Application of Proton Induced Nuclear Reaction to the Analysis of Fluorine in Water Samples

A. H. M. Saadat[1*], A. K. M. Fazlul Hoque[2] and M. D. Hossain[3]

[1]Department of Environmental Science, Jahangirnagar University, Savar, Dhaka 1342, Bangladesh
[2]Bangladesh Atomic Energy Centre, 4 Kazi Nazrul Islam Avenue, Dhaka 1000, Bangladesh
[3]Department of Physics, Jahangirnagar University, Savar, Dhaka 1342, Bangladesh

Abstract

Proton induced gamma emission (PIGE) analytical technique was used to measure the concentration of F in groundwater samples collected from different areas of Kalia thana under Narail district. Proton beam of energy 2.5 MeV obtained from the 3 MV Van de Graaff accelerator at the AECD (Atomic Energy Centre, Dhaka) was used for sample irradiation. 200 ml of water sample mixed with 1.0 gm of cellulose powder is evaporated, and the residue is made into standard pellets that are used as target for the proton beam. The characteristic gamma emitted from the exited nuclei of the irradiated samples was detected by a HPGe spectrometer system. Concentrations were obtained by comparing the PIGE gamma yields with that of the standards prepared in the same laboratory. The concentration ranged from 0.71-4.26 mg/L with the mean of 1.73 mg/L. The highest concentration of F is found at East Durgapur which is 4.26 mg/L and much above the WHO recommended maximum of 1.5 mg/L. The results of the experiments were discussed in the light of elemental deficiencies or the toxicities in the groundwater and the likely impact they may have on the health of the population at that area.

Introduction

The contamination of water supply and food with trace elements, arising from the geological bearing minerals, modern agriculture practices and industrial developments, may have, in the long run, deleterious effects on the health and welfare of human population of a country. This concern has stimulated increasing interest in the study of the trace elements related to the human health and their movement in the environment and to determine their maximum permissible intakes by human through the food chain and drinking water. Fluorine, one of the 15 generally accepted essential elements, has long been recognized as a constituent of bones, teeth, soft tissues and body fluids. Criteria of adequacy and tolerance present particular problems with fluorine. Fluorine confers improved resistance to dental carries and is also necessary in the maintenance of normal skeleton and in the reduction of osteoporosis in the mature adult population[1]. On the other hand, excess fluoride intake causes fluorosis, which is more common than fluorine deficiency. Therefore, fluorine is recognized as an essential trace element, but it becomes toxic if the intake is prolonged and is in excess[2].

In India estimated 62 million people are sick due to fluorosis of which 6 million are children bellow the age of 14 years. Excess of fluoride and associated health problems exist in 15 states out of the 32 states and Union Territories. Central Ground Water Authority (CGWA) of India has warned the people not to consume groundwater from shallow water bearing zones up to 30 meters in six blocks of the National Capital Territory of Delhi. Today 'Fluorine Free Drinking Water' is one of the most desired campaigns in many countries like India, Ireland, Chile, South Africa, etc.

To mitigate the fluoride problem different National and International agencies and NGOs such as WHO, UNICEF, FAO, USAID, Rajiv Gandi National Drinking Water Mission, Public Health Engineering Departments, All India Institute of Medical Sciences, Fluorosis Research and Rural Development Foundation, etc., have been working in different states of India[2,3].

The fluorine content in groundwater in India, especially in the States bordering Bangladesh may make us curious about the situation in Bangladesh. There is a distinct possibility to have fluorine-bearing minerals in the groundwater of Bangladesh. The geological structure of Bangladesh is very similar to India, and it is situated bellow the affected states of India. It is therefore likely that the groundwater in Bangladesh is affected by natural fluorine and this may adversely affect the health of the population[4].

In Bangladesh no significant study has been done yet in this regard. The people are unaware of the effects of fluorine. The fluorine content of the drinking water of Dhaka City supply has been reported using Zirconium-Alizarin spectrophotometric method more than a decade ago[4]. In a recent study on the water of different city supplies of Bangladesh the concentration of F is found to lie in the range 0.03-1.10 mg/L[2]. It has become essential to determine the fluorine intake of Bangladeshi population in order to assess the fluorine deficiency or its hazard. With this in view the present research program has been undertaken.

Proton induced Gamma-ray Emission (PIGE) methodology developed at the Van de Graaff Accelerator Laboratory of AECD for the analysis of fluorine in groundwater samples has been used in this study. PIGE is a nuclear reaction based process in which a change in the composition and/or in the energy of target nuclides is brought about by bombarding with a high-energy proton beam. If a sample is irradiated with protons of energy in MeV range, the low-lying states of sample nuclei are excited. These nuclei de-excite by emitting gamma-rays, which are characteristics of the particular nuclide and thus 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[4-9].

Theory

The concentration of an element in a sample can be obtained from the PIGE yield using the known yield from a standard. 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[10]. The yields are obtained from the relation:

$$Y = \frac{NQh^2\varepsilon}{2k2m_p E_p} g\Gamma_r$$

where ε 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.

Experimental

a) Instrumentation

The experimental setup 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.
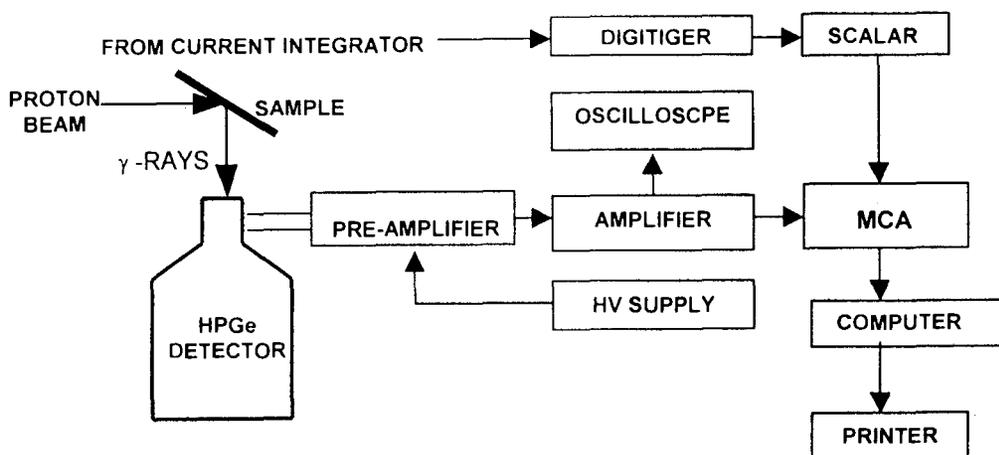

Figure: 1 Schematic diagram of the data acquisition setup.

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 pre-amplifier, 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 1.

The proton beam current was maintained at 10-15 nA and each target was irradiated for a fixed charges of 20 µC. The count rate was kept below 2000 cps to avoid the occurrence of sum peaks in the spectrum.

b) 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 S-3 sample target at the energy 2.9 MeV is shown in Figure 2. The contributions to the background come from the natural radiation, beam induced radiation
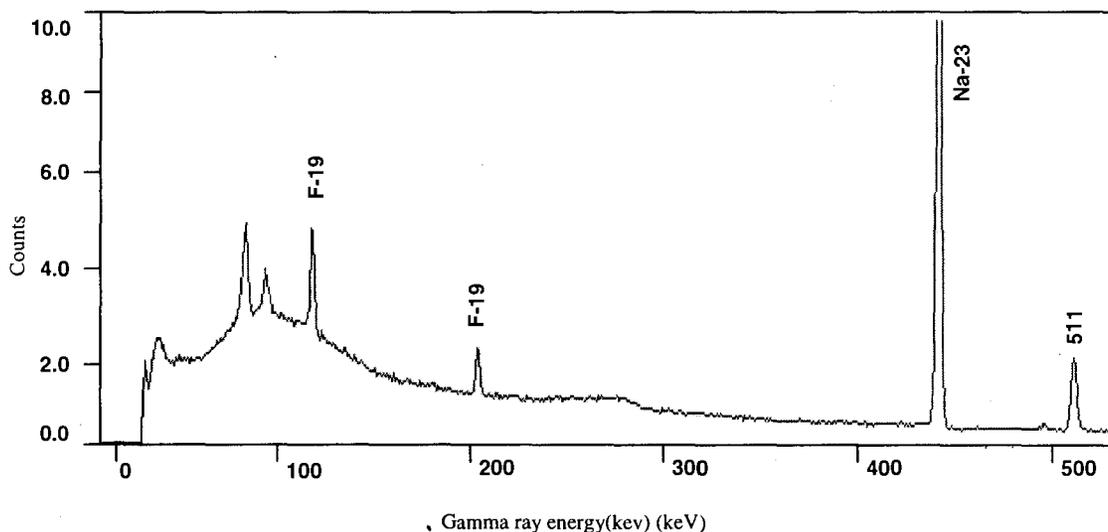

Figure 2 : A typical spectrum of the external PIGE from S-3 target at the energy 2.9 MeV

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.

c) 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.

d) 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 γ-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 reference[4] and the relative efficiencies were obtained by dividing the normalized quantities by these intensities.

e) Concentration Calibration

In order to determine the concentration of F in water samples the concentration calibration curve was obtained by using Analar grade NaF with concentration ranging from 10 to 1000 mg/L in a cellulose mixture.
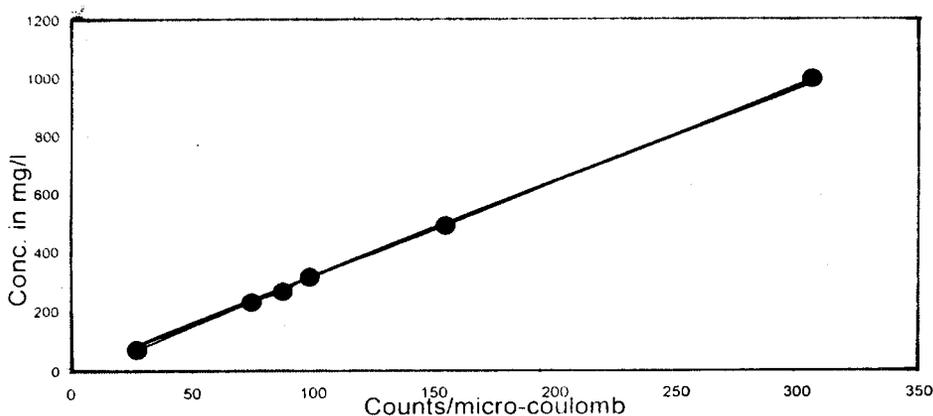

Figure 3: Calibration curve for the determination of F in water residue.

Results and Discussion

10 water samples were analyzed and the concentration of F was measured and are given in Table 1.

Table 1: Measured concentration of trace elements in soil sample

Name of the place	Sample no.	Concentration of F in ground water in mg/L	% error	MDL mg/L
Gobra(South), Narail	AW-1	1.87	10.96	
Gobra(North), Narail	AW-2	1.99	14.43	
Kharrial, Kalia, Narail	AW-3	0.78	12.86	
Kharrial, Kalia, Narail	AW-4	1.77	7.23	
West Uzirpur	AW-5	1.19	14.13	0.08
East Uzirpur	AW-6	1.63	8.86	
East Durgapur	AW-7	4.26	11.01	
West Durgapur	AW-8	1.85	7.59	
Tarapur, Kalia, Narail	AW-9	1.27	10.53	
Fultala Bazar, Khulna	AW-10	0.71	28.06	

The minimum detection limit, which is a measure of the sensitivity, was also measured.
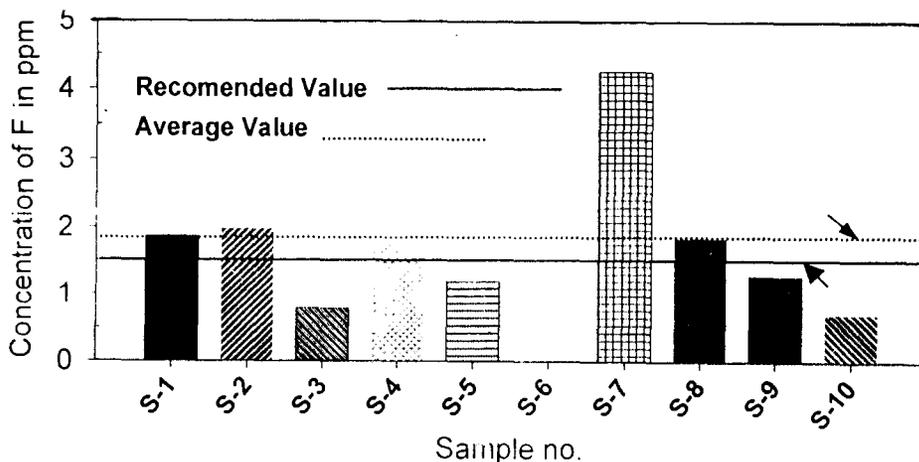
Figure: 5 F concentration in different samples

Fluorine has attracted serious attention in recent years because of the apparent role it plays in human health. Plants, especially from the acidic soils readily absorb fluoride ions, but it is highly toxic for several species of plants[11,12]. The F content measured in the present experiment lies in the range of 0.71 mg/L to 4.26 mg/L with a mean of 1.73 mg/L, the maximum recommended value for Bangladesh given by WHO being 1.5 mg/L[2]. The MDL for F is found to be 0.08 mg/L. From the present study it is found that 60% of the studied samples contain higher fluorine than the WHO recommended maximum. The highest concentration of fluorine is found in the groundwater of East Durgapur under Kalia, Narail, that is 4.26 mg/L.

The data obtained as regards F concentration from the present measurements can serve as a guide to ascertain the quality of drinking water in terms of F content. It can also be useful in detecting F hazard or deficiency that may exist in rural areas of Bangladesh. Further study is required to get detail data about the area having high concentration of F in groundwater. The data on F concentration in dental enamel may be used to determine F toxicity or deficiency in adult and milk teeth of Bangladeshi population.

Like PIGE, PIXE is elemental but it cannot distinguish between the isotopes of an element. PIGE being a nuclear reaction based technique can differentiate between the isotopes of a element. Another important advantage of PIGE is its wide range of sensitivity, that is, it can measure elemental concentration from several percentage level down to a level of few mg/L.

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.

Acknowledgement

References

[1]   J. Colquhoun, Is there a dental benefit from water fluoride?, *Fluoride,* **279(1),** 13-22 (1994).

[2]   A. K. M. Fazlul Hoque, M. Khaliquzzaman, M. D. Hossain and A. H. Khan, *Fluoride,* **35,** 1-9 (2002).

[3]   S. L. Choubisa, Fluorosis in some tribal villages of Udaipur district (Rajastan), *J. Env. Biol.,* **19,** 341-52 (1998).

[4]   A. K. M. Fazlul Hoque, [Ph. D. Thesis, Jahangirnagar University, Savar, Dhaka 1342, Bangladesh 2000].

[5]   A. H. M. Saadat, A. R. Molla, A. K. M. Fazlul Hoque and M. D. Hossain, *Jahangirnagar Univ. J. Sci.,* **25,** 215-223 (2002).

[6]   F. Yin, Y. Yao, C. C. Liu, M. L. Wen, Developments in the analysis of fluoride 1997-1999, *Fluoride,* **34(2),** 114-25 (2001).

[7]   C. Bertrand, *Proc. Int. Congr. Appl. Chem.,* **C 28,** 28 (1992).

[8]   A. Anttila, R. Hanninen and J. Raisanen, *Radioanal. Nucl. Chem.,* **62,** 293 (1981).

[9]   J. Raisannen, *Nucl. Instr. Methods,* **B40/41** 638 (1989).

[10] S. Abachi and S. Lôkös , *Nucl. Instr. and Meth. in Phy. Sec. A,* **338,** 185 (1994).

[11] E. V. McCollum, E. Orent-Keiles and H. G. Day, *The Knowledge of Nutrition* (The Macmillan, Co. New York), p 463.

[12] W. E. C. Wacker, B. L. Valle, *Mineral Metabolism,* **Vol. II,** Part A (Academic Press, New York), p 483, 1964.