



Elemental analysis of agricultural soil samples by particle induced X-ray emission (PIXE) technique

Paulo E. Cruvinel ^{a,*}, Robert G. Flocchini ^b, Paulo Artaxo ^c, Silvio Crestana ^a,
Paulo S.P. Herrmann Jr. ^a

^a *Embrapa Instrumentação, P.O. Box 741, CEP 13560-970 São Carlos, Brazil*

^b *Crocker Nuclear Laboratory, University of California, Davis, CA 95616-8569, USA*

^c *Instituto de Física – USP, P.O. Box 20516, CEP 01498-970, São Paulo, Brazil*

Abstract

In agriculture, elements essential to vital processes are also called nutrients. A suitable and reliable particle induced X-ray emission (PIXE) methodology for content determination of essential nutrients in soil samples was developed and its effectiveness proved. The PIXE method is applied to intermediate thickness samples, whose mass per area unit are smaller than 1 $\mu\text{g}/\text{cm}^2$. Precision and accuracy of the method was estimated after repeated measurements of a single reference material: CRM PACS-2 (estuarine sediment) with a matrix quite similar to the soil samples measured. This paper reports the results of elemental measurements in soil samples. A discussion of agricultural soil sample preparation for PIXE analysis is also presented. © 1999 Elsevier Science B.V. All rights reserved.

PACS: 07.77.Ka; 07.77.Gx; 07.85.-m

Keywords: PIXE; Nutrients; Agriculture; Soil

1. Introduction

In agriculture, use of fertilizers and higher yielding plant varieties with increased nutrient demand, decreasing availability of farmland rich in trace elements in areas where mixed farming has given way to intensive arable agriculture, and higher stocking rates in pastureland regions, have combined to increase the demand made on the soil's ability to supply trace elements to plants.

Consequently, deficiencies have become more common and attempts to correct them have required a better understanding of the soil chemistry of trace elements [1].

A dividing line separates those nutrients required in greater quantities, or macronutrients, from those elements required in smaller quantities, or micronutrients. This division does not mean that one nutrient is more important than another. But just that they are required in different quantities and concentrations. A typical group of macronutrients consists of N, K, Ca, Mg, P and S, whereas a typical group of micronutrients consists of Cl, Fe, B, Mn, Zn, Cu and Mo. From a

* Corresponding author. Tel.: +55-016-274-2477; fax: +55-016-272-5958; e-mail: cruvinel@cnpdia.embrapa.br

practical standpoint, three of the six essential macronutrients are most often managed by the addition of fertilizers to soils, while the others are usually found in sufficient quantities in most soils and no soil amendments are required to maintain adequate supplies. Thus, from a management perspective only N, P and K are considered primary nutrients, because they are most often limiting factors from a crop production standpoint. All of the other essential macronutrient elements are secondary nutrients because they are rarely limiting and seldom added to soils as fertilizers. The ability of soils to supply secondary nutrients to plants indefinitely is subject to the law of conservation of matter and therefore depends upon nutrient cycling. Continued crop removal of Ca, Mg and S requires replenishment just as essentially as primary nutrients, but less frequently. Ca and Mg are often supplied by mineral weathering of either natural soil materials or aglime, i.e., ground limestone added to correct soil acidity. S is often added to soil as either atmospheric deposition or as impurities in fertilizers. Additionally, many other elements may be present in concentrations greater than minimal plant requirements, plants may also accumulate elements that are not essential nutrients.

It is difficult to identify the most important component in trace element analysis of agricultural soil samples but undoubtedly two of the most critical include sampling and choice of the analytical technique for measuring and identifying nutrients. Important points concern optimizing sample preparation, matrix corrections, time requested for sample analysis, and non-degradation of the inorganic matrix of the soil during sample preparation. From this point of view, several analytical methodologies for elemental analysis in agricultural applications have been explored by investigators, and the particle induced X-ray emission technique (PIXE) successfully employed [2–5]. In the PIXE analysis [6], the number of X-ray photons of a given element provides information on its concentration. In addition, PIXE allows non-destructive, rapid and simultaneous detection of practically all elements heavier than Na.

This paper reports an elemental analysis of agricultural soil samples by PIXE technique and

presents a discussion of agricultural soil sample preparation for PIXE analysis.

2. Material and methods

PIXE analysis of the samples was carried out using a Pelletron accelerator, model 5SDH. This accelerator provides proton energies up to 2.4 MeV. The detector used is a Si(Li) detector from KeveX, model 3000, with resolution of 175 eV at 5.9 keV.

The instruments used for signal processing were a standard electronic pulse handling system, and an ADCAM Analyst, model 100U, multichannel analyzer from EG&G ORTEC. Data were accumulated in a PC-compatible computer and the AXIL code used for data analysis [7]. Absolute accuracy of the analysis system was established through the use of gravimetric thin film standards. Therefore, in order to obtain accurate measurements for the soil sample analysis a standard reference material from National Bureau of Standards was used.

The reference material, i.e., CRM PACS-2, is a sediment standard intended primarily for calibration in the analysis of sediments, soils, or materials of a similar matrix. The certified concentrations of the elements in the standard reference material were obtained using X-ray fluorescence spectrometry. Analysis of a sample requires 400 s of beam time and about 25 s of computer time. Sodium and heavier elements are routinely detected with minimum detectable limits (MDL) ranging from a few ppm to several hundred ppm, when interfering peaks are present.

The soil samples were analyzed using an incident 2.4 MeV proton beam with a typical beam current of 15 nA and charge of 8 μC . Nuclepore filter (25 mm, 0.4 μm) from Costar Corporation was used as a substrate for holding the soil samples for PIXE analysis. Because the 2.4 MeV proton beam cannot penetrate a target deeper than a few microns, all soil samples were crushed identically before aerosolization prior to depositing in a nuclepore filter by means of vaseline coatings. Matrix correction was performed by means of correction

association with a spherical particle size diameter and composition [8].

A sample preparation method has been developed in which the soil sample may be aerosolized and collected onto filter media in the form of a uniform layer of particulate matter. The instrument used for sample preparation as show in Fig. 1 consists of a nuclepore 25 mm, filter holder nestled inside a plastic bag (950 cm³) mixing chamber; an air injection system; a vacuum pump and needle valves. A soil sample is primarily crushed as a powder and placed in the plastic bag. Air is pulled

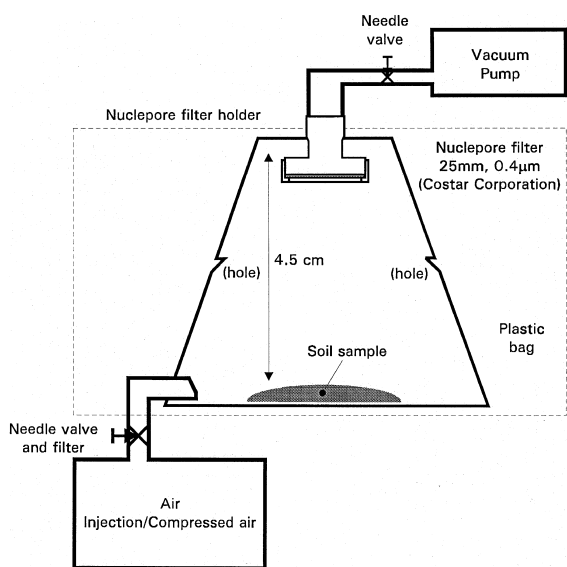


Fig. 1. Schematic diagram of the instrument for agricultural soil sample preparation.

through the mixing chamber by means of an air injection system located downstream from the filter medium onto which the sample is to be deposited. The air flow can be controlled by means of a needle valve and a calibrated flow meter. A flow rate of approximately 15.2 Lpm was used. The soil sample is aerosolized by filtered air introduced into the plastic bag. Besides, we used a vacuum pump connected to the filter holder, which allows a direct deposition of the pulverized soil sample towards the filter medium. Therefore, the matter is deposited onto the filter. Nuclepore filter is located 4.5 cm above the soil sample.

The Atomic Force Microscopy (AFM) technique [9] was used to analyze the soil sample preparation for PIXE analysis. We used a Topometrix Discover TMX 2010 atomic force microscope working in contact mode, with spring constant of approximately 0.06 N/m, and cantilever of Si₃N₄.

We analyzed by PIXE a set of 36 samples collected in the experimental field of Pindorama-SP, Brazil, part of the Agronomic Institute of Campinas, with coordinates of 48°55'W, and 21°13'S, in an area of 5000 m². The soil samples were collected at 5 m intervals with 6 repetitions at a depth of 15 cm from the surface.

3. Results and discussion

Fig. 2 shows two representative topographic images obtained by means of AFM from a nu-

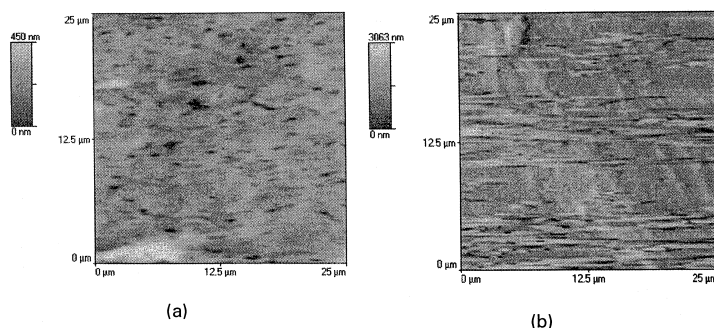


Fig. 2. Representative topographic images obtained by means of AFM with roughness average values in nanometers: nucleopore filter (378 ± 72); nucleopore filter plus soil (2990 ± 73).

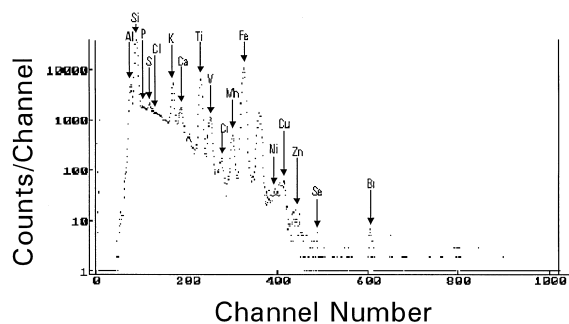


Fig. 3. Typical PIXE spectrum emitted from an agricultural soil sample with lines of several elements.

cleopore filter and a nucleopore filter plus soil. In Fig. 2 were observed the following roughness average values in nanometers (378 ± 72) and (2990 ± 73). These roughness average values show that the soil deposition on the nucleopore filter by means of aerosolization process was reliable and reached soil grain size distribution not larger than $4.0 \mu\text{m}$, i.e., during PIXE analysis the secondary fluorescence effects can be decreased.

A typical PIXE spectrum emitted from a soil sample is shown in Fig. 3. Al ($K_{\alpha} = 1.487 \text{ keV}$), Si ($K_{\alpha} = 1.740 \text{ keV}$), and Fe ($K_{\alpha} = 6.400 \text{ keV}$) are

predominant with respect to P ($K_{\alpha} = 2.015 \text{ keV}$), Cl ($K_{\alpha} = 2.622 \text{ keV}$), K ($K_{\alpha} = 3.312 \text{ keV}$), Ca ($K_{\alpha} = 3.690 \text{ keV}$), Cr ($K_{\alpha} = 5.411 \text{ keV}$), Zn ($K_{\alpha} = 8.631 \text{ keV}$), and the other elements. To demonstrate the applicability of this methodology for elemental analysis of agricultural soil samples, the resulting PIXE spectra were analyzed in order to provide concentration in $\mu\text{g/g}$ and matrix corrections were then implemented.

Table 1 shows the concentrations in $\mu\text{g/g}$ of elements in both agricultural soil sample and reference material. Results obtained for the reference material agree well with those published by the National Bureau of Standards. Fig. 4 shows the spatial variability maps for the concentration of K and P in the Pindoramás agricultural. After PIXE analysis of the agricultural soil samples, the maps were obtained by means of geostatistical procedures. Therefore, the semivariogram functions [10] were also calculated according to:

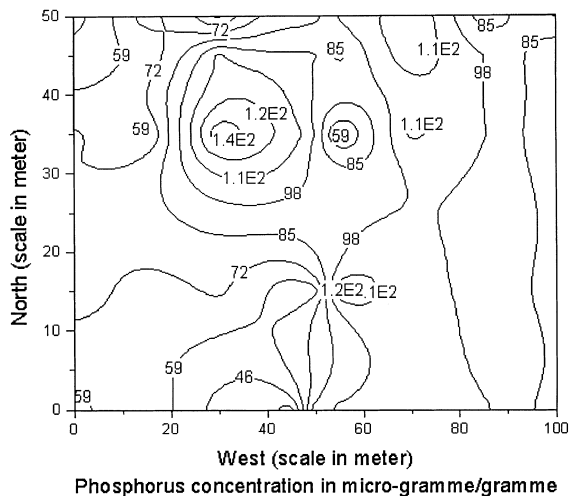
$$\gamma(h) = \frac{1}{2M(h)} \sum_{i=1}^{M(h)} [X(Z_i) - X(Z_{i+h})]^2,$$

where $\gamma(h)$ is the semivariogram; $X(Z_i)$ and $X(Z_{i+h})$ are regionalized variables at spatial

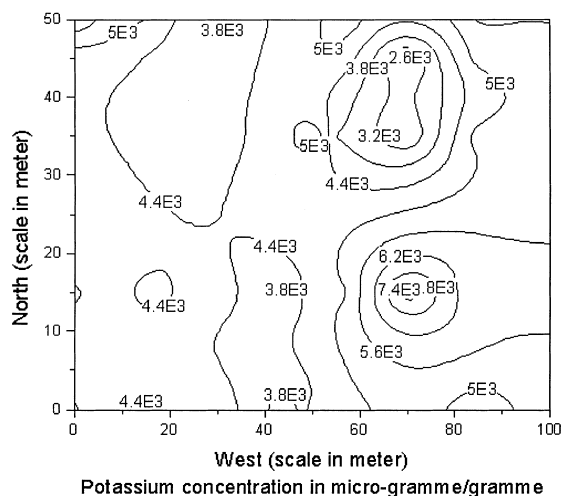
Table 1

PIXE measurements for one soil sample and the CRM PACS-2 reference material (unless otherwise noted the concentration values are in $\mu\text{g/g}$, MDL: minimum detectable limit)

Element	Mean soil sample	Std. dev. soil sample	Mean CRM PACS-2	Std. dev. CRM PACS-2	Mean CRM PACS-2 (certified)	Std. dev CRM PACS-2 (certified)
Al	21 000	1000	13.1%	0.9%	12.5%	0.6%
Si	65 700	3000	—	—	—	—
P	475	24	0.27%	0.04%	0.22%	0.01%
S	180	20	2.2%	0.15%	1.29%	0.13%
Cl	85	6	—	—	—	—
K	5000	300	1.65%	0.10%	1.49%	0.06%
Ca	300	20	2.52%	0.20%	2.75%	0.25%
Ti	4000	200	22	2	19.8	2.5
V	125	15	105	8	133	5
Cr	50	4	83	5	90.7	4.6
Mn	470	20	423	23	440	19
Fe	26 500	1500	5.95%	0.12%	5.85%	0.08%
Ni	530	15	34	4	39.5	2.3
Cu	50	5	285	16	310	12
Zn	20	2	360	25	364	23
Se	MDL	—	—	—	0.92	0.22
Br	MDL	—	—	—	—	—



(a)



(b)

Fig. 4. The two-dimensional maps of the macronutrients K and P and its spatial variability in concentration.

locations Z_i and Z_{i+h} , respectively; and $M(h)$ is the number of pairs of observations having a distance separation h . The semivariogram function is based on the assumption that the mean of the regionalized variable is constant in space, i.e., stationary. Therefore, spherical semivariogram models was fitted for interpolation purposes in order to obtain

the maps shown in Fig. 4. Substantial spatial variability along the agricultural field can be observed. Uncertainties in the concentrations were about 5%. These results show the use of PIXE as a complementary method for investigating sum total of elements in soils and for simultaneously measuring to other potentially interesting elements present in soil samples.

4. Conclusions

In the last few years, nuclear techniques have made an important contribution in the field of soil physics. In this work, the main objective was to demonstrate the suitability of PIXE for determining and measuring total of elements in agricultural soil samples. In comparison to other analytical technique for elemental analysis, the multielemental character of PIXE brings advantage and potentialities to soil science investigators. Furthermore, results of a typical spectrum of soil sample and maps of the spatial variability of the essential macronutrients K and P from a experimental agricultural field were outlined.

Acknowledgements

The work reported in this paper was supported in part by Grants No. 12.094.090 from the Brazilian Enterprise for Agricultural Research (EMBRAPA). Authors also thanks Valentim Monzane for drawing works.

References

- [1] E. D. Brian, Chichester, Wiley, New York, 1980.
- [2] P.E. Cruvinel, R.G. Flocchini, Nucl. Instr. and Meth. B 75 (1993) 415.
- [3] P.E. Cruvinel, R.G. Flocchini, S. Crestana, J.R. Morales, J. Miranda, B.H. Kusko, D.R. Nielsen, Soil Sci. 155 (2) (1993) 100.
- [4] P.E. Cruvinel, E.R. Minatel, Proceedings of the 3rd International Conference on Systems Integration, IEEE Comp. Society (1994) 371.
- [5] P.E. Cruvinel, S. Crestana, P. Artaxo, J.V. Martins, M.J.A. Armelin, Nucl. Instr. and Meth. B 109 (110) (1996) 247.

- [6] T.B. Johansson, R. Arselsson, S.A.E. Johansson, Nucl. Instr. and Meth. B 84 (1970) 141.
- [7] H. Nullens, P. Van Espen, Pro-Axil Users Manual, Canberra Elektronik, Vienna, 1984.
- [8] D.G. Jex, M.W. Hill, N.F. Mangelson, Nucl. Instr. and Meth. B 49 (1990) 141.
- [9] G. Binnig, C.F. Quate, C. Gerber, Phys. Rev. Lett. 56 (1986) 930.
- [10] A.G. Journel, Ch.J. Huijbregts, Academic Press, London, 1978.