

Combined application of INAA and PIXE for studying the regional aerosol composition in Southern Africa

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As part of the SAFARI-92 biomass burning experiment, aerosol collections were carried out with several size-fractionating sampling devices at a number of sites in Southern Africa. One of the samplers used at all ground-based sites was a stacked filter unit (SFU). The SFU samples were analyzed by both INAA and PIXE analysis. The present paper gives an intercomparison of the analytical results obtained in order to assess the accuracy and to check the quality assurance of the analytical procedures. Twenty-one common elements were determined by both INAA and PIXE. Concentrations of 13 elements (i.e., Na, Mg, Al, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Zn and Br) were generally measured with sufficient precision in both techniques for performing the intercomparison. The INAA and PIXE data were compared in terms of PIXE/INAA concentration ratios on a sample by sample basis for the coarse and fine size fraction separately. The atmospheric concentrations for K, Mn and Fe agreed within 5–10%, the agreement between the data for the other common elements was typically better than 15%. Possible explanations for lower than 1.0 ratios for Cl, Br and Na are presented. The common elements were classified into groups according to their detectability and sensitivity in each technique.

Introduction

Tropical atmospheric chemistry and the role of biomass burning is one of the priority areas of research in atmospheric chemistry and its interaction with the biosphere.¹ In order to investigate the characteristics of the tropical biomass burning emissions in the source regions and the transport of air masses from these source regions to the atmosphere over the Atlantic, an internationally coordinated research project – the Southern Tropical Atlantic Regional Experiment (STARE) – was set up. One of its two components, the Southern Africa Fire–Atmosphere Research Initiative (SAFARI) was designed for investigating the impact of savanna fires on atmospheric chemistry, climate and ecology in Southern Africa, and the transport of the emissions across the African continent.

Our contribution to SAFARI-92 involved aerosol collections utilizing several size-fractionating sampling devices at a number of ground-based sites in South Africa, Namibia and Zimbabwe, and from aircraft. Depending upon the sample type, the aerosol samples were analyzed by one or more bulk analysis techniques, including instrumental neutron activation analysis (INAA), particle-induced X-ray emission analysis (PIXE), gravimetry (for the particulate mass), and a light reflectance technique (for black carbon). The analyses of the samples were performed at the Institute for Nuclear Sciences of the University of Gent in Belgium. A detailed interpretation and discussion of the results obtained for the eastern Transvaal, South Africa, is given by Maenhaut et

al.²; a comprehensive evaluation and interpretation of the data from Namibia and Zimbabwe is in preparation. Here, the atmospheric concentrations obtained by INAA and PIXE are compared and discussed in some detail in order to assess the accuracy, and to check the quality assurance of the analytical results. The samples collected by the stacked filter units (SFUs) were analyzed by all the above mentioned analytical techniques, including INAA and PIXE. This paper is, therefore, essentially limited to presenting and discussing the data for the common elements of the two multielement analytical techniques for the SFU samples.

Experimental

Aerosol sampling

The SFU collection device contains two 47 mm diameter Nuclepore polycarbonate filters with pore sizes of 8 μm (Apiezon-coated) and 0.4 μm , placed in series. Upstream of the coarse filter is a pre-impaction stage. The separation principle of the SFU sampler was described earlier.^{3–5} At a flow rate of 15–16 l/min, the pre-impaction stage intercepts particles larger than about 10 μm equivalent aerodynamic diameter (EAD), and the filter with 8 μm pore size (coarse filter) has a 50% collection efficiency at about 2 μm EAD. Consequently, the aerosol particles are separated into a coarse (10–2 μm EAD) and a fine (< 2 μm EAD) size fraction. The SFU samplers were installed in the Etosha National Park (ENP), Namibia, at Victoria Falls, Zimbabwe, and at three sites in the eastern

Transvaal, South Africa, i.e., at Skukuza and Pretoriuskop located within the Kruger National Park, and at Palmer on the Highveld escarpment. Samples were taken continuously on a daily (24 h) basis in August–October 1992 during the dry season. A total of 41 samples were collected at Skukuza, 40 at Pretoriuskop, 42 at Palmer, 45 at Etosha National Park and 32 at Victoria Falls.

Analysis

The INAA procedure was similar to those described in References 6–8. The activation, decay and measuring scheme was optimized to the needs of the multielemental aerosol analysis, and it consists of two activations and five γ -spectrometric measurements. One half of each SFU filter containing about 100 μg of particulate matter was pressed into a pellet. The pellets, together with a nickel foil, were irradiated for 5 minutes at a thermal neutron flux of about $\Phi = 2.6 \cdot 10^{12} \text{ cm}^{-2} \cdot \text{s}^{-1}$ in the Thetis reactor. Each sample was measured twice with a Ge semiconductor detector. The first γ -spectrometric measurement took place after a decay time of 2–3 minutes for a measuring time of 5 minutes and the counting was repeated after a decay time of about 10 minutes for a measuring time of 30 minutes. Between the measurements of the sample, the nickel foil, which served as a flux monitor and a single comparator, was measured for 3 minutes in the same detection geometry as the sample. In order to correct for the changing dead time during the counting, its starting value was held constant throughout the whole measurement by a dead-time stabilizer.⁹ The spectra were evaluated by the computer program LAMAMA. The radionuclides ^{24}Na , ^{27}Mg , ^{28}Al , ^{38}Cl , ^{49}Ca , ^{51}Ti , ^{52}V , ^{56}Mn , ^{66}Cu , ^{80}Br , $^{87\text{m}}\text{Sr}$, $^{116\text{m}}\text{In}$, $^{123\text{m}}\text{Sn}$, $^{125\text{m}}\text{Sn}$, ^{128}I and ^{139}Ba were used for calculating the elemental amounts ($\mu\text{g}/\text{filter}$) via single comparator standardization. The second, about 12 hour activation of the same pellets was performed after cooling for 3–4 weeks. Up to 25 pellets and a multielement standard (a pellet of Whatman 41 filter containing all elements to be measured) were irradiated together at a thermal neutron flux of about $\Phi_{th} = 4.6 \cdot 10^{12} \text{ cm}^{-2} \cdot \text{s}^{-1}$. Each sample was measured three times. After a typical decay time of 2 days, the radionuclides ^{24}Na , ^{42}K , $^{69\text{m}}\text{Zn}$, ^{72}Ga , ^{76}As , ^{82}Br , $^{99\text{m}}\text{Mo}/^{99\text{m}}\text{Tc}$, ^{115}Cd , ^{122}Sb , ^{140}La , ^{153}Sm , ^{187}W and ^{198}Au were counted for a measuring time of 2 hours. To improve the detection limit for several of these radionuclides, the measurement was repeated after 3–6 days (when the bulk of ^{24}Na had decayed) for a measuring time of 4 hours. After a decay period of about 20 days (when the bulk of ^{82}Br had decayed too), the samples were again counted for 12 hours and the radionuclides ^{46}Sc , ^{51}Cr , ^{59}Fe , ^{60}Co , ^{58}Co (formed from ^{58}Ni), ^{65}Zn , ^{75}Se , ^{86}Rb , $^{110\text{m}}\text{Ag}$, ^{124}Sb , ^{134}Cs , ^{131}Ba , ^{141}Ce , ^{152}Eu , ^{177}Lu and ^{233}Pa (formed from ^{232}Th) were measured. The γ -ray spectra

were evaluated by the computer program OLIVE, and elemental amounts were derived by relative standardization. The elemental amounts determined from the five measurements were combined. A number of field blanks were treated with the same INAA procedure and blank amounts were also determined. Mean blank values were calculated for the coarse and fine filters separately, and were subtracted from the corresponding elemental amounts of the samples. Finally, atmospheric concentrations for 39 elements were calculated and expressed in ng per m^3 at standard temperature and pressure (STP; 273.15 K, 1013.2 hPa).

Particulars concerning the experimental setup and the analytical procedure for PIXE analysis of the SFU samples have been described previously.^{10–12} In short, a quarter section of each SFU filter was investigated by bombardment with a beam of protons of 2.4 MeV energy in a vacuum chamber. The beam area and beam current were 0.54 cm^2 and 150 nA, respectively. The X-ray spectra were measured with a composite filter in front of the Si(Li) detector, and were typically accumulated for a preset charge of 60–80 μC . The spectra were fitted for 29 elements (i.e., Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo and Pb) with the computer program AXIL-84.¹³ Elemental amounts were derived by using experimental calibration factors and blank values and, finally, atmospheric concentrations (in ng/m^3 STP) were calculated. Particle size correction factors were applied for the elements Mg and Al (in the fine size fraction 1.4 for Mg, and 1.2 for Al; in the coarse fraction 1.7 for Mg, and 1.4 for Al). These correction factors were deduced on the basis of a previous intercomparison between PIXE and INAA data from SFU samples collected at a continental site.¹⁴

Results and discussion

Twenty-one common elements were determined by both INAA and PIXE. Since the detection limits and precision of INAA and PIXE for the common elements depend on the technique, element and sample composition, the final data for each element in each sample were calculated either by averaging the results from the two independent techniques or by selecting the value from one of the two techniques.

When an element was not detected in INAA or in PIXE, an upper limit (detection limit) was calculated using the $3 \cdot (\text{Background})^{1/2}$ criterion, with the background being taken over the spectral region where the analyte line of the element (γ -ray line or $K_{\alpha}(L_{\alpha})$ line) was expected. For elements that were detected in the blank filters, the net amount (after blank correction) in a real sample was always compared with $3s_{var}$. The standard deviation of the

Table 1. Upper limits (detection limits) in ng/m^3 STP for 21 elements that were measured by both PIXE and INAA in SFU samples

Element	PIXE*		INAA	
	Fine filter	Coarse filter	Fine filter	Coarse filter
Na	110	110	2.1	2.6
Mg	26	25	38	37
Al	6.6	6.6	1.9	2.1
Cl	4.1	6.2	7.5	9.0
K	2.3	2.4	1.2	0.85
Ca	2.6	4.4	45	34
Ti	0.86	0.83	7.4	5.4
V	0.55	0.53	0.025	0.026
Cr	2.9	1.3	4.6	0.58
Mn	0.35	0.40	0.046	0.060
Fe	1.6	2.4	38	39
Ni	0.28	0.28	1.8	1.6
Cu	0.28	0.29	1.7	1.7
Zn	0.21	0.23	1.9	0.79
Ga	0.14	0.13	0.0089	0.0066
As	0.17	0.17	0.028	0.015
Se	0.19	0.18	0.35	0.28
Br	2.3	0.86	1.5	0.61
Rb	0.76	0.43	1.1	1.2
Sr	0.35	0.47	6.9	5.3
Mo	1.1	1.1	0.30	0.16

*The PIXE detection limits are for a preset charge of $60 \mu\text{C}$.

blank value (s_{var}) was derived from the spread in the various individual blank filter values, and thus, it is a measure of the blank variability. When the net amount was less than $3s_{var}$, a detection limit was calculated, which was set at $3s_{var}$. In INAA and PIXE of real samples, the upper

upper limits (detection limits) vary from sample to sample, and are lowest for the lightest-loaded samples (with least aerosol mass). To find out what the minimum values are for our upper limits, a number of blank filters were considered as real samples, and blank corrections were performed. The upper limits in ng/m^3 STP were derived assuming a volume of 19.5 m^3 STP (this was the average volume of the Skukuza samples). The upper limits for the 21 common elements observed by both techniques are presented in Table 1. For the elements that were detected below or near their detection limit in the majority of samples either by one or both techniques, INAA gave more significant results (i.e., lower upper concentrations or smaller relative standard deviations) for fine V, Ga, As, Se and Mo. In these cases, the INAA values were retained in the final data sets. On the other hand, PIXE was more sensitive than INAA for fine Cr, Ni, Cu, coarse Zn and Sr, and, therefore, the PIXE values were included in the final data sets. Typical uncertainties for coarse Br and Rb were similar. For Br, the data obtained by INAA were selected (because of possible Br-loss in PIXE, see later); final Rb values (as an important indicator for biomass burning emissions) were individually evaluated and selected.

Concentrations of 13 elements, i.e., Na, Mg, Al, Cl, K, Ca, Ti, coarse V, coarse Cr, Mn, Fe, fine Zn and Br were generally measured with sufficient precision in both techniques to perform the intercomparison. The median atmospheric concentration for these elements calculated from the final data sets are shown in Fig. 1. The PIXE/INAA comparison was performed in terms of the concentration ratios. Such ratios were calculated for each sample per element, per size fraction and per sampling site,

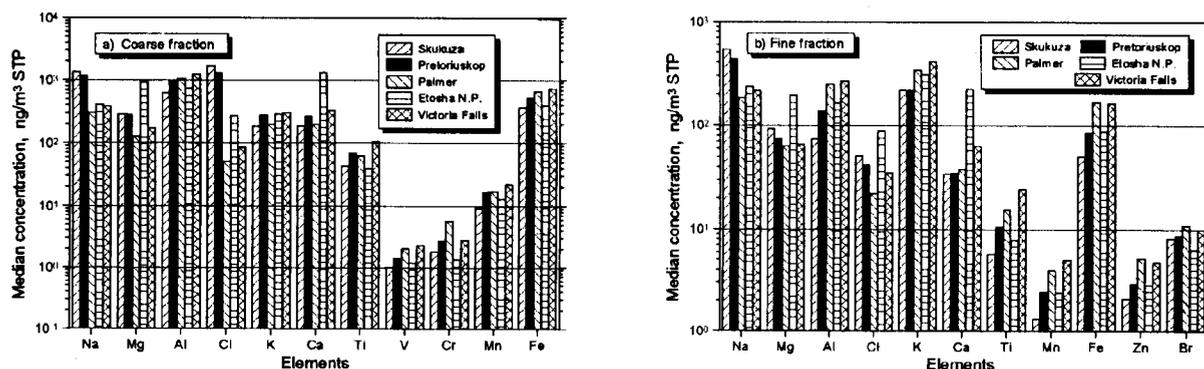


Fig. 1. Median atmospheric concentrations for the common elements in the coarse (a) and fine (b) size fractions for all fixed sampling sites in Southern Africa

limits (particularly those for elements that were not detected in the blank filters) highly depend on the presence of other elements in the sample (because of their impact on the Compton γ -ray background (in INAA) or on spectral interferences (mainly in PIXE)). As a consequence, the

and subsequently the ratios were averaged over all samples at a particular sampling site. In calculating the averages and associated standard deviations, obvious outlier ratios or ratios with a relative standard deviation of larger than 25–30% were excluded. The total number of rejected

Table 2. Average PIXE/INAA concentration ratios and associated standard deviations for selected elements and for the coarse size fraction (overall averages were obtained by averaging the ratios over all sampling sites).

Element	Sampling site					Overall average
	Skukuza	Pretoriuskop	Palmer	Etosha N.P.	Victoria Falls	
Na	0.63 ± 0.08	0.63 ± 0.08		0.61 ± 0.09	0.62 ± 0.11	0.62 ± 0.04
Mg	0.92 ± 0.16	0.90 ± 0.15	0.72 ± 0.12	0.99 ± 0.08	0.79 ± 0.16	0.86 ± 0.06
Al	0.94 ± 0.07	0.97 ± 0.06	1.02 ± 0.05	0.95 ± 0.07	0.99 ± 0.06	0.97 ± 0.03
Cl	0.90 ± 0.08	0.91 ± 0.08	0.99 ± 0.14	0.89 ± 0.09	0.78 ± 0.13	0.90 ± 0.05
K	0.94 ± 0.13	1.00 ± 0.10	1.05 ± 0.10	1.07 ± 0.10	0.09 ± 0.06	1.01 ± 0.04
Ca	0.89 ± 0.14	0.91 ± 0.12	0.97 ± 0.12	1.02 ± 0.12	0.94 ± 0.09	0.94 ± 0.05
Ti	0.84 ± 0.10	0.90 ± 0.11	0.86 ± 0.08	0.83 ± 0.12	0.86 ± 0.08	0.86 ± 0.04
V			0.88 ± 0.13		0.90 ± 0.13	0.89 ± 0.09
Cr		0.82 ± 0.11	0.92 ± 0.15			0.87 ± 0.09
Mn	0.99 ± 0.10	0.96 ± 0.08	0.98 ± 0.07	1.01 ± 0.09	0.93 ± 0.06	0.97 ± 0.04
Fe	1.00 ± 0.07	1.05 ± 0.08	1.01 ± 0.08	1.01 ± 0.13	0.99 ± 0.06	1.01 ± 0.04

Table 3. Average PIXE/INAA concentration ratios and associated standard deviations for selected elements and for the fine size fraction (overall averages were obtained by averaging the ratios over all sampling sites)

Element	Sampling site					Overall average
	Skukuza	Pretoriuskop	Palmer	Etosha N.P.	Victoria Falls	
Na	0.84 ± 0.13	0.88 ± 0.10		0.86 ± 0.09	1.05 ± 0.15	0.91 ± 0.06
Mg	0.91 ± 0.18	0.83 ± 0.08		1.01 ± 0.12		0.92 ± 0.08
Al	0.98 ± 0.08		0.95 ± 0.07	0.94 ± 0.07	0.97 ± 0.06	0.96 ± 0.03
Cl				0.87 ± 0.20	0.65 ± 0.16	0.76 ± 0.13
K	0.98 ± 0.08	1.07 ± 0.07	1.15 ± 0.06	1.07 ± 0.06	1.09 ± 0.06	1.07 ± 0.03
Ca				0.92 ± 0.15	0.77 ± 0.17	0.85 ± 0.11
Ti		0.89 ± 0.16	0.84 ± 0.15	0.74 ± 0.14	0.86 ± 0.10	0.83 ± 0.07
Mn	0.97 ± 0.13	1.00 ± 0.10	0.97 ± 0.08	1.00 ± 0.10	1.01 ± 0.08	0.99 ± 0.04
Fe	0.82 ± 0.13	0.96 ± 0.11	0.93 ± 0.12	0.94 ± 0.10	0.97 ± 0.09	0.92 ± 0.05
Zn	0.83 ± 0.15	0.83 ± 0.13	0.86 ± 0.13	0.79 ± 0.15	0.89 ± 0.16	0.84 ± 0.06
Br	0.51 ± 0.17	0.56 ± 0.16			0.61 ± 0.14	0.56 ± 0.09

outliers remained about 8%. The average PIXE/INAA ratios for the coarse and the fine size fraction are presented in Tables 2 and 3, respectively. The tables also contain overall average ratios and standard deviations, all of which were derived by averaging the concentration ratios over all sampling sites per size fraction. From the observation of the various averaged PIXE/INAA ratios, it can be seen that the associated standard deviations are typically between 10 and 20%. Furthermore, the ratios do not exhibit large variability from site to site, so that meaningful conclusions can be drawn. The average concentration ratios are generally close to 1.0, except for fine Cl and Br, and coarse Na. The correlation of the concentration ratios with the concentration data (observed either by INAA or by PIXE) is insignificant, so the variability in the ratios is not

concentration dependent. Instead, a good to excellent correlation between the INAA and PIXE concentration data was usually obtained even for elements with lower than 1.0 average ratio. For Cl and Br, the deviation from 1.0 is too large to be explained by ordinary analytical error. A Cl- and Br-loss in different samplers was already observed and discussed by other authors, and several possible explanations have been given.^{12, 15-17} Most likely, in our case, the fine Cl and Br were volatilized to a certain extent during the PIXE bombardment of the SFU filters. The coarse Cl was volatilized to a much lesser extent, if at all. For coarse Na, the discrepancy between INAA and PIXE has to be attributed to particle size effects in the PIXE analysis which were not corrected for (in contrast to Mg and Al). The correction factor for the soft Na K_{α}

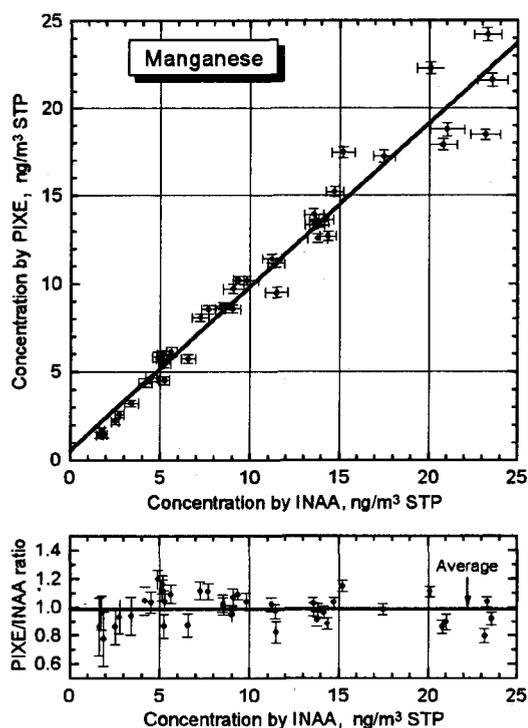


Fig. 2. Correlation between the atmospheric concentrations measured by INAA and PIXE for Mn in the coarse size fraction at the Skukuza site, and the associated PIXE/INAA concentration ratios. The error bars indicate one standard deviation

X-rays is estimated to be about 2 for the coarse particles. Excellent agreement between the INAA and PIXE results was achieved for K, Mn and Fe in both size fractions. The correlations between the concentrations measured by the two techniques, together with the associated concentration ratios, are presented for coarse Mn and fine K at the Skukuza site in Fig. 2 and 3, respectively. The good agreement between the INAA and PIXE data for K, Mn and Fe suggests that these data are accurate to within 5–10%. As a consequence, the final data for those three elements were calculated by averaging the concentrations obtained by both techniques. In some cases, when the concentration pairs resulted in obvious outlier ratios, the concentration values were checked and evaluated (e.g., by investigating the tendencies in concentration time trends, in fine-to-coarse ratios and in enrichment factors with respect to average crustal rock composition), and the most likely value was retained. The agreement between INAA and PIXE data for Fe in the fine samples from Skukuza is fairly good. The INAA value for Fe was near or below the determination limit¹⁸ for several samples; for some other samples the counting statistics in INAA were poor, reaching 15–20%. In view of this, the PIXE data for fine Fe, having a much smaller relative standard deviation of

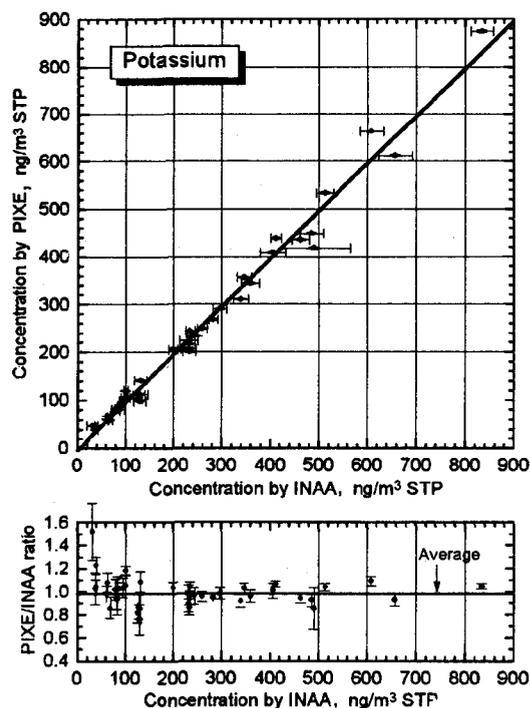


Fig. 3. Correlation between the atmospheric concentrations measured by INAA and PIXE for K in the fine size fraction at the Skukuza site, and the associated PIXE/INAA concentration ratios. The error bars indicate one standard deviation. (The evident individual outlier ratio of 1.52 was excluded when calculating the average PIXE/INAA ratio)

about 2%, were exclusively accepted for that particular sampling site. (The overall average ratio for Fe in the fine size fraction excluding the samples from Skukuza is 0.95 ± 0.04 , cf. Table 3.) For Mg and Ca, there is better agreement between INAA and PIXE for the samples from the ENP site than for the other sampling sites (see Tables 2 and 3). The soil in the region around the ENP sampling site is enriched in Mg and Ca, and this gave rise to elevated atmospheric Mg and Ca concentrations, which could be measured with better precision. The concentrations of the common elements not discussed so far usually agree to within 15%, but the PIXE data tend to be consistently lower than the INAA data. Based on the sensitivity and the relative standard deviations, the INAA results were selected as the final data for Na, Al, Cl, coarse V and fine Br, while the PIXE data were retained for Mg, Ca, Ti, coarse Cr and fine Zn.

The combination of INAA and PIXE can advantageously be used in aerosol studies to extend the number of important elements measured and to evaluate and check the accuracy of the analytical procedures. The present intercomparison of INAA and PIXE shows quite satisfactory agreement and provides strong support for the validity of the analytical techniques. It can be concluded

that no gross systematic error was made during the analytical work and that the analytical data obtained are of high quality. The elements K, Mn, Fe and perhaps also Rb are usually measured in aerosols with similar sensitivities by both INAA and PIXE and, therefore, the independent concentration data can be averaged to obtain the final results. INAA is generally more sensitive and reliable than PIXE for Na, Al, Cl, V, Ga, As, Se and Br and, therefore, the INAA data are to be preferred. PIXE usually gives better precision than INAA for Mg, Ca, Ti, Cr, Ni, Cu, Zn and Sr and, therefore, the PIXE results are normally to be retained in the final data sets. The ultimate data sets created in the way described above are an accurate and reliable source for further statistical evaluation, data reduction and modelling.

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