

## Determination of trace elements in tap water using pixe technique

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### ABSTRACT

Combination of non-destructive proton induced X-ray emission (PIXE) and pre-concentration technique has been employed for the determination of trace elements in tap water. Pre-concentration technique was used to amplify the analytical sensitivity of the trace elements detected by PIXE method. Tap water samples were collected from 15 different locations across Lahore city, Pakistan. The mean concentrations of the trace elements (Mg, S, Cl, K, Ca, Ti, Mn, Fe, Ni, Cu, Zn, As, Br and Sr) in tap water samples were analyzed simultaneously. The concentrations of trace elements were compared with World Health Organization (WHO) guidelines for drinking water quality. The results revealed that most of the trace elements (Mg, S, Cl, K, Ca, Ti, Mn Ni, Cu and Zn) were well within the WHO guidelines. Whereas, the concentration of Fe, As and Br were significantly higher than the WHO safe limits. Therefore, frequent monitoring and further treatment is needed in order to improve the drinking water quality for the areas showing higher trace elements concentrations.

**KEY WORDS:** Tap water, trace elements, PIXE, pre-concentration.

### 1. INTRODUCTION

Water, after air, is the most vital element among the natural resources and crucial for the survival of all living organisms including human, food production, and economic development. As a valuable resource, the quality of water is important for public health as well as for ecosystem habitats. Furthermore, water quality is also closely linked with the communal use of water. Therefore, frequent monitoring of water quality is very important to evaluate its suitability for specific activities such as drinking, swimming or other commercial purposes.

Surface water (rivers, canals or lakes) and groundwater are the main sources of drinking water supplies in Pakistan. Due to arid climate in Pakistan groundwater availability is limited, resulting in shortage of potable water. This problem is more aggravated in big cities by over pumping of groundwater. In addition absence of proper management and monitoring facilities of groundwater aquifers, poor institutional arrangements and lack of a legal framework have intensified the drinking water problems of Pakistan (Aziz, 2005; Hayder, 2009).

During the last two decades, numerous studies have done to understand the distribution of trace elements in drinking water (Khan, 2011). Trace elements are the chemical elements required only in minute amounts by living organisms for normal growth. They are also known as heavy metals because of the high density ( $>5\text{g/cm}^3$ ). Whereas, elevated concentrations of trace elements can make these important trace elements noxious (Gao, 2008). These elements are indestructible in nature. Therefore, the determination of trace elements is exceedingly important for the safety assessment of the drinking water and human health in particular (Batayneh, 2012).

Combination of proton induced X-ray emission (PIXE) and pre-concentration technique is widely used by many researchers for the determination of trace elements in water (Al-Bedri and Al-Jobori, 1991; Yamazaki, 1996; Amartaivan, 2002; Al-Bedri and Ghani, 2010; 2012; 2014). Whereas, in some studies researchers have used PIXE technique without pre-concentration treatment (Futatsugawa, 1994; Thomyasirigul, 2009). PIXE is based on the characteristic X-ray emission of slightly different energy from each element when bombarded by a few MeV particle beam. Generally, it is a sensitive, fast, cheap, simple and nondestructive multi-elemental analysis technique (Cahill, 1980; Johansson and Johansson, 1984; Johansson, 1989; Butalag, 2005). Because of these unique features PIXE technique has been widely used for the analysis of trace elements concentrations in water.

Lahore, with a population of over eleven million, is the capital of Punjab province. Groundwater is the only source of drinking water for the residents, which is extracted and supplied by Lahore Water and Sanitation Authority (LWASA). The groundwater is pumped out from a large number of sites by tube wells from a depth of approximately 200 m, then filtered, purified, chemically treated if necessary and supplied to the households. In this study, PIXE technique was used to determine the concentrations of trace elements in tap water (TW) and examine the competency of PIXE in drinking water quality monitoring. Results obtained from this study were compared with the WHO guidelines of trace elements for drinking water (WHO, 2011).

### 2. MATERIALS AND METHODS

**2.1. Study area:** Lahore is located at latitude  $31^{\circ}32'59''$  N and longitude  $74^{\circ}20'37''$  E with an elevation of 217 masl. It has an area of  $1,772\text{ km}^2$  with a total population of 11,007,835 and is the second largest metropolitan area in

Pakistan. It is located 49 km southeast from the provincial capital Lahore and 312 km from the federal capital Islamabad. Topographically, Lahore is located in the northeastern part of Pakistan on the bank of the river Ravi near the Indian border. The climate of Lahore presents extremes of heat (max. 40.4°C; min. 27.4°C) and cold (max. 19.8°C; min. 5.9°C) and monsoon occurs in the summer, from June until September. The average annual rainfall of Lahore is about 628.8 mm.

**2.2. Sample collection and pre-concentration technique:** TW samples were collected directly from 15 different localities of Lahore city (Figure. 1) in labeled polyethylene bottles without having contact with hands and other materials. The bottles were pretreated with 0.1 N HCl and rinsed twice with tertiary distilled water. Generally, the concentration of trace elements in water ranges from mg/L to µg/L; therefore, pre-concentration treatment of water sample is necessary. As a pre-concentration treatment 100 ml of collected water samples from each site was evaporated in a drying oven at 50°C under controlled environment (Johansson and Campbell, 1988; Al-Bedri and Ghani, 2010). From each sample on an average around 15 mg of dry solid residue was obtained. Dried solid residues from each water sample (5 mg) were then mixed with 20 µL of yttrium nitrate [Y(NO<sub>3</sub>)<sub>3</sub>] solution containing 1.16 mg of Y as internal standard and deposited on a 100 µm thick Mylar sheet over an area of about 1.5 cm<sup>2</sup>. Then the sample was dried and mounted on a pyramid shaped carbon target holder for irradiation in the vacuum chamber and the scattering chamber pressure was fixed at 71 psi. The target holder used in this study able to mount four samples at a time.

**2.3. PIXE analysis:** The samples were irradiated using 2 MV tandem pelletron accelerator (6SDH-2, National Electrostatics Corporation, USA) as shown schematically in fig 2. The target was placed at an angle of 45° with respect to the proton beam from the accelerator. The sample was irradiated by 3.8 MeV collimated proton beam having the diameter of 3mm and 20 nA current. During the whole process, the detector dead time was adjusted to 5%. The samples were irradiated for 20-25 minutes to obtain reasonable counts for each element.

Characteristic X-rays emitted by the target were detected by a Si (Li) energy-dispersive detector (30 mm<sup>2</sup> area and 138 eV energy resolution) and the energy was calibrated using L X-rays of Au. The detector was positioned at a distance of about 15 cm from the target, at right angle to the incident proton beam. Signals from the detector were processed by the usual PIXE electronics and displayed by a multichannel analyzer as channels (energy) versus peak height (counts) spectrum. Moreover, the system was calibrated for K X-rays using known salt mixture containing 12 elements between Z=11 to Z=38 with Y(NO<sub>3</sub>)<sub>3</sub> as internal standard; whereas, L X-rays were calibrated using Ba, Hg and Pb salts. Sensitivity curve relative to Yttrium was plotted and sensitivity value for all elements were tabulated.

### 3. RESULTS AND DISCUSSION

In the present study, to check the validity of experimental technique, a certified reference material Granodiorite Silver Plume (GSP-2) was used in a similar manner described above using Y as the internal standard. Table 1 shows the mean values with the standard deviation of the trace elements concentrations measured in certified reference material. A comparison with the standard values reported by U.S. Geological Survey reference material elucidates that the accuracy of the measurements is within ±1% to ±7%.

Figure.3 shows a typical example of PIXE spectrum observed in water sample. The Yttrium peaks, which are due to internal standard, can be seen very clearly. The concentration of an element was obtained from the following expression:

$$C_e = N_e C_y / N_y S_{ey}$$

Where  $C_e$  is the concentration of the measured element,  $N_e$  is the areal counts of the measured element, and  $N_y$  refers to the areal counts of internal standard respectively,  $S_{ey}$  indicates the relative sensitivity i.e. sensitivity ratio of the analyzed element to the sensitivity of internal standard and  $C_y$  is the concentration of internal standard.

Table.2 demonstrates the range, mean values and standard deviation of the trace elements concentrations present in the TW collected from 15 different localities across the Lahore city compared with the WHO guidelines for drinking water (WHO, 2011). Up till now there is no national drinking water quality standards of Pakistan now and WHO guidelines are followed (Hyder, 2009).

The mean concentrations of the detected trace elements (Mg, Cl, Ca, Mn, Ni, Cu and Zn) in the TW were found relatively lower than WHO guidelines for drinking water. However, the mean concentration of Fe was (116.7 µg/L) higher than the WHO safe limits. This is may be due to corroded pipes of the water distribution system, tanks and pumps; which is supported by the earlier findings (Yamazaki, 2002). Although, Fe is an essential trace element for human metabolic system, increased concentrations of Fe may result in vomiting, metabolic acidosis and neurological changes (Fairbanks, 1971). Moreover, in the samples where As and Br were detected, found to be higher than the WHO safe limits. The concentration of As varied from 11.2 to 37.1 µg/L. Previous studies have also reported the elevated level of As in some parts of Punjab province of Pakistan (Akhter, 2015). The main source As contamination in drinking water is the dissolution of As containing minerals (Toor and Tahir, 2009). Increased concentrations of As in drinking water causes skin discoloration and thickening which may ultimately leads to skin

cancer (Benbrahim-Tallaa and Waalkes, 2008). Numbness of hands and feet along with some digestive problems may also occur as a consequence of excessive intake of As. The concentration of Br ranged from 16-112  $\mu\text{g/L}$  and significantly exceeded the WHO guidelines for drinking water. High amount of Br cause nausea and vomiting, abdominal pain, coma and sometimes even paralysis (WHO, 2003). Excessive Br in water is thought to be the result of the groundwater flowing through silicate mineral deposits (Flury and Papritz, 1993).

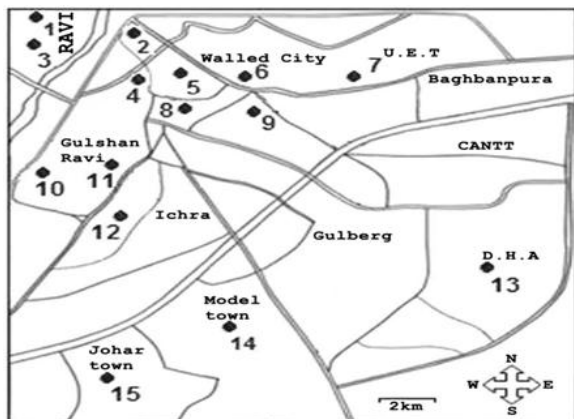


Figure.1. Map showing the sampling points

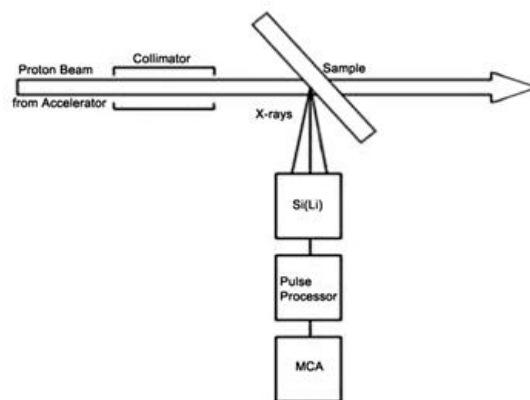


Figure.2. Schematic diagram of the experimental setup

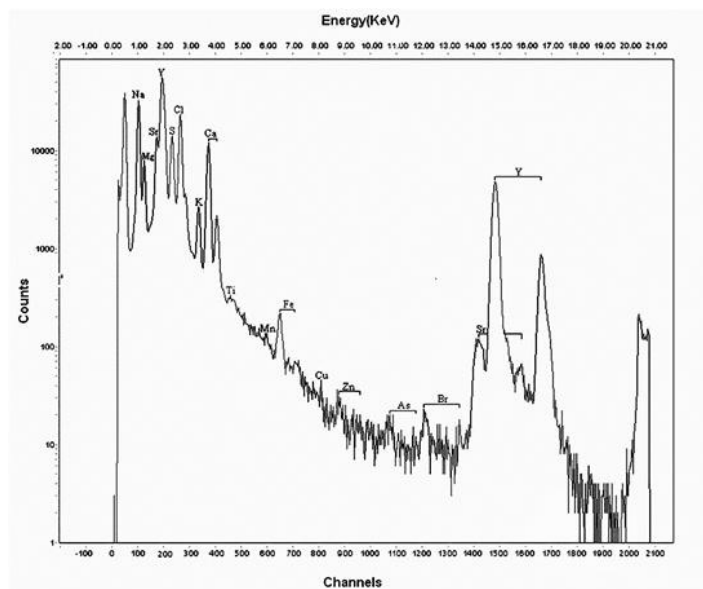


Figure.3.A typical example of PIXE spectrum observed in water sample

Table.1. Comparison between the concentrations of the elements measured in certified reference materials (GSP-2) and the standard values reported by U.S. Geological Survey reference materials used for PIXE analysis

Element	Experimental Value $\pm$ S.D. ( $\mu\text{g/g}$ )	Standard Value $\pm$ S.D. ( $\mu\text{g/g}$ )	Accuracy (%)
Na*	$2.12 \pm 0.09$	$2.06 \pm 0.07$	+2.75
Mg*	$0.58 \pm 0.14$	$0.58 \pm 0.02$	-0.57
Al*	$8.16 \pm 0.13$	$7.88 \pm 0.11$	+3.60
Si*	$30.86 \pm 0.38$	$31.10 \pm 0.04$	-0.78
K*	$4.54 \pm 0.14$	$4.48 \pm 0.12$	+1.34
Ca*	$1.62 \pm 0.06$	$1.53 \pm 0.04$	+5.88
Ti*	$0.40 \pm 0.16$	$0.40 \pm 0.01$	-0.83
Fe*	$3.40 \pm 0.03$	$3.43 \pm 0.11$	-0.78
Mn	$323.33 \pm 16.33$	$320 \pm 20$	+1.04
Sr	$257.33 \pm 13.33$	$240 \pm 10$	+7.22
Zn	$126.33 \pm 12.67$	$120 \pm 10$	+5.28

\* = wt. %, S.D. = Standard deviation

**Table.2. Range and mean concentration in  $\mu\text{g/L}$  of trace elements in the tap water (TW) using PIXE technique compared WHO guidelines for drinking water**

Sampling site	Element concentration ( $\mu\text{g/L}$ )						
	Mg*	S*	Cl*	K*	Ca*	Ti	Mn
1	5.4	8.1	16	0.8	9.6	N.D	N.D
2	23.1	18	50.1	5.4	6.4	N.D	N.D
3	13	11.6	10.2	1.1	4.9	N.D	N.D
4	17.5	9.9	27.4	3.1	13.1	N.D	N.D
5	32.2	21.2	57.6	6.7	19.1	N.D	37.5
6	8.4	7.3	2.1	1.4	17.3	51.5	N.D
7	8.1	9.9	21.6	1.7	9.4	20	31
8	1.7	8.5	2.7	0.78	11.6	N.D	21
9	13.7	18.1	35.7	18.7	8.8	N.D	N.D
10	10.8	7.2	5.8	1.2	22.3	107	25.3
11	11.2	7.6	2.6	1.8	14.5	37.2	13.5
12	8.8	6.3	12.8	1.3	8.7	N.D	N.D
13	21.9	21.5	42.5	2.7	10.4	N.D	N.D
14	17.4	13.7	26.8	1.9	20.6	24.6	26.6
15	6.8	6.9	4.2	0.9	16.2	N.D	21.5
Range ( $\mu\text{g/L}$ )	1.7-32.2	6.3-21.5	2.1-57.6	0.78-18.7	4.9-22.3	20-107	13.5-37.5
Mean $\pm$ S.D( $\mu\text{g/L}$ )	13.33 $\pm$ 7.9	11.72 $\pm$ 5.4	21.21 $\pm$ 18.3	3.29 $\pm$ 4.6	12.86 $\pm$ 5.3	35.9 $\pm$ 35.5	21.3 $\pm$ 10.4
WHO	150	N.S	150	N.S	75	N.S	500

Sampling site	Element concentration ( $\mu\text{g/L}$ )						
	Fe	Ni	Cu	Zn	As	Br	Sr
1	91.3	10	7.5	17.3	11.2	16.1	434
2	34.1	N.D	N.D	N.D	N.D	N.D	468
3	35.5	4.3	N.D	24.9	N.D	51	24
4	44.8	10	N.D	N.D	N.D	N.D	1050
5	210	18.2	N.D	N.D	N.D	31.8	142
6	33.3	13.5	N.D	N.D	N.D	N.D	385
7	164.5	N.D	9.8	N.D	20.3	N.D	563
8	73.3	10.4	9.1	13	N.D	N.D	200
9	96.9	N.D	N.D	N.D	N.D	N.D	307
10	266.5	N.D	N.D	N.D	N.D	N.D	670
11	162.4	16.4	N.D	N.D	34.4	N.D	691
12	42.8	N.D	N.D	17.9	N.D	N.D	117
13	182.8	N.D	N.D	27.6	25.6	112	135.8
14	192.5	N.D	N.D	N.D	N.D	N.D	805
15	120.4	N.D	N.D	105.2	37.1	48.9	603
Range ( $\mu\text{g/L}$ )	33.3-266.5	4.3-18.2	7.5-9.8	13-105.2	11.2-37.1	16.1-112	24-1050
Mean $\pm$ S.D( $\mu\text{g/L}$ )	116.7 $\pm$ 75.4	11.83 $\pm$ 4.6	8.80 $\pm$ 1.8	34.32 $\pm$ 35.1	25.68 $\pm$ 10.6	51.96 $\pm$ 36.4	439.65 $\pm$ 292.8
WHO	100	20	2000	15000	10	10	N.S

\* Mg, S, Cl, K, Ca concentrations are in mg/L and the rest are in  $\mu\text{g/L}$ , N.D = Not detected; N.S = No standard

#### 4. CONCLUSION

The present study attempts to determine the concentrations of trace elements (Mg, S, Cl, K, Ca, Ti, Mn, Fe, Ni, Cu, Zn, As, Br and Sr) in tap water of Lahore using PIXE technique coupled with pre-concentration treatment. Combination of PIXE and pre-concentration technique leads to sensitivity improvement below the ppb level and confirms the competency of PIXE technique in drinking water quality monitoring. Most of the elements (Mg, S, Cl, K, Ca, Ti, Mn, Ni, Cu and Zn) were within WHO guidelines for drinking water. Whereas, Fe, As and Br were found

to be higher in some of the samples. Therefore, regular water quality monitoring and further treatment is needed, especially for the areas showing higher Fe, As and Br concentrations, for ensuring good quality drinking water to the general population.

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## REFERENCES

- Akhtar MM, Zhonghua T, Sissou Z, Mohamadi B, Assess arsenic distribution in groundwater applying GIS in capital of Punjab, Pakistan, *Natural Hazards and Earth System Sciences Discussions*, 3, 2015, 2119-2147.
- Al-Bedri M, Al-Jobori S, Multielement determination in river water by neutron activation analysis, *Journal of Radioanalytical and Nuclear Chemistry*, 147, 1991, 235-241.
- Al-Bedri MB, Ghani IJA, PIXE elemental analysis of mineral, tap and ground water, *International Journal of PIXE*, 20, 2010, 93-100.
- Amartaivan T, Ishii K, Yamazaki H, Takahashi Y, Matsuyama S, Satoh T, Sugihara S, Katoh K, Komori Y, Orihara H, PIXE analysis of trace heavy metals in river and tap water using an ion-exchange cellulose phosphate filter, *International Journal of PIXE*, 12, 2002, 217-223.
- Aziz JA, Management of source and drinking-water quality in Pakistan, *Eastern Mediterranean Health Journal*, 11, 2005, 1087-1098.
- Benbrahim-Tallaa L, Waalkes MP, Inorganic arsenic and human prostate cancer, *Environmental health perspectives*, 116, 2008, 307-318.
- Cahill TA, Proton microprobes and particle-induced X-ray analytical systems, *Annual Review of Nuclear and Particle Science*, 30, 1980, 211-252.
- Fairbanks VF, Fahey JL, Beutler E, Clinical disorders of iron metabolism, 2, Grune and Stratton, New York, 1971, 1-486.
- Flury M, Papritz A, Bromide in the natural environment: occurrence and toxicity, *Journal of Environmental Quality*, 22, 1993, 747-758.
- Futatsugawa S, Hatakeyama S, Saitou Y, Sera K, PIXE analysis of mineral water (effect of sample preservation), *International Journal of PIXE*, 4, 1994, 107-116.
- Gao S, Jin Y, Unverzagt FW, Ma F, Hall KS, Murrell JR, Cheng Y, Shen J, Ying B, Ji R, Matesan J, Trace element levels and cognitive function in rural elderly Chinese, *The Journals of Gerontology Series A: Biological Sciences and Medical Sciences*, 63A, 2008, 635-641.
- Haydar S, Arshad M, Aziz JA, Evaluation of drinking water quality in urban areas of Pakistan: A case study of Southern Lahore, *Pakistan Journal of Engineering and Applied Sciences*, 5, 2009, 16-23.
- Johansson SA, Campbell JL, PIXE: A novel technique for elemental analysis, 20, John Wiley and Sons, Chichester, 1988, 347.
- Johansson SA, PIXE: a novel technique for elemental analysis, *Endeavour*, 13, 1989, 48-53.
- Khan TA, Trace elements in the drinking water and their possible health effects in Aligarh City, India, *Journal of Water Resource and Protection*, 3, 2011, 522-530.
- Thomyasirigul S, Fukuda H, Hasegawa J, Oguri Y, Determination of chromium (VI) in water by PIXE analysis using ion exchange paper - limit of detection and interference by coexisting anions, *International Journal of PIXE*, 19, 2009, 1-8.
- Toor IA, Tahir SN, Study of arsenic concentration levels in Pakistani drinking water, *Polish Journal of Environmental Studies*, 18, 2009, 907-912.
- WHO, Bromate in Drinking-water, Background document for development of WHO Guidelines for Drinking-water Quality, WHO, Geneva, 2005, 10.
- WHO, Guidelines for drinking-water quality, WHO, 4, Geneva, 2011, 1-518.
- Yamazaki H, Ishii K, Takahashi Y, Amartaivan T, Matsuyama S, Satoh T, Sugihara S, Sera K, Jon GC, PIXE elemental analysis of drinking water supplies, *International Journal of PIXE*, 12, 2002, 209-215.
- Yamazaki H, Tanaka M, Tsutsumi K, Ishii K, Iwasaki S, Matsuyama S, Inoue J, Murozono K, Orihara H, A pre-concentration technique for water analysis by PIXE, *International Journal of PIXE*, 6, 1996, 483-492.