

NEW ANALYTICAL METHODS FOR DETERMINING TRACE ELEMENTS IN COAL

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ABSTRACT

New and improved analytical methods, based on modern spectroscopic techniques, have been developed to provide more reliable data on the levels of environmentally significant elements in Australian bituminous thermal coals. Arsenic, selenium and antimony are determined using hydride generation atomic absorption or fluorescence spectrometry, applied to an Eschka fusion of the raw coal. Boron is determined on the same digest using inductively coupled plasma atomic emission spectrometry (ICPAES). ICPAES is also used to determine beryllium, chromium, cobalt, copper, manganese, molybdenum, nickel, lead and zinc, after fusion of a low temperature ash with lithium borate. Other elements of concern including cadmium, uranium and thorium are analysed by inductively coupled plasma mass spectrometry on a mixed acid digest of a low temperature ash. This technique was also suitable for determining elements analysed by the ICPAES. Improved methods for chlorine and fluorine have also been developed. Details of the methods will be given and results of validation trials discussed on some of the methods which are anticipated to be designated Australian standard methods.

INTRODUCTION

Increasing attention is being focussed on the potential environmental impact of trace elements, particularly those of environmental concern, associated with electricity production from coal-fired power plants. As a consequence the impact of trace elements on the surrounding ecology from atmospheric emissions and mobilisation in ash dams is coming under increased scrutiny.

Trace elements of concern to the environment and health have been identified by the United States National Research Council¹. More recently the levels of trace elements in coal have received greater attention with the introduction of legislation, in some countries, which imposes atmospheric discharge limits on a range of environmentally sensitive trace elements. Details of these limits in Australia, Austria, Germany, Italy and the United States of America are given by Clarke and Sloss². Of most significance relating to the impact of trace elements on the environment was the recent amendments to the US Clean Air Act, 1991, which greatly expanded the role of the US Environmental Protection Agency to regulate trace element emissions. Included in the list of 190 hazardous air pollutants were arsenic, antimony, beryllium, cadmium, cobalt, chromium, chlorine, fluorine, mercury, manganese, nickel, lead and selenium together with radionuclides including radon. Although the power industry is not included in the list of source categories, the amendments require the measurement of mercury emissions from coal-fired power plants. The Electric Power Research Institute (EPRI) in the US has carried out a field monitoring project to measure a range of trace elements in the process and discharge streams of power plants to determine the efficiency of control devices to reduce emissions of air toxics³.

The imposition of stricter controls by regulatory bodies on emissions has focussed attention on the levels of environmentally sensitive elements, particularly those designated as air toxics, in thermal coals. As a consequence of this there is an increasing need to accurately specify the levels of these trace elements to satisfy contractual requirements. Australia is the world's largest exporter of coal and the implications of regulations on trace element emissions are for the development of better quality assurance procedures in the specification of the levels of key environmental trace elements in export thermal coals.

Quality assurance requires the application of validated standard methods which guarantee the accuracy and reliability of the analytical data. The problem is that, in most cases, current standard methods do not have the necessary accuracy to specify the levels of environmentally sensitive trace elements at the concentrations normally present in Australian product thermal coals. One reason for this inadequacy of current standard methods is that they are based on long established analytical techniques such as atomic absorption spectrometry (AAS) which lack the sensitivity to provide the necessary quality assurance. AAS is also a single element technique which, in terms of the number of elements identified as environmentally significant, makes it less cost effective than newer multi-element, simultaneous techniques such as inductively coupled plasma atomic emission spectrometry (ICPAES). Over the past decade this technique has become more readily available in commercial laboratories and its suitability for determining many of the designated trace elements has been established.

In view of the pressing requirements for better quality assurance, new analytical methods based on ICPAES has been developed. The current standard methods based on hydride generation-AAS for arsenic and selenium has been revisited and an improved method, based on atomic fluorescence spectrometry, has provided increased sensitivity for these trace elements. These methods are undergoing validation trials with the anticipation that they will be adopted as new Australian standard methods.

Other techniques have also been used to develop reliable methods. These include inductively coupled plasma mass spectrometry (ICPMS) for a range of trace elements including cadmium, nickel, lead, molybdenum, thorium and uranium. Proton induced gamma ray emission (PIGE) has been applied to the determination of fluorine and X-ray fluorescence spectrometry (XRF) for chlorine.

CURRENT STATUS OF STANDARD METHODS

The performance of current standard methods is shown in table 1 where the lower limits of determination of the methods are compared with the means and range values for the key environmental trace elements in Australian export thermal coals as given by Dale and Fardy⁴. In most cases the current methods are inadequate for determinations at the low range values. For cadmium, cobalt, molybdenum, uranium and thorium no standard methods exist.

Table 1. Mean and Range Values for Trace Elements of Environmental Concern in Australian Export Thermal Coals Compared with Lower Limit of Determination (LLD) of Available Standard Methods

Element	Mean*	mg/kg				
		Range		LLD*		
		Low	High	AS	ASTM	ISO
As	2	<1	7	0.5	1	1
B	17	<5	40	20	-	-
Cd	0.09	<0.05	0.22	-	-	-
Hg	0.06	0.01	0.14	0.01	0.01	-
Mo	1.6	0.25	5.5	-	-	-
Pb	7.5	2.5	13	40	10	-
Se	1	<1	2	-	1	-
Mn	30	3	110	30	-	-
Cr	12	5	27	20	5	-
Cu	12	4	23	50	5	-
Ni	14	<9	39	20	10	-
V	26	10	63	100	10	-
Zn	19	3	53	80	50	-
F	120	40	200	50	10	-
Co	5.3	1.6	14	-	-	-
Cl	200	20	630	100	200	-
Sb	0.54	<0.05	1.5	-	-	-
Be	1.4	0.25	5.5	2	0.5	-
U	1.1	0.3	2.1	-	-	-
Th	3.5	1.1	7.7	-	-	-

* AS - Australian Standard

ASTM - American Society for Testing Materials

ISO - International Organisation for Standardisation

METHOD FOR ARSENIC, SELENIUM AND ANTIMONY

This method is based on the current US standard (ASTM D4606-87) which involves the fusion of the raw coal using Eschka's mixture. The elements arsenic and selenium are determined by hydride generation-AAS using matrix matched standards. The new method uses similar conditions for generation of the hydride. However advantage is taken of the higher sensitivity obtained with atomic fluorescence spectrometry. The method has also been found satisfactory for determining antimony and has been validated by analysis of certified reference materials as shown in Table 2.

Table 2. Results for Arsenic, Selenium and Antimony Obtained on Certified Reference Materials using Hydride Generation Atomic Fluorescence Spectrometry

CRM	Arsenic		Selenium		Antimony	
	mg/kg					
	Certified	Found	Found	Certified	Found	Certified
NIST 1632b	3.70 ± 0.28	3.72 ± 0.12	1.30 ± 0.12	1.29 ± 0.11	0.28 ± 0.02	(0.24)
SARM 19	7.65 ± 0.10	7 ± 1	1.12 ± 0.06	1	-	-
SARM 20	-	-	0.75 ± 0.04	0.8 ± 0.2	-	-

This method is currently undergoing validation tests in an interlaboratory trial and is anticipated to be adopted as an Australian standard method.

METHOD FOR BORON

The method developed is based on the Eschka fusion procedure used for arsenic, selenium and antimony. The element is determined using ICPAES using matrix matched standards. The method was validated using South African reference coals as demonstrated by the following results.

Table 3. Results for Boron Obtained on an SARM Reference Coal

CRM	mg/kg	
	Found	Indicated*
18	28	30
19	94	90
20	84	90

* Values are not certified.

This method is also undergoing validation tests and is anticipated to be adopted as an Australian standard.

ICPAES METHOD FOR TRACE ELEMENTS

This method is based on fusion of a 450°C ash of the coal with a mixture of 1 part lithium metaborate to 3 parts lithium tetraborate. The elements chromium, copper, zinc, vanadium, manganese, nickel, cobalt, molybdenum, lead and beryllium are determined using ICPAES with matrix matched standards.

The method has been validated using NIST 1632b and is currently undergoing validation tests in an interlaboratory trial. It is anticipated to be adopted as an Australian standard method.

TRACE ELEMENTS BY ICPMS

This technique has gained popularity over the past decade because of its very high sensitivity and multi-element capability. It has been applied, in this laboratory, to the determination of a wide range of trace elements in coal. The method developed is based on dissolution of a 450°C ash of the coal using a mixture of nitric-hydrochloric-hydrofluoric acids. The elements are determined using appropriate internal standard elements (indium, thallium and enriched stable isotopes of chromium-53 and zinc-68).

This technique has been found suitable for determining a wide range of environmental trace elements including uranium, thorium, cadmium, antimony, lead, nickel, arsenic, beryllium, chromium, cobalt, copper, zinc, vanadium and molybdenum. Of particular significance is the ability to analyse for cadmium, uranium, and thorium (detection limits 0.01, 0.005 and 0.005 mg/kg respectively). There are no standard methods available for these elements because of their low abundances in coal and the lack of sensitivity of more conventional techniques. Cadmium however could possibly be analysed by graphite furnace-AAS.

Although ICPMS instruments are expensive the technique is finding increased popularity in commercial laboratories. It is expected that its application to the determination of trace elements

in coal will receive greater attention because of its high sensitivity and multi-element capability which makes it cost effective.

METHOD FOR CHLORINE

Current methods for chlorine are based on oxygen bomb digestion or fusion followed by determination by ion-selective electrode (AS 1038.8.1, ASTM D4208). There are however, recognised problems with these methods. These relate to the recovery of the chlorine during the sample destruction and the lack of sensitivity of the ion-selective measurement. Evidence of the problems has been highlighted in international interlaboratory comparisons such as the CANSPECS program organised by Energy Resources Canada. The extreme variability of results by laboratories using the same standard method suggests that these methods lack the reliability required by standard methods. This variability is of great concern to Australian coal producers because of disputes that occur between suppliers and buyers.

In recognition of the problems with current methods, a procedure is being developed based on X-ray fluorescence spectrometry (XRF). This procedure has the advantage that it analyses the raw coal and is therefore non-destructive thereby overcoming one of the main deficiencies of current methods.

The suitability of the XRF procedure has been verified by comparison with results obtained by instrumental neutron activation analysis (see Table 4). The lower limit of determination of the XRF method is 30 mg/kg which is below the low range value for Australian coals. Analysis of the NIST 1632b CRM gave a value of 1190 mg/kg which compares favourably with the indicated value of 1230 mg/kg. The new method requires minimal sample preparation (grinding to less than 75 μm and the addition of an internal standard) and is cost effective on the basis of its high sample throughput compared to current standard methods.

Table 4 - Comparison of Chlorine Results Obtained on Coals by XRF and INAA

Sample	Cl (mg/kg)	
	XRF	INAA
1	250	235
2	450	410
3	505	495
4	670	610
5	970	1075

METHOD FOR FLUORINE

The standard method for determining this element is based on destruction of the raw coal by pyrohydrolysis followed by determination with an ion-selective electrode (AS 1038.10.4). This method has limitations in that the problems are associated with the liberation of the fluorine from the sample and the rather poor sensitivity of the ion-selective electrode at the levels normally encountered in coals.

The method used in our laboratory is based on proton induced gamma ray emission using the 2MV van der Graaf accelerator available through the Australian Nuclear Science and Technology Organisation. Previous work³ has verified the application of this technique to the analysis of coal for fluorine. It is based on the irradiation of the raw coal with high energy protons in which the fluorine atoms produce characteristic g-rays. It is therefore non-destructive. Analysis of the NIST 1632a CRM gave a mean value of 183 mg/kg with a standard deviation of 10 mg/kg (12 determinations). The accepted value for this CRM is 178 mg/kg. The detection limit is 5 mg/kg.

PERFORMANCE OF NEW METHODS

The new methods provide the necessary sensitivity to meet the requirements for determining a range of key environmental trace elements in Australian coals. This is demonstrated in Table 5 which compares the lower limit of determination of the new methods and the current standard methods. For most elements, the new methods provide the capability for reliably analysing Australian coals at the levels normally present.

Validation trials are currently in progress involving a number of participating commercial laboratories. Preliminary data suggests that the methods for arsenic, selenium and antimony based on the hydride generation-AFS technique will meet the requirements for acceptance as a standard method as required by Standards Australia. Similar agreement between laboratories for

the boron and ICPAES methods suggests that these will become standard methods. Future efforts will be directed towards the establishment of an Australian standard method based on ICPMS which would account for cadmium, uranium and thorium.

The methods used for chlorine and fluorine are presently considered as reference methods. There needs to be a revision of current methods in view of the discrepancies which occur between laboratories.

Table 5 - Lower Limits of Determination (LLD) for Trace Elements with New Analytical Methods Compared with Standard Methods and the Means and Range Values in Australian Export Thermal Coals

Element	mg/kg				
	Mean	Range		LLD	
		Low	High	New Method	Standard Method
As	2	<1	7	0.03	0.4
B	17	<5	40	3	20
Cd	0.09	<0.05	0.22	0.01	-
Mo	1.6	0.25	5.5	0.2	-
Pb	7.5	2.5	13	0.2	10
Se	1	<1	2	0.03	1
Mn	30	3	110	0.02	-
Cr	12	5	27	0.1	5
Cu	12	4	23	0.2	5
Ni	14	<9	39	2	10
V	26	10	63	0.2	10
Zn	19	3	53	0.2	50
Co	5.3	1.6	14	0.2	-
Cl	200	20	650	50	200
Sb	0.54	<0.05	1.5	0.03	-
Be	1.4	0.25	5.5	0.01	-
U	1.1	0.3	2.1	0.03	-
Th	3.5	1.1	7.7	0.03	-
F	120	40	200	20	50

SUMMARY

The new methods provide adequate sensitivity to reliably determine a range of key environmental trace elements in Australian coals. These methods are based on modern instrumentation which is generally available in commercial laboratories. These new methods address the need for better quality assurance in the specification of trace elements in export coals. This has been as a direct result of increasing concern on the environmental impact of trace elements from coal-fired power plants.

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REFERENCES

1. United States National Research Council. PECH Report, National Academic Press, Washington, D.C. 1980.
2. Clarke, L.B and Sloss, L.L., International Energy Agency Report IEACR/49, London, 1992.
3. Boutacoff, D., EPRI Journal, 5-13, Mar. 1991.
4. Dale, L.S., Lavrencic, S.A. and Fardy, J.J., NERDDP Report EG91/1005, 1991.
5. Clayton, E. and Dale, L.S., Anal. Lett., 18, 1533-1538, 1985.