



## Analysis of Coal Fly Ash using the Dual View Prodigy ICP with a Simple HF Sample Preparation

### 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.

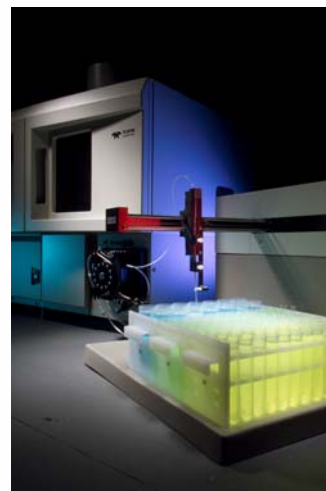
### Elements of Interest

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

### Instrumentation

A **Prodigy** High Dispersion Inductively Coupled Plasma (ICP) Spectrometer equipped with a dual 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 is made of HF resistant materials. The quartz torch is demountable and uses an alumina injector. The spray chamber and nebulizer are both made of plastic. 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	20.0 l/m	
Auxiliary Flow	0.0 l/m	
Plasma View	Axial/Radial	
Torch Type	Quartz Demountable	120-00479-1
Injector	Alumina	318-00071
Nebulizer Pressure	50 psi	
Nebulizer Type	HF Resistant Concentric	318-00107
Spray Chamber	HF Cyclonic	318-00106
Uptake Rate	1.0 ml/min	

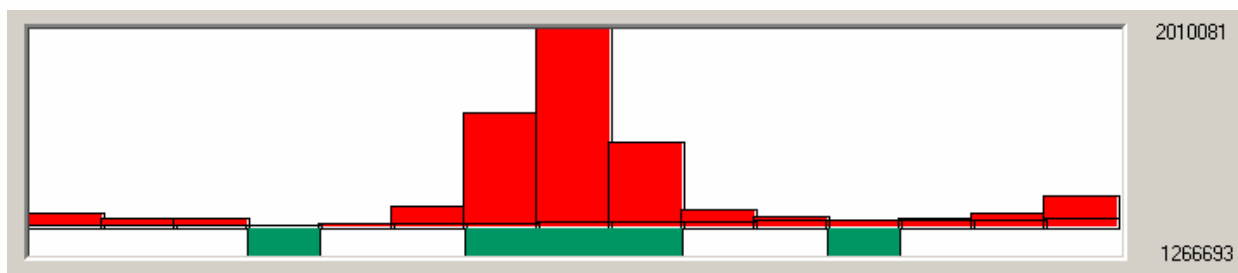
*Table 1. Plasma Parameters*

## 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 later. Elements in **Blue** were determined using the radial view.

The integration times were set to 30 and 15 seconds for the axial and radial views, respectively.

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. K 766 nm Subarray*

Wavelength	LBG X	LBG W	PEAK X	PEAK W	RBG X	RBG W
Line	Left Background Position	Left Background Width	Peak Position	Peak Width	Right Background Position	Right Background Width
<b>Al 308.215 r</b>	3	1	7	3	13	1
<b>Al 396.152 r</b>	1	3	7	3	13	3
As 189.042	6	1	7	3	10	1
As 193.759	6	1	7	3	10	1
<b>Ba 233.527 r</b>	3	1	7	3	13	1
<b>Ba 493.409 r</b>	3	1	7	3	13	1
<b>Ca 315.887 r</b>	3	1	7	3	13	1
<b>Ca 317.933 r</b>	3	1	7	3	14	1
Cr 267.716	3	1	7	3	13	1
Cr 283.563	3	1	7	3	13	1
Cu 324.754	1	1	7	3	13	1
<b>Fe 238.204 r</b>	3	1	7	3	13	1
<b>Fe 259.940 r</b>	3	1	7	3	13	1
<b>K 766.491 r</b>	4	1	7	3	12	1
<b>K 769.897 r</b>	6	1	7	3	10	1
<b>Mg 279.078 r</b>	3	1	7	3	13	1
<b>Mg 285.213 r</b>	3	1	7	3	13	1
Mn 257.610	2	1	7	3	13	1
<b>Na 588.995 r</b>	6	1	7	3	10	1
<b>Na 589.592 r</b>	3	1	7	3	12	1
Ni 231.604	3	2	7	3	15	1
Ni 232.003	3	1	7	3	11	1
Pb 220.353	6	1	7	3	10	1
<b>Si 251.611 r</b>	3	1	7	3	13	1
<b>Si 288.158 r</b>	3	1	7	3	13	1
<b>Sr 407.771 r</b>	3	1	7	3	13	1
<b>Sr 421.552 r</b>	3	1	7	3	13	1
<b>Ti 334.941 r</b>	4	0	7	3	13	1
<b>Ti 336.122 r</b>	3	1	7	3	13	1
<b>Ti 337.280 r</b>	4	1	7	3	13	1
V 292.401	3	1	7	3	13	1
V 310.230	3	1	7	3	13	1
Zn 202.548	5	1	7	3	12	1
Zn 206.200	4	2	7	3	13	1

*Table 2. Element Parameters*

## Sample Preparation

1. Weigh 0.2000g of the coal fly ash sample and place into a Teflon™ beaker.
2. Add sufficient distilled water (DIW) such that the sample is completely covered.
3. Add 5 ml of aqua regia and 2 ml of HF.
4. Cover the beaker with a Teflon™ cover and heat at 95-100°C for two hours. Remove from heat and cool to near room temperature.
5. Using a Whatman 42 filter paper, filter into a 100 ml volumetric flask and dilute to the mark with DIW.

## Calibration Standards

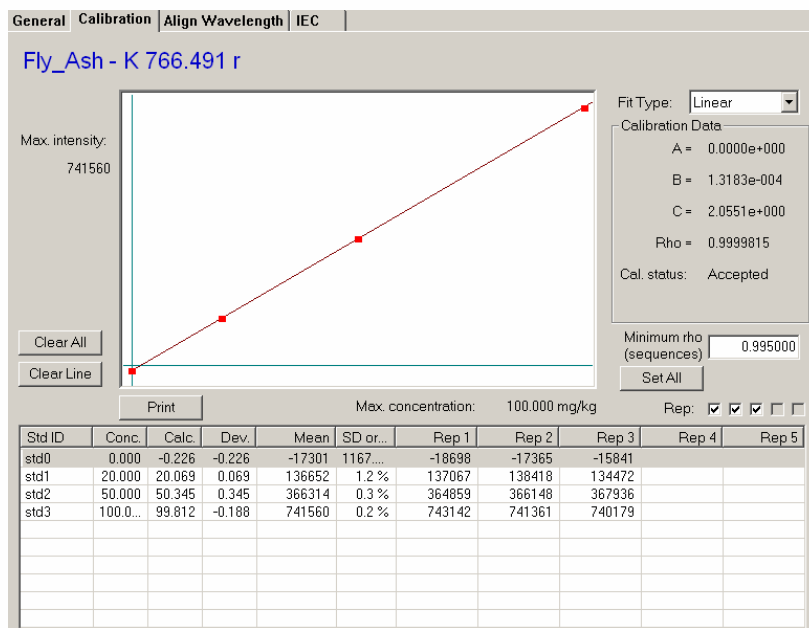
The calibration standard concentrations, in mg/kg, are listed in the table below. Standards were matrix match to the samples as follows:

- Add 5 ml of aqua regia and 2 ml of HF to each standard flask.
- Add the stock standards and dilute to the mark with DIW.

Element	STD0	STD1	STD2	STD3
		mg/kg	mg/kg	mg/kg
Al	0.0	200	400	800
As	0.0	0.20	0.50	1.00
Ba	0.0	1.00	2.00	5.00
Ca	0.0	20	50	100
Cr	0.0	0.20	0.50	1.00
Cu	0.0	0.20	0.50	1.00
Fe	0.0	100.0	200.0	400.0
K	0.0	20.0	50.0	100.0
Mg	0.0	5.0	10.0	20.0
Mn	0.0	0.20	0.50	1.00
Na	0.0	2.00	5.00	10.00
Ni	0.0	0.20	0.50	1.00
Pb	0.0	0.10	0.20	0.50
Si	0.0	250.0	500.0	1000.0
Sr	0.0	1.00	2.00	5.00
Ti	0.0	10.0	20.0	50.0
V	0.0	0.50	1.00	2.00
Zn	0.0	0.20	0.50	1.00

*Table 3. Calibration Standard Concentrations*

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



**Figure 2.** K 766 calibration Curve

## Results

The NIST SRM 1633b Coal fly ash sample was analyzed using the operating parameters described in **Table 1** with the analytical wavelengths and background correction positions listed in **Table 2**. Analysis results are given in **Table 4**. The measured values are in close agreement with the certified NIST values. In addition, elements that were determined at two different wavelengths show excellent agreement between the wavelengths. As is usual with SRM's, elements within values enclosed in parentheses are not certified.

Element	Found	SD	RSD	Unit	Certified Value	SD	% Recovery
Al 308.215 r	14.94	0.073	0.49	wt%	15.05	0.27	99.3
Al 396.152 r	14.80	0.053	0.36	wt%	15.05	0.27	98.4
As 189.042	134.2	3.45	2.57	mg/kg	136.2	2.6	98.5
As 193.759	136.5	4.45	3.26	mg/kg	136.2	2.6	100.2
Ba 233.527 r	736	5	0.73	mg/kg	709	27	103.7
Ba 493.409 r	723	5	0.75	mg/kg	709	27	101.9
Ca 315.887 r	1.56	0.005	0.33	wt%	1.51	0.06	103.5
Ca 317.933 r	1.57	0.006	0.40	wt%	1.51	0.06	104.0
Cr 267.716	194.2	0.17	0.09	mg/kg	198.2	4.7	98.0
Cr 283.563	196.1	0.61	0.31	mg/kg	198.2	4.7	99.0
Cu 324.754	111.0	0.32	0.29	mg/kg	112.8	2.6	98.4
Fe 238.204 r	7.98	0.029	0.36	wt%	7.78	0.23	102.6
Fe 259.940 r	7.89	0.040	0.51	wt%	7.78	0.23	101.4
K 766.491 r	1.91	0.010	0.55	wt%	1.95	0.03	97.9
K 769.897 r	1.94	0.004	0.22	wt%	1.95	0.03	99.4
Mg 279.078 r	0.489	0.002	0.39	wt%	0.482	0.008	101.5
Mg 285.213 r	0.506	0.004	0.71	wt%	0.482	0.008	104.9
Mn 257.610	133.0	1.32	0.99	mg/kg	131.8	1.7	100.9
Na 588.995 r	0.200	0.0010	0.48	wt%	0.201	0.003	99.5
Na 589.592 r	0.198	0.0015	0.75	wt%	0.201	0.003	98.3
Ni 231.604	120.0	1.00	0.83	mg/kg	120.6	1.8	99.5
Ni 232.003	112.3	1.03	0.91	mg/kg	120.6	1.8	93.1
Pb 220.353	72.2	1.3	1.80	mg/kg	68.2	2.6	105.9
Si 251.611 r	22.64	0.123	0.54	wt%	23.02	0.08	98.4
Si 288.158 r	22.80	0.142	0.62	wt%	23.02	0.08	99.0
Sr 407.771 r	994.1	3	0.35	mg/kg	1041	14	95.5
Sr 421.552 r	1004	4	0.44	mg/kg	1041	14	96.5
Ti 334.941 r	0.775	0.001	0.13	wt%	0.791	0.014	98.0
Ti 336.122 r	0.781	0.002	0.22	wt%	0.791	0.014	98.7
Ti 337.280 r	0.775	0.001	0.19	wt%	0.791	0.014	97.9
V 292.401	297.0	1.30	0.44	mg/kg	295.7	3.6	100.4
V 310.230	296.1	0.79	0.27	mg/kg	295.7	3.6	100.1
Zn 202.548	218	0.49	0.22	mg/kg	(210)	-	-
Zn 206.200	219	0.52	0.24	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.

The HF sample introduction system performs without any clogging of the torch or nebulizer.

The image stabilized plasma and the simultaneous data collection of both peak and background data combine to provide precise and stable results.