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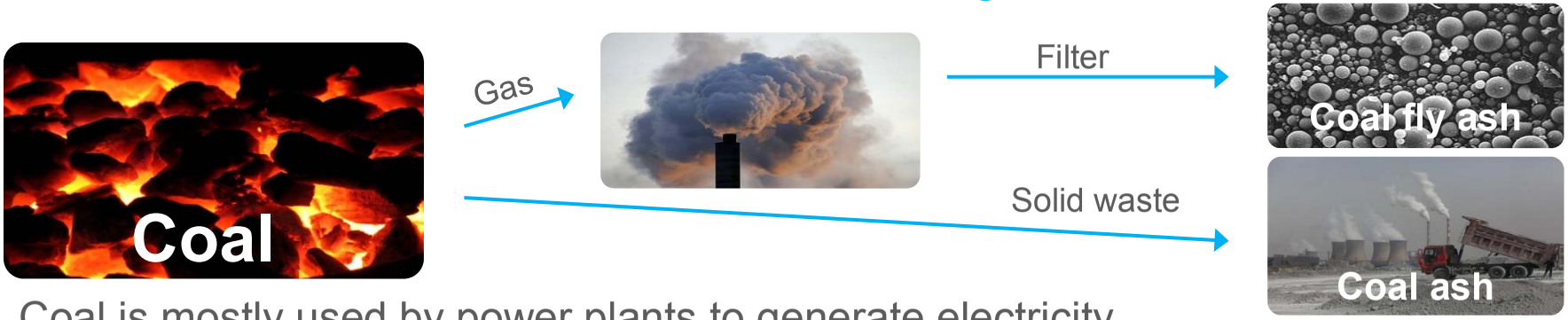
Characterization of **Coal** and **Its By-products** Using Borate Fusions and ICP-OES Analyses

By **Marie-Ève Provencher,** M.Sc. Chemist
USA Sales Manager

Samples from Coal Industry



Coal is mostly used by power plants to generate electricity

Emissions from power plants:

- Gas (fly ash)
- Solid waste (ash)

Why is trace analysis important?

- It helps to know the content of the coal by-products (coal ash and coal fly ash)
- It allows to know the content of the waste from power plants (coal ash and coal fly ash) for an eco-friendly disposal

Certified Reference Materials (CRMs)

- 3 CRMs from coal industry
- High silica and alumina content
- Sample preparation method
  - Acid digestion (not efficient)
  - Harsh acid (HF) (not entirely safe)
  - Fusion

	Coal	Coal ash	Coal fly ash
	NCS FC28127	VS-7177-95	EOP 12-1-02
	China	Russia	Czech Republic
Al	3.47	14.3	16.1
Si	5.61	27.4	22.9

Norms

ASTM D6349

- Sample preparation:
  - Borate fusion
  - Acid digestion ($HF/HNO_3/HCl$)
- ICP-OES
- **Al**, Ba, **Ca**, **Fe**, **K**, **Mg**, Mn, **Na**, P, S, **Si**, Sr and **Ti**

AS 1038.14.1

- Sample preparation:
  - borate fusion
- AA
- **Al**, Ba, **Ca**, **Fe**, **K**, **Mg**, Mn, **Na**, P, S, **Si**, Sr, **Ti** and Zn

Pretreatment of Samples

- Ramp up to 500 °C for 1 hour
- Ramp up to 750 °C for 2 hours
- Hold at 750 °C for 2 hours

	Coal	Coal ash	Coal fly ash
	NCS FC28127	VS-7177-95	EOP 12-1-02
	China	Russia	Czech Republic
LOI	74.3%	0.42%	0.29%

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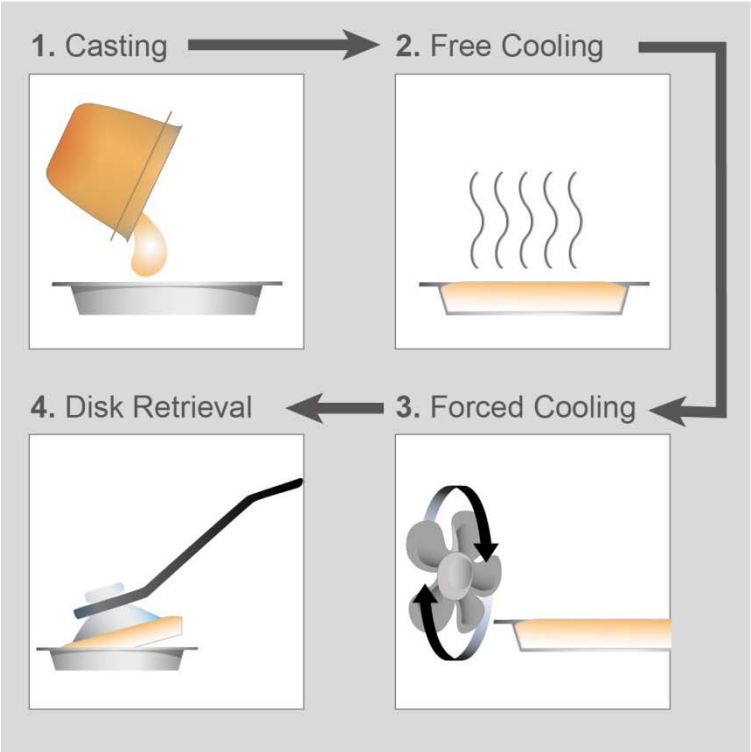
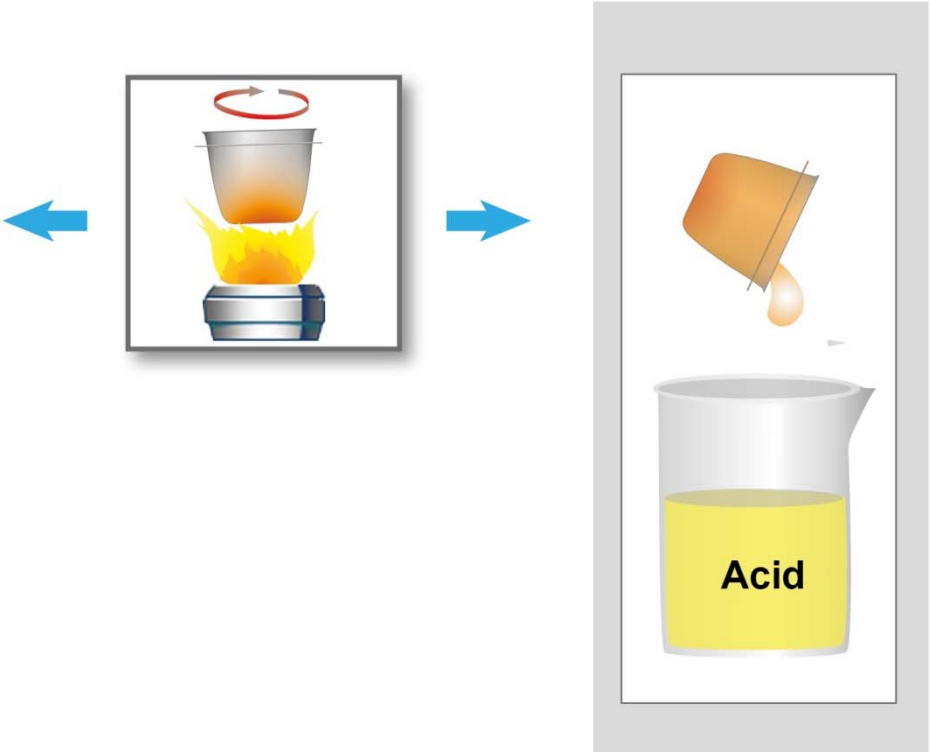
Sample Preparation by Borate Fusion

XRF Analysis



ICP and AA Analysis



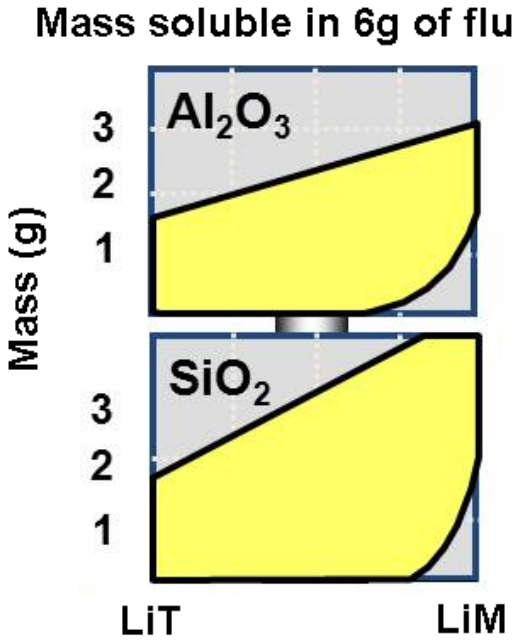
Sample Preparation by Borate Fusion

In a Pt/Au (95%/5%) crucible:

- 0.100 g of ashed sample
- 0.150 g $LiNO_3$
- 1.000 g LiM/1.5%LiBr

Keep in mind:

- Low sample/flux ratio (1/10) for an optimized sample dissolution
- The non-wetting agent allows a complete pouring
- Silica and alumina are very soluble in lithium metaborate



Fusion Technique Instruments

1. Manual

- Meeker burner and rising stand
- Muffle furnace
- Home made

2. Automatic

- Gas fired
- Electric

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Claisse® Automatic Fluxers

ELECTRIC

LeNeo® Claisse® fluxer

Eagon 2® Claisse® fluxer

TheOx® Claisse® fluxer

GAS

M4™ Claisse® fluxer ← Propane & Natural Gas

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Automated Fusion

- LeNeo® fusion instrument
- One fusion position
- Programmable parameters (temperature, duration and agitation):
  - Oxidation step at 800 °C
  - Fast temperature ramp-up (up-to 1200 °C)
  - The fusion steps are completed in 7 minutes

Steps	Duration (min)	Rocking angle	Rocking speed	Temperature (°C)
Oxidation	2	0	0	800
Fusion	1	0	0	1000
Fusion	1	0	0	1050
Fusion	1	20	15	1050
Fusion	1	30	20	1050
Fusion	1	40	30	1050
Pouring	-			
Stirring	6			

Automated Dissolution

The dissolution is completed in 6 minutes:

- Complete pouring
- 90 mL of 10% HNO_3
- Magnetic agitation

Steps	Duration (min)	Rocking angle	Rocking speed	Temperature (°C)
Oxidation	2	0	0	800
Fusion	1	0	0	1000
Fusion	1	0	0	1050
Fusion	1	20	15	1050
Fusion	1	30	20	1050
Fusion	1	40	30	1050
Pouring	-			
Stirring	6			

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Manual Dilution

- Complete to 100 mL
- Add the internal standard
- Dilution 1 in 2
- Final volume at 200 mL

0.5% of total dissolved salt

Analysis by ICP-OES

Instrumentation

- Perkin Elmer® Optima® 7300 DV ICP-OES

Analysis

- Matrix-matched calibration curve
- Internal standards added

Nebulizer	Gem Tip Cross flow
Spray chamber	Scott
Injector	Alumina 2 mm i.d.
RF	1500 W
Argon flow	Plasma: 16 L/min Nebulizer: 0.8 L/min Auxiliary: 0.4 L/min
Sample flow rate	1.0 mL/min

Internal Standards

Internal standard associated with the element:

- Similar ionization potential
- Similar ionization state

Elements of interest			Associated internal standards			Both	
Elements	Wavelength	Ionization potential	Internal standards	Wavelength	Ionization potential	Ionization state	Viewing mode
Al	237.313	6.0	Ga	294.364	6.0	I	Axial
Ca	422.673	6.1	Eu	381.967	5.7	II	Radial
Fe	238.863	7.9	Re	197.248	7.9	II	Axial
K	766.490	4.3	Rb	780.023	4.2	I	Axial
Mg	279.077	7.6	Re	197.248	7.9	II	Axial
Na	589.592	5.1	Ga	294.364	6.0	I	Radial
Si	252.851	8.2	Te	214.281	9.0	I	Axial
Ti	337.279	6.8	Eu	381.967	5.7	II	Axial

Calibration, Method Detection Limits (MDLs) and Linearity

Elements	Wavelength (nm)	View	MDL (mg/L)	Calibration range		Correlation coefficient (pts = 5)
				(Min)	(Max)	
Al	237.313	Axial	0.07	13.8	275	1.0000
Ba	413.065	Axial	0.006	0.25	5.00	1.0000
Ca	422.673	Radial	0.1	6.00	115	1.0000
Fe	238.863	Axial	0.02	6.25	125	1.0000
K	766.490	Axial	0.002	0.900	18.0	0.9997
Mg	279.077	Axial	0.007	0.880	17.5	1.0000
Mn	293.305	Axial	0.001	0.138	2.76	1.0000
Na	589.592	Radial	0.05	0.280	5.50	1.0000
P	177.434	Axial	0.03	1.60	30.0	0.9995
S	181.975	Axial	0.06	2.80	55.0	1.0000
Si	252.851	Radial	0.07	15.0	300	1.0000
Sr	460.733	Axial	0.002	0.330	6.50	0.9999
Ti	337.279	Axial	0.002	2.80	55.0	1.0000
Zn	213.857	Axial	0.003	0.150	3.00	1.0000

Results

- The method has been tested with 3 different types of samples:

Fly ash
Coal ash
Coal

- Accuracy and precision were calculated based on the certified reference value of each CRM (Al, Ca, Fe, K, Mg, Na, Si and Ti)
- Recovery was calculated with samples spiked before fusion (Ba, K, Mn, P, S, Sr and Zn)

Precision and Accuracy in Brown Coal Fly Ash

EOP 12-1-02						
Elements	Certified values (%)	Experimental values (%) n=10	MDL (%)	Precision $t_{0,975;9}$ (%)	Accuracy (%)	RSD (%)
Al	16.1	16.3	0.01	0.1	98.7	0.5
Ca	1.49	1.44	0.02	0.04	96.5	3.9
Fe	5.17	5.21	0.003	0.02	99.2	0.5
K	0.651	0.630	0.0004	0.011	96.7	2.4
Mg	0.581	0.623	0.001	0.002	93.0	0.5
Na	0.361	0.37	0.01	0.01	97.6	3.5
Si	22.9	23.8	0.01	0.4	96.3	3.7
Ti	3.61	3.44	0.0003	0.01	95.3	0.5

Dilution factor: 1994
n = 10

Precision and Accuracy in Coal

NCS FC28127						
Elements	Certified values (%)	Experimental values (%) n=10	MDL (%)	Precision $t_{0,975;9}$ (%)	Accuracy (%)	RSD (%)
Al	3.47	3.37	0.003	0.03	97.1	1.2
Ca	1.88	1.89	0.006	0.04	99.3	2.8
Fe	1.02	1.05	0.0008	0.01	97.4	1.0
K	0.29	0.281	0.0001	0.005	97.0	2.5
Mg	0.28	0.294	0.0004	0.002	94.7	0.8
Na	0.052	0.052	0.002	0.001	99.6	2.2
Si	5.61	6.05	0.004	0.06	92.2	1.3
Ti	0.18	0.173	0.00008	0.002	96.4	1.4

Dilution factor: 513
n = 10

Precision and Accuracy in Coal Ash

VS 7177-95						
Elements	**Certified values (%)***	**Experimental values (%) n=10**	**MDL (%)**	**Precision $t_{0,975;9}$ (%)**	**Accuracy (%)**	**RSD (%)**
Al	14.33	14.0	0.01	0.1	97.7	1.3
Ca	3.49	3.70	0.02	0.06	94.0	2.4
Fe	3.83	3.73	0.003	0.03	97.3	1.0
K	0.49	0.446	0.0004	0.006	91.0	1.9
Mg	0.893	0.874	0.001	0.009	97.9	1.5
Na	0.10	0.11	0.01	0.01	97.6	3.1
Si	27.43	28.6	0.014	0.4	95.7	2.1
Ti	0.36	0.357	0.0003	0.003	99.3	1.2
*Measured as Al but reported as Al_2O_3 on the certificate of analysis provided with material						

Dilution factor: 1992
n = 10

Recovery for the 3 CRMs

Elements	EOP 12-1-02 (brown coal fly ash)			NCS FC28127 (coal ash)			VS 7177-95 (coal)		
	Spiked values	Recovery	RSD	Spiked values	Recovery	RSD	Spiked values	Recovery	RSD
	mg/L	%	%	mg/L	%	%	mg/L	%	%
Ba	1	102	0.4	1	102	1	1	103	0.2
K	3	91	3	5	102	2	3	91	4
Mn	1	102	1	2	100	0.7	1	104	0.6
P	1	99	1	1	103	1	1	101	3
S	1	97	3	5	100	1	1	96	3
Sr	1	96	1	1	100	0.9	1	98	3
Zn	1	100	0.7	1	101	0.9	1	101	1

n = 5

Conclusion

- Great overall accuracy:
  - Minimum (smaller value) 91.0% for K
  - Average 96.6 ± 2.3%
- Great overall recovery:
  - Minimum 91% for K
  - Average 99.5 ± 3.6%

- It is appropriate to use LeNeo instrument to prepare coal samples for ICP-OES analysis in accordance with industry norms

Questions?

maprovencher@claisse.com

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