

Zinc measurements in agricultural field by means of electronics and nuclear instrumentation

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Abstract:- Electronics and computers are rapidly advancing into agricultural systems management. Silicon and software now impact strongly production agriculture as well as industry in general. In the next few decades electronics and computer applications in agriculture will be as significant as were materials and fluids technologies in industrialized economies over the last ten years. A measure of this shift is that the electronics content of agricultural machinery and products used in agriculture will represent a multibillion-dollar market worldwide by the year 2000. For agriculture of the most significant opportunities and solutions lie within the domain of instrumentation applications. The scope and importance of technical developments in the last five years amply demonstrate this benefit. This paper presents the suitability of PIXE to study the trace metal Zinc in soil, showing additionally that many solutions in agriculture lie within the domain of instrumentation development. So far, processes involved in Zn adsorption, as well as for many other elements, are not completely understood. Soil samples were analyzed using both PIXE and the classical procedure of INAA technique for comparison. Results showed that there is a good linear relationship for Zn concentration obtained using these techniques.

Key-Words:- *Agricultural Instrumentation, PIXE, INAA, Micronutrient, Soil Analysis, Zinc, Heavy metal, Trace-elements*

1 Introduction

In the near future, developing and successfully commercializing new agricultural products and services, including those associated with site-specific agriculture, will require organizing increasingly complex partnerships. These partnerships will bring together specialists with many different perspectives and kinds of expertise. The success of agricultural initiatives will depend on the capability of these specialists and the degree to which their activities are coordinated, integrated, and focused. Research and development (R&D) efforts enabling and supporting complex commercial initiatives in agriculture will also be organizationally complex. They will require unusually close relationships in which public institutions and agencies are full partners in commercialization efforts. Like other suppliers and partners in

these efforts, public institutions and agencies will provide unique capabilities and facilities. Differences in organizational characteristics however may make it difficult for some groups to work well together. Like the collective memory of networked computers, partners in the complex value-added partnerships of the future, including those with responsibility for research and technology transfer, must to function as one. This virtual agriculture will depend heavily on networked computers. At present, agriculture is driven by the logistical demands of serving large urban populations. Made up of many highly specialized activities, it involves many different individuals and groups, conceiving, designing, developing, implementing and managing activities once carried out almost entirely by farmers. Farmers themselves are

becoming specialists, functioning with other specialists in the industry of agriculture.

With the advent of accurate, reliable and affordable positioning systems, particularly the Global Positioning System (GPS), the possibility of taking into account within-field spatial and time variability was born, with the promise of both economic and environmental benefit. Parallel advances in sensing systems, in precise application mechanisms and control systems and the information processing power computers have led to the adoption of the concept of precision agriculture. Precision agriculture may be defined as the targeting of inputs to field crops according to locally determined requirements at the meter or even centimeter level. The concept has been technology-led, with technology in place so that spatially variable application of inputs could be implemented in production agriculture. However, interpretation of spatial and time variability and the necessary understanding of instrumentation, soil science, crop science and agronomy on a site-specific basis are very much less well developed. It is widely recognized that substantial research is necessary in these areas in order to give a solid foundation to the whole concept of precision agriculture and its implementation in production agriculture [1].

The use of measurement and control systems design in electronics technology for soil science is a relatively new field. For many years, the most sophisticated apparatus used was an on-off or perhaps a proportional thermostat with a liquid filled bulb. In many instances, particularly in mild climates, plant and animal environments were manually regulated by adjusting curtains, tilt-out panels, dampers, and spray nozzles. Also, electronics applications for environmental control until recently have been largely limited to research uses. Although integrated circuits (ICs) have been available since the early '60s, only in recent years have these powerful building blocks been used in designing analog devices such as amplifiers and filters, and digital logic circuits for instrumentation and measurements systems. Intel Corporation introduced the first

microprocessor, the Intel 4004 [2], only 27 years ago. Its descendents include today's growing personal computer industry and the associated computer revolution. Therefore, the subsequent drop in price of microprocessor-based instrumentation measure and control components has given engineers a versatile tool for systems design. By using a microcomputer as a central part of a system, the engineer can now simplify his task. First, he needs to interface all inputs and outputs, both analog and digital, through appropriate circuitry such as amplifiers, sample and hold, buffers, and so on, to the microcomputer. Once this is done, by changing the software, he can read inputs and control outputs in any way desired. While personal computers are highly visible to the public thanks to considerable coverage by the press, a far greater number of microprocessors are finding their way into industrial controllers, consumer products, and research instruments.

A relevant application of instrumentation in agriculture lies in the determination of supply, availability, and movement of trace-elements in soil/plant ecosystems. In this context, the investigation of suitable techniques for the measurement of the concentration and identification is essential to the development of an understanding of the mechanisms and dynamics of transport and their biological implications. One serious difficulty encountered in attempts to relate trace-elements to plant response is the fact that their concentration in the agricultural soils varies in time and spatially. Thus, to study trace-elements concentration in an agricultural field it is useful to use a large number of samples, at least to have a representative sampling grid of the experimental field. Furthermore when working with a large number of either soil or plant samples, the choice of the analytical technique to measure and identify trace-elements becomes to be another critical point, in terms of optimizing sample preparation, matrix corrections, requested time for each sample analysis, and non-destructive characteristics. Certainly, each analytical techniques

commercially available have their own limitations, however the proton induced X-ray emission technique has been used successfully in agronomic applications [3][4][5][6]. In the field of soil physics, a technique which permits a non-destructive, accurate and fast elemental analysis with a minimum of sample preparation effort is often desired. The composition of soils is extremely diverse and, although governed by many different factors, climatic conditions and parent material predominate most commonly. Although trace elements are minor components of the solid phase, they play an important role in soil fertility. Knowledge of the association of trace elements with particular solid phase and their affinity to each soil constituent is the key to a better understanding of the principles governing their behavior in soils. There are a large number of trace elements in soils, at concentration values in the range of parts per billion and tenths of parts of million. As for biological samples many of them are of great importance for the nutrition of the plants, while others are toxic, and others have an unknown role. Moreover the knowledge of the behavior of polluting trace elements is far from complete.

Zinc (Zn), for example, seems to be distributed rather uniformly in magmatic rocks, and its slight decrease in acid rocks is observed. The Zn occurs chiefly as single sulfides (ZnS), but is also known to substitute for Mg^{2+} in silicates. The solubilization of Zn minerals during weathering produces mobile Zn, mainly in oxidizing environments. Additionally it is easily adsorbed by mineral and organic components and thus, in several soils types, its accumulation in the surface horizons is observed [7]. The Zn balance in surface soils of different ecosystems shows that, in general, the atmospheric input of this metal exceeds its output due to both leaching and the production of biomass. Processes involved Zn adsorption is not yet completely understood. However, there are some generalizations obtained from studies reported in the literature, which show both the adsorption in acid media related to cation

exchange sites and in alkaline media that is highly influenced by organic ligands [8][9][10]. The nucleation of Zn hydroxide on clay surfaces may produce the strongly pH dependent retention of Zn in soils [11]. The adsorption of Zn can be reduced at lower pH, smaller than 7, by competing cations and this results leading to mobilization and leaching of Zn from light acid soils, which has an important practical impact on either the Zn availability or deficiency to plants.

Proton Induced X-ray Emission (PIXE) is an analytical technique based on the ionization of the sample atoms by the incidence of a proton beam and the subsequent emission of X-rays characteristic of the elements present in the sample [12]. The number of X-ray photons of a given element provides information on the amount of this element as little as one part in 10^{-12} g in special cases [13]. It is also able to analyze very small sample quantities down to 10^{-4} g for solids and around 1 μ l for liquids. In addition, it allows the simultaneous detection of all elements heavier than Na, a non-destructive and rapid analysis [14]. Recent developments have expanded the usefulness of PIXE in applications such as geology and material science combining part per million (ppm) elemental sensitivity and sub-millimeter spatial resolution [15][16]. For PIXE analysis the X-ray yield can be obtained using the ionization cross section energy dependence according to the relation:

$$Y_p(E) = (4.968)10^{-17} N_2 x \sigma_p^x(E) Q \Omega \left(\frac{\epsilon}{\sin \Theta_i} \right)$$

Where $Y_p(E)$ is the number of X-ray counts in a peak p for an incident ion energy E, $\sigma_p^x(E)$ is the X-ray production cross section for a peak p, N_2 is the number of target (atoms/cm³), x is the target thickness (μ g/cm²), Q in (μ C) is the total charge hitting the target, Ω is the detector solid angle (steradians), ϵ is the total detection efficiency and Θ_i is the angle between the surface normal and the beam direction [17][18]. Correction factors are required. The first is a loading correction that reflects the transmission of X-rays through a

uniform layer of a filter. The second is a particle size diameter correction associated with a spherical particle of a given diameter and composition [19]. The second correction may become important for quantitative analysis of soils.

Concerning to multielemental analysis techniques on soils, during the last years [20][21][22] the usefulness of the instrumental neutron activation analysis (INAA) have been also pointed out to obtain information about concentrations of a large number of elements simultaneously, and it has been applied to the analyses of soil by several researchers.

This work demonstrates not only the suitability of PIXE as a fast and non-destructive technique useful to measure total Zn content in soil samples from an agricultural field but also a comparison of results with INAA is outlined.

2 Material and Methods

PIXE analysis of the samples was carried out using a Pelletron accelerator, model 5SDH, installed at the Physics Institute of the University of São Paulo, São Paulo, Brazil. This accelerator provides proton energies up to 2.4MeV. The detector used in order to obtain a suitably high sensitivity for each element is one Si(Li) from Kevex, model 3000, with resolution of 175eV in 5.9KeV.

The instruments used for signal processing were a standard electronic pulse handling system, and a ADCAM Analyst, model 100U multichannel analyzer from EG&G ORTEC. Data are accumulated in either a VAX or PC-compatible computer and the AXIL code is used, giving both a spectrum of characteristic X-ray and a smooth background. Figure 1 shows in block diagrams a basic instrumental architecture for PIXE analysis. Absolute accuracy of the analysis system is established through the use of gravimetric thin film standards. Therefore in order to have accurate measurements for the soil samples analysis a standard reference material from National Bureau of Standards was used. This reference material, i.e., CRM PACS-2, is a sediment standard and it is intended primarily to calibrate and use in the analysis of sediments, soils, or materials of a similar matrix. The certified concentration of the elements in that standard reference material was obtained using X-ray fluorescence spectrometry. An average analysis normally requires 400 seconds of beam time and about 25 seconds of computer time. Elements sodium and heavier are routinely detected with minimum detectable limits (MDL) ranging from a few ppm to several hundred ppm, when interferences are present.

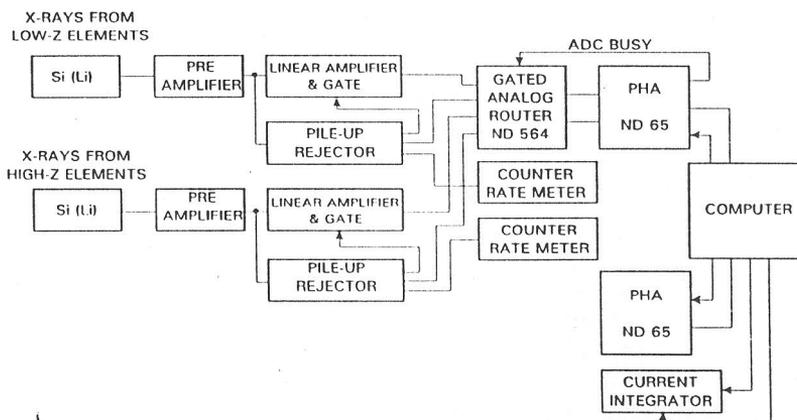


Figure 1 - Block diagrams a basic instrumental architecture for PIXE analysis.

The soil samples were analyzed using an incident 2.4MeV proton beam and both a typical beam current of 15nA and charge of 8 μ C. Because the 2.4MeV proton beam cannot penetrate the target deeper than a few microns all soil samples were crushed identically before analysis. The soil samples were crushed to allow both the penetration of the 2.4MeV proton beam and to decrease the effects of X-ray attenuation by the aggregates of the soil. Nucleopore filter with a thickness of approximately 10⁻²mm was used to hold the crushed soil as a thin layer for PIXE analysis.

INAA [22] were carried out by means of a thermal neutron flow having 5.10¹² neutrons.cm⁻².s⁻¹ for a period of eight hours. Irradiations have been carried out at the IEA-R1 swimming pool type reactor of IPEN-CNEN/SP. Samples and standard of Zn were irradiated together in aluminium tubes. After a minimum cooling time of ten days the γ ray emitted by ⁶⁵Zn(1115 keV) was measured. Samples and standard were placed in close geometry using a solid state EG&G ORTEC model GMX 20190 Ge detector, with a resolution of 1.9keV for the 1332 keV peak of ⁶⁰Co, coupled to an ADCAM 918A multichannel buffer. Analysis of the γ ray spectra were carried out by using appropriate computer programs.

It was analyzed by PIXE soil samples collected in the experimental field of Pindorama-SP, part of the Agronomic Institute of Campinas, i.e., Brazilian Podzol (Palehumult).

The soil samples were collected 5 meters far from each other in a depth of 15cm. For comparison, part of the samples were also analyzed experimentally by INAA.

3 Results and discussion

A typical PIXE spectrum emitted from a soil sample is shown in Figure 2. Fe, Si and Al are predominant with respect to Zn (K_{α} = 8.631 keV, K_{β} = 9.572 keV), Cr, Cl, Ca, K, and the other trace elements. In Figure 2, the

showed pile-up pulse occurred because during signal processing each pulse must be measured individually with reference to a zero level and cannot be measured when superimposed upon either the leading edge or the trailing edge of a nearly coincident pulse. i.e., the fact that pulses from a radiation detector are randomly spaced in time can lead to interfering effects between pulses when counting rates are not low. These effects called pile-up can be minimized by making the total width of the pulses as small as possible.

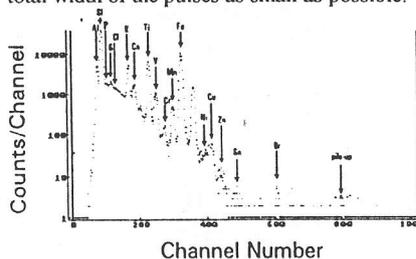


Figure 2 - A typical PIXE spectrum emitted from a soil sample.

The resulting PIXE spectra were analyzed to provide the absolute concentration in μ g/g of the measured elements and matrix correction was implemented. Uncertainties in the concentrations range from 2% for heavy elements to 20% for light elements. Table 1 shows the concentrations in μ g/g of elements in a reference material. Results obtained for the reference material agree well with those published by the National Bureau of Standards. Moreover, the resulting INAA spectra were also analyzed to provide the absolute concentration in μ g/g.

Figure 3 shows a comparison between PIXE and INAA analysis i.e., results for Zn concentration measurements in soils. Considering errors given in Figure 3, the Zn concentration obtained by PIXE seems to correlate well with that obtained by INAA, i.e., with a coefficient of linear correlation $r^2=0.98$. These results confirm the use of PIXE as a complementary method to investigate total Zn in soils as well as to measure, at the same time, others elements

present in soil samples of potential interest to the investigator.

The occurrence of concentrations between 20 $\mu\text{g/g}$ and 30 $\mu\text{g/g}$ was larger than for other values.

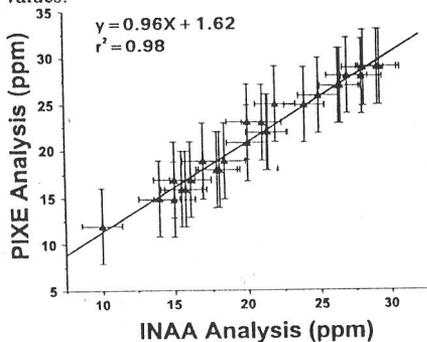


Figure 3 - Comparison between PIXE and INAA analysis.

4 Conclusions

Wide-ranging conclusions with both technological and social implications can now be drawn concerning future agriculture practice. Particularly, in industrialized nations are trends towards greater mechanization and automation will continue and perhaps accelerate. Advances in instrumentation technology, which involves not only instrumentation design but also the development of new methodologies for sustainable agriculture by means of instrumentation application. In this work, we have shown one application and the ability of PIXE in determining and measuring total Zn in soil samples.

Table 1 - PIXE measurements for the CRM PACS-2 reference material, concentrations are in $\mu\text{g/g}$ unless otherwise noted.

Element	Mean CRM PACS-2	Std Dev CRM PACS-2	Mean CRM PACS-2 (Certified)	Std Dev CRM PACS-2 (Certified)
Al	13.1 %	0.9 %	12.5 %	0.6 %
P	0.27 %	0.04 %	0.22 %	0.01 %
S	2.2 %	0.15 %	1.29 %	0.13 %
K	1.65 %	0.10 %	1.49 %	0.06 %
Ca	2.52 %	0.20 %	2.75 %	0.25 %
Ti	22	2	19.8	2.5
V	105	8	133	5
Cr	83	5	90.7	4.6
Mn	423	23	440	19
Fe	5.95 %	0.12 %	5.85 %	0.08 %
Ni	34	4	39.5	2.3
Cu	285	16	310	12
Zn	360	25	364	23
Se	MDL	MDL	0.92	0.22

As a methodology that involves instrumentation, this method showed a good correlation with INAA method for analyses of the total Zn in soil samples. Certainly both techniques have their own analytical limitations when applied to soil. For quantitative analysis of total Zn in soils, the PIXE method requires both the matrix

corrections and codes for spectra reduction, however it takes few minutes to carry out a high number of analyses. In addition detection limits down to 2 $\mu\text{g/g}$ were achieved by the PIXE analysis of total Zn in the soil samples. Besides, results of a typical spectrum of soil samples from an experimental field and

quantitative concentration in $\mu\text{g/g}$ for Zn were outlined.

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