

Stephen M HALEY, Alan D TAPPIN and Mark F FITZSIMONS

School of Earth, Ocean and Environmental Sciences, University of Plymouth, PLYMOUTH PL4 8AA, UK

ABSTRACT

The physico-chemical behaviour of estuarine suspended particulate matter (SPM) is an area of increasing interest, as particles can regulate the speciation and destiny of contaminants and nutrients in the aquatic environment. This study compared the use of Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES) with Scanning Electron Microscopy-Energy Dispersive X-ray Spectrometry (SEM-EDS) in quantifying the elements Al, Fe, Mg, Si, Zn, Mn, Ca, K and Ti in an estuarine Certified Reference Material (CRM).

Sample preparation for ICP-AES analysis involved LiBO_2 fusion in order to release Al. SEM-EDS analysis required the production of polished resin stubs containing the CRM. The analysis of 15 scans from the ICP-AES, and 100 individual particles by SEM-EDS, revealed no significant difference between the medians for Al, Fe, Mg, Ca and K. Good correlation was generally observed between the instrument and reference values. Significant differences were observed between the medians of Mn and Ti, while the Si value was not established as a reliable reference. Trace Zn was not determined by SEM-EDS and the instrument performed poorly on Mn and Ti, which were also present at trace levels.

The ICP-AES values correlated closely with CRM values throughout, except for K, which it undervalued substantially. Qualitative elemental mapping techniques were performed on the SEM-EDS. The results were mainly illustrative but showed potential for further development.

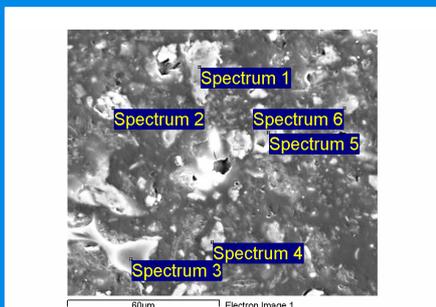


Figure 1. Micrograph of acquired Site of Interest 1 showing embedded specimens and spectrum acquisition targets

INTRODUCTION

Suspended particulate material (SPM) regulates the speciation of many dissolved aquatic species (Doucet *et al.*, 2004). Estuarine SPM, including resuspended sediment, can scavenge metals and organic pollutants, particularly in the low salinity, turbidity maximum zone (TMZ). The role of estuarine SPM may be particularly important due to the effect of regular tidal movements and sporadic meteorological or river flow influences on both organic and non-organic particle concentrations and character (Turner & Millward, 2002). Individual particle analysis is routinely undertaken within the field of aerosol research (Ro *et al.*, 2004). However, little research has been conducted on the elemental characterisation of individual estuarine particles (Menzel *et al.*, 2002).

Scanning Electron Microscopy-Energy Dispersive X-ray Spectrometry (SEM-EDS) is a simple, rapid, non-destructive option for surface elemental analysis. A detection limit of 0.1–0.5 wt. % is possible for most elements and a high spatial resolution (< 10nm) is possible (Goldstain, 2003). It is capable of producing quantitative and qualitative surface elemental data from individual particles (McGuinness, 2003). The topography of a single particle, including its texture and detectable features, can be considered by analysing images of each particle in three dimensions (Pina *et al.*, 2002). This may be particularly useful for considering the spatial distribution of elements on a particle and their mutual depositional and textural relationships. As analysis with SEM-EDS is non-destructive, it allows reproducibility and has the potential to improve the integrity of the data (Reed, 1996).

In this novel study we evaluated the ability of SEM-EDS to provide quantitative elemental data for heterogeneous, estuarine particles. The technique was compared with Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES), a routine method for quantitative particle analysis, using a certified reference material for estuarine sediment.

MATERIALS & METHODS

The Certified reference material (CRM) was prepared by the National Research Council of Canada. The sediment (PACS-2) was collected in the estuarine harbour of Esquimalt, British Columbia, Canada, freeze dried, screened to pass a No. 120 (125µm) screen, blended and bottled. The bottled samples were radiation sterilised with a dose of not less than 2.5 Mrad in order to minimise the effects of any biological activity.

ICP-AES analysis

Sediment samples (0.250 g, n = 5) and a procedural blank were mixed with LiBO_2 (1.0g) and heated in a muffle furnace (15 mins, 900 °C). The melt was immediately poured into pre-cleaned, polypropylene beakers containing nitric acid (4 % v/v, 50 mL) and the solution homogenised.

Solutions were transferred to pre-cleaned 100 mL volumetric flasks and diluted to volume with nitric acid (4% v/v). All calibration solutions and procedural blanks contained LiBO_2 and nitric acid to ensure matrix matching. These solutions were immediately transferred to plastic bottles for elemental determination by ICP-AES.

The ICP-AES was calibrated and optimised for maximum signal strength, 3 mm above the lead coil, for determination of the selected elements. The plasma conditions used were: an r.f. power of 1.00 kW applied to the plasma; flow rates of 15 L min⁻¹ for the plasma gas and 1.5 L min⁻¹ for the auxiliary gas with the nebuliser gas pressure set at 150 kPa, snout purge low. The sample uptake was 1.5 mL min⁻¹ for each of 3 replicate scans.

SEM-EDS analysis

Aluminium SEM specimen stubs were prepared with double-sided adhesive carbon mounting tabs. CRM was deposited onto the mounting tabs and the stubs carbon coated using an Edwards 306 vacuum evaporator (~200 Å). These specimens were utilised to provide topographical images of individual particle surfaces.

For elemental analysis, cured stubs were polished in a three-stage polishing process using increasingly fine grades of Buehler diamond polishing cloths (15 µm, 6 µm and 1 µm respectively) and corresponding diamond suspension compound polishes. The stubs were cleaned, dried and carbon coated (~200 Å) as described above.

Samples were analysed using a Jeol JSM 6100 scanning microscope, combined with an Oxford Instruments INCA EDS suite. The software was calibrated to a Cobalt reference standard embedded in the specimen holder. The accelerating voltage for X-ray intensity measurement and for SEM image observation was 15 kV, using a probe current of 0.3 nA and a mean dead time of 20 %. The acquisition rate was 6 kcps (over 90 s) and the magnification was 1000 x. Twenty two individual sites of interest of a 13,200 µm² area were acquired, with 2–9 (7 µm – 70 µm diameter) particles per site. One hundred particles were analysed in total.

Recalibration was performed at 15 minute intervals. Electron micrographs of each site of interest were produced, indicating individual particles and determination targets (Figure 1), while spectra for individual particles were recorded, as shown in Figure 2.

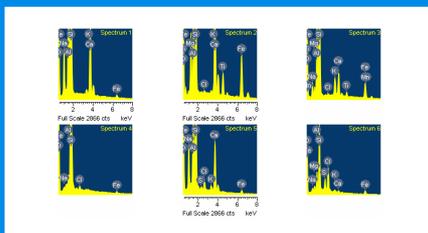


Figure 2. Site of interest 1 spectra showing relative elemental abundance. Element concentration data from each measurement were pooled and expressed for the entire CRM, as shown in Figure 3.

RESULTS & DISCUSSION

The data supplied with the CRM lacked a value for sample size, and this prevented a parametric statistical data analysis. Consequently, the non-parametric Kruskal-Wallis test, which is a comparison of medians, was chosen as a suitable tool for statistical analysis.

The results for 95% confidence interval (CI, Fig. 3) showed a wide variation across the sample set. This is expected, and due to the relative differences in sample size. The SEM-EDS determinations were made on 100 individual particles, whereas the ICP-AES data measured elements extracted simultaneously from thousands of particles. Furthermore, the CRM values were determined after analyses of a large number of individual samples. An improved 95% CI for SEM-EDS analysis might thus be expected to result from substantially increasing the sample size.

Given the various particle sizes within the CRM, it follows that single particle analysis may discriminate against trace constituents. The only two certified element values with a significant difference between medians were Mn and Ti. These elements were present at low concentrations, with Mn cited as present at trace amounts in the CRM documentation. The SEM-EDS 95% CI was relatively large for Mn and Ti (Figure 3), with their respective normality plots indicating the considerable number of nil counts obtained. The apparent increase of variance between SEM-EDS and referenced values for analytes at trace levels appears to concur with the literature in terms of the poor determination capabilities of SEM-EDS of elements at trace levels (Reed, 1996).

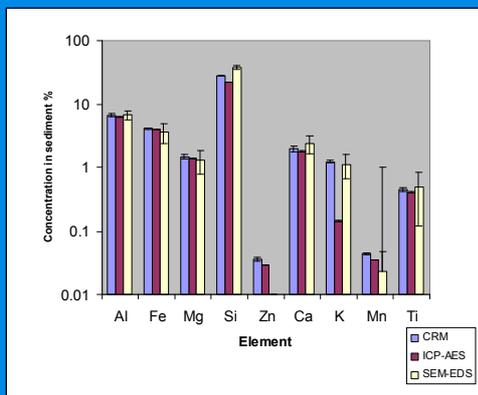


Figure 3. Comparison of means of elemental concentrations in PACS-2 sediment, with reference to accredited CRM data.

It is interesting to note that a strong correlation emerged for non-trace elements between techniques. This may be due, in part, to a random selection procedure for SEM-EDS analysis, which included a range of particle sizes. No significant difference was found between the medians for Al, Fe, Mg, Ca (the Si value was not certified). The K measurement using SEM-EDS was not significantly different from the CRM value, while the ICP-AES value underestimated K. This may have occurred as a result of K volatilization during treatment of the sediment with LiBO_2 (Greenwood & Earnshaw, 1984).

In conclusion, these results suggest that SEM-EDS can provide accurate and precise concentration data for a range of elements embedded in complex estuarine particles. Increasing the number of particles analysed would extend quantitative analysis to trace elements.

ACKNOWLEDGMENTS

We thank the University of Plymouth SEM Unit for help with the SEM-EDS analysis, and Andrew Arnold for help with the LiBO_2 digest. This study was funded by the Leverhulme Trust (grant F/00568/H) for which it is gratefully acknowledged.

REFERENCES

- Doucet, F. J., Maguire, L. & Lead, J. R. (2004) *Anal Chim Acta* 522: 59-71.
- Goldstain, J., *et al.* (2003) *Scanning Electron Microscopy and X-ray Analysis*. Kluwer Academic Publishing, New York.
- Greenwood, N.N. & Earnshaw, A. (1984) *Chemistry of the Elements*. Pergamon Press.
- McGuinness, P. E. (2003) *The Journal of Scanning Microscopies* 25 (4): 221.
- Menzel, N., Schramel, P. and Wittmark, K. (2002) *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* 189 1-4: 94-99.
- Pina, A., Villaseñor, G. T., Jacinto, P. S. and Fernandez, M. M. (2002) *Atmos Env* 36: 5235-5243.
- Reed, S. J. B. (1996) *Electron Microprobe Analysis and Scanning Electron Microscopy in Geology*. Cambridge University Press, Cambridge, 1-4, 183, 184.
- Ro, C. U., Kim, H. & Van Grieken, R. (2004) *Anal Chem* 76: 1322-1327.
- Turner, A. and Millward, G. E. (2002) *Est Coast Shelf Sci* 55: 857-883.