Application Note

Analysis of Samples Related to Nuclear Submarine Operation

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1 Introduction

Eight samples from the Nuclear Division of a company were analyzed. These samples have complex matrices such as salt, concentrated acid, etc. and required high dilution factors when flame AAS is used. This application note will demonstrate the feasibility and simplicity of the ICP technique for this type of analysis.

2 Principle

2.1 Technique used

The elemental analysis of solutions 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

The limits of detection are calculated using the following formula:

$$LOD = k \times BEC \times RSD_B$$

With:
LOD = limits of detection,
k= 3 for the normal 3-sigma values,
BEC = Background equivalent concentration,
RSD_B = 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; thus providing the BEC. The RSD_B is evaluated by running the blank ten times.

3 Instrument specification

The work presented hare was performed on a ULTIMA 2.The specifications of this instrument are listed below in Tables 1 and 2.

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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	
Resolution	5 pm	160-320 nm
	10 pm	320-800 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

4 Operating conditions

The operating conditions are listed in Table 3 below.

Table 3: Operating conditions

Parameter	Condition
RF Generator power	1100 W
Plasma gas flowrate	12 L/min
Auxiliary gas flowrate	0 L/min
Sheath gas flowrate	0.2 L/min
Nebulizer flowrate	2.9 bars, 0.61 ml/min
Sample uptake	1 mL/min
Type of nebulizer	Meinhard (K3 type)
Type of spray chamber	Cyclonic
Argon humidifier	No
Injector tube diameter	3.0 mm

5 Sample description

The sample content are described in Tables 4 through 11.

Table 4: Sample 1
Matrix: $KMnO_4$ 0.6 g/L, pH 2.8 (nitric acid)

Elements	Concentration range (mg/L)
Cr	10 - 100
Fe	0.5 - 20

Table 5: Sample 2
Matrix: $KMnO_4$ 0.6 g/L, pH 2.8 (nitric acid)

Elements	Concentration range (mg/L)
Cr	0.5 - 20
Fe	0.5 - 20

Table 6: Sample 3
Matrix: EDTA disodium 3.46 g/L, Citric acid 2.3 g/L, Tri-Ammonium citrate 0.366 g/L, Armohib 28 0.12 ml/L, pH 3.5

Elements	Concentration range (mg/L)
Fe	50 - 500
Ni	10 - 100
Cr	10 - 100
Co	0.5 - 20
Mn	50 - 500
K	50 - 500

Table 7: Sample 4
Matrix: EDTA disodium 3.46 g/L, Citric acid 2.3 g/L, Tri-Ammonium citrate 0.366g/L, Armohib 28 0.12 ml/L, pH 3.5

Elements	Concentration range (mg/L)
Fe	50 - 500
Ni	10 - 100
Cr	10 - 100
Co	0.5 - 20
Mn	50 - 500
K	50 - 500

Table 8: Sample 5
Matrix: $K_2B_4O_7$ 3.45 g/L, pH 9.2

Elements	Concentration range (mg/L)
Li	0.5 - 20

Table 9: Sample 6
Matrix: $K_2B_4O_7$ 50 ppm, pH 7

Elements	Concentration range (mg/L)
Li	0.01 - 1

Table 10: Sample 7
Matrix: Na 550 ppm, Formate 14,800 ppm, picolinate 5600 ppm, pH 3

Elements	Concentration range (mg/L)
Fe	100 - 1000
Ni	0.5 - 20
Cr	0.5 - 20
Co	0.5 - 20
Mn	50 - 500
K	10 - 100
V	100 - 1000

Table 11: Sample 8
Matrix: Na 385 ppm, Formate 12,300 ppm, picolinate 3905 ppm, pH 3

Elements	Concentration range (mg/L)
Fe	50 - 500
Ni	0.5 - 20
Cr	0.5 - 20
Co	0.5 - 20
Mn	10 - 100
K	10 - 100
V	50 - 500

6 Results

The samples were analyzed first with a fast semi-quantitative method, and then quantitatively with appropriate calibration and analysis conditions. The semi-quantitaive method is made with a calibration at 5 mg/L in deionized water, one replicate and fast acquisition. It allows us to identify the sample by determining the elements of interest and concentration, and identify other elements which may cause matrix effects if present at high concentration or interference. It also allows the estimation of the calibration range for all the elements.

We worked with dilution factors of 10 (samples 1 and 2) or 50 (samples 3-8), and this way were able to analyze all the elements in all samples using a single quantitative method.

Note that the semi-quantitative analyses did not reveal any surprise in terms of unknown elements: With the dilution factor selected, the matrix effect is nonexistent owing to the radial view of the plasma.

The quantitative method was calibrated with multi-element standards (in deionized water, using Spex* standards), as following:

0 / 0.01 / 0.1 / 1 / 10 / 30 mg/L

The example of Cr calibration line is shown figure 1.

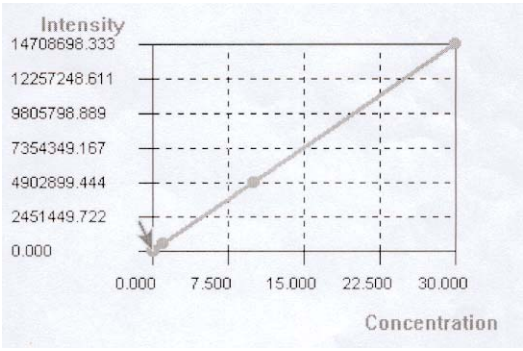

Figure 1: Cr calibration curve

* www.certiprep.com

The wavelengths selected are listed in table 12.

Table 12: Wavelengths

Element	Wavelength
B	249.773
Co	228.616
Cr	267.716
Fe	259.940
K	766.490
Li	670.784
Mn	257.610
Ni	221.647
V	292.402

The acquisition parameters used for quantitative analysis are: Maximum Mode (1 point measured at the top of the peak) 4 seconds and 3 seconds for the background correction. Total analysis is less than 4 minutes, including rinse time (between each sample), and sample transfer time (the autosampler JY AS-421 was used). This is an important benefit compared to flame AAS.

The quantitative results are presented in Tables 13 to 22. Results are given in mg/L in the diluted solutions and results from the semi-quantitative method (S.Q.) to compare, noting that the S.Q. calibration is a simple one with 0 and 5 mg/L, and elements may be out of calibration range. Due to the high dynamic range of the ULTIMA 2 this method gives quite accurate results in a wide range of concentrations, even for traces.

Table 13: Certified Reference Sample 1640, concentrations in the diluted solutions, in mg/L

Sample 1640	Quantitative method		Semi-Quant method	Certified
El	Conc	RSD	Conc	Conc
B	0.3138	0.70	0.2971	0.3011
Co	0.0207	0.37	0.0187	0.02028
Cr	0.0369	1.53	0.0361	0.0386
Fe	0.0324	1.05	0.0295	0.0343
K	0.918	2.23	0.743	0.994
Li	0.0469	0.64	0.044	0.0507
Mn	0.1126	1.22	0.1210	0.1215
Ni	0.0285	0.53	0.0321	0.0274
V	0.0140	2.20	0.0121	0.01299

Table 14: Sample 2 results obtained in sample diluted by 10

Sample 1 diluted /10				In initial sample	
El	Semi-Quant method Conc(mg/l)	Quantitative method Conc(mg/l)	RSD	Conc (mg/l)	Spike (mg/l)
B		0.006	1.44	0.006	
Co		0.000	64.50	0.00	
Cr	5.596	5.206	0,53	52.06	50
Fe	0.0318	0.0254	2,33	0.0254	
K		23.392	0,31	23.392	
Li		0.00	27.90	0.00	
Mn	23.35	20.931	0,89	209.31	
Ni		0,000	19,25	0.00	
V		0,002	1,66	0.003	

Table 15: Sample 2 results obtained in sample diluted by 10

Sample 2 diluted /10				In initial sample	
	Semi-Quant method	Quantitative method			Spike
El	Conc(mg/l)	Conc(mg/l)	RSD	Conc (mg/l)	(mg/l)
B		0.004	1.98		
Co		0.000	358.4		
Cr	0.533	0.530	0.67	5.30	5
Fe	0.0328	0.0254	2.34	0.254	1
K		16.040	0.20		
Li		0.001	58.05		
Mn	22.208	21.038	0.79	210.38	209
Ni		0.000	19.25		
V		0.002	1.66		

Table 16: Sample 3 results obtained in sample diluted by 50

Sample 3 diluted /50				In initial sample	
	Semi-Quant method	Quantitative method			Spike
El	Conc(mg/l)	RSD	Conc(mg/l)	Conc (mg/l)	(mg/l)
B		0.0046	4.36		
Co	0.042	0.0451	0.43	2.26	2
Cr	1.049	1.002	0.94	50.11	50
Fe	4.210	4.239	0.52	211.94	200
K	8.564	9.6771	0.74	483.85	
Li		0.0007	121.67		
Mn	4.351	4.166	0.84	208.31	209
Ni	0.4094	0.4415	0.99	22.08	20
V		0.0018	12.26		

Table 17: Sample 4 results obtained in sample diluted by 50

Sample 4 diluted /50				In initial sample	
	Semi-Quant method	Quantitative method			Spike
El	Conc(mg/l)	Conc(mg/l)	RSD	Conc (mg/l)	(mg/l)
B		0.004	1.87		
Co	0.0172	0.021	1.51	1.03	1
Cr	0.0978	0.103	0.73	5.13	5
Fe	0.0948	0.109	1.37	5.46	5
K	3.284	3.087	1.09	154.35	148
Li		0.001	5.50		
Mn	4.473	4.266	0.81	213.28	209
Ni	0.0420	0.044	1.21	2.20	2
V		0.002	12.99		

Table 18: Sample 5 results obtained in sample diluted by 50

Sample 5 diluted /50				In initial sample	
El	Semi-Quant method Conc(mg/l)	Quantitative method Conc(mg/l)	RSD	Conc (mg/l)	Spike (mg/l)
B	13.262	13.689	0.13	684.47	639
Co		0.000	57.52		
Cr		0.000	111.00		
Fe		0.001	9.28		
K	21.973	23.498	0.51	1174.89	1156
Li	0.0769	0.076	0.62	3.82	4
Mn		0.001	22.31		
Ni		0.000	39.48		
V		0.002	3.92		

Table 19: Sample 6, results obtained in a non diluted sample

Sample 6 non diluted		
El	Quantitative method Conc (mg/L)	Spike (mg/L)
B	9.768	9.3
Co	0.00	
Cr	0.00	
Fe	0.002	
K	16.574	16.7
Li	0.052	0.058
Mn	0.00	
Ni	0.00	
V	0.002	

Table 20: Sample 6 results obtained in sample diluted by 50

Sample 6 diluted /50				In initial sample	
El	Semi-Quant method Conc(mg/l)	Quantitative method Conc(mg/l)	RSD	Conc (mg/l)	Spike (mg/l)
B	0.1689	0.209	0.16	10.44	9.3
Co		0.000	87.58		
Cr		-0.000	203.82		
Fe		0.001	22.59		
K	0.03037	0.361	1.76	18.04	16.7
Li	0.0031	0.0014	18.93	0.070	0.058
Mn		0.001	12.72		
Ni		-0.000	1 208.54		
V		0.001	25.56		

Table 21: Sample 7 results obtained in sample diluted by 50

Sample 7 diluted /50				In initial sample	
	Semi-Quant method	Quantitative method			Spike
El	Conc(mg/L)	Conc(mg/L)	RSD	Conc (mg/L)	(mg/L)
B		0.019	2.05		
Co	0.035	0.0353	1.28	1.77	1.6
Cr	0.1710	0.1702	1.12	8.51	8
Fe	6.953	6.817	1.06	340.86	
K	0.9784	0.9964	0.82	49.82	
Li		-0.000	116.78		
Mn	1.345	1.312	0.35	65.69	64
Ni	0.3533	0.3466	0.46	17.33	16
V	25.661	25.587	0.56	1279.35	

Table 22: Sample 8 results obtained in sample diluted by 50

Sample 8 diluted /50				In initial sample	
	Semi-Quant method	Quantitative method			Spike
El	Conc(mg/l)	Conc(mg/l)	RSD	Conc (mg/l)	(mg/l)
B		0.007	4.78		
Co	0.019	0.0037	7.17	0.18	0.18
Cr	0.0146	0.0195	2.29	0.98	0.9
Fe	0.7943	0.7919	0.78	39.60	
K	0.835	1.072	1.63	53.61	
Li		-0.002	31.23		
Mn	1.553	1.426	0.60	71.31	
Ni	0.0432	0.0400	0.93	2.00	2
V	13.803	13.576	0.92	678.79	

7 Conclusion

The ULTIMA 2 ICP allows simple and rapid analysis using one single analytical method. The simple dilution made here helps to reduce matrix effects and to use a simple calibration in water, covering all the concentration ranges required. Some samples can be analyzed directly without dilution such as example sample 6, owing to the robustness of the plasma.

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