Elemental Scientific

sea*FAST*

Automating Seawater Analysis

seaFAST Brief and System Schematics

Brief

The seaFAST is a high performance, automated sample introduction system for the determination of ultra-trace metals in undiluted seawater and other high matrix samples. It lowers procedural blanks and improves detection limits for a variety of elements through syringe-based sample preconcentration and matrix elimination.

seaFAST Systems

- Fully automated software control
- Seamlessly integrated with ICPMS
- Syringe controlled volumes and flow rates
- Inert fluoropolymer flow paths
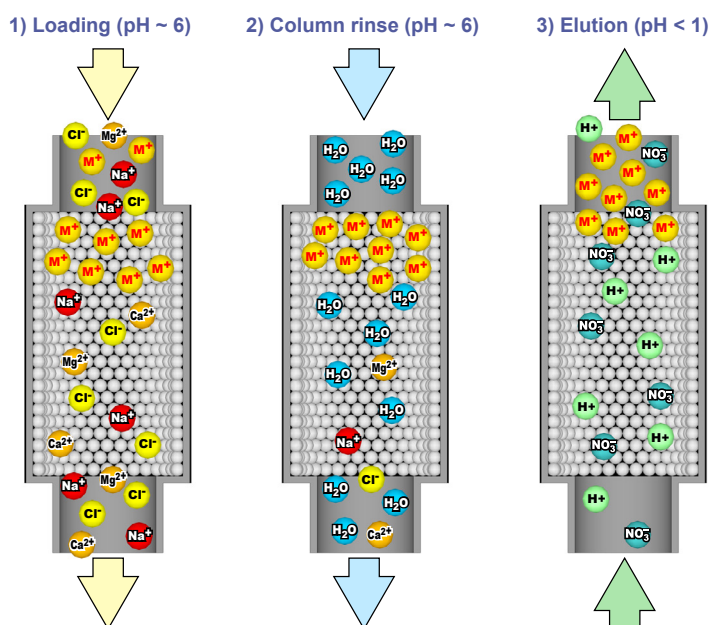- High sample capacity

seaFAST
Preconcentration
Column

1) Loading (pH ~ 6) 2) Column rinse (pH ~ 6) 3) Elution (pH < 1)

Figure 1. Image and schematic of the seaFAST preconcentration column. At a pH ~6, transition row metals are chelated on the preconcentration column, while matrix elements (group 1 and 2) are flushed from the column.

sea*FAST* S2

Dual mode operation allows undiluted samples to be measured directly with a user-specified dilution while loading an aliquot of sample onto a column for automated, inline preconcentration and matrix removal.

Inline

- Elutes sample directly to ICPMS
- Real time data
- High preconcentration factors
- Dual mode operation
- <9 min/sample
- Offline Mode

Offline

- Collects samples for analysis
- Standalone operation
- Steady state signal
- User defined load and elute volumes
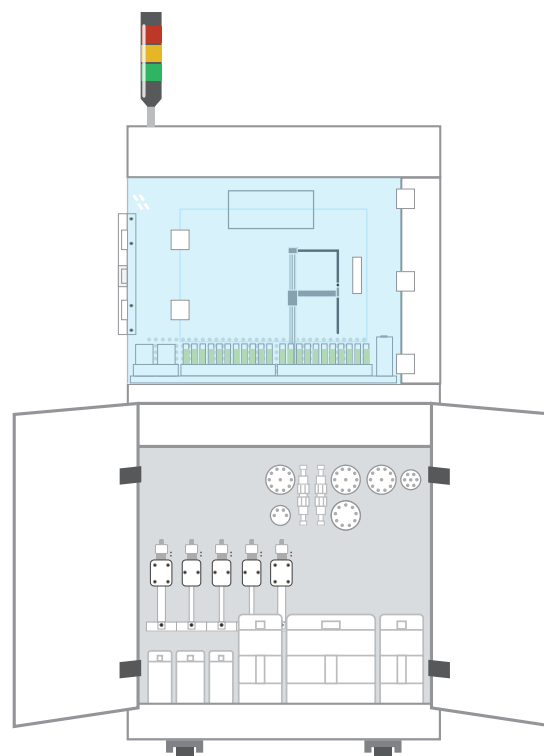- 15 min/sample
- Inline mode for method development

**Figure 2.** sea*FAST* S2 system with integrated mobile stand

sea*FAST* Systems

Features	S2	SP2	SP3
Integrated Mobile Autosampler & Enclosure	✓	✓	✓
Offline Preconcentration	✓	✓	✓
Online Preconcentration	✓	✓	✓
Direct Mode Static Inline Dilution	✓	✓	✓
Hydride Mode			✓
Autocalibration		✓	✓
Autodilution		✓	✓
Auto Matrix Matching		✓	✓

S2: REEs in Seawater

Offline Application

Accurate and precise quantification of Rare Earth Elements (REEs) in open ocean seawater remains a difficult task. This is due to low dissolved analyte concentration (10s of pg L^{-1}), BaO^+ interferences, and a complex matrix (3.5% TDS). The seaFAST S2™ is an ultra-clean, automated, low-pressure ion chromatography system capable of single digit picogram L^{-1} detection limits. In an offline configuration, the automated system buffers user defined volumes (10 to 100 mL) of acidified seawater before loading it onto a column. The matrix is then removed and the concentrated sample is eluted in user defined volumes (250 to 1000 µL) of acid. Rapid sample loading rates combined with low elution volumes provides high concentration factors and unprecedented detection limits (pg L^{-1}).

BATS 20 M
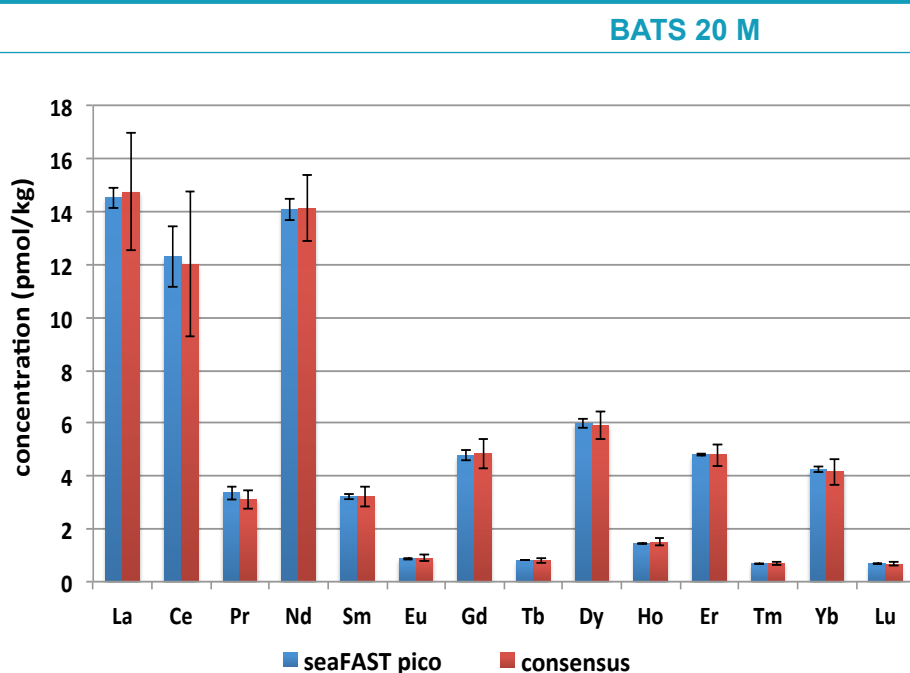
In collaboration with:

Max Planck Research Group for Marine Isotope Geochemistry

Institute for Chemistry and Biology of the Marine Environment (ICBM)

Katharine Pahnke, Melanie Behrens, & Ronja Paffrath

Figure 3. Single digit picomolar (<1 to 15 pM) concentrations of REEs are routinely determined in surface samples (20 M) from the Bermuda Atlantic Time-series Station (BATS). The error bars (2 SD) illustrate the precision of the method, whereas accuracy is demonstrated through agreement with consensus values. Data courtesy of Katharine Pahnke, Melanie Behrens and Ronja Paffrath, Max Planck Research Group for Marine Isotope Geochemistry.
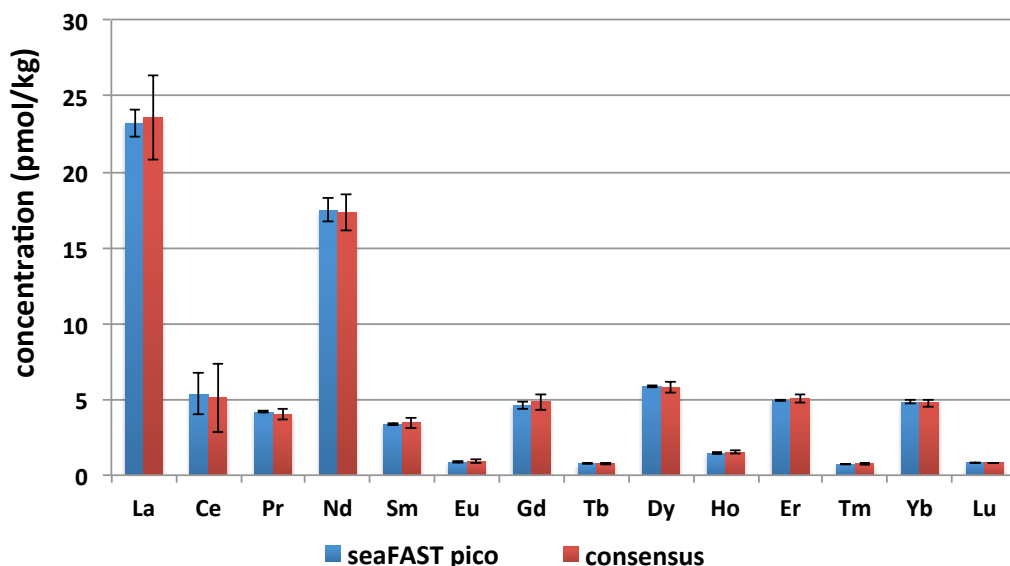
S2: REEs in Seawater

BATS 2000 M

Figure 4. Similar to Figure 3, REEs determined and consensus concentrations for a deep sample (2000 M) from the Bermuda Atlantic Time-series Station (BATS) are plotted. The error bars (2 SD) illustrate the precision of the method, whereas accuracy is demonstrated through agreement with consensus values. Data courtesy of Katharine Pahnke, Melanie Behrens and Ronja Paffrath, Max Planck Research Group for Marine Isotope Geochemistry.
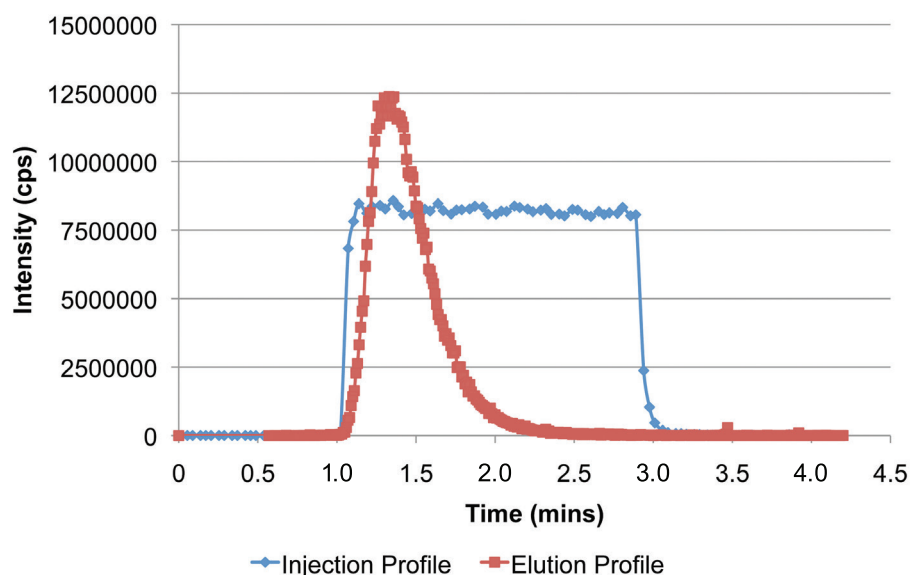
Injection and Elution Profile for Ce

Figure 5. A comparison of a sea*FAST* S2 inline elution profile with a sea*FAST* S2 offline injection is shown above. Offline fraction collection of programmable elution volume is injected to the ICPMS with a micro*FAST* system. A profile collected from a sample eluted in 200 μL and introduced at 100 μL min^{-1} illustrates two minutes of steady state signal.

Quantitative Recovery for a Range of Elution Volumes

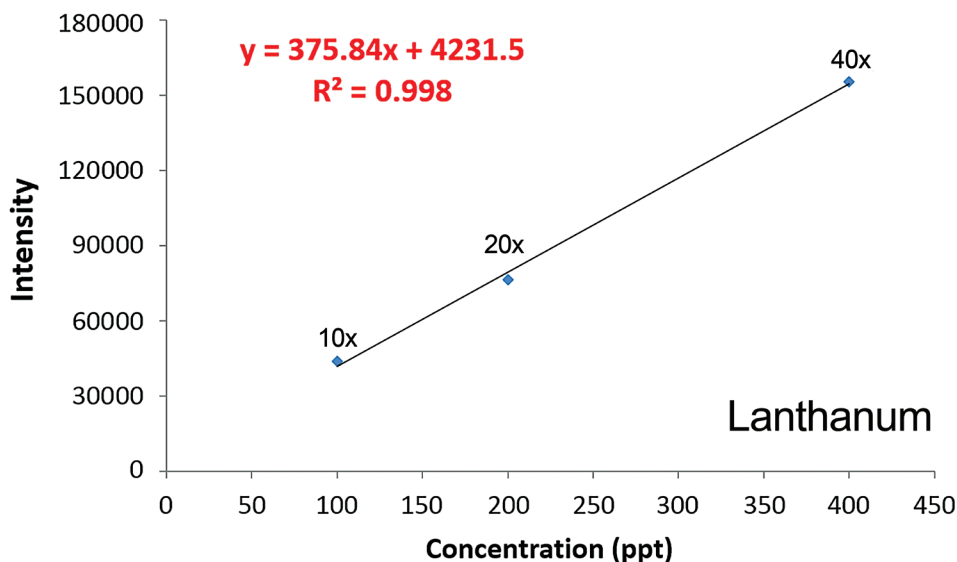$$y = 375.84x + 4231.5$$
$$R^2 = 0.998$$

Figure 6. By adjusting elution volume (1000, 500, to 250 µL), 10 mL of Indian Ocean surface water (with 10 ppt REE spike) is concentrated 10, 20, and 40x. A linear correlation between concentration and intensity indicates that even 250 µLs is sufficient for quantitative recovery.

Quantitative Recovery for a Range of Sample Volumes
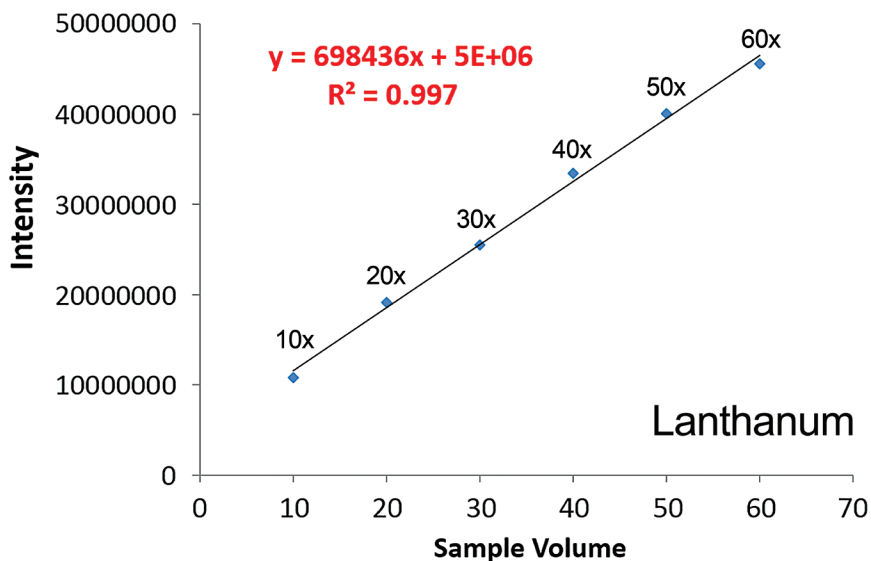

$$y = 698436x + 5E+06$$
$$R^2 = 0.997$$

Figure 7. By adjusting sample volume (10-60 mL), Indian Ocean surface water (with 10 ppt REE spike) eluted in 1 mL is concentrated 10-60x. A linear correlation between concentration and intensity indicates the columns capacity to process large volume samples with quantitative recovery.

S2: REEs in Seawater
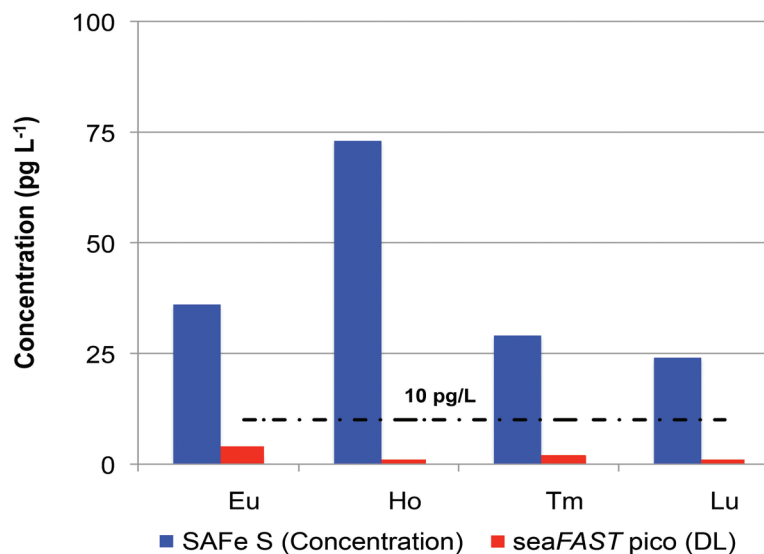
LODs of Selected REEs

Figure 8. Limits of detection are compared to SAFe surface water concentrations. Matrix removal combined with a 20-fold preconcentration factor is sufficient to determine the lowest level of REEs in open ocean seawater.
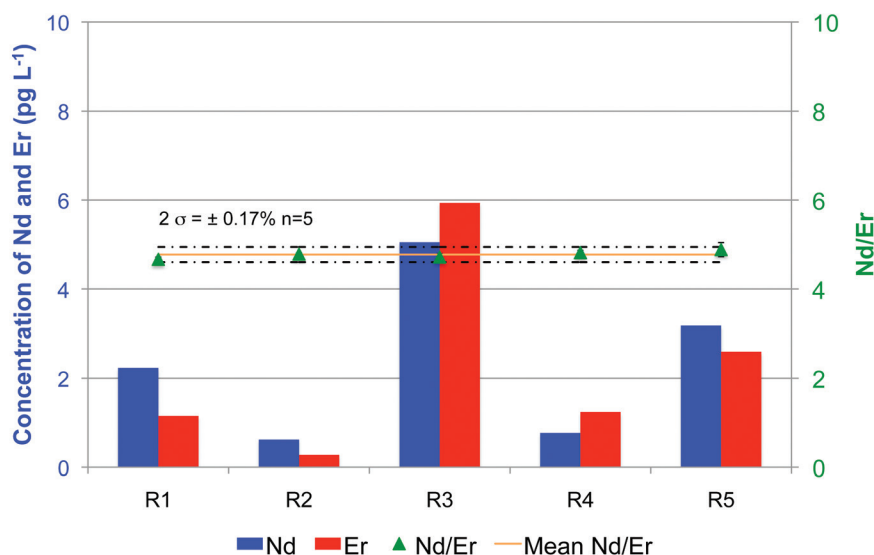
NASS-6 Precision

Figure 9. The interpretation of dissolved REEs requires high quality concentration values from which very precise patterns and elemental ratios can be determined. Three NASS-6 replicates, run on five different analytical dates, indicate good precision for concentration data and better than ±3.5% (2-sigma) for LREE/HREE (Nd/Er) ratios.

S2: Trace Metals in Seawater

Offline Application

Accurate and precise quantification of transition row metals in seawater remains a difficult task due to low dissolved analyte concentration (10s of ng L^{-1}), a complex matrix (3.5% TDS) and difficulty obtaining low procedural blanks. The sea*FAST* S2™ is an ultra-clean, fully automated system with a flouropolymer flow path that reduces blanks by minimizing sample exposure and handling. Rapid sample loading rates combined with small elution volumes provide high concentration factors (~20-100 fold) and unprecedented detection limits (pg L^{-1}).
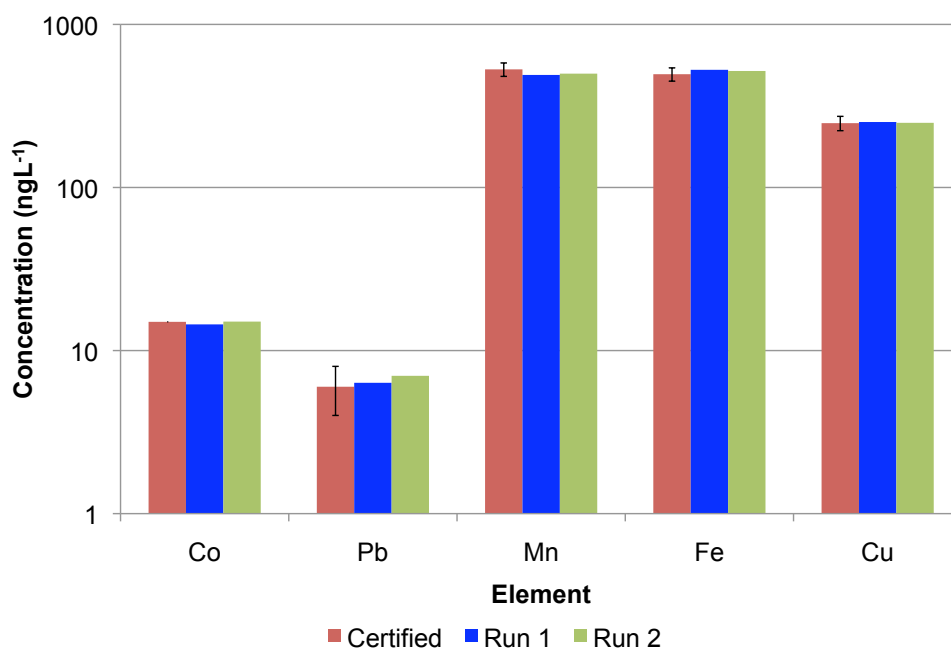
NASS-6

Figure 10. Determined (two separate dates) and certified values for seawater reference material (CRM) NASS-6 are plotted (on a log scale). Excellent agreement between determined and certified values for both low (Pb, 6 ng L^{-1}) and high (Fe and Mn ~500 ng L^{-1}) concentration elements illustrates the accuracy of the method. No internal standard was used.

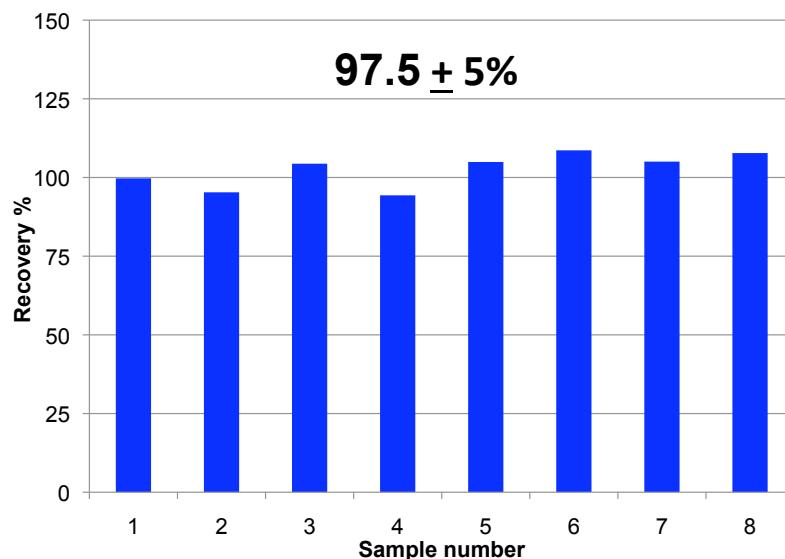# S2: Trace Metals in Seawater

Indium Recovery

Figure 11. Indium is reproducibly and quantitatively recovered from seawater samples making it an excellent Internal Standard (IS) candidate.

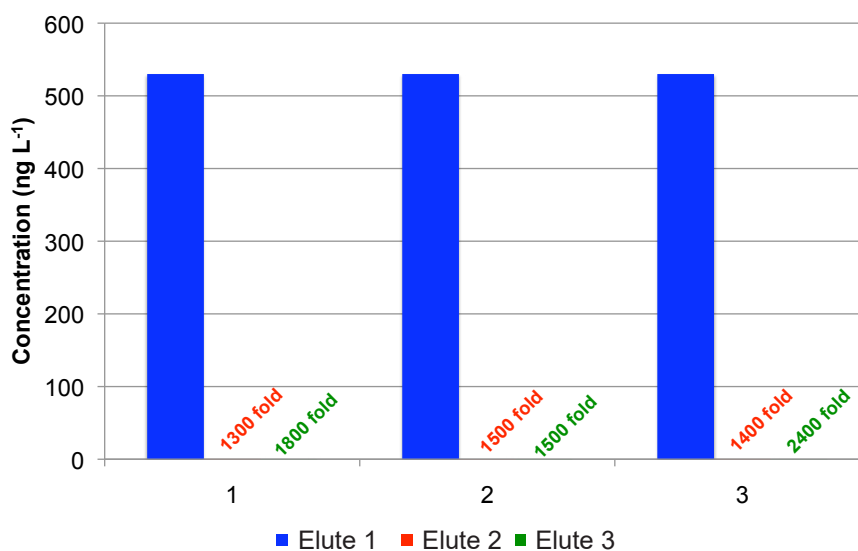## Mn Washout with sea*FAST* S2

Figure 12. Three replicates of a three step elution are plotted. The first step, after loading NASS-6, recovers trace metals from the column. Two subsequent elution steps illustrate greater than a 1000-fold washout, indicating minimal sample to sample carryover. Low carryover is sufficient to measure trace metals in a wide variety of oceanic environments.

S2: Trace Metals in Seawater

Limits of Detection
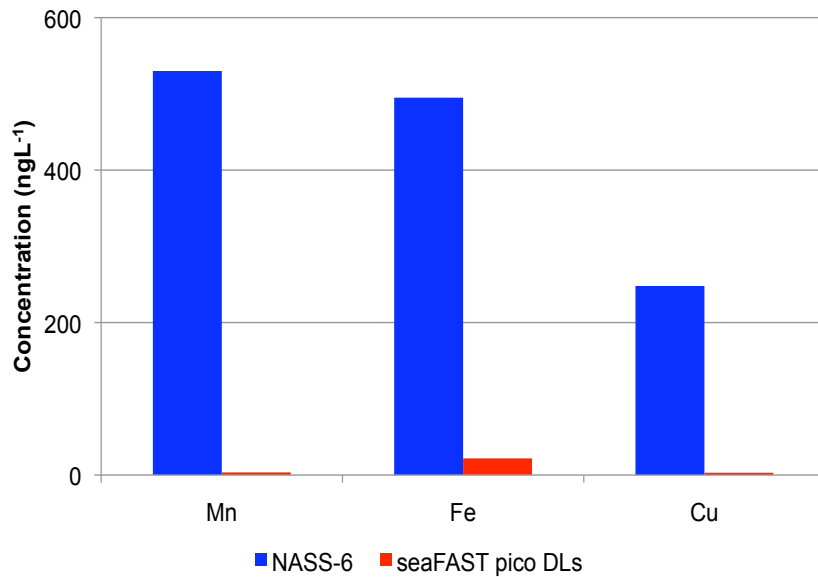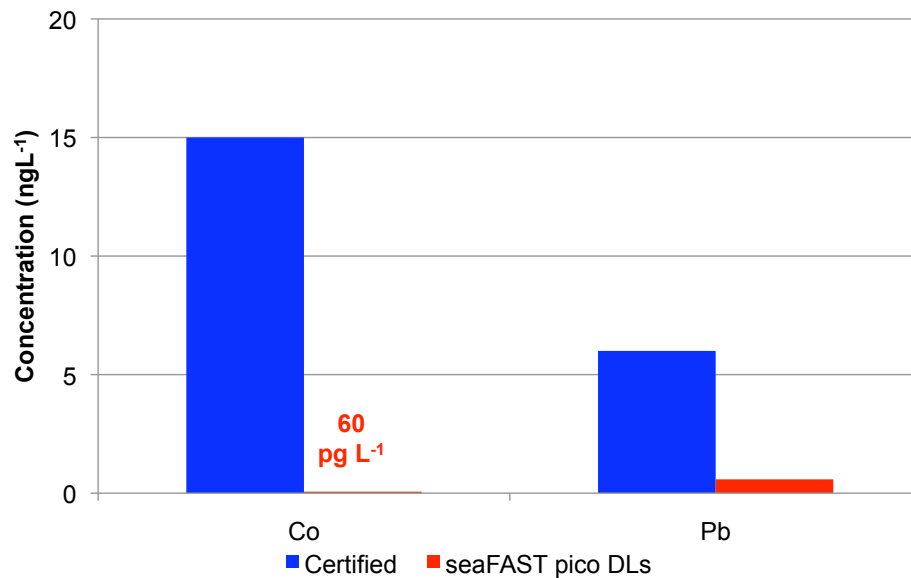

Limits of Detection

Figure 13. Limits of detection are compared to NASS-6 certified values. Matrix removal combined with a 20-fold preconcentration factor is appropriate for many seawater applications. If lower detection limits are required, the system can easily be programmed for larger preconcentration factors.

S2: First Row Transition Metals in Seawater

Inline Application

The sea*FAST* S2 can be operated inline. The automated method loads 10 mL of seawater and elutes the transition row metals directly to an ICPMS. Rapid sample loading rates combined with low elution volumes provide high preconcentration factors (~200 fold) and unprecedented detection limits (pg L^{-1}). The whole process is complete in 9 minutes providing real-time data with invaluable insight into blank reduction and other aspects of method development.
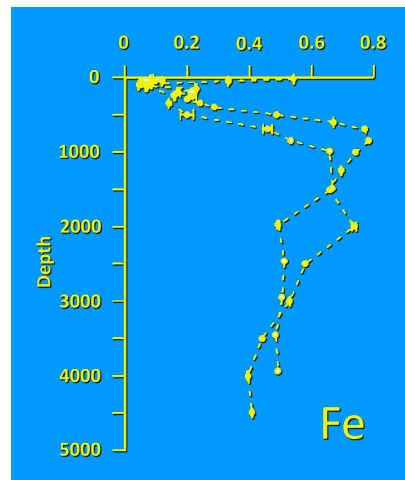
SAFe D Reference Seawater
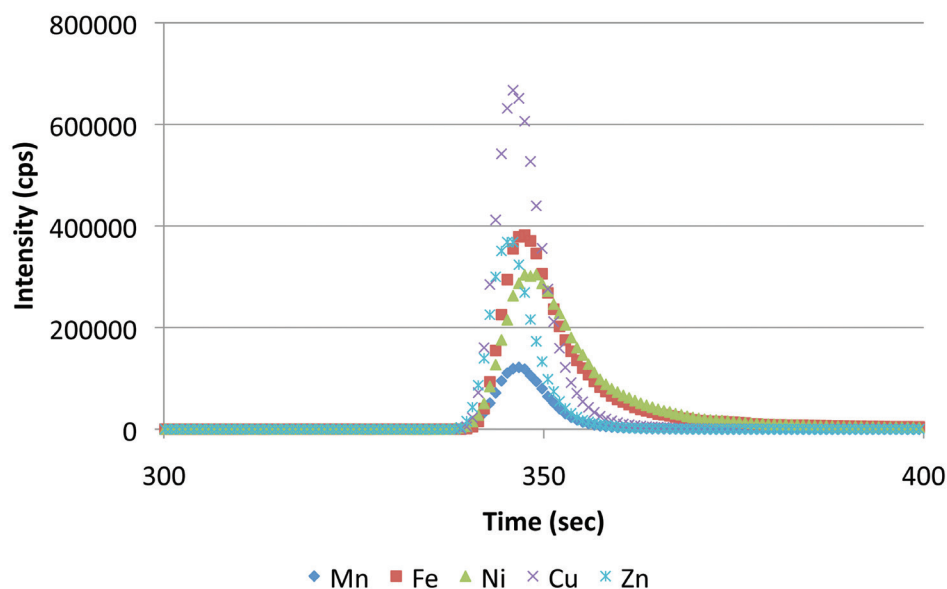
In collaboration with:

The Institute of Marine and Coastal Sciences Rutgers the State University of New Jersey

Robert M. Sherrell, Lisa Fischer, Maria Lagerström and Marie Séguret

Figure 14. Elution profiles for a selection of first row transition metals (2 point running average).

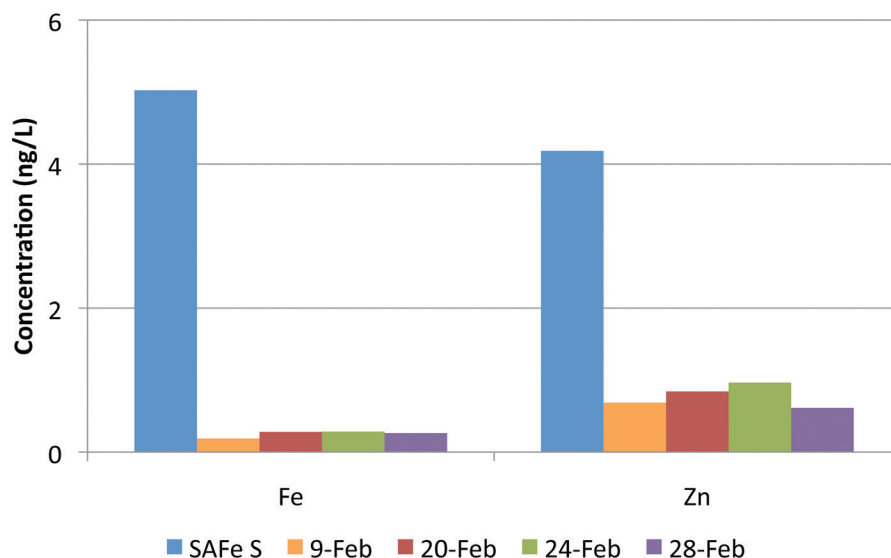# S2: First Row Transition Metals in Seawater

LODs From Multiple Dates

Figure 15. Limits of detection for contamination-prone elements (Fe and Zn) are in the high pg L^{-1} range and are reproducible on a day-to-day basis. These limits of detection are appropriate for determination of ultra-trace metal concentrations in open ocean surface seawater.

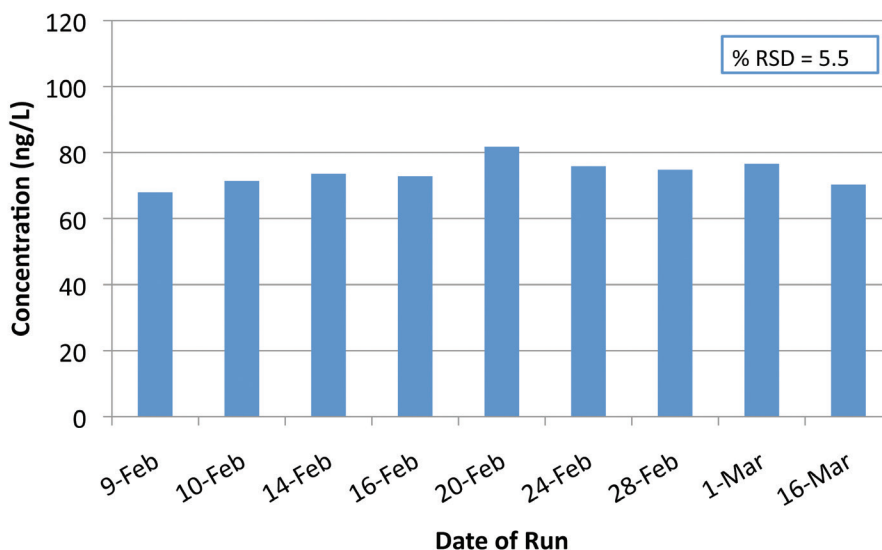## Fe Reproducibility for 8 Runs Over Two Months

Figure 16. An internal laboratory standard of Ross seawater collected from the Southern Ocean is run several times on each of 9 discrete analytical dates. Excellent day-to-day reproducibility is illustrated for Fe, a difficult contamination-prone element.

S2: First Row Transition Metals in Seawater

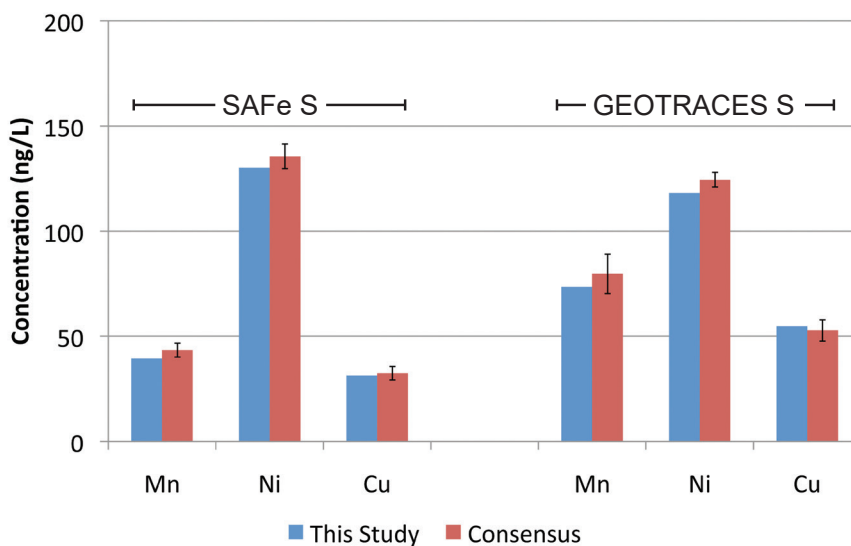## Pacific and Atlantic Surface Waters

Figure 17. Accuracy of Manganese, Nickel and Copper at very low concentrations typical of the open ocean is demonstrated for SAFe and GEOTRACES surface water.

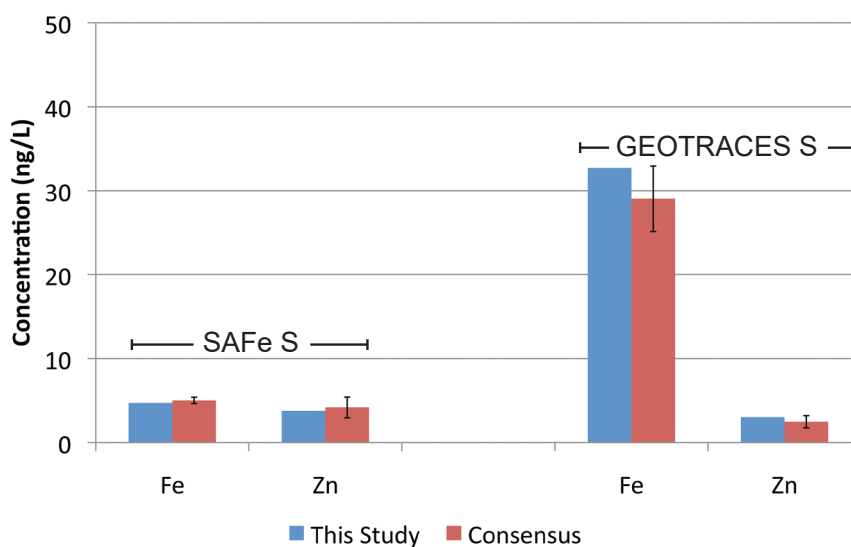## Pacific and Atlantic Surface Water Values

Figure 18. Accuracy of Iron and Zinc at very low concentrations typical of the open ocean is demonstrated for SAFe and GEOTRACES surface water.

Abstract

A sea*FAST* S2 system is used in Preconcentration mode to determine the Cd and Pb concentration in arctic seawater. Validation of the method is illustrated by obtaining Cd and Pb concentrations that agree with the consensus values for SAFe (S and D1) and GEOTRACES (GS and GD) samples. Advantages of the system include the small sample volumes required (12 mL for duplicate analysis) for low level multi element analysis, fast throughput (6 samples per hour) and low procedural blanks.
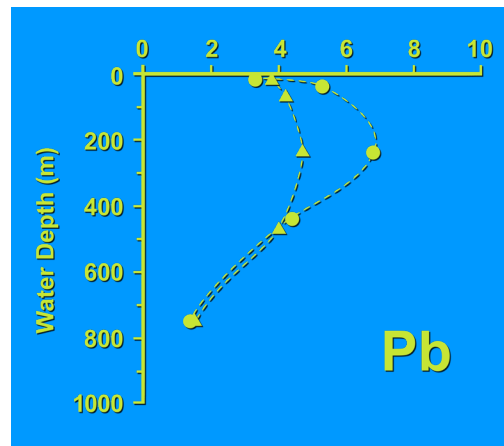
Figure 19. In Preconcentration mode, a chelation column binds transition metals and rare earth elements and then elutes them directly to a low dead volume nebulizer for direct determination by ICPMS.

In collaboration with:

University of Alaska, Fairbanks, AK

Robert Rember, Ana Aguilar-Islas and Marie Séguret

Presented at ASLO 2014 Ocean Sciences Meeting in Honolulu, HI
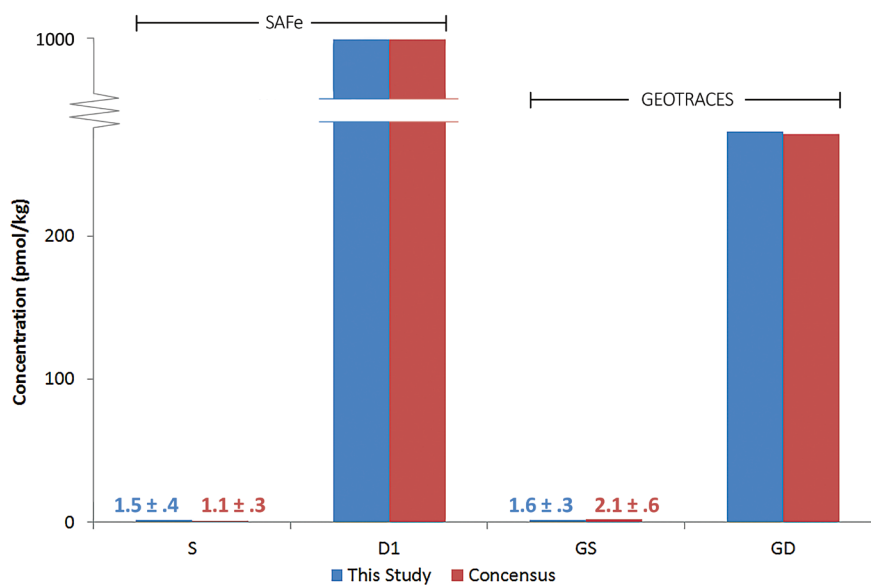
S2: Preconcentration Mode

Dissolved Cadmium

Figure 20. Concentrations of dissolved Cd determined by isotope dilution for SAFe and GEOTRACES reference standards.
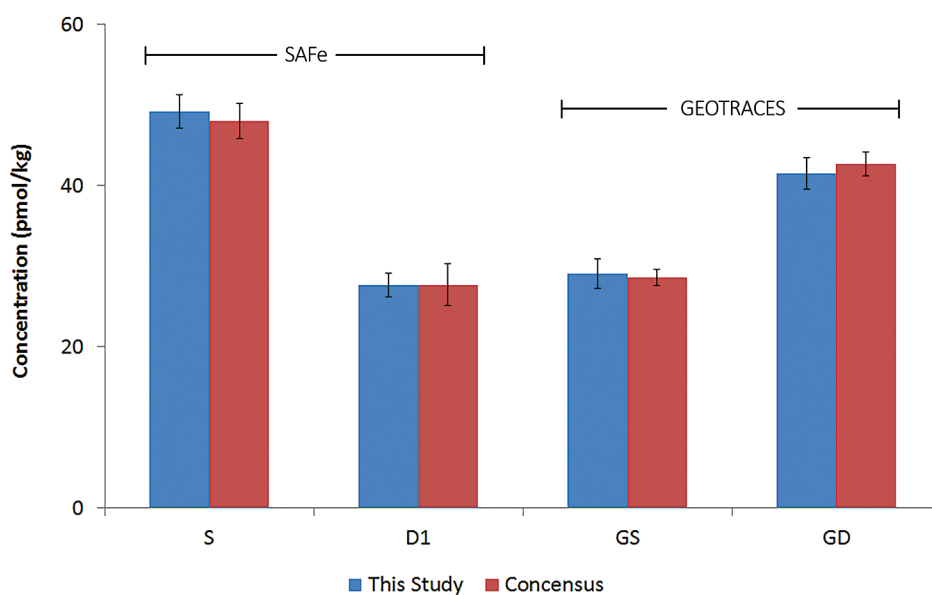
Dissolved Lead

Figure 21. Concentrations of dissolved Pb determined by isotope dilution for SAFe and GEOTRACES reference standards.

S2: Preconcentration & Direct Modes

Abstract

The seaFAST S2 is a high performance, automated sample introduction system for the determination of trace elements in seawater and other high matrix samples by ICPMS. Undiluted samples can be measured directly with a user-specified dilution while simultaneously loading an aliquot of sample onto a column for automated, online preconcentration and matrix removal. Both Direct and Preconcentration modes reduce procedural blanks associated with offline sample preparation; Preconcentration mode dramatically improves detection limits by eliminating matrix effects and increasing sensitivity. The seaFAST S2 offers complete flexibility and can run in Direct, Preconcentration, or both modes by simply selecting the desired mode(s) in the ESI software.

Figure 22. Periodic table showing the possible modes for each element.

Modes

Preconcentration mode:
A chelation column binds transition metals and rare earth elements but allows matrix Na^+, Cl^-, Ca^{2+} and Mg^{2+} ions to be rinsed out. After the preconcentration step, analytes are eluted and detected by ICPMS.

Direct mode:
Sample is automatically diluted inline by high-precision syringe pumps. Dilution reduces matrix effects and allows the determination of elements whose chemistry is not compatible with the preconcentration column.

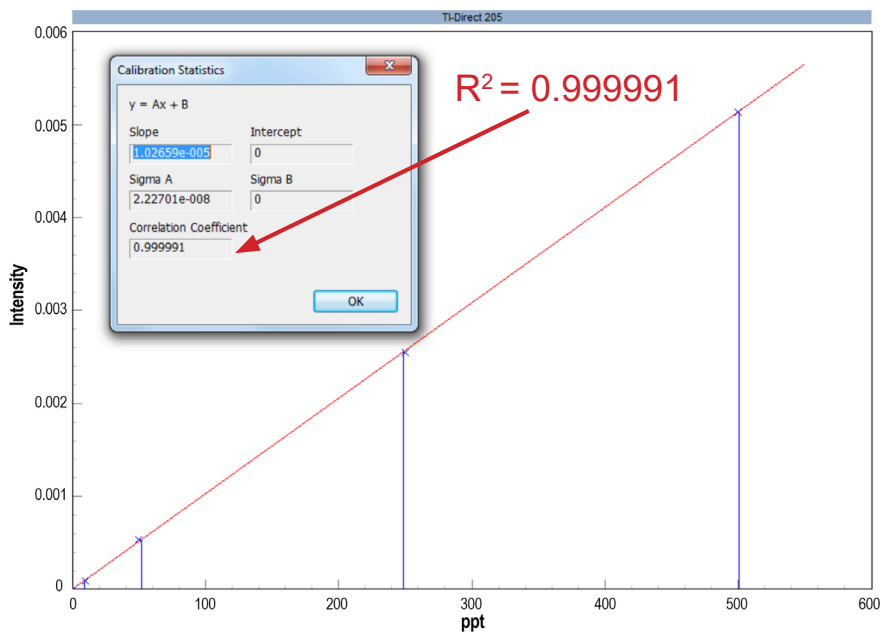# S2: Preconcentration & Direct Modes

Inline Dilution

Figure 23. Direct mode calibration of Tl in 3.5% NaCl. Calibration spikes are 1, 10, 50, 250 and 500 ppt.
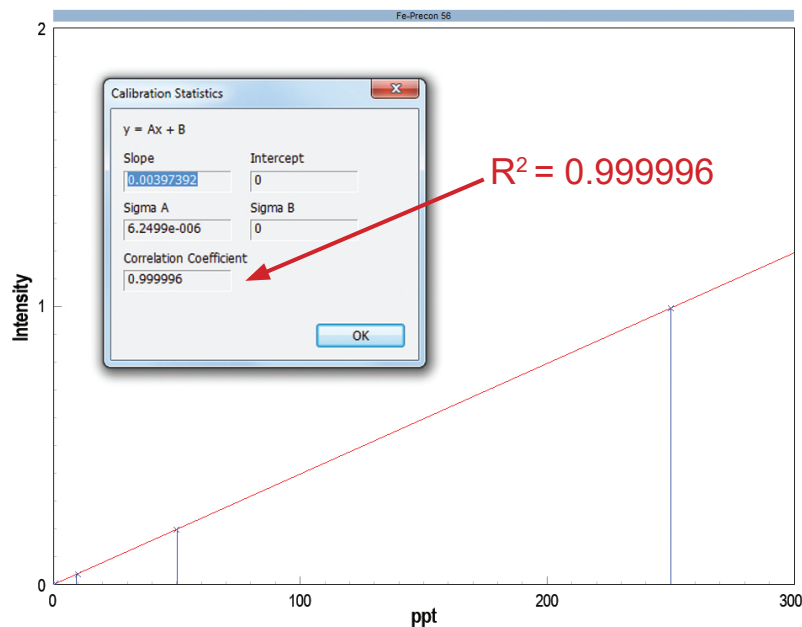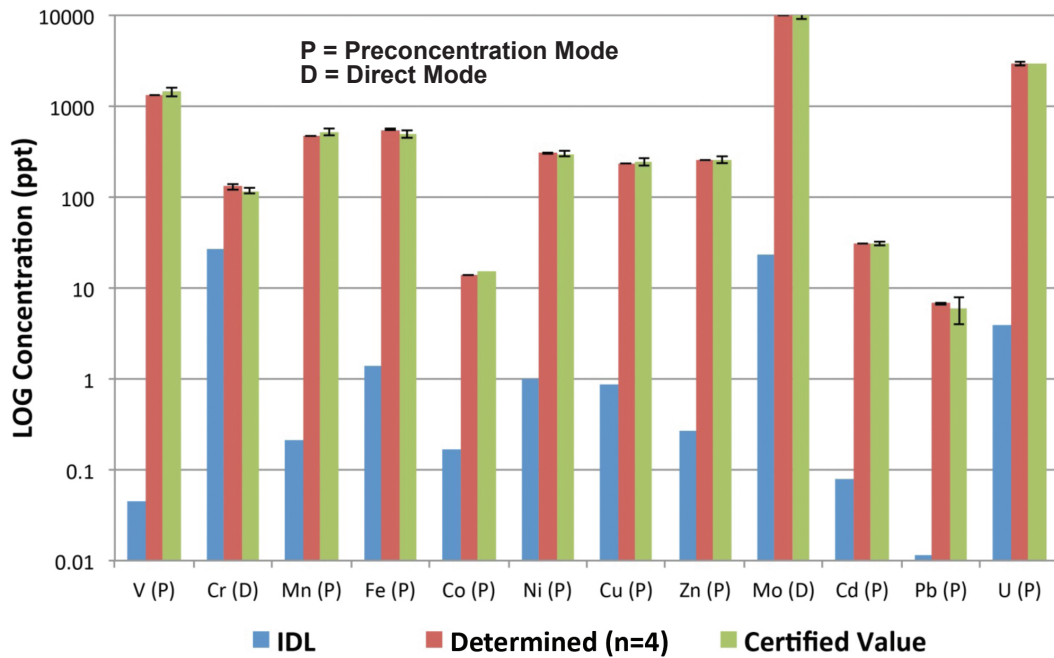
Ultratrace Calibration

Figure 24. Preconcentration mode calibration of Fe in 3.5% NaCl. Calibration spikes are 1, 10, 50 and 250 ppt.

sea*FAST* S2 NASS-6 Determination, DRC, Preconcentration and Direct

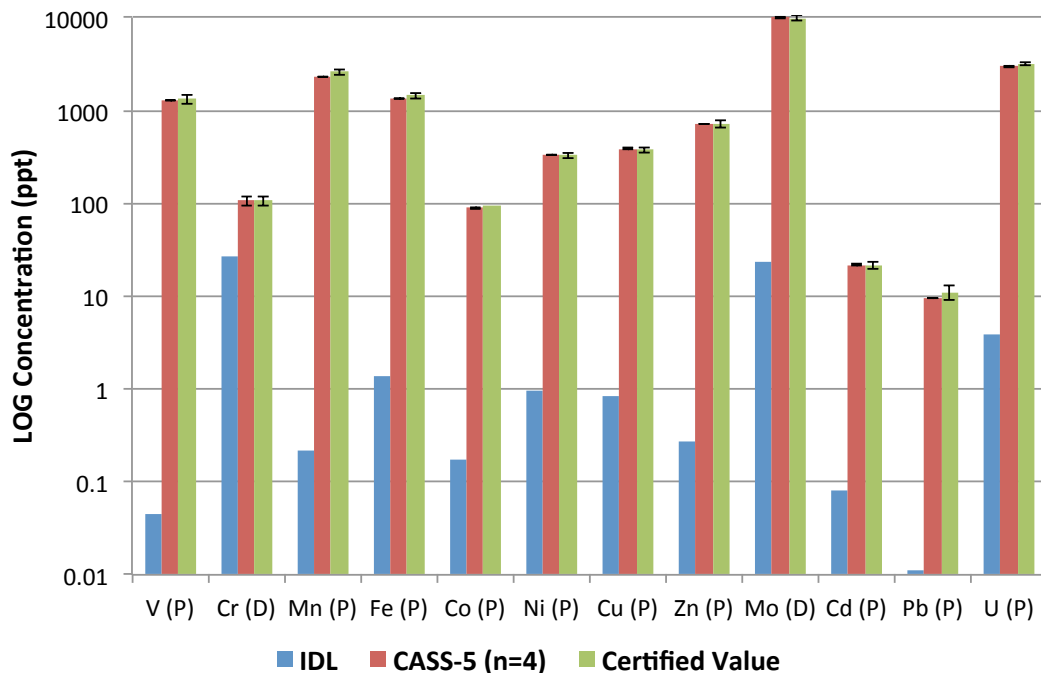## sea*FAST* S2 CASS-5 Determination, DRC, Preconcentration and Direct

Figure 25. Results for NASS-6 and CASS-5 Seawater Reference Materials are shown. Elements determined with the sea*FAST* S2 are accurate and precise for elements with certified concentrations from <10 ppt to >10 ppb.

S2: Preconcentration & Direct Modes

Washout Factors: Co, Cu, Zn, Cd, and Pb

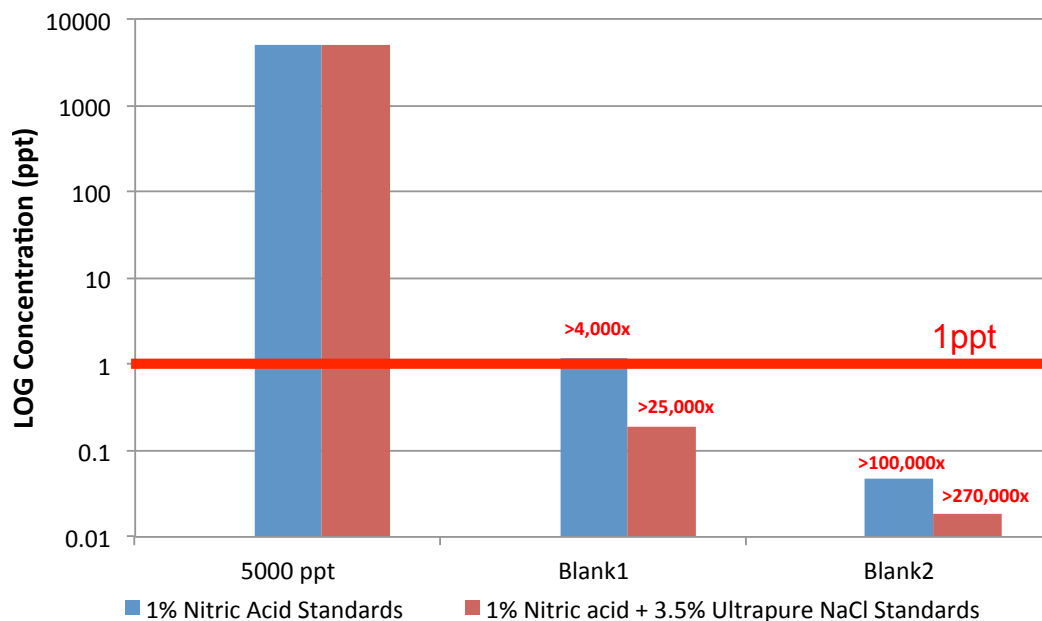**Figure 26.** Washout in Preconcentration mode is excellent with both 1% nitric acid calibration standards and matrix-matched standards. Matrix matching the standards with seaBlank is not required for Preconcentration mode, but it enhances washout.
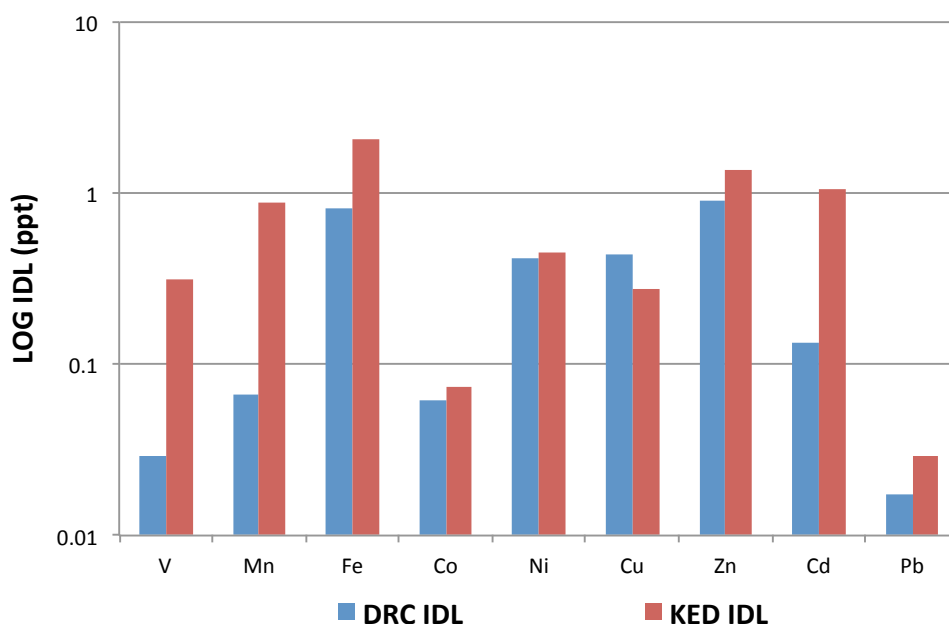
Detection Limits in DRC & KED, Preconcentration Mode

Figure 27. Detection limits are near or better than 1 ppt on a quadrupole ICPMS (n=10, 3σ).

seaFAST SP2: Automated Standard Additions

Brief

A seawater analyzer for ICPMS is described that automatically performs standard additions, preconcentration, and matrix removal to achieve superb accuracy for the determination of trace elements in undiluted seawater, even for challenging elements such as Fe, Zn, and Ag at low or sub-ppt levels. This configuration enables routine analysis of open ocean seawater samples with complete automation.

Figure 28. Periodic table showing the possible modes for each element.

Introduction

Matrix effects from samples with high total dissolved solids (TDS) can cause severe problems for accurate determination of many elements by ICPMS. High dilution factors attenuate the matrix effects but are undesirable when the best detection limits are required. Historically, a variety of advanced techniques have been used to accurately determine trace elements in high TDS samples. One common approach is preconcentration and matrix removal with external calibration, which offers excellent results for elements whose chemistry is compatible with the chosen chelation resin. While this technique is appropriate for many samples types, some samples, such as open ocean seawater, contain concentrations of Fe, Zn, and Ag that are difficult to determine accurately with external calibration. To improve accuracy for these sample types, analytical techniques such as isotope dilution or standard additions are often used.

seaFAST SP2: Automated Standard Additions

In this work, the sea*FAST* SP2 is configured to determine low and sub-ppt Fe, Zn, Ag, and other trace elements in undiluted seawater using completely automated standard additions, preconcentration, and matrix removal. Undiluted seawater is vacuum-loaded onto a 6 mL sample loop, auto-spiked with variable levels of standard (or no spike), and transferred into a second loop for automatic preconcentration and matrix removal.

In order to achieve quantitative chelation of Ag, an alternate sea*FAST* resin is used containing carboxymethylated polyethylenimine immobilized on a hydrophilic methacrylate polymer. This resin offers excellent Ag recovery in high saline matrices while maintaining analytical conditions and performance metrics for other elements similar to those of the standard sea*FAST* resin.
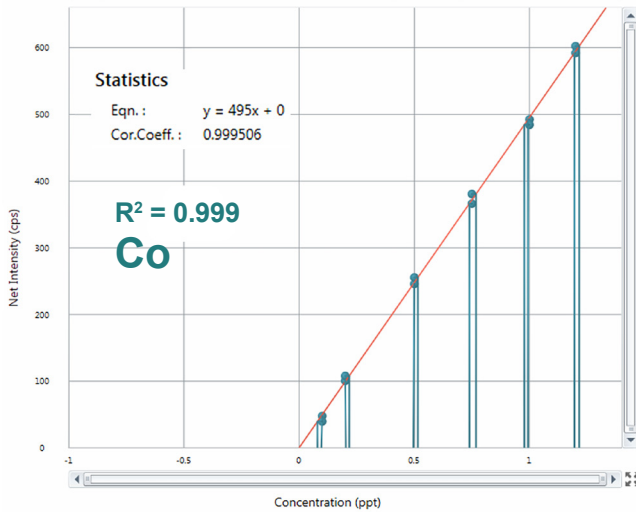
Transient Signals for Co, Zn, and Pb
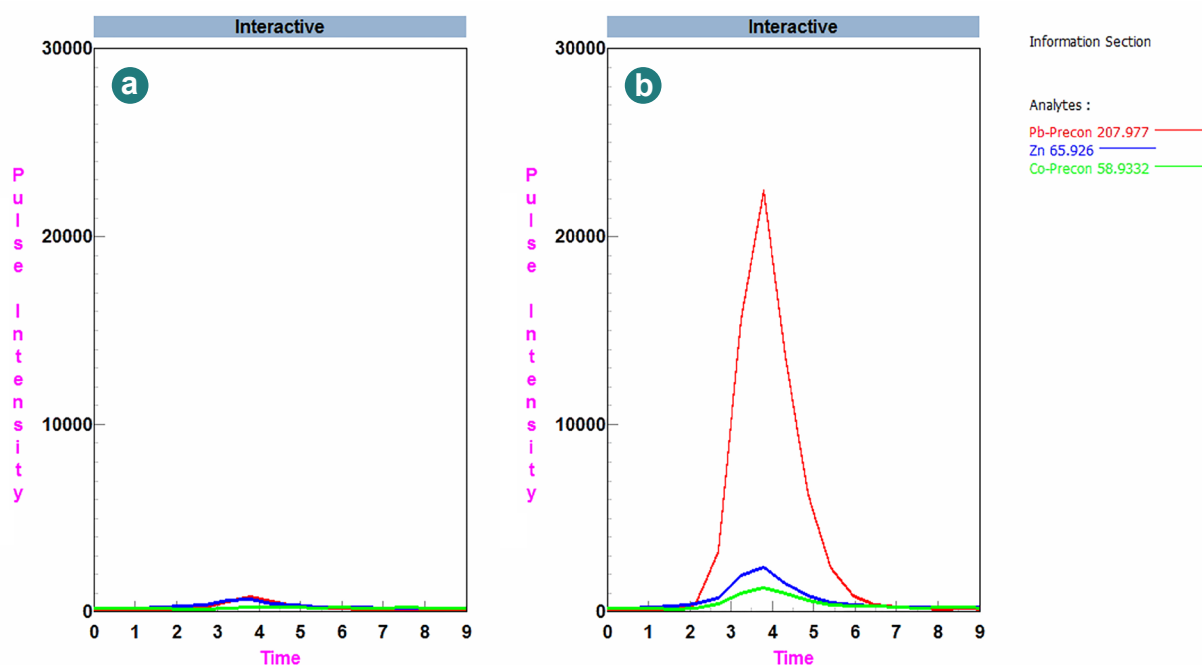
Figure 29. a) Blank acquired by loading air onto the column. b) GSP sample elution profile.
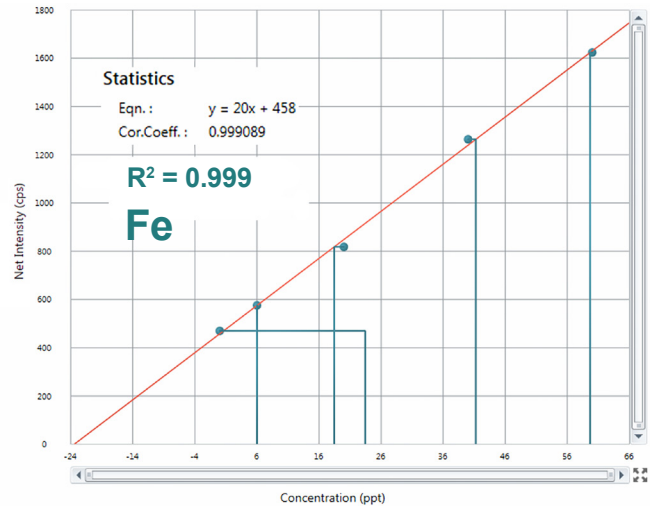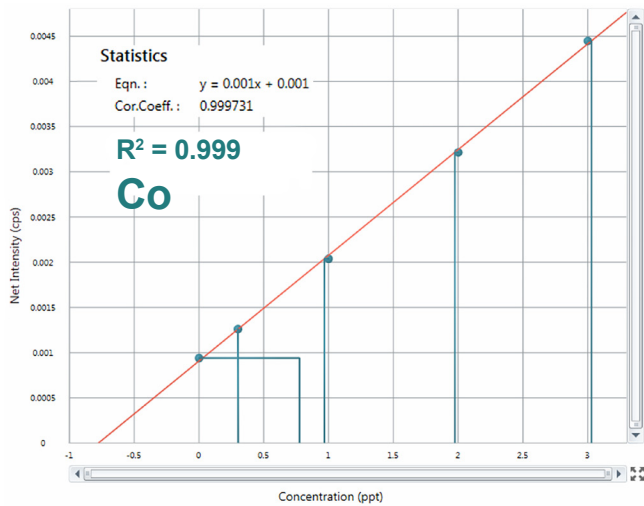
seaFAST SP2: Automated Standard Additions

Sub-ppt Standard Additions Autocalibration

A sub-ppt standard addition calibration prepared by auto-spiking a DI water sample, background subtracted.

Sub-ppt Standard Additions Autocalibration

Automatic standard addition calibrations in GSP for Co and Fe, no blank subtraction.

Figure 30. GEOTRACES GSP Intercalibration North Pacific surface water sample was analyzed by standard addition calibration. SAFe D1 (deep water, 1000 m) Intercalibration North Pacific sample was measured against the standard addition calibration.

seaFAST SP2: Automated Standard Additions

Results
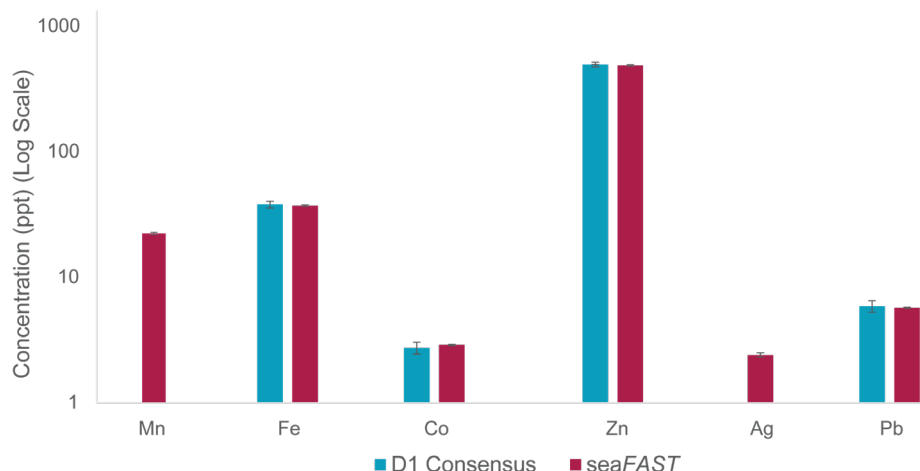
D1 North Pacific Intercalibration Sample, 1000m

	Consensus Value	seaFAST
Mn	na	22.1 ± 0.4
Fe	38 ± 2.3	37.2 ± 0.6
Co	2.74 ± 0.3	2.89 ± 0.04
Zn	496 ± 23	488 ± 7
Ag	na	2.4 ± 0.2
Pb	5.88 ± 0.6	5.70 ± 0.02

Results for D1 measured with sea*FAST* are compared with consensus values, showing excellent agreement. Mn and Ag have no consensus values.

GSP Intercalibration North Pacific

	Determined Concentrations (ppt, *n=5*)	Detection limit (ppt, 3σ, *n=10*)
Mn	43.7 ± 0.8	0.06
Fe	15 ± 2	0.7
Co	0.58 ± 0.05	0.04
Zn	2.6 ± 0.4	0.6
Ag	0.12 ± 0.04	0.02
Pb	13.5 ± 0.3	0.04

Detection limits and results are shown for GSP. Zn results are preliminary due to ongoing investigations of blank reduction/correction.

SLEW-3 SRM Comparison

	Reference (ppt)	seaFAST (ppt)
Ag	1.93 ± 0.1	1.92 ± 0.08

J. Anal. At. Spectrom., 2002,17, 88-93

Since Ag does not have a consensus value in D1, SLEW-3 was analyzed. The sea*FAST* determination is in agreement with that reported by Yang et. al.
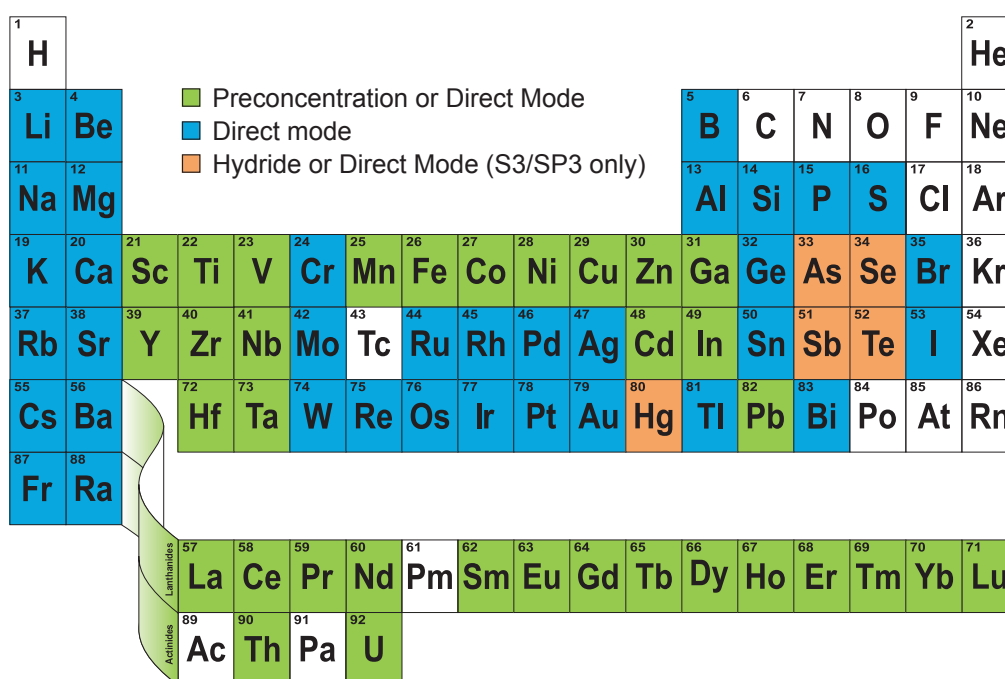
Conclusion

- sea*FAST* SP2 automatically creates standard addition calibrations with no manual sample preparation.
- Results for D1 and SLEW-3 are in good agreement with consensus values. GSP values are consistent with open ocean surface waters.
- sea*FAST* offers unprecedented automation for analysis of seawater samples, even at open ocean concentrations for low and sub-ppt analytes.

seaFAST SP3: Routine Multi-Mode Seawater Analysis

Brief

A new, automated analysis system for ultratrace determination of low and sub-ppt metals in high matrix samples is described. Simple external autocalibration from a single multielement stock standard eliminates common sources of contamination for ultratrace metals determination. Inline, automatic matrix matching provides exceptional accuracy. Metals may be measured in up to three modes: preconcentration and matrix removal, direct analysis with inline dilution, and hydride generation.

Figure 31. Periodic table showing the possible modes for each element.

Introduction

Matrix effects from samples with high total dissolved solids (TDS) can cause severe problems for accurate determination of many elements by ICPMS. High dilution factors attenuate the matrix effects but are undesirable when excellent detection limits are required. Historically, a variety of advanced techniques have been used to accurately determine trace elements in high TDS samples. One common approach is preconcentration and matrix removal, which offers superb results for elements whose chemistry is compatible with the chosen chelation resin. For other elements, manually matching the matrix of calibration blanks and standards to that of the diluted samples can achieve very accurate results in high TDS samples. Lastly, hydride generation improves quantification for elements such as As and Se that are otherwise difficult to determine.

seaFAST SP3: Routine Multi-Mode Seawater Analysis

The new seaFAST SP3 analyzes samples using one or more advanced analytical techniques: preconcentration and matrix removal, direct analysis with inline dilution, and hydride generation. For improved accuracy the seaFAST performs automatic inline matrix matching for calibration blanks, standard, and QC samples, as well as autodiluted samples.
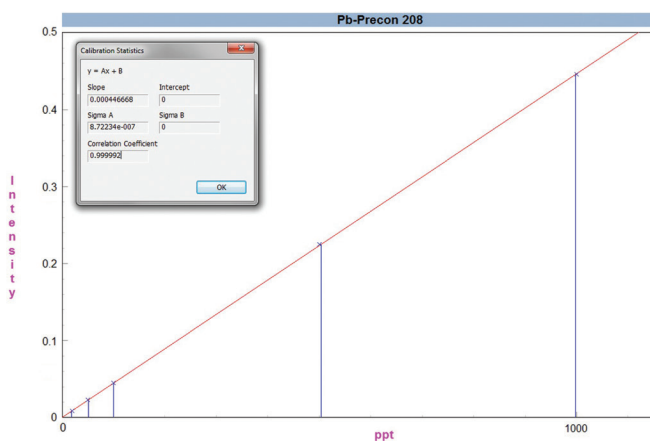
Preconcentration Mode: Pb Calibration Curve

Figure 32. Autocalibration from a single 1000 ppt calibration standard. Calibration curve was matrix matched to ~3% TDS.
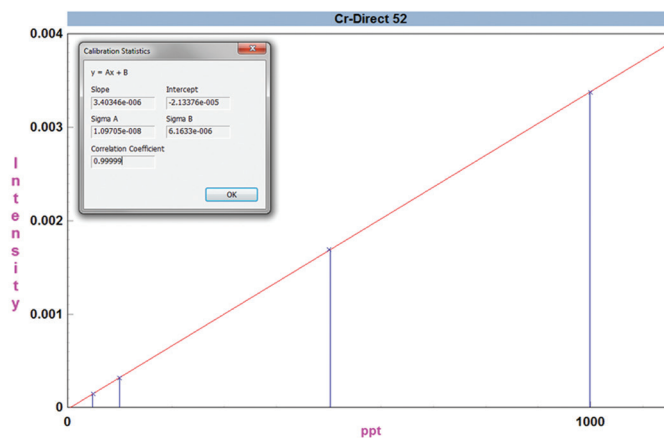
Direct Mode: Cr Calibration Curve

Figure 33. Direct mode with 10x inline dilution: Autocalibration from a single 1000 ppt calibration standard. Calibration curve was matrix matched to ~3% TDS.
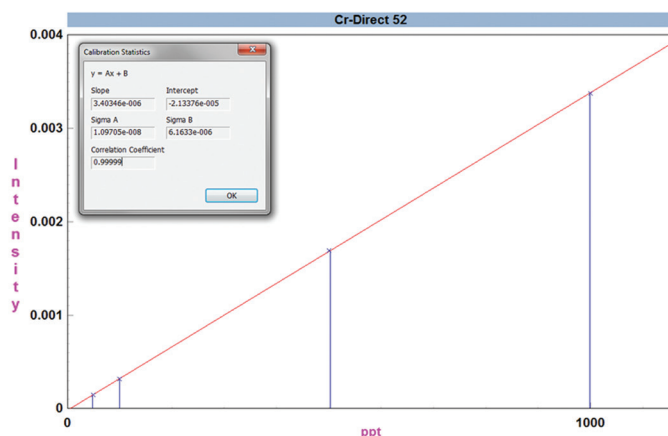
Hydride Mode: As Calibration Curve

Figure 34. Autocalibration from a single 1000 ppt calibration standard. Calibration curve was matrix matched to ~3% TDS.

Preconcentration Mode: Elution of 6 Elements at 1 ppb
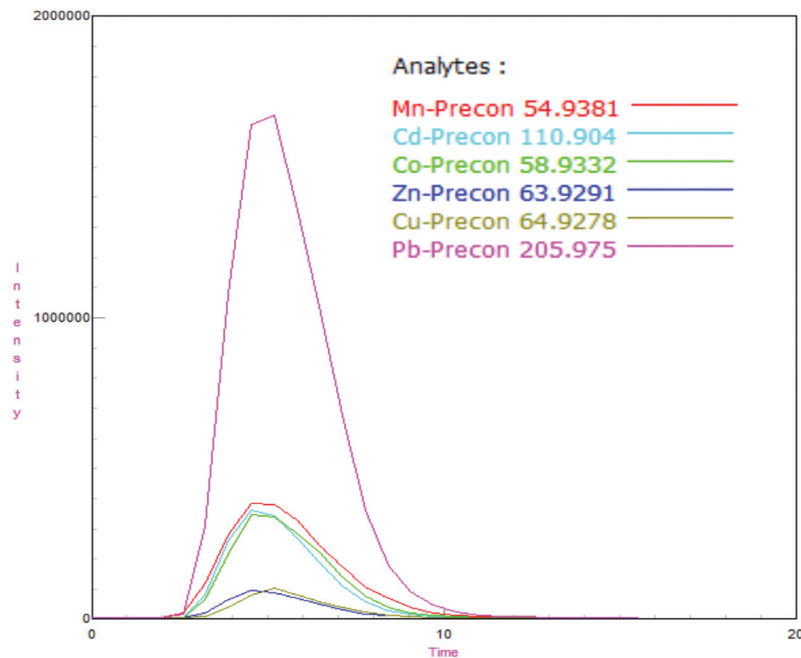

Figure 35. Simultaneous elution of 6 elements in Preconcentration mode at 1 ppb.

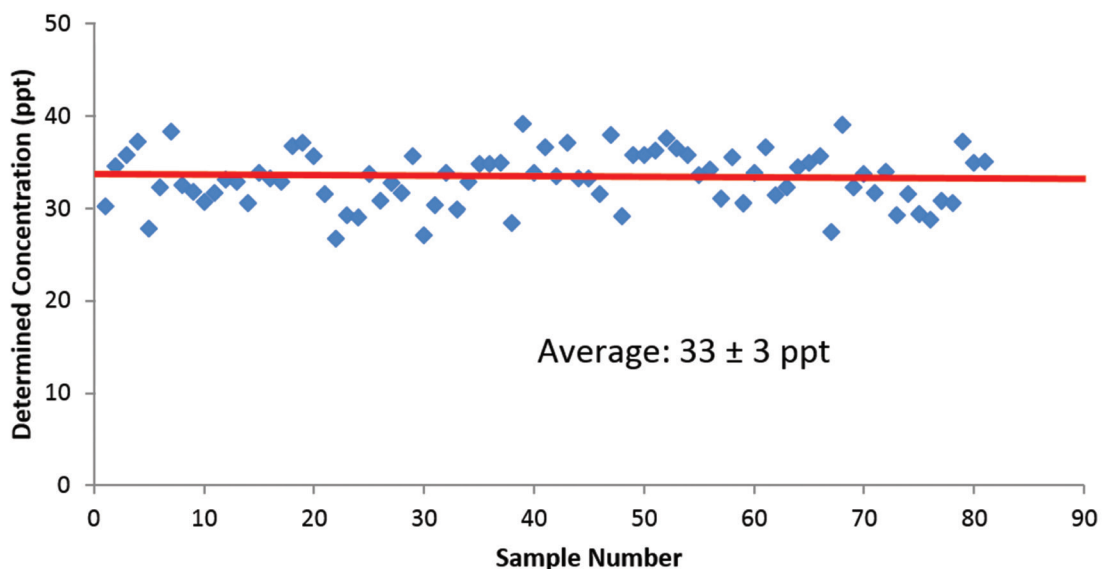**Preconcentration Mode: Elution of 6 Elements at 1 ppb**

Figure 36. Long term stability of Cr in synthetic seawater shows >14 hours of repeated determinations with internal standard correction. Direct mode automatically diluted the sample inline by 10x. The determined concentration in the synthetic seawater was 33±3 ppt.

seaFAST SP3: Routine Multi-Mode Seawater Analysis

Long Term Stability

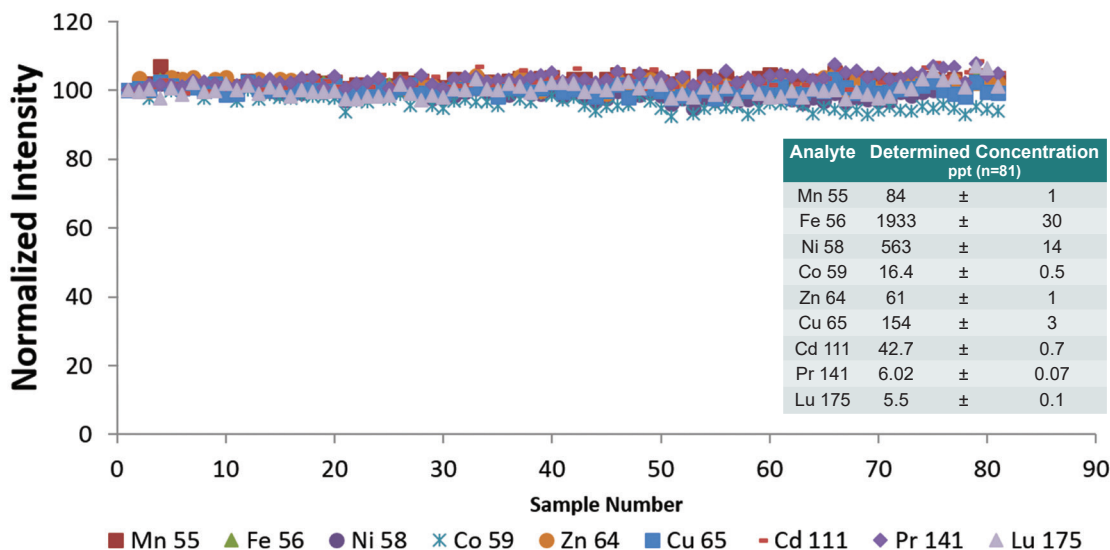| Analyte	Determined Concentration ppt (n=81)		
Mn 55	84	±	1
Fe 56	1933	±	30
Ni 58	563	±	14
Co 59	16.4	±	0.5
Zn 64	61	±	1
Cu 65	154	±	3
Cd 111	42.7	±	0.7
Pr 141	6.02	±	0.07
Lu 175	5.5	±	0.1

Figure 37. Common transition metals and selected rare earth elements (REEs) were determined in synthetic seawater consecutively for over 14 hours (n=81). Auto-matrix-matched blanks and QC standards are not shown, for clarity. Average precision over 14 hours was better than 2% with internal standard correction. REEs were spiked at 5 ppt.
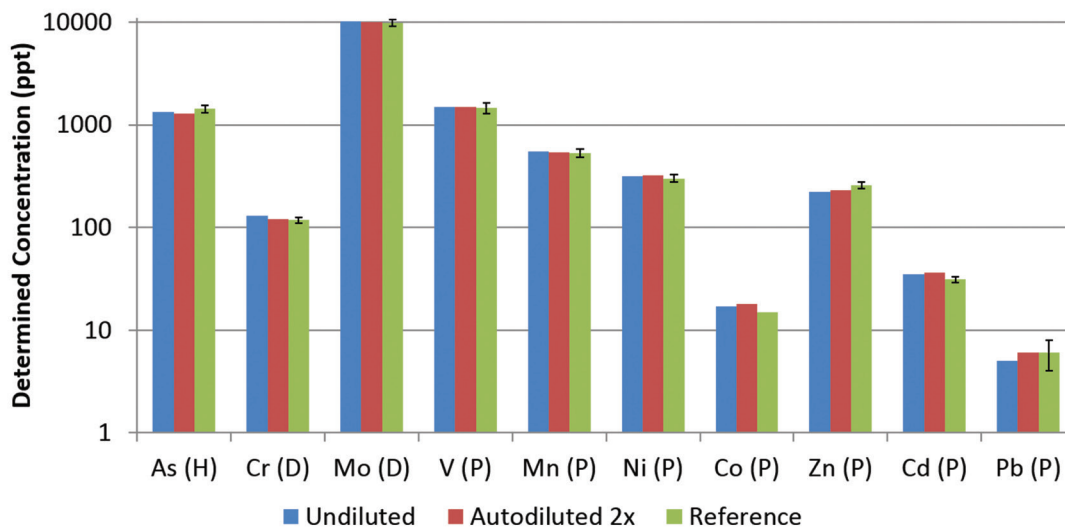
Accuracy

Figure 38. NASS-6 was analyzed in all three modes, Preconcentration (P), Direct with fixed 10x inline dilution (D) and Hydride (H). NASS-6 was run undiluted and with a 2x autodilution using automatic, inline matrix matching with seaBlank ultrapure sodium chloride solution. The *seaFAST* achieves excellent accuracy in all three modes, with and without autodilution.