

Ultra-fast ICP-OES determination of trace elements in water, as per US EPA 200.7

Application note

Environmental

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Introduction

Water quality has a direct impact on the health of all ecosystems, therefore environmental monitoring of water, wastewater and solid wastes for pollutants is an important activity and one that is often subject to strict legislation. ICP-OES is a well established technique that is used as a workhorse in many environmental labs where US Environmental Protection Agency (EPA) methods are run, especially the 200.7 regulation—Determination of Metals and Trace Elements in Water, Solids and Biosolids by ICP-AES. With many hundreds of samples per day to process, many environmental laboratories are constantly looking to improve productivity and reduce operating costs, while maintaining instrument robustness, ease-of-use and analytical performance.

To meet these demands, Agilent has developed the 5100/5110 Synchronous Vertical Dual View (SVDV) ICP-OES, which improves sample throughput by taking a single reading of the vertical plasma for all wavelengths. This leads to faster analysis times and reduced argon consumption. In fact, the 5100/5110 SVDV fitted with next generation of valve technology to



optimize the delivery of the sample to the instrument is up to 55% faster than conventional Dual View (DV) instruments fitted with a valve system. This is due to conventional DV requiring multiple readings (in some cases up to 4 readings) to cover both axial and radial plasma views. Furthermore, the 5100/5110 SVDV uses up to 50% less argon for a comparative EPA 200.7 compliant analysis and, with shorter run times, reduces wear on the sample introduction system (SIS) and torch.

The innovative SVS 2+ Switching Valve System is a 7 port switching valve that more than doubles the productivity of the 5100/5110 ICP-OES by reducing sample uptake, stabilization times, and rinse delays. The SVS 2+, which can be used with the SPS 3 autosampler, includes a positive displacement pump that rapidly pumps sample through the sample loop and features a bubble injector to help with sample washout.

Agilent has introduced unique Dichroic Spectral Combiner (DSC) technology with the 5100/5110 SVDV ICP-OES so that Easily Ionized Elements (EIE) such as sodium and potassium can be measured radially while other elements are measured axially, allowing % level and ppb level elements to be determined at the same time, in the same reading. The DSC achieves this by combining axial and radial light measurements from the vertical plasma, over the entire wavelength range, in a single measurement that is read by the high speed VistaChip II CCD detector.

The vertical torch position of the 5100/5110 leads to excellent plasma robustness and long term stability, especially for challenging sludge and trade wastes samples that can be run using the 200.7 method. The outcome is a reduced number of reruns of samples and quality control (QC) solutions, resulting in even higher sample throughput.

To keep the operation of the 5100/5110 as simple as possible, the instrument includes a plug-and-play torch that automatically aligns the torch and connects all gases for fast start up while ensuring reproducible loading of the torch from operator-to-operator and lab-to-lab. In addition, software applets that include pre-set method templates e.g. compliant with US EPA 200.7 requirements, can be developed using the ICP Expert software to ensure fast startup with minimal user training.

This note describes the use of the Agilent 5100 SVDV ICP-OES for the ultra-fast determination of trace elements in water CRMs following US EPA method 200.7 guidelines. Equivalent results could be obtained on the 5110 instrument.

Instrumentation

All measurements were performed using an Agilent 5100 SVDV ICP-OES with Dichroic Spectral Combiner (DSC) technology that runs axial and radial view analysis of a vertically orientated plasma at the same time. The sample introduction system consisted of a Seaspray nebulizer, single-pass glass cyclonic spray chamber, white-white pump tubing and a standard 1.8 mm injector torch. The instrument uses a solid-state RF (SSRF) system operating at 27 MHz to deliver a robust plasma capable of excellent long term analytical stability. An SPS 3 autosampler with the SVS 2+ switching valve was used to deliver samples to the instrument. The SPS 3 was setup with a 1.0 mm ID probe. The instrument operating conditions used are listed in Table 1 and SVS 2+ settings are given in Table 2.

Tables 1 and 2 list the operating conditions used for the ICP-OES and the SVS 2+ during this analysis.

Table 1. Agilent 5100 SVDV ICP-OES operating parameters

Parameter	Setting
Read time (s)	20
Replicates	2
Sample uptake delay (s)	0
Stabilization time (s)	10
Rinse time (s)	0
Pump Speed (rpm)	12
Fast pump (rpm)	Off
RF power (kW)	1.50
Aux flow (L/min)	1.0
Plasma flow (L/min)	12.0
Nebulizer flow (L/min)	0.7
Viewing height (mm)	5
Background Correction	Off-Peak

Table 2. SVS 2+ Switching Valve System settings

Parameter	Setting
Sample loop size (mL)	1.0
Loop uptake delay (s)	7.0
Uptake pump speed (rpm) - refill	355
Uptake pump speed (rpm) – move	355
Uptake pump speed (rpm) – inject	100
Time in sample (s)	6.6
Bubble inject time (s)	6.8

Sample and standard preparation

Standards were prepared from single element standards and diluted with 1% HNO₃. To validate the method, the following trace metals in drinking water (TMDW) Certified Reference Materials (CRM) were analyzed: TMDW-A, and TMDW-B (High Purity Standards, Charleston, South Carolina, USA).

Interference correction

Environmental samples can contain a wide range of elements at varying concentrations. Inter Element Corrections (IEC) have been established as the preferred correction technique for these spectral interferences in labs running US EPA methods. However, Agilent’s powerful spectral deconvolution Fast Automated Curve-fitting Technique (FACT) can also be used where accepted by local regulators. In this study, IEC factors were setup using the ICP Expert v7 software. Once the factors have been determined, they can be stored in a template and reused in subsequent analyses.

Results and discussion

Linear dynamic range analysis (LDR)

The Vista Chip II detector used in the 5100/5110 ICP-OES has the fastest processing speed (1 MHz) of any charge coupled device (CCD) detector used in ICP-OES and provides a full 8 orders of linear dynamic range by reducing the likelihood of pixel saturation and signal over-ranging. The SVDV configuration with its synchronous measurement of axial and radial signals also aids the upper concentration limit for each analyte beyond which results cannot be reported without dilution of the sample. The results in Table 3 show

the excellent upper concentration limit results for Na and K, which are selected by the DSC to be measured from the radial light, and for the elements which are selected by the DSC to be measured from the axial light, in particular Mg, Ca, and Al. The maximum error for each calibration standard within the linear range cannot exceed 10%.

Table 3. Upper concentration limits for the 5100 SVDV ICP-OES. All measurements were determined in a single analytical run

Element	LDR (ppm)
Ag 328.068	50
Al 308.215	200
As 188.980	50
B 249.772	200
Ba 493.409	25
Be 313.042	5
Ca 315.887	100
Cd 226.502	50
Ce 413.765	100
Co 228.616	100
Cr 205.552	50
Cu 324.754	100
Fe 259.940	50
K 766.491	200
Li 670.784	20
Mg 279.079	500
Mn 257.610	10
Mo 203.846	100
Na 589.592	500
Ni 231.604	50
P 214.914	500
Pb 220.353	200
Sb 206.834	200
Se 196.026	50
Si 251.611	200
Sn 189.925	100
Sr 421.552	2.5
Ti 334.941	25
V 292.401	100
Zn 213.857	10
Tl 190.794	100

Method detection limits (MDL)

The method detection limits (MDL) of each element were determined according to the procedure in EPA Method 200.7 revision 5 (40 CFR, part 136 Appendix B, Section 9.2.1). A standard solution containing analytes at a concentration of 3–5 times the Instrument Detection Limit was measured on three non-consecutive days. Excellent detection limits were obtained for the elements selected by the DSC to be measured in the axial view e.g. As, Pb, and Se. In the same measurement, detection limits for K and Na were equivalent to those from a typical radial measurement.

Table 4. Method detection limits acquired per EPA Method 200.7 guidelines. All MDLs were determined in a single analytical run.

Element	MDL (µg/L)
Al 308.215	2.8
Sb 206.834	3.4
As 188.980	3.7
Ba 493.409	0.1
Be 313.042	0.04
B 249.772	0.9
Cd 226.502	0.2
Ca 315.887	4.7
Ce 413.765	3.7
Cr 205.552	0.5
Co 228.616	0.6
Cu 324.754	0.5
Fe 259.940	0.5
Pb 220.353	1.9
Li 670.784	0.1
Mg 279.079	4.6
Mn 257.610	0.1
Mo 203.846	1.2
Ni 231.604	0.9
P 214.914	8.2
K 766.491	21.6
Se 196.026	3.2
Si 251.611	1.4
Ag 328.068	0.4
Na 589.592	10.1
Sr 421.552	0.1
Ti 334.941	0.1
Tl 190.794	3.6
Sn 189.925	2.5
V 292.401	0.4
Zn 213.857	0.3

CRM recoveries

To test the accuracy of the analytical method, two TMDW CRMs were analyzed. The average of 7 analyses of TMDW-A and TMDW-B are shown in Table 5, showing excellent recoveries for all elements, demonstrating the capability of the 5100 SVDV ICP-OES to analyze trace elements in the axial view, while at the same time measuring Na and K at high levels in radial view.

Sample throughput

To analyze the full suite of elements on a conventional DV instrument would require a measurement in the axial view and one in the radial view, whereas it has been demonstrated that this can all be done in one measurement using the 5100 SVDV ICP-OES.

Running the 5100 SVDV method with the SPS 3 and SVS 2+, it was possible to analyze a sample every 58 seconds which equates to an argon consumption of less than 21 L/sample using the operating parameters outlined in Table 1. This allows more samples to be run every day, and also reduces the cost of argon per sample. This equates to a reduction in argon usage of around 50%, compared to a conventional DV system where 2, 3, or even 4 readings of the sample are required to analyze the entire suite of elements.

Table 5. Recovery of elements in two trace metals in drinking water CRMs using the 5100 SVDV ICP-OES. All analytes were determined in a single analytical run.

Element/ wavelength (nm)	CRM-TMDW-A				CRM-TMDW-B			
	Certified (µg/L)	Measured (µg/L)	SD	Recovery (%)	Certified (µg/L)	Measured (µg/L)	SD	Recovery (%)
Al 308.215	125	131.0	15.7	105	125	125.2	4.8	100
Sb 206.834	55	55.7	1.7	101	55	55.3	3.5	100
As 188.980	55	58.0	2.3	105	10	10.4	2.7	104
Ba 493.409	500	493.9	6.8	99	500	483.3	7.9	97
Be 313.042	15	15.0	0.4	100	15	14.9	0.5	100
B 249.772	150	152.4	0.8	102	150	151.5	1.3	101
Cd 226.502	10	10.0	0.4	100	10	9.9	0.5	99
Ca 315.887	31000	31573	423	102	31000	31411	334	101
Cr 205.552	20	20.2	0.3	101	20	19.8	0.6	99
Co 228.616	25	23.9	0.5	96	25	23.4	0.4	94
Cu 324.754	20	18.8	0.1	94	20	19.1	0.3	96
Fe 259.940	90	98.0	6.4	109	90	95.1	1.9	106
Pb 220.353	20	20.4	1.0	102	20	19.8	0.6	99
Li 670.784	15	13.5	0.3	90	15	14.8	0.3	99
Mg 279.079	8000	8175	54.8	102	8000	8015	62.3	100
Mn 257.610	40	39.5	1.1	99	40	38.4	1.3	96
Mo 203.846	110	110.5	1.4	100	110	109.6	0.8	100
Ni 231.604	60	64.5	3.6	108	60	59.9	1.3	100
K 766.491	2500	2563	19.6	103	2500	2561	35.0	102
Se 196.026	11	11.3	1.3	103	11	11.4	1.8	103
Ag 328.068	2	1.9	0.2	94	2	1.8	0.2	91
Na 589.592	2300	2412	24.9	105	22000	22678	272	103
Sr 421.552	300	308.1	5.1	103	300	305.5	4.0	102
Tl 190.794	10	10.2	2.0	102	10	9.5	2.2	95
V 292.401	35	34.7	0.4	99	35	34.5	0.6	99
Zn 213.857	75	78.8	0.4	105	75	77.6	0.6	103

Long term stability

Long term stability was determined by running a Instrument Performance Check sample every 10 samples, as specified in the US EPA 200.7 method. The plug-and-play vertical torch of the 5100/5110, with Mass Flow Controller control of all plasma gases ensures reproducible torch alignment that contributes to instrument stability over long periods of operation. This is demonstrated in Figure 1, which shows that excellent long term stability was achieved over 12 hours, with all elements having recoveries within $\pm 10\%$ and a %RSD of less than 1.3% over the duration of the worksheet run. Long term stability means that costly quality control (QC) failures and reruns can be minimized.

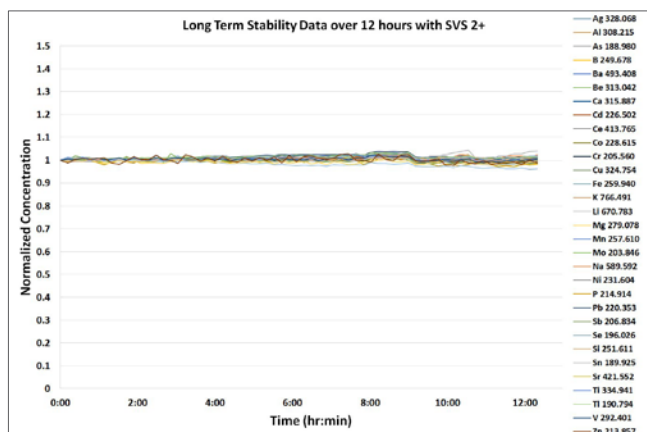


Figure 1. Long term stability over a 12 hour analysis

Conclusions

The Agilent 5100/5110 Synchronous Vertical Dual View (SVDV) ICP-OES, combined with an SPS 3 autosampler and the SVS 2+ switching valve is an ideal instrument to meet the productivity demands of environmental labs working to EPA methodology such as 200.7. The instrumentation achieves an excellent sample-to-sample cycle time of 58 seconds. This enables more samples to be measured each day and reduces argon consumption per sample by 50% per sample.

The 5100/5110 SVDV is up to 55% faster than conventional DV instruments because of the unique ability of the Dichroic Spectral Combiner (DSC) to select and measure axial and radial views of the plasma in one reading rather than the multiple readings required by previous generation DV instruments.

Excellent method detection limits in the $\mu\text{g/L}$ (ppb) range were obtained for all elements in a single run. Good recovery results for 26 elements in two TMDW CRMs were achieved, together with stability better than 1.3% for all elements during a 12 hour period.

The study has shown that the 5100 SVDV ICP-OES delivers accurate results in the quickest possible time. Similar performance would be achieved with the 5110 ICP-OES instrument.

Note: Since this study was completed a new, fully integrated switching valve has been released. The new Advanced Valve System (AVS) offers the following improvements over the previous SVS 2+:

- full hardware and software integration for the simplest operation,
- higher sample throughput, and
- improvement to analytical precision.



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