EWCPS 2017

Reducing the risk of inaccurate results when quantifying trace elements in seawater using ICP-QQQ-MS

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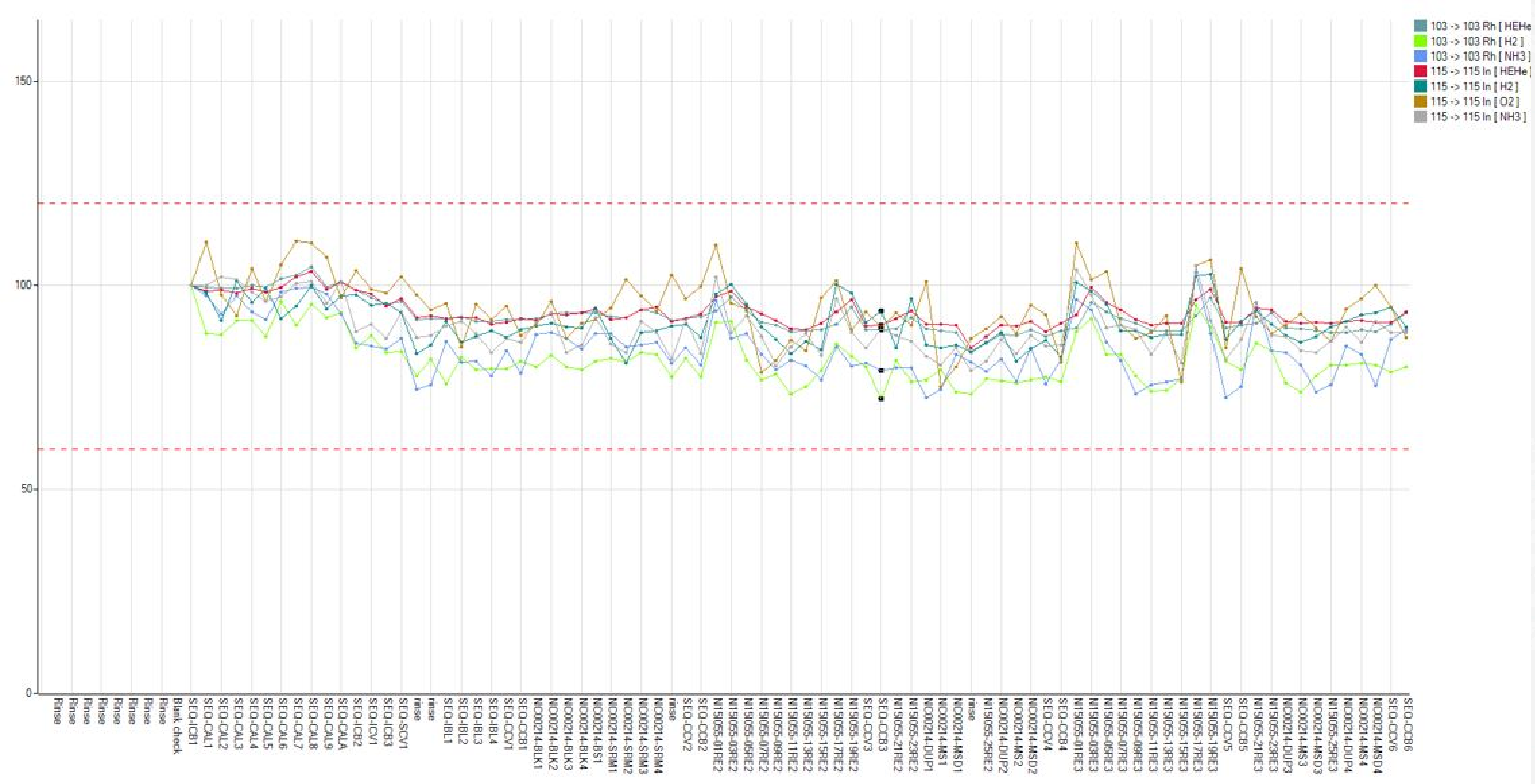
Trace level metals analysis in Seawater

- High total dissolved solids
  - Deposition on ICP-MS interface causing signal stability issues.
  - Decrease of ionization efficiency causing reduced sensitivity.
- Dilution of samples
  - Manual dilution
  - Online dilution - Agilent High Matrix Interface system
  - Decrease in sensitivity
- Column chelation
  - Preconcentrating method that simultaneously removes matrix
  - Not all metals bind to column chelation (example As, Se)
- What are the improvements of using Column Chelation coupled to ICP-QQQ-MS?
  - Double quadrupole mass filter and CRC for removing polyatomic interferences
  - Highly sensitive system resulting in low detection limits
  - Low background
  - Peak integration with Agilent Mass Hunter

Agilent ICP-QQQ-MS HMI System

40 injections of undiluted seawater

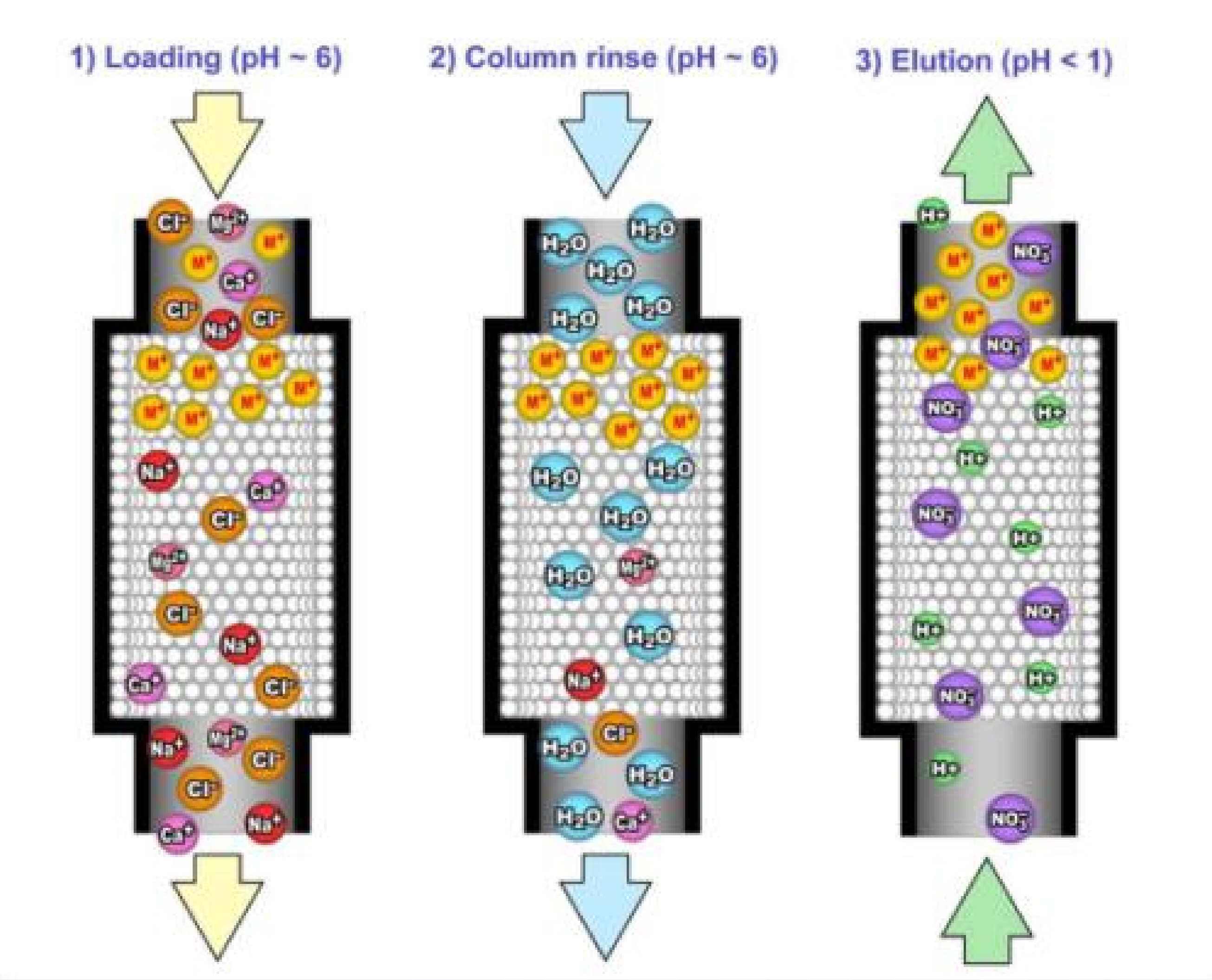


Limit Of Quantitation (LOQ) After Matrix Dilution (HMI vs. Manual)

Analyte / conc (µg/L)	Example Seawater Concentrations*	LOQs with Agilent ICP-QQQ-MS Using HMI (typical)	LOQs with 50x manual Dilution ICP-MS (typical)
Ag	0.003	0.06	0.3
As	1.36	0.06	0.3
Be	0.002	0.1	0.5
Cr	0.183	0.25	1.25
Cu	1.55	0.22	1.1
Sb	0.14	0.1	0.5
Se	0.1	0.11	0.55
Tl	0.011	0.13	0.65
Zn	0.201	1.2	6

*Example concentrations derived from Certified Reference materials from NRC's CASS SLEW NASS

Matrix Removal and Trace Metal Preconcentration Using Online Column Chelation



1. An aliquot of seawater is passed through a column containing a chelating resin.

2. The metals of interest are bound to the resin while non-target ions pass through.

3. The bound metals are then rinsed off the column with a nitric acid solution into the ICP-MS.

Photo credit: Elemental Scientific Inc

LOQ from Column Chelation

(µg/L)	Example seawater concentrations *	LOQs with Agilent ICP-QQQ-MS Using Column Chelation
Cd	0.048	0.004
Co	0.042	0.003
Cu	1.55	0.015
Fe	0.568	0.04
Ni	1.23	0.013
Pb	0.009	0.003
V	2.57	0.012
Zn	0.201	0.015

*Example concentrations derived from Certified Reference materials from NRC's CASS SLEW NASS

Accuracy near detection limit

Reality - do low calibration points recover?

Calibration Recoveries										
Calibration Points	**True value Mn, Ni, Cd, V, Co, Cu, Pb (ng/L)**	**True value Zn (ng/L)**	**Mn**	**Ni**	**Zn**	**Cd**	**V**	**Co**	**Cu**	**Pb**
1	10	50	95%	90%	84%	101%	95%	103%	113%	104%
2	20	100	100%	118%	97%	101%	104%	105%	106%	104%
3	50	250	104%	104%	104%	103%	97%	105%	113%	102%
4	100	500	102%	107%	104%	106%	107%	109%	109%	106%
5	500	2500	103%	106%	103%	105%	100%	105%	104%	102%
6	1000	5000	99%	105%	99%	101%	101%	99%	98%	98%
7	5000	25000	86%	100%	86%	100%	100%	100%	100%	100%
blank		**BEC**	**3**	**6**	**97**	**0.042**	**0.319**	**3.08**	**8.9**	**1.607**

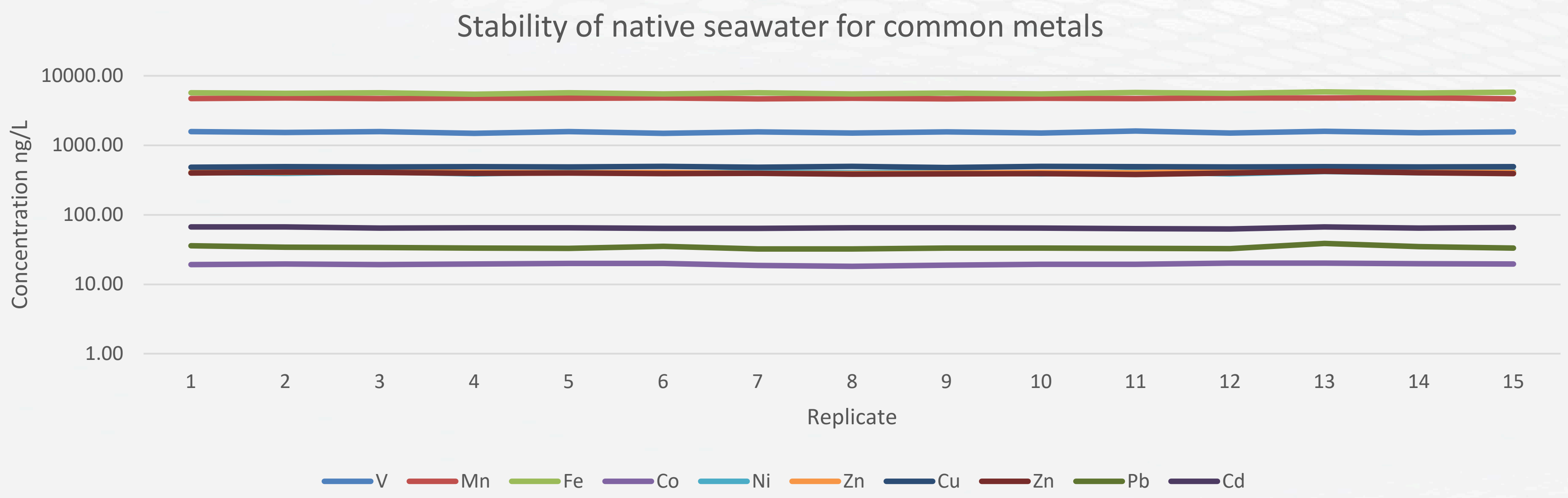
Recovery of CRMs

Certified reference material SLEW-3 (marine estuary CRM from NRC)

SLEW-3								
	V	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**Cd**
Certified Values (ng/L)	2570	1610	568	42	1230	1550	201	48
Analysis	**% Recoveries**							
Day1 Rep1	106%	107%	83%	110%	115%	103%	90%	107%
Day1 Rep2	103%	107%	88%	110%	113%	102%	106%	107%
Day2 Rep1	105%	105%	113%	104%	106%	106%	100%	105%
Day2 Rep2	103%	102%	95%	104%	103%	106%	86%	104%
Day2 Rep3	104%	102%	100%	103%	105%	105%	88%	101%
Day2 Rep4	108%	107%	117%	107%	107%	109%	101%	111%
Day2 Rep5	107%	104%	97%	105%	108%	107%	82%	101%
Day2 Rep6	103%	101%	93%	102%	103%	104%	82%	103%
Day2 Rep7	103%	102%	98%	103%	102%	102%	91%	104%
Day2 Rep8	102%	101%	103%	102%	102%	103%	86%	102%
Average Values	**105%**	**104%**	**99%**	**105%**	**106%**	**105%**	**91%**	**104%**

Precision - Stability

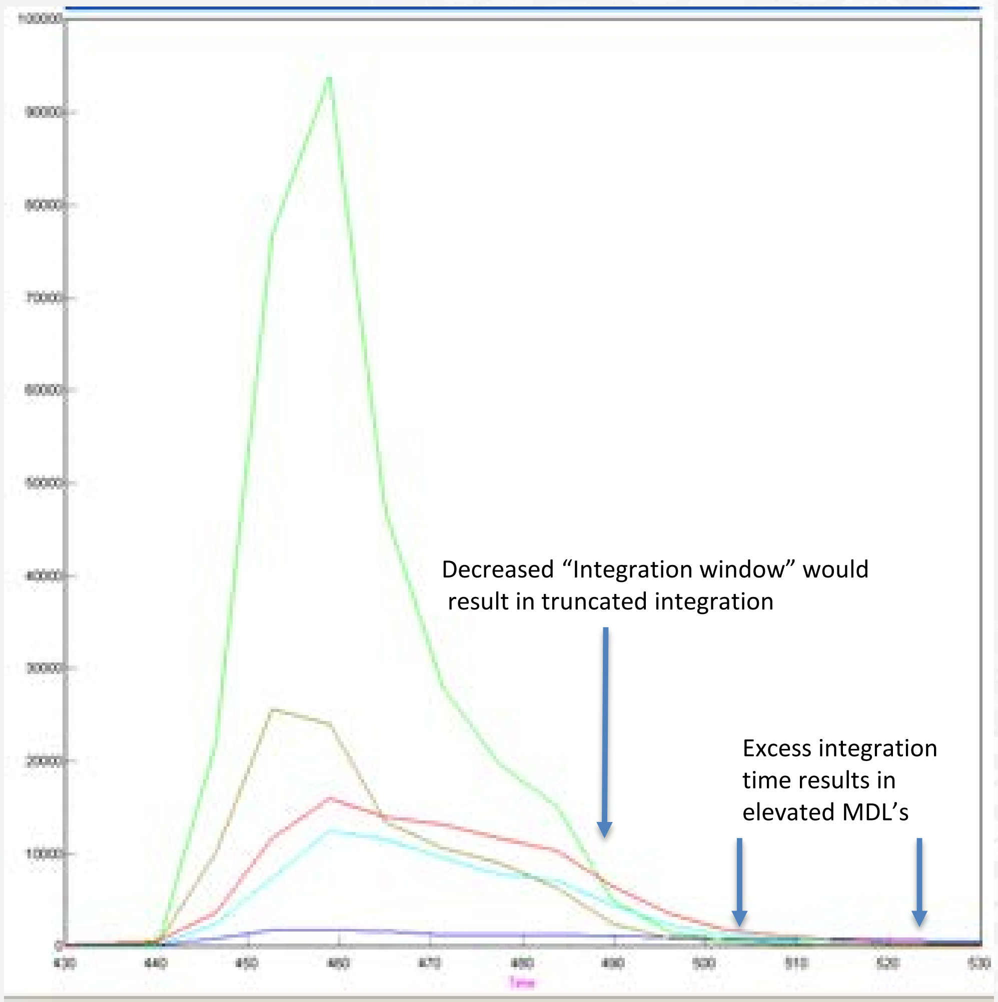
multiple injections using ambient seawater from Puget Sound



	V	Mn	Fe	Co	Ni	Zn	Cu	Zn	Pb	Cd
Average Native Concentration (ng/L)	1543	4748	5644	19	405	411	491	398	34	65
Standard Deviation	40	51	126	1	11	15	6	11	2	1
RSD %	3%	1%	2%	3%	3%	4%	1%	3%	5%	2%

Data Processing

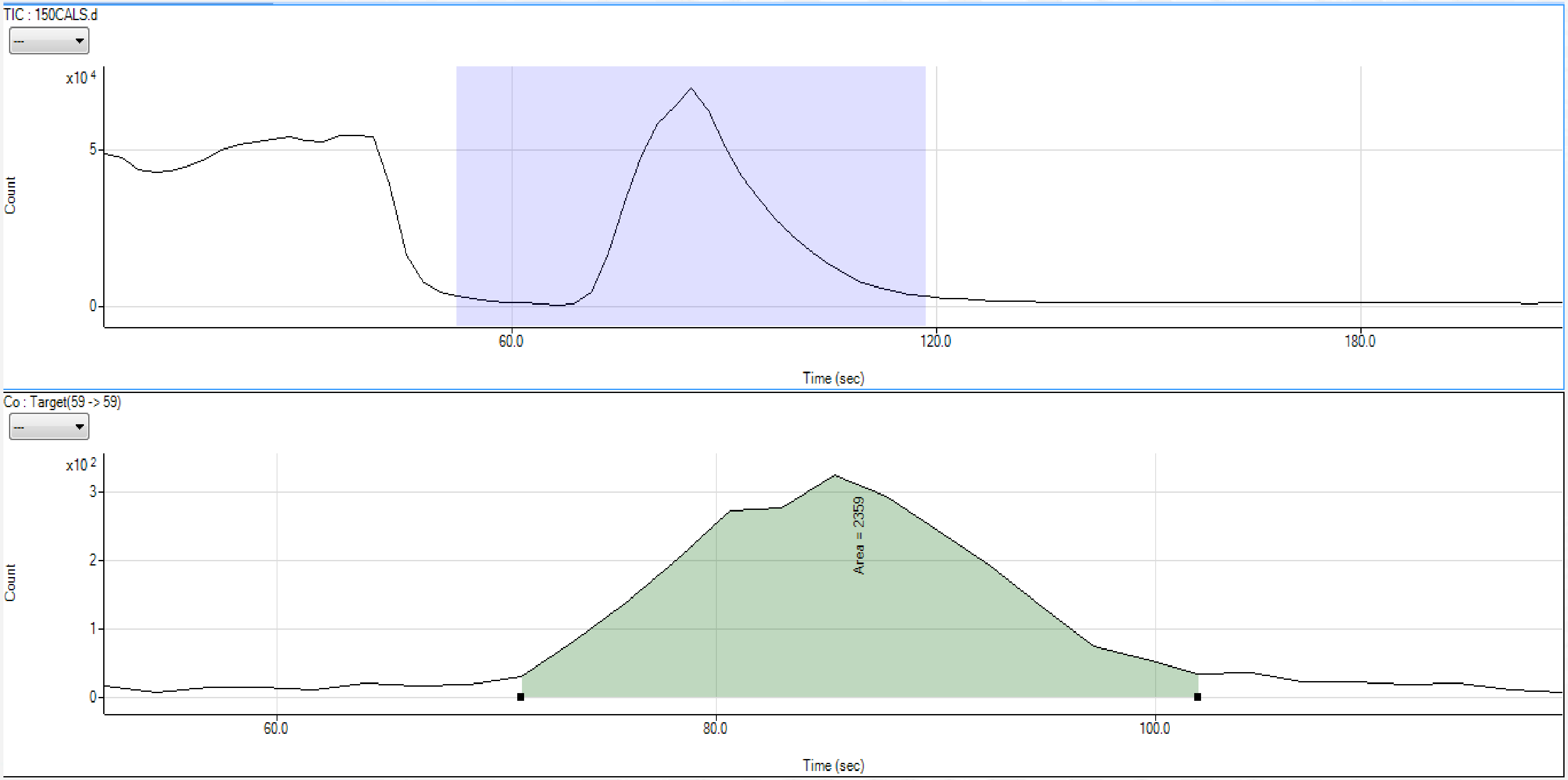
Standard data collection and peak integration



- Using typical ICP-MS software "peak integration" is predefined regardless of peak size or retention
- Excess integration time can increase detection limit
- Short integration time can cause peak cut off biasing data low

Data Processing

Peak integration on ICP-QQQ-MS



Peak integration is completely customizable per analyte per injection for best fit resulting in lower detection limits.

Pristine Seawater – Actual samples

Use of humic acids to test dissolved organic carbon effect on column

- Typical humic content of seawaters are approximately 0.1 mg/L (IAEA ANL-84-78)
- Leonardite (0.1 mg/L)
- Danoke peat (0.1 mg/L)
- Nordic fulvic (0.26 mg/L)
- Elliott Bay (filtered)
- SRFA (Suwannee River Fulvic Acid) (0.37 mg/L)
- Nordic NOM (0.7 mg/L)

Humic acid experimental design

Failure test analysis

- Analyzed at 50x, 25x, and 5x in duplicate.
- Each dilution of humic acid sample had an additional aliquot spiked with analytes of interest.
- Detection limits are based on dilution factor.
  - Note at high dilution factors the increased detection limit may lead to analytical uncertainty because it is near the native concentration.

Elliott bay and SFRA humic acids

Elliott bay					
Analyte	Detection limit ng/L	Dilution			RSD
		50x	25x	5x	
Cd	5.0	ND	ND	ND	NA
Co	10.0	ND	ND	84.3	NA
Cu	10.0	6366.5	6087.5	6270.6	2%
Mn	10.0	ND	ND	228.5	NA
Ni	5.0	[illegible]	152.3	191.1	[illegible]
Pb	5.0	275.7	250.2	209.4	14%
V	5.0	ND	ND	39.3	NA
Zn	60.0	ND	ND	960.7	NA

average matrix spike recovery per dilution		
50x	25x	5x
98%	97%	118%
101%	99%	124%
99%	96%	107%
99%	97%	113%
[illegible]	99%	125%
92%	94%	77%
107%	106%	107%
102%	98%	118%

SRFA					
Analyte	Detection limit ng/L	Dilution			RSD
		50x	25x	5x	
Cd	5.0	ND	ND	ND	NA
Co	10.0	ND	ND	50.2	NA
Cu	10.0	1556.5	1487.5	1668.5	6%
Mn	10.0	ND	372.1	483.7	18%
Ni	5.0	755.0	639.3	820.6	12%
Pb	5.0	1165.7	1172.2	998.5	9%
V	5.0	ND	ND	62.2	NA
Zn	60.0	4797.5	4064.0	3879.2	11%

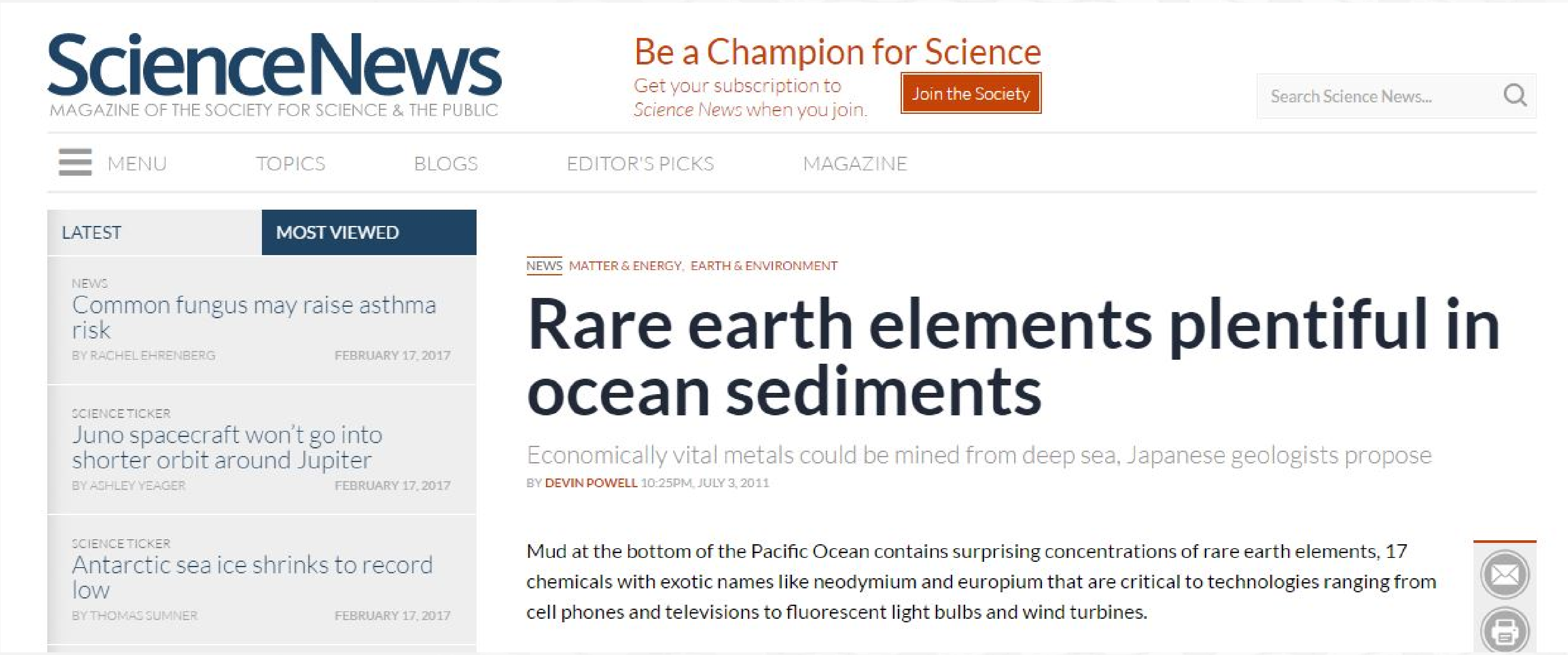
average matrix spike recovery per dilution		
50x	25x	5x
96%	95%	118%
97%	98%	123%
98%	97%	107%
95%	96%	113%
97%	97%	122%
91%	94%	81%
102%	103%	98%
97%	98%	117%

Nordic NOM high organic content water (0.7 mg/L humic acid)

Nordic Nom							
Analyte	Detection Limit ng/L	Dilution			Effects of 5x vs 25x-50x	RSD 50-25	RSD including 5x
		50x	25x	5x			
Cd	5.0	1923	1913	2610	Increase	0%	19%
Co	10.0	3070	2974	3822	Increase	2%	14%
Cu	10.0	57812	56798	81508	Increase	1%	21%
Mn	10.0	67015	66832	82394	Increase	0%	12%
Ni	5.0	14105	14125	20079	Increase	0%	21%
Pb	5.0	5506	5547	4482	Decrease	1%	12%
V	5.0	7339	7301	7252	Similar	0%	1%
Zn	60.0	85108	84529	112931	Increase	0%	17%

Other applications

REE



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Rare earth elements plentiful in ocean sediments

Economically vital metals could be mined from deep sea, Japanese geologists propose

BY DEVIN POWELL 10:25PM, JULY 3, 2011

Mud at the bottom of the Pacific Ocean contains surprising concentrations of rare earth elements, 17 chemicals with exotic names like neodymium and europium that are critical to technologies ranging from cell phones and televisions to fluorescent light bulbs and wind turbines.

- Evaluation of REE levels in all aqueous matrices need ultra low level detection limits

Accuracy

SLEW-3 (non certified values)

Reference Values (ng/L)												
Element	**La**	**Ce**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Yb**	**Lu**
	7.70	6.60	7.93	7.20	0.48	3.10	0.45	3.38	0.91	2.70	1.80	0.29
Recovery												
Rep 1	95%	101%	95%	100%	112%	104%	96%	98%	97%	94%	25%	119%
Rep 2	96%	93%	96%	107%	162%	93%	93%	87%	93%	109%	117%	78%
Rep 3	95%	98%	100%	104%	152%	100%	95%	101%	87%	93%	90%	52%
Rep 4	99%	97%	97%	96%	107%	94%	88%	96%	88%	96%	97%	74%
Rep 5	96%	94%	102%	96%	124%	91%	93%	100%	95%	99%	102%	64%
Rep 6	99%	99%	103%	106%	135%	94%	90%	99%	85%	101%	99%	52%
Rep 7	93%	96%	94%	91%	93%	100%	79%	91%	89%	95%	118%	72%
Rep 8	94%	93%	97%	92%	98%	85%	93%	90%	95%	96%	107%	86%
Rep 9	98%	96%	104%	97%	137%	101%	86%	95%	96%	98%	91%	72%
Rep 10	96%	99%	99%	97%	99%	92%	86%	91%	84%	94%	105%	74%
Average Recovery	**96%**	**97%**	**99%**	**99%**	**122%**	**95%**	**90%**	**95%**	**91%**	**97%**	**95%**	**74%**

GeoReM: Jochum, K. P., Nohl, U., Herwig, K., Lammel, E., Stoll, B. and Hofmann, A. W. (2005), GeoReM: A New Geochemical Database for Reference Materials and Isotopic Standards. Geostandards and Geoanalytical Research, 29: 333–338. doi: 10.1111/j.1751-908X.2005.tb00904.x
http://georem.mpch-mainz.gwdg.de/

Conclusions

Column chelation coupled to QQQ-MS

- Agilent Mass Hunter software allows for better transient signal peak integration
- Preconcentration yields extremely low detection limits of typical metals (ng/L)
- Effective matrix and interference removal
- Analyte list can be expanded to other metals such as REE metals (pg/L)

Questions?

Thank You!!

Agilent, ESI, Brooks Applied Labs, and the Audience