

External particle-induced X-ray emission

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Particle induced X-ray emission (PIXE) technique has been used for a variety of analytical applications with an MeV accelerator. Normally, for PIXE analysis, the sample is kept inside a high vacuum chamber for bombardment with the particle beam from the accelerator. In case of vacuum-incompatible biological and liquid specimens and for large archaeological objects, it is necessary to take the beam outside the chamber in order to carry out the analysis by the so-called external PIXE technique. In such a case, a number of technical issues such as isolation of accelerator vacuum, beam-charge integration for quantitative analysis, sample scanning and X-ray background suppression, etc. are to be addressed. Recently, at the Institute of Physics, Bhubaneswar, an external PIXE set-up has been installed at the 3 MV tandem pelletron accelerator. This note presents the various aspects of the external PIXE set-up along with some of the experimental results, which demonstrate the applicability of this method to different areas to which these studies can be extended.

PARTICLE-induced X-ray emission (PIXE) is a unique technique for performing non-destructive analysis, which is based on the measurements of characteristic X-rays induced by the energetic proton beam (MeV energy scale) directed onto the surface of a specimen¹. This technique has been successfully used for almost three decades for analysis of various types of samples^{2–11}. The reasons for use of PIXE as a method of choice for characterization of various materials are its well-known features like multi-elemental capabilities, small sample mass requirements, high sensitivity, large dynamic range, and simple or virtually no sample preparation method. At the Ion Beam Laboratory, Institute of Physics (IOP), Bhubaneswar, the PIXE technique was first started in 1992. Since then, various environmental^{12–14}, geological^{15,16}, archaeological¹⁷ and biological^{18,19} samples have been analysed using PIXE, and have been reported from time to time. This technique employs the proton beam from the 3 MV tandem pelletron accelerator and samples are irradiated keeping them in vacuum. But, while dealing with specific samples of archaeological (manuscripts, etc.), biological (fishes, teeth, etc.) and geological materials (big rocks, etc.), the prerequisite of pellet-making procedure makes the conventional PIXE technique unusable (either the sample or a part of it needs to be destroyed at the sample-preparation stage itself). To overcome this difficulty, there is need to bring the proton beam outside the accelerator vacuum to carry out analysis by the external PIXE method. The advantage of this method is that the samples of almost any size and type can be analysed 'as such'. This technique has several advantages apart from easy sample handling and positioning in air. Objects of large size and complex structure and shape can be analysed *in situ* without the need of sampling, a fact particularly

valuable for art objects. Also, it is possible to study materials containing volatile compounds, which could otherwise not withstand in vacuum. The risk of damage due to heating is considerably reduced because of efficient cooling by the air or the helium flow. Another positive aspect is that the charging of insulating materials can totally be avoided without the need of a thin conducting coating required when operating under vacuum. Indeed, charging effects can produce potentials up to several tens of keV and accordingly accelerate secondary electrons with a subsequent extension of the bremsstrahlung background to higher energy. The detection limit would then be markedly increased. This note describes the recent development of an external PIXE set-up at IOP and some results of the preliminary experiments that were carried out.

IOP external proton-beam facility

The proton beam of 3 MeV energy obtained from the 3 MV tandem-type pelletron accelerator was collimated by a graphite collimator to a beam size of 3 mm diameter. The beam was extracted into air using a KaptonTM foil at the exit point of a vacuum scattering chamber (8 microns thickness). The scattering chamber has an inner diameter of 80 cm and was designed to cater to the requirements of the external beam as well as for the charged particle reaction studies for nuclear physics experiments. The beam is first focused and centred at the target location inside the scattering chamber and then let through the thin Kapton foil placed at the exit port. The chamber is pumped by a high throughput diffstack pump to maintain a vacuum in the range of 10^{-7} mbar in the chamber and the beam line. The KaptonTM foil is used as exit window due to its several special characteristics like low beam-induced background emission, minimal energy loss and resistance to radiation damage. The beam is

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Figure 1. External PIXE set-up at IOP.

allowed to travel 3 cm in air by which time the energy gets reduced to about 2.4 MeV, and the proton beam then irradiates the samples. The external PIXE set-up is shown in Figure 1. Beam-charge measurement is carried out using a rotating chopper as described by Mando *et al.*^{6,20}. A rotating vane chopper of adjustable length is used for charge measurements²¹. The chopper disc of diameter 15 mm is placed between the exit window and the sample at a distance of 3 mm from the exit window. The chopper vane is fully isolated from the electrical motor as well the beam line using insulation, and is connected to the current integrator for recording the charge. The charge measurement of the chopper is calibrated using the pure copper foil.

For the measurements to be described below, the samples were kept in air over a sample stand (of 5 kg capacity) making an angle of 45° to the beam direction. In case of incompatible big samples, the stand was removed and samples were adjusted (and/or positioned) according to requirement. The samples were irradiated with maximum beam current of 20 nA passing through the 8 µm thick KaptonTM window. A Si(Li) detector (active area 30 mm²) having energy resolution of full-width at half maximum 165 eV at 5.9 keV placed at 90° with respect to the beam direction was used to detect characteristic X-rays emitted from the target. The detector has an active area of 30 mm² and an entrance beryllium window of 8 µm thickness. A 25 µm thick aluminized Mylar absorber (with 6% hole) was kept in front of the detector to attenuate the bremsstrahlung background and the dominant low-energy X-ray peaks. Spectra were recorded using a Canberra S-100 multichannel analyser, which was calibrated with ²⁴¹Am X-ray source.

The data were analyzed with the GUPIX-2000 program. The relationship between characteristic X-ray yield $Y(Z)$ for an element of atomic number Z and its concentration C_z in a given target matrix is

$$Y(Z) = HY_l(Z) C_z Q \epsilon_z t_z,$$

where $Y_l(Z)$ is the computed yield from the database per steradian per unit concentration and per unit integrated beam charge; Q the beam charge; ϵ_z the intrinsic efficiency of the Si(Li) X-ray detector; and t_z the transmission of the X-rays through any absorber placed between the detector and the specimen. The instrumental constant H is the product of the geometric solid angle of the X-ray detector and any systematic normalization factor present in the charge integration system. The instrumental constant H was measured using 3 MeV protons and a wide range of pure single-element standards emitting both K and L X-rays in the energy region 3–26 keV. Thus the X-ray yield (Y) is converted to elemental concentration via a defined standardization technique involving H value, the theoretical yield, detection efficiency and filter transmission values.

Performance and application of the PIXE set-up

Archaeology

One of the important applications of external PIXE is in the analysis of archaeological samples, as these are precious objects and are difficult to be recovered, if damaged. In conventional PIXE technique, it is not always

possible to analyse certain materials like manuscripts, pottery, bone, etc., which require destructive methods involving sample preparation procedure. In some cases, the samples are too large to fit into the vacuum chamber. The study of historical manuscripts can give an idea about the period and the type of ink then used. Another special type of material, i.e. numismatic objects can be well-studied, which can throw light on the mining and minting procedures, type of ore used and may thereby provide knowledge about the socio-economic condition of the contemporary period.

Punch-marked (silver) coins

Punch-marked coins were in use in ancient India between 6th Century BC and 6th Century AD. They are found in different shapes and sizes. On one side, several symbols were punched. Punch-marked coins were recovered from the Suktel river valley, Sakma area, Bolangir district, Orissa identified to be the ancient site of 'Suktimati-pura', the ancient capital city of the Chedi dynasty to which the ancestors of Kharavela belonged. The site is datable to 2nd century BC. Suktel river mingled with Tel river near the confluence of Mahanadi and Tel rivers at Sonepur²². In the Seravanijia Jatak of Buddhist literature, 'Tel' river finds mention as 'Telavahanadi'. It is mentioned in Jataka stories that the Tel river was the source of extensive and hectic trade activities. In the present investigation, an attempt has been made to characterize these ancient punch-marked silver coins using external PIXE technique. Punch-marked coins were exposed to the external proton beam, and an external PIXE spectrum of the coin is shown in Figure 2 *a*. The results show large variations in concentration of elements from sample to sample (Table 1).

Biology

Trace elements have a major role in biological systems and their functions. The concentration of various elements plays an important role in the diagnosis of diseases. As a consequence of trace-element deficiency or abundance, many clinical and pathological disorders can arise in animals and humans. Trace elements may vary with age, sex and dietary habits of patients from a particular region. External PIXE technique can be used to analyse live samples. Figure 2 *b* shows trace elements present in kidney stone taken from a south-Indian male patient. Apart from Ca being the dominant element, other elements like Fe, Cu, Zn and Sr are seen to be present in significant proportions. Attempts are being made by our group to systematically investigate the distribution of trace elements in kidney stones and gallstones using external PIXE technique, and correlate them with the disease conditions.

Table 1. Concentration (%) of various elements in punch-marked coins

Element	Coin 1	Coin 2	Coin 3	Coin 4	Coin 5
K	0.49	0.08	6.4	3.0	0.20
Ca	0.14	0.10	1.1	1.3	4.3
Ti	1.9	0.96	2.5	2.4	0.31
V	1.5	0.86	2.5	2.8	—
Cr	0.85	0.41	1.5	1.6	—
Mn	0.72	0.33	1.2	1.2	1.3
Fe	8.2	3.6	3.4	3.2	2.9
Co	0.65	0.82	0.75	0.60	—
Ni	0.99	0.44	3.1	2.6	0.01
Cu	3.4	2.5	15.9	16.2	63.8
Rb	0.36	0.24	0.52	1.4	—
Ag	79.0	82.3	49.5	57.9	26.2
Pb	1.1	0.8	3.1	2.7	0.45

Environment

Nowadays, many laboratories are involved in environmental research using the PIXE technique. The characterization of fly ash, which is an environmental material of importance, mostly due to its potential for utilization by plants and animals, was studied extensively in our laboratory using this technique. Fly ash is associated with various useful constituents such as Ca, Mg, Mn, Fe, Cu, Zn, Ba, S and P, along with appreciable amounts of toxic elements like Cr, Pb, Hg, Ni, V, As and Ba. The concentration of trace elements in ash is extremely variable and depends on the composition of the parent coal, conditions during coal combustion, efficiency of emission control devices, etc. Figure 2 *c* is a fly ash spectrum taken with the present external PIXE set-up. The study indicates that the external PIXE technique could effectively be used for characterization of fly ash with good sample turnover time. Aerosols are another frequently studied environmental material using vacuum PIXE technique. But this technique causes the loss of volatile elements like mercury. Another practical obstacle being the beam current used for aerosol samples in conventional PIXE is usually less, but could be increased by about four times in the case of external PIXE.

Geology

In geochemical explorations, PIXE has been widely used by several workers, which includes pioneering works of CSIRO (Australia) and Schonland research (South Africa) groups on various materials, including diamond. But due to the requirement of large number of samples to be irradiated in order to achieve better statistics, the conventional PIXE technique requires more sample turnover time. Another aspect, which should not be ignored is the characterization of particular spots of a geological material followed by identification through ore microscopy.

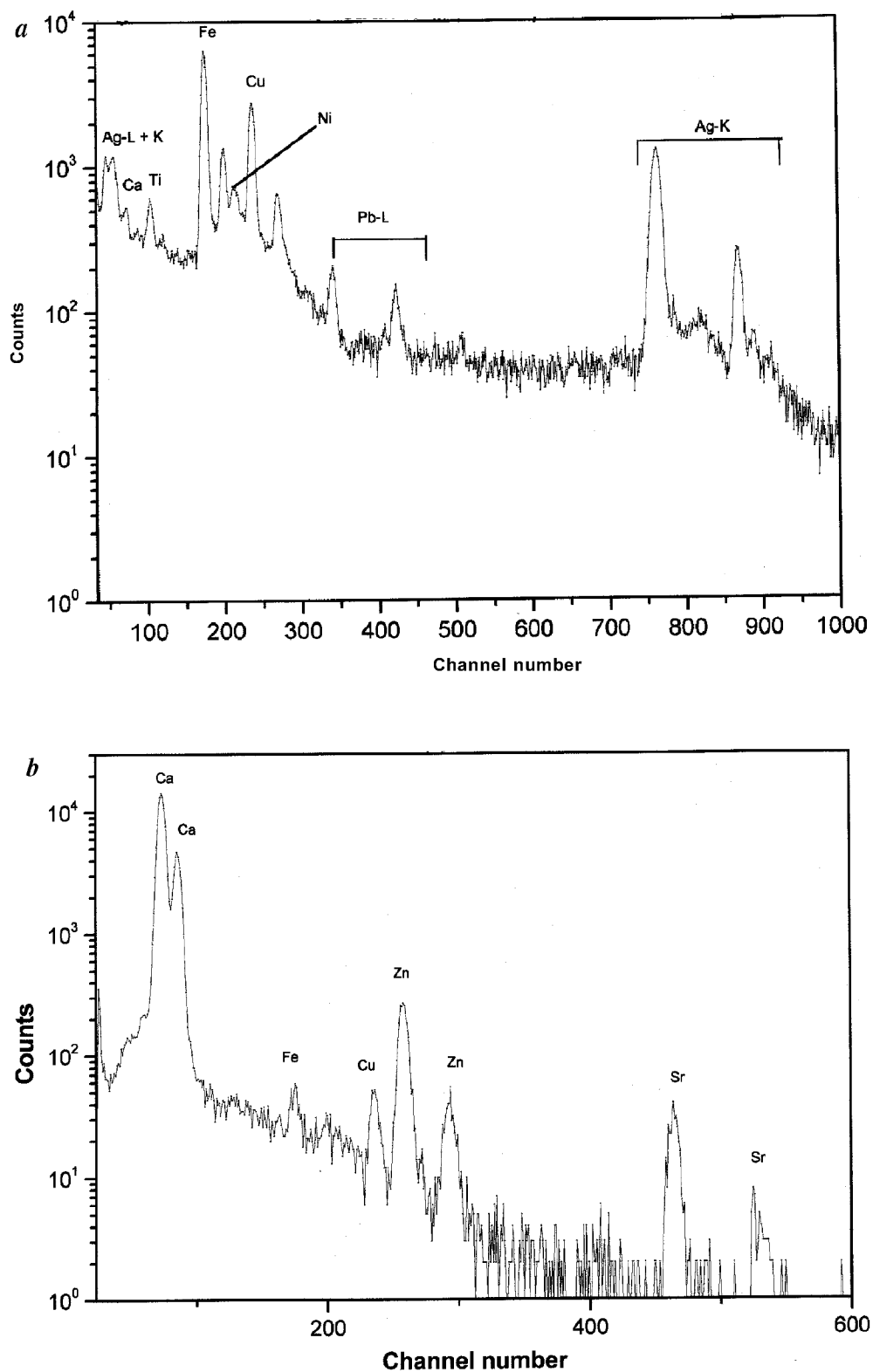


Figure 2. External PIXE spectra of *a*, Punch-marked silver coin; and *b*, Kidney stone.

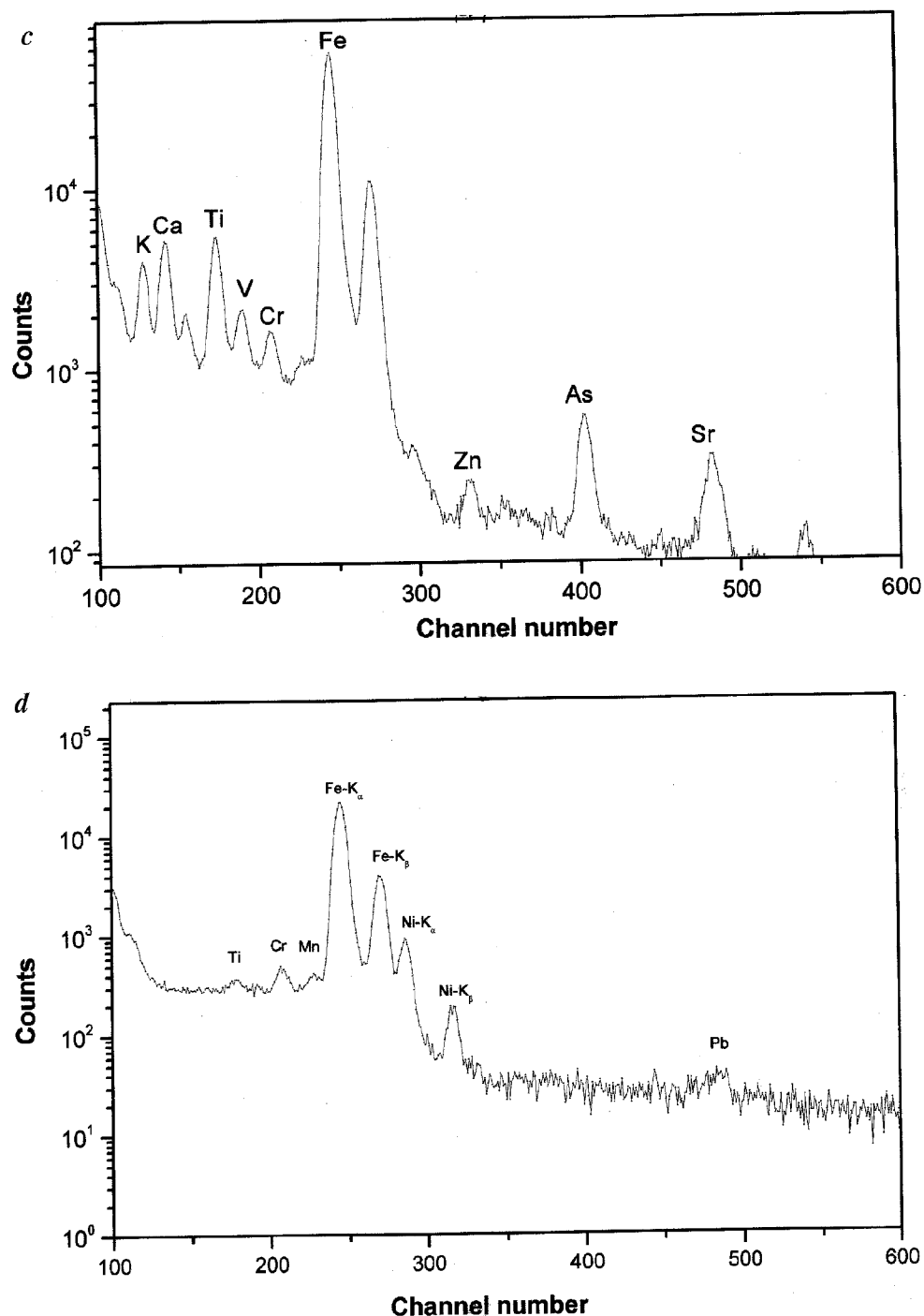


Figure 2. External PIXE spectra of *c*, Fly ash, and *d*, Soapstone.

Previously, our group has reported the use of PIXE¹⁴ and other X-ray techniques¹⁶ on geological materials in finding out the trace elemental ratios, which were used in interpreting the environment of a depositional basin. It is felt that the problem of analysing big samples could be

overcome successfully by the external PIXE technique. Figure 2 *d* is an external PIXE spectrum of soapstone taken using the present set-up, with no sample preparation procedure. Among other elements, Fe is found to be present dominantly in this sample. We are planning to

use the external PIXE set-up to analyse different spots and inclusions observed in geological materials, followed by cross-sectional cutting in order to investigate the distribution of trace elements.

Conclusion

The present note describes some of the preliminary experiments that were carried out using the external PIXE set-up developed at IOP. Collaborations with various archaeological and museum groups have been initiated in order to characterize archaeological materials non-destructively. The present set-up is expected to be useful for various multidisciplinary studies of art objects and other scientific investigations.

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