Application Note

Waste Water and Soil Samples

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1 Introduction

This Application Note examines the analysis of five different wastewater and soil samples, which are listed below.

Sample 1: Distilled water
Sample 2: Wastewater after treatment in wastewater plant (exit)
Sample 3: Wastewater before treatment in the waste plant
Sample 4: Industrial wastewater
Sample 5: Dried soil from agriculture waste, digested with HNO_3 and $HClO_4$
Samples 1-4 contained dilute HNO_3.

The 5 samples were initially analyzed using a semi-quantitative method to identify the elements and their concentration ranges in each sample. Profiles of each element of interest were taken for all the samples, which were used to show the peaks and the relative background levels. Then, quantitative analyses were performed using calibration curves at the appropriate concentration ranges. Finally, the Standard Addition Method was used to obtain results for Sample 5, as this sample may have a much more significant matrix effect.

2 Principle

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.

3 Instrument specification

The work was done on a ULTIMA 2.The specifications of this instrument are listed in Tables 1 and 2.

Table 1: Specification of spectrometer

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 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

4 Semi-quantitative analysis

The analytical approach used in this Application Note was to initially undertake a semi-quantitative analysis to detect the presence of elements and estimate their concentration range, and then perform a quantitative analysis to obtain accurate and precise results.

A semi-quantitative method is integrated into the Analyst software for the ICP. It allows for rapid identification of elements in the sample from a qualitative and quantitative point of view.

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Currently, the method contains 34 elements. Wavelengths have been chosen in order to cover a wide variety of sample types: sensitive lines for most of the elements, except for Ca, Mg; including appropriate background correction positions. A background correction point is placed on both sides of the Pb and Al peaks, in case of high concentration of Al or Ca, respectively. Calibration is performed with 2 points (0 and 5 mg/L in deionized water) and both calibration and analyses are measured with 1 "replicate". The acquisition time is 0.1 s per data point with 7 data points measured to fit a gaussian curve.

With these conditions, a semi-quantitative analysis is undertaken in about 3-4 minutes for the 34 elements and allows the identification of different kinds of samples.

Note: the matrix for the calibration standards may be adjusted (NaCl 100 g/L, 20 % H_2SO_4 ...) according to the samples that need to be analyzed, thus giving more accurate results.

The following plasma conditions were applied. Note that the power is slightly increased to 1200 W from the 1000 W that would be typically used for clean water. This is to minimize matrix effects that may have an influence on signal quantity, as the standards are in deionized water and the samples are waste water/soil and acids.

Table 3: Operating conditions

Parameter	Condition
RF Generator power	1200 W
Plasma gas flowrate	12 L/min
Auxiliary gas flowrate	0 L/min
Sheath gas flowrate	0.17 L/min
Nebulizer gas flowrate	0.76 L/min
Nebulizer flowrate	2.75 bars
Sample uptake	1 mL/min
Type of nebulizer	Cross Flow
Type of spray chamber	Scott
Argon humidifier	No
Injector tube diameter	3.0 mm
Slits	20/15 µm

Note: a Meinhard nebulizer (K3 or C1 type) and cyclonic spray chamber can be used to gain sensitivity if required. The results can be printed and/or exported from the ICP software. To validate the results, a certified sample was analyzed before measuring the samples.

Table 4: Results for sample "Reference 1643-d"

Elements	Concentration	Unit	Certified concentration
Ag 328.068	3.60	µg/L	1.27
Al 394.401	118.60	µg/L	127.6
Al 396.152	120.90	µg/L	127.6
As 189.042	56.10	µg/L	56.02
B 249.773	148.60	µg/L	144.8
Ba 455.403	485.90	µg/L	506.5
Be 313.042	8.60	µg/L	12.53
Ca 317.933	30.92	mg/L	31.04
Cd 228.802	5.20	µg/L	6.47
Co 228.616	22.00	µg/L	25.0
Cr 267.716	15.20	µg/L	18.53
Cu 324.754	20.10	µg/L	20.5
Fe 259.940	74.20	µg/L	91.2
Hg 194.164	< LD		n.c.
K 766.490	2.51	mg/L	2.36
Li 670.784	17.60	µg/L	16.5
Mg 279.806	7.44	mg/L	7.989
Mn 257.610	36.20	µg/L	37.66
Mo 202.030	111.30	µg/L	112.9
Na 589.592	21.06	mg/L	22.07
Ni 221.647	57.20	µg/L	58.1
P 178.229	< LD		n.c.
Pb 220.353	28.60	µg/L	18.15
S 181.978	144.80	µg/L	n.c.
Sb 206.833	34.40	µg/L	54.1
Se 196.026	13.40		11.43
Si 251.611	2.68	mg/L	2.7
Sn 189.989	< LD		n.c.
Sr 407.771	282.60	µg/L	294.8
Ti 337.280	< LD		n.c.
Tl 190.864	9.30	µg/L	7.28
V 292.402	28.80	µg/L	35.1
V 311.071	36.80	µg/L	35.1
W 207.911	< LD		n.c.
Zn 213.856	68.70	µg/L	72.48
Zr 343.823	< LD		n.c.

n.c. means non-certified

Table 5: Results for various samples

Line	Sample 1	2	3	4	5
Ag 328.068	< LD	< LD	< LD	0.010	0.179
Al 394.401	0.235	0.233	0.544	0.143	49.2
Al 396.152	0.271	0.256	0.592	0.120	48.5
As 189.042	< LD	< LD	< LD	< LD	0.016
B 249.773	0.045	0.466	0.216	1.07	0.159
Ba 455.403	0.046	0.076	0.090	0.170	1.30
Be 313.042	< LD	< LD	< LD	< LD	< LD
Ca 317.933	0.969	49.4	38.4	157	645
Cd 228.802	< LD	< LD	< LD	< LD	0.007
Co 228.616	< LD	< LD	< LD	< LD	< LD
Cr 267.716	< LD	< LD	0.003	0.006	2.00
Cu 324.754	0.003	0.066	0.045	0.121	3.75
Fe 259.940	0.016	0.065	0.377	0.490	119
Hg 194.164	< LD	< LD	< LD	0.032	0.479
K 766.490	0.202	5.79	3.427	389	7.40
Li 670.784	< LD	< LD	< LD	< LD	0.110
Mg 279.806	0.066	8.77	6.344	12.3	28.3
Mn 257.610	< LD	0.001	0.040	0.066	1.07
Mo 202.030	< LD	< LD	< LD	< LD	0.013
Na 589.592	1.09	33.3492	25.4	797	3.66
Ni 221.647	< LD	0.0394	0.027	0.0102	1.01
P 178.229	0.024	0.7233	0.400	6.22	42.1
Pb 220.353	< LD	< LD	0.031	< LD	0.632
S 181.978	0.384	10.0	7.19	56.8	26.2
Sb 206.833	< LD	< LD	< LD	< LD	< LD
Se 196.026	< LD	< LD	< LD	< LD	0.020
Si 251.611	0.114	3.10	3.18	6.02	5.62
Sn 189.989	< LD	< LD	< LD	< LD	0.248
Sr 407.771	0.005	0.162	0.117	0.382	1.87
Ti 337.280	< LD	< LD	0.006	< LD	0.785
Tl 190.864	< LD	< LD	< LD	< LD	< LD
V 292.402	< LD	< LD	< LD	< LD	0.181
V 311.071	< LD	< LD	< LD	< LD	0.191
W 207.911	< LD	< LD	< LD	< LD	0.087
Zn 213.856	0.098	0.181	0.184	0.184	6.38
Zr 343.823	< LD	< LD	< LD	< LD	< LD

5 Quantitative analysis

Using the results obtained from the semi-quantitative method, several standards were prepared in the appropriate concentration range for each element:

Table 6: Standard concentration

Element	Standards (mg/L) 0	1	2	3	4	5	6	7
Al	0	0.02	0.05	0.1	1	10	37.3	150
As	0	0.02	0.05	0.1	1	10		
B	0	0.02	0.05	0.1	1	10		
Cd	0	0.02	0.05	0.1	1	10		
Cr	0	0.02	0.05	0.1	1	10		
Cu	0	0.02	0.05	0.1	1	10		
Fe	0	0.02	0.05	0.1	1	10	37.3	150
Mn	0	0.02	0.05	0.1	1	10		
Ni	0	0.02	0.05	0.1	1	10		
Pb	0	0.02	0.05	0.1	1	10		
Se	0	0.02	0.05	0.1	1	10		
Zn	0	0.02	0.05	0.1	1	10		

The plasma parameters are shown in Table 7.

Table 7: Operating conditions

Parameter	Condition
RF Generator power	1100 W
Plasma gas flowrate	12 L/min
Auxiliary gas flowrate	0 L/min
Sheath gas flowrate	0.17 L/min
Nebulizer gas flowrate	0.63 L/min
Nebulizer flowrate	2.84 bars
Sample uptake	1 mL/min
Type of nebulizer	Meihnard C1
Type of spray chamber	Cyclonic
Argon humidifier	No
Injector tube diameter	3.0 mm
Slits	20/15 µm

The combination of a Meinhard C1 nebulizer and cyclonic Spray Chamber for sample introduction was used for optimum sensitivity and detection limits.

Note: sample number 5 was analyzed using the Standard Addition Method, as there may be a more significant matrix effect in this sample, compared to the first four, due to the major elements (650 mg/l of Ca and acids).

Profiles of several samples for Cd are shown below in Figure 1. This demonstrates that the matrix is different because the spectral background is raised in sample 5.

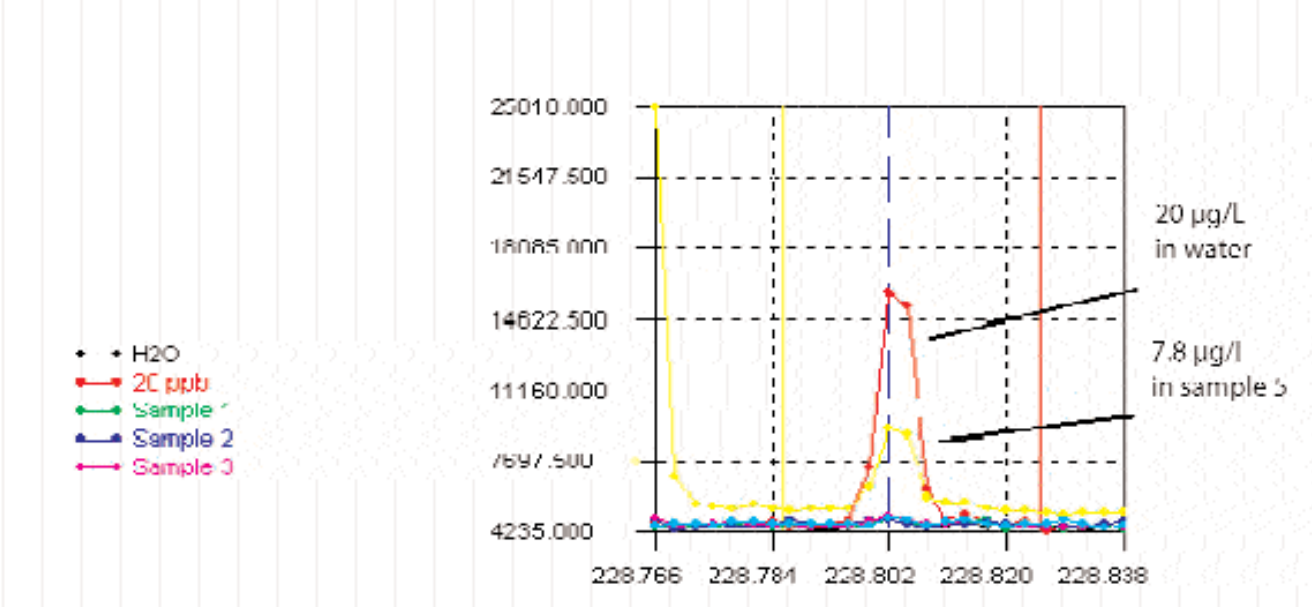

Figure 1: Cd spectrum in sample 5

The methodology of the Standard Addition Method (S.A.M.) is as follows:

· Estimate the approximate concentration for each element of interest (using a rapid semi-quantitative method)

· Prepare a stock solution with all the elements of interest and with appropriate concentrations (2-5 times each element concentration).

· Prepare at least 3 standards: spike the sample with increasing concentrations; then we have the unknown sample which is declared as our blank (standard 0) and 3 standards in the same matrix. Four standards at least in total are recommended.

· Prepare the method in the software, using background correction for baseline correction. When creating the method, it can be set up as a Standard Addition Method

· Run the calibration: the results will be given under the Standard Addition Tab after running the calibration. Alternatively, if the method was not set up as a Standard Addition, the intercept (or BEC) of each curve corresponds to the concentration of the element in the sample

From this calibration, other samples with similar matrix can be analyzed.

The global report of the quantitative analyses is shown below in Tables 8 -13. The following abbreviations are used:
Conc.: from quantitative method;
Conc. (S.Q.): from semi-quantitative method;
Conc. SAM: from standard addition method.

Table 8: Results for Sample 1

Line	Net Intensity	Conc	SD	Unit	RSD(%)	Conc. (S.Q.)
Al 396.152	19 691.33	0.263	0.00459	mg/L	1.74	0.271
As 189.042	52.58	< LD		mg/L		< LD
B 249.773	20 185.33	0.0472	0.00071	mg/L	1.50	0.045
Cd 228.802	318.65	< LD		mg/L		< LD
Cr 267.716	327.00	< LD		mg/L		< LD
Cu 324.754	1 492.67	0.0046	0.00020	mg/L	4.39	0.0034
Fe 259.940	2 589.67	0.0373	0.00033	mg/L	0.89	0.0157
Mn 257.610	2 402.33	0.0018	0.00006	mg/L	3.01	< LD
Ni 221.647	651.67	< LD		mg/L		< LD
Pb 220.353	533.79	< LD		mg/L		< LD
Se 196.026	386.25	< LD		mg/L		< LD
Zn 213.856	108 289.33	0.1047	0.0010	mg/L	0.95	0.0981

Table 9: Results for Sample 2

Line	Net Intensity	Conc	SD	Unit	RSD(%)	Conc. (S.Q.)
Al 396.152	17 524.00	0.2343	0.0036	mg/L	1.53	0.256
As 189.042	155.17	< LD		mg/L		< LD
B 249.773	192 740.00	0.4689	0.0030	mg/L	0.63	0.466
Cd 228.802	386.80	< LD		mg/L		< LD
Cr 267.716	2 058.00	0.0077	0.0005	mg/L	6.50	< LD
Cu 324.754	12 826.00	0.0617	0.0014	mg/L	2.31	0.066
Fe 259.940	6 111.00	0.0852	0.0017	mg/L	1.98	0.065
Mn 257.610	8 728.00	0.0051	0.0001	mg/L	2.54	0.0012
Ni 221.647	9 888.33	0.0381	0.0006	mg/L	1.55	0.039
Pb 220.353	867.49	< LD		mg/L		< LD
Se 196.026	641.92	< LD		mg/L		< LD
Zn 213.856	195 355.00	0.1863	0.0010	mg/L	0.54	0.181

Table 10: Results for Sample 3

Line	NetIntensity	Conc	SD	Unit	RSD(%)	Conc. (S.Q.)
Al 396.152	39 239.67	0.5228	0.0040	mg/L	0.76	0.592
As 189.042	147.58	< LD		mg/L		< LD
B 249.773	92 747.33	0.2245	0.0028	mg/L	1.25	0.216
Cd 228.802	292.22	< LD		mg/L		< LD
Cr 267.716	2 158.33	0.0081	0.0003	mg/L	4.13	0.003
Cu 324.754	9 189.33	0.0434	0.0005	mg/L	1.09	0.045
Fe 259.940	25 223.67	0.3447	0.0047	mg/L	1.36	0.377
Mn 257.610	75 530.67	0.0401	0.0004	mg/L	0.94	0.0402
Ni 221.647	7 890.67	0.0301	0.0004	mg/L	1.21	0.027
Pb 220.353	1 759.30	0.0129	0.0002	mg/L	1.91	0.031
Se 196.026	572.92	< LD		mg/L		< LD
Zn 213.856	194 040.33	0.1851	0.0012	mg/L	0.63	0.184

Table 11: Results for Sample 4

Line	Net Intensity	Conc	SD	Unit	RSD(%)	Conc. (S.Q.)
Al 396.152	10 105.00	0.1358	0.0012	mg/L	0.91	0.12
As 189.042	387.25	0.0035	0.0007	mg/L	21.00	< LD
B 249.773	433 991.00	1.0585	0.0058	mg/L	0.55	1.07
Cd 228.802	361.35	0.00018 (2 * LD)	0.0001	mg/L	53.19	< LD
Cr 267.716	2 086.33	0.0078	0.0008	mg/L	10.40	0.006
Cu 324.754	24 860.33	0.1223	0.0011	mg/L	0.89	0.121
Fe 259.940	36 921.00	0.5036	0.0049	mg/L	0.98	0.49
Mn 257.610	118 608.33	0.0627	0.0004	mg/L	0.67	0.066
Ni 221.647	1 745.67	0.0052	0.0004	mg/L	6.80	0.01
Pb 220.353	618.03	0.0051	0.0021	mg/L	40.49	< LD
Se 196.026	516.25	< LD		mg/L		< LD
Zn 213.856	202 759.33	0.1933	0.0018	mg/L	0.93	0.184

Table 12: Results for Sample 5

Line	Net Intensity	Conc	SD	Unit	RSD(%)	Conc. (S.Q.)	Conc S.A.M.	RSD (%)
Al 396.152	3 794 058.00	50.3999	0.4916	mg/L	0.98	48.54		
As 189.042	2 939.67	0.0216	0.0013	mg/L	6.00	0.016	0.0204	3.4
B 249.773	61 938.00	0.1492	0.0006	mg/L	0.43	0.159	0.166	0.78
Cd 228.802	5 014.01	0.0078	0.0001	mg/L	1.10	0.007	0.0085	0.19
Cr 267.716	557 018.00	2.1941	0.0019	mg/L	0.09	2	2.52	0.66
Cu 324.754	714 754.00	3.6002	0.0154	mg/L	0.43	3.75	4.15	0.77
Fe 259.940	9 214 680.00	125.1386	1.8638	mg/L	1.49	119.4		
Mn 257.610	2 058 893.33	1.0787	0.0075	mg/L	0.70	1.07	1.2	0.45
Ni 221.647	251 921.67	1.0159	0.0147	mg/L	1.45	1.01	1.2	1.23
Pb 220.353	116 931.40	0.8052	0.0053	mg/L	0.66	0.632	1.04	0.95
Se 196.026	1 842.58	0.0107	0.0027	mg/L	25.52	0.02	0.0148	4.2
Zn 213.856	6 970 960.33	6.5373	0.0318	mg/L	0.49	6.38		

Table 13: Results for Standard 0.1

Line	Net Intensity	Conc	SD	Unit	RSD(%)
Al 396.152	7 644.00	0.1031	0.0026	mg/L	2.49
As 189.042	13 906.330.0994	0.0005	mg/L	0.47	
B 249.773	41 796.670.1000	0.0006	mg/L	0.60	
Cd 228.802	61 493.200.0997	0.0008	mg/L	0.80	
Cr 267.716	25 540.000.1002	0.0006	mg/L	0.57	
Cu 324.754	20 453.000.1001	0.0002	mg/L	0.22	
Fe 259.940	6 399.67	0.0891	0.0009	mg/L	1.04
Mn 257.610	181 739.00	0.0957	0.0000	mg/L	0.02
Ni 221.647	25 957.330.1030	0.0009	mg/L	0.85	
Pb 220.353	15 678.110.1087	0.0013	mg/L	1.24	
Se 196.026	11 389.080.0977	0.0003	mg/L	0.29	
Zn 213.856	108 004.00	0.1045	0.0016	mg/L	1.54

The standard at 0.1 mg/l was analyzed to check and validate the calibration at the end of the analyses.

Table 14: Detection limits

Detection limits (µg/L)	LOD Quantitative Method (µg/L) Water	LOD 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 279.553	0.03	0.12
Mg 279.806	1.0	4.0
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
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

6 Conclusion

This application illustrates that both quantitative and semi-quantitative methods give good results in a wide range of concentrations (µg/L levels to hundreds of mg/L). The radial viewing allows the user to minimize matrix effects. Note that the fast and precise semi-quantitative method can be routinely used. For more applications on semi-quantitative analysis of supply water and sludge from animal food see Application Note 25.

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