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IBA methods for characterisation of fine particulate atmospheric pollution: a local, regional and global research problem

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Abstract

The IBA techniques of PIXE, PIGE, RBS and PESA have been used simultaneously to analyse fine particle pollution collected on Teflon filters. This provided a suite of 23 elements from hydrogen to lead which can be used to characterisation and fingerprint pollution sources and estimate their contributions to the total mass loading. These methods have been demonstrated to be applicable for aerosol pollution studies on a local, regional and even globe scale on time frames from a few days to decades.

Keywords: IBA; PIXE; PIGE; RBS; PESA; Fine particle characterisation; Air pollution; ACE Asia

1. Introduction

Ion beam analysis techniques have been applied to the characterisation of fine particulate matter from air pollution for many decades in accelerator laboratories around the world. Their multi-elemental capabilities, high sensitivity, low detection limits, short analysis times and non-destructive properties make them ideal for this type of work. In particular, the simultaneous application of PIXE, PIGE, RBS and PESA can provide quantitative elemental information on a broad range of elements from hydrogen to lead on samples containing only a few micrograms of material [1–5].

Fine particle pollution in the atmosphere is mainly composed of micron, and sub-micron particles from anthropogenic sources such as motor vehicles, biomass and fossil fuel burning and natural sources such as windblown soils and sea spray [2,3]. The characterisation of these fine airborne particles is becoming increasingly important to governments, regulators and researchers due to their impacts on human health [6], their ability to travel thousands of kilometres across countries and more recently for their influence on climate forcing and global warming [7].

In this paper we discuss how the low detection limits and multi-elemental nature of IBA techniques can contribute to a better understanding of fine particle air pollution on local, regional and

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global scales and provide specific examples for each of these key areas.

2. Ion beam analysis methods

Accelerator based ion beam analysis (IBA) methods are ideally suited to the multi-elemental analysis of fine particulates on the appropriate filter media [2–5]. They cover a wide range of elements in the periodic table from hydrogen to lead, they have (μg/g) sensitivity, they have short analysis times (typically 5 min per sample) and are non-destructive, so other techniques like ion chromatography (IC) can be performed after IBA analysis. To cover the broadest possible range of elemental species present on typical filters we apply the four simultaneous IBA techniques of particle induced X-ray emission (PIXE), particle induced gamma ray emission (PIGE), Rutherford backscattering (RBS) and proton elastic scattering analysis (PESA). An 8 mm diameter beam of 10 nA, 2.6 MeV protons from a 3 MV Van de Graaff accelerator was passed through each filter for approximately 5 min. Typical spectra obtained via these four methods on Teflon filter papers are shown in Figs. 1–4.

The X-ray spectrum of Fig. 1 shows a characteristic peak for each element detected and the area of each peak was related to the absolute concentration of that element on the filter. Elements from aluminium to lead were readily detected with

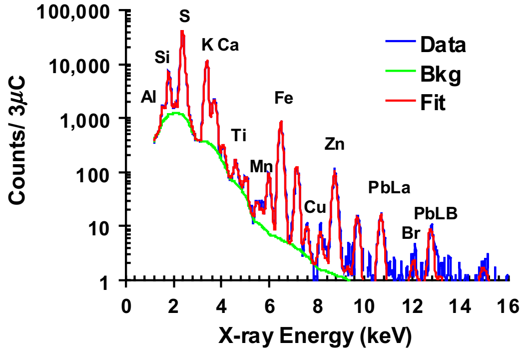

Fig. 1. A typical PIXE spectrum using 2.6 MeV protons for Teflon filters from the Cheju Island site in Southern Korea exposed on 26 May 2002.

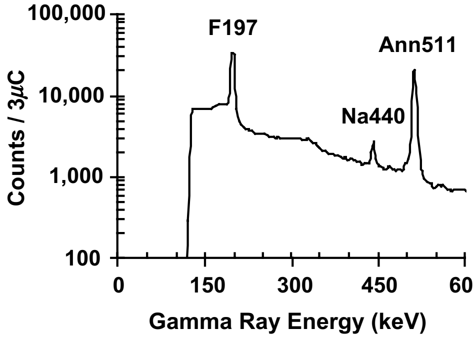

Fig. 2. A typical PIGE spectrum using 2.6 MeV protons for Teflon filters from the Cheju Island site in Southern Korea, exposed on 6 March 2002.

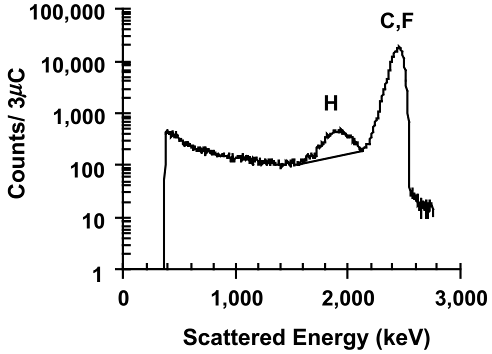

Fig. 3. A typical PESA spectrum using 2.6 MeV protons for Teflon filters exposed on 19 May 2002 at the Sado Island site off the west coast of Japan.

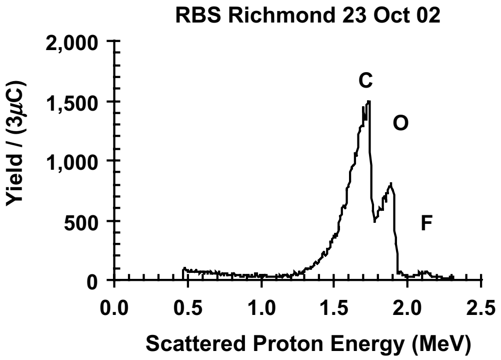

Fig. 4. A typical RBS spectrum for 2.6 MeV backscattered protons (170°) from a Teflon filter exposed for 24 h at Richmond, Sydney during a major dust storm on 23 October 2002.

detection limits down to 1 ng/m^3 of air sampled. The very low backgrounds above X-ray energies of about 4 keV (see Fig. 1) made for particularly low detection limits for elements heavier than calcium in the periodic table [8]. Lighter elements generally have higher cross-sections for (p,γ) and (p,p$'\gamma$) reactions, hence PIGE methods are more sensitive for the lighter elements like sodium and fluorine. The spectrum of Fig. 2 shows characteristic gamma rays for sodium (γ energy 440 keV) and fluorine (γ energy 197 keV) produced when a Teflon filter was bombarded with 2.6 MeV protons. The 511 keV gamma ray annihilation peak was always present and is not related to concentration estimates in this work. Again each peak was characteristic of an element present and its area provided the concentration. PIGE excitation being a nuclear (and not an atomic) process has a lower probability of occurring than PIXE excitation and hence was less sensitive. Minimum detectable limits for sodium and fluorine by PIGE were around 100 ng/m^3 of air sampled.

High energy protons passing through the thin filters have enough energy to scatter off light atoms like hydrogen and carbon and then be detected in the forward direction [1]. The number of forward scattered protons detected in this unique scattering energy range was related to the total hydrogen present in the filter. Fig. 3 shows the ‘hydrogen bump’ to the left and well separated from signatures from other heavier, unresolved, elements present in the filter. This PESA technique is one of the few ways of accurately measuring, in a non-destructive manner, the total hydrogen present in microgram samples. The system was calibrated against thin Mylar films (<6 μm thick) of known hydrogen content and had an ultimate sensitivity of around 20 ng/m^3 of air sampled for hydrogen in thin filters not containing hydrogen (for example Teflon filters). Again the factor limiting the ultimate sensitivity was the background under the ‘hydrogen bump’. This was mainly determined by the collection filter thickness and was the main reason for using thin Teflon filters typically 230 μg/cm^2 thick.

The combination of these four IBA methods provided data on the following 23 elements, H, C, O, F, Na, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Cu, Ni, Zn, Br and Pb. Typical minimum detectable limits (MDLs) range down to less than 1 ng/m^3 of air sampled and experimental errors are around ±7% for most of the elements listed. For much of the work described here volumes of air sampled range from 20 to 32 m^3 and filter areas from 2 to 10 cm^2, hence equivalent MDL concentrations are around 5–20 ng/cm^2 of filter area. A comprehensive discussion of MDLs and errors related to these IBA techniques has been presented elsewhere [8]. The black carbon or soot content was also estimated from (He/Ne) laser absorption techniques [9] applied to each filter before and after exposure and using a mass attenuation coefficient obtained from calibration measurements on acetylene and candle flames of $\varepsilon = 7$ m^2/g [10].

3. Local fine particle pollution

Government legislation requires Local Councils in Australian States to report regularly to Parliament on the State of the Environment. This report must include air quality and impacts of toxic metals from industries on air quality. For example, in Sydney over the past decade lead in air from leaded petrol combustion in cars and from local industry has been a key issue. Sydney reduced lead in petrol from 0.4 g/l pre January 1993 to 0.2 g/l in 1995 and eventually to zero post January 2001. PIXE techniques were used to measure the fine lead (particles with diameters less than 2.5 μm or PM2.5) in air twice weekly, every week since 1992. The mean monthly lead values from these measurements are shown in Fig. 5. There were strong seasonal variations with winter values being four to six times higher than summer values. This was due mainly to differing seasonal meteorological conditions.

Since 1992 the peak winter values as well as the summer minima have dropped significantly in line with the reduction of leaded petrol sales and the reduction of lead in petrol. This is clearly demonstrated in Fig. 6 where the calculated tonnes of lead emitted to air annually from leaded petrol in NSW, Australia and the actual measured annual average lead in fine particulate air are plotted

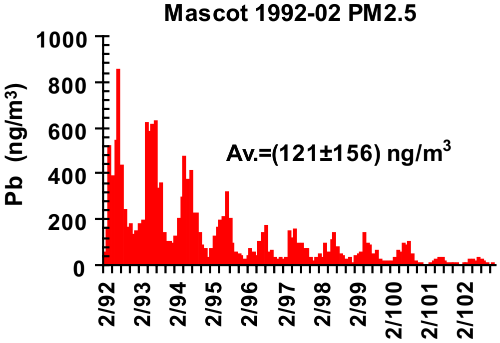

Fig. 5. Mean monthly fine lead levels at Mascot in Sydney from 1992 to June 2002.

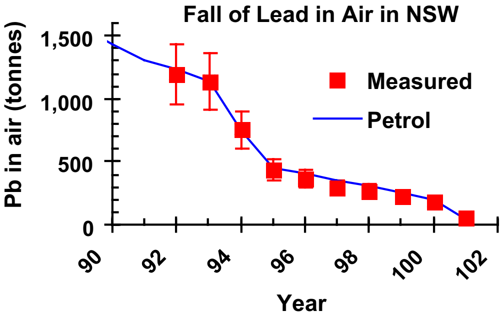

Fig. 6. Lead in Sydney, NSW air from leaded petrol combustion and measured in the fine (PM2.5) particle fraction.

against time. The two datasets have been normalised at 1993 since lead from petrol was measured in tonnes and in air in ng/m^3. The two trends are identical showing that lead in Sydney air was predominantly due to lead from petrol combustion and that new measures have dramatically reduced the lead levels in and around Sydney.

At the same time we were measuring lead we were also measuring some 20 other elements identified by IBA techniques. This enabled statistical methods like factor analysis (FA), principal components analysis (PCA) and positive matrix factorisation (PMF) to be use to identify inter-element associations and generate source fingerprints [2,3,11–13]. Table 1 shows a five factor PCA analysis of the same data set used to determine the lead concentrations at Mascot in Sydney from January 2001 to December 2002 (about 200 points). Elements with high factor loading (bold numbers near unity) have strong associations, should correlate and can be used to identify sources and their fin-

Table 1
Factor loading from a PCA analysis of data from Mascot in Sydney from January 2001 to December 2002

Element	Auto	Soil	Smoke	Sea salt	Industry
Soot	**0.861**	0.267	0.160	−0.077	0.159
Cu	**0.855**	0.078	0.170	−0.062	0.087
Zn	**0.845**	0.082	0.265	−0.002	0.157
Fe	**0.811**	**0.401**	0.208	−0.022	0.187
Mn	**0.797**	0.156	0.177	−0.022	0.024
Ti	**0.630**	**0.692**	0.119	0.029	0.193
Pb	**0.613**	0.068	**0.385**	−0.111	−0.024
Cr	**0.600**	0.158	0.044	−0.198	**0.382**
Br	**0.577**	0.029	**0.660**	0.085	0.205
Al	0.134	**0.945**	0.177	−0.074	0.029
Si	0.211	**0.921**	0.213	0.006	0.118
Ca	0.288	**0.655**	0.194	**0.503**	0.173
K	**0.324**	**0.318**	**0.842**	0.011	0.031
H	**0.280**	0.292	**0.830**	−0.079	0.173
Na	−0.317	−0.028	−0.044	**0.865**	0.104
Cl	−0.257	−0.065	0.042	**0.803**	−0.223
V	0.163	0.081	−0.045	**0.686**	0.025
P	**0.407**	−0.022	0.057	−0.240	**0.806**
S	0.211	0.002	**0.323**	**0.279**	**0.695**
Co	−0.051	**0.350**	0.002	−0.014	**0.609**

These five factors explained 76% of the variance.

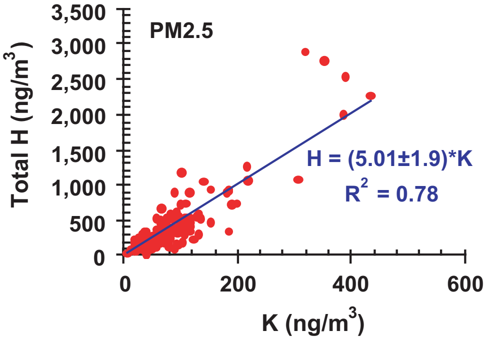

Fig. 7. Correlation plot of H versus K for two year data set from Mascot in Sydney.

gerprints [2,3]. This provides unique information for local Councils and Environmental Protection Agencies beyond the straight total particulate mass measurements. For example in the biomass smoke factor of Table 1, hydrogen (H) from organic material and potassium (K) from vegetation have the highest factor loadings and hence have a strong correlation. Fig. 7 demonstrates that this correlation does indeed exist and shows the power of PCA statistical methods to identify these correlations in multi-dimensional space.

The gradient of plots like Fig. 7 for the range of elements identified in analyses like those of Table 1 allow source fingerprints to be generated [2,3]. Fig. 8 is such a source fingerprint for automobiles at the Mascot site in Sydney. If enough of these sources can be identified and fingerprinted then standard chemical mass balance (CMB) [14] techniques can be applied to determine absolute source contributions.

4. Regional fine particle pollution

On a regional scale we show how IBA techniques were able to quantify a major dust storm in October 2002 during the height of recent Australian droughts. This natural storm covered three Australian states and using IBA techniques we were able to tract and quantify the soil contribution to the total fine particle mass loading at sites separated by hundreds of kilometres. Table 1 showed that soil contained at least five key associated elements, Al, Si, Ti, Ca and Fe being the major ones [15]. The gradient of plots similar that of Fig. 9 enabled us to obtain fractional relationships between these soil elements and to determine a unique soil fingerprint and hence estimate the soil content on the filters [3,4]. Fig. 10 shows this soil content, calculated using the oxide form of these five elements [15], in the fine fraction (PM2.5) for the six month period from July to December 2002 at Richmond in Sydney, Queensland University of Technology, in Queensland and Muswellbrook in northern NSW. These three sites were many hundreds of kilometres apart demonstrating the extent of this dust event. The figure shows the peak in the soil concentration occurred at all three sites on the same day (23 October 2002). The soil concentration ranged from 7 to 20 μg/m^3 across the sites and was many times larger than the average background fine soil which was

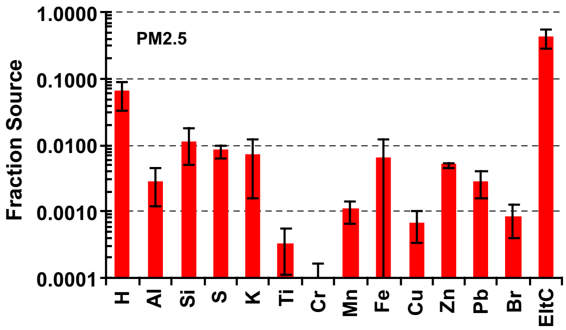

Fig. 8. Estimated automobile fine particle (PM2.5) source fingerprint at Mascot in Sydney.

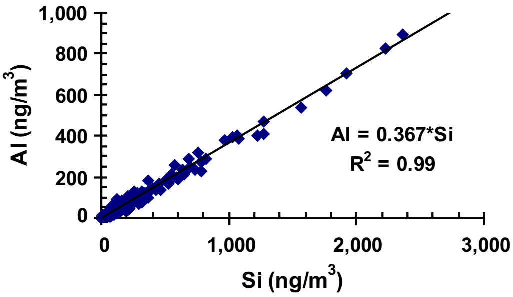

Fig. 9. Al versus Si for all Australian sites from July 2002 to December 2002, including the dust storm of 23 October 2002.

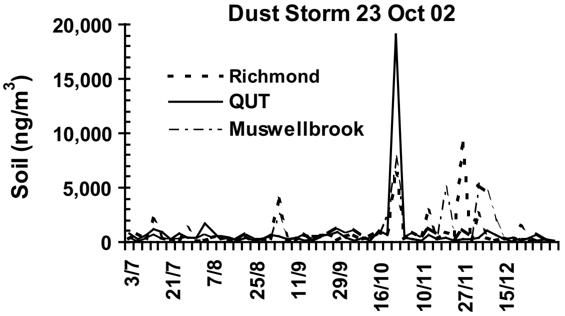

Fig. 10. Fine PM2.5 soil from five key elements at three sites in Australia over 1000 kms apart for July 2002 to December 2002.

generally well below 2 μg/m^3. Other high soil events at selected sites can also be seen in this type of plot but none at all three sites and with the intensity of the 23 October event. The IBA PIXE technique has provided a unique opportunity to study soil absolutely through its multi-elemental capability.

5. Global fine particle pollution

On a global scale ANSTO is currently a collaborator on a major international aerosol characterisation experiment in Asia (ACE-Asia) [16–18]. This project is studying massive airborne dust and industrial pollution from northern and eastern China which is transported, in the northern hemisphere spring time, in an easterly direction across Korea and Japan and even across North America. This fine particle pollution is large enough to have impacts on solar heating of the globe and to directly affect climate forcing [7]. Furthermore different components like sulphate, carbon and soil have different effects on climate forcing. We have been sampling in five Asia countries of Vietnam, China, Philippines, Japan and Korea since January 2001 to study the large scale dust and pollution events originating from these regions [18]. Again IBA techniques have been applied to characterise these events and provide quantitative information on natural and anthropogenic contributions.

For example a time series plot of sulphur from Hanoi, Vietnam shows large sulphur events between 26 and 30 September 2001 (see Fig. 11). A four day back trajectory plot during this time [19,20], shown in Fig. 12, shows this pollution originates from the eastern regions of China and was being transported by prevailing winds across the border into Vietnam [18]. Similar regular annual events have been measured for dust transported from deserts in northern China, near the Mongolian border, across Korea, Japan and round the globe to North America [16].

The average percentage compositions for the major components in the fine particle fraction, for sampling sites at Manila in Philippines, Hong Kong, Cheju Island in Southern Korea, Hanoi in Vietnam and Sado Island off the west coast of Japan are given in Table 2. The large standard deviations reflect the large seasonal variations and

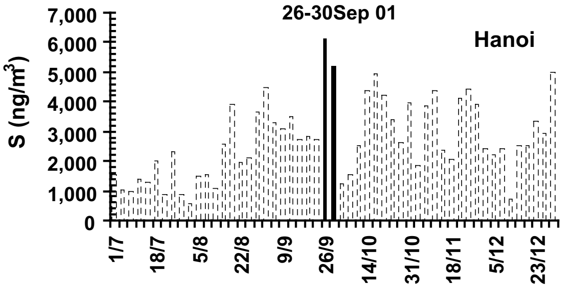

Fig. 11. Highest PM2.5 fine sulphur days in Hanoi site during 2001.

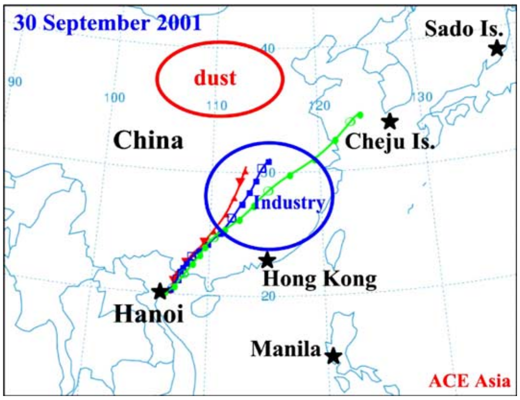

Fig. 12. NOAA 4 day back trajectories out of Hanoi, Vietnam for 500 m (dots), 200 m (squares) and 100 m (triangles) above ground level for 30 September 2001.

Table 2
Average PM2.5 fine aerosol composition for the three ACE-Asia sites for the study period from 1 January 2001 to 31 March 2003

PM2.5	Manila	Hong Kong	Cheju Island	Hanoi	Sado Island
Black carbon (%)	29 ± 11	7.3 ± 5	7.0 ± 6	8.3 ± 3	6.9 ± 4
Soil (%)	3.1 ± 4	7.0 ± 8	10 ± 17	9.5 ± 9	8.9 ± 22
Ammonium sulphate (%)	4.8 ± 10	42 ± 25	39 ± 24	25 ± 14	41 ± 33
Organics (%)	46 ± 21	17 ± 23	15 ± 21	30 ± 25	14 ± 29
Sea salt (%)	4.4 ± 4	8.9 ± 7	7.1 ± 7	3.6 ± 6	11 ± 9
Trace elements (%)	0.60 ± 0.5	0.78 ± 0.3	0.47 ± 0.2	1.4 ± 1	0.43 ± 0.3
Non-soil K (%)	1.1 ± 7	1.4 ± 1.5	0.98 ± 1.3	1.3 ± 0.7	0.73 ± 0.8
Average mass (μg/m^3)	47 ± 24	31 ± 22	20 ± 15	47 ± 31	13 ± 11

not the IBA measurement errors which were much smaller [8]. Although the absolute PM2.5 masses were significantly different at the three sites the percentage compositions for the major components were remarkably similar. All three sites being coastal sites had similar sea salt components. The percentage soil components at Cheju and Sado Islands tended to be higher than at Hong Kong. The average PM2.5 mass loadings at these two sites were affected more by soil from main land China than at the Hong Kong site over the study period. The organic fraction measured at Sado Island was consistently lower than either Hong Kong or Cheju Island sites.

6. Summary

We have demonstrated the power of using multiple IBA techniques to provide multi-elemental analyses of fine particulate dust on thin Teflon filters. In particular, the ability to measure the total elemental concentration and not a subset (like only the soluble part) with no sample preparation on sample masses of only a few hundred micrograms on elements from hydrogen to lead simultaneously is unique. For these types of pollution studies it allows source pollution fingerprints to be estimated and the contribution of these sources to be quantified. This is much more useful and easier to interpret for Local Councils and pollution managers than just the straight elemental concentrations. We have shown examples of how this has been applied on a local scale to follow lead in air reductions over many years, on a regional scale by quantifying dust storms over hundreds of kilometres and finally as inputs for global climate modellers trying to unravel the effects of fine particles on climate forcing around the globe. Over the past ten years and more these IBA techniques have analysed tens of thousands of samples around the world. With the US EPA introducing a fine particle goal for atmospheric pollution in July 1997 and many other countries in Asia, Europe and Australia going down the same path the value of these techniques should continue to be extremely beneficial for many years to come.

Acknowledgements

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