Application Note

Analysis Repeatability of Trace and Major Elements in a Water Sample

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Keywords: environment
Elements: Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Se, Si, Zn

1 Introduction

This Application Note examines the analysis repeatability of trace and major levels of elements in a water sample. The water sample was initially analyzed using a rapid semi-quantitative method to determine the concentration range for all the elements. Five successive analyses were then measured, using a quantitative method, to establish the repeatability of both low and high concentrations.

2 Principle

2.1 Technique used

The elemental analysis of these 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.

3 Sample Preparation

The water samples were stabilized in 1% HNO_3.

4 Instrument specification

The work was performed on a ULTIMA 2 with the specifications shown below.

Table 1: Specification of spectrometer

Parameters	Specifications
Mounting	Czerny-Turner
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

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

The operating conditions of the spectrometer are listed in Table 3.

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Table 3: Operating conditions

Parameter	Condition
Generator power	1050 W
Plasma gas flowrate	12 L/min
Auxiliary gas flowrate	0 L/min
Sheath gas flowrate	0.2 L/min
Nebulizer	0.5 L/min at 2.82 bars
Sample uptake	1 mL/min
Type of nebulizer	Meinhard C1 type
Type of spray chamber	Cyclonic
Argon humidifier	No
Injector tube diameter	3.0 mm

Below you will find calibration curves of some elements, with standards prepared in 1% HNO_3.

5 Calibration

Line: Al, 167.020 nm

Calibr. curve: C = -0.00003408 + 0.00000819 * X

Parameters of curve

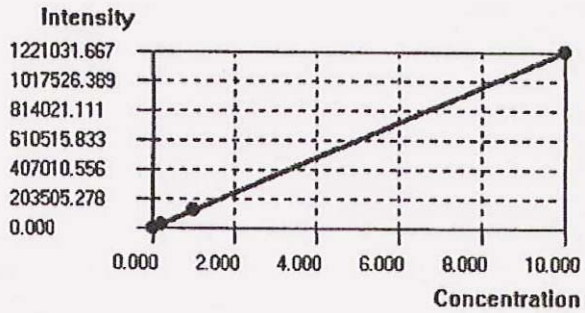
Sigma : 0.011722

BEC : 34.1 ng/l

LOD : ***

Correl. : 1

Weight: not used



#	Sample Name	Intensity	Chem. Conc.	Calc. Conc.		Rel. dev(%)	Valid
1.	Std0	57.33	0	0	mg/l		Yes
2.	Std1	121021.00	1	0.991	mg/l	0.88	Yes
3.	Std10	1221031.6	10	10.00	mg/l	0.007	Yes
4.	StdAlBa0.2	25359.67	0.2	0.208	mg/l	3.84	Yes

Line: As, 189.042 nm

Calibr. curve: C = -0.0003359 + 0.00002343 * X

Parameters of curve

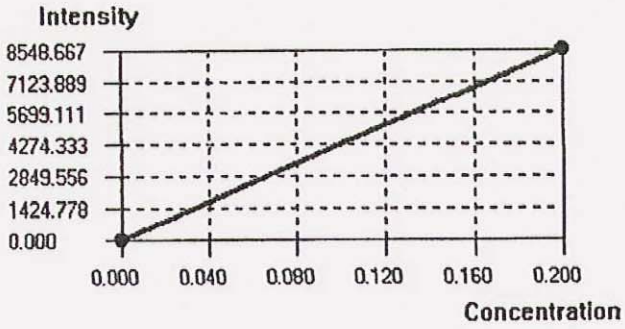
Sigma : 0

BEC : 336 ng/l

LOD : ***

Correl. : 1

Weight: not used



#	Sample Name	Intensity	Chem. Conc.	Calc. Conc.		Rel. dev(%)	Valid
1.	Std0	14.33	0	0	mg/l		Yes
2.	StdQC210.2	8548.67	0.2	0.20	mg/l	0	Yes

Line: P, 178.229 nm

Calibr. curve: C = -0.01449 + 0.000009582 * X

Parameters of curve

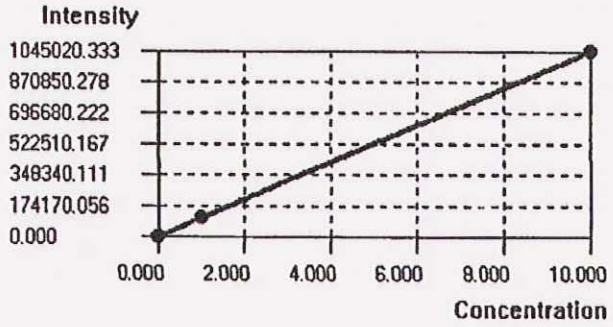
Sigma : 0.012816

BEC : 14.5 µg/l

LOD : ***

Correl. : 1

Weight: not used



#	Sample Name	Intensity	Chem. Conc.	Calc. Conc.		Rel. dev(%)	Valid
1.	Std0	620.67	0	0	mg/l		Yes
2.	Std1	106865.00	1	1.01	mg/l	0.95	Yes
3.	Std10	1045020.3	10	10.00	mg/l	0.009	Yes

Line: **Si, 251,611 nm**

Calibr. curve: C = -0,01586 + 0,00001884 * X

Parameters of curve

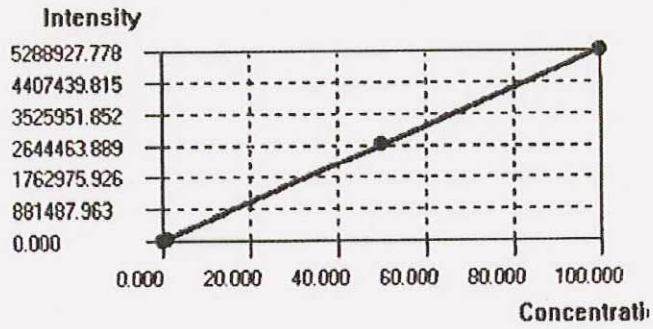
Sigma : 0,13689

BEC : 15,9 µg/l

LOD : ***

Correl. : 0,99997

Weight: 1/sqrt(I)



#	Sample Name	Intensity	Chem. Conc.	Calc. Conc.		Rel. dev(%)	Valid
1.	Std0	331,11	0	0	mg/l		Yes
2.	Std1	58705,56	1	1,09	mg/l	8,99	Yes
3.	Std100	5288927,7	100	99,61	mg/l	0,39	Yes
4.	Std50	2683830,0	50	50,54	mg/l	1,07	Yes

Line: **Zn, 213.856 nm**

Calibr. curve: C = -0.0007182 + 0.000002019 * X

Parameters of curve

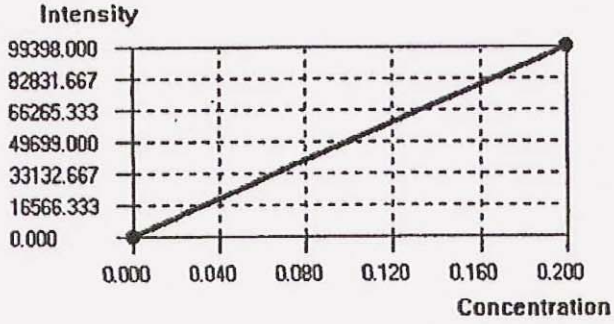
Sigma : 0

BEC : 718 ng/l

LOD : ***

Correl. : 1

Weight: not used



#	Sample Name	Intensity	Chem. Conc.	Calc. Conc.		Rel. dev(%)	Valid
1.	Std0	355.67	0	0	mg/l		Yes
2.	StdQC210.2	99398.00	0.2	0.20	mg/l	0	Yes

6 Wavelength selection and analytical conditions

Table 4: Wavelength and analytical conditions

El	Wavelength (nm)	Measured point	Calculated points	Integration time	Entrance slit (µm)	Exit slit (µm)	Increment (nm)	Mode of analysis
Al	167.020	5	1	0.5	22	15	0.002	Max
Al	396.152	1	1	4.0	22	15	0.002	Max
As	189.042	5	1	0.5	22	15	0.002	Max
B	249.773	5	1	0.5	22	15	0.002	Max
B	182.529	5	1	0.5	22	15	0.002	Max
Ba	455.403	5	1	0.5	22	15	0.002	Max
Ca	317.933	1	1	3.0	22	80	0.002	Max
Cd	228.802	1	1	4.0	22	15	0.002	Max
Co	228.616	5	1	0.5	22	15	0.002	Max
Cr	267.716	5	1	1.0	22	15	0.002	Max
Cu	324.754	5	1	0.5	22	15	0.002	Max
Fe	259.940	5	1	0.5	22	15	0.002	Max
Hg	194.163	1	1	4.0	22	15	0.002	Max
K	766.490	7	5	0.5	22	15	0.002	Gauss
Li	670.784	1	5	3.0	22	15	0.002	Max
Mg	279.806	1	1	3.0	22	80	0.002	Max
Mn	257.610	5	1	0.5	22	15	0.002	Max
Mo	202.03	5	1	0.5	22	15	0.002	Max
Na	589.592	1	1	3.0	22	80	0.002	Max
Ni	221.647	5	1	0.5	22	15	0.002	Max
P	178.229	5	1	0.5	22	15	0.002	Max
Pb	220.353	1	1	4.0	22	15	0.002	Max
S	180.676	1	1	3.0	22	80	0.002	Max
Se	196.026	1	1	4.0	22	15	0.002	Max
Si	251.611	1	1	3.0	22	80	0.002	Max
Zn	213.856	5	1	1.0	22	15	0.002	Max

7 Results

Five independent analyses were undertaken on each sample to test the repeatability on trace, minor, and major elements. Each analysis was made using 3 replicates. The total analysis time for the 20 elemental lines was 7 minutes, including 1 minute for rinse and sample transfer, using the autosampler. This analysis time can be decreased down to 4 minutes if high throughput is required, without causing a large change in the performance. In the Table below, the repeatability for each element is presented. The last column corresponds to the concentration obtained by the semi-quantitative method. The concentrations are expressed in mg/L.

Table 5.1: Al repeatability

	Sample	Cc (mg/L)	RSD(%)	Cc S.Q. (mg/L)
Al 167.020	A 1	0.0327	7.96	
	A 2	0.0352	4.59	
	A 3	0.0330	4.80	
	A 4	0.0338	4.24	
	A 5	0.0345	6.42	
	Mean	0.0338	5.60	0.035
	SD	0.0010		
	RSD	3.09		

Table 5.2: As repeatability

	Sample	Cc (mg/L)	RSD(%)	Cc S.Q. (mg/L)
As 189.042	A 1	0.0034	27.57	
	A 2	0.0044	30.64	
	A 3	0.0053	17.65	
	A 4	0.0040	32.38	
	A 5	0.0054	27.24	
	Mean	0.0043	27.10	< LD
	SD	0.00069		
	RSD	16.14		
Obtained concentration ~ 3.5 * LD				

Table 5.3: B (192 nm) repeatability

	Sample	Cc (mg/L)	RSD(%)	Cc S.Q. (mg/L)
B 182.529	A 1	0.0606	0.68	
	A 2	0.0626	4.73	
	A 3	0.0577	2.59	
	A 4	0.0608	3.63	
	A 5	0.0599	2.13	
	Mean	0.0603	2.75	
	SD	0.0018		
	RSD	2.93		

Table 5.4: B (249) repeatability

	Sample	Cc (mg/L)	RSD(%)	Cc S.Q. (mg/L)
B 249.773	A 1	0.0601	1.18	
	A 2	0.0571	1.47	
	A 3	0.0590	1.74	
	A 4	0.0586	2.26	
	A 5	0.0576	3.10	
	Mean	0.0585	1.95	0.060
	SD	0.0012		
	RSD	2.01		

Table 5.5: Ba repeatability

	Sample	Cc (mg/L)	RSD(%)	Cc S.Q. (mg/L)
Ba 455.403	A 1	0.0258	0.67	
	A 2	0.0253	1.26	
	A 3	0.0258	0.28	
	A 4	0.0260	0.54	
	A 5	0.0255	1.65	
	Mean	0.0257	0.88	0.029
	SD	0.00025		
	RSD	0.99		

Table 5.6: Ca repeatability

	Sample	Cc (mg/L)	RSD(%)	Cc S.Q. (mg/L)
Ca 317.933	A 1	87.24	0.78	
	A 2	87.11	0.19	
	A 3	87.08	0.02	
	A 4	87.33	0.57	
	A 5	87.43	0.49	
	Mean	87.24	0.41	81.69
	SD	0.15		
	RSD	0.17		

Table 5.7: Cd repeatability

	Sample	Cc (mg/L)	RSD(%)	Cc S.Q. (mg/L)
Cd 228.802	A 1	0.00037	14.68	
	A 2	0.00037	20.13	
	A 3	0.00031	24.45	
	A 4	0.00028	17.01	
	A 5	0.00036	19.54	
	Mean	0.00034	19.16	0.001
	SD	0.000043		
	RSD	12.61		
Obtained concentration ~ 3.5 * LD				

Table 5.8: Cr repeatability

	Sample	Cc (mg/L)	RSD(%)	Cc S.Q. (mg/L)
Cr 267.716	A 1	0.00138	6.52	
	A 2	0.00114	15.67	
	A 3	0.00110	10.96	
	A 4	0.00113	3.94	
	A 5	0.00146	10.58	
	Mean	0.00124	9.54	0.002
	SD	0.00017		
	RSD	13.55		

Table 5.9: Cu repeatability

	Sample	Cc (mg/L)	RSD(%)	Cc S.Q. (mg/L)
Cu 324.754	A 1	0.0187	1.94	
	A 2	0.0187	2.83	
	A 3	0.0193	4.62	
	A 4	0.0191	3.17	
	A 5	0.0193	2.44	
	Mean	0.0190	3.00	0.022
	SD	0.00030		
	RSD	1.58		

Table 5.10: Fe repeatability

	Sample	Cc (mg/L)	RSD(%)	Cc S.Q. (mg/L)
Fe 259.940	A 1	0.0530	2.16	
	A 2	0.0530	1.08	
	A 3	0.0540	1.06	
	A 4	0.0531	2.85	
	A 5	0.0550	1.04	
	Mean	0.0536	1.64	0.057
	SD	0.00086		
	RSD	1.61		

Table 5.11: Hg repeatability

	Sample	Cc (mg/L)	RSD(%)	Cc S.Q. (mg/L)
Hg 194.163	A 1	< LD		
	A 2	< LD		
	A 3	< LD		
	A 4	< LD		
	A 5	< LD		
	Mean	< LD		< LD
	SD			
	RSD			

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Table 5.12: K repeatability

	Sample		Cc (mg/L)	RSD(%)	Cc S.Q. (mg/L)
K 766.490	A 1	6.14	1.70		
	A 2		5.87	4.64	
	A 3		6.07	2.61	
	A 4		5.83	1.96	
	A 5		5.80	0.56	
		Mean	5.94	2.29	5.52
		SD	0.15		
		RSD	2.55		

Table 5.13: Mg repeatability

	Sample		Cc (mg/L)	RSD(%)	Cc S.Q. (mg/L)
Mg 279.806	A 1	15.29	0.44		
	A 2	15.35	0.34		
	A 3	15.24	0.60		
	A 4	15.11	0.26		
	A 5	15.21	0.20		
		Mean	15.24	0.37	15.81
		SD	0.09		
		RSD	0.59		

Table 5.14: Mn repeatability

	Sample		Cc (mg/L)	RSD(%)	Cc S.Q. (mg/L)
Mn 257.610	A 1		0.0105	0.41	
	A 2		0.0106	1.54	
	A 3		0.0105	0.27	
	A 4		0.0105	1.62	
	A 5		0.0105	0.99	
		Mean	0.0105	0.97	0.006
		SD	0.00006		
		RSD	0.53		

Table 5.15: Na repeatability

	Sample		Cc (mg/L)	RSD(%)	Cc S.Q. (mg/L)
Na 589.592	A 1		23.52	1.17	
	A 2		23.32	1.12	
	A 3		23.48	0.85	
	A 4		23.05	0.16	
	A 5		22.94	0.29	
		Mean	23.26	0.72	23.81
		SD	0.26		
		RSD	1.10		

Table 5.16: P repeatability

	Sample		Cc (mg/L)	RSD(%)	Cc S.Q. (mg/L)
P 178.229	A 1		0.0680	3.25	
	A 2		0.0658	4.94	
	A 3		0.0670	1.24	
	A 4		0.0670	5.82	
	A 5		0.0664	1.96	
		Mean	0.0669	3.44	0.072
		SD	0.00083		
		RSD	1.24		

Table 5.17: Pb repeatability

	Sample		Cc (mg/L)	RSD(%)	Cc S.Q. (mg/L)
Pb 220.353	A 1		0.00363	14.27	
	A 2		0.00348	8.36	
	A 3		0.00398	6.05	
	A 4		0.00250	16.46	
	A 5		0.00382	6.01	
		Mean	0.00348	10.23	< LD
		SD	0.00058		
		RSD	16.66		
Obtained concentration ~ 2.3 * LD					

Table 5.18: Se repeatability

	Sample	Cc (mg/L)	RSD(%)	Cc S.Q. (mg/L)
Se 196.026	A 1	0.0061	10.23	
	A 2	0.0054	19.73	
	A 3	0.0076	6.76	
	A 4	0.0096	9.94	
	A 5	0.0073	13.02	
	Mean	0.0072	11.94	0.007
	SD	0.0016		
	RSD	22.06		

Table 5.19: Si repeatability

	Sample	Cc (mg/L)	RSD(%)	Cc S.Q. (mg/L)
Si 251.611	A 1	5.95	0.17	
	A 2	5.92	0.56	
	A 3	5.91	0.32	
	A 4	5.88	0.30	
	A 5	5.98	0.45	
	Mean	5.93	0.36	5.5
	SD	0.04		
	RSD	0.64		

Table 5.20: Zn repeatability

	Sample	Cc (mg/L)	RSD(%)	Cc S.Q. (mg/L)
Zn 213.856	A 1	0.00591	1.64	
	A 2	0.00621	2.03	
	A 3	0.00610	0.23	
	A 4	0.00601	1.38	
	A 5	0.00597	0.44	
	Mean	0.00604	1.14	0.008
	SD	0.00011		
	RSD	1.90		

The accuracy of the semi-quantitative results for traces and major elements, even if the calibration is made with two points in water (0 and 5 mg/l), is acceptable for some requirements. The detection limits are listed in Table 6 below, for both quantitative and semi-quantitative methods.

Table 6: Detection limits

Detection limits (µg/L)	DL Quantitative Method (µg/L) Water	DL Semi-quantitative Method (µg/L) Environmental samples
Ag 328.068	0.60	2.50
Al 167.020	0.20	0.80
Al 394.401	1.50	6.0
Al 396.152	1.00	4.0
As 189.042	1.20	5.0
B 249.773	0.30	1.0
Ba 455.403	0.04	0.12
Be 313.042	0.04	0.12
Br 153.114	200	800
Ca 317.933	1.5	6.0
Ca 393.366	0.03	0.12
Cd 228.802	0.09	0.40
Cl 134.664	200	800
Co 228.616	0.21	0.80
Cr 267.716	0.15	0.70
Cu 324.754	0.18	0.80
Fe 259.940	0.20	0.80
Hg 194.164	1.30	6.0
I 178.218	5.0	20.0
I 179.847	20.0	80.0
K 766.490	1.50	6.0
Li 670.784	0.50	2.0
Mg 279.806	1.0	4.0
Mg 279.553	0.03	0.12
Mn 257.610	0.05	0.20
Mo 202.030	0.20	0.80
Na 589.592	0.60	2.50
Ni 221.647	0.30	1.60
P 178.229	1.50	6.0
Pb 220.353	1.50	6.0
S 181.978	3.0	10.0

Table 6: Detection limits, continued

Detection limits (µg/L)	DL Quantitative Method (µg/L) Water	DL Semi-quantitative Method (µg/L) Environmental samples
Sb 206.833	1.50	6.0
Se 196.026	1.50	6.0
Si 251.611	1.50	6.0
Sn 189.989	1.30	6.0
Sr 407.771	0.03	0.12
Ti 337.280	0.15	0.60
Tl 190.864	1.0	4.0
V 292.402	0.20	1.0
V 311.071	0.20	1.0
W 207.911	2.0	8.0
Zn 213.856	0.10	0.50
Zr 343.823	0.30	1.20

8 Conclusion

The analysis presented in this Application Note shows that the semi-quantitative program is accurate for many applications and has the advantage of speed. This mode could be used for screening purposes for a busy laboratory. The second point to note is that the reproducibility of the replicate analysis on 5 identical samples showed standard deviations similar to those achieved when determining the limit of detection. For example, the Pb result shows a deviation of 0.58 ppb over five determinations at 3.5 ppb. In a single run, both traces and high levels can be determined with good accuracy and precision.

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