Extending ICP-MS into the Realm of ICP-OES

The Agilent High Matrix Introduction Accessory for the 7500 Series ICP-MS

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What is "The Realm of ICP-OES" and Why?

What…

- Fast, Multi-element analysis
- TDS as high as 10% or higher
- Detection limits > 1 ppb
- Many interferences can require complex correction equations

Why is OES more matrix tolerant?

- Atomic emission is not subject to ionization suppression
- ICP-OES has no cones to clog or ion lenses to contaminate

Why Use ICP-MS?

Simply

- Much better detection limits (ppt or sub ppt)
- Fewer simpler interferences – mostly eliminated using CRC technology
- One technique is simpler than 2 (or 3)
  - Single sample prep
  - Reduced QA/QC
  - Simplified reporting

But…

- High TDS samples (> 0.1-0.2%) require dilution

Limitations of ICP-MS to high salts

- ✓ High salt samples can result in salt buildup on the cones and interface components resulting is loss of sensitivity and drift.
- ✓ High salts cause suppression of sample response in the plasma
  - Ionization suppression especially from easily ionizable elements (EIEs)

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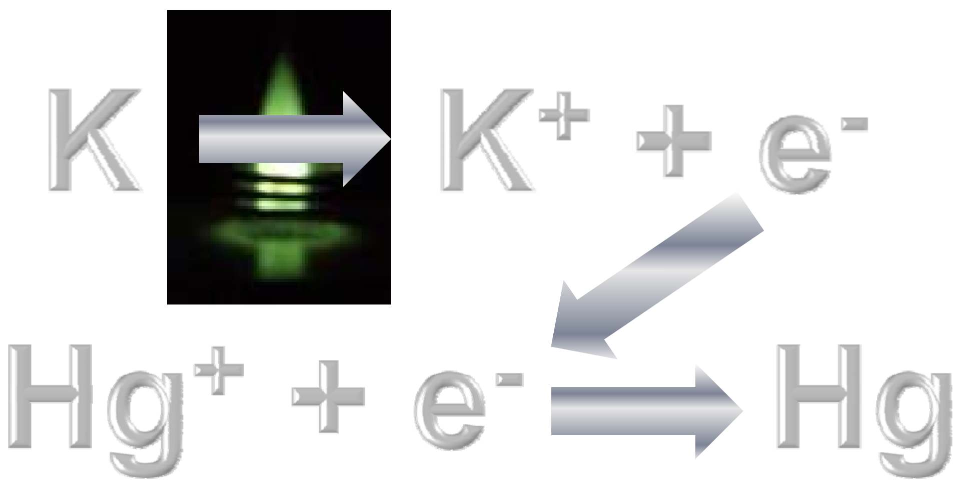
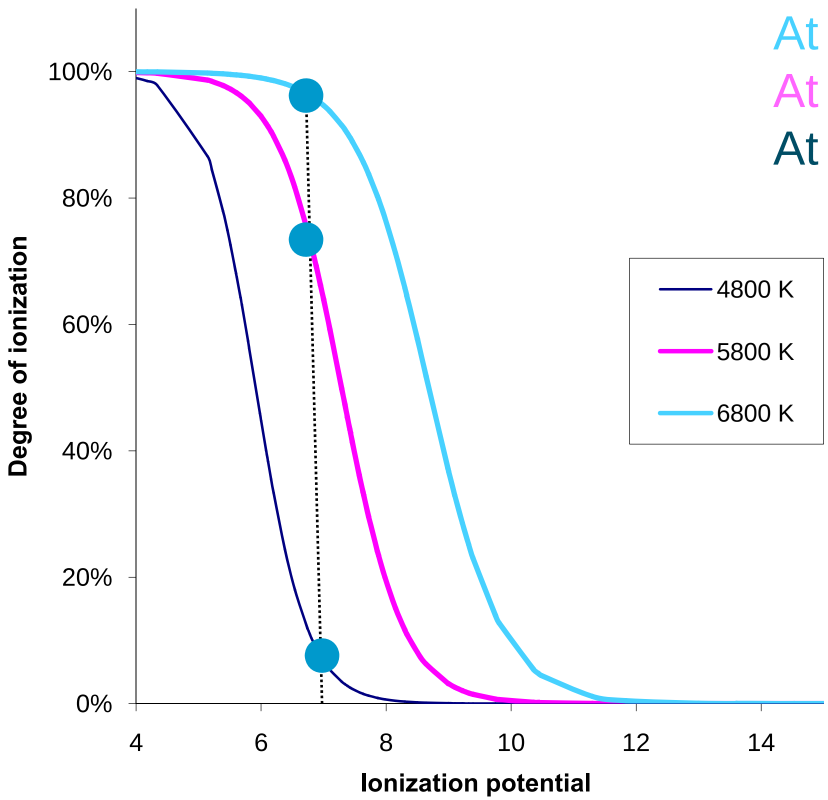


1st IP = 4.341 eV, > 99% ionization results in lots of free electrons

1st IP = 10.437 eV, ionization is suppressed

Limitations of ICP-MS to high salts

✓ Ionization is also suppressed by reduction in plasma temperature



Example: for an element with 1st IP = 7 eV
At 6800 K it is ~98% ionized
At 5800 K it is ~72% ionized
At 4800 K it is only ~8% ionized

Plasma temp is increased by
- Increasing RF Power
- Decreasing carrier gas flow
- Decreasing sample flow

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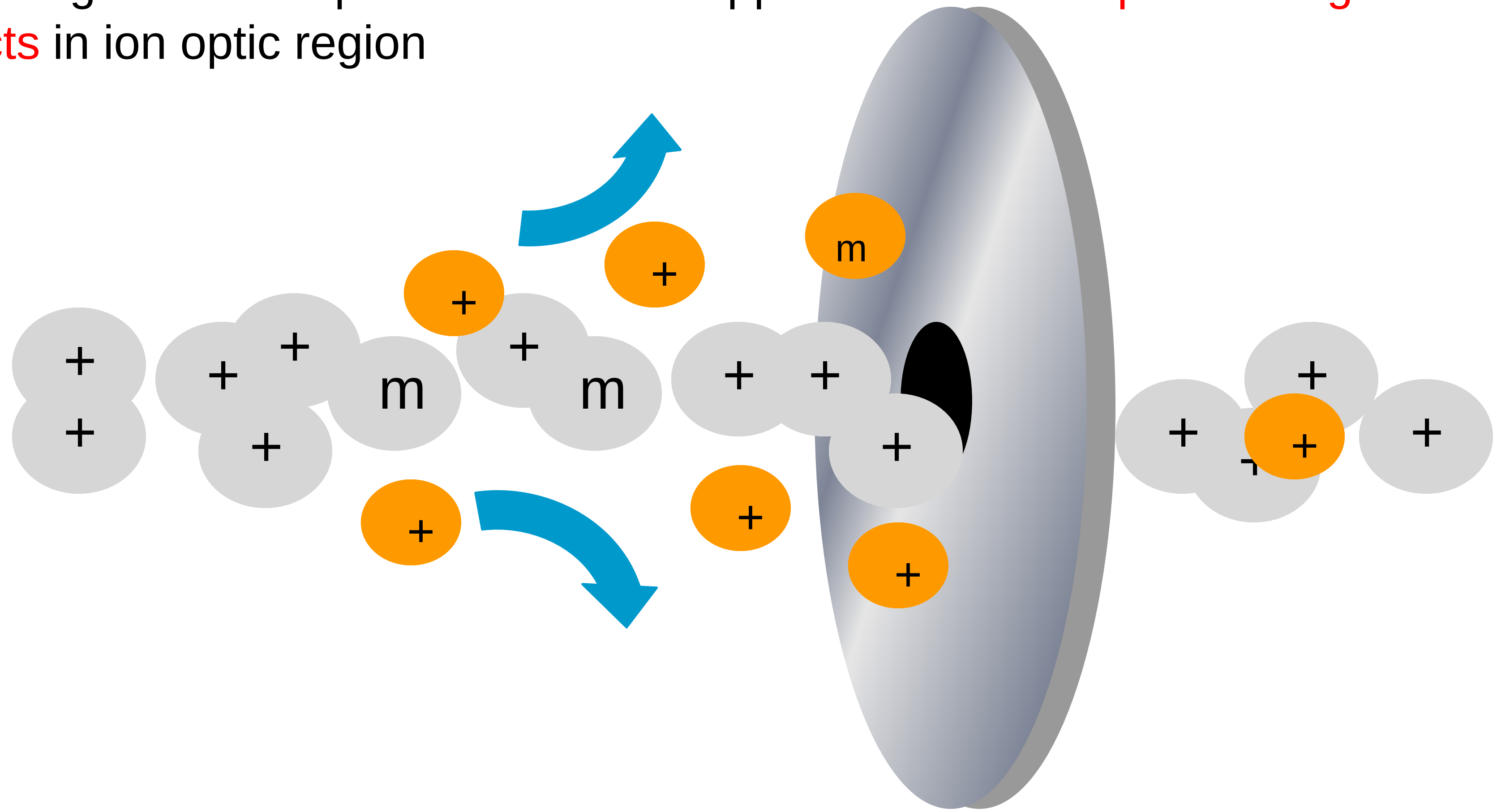
Limitations of ICP-MS to high salts

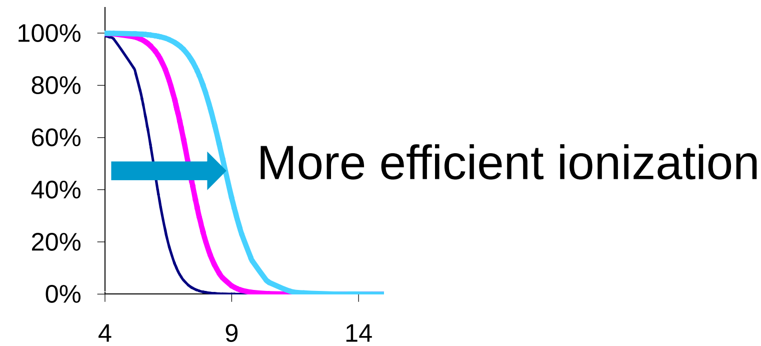
✓ High TDS samples also cause suppression due to space charge effects in ion optic region



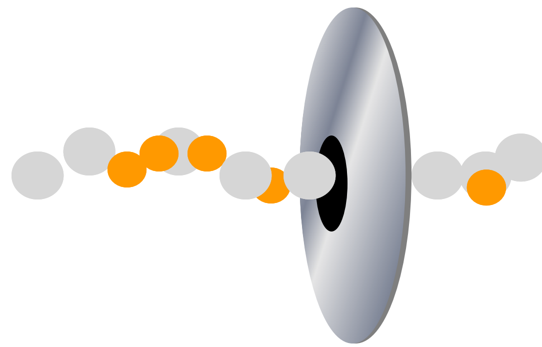
Low mass ions are suppressed by high mass ions

Summary – Overcoming the limitations to ICP-MS Plasma Robustness

Matrix effects can be reduced by:



1. Increasing plasma temperature
   - Higher power
   - Lower carrier gas flow
   - Lower sample flow
2. Reducing matrix load
   - Lower sample flow
   - Sample dilution
     - But conventional dilution does not reduce the solvent (dilute acid or other) which is also a major component of the matrix
     - Other disadvantages to dilution (contamination, time, errors, waste)



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An Alternative to Conventional Dilution

→ Aerosol Dilution

1. Decrease sample flow and carrier gas flow to nebulizer

- Reduces total sample and reduces nebulizer/spraychamber efficiency

2. Make up the flow with a dilution gas added between the spraychamber and torch

- Maintain correct carrier gas flow to torch
- Reduce total amount of water or other solvent going to plasma

Results in hotter, more robust plasma with much lower oxides

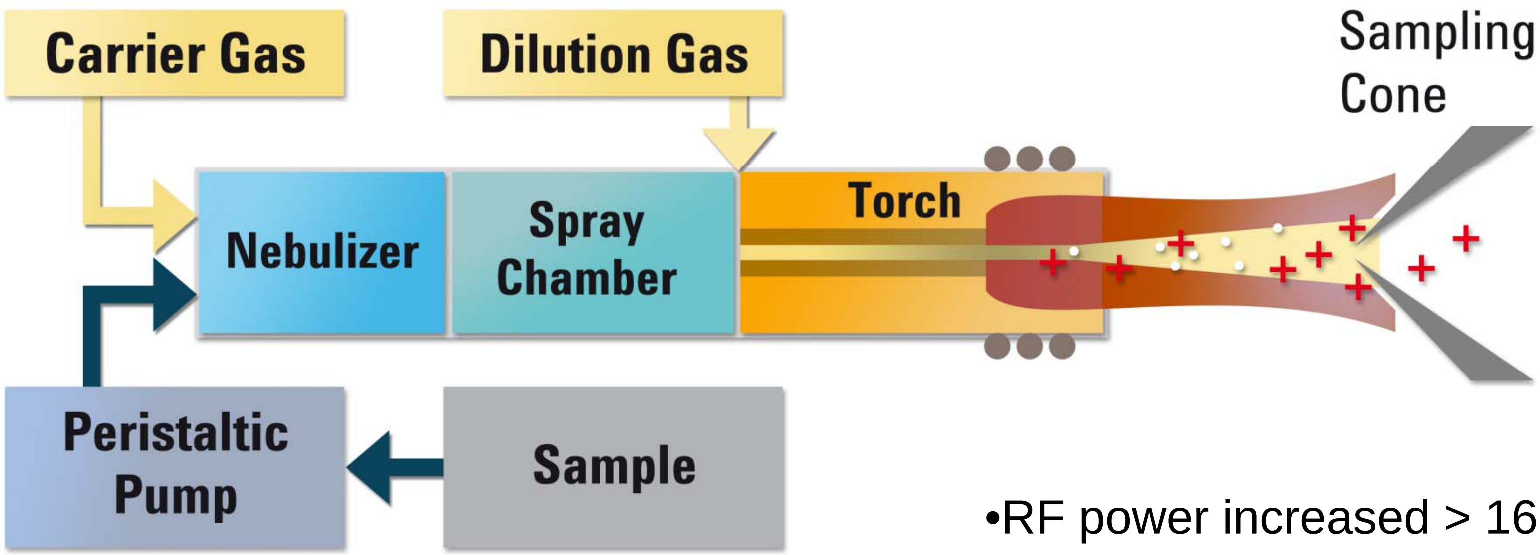
Cannot introduce contamination

Error free (optimized using sophisticated software algorithms)

Virtually instantaneous

The Agilent High Matrix Interface (HMI)

Maximizes Plasma Robustness
Minimizes Matrix Load via "Aerosol Dilution"



- RF power increased > 1600W
- Sample depth increased
- Carrier gas decreased
- Sample flow decreased
- Dilution gas added

Simple Hardware – Sophisticated Software

Variable, reproducible aerosol dilution requires accurate, precise control of several important instrument parameters

- Nebulization efficiency
- Spraychamber efficiency
- Carrier gas/dilution gas flow
- Sample depth
- Plasma temperature
- Applicable over a range of individual instruments in varying conditions

HMI Automation

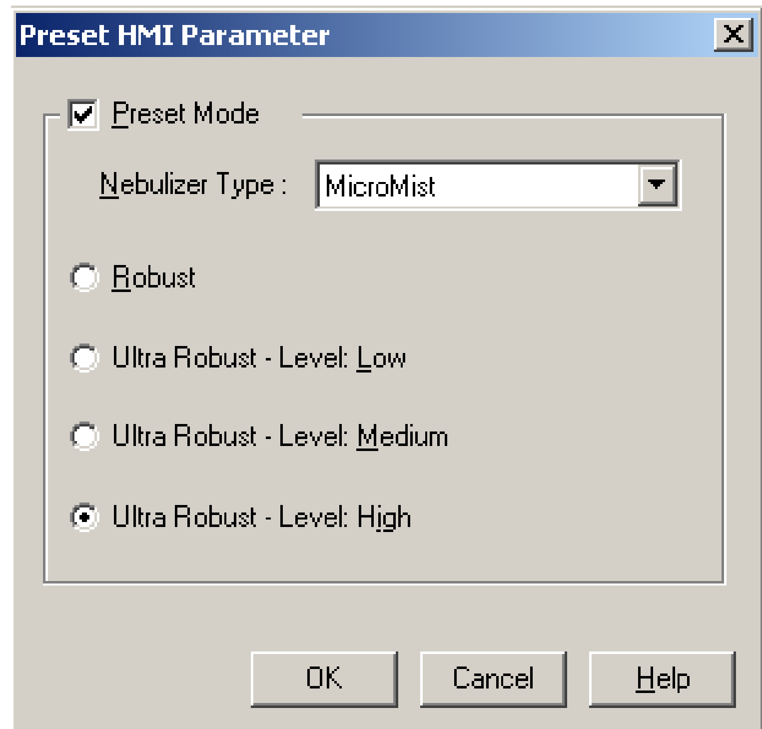
HMI Setup is simple

On installation, the software performs an evaluation of individual instrument characteristics and corrects for any deviations from expected performance.

Then the user simply –

•Select the nebulizer you are using
•Select the level of plasma robustness needed
•Select the level of aerosol dilution needed

•The ChemStation handles all control functions – operation is completely transparent to the user.



Measuring "Plasma Robustness" when using HMI

Typically measured by examining the ability of the plasma to break down or prevent the formation of Metal Oxides such as Cerium Oxide

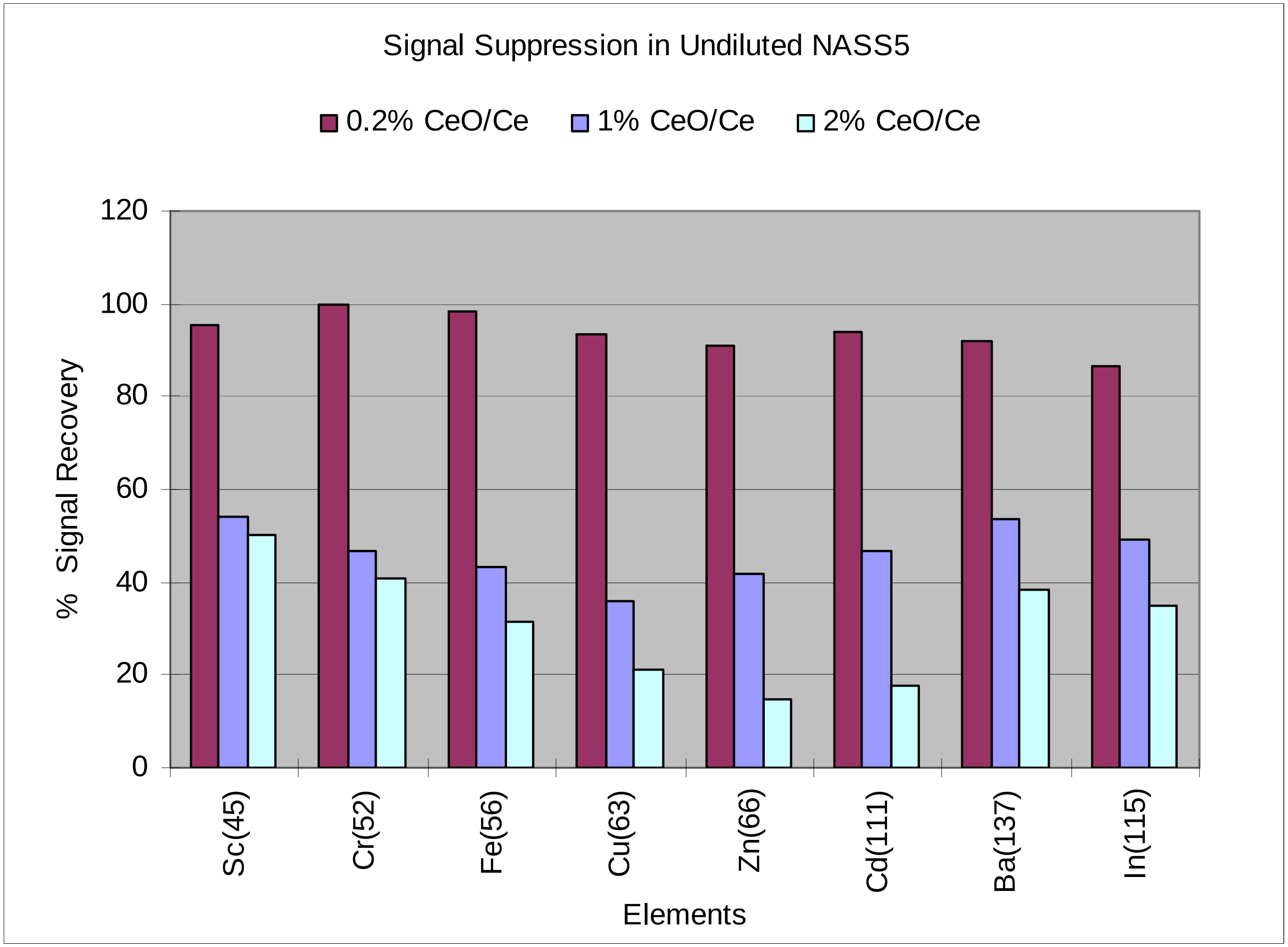
Measure CeO^+/Ce^+ ratio – lower is better

Typical values are 1-3% depending on instrument design and tune conditions

HMI can deliver 0.2% CeO or better

Samples containing 1% TDS or higher can be directly introduced into the ICP-MS without dilution

Signal Suppression as a Function of Cerium Oxide Ratio in Undiluted Seawater



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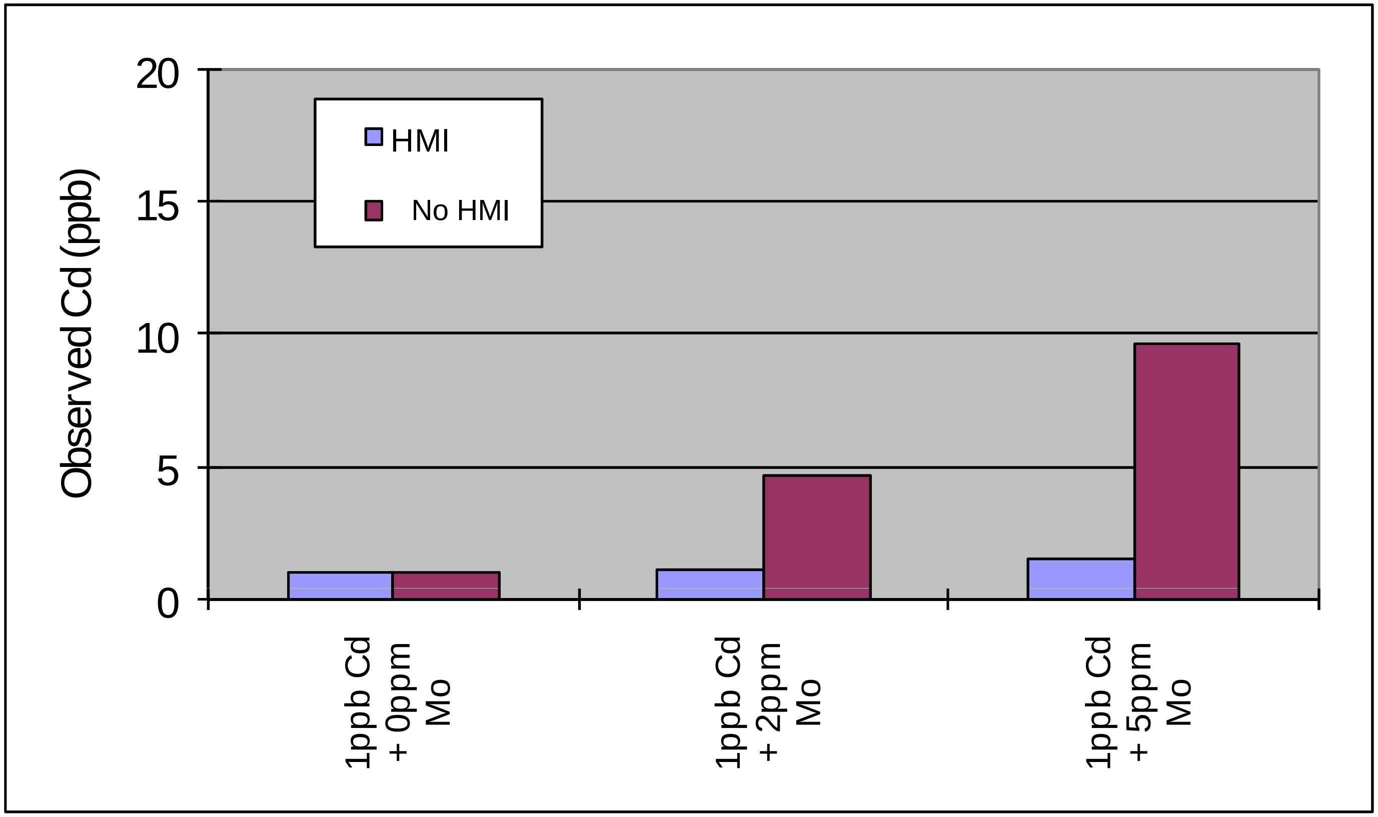
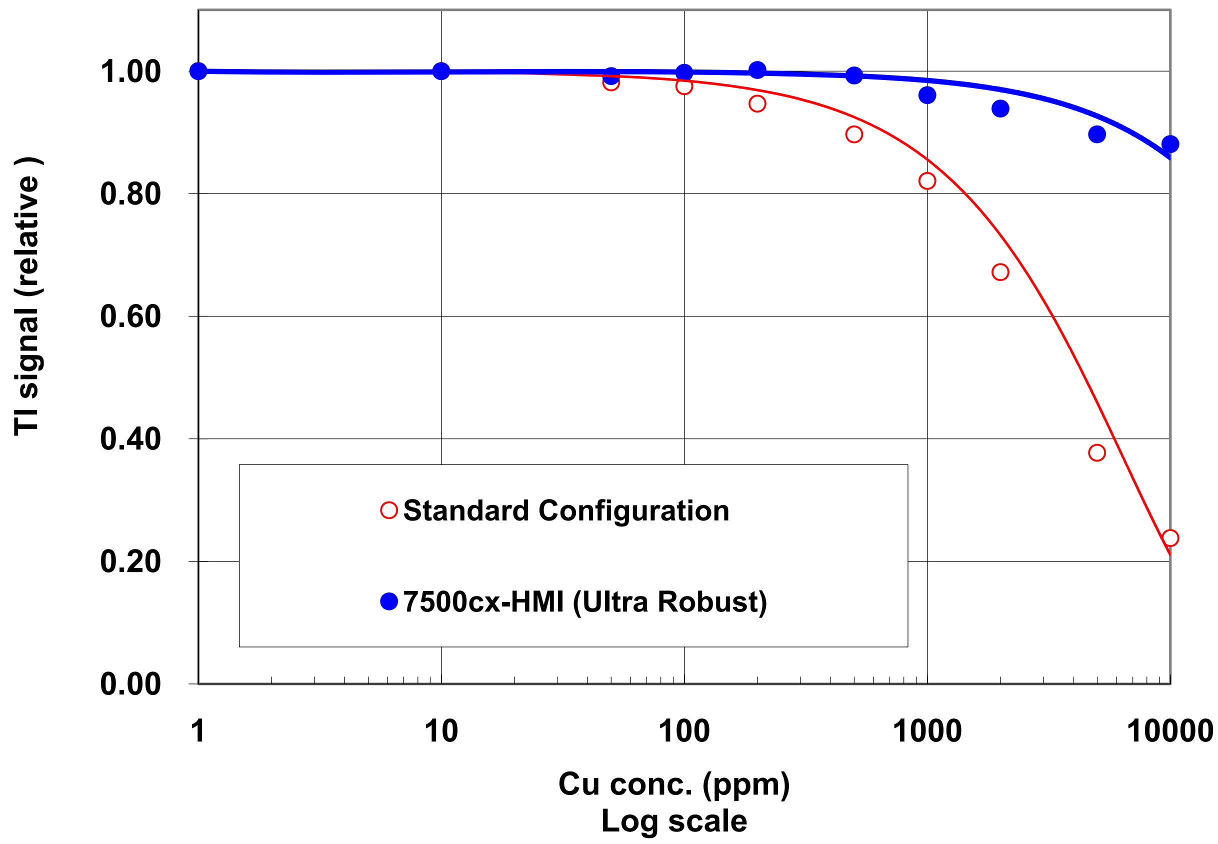
Robust Plasma → Low Oxides → Lower Interferences



Effects of interference from MoO on a 1 ppb Cd spike at increasing Mo concentrations (0 ppm, 2 ppm, 5 ppm) shown for both typical configuration (1% oxides) and HMI equipped 7500cx (0.2% oxides)

Signal Suppression as a function of matrix concentration in standards

Thallium response as a function of increasing copper concentration – with and without HMI



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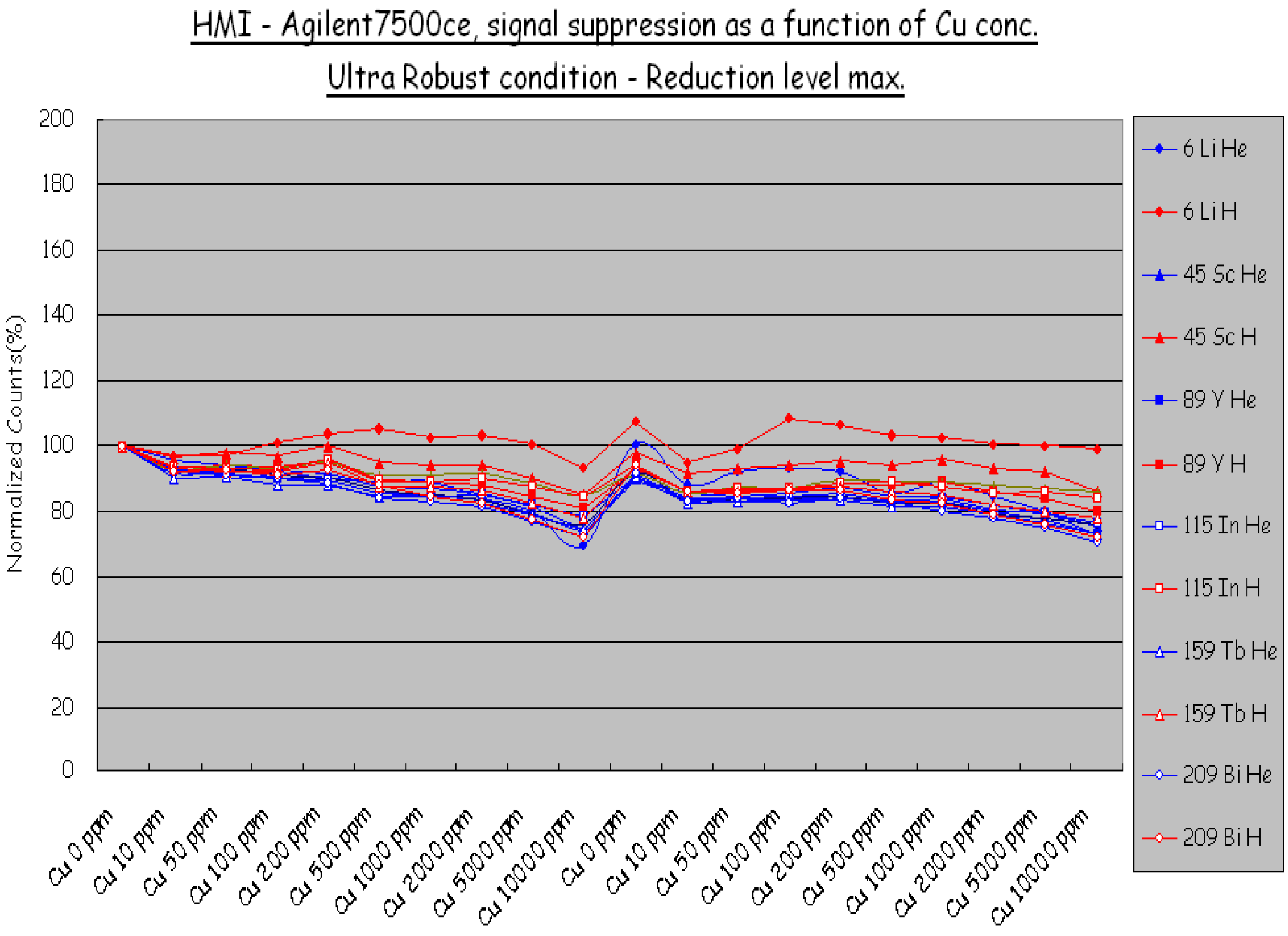
Reduced Suppression in High Concentration Metal Solutions

Suppression is nearly independent of matrix concentration

No need for matrix matching

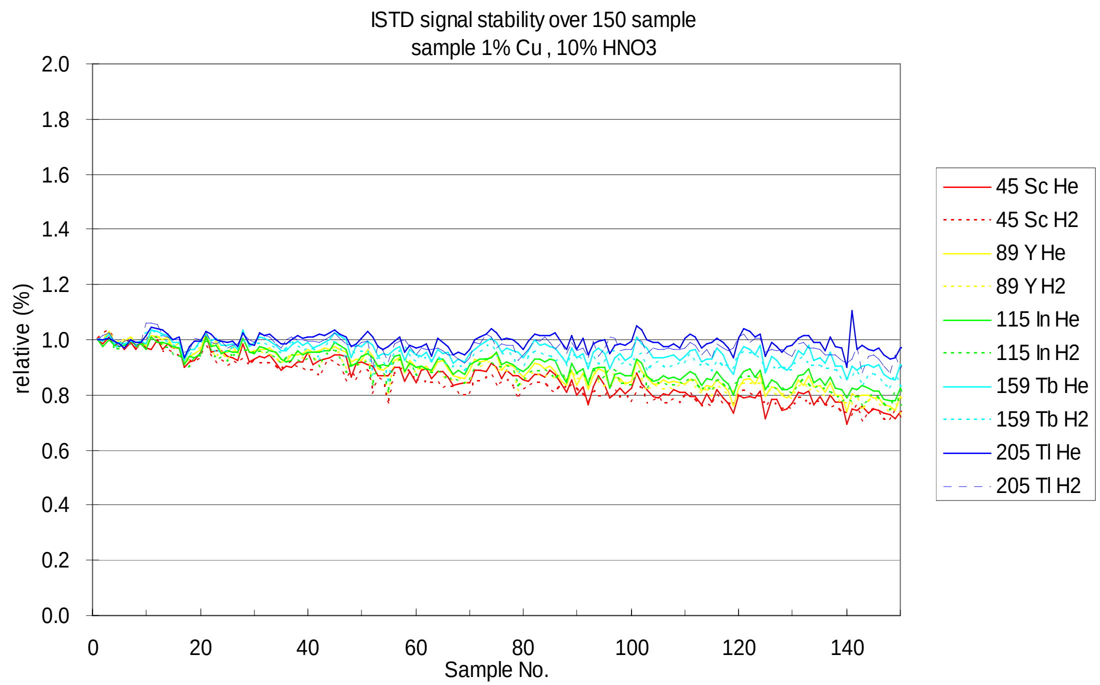
Better, simpler internal standard correction



Reduced Suppression *AND* Improved long term stability in 1% Copper

Internal standard stability in 1% Cu/10% HNO_3 solution over 150 sample sequence

Small amount of drift easily corrected with internal standards



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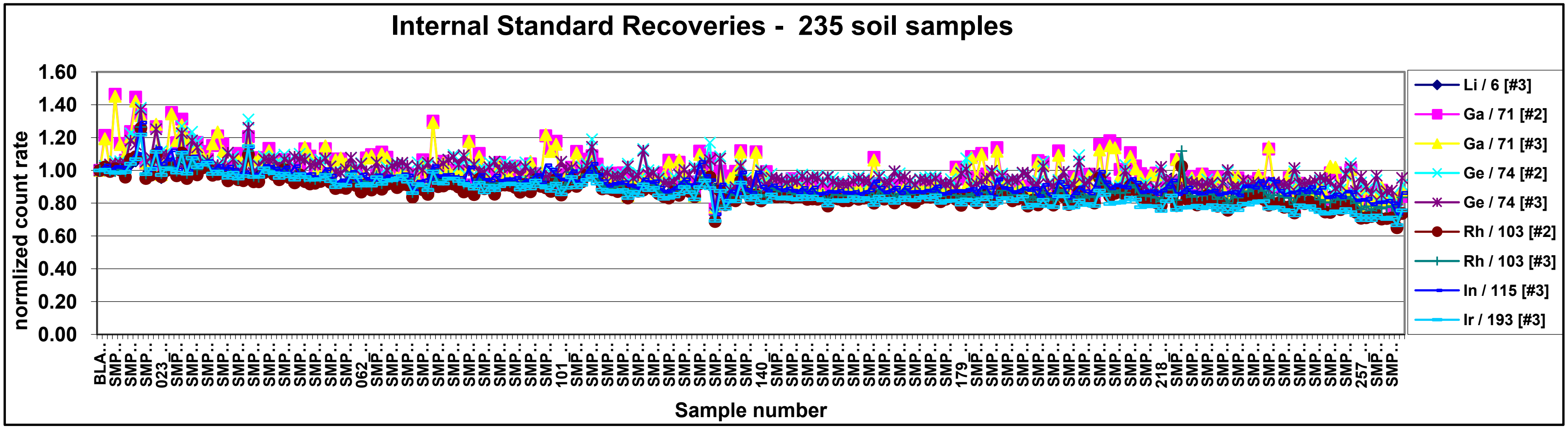
Instrument Detection Limits in Maximum Robustness Mode with HMI

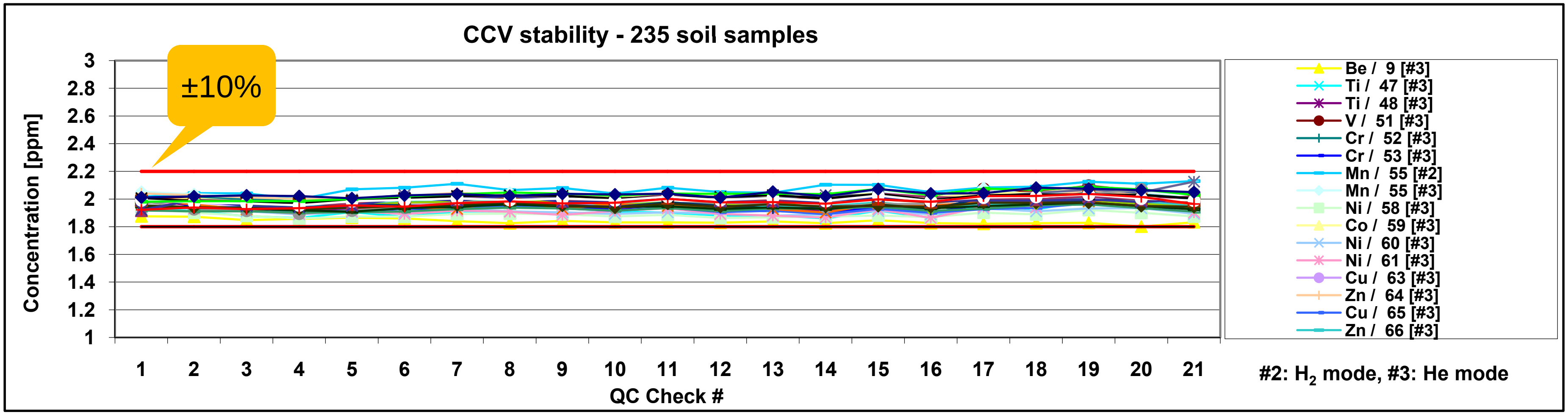
Based on 10 replicates of 1% nitric acid blank
•Ultra robust conditions
•Maximum aerosol dilution

IDLs are significantly better in high TDS samples using HMI than using conventional dilution

Element	*m/z*	int. time (sec)	ORS Mode	ISTD	IDL (ppb) (3-sigma)
V	51	0.3	He	Sc	0.064
Cr	52	1	He	Y	0.030
Mn	55	0.3	He	Y	0.069
Fe	56	0.3	H_2	Y	0.021
Ni	60	3	He	Ge	0.012
Co	59	1	He	Ge	0.003
Cu	63	6	He	In	0.025
Zn	66	3	He	In	0.084
As	75	3	He	Y	0.030
Se	78	9	H_2	Ge	0.035
Mo	98	0.3	He	Tb	0.015
Ag	107	1	He	In	0.007
Cd	111	3	He	In	0.015
Pb	208	1	He	Bi	0.005
U	238	1	He	In	0.001

Internal Standard and Calibration Stability in 23 Hour Sequence of Undiluted Soil Digests





#2: H_2 mode, #3: He mode

Results of replicate (n=10) analyses of two certified reference soil samples (FeNeLab and BCR144R*)

Element	ORS Mode	FeNeLab River Clay			BCR144R Sewage Sludge		
		Measured(1) (ave n=10)	Certified	Rec. % (ave)	Measured(1) (ave n=10)	Certified	Rec. % (ave)
Be 9	He	1.6			0.2		
V 51	He	59.6			13.9		
Cr 52	He	191.9	187	103	88.8	90	99
Co 59	He	19.8	18.7	106	13.6	13.3	102
Ni 60	He	55.7	52.9	105	40.7	44.9	91
Cu 63	He	153.9	156	99	270.0	300	90
Zn 66	He	1031.6	970	106	825.1	919	90
As 75	He	44. 7	44	102	3.2		
Se 78	H_2	2.0			1.7		
Se 78	He	2.4			1.5		
Mo 95	He	1.3			6.9		
Ag 107	He	2.9			8.2		
Cd 114	He	8.5	8.07	105	1.7	1.84	90
Sn 118	He	0.02			36.0	40.8	88
Sb 121	He	1.6			2.8	3.05	92
Te 125	He	0.3			0.1		
Ba 135	He	828.3	817	101	319.2	367	87
Hg 201	He	4.1	3.83	107	3.2	3.11	102
Tl 203	He	1.1			0.1	0.14	
Pb 208	He	297.0	274	108	94.9	96	99

*BCR-144R Domestic Sewage Sludge, IRMM, Belgium and FeNeLab River Clay, FeNeLab, Netherlands

(1) Units in mg kg^{-1}

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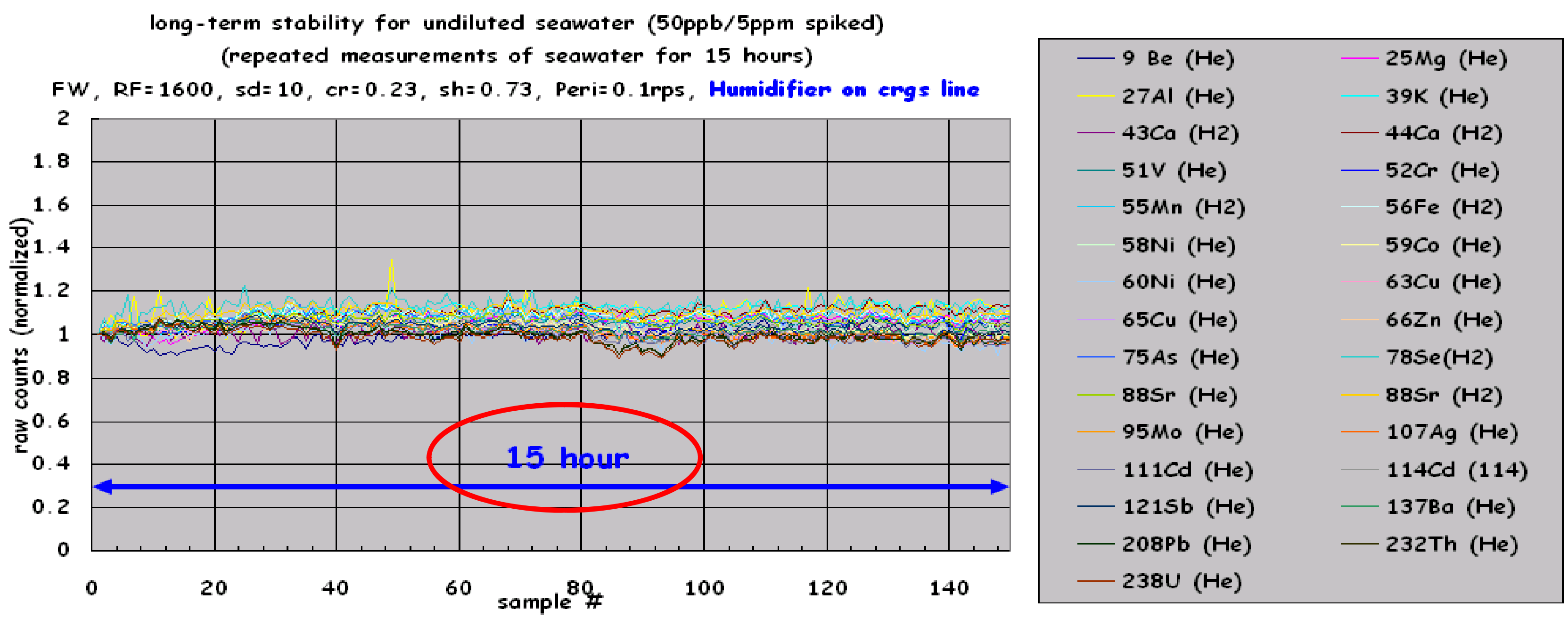
150 Sample Sequence of Undiluted Spiked NASS 5 Seawater – Long-term Stability



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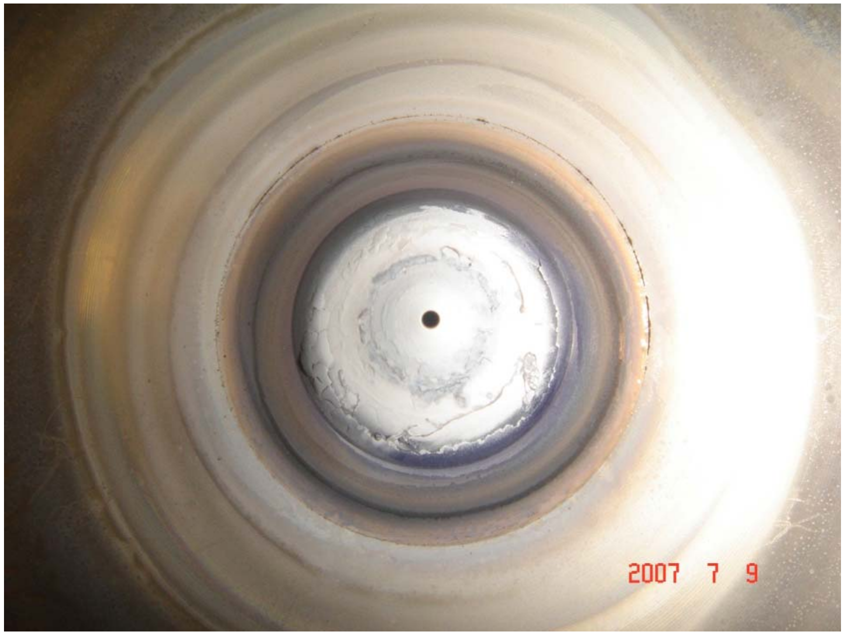
After neat seawater analysis with HMI – No blockage of either Sampler or Skimmer



Sampler

Skimmer

Results - Direct Analysis of Undiluted Seawater SRM
- requires high sensitivity and high matrix tolerance

NASS 5				
Element	*m/z*	Certified (ppb)	Measured (ppb)	Recovery (%)
V	51	1.2	1.194	99.5
Cr	52	0.11	0.119	108.2
Mn	55	0.919	0.920	100.1
Fe	56	0.207	0.231	111.6
Ni	60	0.253	0.275	108.7
Co	59	0.011	0.018	163.6
Cu	63	0.297	0.290	97.6
Zn	66	0.102	0.132	129.4
As	75	1.27	1.415	111.4
Mo	98	9.6	9.586	99.9
Cd	111	0.023	0.027	117.4
Pb	208	0.008	0.006	75.0
U	238	2.6	2.615	100.6

Below DL

Even with maximum aerosol dilution, ambient levels in neat seawater can be accurately measured down to 0.1 ppb or better

Recovery of certified values for JSAC 0121 (high purity aluminum)

Element	m/z	ORS mode	Certified value	Result	
			mg/kg	mg/kg	recovery (%)
Mg	24	He	2.82 ± 0.13	2.841	101
Ti	47	He	1.96 ± 0.07	2.073	106
Cr	52	He	1.13 ± 0.06	1.098	97
Mn	55	He	1.73 ± 0.06	1.730	100
Fe	56	He	9.4 ± 0.3	10.016	107
Cu	63	He	3.48 ± 0.11	3.738	107
Zn	68	He	2.03 ± 0.13	2.117	104
Zr	90	He	2.02 ± 0.13	2.000	99

Samples were prepared by gently dissolving 1 gram of sample into 100 mL of 20% aquaregia and analyzed directly

Recovery of certified values for NIST 398 (unalloyed Cu)

Element	m/z	ORS mode	Certified value	Result	
			mg/kg	mg/kg	recovery (%)
Fe	56	He	11.4 ± 0.5	11.52	101
Ni	60	He	7.0 ± 0.1	7.04	101
Zn	68	He	24 ± 1	24.18	101
As	75	He	25.0 ± 3	27.62	110
Se	78	He	17.5 ± 0.8	17.33	99
Ag	107	He	20.1 ± 0.2	19.75	98
Sn	118	He	4.8 ± 0.6	5.46	114
Sb	121	He	7.5 ± 0.1	7.25	97
Te	125	He	10.1 ± 0.2	10.12	100
Pb	208	He	9.9 ± 0.6	10.15	103
Bi	209	He	2.0 ± 0.3	2.09	105

Samples were prepared by gently dissolving 1 gram of sample into 100 mL of 20% aquaregia and analyzed directly

Recovery of certified values for JSS003-5 (high purity Iron)

Element	m/z	ORS mode	Certified value	Result	
			mg/kg	mg/kg	recovery (%)
Al	27	He	78 ± 6	78.6	101
Cr	52	He	0.1	0.12	115
Mn	55	He	27± 1	26.6	99
Co	59	He	2.2 ± 0.2	2.25	102
Ni	60	He	0.4 ± 0.1	0.35	88
Cu	63	He	15.4 ± 0.5	15.3	99
Mo	95	He	0.7 ± 0.1	0.75	107
Sn	118	He	4.9 ± 0.2	4.92	100
W	182	He	0.4 ± 0.2	0.36	90

Samples were prepared by gently dissolving 1 gram of sample into 100 mL of 20% aquaregia and analyzed directly

Potential Applications

High TDS Samples requiring high sensitivity, few interferences

- Neat seawater
- Soil digests (undiluted)
- High TDS ground waters
- TCLP leachates
- Geological digestions and fusions (no HF)
- RoHS samples
- High purity metals
- HPLC-ICPMS applications requiring high salt buffers

Summary

HMI

1. Significantly improves matrix tolerance of the Agilent 7500 ICP-MS
2. Improves limits of detection in high matrix samples when compared to conventional dilution
3. Improves long term stability in high matrix samples
4. Minimizes or eliminates the need for matrix matching for most sample types
5. Improves the accuracy of internal standard correction
6. Reduces interferences due to metal oxides
7. Reduces system cleaning and maintenance

THANK YOU

Upcoming ICP-MS eSeminars

Environmental ICP-MS - EPA Methods Update

April 9, 2008 – 1:00pm EDT

ICP-MS – The Role of Elemental Mass Spectrometry in Life Sciences Research

May 8, 2008 – 1:00pm EDT