

High Throughput, Low Cost ICP-OES Analysis of Sludge Samples According to US EPA Method 6010C

Application note

Environmental

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Introduction

Many laboratories concerned with the analysis of elements in environmental samples, such as ground waters, industrial wastes, soils, sludge and sediment by ICP-OES, work to United States Environmental Protection Agency (US EPA) method 6010C guidelines. Fast sample throughput and low cost analysis is desirable for these labs but can be challenging to achieve using spectrochemical techniques due to the wide range of elements and their varying concentrations in typical samples.

Traditionally, radial ICP-OES with a vertical torch or a dual view (DV) ICP-OES have been used for the determination of major, minor and trace elements in complex environmental samples. However, the unique Synchronous Vertical Dual View (SVDV) configuration of the Agilent 5100 and 5110 ICP-OES ensures that the instruments can be operated in the best mode for the application (axial, radial, vertical dual view or synchronous vertical dual view) providing full-flexibility with established methods and application requirements [1].



In this study, an Agilent 5100 ICP-OES operating in SVDV viewing mode was used for the analysis of major, minor and trace elements in a certified channel sludge reference material according to method 6010C. An Agilent SVS 2+ Switching Valve System was used with the ICP-OES to improve sample throughput and reduce argon gas consumption per sample. The 6010C method is a performance-based set of guidelines for the analysis of 31 elements in soils, sludge and sediment. 6010C methodology requires the ICP-OES instrument to meet performance criteria for calibration validity, linear dynamic range (LDR) and method detection limits (MDL), as well as a spectral interference checks (ISC) .

Experimental

Instrumentation

All measurements were carried out using an Agilent 5100* SVDV ICP-OES with Dichroic Spectral Combiner (DSC) technology. The DSC improves analysis times by allowing a combination of axial and radial emissions from the plasma to be synchronously directed into the polychromator, with all wavelengths being measured in a single reading. The standard sample introduction system was used, comprising a SeaSpray nebulizer, double-pass glass cyclonic spray chamber and a standard 1.8 mm dual view torch. The instrument's plug and play torch loader automatically aligns the torch and connects gases for fast start up and reproducible performance, irrespective of operator.

An SPS 3 autosampler with the SVS 2+ switching valve was used to deliver samples to the ICP-OES. The innovative SVS 2+ is a 7 port switching valve that increase the productivity of the 5100 ICP-OES by reducing sample uptake, stabilization and rinse delays. The SVS 2+ includes a positive displacement pump that can reach up to 500 rpm and rapidly pumps sample through the sample loop. It also features a bubble injector to reduce sample usage and improve sample washout. A 3 second rinse was used to assist with washout of high concentration elements, such as iron, aluminum and calcium. Instrument operating conditions are listed in Table 1 and SVS 2+ settings are given in Table 2.

*The 5100 ICP-OES has been superceded by the model 5110, which has equivalent performance.

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)	3
Fast pump (80 rpm)	Yes
Background correction	Left and/or right background correction
RF power (kW)	1.4
Nebulizer flow (L/min)	Default (0.70)
Plasma flow (L/min)	Default (12.0)
Aux flow (L/min)	Default (1.0)
Viewing height (mm)	Default (8)

Table 2. SVS 2+ operating parameters

Condition	Setting
Loop uptake delay (s)	5
Uptake pump speed (refill) (rpm)	400
Uptake pump speed (inject) (rpm)	150
Sample loop size (mL)	1.0
Time in sample (s)	4.5
Bubble inject time (s)	4.8

Sample preparation

International Soil-Analytical Exchange (ISE) Channel sludge reference material 859 from de Bilt/Netherlands prepared for the Wageningen Evaluating Programs for Analytical Laboratories (WEPAL) proficiency program was used to check the quality of the analysis.

A Milestone UltraWave was used for microwave digestion of the samples. Extraction (rather than total decomposition) of each sample was carried out according to US EPA method 3051A (Microwave Assisted Acid Digestion of Aqueous Samples and Extracts). Approximately 0.5 g of sample was accurately weighed into microwave vessels followed by addition of 4.5 mL HNO₃ and 1.5 mL HCl. Microwave heating conditions are given in Table 3. After cooling the vessels, the digested solutions were quantitatively transferred to volumetric flasks and brought to 20 mL volume with deionized water. The final acid concentration was 30% Reverse Aqua Regia (R. AR). For each set of the measurements at least one digestion blank containing the same amount of acid as the

samples was prepared for analysis. For each sample material, three replicates were prepared.

Table 3: Parameters used for microwave digestion

Parameter	Setting
Ramp (min)	5.5
Temp (°C)	175
Hold (min)	4.5
Total (min)	10

Calibration standard solutions

Calibration standards were prepared from AccuStandard® solutions, which are suitable for US EPA Contract Laboratory Program (CLP) analysis. The calibration standards and quality control (QC) solutions were diluted with >18 MW/cm³ deionized water and the acid concentration was matched to the acid concentration of the prepared sediment samples (30% v/v). An internal standard solution of 20 ppm Lu and 5 ppm Y was prepared and acid matched to the acid concentration of the samples.

The following are suggested element mixes used for Method 6010C – prepared from the CLP multi-element stock solutions and CLP single element standard solutions.

- CLP Cal-1 Ca, Mg, Na, K
- CLP Cal-2 Cr, Mn, Ni, Zn
- CLP Cal-3 Al, Ba, Be, Co, Cu, Fe, V
- CLP Cal-4 As, Cd, Pb, Se, Tl
- CLP Cal-5 Sb
- CLP Cal-6 Hg, Ag
- CLP Cal-7 B, Mo
- CLP Cal-8 Ce, Li, P, Sn, Ti

Analytical sequence

In order to verify the accuracy and precision of the implementation of Method 6010C, QC samples were analyzed following calibration, during the run, and at the end of the run. Method performance was verified by analysis of an appropriate reference material. The following outlines a typical analytical sequence used in this study:

- Calibrate the instrument using blank and one standard
- Verify the calibration by analyzing the Initial Calibration Verification (ICV) standards, prepared from a purchased second source reference material at a concentration near the midpoint of the calibration range. The acceptance criteria for the ICV standard must be ±10% of the known values for each element.

CLP-ICV-01:	Ag, Ba, Be, Cd, Co, Cu, Fe, Mn, Ni, Pb, Tl, Zn
CLP-ICV-02:	Al, As, Ca, Cr, K, Mg, Na, Sb, V
CLP-ICV-03:	Sb

- Verify the calibration by analyzing the Initial Calibration Blank (ICB), prepared by acidifying reagent water to the same concentration of acid found in the standards and sample. The calibration blank result must be less than two to three times the method detection limit (MDL).
- Verify the lower calibration range (near the quantitation limit) by analyzing the Low-Level Initial Calibration Verification (LLICV) standard, prepared in the same acid matrix using the same standard used for calibration. The acceptance criteria for the ICV standard must be ± 30% of the known values for each element. The analysis data for the LLICV is displayed in Table 6.
- Verify the accuracy of Inter Element Corrections (IEC's) and background corrections by analyzing the Interference Check Solutions (ICS), prepared from known concentrations of the interfering elements and all elements of interest as follows:

ICS A:	containing interfering elements Al, Ca, and Mg at 250 mg/L and Fe at 100 mg/L.
ICS AB:	containing the same interfering elements plus all analyte elements of interest (Ag, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sb, Se, Tl, V and Zn). The measured value for the ICSAB must be within 20% of the true value.

- Verify the calibration after every 10 samples with the Continuing Calibration Verification (CCV) standard, prepared in the same acid matrix using the same standard used for calibration, at the concentration near the midpoint of the calibration curve.

CLP-CCV-01:	Ag, Ba, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, V, Zn
CLP-CCV-02:	As, Cd, Pb, Tl
CLP-CCV-03:	Mo, B
CLP-CCV-04:	P, Ti, Ce, Li, Sn, Sr

- Verify the calibration after every 10 samples with the Continuing Calibration Blank (CCB), prepared by acidifying reagent water to the same concentration of acid found in the standards and sample. The calibration blank result must be less than two to three times the MDL.

Performance characteristics

The initial performance parameters for 31 elements were determined as specified in US EPA Method 6010C using the wavelengths listed in Table 4.

Method Detection Limits

The MDL of each element was determined per the procedure specified method 6010C and was expressed as the minimum concentration of an analyte that can be measured. Solutions spiked with each analyte at a concentration of two to three times the Instrument Detection Limit (IDL) were analyzed ten times and the standard deviation of each analyte concentration was multiplied by 3. The procedure was repeated three times to ensure a better estimate of the MDL was obtained. The results shown in Table 4 are an average of

3 determinations over 3 separate days. Very low MDLs were obtained for all wavelengths.

Linear Dynamic Range (LDR)

Method 6010C requires that upper limit of the ICP linear range be established for each wavelength. The upper limit is considered to have been exceeded when the measured concentration is more than 10% below the true value. For this experiment, standards at the upper limits of the calibration range were prepared, analyzed and quantified against the calibration curves (minimum of three standard concentrations across the range). The results of the LDR are given in Table 4 and the calculated values were within $\pm 10\%$ of the true value.

The results in Table 4 show excellent upper concentration limit results for Na and K and for other elements, such as Fe, Mg, Ca, and Al. A LDR up to 10,000 mg/L in solution for Fe is required for the analysis of tough samples such as sludges, sediment or soils. K 766 shows excellent linearity up to 1000 ppm, as shown in Figure 1.

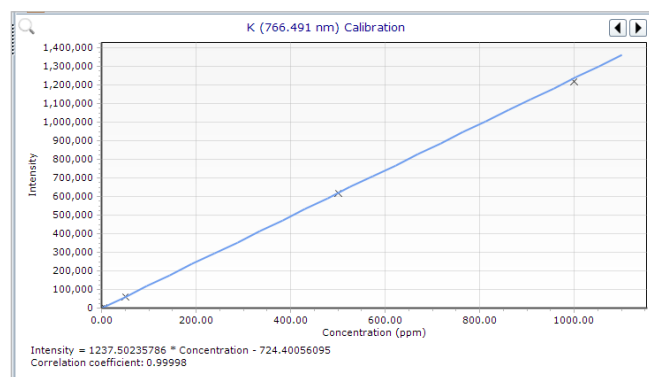


Figure 1. The calibration curve for K 766.491 nm in SVSD mode shows a wide linear range.

The LDR displayed by the 5100 ICP-OES permits the analysis of elements over a wide concentration range, without the need to dilute the samples frequently. This allows analysts to carry out single point calibration, thereby simplifying operation and improving productivity.

Table 4. MDLs (µg/L) in solution for target elements and upper concentration limits (mg/L) acquired per EPA Method 6010C guidelines.

Element and wavelength	LDR (mg/L)	MDL (µg/L)
Ag 328.068	50	0.48
Al 308.215	2000	3.6
As 188.980	50	4.6
B 249.678	200	0.81
Ba 233.527	50	0.18
Be 313.042	5.0	0.04
Ca 318.127	1000	5.9
Cd 214.439	25	0.35
Ce 446.021	100	2.3
Co 228.615	250	0.54
Cr 205.560	100	0.47
Cu 324.754	100	0.42
Fe 273.358	10000	53
Hg 184.887	250	1.4
K 766.491	1000	21
Li 610.365	50	0.31
Mg 279.078	1000	3.5
Mn 257.610	50	0.08
Mo 202.032	50	0.48
Na 588.995	1000	50
Ni 231.476	100	3.7
P 213.618	500	6.3
Pb 220.353	200	3.1
Sb 206.834	200	4.0
Se 196.026	25	5.1
Sn 189.925	100	3.8
Sr 421.552	2.5	0.05
Ti 334.188	25	0.14
Tl 190.794	100	4.4
V 292.401	100	0.73
Zn 213.857	20	0.22

Results and Discussion

Sample analysis

Sediment reference material WEPAL-ISE 859 was analyzed using the Agilent 5100 SVDV ICP-OES. While the samples and standards were matrix matched, an internal standard was also used to improve accuracy. Internal Standards Lu 261.541 and Lu 547.668 were used to correct for the lines selected by the DSC to be measured axially and Y 488.368 was used to correct for the elements measured radially by the DSC, in particular Na and K.

The results for the analysis of the CRM are given in Table 5. Excellent recoveries were obtained from an average of 3 determinations repeated over 3 days.

Fast Automated Curve Fitting (FACT) was used to correct for a Ca interference on Li 610.365.

Table 5. Recovery of elements present in CRM WEPAL-ISE 859 Channel sludge using the 5100 SVDV ICP-OES. All analytes were determined in a single analytical run.

Element and wavelength	Certified (mg/kg)	Measured (mg/kg)	SD	%Recovery
Ag 328.068	(4.68) ^{Inf}	4.70	0.154	101
Al 308.215	28000	27572	0.287	101
As 188.980	38.0	40.0	0.624	107
B 249.678	(29.3) ^{Inf}	29.6	0.045	102
Ba 233.527	(466) ^{Inf}	473	0.027	102
Be 313.042	(1.59) ^{Ind}	1.58	0.025	99
Ca 318.127	31000	31442	1.87	102
Cd 214.439	6.29	5.91	0.031	96
Ce 446.021	(38.9) ^{Inf}	37.4	0.350	97
Co 228.615	13.4	13.6	0.099	100
Cr 205.560	124	129	0.078	104
Cu 324.754	127	129	0.079	101
Fe 273.358	37300	38068	7.51	102
Hg 184.887	1.86	1.81	0.250	97
K 766.491	4560	4502	5.67	99
Li 610.365	(32.2) ^{Inf}	34.5	1.44	107
Mg 279.078	6980	7129	0.574	102
Mn 257.610	847	830.6	0.020	98
Mo 202.032	(1.91) ^{Ind}	1.85	0.154	97
Na 588.995	432	436	37.61	101
Ni 231.476	59.3	60.5	103	102
P 213.618	3810	3727	102.70	98
Pb 220.353	192	176	3.680	92
Sb 206.834	(2.18) ^{Inf}	2.05	0.033	94
Se 196.026	(1.59) ^{Ind}	1.59	0.130	100
Sn 189.925	(21.2) ^{Inf}	19.6	0.366	92
Sr 421.552	(131) ^{Inf}	134	2.67	103
Ti 334.188	(339) ^{Ind}	358	20.54	106
Tl 190.794	(1.19) ^{Inf}	1.21	0.061	101
V 292.401	(50.8) ^{Ind}	50.9	0.816	100
Zn 213.857	816	800	10.6	98

^{Inf} Informative value based on less than 8 results of coefficient of variation higher than 50%.

^{Ind} Indicative value based on at least 8 and less than 16 results or a coefficient of variation between 25% and 50%.

The excellent recoveries demonstrate the capability of the 5100 SVDV to measure elements across a wide concentration range in a single measurement of the sample. Using the DSC, elements present at high concentrations, such as Na and K are measured radially, while elements at trace levels, such as Hg, As and Se are measured axially.

Low Level of Quantitation Verification (LLQC) Standard

A single calibration standard and blank were used to establish the calibration curve and Low Level Check Standards (LLICV and LLCCV) were used to verify the calibration curve. The acceptance criteria for the LLQC standard must be within $\pm 30\%$. The analysis data for the LLICV is displayed in Table 6. The recoveries obtained in this study were all within the required limits.

Table 6. Analysis data for the LLICV standard

Element and wavelength	Measured (mg/L)	%Recovery
Ag 328.068	0.020	98%
Al 308.215	0.020	100%
As 188.980	0.019	96%
B 249.678	0.018	92%
Ba 233.527	0.020	100%
Be 313.042	0.020	98%
Ca 318.127	0.194	97%
Cd 214.439	0.019	96%
Ce 446.021	0.023	116%
Co 228.615	0.019	95%
Cr 205.560	0.020	99%
Cu 324.754	0.019	93%
Fe 273.358	0.218	109%
Hg 194.164	0.021	107%
K 766.491	0.182	91%
Li 610.365	0.019	96%
Mg 279.078	0.019	96%
Mn 257.610	0.021	107%
Mo 202.032	0.017	85%
Na 588.995	0.225	112%
Ni 231.476	0.023	117%
P 213.618	0.022	108%
Pb 220.353	0.021	103%
Sb 206.834	0.020	99%
Se 196.026	0.020	99%
Sn 189.925	0.021	104%
Sr 421.552	0.022	108%
Ti 334.188	0.020	101%
Tl 190.794	0.020	99%
V 292.401	0.020	98%
Zn 213.857	0.020	99%

Interference Check Solutions (ICS)

Channel sludge can contain high concentrations of unknown elements which can cause significant spectral overlaps that need to be identified. The ICP Expert v7 software automatically calculates IEC factors based on the analysis of analyte and interference solutions. These correction factors are then automatically applied to each sample analysis. Two check solutions were analyzed, ICSA and ICSAB. The measured values for the standards (Table 7) are all within the required $\pm 20\%$ of the true concentration limit.

Table 7. Analysis data for the ICSA and ICSAB standards

Element and wavelength	ICSA (mg/L)	ICSAB (mg/L)	Actual	%Recovery
Ag 328.068	<MDL	2.05	2.00	103
Al 308.215	244	247	250	99
As 188.980	<MDL	0.995	1.00	99
Ba 233.527	<MDL	0.548	0.50	110
Be 313.042	<MDL	0.516	0.50	103
Ca 318.127	261	264	250.00	105
Cd 214.439	<MDL	1.01	1.00	101
Co 228.615	<MDL	0.481	0.50	96
Cr 205.560	<MDL	0.526	0.50	105
Cu 324.754	<MDL	0.544	0.50	109
Fe 273.358	100	102	100	102
Mg 279.078	260	263	250	105
Mn 257.610	<MDL	0.536	0.50	107
Ni 231.476	<MDL	0.972	1.00	97
Pb 220.353	<MDL	0.474	0.50	95
Sb 206.834	<MDL	6.19	6.00	103
Se 196.026	<MDL	0.547	0.50	109
Tl 190.794	<MDL	0.951	1.00	95
V 292.401	<MDL	0.496	0.50	99
Zn 213.857	<MDL	0.970	1.00	97

Long term stability

Long term stability was determined by analyzing a Standard Reference Material every 10 samples for eight hours. The 5100 SVDV ICP-OES showed excellent stability over the eight hour run with recoveries for all elements within 10% of the true value. RSD values of less than 1.5% were achieved for all elements over the duration of the run, except for slightly higher RSDs of 2.3% and 2.0% for Hg and Sb respectively. Figure 2 shows that conditions remain stable for all elements during the eight hour sequence.

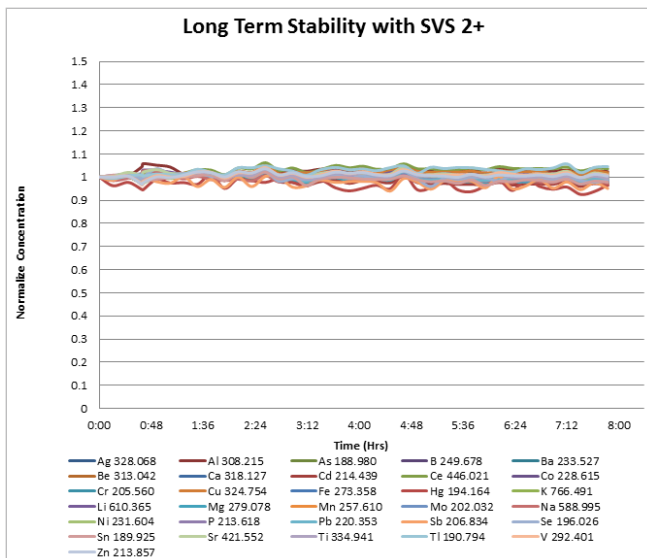


Figure 2. Stability for EPA 6010C elements using an 5100 ICP-OES with SVS 2+ valve.

The solid-state RF (SSRF) system operating at 27 MHz and the vertical torch position of the 5100 leads to excellent plasma robustness and long term stability, especially for challenging sludge samples. The plug and play vertical torch that ensures reproducible torch alignment and Mass Flow Controller control of all plasma gases also contributes to instrument stability over long periods of operation. Long term stability means re-runs of samples and costly QC can be reduced, leading to increased productivity.

Fast sample throughput and low argon consumption

An analysis sequence that adheres to US EPA protocols can be time-consuming as there are a large number of QC solutions that must be analyzed. In this study, the use of DSC technology with the SVS 2+ dramatically reduced the sample-to-sample analysis time to 60 seconds. This equates to 60 samples per hour or 480 samples over an 8 hour day. The total argon consumption for the method was 19 L per sample.

High-throughput laboratories typically measure more than 30 elements per sample and analyze hundreds, even thousands, of samples every day. Running the 5100 SVDV ICP-OES using the SVS 2+ with SPS 3 autosampler reduced the typical sample-to-sample measurement time by 73 seconds compared to the same analysis performed on a 5100 VDV without the SVS 2+ [2].

The rapid sample throughput capabilities of the Agilent 5100 ICP-OES are due to the optimized positioning of the sample introduction system to minimize sample delivery time, the fast Vista Chip 2 detector which reads all wavelengths in a single measurement, and the SVS 2+ Switching Valve System.

Conclusions

Agilent's 5100 or 5110 SVDV ICP-OES with a vertical torch provides the robustness and analytical performance required for the determination of tough environmental samples in accordance with US EPA method 6010C. The unique configuration of the instruments, with synchronous dual view significantly improves sample-to-sample analysis times compared to conventional DV ICP-OES. This produces rapid sample throughput and reduced argon consumption. The SVS 2+ Switching Valve System further improves sample throughput by as much as 73 s compared to conventional sample introduction. Both rinse time and sample analysis time are reduced without any compromise in performance.

In addition to excellent MDLs, spike recoveries, linearity, and excellent long-term stability, a sample to sample analysis time of just 60 seconds per sample was achieved. This enables more samples to be measured each day and reduces argon consumption to just 19 L per sample.

The 5100 or 5110 SVDV ICP-OES fitted with the innovative SVS 2+ is a cost-effective and highly productive system suitable for labs running a wide range of environmental-type samples such as soils, sediments and sludges.

Reference

1. Benefits of a vertically oriented torch— fast, accurate results, even for your toughest samples, Agilent publication, **2014**, publication number 5991-4854EN.
2. Increase productivity for environmental sample analysis using the SVS 2+ Switching Valve System for Agilent 5100 SVDV ICP-OES, Agilent publication, **2015**, publication number 5991-5990EN.



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