

## Applications of proton-induced X-ray emission technique in materials and environmental science

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**Abstract** In this work a complex study of the capabilities of Particle-Induced X-ray Emission (PIXE) technique for the determination of minor constituents of some metallurgical and environmental samples has been done. PIXE analyses have been carried out using a 3 MeV proton beam generated with the aid of the 8.5 MV FN Van de Graaff tandem accelerator of the "Horia Hulubei" National Institute of Physics and Nuclear Engineering (NIPNE) Bucharest. The minor elements identified in the metallurgical samples (steels) using PIXE were: K, Ca, V, Cr, Mn, Fe, Co, Cu, Ni, Zn, W, Ga, As, Pb, Mo, Rb, In, Rh, Zr, Pd, Nb, Sn and Sb. In the investigated environmental samples (vegetal leaves, soil and mosses) PIXE analysis allowed determination of S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, As, Sr, Se, Br, Hg and Pb in concentrations between 0.05-290 mg/kg.

**Keywords:** PIXE technique, environmental samples, metallurgical samples, minor elements

### 1. Introduction

The attractiveness of non-destructive methods and the ability to perform simultaneous multi-elemental determinations has led to an extensive application in different industrial and research laboratories of accurate, precise and sensitive atomic and nuclear analytical techniques such as neutron activation analysis (NAA) [1,2], proton-induced X-ray emission (PIXE) [3-5] and particle-induced gamma-ray emission (PIGE) [6-8]. Despite the significant advances which have been made lately in already established techniques, no technique can be considered a panacea to tackle all sample types and/or determine all elements, so that the selection of the appropriate technique(s) for a particular analytical problem has become a difficult task. In the last years our group activities have been structured on the establishing of the methodology for multi-elemental analysis of metallurgical, biological and environmental materials. The atomic spectrometric technique discussed in this work is PIXE which is a matured analytical technique for minor element analysis in different complex matrices, such as metallurgical and environmental samples.

In PIXE ions from low-energy accelerator are used for the irradiation of the samples. The characteristic X-ray radiation produced is measured by semiconductor detector. In analysis of measured X-ray spectra the concentrations of the elements present in the sample are deduced. In worldwide laboratories PIXE is routinely applied for several interdisciplinary problems: environmental studies [9, 10], analysis of materials [4,5,11], biology and biomedicine [11,12], archaeometry and geology [4,11,13] etc. PIXE method is: multi-elemental, fast, sensitive (ppm), precise and non-destructive. PIXE can be coupled with other ion beam analysis techniques, such as PIGE and Rutherford Backscattering Spectrometry (RBS), and can be completed by NAA [14].

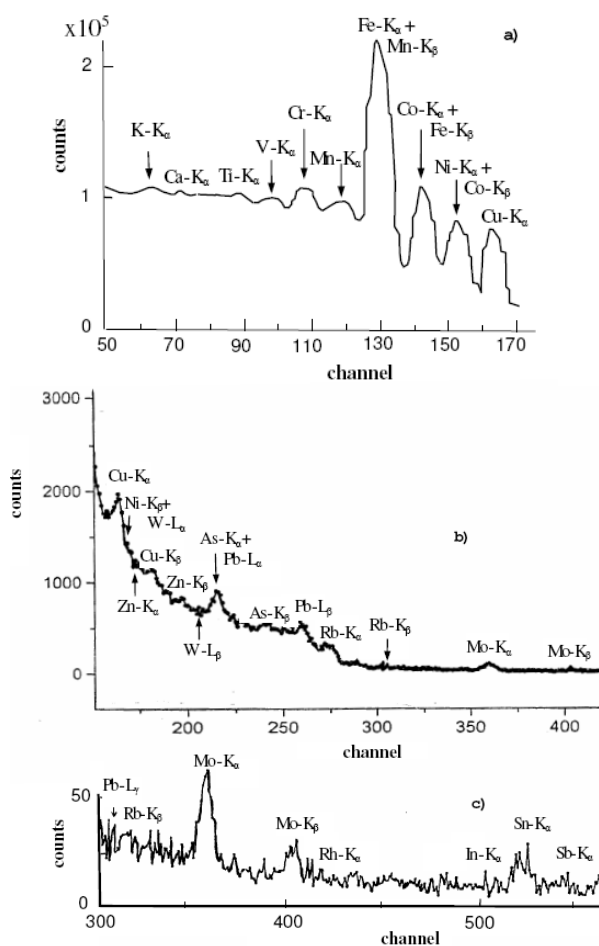
### 2. Experimental

The metallurgical samples and standards were obtained from the MITTAL STEEL Works of Galati (Romania). The used standards were British Chemical Standards BCS Nos. 320 (mild steel: Mo-0.22%; Ni-0.022%; Cr-0.131%; W-0.17%; Sn-0.085%; As-0.031%; Ti-0.021%; Al-0.013%;) and 402/1 (low alloy steel: C-1.2%; Si-0.13%; V-0.15%;

Mn-0.16%; Cu-0.21%; Mo-0.17%; Ni-0.81%; Cr-0.77%; P-0.011%; S-0.032%), Euronorm CRM No. 085-1 (C-670 ppm; Si-80 ppm; P-620 ppm; S-3360 ppm; V-21 ppm; Mn-9770 ppm; Co-190 ppm; Cu-2910 ppm; Zn-25 ppm; Sb-73 ppm and Pb-10 ppm). Sampling of environmental samples - leaves of vegetables, soils and mosses (*Mnium undulatum*) was carried out in the investigated area - the transect from north to south of the Dambovita County. Moss sample preparation procedure was: first, soil was washed off the samples in running water and then the samples were finely cut and dried at a room temperature in a clean box preventing further contamination. After that the dried mosses - with a constant weight have been grained. The obtained powder was mixed with 2  $\mu\text{g}$  of Yttrium (used as internal standard) in 150  $\mu\text{L}$  demineralized water and depicted on Mylar support. A few tens of milligrams of vegetable leaves and soil were weighted and put in 50mL HDPE vials. For each sample an equal volume of 2-4mL  $\text{HNO}_3$  and a few hundreds of microliters  $\text{H}_2\text{O}_2$  and HF were added. In order to assure complete digestion the samples were heated 4 hours at 75°C. After digestion each sample was diluted with a convenient volume of deionized water followed by addition of internal standard (200 $\mu\text{L}$  solution of  $\text{Y}_2\text{O}_3$  in  $\text{HNO}_3$  medium, containing 160.8 $\mu\text{g}$  Y/mL). Volumes of 150 $\mu\text{L}$  were deposited and evaporated on Mylar foil (2,5 $\mu\text{m}$  thickness) fixed on aluminum frames.

PIXE analyses have been carried out using a 3 MeV proton beam generated with the aid of the 8.5 MV FN Van de Graaff tandem accelerator of the "Horia Hulubei" National Institute of Physics and Nuclear Engineering (NIPNE) Bucharest. A 3 nA proton beam current was employed and the exposure time was 30 min. The proton energy of 3 MeV has been chosen based on other authors' studies [3] upon the dependence of the limit of detection on the atomic number of pure elements, this being minimum for almost all targets in the case of 3 MeV protons. Also, we have taken into account the dependence of the X-ray production cross section on the proton energy and the atomic number of the target. The detection system included a 10 mm thick HPGe detector with an energy resolution of 170 eV at 5.9 keV for the X rays and with a 0.13 mm thick beryllium window. The steel plate targets (100-300  $\mu\text{m}$  thick), previously polished and cleaned, and the

prepared environmental samples were mounted in the irradiation chamber at 45° with respect to the beam and the detector's direction. The target chamber had a beryllium window for X rays of 0.1 mm thickness. A thin surface barrier silicon detector was also placed in the chamber, at 135° with respect to the beam direction, in order to detect the backscattered protons for spectra normalization. The X-ray and particle spectra were simultaneously collected and processed off-line with the aid of LEONE computer program.



**Fig.1.** Details of a PIXE spectrum of a standard steel sample irradiated with 3 MeV protons.

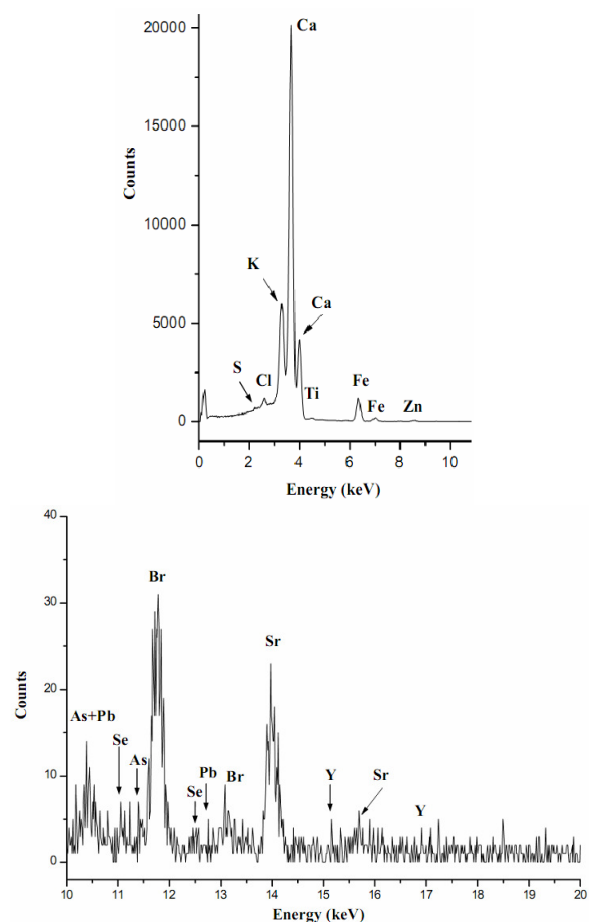
### 3. Results and discussions

Details of the PIXE spectrum obtained during the bombardment of a standard steel sample and a moss sample with 3 MeV protons are presented in Fig. 1 a,b,c and in Fig. 2, respectively. Peaks in the spectrum occur at energies indicative of characteristic X rays and the qualitative analysis is an easy task in PIXE due to the known dependence of X-ray energies with the atomic number of elements, as Moseley's law. The minor and trace elements identified in the iron matrix of the steel samples were: K, Ca, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, W, As, Mo, Rb, In, Rh, Pb, Sn, Sb.

It is worth mentioning that the elements K, Ca, Ti, Cr, Ni, W, As, Mo, Rb, In, Rh, and Sn were not given by the manufacturer for the steel standard Euronorm CRM No. 085-1. Also, some of these elements were identified by NAA (Cr, Ni, W, As, Mo) or PIGE (Ti, Cr, As, Ni, Mo) methods and the results have been published in a previous paper [8]. The limitations of PIXE are the following: i) in the case of analysis of thick steel targets the main problem is the very strong X-ray emission from the iron matrix (Fig. 1 a), which tends to mask the small trace element peaks in the energy spectrum [3]; ii) in the case of the analysis of the elements with  $Z \leq 30$  an interference is frequently encountered between the  $K_{\alpha}$  ( $Z+1$ ) X-ray and the  $K_{\beta}$  ( $Z$ ) X-ray, which have virtually the same energy or between the X-K lines of medium elements and X-L lines of heavy elements (Fig. 1 b). Examples of such overlaps in the case of steel samples are: Co- $K_{\alpha}$  and Fe- $K_{\beta}$ ; Ni- $K_{\alpha}$  and Co- $K_{\beta}$ ; Fe- $K_{\alpha}$  and Mn- $K_{\beta}$ ; As- $K_{\alpha}$  and Pb- $L_{\alpha}$ ; Ni- $K_{\alpha}$  and W- $L_{\alpha}$  etc, and corrections have to be made for quantitative analysis of Co using known  $K_{\alpha}/K_{\beta}$  ratios. In quantitative analysis considerable attention has to pay to matrix effects (non-spectral interferences), ranging from absorption to enhancement, which become important for concentrations bigger than 1% [13]. Matrix effects are well understood in thick target PIXE, and this is an advantage over the optical spectrometric techniques [4].

In the investigated vegetal leaves and soils samples PIXE analysis allowed determination of S, Cl, K, Ca, Ti, Mn, Fe, Ni, Cu, Zn, Sr in vegetable samples and of K, Ca, Mn, Fe, Cu, Zn, Cr, Sr, Mo in related soil samples with the uncertainties of the

data point of the order of 10%. From the Tables 1 and 2 it can be observed the presence of toxic element Sr in soil and leaves of vegetables: the higher concentration of Sr is on the surface of soil and decreases inside the soil. Also calcium, potassium and iron concentrations are higher at the surface soil and decrease inside the soil.



**Fig.2.** Details of a PIXE spectrum of a moss sample irradiated with 3 MeV protons.

The obtained elemental composition of soil can be used to establish the optimal distances to plant the vegetables used in agro-alimentary domain. The obtained results permit to determine the regional extent of heavy metals and toxic elements atmospheric pollution and to identify specially affected areas and local sources of pollution -

industrial processes, thermal power stations, domestic heating systems and motor vehicles. For assessing environmental situation from the point of view of air polluting we applied moss biomonitoring technique in combination with PIXE. Mosses can indicate the presence of elements and their concentration gradients. Most methods used in heavy metals monitoring employ mosses as bioaccumulators and involve sample collection followed by laboratory analysis techniques.

Preliminary results let us to think that the use of mosses constitutes an effective method in air pollution monitoring for several reasons:

- Mosses are small and easy to handle;
- Most of them are evergreen and can be surveyed all year round;
- They have good bioaccumulation ability, particularly for heavy metals, where metal concentrations reflect deposition without the complication of additional uptake via a root system;
- The ability of mosses to accumulate elements in very high concentrations aids chemical analyses of the tissues and may facilitate the detection of

elements present in very low concentrations in the environment;

- Comparisons of fresh samples with herbarium specimens enable retrospective analysis of metal pollution.

The concentrations of heavy and toxic metals in mosses depend on the industrial activity of studied area. PIXE analysis allowed determination of S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, As, Sr, Br, Se and Pb in the samples, as can be seen from the spectra from Fig. 2.

#### 4. Conclusions

The presented PIXE technique is known for its sensitivity, accuracy, precision, simplicity of target preparation and the ability to perform non-destructive multi-elemental analysis of a large number of samples, sometimes quickly, requiring small amounts of material.

Despite these merits, it does suffer from one drawback or another, which are discussed in this paper in the particular case of metallurgical and environmental samples analysis.

**Table 1.** Concentration (mg/100 g fresh sample) of elements in vegetable leaves analyzed by PIXE method

Sample	S	Cl	K	Ca	Ti	Mn	Fe	Ni	Cu	Zn	Sr
<i>Apium graveolens</i> (celery) leaves	18	59	19.6	51	0.098	0.116	0.382	0.006	0.011	0.078	0.017
<i>Apium graveolens</i> (celery) leaves	14.3	51.5	15.78	66.6	0.111	0.172	0.346	nd <sup>x</sup>	0.018	0.088	0.019
<i>Brasica oleracea</i> external leaves (cabbage)	45.6	89	12	7.84	nd <sup>x</sup>	0.098	1.164	0.003	0.053	0.13	0.012
<i>Brasica oleracea</i> external leaves (cabbage)	49	88	10.7	6.7	nd <sup>x</sup>	0.095	1.38	nd <sup>x</sup>	0.061	0.138	0.014
<i>Brasica oleracea</i> inside leaves (cabbage)	21.84	5.99	36.3	11.9	nd <sup>x</sup>	0.022	1.7	0.006	0.054	0.033	0.006
<i>Brasica oleracea</i> inside leaves (cabbage)	28.55	4.75	36	14.22	0.005	0.017	1.88	nd <sup>x</sup>	0.045	0.031	0.008
<sup>x</sup> not detected											

**Table 2.** Concentration (mg/100 g) of elements in soil samples analyzed by PIXE method

Sample	K	Ca	Mn	Fe	Cu	Zn	Cr	Sr	Mo
Soil from surface	37	12	0.07	46	0.005	0.13	0.04	3.6	0.13
Soil from 10 cm deep	27.2	8.12	0.77	35.6	0.007	0.02	0.06	2.6	0.1
Soil from 20 cm deep	23.6	7,80	1.33	31	0.008	0.01	0.16	1.2	0.05

From this work it results that by applying PIXE method, a very good overall picture of the elemental composition of a complex target – such as metallurgical samples (steels) – may be obtained, the limits of detection ranging between 1-100 ppm for the minor elements heavier than iron. It could be a complement of PIGE (particle-induced gamma-ray emission) when the determination of medium and heavy elements content with high sensitivity is necessary. The obtained results in the case of environmental samples permit to determine the regional extent of heavy metals and toxic elements atmospheric pollution and to identify specially affected areas and local sources of pollution.

## 5. References

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