USE OF NEUTRON ACTIVATION ANALYSIS TO MEASURE THE VARIATION IN TRACE ELEMENT CONCENTRATIONS IN A COAL SEAM

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ABSTRACT

Trace element concentrations were measured by neutron activation on 57 run-of-mine coal samples from several locations in seven mines located in the Lithgow seam in the Western Coalfield, Sydney Basin. Twenty-nine of these samples were from a single mine.

Results were tabulated as ratios of the highest to the lowest variance for each element. These variance ratios were compared between mines and for other elements determined by alternative techniques. In general, the variations were not great and a good approximation of the concentrations of most trace elements in the Lithgow seam was obtained by analysing a small number of samples. These results have significance for seam correlation in coal mining and to export sales of coal for power generation.

INTRODUCTION

Increasing attention has been given to the environmental aspects of coal mining and usage in Australia and throughout the world. This has verified the importance of trace elements in coals, especially in their behaviour during combustion, liquefaction and, to some degree, coke-making.

Much is known about the occurrence and levels of elements in Australian coals due to research at CSIRO Division of Fossil Fuels[1,2], BHP Central Research Laboratory[3], State Electricity Commission of Victoria[4] and more recently, at CSIRO Division of Energy Chemistry[5,6]. The behaviour of these elements during coal burning and usage depends to some extent on their occurrence in coal. They can exist in association with organic matter (bound to phenolic, immine or mercapto groups) or as discrete minerals classified into three general groups, silicates, sulphides and carbonates. However, little is known of the trace element variation within a coal seam or whether a seam can be characterised by its trace element pattern. This is particularly important in the export of coal to those countries where environmental matters are of prime concern, such as Sweden and Japan, and where they demand information on the levels of trace elements.

This paper reports the results of a study in which instrumental neutron activation analysis (INAA) was used to measure the variation in the concentration of trace elements in a coal seam. Fifty-seven samples of run-of-mine coal were collected over four years from several locations within seven mines situated on the Lithgow seam. This seam occurs in the Illawarra Coal Measures (Late Permian) of the Western Coalfield on the edge of the Sydney Basin. Twenty-nine of these samples were from a single mine (Location A). Since stable basement conditions have prevailed from Permian times in this area, the degree of folding and faulting is minimal.

EXPERIMENTAL

The trace element profile of these coals were measured by INAA. The elements determined were arsenic, antimony, barium, bromine, cesium, cobalt, europium, hafnium, iron, lanthanum, lutetium, neodymium, samarium, scandium, sodium, terbium, thorium, tungsten, uranium and ytterbium. The full range of elements sensitive to this nuclear technique of analysis was not measured since many of those elements determined by rapid neutron irradiation and counting by high resolution gamma spectrometry were measured by alternative techniques (atomic absorption spectrometry (AAS) and optical emission spectrometry (OES)) in another research program. For this study, samples (100-200 mg in polythene vials) were irradiated for 9 h in the X-6 tube of HIFAR, the AAEC's 15 MW research reactor, at a thermal flux of 5×10^{13} n cm^{-2} s^{-1} and counted on a 100 cm^3, 20% coaxial Ge(Li) detector (Ortec series 8000, FWHM 1.8 keV at 1.332 MeV) coupled to a Canberra Series 40 4096-channel pulse-height analyser, after cooling for 7 and 28 days. The certified NBS standard reference materials SRM1632 (coal) and/or SRM1633 (fly ash) were simultaneously irradiated and counted. Concentration data were calculated by comparative analysis, using a series of FORTRAN programs written by one of the authors (JJF) and processed on an IBM370 computer.

RESULTS AND DISCUSSIONS

The INAA data from the elements listed previously were combined with earlier results obtained by AAS and OES, as well as analytical data for ash, pyritic and total sulphur and carbonate content.

To assess the variation of trace elements within the Lithgow seam, ratios of the highest to lowest variance (mean square deviation of values from their grand average) for each element at Location A were compared to the same ratios determined for all samples from the six remaining mines. Some of these ratios are listed in Tables 1-3.

Data from INAA measurements, listed in Table 1, show very close agreement between most concentration levels from Location A and those from Locations B-G. This was further evidence in Table 2 where other elements determined by OES and AAS showed the same close relationship. These results suggest that during coal formation from plant material, stable climatic conditions dominated the area covered by the Lithgow seam.

Several exceptions are evident from the tabulated results where arsenic and neodymium exhibit a high spread in their concentration data. Although the accuracy of the data for these two elements may be questioned, analytical figures for pyritic sulphur and carbonate levels showed significanlty higher concentrations in Locations B and C. Association of these trace elements with sulphides and carbonates could be the reason for this bias.

Table 3 lists some more spectacular variations from the general trend: variance ratios for iron, manganese and carbonate from other locations much larger than for Location A. Again, this is attributed to the high carbonate levels at Locations B and C, with the accompanying iron levels suggesting the dominant presence of siderite ($FeCO_3$). The association of manganese with carbonate minerals, where it is known to replace iron in siderite, could explain its high values in Table 3.

The extensive chemical data for the Lithgow seam (21 elements on 57 samples) were evaluated statistically. Correlation coefficients were determined between all element and sample pairs, and the matrix of these correlation coefficients was then used in hierarchical cluster analysis programs[7] to identify the association between trace element, and samples. Generally, the trace element classification followed the expected distribution trends between organic, silicates, sulphides and carbonates. No strong clustering occurred between samples from the seven locations.

In general, the variation in most elemental concentrations for run-of-mine coal samples from the Lithgow seam was not great and, hence, a good approximation can be obtained by analysing a small number of samples. This is encouraging news for exporters compelled to supply trace element data with their coal shipments.

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TABLE 1

Variance Ratios from INAA Data

Element	Location A	Other Locations
As	2.3	6.7
Sb	1.4	2.2
Th	1.4	2.2
U	1.4	1.9
Eu	1.5	2.3
Lu	1.3	1.6
Sm	1.5	1.8
La	1.3	1.9
Nd	3.0	5.1
Ba	1.5	3.4
Co	1.6	3.4
Cr	1.3	3.0

TABLE 2

Variance Ratios from OES and AAS Data

Element	Location A	Other Locations
Cd	1.7	2.0
Hg	1.9	3.4
Mo	2.5	3.0
Pb	1.4	2.0
Se	1.4	1.5

TABLE 3

Variance Ratios from Combined Techniques

Component	Location A	Other Locations
Na	2.1	2.9
Fe	3.1	8.3
Mn	4	57
CO_3	2.8	36
Ash	1.2	1.5