

Analysis of Waste Samples According to US EPA Method 6010D

Using the smart features of the Agilent 5800 VDV ICP-OES to simplify method development and quality assure the results



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Introduction

In support of its waste management program, the US Environmental Protection Agency (EPA) has developed various methods to test for contaminants in environmental samples. The test methods are included in the EPA publication: Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, also known as SW-846. Within SW-846, method 6010D outlines the procedure for the determination of 31 elements in soils, sediment, and sludges using ICP-0ES (1). EPA method 6010D is a performance-based method that specifies quality control (QC) criteria for calibration validity, linear dynamic range (LDR), and method detection limits (MDLs). Analysts are advised to use a sample digestion method that is suitable for solids samples, such as the microwave assisted digestion procedure given in EPA method 3051A (2). The sample preparation procedure outlined in 3051A is not a total digestion method but extracts the metals that are available, simulating how the samples may react in the environment.

To manage the large sample loads that are typical of many environmental testing laboratories, ICP-OES users need highly productive instrument performance that is reliable and stable over long periods. The Agilent 5800 ICP-OES meets these demands with a series of smart tools that are accessible from the Agilent ICP Expert instrument-control software (3). The following smart tools are designed to simplify method development, verify results, maximize instrument uptime, and minimize the need to remeasure samples:

- The IntelliQuant Screening function uses data analytics to automatically identify spectral overlaps that can lead to false-positive/biased results. It also recommends the emission wavelength that will give the most accurate result (4).
- Outlier conditional formatting (OCF) compares analytical results from different wavelengths of the same element, providing extra confidence in the results (3). OCF provides a quick visual overview of the results to help laboratories assess and manage the quality of the data set.
- Early maintenance feedback (EMF) allows the user to set up alerts to prompt maintenance after a specified number of samples has been run (3). Tracking instrument health and carrying out maintenance tasks at the right time ensures consistent, high-level analytical performance, even of complex samples such as soils.

In this study, an Agilent 5800 Vertical Dual View (VDV) ICP-OES fitted with an AVS 7 switching valve was used to analyze soil samples according to the EPA 6010D standard method. The samples were prepared according to EPA method 3051A. The elements reported in this study include silver, aluminum, arsenic, boron, barium, beryllium, calcium, cadmium, cerium, cobalt, chromium, copper, iron, mercury, potassium, lithium, magnesium, manganese, molybdenum, sodium, nickel, phosphorus, lead, antimony, selenium, tin, strontium, titanium, thallium, vanadium, zinc, and zirconium.

Experimental

Instrumentation

For fast sample analysis and high sample throughput, an Agilent 5800 VDV ICP-OES fitted with an Agilent AVS 7 seven-port switching valve (5) was used with an Agilent SPS 4 autosampler. The fully integrated AVS 7 uses a high-speed positive displacement pump to rapidly fill the sample loop, speeding up the analysis. The AVS also reduces maintenance and cleaning requirements of the torch, as less sample digest passes through it compared to conventional sample introduction.

The 5800 ICP-OES uses an Agilent Vista Chip III detector. The sophisticated detector provides high-speed continuous wavelength coverage, allowing the analyst to choose multiple wavelengths for each element, without adding a time delay to the analysis.

To ensure the accuracy of the final quantitative method, the IntelliQuant Screening software function was used during method development. IntelliQuant Screening can identify and provide semiquantitative results for up to 70 elements in a sample, as shown by the results for a soil sample (Figure 1). It can also identify spectral interferences that arise from elements present in complex samples.

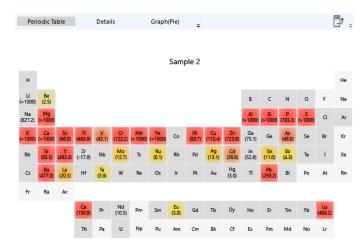


Figure 1. Using IntelliQuant Screening to identify elements in an unknown soil sample digest. The concentration of each element is shown in the periodic table "heat map" view.

Internal standard correction (10 mg/L of yttrium and lutetium) was used to correct for matrix effects and easily ionizable element (EIE) interferences. The 5800 VDV ICP-OES operating conditions are given in Table 1 and the AVS 7 parameters are listed in Table 2.

Table 1. 5800 VDV ICP-OES instrument and method parameters.

Parameter	Radial	Axial			
Read Time (s)	10	10			
Replicates	3	3			
Sample Uptake Delay (s)	0				
Stabilization Time (s)	10	0			
Rinse Time (s)	()			
Pump Speed (rpm)	1	2			
RF Power (kW)	1.	.5			
Aux Flow (L/min)	1				
Plasma Flow (L/min)	12				
Nebulizer Flow (L/min)	0	.7			
Viewing Height (mm)	8	NA			
Nebulizer	SeaSpray concentric				
Spray Chamber	Double pas	ss cyclonic			
Torch	Easy-fit demountable VDV, 1.8 mm injector				
Sample Pump Tubing	White-white				
Internal Standard Pump Tubing	Black-black				
Waste Pump Tubing	Blue-blue				
Background Correction	Off Peak	left/right			

Table 2. AVS 7 switching valve system parameters.

Parameter	Setting
Sample Loop Size (mL)	1.5
Pump Rate - Uptake (mL/min)	36
Pump Rate - Inject (mL/min)	4
Valve Uptake Delay (s)	7
Bubble Inject Time (s)	2
Pre-emptive Rinse Time (s)	1

IntelliQuant Screening as a method development and troubleshooting tool

IntelliQuant Screening was used to assist with method development, particularly to determine the linear dynamic range (LDR) required for the application and for wavelength selection. Being sure that the calibration range and LDR are appropriate for the analysis minimizes the need to further dilute and remeasure any samples that exceed the LDR.

For wavelength selection, two unknown soil samples were digested and measured using IntelliQuant Screening. Following the analysis, the software assigns a star-ranking to the different element wavelengths, as shown in the example

for arsenic in Figure 2. The As 188.980 nm line received the best star ranking due to a background shift on the As 193.696 nm wavelength. Hovering over the "?" symbol displays reasons for the poor rating on a wavelength. For example, As 197.198 nm is interfered by V 197.199 nm, so received only one star.

Element	Used	Flags	Wavelength	Rating		Concentration	Intensity	Background	
As									^
	~		188.980	***		63.74	3200.2	1950.6	
			193.696	***		80.14	3045.7	4197.4	
			197.198	*	?	66.29	2743.6	3529.5	
			200.334	**		52.13	737.9	2455.0	~

Figure 2. IntelliQuant star ranking for As helps with wavelength selection.

Identifying any potential interferences before running the quantitative method reduces the need for sample remeasurements due to interferences. IntelliQuant Screening can be used as a troubleshooting tool to identify the reason for any inaccurate or inconsistent results, however for additional assurance, IntelliQuant (6) can also be run in real time on every sample. The IntelliQuant function provides valuable insight into the sample composition by identifying which elements are present, increasing confidence in the quantitative analytical results with only a short amount of added measurement time.

Reference materials and samples

Standard reference material (SRM) NIST 2711a Montana II soil (with moderately elevated trace element concentrations) was used to validate the 5800 ICP-OES method. A silica sand matrix blank, purchased from Sigma Aldrich, and a soil sample, collected from Melbourne, Australia, were used during method development and for the matrix spike test.

Sample preparation

The soil SRM, soil, and silica matrix samples were prepared for analysis according to the guidelines given in EPA 3051A. Around 0.5 g of each sample was accurately weighed and transferred to a clean PTFE microwave vessel. Samples were left to predigest in 0.1 mL of 18 M Ω de-ionized water (DIW) and 6 mL of HNO $_3$ (Merck) for approximately 15 minutes. The vessel was then capped and placed in a Mars 6 Microwave Digestion System (CEM Corporation, NC, USA) for digestion using the program given in Table 3. Once cool, the solutions were made up to 25 mL with DIW. The samples were thoroughly mixed using a vortex mixer for 10 minutes at 3000 rpm to give a final sample matrix of 24% HNO $_2$.

Table 3. Microwave method parameters.

Parameter	Value
Power (W)	0-1200
Temperature (°C)	175
Ramp Time (min)	5
Hold Time (min)	4.5

Calibration and linear dynamic range

Calibration standards were prepared from Agilent single element stock solutions into a matrix of 24% $\rm HNO_3$ to match the matrix of the diluted samples after digestion. Single point linear calibrations were used for all elements, with major elements calibrated using a 250 mg/L standard and minor elements using a 5 mg/L standard. To ensure that the calibrations were linear per the 6010D method, a linearity study was completed for all elements. The LDR concentration was given as the maximum concentration measured for each element.

Figure 3 shows the linearity of the calibration for Fe 273.358 nm. The data shows that Fe 273.358 is linear (the relative standard error is 1.9%) to at least 10,000 ppm in solution. With a nominal sample mass of 0.5 g, and nominal sample volume of 25 mL, the linear range for Fe is 50% in sample. EPA 6010D states that for a linear study, the solutions must read within $\pm 10\%$ of the expected value.



Figure 3. Linearity of Fe 273.358 nm.

Background correction and interference correction

The analysis of complex samples such as soils and wastes can be hindered by spectral interferences. These background structures can be automatically corrected by modeling the background to each analyte peak using the fitted background correction (FBC) or Fast Automated Curve-fitting Technique (FACT). Both techniques are included in the ICP Expert software. However, off-background correction and inter element corrections (IEC) are typically used by analysts running 6010D method, so that correction technique was used in this study. An example for the off-peak background correction for Ag 328.068 nm is shown in Figure 4.

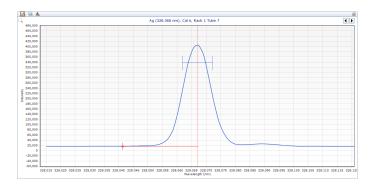


Figure 4. Off-peak background correction for Ag 328.068 nm.

Quality control using OCF

The OCF function of the ICP Expert software was used during the QC assessment of the data. Figure 5 shows that the element concentration %RSD for As has exceeded the limit, as indicated by the flag (F). Arsenic 193 and 197 lines are reporting lower results than As 188. The result-concentration %RSD flag (B) provides further information. The B flag indicates that the replicate %RSD is greater than the target (set) value of 3%. If needed, users can change the acceptance value for %RSD.

Using the IntelliQuant Screening data collected during method development, confidence can be gained in the result for As 188.980 nm (Figure 2). This extra insight avoids the need to remeasure the SRM due to differing results. The expected concentration for As in the SRM is 7.82 mg/L. To ensure that any potential data-related issues or QC failures are identified quickly, the OCF function can be set up in real time to display only results that have been flagged.



Figure 5. The OCF function identifies potentially problematic results.

The QC protocol guidance outlined in EPA 6010D, which is designed to assure the quality of the results, was used in this application.

Results and discussion

Instrument and method detection limits

Instrument detection limits (IDL) were determined using the 5800 VDV ICP-OES operating conditions given in Table 1. Once established, a spiked solution was prepared at a concentration of four times the IDL (US EPA 6010D suggests 3–5 time the IDL) in the same matrix as the calibration solutions. To determine the method detection limit (MDL), the solution was analyzed 10 times on three days. The MDL was calculated as three sigma of the spiked measurement (Table 4).

Table 4. MDLs in solution and in the sample.

Element and Wavelength	MDL in Solution (mg/L)	MDL in Sample (mg/kg)	Element and Wavelength	MDL in Solution (mg/L)	MDL in Sample (mg/kg)
Ag 328.068	0.0006	0.0293	Mg 279.800	0.0052	0.262
Al 237.312	0.0286	1.43	Mn 257.610	7E-05	0.00327
As 188.980	0.0045	0.225	Mo 202.032	0.0009	0.0446
B 208.956	0.0013	0.0655	Na 589.592	0.0081	0.406
Ba 233.527	0.0002	0.00955	Ni 231.604	0.0007	0.0347
Be 313.107	3E-05	0.00167	P 213.618	0.007	0.352
Ca 315.887	0.0041	0.207	Pb 220.353	0.0025	0.125
Cd 214.439	0.0001	0.0061	Sb 206.834	0.0061	0.304
Ce 418.659	0.0032	0.158	Se 196.026	0.0092	0.46
Co 230.786	0.0007	0.0356	Sn 189.925	0.0012	0.062
Cr 205.560	0.0005	0.0229	Sr 216.596	0.0007	0.0348
Cu 327.395	0.0008	0.042	Ti 334.188	0.0003	0.015
Fe 273.358	0.292	14.6	TI 190.794	0.0055	0.274
Hg 194.164	0.001	0.0484	V 292.401	0.0007	0.0368
K 766.491	0.0811	4.06	Zn 206.200	0.0003	0.0164
Li 670.783	0.0105	0.525	Zr 343.823	0.0003	0.0125

Lower limit of quantitation (LLOQ)

To assess the precision and bias of the method over time, the LLOQ was determined by measuring a low-level spiked sample 10 times. The same solution used to determine the MDLs was used to determine the LLOQ. The 5800 method met the method acceptance criteria (data not shown), which state that the average recovery of the spiked samples is required to be within ±35% of the expected value and a relative standard deviation of <20%.

Initial calibration blank (ICB) and continuing calibration blank (CCB)

The ICB and CCB are used to test the accuracy of the calibration, and to check for potential contaminants in the reagents used to prepare the calibration standards. EPA method 6010D states that the ICB and CCB must report less than half the LLOQ for the target elements and less than the LLOQ, respectively. The results in Table 5 show that the criteria were met for all elements in this application.

Interference check solutions (ICSA and ICSAB)

The ICSA is used to ensure that the IECs correct interferences from major elements accurately. The ICSA solution contains 500 mg/L each of Al, Ca, and Mg, and 200 mg/L of Fe. The 6010D method states that the absolute value of the concentration for target analytes should be less than ± the LLOQ. Daily analysis of the ICSA solution checks that elements that are typically present at high concentrations aren't causing interferences on target analytes, and that the IECs are still valid. An ICSAB solution is also used to check the validity of the IECs. The ICSAB solution contains the same concentration of Al, Ca, Fe, and Mg as the ICSA solution, plus 1 mg/L of each of the application's target analytes. Results for target analytes must be within ±20% of the expected value.

The ICSA and ICSAB results in Table 5 show that the 5800 VDV ICP-0ES method met the 6010D method requirements.

Initial calibration verification (ICV) and continuing calibration verification (CCV)

The ICV and CCV solutions were both made from a separate source (CPAChem Ltd.) to the calibration standards. Multi-element stock solutions were diluted into the same matrix as the calibration standards using DIW. A low-level quality control (LLQC) solution was prepared as a 1 in 25 dilution of the ICV in the same matrix as the calibration standards. The CCV was analyzed after every 10 samples to ensure the ongoing validity of the calibration. All elements reported recoveries within the EPA 6010D acceptance criteria of $\pm 10\%$ of the true value for the ICV and CCV, and $\pm 20\%$ of the true value for the LLQC (Table 5).

Table 5. Results and recoveries for all QC samples achieved using the 5800 VDV ICP-OES.

	ICB	ССВ	ICSA		ICSAB			ICV		LLQC		
	(mg/L)	(mg/L)	(mg/L)	Measured (mg/L)	Expected (mg/L)	Recovery (%)	Measured (mg/L)	Expected (mg/L)	Recovery (%)	Measured (mg/L)	Expected (mg/L)	Recovery (%)
Ag 328.068	<0.5*LLOQ	<ll0q< td=""><td><ll0q< td=""><td>1.02</td><td>1.00</td><td>102</td><td>1.15</td><td>1.25</td><td>92</td><td>0.0479</td><td>0.05</td><td>96</td></ll0q<></td></ll0q<>	<ll0q< td=""><td>1.02</td><td>1.00</td><td>102</td><td>1.15</td><td>1.25</td><td>92</td><td>0.0479</td><td>0.05</td><td>96</td></ll0q<>	1.02	1.00	102	1.15	1.25	92	0.0479	0.05	96
Al 237.312	<0.5*LLOQ	<ll0q< td=""><td>496</td><td>506</td><td>500</td><td>101</td><td>96.5</td><td>100</td><td>97</td><td>3.87</td><td>4</td><td>97</td></ll0q<>	496	506	500	101	96.5	100	97	3.87	4	97
As 188.980	<0.5*LLOQ	<ll0q< td=""><td><ll0q< td=""><td>1.03</td><td>1.00</td><td>103</td><td>1.27</td><td>1.25</td><td>102</td><td>0.0493</td><td>0.05</td><td>99</td></ll0q<></td></ll0q<>	<ll0q< td=""><td>1.03</td><td>1.00</td><td>103</td><td>1.27</td><td>1.25</td><td>102</td><td>0.0493</td><td>0.05</td><td>99</td></ll0q<>	1.03	1.00	103	1.27	1.25	102	0.0493	0.05	99
B 208.956	<0.5*LLOQ	<ll0q< td=""><td><ll0q< td=""><td>0.947</td><td>1.00</td><td>95</td><td>2.48</td><td>2.5</td><td>99</td><td>0.103</td><td>0.1</td><td>103</td></ll0q<></td></ll0q<>	<ll0q< td=""><td>0.947</td><td>1.00</td><td>95</td><td>2.48</td><td>2.5</td><td>99</td><td>0.103</td><td>0.1</td><td>103</td></ll0q<>	0.947	1.00	95	2.48	2.5	99	0.103	0.1	103
Ba 233.527	<0.5*LLOQ	<ll0q< td=""><td><ll0q< td=""><td>0.976</td><td>1.00</td><td>98</td><td>1.22</td><td>1.25</td><td>98</td><td>0.0488</td><td>0.05</td><td>98</td></ll0q<></td></ll0q<>	<ll0q< td=""><td>0.976</td><td>1.00</td><td>98</td><td>1.22</td><td>1.25</td><td>98</td><td>0.0488</td><td>0.05</td><td>98</td></ll0q<>	0.976	1.00	98	1.22	1.25	98	0.0488	0.05	98
Be 313.107	<0.5*LLOQ	<ll0q< td=""><td><ll0q< td=""><td>0.95</td><td>1.00</td><td>95</td><td>0.126</td><td>0.125</td><td>101</td><td>0.00502</td><td>0.005</td><td>100</td></ll0q<></td></ll0q<>	<ll0q< td=""><td>0.95</td><td>1.00</td><td>95</td><td>0.126</td><td>0.125</td><td>101</td><td>0.00502</td><td>0.005</td><td>100</td></ll0q<>	0.95	1.00	95	0.126	0.125	101	0.00502	0.005	100
Ca 315.887	<0.5*LLOQ	<ll0q< td=""><td>501</td><td>497</td><td>500</td><td>99</td><td>25.3</td><td>25</td><td>101</td><td>1.01</td><td>1</td><td>101</td></ll0q<>	501	497	500	99	25.3	25	101	1.01	1	101
Cd 214.439	<0.5*LLOQ	<ll0q< td=""><td><ll0q< td=""><td>0.941</td><td>1.00</td><td>94</td><td>0.49</td><td>0.5</td><td>98</td><td>0.0195</td><td>0.02</td><td>98</td></ll0q<></td></ll0q<>	<ll0q< td=""><td>0.941</td><td>1.00</td><td>94</td><td>0.49</td><td>0.5</td><td>98</td><td>0.0195</td><td>0.02</td><td>98</td></ll0q<>	0.941	1.00	94	0.49	0.5	98	0.0195	0.02	98
Ce 418.659	<0.5*LLOQ	<ll0q< td=""><td><ll0q< td=""><td>1.05</td><td>1.00</td><td>105</td><td>2.47</td><td>2.5</td><td>99</td><td>0.0986</td><td>0.1</td><td>99</td></ll0q<></td></ll0q<>	<ll0q< td=""><td>1.05</td><td>1.00</td><td>105</td><td>2.47</td><td>2.5</td><td>99</td><td>0.0986</td><td>0.1</td><td>99</td></ll0q<>	1.05	1.00	105	2.47	2.5	99	0.0986	0.1	99
Co 230.786	<0.5*LLOQ	<ll0q< td=""><td><ll0q< td=""><td>0.925</td><td>1.00</td><td>93</td><td>4.83</td><td>5</td><td>97</td><td>0.189</td><td>0.2</td><td>95</td></ll0q<></td></ll0q<>	<ll0q< td=""><td>0.925</td><td>1.00</td><td>93</td><td>4.83</td><td>5</td><td>97</td><td>0.189</td><td>0.2</td><td>95</td></ll0q<>	0.925	1.00	93	4.83	5	97	0.189	0.2	95
Cr 205.560	<0.5*LLOQ	<ll0q< td=""><td><ll0q< td=""><td>0.952</td><td>1.00</td><td>95</td><td>2.42</td><td>2.5</td><td>97</td><td>0.0969</td><td>0.1</td><td>97</td></ll0q<></td></ll0q<>	<ll0q< td=""><td>0.952</td><td>1.00</td><td>95</td><td>2.42</td><td>2.5</td><td>97</td><td>0.0969</td><td>0.1</td><td>97</td></ll0q<>	0.952	1.00	95	2.42	2.5	97	0.0969	0.1	97
Cu 327.395	<0.5*LLOQ	<ll0q< td=""><td><ll0q< td=""><td>0.952</td><td>1.00</td><td>95</td><td>2.34</td><td>2.5</td><td>94</td><td>0.0899</td><td>0.1</td><td>90</td></ll0q<></td></ll0q<>	<ll0q< td=""><td>0.952</td><td>1.00</td><td>95</td><td>2.34</td><td>2.5</td><td>94</td><td>0.0899</td><td>0.1</td><td>90</td></ll0q<>	0.952	1.00	95	2.34	2.5	94	0.0899	0.1	90
Fe 273.358	<0.5*LLOQ	<ll0q< td=""><td>199</td><td>203</td><td>200</td><td>102</td><td>49.1</td><td>50</td><td>98</td><td>2.04</td><td>2</td><td>102</td></ll0q<>	199	203	200	102	49.1	50	98	2.04	2	102
Hg 194.164	<0.5*LLOQ	<ll0q< td=""><td><ll0q< td=""><td>0.974</td><td>1.00</td><td>97</td><td>0.976</td><td>1</td><td>98</td><td>0.0446</td><td>0.04</td><td>112</td></ll0q<></td></ll0q<>	<ll0q< td=""><td>0.974</td><td>1.00</td><td>97</td><td>0.976</td><td>1</td><td>98</td><td>0.0446</td><td>0.04</td><td>112</td></ll0q<>	0.974	1.00	97	0.976	1	98	0.0446	0.04	112
K 766.491	<0.5*LLOQ	<ll0q< td=""><td><ll0q< td=""><td>1.03</td><td>1.00</td><td>103</td><td>24.1</td><td>25</td><td>96</td><td>1.17</td><td>1</td><td>117</td></ll0q<></td></ll0q<>	<ll0q< td=""><td>1.03</td><td>1.00</td><td>103</td><td>24.1</td><td>25</td><td>96</td><td>1.17</td><td>1</td><td>117</td></ll0q<>	1.03	1.00	103	24.1	25	96	1.17	1	117
Li 670.783	<0.5*LLOQ	<ll0q< td=""><td><ll0q< td=""><td>0.958</td><td>1.00</td><td>96</td><td>1.19</td><td>1.25</td><td>95</td><td>0.0429</td><td>0.05</td><td>86</td></ll0q<></td></ll0q<>	<ll0q< td=""><td>0.958</td><td>1.00</td><td>96</td><td>1.19</td><td>1.25</td><td>95</td><td>0.0429</td><td>0.05</td><td>86</td></ll0q<>	0.958	1.00	96	1.19	1.25	95	0.0429	0.05	86
Mg 279.800	<0.5*LLOQ	<ll0q< td=""><td>493</td><td>511</td><td>500</td><td>102</td><td>24.1</td><td>25</td><td>96</td><td>0.962</td><td>1</td><td>96</td></ll0q<>	493	511	500	102	24.1	25	96	0.962	1	96
Mn 257.610	<0.5*LLOQ	<ll0q< td=""><td><ll0q< td=""><td>0.978</td><td>1.00</td><td>98</td><td>1.25</td><td>1.25</td><td>100</td><td>0.0502</td><td>0.05</td><td>100</td></ll0q<></td></ll0q<>	<ll0q< td=""><td>0.978</td><td>1.00</td><td>98</td><td>1.25</td><td>1.25</td><td>100</td><td>0.0502</td><td>0.05</td><td>100</td></ll0q<>	0.978	1.00	98	1.25	1.25	100	0.0502	0.05	100
Mo 202.032	<0.5*LLOQ	<ll0q< td=""><td><ll0q< td=""><td>0.928</td><td>1.00</td><td>93</td><td>1.17</td><td>1.25</td><td>94</td><td>0.0473</td><td>0.05</td><td>95</td></ll0q<></td></ll0q<>	<ll0q< td=""><td>0.928</td><td>1.00</td><td>93</td><td>1.17</td><td>1.25</td><td>94</td><td>0.0473</td><td>0.05</td><td>95</td></ll0q<>	0.928	1.00	93	1.17	1.25	94	0.0473	0.05	95
Na 589.592	<0.5*LLOQ	<ll0q< td=""><td><ll0q< td=""><td>1.13</td><td>1.00</td><td>113</td><td>24.5</td><td>25</td><td>98</td><td>0.984</td><td>1</td><td>98</td></ll0q<></td></ll0q<>	<ll0q< td=""><td>1.13</td><td>1.00</td><td>113</td><td>24.5</td><td>25</td><td>98</td><td>0.984</td><td>1</td><td>98</td></ll0q<>	1.13	1.00	113	24.5	25	98	0.984	1	98
Ni 231.604	<0.5*LLOQ	<ll0q< td=""><td><ll0q< td=""><td>0.919</td><td>1.00</td><td>92</td><td>2.36</td><td>2.5</td><td>94</td><td>0.0921</td><td>0.1</td><td>92</td></ll0q<></td></ll0q<>	<ll0q< td=""><td>0.919</td><td>1.00</td><td>92</td><td>2.36</td><td>2.5</td><td>94</td><td>0.0921</td><td>0.1</td><td>92</td></ll0q<>	0.919	1.00	92	2.36	2.5	94	0.0921	0.1	92
P 213.618	<0.5*LLOQ	<ll0q< td=""><td><ll0q< td=""><td>1.11</td><td>1.00</td><td>111</td><td>12.9</td><td>12.5</td><td>103</td><td>0.507</td><td>0.5</td><td>101</td></ll0q<></td></ll0q<>	<ll0q< td=""><td>1.11</td><td>1.00</td><td>111</td><td>12.9</td><td>12.5</td><td>103</td><td>0.507</td><td>0.5</td><td>101</td></ll0q<>	1.11	1.00	111	12.9	12.5	103	0.507	0.5	101
Pb 220.353	<0.5*LLOQ	<ll0q< td=""><td><ll0q< td=""><td>0.917</td><td>1.00</td><td>92</td><td>4.65</td><td>5</td><td>93</td><td>0.185</td><td>0.2</td><td>93</td></ll0q<></td></ll0q<>	<ll0q< td=""><td>0.917</td><td>1.00</td><td>92</td><td>4.65</td><td>5</td><td>93</td><td>0.185</td><td>0.2</td><td>93</td></ll0q<>	0.917	1.00	92	4.65	5	93	0.185	0.2	93
Sb 206.834	<0.5*LLOQ	<ll0q< td=""><td><ll0q< td=""><td>1.02</td><td>1.00</td><td>102</td><td>5.19</td><td>5</td><td>104</td><td>0.204</td><td>0.2</td><td>102</td></ll0q<></td></ll0q<>	<ll0q< td=""><td>1.02</td><td>1.00</td><td>102</td><td>5.19</td><td>5</td><td>104</td><td>0.204</td><td>0.2</td><td>102</td></ll0q<>	1.02	1.00	102	5.19	5	104	0.204	0.2	102
Se 196.026	<0.5*LLOQ	<ll0q< td=""><td><ll0q< td=""><td>1.03</td><td>1.00</td><td>103</td><td>0.502</td><td>0.5</td><td>100</td><td>0.0224</td><td>0.02</td><td>112</td></ll0q<></td></ll0q<>	<ll0q< td=""><td>1.03</td><td>1.00</td><td>103</td><td>0.502</td><td>0.5</td><td>100</td><td>0.0224</td><td>0.02</td><td>112</td></ll0q<>	1.03	1.00	103	0.502	0.5	100	0.0224	0.02	112
Sn 189.925	<0.5*LLOQ	<ll0q< td=""><td><ll0q< td=""><td>0.987</td><td>1.00</td><td>99</td><td>2.39</td><td>2.5</td><td>96</td><td>0.0946</td><td>0.1</td><td>95</td></ll0q<></td></ll0q<>	<ll0q< td=""><td>0.987</td><td>1.00</td><td>99</td><td>2.39</td><td>2.5</td><td>96</td><td>0.0946</td><td>0.1</td><td>95</td></ll0q<>	0.987	1.00	99	2.39	2.5	96	0.0946	0.1	95
Sr 216.596	<0.5*LLOQ	<ll0q< td=""><td><ll0q< td=""><td>0.963</td><td>1.00</td><td>96</td><td>2.43</td><td>2.5</td><td>97</td><td>0.0973</td><td>0.1</td><td>97</td></ll0q<></td></ll0q<>	<ll0q< td=""><td>0.963</td><td>1.00</td><td>96</td><td>2.43</td><td>2.5</td><td>97</td><td>0.0973</td><td>0.1</td><td>97</td></ll0q<>	0.963	1.00	96	2.43	2.5	97	0.0973	0.1	97
Ti 334.188	<0.5*LLOQ	<ll0q< td=""><td><ll0q< td=""><td>1.01</td><td>1.00</td><td>101</td><td>0.497</td><td>0.5</td><td>99</td><td>0.0201</td><td>0.02</td><td>101</td></ll0q<></td></ll0q<>	<ll0q< td=""><td>1.01</td><td>1.00</td><td>101</td><td>0.497</td><td>0.5</td><td>99</td><td>0.0201</td><td>0.02</td><td>101</td></ll0q<>	1.01	1.00	101	0.497	0.5	99	0.0201	0.02	101
TI 190.794	<0.5*LLOQ	<ll0q< td=""><td><ll0q< td=""><td>0.981</td><td>1.00</td><td>98</td><td>2.47</td><td>2.5</td><td>99</td><td>0.101</td><td>0.1</td><td>101</td></ll0q<></td></ll0q<>	<ll0q< td=""><td>0.981</td><td>1.00</td><td>98</td><td>2.47</td><td>2.5</td><td>99</td><td>0.101</td><td>0.1</td><td>101</td></ll0q<>	0.981	1.00	98	2.47	2.5	99	0.101	0.1	101
V 292.401	<0.5*LLOQ	<ll0q< td=""><td><ll0q< td=""><td>1.03</td><td>1.00</td><td>103</td><td>2.54</td><td>2.5</td><td>102</td><td>0.1</td><td>0.1</td><td>100</td></ll0q<></td></ll0q<>	<ll0q< td=""><td>1.03</td><td>1.00</td><td>103</td><td>2.54</td><td>2.5</td><td>102</td><td>0.1</td><td>0.1</td><td>100</td></ll0q<>	1.03	1.00	103	2.54	2.5	102	0.1	0.1	100
Zn 206.200	<0.5*LLOQ	<ll0q< td=""><td><ll0q< td=""><td>0.964</td><td>1.00</td><td>96</td><td>0.508</td><td>0.5</td><td>102</td><td>0.0197</td><td>0.02</td><td>99</td></ll0q<></td></ll0q<>	<ll0q< td=""><td>0.964</td><td>1.00</td><td>96</td><td>0.508</td><td>0.5</td><td>102</td><td>0.0197</td><td>0.02</td><td>99</td></ll0q<>	0.964	1.00	96	0.508	0.5	102	0.0197	0.02	99
Zr 343.823	<0.5*LLOQ	<ll0q< td=""><td><ll0q< td=""><td>0.999</td><td>1.00</td><td>100</td><td>1.24</td><td>1.25</td><td>99</td><td>0.0492</td><td>0.05</td><td>98</td></ll0q<></td></ll0q<>	<ll0q< td=""><td>0.999</td><td>1.00</td><td>100</td><td>1.24</td><td>1.25</td><td>99</td><td>0.0492</td><td>0.05</td><td>98</td></ll0q<>	0.999	1.00	100	1.24	1.25	99	0.0492	0.05	98

SRM and matrix spike (MS) recovery tests

Table 6 outlines the results for the soil SRM 2711a. All elements were measured within ±10% of the expected concentration, except antimony (Sb). As hydrochloric acid was not used in this digestion, it was expected that the Sb would report low. Recovery results for Sb are presented in EPA 3051A, where figure 3 show the effects of hydrochloric acid on Sb during digestion (3).

To determine the accuracy of the measurement of all elements in a clean matrix, a silica sand sample spiked prior to digestion was used as an MS sample. The MS recovery results for all elements, including Sb, are within the $\pm 25\%$ method acceptance criteria, as shown in Table 6. The spike level includes a weight/volume correction.

Table 6. Results for SRM 2711a and silica sand matrix spike sample.

		SRM 2711a (n=6)			Silica Sand (Matrix Spike)				
	Measured (mg/kg)	Expected (mg/kg)	Recovery (%)	Measured (mg/kg)	Matrix Spike (mg/kg)	Spike Level (mg/kg)	Recovery (%)		
Ag 328.068	5.45	5.5	99	0.966	2.35	1.25	111		
Al 237.312	13200	13200	100	240	5520	5000	106		
As 188.980	90.3	89	101	<ll0q< td=""><td>10.6</td><td>10</td><td>106</td></ll0q<>	10.6	10	106		
B 208.956	4.54	NA		0.612	6.08	5	109		
Ba 233.527	181	190	95	1.53	109	100	107		
Be 313.107	0.991	0.93	107	<ll0q< td=""><td>0.514</td><td>0.5</td><td>103</td></ll0q<>	0.514	0.5	103		
Ca 315.887	15200	14000	109	66.9	10500	10000	104		
Cd 214.439	49.4	47	105	0.0578	1.5	1.5	96		
Ce 418.659	39.1	NA		1.18	27.5	25	105		
Co 230.786	7.25	7.5	97	<ll0q< td=""><td>9.71</td><td>10</td><td>97</td></ll0q<>	9.71	10	97		
Cr 205.560	15.5	15	103	0.293	50.7	50	101		
Cu 327.395	121	130	93	2.53	102	100	99		
Fe 273.358	15800	15000	105	123	10400	10000	103		
Hg 194.164	6.7	7.4	91	<ll0q< td=""><td><ll0q< td=""><td>0.25</td><td><lloq< td=""></lloq<></td></ll0q<></td></ll0q<>	<ll0q< td=""><td>0.25</td><td><lloq< td=""></lloq<></td></ll0q<>	0.25	<lloq< td=""></lloq<>		
K 766.491	4010	3900	103	129	1420	1250	103		
Li 670.783	12.8	NA		<ll0q< td=""><td>11.1</td><td>10</td><td>111</td></ll0q<>	11.1	10	111		
Mg 279.800	6000	5700	105	25.1	4980	5000	99		
Mn 257.610	489	460	106	1.08	258	250	103		
Mo 202.032	0.331	NA		<ll0q< td=""><td>0.58</td><td>0.5</td><td>116</td></ll0q<>	0.58	0.5	116		
Na 589.592	187	180	104	54.3	600	500	109		
Ni 231.604	15.5	15	103	0.396	24.2	25	95		
P 213.618	713	NA		9.15	4030	3750	107		
Pb 220.353	1230	1300	95	2.03	192	200	95		
Sb 206.834	<lloq< td=""><td>4.9</td><td></td><td><ll0q< td=""><td>3.18</td><td>3</td><td>106</td></ll0q<></td></lloq<>	4.9		<ll0q< td=""><td>3.18</td><td>3</td><td>106</td></ll0q<>	3.18	3	106		
Se 196.026	1.69	1.7	99	<ll0q< td=""><td>2.37</td><td>2.5</td><td>95</td></ll0q<>	2.37	2.5	95		
Sn 189.925	<lloq< td=""><td>NA</td><td></td><td><ll0q< td=""><td>1.17</td><td>1</td><td>117</td></ll0q<></td></lloq<>	NA		<ll0q< td=""><td>1.17</td><td>1</td><td>117</td></ll0q<>	1.17	1	117		
Sr 216.596	33.7	NA		0.742	105	100	104		
Ti 334.188	52.2	NA		7.01	108	100	101		
TI 190.794	2.12	2.1	101	<ll0q< td=""><td>2.51</td><td>2.5</td><td>100</td></ll0q<>	2.51	2.5	100		
V 292.401	25.3	28	90	<ll0q< td=""><td>55.4</td><td>50</td><td>111</td></ll0q<>	55.4	50	111		
Zn 206.200	363	350	104	3.7	503	500	100		
Zr 343.823	14.1	NA		0.926	13.3	12.5	99		

Long-term stability

To determine the stability of the 5800 VDV ICP-OES, 272 solutions were analyzed over a six-hour period. The solutions consisted of two digested soil samples and the ICV solution. To show the stability of the instrument over an extended run, the recovery of the ICV solution was plotted against time (Figure 6). All results for the ICV were within ±10% of expected values, and the RSD was <2% for all elements.

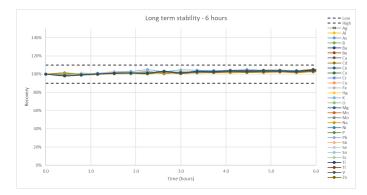


Figure 6. Long-term stability test showing recovery of the ICV solution analyzed over a six-hour period.

Early maintenance feedback

Analyzing complex sample types such as soils, sediments. and sludges can be tough on the sample introduction system of an ICP-OES over extended analytical runs. Long runs can result in deteriorating analytical performance, high consumable costs, and unplanned instrument downtime. Scheduling maintenance tasks according to the number of solutions measured, rather than elapsed time can reduce these impacts. The EMF function allows the user to set up an alert for a maintenance task after a specified number of samples. Recommended alert settings for specific sample types can be generated automatically. The alert system will result in more frequent instrument maintenance when measuring complex samples, such as soils, ensuring consistent analytical performance. Figure 7 shows an example of the maintenance counters in the ICP Expert software. A color-coding system shows which activities should be done immediately (red), and which are lower priority (green). EMF provides seven default maintenance counter presets for general, high total dissolved solids (TDS), and organic applications, as the type of sample will affect the sample introduction and consumables differently. Also, if a user wants to monitor a specific parameter, custom counters can be set up.

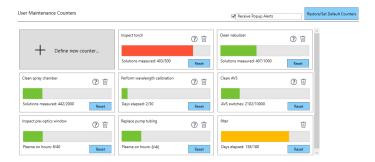


Figure 7. The EMF system monitors critical instrument parameters to maintain optimum analytical performance and reduce sample remeasurement.

Conclusion

Accurate, routine measurement of soils, sediments, and sludges can be carried out using an Agilent 5800 VDV ICP-OES with an AVS 7 switching valve in accordance with US EPA method 6010D. The AVS 7 reduces the maintenance requirements on the VDV torch and improves sample throughput.

The high performance of the 5800 VDV ICP-OES was demonstrated by the recovery data of 23 elements in a soil SRM and recoveries for all 32 elements in a matrix spike sample. Antimony did not recover in the soil SRM digest as HCl was not used during the digestion. However, the matrix spike test showed that good recovery of antimony was possible if it had been solubilized during digestion. All other SRM recoveries were within $\pm 10\%$ of the expected value, demonstrating the accuracy of the method.

Smart tools developed for the ICP Expert instrument control software add an extra layer of QA/QC to the analysis. IntelliQuant Screening was used during the method development and helped to identify appropriate wavelengths and avoid spectral interferences where possible. The OCF function gave a quick visual flag of any results that needed further attention, allowing troubleshooting of individual results. To maximize instrument performance and minimize unplanned downtime, the EMF function was used to generate alerts for maintenance tasks, based on the number of samples run.

Other benefits of the 5800 VDV ICP-OES for the accurate measurement of metals in soil, sediment, and sludge samples include:

- Stable results over an extended analytical period without the need to recalibrate, as shown by the six-hour QC stability-test results.
- Interference correction using inter-element corrections (IEC) and off-peak background correction.

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- Reduce Costs and Boost Productivity with the Advanced Valve System (AVS) 6 or 7 Port Switching Valve System, Agilent publication, <u>5991-6863EN</u>
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Note: The Agilent 5800 VDV ICP-OES requires ICP Expert Pro pack software to access IntelliQuant Screening and to operate the AVS 7 switching valve system. All these features are standard with the Agilent 5900 SVDV or Agilent 5900 VDV ICP-OES systems.

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