Analysis of Environmental Samples with the Agilent 730-ES Following US EPA Guidelines

Application Note

Inductively Coupled Plasma-Optical Emission Spectrometers

Author

Vincent Calderon

Introduction

The United States Environmental Protection Agency (EPA) Contract Laboratory Program (CLP) defines the analytical methods accepted for the isolation, detection and quantitative measurement of 23 target analytes (including mercury) and cyanide in both water and soil/sediment environmental samples [1]. Data from the Statement of Work (SOW) for Multi Media, Multi Concentration Inorganic Analysis (ILM05.3) is used to define the nature and extent of contamination, and determine appropriate cleanup actions, emergency response actions and enforcement/litigation activities [2].

This application note describes the use of the Agilent 730-ES to carry out the US EPA/CLP compliant analysis of water samples.

Instrumentation

The Agilent 730-ES with custom-designed CCD detector was used, providing true simultaneous measurement for fast, precise and accurate analysis. The MultiCal feature in the ICP Expert II software extends the linear range, allowing the measurement of elements from microgram per litre to percentage levels from a single plasma view. The optical system is thermally stabilized and contains no moving parts, ensuring excellent long-term stability.

An Agilent Switching Valve System (SVS) with the Agilent SPS3 autosampler was used to improve the efficiency of sample introduction, increasing sample throughput and reducing analysis time.

ILM05.3 Exhibit D recommends the use of an ionization buffer if ionization effects are pronounced. The potential for ionization interference caused by easily ionized elements (Na, K and Ca) was addressed by adding a solution containing 1% caesium (ionization buffer) online to the sample stream [3].

Materials and Reagents

Calibration and Quality Control (QC) solutions were prepared from Inorganic Ventures, Inc. custom-grade multi-element solutions, including the Superfund CLP ICP Kit for ILM05.2. NIST certified standard reference material 1643e Trace Elements in Water was measured as a Laboratory Control Sample. The Superfund CLP ICP Kit for ILM05.2 contained the following solutions:

Table 1. Superfund CLP ICP Kit for ILM05.2

Solution	**Conc (mg/L)**	**Elements**	**Purpose**	**Required dilution**
CLPP-CAL-1	5000	Ca, Mg, K.Na	Calibration standard	1:100
	2000	Al, Ba		
	1000	Fe		
	500	Co, Mn, Ni, V, Zn		
	250	Ag, Cu		
	200	Cr		
	50	Be		
CLPP-CAL-2	1000	Sb	Calibration standard	1:100
CLPP-CAL-3	1000	As, Pb, Se, Ti	Calibration standard	1:100
	500	Cd		
CL-AES-CRQL	500	Ca, Mg,K	CRQL (CRI)	1:100
	20	Al, Ba		
	10	Fe		
	6	Sb, Zn		
	5	Co, V		
	4	Ni		
	3.5	Se		
	2.5	Cu,Ti		
	1.5	As, Mn		
	1	Cr, Pb, Ag		
	0.5	Be, Cd		
CLPP-ICS-A	5000	Al, Ca, Mg	ICSA	1:20
	2000	Fe		
CLPP-ICS-B4	100	Cd, Ni, Zn	ICSAB	1:100
	60	Sb		
	50	Ba, Be, Co, Cr, Cu Mn, V		
	20	Ag		
	10	As, Ti		
	5	Pb, Se		
QCP-CICV-1	2500	Ca, Mg, K, Na	ICV, CCV	1:500 (ICV) 1:100(CCV)
	1000	Al, Ba		
	500	Fe		
	250	Co, Mn, Ni, Zn		
	125	Ag, Cu		
	100	Cr		
	25	Be		
QCP-CICV-2	500	Sb	ICV, CCV	1:500 (ICV) 1:100 (CCV)
QCP-CICV-3	500	As, Pb, Se, Ti	ICV, CCV	1:500 (ICV) 1:100 (CCV)
	250	Cd		
CLPP-SPK-1	2000	Al, Ba	Matrix spike	1:1000
	1000	Fe		
	500	Co, Mn,Ni, V, Zn		
	250	Cu		
	200	Cr		
	50	Ag, Be		
CLPP-SPK-5	100	Sb	Matrix spike	1:1000
	50	Cd, Se, Ti		
	40	As		
	20	Pb		

Standard and Sample Preparation

The calibration and QC solutions were diluted with >18 MΩ/cm^3 deionized water and stabilized in 1% v/v HNO_3 and 5% v/v HCl (both Merck Ultrapur). The sample solutions were also prepared in 1% v/v HNO_3 and 5% v/v HCl.

The calibration blank was prepared from >18 MΩ/cm^3 deionized water in 1% v/v HNO_3 and 5% v/v HCl (both Merck Ultrapur).

A 1% w/v ionization buffer solution was prepared from Merck Tracepur $CsNO_3$ and stabilized in 1% v/v HNO_3 (Merck Ultrapur). The solution was introduced online to the sample line using a spare channel on the peristaltic pump. A "Y-connector" located between the nebulizer and peristaltic pump was used to add the ionization buffer solution to the sample stream.

Conditions

The instrument operating conditions are shown in Table 2.

Table 2. Instrument Operating Conditions

Parameter	Setting
Power	1.4 kW
Plasma gas flow	15 L/min
Auxiliary gas flow	1.5 L/min
Spraychamber type	Glass cyclonic
Torch	Standard axial torch
Nebulizer type	SeaSpray
Nebulizer gas flow	0.75 L/min
Pump tubing	Sample: white-white (1.02 mm id) Waste: blue-blue (1.65 mm id) Buffer/reference (internal standard) element: black-black (0.76 mm ID)
Pump speed	12 rpm
Sample uptake	2.5 mL
Replicate read time	30 s
Number of replicates	2
Sample delay time	25 s
Switching valve delay	22 s
Stabilization time	10 s
Fast pump	On
Background correction	Off-peak

Table 3 shows the background correction points used.

Table 3. Off-Peak Background Correction Points Used

Element	BC point left (nm)	BC point right (nm)
Ag 328.068	0.031	n.u.
Al 237.312	0.022	n.u.
As 188.980	0.0100	n.u.
Ba 585.367	0.068	0.066
Be 313.042	n.u.	0.032
Ca 315.887	n.u.	0.033
Ca 370.602	n.u.	0.041
Cd 214.439	0.015	0.018
Co 228.615	n.u.	0.023
Cr 267.716	0.024	n.u.
Cu 324.754	n.u.	0.033
Fe 238.204	n.u.	0.021
Fe 258.588	0.020	n.u.
K 404.721	n.u.	0.030
K 769.897	n.u.	0.088
Mg 285.213	0.029	n.u.
Mn 257.610	0.024	n.u.
Na 330.237	0.030	n.u.
Na 589.592	0.066	0.078
Ni 231.604	n.u.	0.022
Pb 220.353	0.010	0.012
Sb 206.834	n.u.	0.018
Se 196.026	0.010	n.u.
Tl 190.794	0.013	n.u.
V 292.401	0.032	n.u.
Zn 206.200	n.u.	0.018

Note: n.u. indicates "not used"

Discussion

Method Detection Limits (MDL) and Contract Required Detection Limits (CRDL)

The MDL of each element was determined following the procedure defined in 40 CFR, part 136, as specified in Section 12.10.1.1 of Exhibit D in ILM05.3 Statement of Work. A standard solution containing analytes at a concentration of 3 to 5 times the instrument manufacturer's suggested IDL, was measured on 3 non-consecutive days. A replicate read time of 30 seconds was found to be sufficient to meet the contract required detection limits (CRDLs) as specified in Section 12.10.1.2, Exhibit D of ILM05.3 Statement of Work. These

CRDLs are reported in Table 4. Note that in this application, the instrument operating parameters were optimized for low wavelength elements. When the conditions were optimized for the higher wavelength elements such as Na and K, MDLs improved by up to four times for those elements.

Table 4. Method Detection Limits

Element wavelength	CRDL (µg/L)	CRQL ILM05.3 (µg/L)	MDL required LM05.3 (µg/L)	MDL obtained (µg/L)	Result
Ag 328.068	5	10	5	0.5	Pass
Al 237.312	200	200	100	5	Pass
As 188.980	5	10	5	1	Pass
Ba 585.367	20	200	100	0.6	Pass
Be 313.042	1	5	2.5	0.009	Pass
Ca 315.887	5000	5000	2500	1	Pass
Cd 214.439	2	5	2.5	0.09	Pass
Co 228.615	5	50	25	0.4	Pass
Cr 267.716	5	10	5	0.2	Pass
Cu 324.754	5	25	12.5	0.7	Pass
Fe 238.204	100	100	50	0.3	Pass
K 769.897	5000	5000	2500	2	Pass
Mg 285.213	5000	5000	2500	0.4	Pass
Mn 257.610	10	15	7.5	0.06	Pass
Na 589.592	5000	5000	2500	0.6	Pass
Ni 231.604	20	40	20	0.7	Pass
Pb 220.353	3	10	5	0.8	Pass
Sb 206.834	5	60	30	1	Pass
Se 196.026	5	35	17.5	1	Pass
Tl 190.794	5	25	12.5	1	Pass
V 292.401	10	50	25	0.3	Pass
Zn 206.200	10	60	30	0.5	Pass

The reproducibility of the Agilent 730-ES is demonstrated in Table 5. Included are the key low wavelength elements As, Pb, Sb, Se and Tl. The readback of the reagent blank solution spiked with 5 µg/L of analyte shows the excellent reproducibility of the Agilent 730-ES near method detection limit levels.

Table 5. Readback of Reagent Blank + 5 µg/L Analyte

Run 1	As 188.980	Se 196.026	Sb 206.834	Tl 190.794	Pb 220.353
R.Blk + 5 µg/L	5.21	4.65	5.49	5.48	5.26
R.Blk + 5 µg/L	5.12	4.20	5.49	5.06	5.42
R.Blk + 5 µg/L	5.51	4.67	5.67	4.71	5.13
R.Blk + 5 µg/L	5.13	5.20	5.76	4.68	5.44
R.Blk + 5 µg/L	5.60	5.14	4.87	5.48	5.15
R.Blk + 5 µg/L	5.22	4.70	5.90	4.54	5.53
R.Blk + 5 µg/L	4.94	5.12	5.07	5.19	5.80
SD	0.23	0.36	0.37	0.39	0.24
MDL – µg/L	0.73	1.14	1.17	1.21	0.74
Average conc	5.25	4.81	5.46	5.02	5.39

Run 2	As 188.980	Se 196.026	Sb 206.834	Tl 190.794	Pb 220.353
R.Blk + 5 µg/L	5.63	5.18	4.73	4.75	5.00
R.Blk + 5 µg/L	4.52	4.97	5.30	5.17	5.16
R.Blk + 5 µg/L	4.65	5.13	5.17	4.92	4.67
R.Blk + 5 µg/L	5.32	4.69	4.71	5.22	5.40
R.Blk + 5 µg/L	5.58	4.06	5.53	5.38	4.70
R.Blk + 5 µg/L	4.70	4.62	5.01	5.63	5.39
R.Blk + 5 µg/L	5.42	5.10	4.63	4.74	4.97
SD	0.48	0.40	0.34	0.33	0.30
MDL – µg/L	1.49	1.26	1.07	1.04	0.93
Average conc	5.12	4.82	5.01	5.12	5.04

Run 3	As 188.980	Se 196.026	Sb 206.834	Tl 190.794	Pb 220.353
R.Blk + 5 µg/L	5.50	4.50	4.69	5.22	5.18
R.Blk + 5 µg/L	5.06	5.13	4.71	4.78	4.98
R.Blk + 5 µg/L	4.89	5.08	5.71	4.25	5.06
R.Blk + 5 µg/L	5.51	5.31	5.46	4.92	5.57
R.Blk + 5 µg/L	4.96	5.54	5.17	4.70	5.46
R.Blk + 5 µg/L	5.10	5.20	4.41	5.12	5.45
R.Blk + 5 µg/L	4.80	5.37	4.74	4.61	5.63
SD	0.28	0.33	0.47	0.33	0.26
MDL – µg/L	0.89	1.04	1.48	1.03	0.81
Average conc	5.12	5.16	4.98	4.80	5.34

Linear Range Analysis (LRA)

The LRA represents the upper concentration limit for each analyte of the ICP-OES linear range beyond which results cannot be reported without dilution of the sample. The maximum error for each calibration standard within the linear range cannot exceed 5% [4]. Table 6 shows the results for the LRA.

Using the MultiCal feature, a second less sensitive wavelength was added for the elements K, Na, Ca, and Fe, as shown in Table 6. To extend the linear dynamic range further during the analysis, MultiCal automatically assigns sample results to the appropriate wavelength. In the same way, QCP tests and actions are applied only to those wavelengths for which the results fall within the specified LDR.

It should be noted also, the LDR can be extended even further by using the online over-range dilution capability of the SPS3 autosampler and diluter accessory in conjunction with MultiCal.

Table 6. Linear Range Analysis

Element	Curve type	Minimum conc. (mg/L)	Maximum conc. (mg/L)
Ag 328.068	Linear	0	50
Al 237.312	Linear	0	200
As 188.980	Linear	0	100
Ba 585.367	Linear	0	200
Be 313.042	Linear	0	10
Ca 315.887	Linear	0	200
Ca 370.602	Linear	0	2000
Cd 214.439	Linear	0	10
Co 228.615	Linear	0	100
Cr 267.716	Linear	0	100
Cu 324.754	Linear	0	100
Fe 238.204	Linear	0	200
Fe 258.588	Linear	0	1000
K 404.721	Linear	100	2000
K 769.897	Linear	0	100
Mg 285.213	Linear	0	50
Mn 257.610	Linear	0	50
Na 330.237	Linear	50	2000
Na 589.592	Linear	0	100
Ni 231.604	Linear	0	100
Pb 220.353	Linear	0	100
Sb 206.834	Linear	0	100
Se 196.026	Linear	0	100
Tl 190.794	Linear	0	100
V 292.401	Linear	0	100
Zn 206.200	Linear	0	100

Note: The US EPA recommends that the maximum silver concentration is limited to 2 mg/L.

Inter-Element Correction (IEC) and Interference Check Samples (ICSA and ICSAB)

Inter-Element Correction factors are commonly used in ICP-OES to compensate for spectral interferences that may arise on analyte wavelengths. Interference Check Samples (ICS) are used to confirm that interfering elements likely to be encountered in environmental samples do not cause inaccurate determination of analyte concentrations.

To verify that inter-element and background correction factors are accurate, the interference check samples (ICS) must be analyzed and reported for all elements and interferents. ILM05.3 SOW states that the determined concentration of an analyte in the ICSA must be within ± 2 × CRQL. All analytes in the ICSAB must be recovered to within ± 20% of their true value. Tables 7 and 8 show the results for all target elements in ICSA and ICSAB without applying IEC factors. Since the measured concentrations for both solutions meet the specified requirements, inter-element corrections were not needed for the application on the Agilent 730-ES.

Table 7. Interference Check Sample A

Element	CRQL ILM05.3 (µg/L)	ILM05.3 ± limit (µg/L)	ICSA (µg/L)	Result
Ag 328.068	10	20	-10	Pass
As 188.980	10	20	-2	Pass
Ba 585.367	200	400	-0.4	Pass
Be 313.042	5	10	0.1	Pass
Cd 214.439	5	10	0.4	Pass
Co 228.615	50	100	1	Pass
Cr 267.716	10	20	0.2	Pass
Cu 324.754	25	50	2	Pass
Mn 257.610	15	30	2	Pass
Ni 231.604	40	80	3	Pass
Pb 220.353	10	20	-3	Pass
Sb 206.834	60	120	15	Pass
Se 196.026	35	70	11	Pass
Tl 190.794	25	50	-0.4	Pass
V 292.401	50	100	6	Pass
Zn 206.200	60	120	3	Pass

Table 8. Interference Check Sample AB

Element	Expected ICSAB (mg/L)	Found ICSAB (mg/L)	% recovery ICSAB	Result
Ag 328.068	0.20	0.21	106	Pass
As 188.980	0.10	0.097	97	Pass
Ba 585.367	0.50	0.51	102	Pass
Be 313.042	0.50	0.50	99	Pass
Cd 214.439	1.01	0.98	97	Pass
Co 228.615	0.50	0.49	98	Pass
Cr 267.716	0.50	0.50	100	Pass
Cu 324.754	0.50	0.52	104	Pass
Mn 257.610	0.50	0.51	102	Pass
Ni 231.604	1.01	0.99	98	Pass
Pb 220.353	0.05	0.045	90	Pass
Sb 206.834	0.60	0.63	105	Pass
Se 196.026	0.05	0.06	118	Pass
Tl 190.794	0.10	0.09	91	Pass
V 292.401	0.50	0.51	101	Pass
Zn 206.200	1.01	0.99	98	Pass

Laboratory Control Sample (LCS)

An LCS obtained from the US EPA must be analyzed to demonstrate that sample preparation procedures are appropriate for the sample type. With the exception of silver and antimony, the percentage recovery for the LCS must not fall outside the control limits of 80–120%. If an LCS cannot be obtained from the US EPA, the Initial Calibration Verification (ICV) solution may be used [4].

For this application, NIST 1643e Trace Elements in Water was used as the LCS. Table 9 shows the percentage recovery for all target elements falling within the US EPA requirements.

Duplicate Sample Analysis

The reproducibility of the sample preparation was determined by performing a duplicate sample analysis. A duplicate pair was created by processing two aliquots of the same sample through the sample preparation procedure. A control limit of 20% for the Relative Percentage Difference (RPD) applies for samples with a concentration greater than or equal to 5 x CRQL. For samples with a concentration less than 5 x CRQL but greater than the CRQL, an absolute difference in concentration of ± CRQL applies. If the sample has concentrations less than the CRQL, the difference is not reported. Tables 9 and 10 show the RPDs for the NIST 1643e certified standard reference material and a local water sample with all target analytes meeting the required US EPA specifications.

Spike Sample Analysis (Matrix Spike)

The spike sample analysis is designed to provide information about the effect of the sample matrix on the digestion and/or measurement methodology. Exhibit D (ICP-OES) of the ILM05.3 document states the spiking levels required for each of the analyzed elements. The spike recoveries must fall within the limits of 75–125%. A post-digestion spike may need to be performed if the recoveries do not fall within these limits [4].

Tables 9 and 10 below show the matrix spike recoveries for the NIST 1643e certified standard reference material and a local water sample with all target elements falling within the US EPA requirements.

Table 9. LCS Analysis

Element wavelength	NIST 1643e certified (mg/L)	NIST 1643e measured LCS (mg/L)	LCS % recovery	NIST 1643e) duplicate LCS measured (mg/L)	Control limit	% RPD or difference (mg/L)	Sample spike measured (mg/L)	Added QC spike conc. (mg/L)	% spike recovery
Ag 328.068	0.001062	< CRQL	–	< CRQL	–	–	0.0443	0.0430	103.0%
Al 237.312	0.1418	0.151	106.6	0.160	CRQL	0.009	1.93	1.72	104.3%
As 188.980	0.06045	0.0590	97.5	0.0575	20%RPD	2.42%	0.0923	0.0379	97.8%
Ba 585.367	0.5442	0.554	101.9	0.561	CRQL	0.007	2.35	1.72	106.8%
Be 313.042	0.01398	0.0140	100.0	0.0142	CRQL	0.0002	0.0585	0.0430	105.6%
Ca 315.887	32.3	32.0	99.0	32.1	20%RPD	0.560%	–	–	–
Cd 214.439	0.006568	0.00642	97.8	0.00645	CRQL	0.00003	0.0558	0.0473	105.2%
Co 228.615	0.02706	0.0280	103.5	0.0283	CRQL	0.0003	0.484	0.430	106.6%
Cr 267.716	0.0204	0.0209	102.4	0.0211	CRQL	0.0003	0.203	0.172	106.8%
Cu 324.754	0.02276	0.0229	100.7	0.0242	CRQL	0.0013	0.247	0.215	104.9%
Fe 238.204	0.0981	0.105	106.8	0.104	CRQL	0.001	1.03	0.859	108.5%
K 769.897	2.034	2.11	103.7	2.13	CRQL	0.02	–	–	–
Mg 285.213	8.037	8.55	106.4	8.65	CRQL	0.10	–	–	–
Mn 257.610	0.03897	0.0410	105.1	0.0411	CRQL	0.0001	0.503	0.430	108.2%
Na 589.592	20.74	21.6	104.1	20.9	CRQL	0.7	–	–	–
Ni 231.604	0.06241	0.0629	100.9	0.0639	CRQL	0.001	0.516	0.430	106.1%
Pb 220.353	0.01963	0.0207	105.7	0.0202	CRQL	0.0005	0.0385	0.0189	100.7%
Sb 206.834	0.0583	0.0596	102.2	0.0608	CRQL	0.0012	0.144	0.0946	93.6%
Se 196.026	0.01197	< CRQL	–	< CRQL	–	–	0.0561	0.0473	118.5%
Tl 190.794	0.007445	< CRQL	–	< CRQL	–	–	0.0542	0.0473	114.6%
V 292.401	0.03786	0.0389	102.7	0.0388	CRQL	0.0001	0.486	0.430	104.7%
Zn 206.200	0.0785	0.0803	102.3	0.0820	CRQL	0.0017	0.538	0.430	107.7%

Table 10. Local Water Analysis

Element wavelength	Melbourne tap water measured (mg/L)	Duplicate measured (mg/L)	Control limit	% RPD or difference (mg/L)	Sample spike measured (mg/L)	Added QC spike conc. (mg/L)	% spike recovery
Ag 328.068	< CRQL	< CRQL	–	–	0.0484	0.0491	98.6
Al 237.312	0.0934	0.0944	CRQL	0.001	2.11	1.96	103
As 188.980	< CRQL	< CRQL	–	–	0.0395	0.0361	109
Ba 585.367	0.0180	0.0172	CRQL	0.00078	2.05	1.96	104
Be 313.042	< CRQL	< CRQL	–	–	0.0513	0.0491	104
Ca 315.887	3.64	3.63	CRQL	0.01	–	–	–
Cd 214.439	< CRQL	< CRQL	–	–	0.0486	0.0451	108
Co 228.615	< CRQL	< CRQL	–	–	0.510	0.491	104
Cr 267.716	< CRQL	< CRQL	–	–	0.206	0.196	105
Cu 324.754	0.162	0.161	20% RPD	0.40%	0.412	0.246	102
Fe 238.204	0.0935	0.0912	CRQL	0.0023	1.10	0.982	102
K 769.897	0.598	0.596	CRQL	0.002	–	–	–
Mg 285.213	1.115	1.112	CRQL	0.003	–	–	–
Mn 257.610	0.00617	0.00611	CRQL	0.00006	0.524	0.491	105
Na 589.592	4.075	4.073	CRQL	0.002	–	–	–
Ni 231.604	< CRQL	< CRQL	–	–	0.516	0.491	105
Pb 220.353	< CRQL	< CRQL	–	–	0.0201	0.0180	112
Sb 206.834	< CRQL	< CRQL	–	–	0.101	0.0901	112
Se 196.026	< CRQL	< CRQL	–	–	0.0493	0.0451	109
Tl 190.794	< CRQL	< CRQL	–	–	0.0474	0.0451	105
V 292.401	< CRQL	< CRQL	–	–	0.503	0.491	102
Zn 206.200	0.00589	0.00685	CRQL	0.00096	0.530	0.491	107

Quality Control (QC) Tests

The QC tests outlined in ILM05.3 are designed to ensure accuracy and precision in the results obtained. Refer to Exhibit D – Part A "Analytical Methods for Inductively Coupled Plasma – Atomic Emission Spectroscopy" for detailed explanations of the QC tests. The following QC solutions were used in this work.

Initial Calibration Verification (ICV)

The ICV test is run directly after the initial calibration to check the validity of the calibration standards. The ICV solution is obtained from the EPA or a secondary source. It must not be prepared from the same solution as the calibration standards. The recoveries of all target elements must be within the control limits of 90–110%.

Continuing Calibration Verification (CCV)

The Continuing Calibration Verification test is used to ensure the validity of the calibration throughout the analysis and is carried out at a frequency of 10% (every 10 analytical samples) or every two hours, whichever is more frequent. The CCV is also measured at the beginning, but not before the ICV, and at the end of the analysis. The recoveries of all target elements must be within the control limits of 90–110%.

Contract Required Quantitation Limit (CRQL) Check Standard (CRI)

A standard at the CRQL (CRI) must be analyzed to verify the instrument calibration at low analyte concentrations. The CRQL is the minimum level of quantification acceptable under the contract Statement of Work (SOW). The CRI is measured immediately after the ICV/ICB followed by the ICS. The CRI must be run for every wavelength used for the analysis, except Al, Ba, Ca, Fe, Mg, Na and K. The recoveries of all CRI target elements must not fall outside the control limits of 70–130% and 50–150% for antimony, lead and thallium.

Initial and Continuing Calibration Blank (ICB/CCB)

The ICB/CCB must be measured to ensure that adequate washout is being achieved and sample is not being carried over. The absolute value of the calibration blanks (ICB/CCB) must not exceed the CRQL. The ICB is measured directly after the ICV and the CCB is measured directly after the CCV.

Table 11 shows the results for the QC tests. All tests meet the required US EPA specifications.

Table 11. ICV, CCV, CRI Test Solution Results

Element wavelength	ICV conc (mg/L)	Measured ICV conc (mg/L)	% R	CCV conc (mg/L)	Measured CCV conc (mg/L)	% R	CRI conc (mg/L)	Measured CRI conc (mg/L)	% R
Ag 328.068	0.247	0.268	108	1.25	1.37	110	0.0101	0.0108	107
Al 237.312	1.98	2.00	101	10.0	10.3	103	0.201	0.200	99.1
As 188.980	0.994	1.02	102	5.03	4.95	98.5	0.0151	0.0168	111
Ba 585.367	1.98	2.07	105	10.0	10.3	103	0.201	0.203	101
Be 313.042	0.0495	0.0504	102	0.250	0.254	101	0.00503	0.00520	103
Ca 315.887	4.95	5.12	103	25.0	25.7	103	5.03	5.13	102
Cd 214.439	0.497	0.523	105	2.51	2.55	101	0.00503	0.00518	103
Co 228.615	0.495	0.508	103	2.50	2.58	103	0.0503	0.0519	103
Cr 267.716	0.198	0.206	104	1.00	1.04	104	0.0101	0.0102	102
Cu 324.754	0.247	0.256	103	1.25	1.32	105	0.0251	0.0258	103
Fe 238.204	0.990	1.03	104	5.00	5.16	103	0.101	0.103	102
K 769.897	4.95	5.30	107	25.0	26.5	106	5.03	5.31	106
Mg 285.213	4.95	5.26	106	25.0	26.5	106	5.03	5.34	106
Mn 257.610	0.495	0.518	105	2.50	2.58	103	0.0151	0.0161	107
Na 589.592	4.95	5.41	109	25.0	26.8	107	5.03	5.42	108
Ni 231.604	0.495	0.519	105	2.50	2.59	104	0.0403	0.0412	102
Pb 220.353	0.994	1.01	102	5.03	4.98	99.0	0.0101	0.0104	104
Sb 206.834	0.979	1.03	105	5.02	5.21	104	0.0604	0.0619	102
Se 196.026	0.994	1.04	104	5.03	5.02	99.8	0.0352	0.0379	108
Tl 190.794	0.994	1.01	102	5.03	4.99	99.2	0.0251	0.0233	92.7
V 292.401	0.495	0.511	103	2.50	2.57	103	0.0503	0.0507	101
Zn 206.200	0.495	0.521	105	2.50	2.59	104	0.0604	0.0621	103

Long-Term Stability

Long term stability over 8 hours was measured with a repeatability of 0.75% RSD found for most elements up to a maximum of 0.98% for cadmium. As shown in Figure 1, all CCV recoveries over the 8 hour period were easily within specified limits.

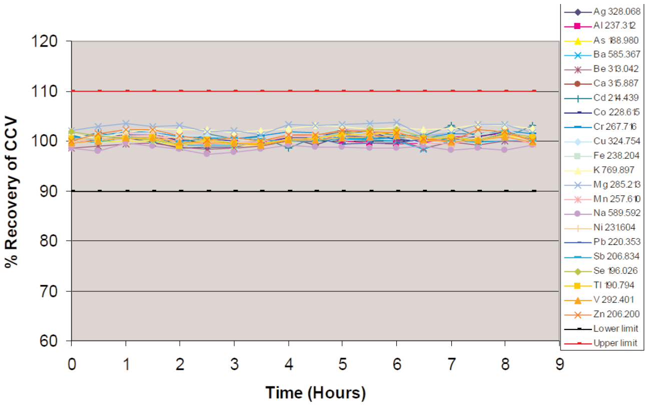

Figure 1. Long-term stability of the Agilent 730-ES over 8 hours.

Speed of Analysis

Due to the requirements set by the US EPA, a large number of QC solutions must be measured to ensure compliance to US EPA methodology, making these types of analyses time-consuming. However, the Agilent 730-ES Simultaneous ICP-OES has shown that all US EPA requirements can be met with an analysis time of 2 minutes and 25 seconds per solution.

Conclusion

This work has demonstrated the ability of the Agilent 730-ES Simultaneous ICP-OES with axially-viewed plasma, to meet the environmental regulations set by the US EPA for waters and wastewaters.

The Agilent 730-ES provides the advantage of being able to achieve this requirement from a single viewed plasma system. This reduces time delays and costs related to repeating analyses with other techniques or multiple measurements when using dual viewed ICP-OES systems. The use of a switching valve also decreases analysis time by providing more efficient introduction and washout of the sample from the sample introduction system.

MultiCal was used to extend the linear dynamic range of Ca, Fe, K and Na without requiring the sample to be diluted or measured separately with radial viewing. The suitability of this approach was proven with the CRI and Linear Dynamic Range tests. Using standard US EPA conditions, it was also shown that successful compliance with the Interference Correction Standards tests could be achieved without Inter-Element Correction factors.

The ICP Expert II software provides complete automation of all US EPA protocols, and the capability to customize QC protocols to meet the requirements of other regulatory bodies. The Agilent 730-ES ICP-OES was shown to meet all regulatory requirements of USEPA ILM05.3 in a single, fast and fully automated analysis.

References

1. http://www.epa.gov/superfund/programs/clp/ilm5.htm
2. "Multi-Media, Multi-Concentration, Inorganic Analytical Service for Superfund (ILM05.3)". EPA Publication 540-F-04-001, 2004.
3. C. Dubuisson, E. Poussel, J-M. Mermet, "Comparison of axially viewed and radially viewed inductively coupled plasma atomic emission spectrometry in terms of signal-to-background ratio and matrix effects". Journal of Analytical Atomic Spectrometry, 1997, 12, 281-286.
4. US EPA Contract Laboratory Program, Statement of Works for Inorganics, Multi-Media, Multi-Concentration, Document Number ILM05.3.

Further Reading

1. S. Bridger, M. Knowles, "A Complete Method for Environmental Samples by Simultaneous Axially Viewed ICP-AES following US EPA Guidelines". Varian ICP-OES At Work No. 29, January 2000.
2. I. Szikla, "Determination of 22 elements following US EPA guidelines with a new megapixel CCD ICP-OES". Varian ICP-OES At Work No. 30.
3. V. Calderon, "Analysis of environmental samples with the Varian 710-ES following US EPA guidelines". Varian ICP-OES Application Note No. 39.

For More Information

For more information on our products and services, visit our Web site at www.agilent.com/chem

www.agilent.com/chem

Printed in the USA
November 1, 2010
IO-038

Agilent Technologies