


Trace Elemental Analysis of Produced and Flowback Waters

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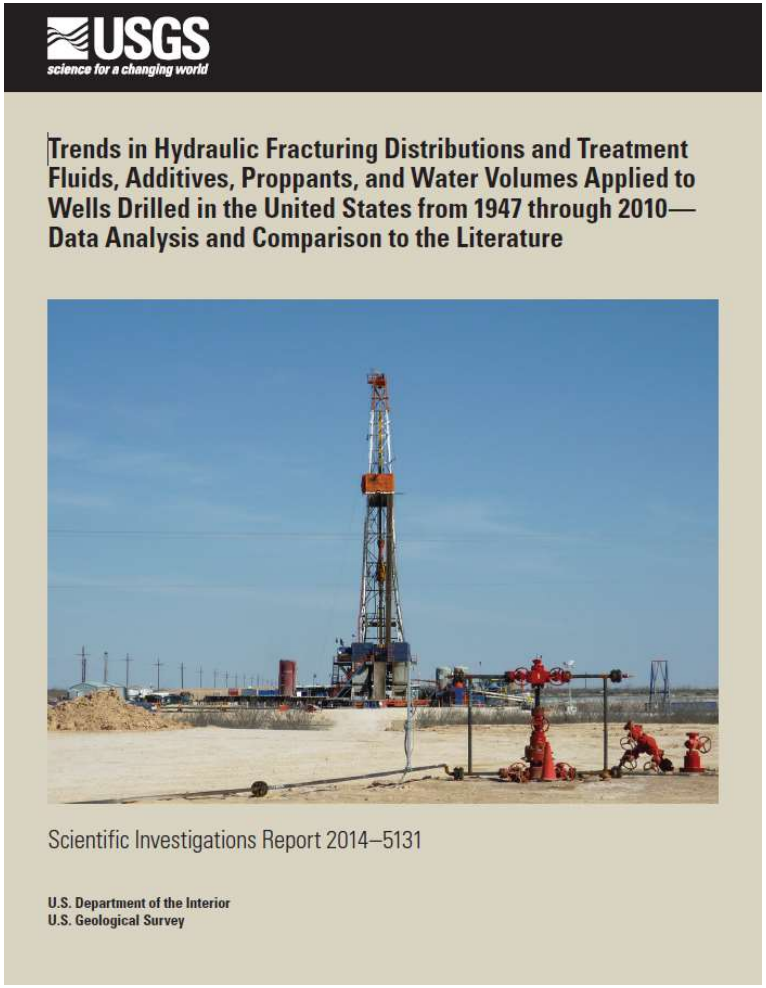
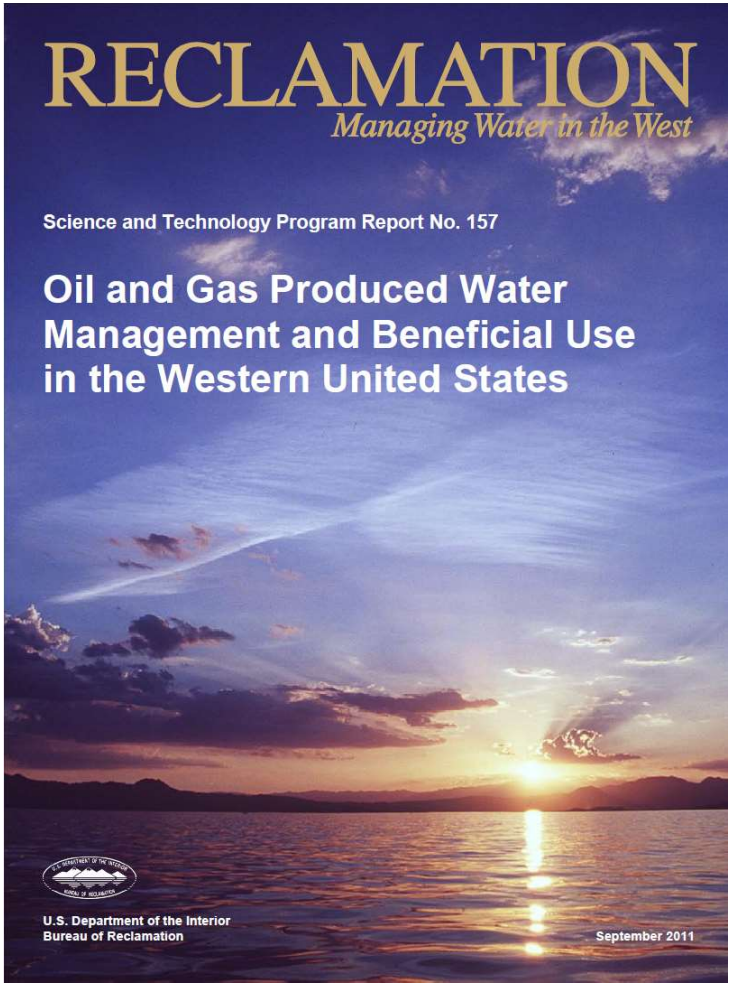
Introduction

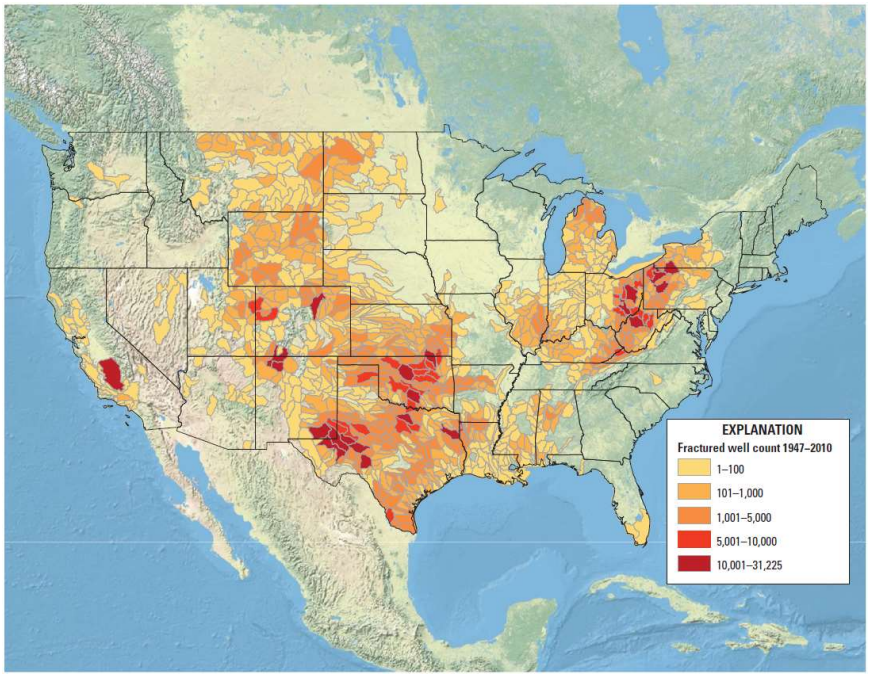
- Why is this a concern?
- Analytical Challenges
  - Total Dissolved Solids (TDS)
  - Interference Control
  - Quantitation Limits
- Instrumental Solutions

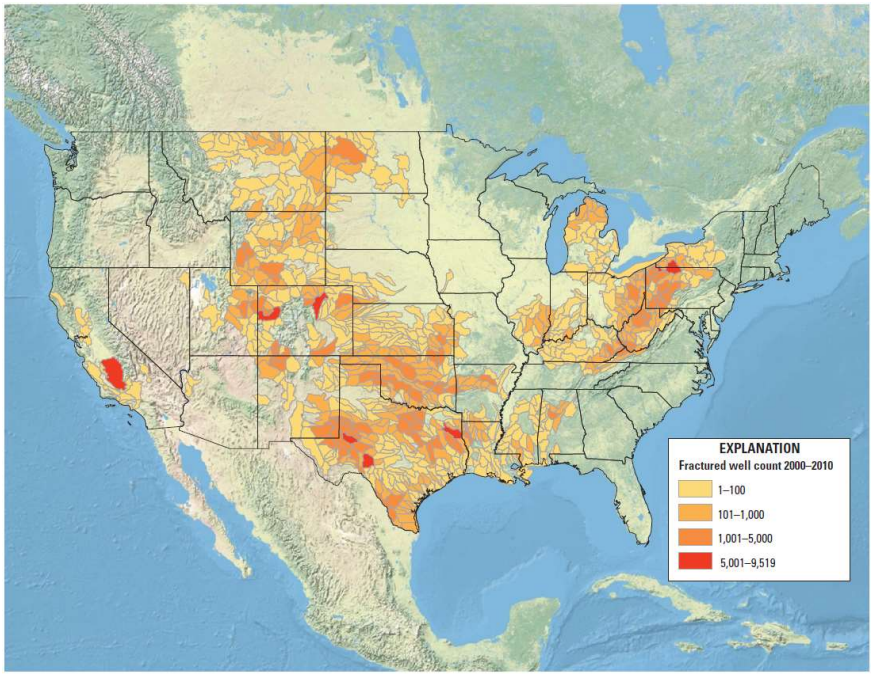
Recent Studies





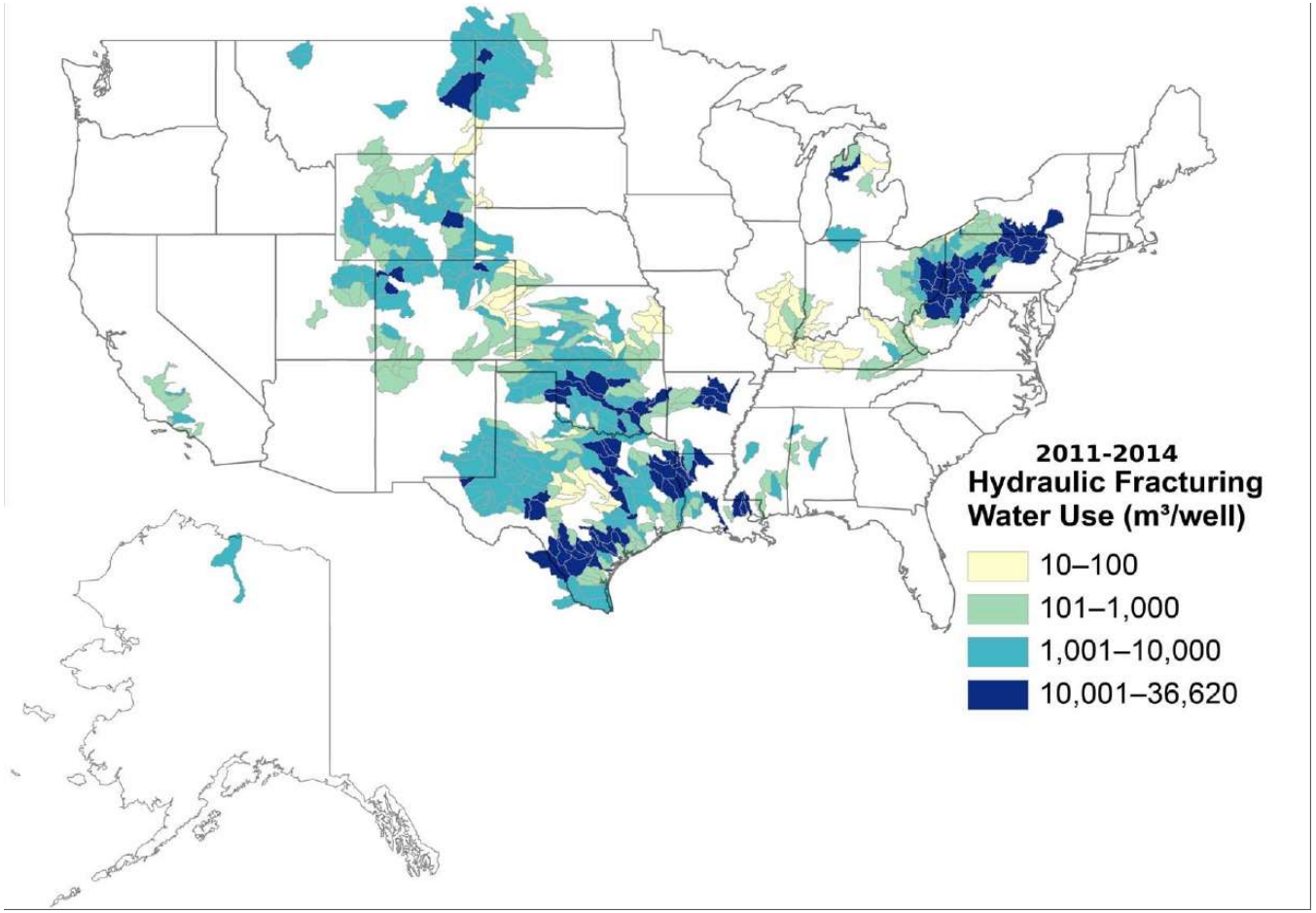
Hydraulically Fractured Wells





USGS 2014-5131

Water Use is on the Rise



- Water use is as high as 9.7 million gallons per well

USGS 2015

Analytical Challenges of Produced Waters

- High Total Dissolved Solids (TDS) (USGS 2002)
  - 1,000 mg/L to 400,000 mg/L
  - Chloride up to 250,000 mg/L
  - Sodium up to 150,000 mg/L
  - Calcium up to 74,000 mg/L
  - Sulfate up to 15,000 mg/L
- High Carbon Content
  - TOC up to ~2,000 mg/L
  - Total Oil up to ~500 mg/L
- Variable concentration of target elements
  - ND to several ppm

Pre-Treatment Adds to the Challenge

- Water is often treated prior to use
  - Corrosion inhibitors
  - Bacterial inhibitors
  - Scale inhibitors
  - Emulsion breakers
  - Anti-Foaming Agents
- Water requires treatment after use

Agilent's History in ICP-MS
30 Years of ICP-MS Innovation

Enabling high sensitivity metal analysis

PMS series

First computer-controlled ICP-MS

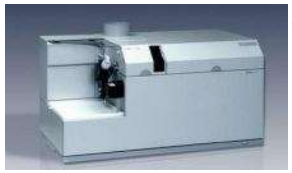
Enabling routine robust ICP-MS analysis

4500

First benchtop ICP-MS
Cool plasma

Enabling control of common interferences

7500



9 orders detector
ORS cell

Enabling ease of use and productivity

7700

HMI
ISIS-DS
MassHunter SW

A new era in ICP-MS performance

7900

UHMI
ODS detector
ISIS 3

Enabling simplified ICP-MS workflows

7800

Solution ready
Method automation

Enabling controlled reaction chemistry

8800 ICP-QQQ

World's first ICP-QQQ

Flexible, high performance MS/MS

New 8900 ICP-QQQ

Second generation ICP-QQQ

#1 selling ICP-MS !

1987 1994 2000 2009 2012 2014 2015 **2016**

Agilent 7900 ICP-MS

Improved Concentration Power (I.C.P. Mode)

1) Matrix Tolerance

Ultra High Matrix Introduction System (UHMI)

Handles tough sample matrices better than any other ICP-MS. Highest total dissolved solids(TDS) capability up to 25%

Reduces sample prep time and error

- Better long-term stability

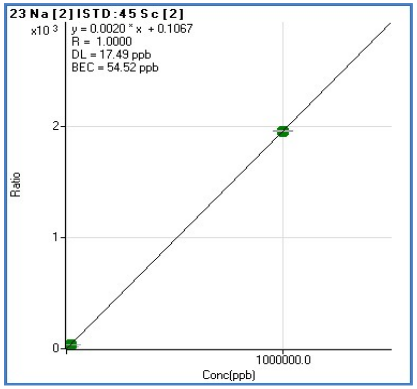
2) Interface Design

Specially designed interface for improved matrix tolerance and at higher sensitivities.

Specially designed for higher sensitivity at lower oxides

- Great performance and low polyatomic formation
- Easy access to the interface for ease of use and maintenance.

3) Orthogonal Detector



Orthogonal Detector (11 orders dynamic range)

From 0.1ppt to 1%

- Simplifies method development
- Easy sample prep.
- Improves productivity

The UHMI's matrix tolerance, the specially designed interface and the Orthogonal Detector's dynamic range gives the 7900 the capability of the I.C.P. mode.

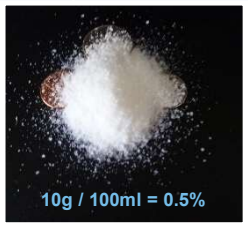
Introducing the Agilent UHMI

UHMI (ultra High Matrix Interface) – much more than just a simple T-piece

UHMI uses optimized gas mixing geometry and sophisticated plasma/gas-flow tuning algorithm to set reproducible conditions for predictable aerosol dilution rate

The Big Four Spiked at Different Salt Content

NaCl Amount	75 As [25 ppb]	114 Cd [50 ppb]	208 Pb [50 ppb]	201 Hg [1 ppb]
0%	26.9	49.2	49.7	0.85
0.5%	24.2	49.0	50.1	0.99
1%	24.8	51.5	50.2	0.93
1.5%	25.5	50.0	50.5	0.88
2%	24.6	50.0	49.7	1.03
5%	25.4	48.7	50.7	0.89
10%	22.8	46.1	49.8	0.91
25%	26.2	45.4	49.0	0.96
Average	**25.1**	**48.7**	**50.0**	**0.93**
% RSD	**5%**	**4%**	**1%**	**6%**
% Recovered	**100%**	**97%**	**100%**	**93%**



Processes of Interference Removal in Collision/Reaction Cell

Collisional Dissociation

- Limited in ICP-MS, as collision energy must be higher than bond dissociation energy

Reaction

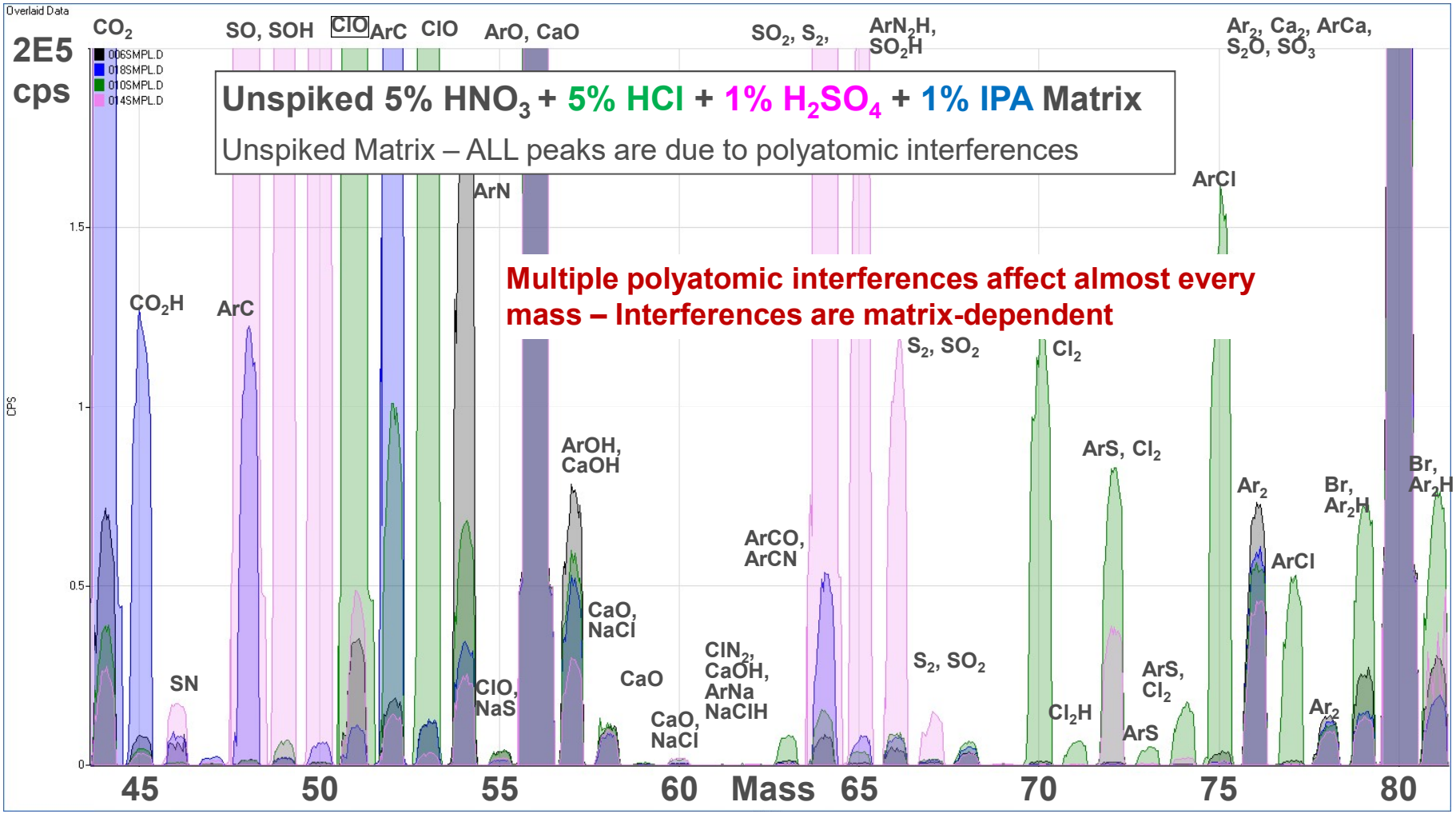
- Can be very efficient – up to 9 orders reduction – but can also be non-selective. Highly reactive gases may react with analytes, matrix components and residual cell contamination, giving analyte loss and the formation of complex cluster ions

Energy Discrimination

- Useful in complex, variable and unknown matrices, as interference removal occurs, regardless of the level, source and chemistry of the interfering species. Can use inert cell gas, so no reaction with analytes and no formation of new cluster ions

Polyatomic Interferences in No Gas Mode

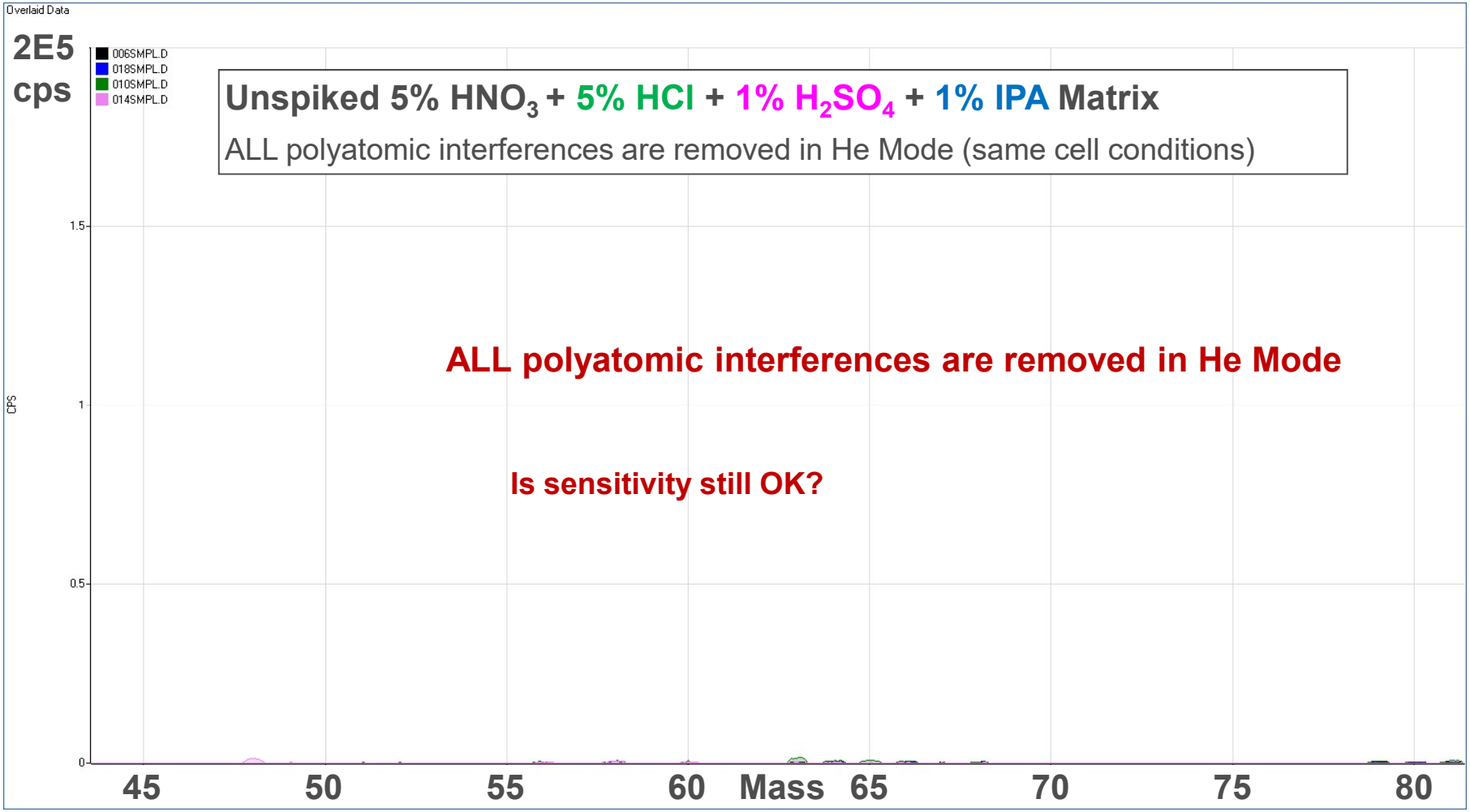
Color of spectrum indicates which matrix gave each interfering peak



No Gas Mode

Polyatomic Interferences in He Mode

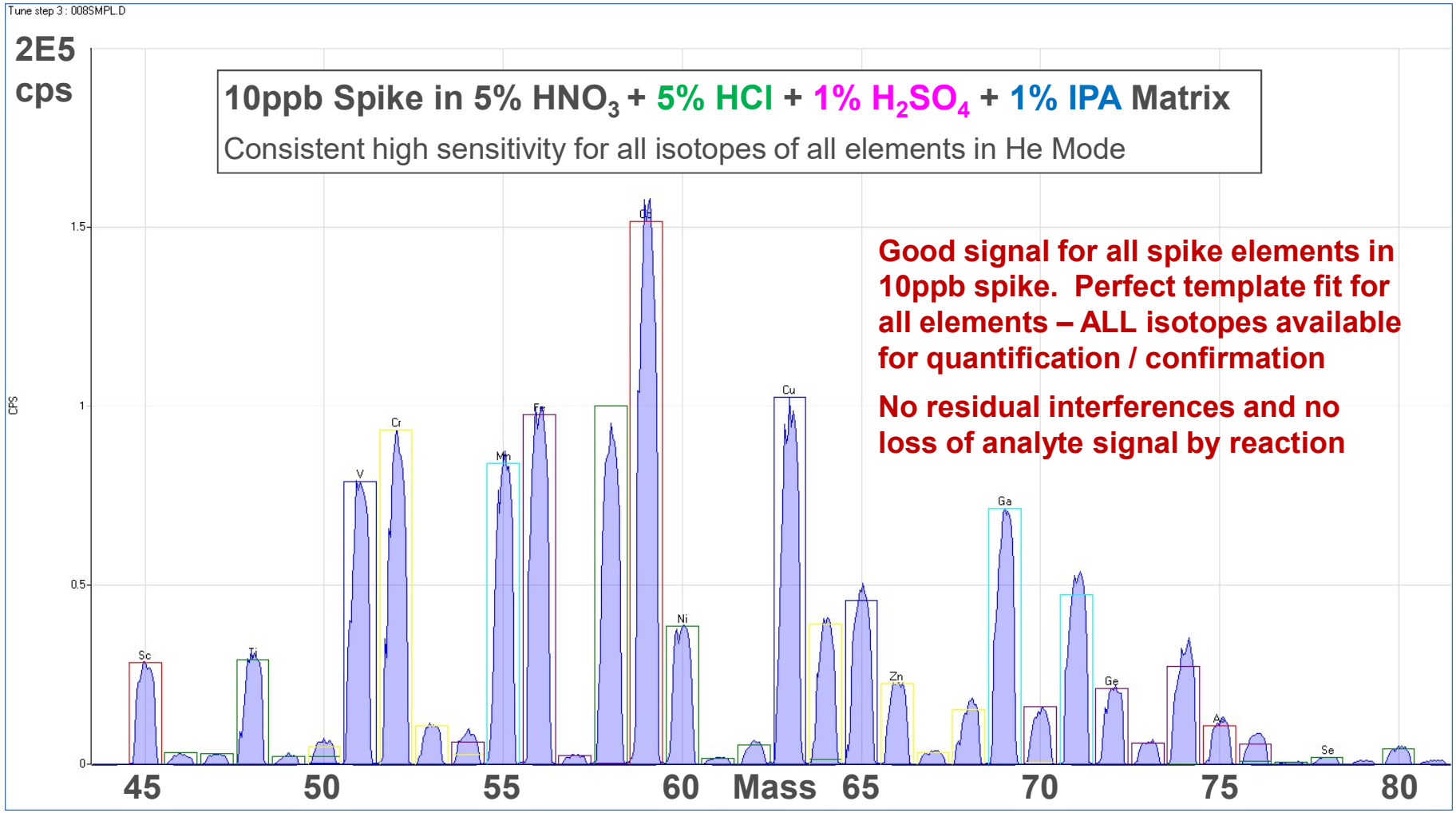
Color of spectrum indicates which matrix gave each interfering peak



He Mode

Matrix Mix with Spike (10ppb) in He Mode

Consistent sensitivity and perfect template match for all elements

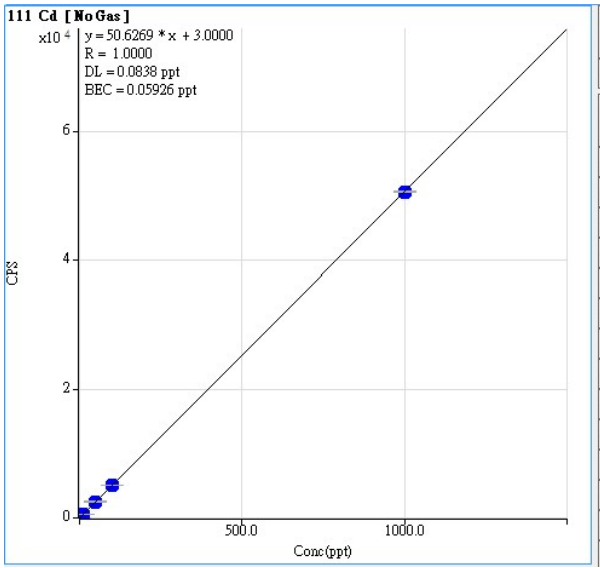


He Mode

Far Wider Dynamic Range Than Any Other ICP-MS

11 orders - low and high level calibrations in a single run

Cd (1ppt - 1ppb) and Na (100ppb - 10,000ppm (1%)) in the same run



Analyte Information (111 Cd [No Gas])

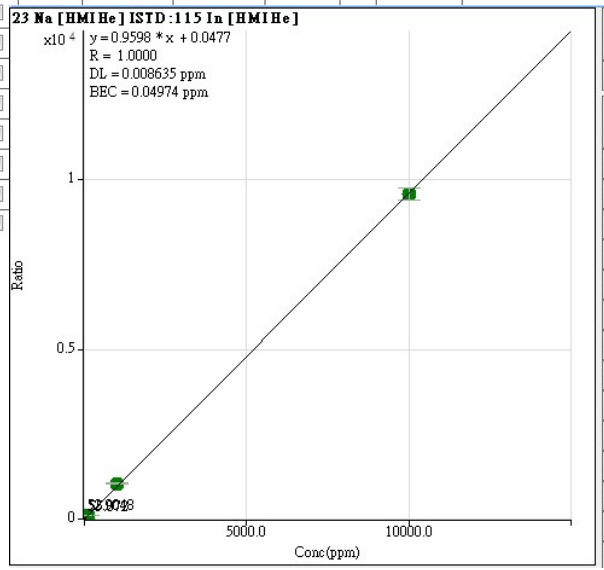
Current Sample	Calc Conc.	CPS	Ratio	Det.	Conc. RSD
1ppbBeAsCdHgPb	1000.006	50630.23		P	0.4

Calibration

Level	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1		0.000	0.000	3.00		P	47.1
2		1.000	0.960	51.60		P	14.9
3		10.000	10.078	513.21		P	3.8
4		50.000	49.851	2526.83		P	2.9
5		100.000	100.008	5066.11		P	2.2
6		1000.00	1000.006	50630.23		P	0.4
7							
8							
9							
10							
11							
12							
13							
14							

Both calibrations are linear.

Total **concentration range** covered from Cd blank (BEC of <0.1ppt) to Na top standard (1%) is 11 orders



Analyte Information (23 Na [HMI He] ISTD: 115 In [HMI He])

Current Sample	Calc Conc.	CPS	Ratio	Det.	Conc. RSD
rinse	55.072	3281161.01	52.9048	A	31.7

Calibration

Level	Rjct	Conc.	Calc Conc.	CPS	Ratio	Det.	RSD
1		0.000	0.000	1944.19	0.0477	P	5.8
2		0.100	0.109	6393.55	0.1528	P	2.9
3		1.000	1.049	43220.26	1.0541	P	1.3
4		10.000	10.192	421823.28	9.8296	P	3.2
5		100.000	99.124	4004216.88	95.1848	A	1.7
6		1000.00	1089.335	40455458.40	1,045.570	A	1.5
7		10000.0	9991.075	328778051.1	9,589.288	A	3.7
8							
9							
10							
11							
12							
13							
14							

Concentration range (11 orders) and upper measurement limit (>1%) are at least 10x better than any other ICP-MS

Experimental

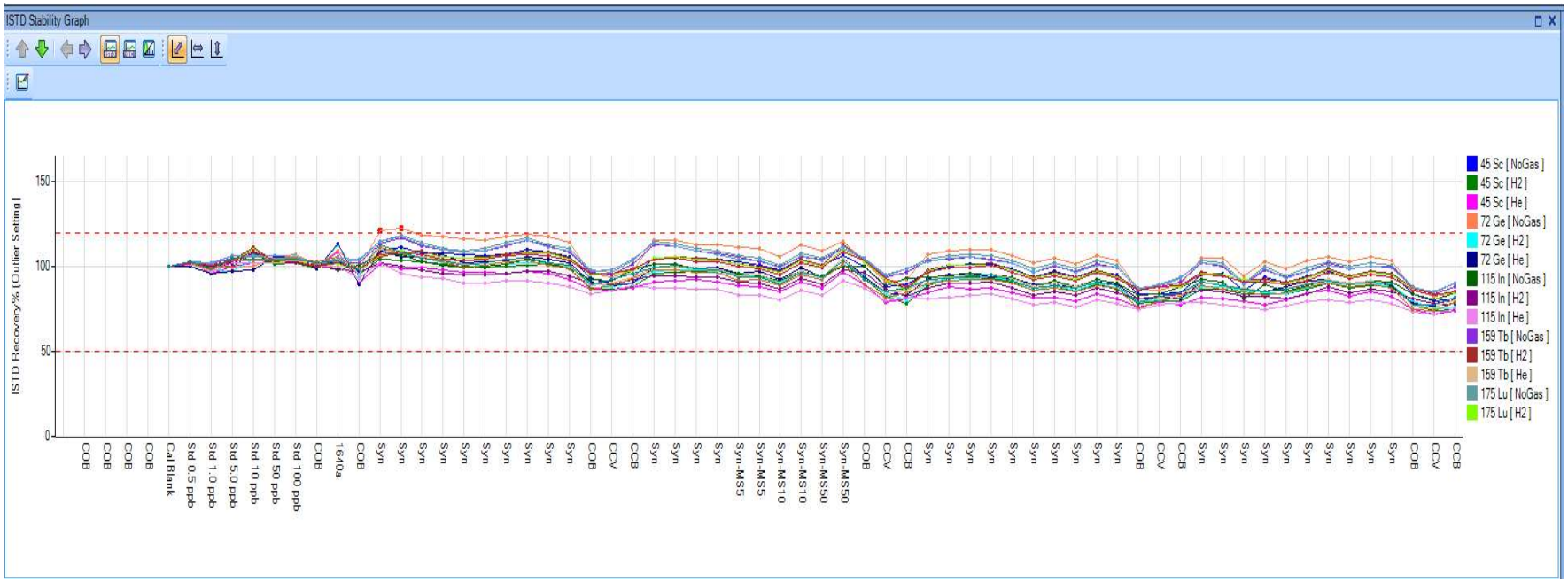
This study used He or H_2 cell mode for most elements and no gas mode for low mass elements.

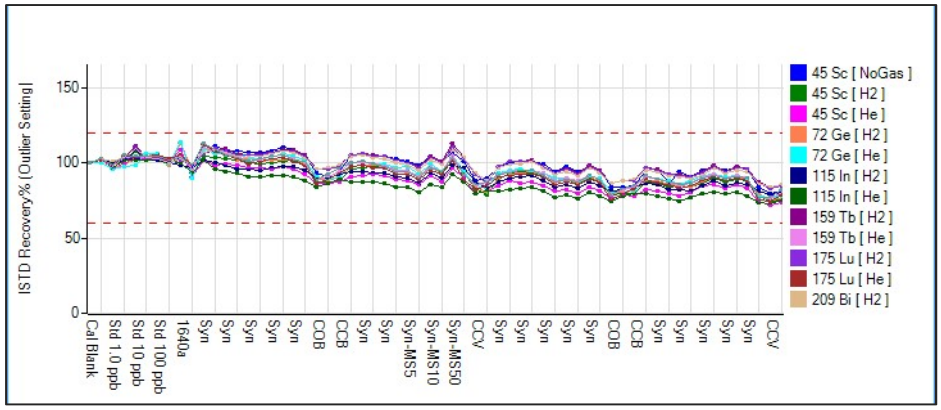
A synthetic sample was analyzed for ~8 hours to demonstrate stability, and was spiked to demonstration accuracy.

Pre-Set Plasma conditions and AutoTune features were used.

Results

Run Stability over 8 hours





Results

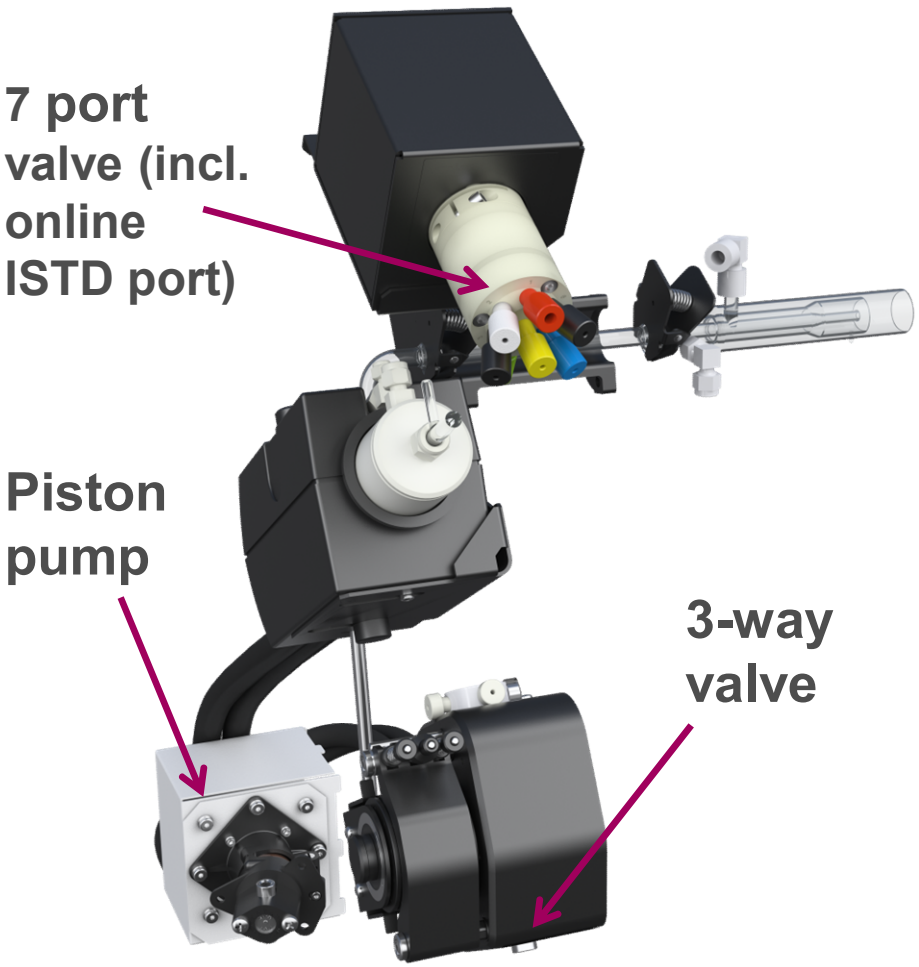
Stability and Recovery Statistics

Isotope/ Element	RSD %	MS %R	MSD %R
9 Be	4.2%	96%	94%
23 Na	1.4%	NA [1]	NA [1]
24 Mg	1.0%	NA [1]	NA [1]
27 Al	1.3%	NA [1]	NA [1]
39 K	1.0%	NA [1]	NA [1]
44 Ca	1.1%	NA [1]	NA [1]
51 V	1.2%	100%	97%
52 Cr	1.0%	100%	98%
55 Mn	1.2%	100%	94%
56 Fe	1.7%	NA [1]	NA [1]
59 Co	1.6%	103%	100%
60 Ni	1.7%	105%	101%
63 Cu	1.6%	106%	100%
66 Zn	1.0%	106%	103%
75 As	1.9%	103%	104%
78 Se	3.1%	102%	102%
95 Mo	0.8%	NA [1]	NA [1]
107 Ag	4.4%	104%	101%
111 Cd	6.7%	102%	100%
121 Sb	17%	111%	112%
137 Ba	3.7%	103%	101%
205 Tl	11%	104%	104%
208 Pb	0.8%	105%	102%
232 Th	1.4%	103%	101%
238 U	4.8%	101%	100%

Note 1 - Concentration too high to spike appropriately.

Integrated Sample Introduction System

Fully compliant multi-mode EPA 6020 analysis in <1 minute



- Close-coupled valve – very short tube length so minimal stabilization/rinse delay
- Piston pump for faster sample uptake
- 3-way valve to switch between on-line ISTD or tune solution
- ISIS is now compatible with Startup auto-optimization functions and full autotune
- With Intelligent Sequencing, ICP-QQQ is suitable for routine, high-throughput analysis

Introduction

Faster analysis, improved ease-of-use, superior matrix tolerance

Combing the unique benefits from each of the following provides much faster analysis, improved ease-of-use and superior matrix tolerance:

- Agilent 7900 ORS^4 He mode collision cell
  - For interference removal
- Ultra High Maxtrix Introduction (UHMI)
  - Aerosol dilution
- ISIS 3
  - Discrete sampling to achieve the best possible productivity

Experimental
Operating conditions

Table 1. Agilent 7900 ICP-MS operating conditions

ICP-MS parameters	No gas mode	He mode
RF power (W)	1600	
Carrier gas flow (L/min)	0.77	
Dilution gas flow (L/min)	0.28	
Lens tune	Autotune	Autotune
Cell gas flow (mL/min)	0.0	4.3
Energy discrimination (V)	5.0	
Number of elements	1 analyte, 1 ISTD	25 analytes, 6 ISTDs
Total acquisition time (3 reps) (seconds)	41	

Experimental
ISIS-DS operation

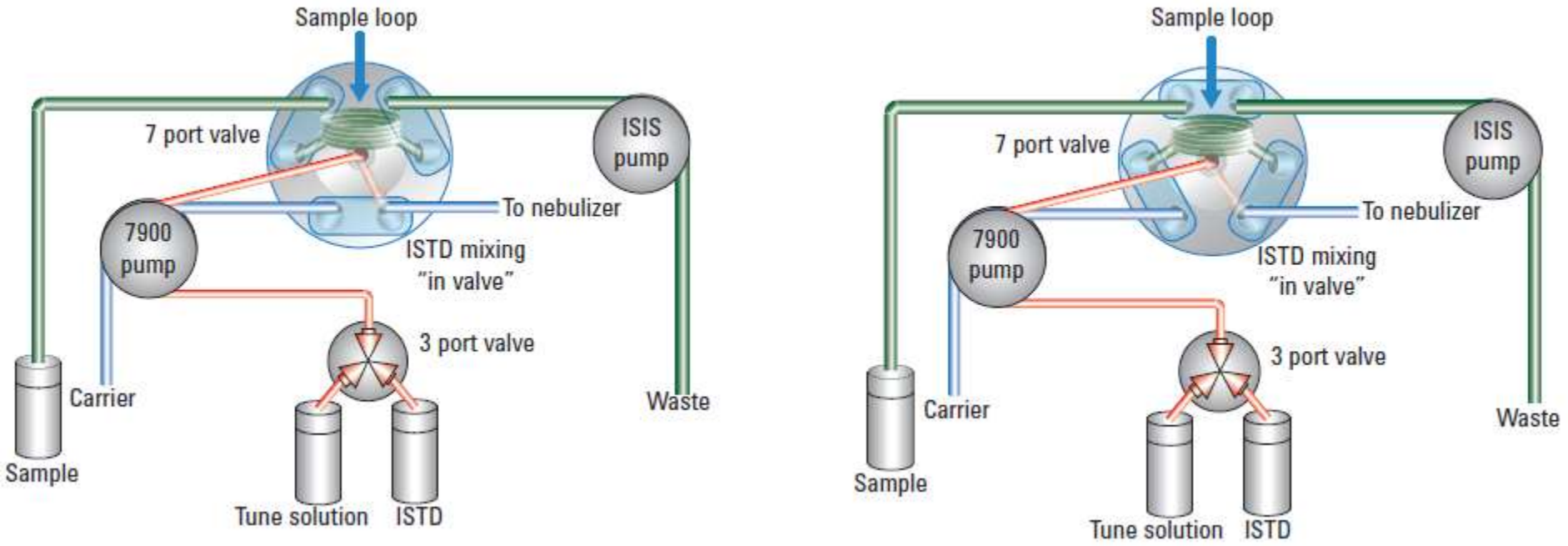


Figure 1. Overview of ISIS-DS operation. Valve in load position (upper left) and inject position (upper right). Actual analyte and internal standard signals during ISIS 3 operation are shown in lower plot with annotation (shown on next page).

Experimental
ISIS-DS operation

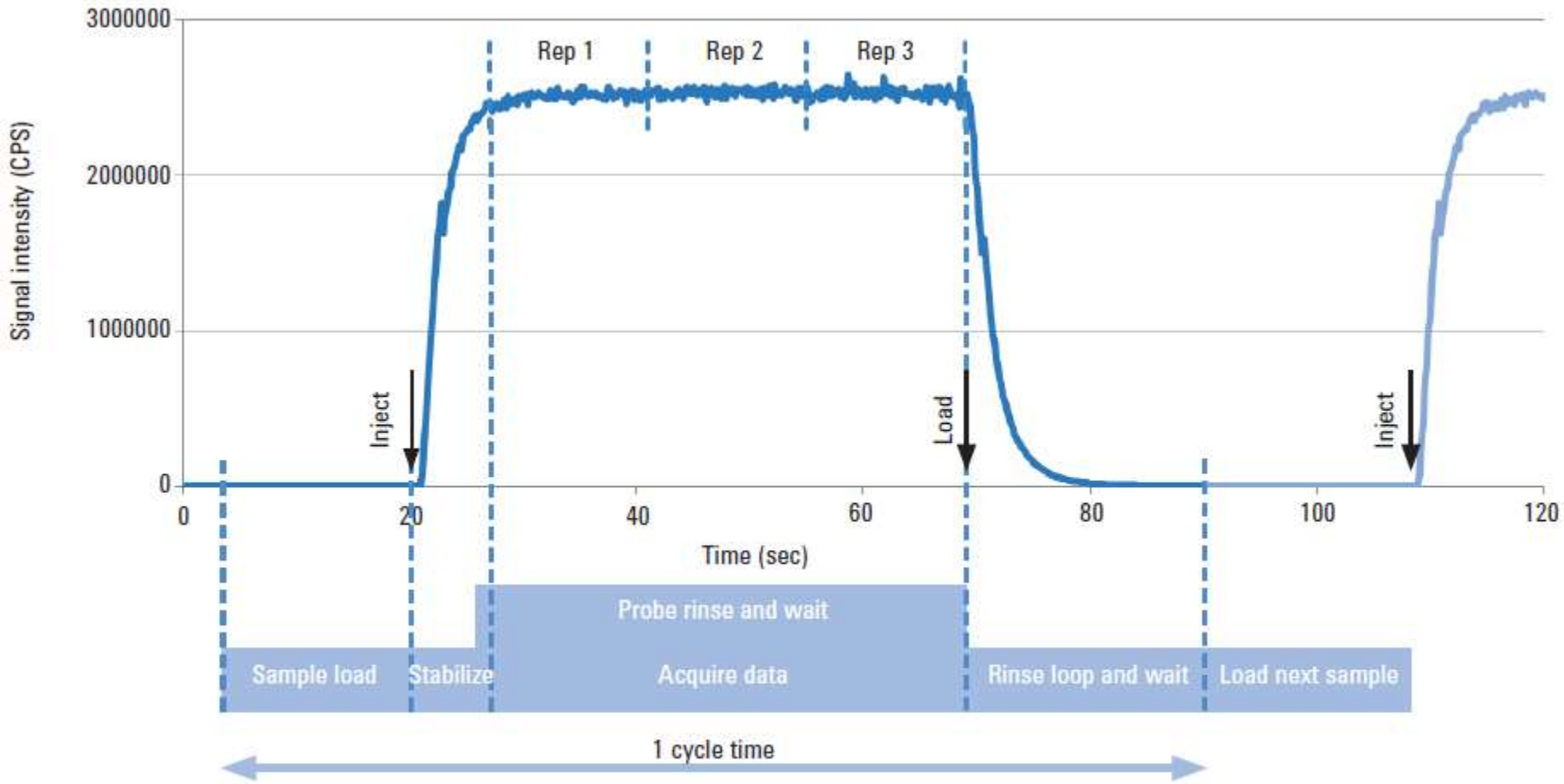


Figure 1 continued. Actual analyte and internal standard signals during ISIS 3 operation are shown with annotation.

Results

This study used He cell mode for most elements and no gas mode for low mass elements.

383 samples were measured in 9 hours and 35 minutes with a run-to-run time of 90 seconds per sample.

The throughput was increased by ~30% compared to a similar study carried out using a 7700x ICP-MS with ISIS 2.

Results
Meeting EPA QA/QC requirements

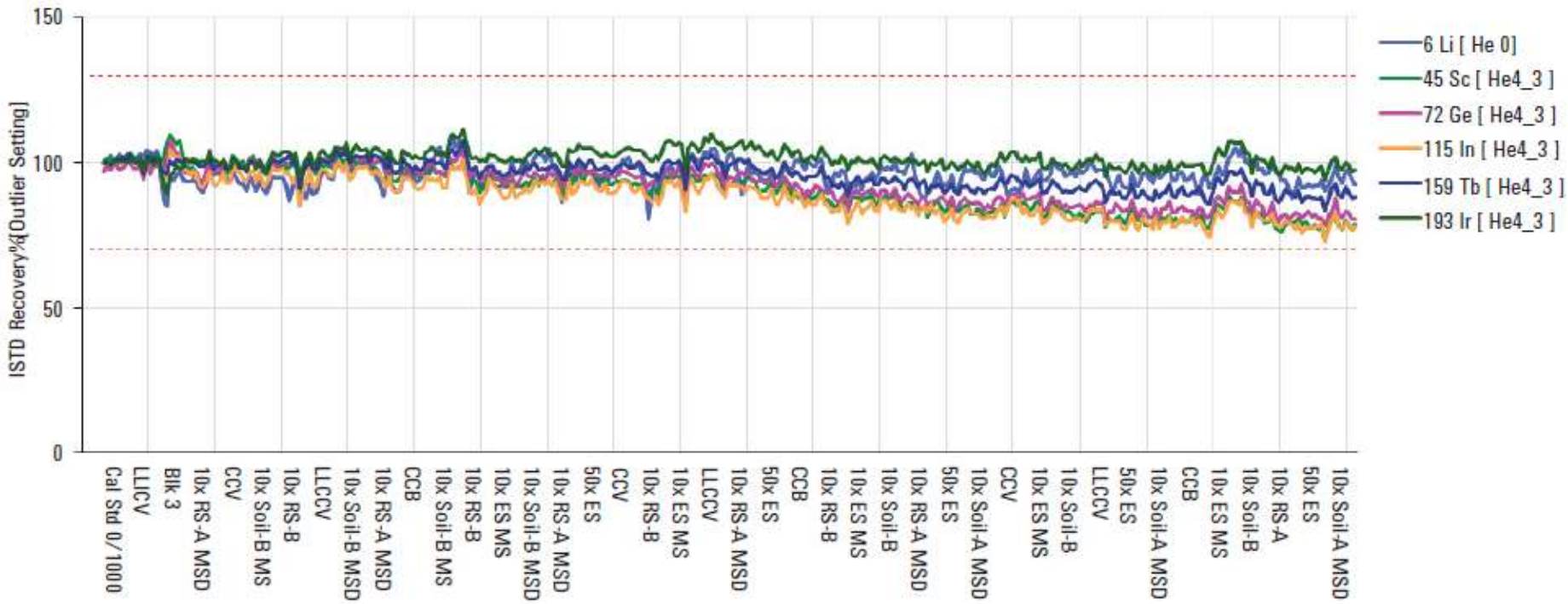


Figure 4. Internal standard recoveries normalized to the calibration blank for all samples. Due to limited space, not all sample names are shown. No internal standard failures occurred.

Results and discussion
Recovery of certified reference values

Table 4. Mean measured values, recoveries, percent Relative Standard Deviations (%RSDs) for all certified elements in the six CRMs analyzed. Blank cells indicate no certified value.
* Concentration of 1/10 diluted solution. ND: less than detection limit

Isotope/ Element	NIST 1640a (n=7)			River Sediment A (1/10, n=14)*			River Sediment B (1/10, n=14)*		
	Mean conc. (ppb)	%RSD	Mean recovery (%)	Mean conc. (ppb)	%RSD	Mean recovery (%)	Mean conc. (ppb)	%RSD	Mean recovery (%)
9 Be	2.80	2.4	93	0.026	9.8		ND		
23 Na	3,112	2.0	107	5,326	1.8	107	5,610	1.6	112
24 Mg	1,062	1.7	101	7,375	1.8	105	13,130	1.3	109
27 Al	57.8	4.4	109	25,180	1.3	101	61,460	0.6	102
39 K	561	5.4	97	14,730	2.4	98	20,220	2.3	101
44 Ca	5,373	3.2	97	29,050	1.8	97	28,960	1.6	97
51 V	15.4	1.5	103	25.5	1.1	102	104	0.7	104
52 Cr	40.5	1.6	101	30,950	1.1	103	1,592	0.9	106
55 Mn	40.0	1.7	100	786	2.2	98	587	1.1	98
56 Fe	44.2	5.7	121	122,000	0.9	102	41,610	0.6	104
59 Co	20.7	2.1	103	12.1	1.5	121	16.3	1.3	109
60 Ni	25.7	1.8	103	52.2	1.4	104	52.8	1.4	106
63 Cu	87.9	2.0	103	101.9	1.7	102	104	1.4	104
66 Zn	56.1	1.3	102	1,454	0.9	97	493	0.8	99
75 As	7.99	1.4	100	60.2	1.3	100	20.4	1.4	102
78 Se	18.5	5.1	93	2.28	5.7	114	0.95	10.5	95
95 Mo	45.8	2.0	101	0.074	7.0		0.17	4.8	
107 Ag	8.25	2.8	103	ND			0.17	2.3	
111 Cd	3.97	1.8	100	10.2	1.1	102	3.18	2.4	106
121 Sb	5.07	1.8	100	50.7	0.7	102	4.22	0.9	106
137 Ba	147	1.1	98	49.3	0.7	99	392	0.5	98
201 Hg	ND			ND			0.023	10.9	
205 Tl	1.58	3.0	98	0.99	1.4	99	1.15	1.6	115
208 Pb	12.5	4.4	104	742	1.8	106	212	1.7	106
232 Th	0.002	40		2.04	2.6	102	9.93	2.3	99
238 U	25.2	3.8	100	1.02	3.1	102	3.02	2.9	101

Conclusions

Long sequences of high Total Dissolved Solids (TDS) samples can be analyzed with high accuracy, precision, and long term stability using the Agilent 7900 ICP-MS.

This was shown by combining the benefits of He mode for removing polyatomic interferences with the UHMI for highly robust plasma conditions, and the ISIS 3 discrete sampling system.

Key Considerations

- Preservation
  - Off-gasing when adding acids
  - Verify pH post preservation
  - Precipitation
- Digestion
  - Closed vessel vs open vessel
  - Consider adding H_2O_2 and HCl
- High Quality Standards and Reagents
  - Only as good as your blanks
  - Standard stability
- Complimentary Techniques

Questions?

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