

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

Pooja S. Dhorge¹ · R. Acharya¹ · N. S. Rajurkar² · Vikas Chahar³ · Vishal Tuli³ · A. Srivastava³ · P. K. Pujari¹

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Abstract Particle induced gamma-ray emission method was used to quantify total fluorine (F) concentrations in soil and food samples obtained from fluoride affected as well as non-affected areas of Punjab state, India. Samples, standards and reference materials in pellet form with lithium as in situ current normalizer were irradiated using 4 MeV proton beam from the tandem particle accelerator. Characteristic prompt gamma rays at 197 keV from ¹⁹F and 478 keV from ⁷Li were measured using a HPGe detector system. Fluorine concentrations in soil and food samples were 279–3138 and 51–211 mg kg⁻¹, respectively.

Keywords Fluorine · Soil · Food · Reference materials · PIGE · Gamma-ray spectrometry

Introduction

Fluorine (F) is an essential as well as toxic trace element and it is present ubiquitously in the environment. The toxicity of fluorine in the form of fluoride is associated with its high chemical and biological activity in human body [1]. Fluoride (F⁻) gets absorbed in the gastrointestinal tract

and rapidly migrates across the biological membranes. It negatively influences many metabolic, structural, and cellular functions. The toxic effect of fluoride includes induction of inflammatory reactions, cell contractile responses, inhibition of protein synthesis, cell cycle progression, oxidative stress and DNA damage [2]. Many of these cellular events ultimately lead to cell death or apoptosis. F is found in the form of fluoride in soil and water. Small amount of fluoride is beneficial in preventing dental carries (1–1.5 mg L⁻¹) which strengthens the enamel; whereas its long exposure is found to be harmful to bones and teeth. Fluoride is considered to be beneficial in drinking water at a level of about 0.7 mg L⁻¹ but it is harmful once it exceeds the safe limit of 1.5 mg L⁻¹ set by World Health Organization [3]. It has been reported that fluoride concentration in the range of 1.5–4 mg L⁻¹ causes dental fluorosis [4], whereas prolonged exposure at higher concentrations i.e., 4–10 mg L⁻¹ leads to skeletal fluorosis [5]. It has been reported by Central Ground Water Board (CGWB, Ministry of Water Resources, River Development and Ganga Rejuvenation) of the Government of India that the states of Andhra Pradesh, Bihar, Delhi, Gujarat, Haryana, Jammu and Kashmir, Karnataka, Kerala, Madhya Pradesh, Maharashtra, Odisha, Punjab, Rajasthan, Tamil Nadu, and Uttar Pradesh are affected by fluoride related toxicity [6]. In the state of Punjab [7], the present study area, there are 11 districts namely Amritsar, Bhatinda, Faridkot, Fatehgrah Sahib, Ferozepur, Gurdaspur, Mansa, Moga, Muktasar, Patiala, and Sangrur, which have shown fluoride concentration in ground water higher than the permissible limit of 1.5 mg L⁻¹. It is known that main sources of fluorine in human body are water and food and they provide about 40% of the intake of total F [8]. The main sources of fluoride in soil are minerals like fluorite, fluorapatite, apatite, biotite, tourmaline, muscovite,

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

✉ N. S. Rajurkar
nlimma@rediffmail.com

¹ Radiochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India

² Department of Chemistry, Savitribai Phule Pune University, Ganeshkhind, Pune 411007, India

³ Department of Chemistry, Panjab University, Chandigarh 160014, India

phlogopite and cryolites [3], which are present in the earth's crust. Fluorine is also known to be present in significant amount in products of coal combustion [9] besides pesticides [10] and fertilizers [11].

Various factors that govern the release of fluoride into water from fluoride-bearing minerals are (i) the chemical constituents present in the water, (ii) the presence and accessibility of fluoride minerals to water, and (iii) the contact time between the source mineral and water [12]. Overall water quality (e.g., pH, hardness, and ionic strength) also plays a key role by influencing mineral solubility, complexation and sorption/exchange reactions [13]. The irrigation of soil using fluoride rich water may further lead to increase in the fluoride content of the soil in addition to fluorine derived from use of agrochemicals. Therefore, it becomes essential to determine concentration of total F in soil, used for cultivation. Wet-chemical techniques like potentiometry [14], colorimetry, fluoride ion selective electrode [15, 16] and ion chromatography [17] are routinely used to determine trace concentration of F in water. However, samples like soil and food are not favorable matrices for these techniques. These methods are based on chemical dissolution/separation followed by detection. Thus, for solid samples the above mentioned chemical technique are destructive in nature, time consuming and requires tedious chemical treatments which may lead to contamination or evaporation of F. In view of this, a technique which can determine F non-destructively i.e., using directly solid samples without any chemical dissolution is preferred. In this respect, particle induced gamma-ray emission (PIGE) [18, 19], an ion beam analysis (IBA) technique, is suitable for determination of low concentration of fluorine using smaller mass of the sample. PIGE is an accelerator based isotope specific online technique for low Z elements which involves measurement of prompt gamma-rays from nuclear reactions like $(p, p'\gamma)$, $(p, \alpha\gamma)$, (p, γ) and $(p, n\gamma)$ [18]. Using low energy proton beam (2–5 MeV), It is capable of determining low Z elements ($3 \leq Z < 17$, except for C, N and O) [18–22]. The determination of C, N, O by PIGE is possible though with poor (higher) detection limits due to use of less abundant isotopes like ^{13}C and ^{18}O [18]. However, at higher proton energy (>7 MeV) C, N and O can easily be determined at low (trace) concentration levels [18, 22]. Main advantage of the PIGE method is direct use of solid samples [23–25]. PIGE has been extensively applied for the determination of total fluorine in various fields like pharmaceuticals [26] glass [27–30], aerosols [31], geological [32, 33] and biological samples [24, 34–36], geological and environmental reference materials [37] along with thin films and functionalized carbon nanotubes [38]. For determination of F contents, PIGE is preferred over techniques like particle induced X-ray emission

(PIXE), X-ray fluorescence (XRF) and neutron activation analysis (NAA), which are not routinely used due to low energy X-ray of F (for X-ray based techniques) or short half-life (^{20}F , 11.4 s) (for NAA). Other techniques which can determine fluorine in samples like soil are colorimetry, spectrophotometry and F-ion-sensitive electrode [39], whereas direct solid sample analysis can be carried out by high-resolution graphite furnace molecular absorption spectrometry [40]. In the present study, the concentrations of F in soil and food samples, obtained from fluoride affected as well as non-affected areas districts of Punjab state, were determined using in situ current normalized PIGE method. Experimental methodology, results of F concentrations, total uncertainties and 3σ detection limits are presented.

Experimental

Sample collection and preparation

Soil samples

Soil samples were collected from different locations of Punjab at a depth ranging from 5 to 30 cm by using normal Auger method. The samples were dried below 60 °C for 12 h and ground into fine powder by using an agate mortar. Powder samples were homogeneously mixed with cellulose and constant amount of Li_2CO_3 . The samples thus obtained were pressed using a hydraulic press to get pellet of uniform thickness.

Food samples

To estimate the F contents and also possible uptake in food samples grown in the very same soil, food samples (rice) from the same locations were also collected for analysis. Samples were dried at 60 °C and powdered. Powder samples were homogeneously mixed with cellulose and constant amount of Li_2CO_3 . The samples thus obtained were pressed using a hydraulic press to get pellet of uniform thickness.

Standards and reference materials

Standards for F were prepared by mixing homogeneously varying amount of NaF (100–3000 mg kg^{-1}) and constant amount of lithium carbonate (Li_2CO_3) (about 10 mg of Li) in cellulose matrix. Reference materials were prepared in similar way to that of soil samples. Accelerator based experiments might be associated with variation in the beam current during the irradiation. Therefore, beam current measurement and normalization is a key aspect in PIGE.

The normalization can be done either by measuring the beam current directly from conducting target or by making use of Rutherford back scattering (RBS) [41] or from the target (powdered sample) mixed with graphite, if target is non-conducting. In present work, current was normalized by externally adding the Li in the form of Li_2CO_3 to monitor current fluctuations in it. The in situ current normalizer works in the principle as given here: the relative count rate per mg kg^{-1} (ppm) of Li (current normalizer) of sample to sample or sample to standard is directly proportional to beam current fluctuation, if any, provided Li is homogeneously distributed in the sample. The condition for selecting an element as the current normalizer is that it is sensitive towards PIGE and it should not be present in the sample of interest. PIGE experiments were carried out at FOTIA, BARC, Mumbai. Some of the experiments were carried out at 3 MV Tandatron at IOP, Bhubaneswar. The target pellets in cellulose matrix with added Li were irradiated, under high vacuum (10^{-6} torr) conditions, and the characteristic gamma rays at 197 and 1236 keV from ^{19}F ($p, p'\gamma$) ^{19}F and at 478 keV from ^7Li ($p, p'\gamma$) ^7Li were measured using 30% relative efficiency high purity germanium (HPGe) detector coupled with PC based 8 k multi-channel analyzer (MCA). The detector was placed perpendicular to the direction of beam axis at a distance of 7 cm from the target ladder. The time of irradiation was kept 30–60 min depending on the F concentration and also for getting higher counts under the peaks of interest. The PIGE spectra for soil and food samples are given in Figs. 1 and 2, respectively. The gamma-ray spectra obtained from different samples were analyzed using peak-fit PHAST software [42]. The counts under the peaks of 197 and 478 keV were in the range of 10,000–50,000 so as to get higher counts (peak area) of interest and to get minimum or low counting statistical error.

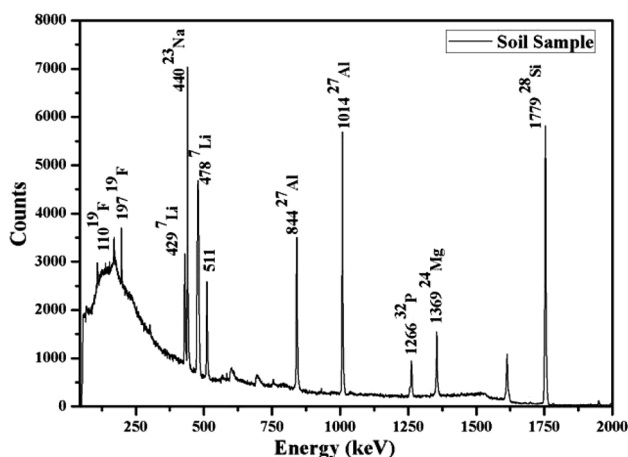


Fig. 1 PIGE spectrum of a soil sample using 4 MeV proton beam showing F and Li peaks ($t_m = 900$ s)

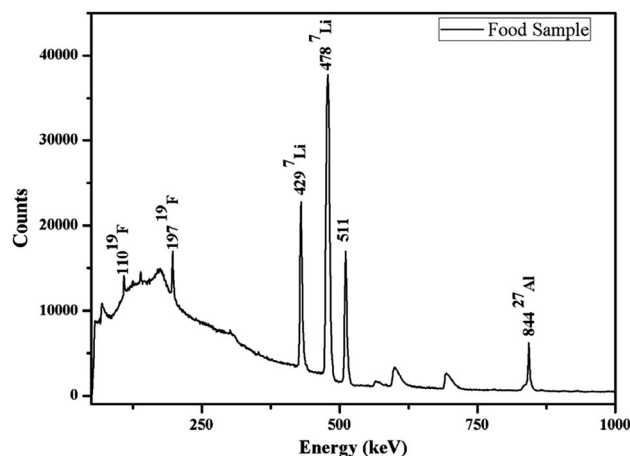


Fig. 2 Typical PIGE spectrum of a food sample using 4 MeV proton beam showing F and Li peaks ($t_m = 3250$ s)

Calculations

Relative method was used for the determination of absolute concentration of F. Concentration of F was determined using Eq. (1).

$$C_x \text{ (mg kg}^{-1}\text{)} = \frac{[\text{CPS}_x/S_{CN}]_{\text{sample}}}{S_{x,N}} \tag{1}$$

where C_x is the concentration of analyte of interest (in this case F), CPS_x is counts per second at 197 keV from ^{19}F , S_{CN} is sensitivity of current normalizer using 478 keV from ^7Li and $S_{x,N}$ is current normalized sensitivity of F using count rate of 197 keV of F standard and sensitivity of current normalizer Li.

Current normalized sensitivity of F ($S_{x,N}$) was determined using Eq. (2),

$$S_{x,N} = \frac{(\text{CPS})_x}{C_x \times S_{CN}} \tag{2}$$

where $(\text{CPS})_x$ is the count rate of 197 keV gamma-ray of ^{19}F , C_x is the concentration of F in mg kg^{-1} in the pellet and S_{CN} is the sensitivity of current normalizer (Li) obtained using following Eq. (3),

$$S_{CN} = \frac{(\text{CPS})_{\text{Li}}}{C_{\text{Li}}} \tag{3}$$

where $(\text{CPS})_{\text{Li}}$ is the count rate of 478 keV gamma-rays of Li, and C_{Li} is the concentration of Li in mg kg^{-1} in the pellet. Further details of calculations can be found in our earlier publications [19–21]. The concentration of F in soil samples was determined using the sensitivity of F obtained from the Eq. 1. For normalizing the effect of beam current fluctuations, the in situ current normalizing element (Li) was added in constant amount to each target of sample and standard.

The 3σ detection limit of F in the present method was calculated by standard calculation equation using sample background counts and elemental sensitivity at 197 keV peak of F obtained using 4 MeV proton beam as reported earlier in our previous paper [19, 20].

Results and discussion

The results of F concentrations of three RMs namely AGV-1, G-2 and 2695 (H) obtained by in situ current normalized PIGE method are given in Table 1. The concentrations are in the range on 426–1257 mg kg⁻¹ and the

percent deviations are in the range of ± 0.2 –2.5%, with respect to the certified values. The propagated uncertainties on the results are in the range of ± 2 –5%, which are due to counting statistics of peak areas of 197 keV (¹⁹F) of sample and standard as well as 478 keV of in situ current normalizer (⁷Li) and uncertainties on their corresponding masses.

The standardized method was applied to a total of 27 soil and 26 food (rice) samples for determining total F concentration. Concentrations of F determined in soil and food samples are in the range of 279–3138 mg kg⁻¹ (Table 2) and 51–211 mg kg⁻¹ (Table 3), respectively. The associated propagated (as described earlier)

Table 1 Determined concentrations of F (mg kg⁻¹) in three reference materials by PIGE method: method validation

RM code	Matrix	This work	Certified value	% Deviation
USGS CRM AGV-1	Rock	426 ± 20	425 ± 50	+0.24
NIST SRM 2695 (H)	Grass	284 ± 13	277 ± 27	+2.5
USGS CRM G-2	Rock	1257 ± 39	1280 ± 80	-1.8

Table 2 Determined concentrations of F (mg kg⁻¹) in soil samples by PIGE method

Samp. no.	District	Location	Concentration (mg kg ⁻¹)	Propagated uncertainty (%)
S1	Amritsar	Verka	917 ± 14	1.2
S2	Bathinda	Modh	1462 ± 22	1.5
S3	Barnala	Sehna	1027 ± 14	1.4
S4	Bhatinda	Talwandi sabu	695 ± 9	1.4
S5	Chandigarh	Chandigarh	452 ± 6	1.3
S6	Faridkot	Faridkot	3138 ± 74	2.4
S7	Faridkot	Koth Kupra	834 ± 12	1.4
S8	Fatehgarh Sahib	Amloh	1430 ± 21	1.4
S9	Fazilka	Fazilka	853 ± 16	1.9
S10	Ferozpur	Ahal khurd	1797 ± 27	1.5
S11	Gurdaspur	Dhariwal	500 ± 8	1.6
S12	Gurdaspur	Gurdsarpur	761 ± 11	1.4
S13	Hoshiarpur	Hoshiarpur	279 ± 4	1.2
S14	Jalandhar	Phillaur	511 ± 6	1.2
S15	Kapurthala	Kapurthala	396 ± 5	1.2
S16	Ludhiana	Mangat	945 ± 15	1.6
S17	Mansa	Peekhi	1105 ± 17	1.5
S18	Mansa	Jhuhir	947 ± 13	1.4
S19	Moga	Moga	1570 ± 27	1.7
S20	Mohali	Derabasi	869 ± 13	1.5
S21	Muktsar	Muktsar	1490 ± 25	1.7
S22	Nawanshahr	Andh	307 ± 5	1.4
S23	Patiala	Patiala	1198 ± 21	1.8
S24	Patiala	Nabha	611 ± 7	1.2
S25	Ropar	Chamkur sahib	384 ± 5	1.2
S26	Sangrur	Lehragaga	1717 ± 38	2.2
S27	Taran taran Sahib	Valtoha	364 ± 4	1.1

Table 3 Determined concentrations of F and detection limits (mg kg^{-1}) in food samples by PIGE method

No.	District	Location	Concentration (mg kg^{-1})	3σ detection limit (mg kg^{-1})
F1	Amritsar	Walipur	54 ± 2	17
F2	Barnala	Barnala	179 ± 5	22
F3	Faridkot	Jaitho	77 ± 2	15
F4	Faridkot	Rorikaapur	137 ± 3	18
F5	Fatehgarh Sahib	Lohari kalan	194 ± 5	25
F6	Fatehgarh Sahib	Dhangeri	53 ± 2	15
F7	Fatehgarh sahib	Lohari kalan	75 ± 2	15
F8	Fatehgarh Sahib	Dhan Geri	211 ± 5	24
F9	Firozpur	Gati harike	86 ± 2	13
F10	Firozpur	Kalhewala	64 ± 2	15
F11	Firozpur	Chat tibbi tayab	80 ± 2	14
F12	Firozpur	Sodhe ke	58 ± 2	14
F13	Hoshiarpur	Maujowal	63 ± 2	18
F14	Jalandhar	Bangiwal	56 ± 2	18
F15	Kapurthala	Kurshedpur	68 ± 3	16
F16	Ludhiana	Hujra	96 ± 3	17
F17	Ludhiana	Gosal	82 ± 3	12
F18	Ludhiana	T. Kalan	160 ± 4	20
F19	Rupnagar	Mehendalikalan	75 ± 3	9
F20	Rupnagar	Hasanpur	93 ± 3	17
F21	Sangrur	Lasoi	123 ± 4	19
F22	Sangrur	Sunam	51 ± 2	10
F23	Sangrur	Lasoi	57 ± 2	15
F24	Sangrur	Sunam	39 ± 2	10
F25	Fazilka	Abhor	93 ± 3	19
F26	Firozpur	Sodhe ke	204 ± 5	22

uncertainties are in the range of 1.1–2.4% for soil samples and 2–5% for food samples due to their varying concentrations. To the best of our knowledge literature data about safe limit of F (in mg kg^{-1}) in soil and food are not available like permissible limit for drinking water. The F concentrations in soil samples reported are in the range of about 20–1000 mg kg^{-1} , and based on this data it can be stated that soil samples analyzed have higher concentration of F than the control/uncontaminated soil. These results indicate that the soil samples are contaminated with fluoride. From literature data on food and diet samples [8, 16, 43], it was difficult to find F concentration data in rice samples. However, the reported data on F in diet/food samples (except for rice) are in the range of 10–30 mg kg^{-1} [8, 16, 43]. Based on these results, it can be stated that the higher concentrations of F (51–211 mg kg^{-1}) in the rice samples might be due to fluoride contaminated soil and water in the study areas. We have attempted to find correlation of F concentration between soil and food from same location and it was observed that F concentration in food to soil are in the

range of 3–21% indicating no direct correlation from our observed results. The detection limits of F by the present method (4 MeV proton beam, about 20 nA current, 30% HPGe detector at about 7 cm distance) are in the range of 10–50 and 9–24 mg kg^{-1} for soil and food samples, respectively. The detection limit values of F in food samples are given in Table 3.

The in situ current normalized PIGE method is advantageous as it does not need another set up/method for current measurement. PIGE method used here is promising for determination of low to high concentrations of F in food (biological/organic matrix) and soil samples as it does not need sample dissolution like other conventional wet-chemical methods. The advantages of the method are: small sample size, non-destructive in nature, on-line measurement thus less turn-around time and high sensitive particularly for F. It is also free from spectral interference as no peak at 197 keV was observed from cellulose matrix. From our work it can be concluded that PIGE is the best as well as simple method for precise and accurate determination of low concentration of F in solid powder samples (Table 4).

Table 4 Correlation of fluorine concentration among soil and food samples collected from same locations

Sr. no.	District	Soil (mg kg ⁻¹)	Food (mg kg ⁻¹)	Ratio of F in food/soil (%)
1	Faridkot	3138	77	2.5
2	Sangrur	1717	68	4.0
3	Ferozepur	1797	72	4.0
4	Amritsar	917	54	5.9
5	Fatehgarh Sahib	1430	107	7.5
6	Fazilka	853	93	10.9
7	Hoshiarpur	297	63	21.2
8	Jalandhar	511	56	11.0
9	Ludhiana	945	113	12.0
10	Faridkot	834	137	16.4
11	Kapurthala	396	68	17.2
12	Barnala	1027	179	17.4

Conclusions

PIGE method using 4 MeV proton beam from FOTIA has been optimized for determination of trace to minor concentration of fluorine in food and soil samples obtained from fluoride affected and non affected areas. The method applied to three reference materials as a part of quality control exercise and the results are in good agreement with that of certified values. Our results on F concentrations will serve as data base for our future work as well as for other researchers.

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References

1. Tebbutt THY (1983) Relationship between natural water quality and health. UNESCO, Paris
2. Agalakova NI, Gusev GP (2012) Molecular mechanisms of cytotoxicity and apoptosis induced by inorganic fluoride. *ISRN Cell Biol* 2012:1–6. doi:10.5402/2012/403835
3. Fawell J, Bailey K, Chilton J et al (2006) Fluoride in drinking-water. WHO, Cornwall
4. Salah H, Arab N (2007) Application of PIGE to determine fluorine concentration in human teeth: contribution to fluorosis study. *J Nucl Radiochem Sci* 8:31–34
5. Reddy DR (2009) Neurology of endemic skeletal fluorosis. *Neurol India* 57:7–12. doi:10.4103/0028-3886.48793
6. Susheela AK (1999) Fluorosis management programme in India. *India Curr Sci* 77:1250–1256
7. State Profile, Ground Water Scenario of Punjab, Central Ground Water Board, Punjab, http://cgwb.gov.in/gw_profiles/st_Punjab.htm. Accessed 15 July 2016
8. Farooqi AS, Arshed W, Akanle OA et al (1992) Fluorine determination in diet samples using cyclic INAA and PIGE analysis. *J Radioanal Nucl Chem* 161:71–78. doi:10.1007/BF02034881
9. Ando M, Tadano M, Yamamoto S et al (2001) Health effects of fluoride pollution caused by coal burning. *Sci Total Environ* 271:107–116. doi:10.1016/S0048-9697(00)00836-6
10. Singh K, Lataye DH, Wasewar KL (2013) Removal of fluoride from aqueous solution: status and techniques. *Desalination Water Treat* 51:3233–3247. doi:10.1080/19443994.2012.749036
11. Eyde B (1985) Determination of fluoride in fertilizers by means of the ion-selective electrode. *Anal Chem* 320:41–44
12. Thesai S, Krishnasamy J, Sundaram R et al (2014) Incidence and effects of fluoride in Indian natural ecosystem: a review. *Adv Appl Sci Res* 5:173–185
13. Vithanage M, Bhattacharya P (2015) Fluoride in drinking water: health effects and remediation, vol 5. *Environmental chemistry for a sustainable world*. Springer, New York, pp 105–151. doi:10.1007/978-3-319-11906-9_4
14. Light TS, Mannion RF (1969) Microdetermination of fluorine in organic compounds by potentiometric titration using a fluoride electrode. *Anal Chem* 41:107–111
15. Eyde B (1983) Determination of acid soluble fluoride in soils by means of an ion-selective electrode. *Fresenius Z Anal Chem* 316:299–301. doi:10.1007/BF00468924
16. Ponikvar M, Stibilj V, Žemva B (2007) Daily dietary intake of fluoride by Slovenian Military based on analysis of total fluorine in total diet samples using fluoride ion selective electrode. *Food Chem* 103:369–374. doi:10.1016/j.foodchem.2006.07.032
17. Saha JK, Kundu S (2003) Determination of fluoride in soil water extract through ion chromatography. *Commun Soil Sci Plant Anal* 34:181–188. doi:10.1081/CSS-120017424
18. Räsänen J (2009) “Particle induced gamma emission: PIGE” (Chapter 7). In: Wang Y, Nastasi M (eds) *Handbook of modern ion beam materials analysis*. Materials Research Society, Warrendale, pp 147–176
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* 302:1461–1464. doi:10.1007/s10967-014-3661-5
20. Chhillar S, Acharya R, Pai RV et al (2012) A simple and sensitive particle induced gamma-ray emission method for non-destructive quantification of lithium in lithium doped Nd₂Ti₂O₇ ceramic sample. *J Radioanal Nucl Chem* 293:437–441. doi:10.1007/s10967-012-1764-4
21. Chhillar S, Acharya R, Vittal Rao TV et al (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* 298:1597–1603. doi:[10.1007/s10967-013-2609-5](https://doi.org/10.1007/s10967-013-2609-5)
22. 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* 305:463–467. doi:[10.1007/s10967-015-4037-1](https://doi.org/10.1007/s10967-015-4037-1)
 23. Roelandts I, Robaye G, Weber G, Delbrouck-Habaru JM (1986) The application of proton-induced gamma-ray emission (PIGE) analysis to the rapid determination of fluorine in geological materials. *Chem Geol* 54:35–42
 24. Samudralwar DL, Robertson JD (1993) Determination of major and trace elements in bones by simultaneous PIXE/PIGE analysis. *J Radioanal Nucl Chem* 169:259–267
 25. Savidou A, Aslanoglou X, Paradellis T, Pilakouta M (1999) Proton induced thick target γ -ray yields of light nuclei at the energy region $E_p = 1.0$ – 4.1 MeV. *Nucl Instrum Methods B* 152:12–18
 26. 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
 27. Chhillar S, Acharya R, Sodaye S et al (2012) Application of particle induced gamma-ray emission for non-destructive determination of fluorine in barium borosilicate glass samples. *J Radioanal Nucl Chem* 294:115–119. doi:[10.1007/s10967-011-1525-9](https://doi.org/10.1007/s10967-011-1525-9)
 28. Elekes Z, Uzonyi I, Gratuze B et al (2000) Contribution of PIGE technique to the study of obsidian glasses. *Nucl Instrum Methods B* 161–163:836–841
 29. Mosbah M, Metrich N, Massiot P (1991) PIGME fluorine determination using a nuclear microprobe with application to glass inclusions. *Nucl Instrum Methods B* 58:227–231
 30. Venkatesh K, Chhillar S, Kamble GS et al (2014) Determination of boron concentration in borosilicate glass, boron carbide and graphite samples by conventional wet-chemical and nuclear analytical methods. *J Radioanal Nucl Chem* 302:1425–1428. doi:[10.1007/s10967-014-3552-9](https://doi.org/10.1007/s10967-014-3552-9)
 31. Macias ES, Radcliffe CD (1978) Proton induced γ -ray analysis of atmospheric aerosols for carbon, nitrogen, and sulfur composition. *Anal Chem* 50:1120–1124
 32. Valkovic O, Jaksic M, Fazinic S et al (1995) Quality control of PIXE and PIGE nuclear analytical techniques in geological and environmental applications. *Nucl Instrum Methods B* 99:372–375
 33. Roelandts I, Robaye G, Weber G et al (1987) Determination of fluorine by proton-induced gamma-ray emission (PIGE) spectrometry in igneous and metamorphic charnockitic rocks from Rogaland (S. W. Norway). *J Radioanal Nucl Chem* 112:453–460. doi:[10.1007/BF02132377](https://doi.org/10.1007/BF02132377)
 34. Farooqi AS, Arshed W, Akanle OA et al (1992) Fluorine determination in diet samples using cyclic INAA and PIGE analysis. *J Radioanal Nucl Chem* 161:71–78
 35. Carvalho ML, Karydas AG, Casaca C et al (2001) Fluorine determination in human healthy and carious teeth using the PIGE technique. *Nucl Instrum Methods B* 179:561–567
 36. Sastri CS, Banerjee A, Sauvage T et al (2013) Fluorine determination in different types of ivory by PIGE technique. *J Radioanal Nucl Chem* 298:311–315. doi:[10.1007/s10967-012-2410-x](https://doi.org/10.1007/s10967-012-2410-x)
 37. Roelandts I (1985) Determination of fluorine in eighty international geochemical reference samples by proton induced gamma ray emission spectrometry (PIGE). *Geostand Newsl* 9:191–197
 38. Barthos R, Méhn D, Demortier A et al (2005) Functionalization of single-walled carbon nanotubes by using alkyl-halides. *Carbon* 43:321–325. doi:[10.1016/j.carbon.2004.09.018](https://doi.org/10.1016/j.carbon.2004.09.018)
 39. Xie ZM, Ye ZH, Wong MH (2001) Distribution characteristics of fluoride and aluminum in soil profiles of an abandoned tea plantation and their uptake by six woody species. *Environ Int* 26:341–346. doi:[10.1016/S0160-4120\(01\)00010-1](https://doi.org/10.1016/S0160-4120(01)00010-1)
 40. Borges AR, François LL, Welz B et al (2014) Determination of fluorine in plant materials via calcium mono-fluoride using high-resolution graphite furnace molecular absorption spectrometry with direct solid sample introduction. *J Anal At Spectrom* 29:1564–1569. doi:[10.1039/c4ja00067f](https://doi.org/10.1039/c4ja00067f)
 41. Tripathi R, Sodaye S, Tomar BS (2004) Oxygen determination in metal foils using backscattering spectrometry. *Nucl Instrum Methods A* 533:282–286. doi:[10.1016/j.nima.2004.06.173](https://doi.org/10.1016/j.nima.2004.06.173)
 42. Mukhopadhyay PK (2001) The operating software of the PHAST PC-MCA Card. Proceedings of symposium on intelligent nuclear instrumentation-2001, Bhabha Atomic Research Centre, Mumbai
 43. Gurkan R, Altunay N, Korkmaz S (2015) A new preconcentration procedure to quantify total acid hydrolyzed fluoride in selected beverages and food by spectrophotometry. *Anal Methods* 7:5081–5091. doi:[10.1039/c5ay00672d](https://doi.org/10.1039/c5ay00672d)