Application Note

Fast Analysis of Waste Water using ACTIVA-M ICP-AES

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1 Introduction

The control of water pollution is essential because it is necessary to maintain the quality of water for both mankind and other living organisms. Water can be affected in quality by several pollution sources such as untreated human and animal waste, agricultural fertilizers, and a myriad of industrial waste sources. There is a wide range of contaminants, pathogens, non pathogenic bacteria, organic or inorganic particles… ICP-AES is well adapted for the determination of inorganic elements in waste water as it allows fast and accurate determination of many elements of the periodic table with low detection limits.

This application flash will describe the analysis of 17 elements, using several lines for some elements, in waste waters using the ACTIVA-M ICP-AES. This instrument is well adapted for this analysis due to its configuration, vertical torch and excellent sensitivity thanks to the Total Plasma View. Recoveries on a Certified Reference Standard as well as detection limits will be given in this application note. A focus will be made on analysis time and Argon consumption.

2 Sample preparation

The analysis was done using external calibration with a multi-element standard solution from Spex. All dilutions were done in 2% HNO_3. The accuracy of the method was evaluated using a Certified Reference Standard, EU-L-2 diluted 1:100 prior to analysis.

3 Instrument and operating specifications

The characteristics of the ACTIVA-M used for the analysis are given in Table 1.

Table 1: Specification of the ACTIVA-M ICP spectrometer

Parameter	Specification
Optical Mounting	Czerny Turner
Focal Length	0.64 m
Gratings: number of grooves per mm	Dual back-to-back gratings 4343 g/mm 2400 g/mm
Resolution	< 10 pm 120-430 nm < 18 pm 430-800 nm
Thermoregulation	32 ± 0.1°C
Type of generator	40.68 MHz Solid state, water-cooled
Torch	Vertical Radial view with Total Plasma View*

* Total Plasma View: Measurement of the whole Normal Analytical Zone of the plasma for enhanced sensitivity and freedom from interferences.

Table 2: Specification of the sample introduction system

Parameter	Specification
Nebulizer	Concentric glass nebulizer
Spray chamber	Cyclonic glass spray chamber
Sample uptake	1 mL/min
Pump tubing	Black-black pump tubing for sample Grey-grey pump tubing for drain

The ACTIVA-M is equipped with a unique fully demountable torch, 3 mm i.d. alumina injector and the HORIBA Jobin Yvon patented sheath gas device. The 3 mm i.d. injector increases the residence time of the sample in the plasma, leading to enhanced sensitivity and reduced matrix effects, while the sheath gas reduces the contact between the injector and the sample, eliminating deposit issues and memory effects.

A concentric glass nebulizer and a cyclonic spray chamber were used to ensure enhanced sensitivity, shorten stabilization and reduce rinsing time. The use of the cyclonic spray chamber is possible, even with high amounts of total dissolved solids because no depositions occur due to the large injector bore and the sheath gas.
The plasma parameters and gas flows are optimized to obtain the best sensitivity along with long term stability and are given in Table 3.

Table 3: Operating conditions of the spectrometer

Parameter	Specification
RF generator power	1100 W
Plasma gas	12 L/min
Auxiliary gas	0 L/min
Sheath gas	0.2 L/min
Nebulizer pressure/argon flow	0.8 L/min

The integration time used was 5 seconds for all wavelengths. The whole sequence was run with the AS-500 autosampler for fully automated analysis.

4 Analytical results

Detection limits were estimated using a 2% HNO_3 blank. This blank was analyzed 5 times using 10 replicates for each determination. The detection limit was estimated using the following definition:

DL = 3 x sB, where DL is the detection limit in µg/L and s_B is the standard deviation, in µg/L of the 10 measurements of the blank.

The Certified Reference Standard, EU-L-2 was also analyzed to check the accuracy of the method and the stability was evaluated using this same sample analyzed over 3 hours.

4.1 Detection limits

The detection limits, calculated according to the formula already described, are given in Table 4. The value given in this table is the mean of the 5 independent measurements.

To take full benefit of the CCD detection, many lines were used for several elements. It allows increasing the confidence in the results obtained because it is then possible to check whether some spectral interference occurs or not. Due to the very low detection limits required for waste waters, however, it is not possible to use several lines for all the elements.

Detection limits are given for each element on the basis of the most sensitive line used during the analysis.

Table 4: Detection limits in µg/L estimated on a blank

Element	Wavelength (nm)	Detection Limit(µg/L)
Ag	338.289	0.25
As	188.979	7.0
Ba	230.425	0.15
Cd	228.802	0.15
Co	228.615	0.45
Cr	205.571	0.70
Cu	327.395	0.50
Hg	194.163	3.0
Mo	202.030	0.70
Ni	231.604	0.55
Pb	220.353	5.0
Sb	217.581	2.5
Se	196.026	11
Sn	189.926	3.2
Ti	334.941	0.13
V	309.311	0.12
Zn	213.857	0.20

The detection limits are excellent, even with the short integration time used. This is due to the design of the spectrometer. The radial viewing mode with the Total Plasma View concept associated with the 3 mm i.d. injector, which increases the residence time of the sample into the plasma, lead to unmatched sensitivity. The low noise high performance CCD detector allow the detection of weak signals for low concentration determination, ensuring excellent stability and repeatability.

4.2 Certified Reference Standard Analysis

The EU-L-2 Certified Reference Standard sample was analyzed after a 1:100 dilution as mentioned on the certificate of analysis. The dilution was made using 2% HNO_3 blank to match the standard preparation. Results of the quantitative analysis for each line used as well as recoveries are given in Table 5.

Table 5. Results of the quantitative analysis for EU-L-2 and recoveries

	EU-L-2	Consensus Value mg/L	Recovery %
Ag 328.068	< DL	-	
Ag 338.289	< DL	-	
As 188.979	0.080	0.08	100
Ba 230.425	0.125	0.124	100
Ba 233.527	0.124	0.124	100
Cd 226.502	0.024	0.023	104
Cd 228.802	0.025	0.023	107
Co 228.615	0.083	0.081	103
Co 230.785	0.080	0.081	98
Cr 205.571	0.060	0.06	100
Cr 206.562	0.062	0.06	103
Cu 224.700	0.103	0.105	98
Cu 327.395	0.103	0.105	98
Hg 194.163	< DL	-	
Mo 201.511	0.041	0.04	102
Mo 202.030	0.040	0.04	99
Ni 227.021	0.081	0.082	99
Ni 230.300	0.081	0.082	99
Ni 231.604	0.084	0.082	102
Ni 232.003	0.080	0.082	98
Pb 220.353	0.040	0.041	97
Sb 206.833	0.019	0.019	102
Sb 217.581	0.019	0.019	99
Se 196.026	0.029	0.027	107
Sn 189.926	< DL	-	
Ti 308.804	< DL	-	
Ti 334.903	< DL	-	
Ti 334.941	< DL	-	
Ti 336.122	< DL	-	
Ti 337.280	< DL	-	
Ti 338.377	< DL	-	
V 309.311	0.051	0.049	104
V 311.838	0.048	0.049	99
Zn 202.548	0.024	0.023	103
Zn 213.857	0.022	0.023	94

Results obtained are very close to the certified values and recoveries are excellent, with good RSD even on elements close to the detection limit such as Selenium and Antimony, thus proving the ability of the CCD detector to measure such levels of concentration with a good repeatability.

4.3 Stability test

A stability test was performed on the Certified Reference Standard with 4 determinations at 1 hour intervals. The graphic of the normalized concentrations is given in Figure 1 (see next page).

The stability of the ACTIVA-M on such concentrations is very good with deviations less than 3% from the mean of the 4 values and long term RSD less than 2% for all the lines.

7 Analysis time and Argon consumption

The total analysis time with the ACTIVA-M for the determination of 17 elements using 35 wavelengths is less than 3 minutes (2 minutes and 55 seconds exactly). This time was evaluated on a fully automated analysis using the AS-500 autosampler and taking into account the sample transfer time, the stabilization time and the rinsing time.
The determination of hundreds sample per day is then possible using the ACTIVA-M and the AS-500.

Due to the vertical torch configuration of the ACTIVA-M, the Argon flow required for the analysis is very low, ensuring a reduction of the operating cost. The design of the optics also allows using low nitrogen flow to ensure an efficient purge to increase the sensitivity in the UV part of the spectrum. The total Argon consumption per minute is only 13 L/min and 0.5 L/min of Nitrogen is used for the optics. The amount of gas needed for the determination of a single sample is only 40 liters of Argon and 1.5 liters of Nitrogen.

Compared to other ICP-AES systems, using the ACTIVA-M and the AS-500 can save up to 50% on gas cost, greatly decreasing the operating cost of the instrument.

Moreover, the use of a vertical torch decreases the operating costs by reducing the need to change the glassware. The savings observed are in the range 75 to 470% per year when comparing HORIBA Scientific ICP-AES with other ICP-AES instruments, contributing to the decrease in the total cost of an analysis.

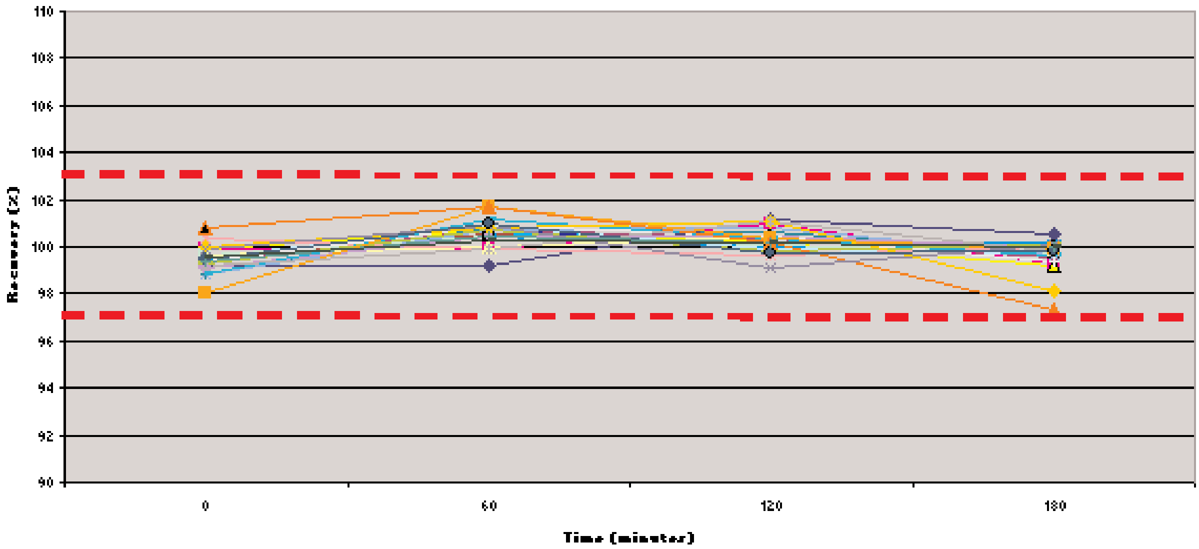

Figure 1: Stability test on EU-L-2 expressed as µg/g in the sample

8 Conclusion

The ACTIVA-M is suited to the analysis of environmental samples. The high performance low noise CCD detector allows reducing the integration time without degrading performances. Detection limits are kept at a low level, unrivaled for a radial viewing ICP-AES.

Stability is excellent, even on low concentrations, as observed on the Certified Reference Standard. The combination of the short integration time and the vertical torch design reduces the Argon consumption and the total analysis time, greatly decreasing the operating costs mainly due to lower gas consumption and fewer spare parts needed.

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