Pact 33 - I.b.2 : N. Rose, J. Watt, S. Juggins, M.A.R. Munro and R.W. Battarbee

The Characterisation of Carbonaceous Particles Derived from Fossil-fuel Combustion

High temperature combustion of coal and oil gives rise to the emission of both gases (SO_2, NO_x, CO_2) and particles. The particulate fraction is collectively referred to as fly-ash and includes particles of different types (carbonaceous, alumino-silicate) and different sizes (< 1 µm - > 50 µm) (Fig. 1). Emitted particles are widely dispersed in the environment, and are found in lake sediments (Goldberg *et al.*, 1981 ; Wik *et al.*, 1986 ; Battarbee *et al.*, 1988), soils (Wik and Renberg, 1987) and on buildings (Del Monte *et al.*, 1984). Since they are extremely resistant to decay their relative abundance in lake sediments can be used both to map the distribution and reconstruct the history of particle pollution (Wik and Renberg, 1987), Renberg and Wik, 1985).

They are also useful as surrogates for sulphur deposition and the excellent agreement between the incidence of lake acidification and the abundance of carbonaceous particles in lake sediments has enabled palaeolimnologists to argue strongly for acid deposition as the main cause of lake acidification (Battarbee *et al.*, 1988, 1989).

Although alumino-silicate particles are more abundant (Rose, 1990a) carbonaceous particles are easier to distinguish from other particles in sediments and can be extracted more effectively using chemical digestion techniques (Rose, 1990b). Particles can be enumerated by direct counting using light microscopy or automatically using program-driven scanning electron microscopy. However, existing quantitative techniques make no attempt to differentiate carbonaceous particles according to fuel type.

Examination of individual particles show characteristic differences between oil and coal. Oil particles are often smaller, more spherical, and more porous than coal particles, and often have a convoluted or layered surface texture, and chemically, coal is frequently characterised by titanium, and oil by vanadium peaks in EDS spectra (Fig. 2 a,b).

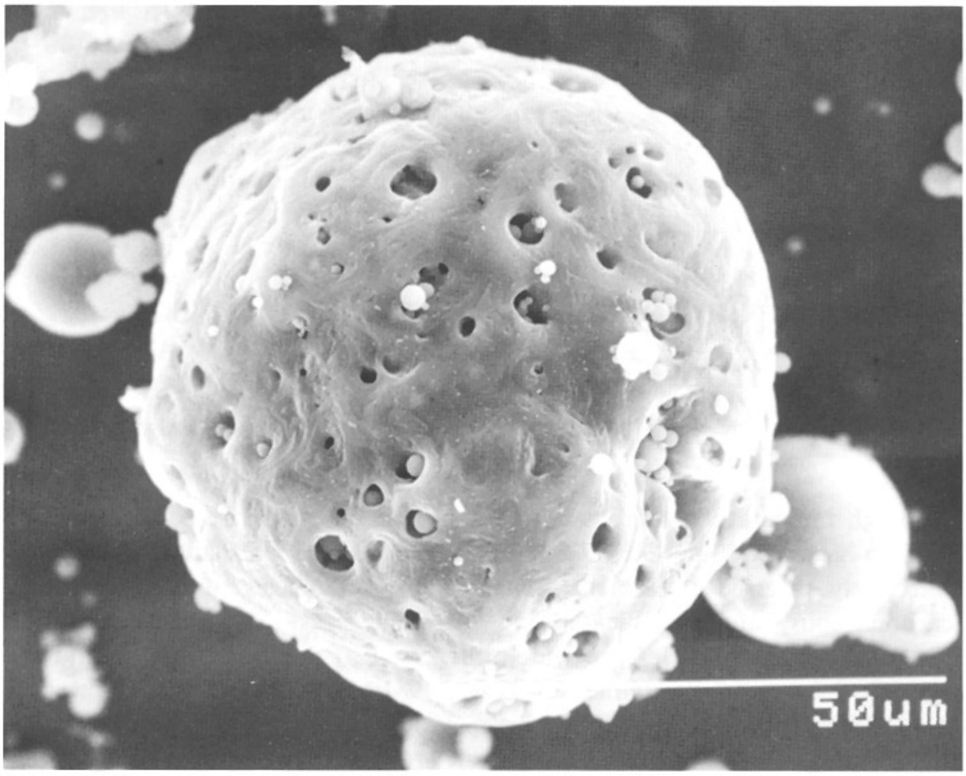

Fig. 1. Scanning electron micrograph of a carbonaceous particle from a coal-fired power station. A number of inorganic ash particles are also shown.

Unfortunately neither the morphological distinctions nor these simple vanadium/titanium criteria are reliable since these characters are not exclusive to the respective types (Fig. 2c). Consequently we have developed additional criteria for differentiating between oil and coal types based on the examination of large numbers of reference particles obtained from oil and coal-fired power stations. We have used automated SEM/EDS analysis of these reference particles to construct a calibration dataset that can be used to distinguish oil from coal particles in fossil samples and mixed samples of unknown provenance.

We obtained fly-ash samples from 5 oil-fired and 5 coal-fired power stations in the UK and one sample from a peat-fired power station in the Republic of Ireland. Each sample was dispersed in a column of alcohol and drawn onto a 0.4 μm nuclepore filter. The filters were mounted onto glass slides using a colloidal graphite paint and coated with a thin layer of carbon. Samples were analysed automatically using a JEOL 733 Superprobe in conjunction with an image analysis program (DIGISCAN) to control data acquisition. In this way large numbers of particles can be processed rapidly

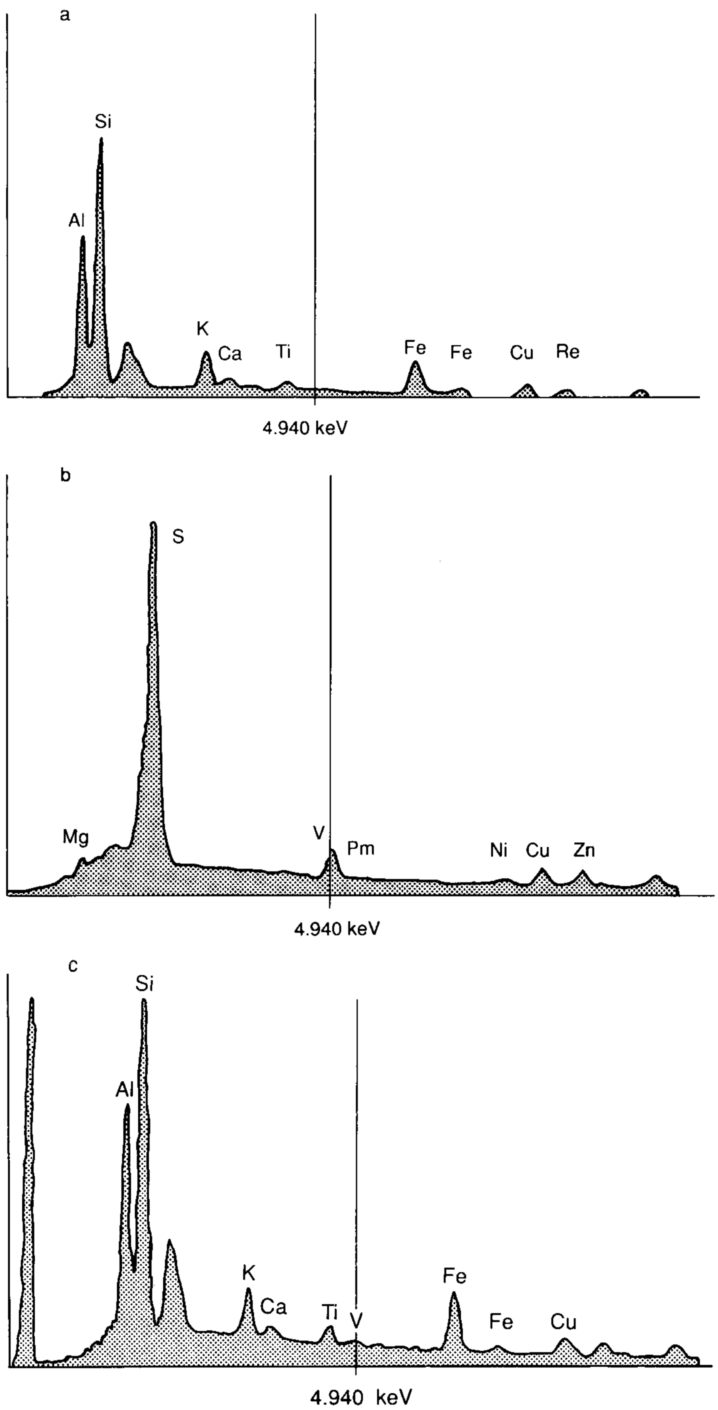

Fig. 2. EDS spectra of carbonaceous particles from (a) coal, (b) oil, and (c) coal. (c) shows the presence of both V and Ti.

and objectively to create a large dataset suitable for the use of multivariate statistical techniques.

Data on location, size and shape for each particle together with EDS results for up to 25 user-defined regions of interest were obtained. A number of these regions were used for background correction and for correction due to major overlaps between elemental peaks. Results were expressed as a percentage of the total X-rays detected in the elemental windows (after correction) and a window file containing definitions of regions of interest and correction factors was created. The key elements included were Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu and Zn.

A particle classification scheme was then developed using the total dataset to create subdivisions. This was achieved by plotting pairs of variables against each other to identify populations or groupings belonging to a single fuel type. For example when sulphur was plotted against vanadium three discrete groups were observed : a high (> 18 %) vanadium group composed entirely of oil particles ; a high (> 60 %) sulphur group of oil particles ; and a group low in both these elements which included all the coal particles and some oil particles. In this way the high vanadium and sulphur groups were ascribed to oil and removed from analysis. Other elements (e.g. iron and calcium) were then used to split the remainder until all the particles were placed into the correct fuel grouping. This procedure was carried out for oil against peat, coal against peat as well as coal against oil, and a single classification scheme with 12 different categories, each with a characteristic chemistry, was set up (Fig. 3). With this scheme over 85 % of the reference particles were placed in their correct fuel group.

Despite the apparent success of this procedure there are several disadvantages : the splits are subjective since they are based on visually distinct clusters ; one group of particles with very low X-ray counts could not be differentiated into coal or oil ; and the sub-groups identified may be artificial, related more to the order in which the elements were used in the classification rather than to the existence of naturally discrete groups.

In order to improve this performance multivariate discriminant analysis was used. This is a statistical technique that can be used to find a multivariate axis along which the differences between two groups can be maximised. Analysis of the combined oil and coal reference material using this technique showed a clear bimodal separation between coal and oil particles (Fig. 4). To assess the performance of this separation in assigning particles to their correct fuel type 200 particles were randomly selected from coal and oil sources and the discriminant analysis was re-applied. The results on this test set showed that over 93 % of these particles were correctly classified.

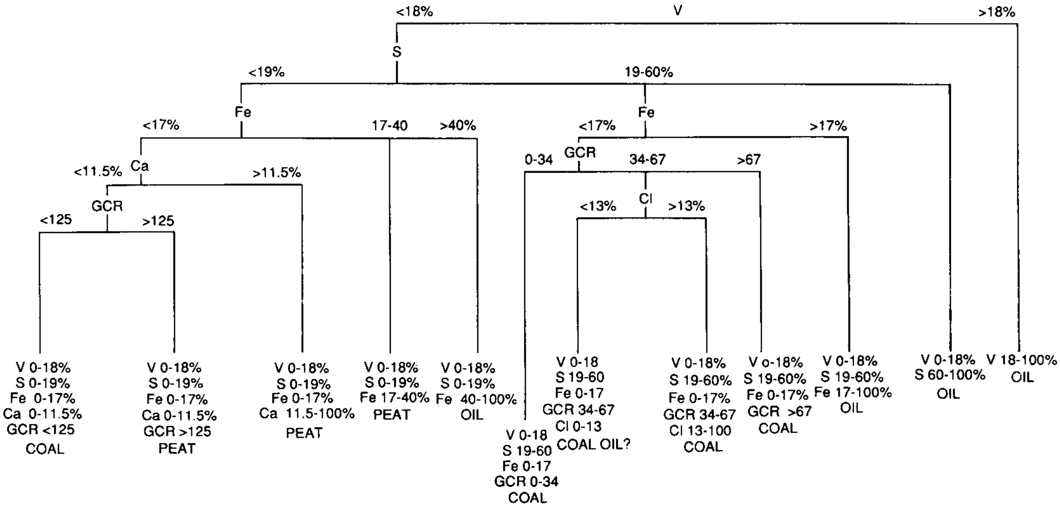

Fig. 3. A classification scheme for carbonaceous particles using EDS-derived chemistry.

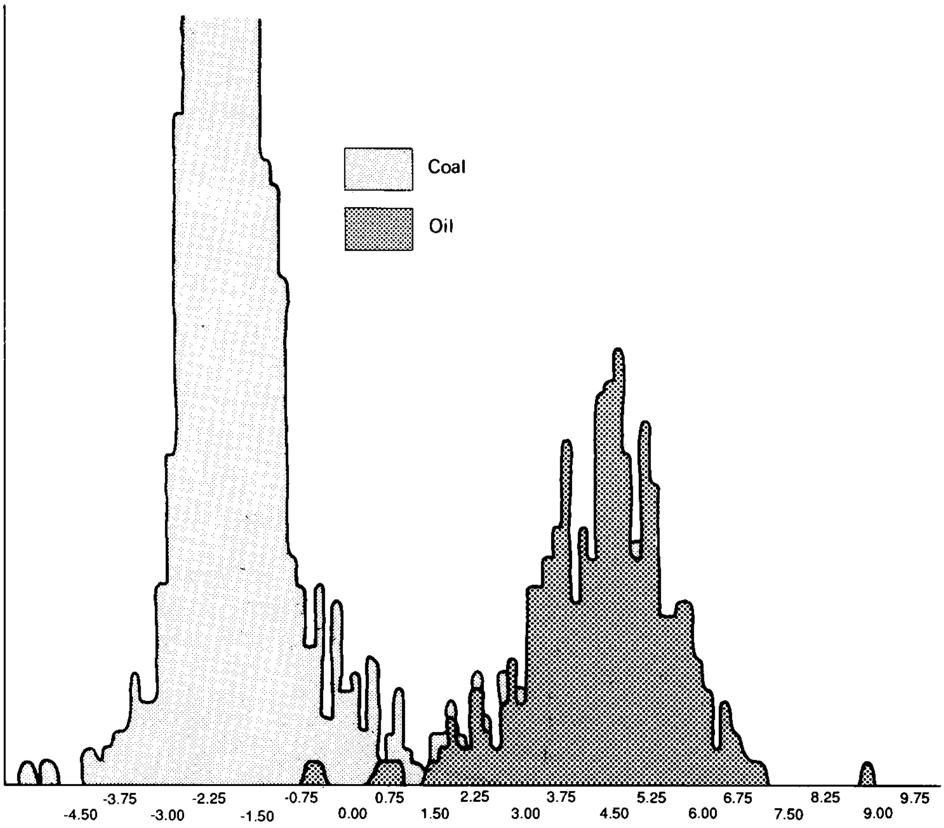

Fig. 4. Graphical representation of the coal/oil characterisation using multivariate discriminant analysis.

The method was then used to characterise the carbonaceous particles extracted from a lake sediment sample from Loch Tinker in Scotland, an acidified lake approximately 45 km downwind from the city of Glasgow. The sediment sample was taken from the 1.5 cm to 2.0 cm depth of a core representing 1971-74 AD. Using the reference dataset of previously classified coal and oil particles approximately 550 particles extracted from the sediment were classified. The results indicated that 80 % of the particles were from coal combustion and 20 % from oil. This conclusion was supported by the results of inorganic fly-ash analysis on the same sediment sample which showed that the ratio of inorganic ash spheres to carbonaceous particles in the sample was 8 : 1. Because oil-combustion produces very few inorganic ash particles but coal combustion produces both kinds of particle in approximately this ratio a predominantly coal origin for the particles at this site was confirmed.

The particles themselves rarely occur in sufficient concentration to cause environmental damage but they are excellent tracers for other pollutants associated with fossil-fuel combustion, especially sulphur (Wik and Renberg, 1987 ; Rose, in press). Characterisation of carbonaceous particles into coal and oil types greatly enhances their value as pollution indicators in both time and space since they can potentially be used to identify acid deposition sources on both regional and national scales. For example, the presence of coal-derived carbonaceous particles in soils and lake sediments of southern Norway would indicate a pollution source external to the country since coal is not burnt in Norway. Equally current work attempting to characterise particles produced by the combustion of brown coal will help to trace air pollution from Central and Eastern Europe, and analysis of particles from dated lake sediment cores can be used to reconstruct trends in the relative proportions of contamination associated with different fuel-types (and countries) as levels of SO_2 emissions are reduced in Europe over the next two decades.

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