Particle-induced X-ray emission analysis of IAEA standard reference materials, NIST standard reference materials and soils and sediments of Bangladesh

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Abstract— **This study shows that twenty-six elements (Na, Mg, Al, Si, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Ga, As, Br, Rb, Sr, Y, Zr, Nb, Ba, Hg, and Pb) in very small quantities of international atomic energy agency standard reference materials (IAEA-SRM-Soil-7, IAEA-SRM-SL-1, IAEA-SRM-SL-3), national institute of standard and technology standard reference materials (NIST-SRM-1633b and NIST-SRM-1632b) are determined by particle-induced x-ray emission (PIXE) with reasonable accuracy. PIXE also applied to the determination of multi-elements in soils and sediments of Bangladesh. This study shows that PIXE using the powdered internal standard method can be used for the rapid identification of the environmental pollutants especially elevated levels of chromium and arsenic in soils and sediments of Bangladesh.**

Keywords— ***PIXE • IAEA and NIST SRM • Soils • Sediments• Multi-elements • Toxic chromium and arsenic***

I. Introduction

During the last few decades, reactors and accelerators have been using for the development of numerous analytical techniques to determine the multi-elements in different sample matrices. There are two non-destructive techniques of neutron activation analysis: instrumental neutron activation analysis (INAA) and prompt gamma-ray analysis (PGA) [1-5, 21]. Multi-element analysis can be also performed by particle or proton-induced X-ray emission (PIXE) using an accelerator, which is based on the detection of characteristics X-ray. PIXE has become an effective technique in the multi-element analysis of both thick and thin target samples [6]. Recently, PIXE has been accepted among researchers in the field of bio-medicine owing mainly to its high sensitivity with simultaneous, multi-elemental analysis of the exceedingly small amount of samples [7]. Nowadays, researchers have been using PIXE for elemental concentrations (especially high Z-elements) determinations in powdered samples and the field of study has been growing rapidly in versatile matrices. It becomes more strong, indispensable, and popular methods for materials characterizations. The research for analysis of heavy matrix elements in soil, ash, and aerosol is very essential in numerous fields (mineralogy, geology, environmental science, and archaeology, etc.) [8]. It is necessary to get the mean concentration of constituents in geological rock samples, a certain amount of matrix need to be taken and grinding it to a fine powder. It was very difficult to analyze quantitatively such types of the powdered sample by PIXE, but X-ray fluorescence analysis was usually used for this determination. Though the sample preparation process is simple for X-ray fluorescence analysis until now it is rather complicated with respect to PIXE analysis. Additionally, a very small amount of sample is required for PIXE analysis (less than a few mg) on the other hand, X-ray fluorescence analysis requires generally more than 0.5 g sample. Moreover, PIXE has better sensitivity than the X-ray fluorescence analysis. Therefore, for analyzing powdered samples by PIXE, a suitable method for sample preparation is essential to be developed. A powdered internal standard method is developed by Sera K et al. [9] combining with correction for the self-absorption of X-rays to environmental, geological, and biological samples. It was found that the method is very effective even the target is thick enough in which the particles overlap with each other. The method is also applicable for samples prepared by grinding of different particles size.

The objective of this work is to determine the multi-elements in geological samples (sediments & soils) of Bangladesh by PIXE using the powdered internal standard method developed by Sera K et al. [9]. Since the environmental pollution problem has been becoming worst day-by-day in Bangladesh. Chromium and arsenic are highly toxic elements and long term exposers by both these elements can cause serious adverse effects on human health. It is obviously needed to find out the more accurate and rapid method for environmental sample analysis to detect the sources of pollutants (e.g. As and Cr). If it is seen that PIXE as well as powdered internal standard method is suitable for geological sample analysis, then in future this method can be applied in parallel to INAA to overcome the national pollution problem in the right perspective. IAEA geological standard reference materials are being used as a standard for many

research purposes in the different laboratories of the world. But in the IAEA-SRM-Soil-5, Soil-7 and lake sediment SL-1 and SL-3 some major, minor, and trace constituents have not certified [10-13]. So, this study also emphasizes the determination of the non-certified trace, minor and major elements in that SRM's using PIXE and finally to compare with other methods (INAA, PGA).

II. PRINCIPLES OF PIXE

While a target material is being irradiated using an accelerator, the characteristic X-rays emitted from the material is to be detected in PIXE. A charged particle, which is produced in an accelerator, loses energy mainly by exciting electrons in the atoms as it passes through the material. An unstable electron atomic configuration has occurred while the electrons in the inner shells of the atom (mostly the K and L shells) are given adequate energy to them to be ejected. To fill these vacancies, electrons are 'drop-down' from higher shells of the atom and consequences of these discharges excess energy in the form of X-rays. Therefore, these characteristic X-rays can be used to identify of the elemental composition. Then again, the majority elements in the matrix down to nearly 1 ppm (part-per-million) can be determined by measuring the intensities of characteristic X-rays. Protons produced from an accelerator of 2-3 MeV is generally used for sample irradiation purposes. The yield of X-ray production for proton impact as a function of proton energy is given by

$$\sigma_p = \sigma_i \omega k$$

where σ_i represents the ionization cross-section, ω is the fluorescence yield and k is the relative line intensity of possible transitions to fill an inner-shell vacancy.

Table 1 List of samples analyzed in this work (PIXE)

Sample no.	Name of sample	Location	Depth (cm)	Mass (g)
1	Soil	Madhupur, Tangail	50	0.1024
2	Soil	Madhupur, Tangail	Surface	0.1020
3	Soil	Madhupur, Tangail	Surface	0.1039
4	Soil	Madhupur, Tangail	Surface	0.1013
5	Soil	Madhupur, Tangail	Surface	0.1032
6	Soil	Savar, Dhaka	10	0.1027
7	Soil	Savar, Dhaka	Surface	0.1016
8	Soil	Savar, Dhaka	100	0.1016
9	Soil	Savar, Dhaka	150	0.1022
10	River sediment	Gheore, Manikganj	-	0.1034
11	Tannery sediment	Tannery area, Dhaka	-	0.1029
12	Tannery sediment	Tannery area, Dhaka	-	0.1028
13	Soil	Sonargaon, Narayanganj	Surface	0.1002
14	Soil	Sonargaon, Narayanganj	61	0.1038
15	Soil	Sonargaon, Narayanganj	Surface	0.1011
16	Soil	Sonargaon, Narayanganj	Surface	0.1032
17	Soil	Sonargaon, Narayanganj	Surface	0.1015
18	Soil (near tube-well)	Muradnagar, Comilla	Surface	0.1008
19	Soil (near tube-well)	Muradnagar, Comilla	Surface	0.1006
20	IAEA-SRM-Soil-7	Near Ebensee, Upper Austria	10	0.1038
21	IAEA-ARM-SL-1 (Lake sediment)	Sardis Reservoir, Panola country, Mississippi, USA	1500	0.1032
22	NIST-SRM-1633b (Coal fly ash)	-	-	0.1018
23	NIST-SRM-1632b (Bituminous coal)	-	-	0.1021
24	IAEA-SRM-SL-3 (Lake sediment)	Neusiedlersee, Vienna, Austria	-	0.1015

The product of the electron binding energy squared (u_i^2) and the ionization cross-section (σ_i), $u_i^2 \sigma_i$ is plotted (y-axis) versus the expression $T/\lambda u_i$ (x-axis), where T is the proton energy and λ is the ratio of the proton mass to the electron mass. The K and L ionization cross sections are obtained from the y-axis (a plot of the K and L ionization cross sections in proton impact) [14].

By means of heavy-ion impact, the yield of X-ray production can be increased. With identical velocity ions, the cross-section for X-ray production is proportional to Z^2 (Z represents the atomic number).

III. EXPERIMENTAL PREPARATION OF THE SAMPLES

The samples analyzed in this work using PIXE are listed in Table 1. At first a few hundred grams of soil samples were

collected from different areas of Bangladesh. The sediment sample was collected from the tannery industry area of Bangladesh. At first the soil and sediment samples were naturally dried in a clean room separately and then each sample was again dried in an oven at a temperature of about 50^0C until they attained constant weight. An agate mortar was used to make powder samples from the dried each soil and sediment samples separately for ensuring the homogeneity of the samples. The IAEA-SRM-Soil-7 was an aliquot of a homogeneous powder prepared by IAEA [11]. Other IAEA standard reference materials were also originally supplied as a homogeneous powder. Standard reference material coal fly ash 1633b and bituminous coal 1632b were a homogeneous powder prepared by the NIST, Gaithersburg, USA.

For PIXE analysis, about one hundred mg of sample and about 10 mg palladium-carbon (5% palladium) powder (added as an internal standard) were homogenized in an agate mortar. To prepare the thinnest target, around 0.1 mg of powder sample to be taken and putting it onto a 4 µm-thick polypropylene (pp) film (pp film was previously fixed on the 500 µm thick Mylar holder by glue), and approximately 1 µl of 10% collodion solution diluted with ethyl alcohol to be dropped onto it for fixing and smoothing. To avoid the overlapping of the small particles with each other the procedure mentioned earlier was used for the preparation of very thin targets.

IV. SAMPLE IRRADIATION BY BABY CYCLOTRON AND COUNTING

Japan Radioisotope Association (RIA) has established a baby cyclotron (small size) at Nishina Memorial Cyclotron Center (NMCC) for positron emission tomography (PET), Cyclotron Research Center, Iwate Medical University, Takizawa, Japan. This facility also uses for material characterizations and other research works. This baby cyclotron delivers a 2.9 MeV- proton beam on a target after passing through a beam collimator, which defines spot size of the beam. In this study it was 6 mm in diameter. Proton beam with 2.9 MeV from this baby cyclotron was used for the bombardment of thin target film. Silicon lithium, Si (Li) semiconductor detectors coupled with multi-channel analyzers were used for the detection of induced characteristic X-rays and spectra analysis. Two-detector measuring system reported by Sera K et al. [7] was used for simultaneous measurement of multi-elements (as shown in Fig. 1). For the detection of X-rays of energy greater than those of K-K$_\alpha$ the No. 1 Si (Li) detector (0.025 mm Be window and a 6 mm active diameter) with a 500 µm-thick Mylar absorber (in some cases the Mylar absorber thickness were varied) was used. For the measurement of lower-energy X-rays No. 2 Si (Li) detector (0.008 mm Be window & a 4 mm active diameter) without absorber but with an X-ray collimator was simultaneously used. Measurements were carried out by irradiating a sample from the back and the front side of the target with respect to the No. 1 detector in this study. The detailed geometric arrangement is shown in Fig. 1. Iterative calculation using the ratio of calcium concentration achieved from the back irradiation to that from the surface irradiation was used to get the effective thicknesses for self-absorption of the targets. Typical beam currents were few nA for the thinnest sample. The typical measuring time was 5-15 minutes in this work.

V. SPECTRUM ANALYSIS BY SAPIX

The data acquisition system with two detectors are shown in the schematic diagram Fig. 2. Japan NEC PC-9801 personal computer was used for receiving the spectrum data from the two-pulse height analyzer (PHA). The computer code SAPIX developed by Sera K and Futatsugawa S [15] was used for spectrum analysis. In the present investigation the elemental concentrations in all samples were calculated using the quantitative software package SAPIX.
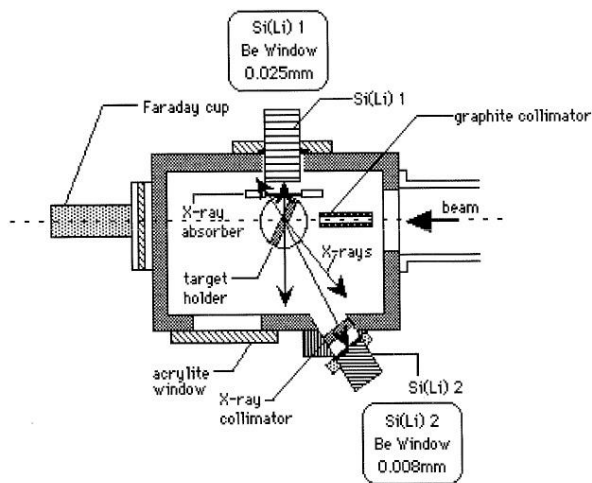

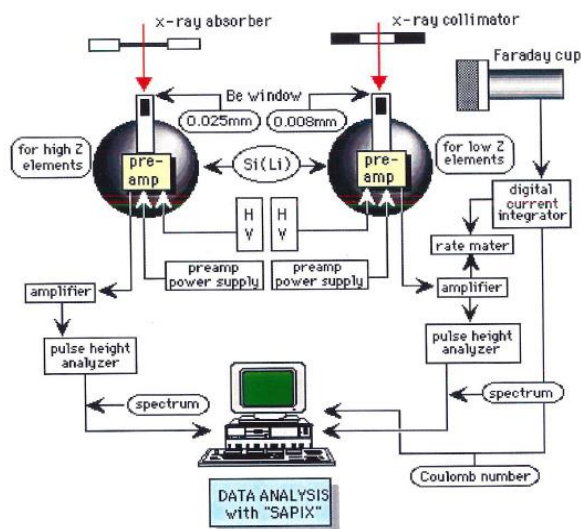**Fig. 1** Geometric arrangement of a proton beam, a target and the two Si (Li) detectors

Fig. 2 Schematic diagram of the data acquisition system with two detectors

VI. RESULTS AND DISCUSSION

A. Accuracy of the analytical results:

In order to assess the accuracy of the PIXE method, IAEA standard reference material Soil-7 and NIST standard reference material 1633b (coal fly ash) were analyzed two times. The analytical results are shown in Table 2. The analytical results for these samples were also compared with the literature values (shown in Fig. 3 and Fig. 4). From Fig. 3 it is seen that the

elemental concentrations of Al, Si, Ca, Mn, Fe, Zn, Rb, Sr, Y, Zr, Nb and Pb in IAEA-SRM-Soil-7 are consistent (within 10%) with the literature values. The concentration of K, Ti and As in IAEA-SRM-Soil-7 are in agreement (within 20%) with the literature values. The concentration of major elements Na and Mg are largely deviated from the literature values although the literature values are not certified. Fig. 3 also shows the reproducibility of the data of this sample. The reproducibility of the data of this sample is in general not good. Probably due to the difficulty of the preparation of very thin and uniform film of the target or due to difficulty of preparation of very fine soil powder sample for PIXE

experiment. The elemental concentrations of multi-elements in NIST-SRM-1633b (coal fly ash) are compared with the literature values (shown in Fig. 4). This figure shows that the concentrations of most of the elements except Na, Mg and Pb are in generally consistent within 20% of the literature values. The data reproducibility of this sample is in generally very good except Fe. The cause might be difficult to prepare very fine powder since iron is metal. This study shows that the determination of toxic trace (few ppm) element Cr in soil sample and coal fly ash is not reliable by PIXE. The other toxic trace element as in soil sample and coal fly ash can determine by PIXE with reasonable accuracy.

Table 2 Elemental concentrations for the IAEA-SRM-Soil-7 and NIST-SRM-1633b (coal fly ash) determined in this study by PIXE with the certified values unless otherwise indicated

Element	X-ray line (used)	IAEA-SRM-Soil-7				NIST-SRM-1633b (coal fly ash)			
		This work			Lit. value[a]	This work			Lit. value[b]
		1st meas.	2nd meas.	Wtd. Mean		1st meas.	2nd meas.	Wtd. Mean	
Na	K_α	1503±121	1479±194	1496±103	2400*	2617±208	3183±321	2784±175	2010±30
Mg	K_α	4167±158	7893±334	4848±143	11300*	1454±183	2285±332	1648±160	4820±80
Al	K_α	38871±1190	52032±1686	43247±972	47000*	139189±4483	150143±4723	144381±3251	150500±2700
Si	K_α	128076±3877	195570±6238	146883±3293	180000*	177640±5710	214074±6686	193006±4342	230200±800
S	K_α	604±43	535±70	585±37	-	2089±97	2060±132	2079±78	2075±11
Cl	K_α	228±50	605±152	265±47	-	†	†	-	-
K	K_α	7850±255	10029±360	8578±208	12100*	16083±539	19485±653	17462±416	19500±300
Ca	K_α	149000±4492	203523±6501	166619±3696	163000*	13547±460	16375±564	14677±356	15100±600
Ti	K_α	2391±107	4738±210	2875±95	3000*	6845±388	9912±380	8410±271	7910±140
Cr	K_α	119±10	n. d.	(119±10)	60	254±23	628±124	266±23	198.2±4.7
Mn	K_α	596±29	1331±80	681±27	631	†	†	-	131.8±1.7
Fe	K_α	26981±1146	42583±1382	33338±882	25700*	74629±4134	119936±4158	97151±2932	77800±2300
Ni	K_α	†	n. d.	-	26*	105±20	†	(105±20)	120.6±1.8
Cu	K_α	20.7±5.1	†	(20.7±5.1)	11	108±10	112±13	109±8	112.8±2.6
Zn	K_α	98±5	112±7	103±4	104	170±9	202±13	180±7	210**
Ga	K_α	†	13.9±4.4	(13.9±4.4)	10*	40.8±4.9	63.5±8.3	46.7±4.2	-
As	K_α	20.8±2.5	11.4±3.3	17.4±1.9	13.4	111±6	112±8	111±4.8	136.2±2.6
Br	K_α	12.6±2.0	10.5±2.4	11.7±1.5	7*	12.3±3.4	n. d.	(12.3±3.4)	2.9**
Rb	K_α	45.3±3.3	50.4±4.3	47.2±2.6	51	115±7	154±10	128±6	140**
Sr	K_α	100±5	111±6	105±4	108	855±31	998±40	909±25	1041±14
Y	K_α	19.7±2.3	n. d.	19.7±2.3	21	62.1±5.3	n. d.	(62.1±5.3)	-
Zr	K_α	152±9	195±18	161±8	185	180±15	97±35	167±14	-
Nb	K_α	10.9±2.7	†	(10.9±2.7)	12*	48.5±6.1	49.1±9.9	48.7±5.2	-
Ba	K_α	†	†	-	159*	899±112	569±116	740±81	709±27
Hg	L_α	58.5±8.9	44.9±14.9	54.9±7.6	0.04*	40.6±12.7	†	(40.6±12.7)	0.141±0.019
Pb	L_α	58.8±9.6	81.5±12.9	66.9±7.7	60	89.9±20.6	102±29	93.9±16.8	68.2±1.1

n.d not determined, † very high error, [a]certified values [11], *non-certified values [11], [b]certified values [16], **non-certified values [16], ( ) data from only one meas

VII MULTI-ELEMENT ANALYSIS IN THE IAEA AND NIST STANDARD REFERENCE MATERIALS (SRM)

The concentrations of multi-elements in lake sediments IAEA-SRM-SL-1, IAEA-SRM-SL-3 and bituminous coal NIST-SRM-1632b were determined in this study by PIXE are shown in Table 3 and Table 4 with literature values. The concentration values for all elements in IAEA-SRM-SL-1 and IAEA-SRM-SL-3 were also plotted for comparison with those reported in the literature (shown in Fig. 5). In IAEA-SRM-SL-1 the literature values for the elements Ti, Mn, Fe, Zn, As, Rb and Ba are recommended with a high degree of confidence but the literature values of all other elements in this sample are information values (shown in Table 3). From

Fig. 5 it is seen that the concentrations determined in this study for the elements Ca, Ti, Cu, Zn, Ga and Rb are good agreement (±10%) with the literature values [12]. On the other hand concentrations for K, Mn, Fe, As and Sr are consistent within ±20% of the literature values [12]. The concentration values of Na, Mg, Al, S, Cl, Cr, Br, Y, Zr, Ba and Pb in IAEA-SRM-SL-1 determined in this study are largely deviated from the literature values. Since the literature values of these above mentioned elements except Ba are information values only so probably the large deviation of the concentrations of these elements is for that reason. From Table 3 it is seen that in IAFA-SRM-SL-3 the literature values of K, As, Rb and Sr are recommended values, all other elements listed in that table are information

values and there are several elements have no literature values. Figure 5 shows that in IAEA-SRM-SL-3 the concentrations of K, Ti, Cr and Sr determined in this study are in good agreement (±10%) with the literature values [13]. The concentration values of Fe, Rb and Ba are consistent within ±20% of the literature values. The other elements concentrations in this sample are largely deviated from the literature values. These large deviations are most probably due to the unreliable literature values (information values).
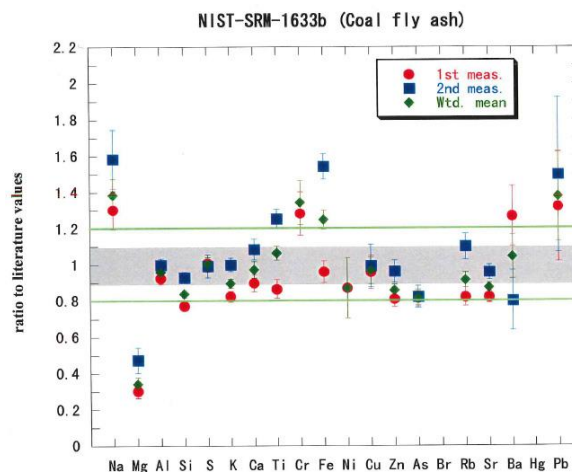
Table 3 Comparison of Elemental concentrations for the IAEA-SRM-SL-1 and IAEA-SRM-SL-3 determined by PIXE with the certified values. The literature values are recommended with a relatively high degree of confidence unless otherwise indicated

Element	X-ray line (used)	IAEA-SRM-SL-1 Concentration (ppm)		IAEA-SRM-SL-3 Concentration (ppm)	
		This work	Lit. value[†]	This work	Lit. value[‡]
Na	K_α	2691±219	(1720±120)	5064±190	(6690)
Mg	K_α	3483±212	(29000)	20306±621	(27000)
Al	K_α	117135±4452	(89000)*	17961±560	(24500)
Si	K_α	235575±8929	-	248241±7466	-
S	K_α	613±67	(12000)	1331±60	-
Cl	K_α	417±80	(10)*	790±67	-
K	K_α	12282±484	(15000)	7732±254	8740
Ca	K_α	2342±129	(2500)	147786±4450	(111100)
Ti	K_α	5158±277	5170±370	2591±174	(2610)
Cr	K_α	194±20	(104±9)	40.5±16.3	37.2±1.9**
Mn	K_α	3943±209	3460±160	448±39	-
Fe	K_α	81428±4229	67400±1700	12994±802	11000±1000
Cu	K_α	28.9±7.5	(30±5.6)	13.4±3.2	-
Zn	K_α	214±10	223±10	31.4±2.6	-
Ga	K_α	25.9±4.1	(24)	6.1±1.6	-
As	K_α	22.1±3.6	27.5±2.9	4.2±1.2	3.2
Br	K_α	9.23±2.78	(6.82±1.73)	8.9±1.3	(5.6)
Rb	K_α	101±6	113±11	30.7±2.3	38.8
Sr	K_α	69.3±5.7	(80)	473±16	470
Y	K_α	23.1±3.6	(85)	19.2±1.9	-
Zr	K_α	161±11	(241)	942±32	248±38**
Nb	K_α	-	(17)*	7.4±2.5	-
Ba	K_α	446±111	639±53	245±45	207±25**
Hg	L_α	-	(0.13)	25.8±5	-
Pb	L_α	89.2±14	(37.7±7.4)	13.7±4.8	-

[†]Literature values [12], [‡]Literature values [13], ( ) Information values only, *Only one data, **Ref [17]
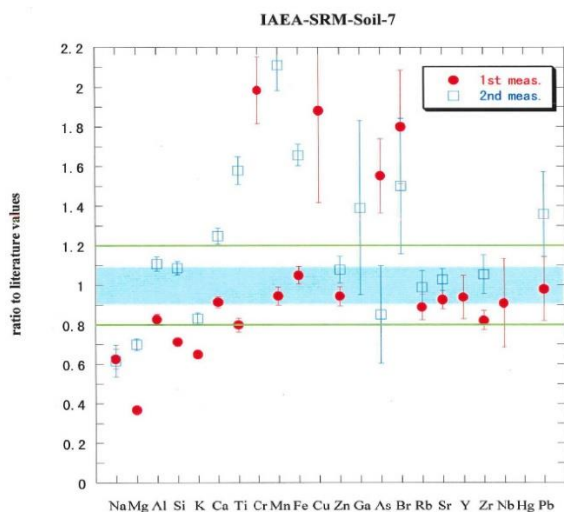
Fig. 3 Comparison of elemental concentrations determined in IAEA-SRM-Soil-7 with literature values and reproducibility of the data for different irradiations at the same position on different days
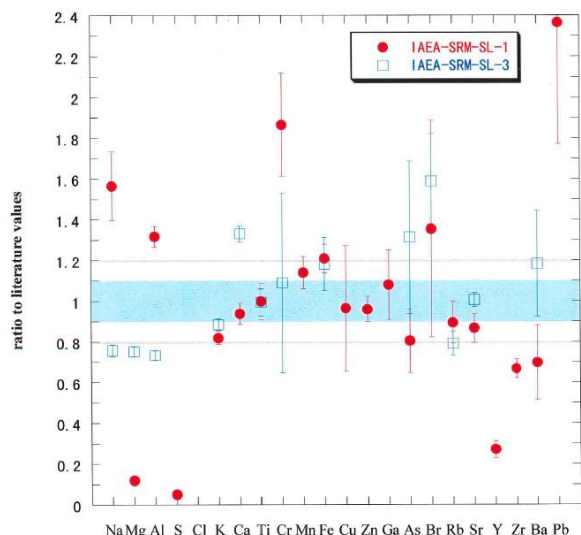

Fig. 4 Comparison of elemental concentrations determined in NIST-SRM-1633b with literature values and reproducibility of the data for different irradiations at the same position on different days

Table 4 Comparison of Elemental concentrations for the NIST-SRM-1632b (bituminous coal) determined by PIXE with the certified values. The literature values are certified unless otherwise indicated

Element	X-ray line (used)	NIST-SRM-1632b (bituminous coal) Concentration (ppm)	
		This work	Lit. value[†]
Na	K_α	2477±116	515±11
Mg	K_α	183±52	383±8
Al	K_α	11143±374	8550±190
Si	K_α	17271±574	(14000)
S	K_α	21889±728	18900±600
Cl	K_α	1199±65	(1260)
K	K_α	799±40	748±28
Ca	K_α	2612±94	2040±60
Ti	K_α	676±39	454±17
Cr	K_α	26.5±7.2	(11)
Mn	K_α	24.7±10.2	12.4±1
Fe	K_α	9584±426	7590±450
Cu	K_α	11.2±2.2	6.28±0.3
Zn	K_α	21.6±1.8	11.89±0.78
As	K_α	2.62±0.9	3.72±0.09
Br	K_α	24.1±1.6	(17)
Rb	K_α	6.2±1.3	5.50±0.11
Sr	K_α	102±5	(102)
Y	K_α	2.58±0.97	-
Zr	K_α	26.6±3.3	-
Pb	L_α	10.1±3.5	3.67±0.26

[†]Literature values [18], ( ) information values only

Fig. 5 Comparison of elemental concentrations determined in lake sediments IAEA-SRM-SL-1 and IAEA-SRM-SL-3 with literature values

The multi-elements concentrations determined in this study in NIST-SRM-1632b (bituminous coal) are shown in Table 4. The concentrations of multi-elements were plotted for comparison with the literature values (shown in Fig. 6).

From this figure it is seen that very few elements (S, Cl, K, Rb and Sr) are agreement (within ±20%) with the literature values. The concentrations of other elements are not consistent with the literature values. The inconsistent of the elemental concentrations with the literature values most probably due to the difficulty of the coal sample preparation (very thin film) for PIXE.

VIII MULTI-ELEMENT ANALYSIS IN THE SOILS AND
SEDIMENTS OF BANGLADESH

The concentrations of multi-elements (Na, Mg, Al, Si, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Cu, Zn, Ga, As, Br, Rb, Sr, Zr, Nb, Ba, Hg and Pb) in soils and sediments of Bangladesh were determined in this study by PIXE. The analytical results are shown in Table 5. It is seen that the concentration of toxic element Cr in soil sample is very low on the other hand in the tannery sediment (No. 11) it is very high and is consistent (within ±15.7%) with the INAA value determined by Latif SA et al. [19]. The concentration of Cr in river (Gheore, Manikganj) sediment is not so high compare to tannery sediment. This study again reveals that the elevated concentration of Cr in that tannery sediment sample is due to anthropogenic contamination. This study also shows that the higher levels of Cr can be easily determined in sediments by PIXE. The elevated levels of another toxic element As were

determined in the soil samples (No. 18 & 19, near tube-well) collected from Comilla district. This study shows that the higher levels of As in that soil samples may be due to the direct contamination of the tube-well water. The concentration of As in the tannery sediment (No. 11) is consistent (within ±14.3%) with the INAA value determined by Latif SA et al. [19]. This study further reveals that the higher levels of As can be determined in soils and sediments by PIXE.

CONCLUSION

This study shows that 26 elements (Na, Mg, Al, Si, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Ga, As, Br, Rb, Sr, Y, Zr, Nb, Ba, Hg and Pb) in very small amounts of IAEA-SRM-Soil-7 are determined by PIXE with reasonable accuracy. The literature values [11] for most of the elements mentioned above of the IAEA-SRM-Soil-7 sample are non-certified except Cr, Mn, Cu, Zn, As, Rb, Sr, Y, Zr and Pb. This study reports the concentration of the elements in the investigated IAEA and NIST standard reference materials for the certification especially for the non-certified elements.

Recently, PIXE as well as XRF methods were applied for the assessment of contaminants in aerosols by Diaz et al. 2014 [20]. Since PIXE is also an online process and multi-element character then it can be used for determining the elevated levels of toxic element arsenic and chromium as well as other elements in soils and sediments. This study also shows that PIXE using powdered internal standard method developed by Sera K et al. [9] is an alternative method of INAA for the rapid identification of the environmental pollution problem due to

higher levels of chromium arises from tannery industries as well as other sources and elevated arsenic contamination problem in Bangladesh.
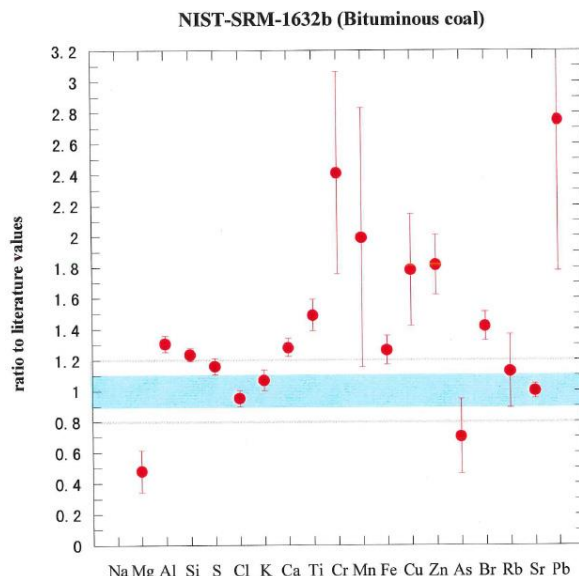

Fig. 6 Comparison of elemental concentrations determined in NIST-SRM-1632b with literature values

Table 5 Elemental concentrations (ppm) determined in soil and sediment samples collected from different areas of Bangladesh using PIXE

Element	X-ray line (used)	Soil (1)	Soil (2)	Soil (3)	Soil (4)	Soil (5)	Soil (6)	Soil (7)
Na	K_α	1455±209	1627±190	1495±117	2917±282	981±150	1979±202	1880±202
Mg	K_α	1965±231	1913±208	925±113	2202±277	922±154	1476±207	1518±202
Al	K_α	88620±231	86659±2711	42776±1333	80069±2615	45108±1444	70130±2231	51706±1689
Si	K_α	260864±8154	260892±8094	345473±10728	351546±11329	230154±7247	270837±8505	367875±11808
S	K_α	239±73	112±63	†	†	183±52	195±71	†
Cl	K_α	†	376±123	221±85	634±158	†	465±135	†
K	K_α	17542±592	17399±586	18729±611	15573±543	11941±415	16529±571	17835±636
Ca	K_α	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.
Ti	K_α	6153±236	6566±238	4557±160	4932±207	5292±198	5803±224	6304±239
Cr	K_α	n. d.	n. d.	n. d.	n. d.	†	†	†
Mn	K_α	1598±90	1929±96	1798±70	660±71	1078±70	1697±97	1856±99
Fe	K_α	71693±2361	72950±2359	29860±932	45789±1532	46606±1539	62943±2067	38138±1276
Cu	K_α	18.0±6.0	16.9±5.5	9.5±2.8	†	†	†	†
Zn	K_α	49.9±5.2	45.6±4.7	31.7±2.6	42.4±5.0	28.9±4.0	60.7±5.7	28.3±4.1
Ga	K_α	21.5±4.3	22.8±4.0	10.9±1.9	12.7±3.9	17.9±3.5	26.5±4.5	†
As	K_α	†	†	5.5±1.3	8.6±2.7	†	9.3±3.0	†
Br	K_α	†	†	5.6±1.1	†	†	†	†
Rb	K_α	152±7.9	161±7.8	94.7±4.1	124±8	97.4±5.9	140±8	109±7
Sr	K_α	34.4±3.8	39.0±3.8	36.2±2.4	30.2±4.0	20.9±3.2	44.1±4.4	30.2±3.8
Zr	K_α	138±16	360±23	527±22.5	197±19.3	622±33	356±26	441±28
Nb	K_α	14.4±4.6	24.3±4.9	9.2±2.9	†	†	21.9±5.8	20.9±5.6
Ba	K_α	n. d.	640±82	378±60	529±123	n. d.	†	n. d.
Hg	L_α	n. d.	n. d.	†	n. d.	n. d.	†	n. d.
Pb	L_α	51.8±11.9	75.9±10.8	24.7±5.1	†	†	50.7±11.6	†

(Continued)

Table 5 (continued)

Table 5 Elemental concentrations (ppm) determined in soil and sediment samples collected from different areas of Bangladesh using PIXE

Element	X-ray line (used)	Soil (8)	Soil (9)	River sediment (10)	Tannery sediment (11)	Tannery sediment (12)	Soil (13)
Na	K_α	16111±2250	2223±241	5770±275	5737±206	6532±504	7493±397
Mg	K_α	24193±2569	2371±262	7262±312	2633±105	4552±448	10211±467
Al	K_α	n. d.	114687±3603	49403±1576	7248±243	38844±1533	84015±2752
Si	K_α	n. d.	323465±10083	280308±8786	204293±6190	272390±10074	365257±11786
S	K_α	†	n. d.	†	4284±139	9716±599	†
Cl	K_α	†	1175±170	†	4196±141	622±297	781±192
K	K_α	170936±5740	19157±638	16576±545	4802±166	14447±608	23104±789
Ca	K_α	n. d.	n. d.	13700±457	42473±1293	21611±872	10279±385
Ti	K_α	62780±2424	7710±287	4135±172	1588±74	3075±221	4860±223
Cr	K_α	1761±693	†	321±76	12958±551	†	†
Mn	K_α	434±70	3507±164	1198±75	30992±1315	901±137	1085±84
Fe	K_α	86749±2927	83229±2778	54894±1800	†	34815±1389	54179±1830
Cu	K_α	†	21.9±7.2	†	39.0±4.1	113±16	26.3±7.3
Zn	K_α	45.8±5.7	56.3±6.2	59.9±4.5	79.4±4.0	961±45	112±8
Ga	K_α	25.6±4.8	20.9±5.1	16.9±3.6	†	n. d.	17.6±4.8
As	K_α	†	†	†	5.1±1.6	n. d.	n. d.
Br	K_α	†	n. d.	n. d.	†	n. d.	†
Rb	K_α	153±9	152±9	103±6	25.1±2.3	n. d.	118±8
Sr	K_α	30.2±4.0	43.9±4.7	161±8	117±5	n. d.	126±8
Zr	K_α	361±27	676±40	402±27	90.5±5.8	n. d.	146±21
Nb	K_α	†	†	17.4±4.9	†	n. d.	17.7±5.7
Ba	K_α	†	†	341±91	107±42	†	†
Hg	L_α	n. d.	n. d.	†	21.5±5.7	n. d.	n. d.
Pb	L_α	47.1±12.1	83.3±13.8	37.7±9.1	42.3±6.3	110835±4334	117±14.7

(Continued)

Table 5 (continued)

Table 5 Elemental concentrations (ppm) determined in soil and sediment samples collected from different areas of Bangladesh using PIXE

Element	X-ray line (used)	Soil (14)	Soil (15)	Soil (16)	Soil (17)	Soil (18)	Soil (19)
Na	K_α	7020±358	7030±460	5915±270	8153±367	6747±343	6165±321
Mg	K_α	16219±598	10022±532	6684±293	7326±348	8338±385	9118±394
Al	K_α	111566±3501	79262±2663	59359±1882	65685±2115	63302±2060	60924±1957
Si	K_α	360663±11230	337382±11082	294995±9240	319891±10145	348851±11155	302230±9553
S	K_α	286±84	524±116	†	†	344±89	†
Cl	K_α	552±160	†	1002±135	1078±153	621±176	979±167
K	K_α	30010±960	23185±812	22984±741	19307±643	20569±700	18225±605
Ca	K_α	9984±352	13375±502	11557±395	10195±362	8322±316	8501±307
Ti	K_α	6343±245	5012±245	4117±168	4386±186	4839±211	4902±200
Cr	K_α	†	†	277±69	221±76	300±88	222±67
Mn	K_α	1444±92	1141±109	1169±66	1186±82	1271±86	1163±80
Fe	K_α	77872±2613	62576±2272	48780±1571	54578±1831	50663±1682	56068±1843
Cu	K_α	100±31	†	27.7±4.9	20.8±6.0	†	†
Zn	K_α	122±8	108±9	71.9±4.9	64.1±5.7	102±7	98.2±6.5
Ga	K_α	27.2±4.8	†	17.5±3.4	25.6±4.3	23.9±4.4	23.6±4.2
As	K_α	13.1±3.1	†	†	†	18.8±3.2	43.7±3.8
Br	K_α	†	†	†	†	†	14.7±2.5
Rb	K_α	177±9	130±10	112±6	113±7	126±7	109±7
Sr	K_α	128±7	140±10	135±7	137±8	108±7	115±7
Zr	K_α	110±16	337±35	341±23	659±37	180±20	462±30
Nb	K_α	15.9±5.4	n. d.	†	21.8±5.9	n. d.	†
Ba	K_α	598±141	485±126	338±57	485±125	357±98	298±95
Hg	L_α	†	n. d.	†	†	†	n. d.
Pb	L_α	36.9±11.8	55.3±15.3	36.8±8.1	26.9±9.7	35.2±12.1	†

The number in parentheses are indicated the sample number, n.d. not detected, † very high error (≥40%)

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