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ELEMENTAL ANALYSIS OF GROUND WATER USING PIXE AND PIGE TECHNIQUES

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Water is the most important source of minerals for both human beings and animals. But at the same time, water is also a source of disease due to the contamination of various elements. Therefore, knowledge of the elemental content of water is important. In this work, water samples were collected from areas around Chandigarh and Bathinda district, Panjab, India. Proton-induced X-ray emission (PIXE) and proton-induced gamma-ray emission (PIGE) techniques were used for the determination of heavy and light trace elements, respectively, in wide varieties of water samples. A large number of elements, namely F, Na, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Cu, Zn, As, Pb, and U were detected in the samples and results are discussed.

Keywords: PIXE; PIGE; water samples.

1. Introduction

Water pollution is one of the major threats to public health in India, because drinking water quality is poorly managed and monitored. Drinking water sources, both surface and groundwater are contaminated with toxic metals and pesticides throughout the country. Human activities like improper disposal of municipal and industrial effluents and indiscriminate applications of agrochemicals in agriculture are the main factors contributing to the deterioration of water quality. In the present investigation, we have taken up a study of the trace element concentrations in water samples collected from tube wells situated on cultivated farms and village settlements near Chandigarh and Bathinda districts of Panjab (India). These two regions were selected for trace element analysis to do the comparative study between two regions and find out the reasons behind water contamination in Bathinda district, where people are facing serious health problems due to contaminated water.

The most popular methods for determination of heavy elements in environmental samples include atomic absorption spectrometry (AAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES). But the need for the exhaustive and time consuming sample preparation for these techniques, has led to increasing interest toward X-ray and γ-ray emission based techniques, viz., proton induced X-ray emission (PIXE) and proton induced gamma-ray emission (PIGE) for the environmental sample investigations. PIXE is a well established highly sensitive, nondestructive and multielemental analytical method.[1] It has been employed for simultaneous analysis of heavy elements in medical, biological, geological, archeological and environmental science.[4–9] However, K and L lines corresponding to elements with $Z < 17$ have low energy, suffer large absorption and therefore have very low detection efficiency. In practice, we utilize PIGE in the analysis of light elements lithium, boron, fluorine, sodium, etc. which are often difficult to determine by PIXE technique.[10]

2. Sample Collection and Preparation

Water samples were collected from the (a) villages and dams near Chandigarh (sites S1 to S6) and, (b) villages of Bathinda district (sites S7 to S12). Chandigarh is located near the foothills of the Shivalik range of the Himalayas in northwest India and the exact cartographic co-ordinates of Chandigarh are 30.74°N 76.79°E. Bathinda is in the northwestern region of India and is a part of the Indo-Gangetic alluvial plains. The exact cartographic co-ordinates of Bathinda are 30.20°N 74.95°E. Water samples were collected in polythene bottles which were cleaned thoroughly with water, 1N nitric acid and then by deionized water (18 MΩ water). For sample preparation, technique similar to the one used by Aprilesi *et al.*[11] was followed. 50 ml of each of the water samples were taken in a beaker and 2.5 ml of saturated NaDDTC (sodium diethyldithio carbamate $C_5H_{10}NaS_2H_2O$) was added to precipitate the metal contents as their respective carbamates. The precipitates thus formed were collected on 25 mm diameter nuclepore filters of pore size 0.4 μm, by vacuum filtration, using a millipore vacuum filtration unit. A thin uniform layer was formed on the membrane that is used as the target for the PIXE and PIGE measurements.

3. Experimental Set-up

3.1. *PIXE experimental set-up*

Water samples collected in June and September, 2010 were analyzed for trace elements using PIXE and PIGE techniques.[1–3] PIXE measurements were performed at Surface and Profile Measurement Laboratory at National Centre for Compositional Characterization of Materials (NCCCM), BARC, Hyderabad using the 3 MV tandetron accelerator.[12] In PIXE experiments, a well collimated 2.4 MeV proton beam of diameter 5 mm and current 5–7 nA was incident normally on targets placed inside a scattering chamber. The X-rays were detected by a planar high purity germanium (HPGe) detector (Eurisys Measures type EGX100-01, Be window thickness 40 μm) placed at 45° to the beam axis. The resolution of the detector was found to be 150 eV at 5.9 keV. To reduce high count rate, a Mylar (40 μm) has been used as absorber. An electron suppressor with -900 V was placed in front of the samples.

3.2. *PIGE experimental set-up*

A 2.4 MeV proton beam with a current of 4–5 nA was used to bombard the samples. Proton beam was produced from Single Dee Cyclotron situated at Panjab University, Chandigarh, India.[13] The beam size at the target position was 2 mm in diameter. The target was positioned at 90° w.r.t. the beam direction and the characteristic γ-rays emitted from the samples were detected by an ORTEC HPGe detector (FWHM 1.9 keV at 1332 keV) placed at 135°. The absolute efficiency was determined by means of calibrated radioactive sources of ^{133}Ba and ^{152}Eu, placed at target position.

4. Data Analysis

4.1. *PIXE analysis of water samples*

The obtained PIXE spectra corresponding to different samples were analyzed using GUPIX software package.[14] This package has provision to convert the X-ray intensities into elemental concentrations using a standardization technique involving fundamental parameters, predetermined instruments, constants, and input parameters such as solid angle, charge collected, etc. The GUPIX software determines the intensities of characteristic X-ray peaks in a PIXE spectrum by fitting a theoretical spectrum to the measured spectrum using a nonlinear least-squares technique. The theoretical spectrum is generated by using data base of K, L and M X-ray energies, fluorescence and Koster Cronig probabilities and relative X-ray intensities. The concentration of element is given as

$$C_Z = \frac{Y_m}{Y_t H Q \varepsilon T}\,, \tag{1}$$

where Y_m and Y_t are the measured and theoretical X-ray yields, respectively, Q is the real charge accumulated, ε is the intrinsic efficiency of the detector and T is the transmission through any filter or absorber between target and the detector. H value[15] is the product of detector solid angle and a charge correction factor and is determined by analyzing a standard reference material. For the calibration of setup, standard foils of $_{28}$Ni, $_{57}$La and $_{66}$Dy of thickness 340, 57.3 and 60 μg/cm^2, respectively were used. X-ray spectrum was obtained from these foils using the proton beam. These spectrums were used in the GUPIX, in which initially $H = 1$ is used. After fitting the spectrum of the standard foil, GUPIX generates the concentration of the element. After taking the ratio of calculated concentration to the known concentration of the standard sample, the H value is calculated. It does not depend on the atomic number of the standard. We used the three standards to include uncertainty, if any, in the efficiency of the detector for different energy range. For the standard samples, the energies used in the calibration are in the range of 4 to 8 keV. But we found that the measured H-values for the three samples are almost same and it was found to be $4.302 \times 10^{-3} \pm 2.33 \times 10^{-4}$. Thus, the X-ray yield (Y) is converted to elemental concentration via a defined standardization technique involving H value, the theoretical yield, detector efficiency and filter transmission values.

4.2. *PIGE analysis of water samples*

For the analysis of water samples, the gamma yield Y emitted by an isotope i of an element within thin target bombarded by a proton beam of energy E is calculated using the following equation:[16]

$$Y(E) = \varepsilon_{\mathrm{abs}}(E_\gamma) N_P \sigma(E) f_m f_i N_{av} A^{-1} \Gamma \,, \qquad (2)$$

where $\varepsilon_{\mathrm{abs}}(E_\gamma)$ is the absolute efficiency of the detection system at the emitted energy E_γ, N_P the number of incident protons and $\sigma(E)$ is the nuclear reaction cross-section at the incident proton energy E. The parameters f_m, f_i, N_{av} and A^{-1} represent the mass fraction of the element, the abundance of the isotope i related to the gamma emission, the Avogadros number and the inverse of the atomic mass of the element, respectively. Here Γ is the thin sample thickness and measured in $\mu\mathrm{g/cm}^2$. From the gamma-ray yield $Y(E)$, a partial thickness Γ of the film was calculated for all the studied elements. Their concentrations were then determined by considering the area of the polycarbonate filters and the volume of water filtered during each sample preparation.

5. Results and Discussion

PIXE and PIGE spectra of one of the samples under study are shown in Figs. 1 and 2, respectively. To establish the reliability of our system, NIST water sample [SRM 1643d] was analyzed for trace elements using PIXE. The results of the analysis of the sample from NIST water standard are in good agreement with those of the certified values as shown in Table 1. The concentrations of various elements of interest in the samples collected from different locations near Chandigarh (sites S1 to S6) and Bathinda region (sites S7 to S12) are given in Table 2. The overall errors in the measured concentration values for various elements have been estimated to be in the range of 5–10%. The errors are attributed to uncertainties in the fundamental parameters and efficiency calibration. Elements such as S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Cu, Zn, As, Pb and U are measured with different concentrations using the PIXE technique while Na and F concentrations were determined by the PIGE technique.

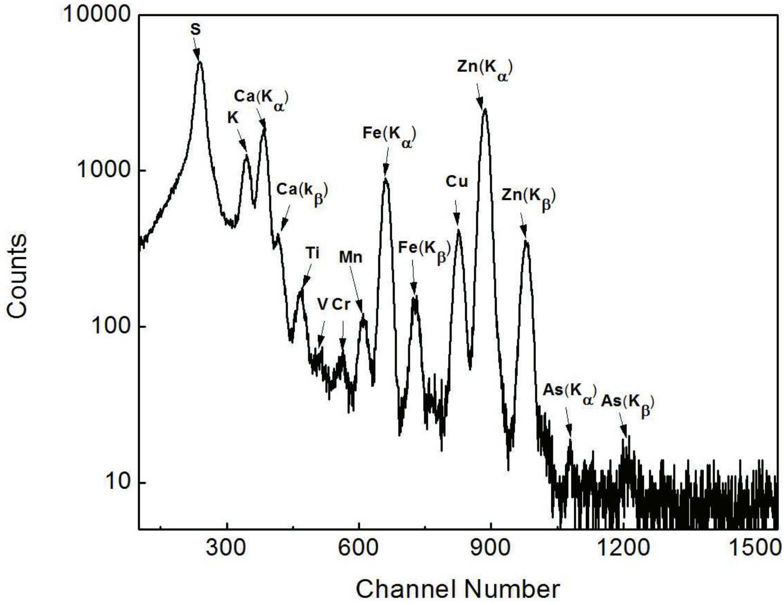

Fig. 1. PIXE spectrum of a water sample under study.

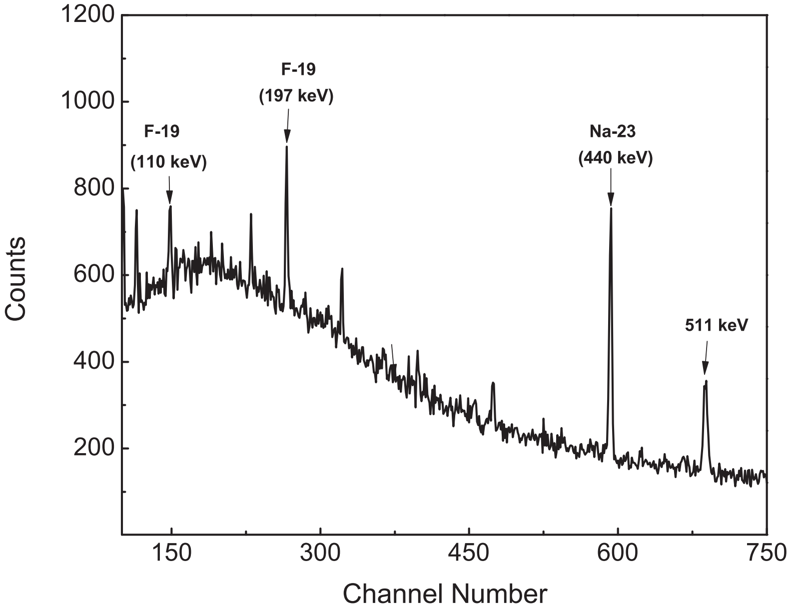

Fig. 2. PIGE spectrum of a water sample under study.

Table 1. PIXE measurements of NIST standard "Trace elements in water" [SRM1643d].[a] Percent errors are given in parenthesis.

Element	Experimental value	Certified value
Na	21.1(5)	22.0(2.9)
K	2.7(10.3)	2.3(1.5)
Ca	31.6(9)	31.0(1.6)
Cr	19.1(4)	18.53(1.1)
Mn	93.0(6)	91.2(4.3)
Fe	92(5.4)	91.0(4.4)
Ni	61.4(6)	58.1(4.7)
Cu	22.6(5.2)	20.5(20.5)
Zn	71.2(3.9)	72.5(1.0)
As	53.2(5.1)	56.02(1.3)
Se	10.4(7)	11.43(1.5)
Pb	16.3(5.3)	18.1(3.3)

[a] Na, K and Ca concentrations are in ppm while the rest are in ppb.

In this study, the range distribution for F concentration is between 0.49 and 0.72 ppm. The optimal drinking water concentration of fluoride for dental health is generally between 0.5 and 1.0 ppm and depends upon the volume of drinking water consumed and the uptake and exposure from other sources. These values are based on epidemiological studies conducted over the past 70 years in communities in many countries with natural and added fluoride in their drinking water. In this concentration range the maximum caries preventative effect is achieved while minimizing the levels of dental fluorosis. The WHO[17] drinking-water guideline value for fluoride is 1.5 ppm. Sodium content in water lies in the range 10–50 ppm whereas the optimum value is 20 ppm. High concentrations of sodium in water bodies mean high total minerals and tend to increase the corrosive action of water. Light elements detected by PIXE are S, Cl, K, Ca and their concentrations are in the range 108–1288 ppb, 21–75 ppb, 9.8–291.4 ppb and 56–1759 ppb, respectively. Concentrations of S and Cl are found to be maximum at the site S10, Bahadurpur village of district Bathinda. Sulfur is found in naturally occurring minerals in some soil and rock formations that contain groundwater. Chlorides are leached from various rocks into soil and water by weathering. Concentration of potassium is maximum at Mirzapur dam (site S3) and calcium is found to be maximum in Bhucho Mandi village (site S11) of Bathinda district. Potassium and calcium are metals common in rocks found in continents. Sources of potassium in underground water include weathering and erosion of potassium-bearing minerals, such as feldspar, leaching of fertilizer and sea water, in areas susceptible to saltwater intrusion.

Iron, copper, manganese and zinc are important micronutrients that are in trace amounts and their concentrations are shown in Fig. 3. Elevated concentrations of

Table 2. Experimental results for elemental concentrations (ppb).

Element	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12
F	[a]BDL	490.4 ±5.5	722.0 ±7.6	BDL	BDL	454.0 ±5.2	BDL	BDL	553.0	BDL ±9.7	BDL	BDL
[b]Na	18.0 ±1.5	24.0 ±2.1	36.1 ±2.9	1.9 ±0.2	12.7 ±1.0	BDL	16.1 ±1.0	49.3 ±2.1	20.3 ±1.7	45.3 ±3.9	34.7 ±2.7	13.1 ±1.1
S	532.9 ±50.2	117.8 ±10.3	209.0 ±20.5	308.0 ±25.4	108.0 ±10.6	523.6 ±50.5	407.6 ±35.5	529.0 ±49.4	453.4 ±37.3	1288.0 ±126.0	391.2 ±29.2	256.0 ±25.2
Cl	71.4 ±5.4	26.3 ±3.4	23.2 ±2.7	42.5 ±3.9	28.6 ±3.0	41.5 ±4.3	23.2 ±1.8	28.6 ±2.7	21.0 ±1.6	75.0 ±6.7	46.8 ±3.6	45.4 ±4.5
K	86.5 ±8.5	53.5 ±3.6	291.4 ±18.0	BDL	19.0 ±1.3	17.6 ±1.1	9.8 ±0.5	7.87 ±0.3	36.2 ±3.4	77.0 ±6.3	9.9 ±8.1	26.8 ±2.4
Ca	167.8 ±13.5	639.0 ±64.0	462.0 ±40.3	424.0 ±36.4	129.5 ±9.9	56.0 ±4.3	162.7 ±16.3	44.2 ±3.7	308.0 ±21.0	114.0 ±10.3	1759.0 ±171.2	150.7 ±13.5
Ti	13.5 ±1.3	13.8 ±1.1	57.0 ±3.4	BDL	4.6 ±0.4	0.5 ±0.03	1.4 ±0.1	1.3 ±0.1	21.7 ±0.2	8.5 ±0.7	5.2 ±0.4	13.0 ±1.2
Cr	7.8 ±0.7	BDL	7.0 ±0.6	1.4 ±0.1	2.4 ±0.2	3.9 ±0.3	1.9 ±0.2	2.8 ±0.3	4.7 ±0.4	2.9 ±0.2	7.3 ±0.5	6.1 ±0.4
Mn	15.3 ±1.3	157.7 ±13.7	79.4 ±4.5	16.3 ±1.3	9.3 ±1.0	28.4 ±2.7	11.66 ±1.0	99.9 ±9.4	297 ±25.2	98.7 ±9.4	149.7 ±10.3	406.8 ±35.5
Fe	318.8 ±30.4	360.5 ±32.4	883.0 ±80.1	186.6 ±15.7	206.8 ±16.8	24.9 ±2.3	48.8 ±4.3	73.7 ±5.8	113 ±10.0	142.7 ±11.4	457.7 ±40.9	778.0 ±37.3
Ni	3.9 ±0.3	BDL	2.3 ±0.2	BDL	1.0 ±0.05	BDL	1.1 ±0.1	2.57 ±0.2	BDL	1.6 ±0.1	3.6 ±0.3	7.0 ±0.7
Cu	16.8 ±1.5	15.9 ±1.3	21.4 ±2.0	71.1 ±4.5	98.3 ±8.1	12.6 ±1.0	78.9 ±7.6	209.7 ±15.8	73.4 ±7.2	125.5 ±12.0	129.9 ±12.6	151.0 ±13.5
Zn	103.6 ±10.3	59.5 ±5.2	69.7 ±6.3	16.2 ±1.5	90.2 ±8.5	40.9 ±4.3	396.0 ±36.0	29.8 ±2.5	75.0 ±6.7	738.9 ±7.4	78.3 ±7.6	17.4 ±1.6
As	BDL	BDL	BDL	BDL	BDL	4.5	BDL ±0.4	BDL	10.9	8.55 ±1.3	4.27 ±0.7	BDL ±0.4
Se	1.8 ±0.1	BDL	1.2 ±0.1	BDL	BDL	BDL	15.3 ±1.3	5.4 ±0.5	BDL	7.7 ±0.6	14.9 ±1.3	BDL
Pb	BDL	1.83 ±0.1	BDL	BDL	1.5 ±0.1	BDL	5.14 ±0.5	5.34 ±0.5	BDL	4.1 ±0.4	BDL	BDL
U	3.6 ±0.3	BDL	BDL	BDL	BDL	BDL	12.4 ±1.1	15.7 ±1.3	BDL	3.7 ±0.3	10.3 ±1.3	BDL

[a] BDL is below detection limit.

[b] Na concentration is in ppm.

Sampling sites: S1: Karanpur Village; S2: Pinjore; S3: Mirzapur Dam; S4: Indo global Coll.; S5: Baddi industries; S6: Seswan Dam; S7: Goniana Mandi; S8: Harraipur; S9: Kiratpur; S10: Bahadarpur Village; S11: Bhucho Mandi; S12: Bajakhana.

Cu and Zn in tap water are usually due to corrosion of pipes and plumbing. In this study, the range distribution was 12.6 to 151 ppb for Cu and 16.2 to 738.9 ppb for Zn. None of the concentrations exceeded the WHO limits of 2000 ppb and 3000 ppb for Cu and Zn, respectively. Copper concentration is maximum at Bajakhana

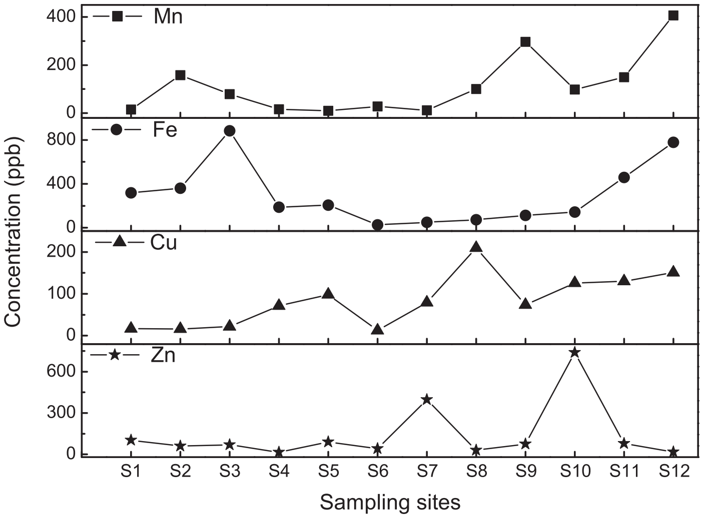

Fig. 3. Concentration of heavy elements in water samples.

village (site S12) of Bathinda district whereas zinc concentration is maximum at site (S10) Bahadurpur village of Bathinda district. At normal concentration, copper is a biologically important trace element; at elevated concentration it is toxic for living organisms.

The desirable and maximum permissible limit of iron in the drinking water is 100 and 1000 ppb, respectively. The concentration of iron in the water samples of the study area ranged between 24.9–883 ppb, which shows that iron content in all the samples is below the maximum permissible limit. Concentration of iron is maximum at site S3 (Mirzapur dam). The desired and permissible level of manganese in drinking water is 50 ppb to 500 ppb, respectively. The concentration of manganese in the groundwater of the area ranged from 9.3–406.8 ppb. The groundwater of the area thus does not appear to be a manganese hazard. Manganese concentration is maximum at Bajakhana village (site S12) of Bathinda district.

Among other heavy metals, As and Pb are highly toxic and classified as a possible human carcinogens. Graphical representation of concentrations of As, Se, Pb and U are shown in Fig. 4. Arsenic concentration is maximum at site S9 (Kiratpur village) of Bathinda district and it is above the permissible limit of 10 ppb specified by WHO. Arsenic is introduced into water through the dissolution of minerals and ores, and concentrations in groundwater in some areas are elevated as a result of erosion from local rocks. Long term exposure to arsenic or its compounds can cause skin and liver cancer. Selenium concentration is found to be maximum at site S7 (Goniana Mandi village of Bathinda district) and it is above the WHO limit of 10 ppb, whereas concentrations of lead and uranium are found to be maximum at Harraipur village of Bathinda district (site S8).

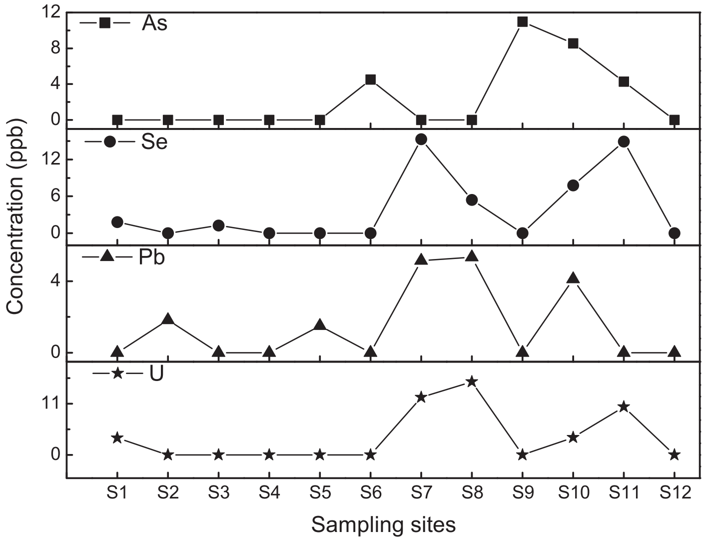

Fig. 4. Concentration of toxic elements in water samples.

Concentration of lead in water samples of the study area is from 1 to 6 ppb that is below the permissible limit of 10 ppb set by WHO. The main source of lead in groundwater is from the rocks containing lead sulfide and oxides. The household plumbing fixture made up of lead may contribute lead in the drinking water. Concentration of uranium at S8 site is found to be above the WHO limit of 15 ppb. The high uranium content in Bathinda waters can be due to the affect of the granite rock intrusions, in which the average value of uranium content was found to be 27.3 mg/Kg.

Results indicate that the concentrations of toxic heavy metals are at elevated levels in the villages of Bathinda district as compared to the locations near Chandigarh. Many health hazards like autism, cerebral palsy, sub normal physical growth of special children of Bathinda region and growing incidences of cancer, all are surprisingly blamed on uranium and other metal toxicity in ground water.[18]

6. Conclusion

We have applied PIXE–PIGE analyses with preconcentration method in determination of elemental content of water samples collected from Panjab region of India. Various elements detected were F, Na, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu and Zn. Toxic elements like As, Se, Pb and U were also detected in some of the samples, most of which are collected from Bathinda district. One of the major advantages of combined PIXE–PIGE analyses is its ability to provide simultaneous multielement quantification. The method offers true multielement analysis during a single analysis with high sensitivity, precision, and accuracy. In this study, prompt gamma-ray analysis and PIXE analysis have been employed for water sample analysis and this combination was found to be effective and accurate.

Trace elements are generally present in small concentration in natural water system. Their occurrence in groundwater and surface water can be due to natural sources such as dissolution of naturally occurring minerals containing trace elements in the soil zone or the aquifer material or to human activities such as mining, fuels, smelting of ores and improper disposal of industrial wastes. This study has shown that the trace element quality of waters in Chandigarh region is generally good, most of the elements satisfying the WHO regulations for drinking waters. However, elevated levels of As, Se and U in some of the samples collected from Bathinda region indicate that there is need to control these elements at their source as they could constitute a threat to human health. Presence of excess of uranium and other toxic elements in drinking water samples from Bathinda area can be the cause of a large number of cancer deaths in the area. However a more detailed study is required in the area where the scientists from different disciplines including Medical Sciences should work together in a collaborative manner to find the solution of this serious problem.

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