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Use of laser ablation ICP-MS to determine trace element distributions in coals, with special reference to V, Ge and Al

D.A. Spears [a,*], A.G. Borrego [b], A. Cox [a], R.M. Martinez-Tarazona [b]

[a] *Centre for Analytical Science, Department of Chemistry, University of Sheffield, Sheffield, UK*
[b] *Instituto Nacional del Carbon, (CSIC), C/Francisco Pintado Fe No 26, 33011, Oviedo, Spain*

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Abstract

Laser ablation ICP-MS has been used to produce element profiles from polished coal samples. The elements analysed (V, Ge, Ni, Cu, Zn, Sr and Ba) were those known to have an organic association, with the addition of Al and Fe as controls on the clay and pyrite abundances. The element profiles were compared with the petrography and a statistical analysis was also carried out. Sporinite was found to have low trace element concentrations, inertinite higher concentrations of detrital elements and vitrinite higher concentrations of V, Ge and Al. The relationships between these elements are explored and all are thought to be present in the organic matter and not as minerals. It is thought that these elements became concentrated during diagenesis, with the possibility that some of the Al could be residual. The Cu/Ni ratio in the pyrite is relatively constant, suggesting constant ionic proportions during diagenesis, and possibly a seawater source.

Keywords: ICP-MS; Coal maceral; Trace elements; Element affinity; Coal petrography

1. Introduction

The utilisation of coals releases trace elements into the environment and concentrations are increased above the natural background levels, raising the possibility of an impact on ecosystems. It is not only absolute concentrations in coals that are important but also the distribution of trace elements within the coal. The mode of occurrence, and association with other elements, are important factors in influencing the fate of elements during combustion. In addition, if the association of trace elements with specific minerals and macerals is known, there is the possibility of reducing concentrations by selected mining and coal-cleaning. Information on the distribution of trace elements within the coal also enables predictions to be made for other coals. In addition to the applied aspects, more precise information on the location of elements within the coal leads to a better understanding of geochemical processes during deposition and diagenesis.

One aim of the present study was to explore the potential of LA ICP-MS as an analytical tool for the in situ trace element analysis of minerals and macerals in coals. Laser ablation inductively coupled plasma-mass spectrometry (LA ICP-MS) offers the possibility of directly analysing individual, micron-sized coal components down to the ppm level using polished sections or blocks and, therefore, free from the need to separate components. The technique of LA ICP-MS is rapidly evolving and is now widely used in the fields of environmental and biological analysis. Lyons et al.

* Corresponding author.
E-mail address: d.a.spears@sheffield.ac.uk (D.A. Spears).

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(1990) used this approach in an examination of macerals in the UK Swallow Wood Coal, which comes from the same coalfield as one of the coals in the present study. Barium, Ca, Dy, Li, Mg, Sr and Y were present in higher concentrations in fusinite than in either vitrinite or cutinite. Vitrinite had more Ti, V, Cr and Ca than cutinite and both had more Cr, Sc, Ti and V than fusinite. The elements were believed to have a mineral-matter (inorganic) origin with the possible exception of Al, K, Fe, Ga and Sr in the vitrinite and cutinite. Only some of these elements have been analysed in the present work, because not all are believed to have a significant organic association. Querol and Chenery (1995) used LA ICP-MS to obtain trace element analyses of individual grains in polished blocks of coal. In addition to sulphide minerals, the macerals vitrinite, liptinite and fusinite were also analysed. Booth et al. (1999) used LA ICP-MS in a scanning mode to obtain average analyses for elements in coal samples to augment conventional analytical methods. The elements analysed, including Hg, Cd and Sb, were those for which detection limits were not sufficiently low using conventional XRF. The limits of detection achieved with the LA ICP-MS were in the µg/kg range (ppb). The scanning mode of the LA ICP-MS was also adopted for the analysis of fly ash particles (Spears, 2004). The data were statistically analysed to overcome a problem associated with the small mean grain size of the particles (8 µm). Although the laser has a minimum beam diameter of 10 µm, a larger beam diameter was adopted to ensure that the sensitivity of key elements was not adversely affected.

Direct analysis of in situ minerals and macerals is also possible using electron beam methods, but many of the trace elements of interest fall below detection limits. In an electron microprobe investigation of the trace element composition of pyrite and marcasite in some UK coals (White et al., 1989) the minimum detection limit of 100 ppm was too high and analyses were completed using the synchrotron XRF at Brookhaven, New York. In another study of pyrite and marcasite in coal using the electron microprobe, Ruppert et al. (2005) recorded a detection limit of 0.05 wt.% for As, which was acceptable because As concentrations were relatively high. The detection limits for the synchrotron are in sub-ppm range, but instruments such as this, and ion microprobes, are not readily available, whereas laser ablation ICP-MS is increasingly becoming more common.

Indirect methods are usually used to determine the distribution of trace elements in coals and either make use of the natural variation in a suite of coals or involve fractionating the coals using chemical or physical methods. A number of methods are described in Davidson (2000) for the analysis of single coals. Using the latter approach the composition of the organic matter in one of the present coals was determined (Spears and Booth, 2002; Spears, 2002). The calculated trace element distributions are shown in Table 1, together with the analysis of the whole coal. Statistically analysing the trace element data from a suite of coals is a long-established method to obtain element associations. This was done for a representative of UK coals by Spears and Zheng (1999) and most recently for other coals and lignites by Chatziapostolou et al. (2006), Kalkreuth et al. (2006) and Song et al. (2007). There is considerable current interest in trace elements in coals as these, and other recent papers demonstrate (for example Brownfield et al., 2005; Wagner and Hlatshwayo, 2005; Dai et al., 2006; Parzentny and Lewinska-Preis, 2006; Yang, 2006; Hower et al., 2007). These are important papers that focus more on a comprehensive range of trace elements and comparisons with other coals, including global averages, than is the case in the present work. The aims of this work, are on the one hand, to demonstrate the usefulness of LA ICP-MS as an

Table 1
To show the calculated percentage distribution of trace elements between organic matter, the clay fraction and pyrite in the Eggborough coal

	Organic (%)	Clay (%)	Pyrite (%)	Bulk pf (ppm)
V	68	32	0	90
Cr	37	63	0	47
Ni	51	28	21	36
Cu	49	16	36	47
Zn	31	37	31	33
Ga	35	65	0	8
Ge	93	7	0	5
As	9	2	89	27
Se	46	6	48	1.3
Br	100	0	0	41
Rb	0	100	0	28
Sr	40	60	0	45
Y	33	67	0	10
Zr	18	82	0	38
Nb	23	77	0	2.9
Mo	27	5	68	3.2
Sn		100		1
Sb	36	29	35	1.3
Ba	13	87	0	121
La	1	99	0	10
Ce	16	84	0	20
Sm	0	100	0	9.2
Pb	32	19	48	19
Th	0	100	0	3.5

The calculation method was outlined in Spears et al. (1999a) and extended in Spears (2002). The calculated values are from the latter publication as is the bulk composition in the final column.