Pittsburgh rainwater analysis by PIXE[1]

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ABSTRACT

Concentrations of thirteen elements in rainwater from the Pittsburgh, Pa., area were analysed by Charged Particle Induced X-ray Emission (PIXE). They were compared to rainwater in a rural area and air particulates in Pittsburgh. Local and non-local contributions are discussed. Washout ratios were calculated and found to be larger for smaller size particles, contrary to general belief. This work demonstrates the convenience of using PIXE.

Introduction

The quality of rainwater has been widely studied in the past because of its possible relationship with the existence and scrubbing of air pollution particulates, and also for meteorological reasons. Most of these studies have involved light elements (below calcium) and studies on heavy elements are relatively few. In a city like Pittsburgh, Pa., where heavy element pollutants are continuously emitted from industrial sources (i.e. Fe) and from the heavy traffic (i.e. Pb), information on heavy elements in rainwater should be important. In this paper, the results of such a study will be presented. These data then are compared to data of air pollution particulates in the same area and rainwater in a rural area.[2] In addition, this work demonstrates the relative ease of this kind of study, involving many samples by using Particle Induced X-ray Emission Analysis (PIXE). Since the original paper by Johansson et al. (1970), there have been many attempts to use PIXE in different applications. Its advantage is that information of a wide range of elements can be obtained simultaneously. Problems usually encountered are (1) sensitivity, (2) accuracy (reproducibility), and (3) preparation of thin targets. One will see that all these problems are minimal for rainwater analysis.

Experimental

Three different types of samples were analysed: rainwater in Pittsburgh, rainwater in the rural area, and air particulates in Pittsburgh. The air particulates samples were collected on top of a building approximately 100 ft. above street level. A total of thirty samples were taken through a period from December 1972 to February 1973. The samples of rainwater from Pittsburgh were collected on top of the same building. They represented a total of twenty-one rainfall events in the period from January 1974 to July 1974. And the samples of the rainwater from the rural area were collected at ground level. They consisted of nine rainfall events for a period between April 1973 and July 1973. More details of the meteorological conditions can be found in Frohliger et al. (1973) and Kane (1974).

Rainwater samples were collected with samplers shown in Fig. 1. The funnel and bottle were made of polyethylene. The sampler was put on a sampling stand, five feet above the ground. It was covered with plastic to minimize dust settling except during rainfalls. The sample was taken out, sealed and frozen for storage immediately after the rainfall. Further details are given in a publication by Frohliger (1973) who took care of sample collection.

[1] Supported by the National Science Foundation.

[2] This is a rectangular area bounded by Uniontown, Pa., on the northwest, Morgantown, W.Va., on the southwest, Mt. Storm, W.Va., on the southeast and Luke, Md., on the northeast; it is about 80 miles southeast of Pittsburgh.

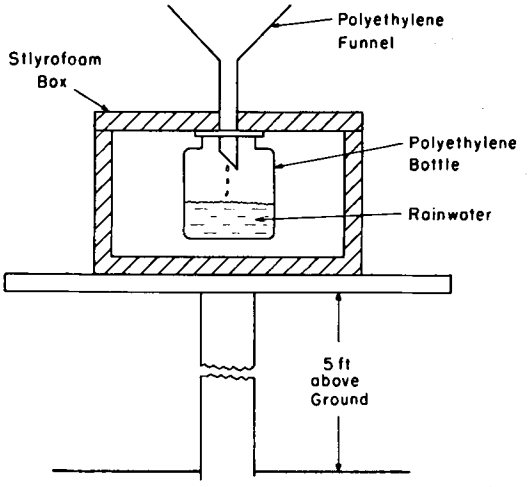

Fig. 1. Rainfall collector used.

In making targets, a vanadium standard solution was added to 50 ml of rainwater sample to a concentration ~2 mg/l, such that the original vanadium concentration was negligible (an estimation of original vanadium concentration in rainwater can be made from Gladney et al. (1972) and Zoller et al. (1973)). The 50 ml sample was then concentrated to ~1.5 ml by evaporation with heating. The heating was controlled so that no boiling occurred in order to minimize possible losses of heavy elements. Approximately 0.5 ml of this final volume was transferred to a mylar target backing and left to dry under cover at room temperature. This procedure produced targets of thicknesses ≤ 50 $\mu g/cm^2$, thin enough for PIXE. The mylar backing used had a thickness of 200 $\mu g/cm^2$. Contamination of the mylar was monitored at different times. Except for phosphorus, all other contaminants were found to be either below the detection limits or well below the levels that would be observed in rainwater samples.

Particulate samples were collected by pulling air through Nuclepore filter disks with a small carbon-vane pump. Air flow, as measured with a rotameter, was approximately 6 liters/min. The Nuclepore disks used were 25 mm in diameter and had a 5 μ pore size. These filters were thin enough to be used directly as targets. The purity was checked regularly and no contamination of heavy elements was found.

PIXE was then performed on these rainwater and air particulates samples. Particles used to excite the X-rays included 6 MeV and 4 MeV alpha particles and 6 MeV protons. Fluorescent X-rays were detected by a Si(Li) detector with energy resolution of ~210 eV. Average detection times were 25 min per target. A typical spectrum is shown in Fig. 2. Energy spectra were analysed by using computer programs XRAFIT to extract peak positions and peak areas and RESULT to convert peak positions to X-ray energies and peak areas to concentrations. Concentrations were determined by comparing to the vanadium standard. All targets were made in duplicate to check for accuracy. Usually, they were better than 20% as shown in Fig. 3.

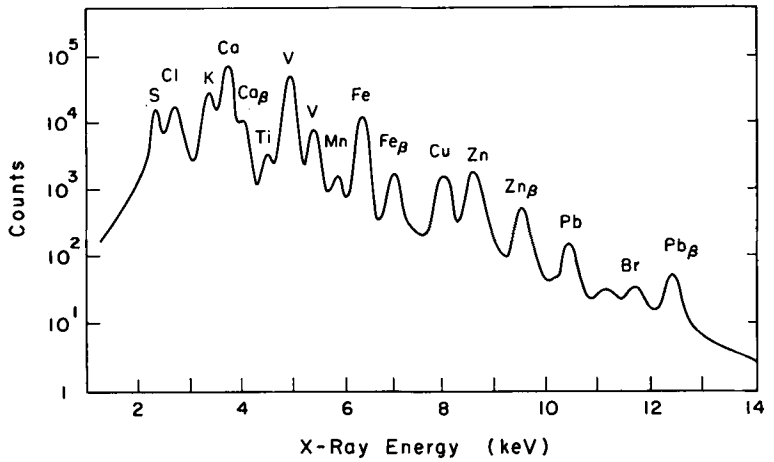

Fig. 2. A raw spectrum of PIXE on Pittsburgh rainwater with 6 MeV alpha particles. 5 mil mylar was used as absorber.

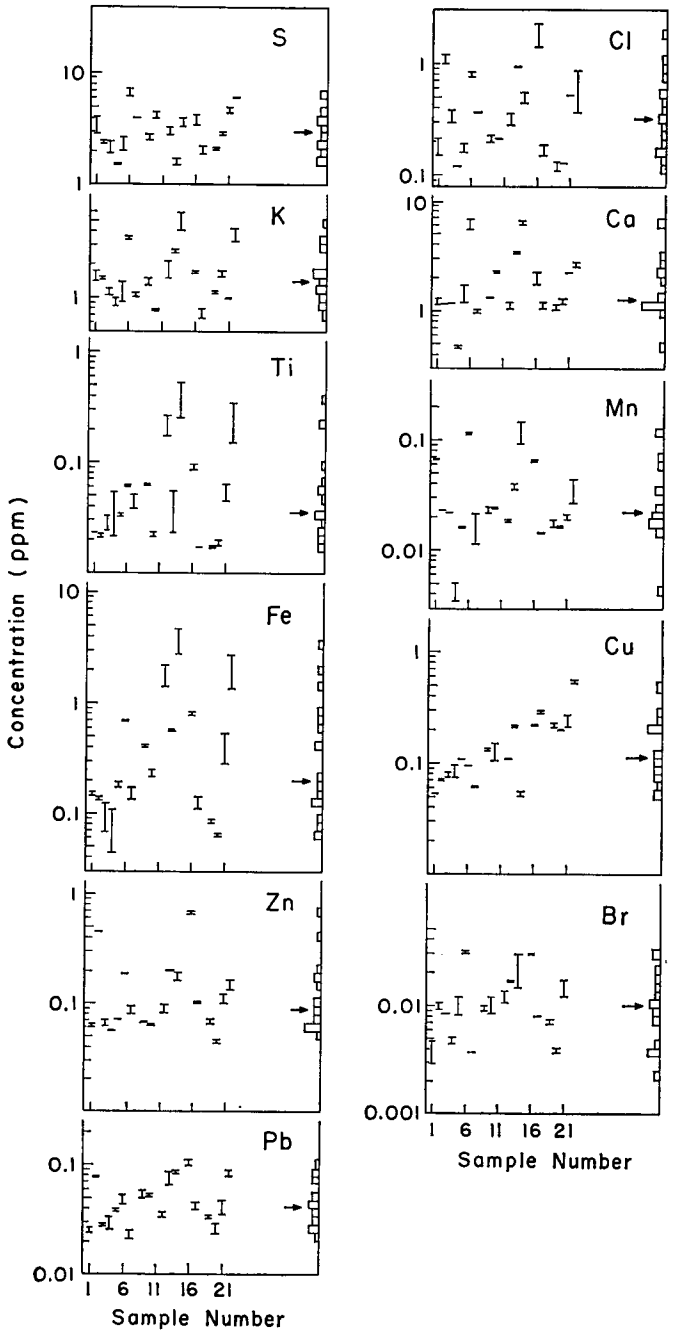

Fig. 3. Concentrations in ppm of different elements. Results for duplicates of the same sample were shown and formed the error bar. Distributions in log scale of concentrations were shown with arrows pointing at the centroids of the distributions.

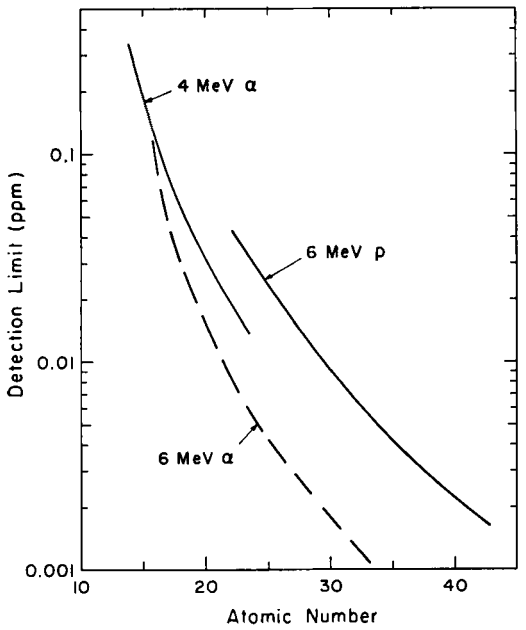

Fig. 4. The PIXE detection limits in ppm for different types of incident projectiles.

The mass detection limit of PIXE has been discussed in detail by Herman et al. (1973). It can be defined as the minimum mass of target material which produces a signal to background ratio better than a certain constant (30% in this work). This definition assumes all the mass on the target is in the beam so will not change among targets. The practical detection limit expressed in parts per million (ppm), shown in Fig. 4, will depend on the target for the following reasons: (1) the volumes of samples transferred to individual targets are different, so the conversions between mass and ppm are not the same for different targets; (2) the beam may be hitting only part of the mass on the target. Deviations will be up to 50% among different targets.

Self absorption of the samples is considered theoretically according to the thin-specimen criterion (Rhodes et al., 1972):

$$\Sigma_i \mu_i m_i \leqslant 0.1$$

where μ_i is the mass absorption coefficients (cm^2/g) and m_i is the mass per unit area (g/cm^2) of different elements on the target. Using the elemental composition from a major element analysis of Pittsburgh air particulates (Shabason & Cohen, 1972) and approximating the total thickness with 1 mg/cm^2, $\Sigma_i \mu_i m_i$ is calculated to be 0.071 and 0.22 for 6 keV and 4 keV X-rays respectively, which in turn means more than 90% and 80% X-ray transmission respectively. In other words, for air particulate samples, having thicknesses ~ 750 $\mu g/cm^2$, self-absorption effects will not contribute significantly for X-rays emitted from elements heavier than calcium. For rainwater samples, thicknesses were much less so, X-rays from all elements are practically self-absorption-free.

Results

The results for Pittsburgh rainwater are displayed in Fig. 3. The X-axis is the number of the sample. Results for duplicate targets are shown and form the error bars of the experiment. Distributions in concentration are presented in steps of 20%. The center arrow is the centroid of the distribution.

The results of the analysis of Pittsburgh rainwater, Pittsburgh air particulates and rural area rainwater are also tabulated in Table 1. Only concentrations of elements appearing in more than 90% of the samples are reported, except for those with a number in brackets following. They are elements found only occasionally, and the ratio is the number of samples in which this element was found over the total number of samples analysed. The main reason why they were not found in the rest of the samples is because of too low a concentration. The numbers given then were only the average from samples where observation was possible. K is the centroid of the distribution and ΔK is the ratio of the second maximum concentration to the second minimum concentration. Elements not listed in the Table are missing for one of the following reasons: (1) the sensitivity of the experiment was not sufficient; (2) the element appeared in less than 90% of the samples; (3) there were interferences among X-rays of different elements; and (4) there were contaminations from other sources, i.e. phosphorus in mylar.

Discussion

Pittsburgh is one of the major industrial cities in the United States, especially for the steel

Table 1. *Elemental contents in air particulates and rainwater samples*

K is the centroid of the distribution as shown in Fig. 2. All values for rainwater are in ppm. Values for air particulates are in relative weight with arbitrary normalization. ΔK is the ratio of the second maximum concentration to second minimum concentration

	Pittsburgh air particulate K (rel. units)	ΔK	Pittsburgh rainwater K (ppm)	ΔK	Rural area rainwater K (ppm)	ΔK
Al	No analysis performed		0.62	16	0.21 (8/34)	
Si			1.3	38	0.7	6.6
S			2.9	4.0	2.8	8.0
Cl			0.33	8.2	0.29 (6/34)	
K			1.4	4.0	0.39	5.0
Ca			1.2	6.6	0.71	4.0
Ti	0.042	5.6	0.036	13	Below sensitivity	
Mn	0.027	32	0.022	8.0		
Fe	0.645	11	0.20	30	0.078	13
Cu	0.007	11	0.12	5.6	0.15	13
Zn	0.028	9.5	0.088	7.0	0.082	14
Pb	0.040	9.5	0.041	3.4	0.019	5.8
Br	0.017	16	0.0096	8.0	0.0035	

industry, which introduces high SO_2 and iron levels into the atmosphere. As shown by Wedberg et al. (1974), the traffic in Pittsburgh constitutes another major source of air pollution, i.e. Pb and Br contaminants. These factors have made air in Pittsburgh unsatisfactory in general, and the average air particulates level is ~ 120 $\mu g/m^3$. On the contrary, particulate level in the rural area is only ~ 40 $\mu g/m^3$ on the average, very much lower than in Pittsburgh.

Before comparing data in Table 1, one irregularity in the Table will be discussed. The Cu levels both in Pittsburgh and the rural area appeared to be at least ten times higher than values reported previously (Rhodes et al., 1972; Granat et al., 1972; Gatz, 1972). This can be observed also in the comparison of ratios of Cu to other heavy elements in Pittsburgh rainwater and air particulate data. Contamination was suspected. The low Cu levels of polyethylene and glassware (Robertson, 1968) showed that the containers used were a very improbable source for this high level contamination. Also, as discussed in the Experimental section, the mylar backing should not be a possible source. Under these circumstances, the Cu levels were accepted although further studies are under consideration.

Comparison between rainwater qualities from Pittsburgh and the rural area shows that the sulfur concentrations are very close in these two places. This seeming lack of local effect for sulfur is particularly interesting for discussion. The sulfate contents in samples of this work have been analysed also by a titration method and reported by Frohliger (1973) and Kane (1974). The sulfur content found is in agreement with this work and again shows a lack of local contributions. The fact that the SO_4 is a synoptic effect not greatly influenced by local conditions has been pointed out by them and a Swedish group (Rodhe et al., 1972). They also pointed out that SO_2 emitted in the local vicinity does not have time to convert to sulfate. This means that rainfall is not an effective scrubber for SO_2 in the atmosphere. Besides sulfur, other elements do show a general increase in concentration from rural rainwater to Pittsburgh rainwater which is an indication of local contributions. This is even more obvious for the particularly high increases for Pb–Br and Al–Fe which can be explained easily by traffic and industrial output respectively.

Reasonable agreement was obtained by comparing the relative quantities of different elements in air particulates and rainwater in Pittsburgh (except for Cu), which indicates a strong correlation between the two.

Correlations of different elements are shown in Fig. 5. Several observations can be made. Firstly, comparing (*a*) and (*b*) and (*c*) and (*d*)

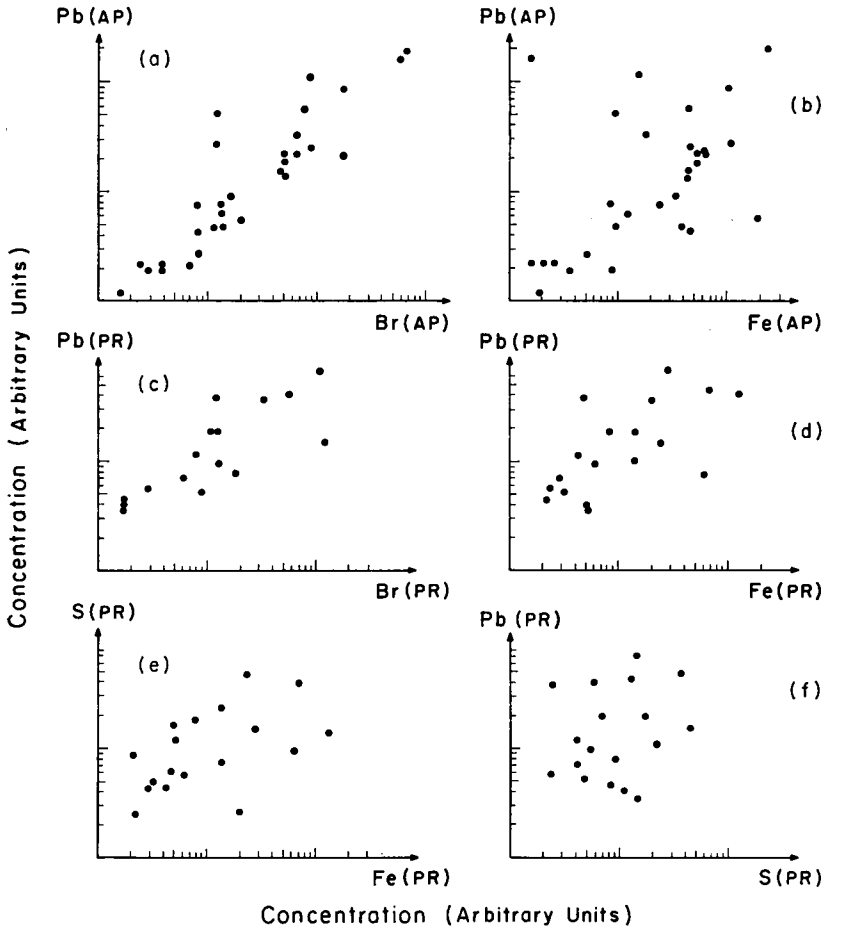

Fig. 5. Correlations between different elements; AP = air particulates in Pittsburgh, PR = Pittsburgh rainwater.

we observe a better correlation between Pb–Br than between Pb–Fe in both Pittsburgh and the rural area. This can be explained by the fact that Pb and Br come from the same source, traffic, which is different from the source of Fe, namely industry. Secondly, air particulates samples have a better correlation between Pb–Br than rainwater samples and the correlation for air particulates is excellent. This confirms that traffic is the source of Pb–Br and indicates that local traffic has a more direct effect on air particulate than on rainwater. Thirdly, S–Fe is less correlated than Pb–Br in the rainwater samples because of the strong non-local effect of sulfur discussed previously. But by comparing (*e*) and (*f*), a better correlation between Fe–S than between Pb–S still exists. This serves as a weak indication that Fe and S originate from the same source.

Washout is a major mechanism for local air

Table 2. *Relative washout ratios normalized to Fe*

	Washout ratio
Ti	2.7
Mn	2.6
Fe	1.0
Cu	53.6
Zn	10.0
Pb	3.2
Br	1.8

particulates to affect the rainwater quality. Washout ratio for a certain element is defined as:

$$\frac{\text{the concentration of the element in rainwater}}{\text{the weight of the element per unit volume of air}}$$

In our case, the relative washout ratios are calculated in Table 2 by taking the ratio of K values and normalized to Fe. These numbers do not show evidence to support the general belief that the washout ratio is higher for industrial output, i.e. Fe, than for traffic contributions, i.e. Pb, Br, because industrial particulates have larger particle sizes compared to the sub-micron sizes from traffic contributions. Since the washout ratio is known to depend on many other factors besides particle size, i.e. size of raindrops, duration and total volume of rainfall, and the relative efficiencies of collecting different particle sizes for the filter used are important here, further work is necessary to resolve this discrepancy.

As shown in the Experimental section, PIXE has enough sensitivity and accuracy for this type of work. Approximately 50 targets can be irradiated in 24 hours. Analysis time is minimal when it is done by computer. Target making is easy. The most important advantage is its ability to obtain information on a large number of elements and samples simultaneously. Therefore, in comparing with other types of analysis, this technique seems very favorable.

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АНАЛИЗ ДОЖДЕВОЙ ВОДЫ В ПИТТСБУРГЕ С ПОМОЩЬЮ PIXE

С помощью рентгеновской эмиссии, индуцируемой заряженными частицами (PIXE) анализировались концентрации 13 элементов в дождевой воде в районе Питтсбурга, Пенсильвания. Эти концентрации сравнивались с определенными в воде в сельской местности и в твердых частицах в воздухе. Обсуждаются локальные и нелокальные влияния. Были вычислены скорости вымывания, которые найдены бо́льшими для частиц меньшего размера в противовес общему мнению. Работа показывает удобства использования PIXE.