Journal of Radioanalytical and Nuclear Chemistry (2020) 325:923–931
https://doi.org/10.1007/s10967-020-07266-7

# Development of an external (in air) in situ current normalized particle induced gamma-ray emission method utilizing 3.5 MeV proton beam from FOTIA for rapid quantification of low Z elements in glass and ceramic samples

**S. K. Samanta[1] · Sk Wasim Raja[1,2] · V. Sharma[1] · Priya S. Girkar[1] · R. Acharya[1,2] · P. K. Pujari[1,2]**

Received: 5 March 2020 / Published online: 6 July 2020


**Abstract**
An external particle induced gamma-ray emission (in air) PIGE facility has been set up for the first time at FOTIA, BARC for rapid and non-destructive quantification of low Z elements. Proton beam of energy of 3.5 MeV was obtained on the target using a 25 µm Tantalum window and Ta collimator of 5 mm diameter. The in situ current normalized PIGE method was validated by quantifying low Z elements in a mixed synthetic standard and in two (certified / standard) reference materials namely USGS CRM G2 and NIST SRM 620. The external PIGE method was applied to lithium-based ceramics, boron carbide and soda-lime and borosilicate glass samples for quantification of low Z elements.

**Keywords** External PIGE · Tantalum window · Lithium based ceramics · Boron carbide ($B_4C$) · Soda-lime and borosilicate glasses · In situ current normalizer

## Introduction

Spectroscopic and wet-chemical analytical methods like atomic absorption spectroscopy (AAS), inductively coupled plasma optical emission spectroscopy (ICP-OES), ICP mass spectrometry (ICP-MS) and chromatographic techniques (IC and HPLC) are well known and often routinely used for chemical analysis of diverse matrix samples. Most of the techniques described here are capable of quantifying elements at low concentration levels but they are destructive in nature involving chemical dissolution and/or separation using strong or corrosive acids. Requirement of reagent blank correction and correction for matrix effect are some of the difficulties associated with the above-mentioned techniques. From the eco-friendly point of view as well as for preservation of cultural heritage and also forensic including nuclear forensic evidences, direct sample analysis without any dissolution/destruction has gained importance in the last few decades due to no reagent blank correction and non-destructive nature with no or minimal sample handling. Solid samples are analyzed by X-ray fluorescence (XRF), nuclear analytical techniques (NATs) namely neutron activation analysis (NAA) [1, 2], prompt gamma-ray NAA (PGNAA) [3], photon activation analysis (PAA) and charge particle activation analysis (CPAA) [4], laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) [5], laser induced breakdown spectrometry (LIBS) and ion beam analysis (IBA) techniques like particle induced X-ray/gamma-ray emission (PIXE/PIGE) [6–10]. NATs like NAA and PGNAA are isotope specific in nature having several advantages like simultaneous multielement determination, often non-destructive in nature, negligible matrix effect, high sensitivity and selectivity, and inherent precision and accuracy. NAA using reactor neutrons is capable to determine medium and high Z elements whereas PIGE is a suitable technique for quantifying low Z elements starting from Li to S utilizing low energy proton beams (2–5 MeV) [7–10]. PIGE using proton beam involves online measurement of prompt gamma-rays from isotopes of elements through inelastic scattering (p, p'γ) or nuclear reactions such as (p, γ), (p, nγ) and (p, αγ). Quantifying low Z elements with high

✉ R. Acharya
racharya@barc.gov.in; racharyabarc@gmail.com

[1] Radiochemistry Division, Bhabha Atomic Research Centre, Mumbai 400085, India

[2] DAE, Homi Bhabha National Institute, Anushaktinagar, Mumbai 400094, India

sensitivity makes PIGE complementary to energy dispersive XRF, PIXE and NAA. PIGE using conventional vacuum chamber experiment demands high vacuum ($> 10^{-6}$ torr), sample in pellet form as well as definite geometry in order to fix it on the sample ladder. If external IBA/PIGE is used, PIGE method becomes rapid thus reducing the turnaround time of analysis as well as it overcomes the above-mentioned sample preparation and irradiation limitations of conventional PIGE using vacuum chamber. In the external beam, ion beam is taken to air through a window and a collimator and used for the PIGE and PIXE experiments. Thus it allows analyzing samples of any size and shape including large size samples even with no sample preparation at all.

IBA techniques with external (in air) proton beams are being used for last few decades with beam energies varying from 1.5 to 4.5 MeV [11]. Extraction of beams is carried out through commercially available 100–200 nm thick $Si_3N_4$ membranes having size between 10 $\mu m^2$–1 $mm^2$. The beam current for these systems is in the order of few nA. There are instances of calculations of external scattered beam dose rates as well as direct exposure dose rates by Doyle et al. [12] through radionuclide production in air using 3.1 MeV $^3He^+$ and 4.5 MeV $H^+$ having beam current of 1 nA. The range in air for 4.5 MeV proton beams was estimated to be 30 cm. The straggling of beams, in air, accompanied by energy loss is the main reason for beam divergence at longer distance from the exit window. In order to avoid significant broadening of beams, 200 nm thick $Si_3N_4$ or diamond membranes are used as exit foils. The evaluation of radiation dose while performing ion beam analysis using external proton beams was carried out by setting up of external beam facility at University of Gottingen [13]. The beam is either extracted into air or into a Helium atmosphere (balloon gas). External Faraday cup was installed for measuring beam current. The samples for PIXE measurements were kept at 5 mm distance from $Si_3N_4$ membrane with the X-ray detector aligned at 45° to the sample normal. The distance between the sample and detector window was 40 mm [13].

The combined PIXE/PIGE along with IBIL (Ion beam induced luminescence) utilizing external proton beams from IPNAS cyclotron at the University of Liege was applied for the analysis of Merovingian glass beads [14]. The beam of 3 nA was extracted through 100 nm thick silicon nitride ($Si_3N_4$) window having energy of 3 MeV [14]. The beam current was monitored by annular detector to measure the backscattered particles on the collimator placed before the exit window. The collimator was made up of brass and covered by thin layer of gold for backscattering proton beams. The AGLAE facility of the Louvre laboratory in France utilized a 2 MV tandem accelerator (Pelletron 6SDH-2) to extract 3 MeV protons of 20 μm in diameter to carry out PIXE, PIGE and RBS simultaneously using the same analyzed spot on the sample [15].Elemental imaging of rocks using the above facility had also been reported [16]. Information regarding proton induced γ-ray yields for light elements infers about the analytical sensitivity towards the detection of the elements. The γ-ray yields for low Z elements (F, Na and Al) in aerosol samples were measured as a function of proton beam energy using external proton beam facility at LABEC laboratory in Florence, Italy [17]. The beam was extracted in atmosphere through a 7.5 μm thick Upilex window, glued on a steel nozzle and the samples were placed 1 cm from the exit window [17]. For external PIXE setup the space between the X-ray detector and sample were saturated by helium gas to minimize the absorption of the emitted radiation. For PIGE, the HPGe detector was placed at 8 cm from the target at an angle of 125° with respect to the external proton beam. However, the set up was later upgraded using a better silicon drift detector (SDD) and more resistant $Si_3N_4$ window to obtain minimum detection limits in rapid measurement of aerosol samples [18, 19].

Non-destructive, non-invasive and multielemental nature of analysis are unique features for several IBA techniques. PIXE and PIGE methods are utilized for analytical applications in a wide range of fields including biomedical, environmental and material sciences. IBA along with elemental mappings/tomography are essential for analysis of archaeological artifacts [20] or cultural heritage samples [14, 15] exhibiting not only diverse elemental composition and structure but also surface and depth inhomogeneities. There is a requirement of a dedicated external proton beam set up for the qualitative as well as quantitative analysis of such kind of "as received" samples with enhanced sensitivity because it does not employ any restrictions upon size, shape, weight and conductive nature of the samples. In other words, external PIXE/PIGE set up in which beam is taken in air is more advantageous with respect to conventional PIXE/PIGE in vacuum towards rapid assay of nonstandard geometry samples without requirement of vacuum chamber where samples can be returned back in as received form from the user. A few representative paintings of contemporary Greek painters were analytically diagnosed using external IBA facilities at Demokritos tandem accelerator [21]. The beam was appropriately collimated from the exit point with $Si_3N_4$ window having ~ 1 mm in diameter at the beam exit point. Such a kind of arrangements was used by Yasuda et al. for simultaneous PIXE and PIGE measurements [22].

We have optimized conventional PIGE method using low energy proton beams (using a vacuum chamber) for quantification of low Z elements (like Li, B, F, Si and Al) in a variety of samples including glass, ceramics, alloys and sediments [23–26]. Due to low X-ray energy of Li and B, X-ray based techniques like PIXE, EDXRF or TXRF are not suitable. Li cannot be estimated by PGNAA or Conventional NAA due to unfavorable nuclear properties but Boron can be easily quantified by PGNAA due to its high neutron

absorption cross section. PIGE has good analytical sensitivities for estimation of Li and B along with other low Z elements. Measurement of beam current for current normalization in PIGE for concentration calculations is always a challenging task which has been overcome by the use of an in situ current normalizer (an element not present in sample) mixed in the sample [27]. The development of in situ current normalized PIGE does not require additional structural set up for measuring current thus making it simpler for analysis. RBS method or conducting sample in graphite is used for measuring beam current in external PIGE [18]. Direct beam current in external PIXE-PIGE is difficult to measure accurately due to ionization of air molecules along the beam path in atmosphere. So, beam current integration was carried out using Ar $K_\alpha$ X-ray line because the spectral line is very distinct with constant yield when Ar in air is bombarded by proton beam of same energy at a stable air pressure [28]. Another method of indirect charge measurement in external PIXE has been reported by J-O Lill where light emission from excited $N_2$ molecule in air was monitored [29].

In the present work, an external (in air) PIGE facility has been set up for the first time in FOTIA, BARC, Mumbai using thin tantalum foil as window material. In situ current normalized external PIGE method was standardized and validated by analyzing a synthetic multielement standard and two certified/standard reference materials from USGS (CRM G2, rock matrix) and NIST (SRM 620, soda lime flat glass) for low Z elements like Li, B, Na, Mg, Al, Si and Ti. The method was applied to three different matrix samples (glass and lithium and boron-based ceramics), which are difficult to be analyzed non-destructively by other analytical method. These samples were analyzed by the external (in air) PIGE by measuring prompt γ-rays of low Z elements with less turnaround time as well as with a simple experimental set up.

## Experimental

### Development of an external (in air) PIGE facility at FOTIA, BARC

The initial energy of proton beam in FOlded Tandem Ion Accelerator (FOTIA) was 5 MeV. The 5 MeV proton beam was channeled through a separate beam line having current of 50 nA. The beam line was connected to one end of the sample chamber and external beam exit was set up at the other end of the chamber. At the exit point of the beam, tantalum (Ta) window (Fig. 1a) of 25 µm thick was fixed on the steel flange. The Ta window, which holds the vacuum as well as allows proton beam to come out which is lesser energy by 1.25 MeV than actual beam energy. The original beam size of 5 mm falls on the Ta window and extracted. For our experiment, to make the proton beam focused at the exit side of the window, a thicker tantalum with 5 mm circular hole is tightly fixed, and in this way a collimated beam is extracted for the experiment. The energy of 5 MeV proton beam from Ta window was reduced to ~ 3.75 MeV. The target was placed on a Perspex sample stand in air at a distance of 1.5 cm from the Ta window perpendicular to the beam line. The final energy of proton beam falling on the target was ~ 3.5 MeV. The prompt gamma rays from proton induced nuclear reactions were measured using a 50% relative efficiency high purity germanium (HPGe) detector placed near (5 cm distance) the sample holder (Fig. 1b). The detector was placed 90° to the beam direction. The output from the detector was taken outside beam hall through a cable wire followed by connection to MCA based PC. Both radiological as well as chemical safety was maintained during the online measurement of gamma rays in PIGE.

### Sample preparation, irradiation, measurements and calculations

Samples like $Li_2TiO_3$, $LiAlO_2$, $Li_2SiO_3$, $Li_2SO_4$, $B_4C$ (natural) and two numbers of each soda-lime (automobile) and

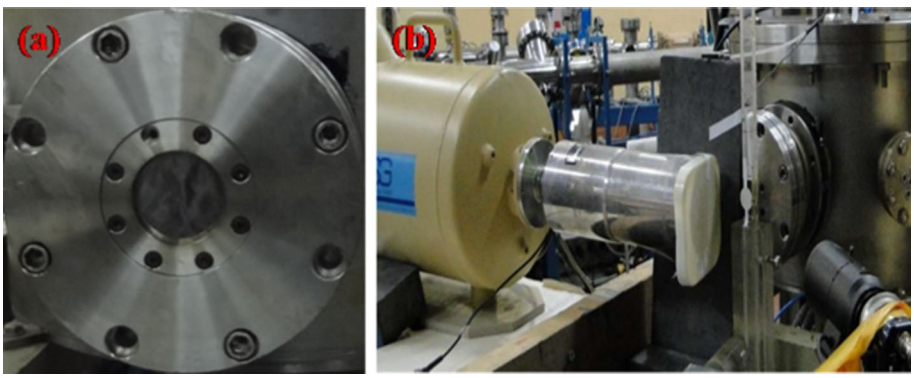


**Fig. 1** **a** Tantalum window of (25 µm thick) used for the extraction of proton beam. **b** External (in air) PIGE setup with a sample holder (for hanging pellets) and HPGe detector (for detecting prompt γ-rays from samples during proton irradiation)

borosilicate glass samples of about 100 mg were taken in powdered form and mixed homogenously with cellulose along with constant amount of Fluorine (in the form of $CaF_2$ in cellulose matrix) as the in situ current normalizer. The resultant homogenous mixture was pelletized using 2 ton hydraulic press. A mixed standard with various stoichiometric compounds of low Z elements ($SiO_2$, $Al_2O_3$, $Na_2CO_3$, MgO, $TiO_2$, $Li_2CO_3$ and $H_3BO_3$) and individual elemental standard with F as in situ current normalizer were prepared for method validation. Standards were mixed with cellulose and $CaF_2$ (as in situ current normalizer) and pelletized in a similar way. The total mass of the pellets were 650 mg for standards and samples. The above samples along with two reference materials (NIST SRM 620 and USGS CRM G2) were irradiated separately for 15–30 min in external proton beam in air having 3.5 MeV energy from FOTIA. The prompt gamma rays from proton induced reactions were measured using a 50% relative HPGe detector having resolution of 2.0 keV at 1332 keV of $^{60}$Co. The peak areas of the sample and standard were analyzed by peak-fit method (i.e., Gaussian shape and low exponential tail model) using Pulse Height Analysis Software (PHAST) developed at BARC. The γ-ray energy along with the nuclear reactions and literature available thick target γ-ray yield (at 4 MeV proton beam) of low Z elements of interest are given in Table 1 in order to get an idea on comparative elemental sensitivity. In comparative method of calculation using count rate of analyte and standard element, the count rate of gamma-ray of interest is normalized with current. Instead of absolute current measurement, we have developed and optimized an in situ current normalization approach in our laboratory by externally adding an element like F (in the form of $CaF_2$ in this case) with the sample and standard in constant amount [25, 27, 30]. The element of choice is that it should not be present in the sample and it should have good analytical sensitivity in PIGE. As both the sample and standard pellets contain the the same in situ current normalizer, the proton induced gamma-ray from it (197 keV from $^{19}$F) as well as from analyte is measured simultaneously, The in situ current normalization works in the assumption that the variation of count rate of 197 keV or count rate of 197 keV per unit mass of current normalizer (F) is proportional to the variation of beam current. In this process, current normalized count rate of analyte is obtained for concentration calculation by relative method of PIGE. Equation 1 shows the relative method of concentration calculation in sample using current normalized count rate for both sample and standard.

$$C_{x,\mathrm{sam}} = C_{x,\mathrm{std}} \times \frac{\left(\mathrm{CPS_{CN}}\right)_{x,\mathrm{sam}}}{\left(\mathrm{CPS_{CN}}\right)_{x,\mathrm{std}}} \quad (1)$$

where,

$$\mathrm{CPS_{CN}} = \mathrm{CPS}/S_{\mathrm{CN}}$$

$$S_{\mathrm{CN}} = \frac{\text{CPS of Current Normalizer}}{C_{\mathrm{CN}}\left(\mathrm{mg\,kg^{-1}}\right)}$$

where $(\mathrm{CPS_{CN}})_x$ is the current normalized (CN) count rate of a particular analyte '$x$' in sample (sam) and standard (std), $C_x$ and $C_{\mathrm{CN}}$ are the concentrations of analyte '$x$' and current normalizer (F), respectively and $\mathrm{S_{CN}}$ represents the sensitivity of current normalizer. Details of the calculations can be found in our earlier published papers [27, 30].

**Table 1** Relevant nuclear data of PIGE for low Z elements

| Element | Reaction | Energy (keV) | Thick target γ-ray yield at 4 MeV proton |
|---|---|---|---|
| Lithium | $^{7}$Li(p,p'γ)$^{7}$Li | 478 | $1.1 \times 10^{8}$ |
| Boron | $^{10}$B(p,αγ)$^{7}$Be | 429 | $1.1 \times 10^{7}$ |
| | $^{10}$B(p,p'γ)$^{10}$B | 718 | $3.0 \times 10^{6}$ |
| | $^{11}$B(p,p'γ)$^{11}$B | 2125 | $1.1 \times 10^{6}$ |
| Fluorine | $^{19}$F(p,p'γ)$^{19}$F | 197 | $4.3 \times 10^{7}$ |
| Sodium | $^{23}$Na(p,p'γ)$^{23}$Na | 440 | $3.9 \times 10^{7}$ |
| Magnesium | $^{24}$Mg(p,p'γ)$^{24}$Mg | 585 | $1.2 \times 10^{6}$ |
| | $^{24}$Mg(p,p'γ)$^{24}$Mg | 1369 | NA |
| Aluminium | $^{27}$Al(p,p'γ)$^{27}$Al | 844 | $1.1 \times 10^{6}$ |
| | $^{27}$Al(p,p'γ)$^{27}$Al | 1014 | $1.6 \times 10^{7}$ |
| Silicon | $^{28}$Si(p,p'γ)$^{28}$Si | 1779 | $1.0 \times 10^{7}$ |
| Titanium | $^{48}$Ti(p,p'γ)$^{48}$Ti | 983 | $6.15 \times 10^{7}$ |

## Results and discussion

### External PIGE set up using tantalum as window material

For the first time in our accelerator centre (FOTIA), we have set up indigenously an external (in air) PIGE facility using Tantalum as window for extraction of beam into air. The choice of Tantalum (Ta) window is advantageous than world-wide used Al, Ti and $Si_3N_4$ (Silicon Nitride) windows, as these window elements are mostly our analyte of interest and thus if we use any one of these windows, we cannot determine that element of interest in the samples. Thus thin Ta is a better or unique choice for our case than other window materials used elsewhere in the world. Since Ta is a high Z element, we have used 25 μm thick window and to get about 4 MeV proton beam, the starting energy before window material was 5 MeV proton beam. The exit energy in the air (3.75 MeV) and current on the target (10–50 nA) were suitable for our work on the determination of low Z elements in various samples of interest. The choice of Ta window to

extract the beam is also somewhat unique because the two prominent gamma rays are at 135 and 165 keV from the inelastic scattering from $^{181}$Ta (p,p'γ)$^{181}$Ta and they do not interfere in the analysis of most of the samples of interest. In addition, another advantage is that any one gamma-ray of Ta could be used as an external beam monitor for quantitative estimation of elemental concentration.

## Method optimization and validation for low Z elements

Our laboratory has previously optimized conventional in situ current normalized PIGE method using sample pellet irradiation in vacuum chamber. The new experimental setup using external (in air) PIGE with 3.5 MeV proton beam gave us opportunity to analyze the samples in faster and simpler way with minimum experimental arrangements due to no requirement of sample irradiation in vacuum. The variation in beam current, if any, during experiment was monitored by the in situ current normalizer element thoroughly mixed along with the sample. The external PIGE method was standardized as well as validated by analyzing synthetic mixed standard for many low Z elements as well as two certified/standard reference materials (CRM/SRM) obtained from USGS (rock matrix) and NIST (glass matrix). The results of concentrations of low Z elements (Li, B, Na, Mg, Al, Si and Ti) in mixed standard are shown in Table 2 and the determined concentrations are found in good agreement with the calculated concentrations in the pellet and the percentage deviations are in the range of ± 0.3–6%. Method validation was also carried out using USGS G2 (geological CRM) and its PIGE spectrum is shown in Fig. 2. Concentrations of Si, Na and Al were determined in USGS G2 using the certified concentration of F (already present in CRM) as the in situ current normalizer in external PIGE and elemental concentrations are given in Table 3. The percentage deviations of determined values of low Z elements with respect to certified values are within ± 6% and zeta score values (at 95.5% confidence level) are within 1, indicating a good accuracy of the standardized external in situ current normalized PIGE method. Results of NIST SRM 620 (soda-lime flat glass), which is also a part of method validation, are given in later Section (Table 5) in application of external PIGE to glass samples.

**Table 2** Method validation using mixed synthetic elemental standard by external PIGE using F as in situ current normalizer

| Element | $E_\gamma$ (keV) | Obtained conc. (%) | Expected conc. (%) | Deviation (%) |
|---|---|---|---|---|
| Li | 478 | 0.681 ± 0.003 | 0.68 | −0.3 |
| B | 718 | 1.50 ± 0.03 | 1.58 | −4.7 |
| | 2125 | 1.61 ± 0.04 | 1.58 | 1.9 |
| Na | 440 | 3.85 ± 0.02 | 3.89 | −1.2 |
| Mg | 585 | 11.0 ± 0.2 | 10.9 | 0.6 |
| Al | 1014 | 4.77 ± 0.04 | 4.98 | −4.3 |
| Si | 1779 | 13.24 ± 0.10 | 13.23 | 0.02 |
| Ti | 983 | 11.85 ± 0.13 | 11.1 | 6.6 |

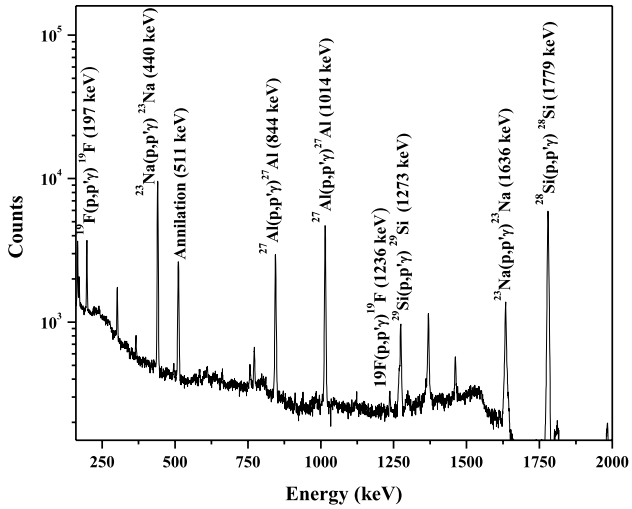


**Fig. 2** Prompt Gamma-ray spectrum of geological certified reference material (USGS-G2) showing major elements (Na, Si and Al)

## Application of external PIGE for quantification of low Z elements in lithium and boron based ceramics

The in situ current normalized PIGE was applied to lithium sulphate standard as well as three different lithium-based ceramics namely lithium titanate, lithium aluminate and lithium silicate, which are potential fusion reactor blanket materials for production of tritium. Prompt γ-ray spectra obtained in external PIGE with 3.5 MeV proton beam for lithium-based ceramics namely lithium titanate and lithium aluminate are shown in Fig. 3a, b, respectively. The Li concentrations obtained in various samples are in the range of 10.1–15.8 wt%, whereas Si, Ti and Al concentrations are in the range of 32.3–41.7 wt% (Table 4). The concentration determined is in good agreement (within ± 6% except for Ti concentration) with the calculated concentration (assuming the compounds to be 100% purely stoichiometric. The uncertainties reported in Table 4 are propagated uncertainties (at ± 1 s limit) and the values are within ± 5% (from a single sample analysis). The propagated uncertainties were evaluated using the parameters namely (1) counting statistics of sample, standard and in situ current normalizer, (2) uncertainties on their corresponding masses, and (3) uncertainty on the concentration of standard. Compared to our earlier work on lithium and other low Z (Al and Ti) quantification

**Table 3** Determination of major elemental concentration in USGS CRM G2 taking F as in situ current normalizer in external (in air) PIGE for method validation

| Oxide | $E_\gamma$ (keV) | Determined conc (%) | Certified value (%) | % Error | Zeta score |
|---|---|---|---|---|---|
| $Na_2O$ | 440 | 3.90 ± 0.11 | 4.08 ± 0.13 | − 4.3 | 1.0 |
| $Al_2O_3$ | 1014 | 16.2 ± 0.7 | 15.39 ± 0.30 | 5.2 | 1.1 |
| $SiO_2$ | 1779 | 67.2 ± 1.6 | 69.14 ± 0.30 | − 5.7 | 1.2 |

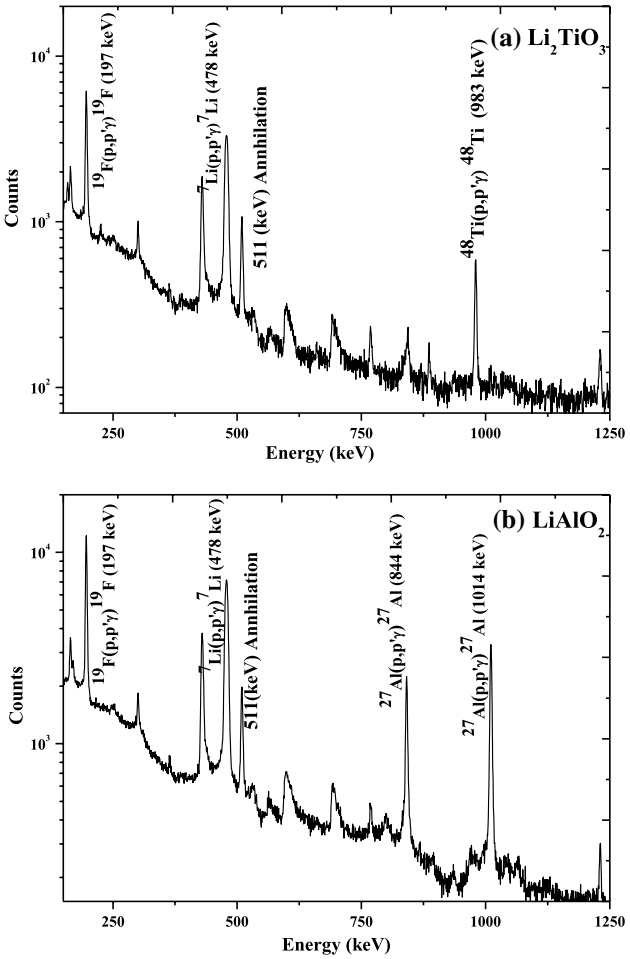


**Fig. 3** Typical gamma spectra of **a** lithium titanate ($Li_2TiO_3$) and **b** lithium aluminate ($LiAlO_2$) in external PIGE (in –air proton beam irradiation) along with F as in situ current normalizer

using 4 MeV proton beam in conventional PIGE in lithium doped $Nd_2Ti_2O_7$ [31] and $Li_2TiO_3$ and $LiAlO_2$ [32, 33], the experiments were really simple and faster using present method and experimental set up. Apart from lithium, boron is used an important neutron absorber/control material in fission reactors. Boron and its isotopic composition are very important information, and our laboratory has performed this work previously by conventional (in-beam) PIGE [34, 35]. The neutron absorbers like titanium based refractory borides and boron carbide ceramics have got immense applications in nuclear fields as neutron shielding, control/shutoff rods, neutron sensors, and nuclear material storage. Chemical quality control (CQC) of these finished materials is required for their acceptability in order to have safe operation of nuclear reactors. Application of boron-based ceramics towards nuclear industry depends upon its specific isotopes ($^{10}B$ and $^{11}B$). As a part of CQC and application of external PIGE, total boron concentration has been determined in natural $B_4C$ sample. A typical γ-ray spectrum indicating three γ-ray peaks (429 and 718 keV from $^{10}B$ and 2125 keV from $^{11}B$) is shown in Fig. 4. The concentration of total B along with combined uncertainty (less than ± 3%) is given in Table 4. The additional advantage of PIGE method is that γ-rays of $^{10}B$ and $^{11}B$ can be used for isotopic composition (IC) of boron simultaneously with total boron concentration determination.

## Application of external PIGE for quantification of low Z elements in NIST SRM 620 and soda-lime and borosilicate glass samples

Glasses are complex matrix samples used in various fields including nuclear industry as a vitrifying matrix [36] as well as they are often studied/used as forensic objects. Two different kinds of glasses namely, soda-lime and borosilicate are found to be extensively used for various applications. Figure 5 shows the prompt γ–ray spectrum of one soda-lime glass sample in PIGE using 3.5 MeV proton beam. External PIGE method validation for glass samples was carried out by analyzing the soda-lime glass standard reference material (SRM 620) from NIST and the results of Si, Na, Al and Mg are found to be within 2% deviations from certified values and zeta-score values are within ± 1 as shown in Table 5. In addition to this, two soda-lime (automobile) and two borosilicate glass samples were analyzed (as shown in Table 5) as a part of application of external PIGE. The determined concentrations of oxides of Si, Na, Al and Mg (in wt %) in soda-lime glass and oxides of Si, B and Na in borosilicate glass samples given in Table 6. The analysis was performed by external PIGE with F as the in situ current normalizer. The propagated uncertainties are found be less than ± 3%. The overall propagated uncertainties (at ± 1 s limit) for the determined low Z elements (Li to Si) in all

**Table 4** Determined concentrations of low Z elements in lithium and boron based ceramics by in situ current normalized external PIGE using F as in situ current normalizer

| Sample or stoichiometric compound | Element | $E_\gamma$ (keV) used | Determined conc. (%) | Calculated conc. (%) | % Deviation |
|---|---|---|---|---|---|
| $Li_2TiO_3$ | Li | 478 | 13.8 ± 0.3 | 12.6 | 9.6 |
| | Ti | 983 | 41.1 ± 1.3 | 43.6 | −5.8 |
| $LiAlO_2$ | Li | 478 | 10.10 ± 0.14 | 10.5 | −3.8 |
| | Al | 1014 | 41.7 ± 1.4 | 40.9 | 1.9 |
| $Li_2SiO_3$ | Li | 478 | 15.8 ± 0.7 | 15.4 | 2.6 |
| | Si | 1779 | 32.3 ± 1.5 | 31.1 | 3.9 |
| $Li_2SO_4$ | Li | 478 | 11.9 ± 0.5 | 12.6 | −6.2 |
| $B_4C$ | B | 718 | 77.8 ± 2.3 | 78.3 | −0.6 |
| | | 2125 | 76.2 ± 2.3 | 78.3 | −2.7 |

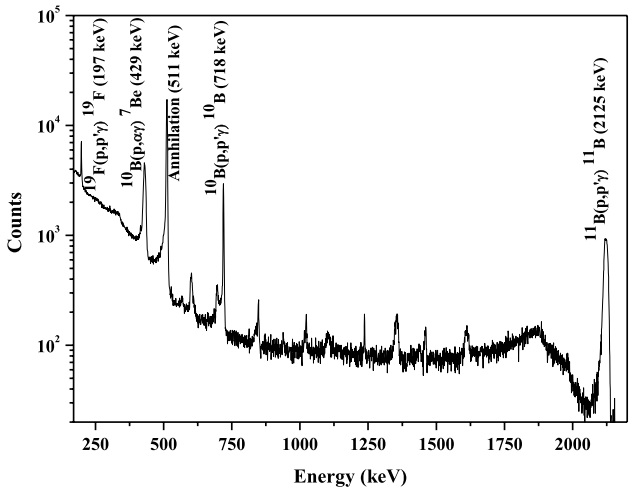


**Fig. 4** Prompt Gamma-ray spectrum of $B_4C$ in PIGE indicating the γ-ray energies at 429, 718 and 2125 keV

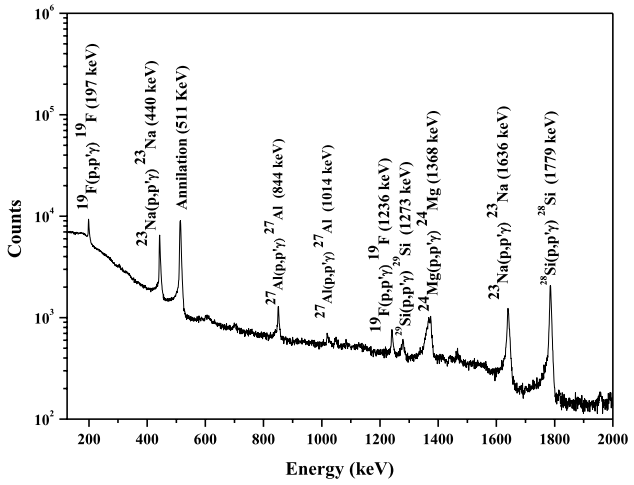


**Fig. 5** Prompt gamma-ray spectrum of a Soda-lime glass sample in external PIGE (in—air proton beam irradiation)

samples, standards and reference materials are found to be in the range of ± 1–5%.

## Conclusions

An external PIGE facility has been set up at FOTIA of BARC using 3.5 MeV proton beam (5 mm beam size) in air obtained using thin tantalum window and tantalum collimator at the beam exit side. We have standardized in situ current normalized external PIGE method by determining low Z elements of interest through analysis of CRM/SRM (for method validation) and applied to three different matrices namely lithium based ceramics, boron carbide and soda-lime and borosilicate glasses for simultaneous quantification of low Z elements. External proton beam current normalization was carried out by an in situ approach using F in the form of $CaF_2$, where the count rate at 197 keV of $^{19}F$ was utilized to get current normalized count rate at gamma-ray peak of interest of low Z element. Overall experimental arrangement was found to be simple and prompt γ-ray measurement of low Z elements could be performed with less turnaround time compared to conventional vacuum chamber PIGE method. The present work also demonstrates the prospective of external (in air) PIGE setup towards rapid quantification of low Z elements in diverse matrices without requirement of vacuum chamber. The external PIGE has the capability for CQC of non-standard geometry samples of lithium and boron-based ceramics. From our results, it is understood that glass samples can be examined without destruction to easily know whether they are soda-lime or borosilicate. The external PIGE method has capability to analyze "as received" as well as large and non-standard geometry samples as there is no restriction in sample shape and sizes since the experiment is carried out in air. In addition to non-destructive analysis of nonstandard geometrical samples by external PIGE, the samples can be returned back

**Table 5** External PIGE method validation by analyzing NIST SRM 620 (Soda-lime glass) and determined major elemental concentration

| Oxide | $E_\gamma$ (keV) | Determined conc (%) | Certified value (%) | % Error | Zeta score |
|---|---|---|---|---|---|
| $Na_2O$ | 440 | 14.1 ± 0.2 | 14.39 ± 0.06 | − 2.0 | 0.7 |
| MgO | 585 | 3.76 ± 0.07 | 3.69 ± 0.05 | 1.9 | 0.5 |
| $Al_2O_3$ | 1014 | 1.79 ± 0.04 | 1.80 ± 0.03 | − 0.6 | 0.1 |
| $SiO_2$ | 1779 | 72.3 ± 0.8 | 72.1 ± 0.08 | 0.3 | 0.1 |

**Table 6** Determined concentration of nominal compounds containing low Z elements in soda-lime and borosilicate glass samples

| Oxide (wt%) | $E_\gamma$ (keV) | Automobile (Soda-lime) glass (SG-1) | Automobile (Soda-lime) glass (SG-2) | Borosilicate glass (BG-1) | Borosilicate glass (BG-2) |
|---|---|---|---|---|---|
| $Na_2O$ | 440 | 13.5 ± 0.1 | 13.1 ± 0.1 | 25.2 ± 0.2 | 20.1 ± 0.2 |
| MgO | 585 | 4.08 ± 0.08 | 4.37 ± 0.08 | ND | ND |
| $Al_2O_3$ | 1014 | 1.15 ± 0.01 | 1.85 ± 0.04 | ND | ND |
| $SiO_2$ | 1779 | 73.9 ± 0.5 | 72.1 ± 1.2 | 51.9 ± 0.9 | 58.1 ± 0.8 |
| $B_2O_3$ | 2125 | ND | ND | 21.9 ± 0.4 | 22.1 ± 0.5 |

*ND* not detected (either below detection limit or not expected to be present)

to the user after analysis as no radioactivity is generated in the sample using this low energy proton beam. External PIGE keeps promise for its application to environmental, biological, geological, forensic and archaeological samples along with energy/nuclear based materials like alloys, oxides and carbides containing low Z elements.

**Acknowledgements** Authors thank Dr. S. Krishnagopal, Head, IADD, Mr. A. Agarwal, OIC, FOTIA, IADD and FOTIA operation crews for their support and co-operation during experiment. Authors thank TIFR target laboratory for providing us thin Tantalum used as window material for extraction of proton beam in air at FOTIA. Authors thank Dr. A.K. Gupta, NPD, BARC and Dr. S. Sodaye, RCD, BARC for their help towards external PIGE set up at FOTIA. Mr. V. Sharma is thankful to Council of Scientific and Industrial Research (CSIR), New Delhi, for Junior Research Fellowship (JRF) and he sincerely thank Director, RC&IG and Head, Radiochemistry Division, BARC and Principal, K.C. College, Mumbai for their support and encouragement.

## References

1. Acharya RN, Nair AGC, Reddy AVR, Manohar SB (2002) Validation of a neutron activation analysis method using k0-standardization. Appl Radiat Isot 57(3):391–398
2. Dasari KB, Acharya R, Swain KK, Lakshmana Das N, Reddy AVR (2010) Analysis of large and non-standard geometry samples of ancient potteries by internal monostandard neutron activation analysis using in situ detection efficiency. J Radioanal Nucl Chem 286(2):525–531
3. Acharya R (2009) Prompt gamma-ray neutron activation analysis methodology for determination of boron from trace to major contents. J Radioanal Nucl Chem 281(2):291–294
4. Sippel RF, Glover ED (1960) Sedimentary rock analysis by charged particle bombardment. Nuclear Instruments and Methods 9(1):37–48
5. Grainger MNC, Manley-Harris M, Coulson S (2012) Classification and discrimination of automotive glass using LA-ICP-MS. J Anal At Spectrom 27(9):1413–1422
6. Šmit Ž, Milavec T, Fajfar H, Rehren T, Lankton JW, Gratuze B (2013) Analysis of glass from the post-Roman settlement Tonovcov grad (Slovenia) by PIXE–PIGE and LA-ICP-MS. Nucl Instrum Methods Phys Res Sect B 311:53–59
7. Valković O, Jakšić M, Fazinić S, Valković V, Moschini G, Menapace E (1995) Quality control of PIXE and PIGE nuclear analytical techniques in geological and environmental applications. Nucl Instrum Methods Phys Res Sect B 99(1):372–375
8. Macias ES, Radcliffe CD, Lewis CW, Sawicki CR (1978) Proton induced.gamma.-ray analysis of atmospheric aerosols for carbon, nitrogen, and sulfur composition. Anal Chem 50(8):1120–1124
9. Volfinger M, Robert JL (1994) Particle-induced-gamma-ray-emission spectrometry applied to the determination of light elements in individual grains of granite minerals. J Radioanal Nucl Chem 185(2):273–291
10. Savidou A, Aslanoglou X, Paradellis T, Pilakouta M (1999) Proton induced thick target γ-ray yields of light nuclei at the energy region Ep = 1.0–4.1 MeV. Nuclear Instrum Methods Phys Res Sect B Beam Interact Mater Atoms 152(1):12–18
11. Giuntini L (2011) A review of external microbeams for ion beam analyses. Anal Bioanal Chem 401(3):785–793
12. Doyle BL, Walsh DS, Lee SR (1991) External micro-ion-beam analysis (X-MIBA). Nucl Instrum Methods Phys Res Sect B 54(1):244–257
13. Hofsäss H (2018) Evaluation of the radiation hazard for ion-beam analysis with MeV external proton beams (X-IBA). Nucl Instrum Methods Phys Res Sect B 427:53–59
14. Mathis F, Othmane G, Vrielynck O, Calvo del Castillo H, Chêne G, Dupuis T, Strivay D (2010) Combined PIXE/PIGE and IBIL with external beam applied to the analysis of Merovingian glass beads. Nucl Instrum Methods Phys Res Sect B 268(11):2078–2082
15. Beck L, Pichon L, Moignard B, Guillou T, Walter P (2011) IBA techniques: examples of useful combinations for the characterisation of cultural heritage materials. Nucl Instrum Methods Phys Res Sect B 269(24):2999–3005
16. Calligaro T, Coquinot Y, Pichon L, Moignard B (2011) Advances in elemental imaging of rocks using the AGLAE

external microbeam. Nucl Instrum Methods Phys Res Sect B 269(20):2364–2372
17. Calzolai G, Chiari M, Lucarelli F, Nava S, Portarena S (2010) Proton induced γ-ray emission yields for the analysis of light elements in aerosol samples in an external beam set-up. Nucl Instrum Methods Phys Res Sect B 268(10):1540–1545
18. Lucarelli F, Calzolai G, Chiari M, Giannoni M, Mochi D, Nava S, Carraresi L (2014) The upgraded external-beam PIXE/PIGE set-up at LABEC for very fast measurements on aerosol samples. Nucl Instrum Methods Phys Res Sect B 318:55–59
19. Lucarelli F, Calzolai G, Chiari M, Nava S, Carraresi L (2018) Study of atmospheric aerosols by IBA techniques: the LABEC experience. Nucl Instrum Methods Phys Res Sect B 417:121–127
20. Pichon L, Beck L, Walter P, Moignard B, Guillou T (2010) A new mapping acquisition and processing system for simultaneous PIXE-RBS analysis with external beam. Nucl Instrum Methods Phys Res Sect B 268(11):2028–2033
21. Sokaras D, Bistekos E, Georgiou L, Salomon J, Bogovac M, Aloupi-Siotis E, Paschalis V, Aslani I, Karabagia S, Lagoyannis A, Harissopulos S, Kantarelou V, Karydas A-G (2011) The new external ion beam analysis setup at the Demokritos Tandem accelerator and first applications in cultural heritage. Nucl Instrum Methods Phys Res Sect B 269(5):519–527
22. Yasuda K, Nomachi M, Sugaya Y, Yamamoto H, Komatsu H (2011) Progress of in-air microbeam system at the Wakasa Wan Energy Research Center. Nucl Instrum Methods Phys Res Sect B 269(20):2180–2183
23. Chhillar S, Acharya R, Mishra RK, Kaushik CP, Pujari PK (2017) Simultaneous determination of low Z elements in barium borosilicate glass samples by in situ current normalized particle induced gamma-ray emission methods. J Radioanal Nucl Chem 312(3):567–576
24. Sharma V, Acharya R, Samanta SK, Goswami M, Bagla HK, Pujari PK (2020) Chemical characterization of soda-lime glass samples by in situ current normalised PIGE and conventional INAA methods for forensic applications. J Radioanal Nucl Chem 323:1451–1457
25. Chhillar S, Acharya R, Sodaye S, Sudarshan K, Santra S, Mishra RK, Kaushik CP, Choudhury RK, Pujari PK (2012) Application of particle induced gamma-ray emission for non-destructive determination of fluorine in barium borosilicate glass samples. J Radioanal Nucl Chem 294(1):115–119
26. Dhorge PS, Acharya R, Rajurkar NS, Chahar V, Tuli V, Srivastava A, Pujari PK (2017) Quantification of trace fluorine concentrations in soil and food samples from fluoride affected region by in situ current normalized particle induced gamma-ray emission method. J Radioanal Nucl Chem 311(3):1803–1809
27. Chhillar S, Acharya R, Sodaye S, Pujari PK (2014) Development of particle induced gamma-ray emission methods for nondestructive determination of isotopic composition of boron and its total concentration in natural and enriched samples. Anal Chem 86(22):11167–11173
28. Li XF, Wang GF, Chu JH, Yu LD (2012) Charge integration in external PIXE–PIGE for the analysis of aerosol samples. Nucl Instrum Methods Phys Res Sect B 289:1–4
29. Lill JO (1999) Charge integration in external-beam PIXE. Nucl Instrum Methods Phys Res Sect B 150(1):114–117
30. Acharya R, Pujari PK (2018) Development and applications of in situ current normalized PIGE method using proton beams for quantification of low Z elements. J Radioanal Nucl Chem 318(3):1727–1735
31. Chhillar S, Acharya R, Pai R, Sodaye s, Mukerjee S, Pujari P (2012) A simple and sensitive particle induced gamma-ray emission method for non-destructive quantification of lithium in lithium doped $Nd_2Ti_2O_7$ ceramic sample. J Radioanal Nuclear Chem 293:437–441
32. Chhillar S, Acharya R, Tripathi R, Sodaye S, Sudarshan K, Rout PC, Mukerjee SK, Pujari PK (2015) Compositional characterization of lithium titanate ceramic samples by determining Li, Ti and O concentrations simultaneously using PIGE at 8 MeV proton beam. J Radioanal Nucl Chem 305(2):463–467
33. Chhillar S, Acharya R, Rao T, Bamankar Y, Mukerjee S, Pujari P, Aggarwal S (2013) Non-destructive compositional analysis of sol–gel synthesized lithium titanate ($Li_2TiO_3$) by particle induced gamma-ray emission and instrumental neutron activation analysis. J Radioanal Nucl Chem. https://doi.org/10.1007/s10967-013-2609-5
34. Raja SW, Acharya R, Pujari PK (2020) Application of PIGE method for quantification of total boron in neutron absorbers and shielding materials and isotopic composition in in-house prepared enriched boron carbide samples. J Radioanal Nucl Chem. https://doi.org/10.1007/s10967-020-07011-0
35. Acharya R, Raja SW, Chhillar S, Gupta J, Sonber JK, Murthy TSRC, Bhushan KS, Rao Radhika M, Majumdar S, Pujari PK (2018) Non-destructive quantification of total boron and its isotopic composition in boron based refractory materials by PIGE and an inter-comparison study using TIMS and titrimetry. J Anal At Spectrom 33(5):784–791
36. Shih PY (2003) Properties and FTIR spectra of lead phosphate glasses for nuclear waste immobilization. Mater Chem Phys 80(1):299–304