ELEMENTAL ANALYSIS OF ARABLE SOIL BY PROTON INDUCED GAMMA EMISSION (PIGE) TECHNIQUE

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ABSTRACT

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Proton Induced Gamma Emission (PIGE) technique was employed for analyzing low Z elements (Na, Mg and F etc.) in arable soil. The soil samples were collected from the arable fields of Norshindi, Sylhet and Chittagong districts. Proton beam from the horizontal type 3 MeV Van de Graff accelerator at the AECD was used for irradiating the soil samples. The proton beam of energy 2.5 MeV was used with a beam current of 20 nA. A HPGe detector along with the associated equipment, such as pre-amplifier, amplifier, PC, MCA was used for the detection of gamma rays from the PIGE reactions in the irradiate soil samples. The PIGE reactions $^{19}F(p, p', \gamma)^{19}F$, $^{25}Mg(p, p', \gamma)^{25}Mg$ and $^{23}Na(p, p', \gamma)^{23}Na$ were used for the determination of the yields and hence the concentrations and sensitivities for the elements Na, Mg, and F. The concentrations were obtained at the ppm level by comparing with the certified values of the IAEA standard soil –7. The experimental results were compared with the optimum concentrations of the above elements in arable soil. Mg and Na were found at a slightly toxic level in some soil samples and F was found rather at a high concentration in some samples.

Key words: Proton Induced Gamma Emission (PIGE), HPGe detector, MCA and ppm.

INTRODUCTION

All plants and animals, including man ultimately depend on the soil for their supply of mineral nutrient. With plants this relationship is direct and is simplified by the fact that the plant is stationary. On the other hand, grazing animals may derive their minerals from a variety of soil types and plant species. In this way any disabilities associated with particular soils would tend to be minimized or even eliminated. Intensification of production imposes restrictions on movements and some animals may become dependent on a single soil type, or a narrower range of soil types, which may be incapable, without appropriate treatment, of sustaining the health, fertility and productivity of stock. It is a fact that animals did not thrive and suffered various disorders when restricted to some particular areas, and remained healthy in other areas. This is because areas considered satisfactory for stock and those classed as unhealthy were often adjacent, which would minimize the climatic differences as causal factors. Furthermore, animals transferred from unhealthy areas usually recovered, which suggested the existence of nutritional differences in soils.

Investigations carried out during the last half-century have shown that many of nutritional maladies of the type just mentioned result from the inability of the soils of the affected areas to supply the mineral needs of man and his domestic animals. Nutritional abnormalities involving the trace elements may arise as simple gross deficiencies or excesses of single element.

With minor exceptions, all of the mineral elements, which enter into the composition of terrestrial plants, come from soil. In the past the discussions of the absorption of mineral salts by plants was mainly focused on soil solution. Recent advances in soil science have made it clear that the mineral salts dissolved in the soil solution are not the only ones, which must be considered in any evaluation of the mineral salt of soils.

The mineral portion represents an essential part of the soil material, its abundance in the solid phase being usually as high as 95 to 99 percent. It is formed by the weathering of different rocks in surface layers of the earth's crust; as regards grain size it is a poli dispersed system with respect to the elementary composition. The mineral portion contains essentially all the natural elements but only eight elements are present with abundances exceeding 1%: O (46.6 %), Si (27.7 %), Al (8.1 %), Fe (5.0 %) Ca (3.7 %) Na (2.8 %), K (2.6%), Mg (2.1 %). Among the macrobiogenic elements, mineral particles supply plants with Ca, K, Mg, and P. In plant tissues nutrient elements such as C, H, N, P, K, Ca, Mg, S, Fe, B, Mo, Cl, Mn, Cu, Zn, F and Li may be found.

The major part of the earth's crust consists of light elements. The important micronutrients in the soils such as fluorine, boron, lithium, etc. play a vital role in life. The depletion of the soil nutrients and its effect on the productivity is also a major concern in the world today. The elements like nitrogen, zinc, phosphorus, and boron play vital roles in the fertility of the land and thus in the productivity (Walter Stiles, 1961). The knowledge of elemental contents of soil is important because the soil is the most important source of minerals for both human being and plants. Many diseases are caused due to the imbalance of supply of the mineral needs.

The detection of γ-rays depends on the energy range and the resolution of the detector. The most advanced state of the available for gamma spectrometry is the High Purity Germanium (HPGe) detector and this most advanced semiconductor technology is available for resolving the closely lying monoenergetic groups of γ-rays. The resolution of these detectors is less than 2 keV at 1332 keV. With the advancement of gamma spectrometry, PIGE method has become an attractive analytical tool for the detection of elements, especially the light elements in different matrices.

The scope of the application of the PIGE technique has been increased recently by many folds and is now used in many laboratories around the world for elemental analysis of the samples of environmental, biological, human health, agricultural, geological and archeological interest. PIGE method has been widely used for the light elements such as, carbon, nitrogen, oxygen, fluorine, boron, silicon, scandium, etc. in the biological and environmental samples. PIGE can also be used in analyzing heavy metals, alloys, glasses and ceramics. An important advantage of the method is its ability to determine simultaneously and accurately carbon, nitrogen and oxygen, which are the main components of biomedical and organic samples (Levertt, 1982, Forbes *et al*.. 1954).

Most of the people in Bangladesh depend on cultivation. But cultivation depends on the nature of the soil. All soils are not suitable for cultivation. Generally soft soils i.e. arable soils are used for cultivation. The light mineral elements are an important factor for growing plants and crops. The presence of mineral elements differs from location to location. Thus different plants and crops grow well at different locations. For example banana grows well in Norshindi, Mymenshing etc. because the concentration of P in the soil in these regions is conductive to its cultivation. But it does not grow well in Rangpur, Dinajpur Rajshahi etc. areas because of the deficiency of P in the soils there. Thus, if we know the concentrations of the mineral elements present in the soil in a region, we can easily say which plants will grow well in that region. The present work aims to determine the concentrations of the natural light elements in soil samples collected from the arable fields of Norshindi, Sylhet and Chittagong districts. So, the prime object of this study is to apply PIGE method to study low Z elements such as Na, Mg and F etc. in arable soil samples.

MATERIALS AND METHODS

The arable soils were collected form different places in Bangladesh. A total of 33 samples were collected, 14 samples from Norshindi, 12 samples from Sylhet and the rest from Chittagong. Proton beam from the horizontal type 3 MeV Van de Graff accelerator at the Atomic Energy Commission, Dhaka, was used for irradiating the soil samples. Proton Induced Gamma Emission (PIGE) is a nuclear reaction based analytical technique has been developed at the Atomic Energy Commission, Dhaka. The purpose of the development of the technique is to apply it for analyzing the low Z elements in the range of $3 \leq Z \leq 21$.In the present study the proton induced nuclear reaction based analytical technique (PIGE) has been used in analyzing soil samples. PIGE analytical technique involves means of exciting the nuclei of a sample to emit gamma rays and the means to detect and identify them so that their measured intensities can be converted to their elemental concentrations in the sample. The number of characteristic γ-rays produced per unit incident charge per unit solid angle at particular proton energy is directly proportional to the number of atoms in the target material. The number of characteristic γ-rays produced is also dependent on the reaction cross-section and the stopping power of the sample material. The concentration of the element (isotope), C_s can be calculated from the gamma ray yield Y_s for a certain γ-ray energy peak in a sample and the yield from a standard Y_{st} using the formula,

$$C_s = C_{st} \frac{S_s Y_s}{S_{st} Y_{st}} \qquad (1)$$

Where, C_s is the concentration of the sample,

C_{st} is the concentration of the standard sample,

S_s is the stopping power of the sample,

S_{st} stopping power of the standard,

Y_s is the yield of the sample,

Y_{st} is the yield of the standard.

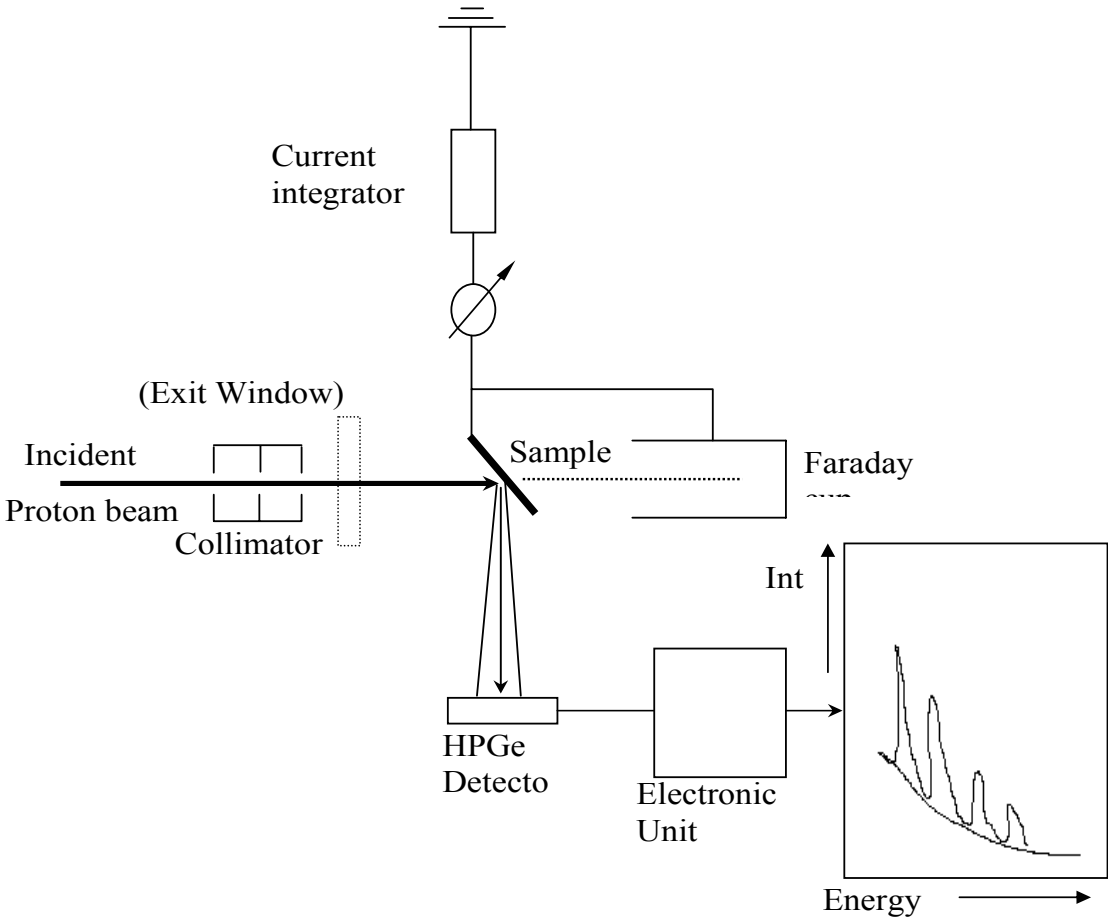

Figure 1. Schematic of PIGE setup with basic physical parameters

PIGE technique has been developed utilizing the proton beam from the 3 MeV Van de Graaff accelerator, which is a horizontal type (KN3000) accelerator and proton beam of energy upto 3 MeV can be obtained from it. Two collimators of 2mm diameter each and a 4 mm cleanup aperture were used. The target sample was irradiated in air (i.e., external beam).

Kapton foils of 1.12-mg/cm^2 thickness were used to extract the proton beams from the beam port into the air. The kapton windows of such thickness were found to be sufficiently strong to withstand about 400 μC of charge collected at proton beam current of 10-20 nA at an energy of 3 MeV on an area of ~3mm^2 without any deterioration of the high vacuum in the beam port. The beam spot was about 2 mm in diameter at the exit window.

In the case of external beam, the energy of the proton beam on the target was found to be about 2.3 MeV after losing its energy in the kapton foil and the air between the exit window and the sample. In order to obtain the total proton charges incident on the sample, the current on the target and the kapton window was monitored. The window frame was insulated from the beam port and the collimator. This arrangement is reproducible for the measurement of total charge on the target (Wahiduzzaman, *et.al.*1988). The setup was designed to hold 35 mm slide frames for solid samples at an angle of 450 with the beam direction. The characteristics γ-rays were detected at 900 with respect to the beam direction. A plastic absorber (44 mg/cm^2 thickness) was used to reduce the background due to the presence of argon in the air around the targets.

A beam area of 0.106 cm^2 on the sample was used for external beam experiments. The irradiation current was maintained within 10-20 nA and each of the target was irradiated for a preset charge of 80 μC depending on the net counts. The count rate was kept below 2000 cps in order to avoid the occurrence of sum peaks.

The HPGe detector having an efficiency 12.3% at 1332 keV energy and a resolution of 1.9 keV for 1332 keV peak (the manufacture's value for the resolution is 1.75 keV), was used to detect the γ-rays. The high voltage power supply, which has an output voltage up to 5 kV (dc.), was used for reverse biasing the detector (MacArthur, *et al.* 1983)

Many computer codes such as GAMANAL, SAMPO, HYPERMET, APTEC, EGM, GAUSS VIII, etc are available for analysing the spectra. Software from APTEC (Ali, *et al*., 1997) was used for data acquisition, display, identification of the elements through energy calibration, analysis of the γ-ray peaks and report generation. APTEC software incorporates PCMCA/SUPER software-version 6.31, the operation of which includes smoothing the spectra, location of the centroid, energy calibration, determination of FWHM and FWTM (full width at tenth maximum), polynomial background fit, integral/net counts, etc. Another OSQ/Professional option that automates the energy vs. channel, FWHM vs. channel and efficiency vs. energy calibration and provides detailed error analysis report.

In the present experiment several point sources such as ^{22}Na, ^{60}Co and ^{137}Cs, have been used for the calibration of energy E. The PC based MCA with APTEC software is used to have an energy calibration function to provide a linear calibration scale for the energy axis.

RESULTS AND DISCUSSION

The results of PIGE measurements of the concentrations and the Minimum Detection Limit (MDL) of three trace elements ^{23}Na, Mg, and ^{19}F in the arable soil are presented in Table 1. The results for the isotopic concentrations of Mg are given in the Table 2. Since PIGE technique is a multi-elemental analytical technique, a number of strong gamma ray lines at different energies in the spectrum of each sample were observed. We were not interested in all the energy lines observed; we were interested specially in 197, 440 and 585 keV lines. In the PIGE experiments, each element has the possibility of undergoing several nuclear reactions. But only the reactions with highest yields were considered.

It was observed that Mg is present in 14 samples which were collected from Norshindi and its concentration is found to be relatively high. The concentration of Na in these samples is lower than that of the Mg. And the concentration of F has the lowest value among the three elements detected (Table 1).

From the Table 1 it was also observed that Mg has not been found at all in the other 19 samples which were collected from Sylhet and Chittagong. The concentration of Na in these samples is found to be higher than that of the F. Proton beam of higher energy (> 2.5 MeV) might have produced higher yields in gamma peaks.

PIGE reaction may occur with all the isotopes of a particular element present in the sample. In the case of Mg, the relative abundances of the three isotopes are 79%, 10% and 11% .The concentrations of ^{19}F, ^{23}Na, ^{24}Mg, ^{25}Mg and ^{26}Mg have been calculated using the certified values for them obtained from the IAEA-standard soil-7 (Table 2).

The measured Mg content of the 14 soil samples collected from Norshindi lies in the range of 9868- 57186 ppm whereas the optimum Mg content for soil is 6000 ppm. In all the 14 samples the Mg content is found to be higher than the required optimum value and the soil therefore seems to be slightly toxic in Mg. The concentration for ^{24}Mg has been found to be in the range of 7798-45177 ppm, for ^{25}Mg 987-5719 ppm and for ^{26}Mg 1086-6290 ppm (Table-2). The MDL for ^{24}Mg has been found to be in 1087 ppm, for ^{25}Mg 138 ppm and for ^{26}Mg 151 ppm. In the other 19 samples no Mg is found. Blood serum contains 2 to 3% of Mg and in the erythrocytes slightly more. On a dry basis bone contains about 1.5% $Mg_3(PO_4)_2$. Soft tissues contain three to five times as much Mg as Ca. Rat muscle, for instance, has 29.6 mg of Mg and 5.7 mg of Ca per 100 g of wet tissue (Tufts and Greenberg., 1938)

The primitive effects of Na salts lie with osmotic adjustment, with the likelihood that there is direct or indirect activation of unidentified enzymes of C4 and CAM metabolism (Carkson *et al.,* 1980). The Na content of the 14 soil samples collected from Norshindi lies in the range of 84 - 41789 ppm whereas the optimum Na content for the soil is 6300 ppm. Some of the soil samples in this region appear to be toxic in Na and are not suitable for animals and plants. The MDL for Na has been found to be less than 1 ppm. The Na content of the other 19 soil samples collected from Sylhet and Chittagong lies in the range of 2538-34603 ppm. Some of these soil samples appear to be toxic in Na. The MDL for Na has been found to be less than 1 ppm.

The F content of the 14 soil samples collected from Norshindi lies in the range of 30 – 6224 ppm whereas the standard content in the soil is 480 ppm. Some of the soil samples in this region appear to be toxic in F and are not suitable for animals and plants. The MDL for F has been found to be less than 1 ppm. The F content of the other 19 soil samples collected from Sylhet and Chittagong lies in the range of 1213-6593 ppm. These soil samples also appear to be toxic in F. The MDL for F has been found to be 31 ppm (Table 1). Fluorine has attracted much attention in recent years because of the apparent role it plays health in human. Fluoride ions are readily absorbed by plants, especially from the more acid types of soils, but in any appreciable concentration they are highly toxic concentrations as low as 10 PPM of fluorine in solution cultures is found to be toxic to several species of plants.

Large fluctuations in errors in the measured values of concentrations of the elements were observed (Table 1). There may be several reasons for these fluctuations.

All the present experiments were done at fixed proton energy of 2.5 MeV, which was perhaps not high enough for exciting all the elements present in the samples. Proton beam of higher energy (>2.5 MeV) might be required to excite all the elements and isotopes present in the target samples. Moreover, if the intensity of the emitted gamma-line is weak then the experiments have to be done over

a long period of time to obtain statistically significant number of counts in the gamma peaks. For very weak peaks the time required for accumulation of statistically significant counts might at times become prohibitively long and expensive.

Proper selection of peak areas can reduce the corresponding errors. Sharper the peaks in the spectrum the better would be the selection. The errors are relatively high in the case of fluorine measurements, because in most cases the peak of γ- ray lines of energies 110 & 197 keV near the Compton edge was not sufficiently sharp. Proton beam of higher energy or larger time for an experiment might have been able to overcome this difficulty.

Errors may also arise due to fluctuations in high voltage power supply, inability of the preamplifier to extract properly the weak current signal from the detector, inadequate analyzing power of MCA for which an energy peak may be shifted from its proper position and become broaden.

Table 1: Experimental results for elemental concentrations

Sample No.	F			Na			Mg		
	Conc. in ppm	MDL	% error	Conc. in ppm	MDL	% error	Conc. in ppm	MDL	% error
Soil-1	4598	33	1.36	29825	29	0.39	41196	2240	10.56
Soil-2	6224	37	1.15	39740	32	0.34	41196	2240	10.56
Soil-3	5342	36	1.28	41789	31	0.33	49128	2396	8.53
Soil-4	5621	36	1.27	38348	32	0.34	56045	2576	7.75
Soil-5	5074	35	1.41	39639	31	0.34	52108	2430	8.65
Soil-6	5306	34	1.41	40050	29	0.34	57186	2274	7.95
Soil-7	4882	64	2.48	37080	55	0.62	46182	4339	14.05
Soil-8	4889	43	1.85	35823	37	0.44	55172	2937	8.68
Soil-9	3710	34	1.68	19532	32	0.5	29934	2648	14.97
Soil-10	3183	44	2.75	17709	43	0.68	17133	BDL	28.45
Soil-11	5198	57	2.13	25835	55	0.62	49873	4373	14.04
Soil-12	5185	68	2.14	26603	62	0.66	48751	5298	15.56
Soil-13	5762	52	1.5	21084	48	0.62	47703	3796	11.62
Soil-14	30	0.5	2.61	84	0.2	0.7	9868	1376	17.63
Soil-15	1916	91	6.65	12937	84	1.64	BDL	BDL	BDL
Soil-16	1213	53	6.56	2538	52	3.85	BDL	BDL	BDL
Soil-17	1669	66	6.36	4108	65	2.98	BDL	BDL	BDL
Soil-18	4760	109	3.86	29141	97	1.05	BDL	BDL	BDL
Soil-19	4780	87	3.11	29186	78	0.84	BDL	BDL	BDL
Soil-20	4448	113	4.14	34603	100	0.97	BDL	BDL	BDL
Soil-21	6564	65	1.89	28665	62	0.63	BDL	BDL	BDL
Soil-22	6593	56	1.61	28650	53	0.54	BDL	BDL	BDL
Soil-23	1751	61	5.82	7639	59	1.86	BDL	BDL	BDL
Soil-24	3371	45	2.69	4024	44	2.24	BDL	BDL	BDL
Soil-25	3449	35	1.98	3995	34	1.8	BDL	BDL	BDL
Soil-26	3450	31	1.61	4024	30	1.56	BDL	BDL	BDL
Soil-27	2292	63	4.43	7289	60	2.09	BDL	BDL	BDL
Soil-28	2202	46	3.84	10451	44	1.11	BDL	BDL	BDL
Soil-29	2083	41	3.76	2932	43	2.5	BDL	BDL	BDL
Soil-30	1649	57	5.22	14513	55	1.01	BDL	BDL	BDL
Soil-31	1651	45	4.16	14464	44	0.81	BDL	BDL	BDL
Soil-32	1912	62	4.28	28103	59	0.65	BDL	BDL	BDL
Soil-33	3192	122	5	12755	117	1.98	BDL	BDL	BDL

MDL: Minimum Detection Limit, BDL: Below Detection Limit

Table 2: Isotopic Concentration of Magnesium

Sample No.	Conc.of ^{24}Mg in ppm	Conc.of ^{25}Mg in ppm	Conc.of ^{26}Mg in ppm	Total Conc of Mg in ppm
Soil-1	32545	4120	4532	41196
Soil-2	32545	4120	4532	41196
Soil-3	38811	4913	5404	49128
Soil-4	44275	5604	6165	56045
Soil-5	41165	5211	5732	52108
Soil-6	45177	5719	6290	57186
Soil-7	36484	4618	5080	46182
Soil-8	43586	5517	6069	55172
Soil-9	23648	2993	3293	29934
Soil-11	39400	4987	5486	49873
Soil-12	38513	4875	5363	48751
Soil-13	37685	4770	5247	47703
Soil-14	7796	987	1086	9868

CONCLUSION

The proton induced nuclear reaction based analytical technique is more suitable for analyzing light elements like lithium(Li), boron(B), fluorine(F), magnesium(Mg), scandium(Sc), chlorine(Cl), phosphorus(P), and sodium(Na), which are often difficult to determine by other analytical techniques. Multielemental proton induced nuclear reaction based analytical technique (PIGE) is very suitable for the measurement of light elements. The results of concentration measurements of Mg, Na and F on arable soil samples using PIGE technique though reliable is not however comprehensive enough to draw any definite conclusion about the toxicity or deficiency of these elements. Comprehensive elemental analysis of the soil of these regions should be carried out so that maps of these regions can be constructed showing their concentrations.

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