Application Note

Fast Elemental Determination of Environmental Samples with ICP-OES

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1 Introduction

Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES) is an efficient analytical process for the determination of inorganic pollutants in environmentally relevant matrices. With the establishment of EPA Method 200.7, ISO 11885: 1997 and DIN 38 406, Part 22 the application of this technique has been selected as the standard method of analysis for water, wastewater and sludge. Customer applications may vary from one lab to the next: monitoring toxic elements in effluents or sludges, leachates from wastes, and even air particulates in the working atmosphere.

The application of ICP-OES is described for wastewaters analyzed using DIN 38 406, Part 22 for the following 33 elements:

Ag	Be	Cr	Mg	P	Si	W
Al	Bi	Cu	Mn	Pb	Sn	Zn
As	Ca	Fe	Mo	S	Sr	Zr
B	Cd	K	Na	Sb	Ti	
Ba	Co	Li	Ni	Se	V	

Chemical matrix effects in ICP-OES are very small compared to other analytical procedures. This means that similar analytical procedures can be applied even with large variations in composition. Therefore, similar ICP methods are suitable for the analysis of water with large differences in dissolved solids (e.g. drinking, ground, surface and wastewater, sludge, sediment and ash).

2 Standard preparation

10 mg/L multi-elemental standards were prepared in 5% (v/v) HNO_3 from single elemental solutions (SpexCertiprep*). To ensure of the compatibility of the elements; seven standards solutions were prepared. Standard VII (250 mg/L) was used for the analysis of air particulates.

Table 1: Standard composition

Standard	Elements
Standard I	Al, Be, Cd, Co, Cr, Cu, Fe, Pb, Li, Mn, Mo, Ni, V, Zn, Bi, Si, Sr, W, Zr
Standard II	Sn, Ti, As, Se, Sb
Standard III	Ba
Standard IV	Ag
Standard V	B
Standard VI	Ca, Mg, Na, K, S, P
Standard VII	Fe, Si, Al

3 Instrument specification

The JY ULTIMA 2 CE spectrometer was used to perform these analyses. The specifications of this instrument are given in Tables 2 and 3.

Table 2: Specification of polychromator

Parameters	Specifications
Mounting	Paschen Runge
Focal length	0.5m
Nitrogen purge	Yes
Variable resolution	Yes
Grating number of grooves	3600 gr/mm
1st order resolution	0.022 nm
2nd order resolution	0.011 nm
Order	2nd order

(*www.certiprep.com)

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Table 3: Specification of monochromator

Parameters	Specifications
Mounting	Czerny Turner
Focal length	1m
Nitrogen purge	Yes
Variable resolution	Yes
Grating number of grooves	2400 gr/mm
Order	2nd order

Table 4: Specification of RF Generator

Parameters	Specifications
Type of generator	Solid state
Observation	Axial
Frequency	40.68 MHz
Control of gas flowrate	by computer
Control of pump flow	by computer
Cooling	air

4 Operating conditions

The operating conditions are listed in Table 5 below.

Table 5: Operating conditions

Parameter	Condition
RF Generator power	1200 W
Plasma gas flowrate	12 L/min
Auxiliary gas flowrate	0.2 L/min
Sheath gas flowrate	0.2 L/min
Nebulizer flowrate	3 bars, 0.85 ml/min
Sample uptake	1 mL/min
Type of nebulizer	Meinhard and USN
Type of spray chamber	Cyclonic
Argon humidifier	Yes
Injector tube diameter	3.0 mm

5 Wavelength selection and analytical conditions

The line with the highest sensitivity was used for all elements, as there were no particular interference problems. The analysis conditions were the same for all elements.

Table 5: Analytical conditions

Elements	Integration time on peak (sec)	Integration time for background (sec)
All elements	40	13

6 Discussion

Several examples of ICP-OES for environmental analysis are presented in the following sections.

6.1 Waste Water

A major problem encountered with this method was the sensitivity for Pb and Se. Background correction was used to compensate for matrix effects that affect the linearity and the accuracy.
The major parameters that influence these matrix effects are the RF generator power, the nebulizer gas and the diameter of the injector tube. An increase in the power produces less matrix effects and enhances sensitivity for elements like Pb, Cd, As, Se. This is the reason the power was set to 1200 W. To minimize matrix effects, one can also decrease the nebulizer gas. However, it was preferred not to modify this parameter, as it would have affected the sensitivity.

6.2 Background Corrections

The following samples were prepared to set background corrections:
1) 10 ppm of the analytes,
2) 200 ppm Fe, 500 ppm Ca, Al, Mg and 1 ppm of the analytes.

Note: Setting two background points for an element (such as Pb and Se) increased the Relative Standard Deviation (RSD) of the measurements, which degraded the detection limits. The positions in nm used on the JY ULTIMA 2 CE are listed in Table 7.

Table 7: Background correction points

Elements	Wavelength (nm)	Background correction (nm)
As	193.695	+ 0.096
B	208.959	- 0.039
Ba	233.527	- 0.108
Be	313.042	- 0.116
Cd	226.502	+ 0.066
Co	228.616	- 0.108
Cr	267.716	- 0.039
Cu	324.754	- 0.108
Fe	271.441	+ 0.100
Mn	257.610	+ 0.096
Mo	202.032	- 0.039
Ni	231.604	+ 0.066
Sr	407.771	- 0.108
V	311.071	+ 0.066
Zn	213.856	- 0.039
Ca	317.933	- 0.108
K	766.490	- 0.108
Mg	279.079	- 0.108
Na	589.592	+0.096
Al	308.215	- 0.039
Ti	337.279	- 0.108
Sn	189.926	- 0.108
Tl	190.800	- 0.108
Se	196.020	- 0.0507/+ 0.096
Sb	206.833	+ 0.096
Pb	220.353	- 0.039/+0.039
Ag	328.068	+ 0.096
Sc	361.384	-0.108
Li	670.776	-0.108

6.3 Linearity

The linear range for each element must be determined by calibrating with a high standard (1 ppm). Only a two-point linear calibration curve must be used. To be considered linear, a solution must be read back at ± 5% of the standard value. Al, Mg, Ca, Fe must be linear to 600 ppm.

The linear range was measured for the major elements: Fe, Al, Mg and Ca. The linear ranges were determined by calibrating with the high standard (1 ppm) and by analyzing 600 ppm of the analytes. An internal standard was NOT used. This would improve the accuracy. The results are given in Table 8.

Table 8: Linear range with 1 ppm calibration

Elements	Mg	Fe	Al	Ca
Conc. Found (ppm)	625.8	573.6	544.0	533.5
Accuracy (%)	4.3	4.4	9.3	11.1

Table 9 gives the linear range obtained previously with a different calibration. The linear ranges were determined by calibrating with single element solutions:

0 & 100 ppm of Mg
0 & 10 ppm of Fe
0 & 1 ppm of Al
0 & 100 ppm of Ca

Table 9: Linear range with single element calibration

Elements	Mg	Fe	Al	Ca
Conc. Found (ppm)	608.6	597.1	567.6	574.1
Accuracy (%)	1.4	0.5	5.4	4.3

6.4 Linearity Test

The linearity was also tested with the 29 other elements at 10 ppm: the results of the measurements are given in Table 10.

Table 10: Linearity data

Elements	Concentration found (ppm)	Accuracy (%)
Sn	10.849	8
Tl	10.751	7
As	10.341	3
Se	10.087	1
Mo	10.914	9
Sb	10.443	4
B	10.170	2
Zn	10.379	4
Pb	10.857	9
Cd	10.952	10
Co	10.967	10
Ni	11.031	10
Ba	10.951	9
Mn	10.867	9
Cr	10.904	9
Fe	10.873	9
Mg	9.976	0.2
Al	9.537	5
V	10.538	5
Be	10.616	6
Ca	11.106	11
Cu	10.147	1
Ag	10.282	3
Ti	10.379	4
Sc	10 381	4
Sr	10.264	3
Na	8.260	17
Li	11.609	16
K	8.077	19

6.5 Limits of Detection in µg/L (at 3 sigma)

All the calibrations were done with 1000 ppb multi-element solutions (See Above). Table 11 shows the US EPA Contract Required Detection Limits (CRDL) and the LOD reached by the JY ULTIMA 2 CE with pneumatic nebulization and with Ultrasonic Nebulization (USN). All the detection limits required by the US EPA are achieved. N.A. indicates there is no value established for this element.

The spectrometer was calibrated, for all elements, using a blank sample and a 1 mg/L standard solution. Table 12 presents the values for SRM 1643b in ppb.

Table 11: Detection Limits

Elements	ULTIMA 2CE	ULTIMA 2CE USN	CRDL
Al	1	0.3	200
Ag	0.3	0.06	10
As	2.8	0.4	10
B	0.2	0.03	N.A.
Ba	0.24	0.05	200
Be	0.43	0.04	5
Ca	0.03	0.01	5000
Cd	0.17	0.05	5
Co	0.49	0.06	50
Cr	0.52	0.07	10
Cu	0.63	0.06	25
Fe	0.27	0.05	100
K	2.0	0.5	5000
Li	0.08	0.02	N.A.
Mg	0.036	0.009	5000
Mn	0.08	0.03	15
Mo	0.39	0.05	N.A.
Na	2.0	0.5	5000
Ni	0.7	0.12	40
P	2.2	0.9	N.A.
Pb	2.3	0.6	3
S	1.4	0.5	N.A.
Sb	2.5	0.7	60
Sc	0.08	0.02	N.A.
Se	3.5	0.7	5
Sn	1.4	0.4	N.A.
Sr	0.007	0.002	N.A.
Ti	0.18	0.05	N.A.
Tl	2.5	0.5	10
V	0.4	0.06	50
Zn	0.26	0.05	20
Zr	0.07	0.02	N.A.

Table 12: Results for SRM 1643b

Elements	Certified Values	Measured Values
As	(49)*	45 ± 5
B	(94)	97 ± 1
Ba	44 ± 2	43 ± 0.4
Be	19 ± 2	18 ± 0.2
Cd	20 ± 1	20 ± 0.2
Co	26 ± 1	26 ± 1
Cr	18.6 ± 0.4	18 ± 0.4
Cu	21.9 ± 0.4	21.9 ± 0.3
Fe	99 ± 8	101 ± 1
Mn	28 ± 2	26 ± 0.4
Mo	85 ± 3	86 ± 2
Ni	49 ± 3	48 ± 1
Sr	227 ± 6	222 ± 4
V	45.2 ± 0.4	45 ± 1
Zn	66 ± 2	67 ± 1

* Not Certified Values

6.6 Sewage Sludge

Sewage sludge was dissolved with aqua regia (2.5 g of sample was heated under reflux in 25 mL aqua regia for 1 hour and then diluted to 200 ml). With this technique, not all of the sample may be completely dissolved, particularly the elements Al, Be, Ti and V. In the following analysis, the six elements common to sewage sludge are determined for BCR Standards 144 and 145. Because of the high Ca and Fe content, it is convenient to dilute the sample and to make a matrix adjustment. The spectrometer was standardized with a blank sample and a 1 mg/L multi-element standard for Cd, Cr, Cu, Ni and Pb and with a 10 mg/L standard for Zn.

Table 13: Results for BCR 144 and BCR 145

Elements	BCR 144	BCR 144	BCR 145	BCR 145
Cd	3.4	3.3	18	17.2
Cr	(485)*	414	(105)*	77
Cu	713	724	429	419
Ni	942	964	41.4	39.2
Pb	495	481	349	338
Zn	3143	3095	2843	2792

* Not Certified Values

6.7 Air Particulates

250 mg of an air particulate sample was dissolved in 5 ml HNO_3 and 1 ml HF under pressure. The clear solution was diluted to 250 mL. Table 14 gives the analyzed elements, the standards used, as well as the certified and measured values.

Table 14: Analysis of certified air particulate SRM 1633a

Elements	StdLow (mg/L)	STDHigh (mg/L)	Certified Value %	Mesaured Value %
Ca	0	10	1.11	1.12
Fe	50	250	9.40	9.21
K	0	10	1.88	1.91
Mg	0	10	0.455	0.438
Na	0	10	0.17	0.17
Si	100	250	22.8	22.1
Al	100	250	(14)*	13.96
Ba	0	10	(0.15)*	0.13
Ti	0	10	(0.8)*	0.89
As	0	1	145	153
Cr	0	1	196	190
Cu	0	1	118	114
Ni	0	1	127	123
Sr	0	1	830	820
Zn	0	1	220	223
Be	0	1	(12)*	13
Co	0	1	(46)*	54

* Not Certified Value

7 Summary

The detection limits passed the criteria set by the US EPA. The use of an internal standard would improve the accuracy of the measurements. However, if the user does not require accuracy better than 5%, this analytical method (without internal standard) shows the possibility to replace Graphite Furnace Atomic Absorption by ICP. The simplicity of this method shows that the JY ULTIMA 2 CE can be used for routine analysis of environmental samples.

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