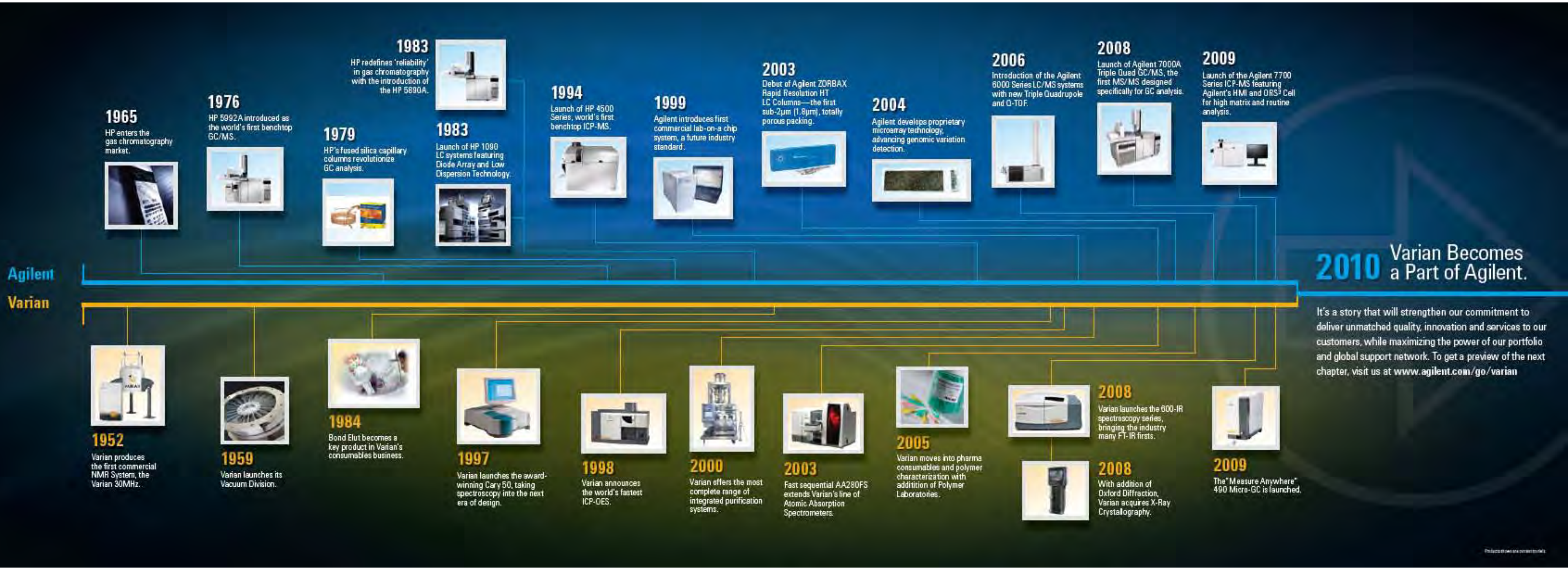
Today's Agilent – New Atomic Spectroscopy Solutions for Environmental Laboratories

2010 – Varian Becomes a Part of Agilent

A Heritage of Innovation: Varian & Agilent



Today's Agilent: Atomic Spectroscopy
More choices

The addition of the Varian Atomic Absorption (AA) and ICP-OES products to Agilent's ICP-MS products provides a complete portfolio for routine and research analysis in environmental, food, agriculture, clinical, pharmaceutical, product safety, semiconductor, chemical/petrochemical, geochemical/mining, metals, academic/research and other applications.

Agilent provides the best choice for every lab through:

- A full range of atomic spectroscopy instrumentation
- Optimal product offering for any budget / application
- Continued focus on reliability and performance

Today's Agilent: Atomic Spectroscopy

World's best, most complete atomic spectroscopy portfolio!

ICP-OES

ICP-MS

AA

Key Features - Atomic Spectroscopy Products

AA, ICP-OES, ICP-MS

Single element

FAA	Flame Atomic Absorption	Very fast; good elemental coverage, single-element; DLs typically 10's to 100's ppb; low cost.
GFAA	Graphite Furnace Atomic Absorption	Slow; select elemental coverage, single-element; DLs typically 10's to 100's ppt; higher cost.

Multi-element

ICP-OES	ICP Optical Emission Spectroscopy	Very fast; can measure most elements, multi-element; DLs typically single ppb; more expensive.
ICP-MS	ICP Mass Spectrometry	Fast; can measure almost all elements, including Hg, multi-element; DLs typically single- or sub-ppt; most expensive.

AA, ICP-OES and ICP-MS are each utilized for routine inorganic analysis.

Agilent Atomic Absorption

The world's fastest flame AA; the world's most sensitive furnace AA

- Superior flame, graphite furnace, and vapor generation—or a combination of techniques—let you exactly match your analytical needs and your budget
- Patented "Fast Sequential" capability lets you measure multiple elements in each sample—doubling productivity and lowering the cost per analysis
- Patented transverse AC modulated Zeeman GFAA provides unmatched background correction and performance
- Easy-to-use software and rugged, reliable hardware simplify operation and maximize uptime

Agilent ICP-OES

The world's most productive high performance simultaneous ICP-OES

- Continuous wavelength coverage provides extended dynamic range and reduced interferences, giving you maximum confidence in your results
- Robust plasma ensures reliable and reproducible results—even with the most complex matrices
- One view, one step measurement of major, minor, and trace elements, plus the fastest warm-up, increases throughput and productivity

Agilent ICP-MS

Unmatched matrix tolerance and unparalleled interference removal

- Patented High Matrix Introduction (HMI) technology increases matrix tolerance up to 10x to handle the toughest samples with ease!
- Third generation collision cell design with helium collision mode effectively removes polyatomic interferences, ensuring more accurate results in unknown or complex sample matrices
- Delivers the highest productivity in the most demanding lab environments

New Atomic Spectroscopy Solutions for Environmental Laboratories

- Determination of Hg in Environmental Samples using Cold Vapor AA
- Analysis of Environmental Samples by Simultaneous Axial ICP-OES following USEPA Guidelines
- The Agilent 7700x ICP-MS and Environmental Monitoring
- Preview - Flue Gas Desulfurization (FGD) Wastewaters by ICP-MS

Overview of Vapor Generation Technique

- Analyze metals which form volatile hydrides
  – As, Se, Sb, Bi, Te, Sn
- Analyze mercury
  – Cold vapor technique
- Extremely sensitive technique
- Chemically reduce the element to gaseous hydride or free Hg
- Dissociate hydride in heated quartz cell

The Measure of Confidence
Agilent Technologies

Advantages of Vapor Generation Technique

- Faster than Zeeman graphite furnace technique
  - 50 – 70 analyses per hour

- Analyte is removed from matrix
  - Eliminating matrix interferences
  - Minimizing background
  - Can easily analyze matrices that are difficult to run by graphite furnace

- 100 % sampling efficiency
  - Detection limits in the sub-ppb range
  - Extremely sensitive for ultra-trace Hg

- Excellent in run precision
  - Typically 1 – 2 % RSD

Water Samples

- Four water samples were prepared following EPA method 245.1 CLP
  - Water samples were supplied from an independent environmental laboratory
  - No certified values were available
    - 50 mL of sample was split into two 25 mL aliquots
    - One aliquot was spiked with 2 μg/L of Hg

Solid Samples

- Two solid samples were prepared following EPA method 245.5 CLP for mercury in soil/sediment
  - NIST river sediment and NIST metals in fish
  - Certified values for mercury were available

Instrument Parameters for Cold Vapor

- Reductant container:
  - 25 % (w/v) stannous chloride ($SnCl_2$) in 20 % (v/v) HCl
  - Add 100 mL concentrated HCl directly to 125 g $SnCl_2$ and warm the mixture on hot plate until dissolution is complete. Dilute to 500 mL
- Acid container:
  - DI water
- Measurement parameters at 253.7 nm line:
  - Delay time = 60 sec to allow for the reaction of the $SnCl_2$ to stabilize
  - Measurement time = 3 sec (3 replicates)
- Calibration standard concentrations:
  - 1 µg/L, 5 µg/L, 10 µg/L and 20 µg/L

Results of Hg Detection Limit Study

- Standard deviation of ten 0.5 µg/L solutions = 0.03 µg/L
  - 3 sigma instrument detection limit = 0.09 µg/L
- Standard deviation of ten prepared 1 µg/L Hg solutions = 0.11 µg/L
  - 3 sigma method detection limit = 0.33 µg/L
- Characteristic concentration = 0.23 µg/L

Sample Results

Water Samples

NIST Samples (solids)

Sample ID	Measured Value (mg/L)	Matrix Spike % Recovery		Sample ID	Certified Value (mg/kg)	Valid Range (mg/kg)	Measured Value (mg/kg)
1	0.81	125		River Sediment	1.1	0.6-1.6	0.97
2	8.53	96		Duplicate			0.97
3	0.38	125		Fish	2.52	1.24-3.8	1.6
4	0.55	119		Duplicate			1.68

Matrix spike conc. = 2.0 μg/L

Summary

- Vapor generation AA is an alternative technique for the determination of Hg at ug/L concentrations in environmental samples

- Vapor generation can be a complementary technique for ICP-OES or Zeeman graphite furnace AA
  - Similar performance for Hg and hydride elements can be obtained by direct analysis using ICP-MS, if sample prep is compatible (must include HCl)

- Vapor generation accessories for AA, ICP-OES and stand-alone Hg analyzers are available

Analysis of Environmental Samples by Simultaneous Axial ICP-OES following USEPA Guidelines

US EPA CLP SOW ILM05.3/05.4

Determine:

- 22 target analytes in water
  - Hg not determined by ICP-OES
- NIST Certified Standard Reference Material 1643e Trace Elements in Water
- Melbourne drinking (tap) water

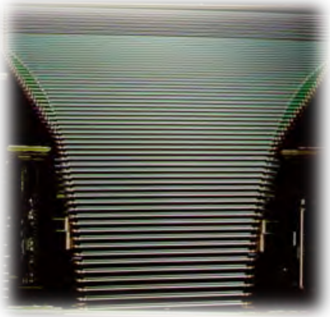
Purpose:

- Provide analytical data of known and documented quality
- Environmental Regulations
  - Extent of contamination
  - Determine cleanup actions
  - Emergency response and remedial actions
  - Enforcement/Litigation activities
  - Hazardous waste site investigations

Instrumentation

Agilent 730-ES simultaneous CCD ICP-OES

- Axial configuration
- VistaChip custom-designed and patented CCD detector
- Continuous wavelength coverage from 167 to 785 nm
- High efficiency 40 MHz RF generator
- Cooled-Cone Interface (CCI) displaces cooler tail of plasma
  - Increases linear dynamic range and reduces interferences
- SVS1 Switching Valve System for greater productivity



Sample Types and Preparation

Sample Types

- Certified Reference Material - NIST SRM 1643e Trace Elements in Water
- Melbourne drinking (tap) water

Sample, Standard and QC Preparation

- Matrix was 1% v/v HNO_3 and 5% v/v HCl (Merck Ultrapur™)

Calibration Standards & QC 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

Instrument Setup

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
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
Sample volume consumed	2.5 mL per sample

Method Detection Limits

Element	CRDL (µg/L)	MDL obtained (µg/L)	Element	CRDL (µg/L)	MDL obtained (µg/L)
Ag 328.068	5	**0.5**	K 766.491	5000	**0.8**
Al 396.152	200	**0.6**	Mg 285.213	5000	**0.4**
As 188.980	5	**1**	Mn 257.610	10	**0.06**
Ba 233.527	20	**0.1**	Na 589.592	5000	**0.6**
Be 313.042	1	**0.009**	Ni 231.604	20	**0.7**
Ca 315.887	5000	**1**	Pb 220.353	3	**0.8**
Cd 214.439	2	**0.09**	Sb 206.834	5	**1**
Co 228.615	5	**0.4**	Se 196.026	5	**1**
Cr 267.716	5	**0.2**	Tl 190.794	5	**1**
Cu 324.754	5	**0.7**	V 292.401	10	**0.3**
Fe 259.940	100	**0.3**	Zn 213.857	10	**0.1**

ALL ELEMENTS MEET CRDL* REQUIREMENTS

* Contract Required Detection Limit

Interference Check Sample A (ICSA)

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 217.582	60	120	10	**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**

ICSA interference matrix solution contains high mg/L levels of Al, Ca, Mg and Fe

LIMIT = 2 x CRQL*   ALL ELEMENTS PASS

* Contract Required Quantitation Limit

Interference Check Sample AB (ICSAB)

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	96	**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 217.582	0.60	0.63	104	**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**

Limit = 80-120% **ALL ELEMENTS PASS**

ICSAB is ICSA interference matrix solution spiked with analyte elements

Laboratory Control Sample (LCS)

NIST SRM 1643e Trace Elements in Water

Element	NIST 1643e Certified (mg/L)	NIST 1643e Measured LCS (mg/L)	LCS %Recovery	Element	NIST 1643e Certified (mg/L)	NIST 1643e Measured LCS (mg/L)	LCS %Recovery
Ag 328.068	0.001062	<CRQL	**-**	K 769.897	2.034	2.11	**103.7**
Al 237.312	0.1418	0.151	**106.6**	Mg 285.213	8.037	8.55	**106.4**
As 188.980	0.06045	0.0590	**97.5**	Mn 257.610	0.03897	0.0410	**105.1**
Ba 585.367	0.5442	0.554	**101.9**	Na 589.592	20.74	21.6	**104.1**
Be 313.042	0.01398	0.0140	**100.0**	Ni 231.604	0.06241	0.0629	**100.9**
Ca 315.887	32.3	32.0	**99.0**	Pb 220.353	0.01963	0.0207	**105.7**
Cd 214.439	0.006568	0.00642	**97.8**	Sb 217.582	0.0583	0.0602	**103.2**
Co 228.615	0.02706	0.0280	**103.5**	Se 196.026	0.01197	<CRQL	**-**
Cr 267.716	0.0204	0.0209	**102.4**	Tl 190.794	0.007445	<CRQL	**-**
Cu 324.754	0.02276	0.0229	**100.7**	V 292.401	0.03786	0.0389	**102.7**
Fe 238.204	0.0981	0.105	**106.8**	Zn 206.200	0.0785	0.0803	**102.3**

Limit = 80-120% **ALL ELEMENTS PASS**

Spike Sample Analysis

Melbourne drinking (tap) water

Element	Sample Measured (mg/L)	Sample + Spike Measured (mg/L)	Added Spike Conc. (mg/L)	Spike % Recovery	Element	Sample Measured (mg/L)	Sample + Spike Measured (mg/L)	Added Spike Conc. (mg/L)	Spike % Recovery
Ag 328.068	<CRQL	0.0484	0.0491	**98.6**	K 769.897	0.597	-	-	**-**
Al 237.312	0.0939	2.11	1.96	**103**	Mg 285.213	1.114	-	-	**-**
As 188.980	<CRQL	0.0395	0.0361	**109**	Mn 257.610	0.00614	0.524	0.491	**105**
Ba 585.367	0.0176	2.05	1.96	**104**	Na 589.592	4.074	-	-	**-**
Be 313.042	<CRQL	0.0513	0.0491	**104**	Ni 231.604	<CRQL	0.516	0.491	**105**
Ca 315.887	3.64	-	-	**-**	Pb 220.353	<CRQL	0.0201	0.018	**112**
Cd 214.439	<CRQL	0.0486	0.0451	**108**	Sb 217.582	<CRQL	0.101	0.0901	**112**
Co 228.615	<CRQL	0.51	0.491	**104**	Se 196.026	<CRQL	0.0493	0.0451	**109**
Cr 267.716	<CRQL	0.206	0.196	**105**	Tl 190.794	<CRQL	0.0474	0.0451	**105**
Cu 324.754	0.162	0.412	0.246	**102**	V 292.401	<CRQL	0.503	0.491	**102**
Fe 238.204	0.0924	1.1	0.982	**103**	Zn 206.200	0.00637	0.53	0.491	**107**

Limit = 75-125% **ALL ELEMENTS PASS**

Duplicate Sample Analysis

Element	NIST 1643e LCS Measured (mg/L)	NIST 1643e Duplicate LCS Measured (mg/L)	Control Limit	%RPD or Difference (mg/L)
Ag 328.068	<CRQL	<CRQL	-	**-**
Al 237.312	0.151	0.160	CRQL	**0.009**
As 188.980	0.0590	0.0575	20%RPD	**2.42%**
Ba 585.367	0.554	0.561	CRQL	**0.007**
Be 313.042	0.0140	0.0142	CRQL	**0.0002**
Ca 315.887	32.0	32.1	20%RPD	**0.560%**
Cd 214.439	0.00642	0.00645	CRQL	**0.00003**
Co 228.615	0.0280	0.0283	CRQL	**0.0003**
Cr 267.716	0.0209	0.0211	CRQL	**0.0002**
Cu 324.754	0.0229	0.0242	CRQL	**0.0013**
Fe 238.204	0.105	0.104	CRQL	**0.001**

LIMITS

Concentration (Element) $\geq$ 5xCRQL: *20% RPD*

Concentration (Element) < 5xCRQL but > CRQL: $\pm$ *CRQL*

Concentration (Element) < CRQL: *Difference not reported*

ALL ELEMENTS PASS

Duplicate Sample Analysis

Element	NIST 1643e LCS Measured (mg/L)	NIST 1643e Duplicate LCS Measured (mg/L)	Control Limit	%RPD or Difference (mg/L)
K 769.897	2.11	2.13	CRQL	**0.02**
Mg 285.213	8.55	8.65	CRQL	**0.10**
Mn 257.610	0.0410	0.0411	CRQL	**0.0001**
Na 589.592	21.6	20.9	CRQL	**0.7**
Ni 231.604	0.0629	0.0639	CRQL	**0.0010**
Pb 220.353	0.0207	0.0202	CRQL	**0.0005**
Sb 206.834	0.0596	0.0608	CRQL	**0.0012**
Se 196.026	<CRQL	<CRQL	-	**-**
Tl 190.794	<CRQL	<CRQL	-	**-**
V 292.401	0.0389	0.0388	CRQL	**0.0001**
Zn 206.200	0.0803	0.0820	CRQL	**0.0017**

LIMITS

Concentration (Element) $\geq$ 5xCRQL: *20% RPD*

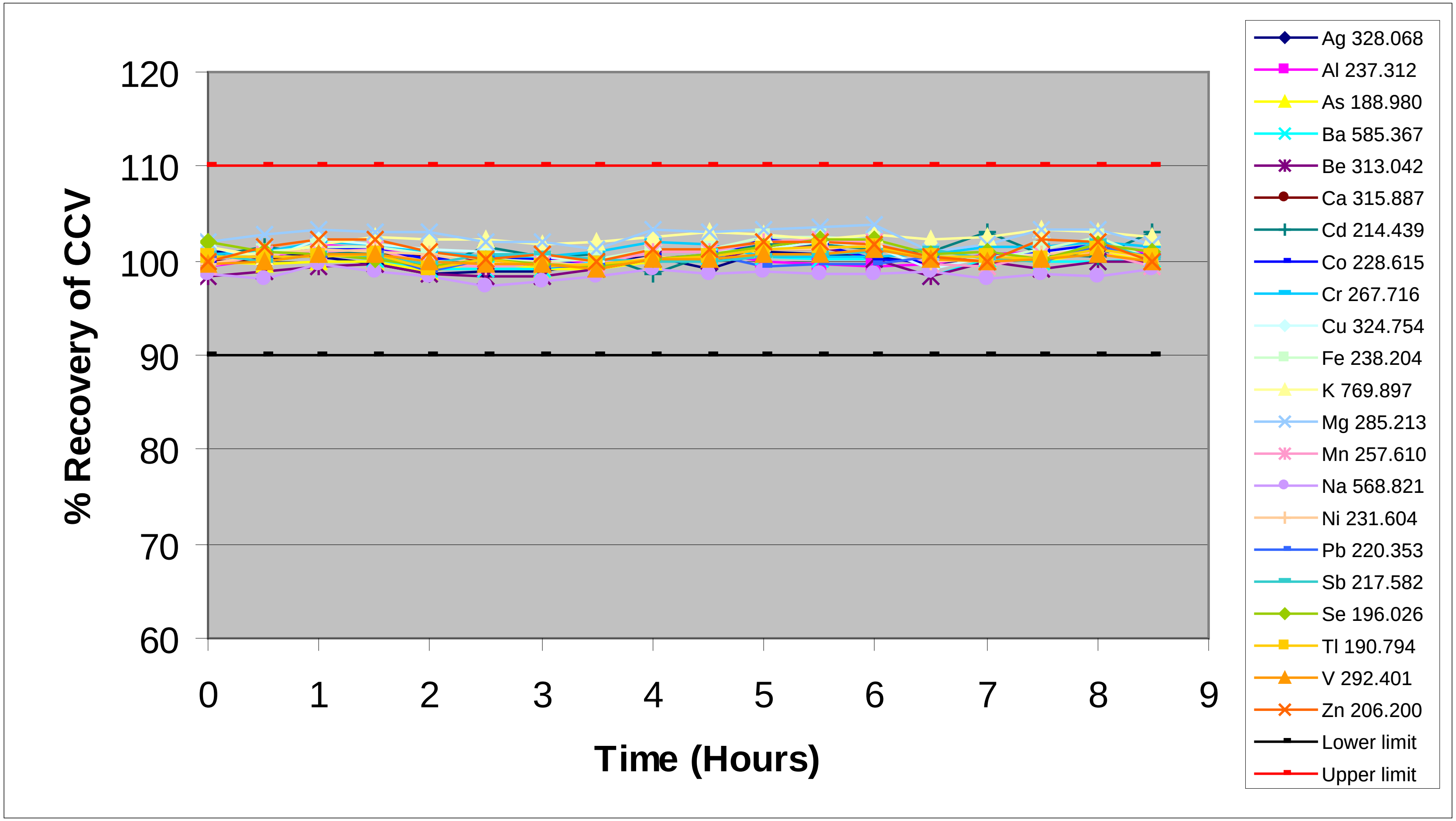
Concentration (Element) < 5xCRQL but > CRQL: *$\pm$ CRQL*

Concentration (Element) < CRQL: *Difference not reported*

ALL ELEMENTS PASS

Long Term Stability

Continuing Calibration Verification (CCV)



Long-term precision (RSD): 0.98% MAX

Speed of Analysis

Strict US EPA requirements require a large number of QC solutions

- Analysis is time consuming

Agilent 730-ES Total Analysis Time

- 2 minutes and 25 seconds per sample

Conclusion

The world's most productive high performance simultaneous ICP-OES, the Agilent 730-ES, with productivity enhancing SVS1 accessory, meets the stringent requirements of US EPA CLP SOW ILM05.3/05.4 in an analysis time of less than 2.5 minutes per sample.

Note: Requirements for ICP-OES methods 200.5, 200.7 and 3020B are also met by Agilent 700-ES series instrument systems.

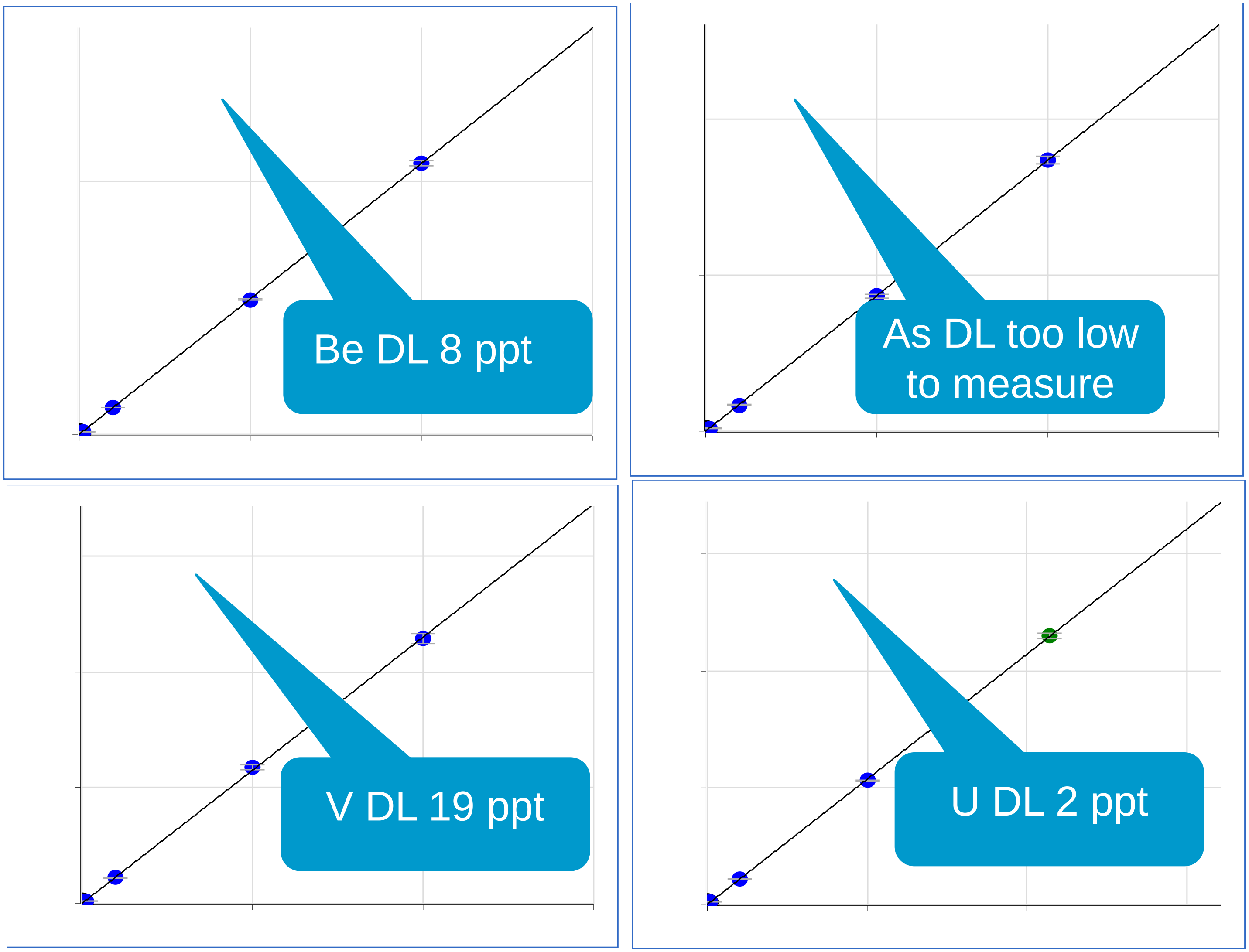
The Agilent 7700x ICP-MS

Smaller, Simpler, Faster, more Accurate, more Sensitive, and more Robust than ever

Designed for environmental analysis -

- Newly designed ORS^3 collision cell for simple, reliable removal of all polyatomic interferences under a single set of conditions, even in complex, unknown matrices
- Standard, built-in High Matrix Introduction (HMI) system permits % level TDS samples to be run directly and routinely
- Optional ISIS-DS discrete sampling accessory for ultimate productivity and stability when running very high matrix samples

ORS³ - Superior Interference Removal Under Generic, Universal Conditions (3 sigma MDLs in 1% nitric / 0.5% HCl)



4 tough elements over entire mass range

Difficult Cl based interferences removed from V and As under the same cell conditions

High and low mass sensitivity in no gas mode preserved

Drinking Water Detection Limits

Helium and no gas only

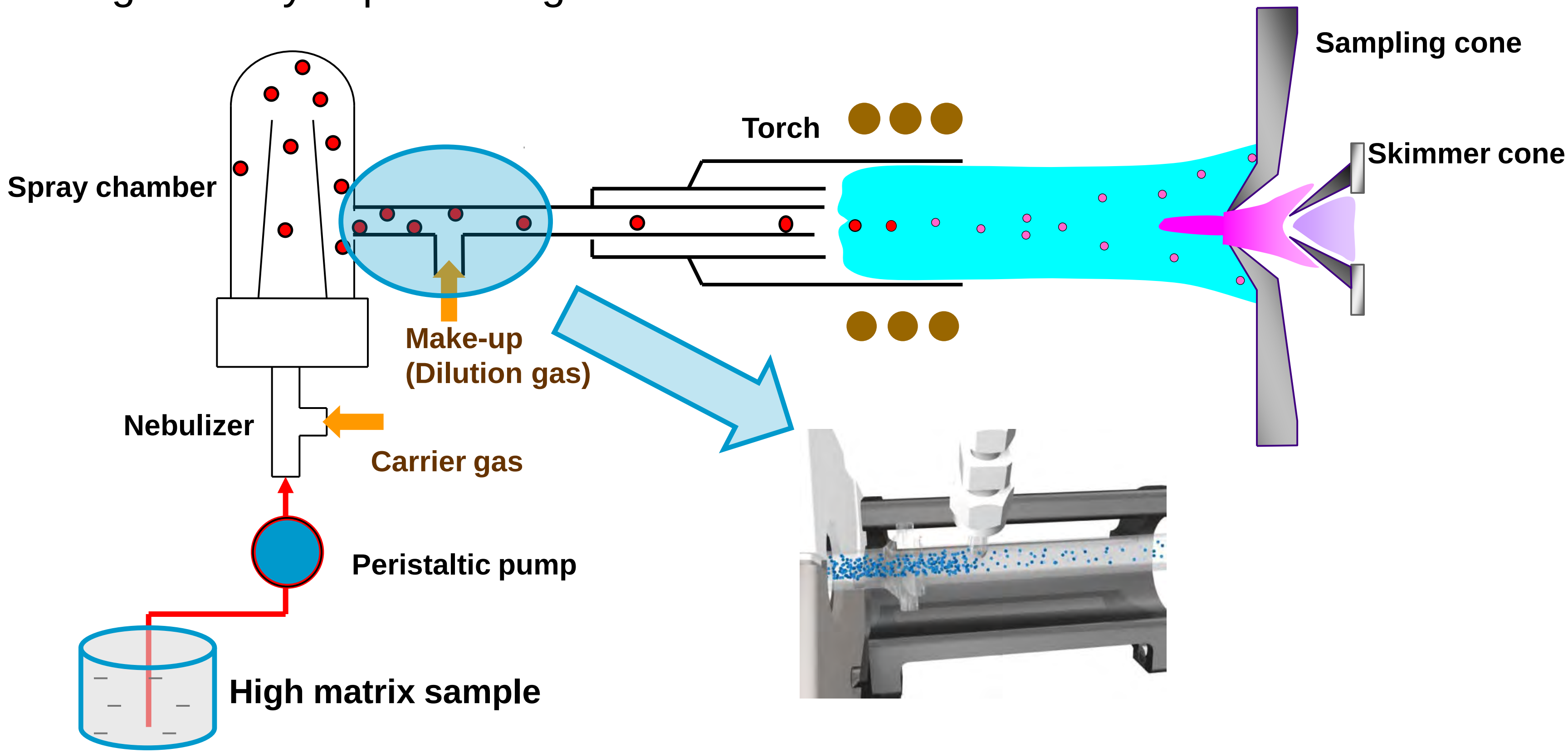
Mass	Element	MDL (ppt)	Cell mode		Mass	Element	MDL (ppt)	Cell mode
9	Be	**5.2**	No gas		66	Zn	**14.0**	He
11	B	**5.0**	No gas		75	As	**11.9**	He
23	Na	**58.5**	No gas		78	Se	**17.6**	He
24	Mg	**2.8**	No gas		88	Sr	**2.1**	He
27	Al	**7.9**	No gas		95	Mo	**6.9**	He
39	K	**76.9**	He		107	Ag	**2.3**	He
42	Ca	**57.8**	He		111	Cd	**2.9**	He
51	V	**14.3**	He		121	Sb	**6.1**	He
52	Cr	**4.3**	He		137	Ba	**5.7**	He
55	Mn	**8.5**	He		202	Hg	**1.2**	He
56	Fe	**14.8**	He		205	Tl	**2.4**	He
59	Co	**4.4**	He		208	Pb	**1.3**	He
60	Ni	**14.7**	He		232	Th	**1.8**	He
63	Cu	**2.7**	He		238	U	**1.7**	He

3 sigma MDLs based on 7 replicates (ppt)

Note: Fe and Se detection limits are less than 20 ppt in helium mode

HMI (High Matrix Introduction) System

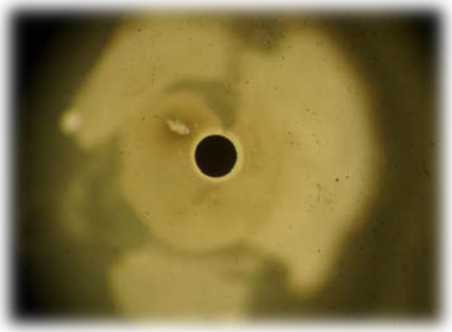
- HMI combines aerosol dilution and highly robust plasma conditions
- Robust conditions are very hot plasma combined with carrier gas flow and sampling location automatically optimized to maximize dilution of ions within the plasma
  - Significantly reduced oxides (CeO^+/Ce^+ ~0.2% or less)
  - Significantly improved high matrix tolerance

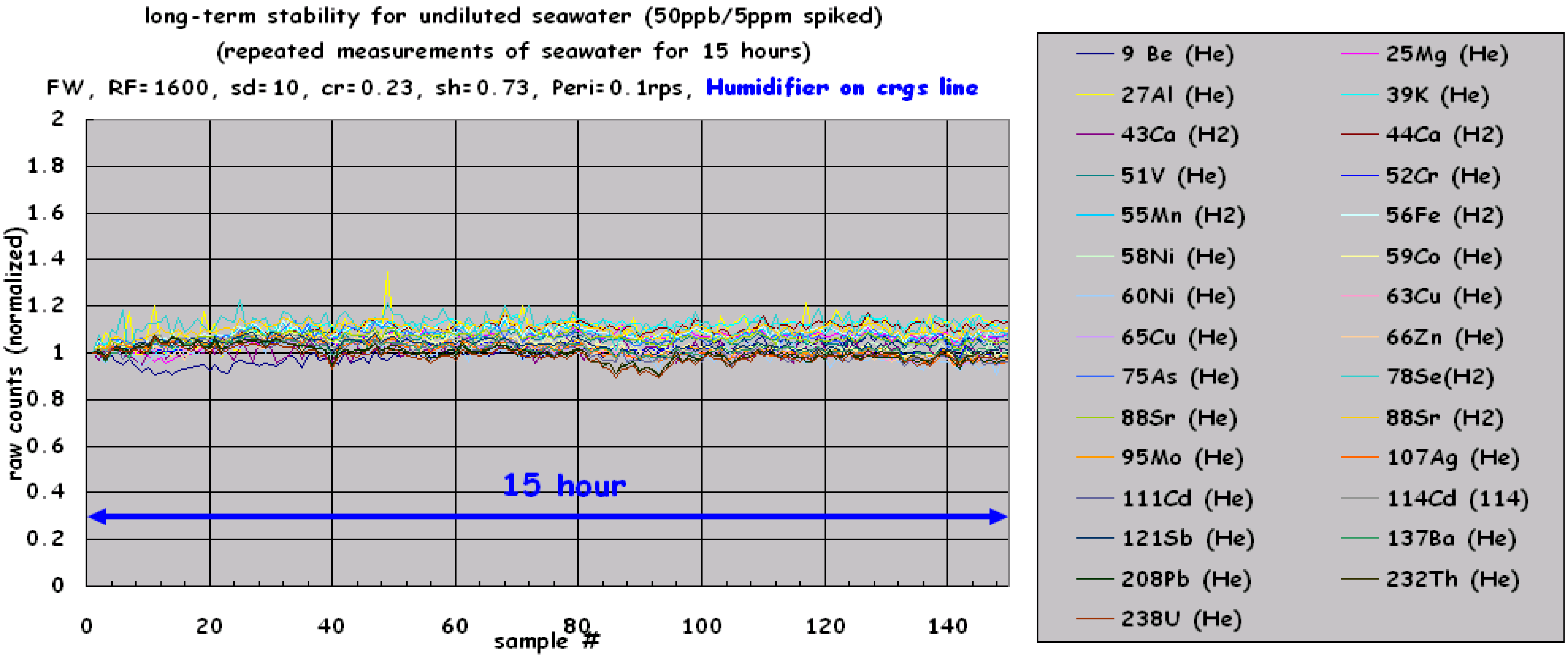


Analysis of ***Undiluted*** Seawater using HMI

Excellent long term stability (>150 samples)
No ICP-MS has ever measured undiluted seawater successfully before!

Skimmer after test

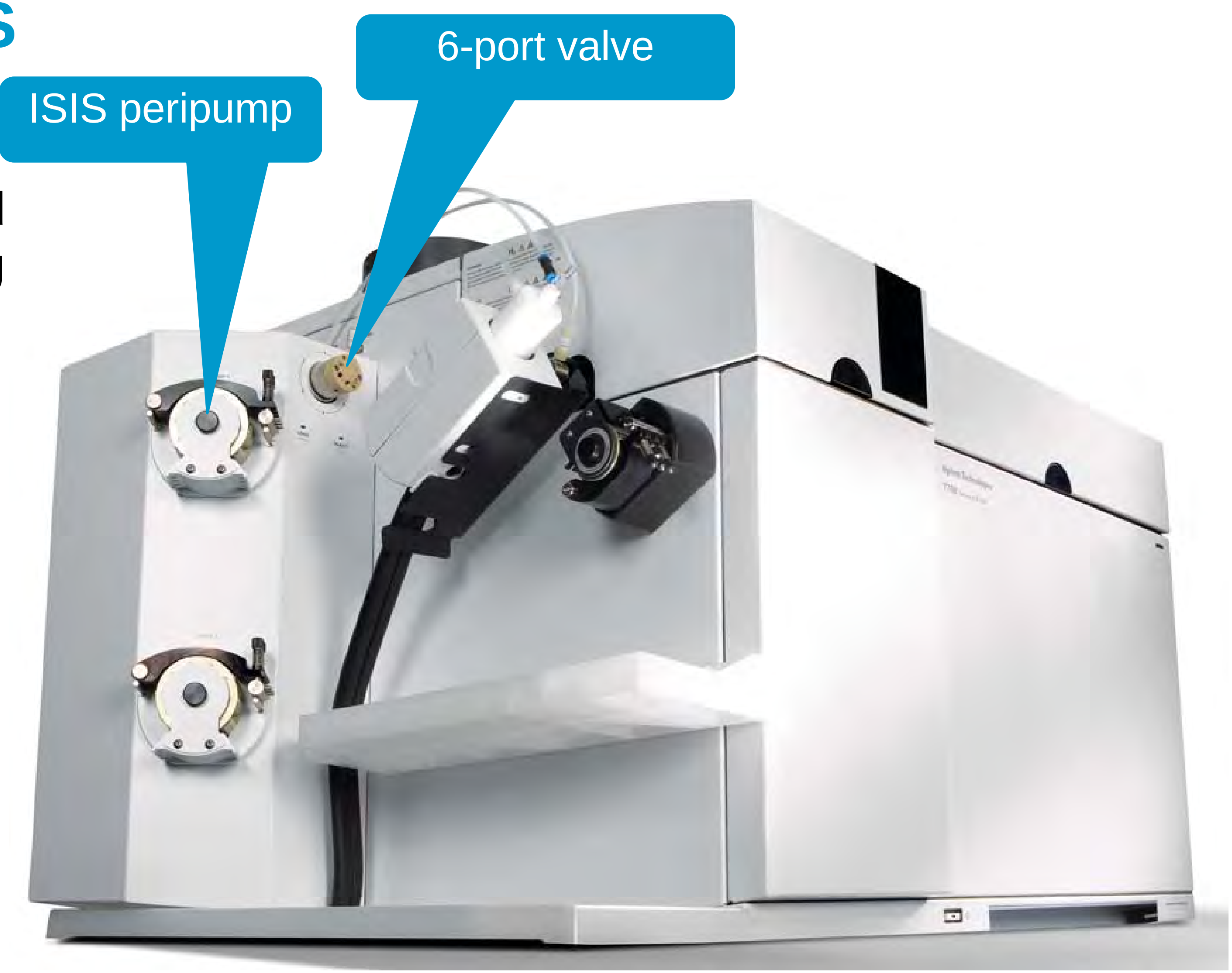




ISIS-DS High Speed Discrete Sampling for the 7700 ICP-MS

Fully integrated, Agilent supported discrete sampling for the 7700

Requires one ISIS peripump and 6-port valve



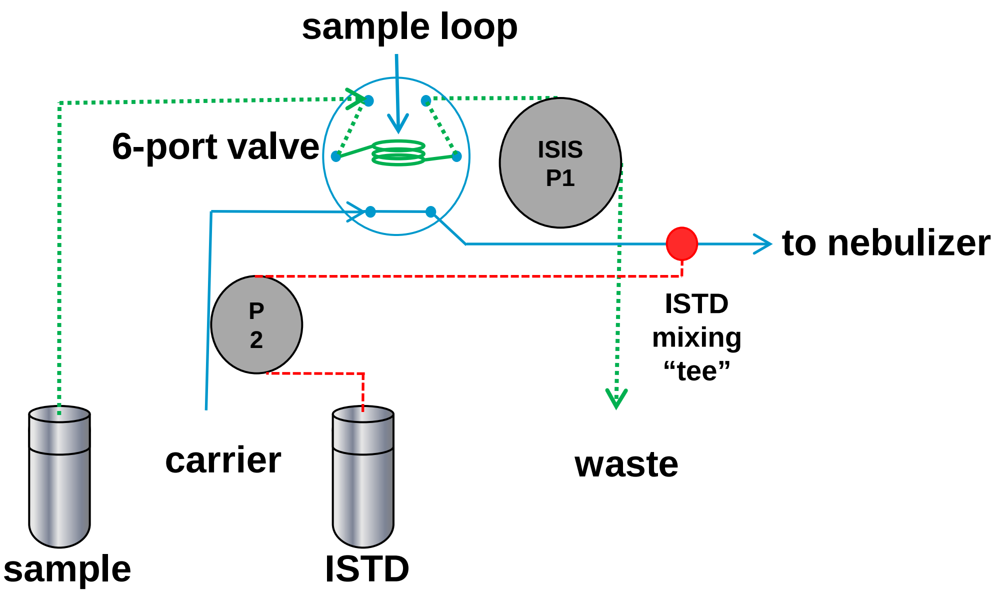
Performance Advantages of Discrete Sampling

(in addition to much faster run times)

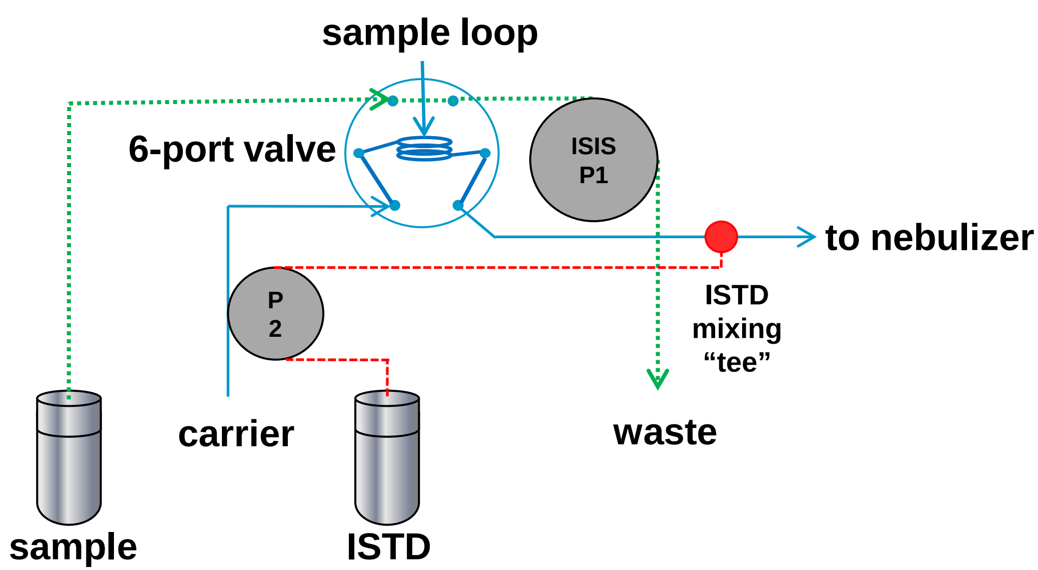
Significantly reduced exposure of ICP-MS to high TDS samples	•Reduced signal drift •Reduced cleaning and maintenance •Ability to run much higher matrix samples routinely
Constant nebulization speed	• Longer peripump tube life • Improved precision
Elimination of peristaltic pump tubing from sample path	• Reduced contamination • Better rinseout
Absolutely constant internal standard addition	• Improved internal standard correction

ISIS-DS Configuration

Load Loop



Inject Sample



Ultimate Speed Plus Ultimate Matrix Tolerance

ISIS-DS plus HMI

Seamless Integration of High Speed Discrete Sampling with Online Aerosol Dilution

Fully compliant EPA 6020 analysis for ultra high matrix samples in under 2 minutes per sample

- No sample dilution
- No matrix matching of standards or blanks
- ICP-MS sensitivity and data quality
- ICP-OES speed and matrix tolerance

Combining ORS³ + HMI + ISIS-DS for Ultimate Performance and Productivity

Eliminating the need for H_2 mode results in faster acquisition which when coupled with ISIS-DS results in the fastest collision cell ICP-MS ever.

31 elements including internal standards, 3 replicates, EPA compliant analysis in 75.6 seconds run to run.

Plasma	**Robust mode – 1550 Watts**
Nebulizer	Glass concentric (standard)
Number of elements (including internal standards)	31
ORS Mode	He - 4 mL/min (single mode)
Integration time per point	0.1 seconds (all elements)
Points per peak	1
Replicates	3
Total acquisition time (3 reps)	26 seconds
Loop volume	300µL
Loop rinse and fill time	8-10 seconds
Acquisition delay (after valve rotation to inject)	15 seconds
Available acquisition time	30 seconds

Multi-Vendor Round Robin Analysis

4 Sample types (75 samples each + QC = 114 runs each)

- 75 water samples
- 75 soil digests (undiluted)
- 75 TCLP extracts (undiluted)
- 75 seawater samples (undiluted)

- 47 elements including Internal Standards
- 2 cell modes - He for all elements except Se and Si (H_2)
- Total run time 2.97 minutes, sample to sample (3 replicates)
- A single HNO_3/HCl calibration was used for all 4 sample types

No matrix matching, no optimized tuning or calibration

Elements	Cal 1	Cal 2	Cal 3	Cal 4	Cal 5	Cal 6	Cal 7	CCV
Trace elements (ppb)	Blank	0.2	1	2	20	100	200	100
Na, K, Ca, Mg, Fe, Si (ppb)	Blank	20	100	200	2000	10,000	20,000	10,000
B, P (ppb)	Blank	1	5	10	100	500	1000	500

Significantly Extended Dynamic Range with HMI

Accurately measure elements at up to 5000x the upper calibration concentration

Element	Highest Calibration (mg/L)	Linear Range Standard Conc (mg/L)	Measured value (mg/L)	Recovery %
Aluminum	0.2	1000	**1081.0**	**108.1%**
Antimony	0.2	10	**9.2**	**91.7%**
Arsenic	0.2	10	**10.8**	**108.3%**
Barium	0.2	10	**10.5**	**105.3%**
Beryllium	0.2	10	**10.7**	**107.3%**
Boron	1	10	**9.5**	**95.4%**
Cadmium	0.2	10	**10.5**	**104.7%**
Calcium	20	1000	**1014.0**	**101.4%**
Chromium	0.2	10	**10.7**	**106.9%**
Cobalt	0.2	10	**11.0**	**109.5%**
Copper	0.2	100	**109.3**	**109.3%**
Iron	20	1000	**977.4**	**97.7%**
Lead	0.2	200	**207.9**	**104.0%**
Lithium	0.2	10	**10.8**	**108.4%**
Magnesium	20	1000	**1014.0**	**101.4%**
Manganese	0.2	10	**10.8**	**108.1%**
Nickel	0.2	10	**10.9**	**108.8%**
Phosphorus	20	500	**486.4**	**97.3%**
Potassium	20	1000	**982.3**	**98.2%**
Selenium	0.2	10	**10.2**	**101.5%**
Silicon	1	500	**462.0**	**92.4%**
Silver	0.2	10	**8.4**	**84.0%**
Sodium	20	1000	**956.3**	**95.6%**
Strontium	0.2	10	**10.5**	**105.1%**
Thallium	0.2	10	**10.3**	**103.1%**
Thorium	0.2	10	**10.2**	**101.7%**
Tin	0.2	20	**20.9**	**104.7%**
Titanium	0.2	10	**9.8**	**97.7%**
Uranium	0.2	10	**10.3**	**103.4%**
Vanadium	0.2	10	**10.6**	**105.7%**
Zinc	0.2	50	**52.0**	**103.9%**
Zirconium	0.2	10	**10.6**	**105.8%**

Accuracy and Precision

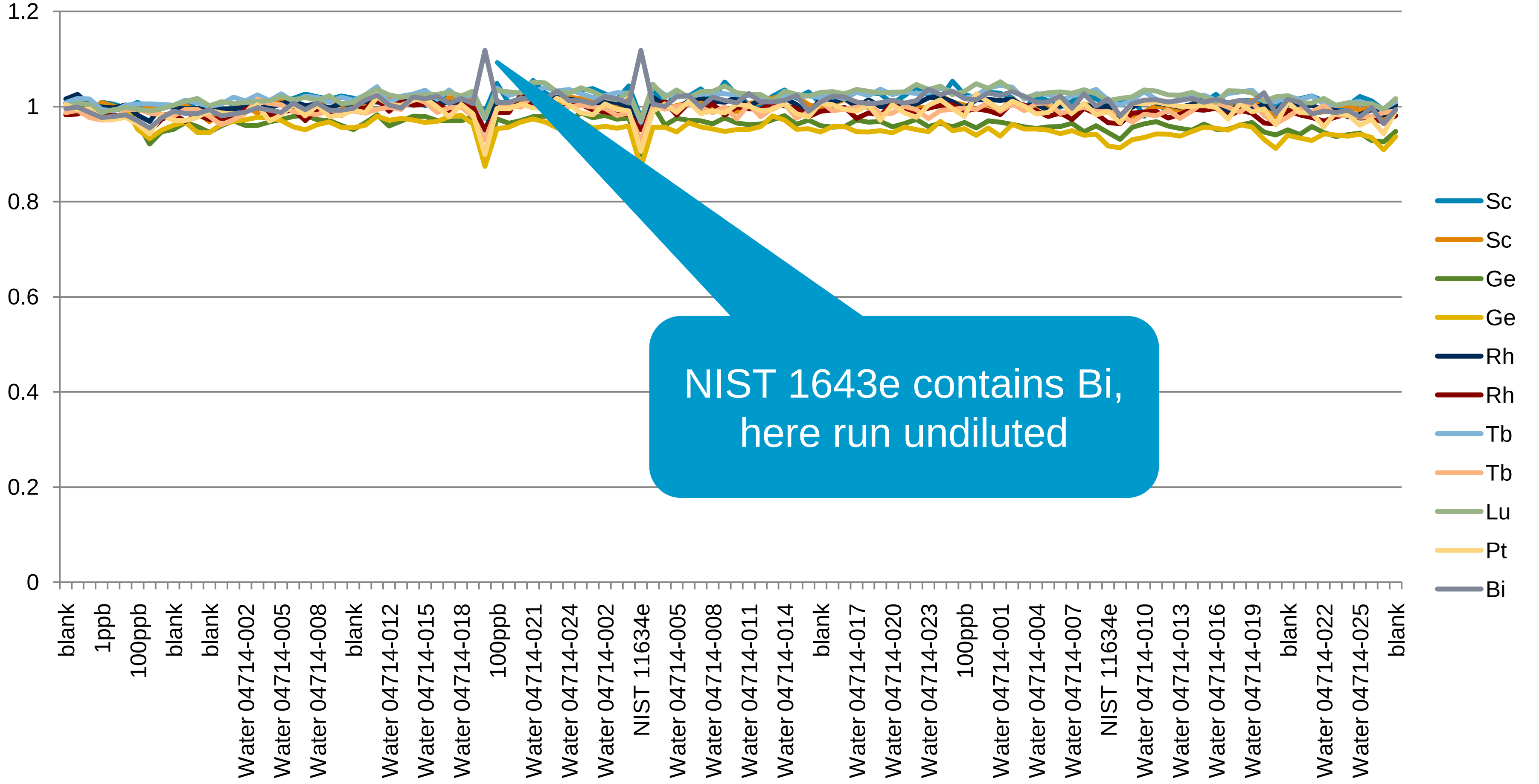
NIST 1643e Trace Elements in Water

Mass/Element	Mean measured value (µg/L)	RSD (%)	Certified value (µg/L)	Recovery (%)
9 Be	13.8	**2.5**	14.0	101.0%
23 Na	22689.2	**2.0**	20740.0	109.4%
24 Mg	7300.3	**2.1**	8037.0	90.8%
27 Al	142.3	**3.3**	141.8	100.4%
39 K	1837.8	**1.1**	2034.0	90.4%
43 Ca	32170.1	**0.7**	32300.0	99.6%
51 V	37.8	**1.1**	37.9	99.8%
53 Cr	19.2	**1.7**	20.4	93.9%
55 Mn	38.0	**0.9**	39.0	97.6%
56 Fe	98.1	**3.9**	98.1	100.0%
59 Co	28.8	**0.7**	27.1	106.4%
60 Ni	59.2	**0.8**	62.4	94.9%
63 Cu	23.2	**0.8**	22.8	101.9%
66 Zn	70.0	**0.5**	78.5	89.2%
75 As	54.3	**0.9**	60.5	89.8%
78 Se	10.0	**3.4**	12.0	83.2%
95 Mo	121.7	**1.1**	121.4	100.3%
107 Ag	1.1	**1.4**	1.1	101.1%
111 Cd	6.2	**0.8**	6.6	94.3%
121 Sb	59.5	**0.9**	58.3	102.0%
205 Tl	7.4	**0.8**	7.4	100.0%
208 Pb	19.6	**0.9**	19.6	99.7%

%RSD for 26 replicate analyses spread over a sequence of 216 samples

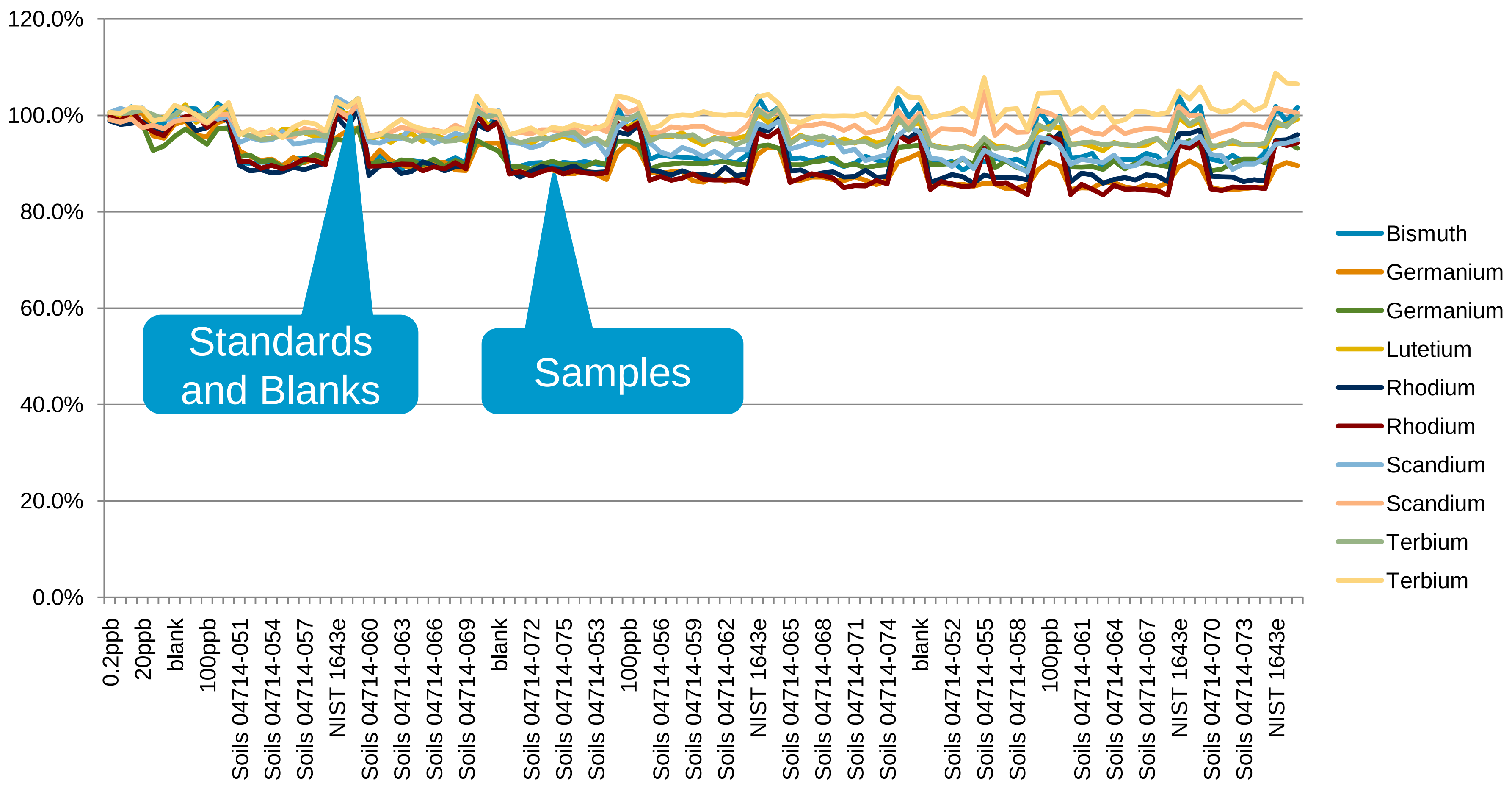
Internal Standard Recoveries

High TDS Water Samples



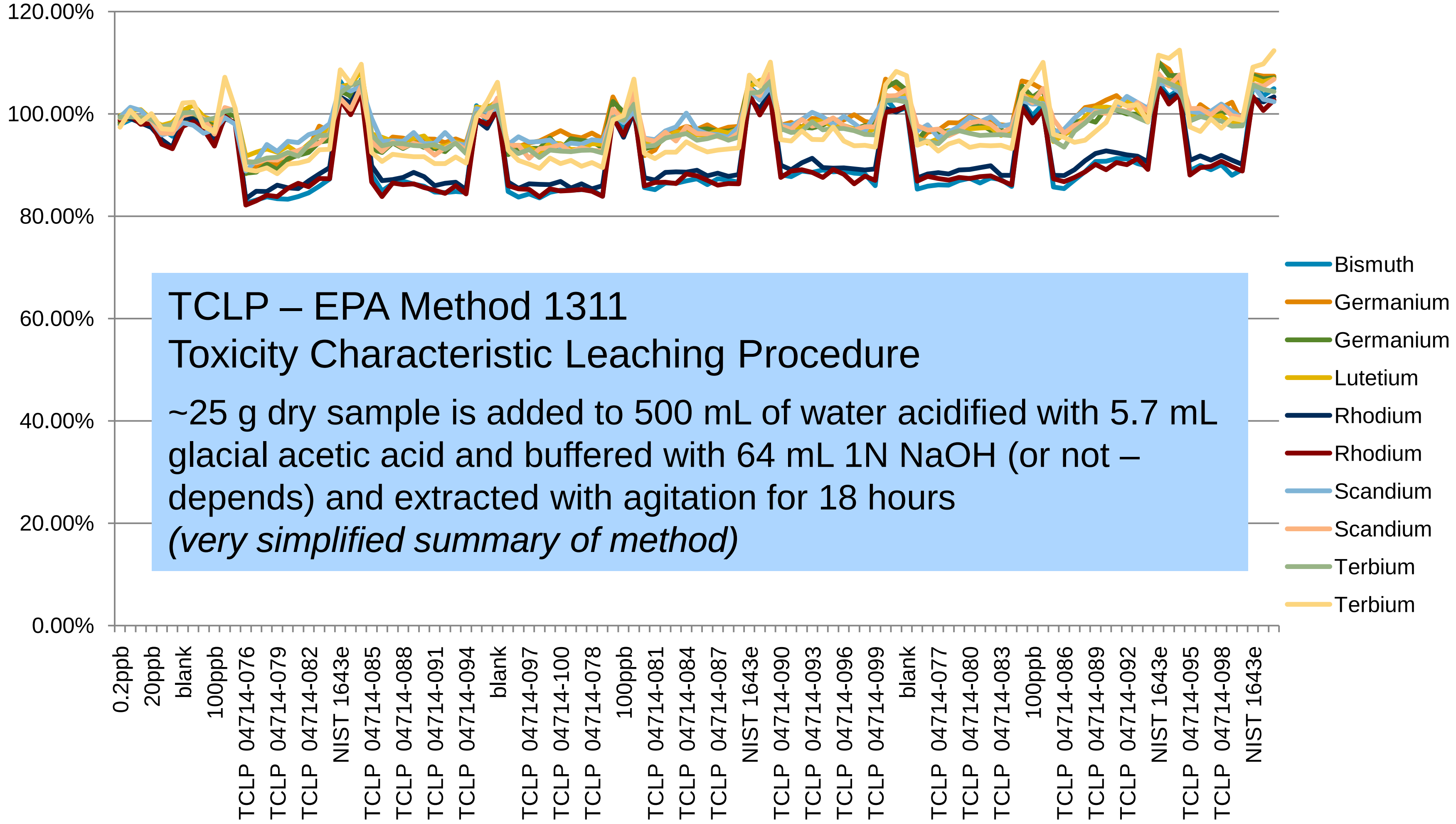
Internal Standard Recoveries

Undiluted Soil Digests



Internal Standard Recoveries

Undiluted, Undigested TCLP Extracts

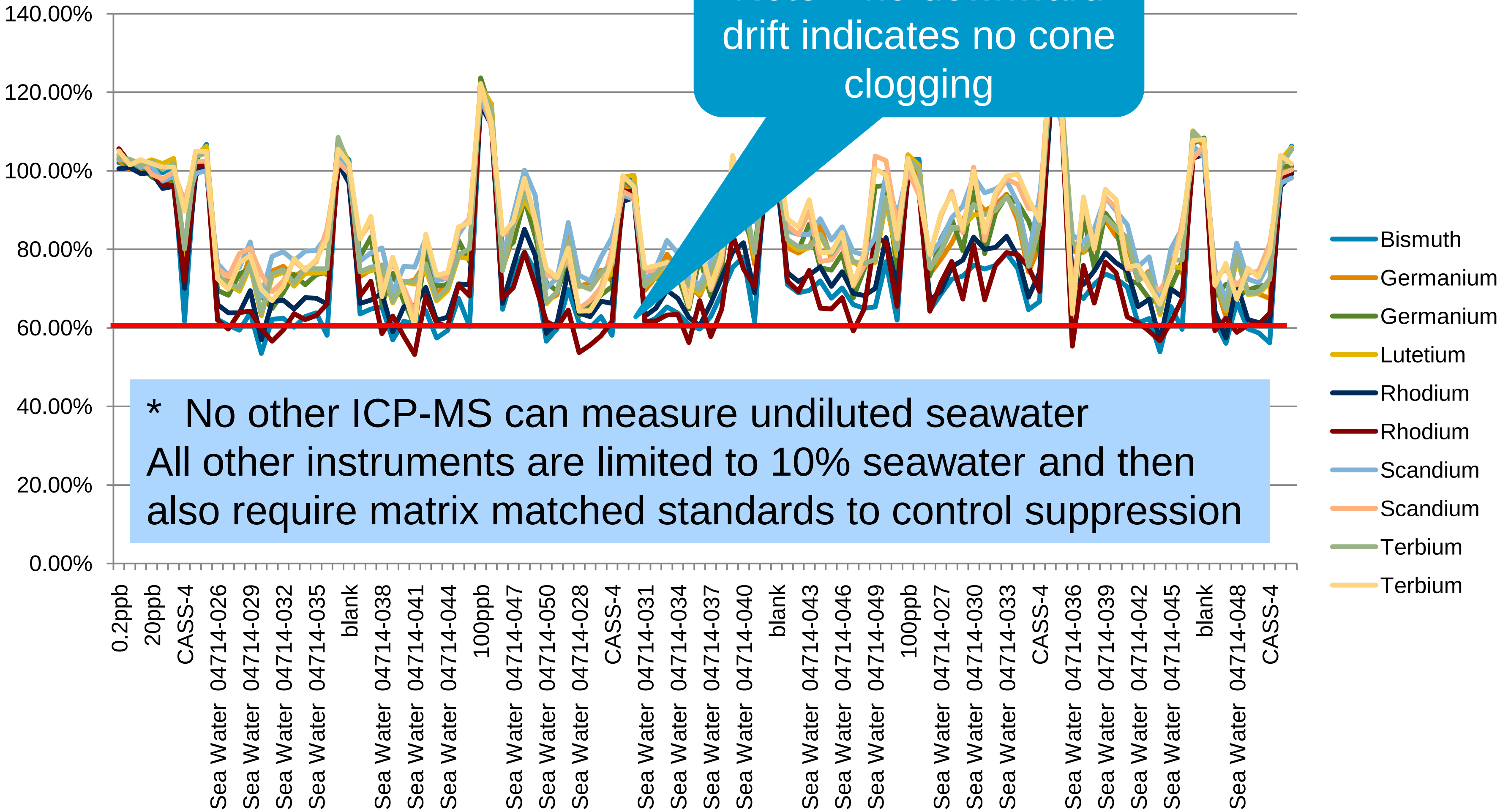


TCLP – EPA Method 1311
Toxicity Characteristic Leaching Procedure

~25 g dry sample is added to 500 mL of water acidified with 5.7 mL glacial acetic acid and buffered with 64 mL 1N NaOH (or not – depends) and extracted with agitation for 18 hours
(very simplified summary of method)

Internal Standard Recoveries

Undiluted* Seawater Samples



* No other ICP-MS can measure undiluted seawater
All other instruments are limited to 10% seawater and then also require matrix matched standards to control suppression

Sample Cone After 75 Undiluted Seawater Samples

This is the reason there was no downward drift. No blockage of sampling orifice.

CCV Recoveries

Water Samples and Soil Digests

	Water Samples		Soil Digests*	
Element	Mean (n=9)	%RSD	Mean (n=9)	%RSD
Aluminum	101.16%	3.15%	99.74%	2.59%
Antimony	101.71%	2.57%	100.54%	1.60%
Arsenic	99.79%	2.15%	102.21%	1.79%
Barium	100.71%	2.68%	100.79%	2.29%
Beryllium	102.21%	2.73%	106.35%	5.04%
Boron	99.24%	2.00%	101.06%	3.14%
Cadmium	101.12%	2.15%	100.79%	2.19%
Calcium	101.68%	3.26%	100.45%	2.11%
Chromium	101.26%	1.93%	103.25%	2.76%
Cobalt	99.85%	1.70%	103.23%	2.82%
Copper	99.28%	2.62%	104.10%	2.41%
Iron	101.58%	2.10%	102.04%	2.62%
Lead	101.83%	2.23%	102.34%	3.15%
Lithium	102.38%	2.55%	104.37%	4.33%
Magnesium	102.92%	2.67%	103.90%	2.89%
Manganese	100.45%	2.48%	100.62%	1.48%

	Water Samples		Soil Digests*	
Element	Mean (n=9)	%RSD	Mean (n=9)	%RSD
Molybdenum	100.01%	2.49%	100.22%	2.29%
Nickel	100.34%	1.94%	102.42%	2.98%
Phosphorus	100.55%	2.49%	97.34%	2.53%
Potassium	102.01%	1.44%	102.57%	1.63%
Selenium	101.24%	1.52%	103.06%	1.99%
Silicon	101.59%	1.16%	94.07%	4.21%
Silver	100.94%		101.91%	2.68%
Sodium	101.44%	2.21%	103.59%	2.96%
Strontium	100.82%	3.16%	98.37%	2.18%
Thallium	101.31%	1.82%	101.83%	2.78%
Thorium	100.89%	2.37%	100.15%	3.40%
Tin	100.54%	2.73%	101.13%	2.28%
Titanium	100.31%	2.13%	100.34%	1.87%
Uranium	102.38%	2.75%	102.23%	3.36%
Vanadium	99.90%	2.35%	102.09%	2.31%
Zinc	99.99%	2.26%	102.20%	1.71%
Zirconium	100.35%	2.19%	99.79%	2.11%

* Undiluted

CCV Recoveries

TCLP Extracts and Seawater Samples

	TCLP Extracts*		Seawater*	
Element	Mean (n=9)	%RSD	Mean (n=9)	%RSD
Aluminum	101.90%	2.02%	94.70%	1.97%
Antimony	98.84%	1.63%	98.67%	1.76%
Arsenic	99.43%	2.28%	97.05%	1.55%
Barium	99.46%	1.77%	97.81%	1.94%
Beryllium	100.13%	0.92%	96.22%	3.12%
Boron	103.93%	1.66%	119.84%	4.35%
Cadmium	98.75%	1.42%	99.29%	1.79%
Calcium	99.95%	1.42%	100.08%	1.56%
Chromium	99.32%	1.49%	100.15%	1.51%
Cobalt	99.75%	1.50%	100.71%	1.71%
Copper	98.85%	1.96%	95.78%	1.66%
Iron	100.01%	0.96%	99.52%	1.80%
Lead	99.54%	1.44%	98.85%	1.66%
Lithium	99.76%	1.51%	95.22%	2.39%
Magnesium	102.51%	1.52%	100.10%	1.76%
Manganese	98.80%	1.33%	100.40%	1.62%

	TCLP Extracts*		Seawater*	
Element	Mean (n=9)	%RSD	Mean (n=9)	%RSD
Molybdenum	98.44%	1.39%	95.29%	1.48%
Nickel	100.31%	1.26%	99.59%	2.24%
Phosphorus	99.37%	1.78%	99.02%	1.44%
Potassium	101.52%	1.49%	100.63%	3.08%
Selenium	100.37%	1.23%	100.09%	1.99%
Silicon	103.20%	1.25%	101.82%	2.30%
Silver	98.64%	1.59%	96.63%	1.73%
Sodium	N/A	N/A	N/A	N/A
Strontium	98.24%	1.70%	96.28%	1.20%
Thallium	99.25%	0.91%	98.31%	1.51%
Thorium	99.66%	1.26%	92.19%	1.80%
Tin	99.68%	1.77%	98.78%	1.77%
Titanium	99.13%	1.44%	99.74%	1.68%
Uranium	98.80%	1.06%	96.73%	1.73%
Vanadium	99.10%	1.82%	100.43%	1.37%
Zinc	99.52%	2.61%	95.54%	1.57%
Zirconium	97.98%	1.64%	94.25%	1.26%

* Undiluted

Flue Gas Desulfurization (FGD) Wastewaters

New EPA SOP available

This application is getting a LOT of attention as the electric power industry is being forced to comply with clean air act policies to reduce sulfur emissions from coal fired electric generation plants*.

In removing sulfur and other contaminants from the stack emissions, these plants generate wastewater that is highly contaminated not only with sulfur, but high concentrations of mineral elements and trace levels of many other metals.

EPA has developed a Standard Operating Procedure using an Agilent 7700x ICP-MS with He Collision Cell for the determination of toxic trace elements in FGD wastewaters.

**EPA 821-R-09-008 - Steam Electric Power Generating Point Source Category: Final Detailed Study Report,* October of 2009. http://www.epa.gov/waterscience/guide/steam/finalreport.pdf

FGD Method Elements, Isotopes and Cell Mode

Only No gas, He *(or H_2 alternatively)* modes are permitted

No other reactive gases or gas mixtures are allowed – highly reactive cell gases (NH_3, O_2…) give unreliable results

Mass	Element of Interest	Analysis mode
27	Aluminum	No gas or He
75	Arsenic	He
111	Cadmium	He
52	Chromium	He
63	Copper	He
208 (+207, 206)	Lead	No gas or He
24	Magnesium	No gas or He
55	Manganese	He
60	Nickel	He
39	Potassium	No gas or He
78	Selenium	He (H_2)
107	Silver	He
23	Sodium	No gas or He
205	Thallium	No gas or He
51	Vanadium	He
66	Zinc	He

It is possible to use a single cell mode – He mode for ALL analytes in this method.

No analyte-specific or matrix-specific optimization is required.

ALL analytes are measured at their preferred isotopes, regardless of the matrix

Synthetic FGD Interference Check Solution is a New Requirement

– **Mixed Interference Check Solution (Synthetic FGD Wastewater)**

- Chloride - 5,000 mg/L
- Calcium - 2,000 mg/L
- Magnesium - 1,000 mg/L
- Sulfate - 2,000 mg/L
- Sodium - 1,000 mg/L
- Butanol - 2,000 ppm

The combination of the highly robust plasma of the Agilent 7700x with HMI and ISIS discrete sampling allows routine analysis of this interference check solution and samples containing similar levels of dissolved solids UNDILUTED!

FGD-ICS-A Analyzed once per day

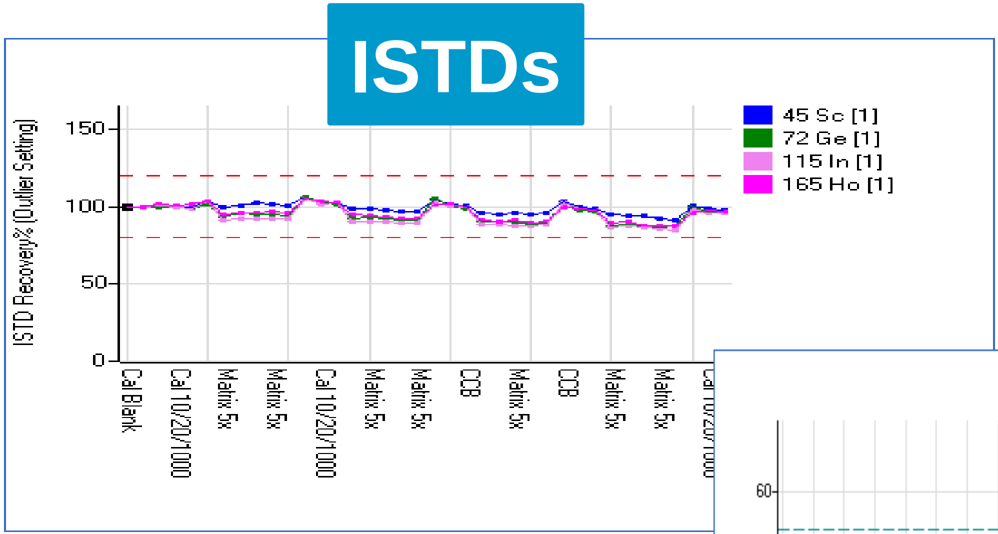
- ISTDs must meet 60-125% requirements and analytes must be less than reporting limits

FGD-ICS-AB is “A” solution spiked with analyte elements at 40 ppb *(exceptions are Zn – 0.4 ppm and Al - 4.0 ppm)*

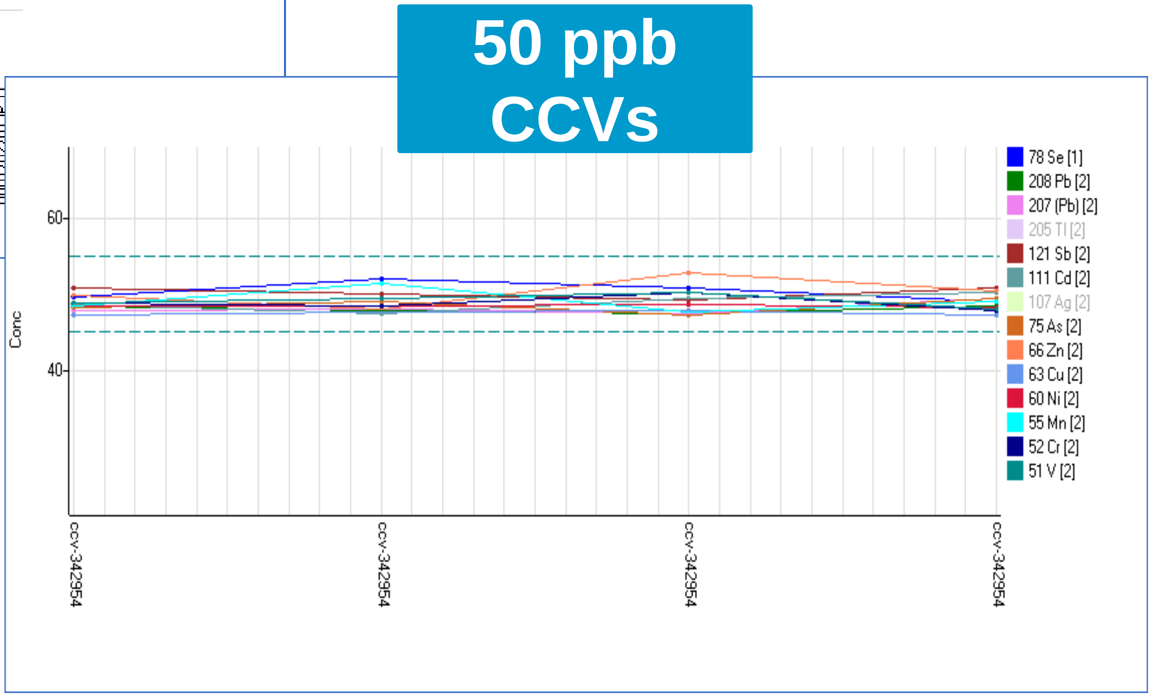
- Must recover within 70–130 %

Internal Standard Recovery and CCV Stability

Repeated Analysis of FGD Interference Check Samples



Excellent ISTD and CCV recoveries



No ICP-MS Has Ever Been Able To Run Undiluted Samples Like This Before

"I think the interesting thing for users is that, yes, you can analyze this kind of matrix by ICP-MS!"

Richard Burrows, PhD

Director of Technology

TestAmerica, Inc.

Conclusions

ISIS-DS can significantly improve sample throughput with no compromise in analytical performance

- More samples per shift - up to 380 analyses in 8 hours

Reduced interface exposure to sample matrix reduces signal drift and improves short and long term precision.

- Fewer recalibrations, fewer sample re-runs
- Less frequent need for cone cleaning and interface maintenance

When coupled with Agilent's HMI (High Matrix Introduction), ISIS-DS can provide very rapid analysis of samples containing percent level TDS, without special optimizations

- Analyze samples prepared for ICP-OES with ICP-MS
- Better DLs and fewer potential interferences compared to ICP-OES, however, more expensive than ICP-OES

New Atomic Spectroscopy Solutions for Environmental Laboratories

- Determination of Hg in Environmental Samples using Cold Vapor AA
- Analysis of Environmental Samples by Simultaneous Axial ICP-OES following USEPA Guidelines
- The Agilent 7700x ICP-MS and Environmental Monitoring
- Preview - Flue Gas Desulfurization (FGD) Wastewaters by ICP-MS

Summary

AA, ICP-OES and ICP-MS are each utilized for routine inorganic analysis. Most important factors in choosing the correct technique are detection limits, required analyte coverage, sample matrix / throughput and budget.

CLEARLY BETTER TOGETHER

AA, ICP-OES, ICP-MS – all together now at Agilent

THANK YOU

QUESTIONS?