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# Merits of EPA Method 1640:

## Preconcentration and matrix removal of seawaters for trace metals analysis with a ICP-QQQ-MS detection system

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# Trace Metals in Seawater

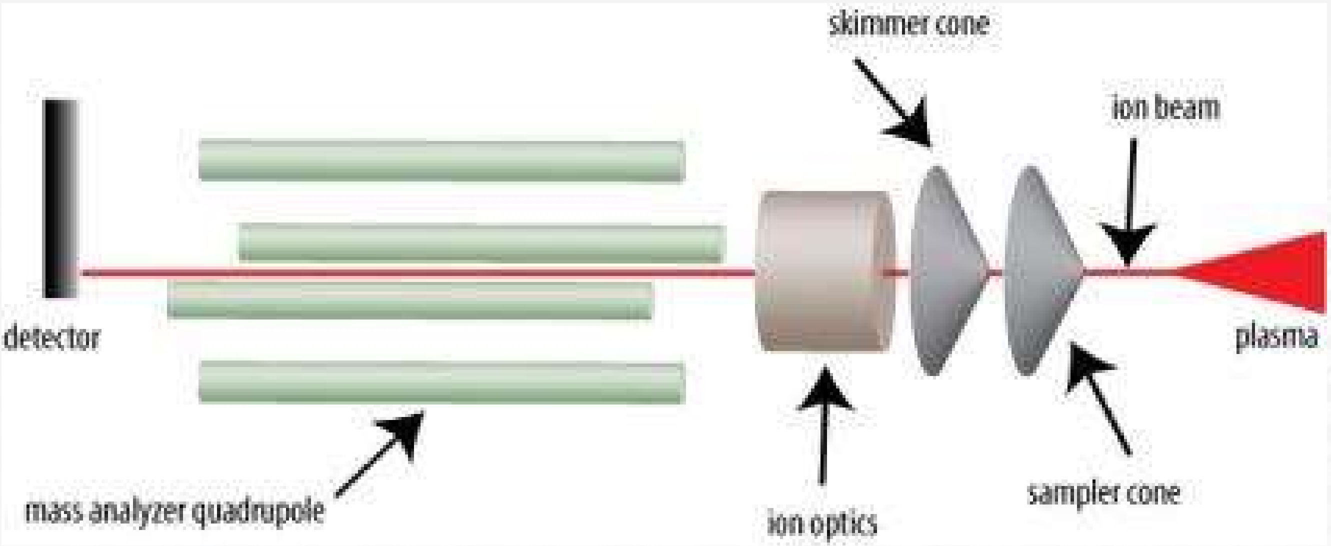
Potential Sources Include: Industrial wastewater, urban stormwater, agricultural runoff, petroleum exploration, marine paints

Monitoring for <u>minor</u> changes in metals concentrations is critical to developing accurate environmental assessments or evaluating the effectiveness of various pollution control and remediation technologies

# ICP-MS

The inductively coupled plasma – mass spectrometer (ICP-MS)

- Accurate and precise
- Right technology when used by trained personnel



# Ambient Levels of Metals in Seawater and Typical ICP-MS Detection Limits

| Element | Example seawater concentrations from CRMs (µg/L) | Typical BAL MDLs in freshwater (µg/L) |
|---|---|---|
| Ag | 0.003 | 0.006 |
| As | 1.4 | 0.006 |
| Be | 0.002 | 0.01 |
| Cd | 0.048 | 0.004 |
| Co | 0.05 | 0.004 |
| Cr | 0.2 | 0.025 |
| Cu | 1.6 | 0.022 |
| Fe | 0.6 | 0.28 |
| Ni | 1.2 | 0.023 |
| Pb | 0.01 | 0.005 |
| Sb | 0.14 | 0.01 |
| Se | 0.1 | 0.011 |
| Tl | 0.01 | 0.013 |
| V | 2.6 | 0.012 |
| Zn | 0.2 | 0.12 |

# Polyatomic Interferences

- Molecules that have the same nominal mass as the analyte of interest
- Potentially cause in high-biased data
- Potentially result in elevated method detection limits if the sample and interferant is diluted

| Analyte | Potential Interferences |
| --- | --- |
| $As^{75}$ | $^{40}Ar^{35}Cl^{+}$, $^{38}Ar^{37}Cl^{+}$, $^{23}Na^{12}C^{40}Ar^{+}$ |
| $Cr^{52}$ | $^{35}Cl^{16}O^{1}H^{+}$ |
| $Co^{59}$ | $^{36}Ar^{23}Na^{+}$ |
| $Cu^{63}$ | $^{23}Na^{40}Ca^{+}$ |
| $V^{51}$ | $^{35}Cl^{16}O^{+}$ |

# Physical Interferences

Seawater contains approximately 3% total dissolved solids (TDS), mainly in the form of sodium, magnesium, and chloride ions.

- These salts will rapidly deposit in and around the sampler and skimmer cones, as well as the ion optics, resulting in signal stability issues.
- Dilution of these interferences will cause an increase in detection limits.
- The elevated salt content also decreases the ionization efficiency of the plasma, causing reduced sensitivity.

Internal Standard Response (counts-per-second, CPS)

| | Sc | Ge | In | Tm |
|---|---|---|---|---|
| DI water | 889,432 | 582,996 | 1,952,339 | 1,904,518 |
| Natural Seawater | 142,518 | 88,369 | 583,276 | 812,010 |
| Recovery (%) | 16 | 15 | 30 | 43 |

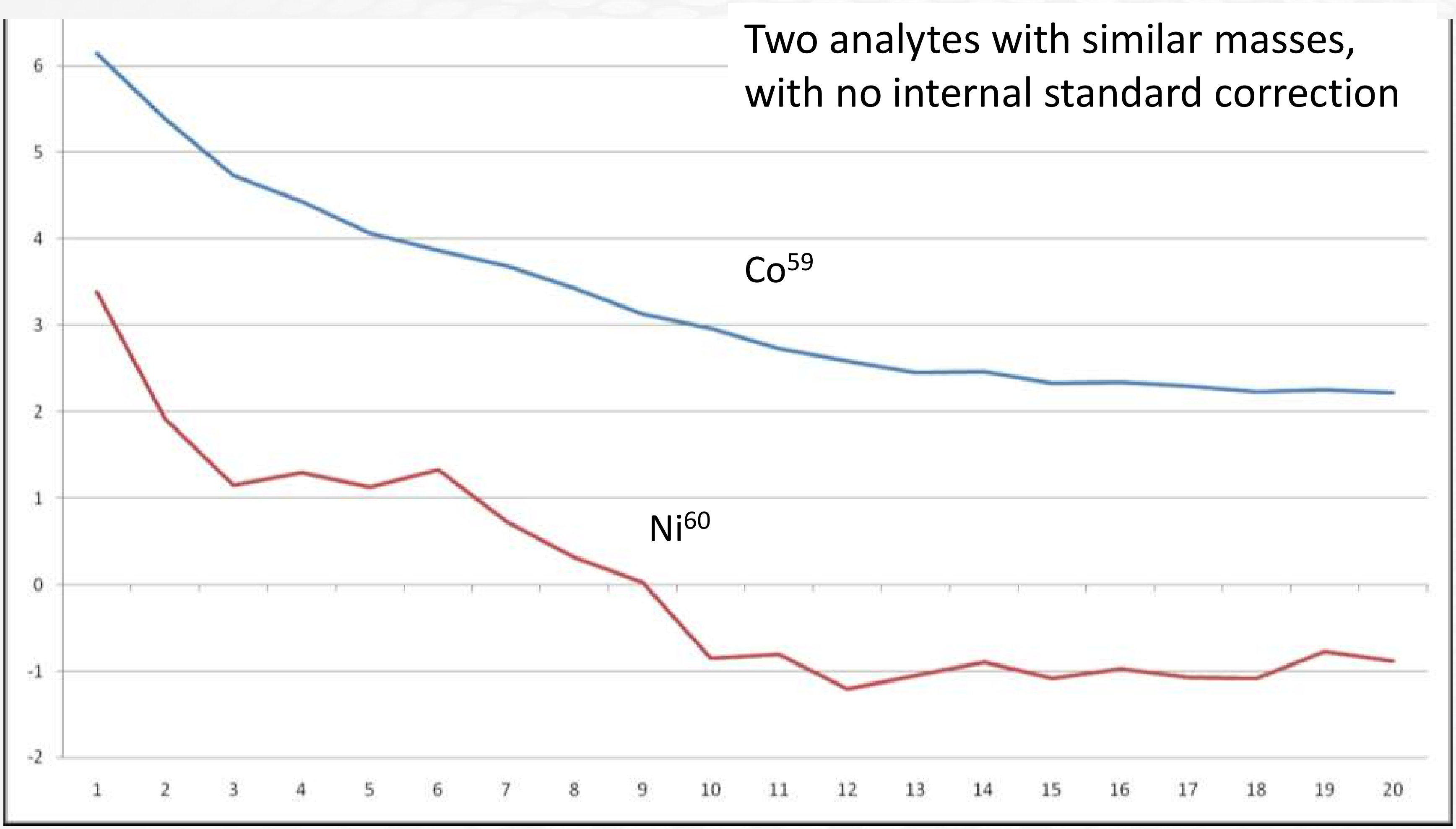
# Instrument Degradation

Before

After

Example pictures of cones from an ICP-MS after 20 replicates of undiluted seawater analysis

# Replicate Analyses Demonstrating Decreasing Response of Seawater



# Resulting MDLs After Matrix Dilution

| Element | Example seawater concentrations from CRMs (µg/L) | MDLs with Typical 50x Dilution ICP-MS (µg/L) | Est. MDLs with ICP-QQQ-MS using HMI (µg/L) |
|---|---|---|---|
| Ag | 0.003 | 0.3 | 0.06 |
| As | 1.4 | 0.3 | 0.06 |
| Be | 0.002 | 0.5 | 0.1 |
| Cd | 0.048 | 0.2 | 0.04 |
| Co | 0.05 | 0.2 | 0.04 |
| Cr | 0.2 | 1.3 | 0.25 |
| Cu | 1.6 | 1.1 | 0.22 |
| Fe | 0.6 | 14 | 2.8 |
| Ni | 1.2 | 1.2 | 0.23 |
| Pb | 0.01 | 0.3 | 0.05 |
| Sb | 0.14 | 0.5 | 0.1 |
| Se | 0.1 | 0.6 | 0.11 |
| Tl | 0.01 | 0.7 | 0.13 |
| V | 2.6 | 0.6 | 0.12 |
| Zn | 0.2 | 6 | 1.2 |

# HMI – High Matrix Interface

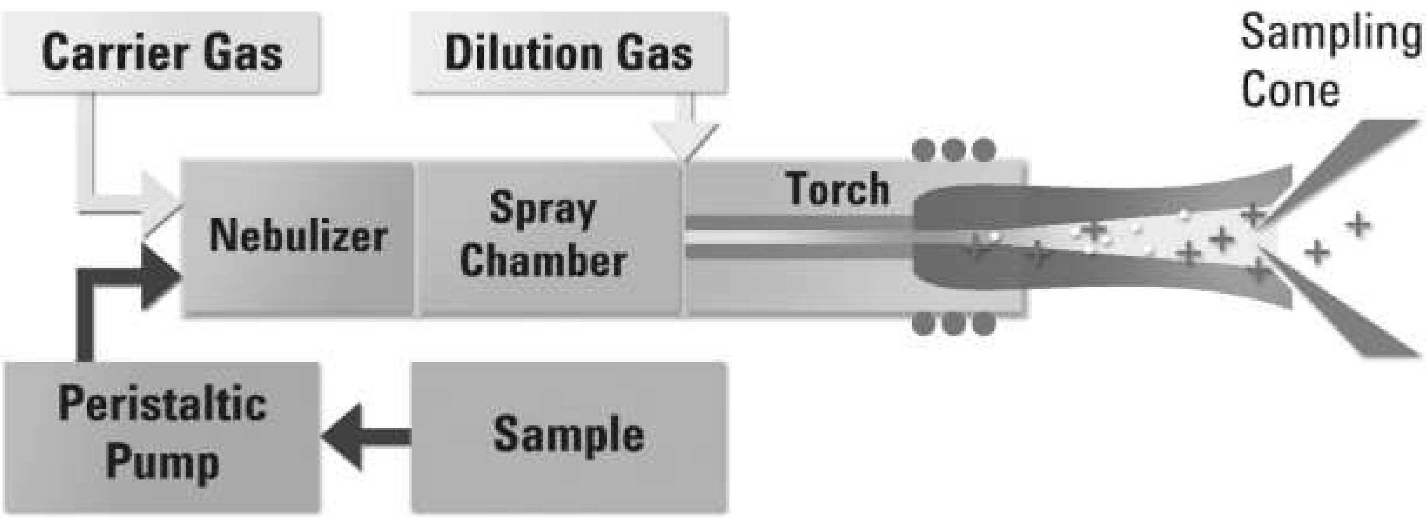
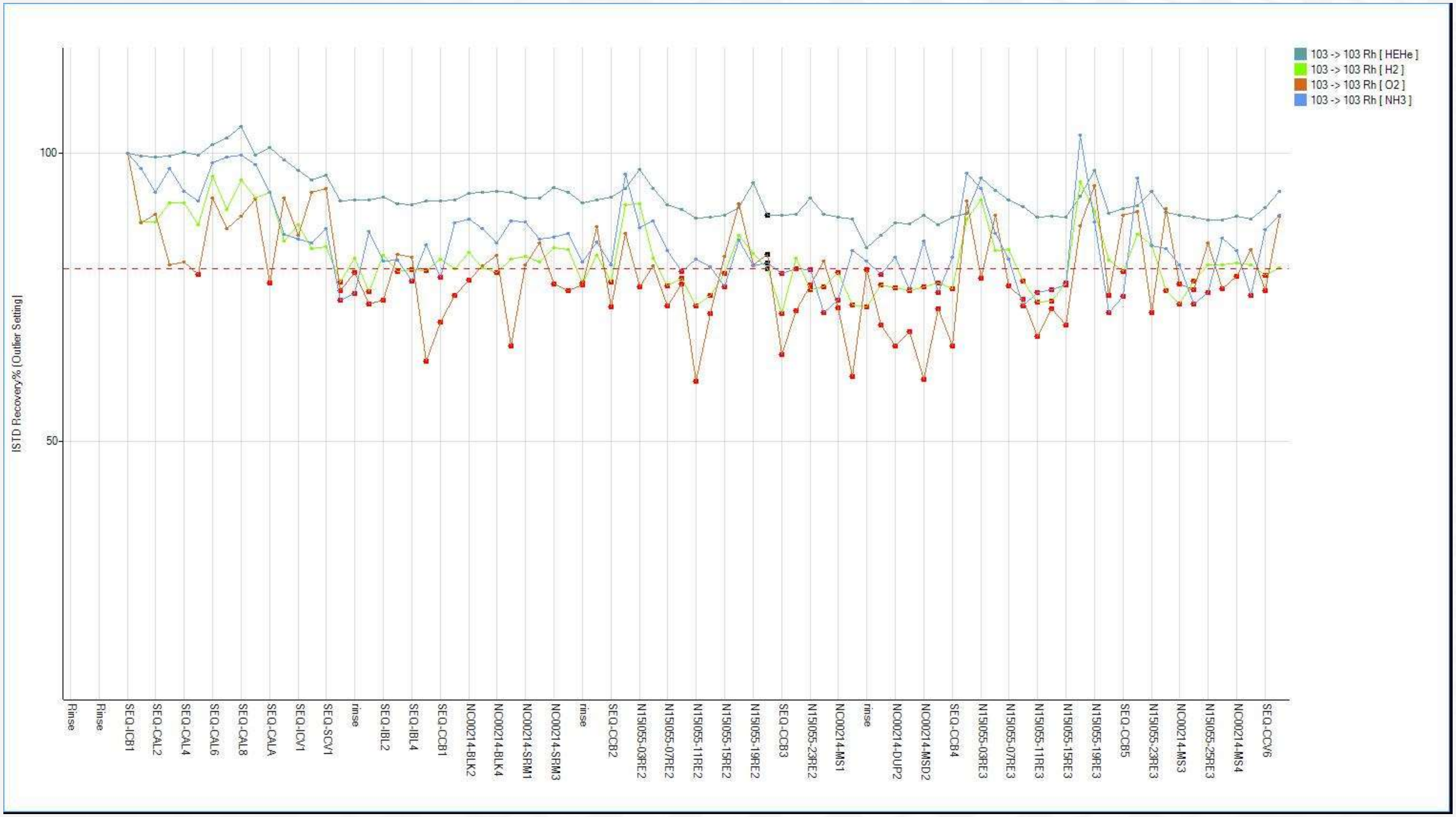



**Figure 1.** Block diagram of HMI component layout.

Agilent online technical library: https://www.agilent.com/cs/library/technicaloverviews/public/5989-7737EN.pdf

# Agilent ICP-QQQ-MS HMI System

## High Matrix Interface



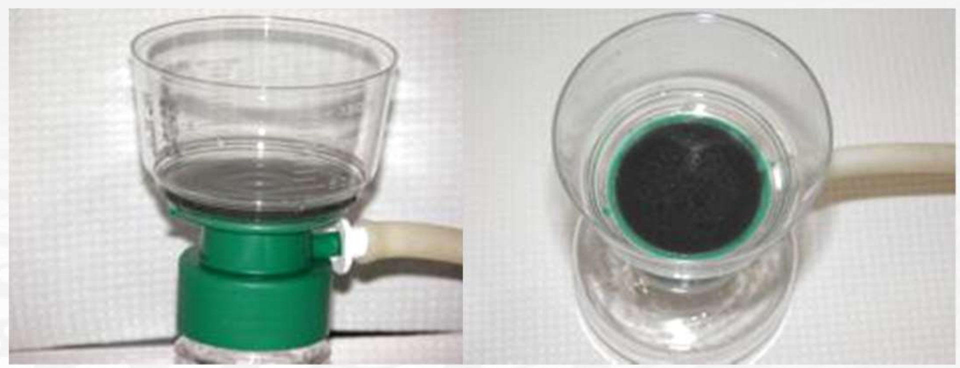
# EPA Method 1640 Overview

- Drafted specifically for seawater analysis by ICP-MS
- Includes several options for preconcentration techniques that also eliminate most matrix interferences
  - Reductive precipitation (RP)
  - Ammonium pyrrolidinedithiocarbamate co-precipitation (APDC)
  - Online column chelation

# APDC and Reductive Precipitation

A preparation technique whereby a catalytic solution of iron and palladium (RP) or cobalt(II) chloride (APDC) is added to the seawater sample, followed by ammonium hydroxide and a borohydride solution, resulting in the precipitation of metals that complex with the reagents.

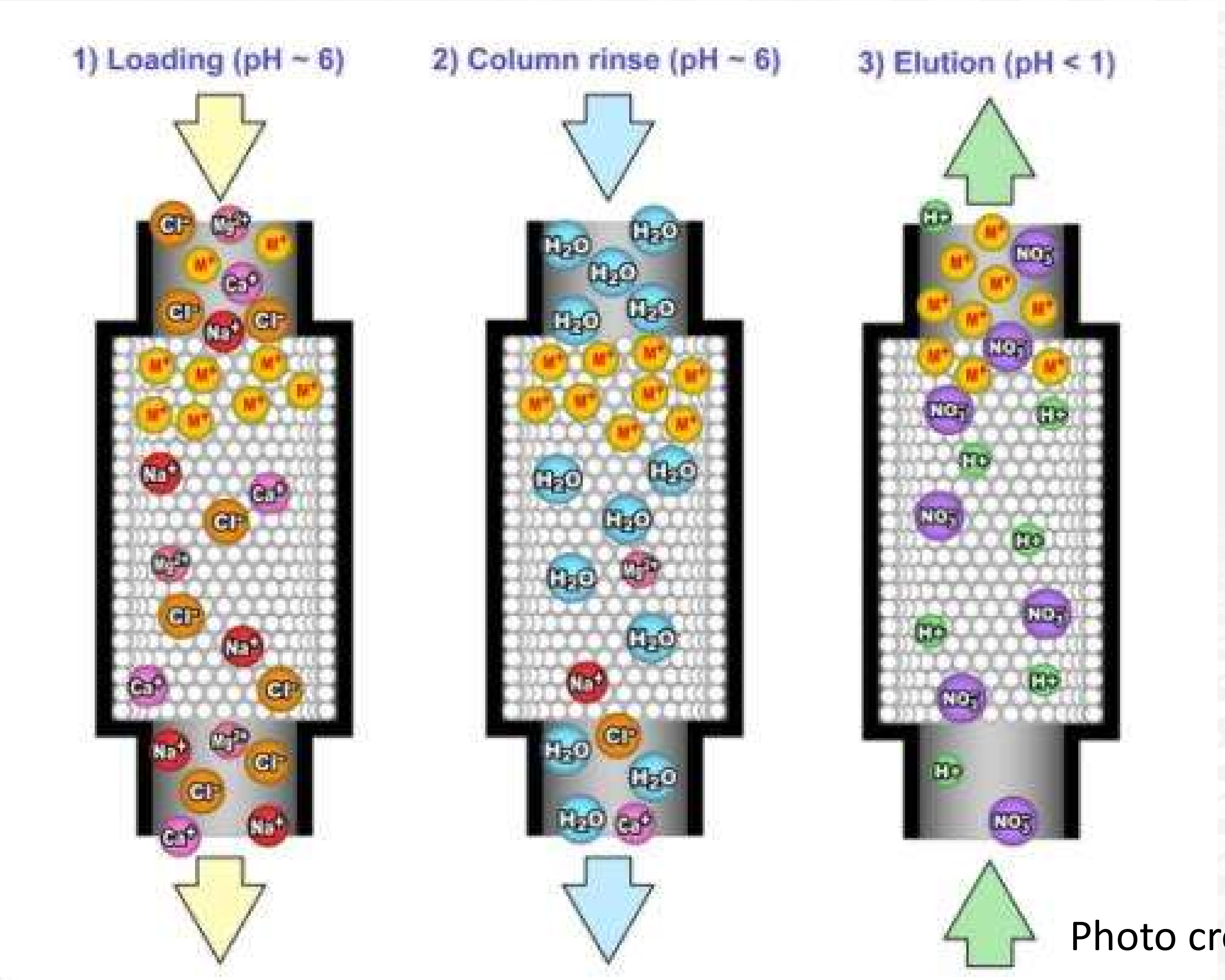
The precipitate is then filtered, allowing the salts and TDS to pass through the filter. The precipitated metals are then re-digested into solution using concentrated nitric acid.



# APDC and Reductive Precipitation Sample Preparation Techniques

- Pros
  - Low detection limits due to preconcentration
  - Removes analyte of interest from saline matrix
- Cons
  - Requires large initial volume
  - Time and labor intensive (off-line)
  - Elevated risk of contamination

# Matrix Removal and Trace Metals Preconcentration Using On-line Column Chelation




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

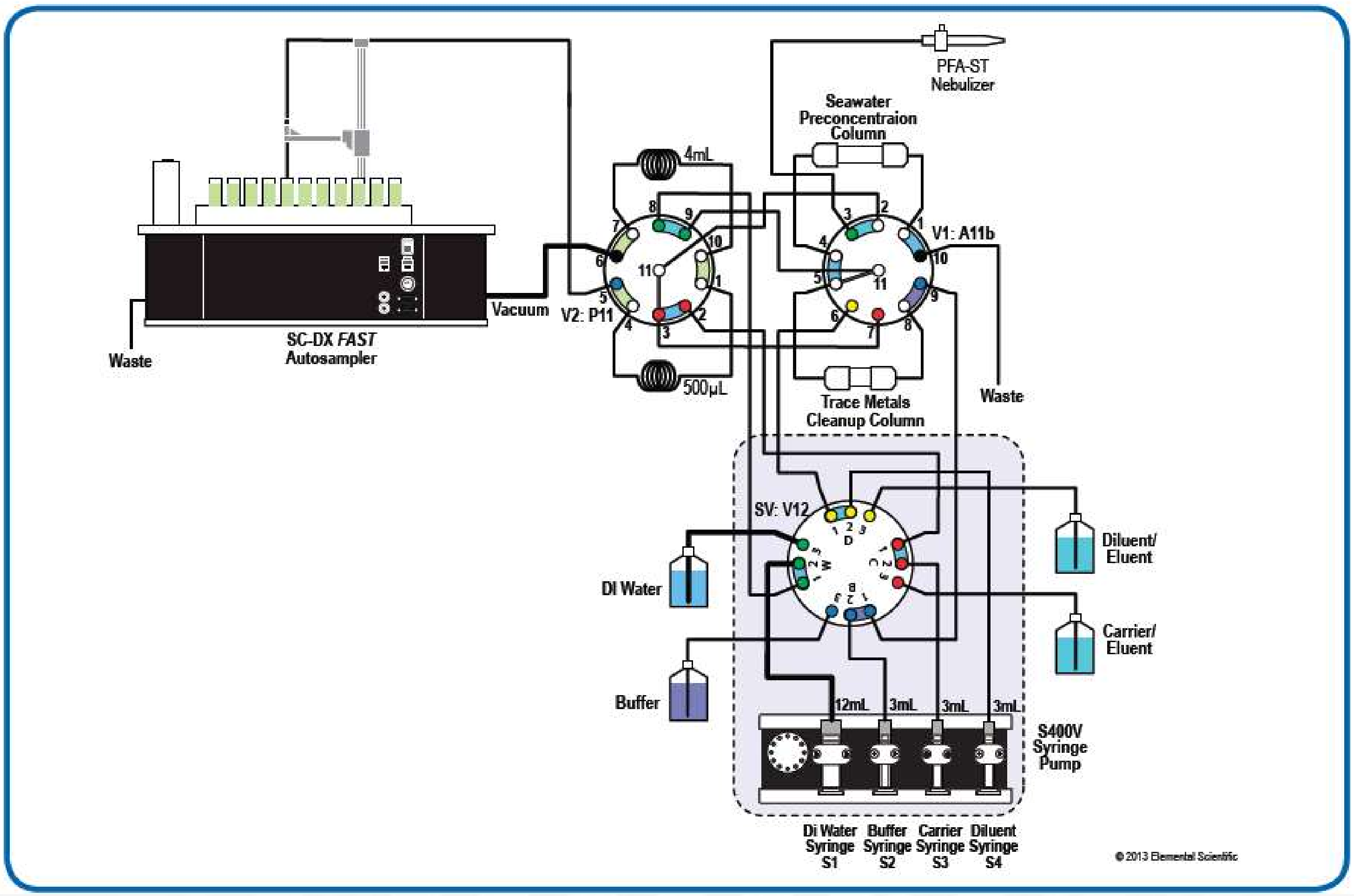
2. The metals of interest are bound to the resin, while salts and other TDS pass through

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

Photo credit: Elemental Scientific Inc.

# ESI SeaFAST - A Complex System

## seaFAST S2 Diagrams



# Common Metals in Seawater

- Typical metals that are accurately quantified by column chelation method:

  Co, Cd, Cu, Fe, Mn, Ni, Pb, V, and Zn

- Not all metals bind efficiently to the column
- What are the improvements possible by using Column Chelation coupled to ICP-QQQ-MS?

# MDLs using Column Chelation coupled to ICP-QQQ-MS

- Analysis of 8 method blanks
- MDL = method blank average + 3x standard deviation of method blanks

| | V | Mn | Co | Ni | Cu | Cd | Pb |
|---|---|---|---|---|---|---|---|
| MDL (ng/L) | 1.6 | 0.37 | 0.094 | 0.30 | 4.26 | 0.026 | 0.017 |

Note change in units from µg/L (parts-per-billion, ppb) to ng/L (parts-per-trillion, ppt)

# Limits of Quantitation (LOQs)

Reality - do lowest calibration points produce acceptable recoveries?

## Calibration Standard Recoveries

| Calibration Point | True value (ng/L) | Zn True value (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 |

# Accuracy of Column Chelation

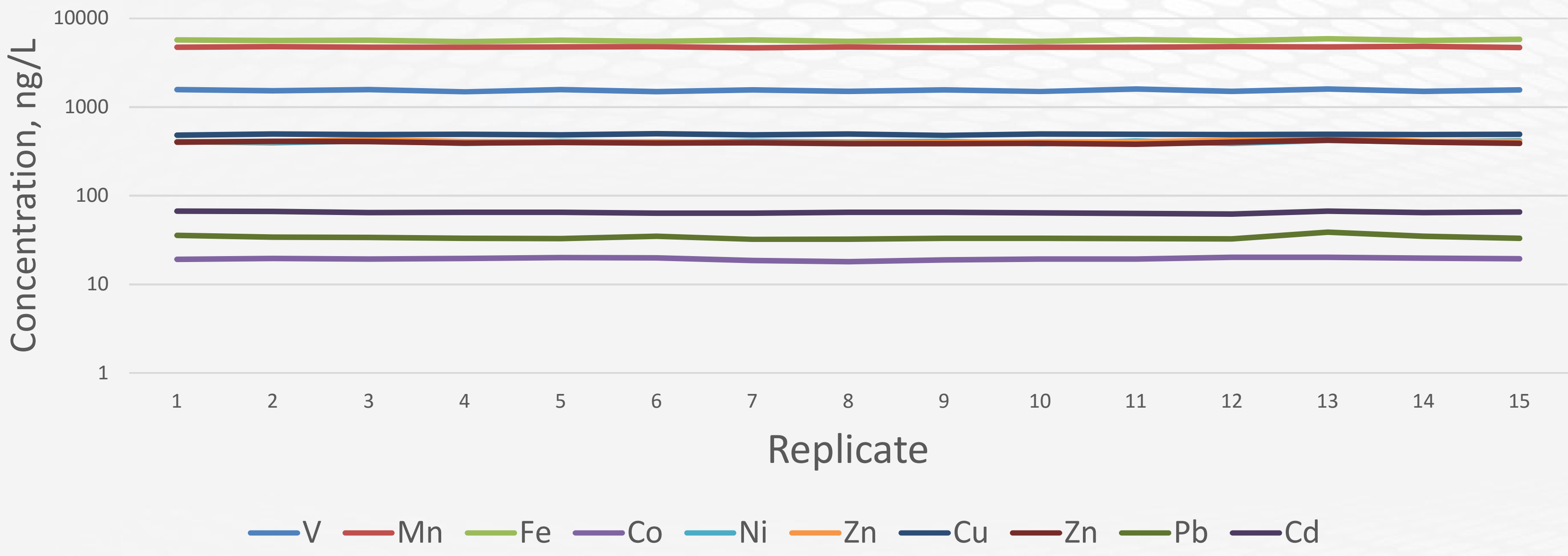
| SLEW-3 (estuarine water CRM from NRCC) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | V | Mn | Fe | Co | Ni | Cu | Zn | Cd |
| Certified Value (ng/L) | 2570 | 1610 | 568 | 42 | 1230 | 1550 | 201 | 48 |
| | | | | | | | | |
| **Analysis** | **Recoveries** | | | | | | | |
| Day1 Rep1 | 106% | 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 | 105% | 104% | 99% | 105% | 106% | 105% | 91% | 104% |

# Accuracy of Column Chelation

| NASS-6 (Nearshore seawater CRM from NRCC) | | | | | | | |
|---|---|---|---|---|---|---|---|
| | V | Mn | Fe | Co | Ni | Cu | Cd |
| Certified Value (ng/L) | 1460 | 530 | 495 | 15 | 301 | 248 | 31 |
| | | | | | | | |
| **Analysis** | **Recoveries** | | | | | | |
| Day1 Rep1 | 83% | 99% | 77% | 108% | 101% | 92% | 101% |
| Day1 Rep2 | 86% | 102% | 84% | 105% | 112% | 95% | 99% |
| Day1 Rep3 | 83% | 105% | 116% | 132% | 110% | 96% | 103% |
| Day1 Rep4 | 89% | 101% | 97% | 107% | 113% | 97% | 88% |
| Day1 Rep5 | 85% | 101% | 83% | 108% | 106% | 95% | 100% |
| Day1 Rep6 | 89% | 101% | 89% | 105% | 111% | 97% | 101% |
| Day1 Rep7 | 88% | 101% | 82% | 105% | 111% | 93% | 94% |
| Day2 Rep1 | 83% | 95% | 76% | 92% | 93% | 93% | 98% |
| Day2 Rep2 | 85% | 92% | 78% | 96% | 95% | 93% | 91% |
| Average | 86% | 100% | 87% | 106% | 106% | 95% | 97% |

# Precision - Stability

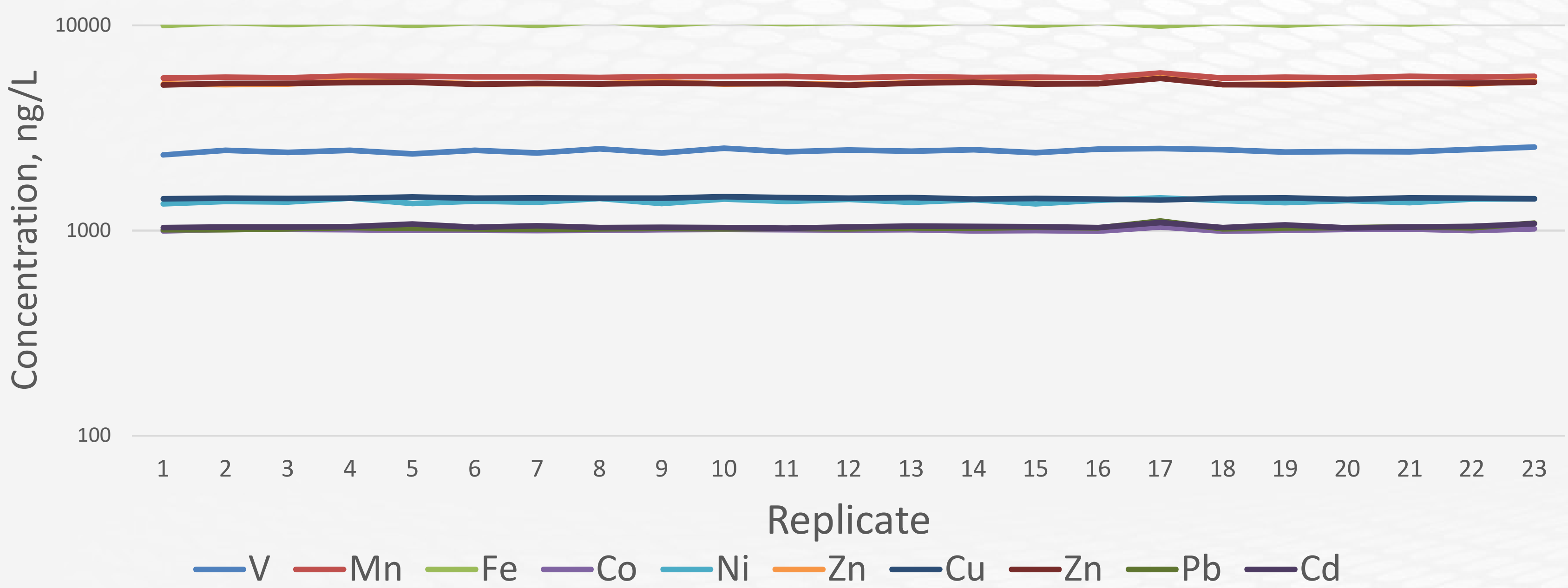
## Multiple injections using ambient seawater from Puget Sound




| | V | Mn | Fe | Co | Ni | Zn | Cu | Zn | Pb | Cd |
|---|---|---|---|---|---|---|---|---|---|---|
| Ave. Conc. (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% |

# Precision - Stability

## Multiple injections using spiked seawater from Puget Sound




| | V | Mn | Fe | Co | Ni | Zn | Cu | Zn | Pb | Cd |
|---|---|---|---|---|---|---|---|---|---|---|
| Ave. Conc. (ng/L) | 2445 | 5608 | 10222 | 1006 | 1393 | 5233 | 1436 | 5215 | 1030 | 1045 |
| Standard Deviation | 53 | 65 | 187 | 10 | 30 | 95 | 12 | 81 | 24 | 17 |
| RSD | 2% | 1% | 2% | 1% | 2% | 2% | 1% | 2% | 2% | 2% |

# Matrix Effects

## Evaluating matrix effects using spiked samples

**(Replicate concentration - Mean assigned concentration) / Spike concentration**

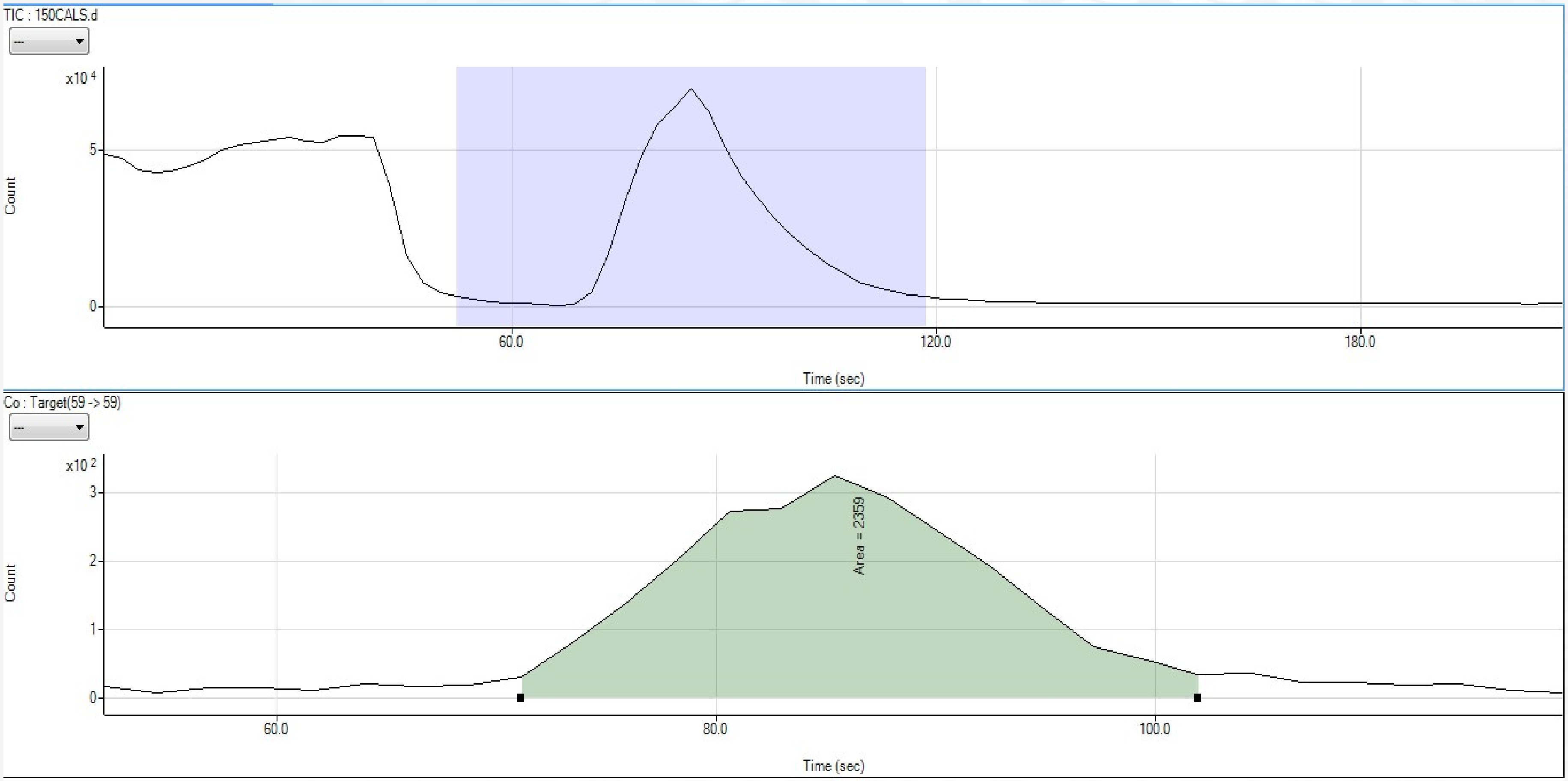
| Replicate | V | Mn | Fe | Co | Ni | Zn | Cu | Zn | Pb | Cd |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 79% | 79% | 87% | 97% | 94% | 95% | 94% | 95% | 97% | 97% |
| 2 | 91% | 84% | 94% | 99% | 98% | 95% | 95% | 96% | 98% | 97% |
| 3 | 86% | 81% | 89% | 99% | 97% | 95% | 94% | 96% | 98% | 97% |
| 4 | 92% | 91% | 94% | 99% | 103% | 99% | 95% | 97% | 100% | 98% |
| 5 | 82% | 89% | 87% | 98% | 95% | 97% | 96% | 98% | 99% | 101% |
| 6 | 91% | 85% | 94% | 98% | 99% | 96% | 95% | 95% | 99% | 97% |
| 7 | 84% | 85% | 87% | 98% | 97% | 96% | 95% | 96% | 98% | 99% |
| 8 | 96% | 83% | 96% | 98% | 103% | 96% | 94% | 95% | 98% | 97% |
| 9 | 84% | 88% | 87% | 99% | 95% | 98% | 95% | 97% | 99% | 97% |
| 10 | 97% | 88% | 96% | 99% | 102% | 95% | 97% | 96% | 98% | 97% |
| 11 | 88% | 90% | 91% | 99% | 98% | 96% | 95% | 96% | 99% | 96% |
| 12 | 93% | 81% | 94% | 99% | 102% | 95% | 95% | 94% | 99% | 97% |
| 13 | 89% | 87% | 89% | 99% | 97% | 97% | 96% | 97% | 99% | 99% |
| 14 | 93% | 82% | 97% | 98% | 101% | 98% | 93% | 98% | 99% | 98% |
| 15 | 85% | 84% | 87% | 98% | 94% | 96% | 94% | 95% | 100% | 98% |
| 16 | 95% | 81% | 95% | 97% | 100% | 96% | 93% | 96% | 100% | 97% |
| 17 | 97% | 111% | 86% | 102% | 104% | 103% | 92% | 102% | 108% | 103% |
| 18 | 93% | 79% | 94% | 97% | 99% | 95% | 94% | 95% | 98% | 97% |
| 19 | 87% | 85% | 88% | 98% | 96% | 95% | 95% | 95% | 100% | 100% |
| 20 | 89% | 80% | 95% | 99% | 99% | 95% | 93% | 96% | 100% | 97% |
| 21 | 88% | 90% | 90% | 100% | 96% | 97% | 95% | 96% | 101% | 98% |
| 22 | 94% | 84% | 96% | 98% | 102% | 95% | 94% | 97% | 100% | 98% |
| 23 | 101% | 90% | 95% | 100% | 102% | 99% | 94% | 98% | 105% | 101% |
| Mean Recovery | 90% | 86% | 92% | 99% | 99% | 96% | 95% | 96% | 100% | 98% |

# Advantages of Using the ESI SeaFAST Coupled to the Agilent 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

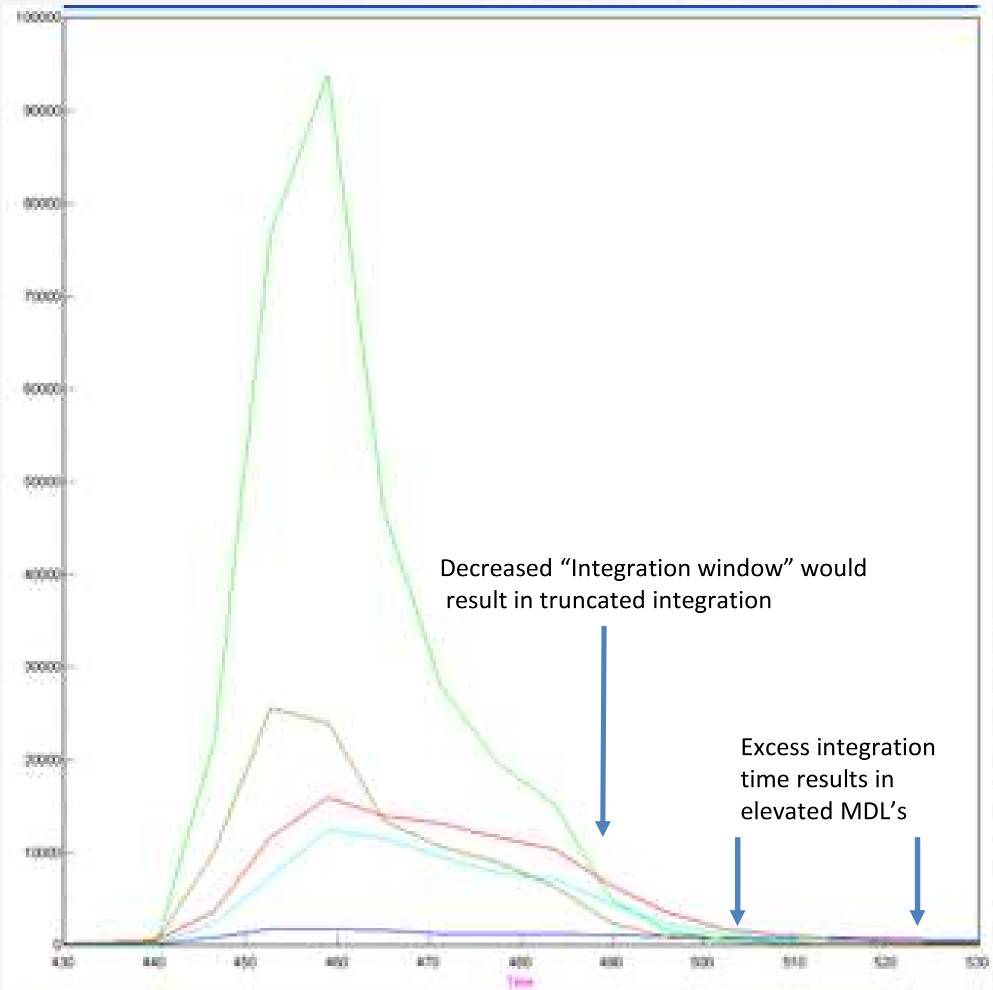
# Data Processing

## Peak integration on ICP-QQQ-MS with Mass Hunter



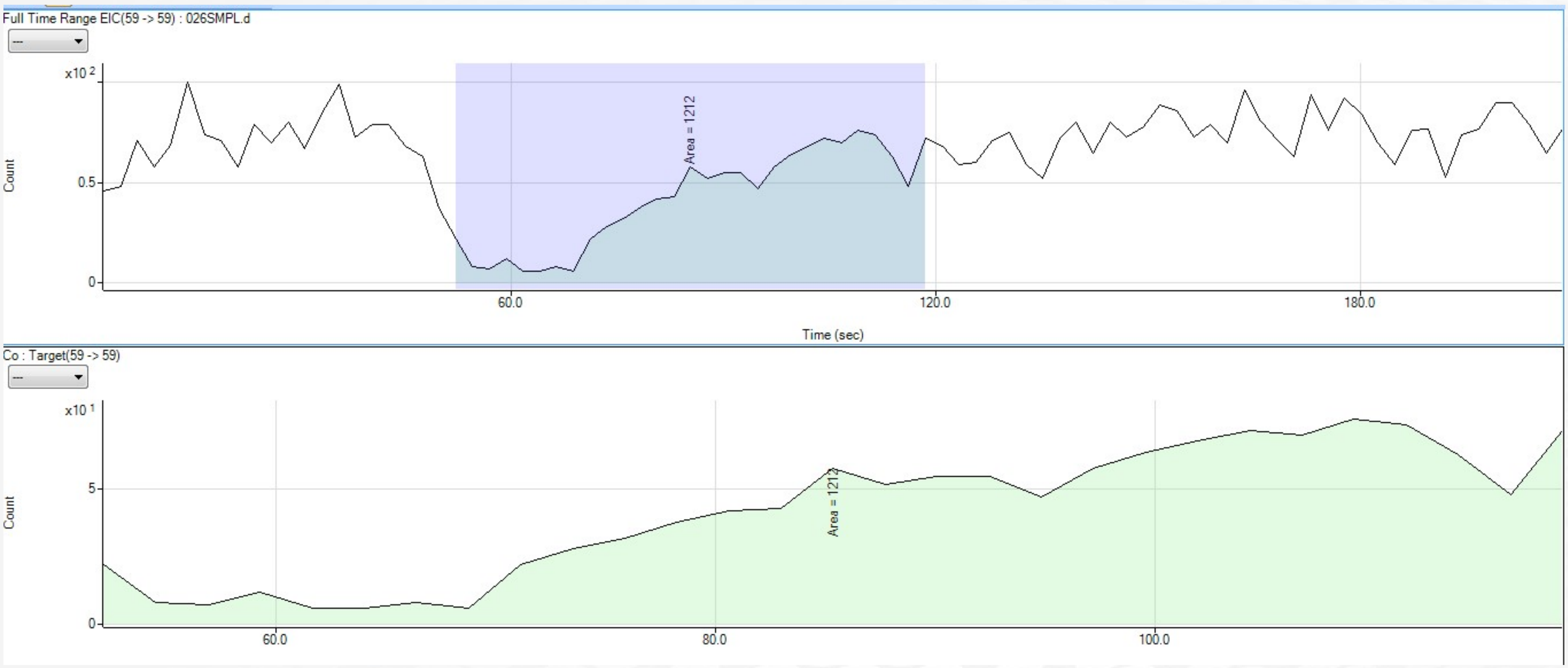

Peak integration is completely customizable per analyte per injection for best fit, resulting in lower detection limits

# Data Processing




- Using other ICP-MS software, “peak integration” is predefined regardless of peak size or retention time
- Excess integration time can increase detection limits
- Short integration time can cause peak cut-off resulting in low-biased data

# Low Background on the ICP-QQQ-MS



# Ahead of the Curve

## Rare Earth by Column Chelation

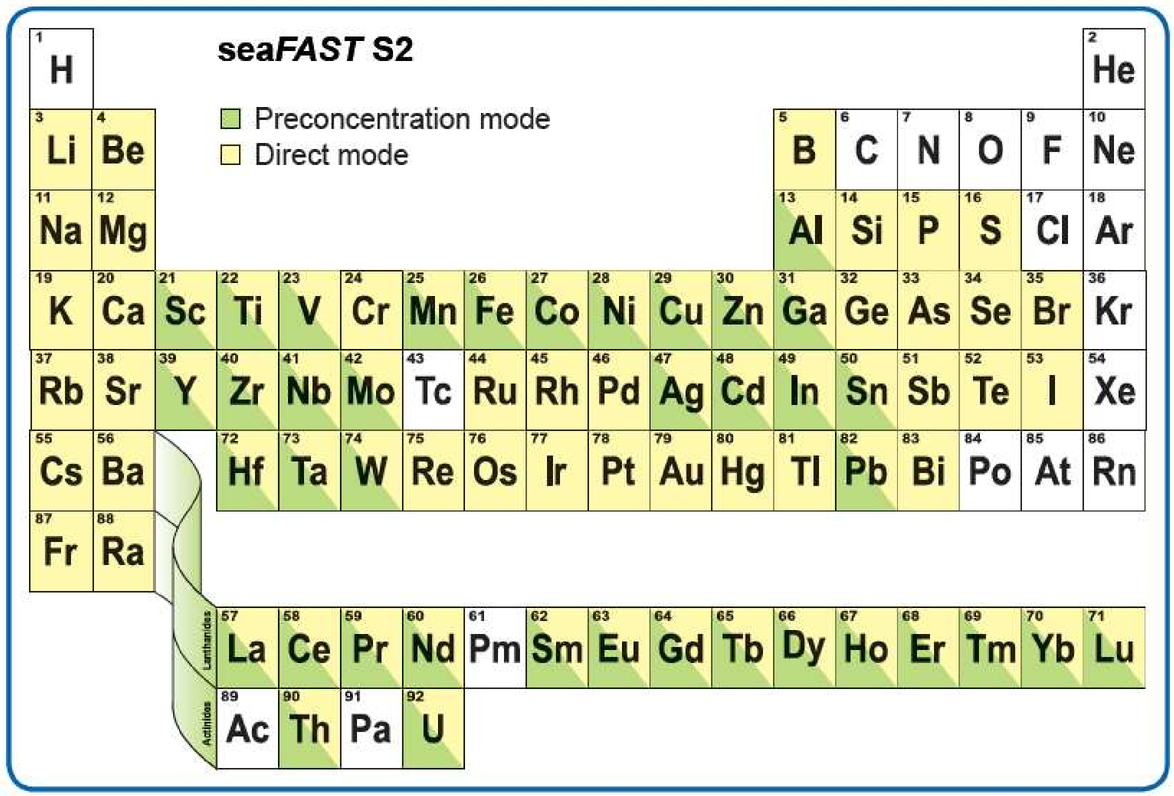



**Diagram 1.** Elements analyzed using the sea*FAST* S2 system

# Why?

- Deep sea mining regulation
  - International seabed authority
  - Earth magazine
- Evaluation of REE concentrations in all aqueous matrices need ultra-low level detection limits

1. http://www.isa.org.jm/files/documents/EN/Seminars/2012/Hein-2.pdf
2. http://www.earthmagazine.org/article/staking-claim-deep-sea-mining-nears-fruition

# MDLs

## In parts-per-quadrillion (ppq)

- Analysis of 8 method blanks
- MDL = method blank average + 3x standard deviation of method blanks

| | La | Ce | Sm | Eu | Gd | Tb | Dy | Ho | Er | Yb | Lu |
|---|---|---|---|---|---|---|---|---|---|---|---|
| MDL (pg/L) | 1.6 | 3.8 | 2.3 | 1.4 | 0.8 | 2.7 | 2.6 | 3.4 | 3.2 | 0.4 | 2.2 |

# LOQs

## Recovery of lowest calibration points

| Calibration Point | True Value (pg/L) | | La | Ce | Sm | Eu | Gd | Tb | Dy | Ho | Er | Yb | Lu |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 100 | | 80% | 58% | 78% | 53% | 107% | 103% | 76% | 95% | 100% | 96% | 79% |
| 2 | 200 | | 91% | 92% | 94% | 52% | 102% | 89% | 119% | 102% | 96% | 73% | 85% |
| 3 | 500 | | 97% | 106% | 126% | 89% | 98% | 113% | 117% | 107% | 98% | 72% | 89% |
| 4 | 1000 | | 104% | 97% | 96% | 94% | 110% | 96% | 107% | 101% | 97% | 91% | 97% |
| 5 | 5000 | | 111% | 114% | 87% | 102% | 101% | 98% | 98% | 103% | 98% | 108% | 103% |
| 6 | 10000 | | 101% | 100% | 103% | 100% | 99% | 100% | 100% | 100% | 100% | 108% | 99% |
| | | | | | | | | | | | | | |
| Blank | BEC | | 78 | 136 | 6 | 0 | 9 | 6 | 30 | 0 | 13 | 0 | 2 |

# Accuracy

## SLEW-3 Estuarine Water CRM (non-certified values)

| Reference Values (ng/L) | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 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 |
| **Recoveries** | | | | | | | | | | | | |
| 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 | 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/

# Accuracy

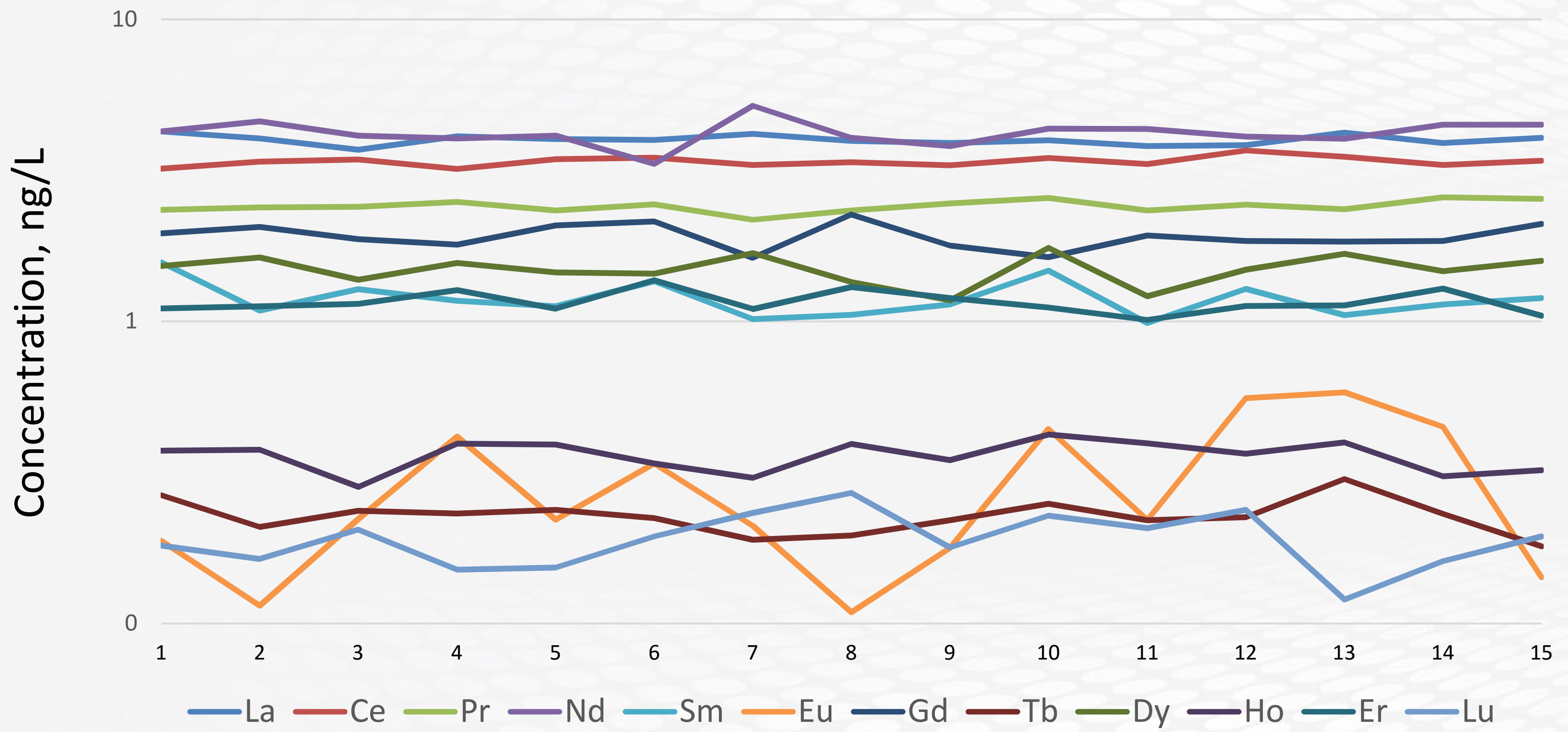
## NASS-6 Seawater CRM (non-certified values)

| Reference Values (ng/L) | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | La | Ce | Nd | Sm | Eu | Gd | Tb | Dy | Ho | Er | Yb | Lu |
| | 12.700 | 6.200 | 6.000 | 0.810 | 0.200 | 1.000 | 0.200 | 1.600 | 0.310 | 1.700 | 1.300 | 0.260 |
| **Recoveries** | | | | | | | | | | | | |
| Rep 1 | 76% | 60% | 92% | 177% | 114% | 154% | 120% | 106% | 116% | 77% | 208% | 108% |
| Rep 2 | 80% | 67% | 107% | 171% | 370% | 156% | 126% | 92% | 145% | 77% | 47% | 83% |
| Rep 3 | 86% | 78% | 133% | 90% | 238% | 229% | 97% | 97% | 108% | 78% | 116% | 37% |
| Rep 4 | 81% | 64% | 112% | 127% | 182% | 146% | 89% | 90% | 127% | 76% | 111% | 74% |
| Rep 5 | 81% | 68% | 109% | 150% | 57% | 130% | 95% | 97% | 114% | 79% | 104% | 87% |
| Rep 6 | 82% | 69% | 120% | 149% | 74% | 131% | 140% | 89% | 120% | 77% | 79% | 92% |
| Rep 7 | 81% | 69% | 95% | 142% | 167% | 129% | 110% | 78% | 132% | 81% | 124% | 104% |
| Rep 8 | 78% | 61% | 119% | 150% | 106% | 150% | 101% | 96% | 120% | 74% | 82% | 75% |
| Rep 9 | 77% | 62% | 102% | 125% | 243% | 137% | 108% | 102% | 130% | 75% | 56% | 55% |
| Average | 80% | 66% | 110% | 142% | 172% | 151% | 110% | 94% | 124% | 77% | 103% | 80% |

**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/

# Precision – Stability for REEs

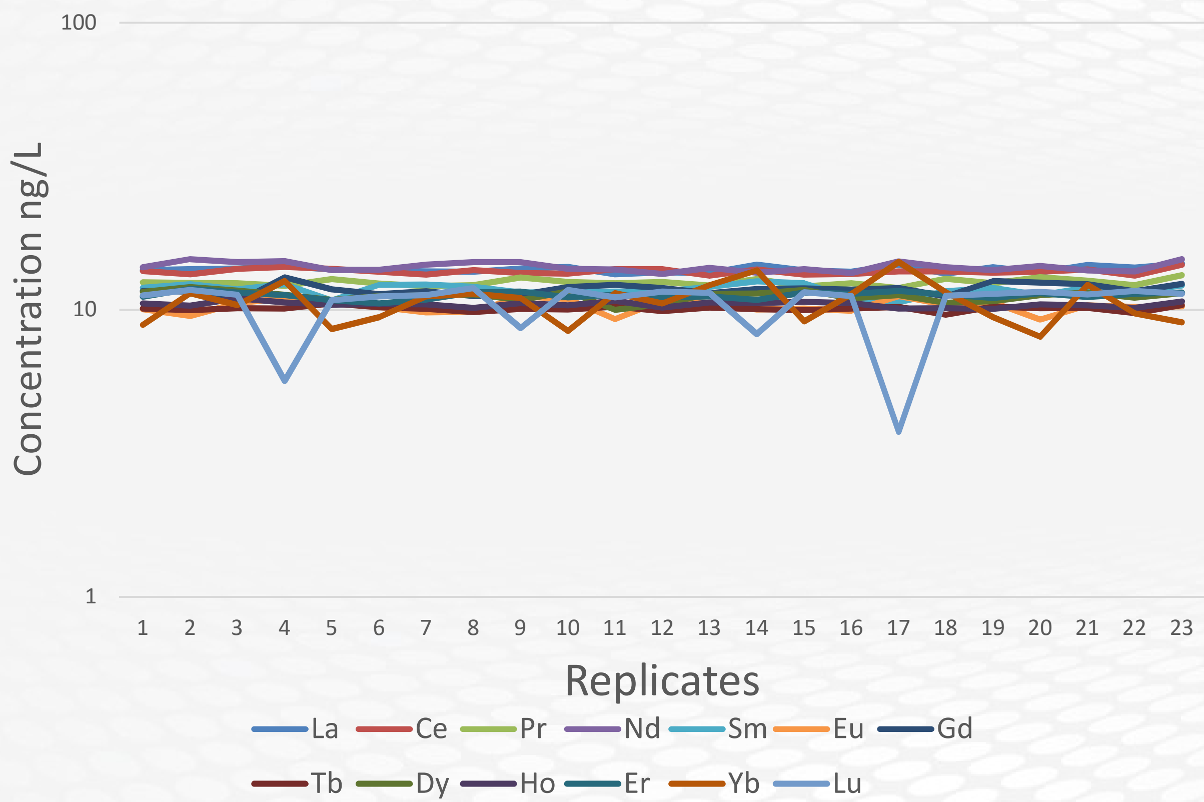
## Multiple injections using ambient seawater from Puget Sound




| | La | Ce | Pr | Nd | Sm | Eu | Gd | Tb | Dy | Ho | Er | Yb | Lu |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ave., ng/L | 4.0 | 3.4 | 2.4 | 4.2 | 1.2 | 0.3 | 1.9 | 0.2 | 1.5 | 0.4 | 1.2 | 1.0 | 0 |
| SD | 0.15 | 0.13 | 0.11 | 0.41 | 0.17 | 0.16 | 0.18 | 0.03 | 0.17 | 0.04 | 0.10 | 0.51 | 0 |
| RSD | 4% | 4% | 4% | 10% | 14% | 54% | 10% | 13% | 11% | 12% | 9% | 50% | 21% |

# Precision – Stability for REEs

## Multiple injections using spiked seawater from Puget Sound




| | La | Ce | Pr | Nd | Sm | Eu | Gd | Tb | Dy | Ho | Er | Yb | Lu |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ave., ng/L | 14 | 14 | 12 | 14 | 12 | 10 | 12 | 10 | 11 | 10 | 11 | 11 | 11 |
| SD | 0.3 | 0.3 | 0.3 | 0.5 | 0.5 | 0.5 | 0.5 | 0.2 | 0.5 | 0.2 | 0.3 | 1.7 | 2.1 |
| RSD | 2% | 2% | 3% | 4% | 4% | 5% | 4% | 2% | 4% | 2% | 3% | 16% | 20% |

# Matrix Effects

## Evaluating matrix effects using analytical spikes

**(Replicate concentration - Mean assigned concentration) / Spike concentration**

| Replicate | La | Ce | Pr | Nd | Sm | Eu | Gd | Tb | Dy | Ho | Er | Yb | Lu |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 98% | 103% | 101% | 99% | 108% | 98% | 97% | 99% | 101% | 102% | 100% | 79% | 110% |
| 2 | 99% | 99% | 100% | 108% | 111% | 92% | 97% | 98% | 105% | 100% | 107% | 104% | 116% |
| 3 | 99% | 105% | 100% | 105% | 106% | 103% | 87% | 99% | 102% | 106% | 103% | 94% | 111% |
| 4 | 102% | 107% | 97% | 106% | 111% | 107% | 111% | 99% | 98% | 103% | 101% | 116% | 55% |
| 5 | 98% | 105% | 104% | 96% | 96% | 103% | 99% | 103% | 93% | 101% | 96% | 76% | 106% |
| 6 | 98% | 102% | 100% | 96% | 110% | 99% | 94% | 100% | 97% | 101% | 94% | 84% | 110% |
| 7 | 96% | 99% | 97% | 102% | 111% | 95% | 97% | 99% | 98% | 101% | 97% | 101% | 111% |
| 8 | 96% | 104% | 98% | 105% | 109% | 96% | 93% | 96% | 98% | 98% | 104% | 104% | 117% |
| 9 | 100% | 101% | 106% | 105% | 103% | 109% | 94% | 98% | 93% | 102% | 104% | 100% | 85% |
| 10 | 101% | 100% | 101% | 97% | 104% | 106% | 101% | 98% | 101% | 100% | 99% | 74% | 115% |
| 11 | 93% | 105% | 100% | 96% | 104% | 90% | 103% | 101% | 85% | 104% | 101% | 104% | 109% |
| 12 | 95% | 105% | 101% | 91% | 104% | 105% | 100% | 97% | 90% | 98% | 99% | 95% | 114% |
| 13 | 95% | 98% | 98% | 98% | 108% | 103% | 95% | 100% | 99% | 103% | 100% | 112% | 113% |
| 14 | 104% | 105% | 104% | 93% | 114% | 97% | 99% | 98% | 99% | 102% | 97% | 127% | 80% |
| 15 | 97% | 99% | 97% | 97% | 112% | 98% | 100% | 98% | 102% | 103% | 103% | 81% | 113% |
| 16 | 96% | 100% | 100% | 92% | 98% | 96% | 98% | 99% | 95% | 102% | 102% | 103% | 110% |
| 17 | 104% | 102% | 95% | 105% | 95% | 109% | 100% | 100% | 98% | 98% | 105% | 137% | 36% |
| 18 | 94% | 102% | 104% | 99% | 104% | 101% | 92% | 94% | 91% | 98% | 102% | 105% | 110% |
| 19 | 101% | 101% | 100% | 96% | 107% | 103% | 107% | 100% | 92% | 97% | 98% | 84% | 112% |
| 20 | 95% | 102% | 106% | 100% | 101% | 90% | 105% | 99% | 98% | 101% | 103% | 70% | 114% |
| 21 | 103% | 105% | 102% | 95% | 107% | 101% | 104% | 99% | 100% | 100% | 99% | 112% | 111% |
| 22 | 100% | 98% | 98% | 94% | 104% | 99% | 97% | 95% | 95% | 98% | 102% | 87% | 115% |
| 23 | 105% | 110% | 108% | 108% | 110% | 100% | 104% | 102% | 99% | 104% | 103% | 80% | 112% |
| Average | 99% | 102% | 101% | 99% | 106% | 100% | 99% | 99% | 97% | 101% | 101% | 97% | 104% |

# Summary

## Merits of EPA 1640 column chelation coupled to ICP-QQQ-MS

- Undiluted analysis of seawater samples
- Preconcentration yields extremely low detection limits of typical metals (ng/L)
- Effective matrix and interference removal
- Accurate and precise analysis of seawater
- Future potential of extremely low detection limits for select REE metals (pg/L)

# Questions?

Thank you!!

Agilent, ESI, Brooks Applied Labs, and the Audience