Analysis of Environmental Samples Following US EPA Guidelines Utilizing a New Simultaneous CCD Detector ICP-OES System

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Introduction

The United States Environmental Protection Agency (US EPA) Contract Laboratory Program (CLP) defines the analytical methods accepted for the isolation, detection and quantitative measurement of target analytes in both water and soil / sediment environmental samples. 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.[1]

This poster describes the use of a new simultaneous CCD detector ICP-OES system to carry out the US EPA / CLP compliant analysis of water samples.

[1] ILM05.3, EPA Publication 540-F-04-001, 2004.

US EPA ILM05.3

Determine

- 22 target analytes in water
- NIST Certified Standard Reference Material 1643e Trace Elements in Water
- Melbourne drinking (tap) water

Purpose

1. Provide analytical data of known and documented quality
2. Environmental Regulations

- Extent of contamination
- Determine cleanup actions
- Emergency response and remedial actions
- Enforcement/litigation activities
- Hazardous waste site investigations

Three New ICP-OES Instruments

Varian 710/715-ES
- Entry level system with CCD detector
- A fully featured ICP-OES for laboratories with moderate or small sample loads

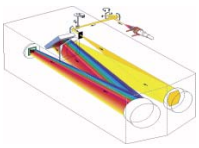
Varian 720/725-ES
- High sample throughput
- Ultimate in performance
- Flexibility to upgrade in the future for higher productivity and performance

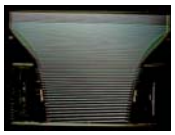
Varian 730/735-ES
- Highest sample throughput
- Ultimate in performance

The **Varian 730-ES simultaneous CCD ICP-OES** was utilized for this study. The 730-ES has an axial view plasma. I-MAP technolology exactly matches the detector to the echelle optics image and provides continuous wavelength coverage from 167 to 785 nm. The 730-ES features a high efficiency 40 MHz RF generator and low gas consumption. Its Cooled-Cone Interface (CCI) displaces the cooler tail of plasma leading to reduced interferences and increased linear dynamic range. The system includes MFC nebulizer gas, 4 channel pump and the SVS1 Switching Valve System as standard for maximum productivity.

700-ES Series Optical Design

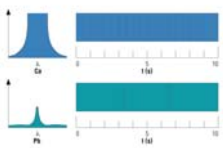
Computer-optimized echelle optical design provides complete wavelength coverage utilizing a single detector and single entrance slit. All wavelengths are captured in one reading. Minimal number of optical components provide high light throughput and excellent signal-to-noise levels. The polychromator is thermostatted to 35°C for stability and fast start-up.





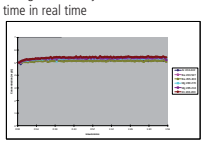
The 730-ES features a custom-designed and patented CCD detector with pixels arranged to exactly match the 2-dimensional echelle image (I-MAP technology). Duplex readout circuitry halves readout time. Processing electronics are 40 times faster with a 1 Megahertz pixel processing speed. The detector is Peltier cooled to -35°C for low noise leading to improved detection limits. Processing electronics are off-chip for high QE.

Adaptive Integration Technology



True Simultaneous Measurement

- Simultaneous measurement of all wavelengths, background signal and internal standard irrespective of signal intensity
- AIT automatically adjusts measurement time in real time
- Achieves optimum signal-to-noise ratio
- Prevents over range signals
- 1 ms to 100 s read times provide wide dynamic range
- Ideal for time resolved / specifiation type applications



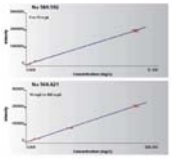
Less than 10 minutes of warm-up time is required

MultiCal

Manages the data collected when using alternate wavelengths:

- Combine element data of strong and weak lines for extended working range
- Measure multiple wavelengths of similar sensitivity for confirmation of results
- Take the mean, weighted mean or median result
- Take the minimum result – most likely to be least interfered result
- Automatically performs calculations on data, e.g. ratios, water hardness

Sample Labels	Na Mean mg/L mg/kg	Na 568.821 mg/L mg/kg	Na 589.592 mg/L mg/kg
Blank	0.00	0.00	0.00
20ppb CCS4+6	0.02		0.02
100ppb CCS4+6	0.10		0.10
1ppm CCS4+6	1.00		1.00
10ppm CCS4+6	10.00	10.00	10.00
50ppm Var Major	50.00	50.00	
200ppm Var Major	200.0	200.0	
500ppm Var Major	500.0	500.0	
Whole Milk Powder	3485	3485	
Whole Milk PowderDup	3565	3565	
Rice Flour 10b	17.20		17.20
Rice Flour 10b Dupl	17.08		17.08

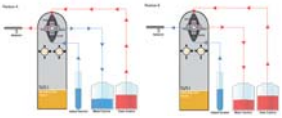


4 Port Switching Valve System (SVS1)

Provides shorter sample uptake and more efficient washout. SVS1 is compatible with SPS-3 and Cetac ASX-520 autosamplers and is controlled by the ICP Expert II software. Sample introduction is rinsed while next sample is introduced, leading to reduced carry over, increased sample throughput and lower cost per analysis.

Four Software Triggers

1. Start Run: ***Position A (instant rinse)***
2. At Start Uptake Delay + user specified time delay: ***Position B (sample)***
3. End Solution Measurement: ***Position A (instant rinse)***
4. End Run: ***Position B (autosampler rinse)***

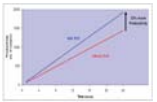


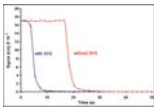
Features and Benefits of SVS1

33% improvement in productivity
- 25% reduction in argon use
- 25% reduction in torch use
- Extra 460 samples/day

Faster analysis times – but longer rinse times!
- Reduces contamination
- Improves accuracy

Reduces sample loading
- Less torch wear and salt build-up
- Improves long term stability for high TDS sample





Sample Type and Preparation

Certified Reference Material
- NIST SRM 1643e Trace Elements in Water

Melbourne drinking (tap) water

Sample matrix was 1% v/v HNO_3 and 5% v/v HCl

Calibration, QC and Buffer Solutions

Prepared from Inorganic Ventures Inc, custom-grade multi-element solutions

Superfund CLP ICP Kit for ILM05.2
- CLPP-CAL-1, CLPP-CAL-2, CLPP-CAL-3
- CLP-AES-CRQL, CLPP-ICS-A, CLPP-CAL-ICS-B4
- CLPP-SPK1, CLPP-SPK-5
- QCP-CICV-1, QCP-CICV-2, QCP-CICV-3

Ionization buffer
- Merck Tracepur™ $CsNO_3$. 1% w/v final solution

Calibration standards, QC solutions and ionization buffer
- Diluted with >18MW/cm³ deionized water (Millipore systems)
- 1% v/v HNO_3 (Merck Ultrapur™)
- 5% v/v HCl (Merck Ultrapur™)

Read Back of Blank + 5 mg/L Analyte

	As	Se	Sb	Tl	Pb
Run 1					
Avg. Conc	5.25	4.81	5.46	5.02	5.39
Run 2					
Avg. Conc	5.12	4.82	5.01	5.12	5.04
Run 3					
Avg. Conc	5.12	5.16	4.98	4.80	5.34

Instrument Parameters

Power	1.4 kW	Plasma gas flow	15 L/min
Auxiliary gas flow	1.5 L/min	Spray chamber type	Glass cyclonic
Torch	Standard axial torch	Nebulizer type	SeaSpray
Nebulizer gas flow	0.75 L/min	Pump speed	15 rpm
Sample uptake	2.5 mL	Replicate read time(s)	30
No. of replicates	2	Sample delay time(s)	25
Switching valve delay(s)	22	Stabilization time(s)	10
Rinse time(s)	30	Peristaltic pump type	4 Channel
Background Correction	1 or 2 point off-peak		

Method Detection Limits

Element Wavelength	CRDL (µg/L)	CRQL ILM05.3 (µg/L)	MDL Required ILM05.3 (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

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	0.50%	-	-	-
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%

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

Interference Check Sample A

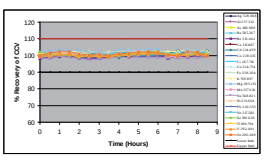
Element	CRQL ILM05.3 (µg/L)	ILM05.3 ± limit (µg/L)	ICSA (µg/L)	Result
Ag 328.068	10	20	-10	Pass
As 188.980	10	20	-2	Pass
Ba 585.367	200	400	-0.4	Pass
Be 313.042	5	10	0.1	Pass
Cd 214.439	5	10	0.4	Pass
Co 228.615	50	100	1	Pass
Cr 267.716	10	20	0.2	Pass
Cu 324.754	25	50	2	Pass
Mn 257.610	15	30	2	Pass
Ni 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

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

Continuing Calibration Verification (CCV)

Long-term precision (RSD): 0.98% MAX



Summary

Strict US EPA requirements for CLP laboratories
- Large number of QC solutions
- Analysis is time consuming

Varian 730-ES total analysis time - 2 minutes and 25 seconds per sample.

Varian 730-ES simultaneous ICP-OES with productivity enhancing SVS1 accessory, meets the stringent requirements of US EPA method ILM05.3 while providing increased sample throughput and lower cost per analysis.

Inspiring Excellence