



Analysis of Coal Fly Ash using the Radial Prodigy ICP and a Lithium Metaborate Fusion Sample Prep

Introduction

Fly ash is a by-product of coal-fired power plants and can be a major source of air pollution. Approximately 600 million tons of fly ash is produced annually worldwide. Most of it will be placed in landfills where potential ground water contamination is a concern, resulting in the need for metals analysis. Other uses of fly ash include cement, flowable fill, raw feed as clinker, soil modification/stabilization, and agriculture. Fly Ash is considered a non-hazardous solid waste.

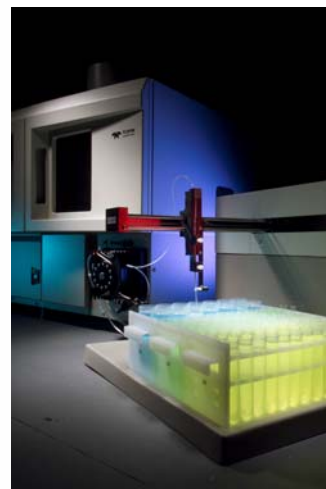
Elements of Interest

In this work, the following elements were measured in coal fly ash: Al, Ba, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Si, Sr, Ti, V and Zn.

Instrumentation

A **Prodigy** High Dispersion Inductively Coupled Plasma (ICP) Spectrometer equipped with a radial view torch and an 88-position autosampler was used to generate the data for this application note.

The **Prodigy** is a compact bench-top simultaneous ICP-OES system featuring an 800 mm focal length Echelle optical system coupled with a mega-pixel Large Format Programmable Array Detector (L-PAD). At 28 x 28 mm, the active area of the L-PAD is significantly larger than any other solid-state detector currently used for ICP-OES. This combination allows **Prodigy** to achieve significantly higher optical resolution than other solid-state detector based ICP systems. The detector also provides continuous wavelength coverage from 165 to 1100 nm permitting measurement over the entire ICP spectrum in a single reading without sacrificing wavelength range or resolution. This detector design is inherently anti-blooming and is capable of random access, non-destructive readout that results in a dynamic range of more than 6 orders of magnitude. For applications that require the measurement of chlorine, bromine or iodine an optional halogen detection system is available.



The **Prodigy** uses a 40.68 MHz free running, water-cooled oscillator, allowing it to handle even the most difficult sample matrices. A high sensitivity sample introduction system ensures that sufficient and steady emission signals are transmitted to the spectrometer. The torch and sample introduction system are uniquely integrated into the optical system through **Prodigy's** innovative Image Stabilization system, which treats the torch as an optical component by rigidly attaching it to the spectrometer.

The sample introduction system consists of a four-channel peristaltic pump, cyclonic spray chamber with a knockout tube, single piece quartz torch and a Ryton™ V-groove nebulizer. The ICP operating parameters for this work are displayed in **Table 1**.

ICP Parameters

Parameter	Setting	Part Number
RF Power	1.2 kW	
Coolant Flow	18.0 l/min	
Auxiliary Flow	0.0 l/min	
Plasma View	Radial	
Torch Type	Single Piece Quartz	120-00336-3
Nebulizer Pressure	34 psi	
Nebulizer Type	High Solids Concentric	120-00474-1
Spray Chamber	Cyclonic w/ Knockout	120-00475-1
Uptake Rate	1.2 ml/min	

Table 1. Plasma Parameters

Element Parameters

For each analytical wavelength, **Prodigy** uses a 3 x 15 pixel subarray which is typically centered on the wavelength of interest. Background correction points and the analytical peak have both position and width values within the subarray. In **Table 2** below, the position value is designated by “x” in the column header, while “w” indicates the width. The default position for the analytical peak is pixel 7 with a width of 3 pixels. All data in the subarrays are collected simultaneously. In addition, all pixel data are saved, permitting recalculation of results at a later time.

The integration time used was 15 seconds. Where possible, multiple wavelengths were used for each element as an internal check for accuracy.

As an example, typical subarray data are presented in **Figure 1**. This subarray contains the data for K at 766 nm from a NIST 1633b sample. As listed in **Table 2**, the background correction positions are 4 and 12, both with a width of 1 pixel and the peak position is 7 with a width of 3 pixels. (Pixel positions are read from left to right.)

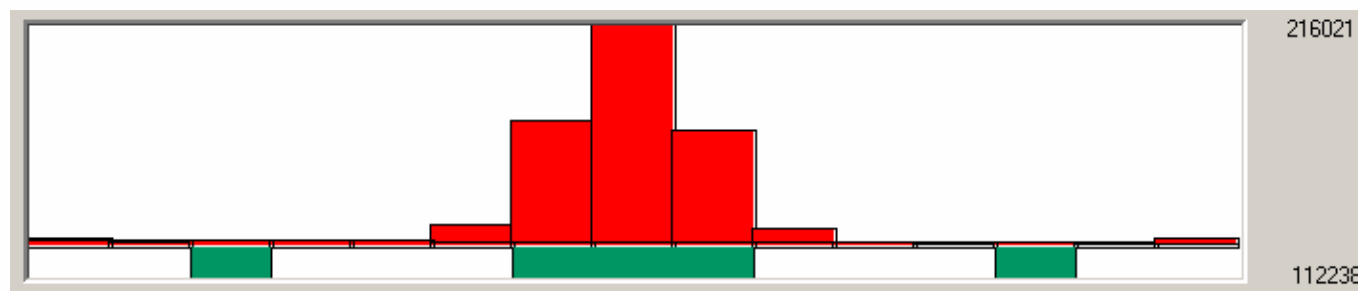


Figure 1. Cr 267 nm Subarray

Element	LBG X	LBG W	Peak	Peak W	RBG X	RBG W
Line	Left Background Position	Left Background Width	Peak Position	Peak Width	Right Background Position	Right Background Width
Al 308.215 r	3	1	7	3	13	1
Al 396.152 r	3	1	7	3	13	1
Ba 233.527 r	3	1	7	3	13	1
Ca 315.887 r	3	1	7	3	13	1
Ca 317.933 r	3	1	7	3	13	1
Cr 267.716 r	3	1	7	3	13	1
Cr 283.563 r	3	1	7	3	13	1
Cu 324.754 r	1	1	7	3	13	1
Fe 238.204 r	3	1	7	3	13	1
Fe 259.940 r	3	1	7	3	13	1
K 766.491 r	3	1	7	3	13	1
K 769.897 r	3	1	7	3	10	1
Mg 279.078 r	3	1	7	3	13	1
Mg 285.213 r	1	1	7	3	13	1
Mn 257.610 r	1	1	7	3	13	1
Na 588.995 r	6	1	7	3	10	1
Ni 231.604 r	3	1	7	3	13	1
Ni 232.003 r	3	1	7	3	13	1
Si 251.611 r	3	1	7	3	13	1
Si 288.158 r	3	1	7	3	13	1
Sr 407.771 r	3	1	7	3	13	1
Sr 421.552 r	3	1	7	3	13	1
Ti 336.122 r	3	1	7	3	13	1
Ti 337.280 r	3	1	7	3	13	1
V 292.401 r	3	1	7	3	13	1
V 310.230 r	3	1	7	3	13	1
Zn 202.548 r	3	1	7	3	12	1
Zn 206.200 r	3	1	7	3	15	1

Table 2. Element Parameters

Sample Preparation

1. Weigh 0.2000 g of the coal fly ash sample and place into a graphite crucible.
2. Add 1.2 g of a mixture of 80% lithium metaborate/ 20% lithium tetraborate fusion flux and mix thoroughly.
3. Fuse the sample/flux mixture in a muffle furnace at 1000°C for 30 minutes. At the halfway point, swirl the crucible to insure all sample/flux mixture is included in the melt. Return the crucible to the muffle furnace to complete the fusion.
4. Add 50 ml of deionized water (DIW), 4 ml of concentrated HNO₃ and a magnetic stirrer to a 150 ml beaker. When the fusion is complete, pour the molten melt into the beaker. Gently heat the beaker on a hot plate while stirring. When the sample is completely dissolved, remove from heat and allow it to cool.
5. Using a Whatman 42 filter paper, filter into a 100 ml volumetric flask and dilute to the mark with DIW.

Calibration Standards

The calibration standard concentrations, in mg/kg, are listed in the table below. Standards were matrix matched to the samples as follows:

- Add 1.2 g of the flux mixture used to fuse the sample to each standard flask.
- Add approximately 30 ml of DIW and 4 ml of HNO₃ to dissolve the flux.

When the dissolution is complete add the stock standards and dilute to the mark with DIW.

Element	STD0	STD1	STD2	STD3
		mg/kg	mg/kg	mg/kg
Al	0	200.0	400.0	800.0
Ba	0	1.00	2.00	3.00
Ca	0	20.0	50.0	100.0
Cr	0	0.200	0.500	1.00
Cu	0	0.200	0.500	1.00
Fe	0	100.0	200.0	300.0
Mg	0	5.00	10.0	20.0
Mn	0	0.200	0.500	1.00
Na	0	2.00	5.00	10.0
Ni	0	0.200	0.500	1.00
Si	0	250.0	500.0	1000
Sr	0	1.00	2.00	5.00
Ti	0	10.0	20.0	50.0
V	0	0.500	1.00	2.00
Zn	0	0.200	0.500	1.00

Table 3. Calibration Standard Concentrations, mg/kg

A typical calibration curve is shown in **Figure 2**.

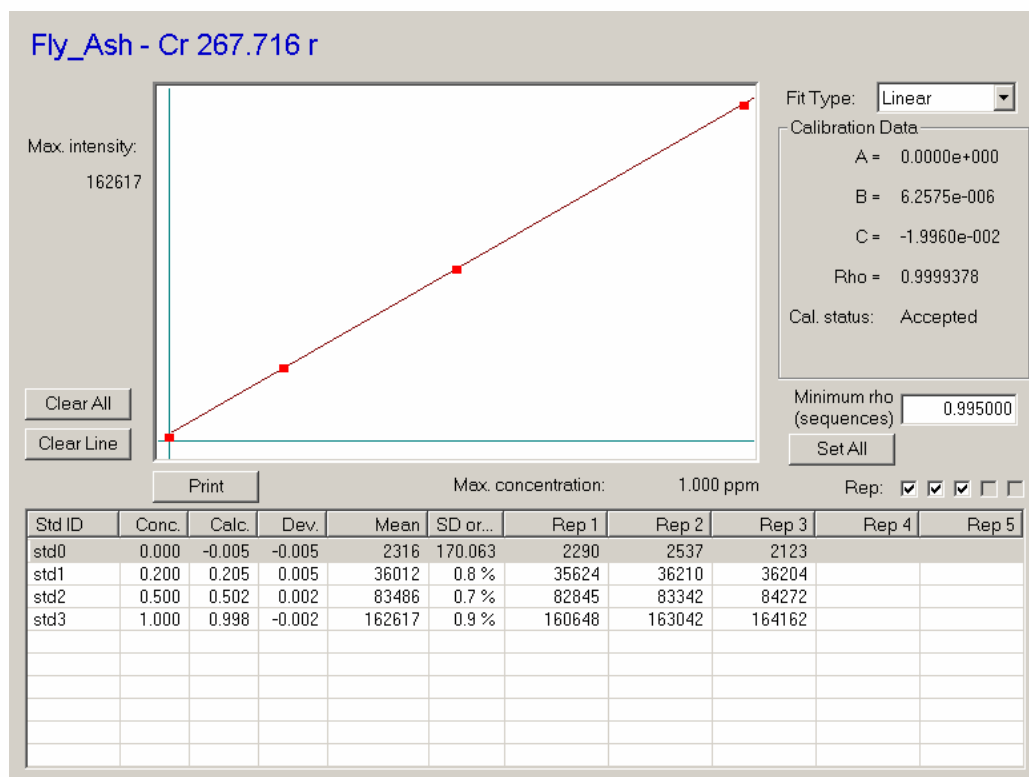


Figure 2. Cr 267 nm Calibration

Results

Validation of the instrument and sample preparation methodology was performed by analyzing a sample of NIST 1633b reference material. The results of this analysis are shown in **Table 4** follows. The measured values are in close agreement with the certified NIST values. Further, the elements that were determined at multiple wavelengths show excellent agreement between the wavelengths.

Sample ID	Line	Found	SD	RSD	Unit	Certificate Value	Recovery%
1633b	Al 308.215 r	15.24	0.09	0.61	wt%	15.05 ± 0.27	101.3
	Al 396.152 r	15.17	0.09	0.61	wt%	15.05 ± 0.27	100.8
	Ba 233.527 r	712	2	0.34	mg/kg	709 ± 27	100.5
	Ca 315.887 r	1.56	0.01	0.82	mg/kg	1.51 ± 0.06	103.0
	Ca 317.933 r	1.57	0.01	0.68	wt%	1.51 ± 0.06	103.8
	Cr 267.716 r	199.8	1.3	0.65	mg/kg	198.2 ± 4.7	100.8
	Cr 283.563 r	197.4	1.0	0.53	mg/kg	198.2 ± 4.7	99.6
	Cu 324.754 r	110.6	0.364	0.33	mg/kg	112.8 ± 2.6	98.1
	Fe 238.204 r	7.79	0.060	0.77	wt%	7.78 ± 0.23	100.1
	Fe 259.940 r	7.91	0.020	0.25	wt%	7.78 ± 0.23	101.7
	K 766.491 r	1.92	0.014	0.71	wt%	1.95 ± 0.03	98.4
	K 769.897 r	1.88	0.015	0.81	wt%	1.95 ± 0.03	96.6
	Mg 279.078 r	0.487	0.004	0.76	wt%	0.482 ± 0.008	101.0
	Mg 285.213 r	0.491	0.001	0.27	wt%	0.482 ± 0.008	101.9
	Mn 257.610 r	132.4	0.54	0.41	mg/kg	131.8 ± 1.7	100.5
	Na 588.995 r	0.207	0.0001	0.24	wt%	0.201 ± 1.7	103.1
	Ni 231.604 r	123.2	0.4	0.31	mg/kg	120.6 ± 0.019	102.1
	Ni 232.003 r	125.0	2.3	1.88	mg/kg	120.6 ± 0.019	103.7
	Si 251.611 r	23.03	0.08	0.35	wt%	23.02 ± 0.08	100.1
	Si 288.158 r	23.27	0.08	0.32	wt%	23.02 ± 0.08	101.1
	Sr 407.771 r	1049	7	0.70	mg/kg	1041 ± 14	100.8
	Sr 421.552 r	1045	4	0.42	mg/kg	1041 ± 14	100.4
	Ti 336.122 r	0.778	0.004	0.51	wt%	0.791 ± 0.014	98.3
	Ti 337.280 r	0.779	0.004	0.54	wt%	0.791 ± 0.014	98.4
	V 292.401 r	301.0	1.9	0.63	mg/kg	295.7 ± 3.6	101.8
	V 310.230 r	301.9	1.7	0.56	mg/kg	295.7 ± 3.6	102.1
	Zn 202.548 r	218.8	2.2	0.88	mg/kg	(210)	-
	Zn 206.200 r	215.7	2.6	1.05	mg/kg	(210)	-

Table 4. NIST 1633b Results

Conclusion

The determination of major and minor elements in coal fly ash by ICP-OES has been described.

The data presented in this report illustrate the ability of the Leeman Labs **Prodigy** High Dispersion ICP to provide an accurate and precise analysis of coal fly ash.