

The Complementarity of PIXE and Synchrotron Induced X-ray Methods for the Characterisation of Combustion Sources Contributing to Urban Air Pollution

David D. Cohen, Rainer Siegele, Ed Stelcer, David Garton

Physics Division, Australian Nuclear Science and Technology Organisation, PMB 1, Menai, NSW, 2234, Australia

Anton Stampfl, Z. Cai, P. Ilinski, W. Rodrigues, D.G. Legnini, W. Yun, B. Lai
Experimental Facilities Division, APS, Argonne National Lab, Argonne, IL, USA

Abstract

Current knowledge of fine-particle airborne pollution concentrations and constituents with diameters below 2.5 μm (PM_{2.5}) is limited. Sources are both natural and man-made. Here we describe two types of experiments performed using the Advanced Light Source (APS) facility at Chicago, and compare the results with PIXE analysis on the same fine particle filters. Firstly, broad beam (2 mm) studies with tuned synchrotron beam energies to help resolve overlapping X-rays and secondly highly focused X-ray beam studies (0.2 μm) of individual fine particles from airborne pollution combustion sources.

Introduction

There currently exists a reasonable body of evidence that fine particle atmospheric pollution, on an urban scale, affects human health [1,2] and on a global scale plays a key role in climate forcing and global climate change [3]. Accelerator based Ion Beam Analysis (IBA) methods are well suited to characterising these fine particles when collected on the appropriate filter papers. Over the past decade considerable research has been going on at the Australian Nuclear Science and Technology Organisation (ANSTO) using four simultaneous IBA techniques, particularly PIXE, PIGE, PESA and RBS to quantify up to 24 elements, including hydrogen, present fine particulate atmospheric urban pollution [4-6].

Ion beam and synchrotron X-ray fluorescence are complementary techniques [7]. PIXE has higher cross sections for low atomic number elements, but for high atomic number elements with K edge energies closer to the beam excitation energy synchrotron radiation cross sections are larger. PIXE is a multi-elemental method and synchrotron excitation has the added advantage that the incident beam energy can be tuned to the K or L edge of a particular element of interest. Furthermore the high brightness of these X-ray sources allows for sub micron spatial resolution with enough yield to analysis for elements within individual sub micron particles.

Here we compare synchrotron induced X-ray emission and PIXE on the same batch of fine particle filters. In particular we are interested in the ability of synchrotron induced X-ray emission to detect arsenic (As) and selenium (Se) which together with sulphur (S) are present in coal combustion products [8]. PIXE, in the presence of large lead (Pb) and bromine (Br) concentrations, was unable to resolve or detect arsenic and selenium at much lower concentrations. The ability to finely tune the synchrotron excitation energy to selectively analysis for As and Se was tested in broad beam mode. Furthermore the high brightness of synchrotron sources allows for sub-

micron focused beams to also be used to analyse individual fine particles for a similar range of elements as determined by PIXE. This spatial resolution is significantly better than anything obtained to date for PIXE analysis using focussed nuclear microprobes. This capability together with the use of standard PIXE analysis routines, such as PIXAN [9], for synchrotron spectrum analysis was also tested.

Fine Particle Sample Collection

Fine particles with diameters less than 2.5 μm (PM_{2.5}) were collected on thin 25 mm stretched Teflon filters from inside the Sydney Basin and around coal fired power stations, outside the Basin, producing power for the Sydney region. These Teflon filters were typically 220 $\mu\text{g}/\text{cm}^2$ thick. Aerosols on these filters were collected over a 24 hour period every Sunday and Wednesday typically containing a several hundred micrograms of sample. All filters were analysed by simultaneous IBA methods for most of the commonly occurring elements including H, C, N, O, F, Na, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Br and Pb at concentrations down to 1 ng/m^3 of air sampled [4-6]. Typically, filter collection areas were 2.27 cm^2 and sampling volumes were 32 m^3 over a 24 hour period so a concentration of 1 ng/m^3 of air sampled corresponded to only 14 ng/cm^2 of material on the filter itself.

Of the 24 or so elements analysed by these IBA methods some key elements related to significant fine particle sources were not present. For example, coal burning produces elemental carbon and sulfur but these elements are also produced by other sources such as motor vehicles, particularly diesel driven vehicles. So to distinguish coal sources from motor vehicles sources we need to include other characteristic tracers like Se and As [8]. However for PIXE analysis the signatures from these elements are completely swamped by signatures from Br and Pb from petrol driven motor vehicles. Typically, in the Sydney region, the measured Pb and Br

concentrations range from 50 to 500 times larger than the As and Se concentrations.

Broad Beam Synchrotron Studies

Synchrotron induced X-ray techniques at the Advanced Photon Source in Chicago were used to detect key elements which were obscured by inter-element interferences during standard PIXE analysis such as (Pb, As and, Pb, Br, Se). This was achieved through appropriate tuning of the excitation beam energy E_{ex} (keV). X-ray production cross sections are larger for elements with their K edge energies E_k adjacent to but just below E_{ex} . For example if the synchrotron excitation energy is $E_{ex}=12.9$ keV, then this is just below the K edge for Br (13.474 keV) and the L edges for Pb (13.035 keV) but above the K edges for As (11.868 keV) and Se (12.658 keV). Hence As and Se K X-rays will be excited with high cross sections and Br and Pb X-rays will not be excited at all.

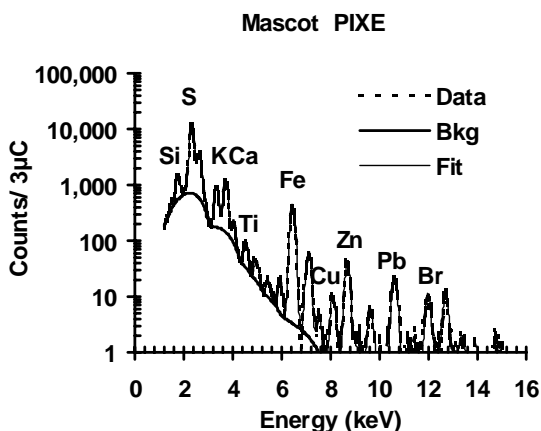


Fig. 1 A typical fitted PIXE spectrum for proton excitation at 2.6 MeV on fine particles from Mascot, Sydney

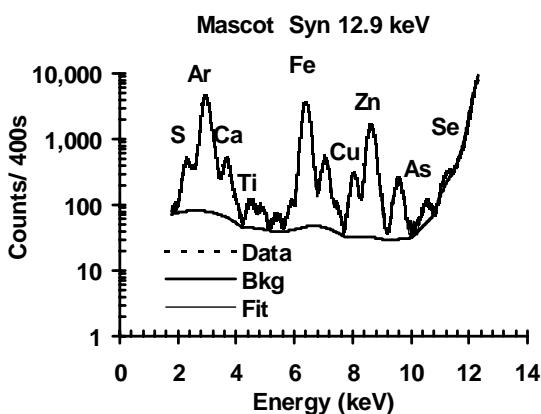


Fig. 2 A typical fitted X-ray spectrum for synchrotron excitation energy $E_x=12.9$ keV on the same filter and the same site as shown in Fig. 1.

The effect on the resulting X-ray spectrum of being able to tune the synchrotron beam in this way is demonstrated in Figs. 1 and 2 where a standard PIXE spectrum and fit are compared with a synchrotron induced spectrum and its corresponding fit on the same filter loaded with fine particles from an urban site at Mascot in the centre of Sydney. Both spectra were fitted using the standard PIXAN fitting routines [9]. Pb (94 ng/m^3) and Br (40 ng/m^3) were present in the PIXE spectrum but not in the synchrotron spectrum. While As (1.2 ng/m^3) and Se (2.3 ng/m^3) were observed only in the synchrotron spectrum with the appropriately tuned excitation energy. The PIXE spectrum was obtained using 2.6 MeV protons in vacuum and the synchrotron spectrum using an excitation energy of 12.9 keV in air. Hence the different shape of the low energy part of spectrum and the presence of the large Argon (Ar) peak in the synchrotron spectrum. The Argon peak was used to normalise run times for all synchrotron spectra. Blank Teflon filters were run in air and used, after normalisation to the Ar peak, to background strip the synchrotron spectra before analysis using the PIXAN routines. Fig. 3 shows a typical background subtracted synchrotron spectrum, obtained using a different filter to the one shown in Figs. 1 and 2. For this filter the As (0.75 ng/m^3) and Se (0.50 ng/m^3) peaks were again clearly identified even in the presence of substantial concentrations of Pb (74 ng/m^3) and Br (35 ng/m^3).

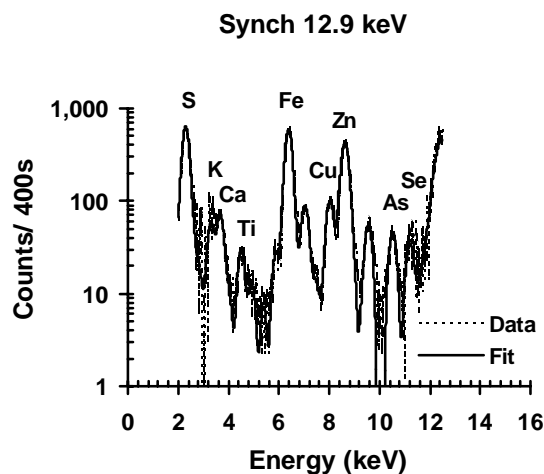


Fig. 3. shows a typical Ar peak and background subtracted spectrum for $E_{ex}=12.9$ keV synchrotron excitation of a fine particle filter.

Broad beam (>2 mm) synchrotron induced data, similar to that shown in Figs. 2 and 3 were collected on over 250 filters from sites affected by coal fired power stations and in urban areas affected by motor vehicles. Absolute elemental yields for synchrotron induced X-rays were obtained by direct comparison with concentrations from PIXE for the same elements on the same filters. Fig. 4 is a plot of the synchrotron elemental yields as a function of elemental K X ray energy for the 13 key common elements S, Cl, K, Ca, Ti, V, Cr, Fe, Cu and Zn. A 3rd order polynomial fit to these data was used to determine

absolute synchrotron concentrations for all other elements not directly measured by this technique. The errors on the points represent one standard deviation and the two dotted lines one standard deviation 'tram lines' about the polynomial fit (solid curve) to the data. The two open circles are the estimated As and Se synchrotron yields obtained by extrapolation of the polynomial fit to the solid circles.

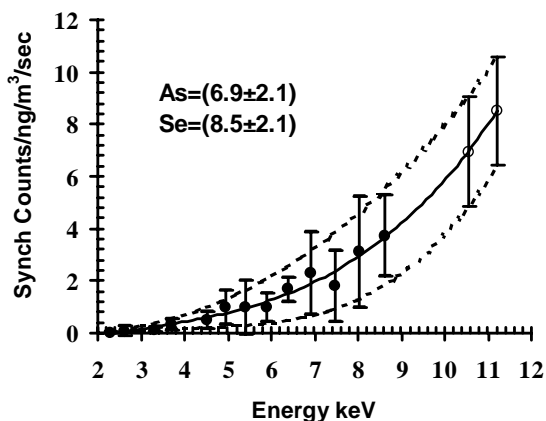


Fig. 4. Calibration plot for $E_x=12.9$ keV for synchrotron counts/ ngm^{-3} / sec for a given trace element X-ray energy.

For this experiment the synchrotron yields for As and Se were (6.9 ± 2.1) and (8.5 ± 2.1) counts/ ngm^{-3} /s respectively. Inspection of the backgrounds under the As and Se peaks in spectra, similar to that shown in Fig. 2, showed that the minimum detectable limits (MDL's) for As and Se using synchrotron excitation were about 0.02 and 0.04 ngm^{-3} respectively. However the background, and their corresponding MDL's, also varied with the mass of material on each filter.

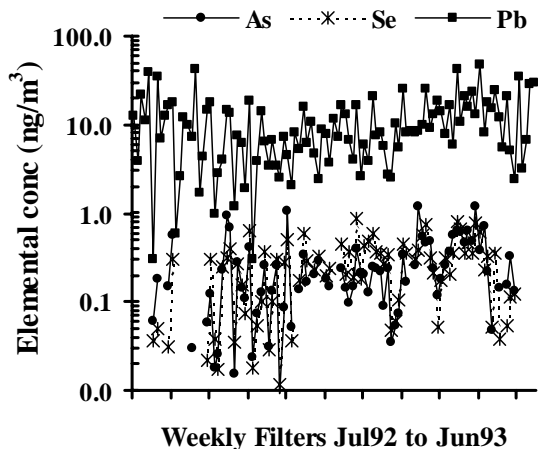


Fig. 5. Typical Pb, As and Se concentrations for a twelve month period at the Muswellbrook site.

Across the several sites monitored and over the 12 month sampling period the average As and Se concentrations were (0.42 ± 0.41) and (0.33 ± 0.36) ngm^{-3} respectively and ranged from 0.02 to 3 ngm^{-3} and 0.02 to 2.5 ngm^{-3} respectively in the presence of Pb up to 250 ngm^{-3} . Fig. 5. shows typical Pb, As and Se concentrations for a twelve month period at the rural Muswellbrook site. Pb concentrations at Muswellbrook were considerably reduced compared inner urban areas affected by motor vehicles (eg Mascot site). However their concentrations were still sufficient to completely interfere with As and Se measured by PIXE and these data could only be obtained by synchrotron induced methods.

Fig. 5 also shows a reasonable correlation between As and Se particularly for concentrations above 0.1 ngm^{-3} . This was most probably due to these elements originating from the same source, coal combustion. The site at Muswellbrook, 150 km north of Sydney, was expected to be most affected by coal-fired power stations, burning several million tonnes of coal per year in the region. This can be verified by the presence of As and Se in association with S from coal burning.

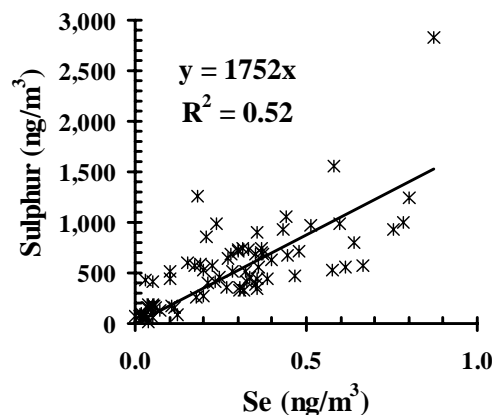


Fig. 6. A plot of sulfur versus selenium concentrations, as measured by synchrotron excitation, for filters affected by a coal-fired power station near Muswellbrook, NSW from July 1992 to June 1993.

Fig. 6 is a plot of S versus Se, both measured by synchrotron excitation, for filters collected at the Muswellbrook site from July 1992 to June 1993. It shows a good correlation between these two elements confirming coal as a major source of S in the region.

Sub-Micron Particle Mapping Studies

The principles described above for broad beam synchrotron excitations are directly applicable to focused sub-microbeam studies. The high brightness of synchrotron sources allows the X-ray beam to be focused to less than $0.2 \times 0.2 \mu\text{m}$ spot sizes which can be scanned over tens of square microns time permitting.

Scanning electron micrographs (SEM) of typical fine particle filters show the presence of two distinct groups of particles on our filters. Namely; fine particles, with diameters much less than $1\ \mu\text{m}$, from combustion sources such as motor vehicles and power stations, and coarser particles, much greater than $1\ \mu\text{m}$ in diameter, from mechanical sources such as windblown dust and seaspray. This is clearly shown in the SEM of Fig. 7 of PM2.5 particles collected on a Nuclepore filter. Over an area of approximately $3 \times 4\ \mu\text{m}$ you see a large ($> 1\ \mu\text{m}$) soil particle in the bottom right with many other fine combustion particles with diameters less than $1\ \mu\text{m}$ and some less than $0.2\ \mu\text{m}$.

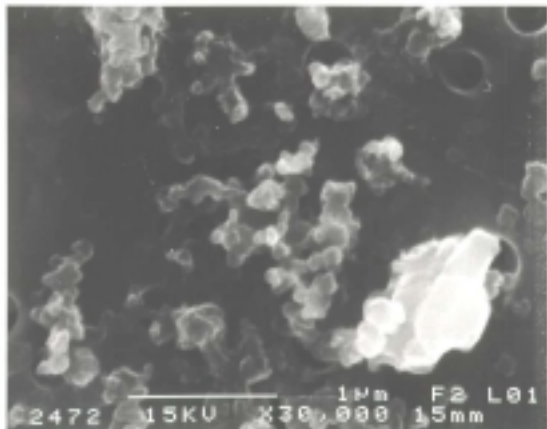


Fig. 7. Scanning electron micrograph (SEM) of typical fine particle (PM2.5) filter collected in the Sydney Basin, magnification 30,000x.

Similar areas and particles have been scanned at the sub-micron X ray facility at the APS, Chicago. The significant advantage being that the X-ray beam energy can be tuned, as with the broad beam studies to only include trace elements of interest. Figs. 8 and 9 show sub-micro beam scans over similar areas to that of Fig. 7 for the elements S and Se at 12.9 keV excitation energy. Each scan took just over 7 hours to complete using a beam spot size of about $0.2 \times 0.2\ \mu\text{m}$ scanned over 16×16 pixels. Full energy X-ray spectra, similar to those of Fig. 2, were obtained for 100 seconds at each pixel in each scan and were further analysed off line to produced maps for up to 15 different elements at a time.

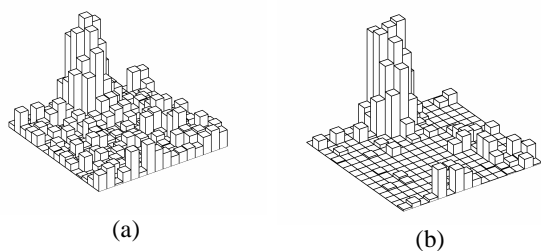


Fig. 8. Sulphur map, (a) region of interest summed, no background removal (b) PIXAN analysis, background removed. Each $0.2 \times 0.2\ \mu\text{m}$ pixel normalised to Argon peak, $E_{\text{ex}}=12.9\ \text{keV}$.

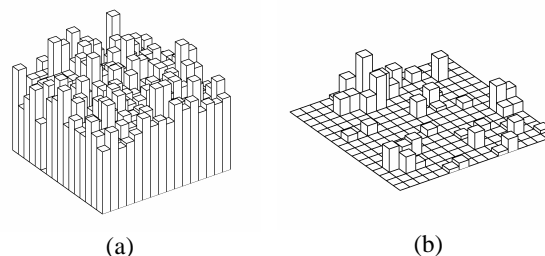


Fig. 9. Selenium map (a) region of interest summed, no background removal (b) PIXAN analysis, background removed. Each $0.2 \times 0.2\ \mu\text{m}$ pixel normalised to Argon peak, $E_{\text{ex}}=12.9\ \text{keV}$.

Traditional X-ray micro beam studies usually place channel markers around elemental peaks of interest and sum up the counts per region of interest to generate two dimensional elemental maps. This technique is reasonable for some elements for proton microprobe studies where the bremsstrahlung backgrounds are low. But for synchrotron induced microbeam work Fig. 2 shows that these backgrounds can be substantial especially for the minor elemental peaks on high backgrounds (Se) or poorly resolved peaks adjacent to other major peaks (S adjacent to Ar).

Here we performed the full PIXAN analysis [8] on each spectrum from each pixel. This had a twofold advantage, firstly the peak areas obtained were each background stripped and secondly if the peak area was less than the MDL the elemental area for that pixel could be set to zero. This had the effect of considerably improving the 2D elemental maps as shown for the S and Se maps in Figs. 8 and 9. Fig. 8b shows a cluster of sulphur particles in a region approximately $0.8 \times 0.8\ \mu\text{m}$ as well as individual sulphur particles less than the defined pixel size on an essentially zero background. Fig. 9 shows effects of the full PIXAN fit, reducing the background and increasing the contrast for selenium elemental maps, an element already occurring at concentrations well below $1\ \text{ng}/\text{m}^3$.

Conclusion

This paper describes some preliminary synchrotron X-ray microbeam studies which yielded many new results regarding the elemental and spatial character of atmospheric fine particles and compares them with the PIXE results previously obtained. Absolute elemental concentrations were obtained for elements not seen by PIXE, and for elements within sub-micron particles. The X ray microprobe facility at the Advanced Photon Source (APS), in Chicago, clearly has the brightness and hence the sensitivity to detect trace elements of interest, not detected by other X-ray methods, in a few minutes of running on samples with a total mass of only a few hundred micrograms or less and even for sub-micron beam spot sizes on individual particles. Furthermore, the ability of the beam energy to be finely tuned to excluded

elements above selected K edges provides a unique opportunity to overcome some adjacent element interferences present in other techniques. One significant drawback was that the submicron beam positioning moved several microns across the sample when the beam excitation energy was changed and retuned making it difficult to precisely scan the same 3x3 μm area and hence get elemental maps from the same scan region. Hopefully this can be overcome for future experiments.

Acknowledgements

We would like to acknowledge funding from the Australian Synchrotron Research Program and to thank, all the 3 MV accelerator staff for assistance throughout many aspects this work.

References

[1]. D. W. Dockery, C. A. Pope, X. Xu, J. D. Spengler, J.H. Ware, M. E. Fay, B. G. Ferris, F.E. Speizer, *New England Journal of Medicine*, 329 (1993) 1753-59.

[2]. C. A. Pope, J. Schwartz and M. Ransom, *Arch. of Environ. Health*, 47 (1992) 211-217.

[3]. *Climate Change 1995; The Science of Climate Change*, Report of Working Group I to the Intergovernmental Panel on Climate Change, IPCC-XI, Rome, 11-15 December 1995.

[4]. D. D. Cohen, *Nucl. Instru. and Methods*, B79 (1993) 385-388.

[5]. D.D. Cohen, G. M. Bailey and R. Kondepudi, *Nucl. Instru. and Methods*, B109 (1996) 218-226.

[6]. D.D. Cohen, *Nucl. Instru. and Methods*, B136 (1998) 14.

[7]. D. D. Cohen, R. Siegele, A. Stampfl, Z. Cai, P. Ilinski, W. Rodrigues, D.G. Legnini, W. Yun, B. Lai, *Proceedings of 11th National Nuclear Techniques of Analysis Conference*, Sydney, Australia, 24-26 November 1999, pp 62-66.

[8]. Z. L. Cheng, K.S. Lam, L.Y. Chan, T.Wang, K. K. Cheng, *Atmospheric Environment* 34 (2000) 2771-2783.

[9]. D. D. Cohen, E. Clayton, *Nucl., Instru. and Methods*, B22 (1987) 55-68.