Proton Induced Gamma Emission Method with the 3 mv van de Graaff Accelerator

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Abstract

Proton induced gamma emission (PIGE) method has been developed at the Accelerator Laboratory of Atomic Energy Centre, Dhaka (AECD) for analyzing low Z elements in the range of 3 to 15. With a view to exploiting the potential of PIGE technique as a tool for practical applications, attempts have been made to find the experimental evidence for its capability and scope. Gamma ray yields from PIGE experiments and the sensitivity for some low Z elements such as lithium, fluorine, boron, sodium, magnesium, silicon, beryllium and oxygen have been measured at proton energy 2.9 MeV in order to assess its capability and to identify its limits. The PIGE method has also been utilized for isotopic speciation of different isotopes of magnesium present in local vegetables to assess its suitability for the analysis of isotopes of different elements present in samples of interest. Present study demonstrates the characteristics of the PIGE method that establish it as a reliable and useful technique capable of rendering analytical services especially in the health and environmental sectors.

Keywords: Analytical method, gamma ray yield, isotopic speciation, MDL, proton induced gamma emission

1. Introduction

Because of better understanding and awareness of pollutants in the environment, it has now become a priority to analyze the materials of practical importance for their elemental constituents. Consequently, there has been a great surge of developing a sensitive analytical method to analyze water, foodstuffs, and vegetables, soil, etc. for both toxic and essential elements, especially at trace level. Accurate determination of concentrations of light elements such as, lithium, boron, fluorine, etc. in water, foodstuffs, vegetables, and other substances when present in trace quantities by chemical methods are difficult and less accurate [1-2]. Proton Induced X-ray Emission (PIXE) has been applied extensively in the laboratory for the analysis of environmental and health related samples, but it is limited to the analysis of heavy elements only [3-5]. Moreover PIXE being elemental, it cannot be used to distinguish between the isotopes of same element. Proton-induced Gamma Emission (PIGE) is however a reliable analytical tool for the analysis of light elements like lithium, boron, fluorine, sodium, magnesium, phosphorus, etc. in environmental and health related samples [6-10].

PIGE is a nuclear reaction based analytical method which is suitable for non-destructive analysis of low mass elements. PIGE analysis is based on the detection of prompt gamma rays emitted from the excited nuclei following the nuclear reactions (p, γ), (p, p$'$ γ), (p, α γ), and (p, n γ) induced by protons [6-7]. The energy of the gamma ray indicates the identity of the isotope and its intensity gives a measure of the concentration of the isotope present in the sample. PIGE method has the advantage of being isotopic in nature with virtually no interference; its sensitivity is high, and it is multielemental. PIGE was developed using proton beam from the 3 MV Van de Graaff Accelerator at AECD [8-10]. Gamma ray yields from PIGE reactions and the sensitivities for some low Z elements were measured to assess its power, limits and scope as an analytical technique. Isotopic speciation of some low Z elements was also done to this end.

2. Materials and Method

Sampling and Sample preparation

For the measurements of the thick target gamma ray yields from PIGE reactions and the PIGE sensitivities for the low Z elements, lithium, boron, fluorine, sodium, oxygen and magnesium the targets were made from chemical compounds MgO (powder), $Mg(PO_4)_2$, NaF_2, LiF_2 and $C_{24}H_{20}BNa$ (Sodium tetraphenyl boron) by pressing them into 10 mm diameter pellets at 3 tons pressure using a Perkin-Elmer pellet maker. Elemental targets of Be-foil were used for beryllium and Si-wafer targets were used for silicon.

In order to demonstrate the capability of PIGE for isotopic analysis, measurements of isotopes of magnesium in locally available vegetables samples were made. Different types of locally available vegetable samples were collected from the kitchen market of Dhaka city for the measurements of isotopes of magnesium in the samples. The list of the vegetables analyzed along with their scientific names is given in Table 1. The samples were sliced into pieces and then freeze-dried. The samples were then finely powdered. After weighing a portion of the powder material, it was pressed into 10 mm diameter pellets with a graduated hydraulic press of 3 tons pressure.

Table 1. List of the vegetables analyzed for isotopes of magnesium.

Sl. No.	Name	Scientific name	Family name
1	Carrot	*Daucas carota*	Umbelliferae
2	Red leaves	*Amaranthus tricolor*	Amaranthaceae
3	Cabbage	*Brassica oleracea*	Cruciferae
4	Spinach	*Beta palonga*	Chenopodiaceae
5	Culiflower	*Brassica oleracea var*	Cruciferae
6	Potato	*Solanum tuberosum*	Solanaceae
7	Gourd	*Lagenaria vulgaris*	Cucurbitaceae
8	Reddish	*Raphanus sativus*	Cruciferae
9	Bean	*Lablab purpureus*	Leguminoceae
10	Brinjal	*Solanum melogena*	Solanaceae
11	Banana	*Musa sapientum*	Musaceae
12	Papya	*Carica papaya*	Caricaceae
13	Tomato	*Lycopersicon Lycopersicum*	Solanaceae
14	Khira	*Cucunis sativus*	Cucurbitaceae

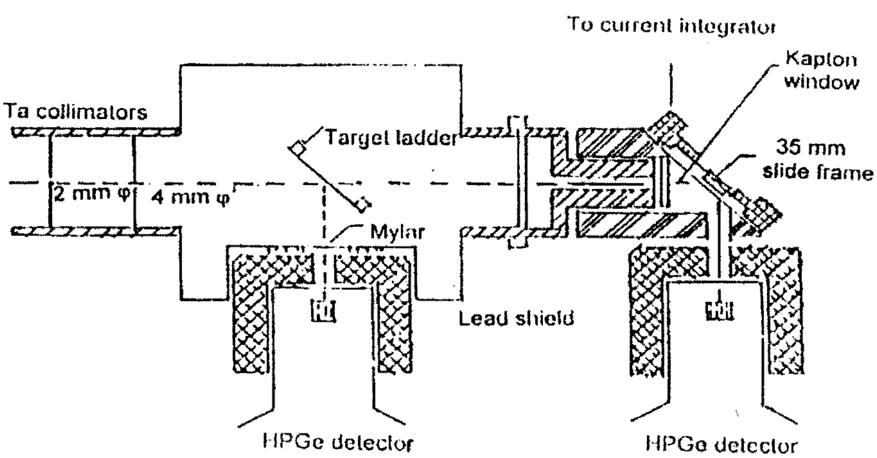

Fig. 1. Schematic diagram of the external/internal beam PIGE experimental setup.

Experiment

The experiment was performed with a proton beam of 2.9 MeV from the 3MV Van de Graaff Accelerator of the Atomic Energy Centre, Dhaka (AECD). The schematic diagram of both the external and internal beam PIGE setup is shown in Fig. 1. Two tantalum collimators of 2 mm diameter each and a 4 mm cleanup aperture, were used to define a finely collimated beam. For external beam measurements, kapton foils of 1.12 mg/cm^2 thickness were used to extract the proton beams from the beam port into the air. The energy of the protons on the target was found to be about 2.3 MeV due to losing energy in the Kapton foil and air between the exit window and the sample. To obtain the total proton charges incident on the sample, the current on the target and the Kapton window was monitored and for this the window frame was insulated from beam port and collimator. The setup was designed to hold 35 mm slide frames for solid samples making an angle of 45° with the beam direction. For the internal beam experiment, the pelletized samples were mounted on a 20×25 mm aluminum target frame with a circular hole of 15 mm diameter at the centre. The vacuum in the target chamber was maintained at about 10^{-5} torr. The chamber itself formed the Faraday cup, which was insulated from the ground in order to measure the proton beam intensity. The γ-ray yields were detected at 90° with respect to the beam direction.

The γ-ray data collection and processing system consisted of a Princeton γ-tech HPGe detector having a FWHM (full width at half maximum) of 1.75 keV at 1332 keV energy, a preamplifier, a main amplifier, a Multichannel Analyzer (MCA) in the pulse height analysis (PHA) mode and an IBM compatible 486 computer. Data acquisition and analysis were done using a spectrum unfolding software from APTEC which provided the analysis of the net peak area including peak centroid, FWHM, background under the peak, range of the peak, and the uncertainties in the counts.

3. Results and Discussion

Measurements of PIGE yields

Thick target PIGE yield for low Z elements lithium, boron, fluorine, sodium, beryllium, silicon, oxygen and magnesium have been measured at proton energy of 2.9 MeV. A beam current of 5-20 nA was used and the count rate was kept below 2000 cps so that sum peaks do not occur.

Table 2. PIGE yield for some low Z elements at 2.9 MeV.

Element	Analyte line (keV)	Reaction	Measured yield at 2.9 MeV per μC. sr	Fitted yield at 2.9 MeV per μC. sr	Lit. [2, 6] yield at 2.4 MeV per μC.sr	Lit. [2, 6] yield at 3.1 MeV per μC. sr
^{7}Li	429	^{7}Li (p, n_1 γ) ^{7}Be	3.6 X 10^5	-	-	9.2 X 10^6
^{7}Li	478	^{7}Li (p, p_1 γ) ^{7}Li	5.1 X 10^6	4.6 X 10^7	2.6 X 10^7	5.6 X 10^7
^{19}F	110	^{19}F (p, p_1 γ) ^{19}F	2.1 X 10^6	4.4 X 10^6	3.5 X 10^5	7.2 X 10^6
[illegible]	197	^{19}F (p, p_2 γ) ^{19}F	4.6 X 10^6	1.2 X 10^7	2.9 X 10^6	2.0 X 10^7
^{10}B	429	^{10}B (p, α_1 γ) ^{7}Be	1.4 X 10^5	6.0 X 10^5	3.5 X 10^6	7.2 X 10^6
^{10}B	718	^{10}B (p, p_1 γ) ^{10}B	2.6 X 10^4	7.0 X 10^5	1.2 X 10^5	1.3 X 10^6
^{11}B	2125	^{11}B (p, p_1 γ) ^{11}B	3.5 X 10^4	-	-	4.8 X 10^6
^{23}Na	440	^{23}Na(p, p_1 γ)^{23}Na	2.9 X 10^6	7.7 X 10^6	3.4 X 10^6	9.6 X 10^6
^{24}Mg	1369	^{24}Mg(p, p_1 γ)^{24}Mg	6.7 X 10^5	4.6 X 10^5	1.5 X 10^5	9.3 X 10^5
^{25}Mg	390	^{25}Mg(p,$p_{2-1}$$\gamma$)^{25}Mg	8.7 X 10^4	3.6 X 10^4	2.4 X 10^4	6.2 X 10^4
^{25}Mg	585	^{25}Mg (p,p_1 γ)^{25}Mg	2.2 X 10^5	1.4 X 10^5	6.7 X 10^4	2.2 X 10^5
^{28}Si	1779	^{28}Si (p, p_1 γ) ^{28}Si	1.4 X 10^5	6.5 X 10^5	2.3 X 10^2	1.2 X 10^6
^{29}Si	1273	^{29}Si (p, p_1 γ) ^{29}Si	8.8 X 10^4	-	1.8 X 10^3	1.2 X 10^5
^{16}O	495	^{16}O (p, γ) ^{17}F	3.3 X 10^3	6.6 X 10^2	9.2 X 10^2	7.3 X 10^2
^{18}O	1983	^{18}O (p, p_1 γ)^{18}O	2.8 X 10^3	-	-	2.1 X 10^3
^{9}Be	415	^{9}Be (p, γ) ^{10}B	3.2 X 10^3	-	0.6 X 10^3	-
^{9}Be	718	^{9}Be (p, γ) ^{10}B	1.9 X 10^4	5.2 X 10^3	5.3 X 10^3	-

In thick targets the characteristic Doppler broadening was observed during the measurement of the 429 keV gamma ray from the nuclear reaction $^{10}B(p,\alpha\gamma)^7Be$. The FWHM of the corresponding peak was 8.5 keV and FWTM was 12.3 keV. For the selected low Z elements such as lithium, boron, fluorine, sodium, beryllium, silicon, oxygen and magnesium several characteristic gamma rays are observed. The intensities of the lines of lithium, boron, fluorine and sodium are the strongest ones and are readily observed even when present in small concentrations. Elements such as silicon and oxygen that give low intensities γ-rays are difficult to detect at trace quantities.

To obtain the absolute yield, corrections were made for absorption of gamma rays in the window of the chamber and detector and the air gap between the detector and the target chamber and also for the detector efficiencies at different gamma ray energies. The yields at 2.9 MeV protons for different elements have also been calculated from the third order polynomial fit of the experimental PIGE yields taken from the literature. The measured and calculated thick target yields of gamma rays per micro-coulomb per steradian along with the literature value for proton energies of 2.4 and 3.1 MeV are listed in Table 2.

Sensitivity of PIGE

The sensitivity or the minimum detection limit (MDL) depends on the detector geometry and efficiency and other experimental factors including the possible effects of interfering reactions and also on the background radiation. MDL is defined as [11-12], MDL $= 3\sqrt{N_b}/S$ where, N_b = No. of counts/μC in the background within an energy

Table 3. Minimum detection limits (MDL) of some low Z elements analysis for Internal and External PIGE for 50 μC charge at 2.9 MeV

Element	Reaction	Analyte line (keV)	MDL (μg/g)	
			Internal beam	External beam
^7Li	$^7Li\ (p, n_1\ \gamma)\ ^7Be$	429	18.42	8.33
^7Li	$^7Li\ (p, p_1\ \gamma)\ ^7Li$	478	23.2	0.56
^{19}F	$^{19}F\ (p, p_1\ \gamma)\ ^{19}F$	110	2.22	1.54
^{19}F	$^{19}F\ (p, p_2\ \gamma)\ ^{19}F$	197	1.12	0.93
^{10}B	$^{10}B\ (p, \alpha_1\ \gamma)\ ^7Be$	429	6.9	3.69
^{10}B	$^{10}B\ (p, p_1\ \gamma)\ ^{10}B$	718	21.72	22.51
^{11}B	$^{11}B\ (p, p_1\ \gamma)\ ^{11}B$	2125	34.99	-
^{23}Na	$^{23}Na(p,\ p_1\ \gamma)^{23}Na$	440	16.73	1.24
^{24}Mg	$^{24}Mg(p, p_1\ \gamma)^{24}Mg$	1369	452.37	865.56
^{25}Mg	$^{25}Mg(p,p_{2\text{-}1}\gamma)^{25}Mg$	390	739.01	740.92
	$^{25}Mg\ (p,p_1\ \gamma)^{25}Mg$	585	394.90	254.98
	$^{25}Mg\ (p,p_2\ \gamma)^{25}Mg$	975	765.07	820.69
^{26}Mg	$^{26}Mg\ (p, \gamma)^{27}Al$	844	54.34	99
	$^{26}Mg\ (p, \gamma)^{27}Al$	1014	21.06	36.42
	$^{26}Mg\ (p,p_1\ \gamma)^{26}Mg$	1809	2997.39	-
^{28}Si	$^{28}Si\ (p, p_1\ \gamma)\ ^{28}Si$	1779	3370.27	18056.29
^{29}Si	$^{29}Si\ (p, p_1\ \gamma)\ ^{29}Si$	1273	471.12	2637.91
^{30}Si	$^{30}Si\ (p, \gamma)^{31}P$	1266		5230.35
^{16}O	$^{16}O\ (p, \gamma)\ ^{17}F$	495	2217.82	6456.77
^{18}O	$^{18}O\ (p, p_1\ \gamma)^{18}O$	1983	84.18	108.68
^{31}P	$^{31}P\ (p, p_1\ \gamma)^{31}P$	1266	31870	30080
^9Be	$^9Be\ (p, \gamma)\ ^{10}B$	415	430470	90810
	$^9Be\ (p, \gamma)\ ^{10}B$	718	104920	20720

interval of two FWHM around the gamma peak and S= Sensitivity of the element.

The MDL for various elements/isotopes were measured for 50 μC of charges (Table-3). At this proton energy the highest sensitivity was obtained for the elements fluorine, boron, lithium, and sodium. It is now possible to measure low Z elements like lithium, fluorine, boron, sodium, magnesium, phosphorus, etc. in the environment related samples with a sensitivity at mg/kg level and the elements, like beryllium, oxygen, magnesium, silicon and phosphorus is at g/kg level.

Isotopic Analysis

In the case of a natural sample PIGE reaction may occur with all the isotopes of the element present in the sample and γ-rays may be produced from each reactions. This feature of PIGE is used to distinguish the different isotopes of a given element and it also allows the quantitative analysis of them. To demonstrate the capability of PIGE for isotopic analysis, measurements of isotopes of magnesium in locally available vegetables samples were made. Experiments were done using internal beam PIGE at 2.9 MeV and each target was irradiated for a preset charge of 50 μC with a beam current of 20 nA. The calculation of the concentration of different isotopes of magnesium has been made using the relation [7]:

$$C_S = C_{St}\,(S_S\,Y_S/S_{St}\,Y_{St}) \quad .... \quad .... \quad (1)$$

where, Y_S and Yst are the gamma ray yields from the sample and standard, C_S and C_{St} are the concentrations and S_S and S_{St} are the stopping powers of the elements in the sample and standard respectively. The stopping powers have been calculated using Stopping and Ranges software package SRIM: version 1997 developed by Ziegler and Biersack [13]. The certified values of NBS SRM 1515 apple leaves, NBS SRM 1573 tomato leaves, NBS SRM 1570 spinach were used as standards for the PIGE measurements. The results are shown in Table - 4.

The measured MDL has been found to be 890 mg/kg, 950 mg/kg and 6353 mg/kg for $^{24,\,25,\,26}$Mg, respectively. The natural abundance of isotopes of $^{24,\,25,\,26}$Mg are 78.99, 10 and 11.01 percent respectively. The agreement between the measured values and that of the natural abundance lies within ±4% for ^{24}Mg and within ±14% for $^{25,\,26}$Mg. The measured ratio of the isotopes of Mg clearly demonstrates the capability of PIGE technique for isotopic speciation of the low Z elements present in natural samples.

Table 4. Concentration of the Isotopes of Magnesium in vegetables obtained from PIGE experiments

Sl. No.	Name of Vegetables	^{24}Mg (%)	^{25}Mg (%)	^{26}Mg (%)	Mg (%)
1	Carrot	0.58	0.063	0.069	0.71
2	Red leaves	0.59	0.081	0.089	0.76
3	Cabbage	0.55	0.058	0.064	0.67
4	Spinach	0.5	0.068	0.075	0.64
5	Culiflower	0.39	0.044	0.046	0.48
6	Potato	0.58	-	-	0.58
7	Gourd	0.6	0.065	0.072	0.74
8	Reddish	0.63	0.067	0.074	0.77
9	Bean	0.65	0.068	0.075	0.79
10	Brinjal	0.56	-	-	0.56
11	Banana	0.57	-	-	0.57
12	Papya	0.59	0.066	0.074	0.73
13	Tomato	0.49	-		0.49
14	Khira	0.63	0.068	0.082	0.78

4. Conclusion

PIGE methodology was developed at the Accelerator laboratory of AECD using proton beam from the 3 MV Van de Graaff Accelerator. The characteristics studied in this work demonstrate that the PIGE method is a useful analytical technique that has the capability of analyzing low Z elements like lithium, beryllium, boron, oxygen, fluorine, sodium, magnesium, silicon and phosphorus in different matrices and to obtain the information about the chemical composition of specimens of different origin such as health, environment, agriculture, etc. The quantification capability of PIGE technique for lithium, boron, fluorine and sodium is at a level of mg/kg while for other elements, like beryllium, oxygen, magnesium, silicon and phosphorus is at level of g/kg. The isotopic speciation studies of low Z elements such as boron, oxygen, magnesium and silicon with PIGE method would depend on their abundance in the sample matrix.

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References

1. R. E. Shroy, H. W. Kraner, K. W. Jones, J. S. Jacobson and L. I. Heller, Nucl. Instr. Methods, **149,** 313 (1978).
2. J. R. Bird and J. S. Williams (eds.), Ion Beams for Materials Analysis, Academic Press, Sydney, Australia, (1989).
3. A. H. Khan, M. Khaliquzzaman, M. B. Zaman, M. Hussain, M. Abdullah and S. Akhter, J. Radioanal. Chem., **57,** 157 (1980).
4. M. Hussain, M. Khaliquzzaman, M. Abdullah, I. Ahmed and A. H. Khan, Int. J. Appl. Radiat. Isot., **31**, 527 (1980)
5. M. Khaliquzzaman, M. B. Zaman and A. H. Khan, Nucl. Instr. Methods, **181**, 209 (1981).
6. J. R. Tesmer and M. Nastasi (eds.), Handbook of Modern Ion Beam Materials Analysis, Materials Research Society, Pittsburgh, Pennsylvania, (1995).
7. G. Deconninck, Introduction to Radioanalytical Physics, Elsevier, Amsterdam, (1978).
8. A. K. M. Fazlul Hoque, Analytical Application of Charged Particle Induced Nuclear Reactions for Low Mass Elemental Analysis, PhD Dissertation, Physics Department, Jahangirnagar University, (2000).
9. A. K. M. Fazlul Hoque, M. Khaliquzzaman, M. D. Hossain and A. H. Khan, Fluoride, **35(3),** 1 (2002).
10. A. K. M. Fazlul Hoque, M. Khaliquzzaman, M. D. Hossain and A. H. Khan, Fluoride, **36(1),** 38 (2002).
11. L. A. Currie, Anal. Chem., **40**, 586 (1968).
12. K. Debertin and R.G. Helmer, Gamma- and X-Ray Spectrometry with semiconductor Detectors, North Holland, Amsterdam, (1988).
13. J. F. Ziegler and J. P. Biersack, SRIM: Stopping and Range of Ions and Matter: Version 1997; Stopping and Ranges of Ions in solid, Pergamon Press, New York, (1990).