Analysis of Coal and Coal Ash using ICP-OES

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Key Words
Coal, coal ash, flue ash, fly ash

Goal

The goal of the application note is to discuss and demonstrate the elemental analysis of coal and coal ash samples using ICP-OES following microwave acid digestion.

Introduction

Despite the recent improvements in, and increasing use of renewable forms of energy, approximately 40% of the world's electricity is still generated by coal fired power stations. This figure is significantly higher in some countries, for example, approximately 70% in India and over 90% in South Africa.

During coal combustion, large amounts of ash are created along with carbon dioxide and other gases. The fine particle ash that rises up with the flue gases is known as fly or flue ash while the heavier ash that does not rise is called bottom ash; collectively these are known as coal ash. Traditionally the fly ash was released into the atmosphere, however, due to its potentially toxic effects it is now generally collected from the flue towers using electrostatic precipitators or other particle filtration equipment. It can then be disposed of or recycled into Portland cement.

The chemical makeup of fly and bottom ash varies significantly and is dependent on the source and composition of the coal being burned. This can include a wide variety of toxic substances from trace amounts to percent levels. In order to protect the environment or the quality and safety of any products it is added to, the composition of the ash product needs to be accurately analysed before it can be recycled or disposed of.

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Instrumentation and method parameters

For this analysis the Thermo Scientific™ iCAP™ 7400 ICP-OES Duo was used, it has full control over the RF power and nebulizer gas flow rate, while the Duo view plasma allows for axial and radial viewing modes to be used for the greatest detection limits and maximum upper analysis ranges. The measurement parameters and sample introduction setup can be seen in table 1.

Table 1. Method parameters and sample introduction setup used

Parameter	Setting	
RF Power	1350 W	
Nebulizer gas flow	0.5 L/min	
Exposure time	Axial	Radial
Low (UV)	15 secs	15 secs
High (Visible)	5 secs	5 secs
Nebulizer	Mira Mist	
Spray Chamber	Glass Cyclonic	
Centre Tube	Glass 2mm I.D.	

A 10 mg/L yttrium internal standard was introduced using the online internal standard kit. This allows the method to compensate for variations in sample matrices along with any changes to the sample introduction. The internal standard wavelengths used can be seen in table 2. The Thermo Scientific™ Qtegra™ software line switching feature was used for the majority of elements, allowing two or more wavelengths to be calibrated at different concentration ranges for the same element, extending the working range of the instrument.

Table 2. Internal standard wavelengths of yttrium used

	Axial	Radial
Low (UV)	224.306 nm	224.306 nm
High (Visible)	371.030 nm	371.030 nm

A range of single element solutions were prepared and analysed in order to observe any spectral interferences that are present. The contributions of any interference present were measured, and Inter Element Corrections (IECs) were applied. This allows the Qtegra software to automatically compensate for these interferences on a sample by sample basis.

Sample Preparation

Two certified reference materials (CRMs) (1 bituminous coal and 1 fly ash, both from the National Institute of Standards and Technology, USA (NIST)) were prepared in triplicate using the following method. The samples were digested by adding 6 ml of 20% hydrochloric acid (HCl) and 2 ml of 20% nitric acid (HNO_3) to approximately 0.1g of solid sample. This was then heated to 220 °C for 35 minutes using a microwave digestion system. Once the samples had cooled they were made up to 25 ml with ultrapure de-ionized water.

Calibration standards were created from 1000 mg/L and 10000 mg/L single element solutions (Fisher Scientific Chemicals, Loughborough, UK) and were matrix matched to the sample digests, i.e. 4.8% HCl and 1.6% HNO_3.

Results

The analytical results of the two CRM samples compared with the certified and reference values (table 3). An empty sample tube was subjected to the same sample digestion method as the samples, this blank was then analysed with 10 replicates. The method detection limits were calculated by multiplying the standard deviation of these 10 replicates by a factor of 3, this was performed in triplicate and an average taken (table 3). Table 3 shows that the analytical results are within ±5% of the certified vales and within ±15% of the reference values, demonstrating the accuracy of this method for the analysis of coal and coal ash samples.

It should be noted that silicon typically constitutes a significant proportion of the composition of these sample types, particularly fly ash. Therefore if the analysis of silicon is required, then a small quantity (0.5ml) of hydrofluoric acid (HF) will need to be added into the digestion procedure, otherwise under recovery of silicon will occur.

Table 3. Analytical results for NIST certified reference materials. *= non certified reference value, (A) = Axial view, (R) = Radial view. Wavelengths for each element are listed in sensitivity order.

Element	Wavelengths (nm)	Method Detection Limit (µg/L)	Units	NIST 1632d (Coal)	Certified / Reference Values	Recovery %	NIST 2690 (Fly Ash)	Certified / Reference Values	Recovery %
Al	167.079 (A) 396.152 (R) 237.312 (R)	0.01	%	*0.791*	*0.912**	*86.7*	12.81	12.35	103.7
As	189.042 (A)	9.4	mg/kg	*6.026*	*6.1**	*98.8*	*27.18*	*26**	*104.5*
B	249.773 (A) 249.678 (R)	6.9	mg/kg	*58.93*	*62**	*95.0*	282.5	NA	-
Ca	422.673 (A) 184.006 (R)	0.001	%	*0.133*	*0.144**	*92.3*	5.526	5.71	96.8
Cd	228.082 (A) 214.438 (R)	0.42	mg/kg	*<0.1*	*0.08**	-	*0.655*	*0.7**	*93.6*
Cr	283.563 (A) 267.716 (R)	4.7	mg/kg	*12.70*	*13.7**	*92.7*	*69.49*	*67**	*103.7*
Cu	324.754 (A) 224.70 (R)	3.4	mg/kg	5.736	5.83	98.4	64.84	NA	-
Fe	259.940 (A) 239.562 (R)	0.003	%	0.779	0.749	104.1	3.442	3.57	96.4
Hg	184.950 (A) 194.227 (A)	0.42	mg/kg	<0.1	0.0928	-	*<0.1*	*<0.003**	-
K	766.490 (A+R)	0.01	%	0.106	0.1094	96.8	1.063	1.04	102.2
Mg	279.553 (A) 285.213 (R)	0.00002	%	*0.034*	*0.039**	89.6	1.561	1.53	102.0
Mn	257.610 (A) 279.482 (R)	2.6	mg/kg	*13.97*	*13.1**	*106.7*	*313.00*	*300**	*104.3*
Na	588.995 (A) 589.592 (A)	6.4	mg/kg	286.5	296.9	96.5	2312.3	2400	96.3
Ni	231.604 (A) 341.476 (R)	0.23	mg/kg	11.99	NA	-	*47.78*	*46**	*103.9*
Pb	220.353 (A) 216.999 (R)	0.96	mg/kg	3.750	3.845	97.5	*35.75*	*39**	*91.7*
Se	196.090 (A)	2.0	mg/kg	*1.418*	*1.29**	*110.0*	*0.732*	*0.8**	*91.5*
Ti	334.941 (A) 338.376 (R)	3.8	mg/kg	487.7	477	102.3	4946	5200	95.1
V	282.402 (A)	0.56	mg/kg	22.77	23.74	95.9	148.3	NA	-
Zn	202.548 (A)	0.11	mg/kg	*14.21*	*12.9**	*110.2*	*117.9*	*120**	*98.2*

Conclusion

The analytical results in table 3 demonstrate that the iCAP 7400 ICP-OES Duo is capable of performing the analysis of coal and fly ash samples. The duo view combined with the features of the Qtegra software such as line switching allow for low detection limits to be achieved whilst maintaining a large working range in a single analytical method. Features and tools such as internal standardization and IECs combined with the adaptable, high efficiency RF generator allow for heavy matrix samples to be accurately analysed without the need for extensive dilutions.

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