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# PARTICLE-INDUCED X-RAY EMISSION SPECTROMETRY OF SIZE-FRACTIONATED ATMOSPHERIC AEROSOLS

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## ABSTRACT

Atmospheric aerosol samples were collected with a stacked filter unit (SFU), which separates the aerosol into a coarse (2-10  $\mu\text{m}$  aerodynamic diameter (AD)) and a fine (< 2  $\mu\text{m}$  AD) size fraction. The samples were analysed by particle-induced x-ray emission (PIXE) spectrometry. Elemental composition and enrichment of the elements were applied for source identification and apportionment. Multivariate statistical methods identified three principal factors, which were assigned to aerosol sources from: mineral dust, biomass burning and sea salt.

**Key words:** PIXE, trace elements, enrichment factors, multivariate analysis.

## 1. Introduction

Aerosols play an important role in the atmosphere. Climate change, stratospheric and tropospheric ozone depletion, acid rain, urban oxidants, visibility and health effects are some of the issues in which they are involved [i,ii]. The link between increased mortality and particulate air pollution even at relatively low concentrations had been well established by the 1990s [iii,iv]. Nowadays, the investigations are focusing on the particularly high risk factors associated with the fine size fraction (PM<sub>2.5</sub>) of aerosols. One subject of special interest is the level of potentially toxic trace elements. Many efforts have been made to identify the elemental composition of atmospheric aerosols and relate them to specific emission sources [v]. The sampling and analysis of these samples is a rather complex task that can be carried out by means of different techniques. A very useful analytical tool in aerosol analysis is particle-induced x-ray emission (PIXE) spectrometry [vi - viii].

In PIXE analysis, the sample is normally irradiated with protons of a few MeV to create inner-shell vacancies. Filling of the vacancies gives rise to the emission of x-ray photons, which are detected by a semi-conductor detector. The non-destructive nature of PIXE and the possibility to simultaneously determine several elements with atomic numbers between  $Z = 11$  and 82 (sodium to lead), with detection limits below 1 ppm make this method very attractive in the aerosol field. Furthermore, PIXE requires only a small amount of sample, only a few tens of  $\mu\text{g}$  of aerosol particles per  $\text{cm}^2$  of collection substrate.

The aim of this work is to present the PIXE analytical methodology and results of the study of trace elements in the coarse and fine fractions of atmospheric aerosol samples at a rural site in South Africa during the dry (biomass burning) season. In addition, the common multivariate receptor modelling approach to the source apportionment of the air pollution is described as well.

## 2. Experimental

The atmospheric aerosol samples were collected with a Gent PM10 stacked filter unit (SFU) sampler. This device separated the particles into coarse (2 - 10  $\mu\text{m}$  aerodynamic diameter (AD)) and fine (< 2

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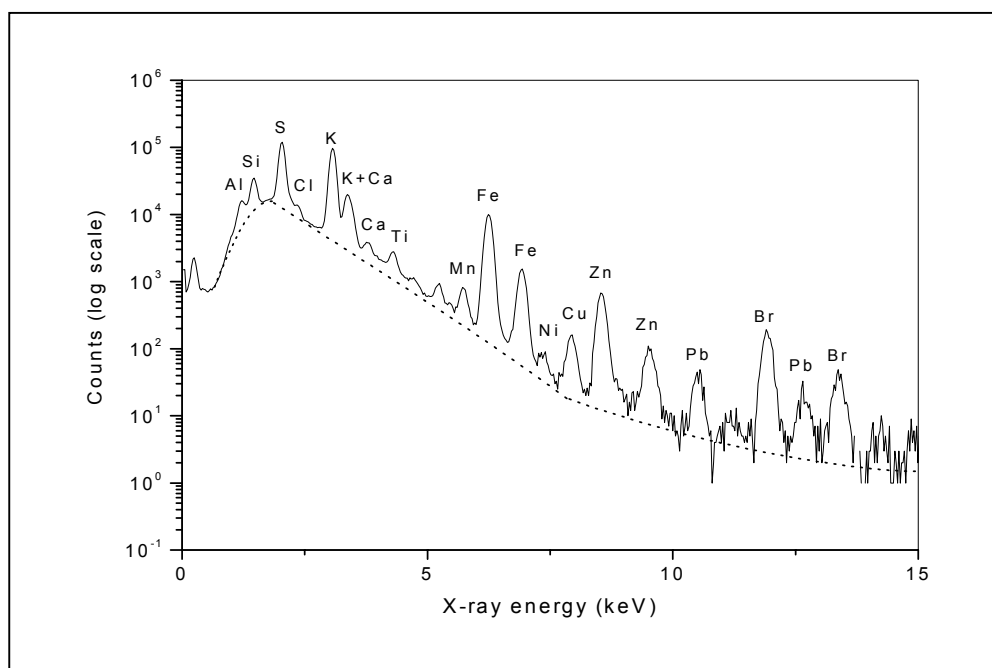
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$\mu\text{m AD}$ ) size fractions. Nuclepore polycarbonate filters were used as collection surfaces. For more details on the collection procedure one is referred to ref. [ix]. After sampling, the filters were placed into Petrislide dishes, sealed carefully and kept in these boxes until analysis. A quarter of each Nuclepore polycarbonate filter was analysed by PIXE.

The PIXE measurements were performed at the Institute for Nuclear Sciences at the Ghent University (Belgium). A lithium drifted silicon (Si(Li)) detector, with a composite “funny filter” [x] in front, was placed 4.3 cm from the target at an angle of  $45^\circ$  with respect to the beam. A proton beam with energy of 2.4 MeV and 150 nA intensity was supplied by a compact isochronous cyclotron, and the area of the beam at the specimen was  $0.54\text{ cm}^2$ . The samples, blanks and standards were irradiated in a vacuum chamber, for approximately 15 minutes with a preset charge of  $100\ \mu\text{C}$ . The spectra were continuously collected by a multi-channel analyzer, transferred to a VAX/VMS computer, and analyzed using the computer program AXIL. The chemometric data analyses in this work were performed by means of the SPSS software package.

### 3. Results and Discussion

A typical PIXE spectrum of an aerosol sample (fine size fraction) is shown in Fig. 1. The peaks, overlayed on the background, for a given element result from a number of transitions to atomic shell vacancies (K and L). The probability of excitation is heavily dependent on the beam energy and the atomic number of the element irradiated, so that it is highest if the incident ion has the same velocity as the shell electron. The background is mainly due to secondary electron bremsstrahlung caused by ejected electrons that are stopped in the sample. This favours the use of a thin sample.



The peak areas for the analyte lines ( $K_{\alpha}$  lines, except for  $\text{Pb } L_{\alpha}$ ) corrected for blank values were used to estimate the atmospheric concentrations (in  $\text{ng}/\text{m}^3$ ) of the elements in the aerosol. The elemental concentrations at a rural site in South Africa averaged over the one-month sampling period, with associated standard deviation (SD), and detection limits (DL) for the fine and coarse size fractions are reported in Table 1. In most of the coarse and fine filters, thirteen elements (Na, Mg, Al, Si, S, Cl, K, Ca, Ti, Mn, Fe, Cu, Zn) were quantified. In addition, several elements in the coarse fraction (P, Ni, Sr) and Br, Pb in the fine fraction were detected in many samples as well. A comparison of the data in the

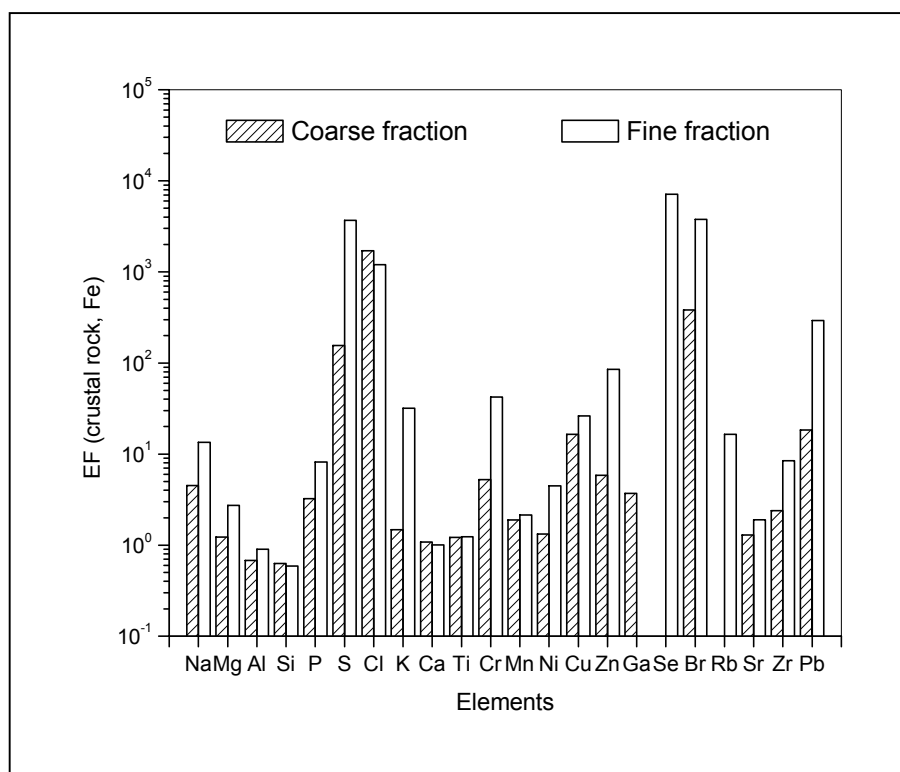
**Table 1. Mean elemental concentrations (in ng/m<sup>3</sup>), standard deviations, number of samples in which the elements were detected and detection limits (V<sub>air</sub>=20 m<sup>3</sup>) for the elements analyzed by PIXE (preset charge=60 μC).**

Elements	Coarse particles			Fine particles			DL[Error! Book mark not define d.]
	Mean	SD	N	Mean	SD	N	
Na	708	488	34	370	210	32	110
Mg	142	78.6	34	55.2	30.7	28	25
Al	307	213	34	71.2	45.0	33	7
Si	967	591	34	159	106	34	13
P	18.9	11.4	32	8.33	3.33	17	5
S	224	96.7	34	932	522	34	7
Cl	1231	1335	34	151	294	27	4
K	212	122	34	804	600	34	2.3
Ca	218	124	34	35.5	18.7	33	2.6
Ti	29.7	18.8	34	5.27	3.42	33	0.8
Cr	2.92	3.42	15	4.09	4.46	19	1.3
Mn	9.90	7.00	34	1.97	1.39	33	0.4
Fe	277	178	34	48.5	32.8	34	1.6
Ni	0.55	0.33	24	0.33	0.10	5	0.28
Cu	5.04	16.9	34	1.40	1.30	29	0.28
Zn	2.28	1.74	34	5.80	4.37	34	0.21
Ga	0.31	0.19	15	< DL	-	0	0.13
Se	< DL	-	0	0.35	0.14	9	0.18
Br	5.30	2.13	11	9.19	6.66	33	0.9
Rb	< DL	-	0	1.44	0.77	19	0.4
Sr	2.69	1.17	34	0.70	0.22	19	0.4
Zr	2.19	1.48	19	1.35	0.83	5	0.6
Pb	1.33	1.06	19	3.70	2.15	33	0.7

two size fractions indicated that some elements, i.e. S, K, Zn, Pb, were principally attached to fine particles. This size fraction is predominantly anthropogenic. The coarse particles, on the other hand, have high concentrations for the crustal elements (Al, Si, Fe, etc.). In PIXE analysis the detection limit and the accuracy of the method depend on the atomic number of the element. Except for Na, Mg and Al, the comparison of the PIXE concentrations and those obtained by instrumental neutron activation analysis (INAA) showed a very small bias of only a few percent and a small random error. Based on this intercomparison, particle size correction factors were introduced for the PIXE data on Mg (1.4 fine fraction, 1.7 coarse fraction) and Al (1.2 fine fraction, 1.4 coarse fraction) [x<sup>i</sup>]. Due to the large uncertainty in the PIXE data for Na, the results for this element are considered as semi-quantitative. Elemental ratios or enrichment factors (EFs) have been extensively used in atmospheric aerosol studies as a mean to identify the major sources of the elements and/or fractionation effects [x<sup>ii</sup>]. For an element in an aerosol sample, the EF relative to a reference element and a natural source composition can be estimated from the expression:

$$EF = (x/z)_{\text{aerosol}} / (x/z)_{\text{source}}$$

where x and z are the concentrations of the element in question and of the reference element. As the source material in EF calculations, the composition of average crustal rock [xiii] has been commonly used. Several elements (Al, Ti, Fe) may be applied as the normalizing element. It was found that EFs vary significantly depending on the choice of the reference element [xiv]. Fig. 2 shows the average enrichment factors estimated (z=Fe). In the coarse fraction, most elements have lower EF than that in the fine fraction. The EF of Mg, Al, Si, Ca, Ti, Mn, Sr is close to 1, suggesting that these elements originate from soil dust dispersal and resuspension. The calculated EF is high (20 - 20000) for S, Se, Br, Pb suggesting that they are of anthropogenic origin. It is noteworthy that the EF of Cl is very high. Although this element can partly be from anthropogenic origin, it is mostly attributable to sea salt at the site.



**Fig. 2. Average crustal enrichment factors for elements in atmospheric aerosols, using Fe as reference element.**

In order to identify and apportion the sources of various elements, PIXE measurements have frequently been combined with some receptor modelling methods. In this work multivariate statistical data analysis was applied. Using principal component and factor analysis, the PIXE data were reduced to few dimensions enabling a better look into the latent structure of the database. This revealed three significant factors, which accounted for 83 % and 78 % of the total variance in the coarse and fine fractions, respectively. The loadings for the various factors in both size fractions were then converted into source profiles. Details on this procedure can be found elsewhere [xv]. According to the elements that are associated with the three factors (Table 2), it is evident that the three aerosol source types are mineral dust, biomass burning and sea salt.

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<b>Table 2. Sources for the detected elements in aerosols.</b>		
Source type	Coarse particles	Fine particles
Mineral dust	Al, Si, Ca, Ti, Fe	Al, Si, Ti, Mn, Fe
Biomass burning	S, Cl, K, Zn, Ca	S, K, Zn, Br
Sea salt	Na, Mg, Cl	Na, Mg, Cl, Ca

#### 4. Conclusion

PIXE is a useful tool for measuring trace elements in atmospheric aerosol samples as well as their distribution among particle sizes. The simultaneous analysis is fast, non-destructive and requires no sample preparation. Since the method requires only samples in the microgram range, it allows the use of air samplers of low size and cost. Furthermore, the method provides the sensitivity for accurate measurements at the nanogram level or less for many important trace metals in the urban atmosphere. In this work the use of a multivariate receptor model has resolved the elemental composition of atmospheric aerosol into components related to emission sources. At the study site, contributions from soil dust, biomass combustion and sea salt aerosol were found.

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