U.P.B. Sci. Bull., Series A, Vol. 81, Iss. 1, 2019 ISSN 1223-7027

PROTON-INDUCED GAMMA-RAY EMISSION FOR DETERMINATION OF LIGHT ELEMENTS IN GLASS (NIST SRM-1412)

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Proton-induced gamma-ray emission (PIGE) has been performed at the Bucharest 3 MV Tandetron^{TM}, using a 3 MeV proton beam energy on thick targets in vacuum. Five light elements (Li, B, Na, Al, Si) have been measured in a known composition glass sample (NIST SRM-1412), based on comparative standards prepared as pellets from high purity chemical compounds (NaCl, $LiNH_2$, $B(OH)_3$), as well as Si single crystal wafer, and certified Al foil (IRMM, Geel, Belgium). The concentration (mass fraction) values obtained are in agreement with NIST certified/information values, being situated in the percent range. This method involves the measurement of the prompt γ-rays 477.6, 718.3, 440, 1014.4, 1779 keV from $^{7}Li(p,p`\gamma)^{7}Li$, $^{10}B(p,p`\gamma)^{10}B$, $^{23}Na(p,p`\gamma)^{23}Na$, $^{27}Al(p,p`\gamma)^{27}Al$, $^{28}Si(p,p`\gamma)^{28}Si$ nuclear reactions, respectively. Peak areas, normalized to the beam charge of the incident protons on the target were used for a quantitative analysis. Stopping powers values of the proton beam in sample and reference standards determined by SRIM program have been considered.

Keywords: Tandem accelerator, IBA, PIGE, gamma spectrometry, nuclear reactions, NIST glass, certified reference materials

1. Introduction

Particle-induced gamma-ray emission (PIGE) with proton beams is a powerful analytical technique based on detection of prompt gamma-rays produced during a proton beam bombardment of solid samples. PIGE could be used to determine the concentration or depth profiling of light elements in a wide variety of samples [1-13]. This technique has been used since the early 1960s for different applications ranging from analysis of fission reactor materials to biomedicine, environment, cultural heritage and, more recently, fusion reactor materials.

However, the main drawback of this method is lack of cross section data. It is known that reliable values of the cross-section data allow the application of the PIGE technique for the analysis of light elements regardless of the standard sample. This process is evolved by integrating the nuclear reaction cross section along the depth of the sample, employing a suitable code [5-7].

For this reason, PIGE quantitative analysis of thick samples is usually performed by comparing the measured data with those of standard samples having

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a similar composition. If the composition of the sample considerably deviates from that of the standard one, serious errors may arise due to different stopping powers of protons in both matrices. Matrix composition of the sample could be determined by using Rutherford Backscattering (RBS) technique in parallel with PIGE in Ion Beam Analysis (IBA) [8].

The aim of this work is to test the application of PIGE technique with 3 MeV protons at the 3 MV Tandetron of IFIN-HH, to determine concentration (mass fraction) of Li, B, Na, Al, and Si light elements in a standard reference material (SRM) glass sample (NIST SRM-1412). The method was applied using comparator standards of certified element concentrations (relative standardization).

2. Experimental

2.1 Samples description

The investigated NIST SRM-1412 sample [14] is a multicomponent glass produced by the National Institute of Standards and Technology (NIST), with elemental composition shown in Table 1. Besides certified concentration values, information ones are given in brackets. The sample's dimensions are of 1 cm^2 and 3 mm thickness (thick target).

As comparator standards for Li, B, and Na, pellets of 1 cm diameter and 1 mm thickness were prepared from high purity chemical compounds powders ($LiNH_2$, $B(OH)_3$, NaCl) using an automatic hydraulic press (Specac Ltd) at 4.5 t. For Al and Si, aluminum foil of certified concentration (IRMM-528RA, Geel, Belgium) and Si single crystal wafer were used.

Table 1

Elemental composition of NIST SRM-1412 multicomponent glass [14] and corresponding element concentration.

Constituent/ Element	Percent by Weight	Uncertainty	Constituent/ Element	Percent by Weight	Uncertainty
SiO_2 Si	42.38 19.81	0.18 0.08	Li_2O Li	(4.50) (2.09)	…. ….
Al_2O_3 Al	7.52 3.98	0.24 0.13	B_2O_3 B	4.53 1.41	0.17 0.05
CaO Ca	4.53 3.24	0.10 0.07	BaO Ba	4.67 4.18	0.16 0.14
MgO Mg	(4.69) (2.83)	…. ….	ZnO Zn	4.48 3.60	0.12 0.10
SrO Sr	4.55 3.85	0.09 0.08	PbO Pb	4.40 4.08	0.17 0.16
Na_2O Na	4.69 3.48	0.07 0.05	CdO Cd	4.38 3.83	0.08 0.07
K_2O K	4.14 3.44	0.10 0.08	Fe_2O_3 Fe	(0.031) (0.022)	…. ….

2.2 Experimental set-up

The experiments were performed at the Horia Hulubei National Institute of Physics and Nuclear Engineering (IFIN-HH) in Bucharest-Magurele, Romania, using the 3 MV Tandetron™ accelerator. It is a last-generation integrated instrument for IBA and ion implantation provided with Cockcroft–Walton high voltage generator. In the actual IBA configuration, PIXE, PIGE and RBS spectra can be registered simultaneously, with automatic control and recording of measurement parameters. A detailed description of the machine has been published [15].

The beam targets were positioned normal to the beam direction on a special target support of 5 cm diameter. PIGE detector was placed at 45^0 with respect to the beam. Measurements were performed in high vacuum (10^{-6} mbar).

The gamma-ray detector used for PIGE was of a GEM10P4-70 coaxial type (energy resolution of 1.75 keV at 1.33 MeV of ^{60}Co, 75 cm^3 active volume, and 10 % relative efficiency). It was situated outside of the experimental chamber, at about 15 cm from the target (the closest position allowed by the IBA chamber of 50 cm diameter, thanks to a special design) [12, 13, 15].

The examined NIST SRM-1412 glass sample as well as comparator standards were irradiated with a 3 MeV proton beam under similar experimental conditions. Current beam of 3-12 nA, electrical charge on target (Q) in the range of 2-27 μC, counting time of 600-3600 s, and counting dead time (τ) in the gamma spectra acquisition lower than 11 % were considered.

2.3 PIGE analysis

The prompt y-rays emitted from a sample under PIGE investigation are always accompanied by an interfering background radiation. Background interferences can come from a variety of sources including terrestrial radiation, cosmic radiation, and contamination in the laboratory. Terrestrial radiation is dominated by naturally occurring radioactive materials (NORM), mainly from the ^{238}U-^{226}Ra and ^{232}Th series, as well as ^{40}K [1, 16, 17]. A spectral interference between ^{25}Mg (585 keV) and the natural background line of 583.2 keV (^{208}Tl) has to be considered in PIGE application on biological samples [12].

The unknown elemental concentrations in the examined sample were determined by comparing the γ-ray yields of the sample with those of appropriate standards (relative standardization), using the following formula [1, 2, 9-13]:

$$C_{Sample} = \frac{Y_{Sample} \cdot S_{Sample(E_{1/2})}}{Y_{S\tan dard} \cdot S_{S\tan dard(E_{1/2})}} \cdot C_{S\tan dard} \qquad (1)$$

were, for sample and standard, respectively, C_{sample} and $C_{standard}$ are element concentrations, Y_{sample} and $Y_{standard}$ are element gamma-ray yields (net peak areas) normalized to the proton beam charge (corrected by counting dead-time), S_{sample} and $S_{standard}$ are stopping powers for proton beam energy $E_{1/2}$.

The gamma-ray spectra were analyzed using Gamma-W [18] and LEONE software (a modified version of a program for complex gamma-ray spectra analysis performed by H. Hanewinkel, Institute for Nuclear Physics of Koln, Germany). These programs provided peak area, peak centroid, FWHM (Full-Width at Half-Maximum), background under the peak, and peak area uncertainty.

The energy $E_{1/2}$ for a named element is the proton beam energy at which the reaction yield, normalized to beam charge, has decreased to half of its value at the incident beam energy E_p (3 MeV, in this work): $Y(E_{1/2}) = Y(E_p)/2$. To assess $E_{1/2}$ for the elements of interest in sample and comparator standards, excitation functions were measured using beam energies between 2.4 and 3 MeV (energy step of 0.1 MeV).

Stopping power values corresponding to proton beam energy $E_{1/2}$ were determined using SRIM code of Anderson and Ziegler [19].

3. Results and Discussion

Fig. 1 presents a PIGE spectrum registered for NIST SRM-1412 glass target irradiated with 3 MeV proton beam (beam charge of 19.0055 μC, beam current of 12 nA, and dead-time of 10.7 %). PIGE reactions for the elements identified in sample are mentioned on the spectrum.

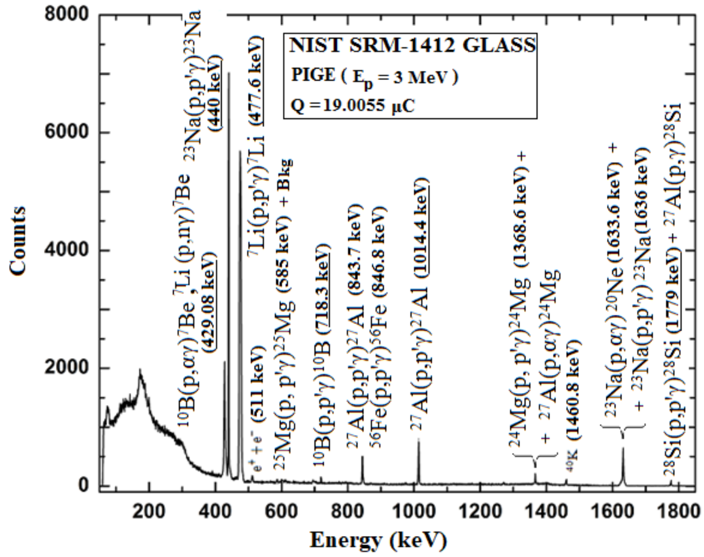

Fig. 1. Experimental γ -ray spectrum obtained from the bombardment of NIST SRM-1412 target with 3 MeV protons.

Table 2 lists the main γ-rays produced by PIGE with 3 MeV protons in the investigated sample, together with possible spectral interferences (competing reactions as well as overlap peaks from nuclear reactions or environmental background).

Table 2

PIGE nuclear reactions with 3 MeV protons measured in NIST SRM-1412 glass sample

Nuclear reaction	E_γ (keV)	Competing reaction / overlap peak
^{7}Li(p,p'γ)^{7}Li	477.6	^{55}Mn(p,nγ)^{55}Fe (*477.2 keV*)
^{10}B(p,αγ)^{7}Be	429.1	^{7}Li (p,nγ)^{7}Be
^{10}B(p,p'γ)^{10}B	718.3	
^{23}Na(p,p'γ)^{23}Na	440.0; 1636.0	
^{23}Na(p,αγ) ^{20}Ne	1633.6	
^{25}Mg(p,p'γ)^{25}Mg	585.0	^{208}Tl (*583.1 keV*)
^{24}Mg(p,p'γ)^{24}Mg	1368.6	^{27}Al(p,αγ)^{24}Mg
^{27}Al(p,p'γ)^{27}Al	843.7; 1014.4	^{26}Mg(p,γ)^{27}Al; ^{56}Fe(p,p'γ)^{56}Fe (*846.8 keV*)
^{29}Si(p,p'γ)^{29}Si	1273.4	
^{28}Si(p,p'γ)^{28}Si	1779.0	^{27}Al(p,γ)^{28}Si; ^{31}P(p,αγ)^{28}Si
^{31}P(p,p'γ)^{31}P	1266.1	
^{56}Fe(p,p'γ)^{56}Fe	846.8	^{27}Al(p,p'γ)^{27}Al (*843.7 keV*)

Tables 3 and 4 present, for sample and comparator standards, respectively, the $E_{1/2}$ and $S_{E1/2}$ values determined for Li, B, Na, Al, and Si in PIGE analysis with 3 MeV protons; PIGE reactions, selected γ-rays (E_γ), and reaction yields (Y) normalized to beam charge, together with their uncertainties are also given in these tables (percent uncertainty, in parenthesis). Elemental mass fractions in comparator standards are inserted in Table 4.

The criterion for the γ-ray selection in PIGE analysis was the emission probability, absence of overlap peaks, and a low background under the peak in the gamma spectrum.

To determine Si content using 1779 keV γ-ray of ^{28}Si(p,p'γ)^{28}Si reaction (Table 2), Al contribution due to ^{27}Al(p,γ)^{28}Si competing reaction was corrected taking into account the ^{27}Al(p,p'γ)^{27}Al complementary reaction in Al target (1014.4 keV/1779 keV yield ratio of 382 ± 5.8 %). P interfering element, not stated in the glass sample (Table 1), was not evidenced in the spectrum at 1266.1 keV peak of ^{31}P(p,p'γ)^{31}P complementary reaction.

Table 3

PIGE reaction yield, $E_{1/2}$, and $S_{E1/2}$ values determined for NIST SRM-1412 glass sample irradiated with 3 MeV protons.

Elem.	Nuclear reaction	E_γ (keV)	Y_{Sample} (counts/μc)	$E_{1/2}$ (MeV)	$S_{E1/2}$ (keV/mg/cm^2)
Li	^{7}Li(p,p'γ)^{7}Li	477.6	16283 ± 163 (1.0)	2.42	98.43 ± 1.28 (1.2)
B	^{10}B(p,p'γ)^{10}B	718.3	100 ± 8 (8.0)	2.50	96.24 ± 8.37 (8.7)

Na	$^{23}Na(p,p'\gamma)^{23}Na$	440.0	6693 ± 161 (2.4)	2.49	96.56 ± 5.89 (6.1)
Al	$^{27}Al(p,p'\gamma)^{27}Al$	1014.4	905 ± 22 (2.4)	2.80	88.95 ± 7.83 (8.8)
Si	$^{28}Si\ (p,p'\gamma)^{28}Si$	1779.0	100 ± 5 (5.2)	2.87	87.24 ± 6.98 (8.0)

Table 4

PIGE reaction yield, $E_{1/2}$, and $S_{E1/2}$ values determined for Li, B, Na, Al and Si comparator standards irradiated with 3 MeV protons.

Elem.	Standard	$C_{Standard}$ (%)	E_γ (keV)	$Y_{Standard}$ (counts/μc)	$E_{1/2}$ (MeV)	$S_{E1/2}$ (keV/mg/cm^2)
Li	$LiNH_2$	30.226	477.6	177472 ± 355 (0.2)	2.50	136.8 ± 3.2 (2.3)
B	$B(OH)_3$	17.49	718.3	788 ± 21 (2.7)	2.45	127.0 ± 6.4 (5.0)
Na	NaCl	39.34	440.0	68986 ± 552 (0.8)	2.51	94.58 ± 1.51 (1.6)
Al	AlCo alloy	98.998	1014.4	20370 ± 143 (0.7)	2.79	87.68 ± 8.77 (1.0)
Si	Si single crystal	100	1779.0	371 ± 14 (3.7)	2.92	86.71 ± 5.20 (6.0)

As could be seen in these tables, similar $S_{E1/2}$ values for the glass sample and standards were determined in the case of Na, Al, and Si (1-2 % bias), while higher $S_{E1/2}$ values for Li and B in standards, by 1.39 and 1.32 times, respectively, were measured.

Table 5 presents the concentration results obtained by PIGE for Li, B, Na, Al, and Si in NIST SRM-1412 glass sample and their assigned values (Table 1). Detection limits for these elements (corresponding to 3σ), were assessed using background area under characteristic peaks in the γ-ray spectrum.

Analytical uncertainties in Table 5 (coverage factor k = 1) were calculated by combining statistical counting uncertainties as well as stopping power uncertainties (originated from $E_{1/2}$ value determination) for sample and standard (percent uncertainty, in parenthesis). Mass fraction uncertainties for comparator standards are considered to be 0.1 %.

Table 5

Elemental concentrations determined by PIGE in NIST SRM-1412 glass sample, compared with assigned values given by U.S. National Institute of Standards and Technology (NIST).

Elem.	$C_{laboratory}$ (%)	$C_{assigned}$ (%)	Detection limit (%)
Li	2.00 ± 0.06 (2.8)	(2.09)	0.0013
B	1.68 ± 0.22 (13.1)	1.41 ± 0.05 (3.8)	0.1200
Na	3.89 ± 0.26 (6.8)	3.48 ± 0.05 (1.5)	0.0070
Al	4.46 ± 0.41 (9.2)	3.98 ± 0.13 (3.2)	0.0400
Si	26.8 ± 3.2 (11.9)	19.8 ± 0.1 (0.4)	0.8300

The concentrations of Li, B, Na, Al, and Si elements determined by PIGE in NIST SRM-1412 glass sample were found to be in agreement with certified/information values, in the uncertainty limits. Analytical uncertainties are situated in the range of 3-13 %.

3. Conclusions

The present measurements at the 3 MV Tandetron of IFIN-HH have confirmed that PIGE is a reliable ion beam analytical technique able to determine with a high accuracy and precision low Z elements like lithium, boron, sodium, aluminum, and silicon at percent levels in a glass type material (thick target).

The highest analytical sensitivity was found for Li and Na, their detection limits being of 13 and 70 ppm (part per million) respectively. For Al, B, and Si, detection limits of 400 ppm, 1200 ppm, and 8300 ppm, respectively, were determined in the investigated glass sample.

Acknowledgements

The author would like to acknowledge Dr. Ana Pantelică and Dr. Dan Pantelică of IFIN-HH for collaboration.

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