PIGE Elemental Analysis of Arable Soil

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Abstract
The elemental concentration of arable soil samples collected from different areas of Savar were measured by proton induced gamma emission (PIGE) analytical technique. The samples were irradiated by the proton beam obtained from the 3MV Van de Graaff accelerator at the AECD (Atomic Energy Centre, Dhaka). The characteristic gamma emitted from the exited nuclei of the irradiated samples were detected by a HPGe spectrometer system. The following elements were detected Na, B, Mg, Sc, Li, Cl, F, and P and their concentrations were obtained by comparing the PIGE gamma yields with that of the standards such as USGS geological standards, AGV-1 and Soil-7. Finally the results of the experiments were discussed in the light of elemental deficiencies or the toxicities in the arable soil of Savar and the likely impact they may have on the growth and yield of specific vegetables grown in the area.

Key Words: PIGE, trace element and arable soil.

Introduction
To ensure sound health and quality of life, elemental analysis of foodstuffs and environmental pollutants and identification of pollution sources are essential. Such studies will help us to understand the environmental pollution and determine the quality of food we consume and their effects on human health. In recent years the study of elements, both major and traces in the environmental samples, foodstuffs and other related samples have become an important field of research.

Earth’s crustal rocks are made up of many substances that we use and that are essential for our health and even for our survival in this planet. Weathering rocks produce soil and cultivation of soil provides most of our foods. Elements with atomic number Z ≤ 15 correspond to about 95% of the total elements in the earth crust [1]. Most of the industrially and commercially important materials are made of light elements. Bulk (>90%) of the constituents of biological materials are also light elements. 26 of the naturally occurring elements are essential for life and eleven of which; namely, C, H, O, N, S, Ca, P, K, Na, Cl, and Mg are low Z elements. Among the 15 recognized trace elements, F and Si are low Z elements. Another low Z

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element is B, which is essential for higher plants. The important micronutrients in the soils such as F, B, Li, etc. play a vital role in our life.

The same element can be both essential and toxic depending on its concentrations. The knowledge of elemental contents of soil, water, foods, vegetables, fruits, drinks, etc. are important, because these are the primary sources of minerals for all living beings and many diseases are caused in men and animals due to mineral deficiency. All elements can become toxic if ingested or inhaled at a sufficiently high level and for a long enough period [2, 3].

The depletion of nutrients and its effects on the productivity of soil is a major concern in the world today. The elements like N, Zn, P and B play a vital role in the fertility of soil and thus in its productivity. To ensure the yield and the food value of the crops the presence or absence of proper nutrients in the soil needs to be ascertained [4]. With the intensification of agriculture, Zn deficiency in the soil has already become a problem in Bangladesh [5] and this could happen for other trace elements as well.

Proton induced Gamma-ray Emission (PIGE) methodology developed at the Van de Graff Accelerator Laboratory of AECD for the analysis of light elements in environmental samples has been used in this study. PIGE analysis is based on the detection of prompt gamma rays emitted from the excited nuclei following the charged particle irradiation of the samples. The energies of the gamma rays identify the elements in a sample and their measured intensities give the amounts in which they are present. PIGE is a rapid, nondestructive technique, which in principle could be used for simultaneous analysis of many elements. PIGE is more suitable for the analysis of the light elements like Li, B and F, which are often difficult to determine by chemical or other ion beam analytical techniques [5-7].

**Theoretical and Analytical Background**

The concentration of an element in a sample can be obtained from the PIGE yield using the known yield from a standard. There are many multi-elemental standards available for the analysis of environmental, biological, medical and geological samples. Synthetic standard samples can also be used for materials’ analysis [8]. A typical PIGE gamma ray spectrum from geological standard soil –7 is shown in Figure 1.
The concentration of an element or its isotope $C_s$ can be calculated from its gamma ray yield $Y_s$ at a certain energy using the yield $Y_{st}$ of a standard from the formula

$$C_s = C_{st} \frac{S_s Y_s}{S_{st} Y_{st}}$$

The stopping powers $S_s$ and $S_{st}$ for the sample and the standard respectively can be obtained from the Stopping and Ranges software package SRIM: version 1997 developed by Ziegler and Biersack or else can be obtained from the literature [8]. The yields are obtained from the relation:

$$Y = \frac{NQh^2 \varepsilon}{2k2m_pE_p} g \Gamma_r$$

where $\varepsilon$ is the efficiency of the detector at a particular energy, $k$ is the loss of energy, $m_p$ is the mass of the proton, and $E_p$ is the proton energy in the lab system.
Procedure

a) Sample preparation

The arable soils were collected from different locations of Savar and labeled. Then the samples were dried in an oven at a temperature of 60°C for about 10 hours. After cooling the samples to the room temperature in a dessicator, the weights were taken. The dried weighted samples were then grinded in a grinder and made into pellets with a pellet maker. These pellets were used as the targets for irradiation with proton beam.

b) Instrumentation

The experimental set up for the PIGE analytical technique comprises of a proton beam of 2.0-2.5 MeV energy from the horizontal type 3 MeV Van de Graaff accelerator, a target chamber with a sample holders and a gamma-ray detection system.

Figure 2  Schematic diagram of the data acquisition setup used in the PIGE analysis

The γ-ray detection and processing system consisted of a Princeton γ-tech HPGe detector having a resolution of 1.75 keV at 1332 keV energy, a preamplifier, a main amplifier, a Multi-channel Analyzer (MCA) in the pulse height analysis (PHA) mode and an IBM compatible 486 computer. A schematic diagram of the data acquisition setup used in the PIGE analysis is shown in Figure 2.
The proton beam current was maintained at 10-15 nA and each target was irradiated for a fixed charges of 100 μC. The count rate was kept below 2000 cps to avoid the occurrence of sum peaks in the spectrum.

![Figure 3 A typical spectrum of the external PIGE from Soil-4 target at the energy 2.9 MeV](image)

c) Data analysis

The analytical information about the presence and the concentrations of the elements in a sample are contained in the peaks of their characteristic γ-ray spectra. A typical spectrum of the external PIGE from Soil-4 target at the energy 2.9 MeV is shown in Figure 3. The contributions to the background come from the natural radiation, beam induced radiation such as the gamma-ray from the elements present in the experimental setup and the target chamber. The trapping of γ-rays in the detector and charge collection losses contribute to the low energy tailing of the peaks.

A computer code obtained from APTEC was used for unfolding of the γ-ray spectra.

Results and Discussion

a) Calibration of the HPGe Detector

For energy calibration sources like $^{60}$Co, $^{137}$Cs, $^{22}$Na were used. The resolution (FWHM) of the detector at 1332 KeV was found to be 1.75 keV.
b) Measurement of Efficiency of the HPGe detector

The efficiency of a detector is a function of the active volume and shape (geometry) of the detector crystal, the source-detector geometry, and the interactions of the $\gamma$-ray with the materials of the detector.

The relative efficiencies curve for the detector in the energy range of 186 - 2448 keV was obtained with a $^{226}$Ra source. It was placed at a distance of 25 cm along the detector axis. The measurement was done for 2 hours to ensure the accumulation of statistically significant number of counts in the peak. The areas under the peak were extracted using standard procedure. The intensities were normalized at the 609.23 keV line, which is the most intense line in the $^{226}$Ra spectrum. The intensities of the gamma lines were taken from the literature [9] and the relative efficiencies were obtained by dividing the normalized quantities by these intensities. 10 soil samples were analyzed and the concentration of the elements Li, Na, F, Cl, B, Mg, Sc, and P were measured and are given in Table 1.

Table 1 Measured concentration of trace elements in soil sample

<table>
<thead>
<tr>
<th>Name of the Element</th>
<th>Average Concentration (ppm)</th>
<th>Minimum detection limit (ppm)</th>
<th>St.deviation (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorine(F)</td>
<td>793.77</td>
<td>22.13</td>
<td>478.44</td>
</tr>
<tr>
<td>Chlorine(Cl)</td>
<td>99.02</td>
<td>-</td>
<td>57.74</td>
</tr>
<tr>
<td>Sodium(Na)</td>
<td>4990</td>
<td>40</td>
<td>3950</td>
</tr>
<tr>
<td>Magnesium(Mg)</td>
<td>9700</td>
<td>360</td>
<td>4900</td>
</tr>
<tr>
<td>Scandium(Sc)</td>
<td>8.72</td>
<td>1.24</td>
<td>5.12</td>
</tr>
<tr>
<td>Boron(B)</td>
<td>75.54</td>
<td>18.99</td>
<td>41.22</td>
</tr>
<tr>
<td>Lithium(Li)</td>
<td>74.13</td>
<td>1.22</td>
<td>37.12</td>
</tr>
<tr>
<td>Phosphorus(P)</td>
<td>709.19</td>
<td>161.88</td>
<td>578.88</td>
</tr>
</tbody>
</table>

The minimum detection limit, which is a measure of the sensitivity, was also measured.

Discussion

Some of the measured elements are essential for both animals and plants, for example B is essential for the yield of some crops like cotton, potato, beans, etc. The properties and significance of the light elements measured in the present experiments are discussed below.
Phosphorous
Large proportion of P present, ranging from 0.2 to 0.8% of the total dry substance in the plants, are found in the fruits and seeds. P is abundant in the meristematic regions of actively growing plants. Large quantities of P are taken up by the plants during the maturation of seeds. The increased demand for P during the flowering time is met by applying phosphate fertilizer to the soil near the base of the plant.

The optimum requirement of P in soil is 0.08% [2], and the measured mean value is 0.07%, which is close to the optimum value. The soil in Savar region is therefore suitable for plants such as banana.

Magnesium
Measured concentration of Mg lie in the range of 0.1-1.76 % with a mean of 0.97 %, the optimum being 0.6 % [2]. The MDL is 0.03 %. Mg is found in all the 10 samples analyzed and the soil in the region is slightly Mg toxic. There is an antagonism between Mg and Ca on the one hand and Mg and K on the other, which means that the increased absorption of one element may result in the diminished absorption of the other. Excess amount of Mg may prove toxic in solution, a condition that may be offset by the presence of sufficient quantities of Ca. The K-deficiency may be induced by heavy applications of Mg.

Sodium and Chlorine
Cl is present in plants as chloride. Nobbe and Siegetrt first suggested that Cl is essential for the growth of buckwheat [4]. Although it remained controversial for many years, but the essentiality of Cl was however established by Maze for Maize, Lipman for various other plants, Eaton for cotton and tomatoes, and Raleigh for beets [10].

Stout et al. demonstrated that Cl is an essential micronutrient for cabbage, lettuce and tomato. Cl deficiency leads to chlorosis in leaves which is followed by necrosis and the growth becomes exceedingly restricted and the plants fail to set fruit.

The particular function of Na in plants is not clear. It however seems that Na can partly, not entirely, replace K as a nutrient. For example, the lowering of the quantity of dry matter produced in a crop due to K deficiency can be partially made up by adding a Na salt [11].
The Na concentrations in the soil samples studied lie in the range of 0.021 to 0.73 % with a mean of 0.49 %, the optimum being 0.63 % [2]. The MDL for Na is found to be 0.04 %.

The Cl content is found to lie in the range of 0.006 to 0.02 % with a mean of 0.01%, the optimum being 0.08 %. The MDL for Cl measured in the soil matrix is found to be 0.001%. The concentration of Cl in the soil of this region is very low and the plants that need Cl for growth do not grow well in this place, consequently the animals in the area may suffer from the diseases related to Cl deficiency.

**Fluorine**

Fluorine has attracted much attention in recent years because of its apparent role in human health. Fluoride ions are readily absorbed by plants, especially from the more acid types of soils, but it is highly toxic if present at a concentration as low as 10 ppm for several species of plants [8]. The F content measured in the present experiment lies in the range of 0.0063 to 0.14 % with a mean of 0.08 %, the optimum being 0.005 %. The MDL for F is found to be 0.0022 %. The concentration of F in the soil of this region is very high and the soil is highly F toxic.

**Boron**

The optimum concentration of B for apples lies between 10-20 ppm, while 30-44 ppm may be toxic with the Jonathan variety. Beans and corn are more sensitive to B toxicity than potato. Orange trees, irrigated with water rich in B, may contain as much as several ppm of B without being injurious to health [3].

A prominent feature of B deficiency is the death of the shoot tip. The leaves exhibit a thick coppery texture, becoming quite brittle and sometimes curling. The roots are stunted in growth and thickened in appearance. Flowering is prevented altogether and flowers fall without producing any seed. There is disintegration in the ground tissues and phloem, which is frequently preceded by their hypertrophy. The xylem is displaced and may be rendered non-functional.

The measured B content in the soil samples studied lie in the range of 0.004 to 0.014 % with a mean of 0.0076 %, the optimum concentration being 0.001 % [2]. B concentration found in the soil samples of Savar is high and toxic and therefore are not suitable for field-grown plants.
Lithium and Scandium
There is no convincing evidence that Li and Sc are essential for plants and animals.

The Li content measured in the soil samples studied lie in the range of 0.0073 to 0.013 % with a mean of 0.0074 %, there is no recommended optimum value. The MDL for Li is found to be 0.00012 %.

The Sc content measured in the soil samples studied lie in the range of 0.0001 to 0.0016 % with a mean of 0.0008 %, the optimum is not known. The MDL for Sc is found to be 0.00012 %.

Conclusion
The Proton induced nuclear reaction based analytical technique is simple and does not require any pretreatment of samples. It is a rapid, nondestructive technique that, in principle, could be used for analyzing any element. It is however more suitable for analyzing light elements that are often difficult to determine by other analytical techniques.

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References