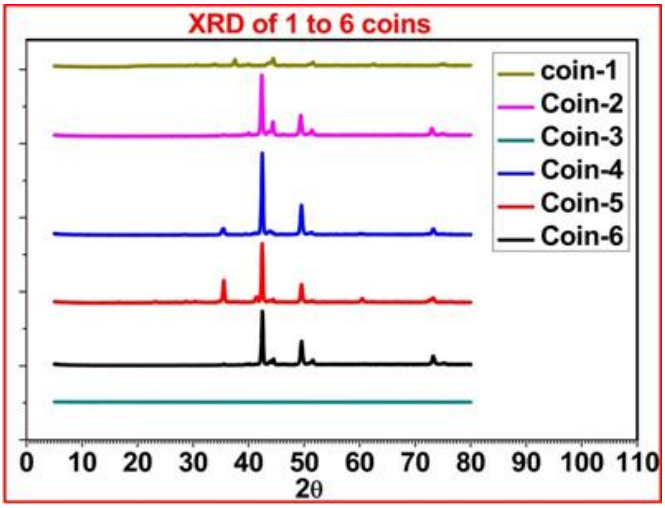

Fig. 7. XRD pattern of Cu and Cu_2O for Reference

An X-ray diffraction pattern is a plot of the intensity of X-rays scattered at different angles by a sample (Fig.5). The coins are scans from 5 to 80̊. The effect of alloying may be seen in the slight shifting of these peaks. The figures show that Cu is the major constituent of almost all coins. The coin 1 to 5 is crystalline phase coin -6 is amorphous in nature. The d value obtained identifies the minerals.

A. Coin-1. Cittrakut Udaypur (1943)

This coin was subjected to half hour scans at theta-2-theta ranging from 5 to 80̊. The three peaks present correspond to the known signature for copper (JCPDS 4-836). The slight peaks are observed. This suggests that texturing throughout the material, likely from the rolling operation to produce the sheet metal.

B. Coin-2. Shri Jiwajirao Shinde Gwalier, Pav-Ana, Sawant (1974)

Reference peaks showed good correspondence to measured peaks. Copper reference peaks were slightly shifted. This shifting effect is likely a result of the Sn and Fe additives whose atomic radii, 145 pm and 140 pm respectively, are larger than that of Cu (135 pm).

C. Coin-3. East India Company ½ PICE (1853)

No peaks are observed indicating amorphous material leading starkly defined textured. In this case the long scan did not reliable clarify the location or relative intensity of peaks. Based on the XRF data we attempted to match alloys and oxide of Fe, as well as Zn and Pb without success

D. Coin-4. Shrimant Maharaj Holaker Indore, Pav-Ana (1943)

This coin was subjected to four one-hour scans: 1 theta-2-theta and 3 at a glancing angle. The major peaks present correspond to the known signature for copper (JCPDS 4-836), cuprites (JCPDS 5-667), and silver (JCPDS 4-783). The slight shifting is observe attributed to effect of Sn in solid solution with either Cu, Ag, or both. There was inhomogeneity in the melting presses.

E. Coin-5. George VI King Emperor, 1/2 PICE (1939)

The major peaks present correspond to the known signature for copper (JCPDS 4-836), cuprite (JCPDS 5-667), silver (JCPDS 4-783), and lead-tin oxide Pb2SnO4 (JCPDS 11-233). The overnight scan allowed us to tentatively identify the as yet unidentified peaks as lead tin oxide.

F. Coin-6. Shri Jiwajirao Shinde Gwalier, Pav-Ana, Sawant (1974)

Near about similar observations are observed as that of coin no 2. The x-ray spectra generated by ED-XRF were interpreted by the analysis software [4] and converted into parts-per-million (PPM), by weight, for 20 elements, including: Si, Al, Fe, Na, Mg, K, Ca, Ti, Mn, Cr, Cu, Ni, Pb, Sr, V, Zn, Ag, and Sn. Prior to commencing XRF testing on the coins, samples of known composition (from the National Institute for Standards and Technology (NIST) were analyzed to test the accuracy and precision of the equipment [5]. Since coins are largely metallic in composition and other elemental data appears unreliable, only data for the six most common metallic elements are reported here (Table 4). Assuming a composition made entirely of these constituents, relative percentages were calculated (Table 5).

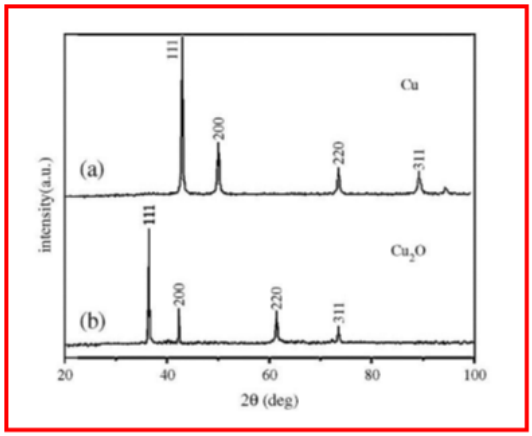

Fig.7. XRD pattern of Cu and Cu_2O for Reference

Coin-1			Coin-2		
Angle (2θ)	D-Value	Intensity (I)	Angle (2θ)	D-Value	Intensity (I)
27.769	3.21009	30.6	28.561	3.12282	28.1
35.550	2.52327	53.9	35.413	2.53269	363
40.119	2.24578	51.2	39.464	2.28154	43.5
42.472	2.12669	3566	41.259	2.18633	58.9
43.879	2.06170	164	42.445	2.12796	5443
44.472	2.03554	349	43.832	2.06377	183
46.372	1.95650	24.2	44.288	2.04357	101

Coin-3			Coin-4		
Angle (2θ)	D-Value	Intensity (I)	Angle (2θ)	D-Value	Intensity (I)
35.575	2.52153	50.7	30.634	2.91604	26.8
40.007	2.25183	137	33.913	2.64120	96.1
42.355	2.13227	3955	37.541	2.39386	403
43.698	2.06978	206	40.037	2.25020	77.1
44.370	2.04001	865	43.536	2.07714	151
46.252	1.96128	36.1	44.419	2.03787	477
49.391	1.84374	1300	62.514	1.48455	102

Coin-5			Coin-6		
Angle (2θ)	D-Value	Intensity (I)	Angle (2θ)	D-Value	Intensity (I)
25.728	3.45990	20.4	28.603	3.11831	18.4
35.536	2.52421	38.6	28.667	3.11152	24.5
38.593	2.33100	19.1	35.507	2.52622	71.5
42.382	2.13096	3020	42.151	2.14213	1238
43.828	2.06394	120	43.544	2.07676	72.6
44.327	2.04190	170	49.182	1.85108	716
50.859	1.79389	52.3	72.722	1.29927	607

PPM (by wt.)	Cu	Zn	Pb	Sn	Fe	Ag
Coin-1	2,891,306	2,947,32	136	--	--	6,129
Coin-2	5,061,974	210,400	--	--	--	9,043
Coin-3	4,305,038	--	19,761	--	750	10,145
Coin-4	2,062,812	5,237	71,871	19,445	27,561	4,831
Coin-5	1,105,732	2,011	11,772	47,182	12,609	6,677
Coin-6	5,961,499	281,543	--	--	--	7,989

Relative Composition (%)	Cu	Zn	Pb	Sn	Fe	Ag
Coin-1	47.15	52.68	0.01	--	--	0.17
Coin-2	96.57	--	--	--	--	0.19
Coin-3	99.25	3.26	0.49	--	0.02	0.24
Coin-4	88.72	0.27	6.83	1.04	2.81	0.32
Coin-5	93.23	0.17	0.99	3.98	1.06	0.56
Coin-6	95.20	--	--	--	--	1.29

CONCLUSION

These important studies did point to the potential for archaeologists and material scientists to gain valuable insight into the atomic structures of coins using advanced XRD techniques. In this research our use of XRD would have been greatly improved by the availability of more reliable compositional tests, though our XRF results were useful for qualitative analysis and comparisons. The XRF results obtained depicts elemental compositions, which shows imperfect technology of casting during those periods. We were also hindered by our inability to access a well-documented history of some of the objects, particularly concerning their possible preservation using chemicals, this issue was compounded by the fact the we were uncertain of the depth of penetration of our diffraction beam. The paper will attempt to look at these scientific methods for studying coins and then, discuss their implications on improving the existing body of research of Indian numismatics. The study may help in understanding

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