



seaFAST



Automating Seawater Analysis

seaFAST

Brief and System Schematics.....	2
S2: REEs in Seawater (Offline)	4
S2: Trace Metals in Seawater (Offline).....	8
S2: First Row Transition Metals in Seawater (Inline).....	11
S2: Preconcentration Mode	14
S2: Direct & Preconcentration Modes	16
seaFAST SP2: Automated Standard Additions.....	20
seaFAST SP3: Routine Multi-Mode Seawater Analysis	24

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 System

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

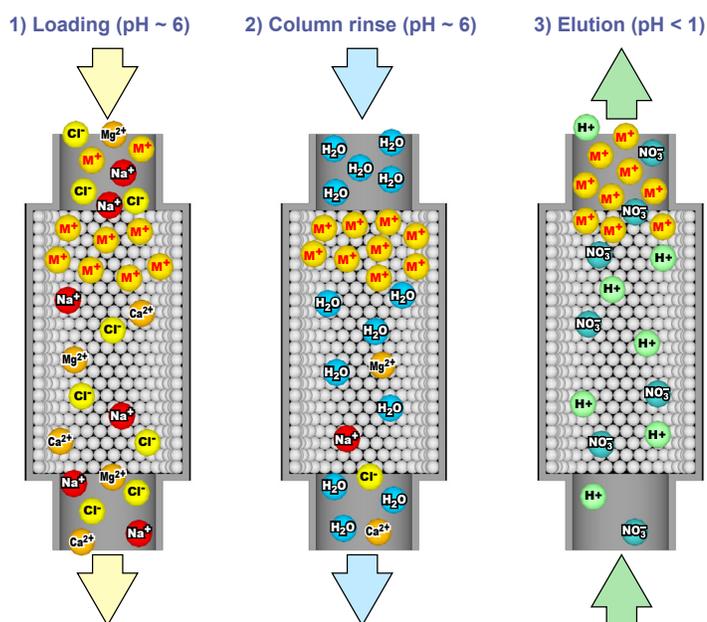
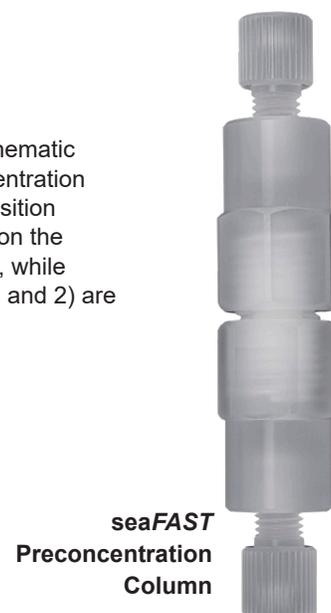


Figure 1. Image and schematic of the seaFAST preconcentration column. At a pH ~ 6, transition row metals are chelated on the preconcentration column, while matrix elements (group 1 and 2) are flushed from the column.



seaFAST 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

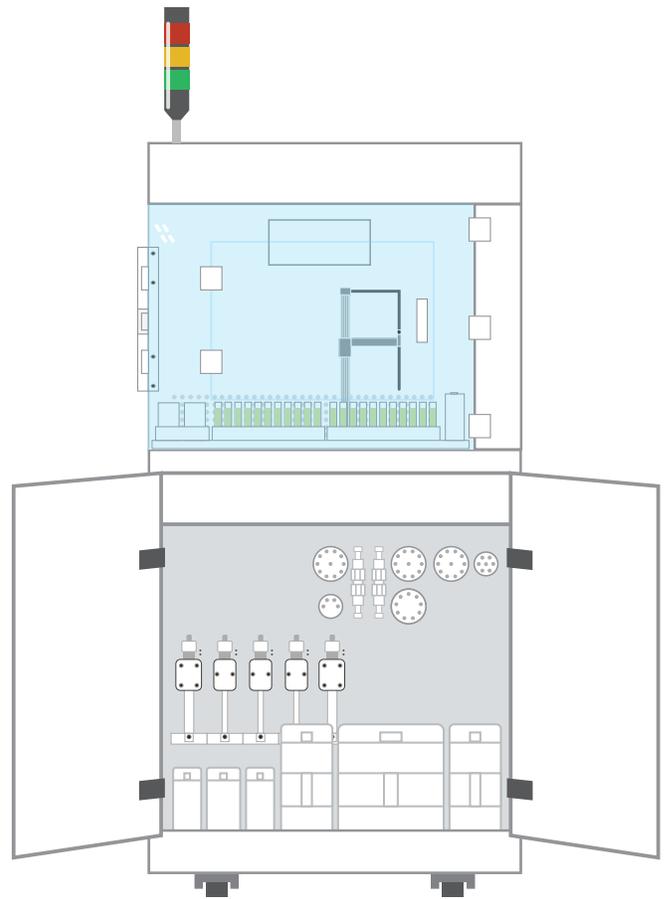


Figure 2. seaFAST S2 system with integrated mobile stand.

seaFAST 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



Photo © Ana Aguilar-Islas

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 100mLs) 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 μLs) of acid. Rapid sample loading rates combined with low elution volumes provides high concentration factors and unprecedented detection limits (pg L^{-1}).

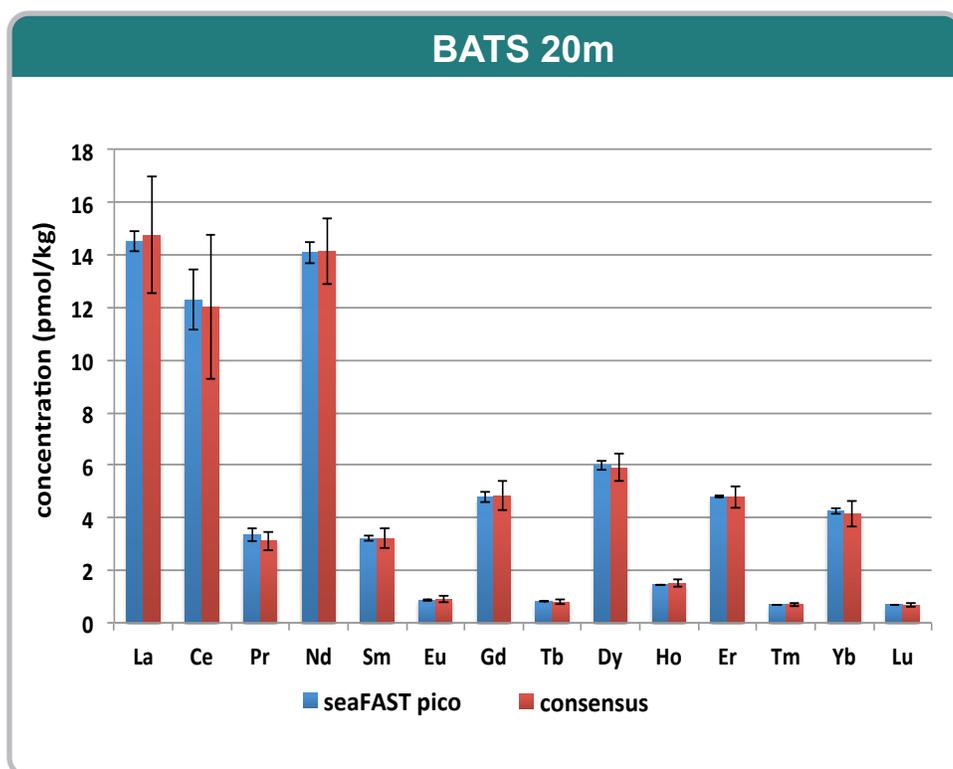


Figure 3. Single digit picomolar (<1 to 15 pM) concentrations of REEs are routinely determined in surface samples (20m) from the Bermuda Atlantic Time-series Station (BATS). The error bars (2 SD) illustrate the precision of the method, whereas accuracy is demonstrated through agreement with consensus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

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

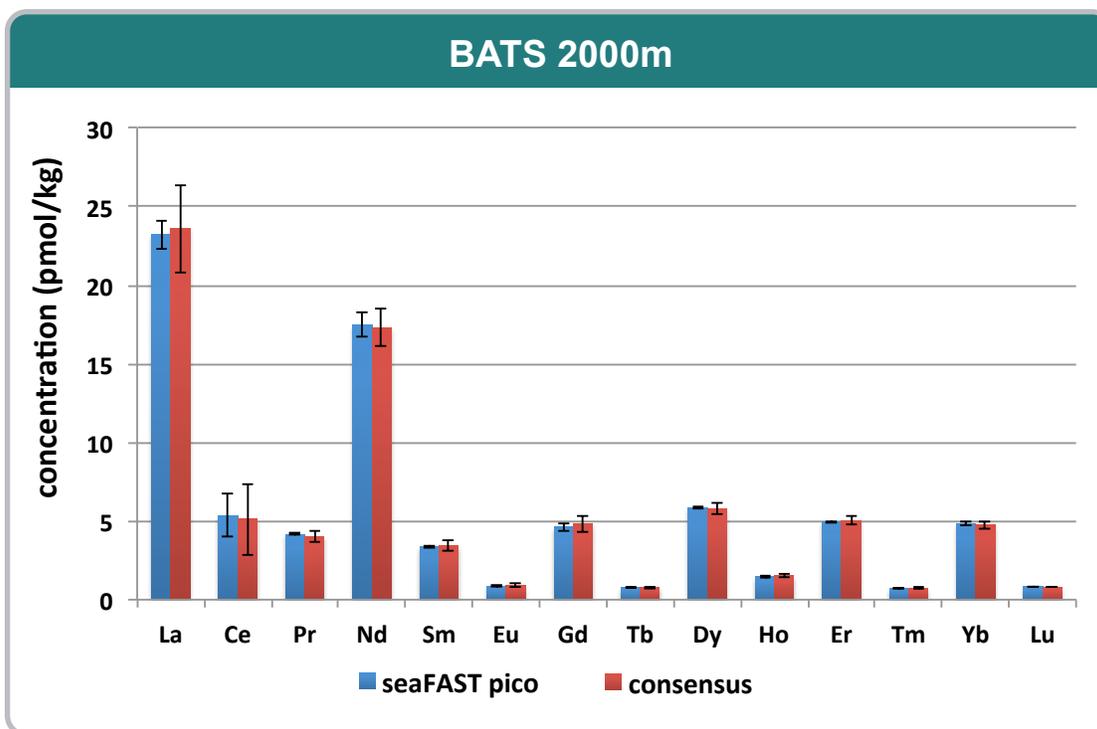


Figure 4. Similar to Figure 3, REEs determined and consensus concentrations for a deep sample (2000m) from the Bermuda Atlantic Time-series Station (BATS) are plotted. The error bars (2 SD) illustrate the precision of the method, whereas accuracy is demonstrated through agreement with consensus values.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

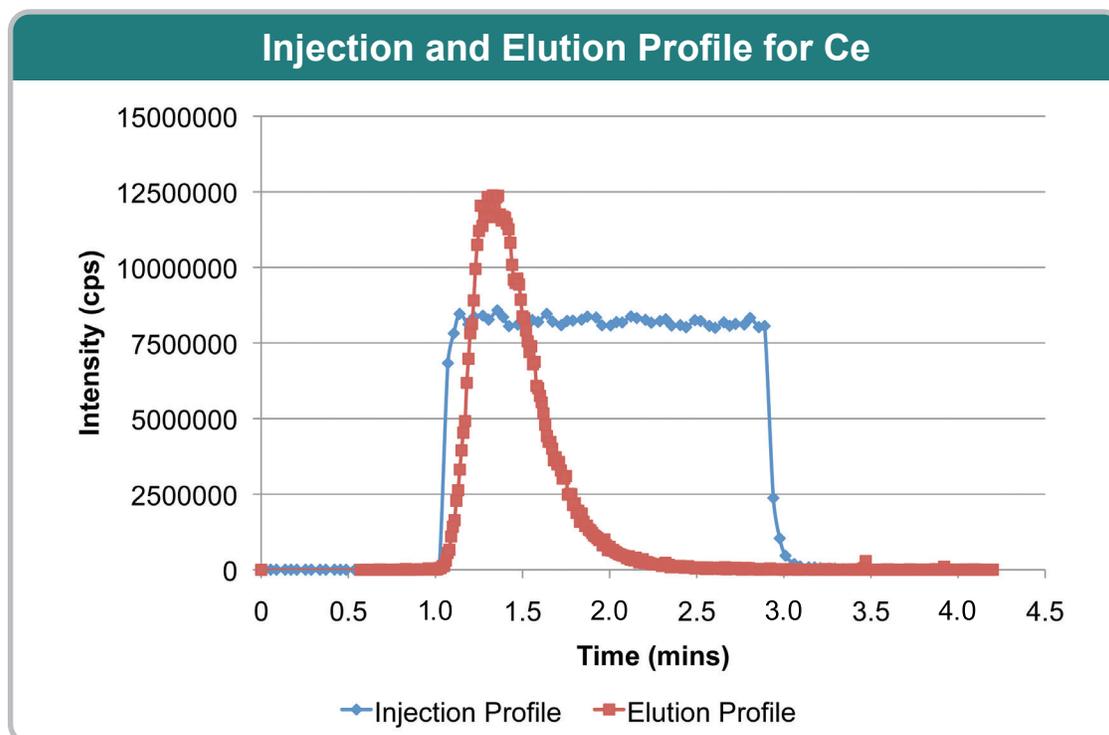


Figure 5. A comparison of a seaFAST S2 inline elution profile with a seaFAST S2 offline injection is shown above. Offline fraction collection of programmable elution volume is injected to the ICPMS with a microFAST system. A profile collected from a sample eluted in 200 μL and introduced at 100 $\mu\text{L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

Quantitative Recovery for a Range of Elution Volumes

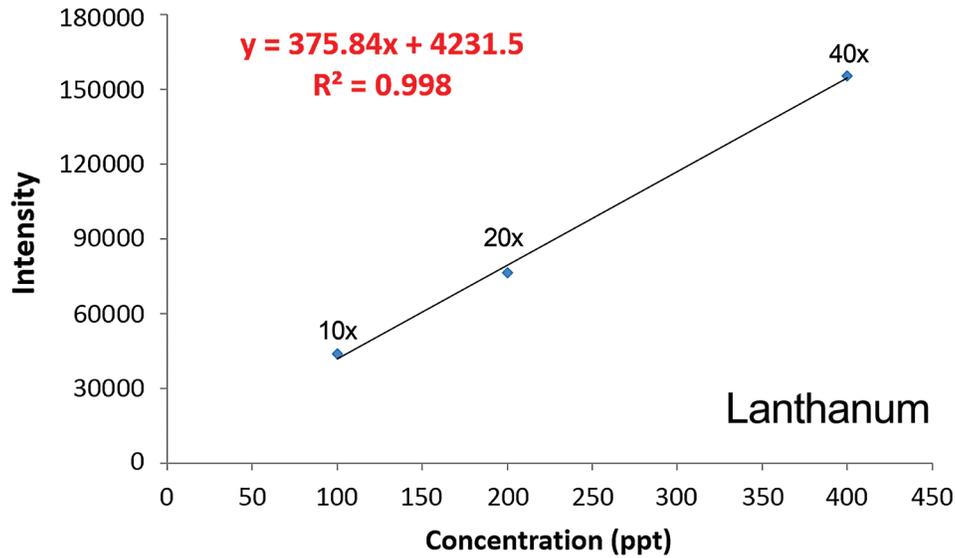


Figure 6. By adjusting elution volume (1000, 500, to 250 μ L), 10 mLs of Indian Ocean surface water (with 10 ppt REE spike) is concentrated 10, 20, and 40x. A linear correlation between concentration and intensity indicates that even 250 μ Ls is sufficient for quantitative recovery.

Quantitative Recovery for a Range of Sample Volumes

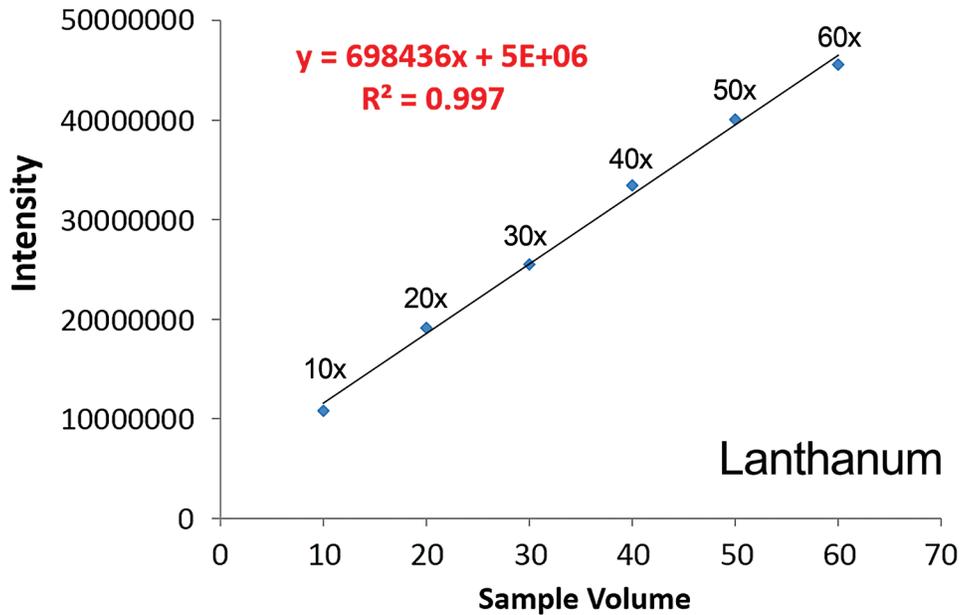


Figure 7. By adjusting sample volume (10 - 60 mL), Indian Ocean surface water (with 10 ppt REE spike) eluted in 1 mL is concentrated 10 - 60x. A linear correlation between concentration and intensity indicates the columns capacity to process large volume samples with quantitative recovery.

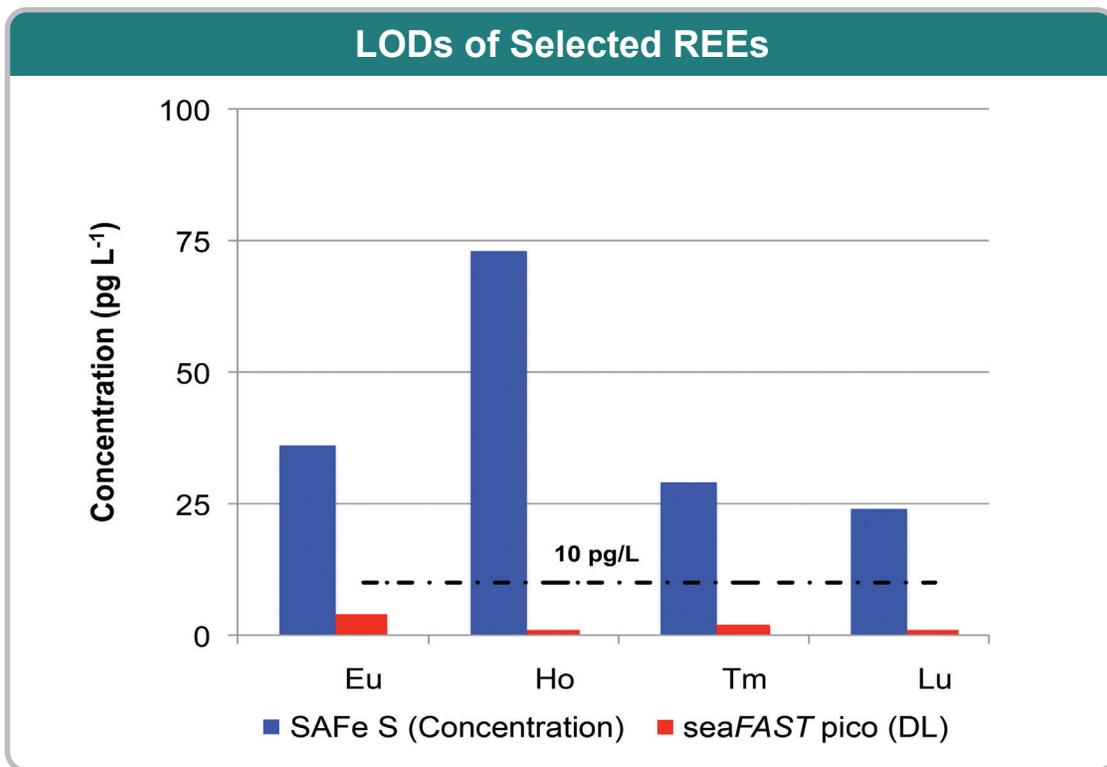


Figure 8. Limits of detection are compared to SAFE surface water concentrations. Matrix removal combined with a 20-fold preconcentration factor is sufficient to determine the lowest level of REEs in open ocean seawater.

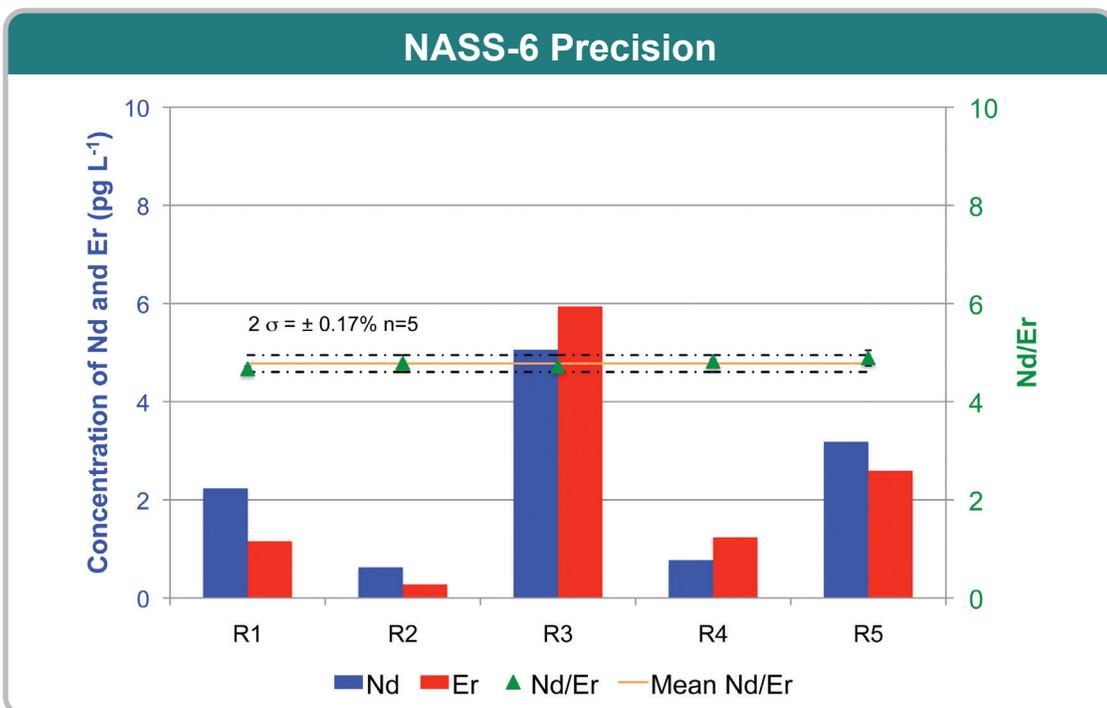


Figure 9. The interpretation of dissolved REEs requires high quality concentration values from which very precise patterns and elemental ratios can be determined. Three NASS-6 replicates, run on five different analytical dates, indicate good precision for concentration data and better than $\pm 3.5\%$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

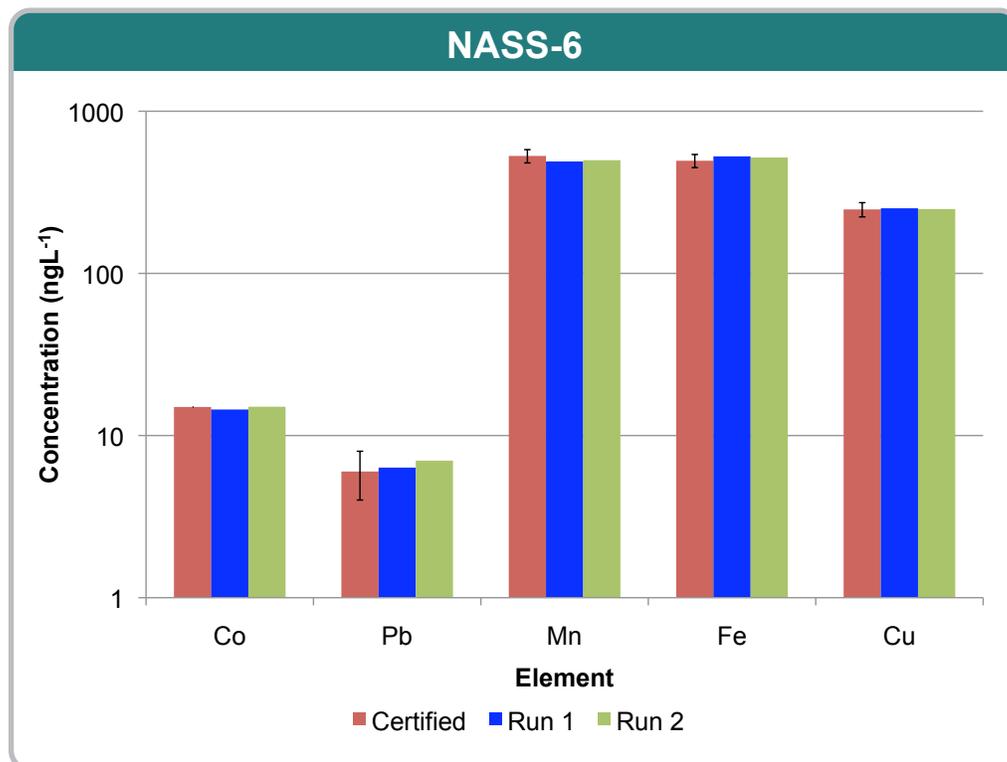
S2: Trace Metals in Seawater



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 seaFAST 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}).

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 $\sim 500 \text{ ng L}^{-1}$) concentration elements illustrates the accuracy of the method. No internal standard was used.



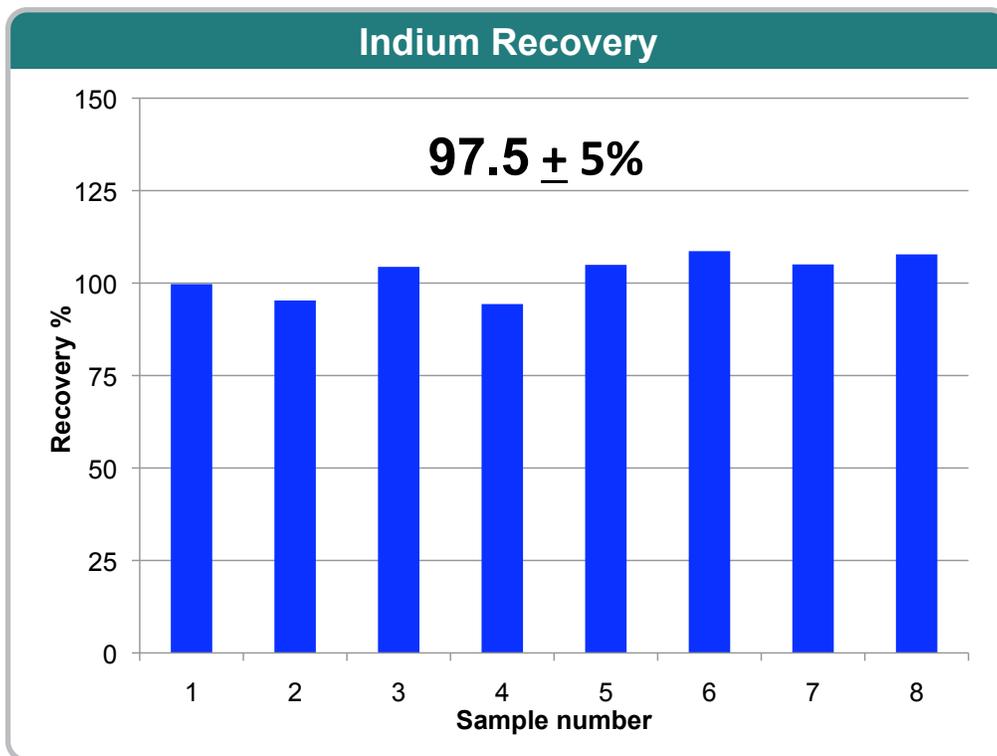


Figure 11. Indium is reproducibly and quantitatively recovered from seawater samples making it an excellent Internal Standard (IS) candidate.

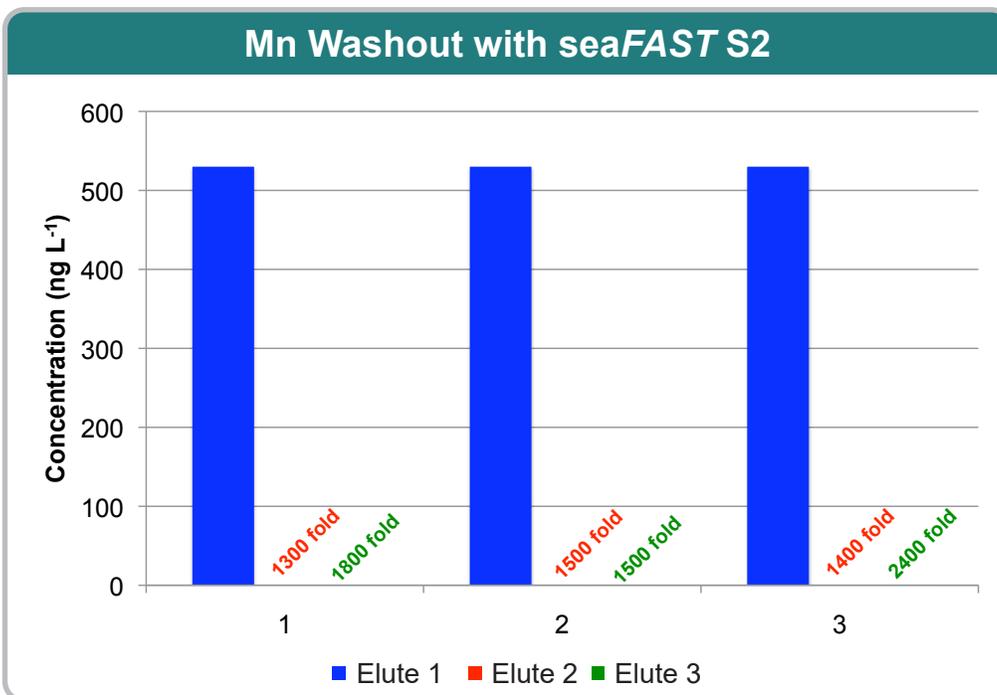


Figure 12. Three replicates of a three step elution are plotted. The first step, after loading NASS-6, recovers trace metals from the column. Two subsequent elution steps illustrate greater than a 1000-fold washout, indicating minimal sample to sample carryover. Low carryover is sufficient to measure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

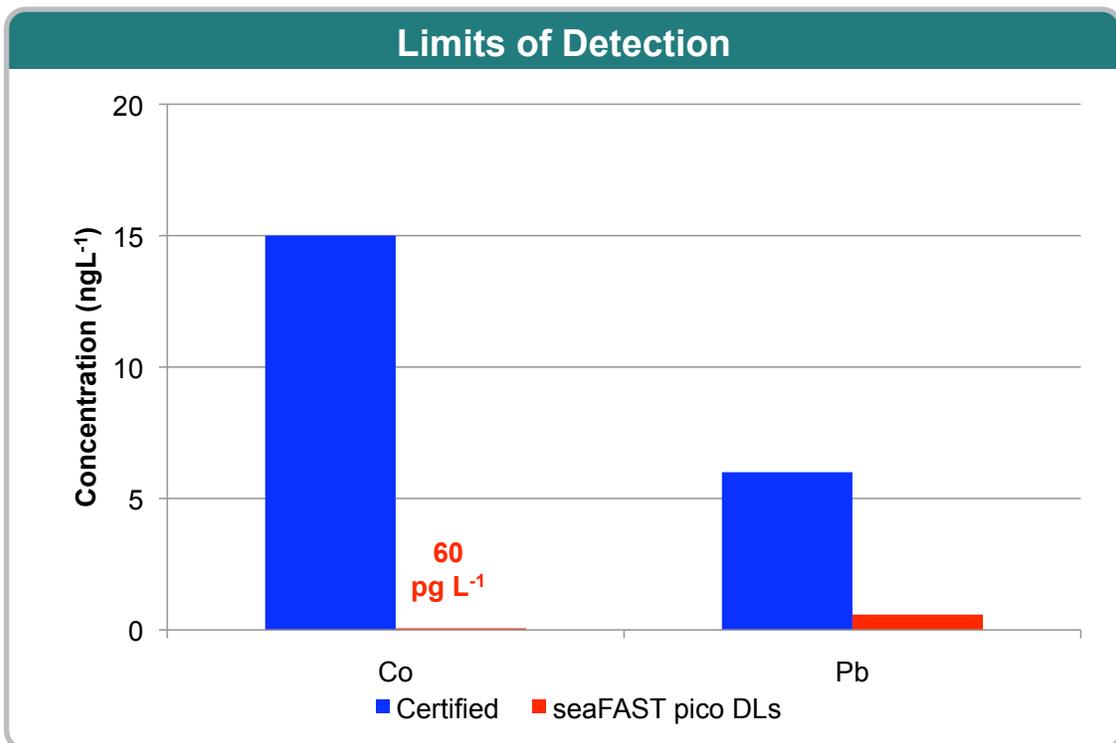
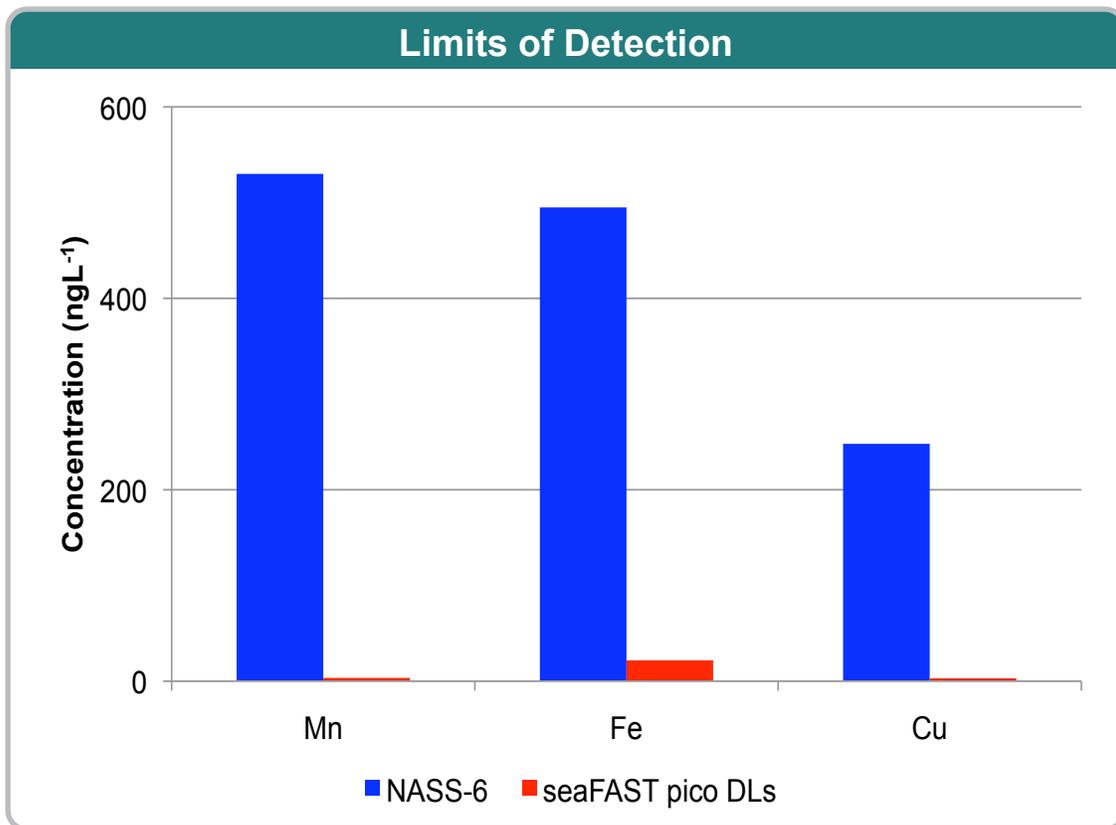
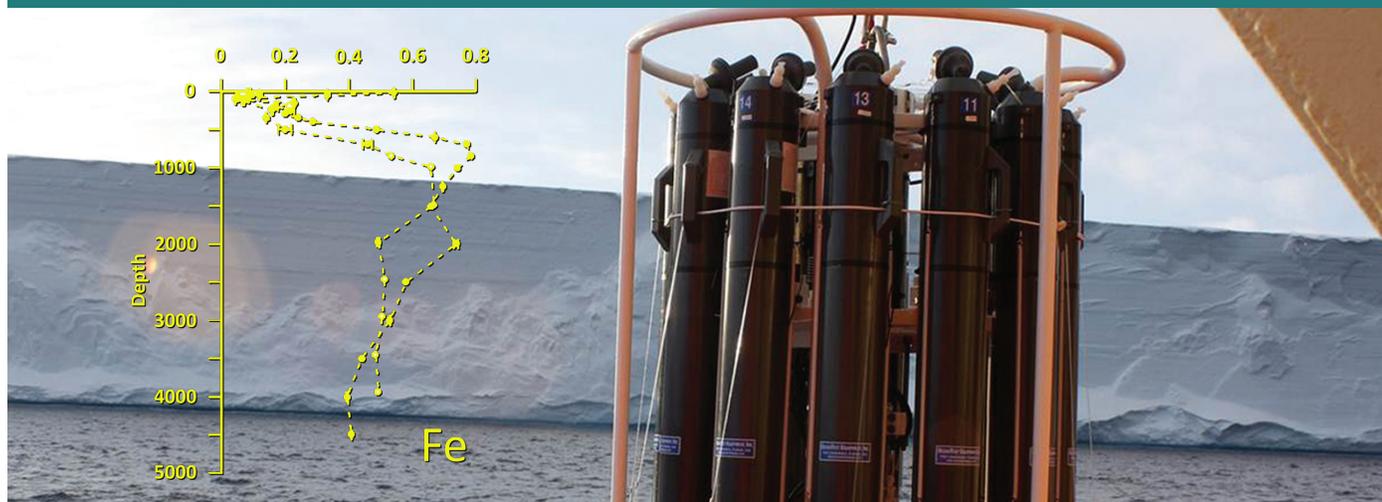


Figure 13. Limits of detection are compared to NASS-6 certified values. Matrix removal combined with a 20-fold preconcentration factor is appropriate for many seawater applications. If lower detection limits are required, the system can easily be programmed for larger preconcentration factors.

S2: First Row Transition Metals in Seawater



Inline Application

The seaFAST 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.

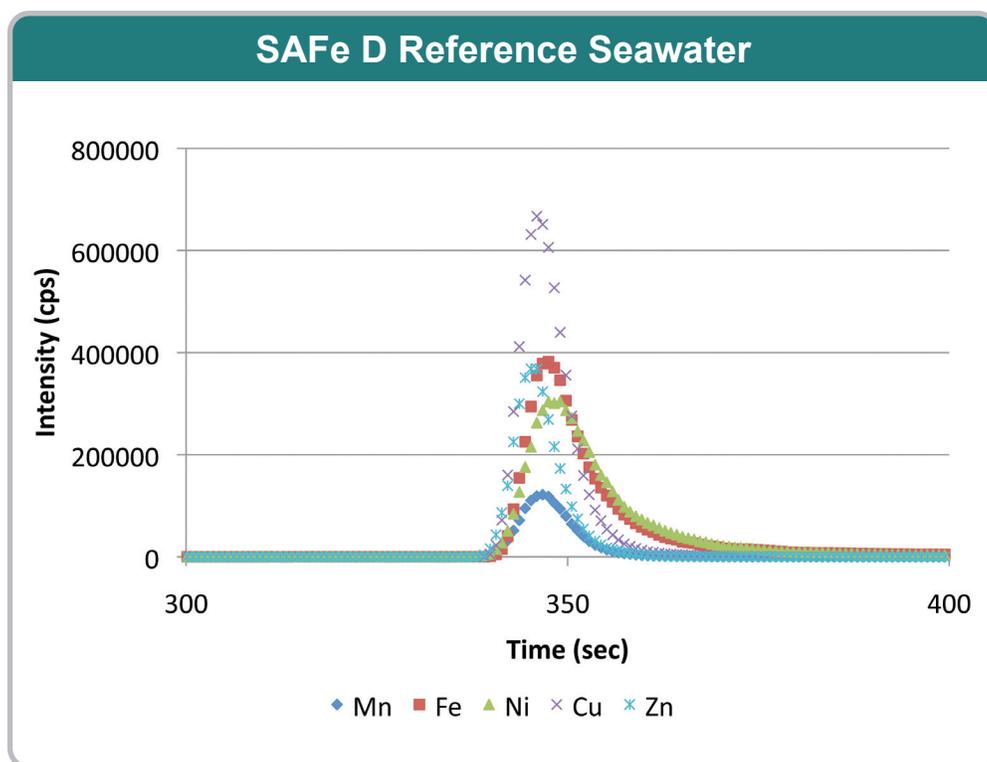
Figure 14. Elution profiles for a selection of first row transition metals (2 point running average).

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



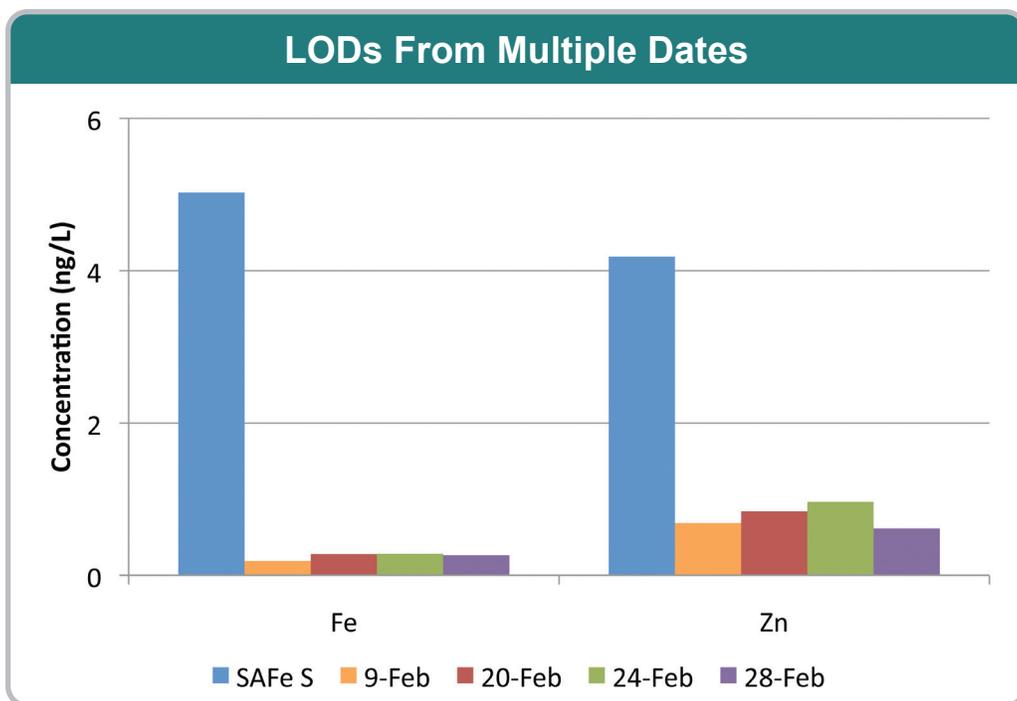


Figure 15. Limits of detection for contamination-prone elements (Fe and Zn) are in the high pg L^{-1} range and are reproducible on a day-to-day basis. These limits of detection are appropriate for determination of ultra-trace metal concentrations in open ocean surface seawater.

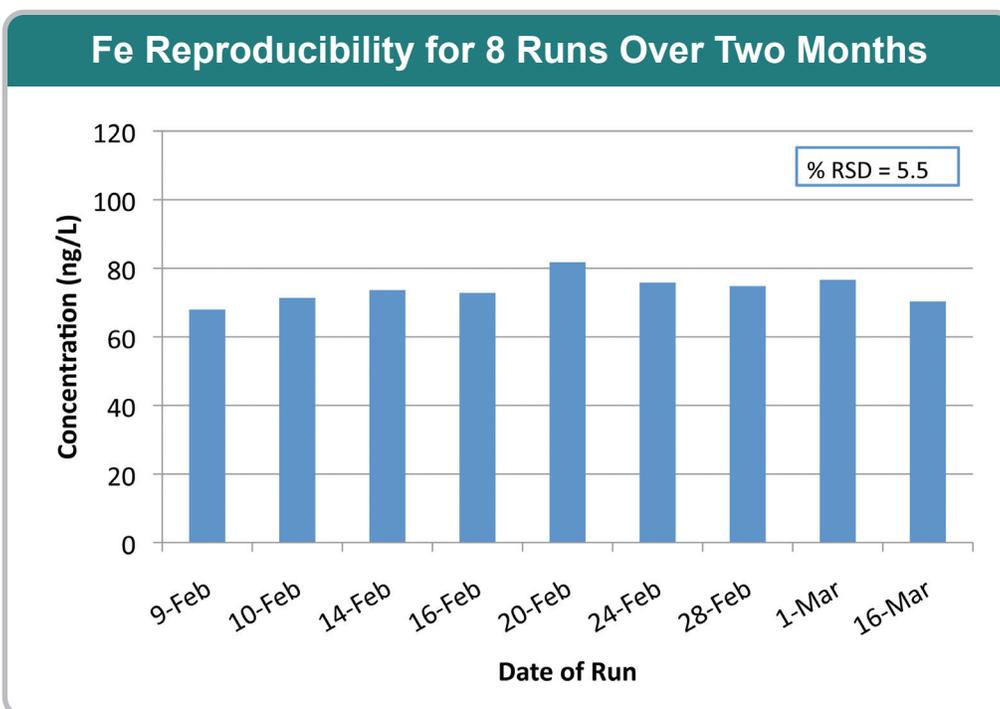


Figure 16. An internal laboratory standard of Ross seawater collected from the Southern Ocean is run several times on each of 9 discrete analytical dates. Excellent day-to-day reproducibility is illustrated for Fe, a difficult contamination-prone element.

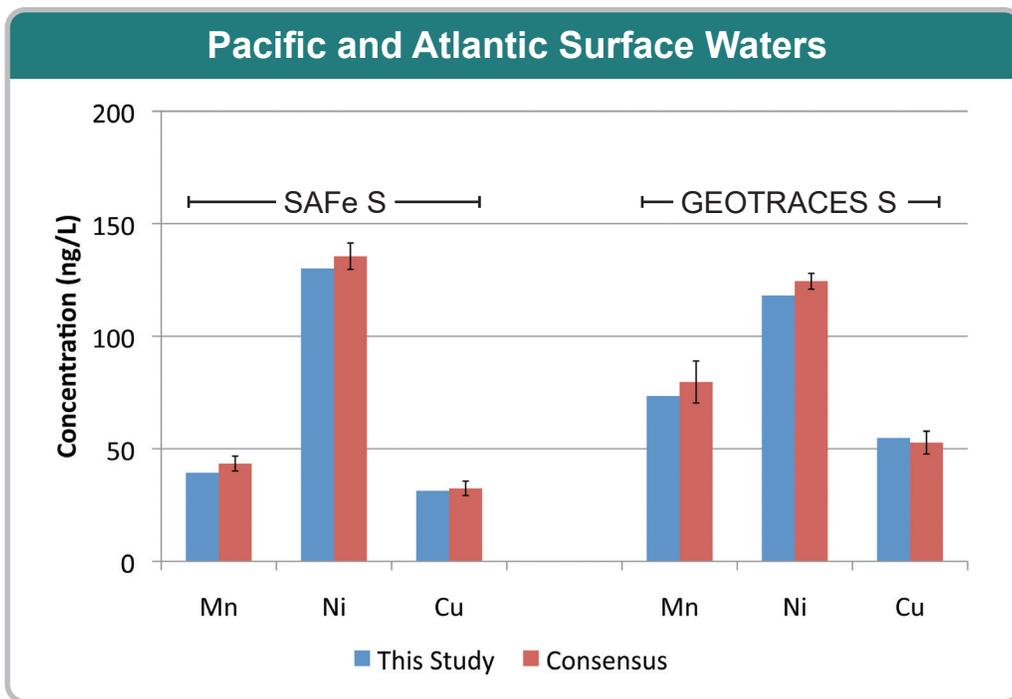


Figure 17. Accuracy of Manganese, Nickel and Copper at very low concentrations typical of the open ocean is demonstrated for SAFe and GEOTRACES surface water.

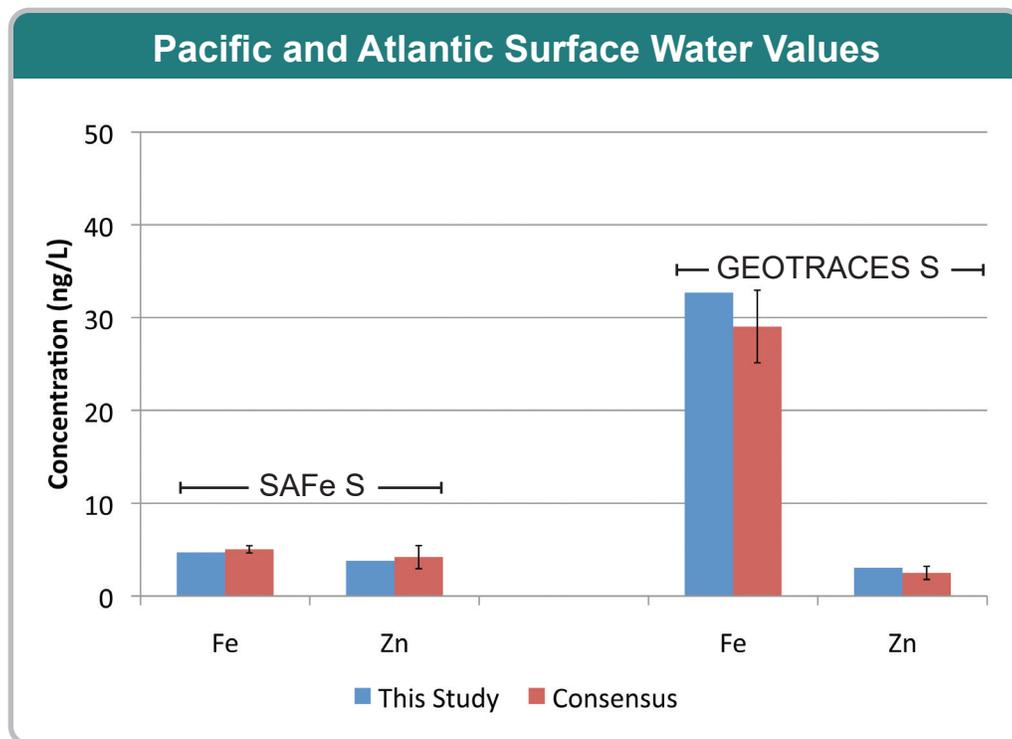


Figure 18. Accuracy of Iron and Zinc at very low concentrations typical of the open ocean is demonstrated for SAFe and GEOTRACES surface water.

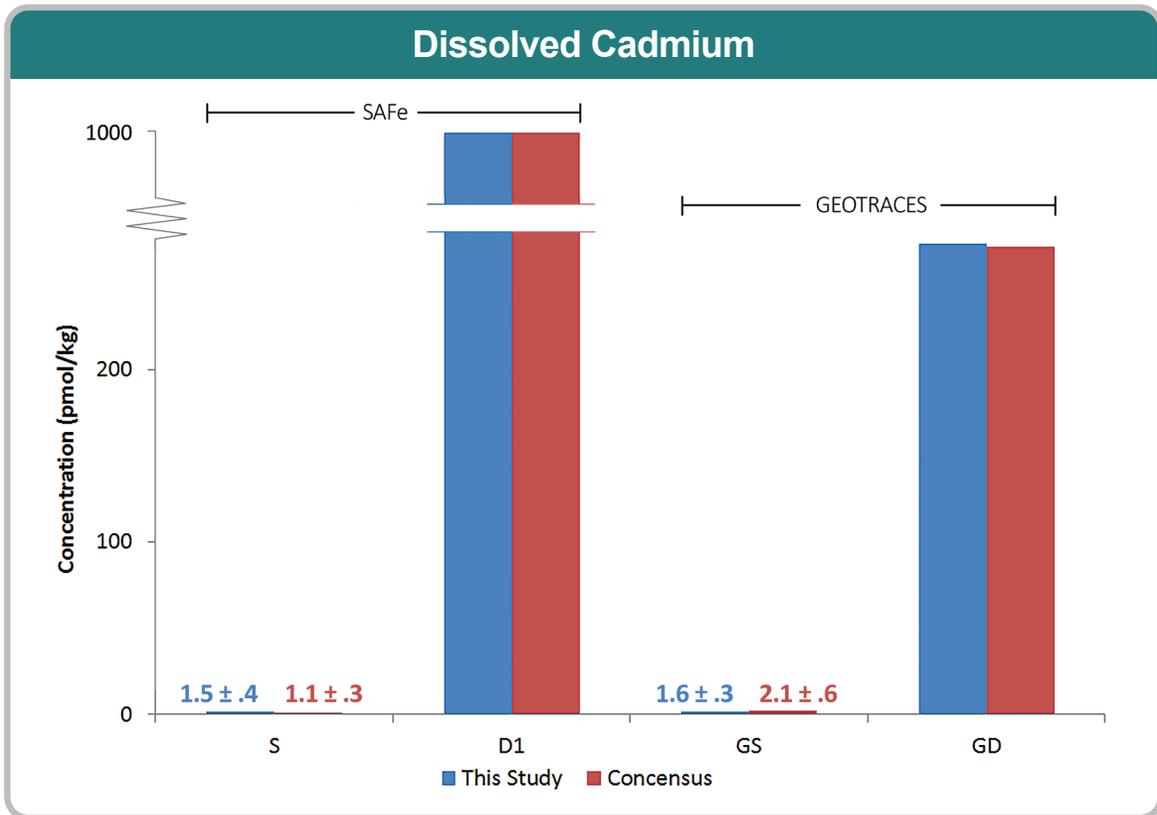


Figure 20. Concentrations of dissolved Cd determined by isotope dilution for SAFe and GEOTRACES reference standards.

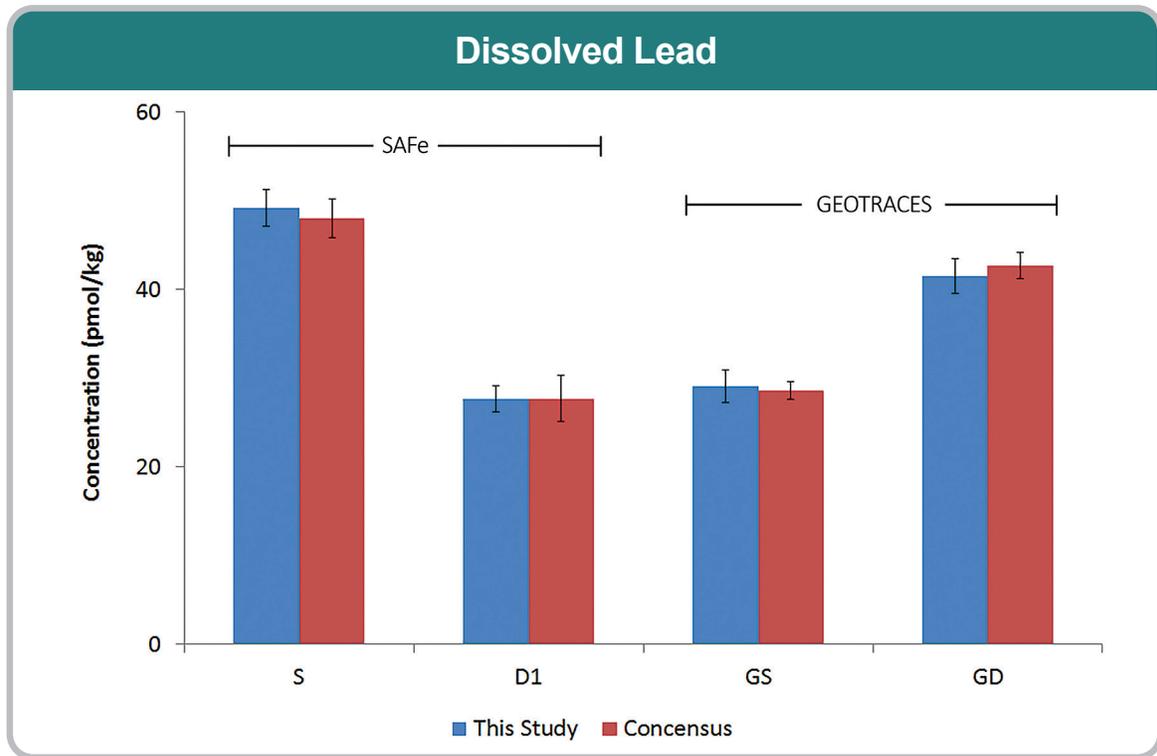


Figure 21. Concentrations of dissolved Pb determined by isotope dilution for SAFe and GEOTRACES reference standards.

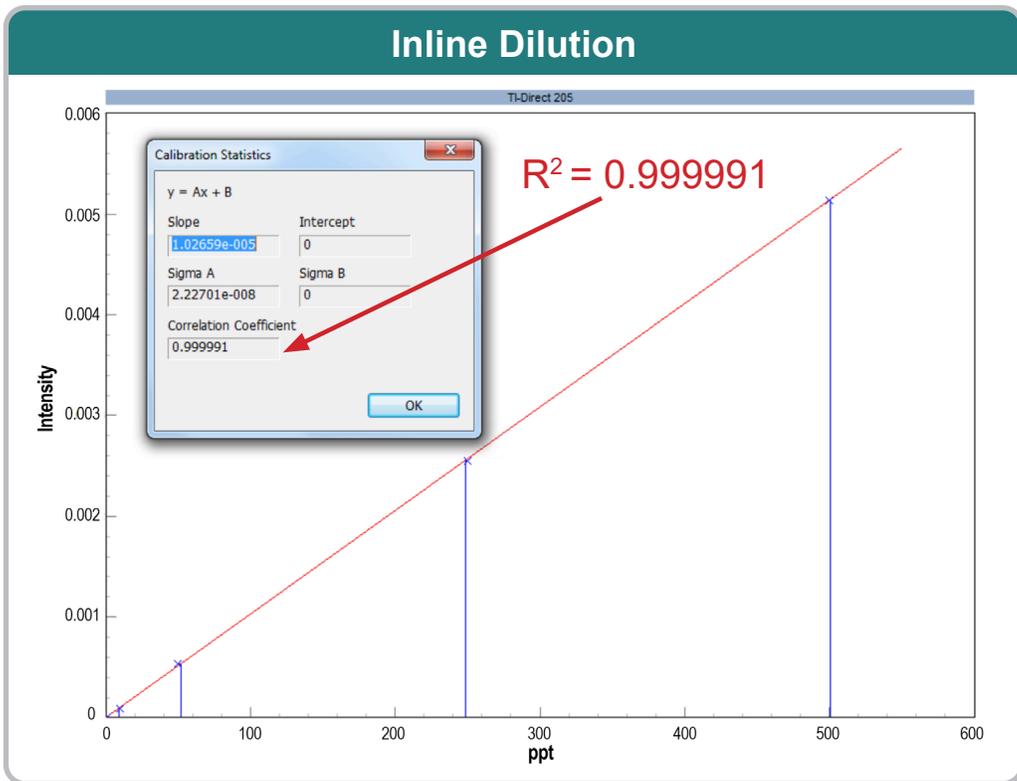


Figure 23. Direct mode calibration of TI in 3.5% NaCl. Calibration spikes are 1, 10, 50, 250 and 500 ppt.

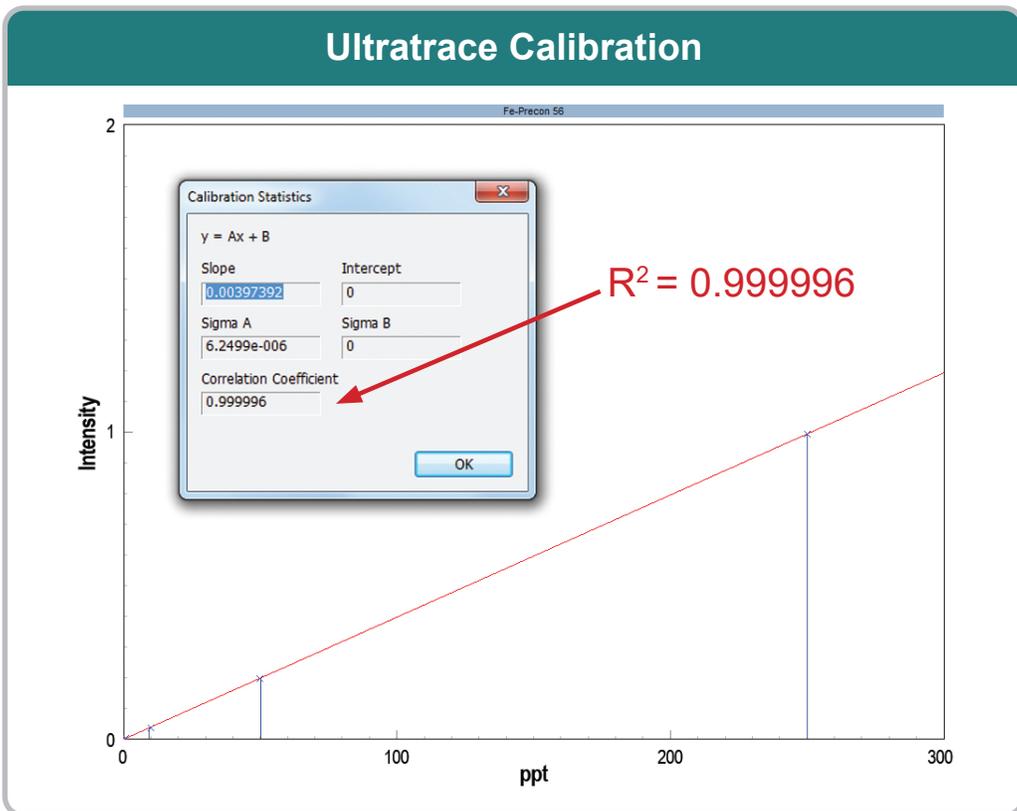
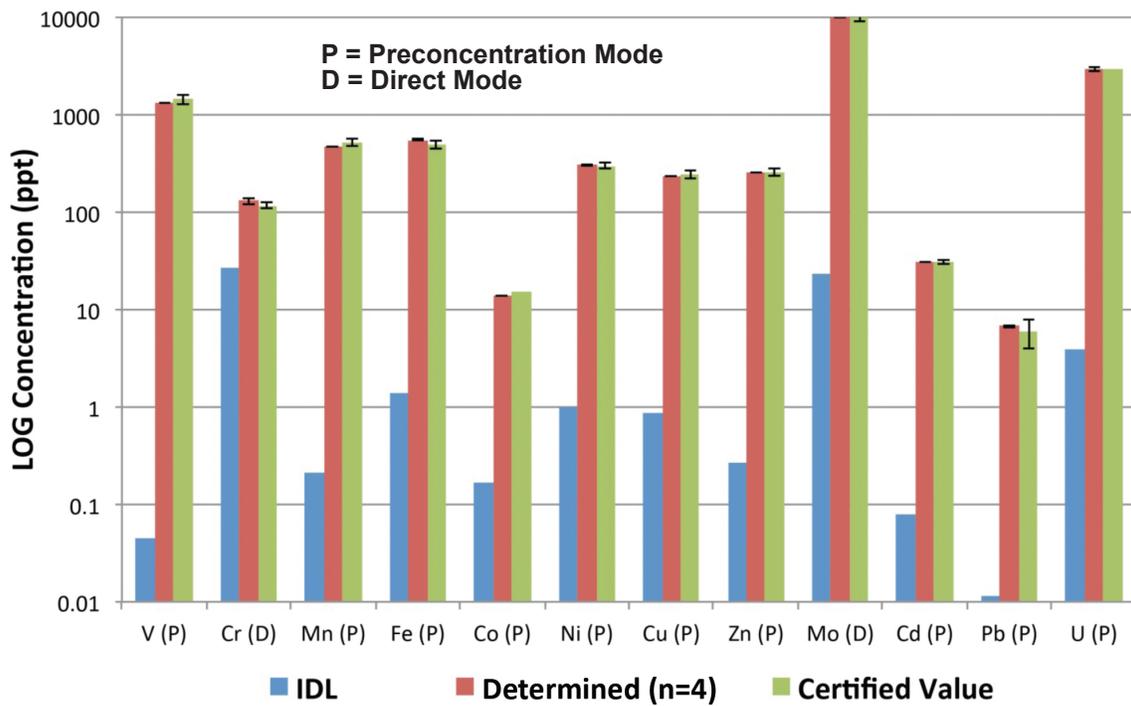


Figure 24. Preconcentration mode calibration of Fe in 3.5% NaCl. Calibration spikes are 1, 10, 50 and 250 ppt.

seaFAST S2 NASS-6 Determination, DRC, Preconcentration and Direct



seaFAST S2 CASS-5 Determination, DRC, Preconcentration and Direct

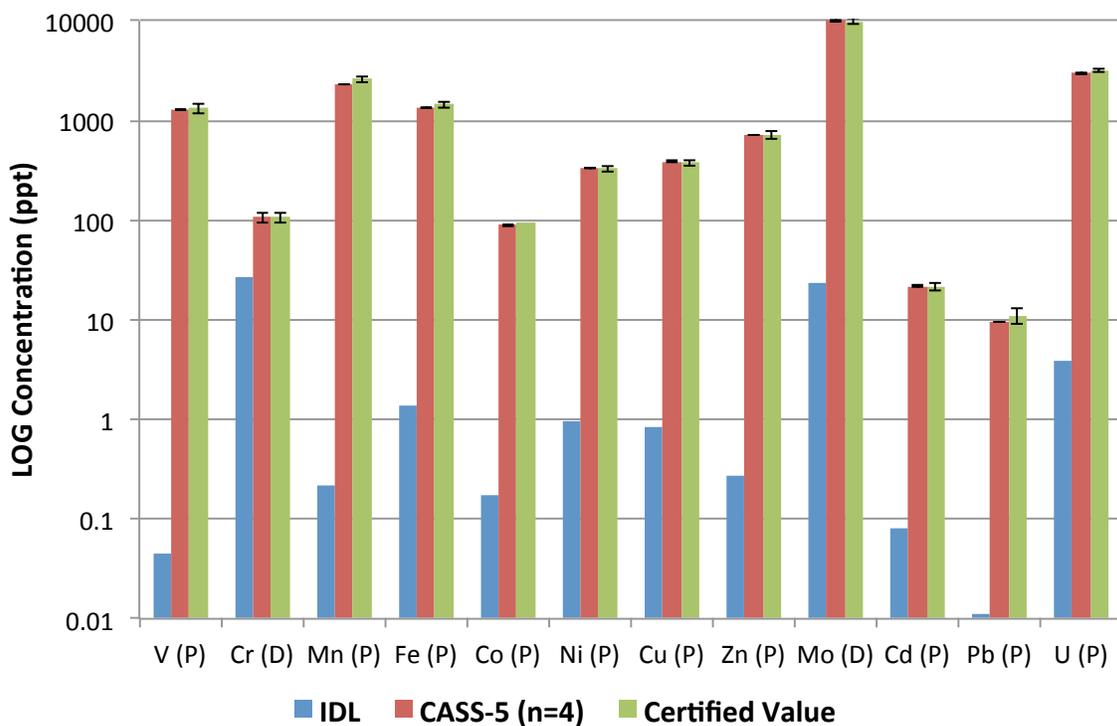


Figure 25. Results for NASS-6 and CASS-5 Seawater Reference Materials are shown. Elements determined with the seaFAST S2 are accurate and precise for elements with certified concentrations from < 10 ppt to > 10 ppb.

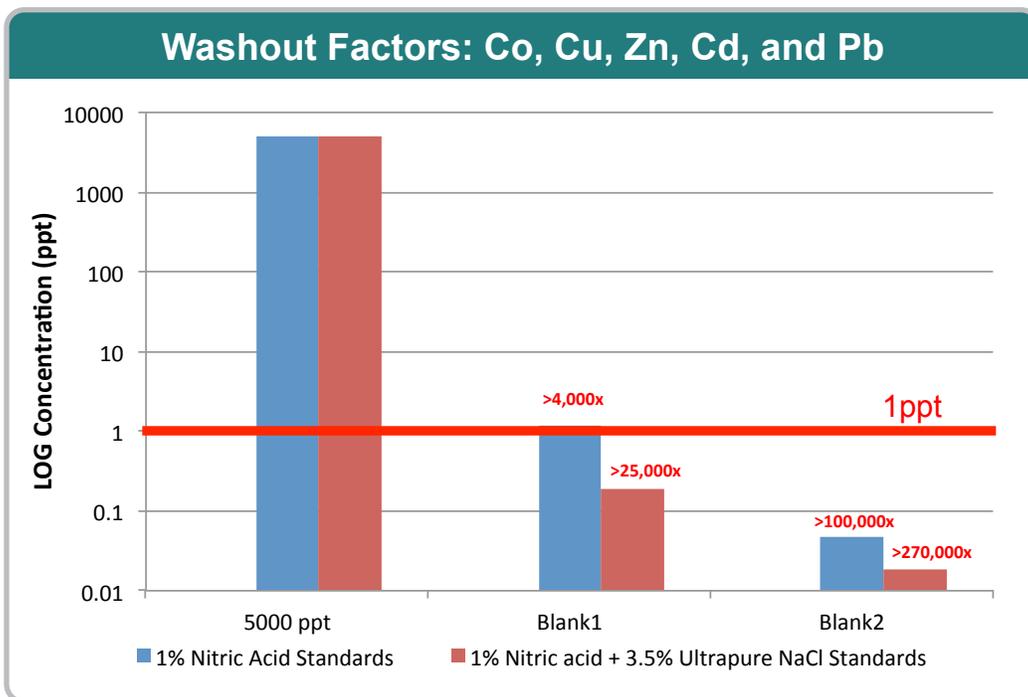


Figure 26. Washout in Preconcentration mode is excellent with both 1% nitric acid calibration standards and matrix-matched standards. Matrix matching the standards with seaBlank is not required for Preconcentration mode, but it enhances washout.

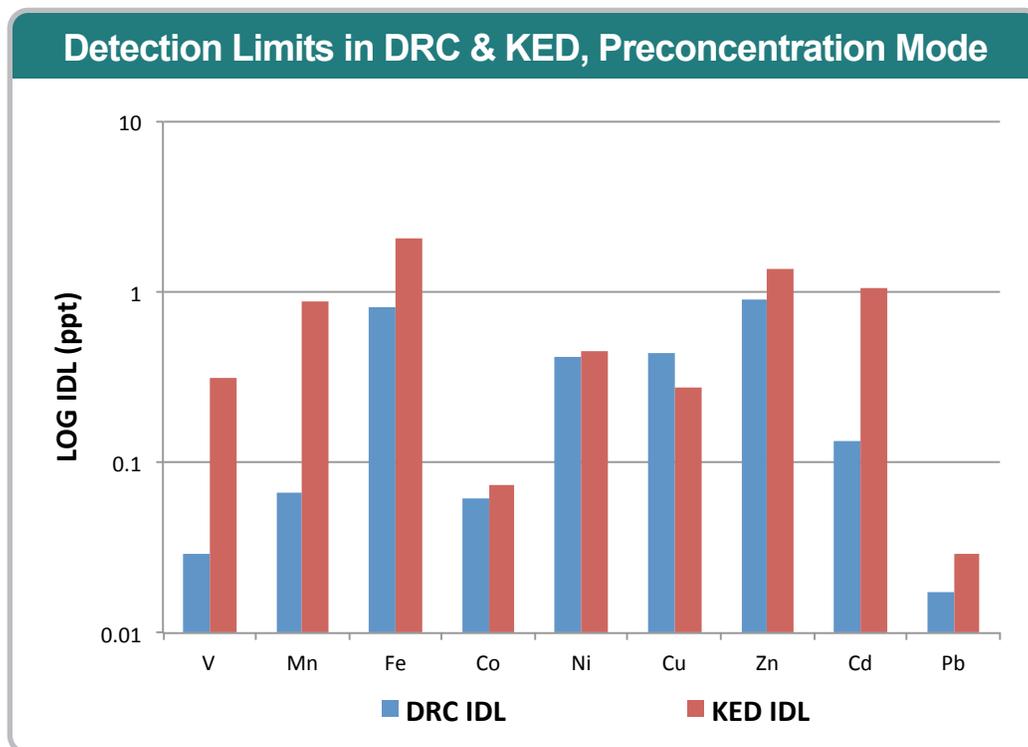


Figure 27. Detection limits are near or better than 1 ppt on a quadrupole ICPMS (n=10, 3σ).



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.

1																	2									
H																	He									
3	4											5	6	7	8	9	10									
Li	Be											B	C	N	O	F	Ne									
11	12											13	14	15	16	17	18									
Na	Mg											Al	Si	P	S	Cl	Ar									
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36									
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr									
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54									
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe									
55	56											72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs	Ba											Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
87	88																									
Fr	Ra																									
		Lanthanides	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71									
			La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu									
		Actinides	89	90	91	92																				
			Ac	Th	Pa	U																				

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.

In this work, the seaFAST 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 seaFAST 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 seaFAST resin.

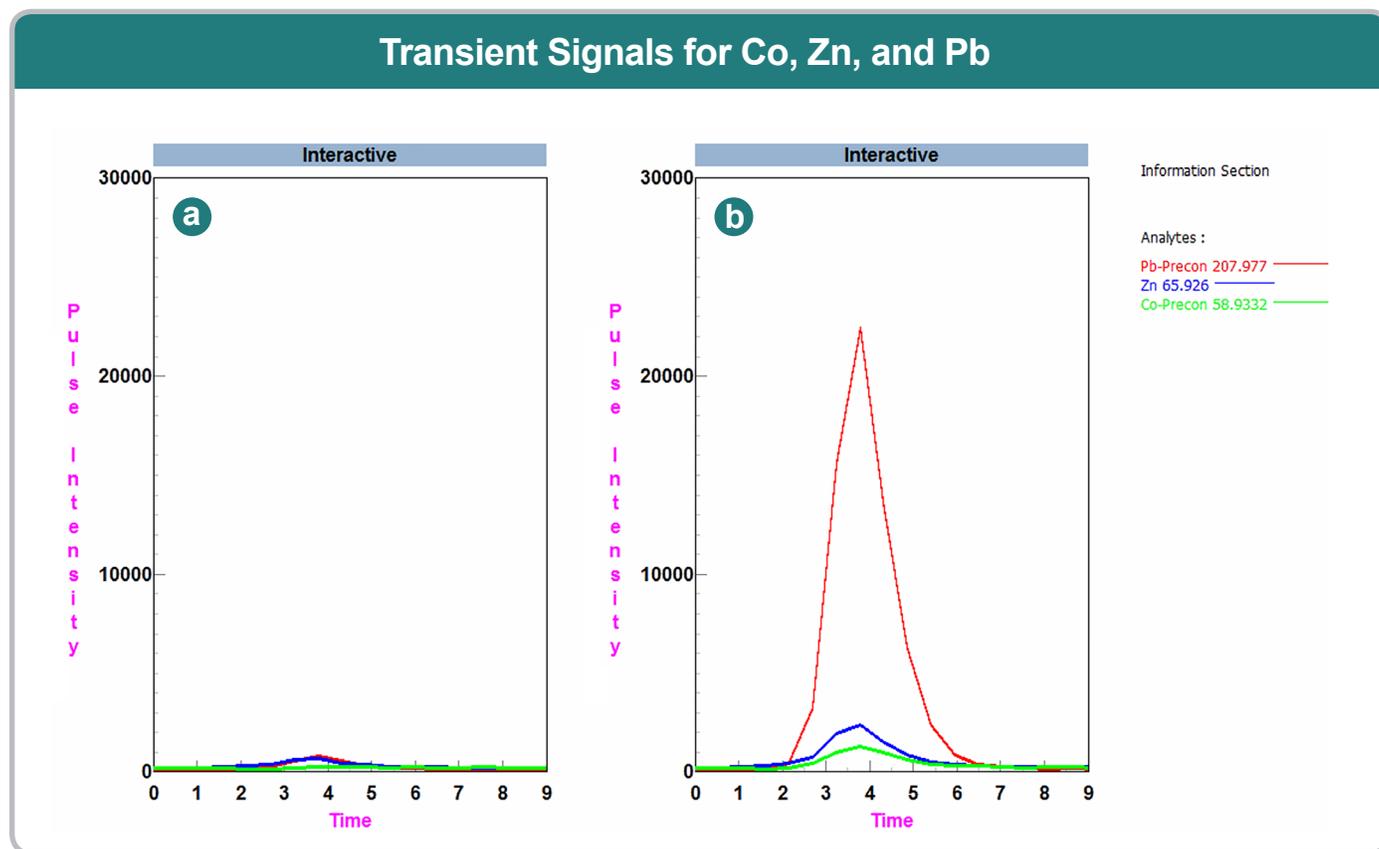
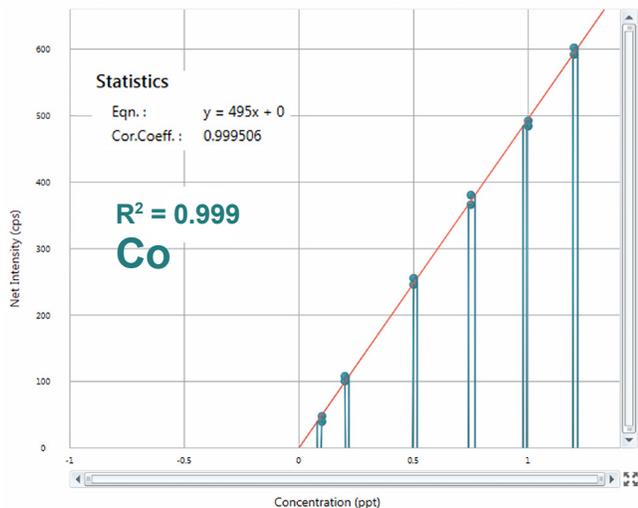


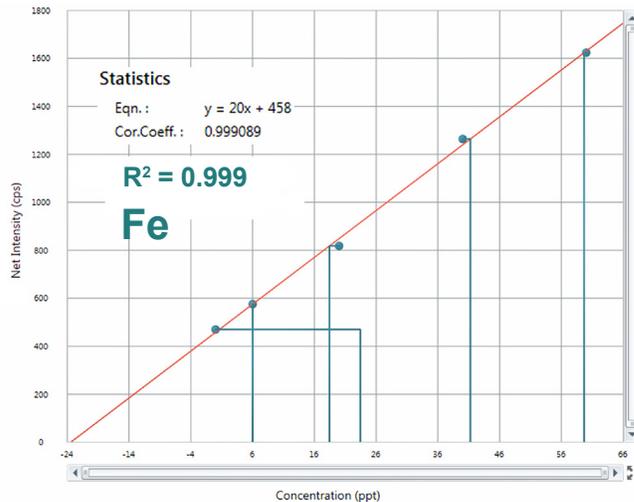
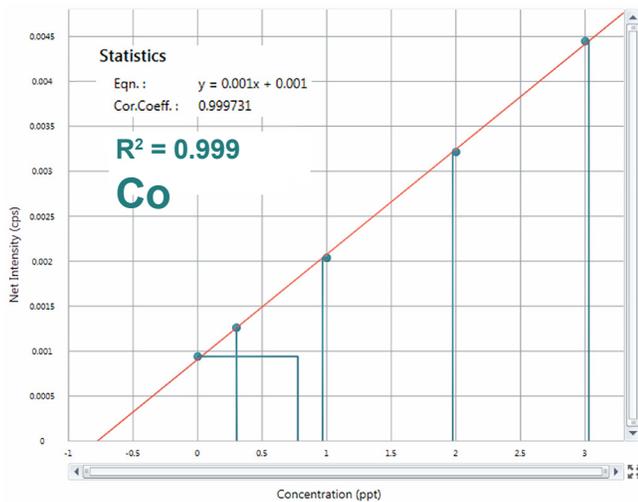
Figure 29. a) Blank acquired by loading air onto the column. b) GSP sample elution profile.

Sub-ppt Standard Additions Autocalibration



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

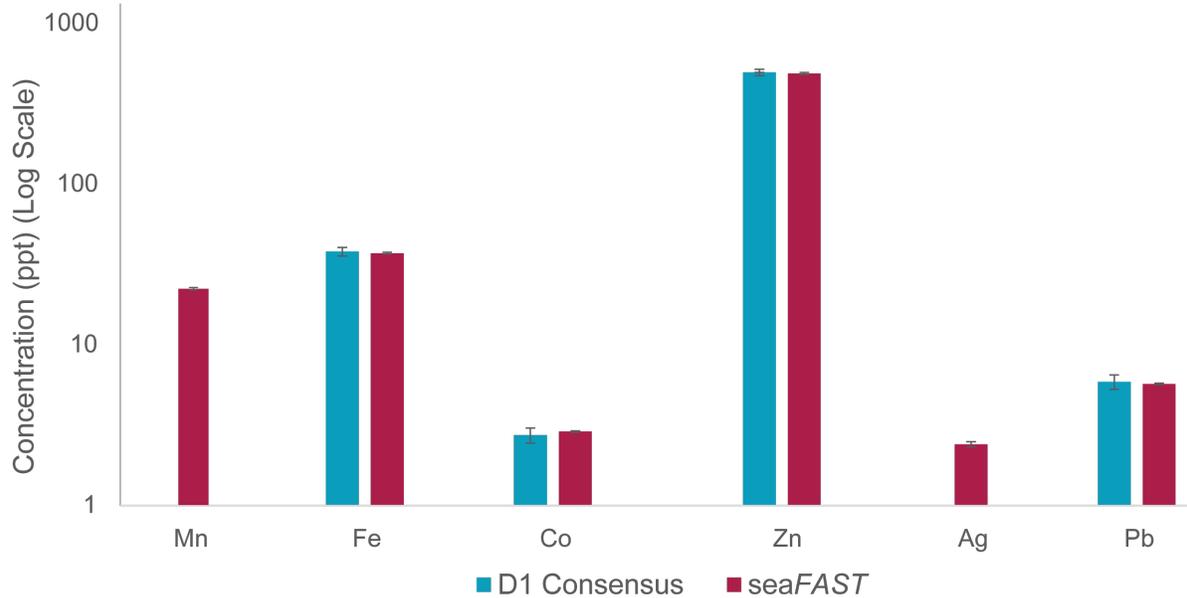
Sub-ppt Standard Additions Autocalibration



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.

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 seaFAST 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

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

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

Conclusion

- seaFAST 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.
- seaFAST offers unprecedented automation for analysis of seawater samples, even at open ocean concentrations for low and sub-ppt analytes.



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.

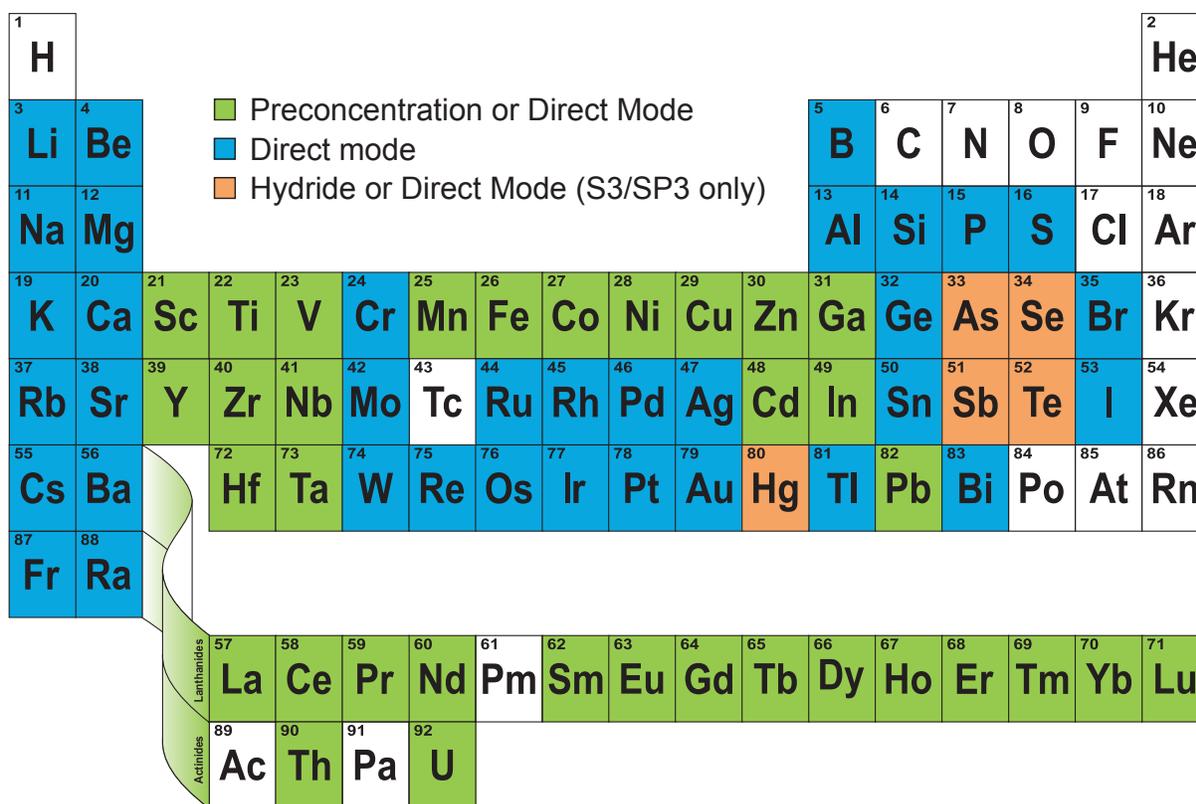


Figure 31. Periodic table showing the possible modes for each element.

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.

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.

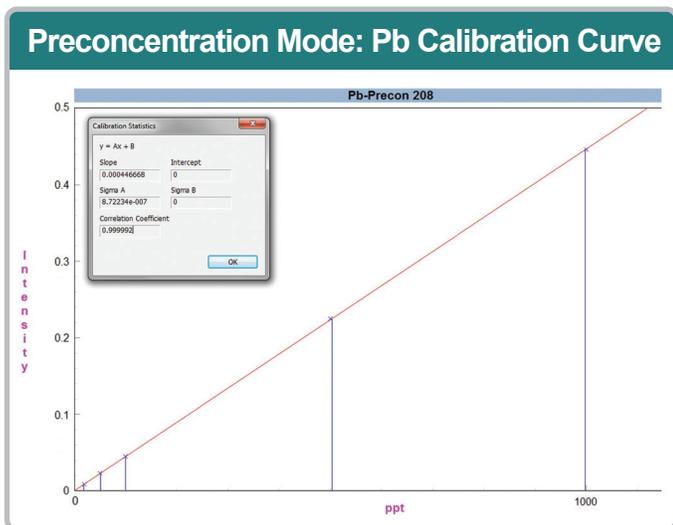


Figure 32. Autocalibration from a single 1000 ppt calibration standard. Calibration curve was matrix matched to ~3% TDS.

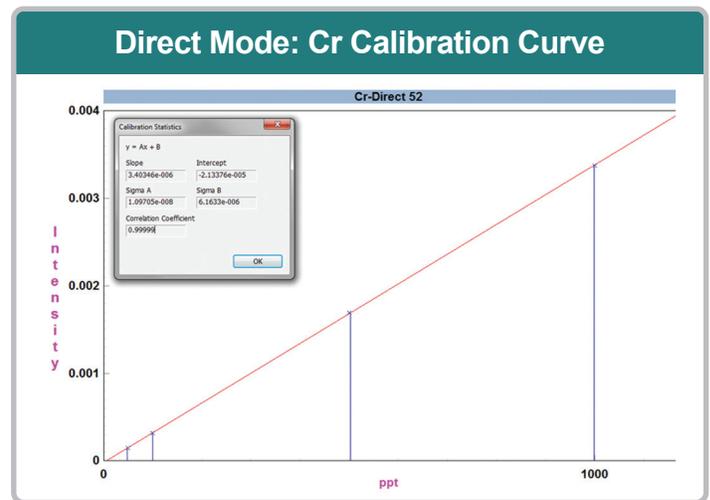


Figure 33. Direct mode with 10x inline dilution: Autocalibration from a single 1000 ppt calibration standard. Calibration curve was matrix matched to ~3% TDS.

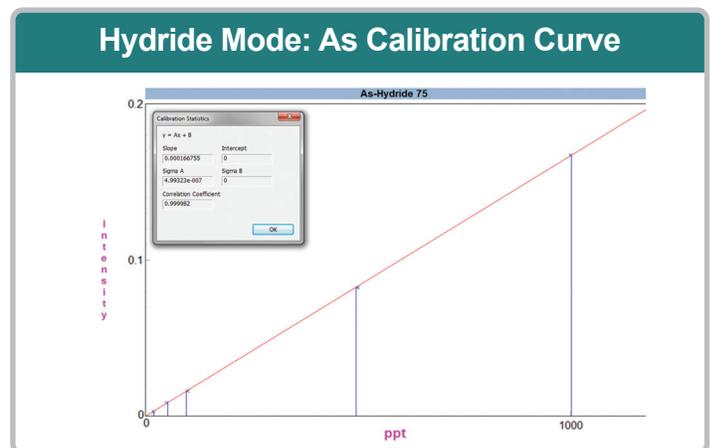


Figure 34. Autocalibration from a single 1000 ppt calibration standard. Calibration curve was matrix matched to ~3% TDS.

Preconcentration Mode: Elution of 6 Elements at 1 ppb

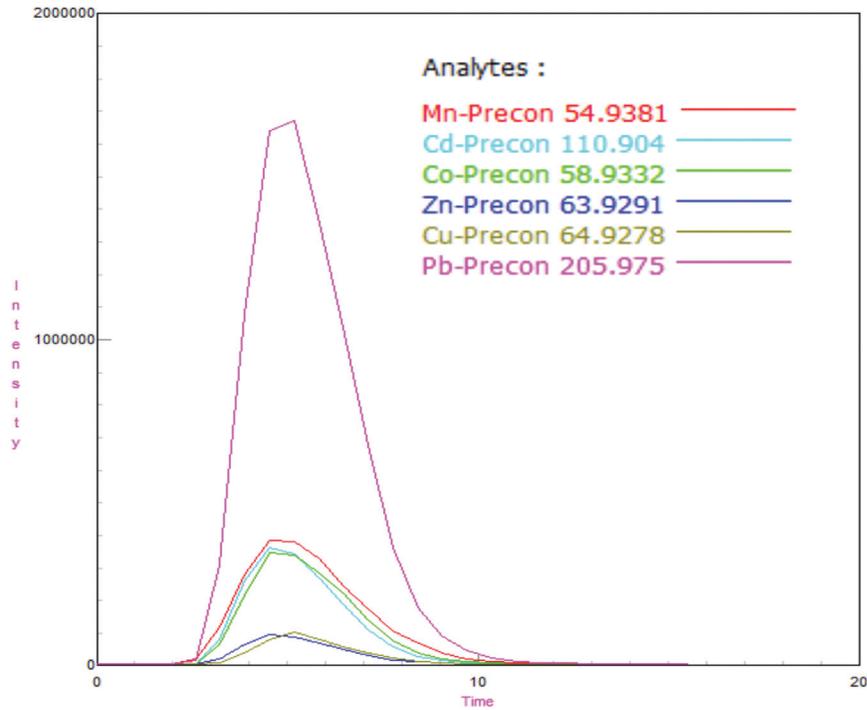


Figure 35. Simultaneous elution of 6 elements in Preconcentration mode at 1 ppb.

Direct Mode: Long Term Stability

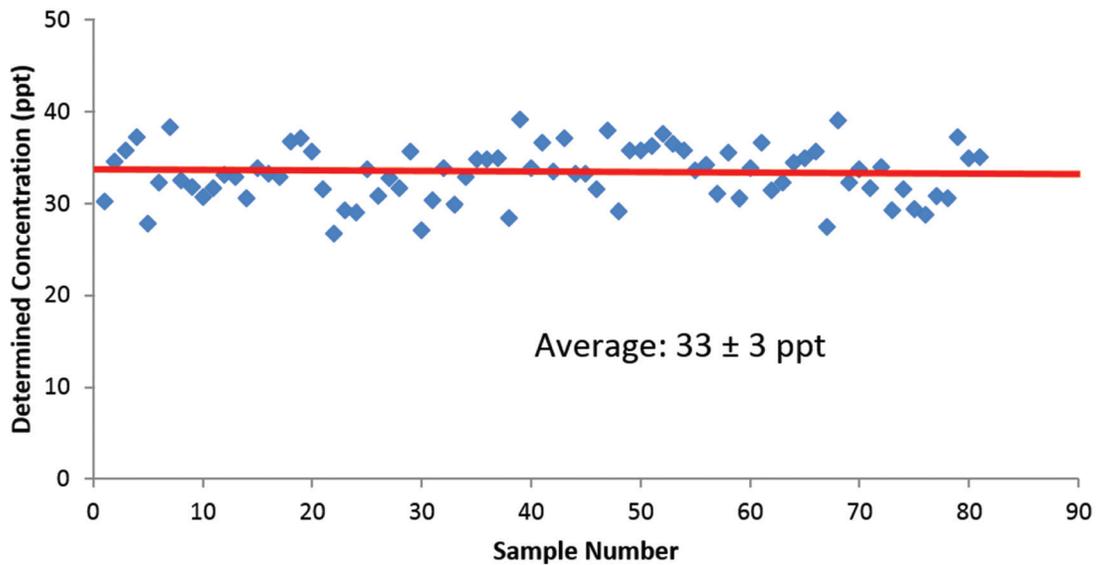


Figure 36. Long term stability of Cr in synthetic seawater shows >14 hours of repeated determinations with internal standard correction. Direct mode automatically diluted the sample inline by 10x. The determined concentration in the synthetic seawater was 33 ± 3 ppt.

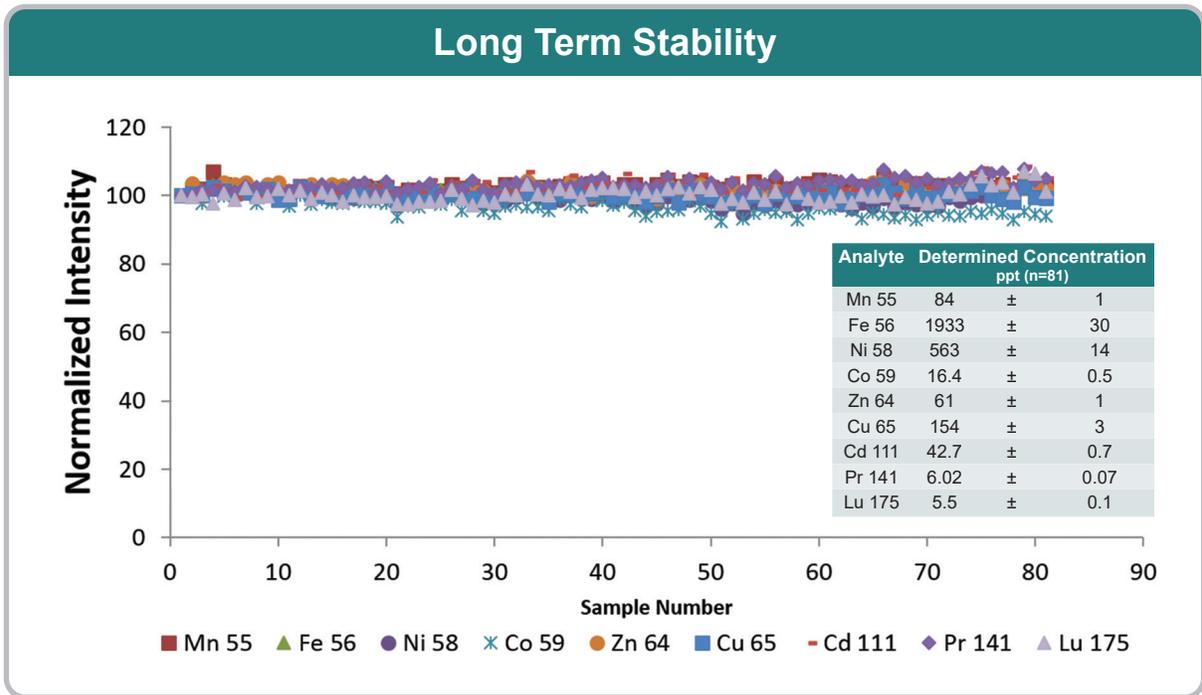


Figure 37. Common transition metals and selected rare earth elements (REEs) were determined in synthetic seawater consecutively for over 14 hours (n=81). Auto-matrix-matched blanks and QC standards are not shown, for clarity. Average precision over 14 hours was better than 2% with internal standard correction.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

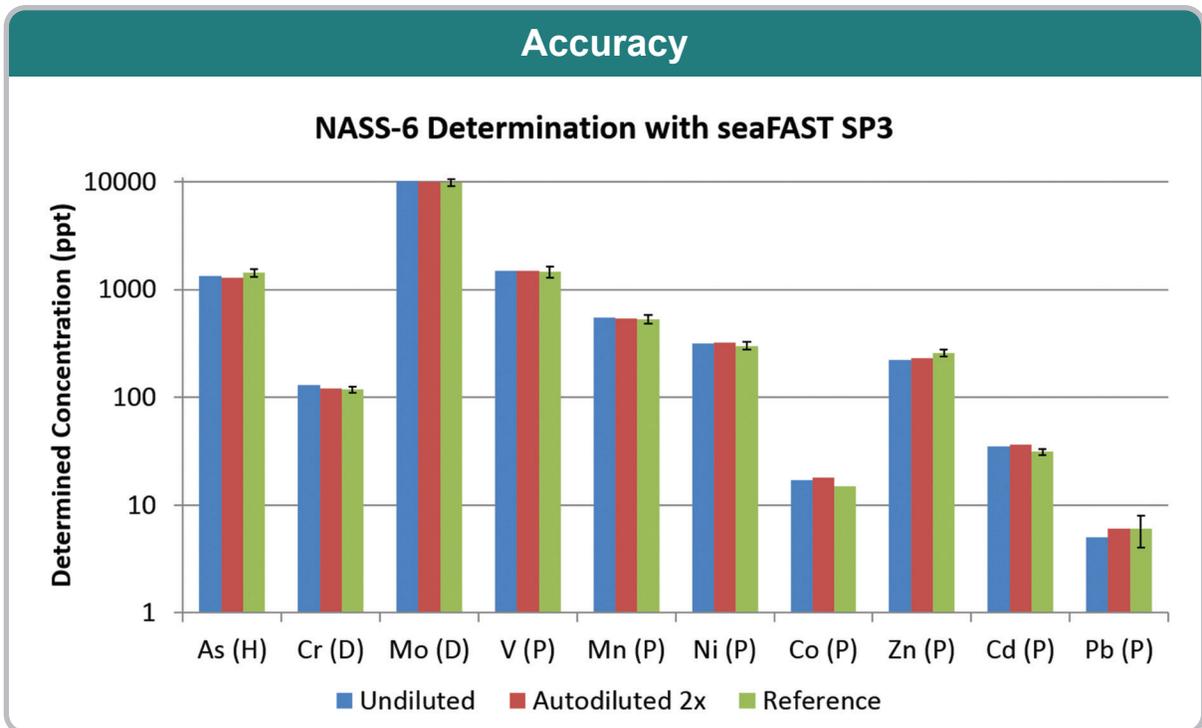
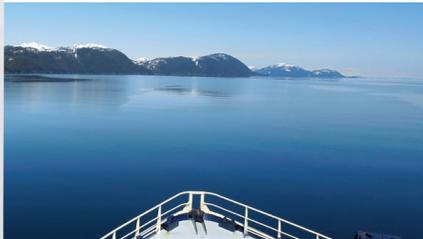


Figure 38. NASS-6 was analyzed in all three modes, Preconcentration (P), Direct with fixed 10x inline dilution (D) and Hydride (H). NASS-6 was run undiluted and with a 2x autodilution using automatic, inline matrix matching with seaBlank ultrapure sodium chloride solution. The seaFAST achieves excellent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



© Elemental Scientific | 7277 World Communications Drive | Omaha, NE 68122
Tel: 402-991-7800 | sales@icpms.com | www.icpms.com