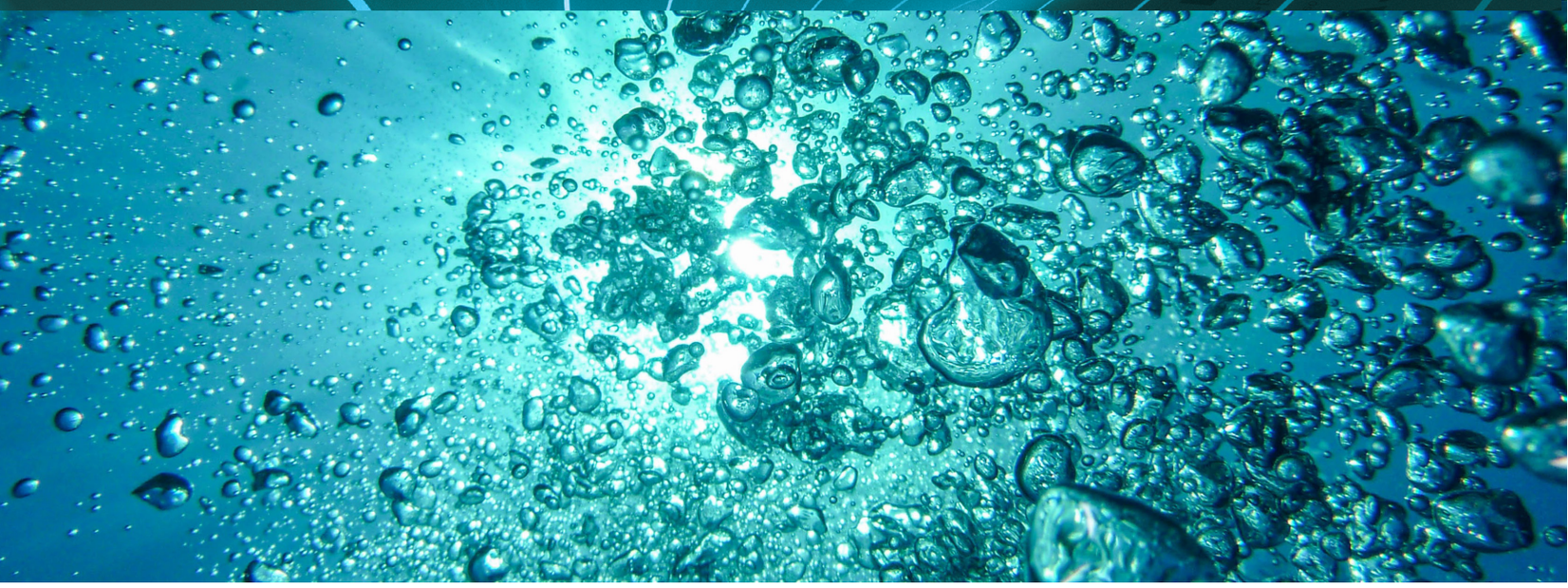

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Automated Processing of Seawater Samples for Iron Isotope Ratio Determination

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Introduction

Bioactive metals, such as iron, act as important nutrients in the ocean and are often present at very low concentrations, which limit phytoplankton growth. In recent years, measurement of the dissolved stable isotope ratio of bioactive metals in seawater has provided insight into the biogeochemical cycling of these elements. Iron isotope ratios, in particular, have been shown to be useful tracers of iron sources across the open oceans [1].

High precision isotope ratio analysis requires sample amounts ranging from 2 to >100 ng, depending on the element and isotopes of interest. Trace and bioactive metals at low natural concentrations (1-100 ng L-1) in seawater pose a significant challenge with respect to sample volume requirements (~1-4 L), the seasalt matrix, and sample processing. Currently, two-step manual processes are employed to first preconcentrate a suite of metals in batch mode and then purify (chromatographically isolate) the metal(s) of interest for isotopic analysis (e.g. [2]), with methods often only optimized for 1 or 2 elements at a time.

Here we investigate a fully automated complete sample processing procedure using a newly developed, large-volume (up to 2 L), seawater preconcentration system in conjunction with a commercially available chromatography system (prep*FAST* MC). The first automation system uses a 200 µL sea*FAST* column to perform a 1000x (400 mL to 400 µL) preconcentration/matrix removal step for a suite of transition row and REEs. The prep*FAST* MC then purifies discrete Cu, Fe, and Zn fractions for isotopic analysis.

Elemental concentrations determined using HR-ICP-MS (Element 2) are used to calculate the total procedural blank, recovery, and carryover. Fe isotope ratios for seawater samples processed by both methods are measured using a HR-MC-ICP-MS (Neptune Plus) and compared for precision and accuracy with samples measured using a published batch extraction and column purification method [2].

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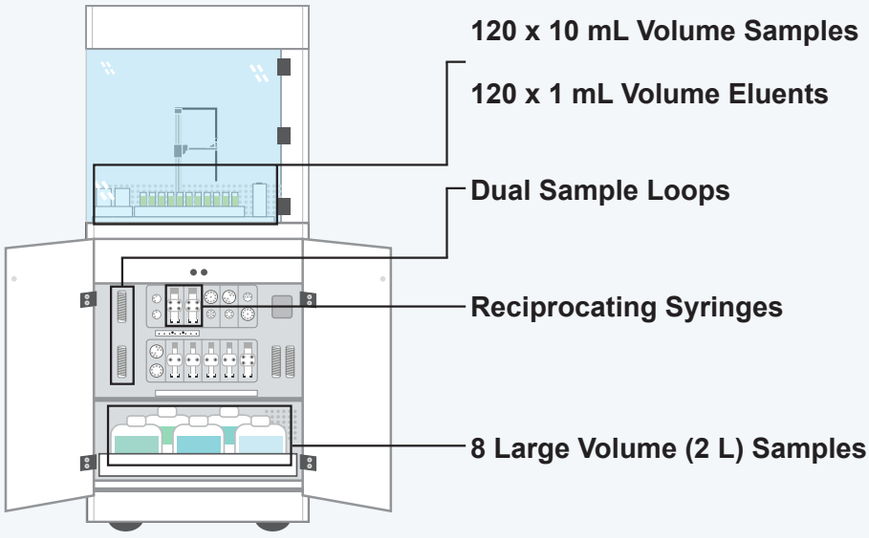
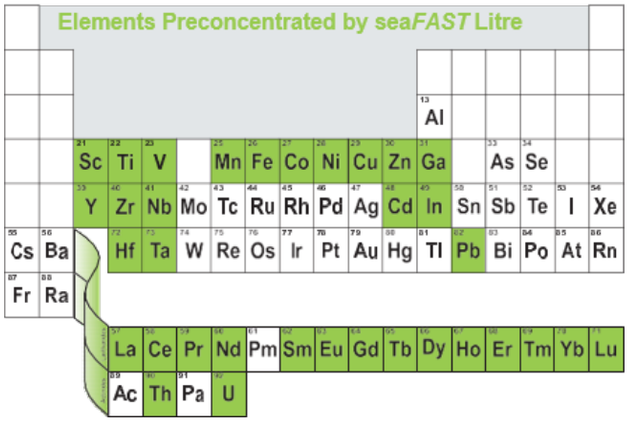
Step 1 - sea*FAST* Litre Preconcentrates Trace Metals from Seawater



Experimental Conditions

- Seawater sample from 3000 m depth,Tropical Western South Atlantic Ocean
- Sample Volume 370 mL
- 200 µL sea*FAST* column
- 600 µL 10M HCl Eluent
- 120 min/sample



Vial+1M HCl dry down Blank

- Cu: 11 pg
- Fe: 23 pg
- Zn: 19 pg

sea*FAST* Litre Blank*

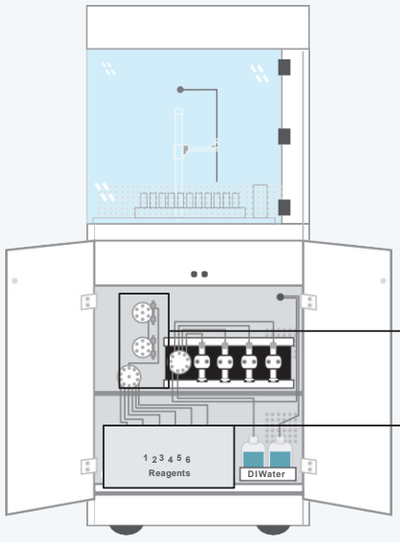
- Cu: 38 pg
- Fe: 134 pg
- Zn: 34 pg

sea*FAST* Litre Recovery*

- Cu: 100.1%
- Fe: 99.8%
- Zn: 98.4%

*Average of 3 samples

Step 2 - prep*FAST* MC Purifies Fractions for Isotopic Analysis

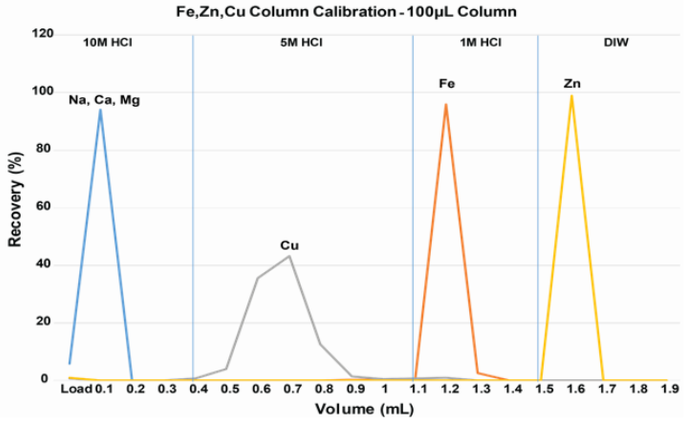


Load sea*FAST* Eluent Directly Into Column

Reagents
- **1M HCl**
- **5M HCl**
- **10M HCl**
- **DI Water**

Experimental Conditions

- Preconcentrated seawater sample eluted in 10M HCl
- Load 600 mL
- 100 µL Fe Zn Cu Column (p/n CF-MC-FeZnCu-0100)
- Load 10M HCl
- Wash 10M HCl
- Elute Cu, Fe and Zn fractions



prep*FAST* MC Blank*

- Cu: 7 pg
- Fe: 119 pg
- Zn: 19 pg

prep*FAST* MC Recovery*

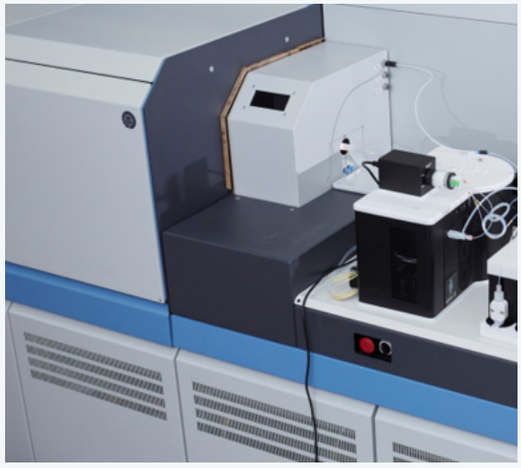
- Cu: 92.8%
- Fe: 99.5%
- Zn: 102.5%

prep*FAST* MC Carryover*

- Cu: 500x
- Fe: 400x
- Zn: 1500x

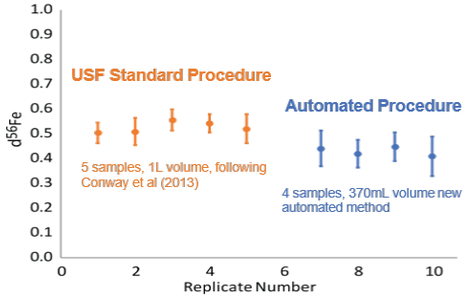
*Average of 3 samples

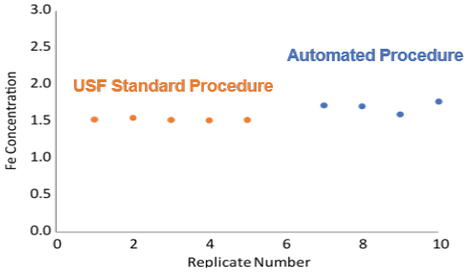
Step 3 - apex Ω Neptune Plus Analyze Sample for Precise Isotopic Ratios



Experimental Conditions

- Neptune Plus with Ni Jet sampler and Al X skimmer cone
- Apex Ω with ~5 L Ar, no N.
- ~120 µL/min ESI PFA neb
- Spiked 1:2 with a 57-58 Fe double spike from isoflex
- Data reduction through typical double-spike calculation following Siebert et al.
- Long-term analytical precision based on repeated analysis of the NIST 3126a standard of 0.36 +- 0.04 permil based on 190 measurements over 15 runs over 2 years.





Conclusions

A novel automated procedure for purification of Cu, Fe and Zn from seawater has been developed and tested for Fe isotope accuracy and precision. The automated method has:

- High recovery
- Low blank
- Low carryover

References

1. *Conway and John, (2014), Nature, 511, 212-215.*
2. *Conway et al., (2013), ACA, 793, 44-52.*

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