CrossMark

Towards rapid and simultaneous quantification of F, Li and Na in "as received" geological samples using PIGE technique

Alice Bejjani[1] · Radwan Sidaoui[1] · Mohamad Roumié[1] · Talal Darwish[2] · Bilal Nsouli[1]

Abstract This work presents a method for simultaneous proton induced gamma-ray emission analysis of fluorine, lithium, and sodium in "as received" geological reference materials. 1.7, 2.4 and 3.0 MeV proton energies were chosen for this study. The choice of the most appropriate incident energy was made after the study of the variation of the signal/background ratio, the limit of detection, the duration of the analysis and the number of counts/μC for each element. Quantitative calculation was achieved using an external standard and the so-called $E_{1/2}$ analytical approach. For this purpose, the thick target yield of the gamma rays at 110, 197, 440 and 478 keV were given between 1.1 and 3.0 MeV proton energies.

Keywords PIGE · Geological samples · Soil contamination · $E_{1/2}$ method · Light elements

Introduction

Elemental analysis of soil samples is important and has become prerequisite step for soil classification and assessment within studies in different areas such as pedology, agronomy and environmental sciences [1–5]. Normally, these studies, which depend on the

quantification of major, minor and trace elements, have to deal with a large number of samples. For instance, proper cartography for land assessment of a small agricultural area (< 1000 km^2) requires hundreds of samples to be analyzed [6]. Therefore, such kind of analysis needs simple, rapid and accurate analytical techniques.

Classical wet analytical techniques, such as atomic absorption spectroscopy (AA) and inductively coupled plasma mass spectrometry (ICP-MS), are used for the study of such type of samples and are known to be highly precise and to have low limits of detection (LOD < 0.1 ppm). However, for analysis of solid samples, such techniques need a laborious preparation procedure (e.g. digestion, purification, extraction, etc.), which becomes expensive and time consuming, especially when a large number of samples are in question [7–9]. Moreover, a technique such as laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), which permits the analysis of geological samples under solid form, still have accuracy limitation coming from several factors: matrix effects, lack of sufficient matrix matched reference materials, the need of quantitative calibration and sensitivity drift correction [10].

Elemental ion-based techniques, such as particle induced X-ray emission (PIXE) and particle induced gamma-ray emission (PIGE), have a high advantage regarding analysis of soil samples. In fact, using these techniques, a soil sample can be analyzed, with high accuracy and precision, in its solid form with minimum sample preparation. PIXE technique is a universal technique commonly used for the multi-elemental quantification of semi-heavy and heavy elements (Na $< Z <$ Pb) in geological and soil matrices [11–14]. The conventional PIGE technique, which uses protons with energies between 1–5 MeV, is a method of choice used for covering the

✉ Alice Bejjani
abejjani@cnrs.edu.lb

1 IBA Laboratory, Lebanese Atomic Energy Commission, National Council for Scientific Research, Airport Road, Riad El Solh, P.O. Box 11-8281, Beirut 11072260, Lebanon

2 National Center for Remote Sensing, National Council for Scientific Research, Riad El Solh, P.O. Box 11-8281, Beirut 11072260, Lebanon

Springer

quantification of light element ($Z < 15$) in "as received solid" samples with different matrices. However, from an analytical point of view, this type of analysis is not an easy task. In fact, such quantification needs to be done with (i) the use of appropriate external or internal standard, (ii) a prior determination of the thick target yield and/or the differential cross section for the emission of the adequate gamma-ray of the element of interest and (iii) the determination of the matrix composition of the analyzed samples. Furthermore, till now, there is no commercial simulation code for data treatment and absolute quantification. Mateus et al. [15] have developed a code for quantitative analysis of light elements in thick samples which to our knowledge still has some drawbacks.

In spite of these analytical difficulties, PIGE technique has been used in the analysis of solid thick samples for its high precision and accuracy. It has been positively tested in different fields for the quantification of species of common interest including applications to plants [16], pharmaceuticals [17, 18], environmental [19–21] and dental sciences [22]. It is also widely used for the determination of fluorine in soil, food and food packaging [19, 23, 24]. Therefore, the PIGE technique can be regarded as a good candidate for multi-elemental analysis of light elements present in solid samples. However, an appropriate compromise has to be found so as to guarantee good precision, high sensitivity, reasonable analysis time and low LOD.

Among others, the quantification of light elements in soil plays an essential role in the classification of soils for agriculture use. For example, lithium, boron and fluorine can be considered as toxic for given concentration [21, 23, 25–27] while sodium soil content is a direct indicator for soil salinity, diversity and dispersivity [28, 29]. When the analysis of Li, B and F in solid samples must be performed by PIGE technique, Na can be analyzed by both elemental IBA techniques i.e. PIGE and PIXE. However, the quantification of Na using PIXE technique needs a precise determination of the matrix composition of the analyzed sample as well as an exact calculation of the self absorption of the Na K-shell photon emission. In addition, the energy of Na K-series X-ray at 1.04 eV is close to the cutoff energy of the Si(Li) detector (in our case) which can highly affect the accuracy of the analysis.

In this work, we present the optimization of the PIGE technique to quantify simultaneously Li, F and Na in geological samples by taking into account the variation of the signal/background ratio, the limit of detection, the duration of the analysis and the number of counts/µC for each element of interest. Based on the work of Kiss et al. [30], we have chosen three different incident proton energies to work with: 1.7, 2.4 and 3.0 MeV. We have examined about ten geological reference samples with different matrices. With these reference materials, covering a large collection of different geological and soil sample types, we will study and discuss the effect of the matrix of each type of samples on the outcomes mentioned above. In addition, we will compare our results (element concentrations and thick target yield) with the ones presented in the literature.

Experimental

Sample preparation for thick target PIGE

Ten different geological reference materials from SARM/CRPG-Nancy (France) have been chosen for this work (GA, UB-N, DR-N, BX-N, GS-N, AC-E, BE-N, AN-G, DT-N and GL-O) [31]. The samples were dried at 378 °K till a constant weight is reached. A mass of 0.5 g of each sample was encircled with an external binder, i.e. the boric acid and then was pressed (2–4 ton/cm^2) into a pellet form. The analysis area (~ 1.2 cm diameter) was binder free. Two homemade standard materials, called LEB1 and LEB2, were made for the determination of $E_{1/2}$. Both are a mixture of the reference material GA with sodium fluoride and lithium carbonate with different quantities. LEB1 contains 6, 15 and 18%, from the total mass weight, of Li, F and Na respectively. LEB2 contains the two-thirds of the above mentioned amounts for the same elements. Pellets from these standard materials have been made using the same method of preparation mentioned above. A very thin ultra pure carbon layer was evaporated on the surface of all samples in order to ensure good surface conductivity as required by in-vacuum ion beam analysis techniques.

PIGE setup and data treatment

Proton beams were obtained from the NEC 1.7 MV 5-SDH tandem accelerator at the Lebanese Atomic Energy Commission. The PIGE experiments were carried out by using a 1.7, 2.4 and 3.0 MeV proton beam. The excitation functions of the gamma-ray emission reaction have been measured using proton beam in the energy range of 1–3 MeV. The beam (~ 3 mm diameter) hits the target at normal incidence. The emitted gamma rays were detected, at 45° referring to the direction of the beam, by an HPGe detector with 40% relative efficiency and FWHM ~ 1.9 keV at 1332 keV. The absolute efficiency curve of the detector was determined by using ^{152}Eu, ^{60}Co and ^{56}Co radioactive sources placed at the target position. The detector has a lead shielding to reduce the background due to natural gamma radiation. In order to have good accuracy in the charge measurement, the target was placed between aluminum wires which act as secondary electron suppressors, biased at -400 V. The distance between the detector and the target was fixed in such a way the dead time

correction during the measurements was less than 3% with a 30–80 nA beam current. The spectra were treated (determination of the peak area with accurate background subtraction) by using the SPECTR computer code (Kalfas 2000-Greece).

Results and discussion

Choice of gamma ray for each element

The choice of the gamma ray for the quantification of each analyzed element was governed by the highest emission cross section and by lack of interference with other gamma-rays from other elements. Based on the work of Savidou et al. and Kiss et al. [30, 32]. and the gamma energy range used in the current work we have chosen 110, 197, 478, and 440 keV as gamma rays emitted via nuclear reaction e.g. $^{19}F(p,p\gamma_{1-0})^{19}F$, $^{19}F(p,p\gamma_{2-0})^{19}F$, $^{7}Li(p,p\gamma_{1-0})^{7}Li$ and $^{23}Na(p, p\gamma_{1-0})^{23}Na$ for the analysis of ^{19}F, ^{7}Li and ^{23}Na, respectively.

Choice of incident ion energy

All analyzed samples have significant difference in their matrices composition. Accordingly, one should optimize the analytical conditions especially if multi-elemental detection of various samples is planned. For example, the choice of the optimum proton energy for F, Li and Na should take into consideration not only the cross section of the production of the chosen gamma ray of each element and its LOD but also the signal to background (S/B) ratio as well as the duration of the analysis time.

Potassium, calcium, aluminum, silicon, magnesium and iron are considered major elements in most geological samples; with a concentration range of each element varying between $\sim$ 1 and 25%. Iron concentration will not affect the background of the PIGE spectra, obtained by using conventional PIGE, as well as Ca and K due to their very low gamma rays production cross section. In contrast, the concentration of Mg, Al and Si can clearly affect the background of the PIGE spectra since they produce prompt gamma rays, with intensity from 2 to 4 orders of magnitude than K and Ca, in the range where the probability of Compton radiation emission is optimal [30].

Therefore, the chosen gamma ray for the studied elements (110 and 197 keV for F, 440 keV for Na and 478 keV for Li) will be drastically affected by the Compton background due to the gamma rays produced from the nuclear reaction ^{25}Mg (p, p'γ) ^{25}Mg (E_γ = 585 keV), ^{26}Mg (p, γ) ^{27}Al and ^{27}Al (p, p'γ) ^{27}Al (E_γ = 844 keV), ^{27}Al (p, p'γ) ^{27}Al (E_γ = 1014 keV), ^{24}Mg (p, p'γ) ^{24}Mg and ^{27}Al (p, $\alpha\gamma$) ^{24}Mg (E_γ = 1369 keV) and ^{25}Mg (p, p'γ) ^{25}Mg (E_γ = 1612 keV). Moreover, the energy of the chosen gamma-rays of F (110 and 197 keV) have energy lower than the gamma rays of Na, B and Li. Therefore, the F gamma rays will be affected by the Compton background due to the gamma rays of those elements.

Figure 1 illustrates three different PIGE spectra for two reference materials obtained at three different incident ion energies (1.7, 2.4 and 3.0 MeV). As it can be seen, a perceptible decrease of the background level is accompanied with the diminution of the incident ion energy. It is well known that the decrease of gamma production leads to an attenuation of the Compton background from various gamma rays. However due the differences between the geological samples composition, this attenuation is not with the same proportion for all the samples. Indeed UB-N matrix is composed mainly from SiO_2 (39%) and MgO (35%) conversely to BX-N matrix which is composed mostly of Al_2O_3 (54%) and Fe_2O_3 (23%).

Signal/background ratio (S/B)

Figure 2 presents the S/B ratio of all the analyzed geological samples using three different incident ions (black for 1.7 MeV, red for 2.4 MeV and green for 3.0 MeV). The background is defined by the SPECTR code by fitting a step function in the area of the peak in question. As it can be noticed from an overview of this figure, the use of 1.7 MeV assures good S/B ratio for sodium and especially for lithium. However, 2.4 MeV gives the best S/B ratio for Fluorine.

Furthermore, in order to demonstrate the influence of the matrix on the values of all obtained ratios, the S/B ratio of Fluorine E_γ = 110 keV of DR-N and GA were compared. Actually, fluorine mass percentage in both samples is 500 ppm. However S/B ratio of fluorine 110 keV gamma ray at 2.4 and 1.7 MeV for GA are nearly the same. This is contrary to S/B ratio of Fluorine 110 keV gamma ray in DRN where the S/B ration at 1.7 MeV is two-third of the one at 2.4 MeV.

Other parameters can still affect the choice of the incident ion energy than the S/B ratio; e.g., limit of detection, duration of the analysis and the number of counts/μC.

Limit of detection (LOD), time of analysis (T) and number of counts/μC (Nb/μC)

During this study the limit of detection

$$LOD = 3C\sqrt{B}I^{-1} \tag{1}$$

has been used [21]. This LOD depends on the number of counts/μC (I), the background under the gamma energy line of the element in question (B) and the concentration of this element (C). An examination of the LOD for the three

Fig. 1 Three different PIGE spectra for UB-N and BX-N geological samples analyzed by 1.7, 2.4 and 3.0 MeV incident proton energy. (Color figure online)
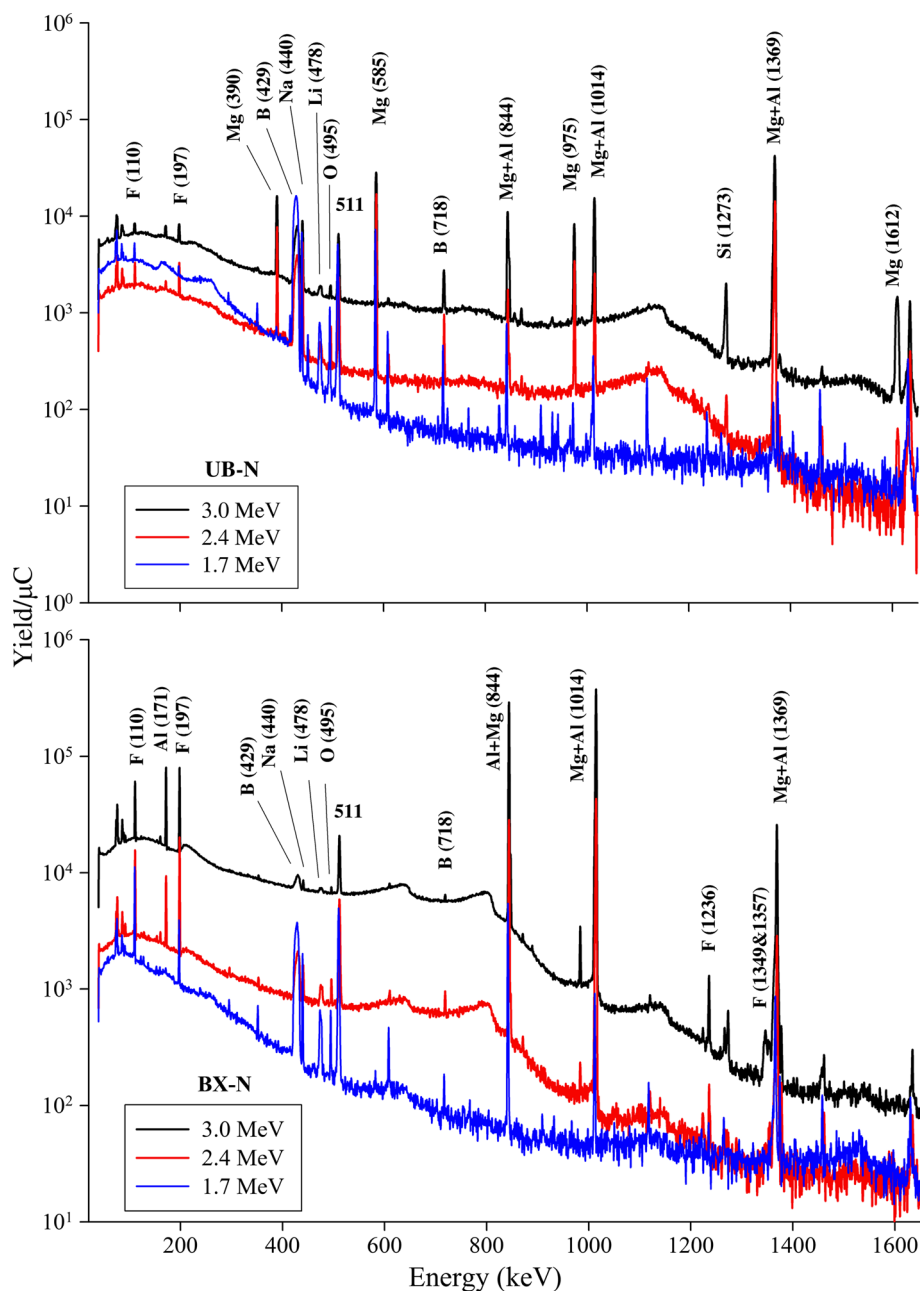
elements in every reference material helped us to make the best choice of the incident ion energy. For instance, a general view into the LOD presented in Table 1 showed that the LODs of fluorine analyzed at 2.4 and 3.0 MeV are 3–8 times better than the LOD of fluorine obtained at 1.7 MeV of incident energy. The smallest LOD of sodium is found at 3.0 MeV in DT-N equal to 22 ppm. However, at 1.7 MeV of incident energy, the LOD of lithium can be less than 4 ppm. So, if one has to choose the best incident ion energy for a multi-elementary study, 3 MeV is not, until now, the best choice although at this energy we noticed the best LOD for Na. Considering that Na is always in high mass percentage comparing to lithium (in ppm

range) especially in geological samples, a difference of few ppm will not certainly affect the detection of Na as it does to lithium detection.

On the other hand, the duration of the analysis has always been considered an important factor in such kind of analysis in addition to the number of counts/μC because the latter reflects the time of analysis and the statistical error as well. Actually, a statistical error around 2–3% can be considered appropriate. For example if 2500 counts in a peak are sufficient to obtain a 2% statistical error, we can accordingly calculate the time we need so the number of gamma rays of the element with the smallest mass percentage in a sample reaches this order. An example on the
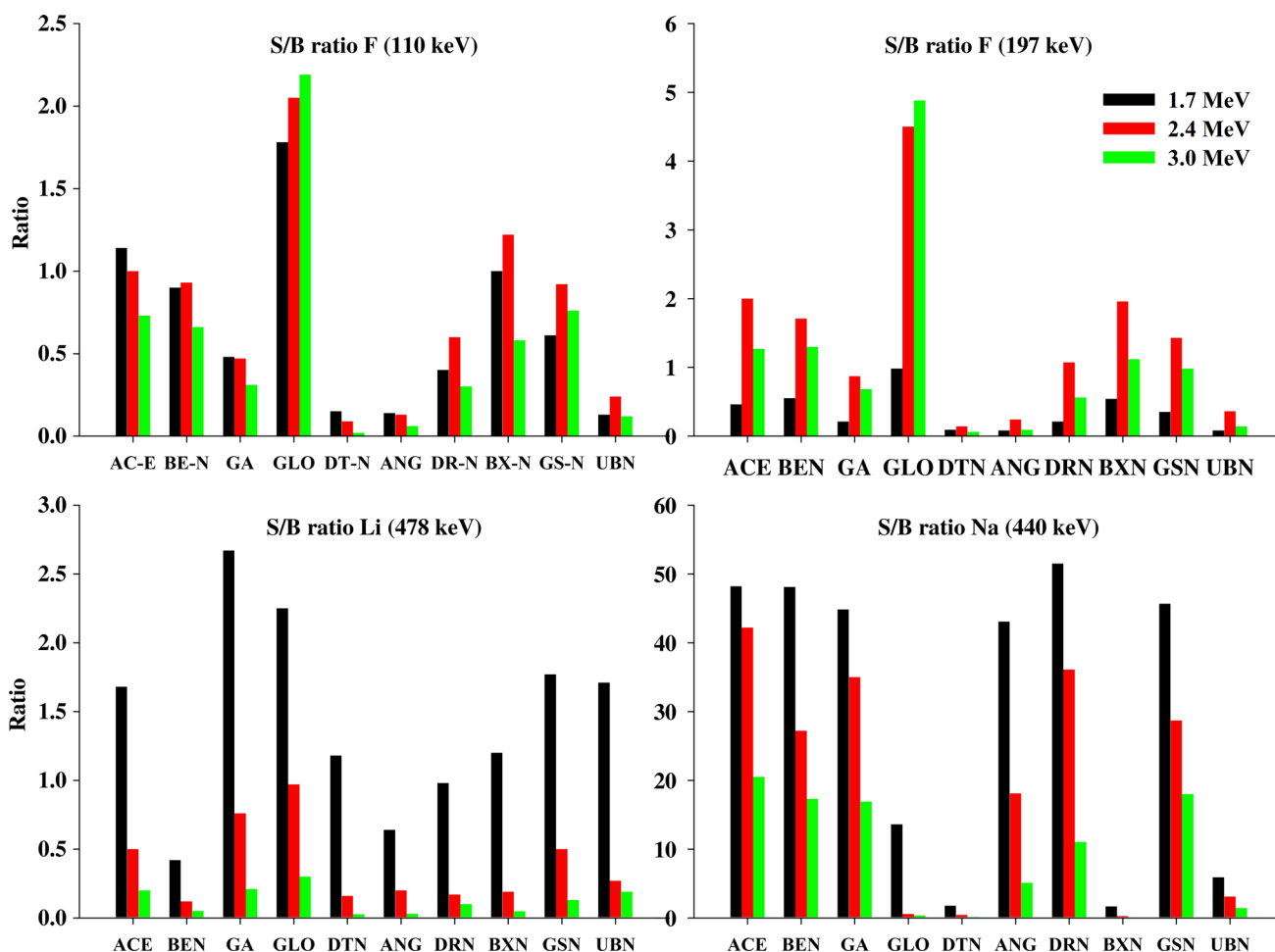
Fig. 2 S/B ratio of F gamma rays of 110 and 197 keV, Li gamma ray of 478 keV, and Na gamma ray of 440 keV in nine geological samples for 1.7 (black bars), 2.4 (red bars) and 3.0 MeV (green bars) proton energies. (Color figure online)

number of counts/μC values of Lithium is illustrated in Table 1. As it can be noticed, at 3.0 MeV, the values of Lithium's number of counts/μC are between 29 and 147. Therefore, to reach the 2500 counts, between 17 and 86 μC of incident ions are needed. In addition, a dead time less than 5% with a current less than 5 nA was considered for the analysis. Hence, the time of analysis must vary between 1 and 5 h to reach the number of counts in a peak with only 2% statistical error.

While the proton energy decreases less gamma emission from the sample is produced. This will reduce the dead time effects thus higher current can be employed. Following this logic, in order to reach this same number of counts at 2.4 MeV proton energy, the time required for the analysis should be between 20 min and 2 h (current $\sim$ 25 nA). At 1.7 MeV, the values of lithium gamma counts are in the range of 8–26 counts/μC. With a 120 nA current, there is no need of more than 13–43 min in order to reach the 2500 counts required. Consequently, results can be

obtained in short time at this latest incident ion energy compared to other incident ion energies.

Furthermore, if one seeks a quantification study with 3% statistical error, the time of analysis will decrease by $\sim$ 45% to reach, in the most unfavorable cases, 126, 56 and 19 min at 3.0, 2.4 and 1.7 MeV, respectively.

In fact, optimization of an analytical technique depends on the outcomes of the study and the real need of the end users. For instance, if light elements' cartography for a whole country is the goal of a study then the incident energy 3 MeV would have been excluded. In that case, the mean time of each analysis could exceed 2 h. In fact, for an agriculture area having a surface area of 1000 km^2, if only 1 sample is taken from a surface area of 1 km^2, the study will need more than 250 days of full accelerator running time.

Following this detailed study, guidelines for the better choice of the incident ion energy can be proposed. This is surely to make PIGE technique a reliable, accurate and

Table 1 LOD and number of counts/µC of F, Li and Na of four reference materials

| | Reference value | 50 µC | | | | | |
| | | 3.0 MeV | | 2.4 MeV | | 1.7 MeV | |
		LOD (ppm)	Counts/µC	LOD (ppm)	Counts/µC	LOD (ppm)	Counts/µC
BE-N							
F (110)	1000 ppm	14	1472	18	607	44	607
F (197)	1000 ppm	8	2254	11	836	102	836
Li	12 ppm	4	29	4	13	4	13
Na	2.44%	29	12,273	38	4619	68	4619
DT-N							
F (110)	40 ppm	18	39	13	19	24	4
F (197)	40 ppm	8	80	8	30	42	2
Li	26 ppm	9	51	6	24	4	8
Na	0.03%	22	135	37	48	94	9
GA							
F (110)	500 ppm	16	560	20	231	48	40
F (197)	500 ppm	10	847	12	329	128	13
Li	90 ppm	7	147	5	81	4	26
Na	3.35%	33	12,400	37	4720	80	809
GS-N							
F (110)	1050 ppm	14	1280	20	516	64	82
F (197)	1050 ppm	10	2032	14	702	148	26
Li	55 ppm	6	105	4	54	4	17
Na	2.80%	32	13,535	42	5056	80	871

The charge consumed in the analysis with 1.7, 2.4 and 3.0 MeV was 50 µC. The reference values of Na are given in % and those of F and Li and the LOD are given in ppm

rapid for a multi-elementary study of a large number of samples.

Depending on the parameters studied above, the choice lays on 3 MeV as incident ion energy for the quantification of Na alone because of low LOD values and high cross section at this energy. However, for multi-elementary study, Na as well as F can be detected and quantified at any incident ion energy. One should notice that if 1.7 MeV is used as incident ion energy the gamma ray 110 keV, instead of 197 keV, is better to consider for the quantification of fluorine. In fact, this gamma ray presented the best limit of detection and the highest number of counts/µC.

In the case of lithium, the increase of signal/background ratio of lithium 478 keV gamma ray with the decrease of incident ion energy was undeniable. Thus, 1.7 MeV should be used for the detection of lithium once present at lowest concentrations.

In order to find the best energy, for simultaneous quantification of Li, F and Na in geological samples, quantification results at the three proton incident energies are tested. This procedure helped also in the assessment of

the $E_{1/2}$ analytical approach. The corresponding results are presented in the following section.

Quantitative analysis

The concentration of each unknown analyzed element i, $C_{sam,i}$, can be given by the following equation [21, 33]:

$$C_{sam,i} = C_{ref,i} Y_{sam}(E_0) S_{sam}(E_{1/2}) [Y_{ref}(E_0) S_{ref}(E_{1/2})]^{-1} \tag{2}$$

where Y_{sam} is the yield of the measured gamma ray at proton energy E_0 and S is the stopping power calculated at proton energy $E_{1/2}$ (the subscripts 'sam' and 'ref' indicate the samples and reference material, respectively). The stopping power is calculated using the Bragg's law by adding up the stopping power of the major element of the matrix of each sample [34, 35]. The $E_{1/2}$ corresponds to the energy for which the thick target yield is half of its value at the incident energy, namely $Y(E_0) = 2Y(E_{1/2})$.

Table 2 shows the $E_{1/2}$ of 3.0, 2.4 and 1.7 MeV for each element in question. These $E_{1/2}$ are graphically calculated

Table 2 Values of $E_{1/2}$, expressed in MeV, for three different proton energies, calculated graphically from F, Li and Na thick-target gamma-ray yields

Proton energy (E_0) (MeV)	$E_{1/2}$ (F) of 110 keV	$E_{1/2}$ (F) of 197 keV	$E_{1/2}$ (Na) of 440 keV	$E_{1/2}$ (Li) of 478 keV
3	2.30	2.52	2.49	2.22
2.4	2.21	2.00	2.01	1.71
1.7	1.31	1.37	1.60	1.29

from the target yields presented in Figs. 3 and 4 of the chosen reactions for the three elements. Thick target yields, using LEB1 as a target, were drawn with 20–50 keV steps between 3.0 and 1.1 MeV. The presented data of fluorine, with both emitted gamma rays of 110 and 197 keV, extend available data from M.J. Kenny et al. work (detector at 135°) [36]. Na and Li data, with emitted gamma rays 440 and 478 keV respectively, complement data from the literature except for the values of Li below 2 MeV where the values, along with those of A. Antilla et al. (at 55°), diverge

from the values found by A. Savidou et al. (at 90°) [32, 37, 38].

Figures 5, 6 and 7 compare values between reference and calculated mass percentage of Li, F and Na, respectively in the eight reference materials for the three chosen incident proton energy. In order to properly evaluate the precision and the accuracy of the analytic strategy adopted, one reference material (GA) was considered as the reference in Eq. 1 for the quantification of Li, F and Na. The error bars of the calculated values cover the peak fitting errors, systematical errors (< 3% for charge integration and
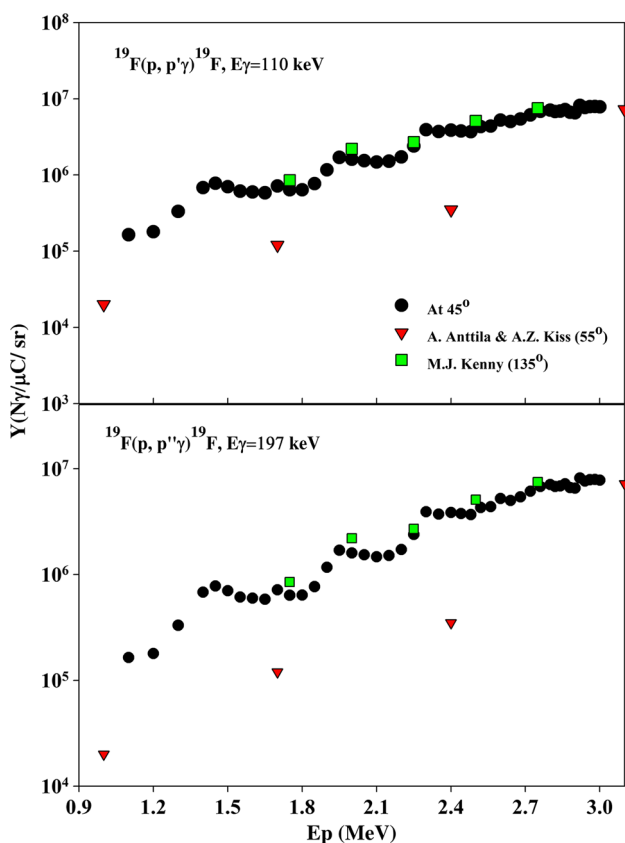

Fig. 3 Thick target yield of F gamma ray of 110 and 197 keV at 45°. Yields from LEB1 target are measured by varying the proton energy from 3000 to 1100 keV in steps between 20 and 50 keV. Data from literature are shown for comparison. The error bars related to experimental statistical and peak fitting uncertainties (< 6%) are smaller than the point symbol dimensions
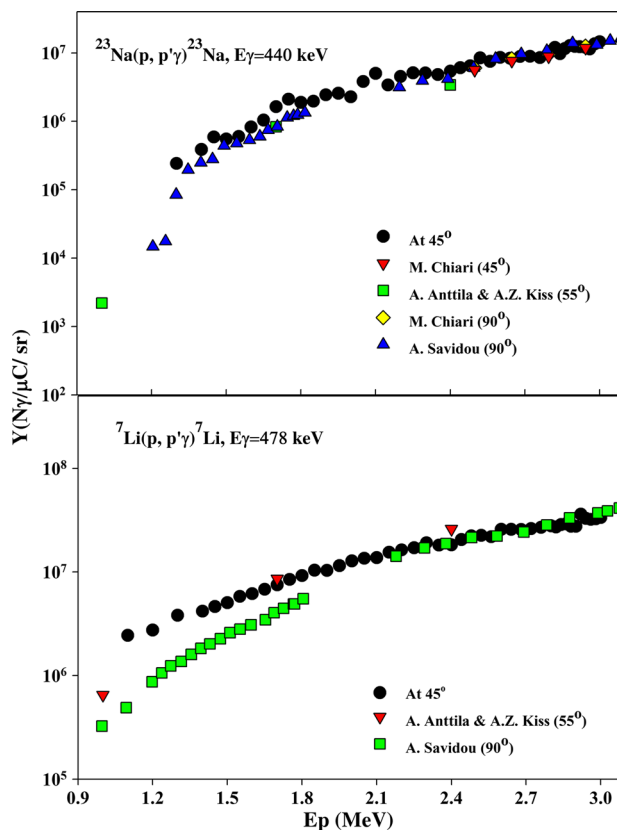
Fig. 4 Thick target yield of Na gamma ray of 440 keV and Li gamma ray of 478 keV at 45°. Yields from LEB1 target are measured by varying the proton energy from 3000 to 1100 keV in steps of 25 keV. Data from literature are shown for comparison. The error bars related to experimental statistical and peak fitting uncertainties (< 6%) are smaller than the point symbol dimensions

Fig. 5 Proposed (by SARM) and calculated values of Li mass percentage concentration in ppm. The error bars of the proposed values designate the 95% confidence limits
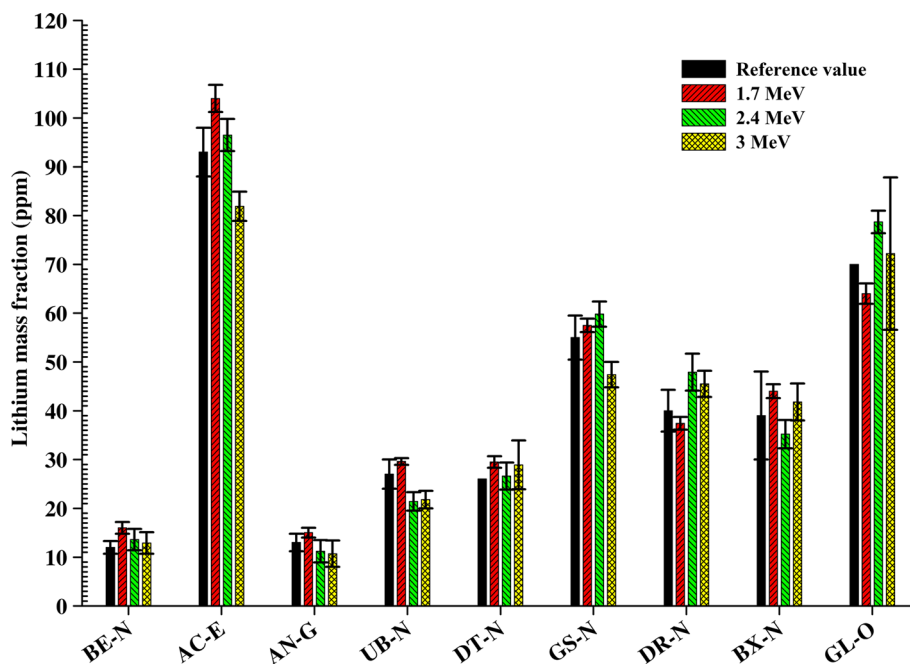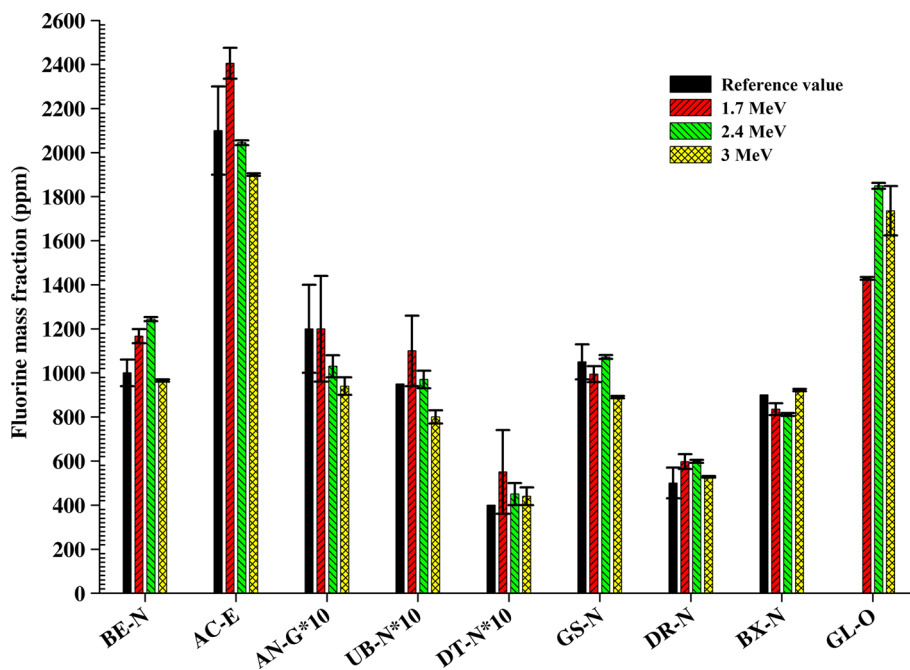

Fig. 6 Proposed (by SARM) and calculated values of F mass percentage concentration in ppm. The error bars of the proposed values designate the 95% confidence limits


detector efficiency) and sample composition uncertainty. Due to the low number of analysis and to the high standard deviation SARM/CRPG did not provide for some of the reference values a 95% confidence level band.

Difference between calculated and reference values of Na for most reference materials does not exceed 10% at 3 MeV and 5% at 1.7 and 2.4 MeV. Only for serpentine (UB-N), kyanite (DT-N) and bauxite (BX-N) type of samples, where Na levels are 10–50 times lower than for the rest of the geological samples (< 900 ppm), the

differences with the reference values have exceeded 20% to even reach 40% (BX-N case at 1.7 and 2.4 MeV). Nevertheless these calculated values were still in the given 95% confidence limits.

The results of lithium and fluorine obtained from the three incident energies are in a good agreement with the given ones. The difference between calculated and reference values haven't exceeded 15% for F for 62–75% of the analyzed geological standards and for Li for 77–82% of the mentioned samples. In fact, some of the reference values

Fig. 7 Proposed (by SARM) and calculated values of Na mass percentage concentration in ppm. The error bars of the proposed values designate the 95% confidence limits
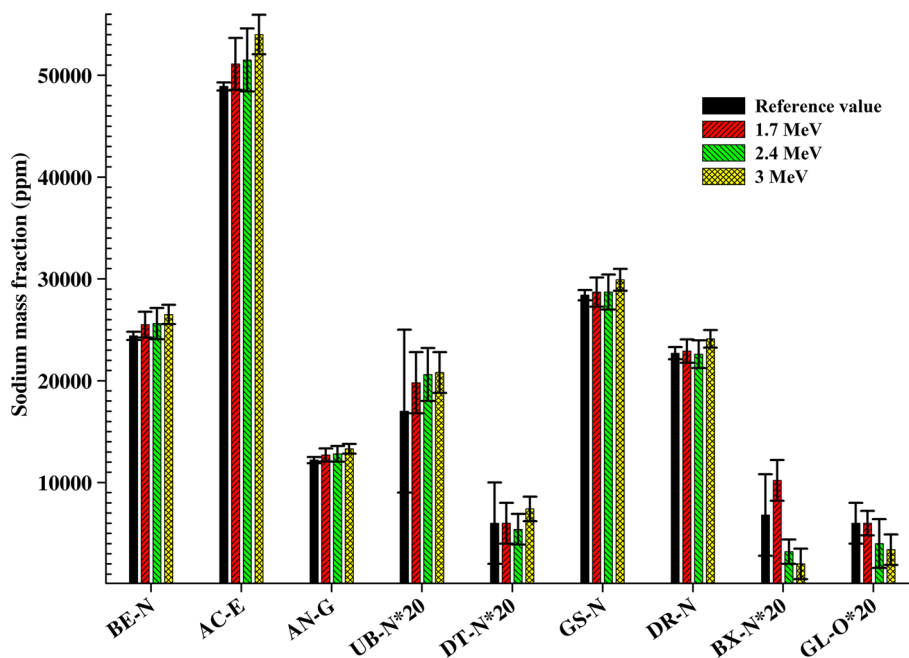
for these trace elements are given with a large 95% confidence level such as the case of Li in the BX-N sample (39 ± 9 ppm). Taking this into account, the calculated values of this latter at the three proton energies can be considered acceptable. In addition, after a closer examination at the calculated values of F we would suggest using 3 MeV proton beam for the analysis of basalt (BE-N), kyanite (DT-N) and diorite (DR-N) types of samples. In fact, for these types the difference between calculated and reference values was less than 10% at 3 MeV and between 12 and 30% at the other utilized proton energies.

Another calculation approach was used in the literature to characterize fluorine in soil. Srivastava et al. and Dhorge et al. have used an internal standard (Li_2CO_3) to quantify fluorine amount in their samples [19, 24]. Moreover, Chhillar et al. have recently published results of F, Li, B and Na simultaneous determination in glass samples by mixing the samples either in cellulose or graphite matrices [39]. We did not consider using these methods in our study because of their lengthier sample preparation procedure. It may not have an influence when only ten samples are in question but when it comes to apply this method to thousands of collected samples such factor cannot be neglected.

Conclusions

In this work, we presented a study aiming to select the most appropriate incident ion energy to be used for rapid simultaneous quantification of F, Li and Na in geological samples. The matrix effect of each sample, the S/B ratio, the LOD, the number of counts/μC and the analysis time

were studied. Their effect on the quantification of some selected soil elements was determined. We also demonstrated the effect of the graphically chosen $E_{1/2}$, from the thick target yield, for each element on the quantitative results.

From the studied parameters, other than the choice of $E_{1/2}$, we concluded that the 3 MeV proton energy is the best to be used for Na quantification. However, we found out that all the three proton energies used have given calculated values very comparable to the reference ones. Using 1.7 and 2.4 MeV proton energies, the accuracy of the results have exceeded the 95%.

For Li and F, all the three chosen incident energies gave calculated values with good agreement with the proposed ones. However, in case of low concentrations of Li and F, 1.7 MeV incident energy is considered as the best choice to conduct any trace analysis. Also, if basalt, kyanite or diorite type of samples are in question, we would suggest working with the 3 MeV proton energy due to the high accuracy (90%) comparing to the other two proton energies.

References

1. Thiffault E, Paré D, Guindon L et al (2013) Assessing forest soil base cation status and availability using lake and stream sediment

geochemistry: a case study in Quebec (Canada). Geoderma 211–212:39–50. https://doi.org/10.1016/j.geoderma.2013.06.006

2. Yanai J, Okada T, Yamada H (2012) Elemental composition of agricultural soils in Japan in relation to soil type, land use and region. Soil Sci Plant Nutr 58:1–10. https://doi.org/10.1080/00380768.2012.658349

3. Navarro FJG, Ortiz-Villajos JAA, Jiménez CJS, Ballesta RJ (2011) Red soil geochemistry in a semiarid Mediterranean environment and its suitability for vineyards. Environ Geochem Health 33:279–289. https://doi.org/10.1007/s10653-010-9340-8

4. Mwalongo D, Mohammed NK (2013) Determination of essential and toxic elements in clay soil commonly consumed by pregnant women in Tanzania. Radiat Phys Chem 91:15–18. https://doi.org/10.1016/j.radphyschem.2013.06.002

5. Zhou J, Wang Y, Yue T et al (2012) Origin and distribution of trace elements in high-elevation precipitation in southern China. Environ Sci Pollut Res 19:3389–3399. https://doi.org/10.1007/s11356-012-0863-7

6. Frangi JP, Richard D (1997) Heavy metal soil pollution cartography in northern France. Sci Total Environ 205:71–79. https://doi.org/10.1016/S0048-9697(97)00184-8

7. Falciani R, Novaro E, Marchesini M, Gucciardi M (2000) Multi-element analysis of soil and sediment by ICP-MS after a microwave assisted digestion method. J Anal At Spectrom 15:561–565. https://doi.org/10.1039/b000742k

8. Butler OT, Cairns WRL, Cook JM, Davidson CM (2017) Atomic spectrometry update—a review of advances in environmental analysis. J Anal At Spectrom 32:11–57. https://doi.org/10.1039/c6ja90058e

9. Angino E, Billings G (1972) Atomic absorption spectrometry in geology. Elsevier, Amsterdam

10. Liu YS, Hu ZC, Li M, Gao S (2013) Applications of LA-ICP-MS in the elemental analyses of geological samples. Chin Sci Bull 58:3863–3878. https://doi.org/10.1007/s11434-013-5901-4

11. Mesjasz-Przybyłowicz J, Przybyłowicz WJ (2011) PIXE and metal hyperaccumulation: from soil to plants and insects. X-Ray Spectrom 40:181–185. https://doi.org/10.1002/xrs.1304

12. Inyang EP, Oketayo OO, Obiajunwa EI (2012) Proton induced X-ray emission analysis of soils with various length of fallow: the effect on soil total elemental composition. Soil Tillage Res 124:178–182. https://doi.org/10.1016/j.still.2012.03.014

13. Markwitz A, Barry B, Shagjjamba D (2008) PIXE analysis of sand and soil from Ulaanbaatar and Karakurum, Mongolia. Nucl Instrum Methods Phys Res B 266:4010–4019. https://doi.org/10.1016/j.nimb.2008.07.010

14. Nsouli B, Darwish T, Thomas JP et al (2004) Ni, Cu, Zn and Pb background values determination in representative Lebanese soil using the thick target PIXE technique. Nucl Instrum Methods Phys Res B 219–220:181–186. https://doi.org/10.1016/j.nimb.2004.01.050

15. Mateus R, Jesus AP, Ribeiro JP (2005) A code for quantitative analysis of light elements in thick samples by PIGE. Nucl Instrum Methods Phys Res B 229:302–308. https://doi.org/10.1016/j.nimb.2004.11.019

16. Devi KN, Sarma HN, Kumar S (2008) Estimation of essential and trace elements in some medicinal plants by PIXE and PIGE techniques. Nucl Instrum Methods Phys Res B 266:1605–1610. https://doi.org/10.1016/j.nimb.2007.12.004

17. Nsouli B, Zahraman K, Bejjani A et al (2006) On the direct quantification of celecoxib in commercial solid drugs using the TT-PIXE and TT-PIGE techniques. Nucl Instrum Methods Phys Res B 249:692–696. https://doi.org/10.1016/j.nimb.2006.03.119

18. Nsouli B, Bejjani A, Della Negra S et al (2010) Ion beam analysis and PD-MS as new analytical tools for quality control of pharmaceuticals: comparative study from fluphenazine in solid dosage forms. Anal Chem 82:7309–7318. https://doi.org/10.1021/ac101247d

19. Srivastava A, Chhillar S, Singh D et al (2014) Determination of fluorine concentrations in soil samples using proton induced gamma-ray emission. J Radioanal Nucl Chem. https://doi.org/10.1007/s10967-014-3661-5

20. Calzolai G, Chiari M, Lucarelli F et al (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 B 268:1540–1545. https://doi.org/10.1016/j.nimb.2010.03.002

21. Nsouli B, Darwish T, Zahraman K et al (2006) Total boron assessment in soil samples from dry Mediterranean region using the thick target-particle induced gamma-ray emission technique. Nucl Instrum Methods Phys Res B 249:566–570. https://doi.org/10.1016/j.nimb.2006.03.056

22. Carvalho ML, Karydas AG, Casaca C et al (2001) Fluorine determination in human healthy and carious teeth using the PIGE technique. Nucl Instrum Methods Phys Res B 179:561–567. https://doi.org/10.1016/S0168-583X(01)00684-X

23. Schaider LA, Balan SA, Blum A et al (2017) Fluorinated compounds in U.S. fast food packaging. Environ Sci Technol Lett 4:105–111. https://doi.org/10.1021/acs.estlett.6b00435

24. Dhorge PS, Acharya R, Rajurkar NS et al (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 311:1803–1809. https://doi.org/10.1007/s10967-016-5118-5

25. Eikmann T, Kloke A, Eikmann S (1993) Environmental medical and toxicological assessment of soil contamination BT. In: Arendt F, Annokkée GJ, Bosman R, Van Den Brink WJ (eds) Contaminated Soil'93: fourth international KfK/TNO conference on contaminated soil, May 3–7, 1993, Berlin, Germany. Springer, Dordrecht, pp 327–336

26. Shahzad B, Mughal MN, Tanveer M, Gupta D (2017) Is lithium biologically an important or toxic element to living organisms? An overview. Environ Sci Pollut Res. https://doi.org/10.1007/s11356-016-7898-0

27. Shahzad B, Tanveer M, Hassan W et al (2016) Plant physiology and biochemistry lithium toxicity in plants: reasons, mechanisms and remediation possibilities—a review. Plant Physiol Biochem 107:104–115. https://doi.org/10.1016/j.plaphy.2016.05.034

28. Munns R, Tester M (2008) Mechanisms of salinity tolerance. Annu Rev Plant Biol 59:651–681. https://doi.org/10.1146/annurev.arplant.59.032607.092911

29. Parameswaran TG, Sivapullaiah PV (2017) Influence of sodium and lithium monovalent cations on dispersivity of clay soil. J Mater Civ Eng. https://doi.org/10.1061/(ASCE)MT.1943-5533.0001877

30. Kiss AZ, Koltay E, Nyakó B et al (1985) Measurements of relative thick target yields for PIGE analysis on light elements in the proton energy interval 2.4-4.2 MeV. J Radioanal Nucl Chem Artic 89:123–141. https://doi.org/10.1007/BF02070210

31. Geostandards. http://helium.crpg.cnrs-nancy.fr/SARM/pages/geostandards.html

32. 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. Nucl Instrum Methods Phys Res B 152:12–18. https://doi.org/10.1016/S0168-583X(98)00962-8

33. 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 Artic 185:273–291. https://doi.org/10.1007/BF02041301

34. Tesmer J, Nastasi Micheal A (1995) Handbook of modern ion beam materials analysis. Materials Research Society, Pittsburgh

35. Ishii K, Valladon M, Debrun J-L (1978) The average stopping power method for accurate charged particle activation analysis. Nucl Instrum Methods 150:213–219. https://doi.org/10.1016/0029-554X(78)90369-5

36. Kenny MJ (1981) Thick target gamma yields from fluorine. Aust J Phys 34:35–42

37. Chiari M, Alves E, Bogdanović Radović I et al (2015) Measurement of proton induced γ-ray emission cross sections on Na from 1.0 to 4.1 MeV. Nucl Instruments Methods Phys Res B. https://doi.org/10.1016/j.nimb.2017.01.043

38. Anttila A, Hänninen R, Räisänen J (1981) Proton-induced thick-target gamma-ray yields for the elemental analysis of the Z = 3–9, 11–21 elements. J Radioanal Chem 62:293–306. https://doi.org/10.1007/BF02517360

39. 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 86:11167–11173. https://doi.org/10.1021/ac5024292