ANALYSIS OF ARCHAEOLOGICAL SAMPLES USING ENERGY DISPERSIVE X-RAY FLUORESCENCE METHOD

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ABSTRACT — A study of pottery samples belonging to different periods is undertaken employing an energy dispersive high resolution X-ray fluorescence spectrometer and 30 mCi ^{238}Pu source. The ratios of Manganese to Cobalt and Iron to the 17.28 keV coherent line intensity are found to vary from period to period. It is found that these ratios are high for the present pottery samples when compared to the earlier periods.

1 – INTRODUCTION

A study of archaeological samples is of interest from the view point of the advancement of civilization and technology adopted during different periods of history. There are several analytical methods employed in this direction. Radio-active carbon dating, thermoluminescence [1] and X-ray fluorescence method (XRF) [2], [3] are a few popular techniques to carry out these studies. Each method is being used with varying degrees of success. The energy dispersive X-ray fluorescence method (ENDXRF) [4], [5] is non-destructive, fast and permits a simultaneous multielement analysis. In recent years, it has become a useful tool for approximate dating of archaeological samples [6]. It makes possible the analysis of rock paintings, glazed surfaces, the determination of elemental concentrations and elemental ratios. It also helps distinguish between genuine and fake samples. There are three types of X-ray fluorescence methods [7], namely, 1) Radioisotope excitation 2) X-ray tube excitation and 3) particle induced X-ray fluorescence (PIXE). The first two methods are referred to as photon induced excitation. The sensitivity limits depend on the mode of excitation used in the analysis of archaeological samples. Several studies [2], [3], [8] on archaeological samples have been carried out employing radioisotopes like Cd-109 and Am-241. The radioisotope excitation method is cheap and the system convenient to handle . However, with this method the sensitivity limits are low when compared to tube excitation. The PIXE method is very expensive and really not necessary for the analysis of archaeological samples inasmuch as the concentration levels of different elements are high and can be easily detected using the first two methods. The present work concerns analysis of archaeological samples belonging to Telangana region of Andhra Pradesh, India and periods ranging from 2500 BC to 600 AD. We have used a 30 mCi ^{238}Pu radioisotope sample as source of exciting radiation and a high resolution XRF spectrometer for the detection and measurement of X-rays. The relative ratios of Mn/Co and Fe/coherent scattered peak intensity, are reported in this paper and the results are discussed.

2 – XRF METHOD

For the present studies, a high resolution XRF spectrometer was used. The spectrometer comprises a 30 mm^2 Si (Li) detector coupled to a low noise FET type preamplifier kept at liquid nitrogen temperature and a 4096 channel analyser with a computer facility. The computer allows data storage and analysis of X-ray spectra.

The block diagram of the XRF system used for the present studies is shown in Fig. 1. The energy resolution (full width at half maximum) is found to be 160 eV at an energy of 5.89 keV — the K-line of ^{55}Mn. The energy standardisation was accomplished by using standard lines from different sources as shown in Fig. 2. The energy calibration plot helps identification of different elements present in any sample. The intensity of a particular X-ray line is measured in terms of the X-ray counts (area under the X-ray peak distribution), the two words being used synony-

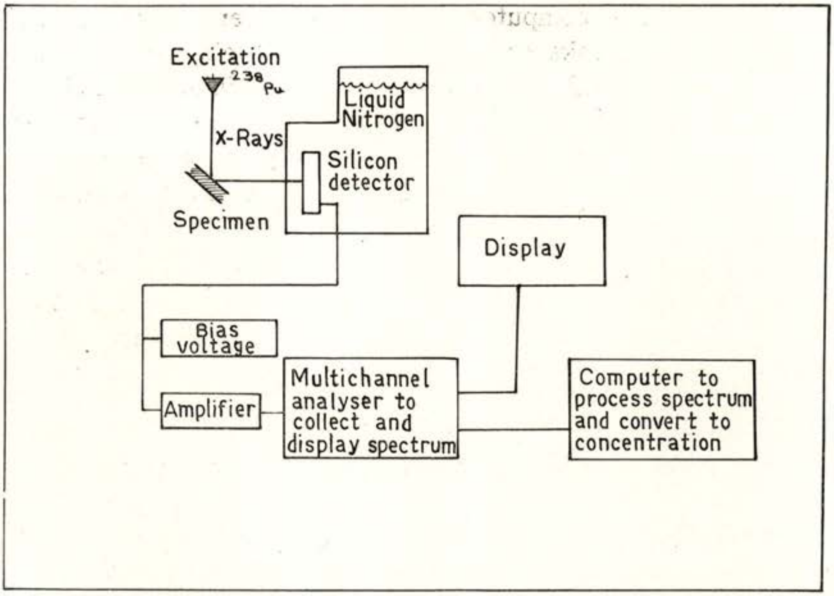

Fig. 1 — Block diagram of the experimental set-up.

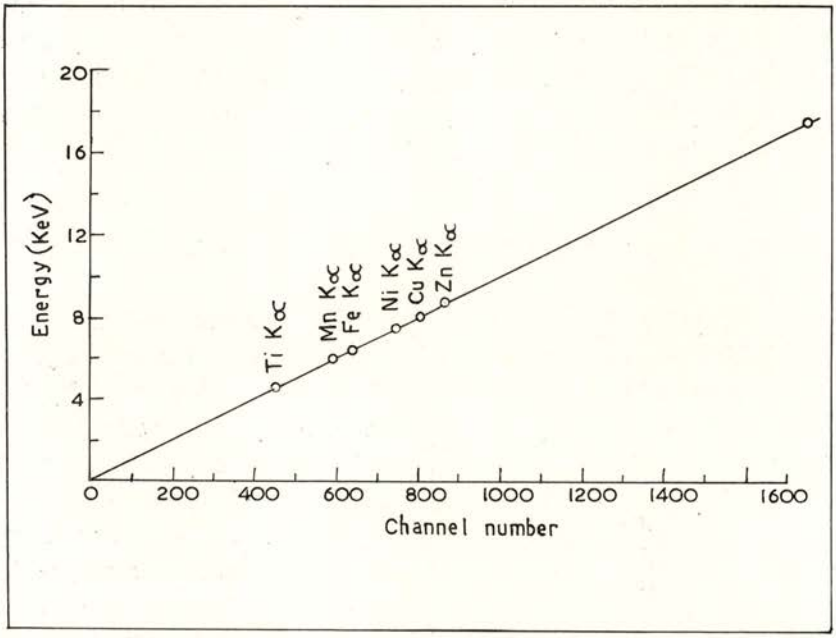

Fig. 2 — Energy linearity characteristic of the system.

mously. Suitable computer programmes were used for the identification of peaks and the corresponding elements, spectrum stripping, backround correction and for obtaining the net peak intensities. Having obtained the individual elemental intensities, the ratios Mn/Co and Fe/17.28 keV intensity can be obtained in a straightforward way. The parameters Mn/Co an Fe/Coherent peak intensity typically label the pottery samples of different ages inasmuch as they decide the colour of the sample and iron is one of the major components of any sample. Also, when one considers ratios, the matrix effects tend to cancel for similar types of samples.

3 – COLLECTION OF ARCHAEOLOGICAL SAMPLES

A total number of about 25 archaeological samples belonging to the Telangana region of Andhra Pradesh were provided by the Department of Archaeology, Government of Andhra Pradesh, India for the present studies. They are pottery samples, have different shapes and surface texture, belong to early historic times and are of neolithic and megalithic types. The depths at which they were collected range from 0.25 meters to 1.7 meters. The samples were used as they were, without any further preparation, for collecting the experimental data, using the XRF system.

4 – RESULTS AND DISCUSSION

Two typical XRF spectra, one from neolithic and one from megalithic samples, are shown in Figs. 3 and 4, respectively. In these figures, the X-ray peaks are identified and labelled by the elements to which they belong. The primary ^{238}Pu source emits X-ray lines ranging from 13 to 17 keV. When X-rays interact with matter, they get scattered by the sample and show up in the XRF spectrum as coherent and incoherent peaks. In the case of coherent peaks, the incident and scattered peak energies are the same, while in the case of incoherent peaks, energies of incident and scattered peaks will be different. For the present purpose the coherent peaks are used in the analysis and the corresponding lines in the

XRF spectrum are labelled by the energies 13.6 and 17.28 keV. The ratio of Fe/coherent peak intensity using the 17.28 keV line was determined for each sample. To look for the matrix effects three pottery samples of different shapes and sizes belonging to the same period were studied. It was found that the Mn/Co and Fe/17.28 keV line ratios were consistent within experimental errors. This suggests saturation of matrix effects for thick samples.

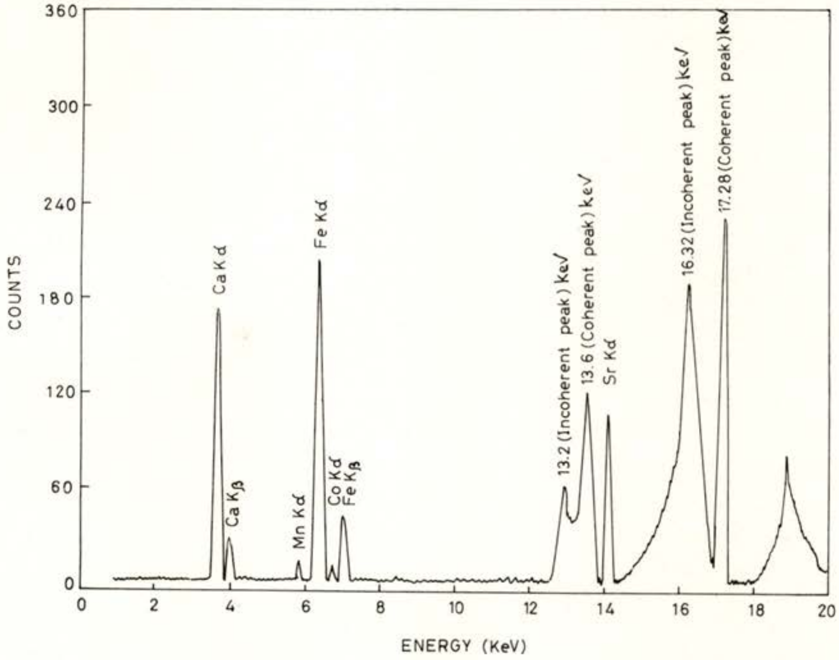

Fig. 3 — A typical X. R. F. spectrum from a Neolithic sample (Period 2500-1000 B. C.).

The results on the Mn/Co and Fe/coherent peak intensity ratios for the different periods characterising the pottery samples are summarized in Table 1. It can be seen, from table 1, that the Mn/Co ratio is very high for present pottery samples as compared to the earlier ones; that being also the case with the Fe/coherent peak intensively ratio. The figures reported in table 1 help to distinguish between present and ancient pottery samples. Table 1 also helps to distinguish between neolithic and megalithic samples.

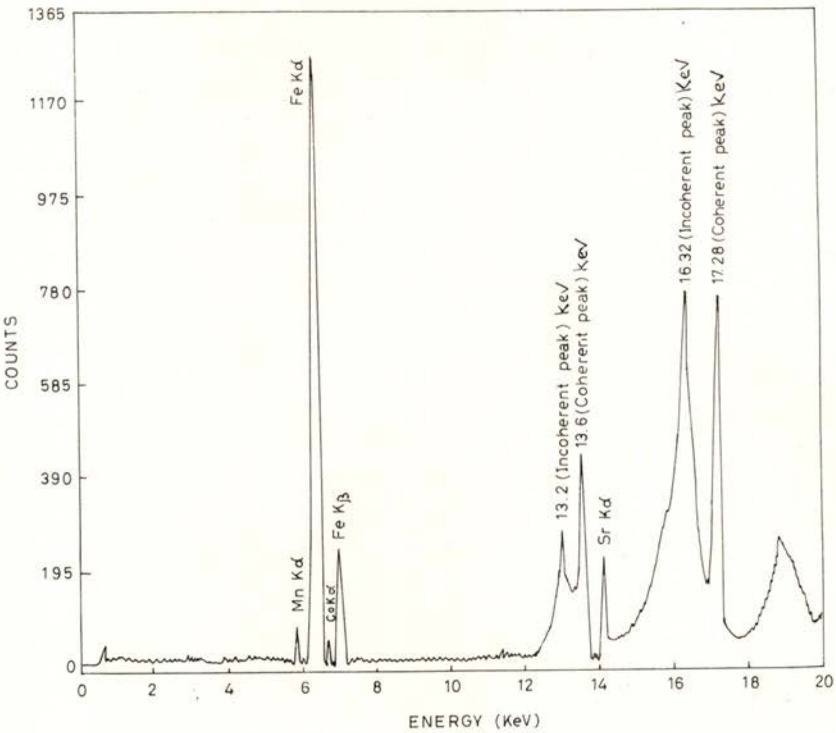

Fig. 4 — A typical X. R. F. spectrum from a Megalithic sample (Period 1000-300 B. C.).

TABLE 1 — Mn/Co and Fe/17.28 (Coh.) Intensity Ratios

No. of Samples	Period	Type	Mn/Co	Fe/17.28 keV
8	2500-1000 B. C.	Neolithic	0.584-0.793	0.906-0.914
8	1000- 300 B. C.	Megalithic	0.385-0.475	1.379-1.407
9	300- 600 A. D.	Historical (Vishnukundan)	0.351-0.405	1.292-1.318
10	Present	—	0.905-1.290	1.688-1.722

5 – CONCLUSION

It is thus illustrated that the energy dispersive X-ray fluorescence method offers a good tool to label pottery samples belonging to different periods.

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REFERENCES

[1] Michels, J. W., *Dating methods in Archaeology*, Seminor press, New York and London, 1973.

[2] Yap, C. T. and Tang, S. M., X-ray fluorescence analysis of modern and recent Chinese porcelains, *Archaeometry*, **26**, 78-81, 1984.

[3] Yap, C. T. and Tang, S. M., X-ray fluorescence analysis of Chinese porcelains from K'ang Hsi to modern times using Cd-109 source, *Appl. Spectroscopy*, **38**, 527-529, 1984.

[4] Goulding, F. S. and Jaklevic, J. M., Photon excited energy dispersive X-ray fluorescence analysis for trace elements, *Ann. Rev. Nucl. Sci.*, **23**, 45-73, 1973.

[5] Technical Report Series No. 115, *Radio-isotope X-ray fluorescence Spectrometry*, International Atomic Energy Agency, Vienna, 1970.

[6] Banks, M. S. and Merrick, J. M., Further analysis of Chinese blue--and-white, *Archaeometry*, **10**, 101-103, 1967.

[7] Bertin, E. P., *Introduction to X-ray spectrometry analysis*, Plenum Press, New York, 1978.

[8] Yap, C. T. and Tang, S. M., Energy dispersive X-ray fluorescence analysis of Chinese porcelains using Am-241, *Archaeometry*, **27**, 1-3, 1985.