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Determination of Fe, Zn, Ag and other trace elements in seawater using automated standard additions, preconcentration, and matrix removal

Poster Presented at Winter Plasma Conference Tucson 2016

Abstract

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.

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 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.

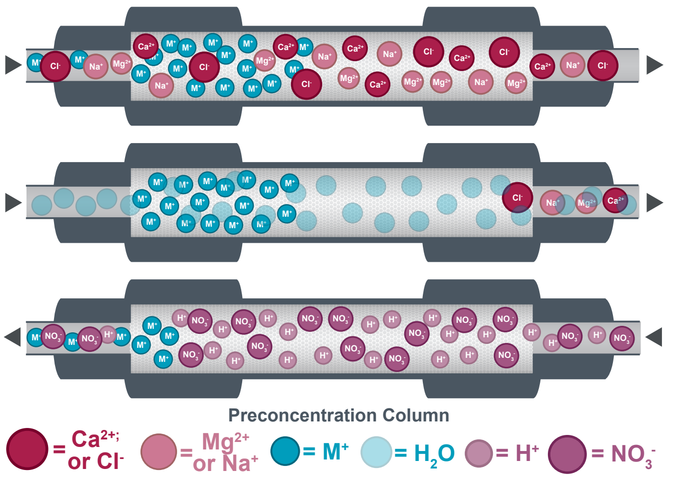
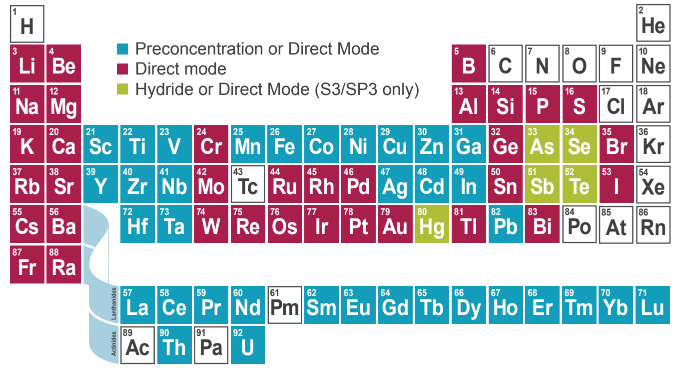


Figure 1. At a pH ~ 6, many metals are chelated on the preconcentration column, while matrix elements are flushed from the column. Metals are eluted directly to the ICPMS with nitric acid.



sea*FAST* Preconcentration Column

Sub-ppt Standard Additions Autocalibration

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

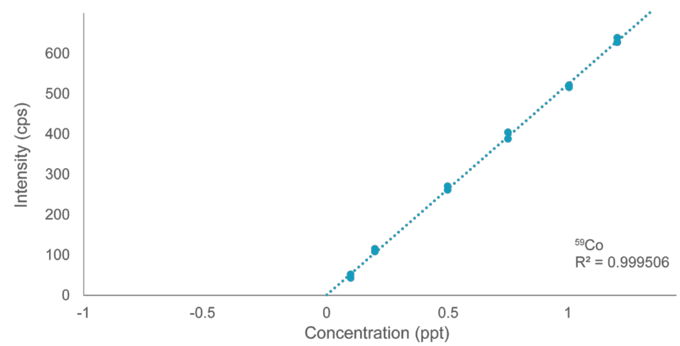


Figure 2. A sub-ppt standard addition calibration prepared by auto-spiking a DI water sample, background subtracted.

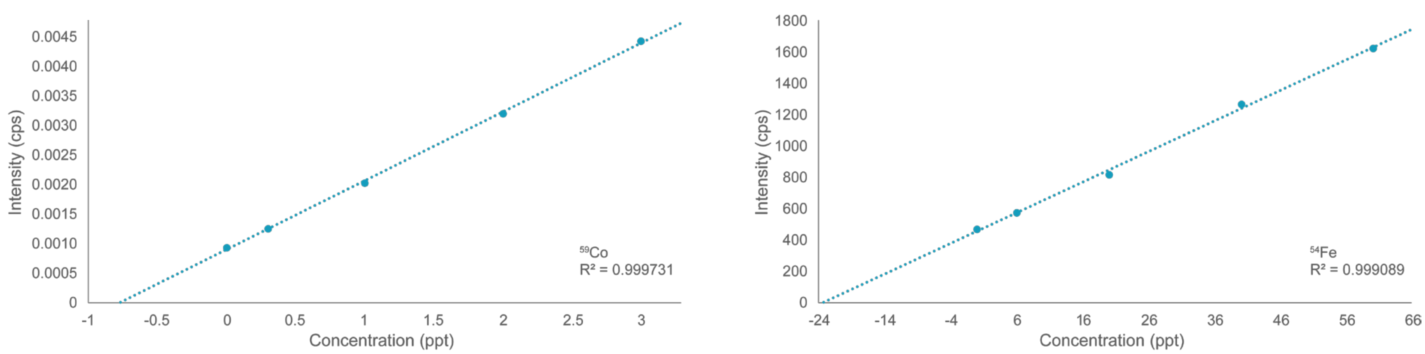


Figure 3. Automatic standard addition calibrations in GSP for Co and Fe, no blank subtraction.

Transient Signals for Co, Zn, and Pb

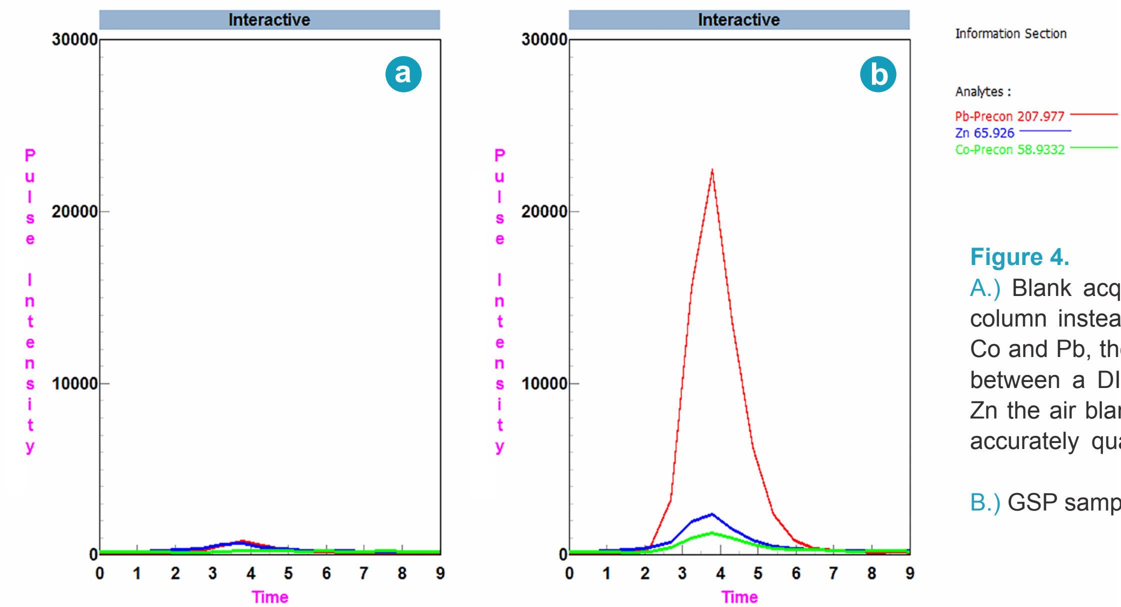


Figure 4.
A.) Blank acquired by loading air onto the column instead of sample or DI water. For Co and Pb, there is no significant difference between a DI water and air blank, but for Zn the air blank is lower. Further studies to accurately quantify the blank are ongoing.

B.) GSP sample elution profile.

Results

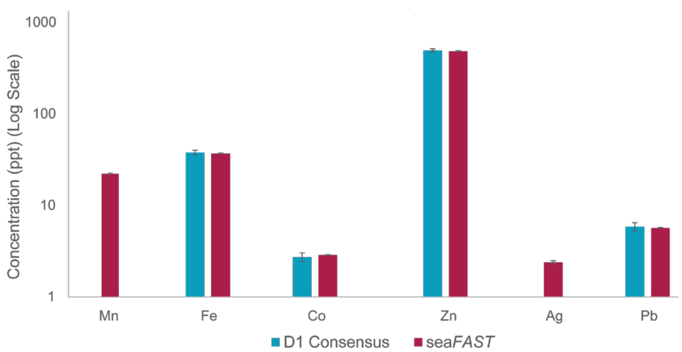


Figure 5. sea*FAST* accuracy compared to D1 Consensus.

Table 1. Results for D1 measured with sea*FAST* on NexION are compared with consensus values, showing excellent agreement. Mn and Ag have no consensus values.

D1 North Pacific Intercalibration Sample, 1000m						
	Consensus Value			**NexION / sea*FAST***		
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

Table 2. 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.

SLEW-3 SRM Comparison						
	Reference (ppt)			**NexION / sea*FAST* (ppt)**		
Ag	1.93	±	0.1	1.92	±	0.08

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

Table 3. Detection limits and results are shown for GSP. Zn results are preliminary due to ongoing investigations of blank reduction/correction.

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

Conclusions

- 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.

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