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Trace elements of soil samples from mining area

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ABSTRACT

The affect of mining activity on the environment has been long of public concern. The present paper deals with the elemental analysis of soil samples from a mine and the area around it, located in E 48°59′ and N 34°11′ in Hamadan province of Iran. Elemental analysis was done using Proton Induced X-ray Emission (PIXE) technique. Spectra analysis and quantification was done using GUPIX software. Besides the major elements Si, P, K, Ca, Mn and Fe the other elements, namely Cl, Ti, V, Cr, Co, Ni, Cu, Zn, Rb, Sr and Pb were also present. Arsenic could be detected in some samples only. The presence of Ba and Ce needs more investigations by other techniques due to overlap of the L X-rays of these elements with the K X-rays of the major elements Mn and Fe, etc. Many elements V, Cr, As and Pb are known to be toxic and needs further understanding and proper handling in the mining process.

1. Introduction

Environmental pollution from mining activity is one of the major concerns globally. Mining generally releases toxic heavy metals such as arsenic (As), cadmium (Cd), lead (Pb) and mercury (Hg). The adverse effects of mining activity on the environment as well as human health have been observed in many areas [1–3]. Metal mining and smelting activities are important sources of heavy metal air pollution, often leading to considerable soil contamination. The contamination of soils by heavy metals may pose long term environmental and health implications. One of the fallout of the mining activities is the production of large quantities of wastes in the process of separation of the benefiting minerals from the whole ore mass. This has led to the creation of mine tailings that are big structures for the deposition of wastes. The quantities of metals in these areas could be an important environmental hazard. Therefore, it is extremely important to have analytical methodologies that allow us to quickly quantify the metal contents of the mineral wastes and also are highly sensitive because the heavier elements, like As, Cd, Pb, and Hg are highly toxic to the human body even at trace level. Particle Induced X-ray Emission (PIXE) is a powerful technique for quantitative analysis because it is non-destructive, multi-elemental (from Na to U), highly sensitive and requires no special sample preparation. Usually proton beams with an energy around 3 MeV, are used in PIXE offering high sensitivity. Development of PIXE with ions other than proton is still continuing [4].

Keeping in view the above consideration, in the present paper, we report the preliminary results on the PIXE analysis of the soil samples collected from a mine and the area around it, located in E 48°59′ and N 34°11′ in Hamadan province of Iran.

2. Experimental methods

2.1. Sample preparation

Seven soil samples for analysis were collected from a mining area situated in Hamadan province of Iran. Three types of samples were collected: (A) residual material after mining process, (B) nearby area of mine and (C) clean area (control sample). The collected soil samples from specific regions were air dried, cleaned and subsequently grounded into fine powder by using a pestle mortar. The powdered samples were thoroughly mixed with high purity graphite powder in the ratio 1:1 by weight. This step is necessary for charge integration with better accuracy and eliminating the problems associated with charging during PIXE measurements [5]. Then self-supporting pellets of 9 mm diameter from the finely pulverized sample were made using a die of stainless steel. A constant pressure of $\sim$20 kN/cm^2 was applied to the die head by using hydraulic press (Paul-Otto-Weber Co., Germany) so as to get pellet of uniform thickness and to reduce the surface effects.

2.2. Experimental setup and data collection

The analysis of the soil samples were carried out by using PIXE technique. A 3 MeV proton beam with a current of 2–3 nA was used to bombard the samples. Proton beam was produced from Single

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Dee cyclotron situated at Panjab University, Chandigarh, India [6]. A multipurpose scattering chamber with 12 in. diameter is designed to carry out Rutherford backscattering (RBS), Particle Induced X-ray Emission (PIXE) and Particle Induced Gamma ray Emission (PIGE) studies. Chamber is attached to the beam line as shown in Fig. 1. The signal from detector was shaped and then amplified and finally, through a pulse height analysis, the energy spectrum was stored and displayed in a multichannel analyzer. 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 X-rays emitted from the samples were detected by an ORTEC HPGe detector (FWHM 150 eV at 5.9 keV) at 45° to the beam line as shown in Fig. 1. For PIXE, energy range to be detected is from 1 keV to 80 keV approximately and HPGe has better efficiency than Si (Li) in this energy range, although resolution is nearly same for both types of detectors. Solid angle for the HPGe detector is $1.13 * 10^{-2}$ Sr. Mylar window of thickness 6 μm is used in front of the detector which acts as an absorber for the X-rays. Absorption of X-rays in the Mylar window is calculated using the formula:

$$\frac{I}{I_o} = e^{(-\mu x)}$$

where I is the intensity of the X-rays after passing through the Mylar window, I_o is the initial intensity of the X-rays, μ is the attenuation coefficient of Mylar and x is thickness of the Mylar foil used. Code XCOM was used to calculate the values of μ. Absorption of the X-rays in the Mylar window comes out to be 91% for 1 keV X-rays, decreases to 30% for 2 keV X-rays and 0.3% for 10 keV X-rays. The beam current was integrated in the sample (for thick targets) and in a Faraday cup behind the target (for thin targets). Each target was irradiated with 3 μC charge approximately. The beam current was kept lower than 3 nA in order to avoid high counting rates at the detector that would reduce the detection sensitivity due to the increase of the background noise. The vacuum obtained inside the experimental chamber was of the order of 10^{-5} Torr. The chamber has two view ports and several other ports for various feed throughs. The GUPIX software is employed to analyze the spectra.

3. Data analysis

The data collected were analyzed using Guelph PIXE code, GUPIX. The detailed features of this code have been explained by Maxwell et al. [7]. The quantitative estimation was done using the thick target option of GUPIX code. The GUPIX software utilizes the Fundamental Parameter Method for the quantitative analysis. For a known experimental geometry the sample composition can be calculated from the measured intensities of the X-ray lines by using known physical parameters like X-ray ionization cross section, mass attenuation coefficient and fluorescent yields. The calculations consider particle stopping powers and the energy dependence of the ionization cross-sections. The absorption of X-rays leaving the target from different depths in a direction to the detector is taken into account. The pellets made from soil samples are infinitesimally thick target for 3 MeV protons; therefore, matrix effects with infinitesimally thick target were applied. The error in the final concentration values is of the order of 5–10% due to the fundamental parameters and efficiency calibration.

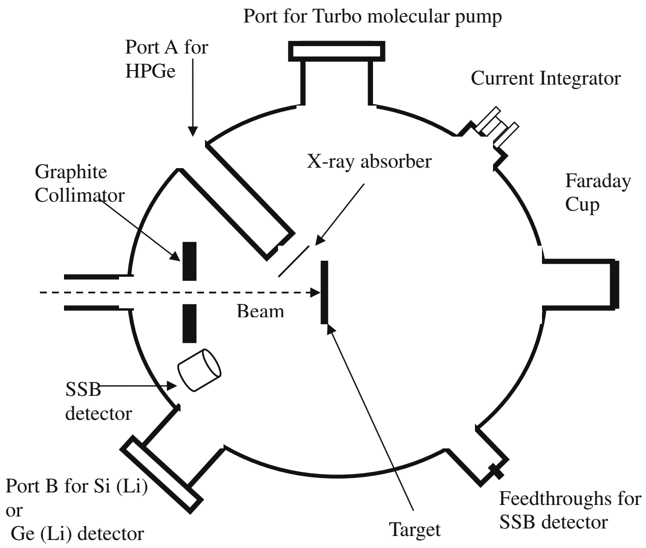

Fig. 1. Schematic diagram of PIXE chamber.

4. Results and discussion

Twenty elements Si, P, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Rb, Sr, Ba, Ce and Pb were observed in these soil samples. Figs. 2a–2c present the typical spectra from (A) residual material after mining process, (B) nearby area of mine and (C) clean area (control

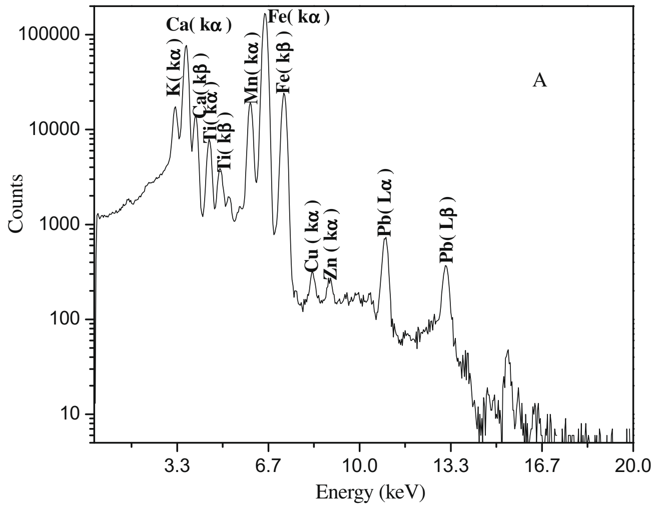

Fig. 2a. Spectrum of residual material after mining process.

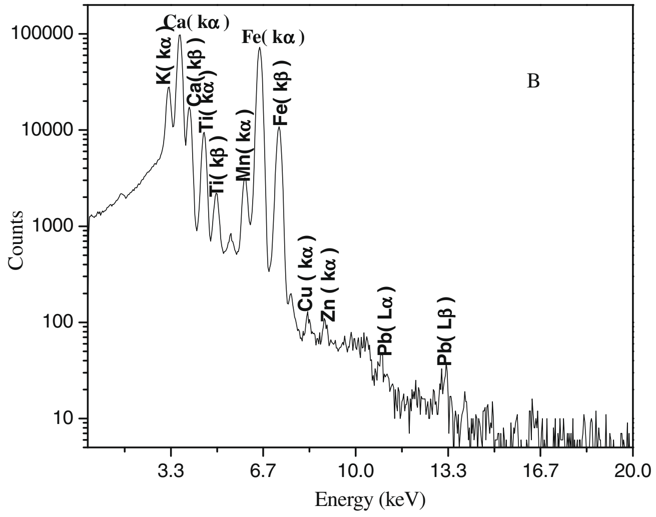

Fig. 2b. Spectrum of nearby area of mine.

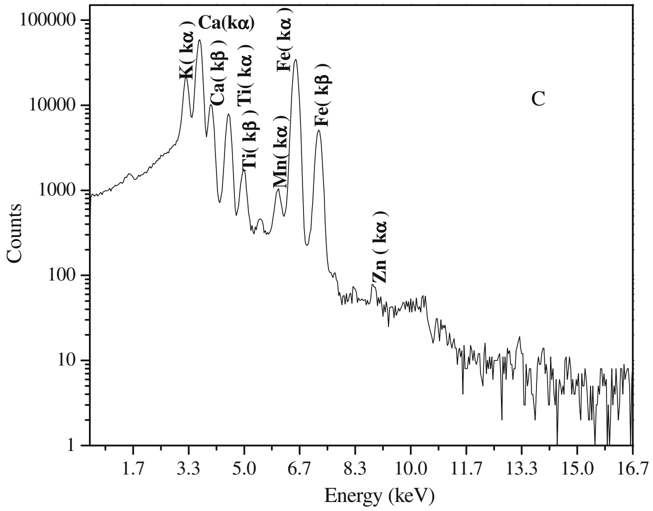

Fig. 2c. Spectrum of control sample.

Table 1
Elemental concentration (in ppm) of the soil samples.

Elements	A1	A2	B1	B2	B3	B4	C
Si	55,764	70,664	71,326	38,501	20,495	85,403	59,019
P	4855	540	5209	1781	2516	6983	5243
Cl	21	1723	21	244	140	262	286
K	6790	8085	11,781	10,727	3039	16,881	9287
Ca	26,249	25,711	32,913	17,112	13,208	27,887	19,643
Ti	888	1070	2325	1743	573	2833	1989
V	57	50	28	48	0	93	19
Cr	22	30	76	44	52	91	47
Mn	5296	3863	760	453	14,051	1613	193
Fe	54,011	45,372	22,995	17,408	163,072	35,480	11,151
Co	201	166	150	93	906	179	60
Ni	37	30	54	43	105	46	20
Cu	82	53	31	22	15	42	12
Zn	88	105	32	53	77	74	21
As	0	0	5	10	0	2	7
Rb	69	101	59	59	1020	138	49
Sr	13	87	9	57	41	0	23
Ba	3869	3415	117	49	8768	1065	0
Ce	212	222	62	50	374	134	46
Pb	3389	2868	86	48	1812	175	0

Table 2
Average concentrations of trace elements in all the three type of samples.

Elements	Atomic No.	A (ppm)	B (ppm)	C (ppm)
Si	14	63,214	65,077	59,019
P	15	2697	4657	5243
Cl	17	97	176	286
K	19	7438	13129	9287
Ca	20	25,980	25,971	19,643
Ti	22	979	2301	1989
Cr	24	26	70	47
Mn	25	4580	942	193
Fe	26	49,692	25,294	11,151
Co	27	184	141	60
Ni	28	34	48	20
Cu	29	67	31	12
Zn	30	96	53	21
As	33	0	6	7
Rb	37	85	85	49
Sr	38	50	36	23
Zr	40	27	202	25
Ba	56	3642	410	0
Ce	58	217	82	46
Pb	82	3128	103	0

sample), respectively. For soil samples Bremsstrahlung in low energy is too high and also due to the Mylar window in front of the detector Si K X-ray peak is not showing up clearly in the spectrum. Table 1 shows the variations in the elemental concentrations of the different samples studied and Table 2 shows the average concentrations of trace elements in all the three type of samples. From Tables 1 and 2 presence of toxic element V, Cr, As and Pb can be seen in the soil after mining process. Whereas the nearby area of mine is slightly affected by the lead traces but the remote areas are safe from it. Arsenic could be detected in some samples only. The presence of Ba and Ce needs more investigations by other techniques due to overlap of the L X-rays of these elements with the K X-rays of the major elements Mn and Fe, etc. The analysis of the soil samples also gives the presence of iron and barium elements in the reasonable amount.

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