Environmental applications of PIXE at the Institute of Physics, UNAM

C. Solís, A. Mireles, and E. Andrade
Instituto de Física, Universidad Nacional Autónoma de México,
Apartado Postal 20-364. 01000 México D.F.,
e-mail: corina@fisica.unam.mx, alibech_m@hotmail.com, andrade@fisica.unam.mx

H. Zolezzi-Ruiz
Instituto de Ciencias del Mar y Limnología, Universidad Nacional Autónoma de México,
Ciudad Universitaria 04510 México, D.F.,
e-mail: zolezzi@icmyl.unam.mx

Recibido el 2 de marzo de 2006; aceptado el 18 de agosto de 2006

The particle induced X-ray emission technique (PIXE), developed by Johansson and colleagues in Lund, Sweden, in the 70's has been used since then in a high number of studies requiring detection and quantification of trace elements at high sensitivity (better than 1 mg/kg). PIXE is grouped among the nuclear analytical techniques because the samples are bombarded with particles (protons generally) accelerated in an accelerator. When protons interact with matter an X-Ray spectrum is produced by the deexcitation of atoms in the sample. From this spectrum the elements contained in the sample as well as their concentrations can be determined. In this work we describe the PIXE technique and several applications in the environmental field developed at the Institute of Physics of the National Autonomous University of Mexico (IFUNAM). These practical applications include field studies for analyses of suspended particles in air using tree leaves, irrigation water quality based on heavy metal analyses, and analyses of trace elements in plants cultivated in waste water irrigated soil.

Keywords: Trace elements; PIXE; biomonitors; heavy metal pollution; Mexico.

La técnica de emisión de rayos X inducida por partículas (PIXE), desarrollada por Johanson y su grupo en Suecia y dada a conocer en 1970, es usada desde entonces para la detección y cuantificación de elementos en numerosos estudios que requieren una alta sensibilidad (<1mg/Kg). Se agrupa con las técnicas de origen nuclear porque las muestras se bombardean con partículas (protones en general) generadas por un acelerador. Cuando los protones interactúan con la muestra, se obtiene un espectro de rayos X producidos por el relleno de vacantes electrónicas de los átomos de la muestra. De este espectro pueden obtenerse tanto los elementos que componen la muestra como su concentración. En este trabajo se describe la técnica de PIXE así como algunas aplicaciones en las ciencias ambientales desarrolladas en el Instituto de Física de la Universidad Nacional Autónoma de México (IFUNAM). Estas aplicaciones prácticas incluyen estudios de campo para el análisis de partículas en el aire usando hojas de árboles, calidad del agua de riego basada en metales pesados, y análisis de elementos traza en plantas cultivadas en suelos regados con aguas residuales.

Descriptores: Elementos traza; PIXE; biomonitores; contaminación por metales pesados; México.

PACS: 82.70.R; 42.62.-b; 80.00; 32.30.Rj

1. Introduction

Trace element analysis based upon the rapid, non-destructive, and multi-element analytical capability of techniques such particle induced X-ray emission (PIXE) has found wide applicability in numerous fields. In the environmental field, in particular, PIXE has a great potential to meet the current and forthcoming demands for trace element analysis.

In PIXE the samples are bombarded with particles (1-4 MeV protons generally) accelerated in an accelerator. When protons interact with matter an X-Ray spectrum is produced by the deexcitation of the atoms in the sample (Fig. 1). From this spectrum, as the one shown in Fig. 2, elements contained in the sample as well as their concentrations can be determined. The high sensitivity of the technique as well as its non destructiveness has made PIXE one of the most suited techniques to study the trace element content of air particulate matter. The same characteristics make PIXE a very useful tool in the analysis of soil, sediments and plants.

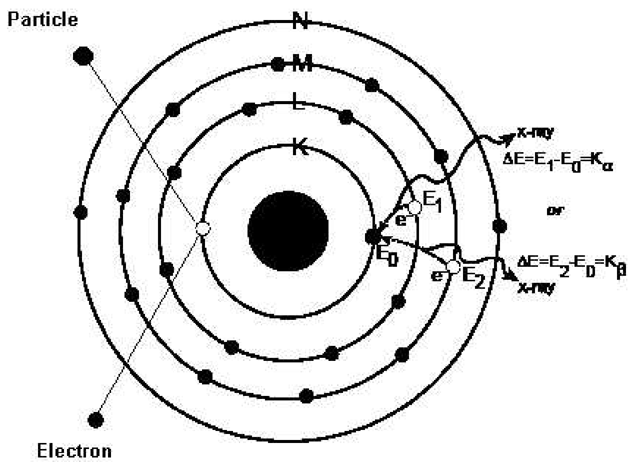

FIGURE 1. Schematic representation of the fundamentals of PIXE.

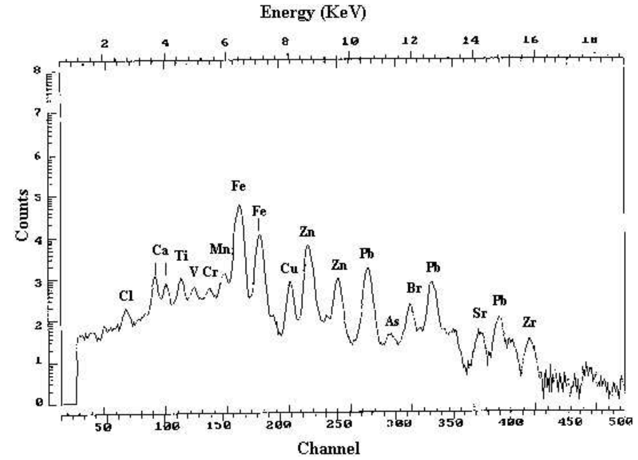

FIGURE 2. PIXE spectrum of an aerosol sample.

In this work we describe the PIXE technique and several applications in the environmental field developed at the Institute of Physics of the National Autonomous University of Mexico (UNAM). These practical applications include field studies for analyses of suspended particles in air using tree leaves, irrigation water quality based on heavy metal analyses, and analyses of trace elements in plants cultivated in waste water irrigated soil.

2. Experimental

PIXE analysis

PIXE analyses are generally performed with protons generated at the 5.5 MV Van de Graff or the 3 MV Pelletron accelerator at the Institute of Physics of the National Autonomous University of Mexico (IFUNAM). Measurements can be done under vacuum or under atmospheric conditions using set-ups developed by colleagues from the Department of Experimental Physics [1-3]. X-ray detection is conducted with an XR-100 Si-PIN Amptek detector for light elements and with a Canberra low-energy Ge detector (using a 38 μm Al foil) for heavy elements. The concentrations of elemental constituents in the sample are calculated from the spectra using the GUelph PIXe (GUPIX) software package [4]. Calibration is performed using pellets of certified reference materials (thick targets) or films of known surface density (MicroMatter films).

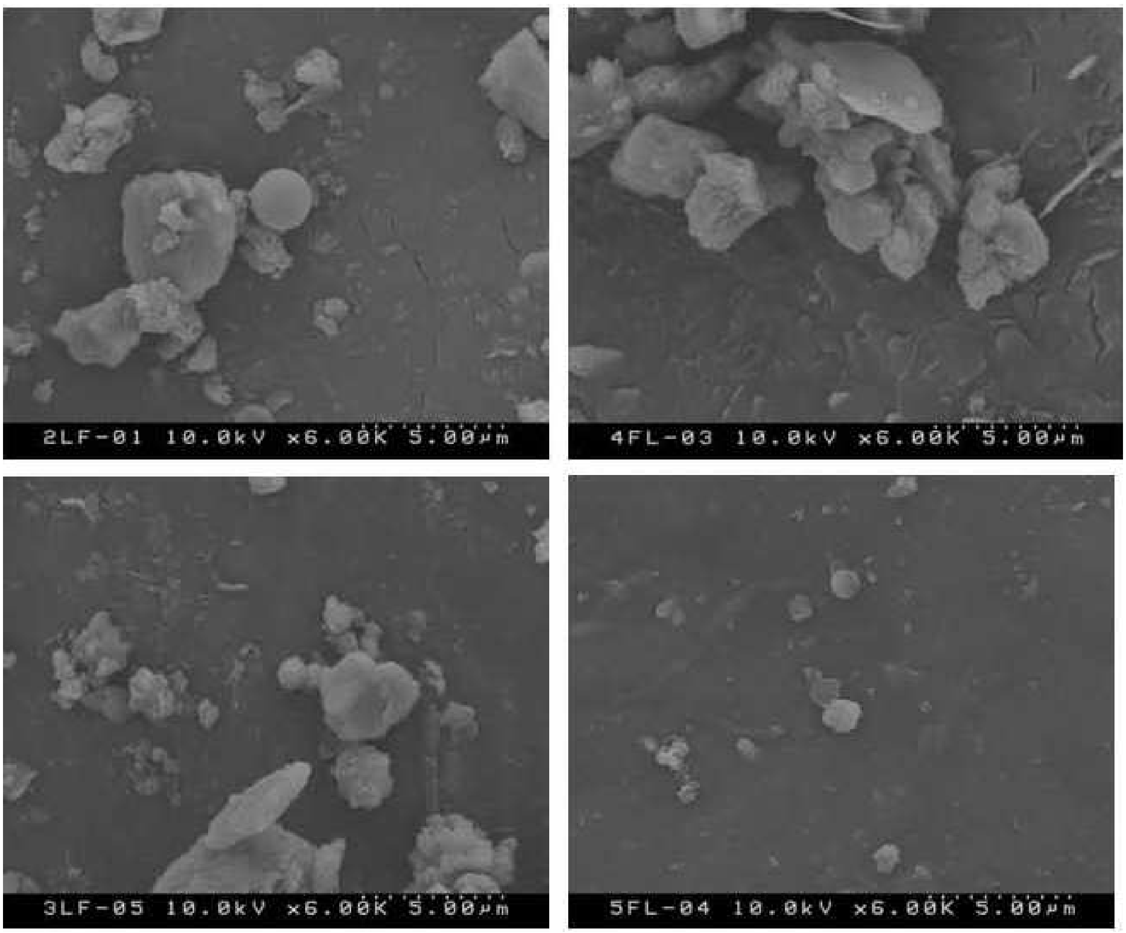

FIGURE 3. SEM image of Wax-leaf privet (Top) in July (left) and March (right) and ficus leaves (bottom) in July (left) and March (right).

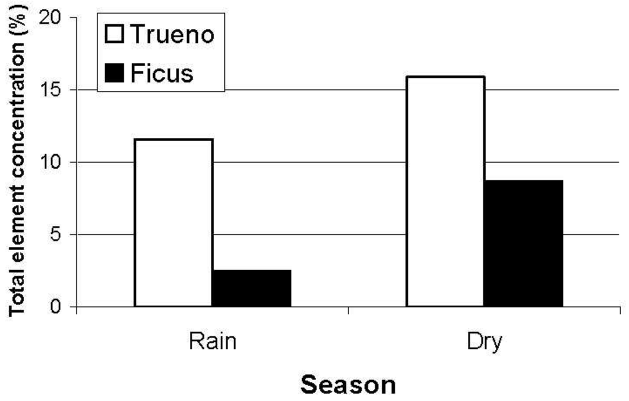

FIGURE 4. Total trace element concentration (in μg/g) in Wax-leaf privet leaves and ficus in rainy and dry season.

Sample preparation

Samples can be prepared as pellets (soils, sediments). Liquid samples can be prepared by depositing a droplet of a few μl onto a filter and letting it dry. Alternatively, a pre-concentration procedure can be followed which involves the precipitation of the trace elements contained in the sample as metal-carbamates complexes and their collection into filters [5]. For the detection of trace elements in plants, a new pre-concentration method was developed. The plant parts in powder were dissolved in 30% peroxide and irradiated with a beam of 248-nm UV photons (5 eV/photon) from an excimer laser (LPX 200, Lambda Physik, Germany). In this process the organic matter is rapidly eliminated through UV photolysis. After the digestion, an aliquot of 50 μl is deposited and dried in a Teflo filter (GELMAN) with palladium as an internal standard. The thin target is analyzed with PIXE under vacuum [6].

3. Applications

3.1. Analyses of suspended particles in air using tree leaves

Trees can be a suitable substrate for atmospheric trace element monitoring, since a significant amount of atmospheric dust is deposited in their leaves [7]. Here we describe a study where leaves from two kinds of trees growing in Mexico City were analyzed by PIXE. We looked at the differences in particulate matter captured between two tree species: Wax-leaf privet (L*igustrum japonicum*) and Weaping fig (*Ficus benjamina*). Tree leaves were collected from a park in downtown, Mexico City (Alameda Park). Collection was

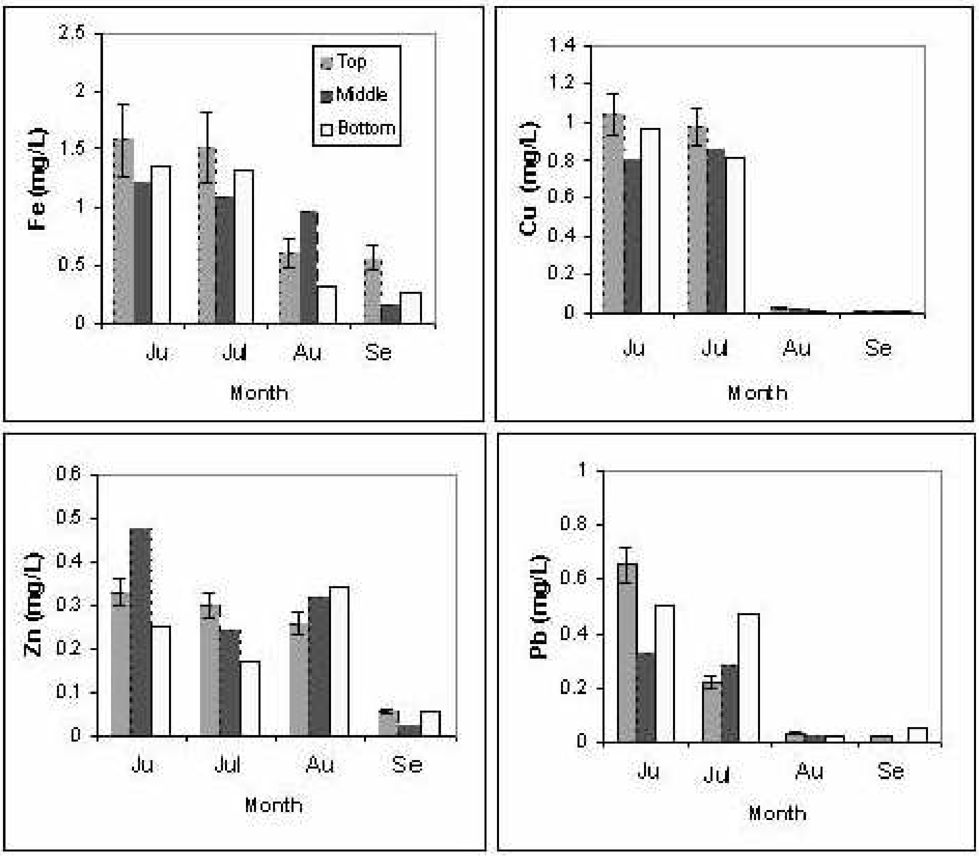

FIGURE 5. Concentrations of Fe, Cu, Zn and Pb in soluble fractions of water samples collected during the beginning and the end of the rainy season. Water was collected at three depths of the Lateral Requena channel at the Mezquital Valley. Maximum limits of total content allowed for irrigation water for these elements are: Fe: 5000.0 μg/L, Cu: 200 μg/L, Zn: 2000 μg/L and Pb: 400μg/L (DOF, 1997).

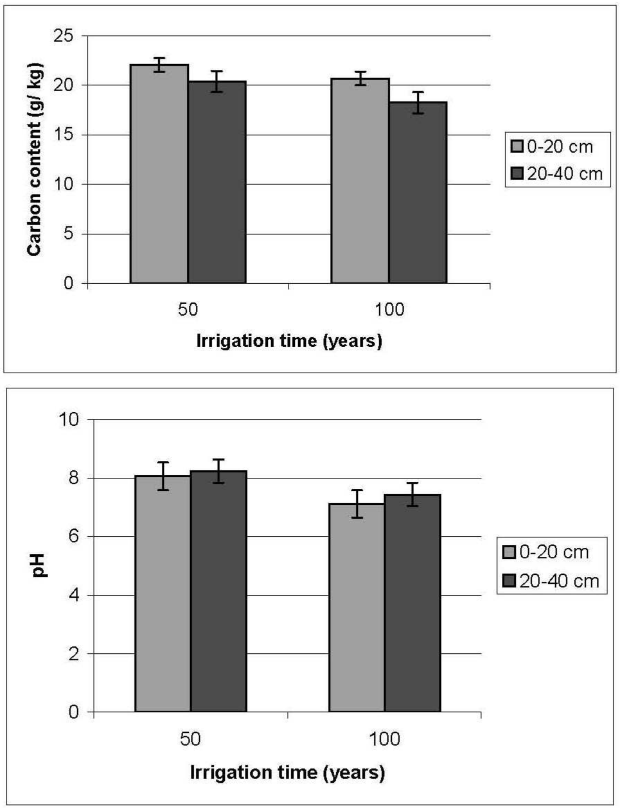

FIGURE 6. Top: Total Organic Carbon (TOC) in g/Kg, at two soil depths in plots irrigated with wastewater for 50 and 100 years. Bottom: Soil acidity (pH) at two depths in plots irrigated with wastewater for 50 and 100 years. Bar is the Standard error.

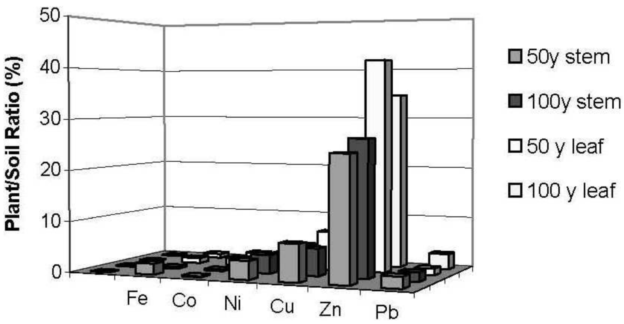

FIGURE 7. Plant/soil ratio (in %) for Fe, Cu, Zn and Pb in stem and leaf of alfalfa plants grown in waste water irrigated soil for 50 and 100 years.

performed at the rainy season (July 2003) and at the dry season (March 2004). Leaves were stored in boxes at -30°C and freeze dried. Some leaves (the top surface) were analyzed by Electron Microscopy in order to identify the morphology, size and number of the deposited particles. For PIXE determination of elemental concentrations, ground dry leaves were digested with nitric acid and an aliquot was deposited in a film as described elsewhere [8]. Figure 3 shows an electron microscope picture of the particulate matter present in the leaves. Some particles can be identified as from soil origin (irregular grains), coal combustion impurities (spherical particles) and carbonaceous particles (round and porous). Less particles are observed in the rainy season (July) compared to the dry season (March). The washing effect of the rain is more effective in ficus leaves than in wax-leaf privet, since less particle density is observed in the former tree during July. This effect is reflected in a lower total element content in ficus relative to wax-leaf privet tree (Fig. 4).

3.2. Irrigation water quality based on heavy metal analyses

In this application we determined the trace element content of irrigation water in the Mezquital Valley. This valley receives wastewater from Mexico City Metropolitan Area since the early 1900's. The irrigation is performed through channels, before being discharged to the Pánuco River. This practice has increased the productivity of the valley, but it has resulted in a change of the natural chemical profiles in some soils as well as in the presence of some toxic elements in food and water. Here we show the contents of Fe, Cu, Zn and Pb in water collected at three depths of the Lateral Requena channel during June and July 2003 (beginning of the rainy season) and during August and September 2003 (end of the rainy season). Water was pre-concentrated with carbamates following a procedure described elsewhere [8]. Figure 5 shows the results obtained from samples taken at the Lateral Requena channel. The metal levels are high in dry season and low during the end of the rainy season. It is important to note that in spite of the high levels, metal contents do not exceed the limits established by the Mexican Regulations NOM-001 ECOL 1996 (DOF 1957).

3.3. Analysis of trace elements in plants cultivated in waste water irrigated soil

PIXE is an attractive technique for total elements analysis in soils and plants since several elements can be analyzed in a high number of samples in times relatively short. In this application the objective was to determine the trace element distribution in agricultural products of soils from the Mezquital Valley that have been irrigated with waste water for long periods of time. Figure 6 shows the organic matter content and pH of soils irrigated for 50 and 100 years. Both parameters decrease with time of irrigation. Figure 7 shows the incorporation ratio of elements such as Fe, Cu, Zn and Pb in stem and leaf of an alfalfa plant. Some elements such as Zn have a higher incorporation ratio than elements such as Fe, Cu or Pb. Also, the accumulation ratio increases with the irrigation period.

4. Conclusions

PIXE is a multielemental, non destructive and highly sensitive technique that allows the detection the presence of many elements in a sample and its relative abundance. This technique combined with adequate sample preparation methods results in improved detection limits rendering it into a powerful tool for environmental analysis.

Acknowledgements

The authors would like to thank K. López, F.J. Jaimes, and E. Zavala, for maintenance and operation of the accelerators, Dr. Katsumi Saitoh from the Akita Prefecture Institute of Environmental Science, Japan, for discussion and performing some leaf analysis and Biol. Graciela Sierra for providing water samples from the Mezquital Valley. This research receives partial support from DGAPA, UNAM Grant IN228603.

1. C. Solís *et al.*, *Nucl. Instr. Meth. B* **150** (1999) 222.
2. G. Guereca and J.L. Ruvalcaba-Sil, *X-Ray Spec.* **34** (2005) 366.
3. J. Miranda, L. Rodríguez-Fernández, O.G. de Lucio, K. López, and J.A. Harada, *Rev. Mex. Fís* **46** (2000) 367.
4. J.A. Maxwell, W.J. Teesdale, and J.L. Campbell, *Nucl. Instr. Meth. B* **95** (1995) 407.
5. C. Solís, J. Sandoval, H. Perez-Vega, and M. Mazari-Hiriart, *Physics Research B* **249** (2006) 592.
6. C. Solís *et al.*, *Nucl. Inst. Meth. B* **24** (2005) 351.
7. K.P. Beckett, Freer-Smith, P.H. and Taylor, *G. Environmental Pollution* **99** (1998) 347.
8. K. Saitoh, K Sera, T Gotoh, and M. Nakamura, *Nucl. Instr. Meth. B* **189** (2002) 86.