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Abstract

The need for elemental analysis especially related to environment has increased in recent years to a great extent. The analytical need has created a worldwide spurt to develop rapid, sensitive and accurate methods for the determination of trace as well as major elements in various environmental related samples. Proton Induced X-ray Emission (PIXE) has been extensively applied for Air pollution related analysis and multi-element analysis of Environmental, Medical, Biological, Agricultural samples, etc. However this method has limitations in detecting elements with $Z<11$ using internal beam technique. The limits of detection of elements such as Na, Al and Si are rather poor because of the self-absorption corrections, which strongly depends on the sample matrix, experimental chamber window thickness and also detector window thickness. External beam method that is used extensively for environmental samples is practically limited to elements with $Z>18$ due to presence of Argon in air. Moreover, very light elements are not detectable at all in practice.

The Proton Induced Gamma Emission (PIGE) technique, based on the detection of gamma-rays following (p, γ), (p, p' γ) and (p, α) reactions leading to the emission of gamma-rays, offer a great potential for elemental analysis, especially for the light elements. To complement PIXE for the analysis of light elements, development of PIGE methodology has been in progress in the Van de Graaff laboratory for some years. Sensitivity of PIGE systems are installation dependent due to background signals which are different for different setups. Over the years the sensitivity of the developed methodology (PIGE) has improved considerably and has now reached a level that can be used for practical applications. In this report the current status of the PIGE setup capabilities have been discussed. Comparative assessments of the present and previous capabilities of the system have been made to illustrate the progress achieved. At present the Dhaka Van de Graaff laboratory has the capability for the analysis of light elements like F, Na, B, Mg, Si, etc. using the PIGE methodology.

Introduction

The possibility of a rapid and nondestructive analysis, providing accurate concentration values for as many elements as possible, is one of the most attractive objectives of ion beam analytical techniques (IBA)[1]. In principle PIXE can detect all elements with $Z > 11$, but for light elements such as Na, Al and Si, the accuracy is rather poor because of the self-absorption corrections, which strongly depends on the sample matrix and morphology. Moreover, very light elements in practice are not detectable at all. This is due to the low x-ray energy from these elements, which can not be detected efficiently by using commercially available detectors.

Among the IBA techniques, PIGE, based on the detection of gamma-rays following proton induced reactions leading to the emission of gamma-rays, offer a great potential for elemental analysis, especially of the light elements using low energy accelerators[2]. Since the energy of the γ-rays are higher PIGE measurement is not affected by self- absorption corrections and is thus much more suitable for the detection of low atomic number elements[3]. Proton induced Gamma Emission (PIGE) technique is also applicable to heavy element determination under certain circumstances. These methods may compete sometimes with PIXE for heavier elements too. Moreover, contrary to elemental character of PIXE, these methods may well be used to distinguish the different isotopes of a given element. The intensities of the lines characteristic of the nuclides are proportional to their concentrations in the bombarded material.

Simplicity, non-destructiveness, multi-elemental capability, rapidity of analysis and accuracy are the main features of the PIGE, which make it an attractive analytical tool. PIGE is very sensitive to the elements having low abundance in nature such as Li, B, and F, but insensitive to the dominating elements such as O, Si, and C. Because of the high sensitivity even for small amounts of material makes it very useful for examination of micro-samples such as in biopsies. There is no significant matrix effect when measurements were done using PIGE method. The method needs minimal preparation of specimen and solid, liquid or gaseous specimen may be used for analysis.

Considerable research is being conducted to ascertain what applications are well suited to the proton induced gamma emission (PIGE) technique. A good number of attempts are being made for elemental analysis of both major and trace elements in various specimens in the

field of biological and medical sciences[4-10], environmental science[10-15], materials science[10], geology[16-18], metallurgy[19-22], semiconductor technology[21], art and archaeology[22], etc. Considerable amounts of efforts are being given to develop the methodology and to utilize this ion beam technique for the analysis of light as well as heavier elements.

The quantitative knowledge of the reaction cross sections for the elemental analysis using PIGE technique is essential for the development of the methodology of PIGE. Reasonable systematic study on the relative thick-target yields of prompt gamma-rays have been reported for the elements Z=3 to 92[23]. The knowledge of the gamma-ray energies and intensities produced by the elements upon the bombardment of protons is necessary for solving possible interferences with other gamma-rays induced in light elements, for which the PIGE techniquc is sensitive. A number of attempts have been made to tabulate the thick target gamma-ray yields [23-26].

The main objectives of the present work is to implement and develop the PIGE methodologies, and to identify the capabilities and limits of the methods developed for the quantitative determination of elemental concentration of low atomic number elements (Z < 20) embedded in different matrices. The basic idea is to expand the application scopes of such nuclear analytical techniques in the laboratory. To achieve the above objective characterization of the High Purity Germanium (HPGe) detector, measurements on PIGE sensitivity of low Z elements and comparative assessments of minimmum detection limits (MDL) of previous and present work, etc. are attempted and reported.

Theory

The observed number of the characteristic gamma-rays at an energy produced from an element in the sample per unit of incident charge and per unit solid angle is directly proportional to the gamma-ray yield for pure material, the number of atoms present, the detector efficiency for the gamma-ray energy, the reaction cross section of the element and is inversely proportional to the stopping power of the matrix.

In general the number N_γ of gamma rays following a nuclear reaction in a homogeneous sample of thickness t i.e. the area of the γ-ray peak from an isotope in a mixture of elements (i.e. in a matrix) neglecting the beam energy straggling and resolution is given by[27]

$$N_\gamma = n_p n_0 \varepsilon \int_{\Delta E} \left[\sigma(E) / S_m(E) \right] dE \qquad (1)$$

where ,

n_p = the number of incident protons,

n_0 = the number density of target atoms,

ε = the detection efficiency including solid angle,

$\sigma(E)$ = the cross section as a function of energy

S_m = the stopping power of the matrix as a function of proton energy

Because the energy loss per unit distance travelled by the incident proton and the reaction yield both vary with the proton energy, a technique has been developed for evaluating the stopping power at the energy where the yield is half that for the incident proton energy and this appears to give reasonably accurate results[22,25,27]. As a rule of thumb Eq.(1) can be written

$$N_\gamma = N_{st} \cdot \frac{F_m}{F_{st}} \cdot \frac{S_{st}}{S_m} \qquad (2)$$

Here

N_{st}= No. of gamma rays obtained from a standard sample having weight fraction F_{St} .

F_{st}= Weight fraction in standard sample

F_m= Weight fraction in sample

S_m and S_{st} are stopping powers at an energy such as that for which γ-ray yield is half of that at E_P

Experiment

The experiment was performed using the beam of protons provided by the 3MeV Van de Graaff Accelerator of the Atomic Energy Centre, Dhaka. A schematic diagram of the internal/external beam PIGE experimental set up is shown in Fig.1. Two collimators of 2 mm diameter each and a 4 mm cleanup aperture, all made of tantalum are used to obtain finely collimated beam. Both the internal and external beam PIGE experiments are being done. In case of internal beam PIGE sample excitation and gamma-ray emission take place in the chamber vacuum. On the other hand sample excitation and gamma-ray emission takes place in a sample holder placed outside the chamber at an atmospheric pressure in case of external beam method. Kapton foils of 1.12 mg/cm^2 thickness are used to extract the proton beams from the beam port into the air.

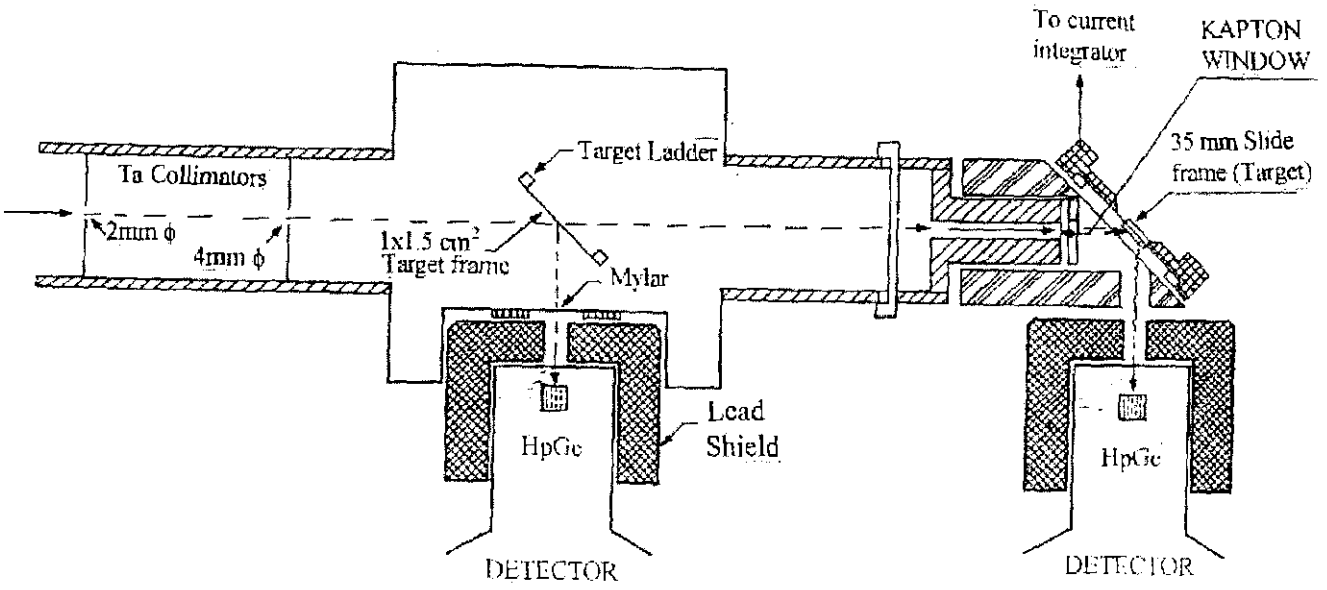

Fig. 1: Schematic diagram of the external/internal beam PIGE experimental system.

The Kapton windows of such thickness are found sufficiently strong to withstand about 400 μC of total charge collection at a beam current from 10-20 nA at 2.5-2.8 MeV protons on an area of ~7mm^2 without deteriotion of high vacuum in the beam port. With a reduced beam current (<10 nA), it is possible to increase the total charge collection without rupture of the Kapton foil. The beam spot is about 2 mm in diameter at the exit window.

To integrate the proton charge bombarding the sample, total current on the target and the Kapton window is monitored. The window frame is insulated from the beam port and the collimator. This arrangement is very reproducible for measurement of total charge on the targets[28].

The set up is designed to hold 35 mm slide frame for solid samples, at an angle of 45° relative to the beam direction and the characteristic γ-rays are detected at 90° with respect to the beam.

For internal beam experiment part of the sample were fixed on a 20X25 mm aluminium target frame with a circular hole of 15 mm diameter at the centre. The target frame is mounted on a target ladder, which can accommodate up to 10 samples at a time. The proton beam were bombarded the sample which is inclined at 45° with respect to the beam direction. The vacuum inside the target chamber was maintained of the order of 10^{-5} torr. The chamber itself forms a Faraday cup insulated from ground for the measurement of proton beam intensity.

The γ-ray data collection and processing system (for both external and internal beam experiments) consists of 47 mm diameter and 38 mm long Princeton Gamma-Tech (PGT) high purity Germanium (HPGe) detector having the resolution FWHM (full width at half maximum) of 1.75 keV and relative efficiency of 12.3% at 1332 keV, preamplifier, main amplifier, 4k channel Multichannel Analyzer (MCA) in pulse height analysis (PHA) mode and an IBM compatible 486 computer. Schematic diagram of the γ-ray detection and data acquisition system used for PIGE analysis is shown in Fig.2.

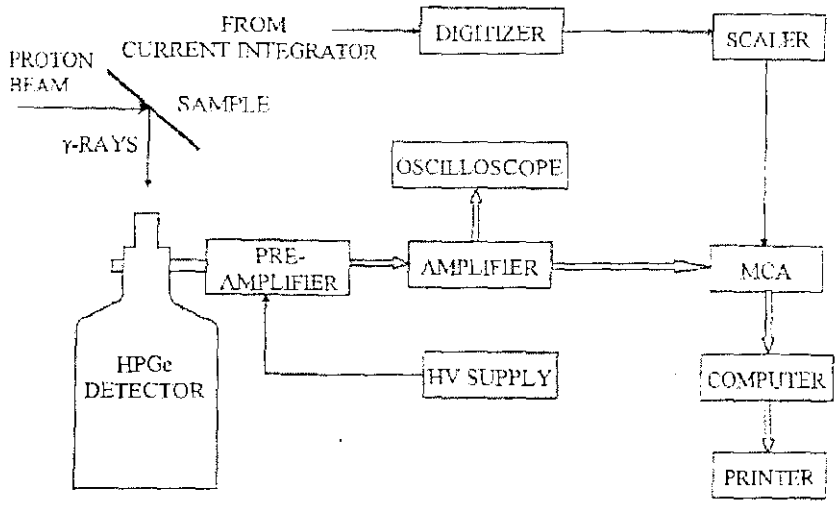

Fig.2: Schematic diagram of the PIGE data acquisition setup used for external/internal beam experiment

For the analysis of the samples the irradiation current is maintained in between 10-30 nA and each of the target is irradiated for a preset charge of 10 – 200 μC depending on the type of sample. The count rate is kept below 2000 cps in order to avoid the occurrence of sum peaks. Some typical PIGE spectra (both external and internal beam) obtained from different samples under the present experimental conditions is illustrated in Fig.3 and 4.

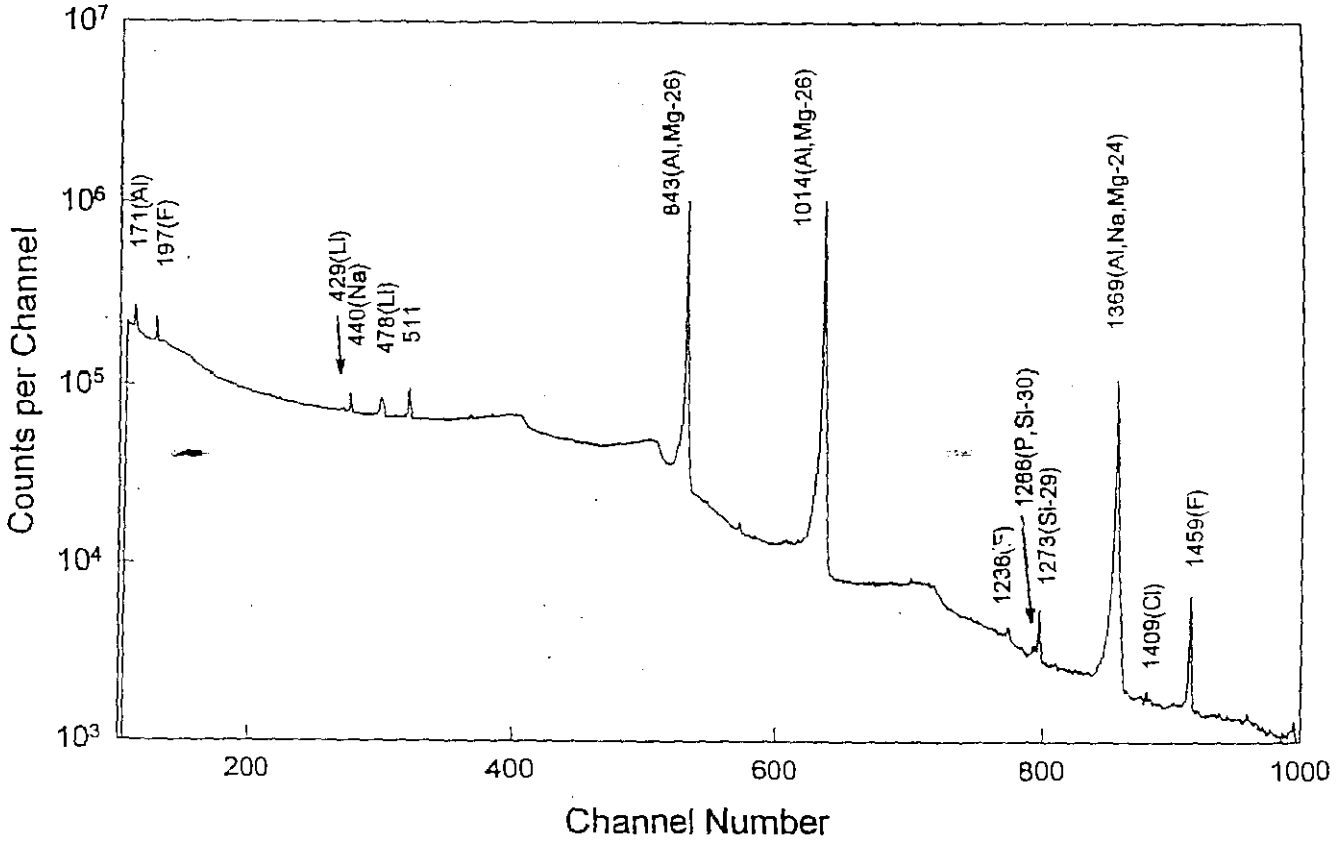

Fig.3: PIGE Spectra from IAEA Standard Soil-7

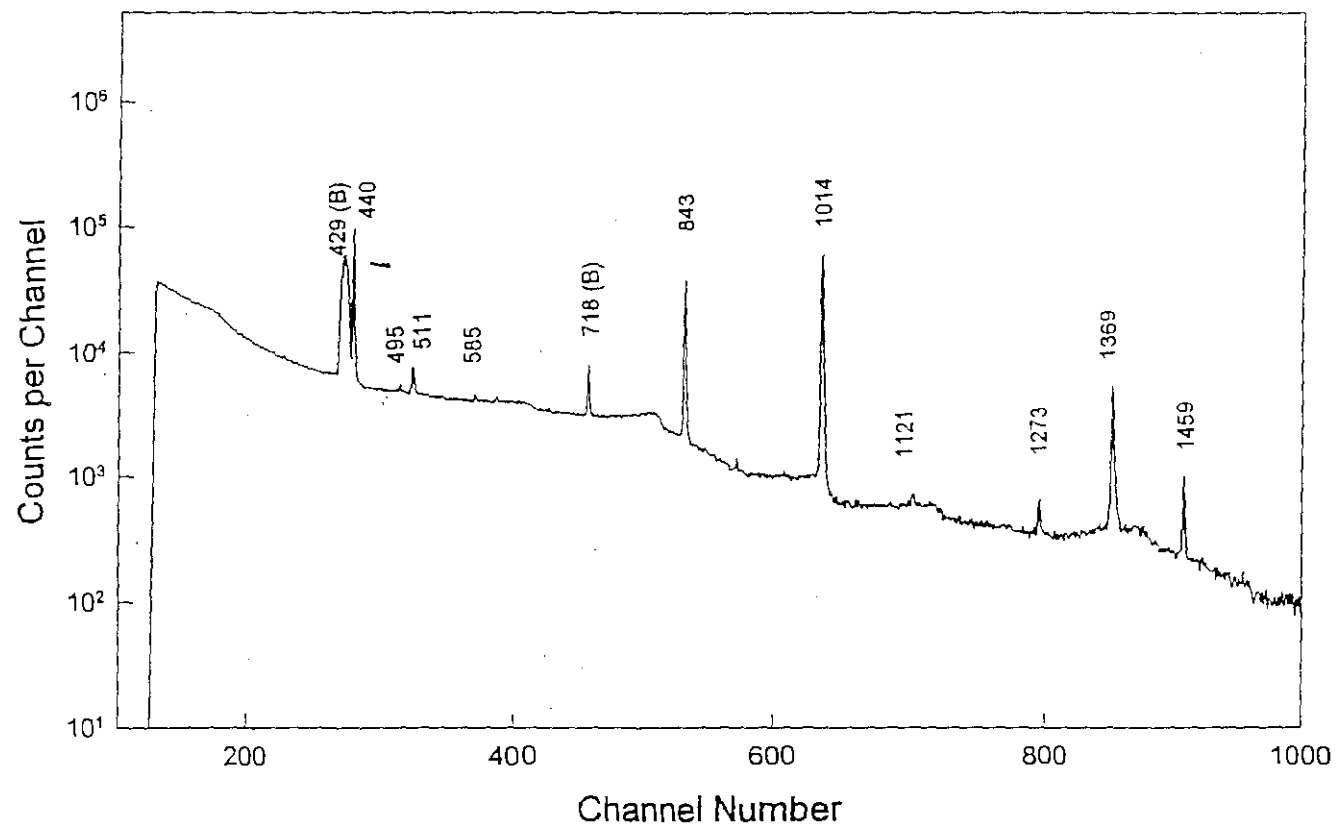

Fig.4: PIGE Spectra from Borosilicate glass

Data analysis

The analytical information on the presence and concentrations of each of the elements present in a sample is confined in the spectrum of characteristic γ-ray peaks. Data acquisition and data analysis is being done using a spectrum unfolding software from APTEC. For the determination of the photo peak energy and the area under the peak using the software, the steps are : (a) energy calibration of the spectrum, (b) identification of the peaks, (c) selection of the peak region, (d) calculation of the gross area, (e) background calculation, and (f) calculation of the net area. The γ-ray spectrum unfolding software provides an analysis report of the net peak intensities including peak centroid, FWHM, background under peak, range of the peak, and uncertainties of the different elements analyzed after performing the above functions. Then necessary corrections like γ-ray absorption corrections, efficiency corrections, etc. were done using the computer programs developed in the laboratory. These net peak intensities are then used to convert them into concentrations.

Results and Discussions

Study of the detector characteristics

The Main Work Horse of the present work is the High Purity Germanium (HpGe) detector. Performance of the HpGe detector is very important for elemental analysis using PIGE technique. The most important parameters characterizing a radiation detector are energy calibration, energy resolution and efficiency. So these characteristics of the HPGe detector have been thoroughly studied.

Energy Calibration

In PIGE the information detected on the energy of γ-rays and the number of photons being emitted from a sample is used to identify the elements presents in the sample and to determine its concentration. For energy measurements the pulse height scale must be calibrated with source emitting photons of known energies.

In the identification of the nuclides it is usually desirable that the energies be accurate to better than 0.1%. To meet this, it is adequate to represent the energy as a linear function of the channel,

$$E(x) = a_1 + a_2.x \qquad (3)$$

Where, x is the channel number and E is the energy. It is sufficient to determine the parameter a_1 and a_2 from only two well-chosen peaks. An improvement in the representation of the energies can often be achieved if several of the gamma-ray lines have known energies. Then a least squares fit, can be carried out to obtain the values of a_1 and a_2.

Energy Calibration was done using the sources ^{60}Co, ^{137}Cs, ^{22}Na . Ist order least square fitting was carried out for the determination of the relationship between the energy of the gamma ray and the channel number. Computational results shown in Fig.5(a) shows that the relationship between the energy of the gamma ray and the channel number is linear. The deviation from linearity is less than 0.1 keV [Fig.5(b)] which is the desired accuracy for the identification of elements.

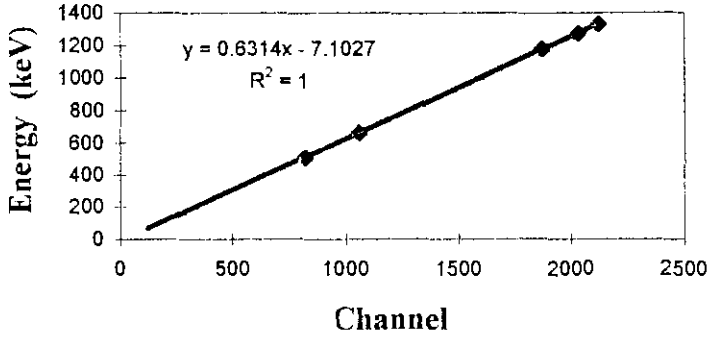

Fig. 5(a) : Energy calibration curve using least square fit.

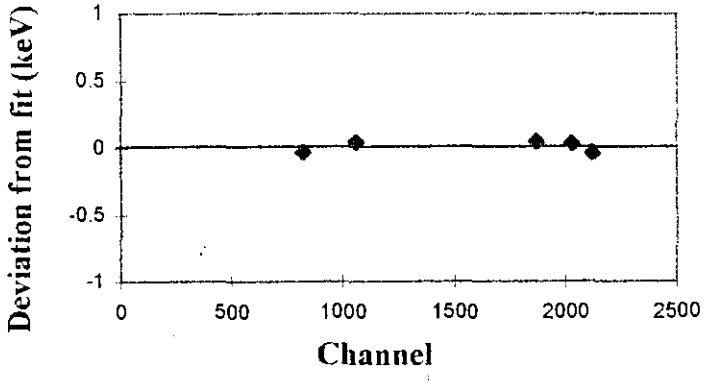

Fig.5(b) : Deviation of measrued gamma energy from fit.

Linearity check of the calibration (shown in Fig.6) has also been done by comparing the calculated and reference energies (from literature)[29] for gamma lines in the spectrum of Ra-226 source. Energy differences of less than 0.1 keV have been obtained in all cases which shows the quality of energy calibration in the energy range of 186 - 2448 keV.

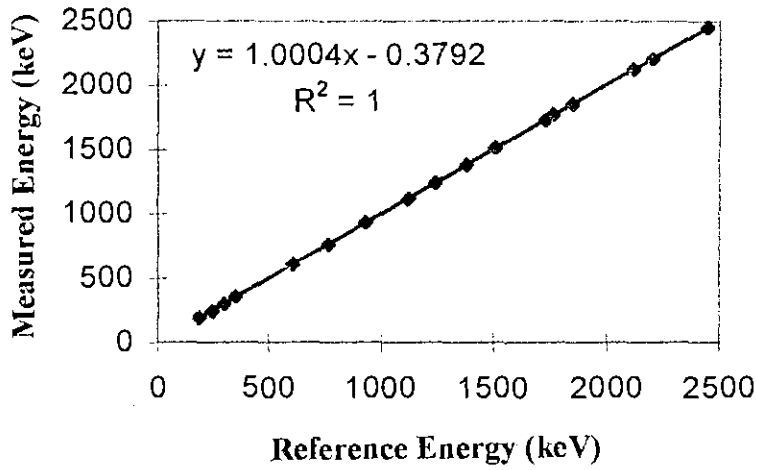

Fig.6 : Linearity of the energy calibration curve (Ra-226).

Resolution of the detector

The FWHM was determined with uncalibrated Co-60 sources at a arbitrary source-detector distance. FWHM at 1332 keV was found 1.9 keV whereas the manufacturer value was 1.8 keV. FWHM of different gamma lines from Ra-226 source were measured. Ist order least square fitting was done which is shown in Fig.7(a). The deviation of the measured FWHM from fit is less than 0.15 keV [Fig.7(b)].

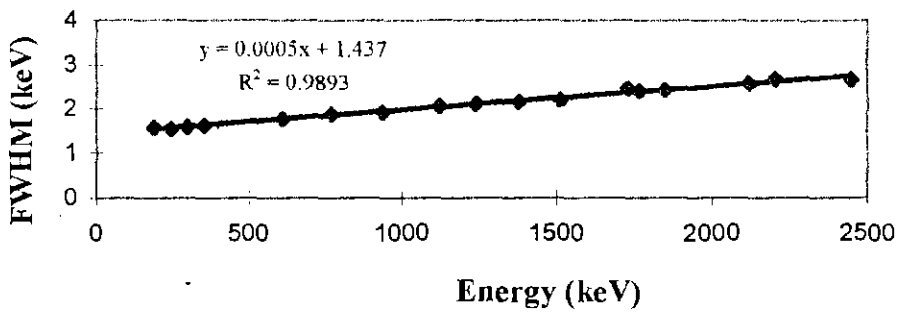

Fig.7(a) : Resolution as a function of energy.

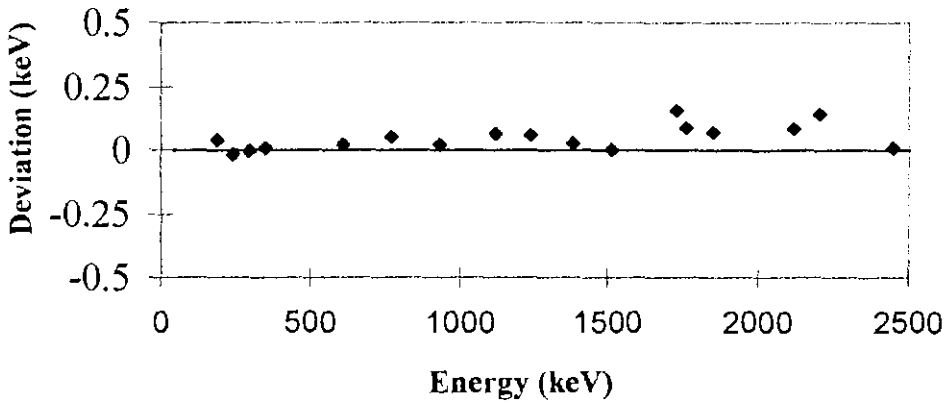

Fig.7(b) : Deviation of measured FWHM from fit.

Efficiency of the detector

The full-energy-peak efficiency depends on the photon energy in a complicated way. At low energies, where the photoelectric effect in the detector material dominates, the energy dependence may be calculated, or at least estimated, as the product of the probability that the photon reaches the detector and the probability that it is absorbed. At higher energies, multi-Compton and pair production events contribute to the full-energy peak. No analytical function which is based on the physical processes in the detector has been derived that can satisfactorily describe the full energy peak efficiency variation for energy above 100 keV. Above 200 keV the data can be approximated by[30]

$$\log \varepsilon = a_0 - a_1 \log(E/E_0) \quad \ldots \quad \ldots \quad (4)$$

where a_0 and a_1 are adjustable positive constants which can be obtained from a linear regression analysis of the set of ($\log \varepsilon_i$, $\log E_i/ E_0$) values. Vano et al.[31] derived the relationship

$$a_1 = 2.14 - 0.629 \log V \ldots \quad \ldots \quad (5)$$

where V is the detector volume in cm^3. This relationship is approximately valid for $V > 10\ cm^3$ and source-detector distances that are not too small [32-33].

But the experimental determination of the detector efficiency with calibration sources is usually easier and more accurate than calculations. The measurement of relative efficiencies of HpGe detector in the energy range of 186.0 - 2448 keV was done using a ^{226}Ra source. The source was placed at distance 25 cm along the detector axis. The counting was done for sufficient time (2 hours) to ensure reasonable statistics in the peak count. The areas were extracted

using standard procedure. The intensities were normalized for 609.23 keV line which is the most intense line in the spectrum. The relative intensities of gamma lines were obtained from literature[29]. The relative efficiencies were then obtained by dividing the normalized intensities by the relative intensities.

A measured efficiency-calibration curve was set up over the whole energy region for which the detector would be used. The plot of the experimental and calculated efficiencies are shown in Fig.8. The agreement between the calculated and measured curve obtained is very good .

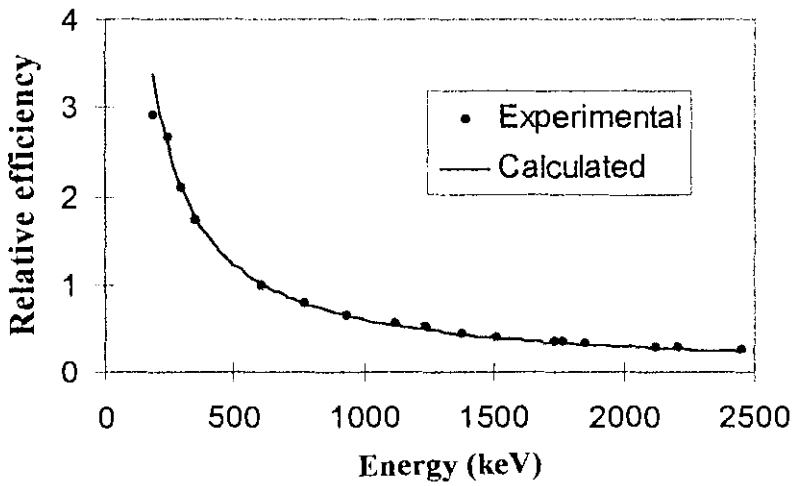

Fig.8 : Relative efficiency as a function of energy.

Sensitivity of PIGE

In case of PIGE proton induced all reactions that are energetically possible are likely to occur, but are subject to the prohibitively large reduction in cross section imposed by the Coulomb barrier. At incident proton energies of a few MeV, the Coulomb barrier inhibits the reaction rate, particularly for heavy element target. The transmission or penetrability coefficient is given by[34]

$$\rho = \exp[-\beta f(x)] \qquad (6)$$

where

$$\beta = \frac{4zZe^2}{h\nu} = 0.63zZ\left[\frac{M/M_P}{E(MeV)}\right]^{1/2}$$

$$f(x)=\left[\cos^{-1}x^{1/2}-\sqrt{x(1-x)}\right]$$

$$x=E/\beta_c$$

$$\beta_c=zZe^2/4\pi\varepsilon_0 R_0$$

β_c = Peak of the Potential Barrier
v = velocity of the particle $(2E0/M)^{1/2}$

To estimate the dependence of possible γ-ray yields on the mass of the target element transmission or penetrability coefficient has been calculated as a function of Z-number for different proton energies and is shown in Fig.9. The nuclear radius has been taken as $R_o = 1.3\ A^{1/3}$ F, and the relationship between Z and A is that given by the line of most stable nuclei in the Chart of Nuclides. It is seen from Fig.9 that the Coulomb barrier penetration factor is substantially smaller than unity, even when the kinetic energy is a few MeV above the Coulomb barrier, which decreases with the increase of Z number. With the increase of the mass of the target elements the PIGE yield decreases substantially. So the detection sensitivities for heavy elements by proton bombardment are low. The technique is more applicable to the analysis of light elements.

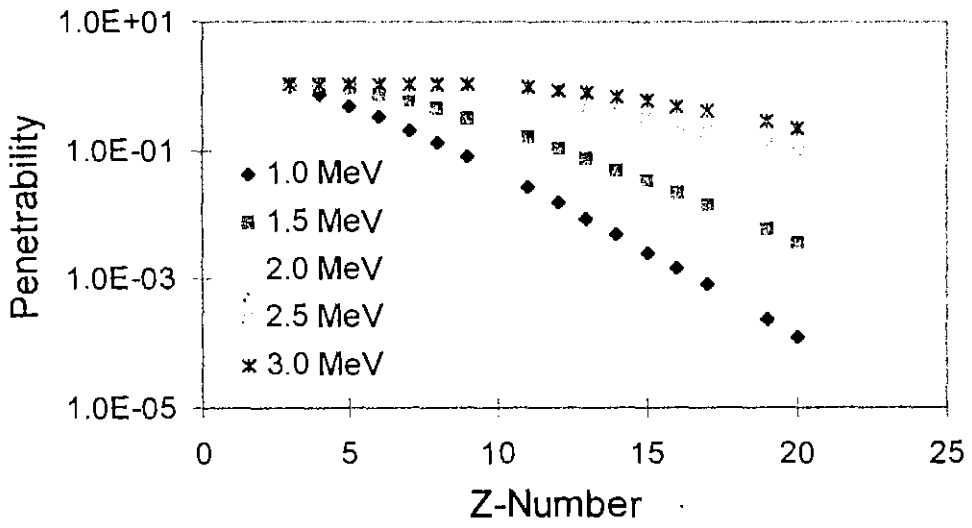

Fig.9: Penetrability as a function of Z-number for (p,p') reaction

The survey of the PIGE yield database also reveals the same. The PIGE sensitivity of some light elements are shown in Table-I on the light of the PIGE reaction cross section data available in the literature at proton energies of 2– 3 MeV[23-26].

Table-I

PIGE Sensitivity of elements at protons of 2.0-2.8 MeV

Isotope	Reaction	Analyte lines (keV)	*Yield at 2.4 MeV (X 10^6)	*Yield at 3.1 MeV (X 10^6)	Sensitivity	Remarks
^{7}Li	$^{7}Li(p,p'\gamma)^{7}Li$	478	26.00	56.00	<1 ppm	High cross section and interference free
^{19}F	$^{19}F(p,p'\gamma)^{19}F$	110 197	0.35 2.90	7.20 20.00		High cross section and interference free
^{23}Na	$^{23}Na(p,p'\gamma)^{23}Na$	440	3.40	9.60		High cross section and interference free
^{10}B	$^{10}B(p,p'\gamma)^{10}B$	429 718	3.50 0.12	7.20 1.30	<10 ppm	Interference with Li
^{24}Mg	$^{24}Mg(p,p'\gamma)^{24}Mg$	1369	0.15	0.93		High cross section, Al – interference
^{25}Mg	$^{25}Mg(p,p'\gamma)^{25}Mg$	390 585	0.02 0.07	0.06 0.22		Interference free
^{27}Al	$^{27}Al(p,p'\gamma)^{27}Al$	171 844 1014	0.01 0.15 0.33	- 2.30 4.60		Interference free Mg interference Mg interference
^{28}Si	$^{28}Si(p,p'\gamma)^{28}Si$	1779	0.0002	1.20	< 50 ppm	Al, P interference
^{31}P	$^{31}P(p,p'\gamma)^{31}P$	1266	0.038	1.60		Si Interference
^{41}K	$^{41}K(p,p'\gamma)^{41}K$	980	0.0005	0.01		Interference free
^{16}O	$^{16}O(p,p'\gamma)^{16}O$	495	0.0009	0.0007	< 1.5 %	Interference free
^{18}O	$^{18}O(p,p'\gamma)^{18}O$	1982	-	0.002		Interference free
^{32}S	$^{32}S(p,p'\gamma)^{32}S$	2230	-	0.005		Interference free

(* Yield for thick samples in protons/μC.Sr)

It is seen from the Table-I, that the most PIGE sensitive elements are Li, F, Na, B, Mg, and Al. The minimum detection limit for the elements Li, F and Na is less than 1 ppm whereas that of B, Mg and Al is less than 10 ppm. The elements Si, P and K can be measured with a

sensitivity of less than 50 ppm. Naturally highly abundant elements like O, N, and C are less PIGE sensitive.

The sensitivity of an element is expressed by the minimum detection limit (MDL) which is defined as

$$MDL = 3\sqrt{N_b}/S \qquad (7)$$

N_b = No. of counts / μC in the background within an energy interval of two FWHM around the gamma peak.

S =Yield measured as (No. of counts per μC) / (element mass per unit area.)

The MDL for some elements in soil matrix (IAEA standard soil-7) were calculated using the above expression at a proton energy of 2.5 MeV using the present set up is shown in Table-II.

Table-II

Minimum Detection Limits in PIGE analysis in soil matrix (IAEA standard soil-7)

at E_P = 2.5 MeV

Element	Analyte line (keV)	MDL
Li	478	0.7 μg/g
O	495	67 mg
F	197	70 μg/g
	1459	34 μg/g
	6129	62 μg/g
Na	440	88 μg/g
	1634	260 μg/g
Mg	585	2.9 mg
Al	844	0.32 mg
	1014	0.22 mg
	1369	0.69 mg
	1781	2.12 mg
Si	1273	39 mg

The preliminary results obtained were very encouraging. The measurements were done at a proton energy of 2.5 MeV and the detector was not shielded properly. The induced gamma rays produced by the chamber materials also contribute to the background signal. Moreover, projectile Bremsstrahlung produced in the Van de Graaff Accelerator itself contributes much to the background. In practical samples MDL decreases due to increased background from

the matrix. However, the Sensitivity of PIGE systems is installation dependent due to background signals that are different for different setups. Hence, the measured sensitivity during previous experiment were somewhat lower than expected.

Over the years the sensitivity of the developed PIGE methodology has improved considerably by manipulating experimental conditions and has reached a level which can be used for practical applications. In the present experiment, the detector is shielded with lead to minimize the background signal and irradiation is being done with elevated proton energy of 2.9 MeV using pure element/oxides. The MDL of various element/isotopes for 50 μC charge at proton energy of 2.9 MeV is shown in Table-III. For this proton energy the highest sensitivity were achieved using present experimental condition for the elements F, B, and Na. These elements could be measured with a measuring time of few minutes. Fluorine is of particular interest, with very high sensitivity, which is difficult to determine by non-ion beam techniques. At present it is possible to measure those elements for many practical applications especially in environmental related samples in the laboratory with a sensitivity of ppm level.

Table – III

Minimum Detection Limits in PIGE analysis at E_P = 2.9 MeV (Samples in the form of elements or oxides)

Element	Analyte line	MDL
F-19	110	9.21 ppm
	197	6.36 ppm
B-10	429	0.60 ppm
B-10	718	15.91 ppm
Na-23	440	16.73 ppm
	1634	8.02 ppm
Be-9	414	430.47 mg/g
	718	104.92 mg/g
Mg-24	1368.82	584.02 ppm
Mg-25	389.56	954.06 ppm
Mg-25	584.8	509.82 ppm
Mg-25	974.61	987.70 ppm
Mg-25	1612.47	1111.41 ppm
Mg-26	843.58	70.16 ppm
Mg-26	1014.28	27.18 ppm
Mg-26	1809.77	3869.62 ppm
O-16	495.28	31241.77 ppm
O-18	1983.08	108.68 ppm
Si-28	1779	3370.2 ppm
Si-29	1273	471.1 ppm

Conclusion

Proton Induced Gamma Emission (PIGE) methodology has been implemented in the Van de Graaff Accelerator laboratory with a view to measure the low Z elements to complement PIXE especially for the analysis of environment related samples. This study reveals that the PIGE methodology could be used as an analytical tool to measure light elements such as Li, F, B, Na in parts per million level. Isotopic analysis of some selected elements (Mg, O, and Si) may also be possible depending on their abundance in the sample. Research work is in progress on the measurements of light elements F and B in environmental related samples like water, soil, vegetables, etc. To demonstrate both prophylactic and toxicological effects related to human health analysis of human teeth has also been undertaken.

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References

1. C. Boni, A. Caridi, E. Cereda, G.M. Braga Marcazzan and P.Redaelli; "Simultaneous PIXE-PIGE analysis of thin and thick samples", Nucl.Instr.Methods, B49(1990)106-110.
2. J. Raisanen; "A rapid method for carbon and oxygen determination with external beam proton induced gammma-ray emission analysis", Nucl.Instr.Methods, B17(1986)344-348.
3. C.Boni, A.Caridi, E.Cereda and G.M.Braga Marcazzan; "PIXE-PIGE analysis of thin Fly-ash samples", Nucl. Instr. Methods, B45(1990)352-355.
4. S.O.Olabanji, M.C.Buoso, D.Ceccato A.M.I.Haque, R.Cherubini, G.Moschini, "PIGE-PIXE analysis of human milk", Nucl.Instr.Methods, B109/110(1996)258-261.
5. G.S.Hall and E.Navon; "Proton induced X-ray and gamma ray emission analysis of biological samples", Nucl.Instr.Methods, B15(1986)629-631.

6. M.Hyvonen-Dabek; "Proton induced prompt gamma-ray emission for determination of light elements in human bone", J.Radioanal. Chem. 63(1981)367-378.

7. G.R.Palmer, J.D.MacArthur and M.A.Singer;"PIXE and PIGE studies of ion diffusion through phospholipid bilayers containing cholesterol",Nucl.Instr.Methods, B45(1990) 337-340.

8. S.O.Olabanji, O. V. Makanju, A. M. I. Haque, M. C. Buoso, D. Ceccato, R. Cherubini, G. Moschini," PIGE-PIXE analysis of chewing sticks of pharmacological importance", Nucl.Instr.Methods, B113(1996)368-372.

9. H.E.Zschau, F.Plier, G.Otto, C. Wyrwich and A.Treide; "Fluorine profiling after application of various anti-caries gels", Nucl.Instr.Methods, B50(1990)74-76.

10. C.Boni, A.Caridi, E.Cereda and G.M.Braga Marcazzan; "A PIXE-PIGE setup for the analysis of thin samples", Nucl.Instr.Methods, B47(1990)133-142.

11. S.Fazinic, M.Jasic, L.Kukec, O.Valkovic, E.Cereda and V.Valkovic; "Light element analysis using PIXE and PIGE spectroscopy", Nucl. Instr. Methods, B68(1992)273-276.

12. J.Raisanen and R.Lapatto; "Analysis of sulphur with external beam proton induced gamma ray emission analysis", Nucl. Instr. Methods, B30 (1988) 90-93.

13. S.K.Biswas, Zs.Fulop, A.Z.Kiss, E.Koltay and E.Somorjai, "Application of PIGE Method for the determination of Sodium and Boron in aerosol samples", ATOMKI-Annual report, (Mar.1991)82-83.

14. L.Asking, E.Swietlicki and L.Grag; "PIGE analysis of sodium in thin aerosole samples", Nucl.Instr.Methods, B22(1987)368-371.

15. G.Robaye, J.M.Delbrouck-Habaru, I.Roelandts, G.Weber, L.Girard-Reydet, J.Morelli and J.P.Quisefit; "PIGE coupled with PIXE for sodium determination in atmospheric aerosol samples", Nucl.Instr.Methods, B6(1985)558-561.

16. Lars-Eric Carlsson; "Accuracy and precision in thick target PIXE-PIGE analysis determined with geological standards", Nucl.Instr.Methods, B3(1984)206-210.

17. J.Vogt, C.Wirth, H.E.Zschau and G.Otto; "Elemental analysis of mineral grains by means of simultaneous use of PIXE, PIGE and proton backscattering", Nucl.Instr.Methods, B68(1992)285-288.

18. S.O.Olabanji, A.M.I.Haque, S.Zandolin, R.T.Ajayi, M.C.Buoso, D.Ceccato, R.Cherubini, D.Zafiropoulos, G.Moschini, "Applications of PIXE, PIGE, SEM and EDAX techniques to the study of geological samples", Nucl.Instr.Methods, B109/110(1996)262-265.

19. I.Borbely-Kiss, M.Jozsa, A.Z.Kiss, E.Koltay, B.Nyako, E.Somorjai, Gy.Szabo and S.Self el Nasr; "Determination of elemental constituents in high voltage insulatorborosilicate glasses under proton bombardment", J. Radioanal.Nucl.Chem., 92/2(1985)391-398.

20. P.Courel, P.Trocellier, M.Mosbah, N.Toulhoat, J.Gosset, P.Massiot and D.Piccot; "Nuclear reaction analysis and electron microanalysis of light elements in minerals and glasses", Nucl.Instr.Methods, B54(1991)429-432.

21. J.D.Robertson, J.B.Bares, N.J.Dudney and R.A.Zuhr; "Ion beam analysis of lithium-ion conduction amorphous electrolyte films", Nucl.Instr.Methods, B56/57(1991)722-725.

22. P.Duerden, J.R.Bird, M.D.Scott, E.Clayton, L.H.Russell and D.D.Cohen,"PIXE-PIGME studies of Artefacts", Nucl. Instr. Methods, 168(1980)447-452.

23. A.Anttila, R.Hanninen and J.Raisanen; "Proton-Induced thick target Gamma-ray yields for the elemental analysis of the Z = 3 - 9, 11 - 21 elements", J. Radioanal. Nucl. Chem., 62(1981)293-306.

24. J.Raisanen and R.Hanninen; "Heavy element (Z>30) thick target gamma-ray yields induced by 1.7 and 2.4 MeV protons", Nucl. Instr. Methods, 205(1983)259-268.