Application Note

Analysis of Dust Samples

Agnès COSNIER
HORIBA Scientific
Longjumeau, France

Keywords: environment
Elements: Cd, Cr, Cu, K, Mo, Na, Ni, Pb, Sb, Sn, Zn, Zr

1 Introduction

This Application Note examines the analysis of dust samples using ICP-AES. There were a number of elements of interest, including the alkalis. ICP-AES is a multi-element technique that allows for the fast analysis of more than 75 elements on the Periodic table.

2 Principle

2.1 Technique used

The elemental analysis of dust samples was undertaken by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). The sample is nebulized then transferred to an argon plasma. It is decomposed, atomized and ionized whereby the atoms and ions are excited. We measure the intensity of the light emitted when the atoms or ions return to lower levels of energy. Each element emits light at characteristic wavelengths and these lines can be used for quantitative analysis after a calibration.

2.2 Wavelength choice

The choice of the wavelength in a given matrix can be made using the profile function, or by using Win-Image, which is rapid semi-quantitative analysis mode using multiple wavelengths. The principle is the same in either case: record the scans of analytes at low concentration, and of the matrix. By superimposing the spectra, we see possible interferences.

2.3 Limits of detection estimation

$$LOD = k * BEC * RSD_0$$

The limits of detection are calculated using the following formula:

With:
LOD limit of detection,
k: equals to 3 for the normal 3-sigma values,
BEC: Background equivalent concentration,
RSD_0: relative standard deviation of the blank.

To calculate the LOD, a calibration curve is constructed using two points, 0 ppm and 5 ppm, or some concentration where the calibration is linear. This calibration provides the BEC. The RSDo is evaluated by running the blank ten times.

3 Sample preparation

Two types of sample preparation were examined. The first method was used for the analysis of Cd, Cr, Cu, Mo, Ni, Pb, Sb, Sn, Zn, and Zr and the second for Na and K.

The composition of the prepared samples was:

Sample 1:
- 2 g/L of dust salt
- 0.2g of fusion salt (H_3BO_3 + K_2CO_3)
- 100mL of 65% HNO_3

Sample 2:
- 0.4 g/L of dust salt
- 50 mL of 37% HCl

HORIBA Scientific

4 Instrument specification

The work was undertaken on a ULTIMA and is also applicable in a ULTIMA 2 ICP spectrometer. The specifications of this instrument are listed below.

Table 1: Specification of spectrometer

Mounting	Czerny-Turner

Parameters	Specifications
Focal length	1 m
Thermoregulation	Yes
Variable resolution	Yes
Nitrogen purge	Yes
Grating number of grooves	2400 gr/mm
Orders	2
1st order resolution	0.005 nm
2nd order resolution	0.010 nm

Table 2: Specification of RF Generator

Type of generator	Solid state

Parameters	Specifications
Observation	Radial
Frequency	40.68 MHz
Control of gas flowrate	By computer
Control of pump flow	By computer
Cooling	Air

5 Operating conditions

The operating conditions are listed in Table 3 below.

Table 3: Operating conditions

	Sample 1	Sample 2
Generator power	1300 W	1100 W
Parameters	**Specifications**	
Plasma gas flowrate	12 L/min	12 L/min
Auxiliary gas flowrate	Not used	Not used
Sheath gas flowrate	0.2 L/min	0.3 L/min
Nebulizer gas flowrate	0.85 L/min	0.85 L/min
Nebulizer flowrate	3.2 bars (47 psi)	3.2 bars (47 psi)
Sample uptake	1 mL/min	1 mL/min
Type of nebulizer	Parallel flow	Parallel flow
Type of spray chamber	Cyclonic	Cyclonic
Argon humidifier	No	No
Injector tube diameter	3.0 mm	3.0 mm

Because the matrix of sample 2 had lower dissolved solids, a lower generator power was used.

6 Wavelength selection and analytical conditions

The most sensitive line for each element was used. In some cases two lines were employed because of known interferences.

Table 4: Analytical conditions

All elements	20 x 15	Gauss	0.2 - 0.5

Element	Slits (μm)	Analysis mode	Integration time (sec)

Wavelengths and background correction points are shown below in table 5.

Table 5: Wavelengths used for analysis

Cd	228.802	0.5
Cr	267.716	0.5
Cu	324.754	0.5
K	766.490	0.5

Element	Wavelength (nm)	Integration time (s)
Mo	202.030	0.5
Na	589.592	0.5
Ni	221.647	0.5
Pb	220.353	0.5
Sb	206.833	0.5
Sn	189.989	0.5
Zn	213.856	0.2
Zr	349.621	0.5

7 Results

7.1 Calibration

Four calibration standards were prepared using the fusion salt and the acid to matrix match the standards to the samples.

For analysis of sample 1 (all concentrations are in mg/L).

Table 6: Standard Concentrations

Element	Std 0	Std 1	Std 2	Std 3
Cd	0	2		
Cr	0	2	20	
Cu	0	2	20	
Mo	0	2		
Ni	0	2		
Pb	0		20	500
Sb	0	2		
Sn	0	2		
Zn	0		20	500
Zr	0	2		
K	0		20	
Na	0	2	20	

Element	Blank	Std 1	Std 2	Std 3

7.2 Limits of detection

The limits of detection are calculated using the formula in 2.3.

Table 7: Limits of detection

Element	Wavelength (nm)	BEC (mg/L)	RSD Blank (%)	LD (µg/L)
Cd	228.802	0.0204	0.23	0.10
Cr	267.716	0.037	0.32	0.40
Cu	324.754	0.052	0.29	0.45
Mo	202.030	0.0158	0.45	0.20
Ni	221.647	0.0206	0.59	0.40
Pb	220.353	0.2359	0.45	3.20
Sb	206.833	0.221	0.54	3.60
Sn	189.989	0.0799	0.63	1.50
Zn	213.856	0.0532	0.44	0.70
Zr	349.621	0.0616	0.28	0.50
K	766.490	0.7982	0.60	14.0
Na	589.592	0.364	0.50	5.50

The limits of detection depend on the level of contaminants. For example, either the standards were contaminated with Cu from the deionized water, acid or fusion salt. The contaminated level is estimated to be 0.362 mg/L.

7.3 Analytical results

Table 8: Results

	Dust			
	Concentration (mg/L)		RSD (%) on 3 replicates	Expected Concentrations
Cd	2.65	1.1		< 2
Cr	2.97	0.5		3 < Cr < 10
Cu	6.33	1.5		3 < Cu < 10
Mo	0.0797		3.3	< 2*
Ni	0.569		0.8	< 2
Pb	129.3	0.1		40 < Pb < 500
Sb	0.369		1.5	< 2
Sn	1.75		0.95	< 2
Zn	459.8		0.6	40 < Zn < 500
Zr	0.0182		2.2	< 2

	Dust		
	Concentration (mg/L)	RSD (%) on 3 replicates	Expected Concentrations
K	12.50	2.2	3 < K < 15
Na	19.50	1.3	3 < Na < 15

We believe that Cd contamination may have occurred. Na is out of the range due to contaminants added during the preparation of the sample.

7.4 Stability test

The sample was measured ten times.

Table 9.1: Results of stability test

	Cd	Cr	Cu	Mo	Ni
	2.5823	2.9108	6.2633	0.0758	0.565
	2.4913	2.9168	6.0706	0.0744	0.5669
	2.7126	2.9013	6.338	0.0797	0.5714
	2.6169	2.9689	6.4002	0.0762	0.5495
	2.7059	2.9818	6.5185	0.0796	0.5682
	2.6771	2.9587	6.3231	0.0824	0.5755
	2.6452	2.9545	6.3928	0.0771	0.5566
	2.6143	2.9861	6.4329	0.0765	0.5728
	2.6385	3.0375	6.2025	0.0774	0.5702
	2.6896	3.0646	6.3647	0.0724	0.5642
RSD (%)	2.5	1.8	2.0 3.7	1.4	
Mean value	2.64	2.97	6.33	0.077	0.57

Table 9.2: Results of stability test

	Pb	Sb	Sn	Zn	Zr
	125.87	0.3517	1.6545	437.757	0.0185
	126.97	0.3268	1.6557	453.570.0187	
	128.37	0.3422	1.7203	456.3194	0.0182
	127.6	0.3821	1.7406	459.1573	0.0179
	132.74	0.3656	1.7027	462.0504	0.0178
	132.49	0.3935	1.8268	456.860.0181	
	132.39	0.3709	1.7156	460.360.0186	
	129.65	0.3629	1.7305	439.050.0183	
	128.3	0.3743	1.748	449.92	0.0177
	129.87	0.371	1.7638	450.28	0.0188
RSD (%)	1.9	5.3	2.9	1.9 2.1	
Mean value	129.43	0.36	1.73	452.53	0.018

Table 9.3: Results of stability test

	K	Na
	13.1726	20.1005
	12.9057	20.5959
	13.1669	19.3722
	12.5343	19.7364
	13.116	18.9523
	12.4106	19.5085
	12.486	19.0537
	13.1377	19.526
	11.8138	19.1854
	12.7337	19.2672
	11.9276	19.4772
	12.5840	19.2672
RSD (%)	3.7 2.4	
Mean value	12.67	19.50

8 Summary

This application report shows that the ICP-AES is a technique suitable for the fast analysis of dust samples for a variety of elements, including alkali elements. The high content of fusion salt doesn't disturb the plasma due to the high power available. Even with the difficult matrix, the limits of detection are excellent.

info-sci.fr@horiba.com
www.horiba.com/scientific

HORIBA Scientific

France: HORIBA Jobin Yvon S.A.S., 16-18 rue du Canal, 91165 Longjumeau Cedex - Tel: +33 (0)1 64 54 13 00 - Fax: +33 (0)1 69 09 07 21 - Email: info-sci.fr@horiba.com
USA: HORIBA Jobin Yvon Inc., 3880 Park Avenue, Edison, NJ 08820-3012. Toll-free: +1-866-jobinyvon - Tel: +1-732-494-8660 - Fax: +1-732-549-5125 Email: info-sci.us@horiba.com
Japan: HORIBA Ltd., Scientific Instruments Sales Dept., Alte-Building Higashi-Kanda, 1-7-8 Higashi-Kanda, Chiyoda-ku, 101-0031 Tokyo - Tel: +81 (0)3 3861 8231 Fax: +81 (0)3 3861 8259 - Email: info-sci.jp@horiba.com
Germany: HORIBA Jobin Yvon GmbH, Hauptstrasse 1, 82008 Unterhaching - Tel: +49 (0)89 46 23 17-0 - Fax: +49 (0)89 46 23 17-99 - Email: info-sci.de@horiba.com
Italy: HORIBA Jobin Yvon Srl, Via Cesare Pavese 35/AB, 20090 Opera (Milano) - Tel: +39 0 2 57 60 30 50 - Fax: +39 0 2 57 60 08 76 - Email: info-sci.it@horiba.com
UK: HORIBA Jobin Yvon Ltd, 2 Dalston Gardens, Stanmore, Middlesex HA7 1BQ - Tel: +44 (0)20 8204 8142 - Fax: +44 (0)20 8204 6142 - Email: info-sci.uk@horiba.com
China: HORIBA Jobin Yvon SAS, Room 1801, Capital Tower No.6, Jianguomenwai Av., Chaoyang District, Beijing 100022 - Tel: +86 (0)10 8567 9966 - Fax: +86 (0)10 8567 9066 Email: info-sci.cn@horiba.com
Other Countries: Tel: +33 (0)1 64 54 13 00 - Email: info.sci@horiba.com