Analysis of Coal Fly Ash with the ProdigyPlus Dual-View ICP-OES

Manny Almeida, ICP/DCA Product Line Manager and Bruce MacAllister, Applications Chemist; Teledyne Leeman Labs

Introduction

Coal fly ash is a fine, powdery material, composed primarily of silica, that is a by-product of the burning of finely ground coal. Produced primarily by coal-fired power plants, it is one of a group of coal burning by-products known as Coal Combustion Residuals (CCRs). Other CCR materials include bottom ash, boiler slag and flue gas desulfurization material.

In 2014, approximately 130 million tons of coal ash was generated in the United States making it one of the largest types of industrial wastes generated.[1] Much of this waste material will be placed in landfills under the requirements of Subtitle D of the Resource Conservation and Recovery Act (RCRA), which defines them as non-hazardous.[2] Fly ash can also be used in different products and materials such as concrete, flowable fill, raw feed as clinker, aggregate substitute material and for soil modification/stabilization. These uses of fly ash are considered beneficial and have favorable environmental impact.

Because the composition of fly ash is directly related to the properties of the coal used for combustion, the potential for trace and major elements leaching from it in both disposal and reuse scenarios can pose an environmental hazard. Consequently, fly ash is tested for metals determination to ascertain its elemental composition.

Experimental

Instrumentation

A Prodigy Plus Inductively Coupled Plasma (ICP) Spectrometer equipped with a dual-view torch configuration and a 120-position CETAC ASX-280 autosampler (Teledyne CETAC Technologies, Omaha NE) was used to generate the data for this application note (Figure 1).

Figure 1 Prodigy Plus ICP-OES and CETAC ASX-280 Autosampler

The Prodigy Plus is a compact, bench-top, simultaneous ICP-OES system featuring an 800 mm focal length Echelle optical system coupled with a mega-pixel CMOS (Complementary Metal Oxide Semiconductor) detector. At 28 x 28 mm, the active area of the CMOS detector is significantly larger than any other solid-state detector currently used for ICP-OES. This combination allows the Prodigy Plus to achieve higher optical resolution and dispersion than other solid-state detector-based ICP systems. The detector 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. Additionally, the high-speed readout of the camera virtually eliminates detector overhead time. Readout time is approximately 1 second, resulting in increased sample throughput.

The detector design is inherently anti-blooming and is capable of random access, non-destructive readout that results in a dynamic range of more than 8 orders of magnitude. For applications that require the determination of chlorine or bromine, an optional halogen detection system is available, extending the wavelength coverage to 135-1100 nm.

The Prodigy Plus uses a 40.68 MHz rugged, free-running, water-cooled RF Generator, allowing it to handle the most difficult sample matrices, as well as common organic solvents.

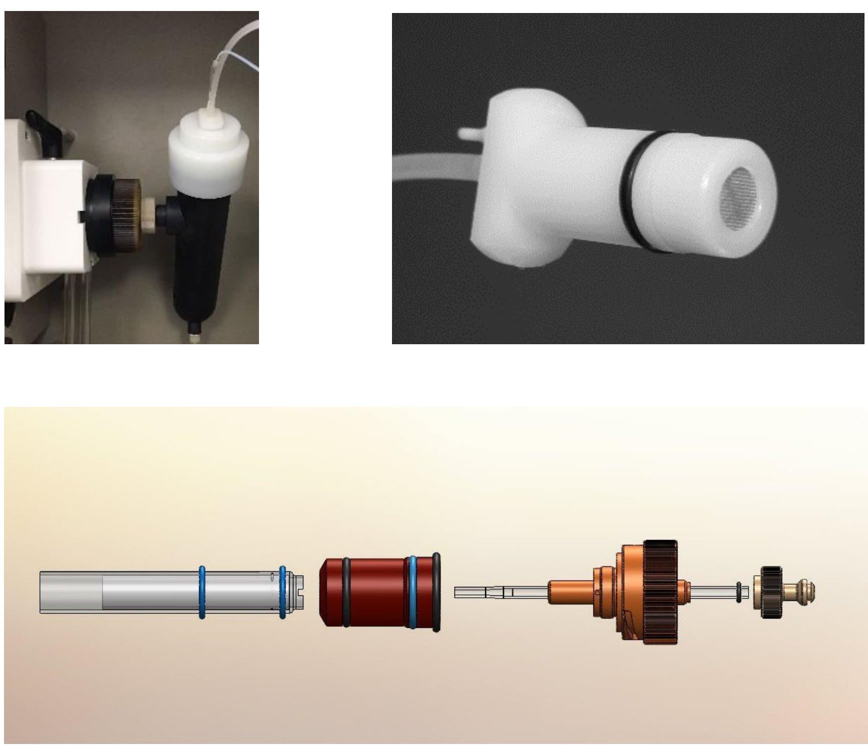
Sample Introduction

For this application note, an HF resistant sample introduction was used, consisting of a Ryton® spray chamber and a Hildebrand Grid nebulizer (Figure 2). The standard quartz sample injector was replaced with one made of HF resistant alumina.

The Hildebrand Grid is an exceptionally versatile nebulizer, capable of running samples in virtually any matrix: aqueous, organic, high-dissolved solids as well as HF. Its design provides high efficiency for good detection limits, as well as resistance to clogging by dissolved solids.

The Prodigy Plus torch is a demountable, low-flow design (Figure 2) capable of operating at up to 20 L/min, should a sample type require a higher flow. To improve torch longevity, the Prodigy Plus uses a short, radial torch for all instrument configurations – radial, axial and dual-view. Viewing ports, slots and extended torch lengths are not used.

Figure 2 Ryton® Spray Chamber, Hildebrand Grid Nebulizer, and Prodigy Plus Torch



Operating Parameters

The Prodigy Plus operating parameters used for this study are shown in Table I. Wavelengths and plasma viewing configuration used are shown in Table II.

Table I Instrument Operating Parameters

Parameter	Setting
RF Power	1.2 kW
Coolant Flow	14 L/min
Auxiliary Flow	0
Torch	Quartz Demountable
Injector	Alumina
Nebulizer Pressure	42 psi
Nebulizer	Hildebrand Grid
Spray Chamber	Ryton™
Sample Uptake Rate	35 rpm
Axial Integration Time	15 s
Radial Integration time	5 s

Table II Analytical Wavelengths

Element	Wavelength, nm	View		Element	Wavelength, nm	View
Al	308.215	Radial		Mn	257.610	Axial
	396.152	Radial			259.372	Axial
As	189.042	Axial		Na	588.995	Radial
	193.759	Axial			589.592	Radial
Ba	233.527	Radial		Ni	231.604	Axial
	493.409	Radial			232.003	Axial
Ca	315.887	Radial		Pb	217.000	Axial
	317.933	Radial			220.353	Axial
Cr	267.716	Axial		Si	251.611	Radial
	283.563	Axial			288.158	Radial
Cu	324.754	Axial		Sr	407.771	Radial
	327.396	Axial			421.552	Radial
Fe	238.204	Radial		Ti	334.941	Radial
	259.940	Radial			336.122	Radial
K	766.491	Radial		V	292.401	Axial
	769.897	Radial			310.230	Axial
Mg	279.078	Radial		Zn	202.548	Axial
	285.213	Radial			206.200	Axial

Method

Sample Preparation

NIST SRM 1633c Coal Fly Ash was prepared using the following procedure:

1. Weigh 0.2000 g of sample and place into a Teflon™ beaker.
2. Add sufficient deionized (DI) water to completely cover the sample.
3. All 5 mL of aqua regia (nitric and hydrochloric acids in a 1:3 ratio) and 2 mL of hydrofluoric acid (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 plastic 100 mL volumetric flask and dilute to 100 g with DI water.

Calibration Standards

Calibration standards were prepared using single element standards from VHG Labs (Manchester, NH). The standards were matrix matched to the sample by adding 5 mL of aqua regia and 2 mL of HF and then diluting to 100 g with DI water. Calibration standards concentrations are presented in Table III.

Table III Calibration Standard Concentrations, mg/kg

Element	Std0	Std1	Std2	Std3
Al	0	200	400	800
As, Cr, Cu, Mn, , Ni Zn	0	0.20	0.50	1.00
Ba, Sr	0	1.00	2.00	5.00
Ca, K	0	20.0	50.0	100
Fe	0	100	200	400
Mg	0	5.00	10.0	20
Na	0	2.00	5.00	10.0
Pb	0	0.10	0.20	0.50
Si	0	250	500	1000
Ti	0	10.0	20.0	50.0
V	0	0.50	1.00	2.00

Results and Discussion

The NIST SRM 1633c Coal Fly Ash sample was analyzed using the operating parameters shown in Table I at the analytical wavelengths and plasma viewing configuration listed in Table II. Analysis results are shown in Table IV. The measured values are in close agreement with the certified NIST values. Additionally, the elements that were determined at two different wavelengths show excellent agreement between results, indicating that there are no spectral interferences (both inter-element or intra-order).

Table IV NIST SRM 1633c Results						
Element	**Concentration**	**SD**	**RSD**	**Units**	**Certified Value**	**% Recovery**
Al 308.215 r	13.08	0.039	0.30	%	13.28	98.5
Al 396.152 r	12.98	0.061	0.47			97.8
As 189.042	186.2	3.347	1.80	mg/kg	186.2	100.0
As 193.759	178.7	1.86	1.04			96.0
Ba 233.527 r	0.111	0	0.20	%	0.1126	98.6
Ba 493.409 r	0.11	0.001	0.59			97.7
Ca 315.887 r	1.348	0.004	0.33	%	1.365	98.8
Ca 317.933 r	1.339	0.005	0.38			98.1
Cr 267.716	272.9	1.326	0.49	mg/kg	258	105.8
Cr 283.563	270.9	0.785	0.29			105.0
Cu 324.754	172.1	0.498	0.29	mg/kg	173.7	99.1
Cu 327.396	169.5	0.786	0.46			97.6
Fe 238.204 r	10.30	0.068	0.66	%	10.49	98.2
Fe 259.940 r	10.28	0.068	0.66			98.0
K 766.491 r	1.754	0.006	0.36	%	1.773	98.9
K 769.897 r	1.733	0.008	0.47			97.7
Mg 279.078 r	0.492	0.002	0.39	%	0.498	98.8
Mg 285.213 r	0.491	0.002	0.33			98.6
Mn 257.610	239.5	0.548	0.23	mg/kg	240.2	99.7
Mn 259.372	239.0	0.605	0.25			99.5
Na 589.592 r	0.163	0.001	0.89	%	0.1707	95.5
Na 588.995 r	0.167	0	0.06			97.8
Ni 231.604	133.0	0.254	0.19	mg/kg	132	100.8
Ni 232.003	130.8	2.129	1.63			99.1
Pb 220.353	94.40	0.803	0.85	mg/kg	95.2	99.2
Pb 217.000	94.29	3.824	4.06			99.0
Si 251.611 r	20.84	0.19	0.91	%	21.3	97.9
Si 288.158 r	20.95	0.133	0.63			98.4
Sr 407.771 r	892.4	2.641	0.30	mg/kg	901	99.0
Sr 421.552 r	889.8	6.791	0.76			98.8
Ti 334.941 r	0.709	0.003	0.45	%	0.724	97.9
Ti 336.122 r	0.703	0.006	0.89			97.1
V 292.401	283.3	0.549	0.19	mg/kg	286.2	99.0
V 310.230	280.6	1.044	0.37			98.1
Zn 202.548	236.1	0.964	0.41	mg/kg	235	100.5
Zn 206.200	235.5	0.727	0.31			100.2

The results indicate that the Teledyne Leeman Labs Prodigy Plus ICP can successfully analyze coal fly ash and similar sample types that require the use of hydrofluoric acid (HF). The dual-view configuration provided the flexibility to use any wavelength in either plasma viewing configuration and was ideal for sample types with concentrations ranging from % to mg/kg (and even µg/kg).

The HF resistant sample introduction system provided excellent sensitivity and precision. The Hildebrand Grid nebulizer is more efficient than many other HF resistant nebulizers and is more rugged. In addition to its HF resistance, the Hildebrand grid is capable of running high levels of dissolved solids (>10%) without clogging, or the need for an argon humidifier.

The CMOS detector was able to capture all sample element emission levels in a single reading and for each plasma viewing configuration, significantly reducing analysis times. Regardless of the intensity difference between the elements, multiple integration times of varying length are never required, nor is a pre-screening to sort wavelengths by intensity necessary. The detector's high readout speed accomplished the collection of over 150 wavelengths in less than 1 second. The Prodigy Plus delivers true low-cost analysis, combining a low-flow torch to reduce argon consumption with short overall analysis time to increase sample throughput. All of these attributes combine to make the Prodigy Plus an ideal instrument for laboratories that analyze samples with wide ranges of analyte concentrations.

References

1. Coal Ash Basics. US Environmental Protection Agency (EPA) [Online]. https://www.epa.gov/coalash/coal-ash-basics (accessed Dec 15, 2016).
2. Final Rule: Disposal of Coal Combustion Residuals from Electric Utilities. US Environmental Protection Agency (EPA) [Online]. https://www.epa.gov/coalash/coal-ash-rule (accessed Dec 15, 2016).