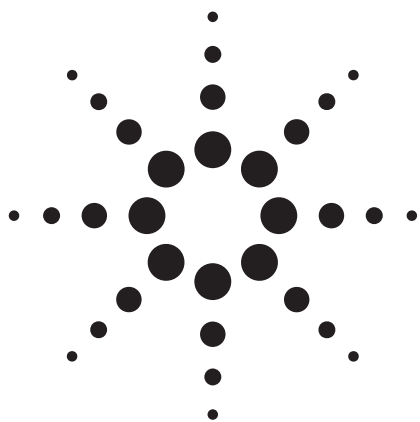




Fast Analysis of Water Samples Comparing Axially-and Radially- Viewed CCD Simultaneous ICP-OES

Application Note

Inductively Coupled Plasma-Optical Emission Spectrometers

Author

Tran T. Nham

Introduction

With the benefits of typically 5–10 fold improvement in detection limits of the axially viewed ICP compared to the conventional radially viewed ICP system [1–5], the applications of axially viewed ICP-OES have been growing rapidly, especially in the area of environmental pollution control. Fast sample throughput is essential for routine water analysis, this study highlights a newly developed axially viewed CCD simultaneous ICP-OES as a high speed analysis tool for the water laboratory.



Agilent Technologies

Experimental

Instrumental

In this work, a Vista AX (axially viewed plasma) CCD simultaneous ICP-OES and a Vista RL (radially viewed plasma) CCD simultaneous ICP-OES were used (Agilent Technologies, Inc.). The Vista features an echelle polychromator with a cross dispersion prism to form a two dimensional diffraction pattern across its focal plane. It is equipped with a custom designed CCD detector -the patented Vista Chip [6].

The polychromator can be purged with a low flow of either argon or nitrogen gas for the detection of low UV wavelengths. With more than 70,000 pixels, the VistaChip covers wavelengths continuously from 167 to 784 nm. The detector has one million pixels per second read out speed, and the read-out circuitry is duplicated on each side of the chip. The signal processing speed of the VistaChip is 80 times faster than a conventional system [7].

The sample introduction system consists of a glass concentric nebulizer and a glass cyclonic chamber. The nebulizer flow is controlled by a mass flow controller.

The operating parameters are shown in Table 1.

Table 1. Instrument Operating Conditions

Power	1.2 kW
Plasma gas flow	15 L/min
Auxiliary gas flow	1.5 L/min
Nebuliser flow	0.75 L/min
Pump rate	15 rpm
Integration time	10 s
Replicates	3
Background correction	Fitted

Reagents and Standards

All chemicals and reagents used were of high purity analytical reagent grade. Standards and blank for detection limit measurements were prepared in 1% v/v HNO₃. Standards and blank for the water analysis were prepared in 3.5 % v/v HNO₃ to matrix match with the NIST water samples.

Results Detection Limits

The detection limits of the system were measured as the concentration giving signals equal to three times the standard deviation of a blank solution. They were measured at an integration time of 10 s and 10 replicate readings over three con-

secutive days to meet the requirements of the US EPA definition of instrument detection limit (IDL) for example, to test compliance against the Contract Required Detection Limit (CRDL). Table 2 illustrates the detection limit of 27 elements with the Vista axially viewed and radially viewed ICP systems. The current CRDL of 22 elements specified by the US EPA is also given in Table 2. The CRDL numbers in brackets indicate proposed changes to the CRDLs under ILMO 5.0 [9].

Table 2. Detection Limits, Current US EPA CRDLs [8] and Proposed CRDLs in Brackets [9]

Element	Wavelength (nm)	IDL axial (µg/L)	IDL radial (µg/L)	CRDL [8,9] (µg/L)
Ag	328.068	0.5	2	10 (5)
Al	396.152	1.5	6	200
As	188.980	3.5	22	10 (5)
B	249.678	0.2	0.5	—
Ba	455.403	0.04	0.3	200 (20)
Be	234.861	0.05	0.3	5 (1)
Bi	223.061	3	18	—
Ca	315.887	1.5	8	5000
Cd	214.439	0.3	1.5	5 (2)
Co	238.892	0.5	4.5	50 (5)
Cr	267.716	0.5	2.2	10 (5)
Cu	324.754	0.3	1.8	25
Fe	259.940	0.4	5	100
K	766.491	0.5	6.5	5000
Mg	279.800	2.2	20	5000
Mn	257.610	0.05	0.3	15
Mo	202.032	0.8	5	—
Na	589.592	0.2	1	5000
Ni	231.604	1.3	10	40 (20)
Pb	220.353	3	25	3
Sb	206.834	2.9	28	60 (5)
Se	196.026	5	35	5
Si	251.430	3.5	32	—
Sr	421.552	0.01	0.1	—
Te	214.282	6	35	—
Tl	190.794	3	24	10 (5)
V	292.401	0.4	3.5	50 (10)
Zn	213.857	0.3	1.0	20 (10)

The detection limits with the axially viewed ICP are generally an order of magnitude better than those from the radially viewed ICP. All detection limits with the axially viewed ICP are lower than the US EPA CRDL.

The detection limit of the radially viewed ICP also meets the majority of the current and proposed CRDL with the exception of As, Tl and Sb. Of course, ICP-OES detection limits can be further enhanced by using alternate sample introduction systems such as vapor generation or ultrasonic nebulization.

Warm Up Time

One of the factors in improving productivity is to shorten the instrument warm up time. The instrument warm up time is defined as the time taken from ignition of the plasma until the system is stabilised and ready for analysis. Figure 1 demonstrates the warm up time from cold start.

As shown in Figure 1, the instrument takes about 35 minutes to stabilize from plasma ignition. While you are waiting for the instrument to warm up, the software allows you to set up a new worksheet, or manipulate the data from the previous runs, or generate a report. The time could also be used for loading samples onto the autosampler.

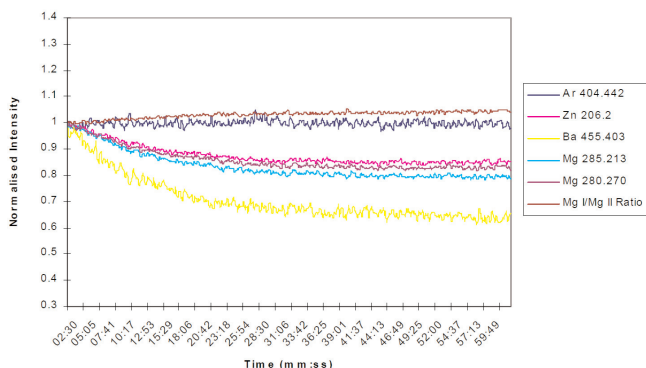


Figure 1. Instrument warm up time.

Ar 404.442 nm, Ba 455.403 nm and Zn 206.200 nm lines were selected together with Mg II 280.270 nm and Mg I 285.213 nm line intensity ratio. These test elements were recommended for drift diagnostics for the ICP.

Sample Throughput Rate

To demonstrate the speed of analysis of the Vista systems, the sample analysis rate was measured under a range of conditions. The sample analysis rate was measured using 25 s sample delay time, 10 s stabilisation time, 30 s rinsing time between samples and fitted background correction. The speed of analysis for 35 elements with 3 replicate readings is shown in Table 3.

Table 3. Sample Throughput Rate

Integration time(s)	Total analysis time(s)	Samples per hour
1	80	45
3	87	41
5	93	38
10	108	33
20	140	26
30	172	21

With an integration time of 10 s, the sample throughput is about 220 samples per 8 hour day which includes calibration of a blank and two standards and recalibration after every 20 samples.

With its automatic data Quality Control Protocols (QCP) software, the Vista can operate unattended 24 hours per day with results tested against acceptance criteria. The instrument need only be stopped for periodic maintenance of the sample introduction system.

Short Term Precision and Long Term Stability

Short term precision of the system was measured with a integration time of 10s and 30 replicates, and is typically 0.5 %RSD or less.

Long term stability was measured by performing a calibration on a multielement standard and a reagent blank, then continuously measuring the standard solution as a sample every 15 minutes without recalibration. Figure 2 shows that the long term stability over 4 hours ranged from 0.21–0.98 %RSD.

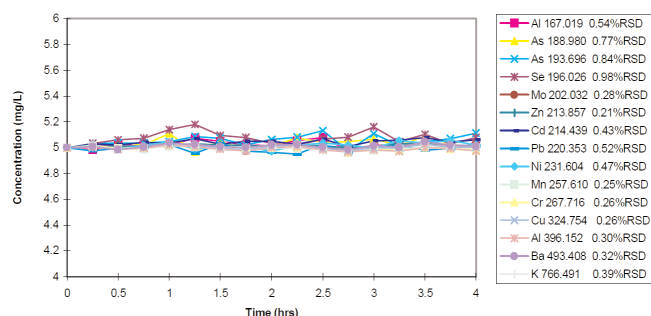


Figure 2. Four hour stability.

Water Analysis

Because of the excellent detection limit capability of the axial system, the water analysis was conducted on this unit. The results of the analysis of NIST SRM 1643C and 1643D water samples for both major and trace elements are listed in Table 4. The measured values compare well with the certified values.

Table 4. Results of Water Analysis by Vista Axial ICP

Element	NIST 1643 C (µg/L)		NIST 1643 D (µg/L)	
	Measured	Certified	Measured	Certified
Ag	2.37 ± 0.22	2.21 ± 0.30	1.31 ± 0.11	1.27 ± 0.06
Al	121.0 ± 2.4	114.6 ± 5.1	127.2 ± 3.6	127.6 ± 3.5
As	79.2 ± 3.9	82.1 ± 1.2	54.5 ± 1.5	56.02 ± 0.73
B	121.9 ± 1.8	119 ± 1.4	138.8 ± 3.6	144.8 ± 5.2
Ba	50.9 ± 0.1	49.6 ± 3.1	495.0 ± 6.0	506.5 ± 8.9
Be	24.2 ± 0.2	23.2 ± 2.2	13.01 ± 0.1	12.53 ± 0.28
Bi	11.3 ± 5.0	(12)	13.5 ± 3.0	(13)
Cd	12.8 ± 0.2	12.2 ± 1.0	6.38 ± 0.38	6.47 ± 0.37
Co	24.7 ± 2.0	23.5 ± 0.8	25.3 ± 0.5	25 ± 0.59
Cu	22.4 ± 2.6	22.3 ± 2.8	21.0 ± 3.0	20.5 ± 3.8
Fe	101.6 ± 3.5	106.9 ± 3.0	80.2 ± 2.0	91.2 ± 3.9
Mn	37.6 ± 0.04	35.1 ± 2.2	40.1 ± 0.68	37.66 ± 0.83
Mo	105.1 ± 2.1	104.3 ± 1.9	110.1 ± 2.0	112.9 ± 1.7
Ni	61.6 ± 1.1	60.6 ± 7.3	60.9 ± 3.0	58.1 ± 2.7
Pb	38.4 ± 0.5	35.3 ± 0.9	19.7 ± 0.8	18.15 ± 0.64
Sb	—	—	56.5 ± 0.9	54.1 ± 1.1
Se	11.8 ± 2	12.7 ± 0.7	14.4 ± 0.6	11.43 ± 0.17
Sr	278.0 ± 1.5	263.6 ± 2.6	315.9 ± 2.4	294.8 ± 3.4
Te	3.6 ± 0.8	(2.7)	1.3 ± 0.4	(1)
Tl	8.5 ± 2.4	(7.9)	7.6 ± 0.5	7.28 ± 0.25
V	29.5 ± 0.9	31.4 ± 2.8	34.3 ± 0.6	35.1 ± 1.4
Zn	89.2 ± 2.6	73.9 ± 0.9	79.1 ± 1.3	72.48 ± 0.65
	mg/L	mg/L	mg/L	mg/L
Ca	37.4 ± 0.3	36.8 ± 1.4	31.21 ± 0.46	31.04 ± 0.50
K	2.27 ± 0.03	(2.3)	2.31 ± 0.02	2.356 ± 0.035
Mg	9.88 ± 0.41	9.45 ± 0.27	8.31 ± 0.17	7.989 ± 0.035
Na	11.62 ± 1.25	12.19 ± 0.36	22.14 ± 0.43	22.07 ± 0.64
Si	—	—	2.84 ± 0.56	(2.7)

Data in parentheses are not certified

Summary

The Vista CCD simultaneous ICP-OES has been shown to be an excellent productivity tool for the water analysis laboratory. The Vista axially-viewed ICP system provides 5-10 times better detection limits than the radially-viewed ICP system, and easily meets the current and proposed CRDLs for the US EPA. The short and long term stability of the Vista are excellent. The measured values of the NIST SRM water samples are in good agreement with the certified values. The Vista instrument provides quick warm up time and fast sample throughput.

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