# Automated, High-volume Preconcentration and Matrix Removal System for Ultratrace Quantification and Isotopic Determination of Trace Elements in Seawater

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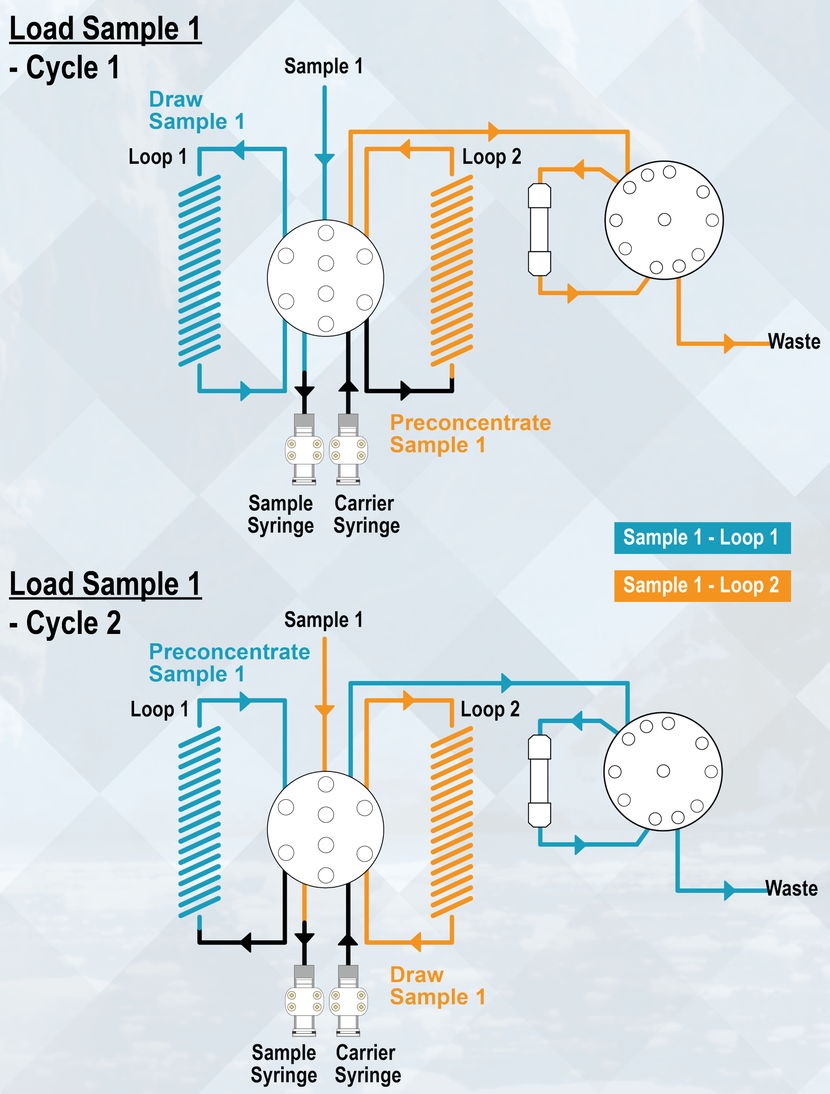
## Abstract

The study of stable isotopes of bioactive trace elements in seawater is a relatively new field of marine chemistry providing insights into marine cycling of these elements. Due to the small variation found in isotope ratios, large volumes of seawater must be preconcentrated to successfully determine differences in ratios for trace elements, making it impractical to process a large number of samples. Furthermore, manual preconcentration techniques have many steps that may introduce contamination and degrade the analytical quality of the determination, making it necessary to further increase sample size. By automating the preconcentration and matrix removal process, blanks are minimized and the required sample volume is decreased, allowing higher throughput sampling and analysis. A new system for automatic preconcentration and matrix removal of large-volume samples (>1 L) is presented which minimizes blanks, increases throughput, and enables routine processing of marine samples for ultratrace quantification and isotopic determination of trace elements in seawater.


## Automatic Sample Preconcentration

- New, high-flow, low-pressure chelation column geometry to allow higher sample throughput.
- Sample volumes from 10 mL to > 1 L may be preconcentrated.
- Automated preconcentration factors > 1000 are possible.
- Samples may be drawn from bottles on the autosampler deck or from bottles connected to a stream selector valve.
- Enclosed, polypropylene cabinet to maintain sample integrity.
- Ultrapure DI water source connected directly to the system for the lowest blanks.
- Ultrapure, fluoropolymer flow path.
- Eliminate contamination from manual sample handling.

## Dual Loop Preconcentration




**To maintain 100% duty cycle for sample loading and enable the automated processing of large samples, a dual loop configuration is used:**

- Load 10 mL sample onto the column from one loop while sample is drawn into a second 10 mL loop
- When sample loading onto the column is completed, switch loops and immediately load the second loop onto the column and draw additional sample into the first loop
- Repeat as desired to increase preconcentration factor.
- After preconcentration and matrix removal, the chelated analytes are eluted into a destination vial using an eluent solution.

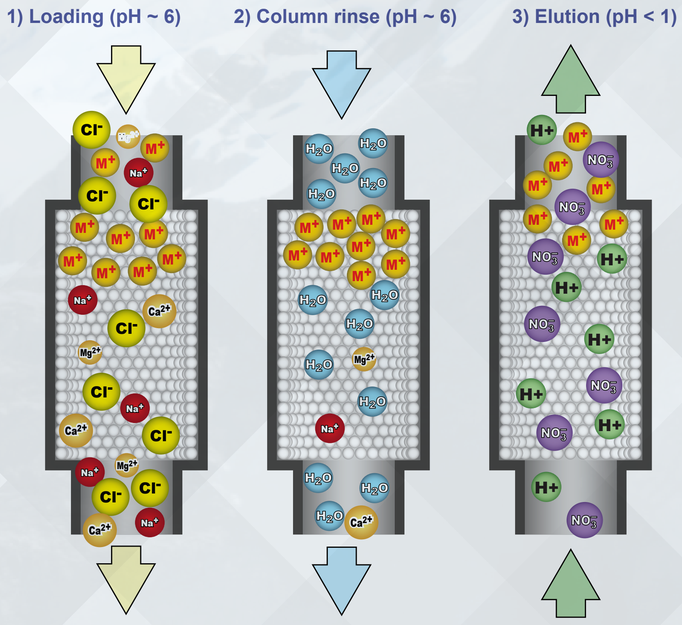
## Analytical Challenges

**Determination of accurate ultratrace elemental concentrations or isotope ratios for elements with low abundance isotopes is a challenging analytical problem in oceanography.**

- Matrix-based polyatomic interferences overlap some isotopes of interest
- Matrix effects from high salinity affect instrument sensitivity with simple direct analysis, even with dilution
- Low concentrations or isotopic abundance limits dilution factor that can be used while still maintaining acceptable accuracy and precision.
- Automated preconcentration and matrix removal provides sufficient analytical improvements to achieve good accuracy and precision for these determinations:
  - Reduction of matrix-based polyatomic interferences
  - Enhanced detection limits
  - Elimination of manual sample preparation

## Preconcentration and Matrix Removal

seaFAST Preconcentration Column




### Step 1

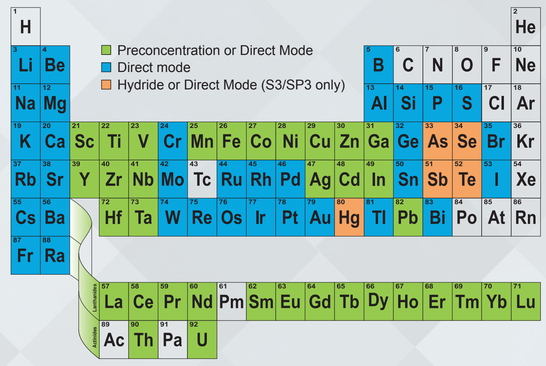
- Inline addition $NH_4OH$ to pH > 6
- Matrix to waste
- Transition metals and rare earth elements are chelated.

### Step 2

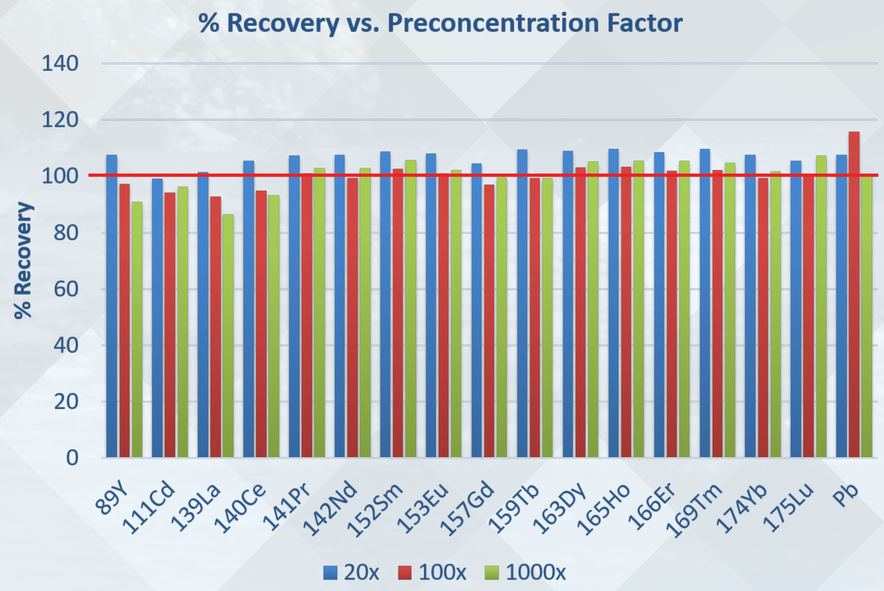
- $H_2O$ washes remaining matrix from column

### Step 3

- Transition metals $M^+$ are eluted into nebulizer with nitric acid $H^+$ $NO_3^-$




## Results




Initial testing for the system using REEs, Cd, and Pb show good recoveries of a 100 ppt standard at preconcentration factors of 20x, 100x, and 1000x (final volume = 1 mL) demonstrating sufficient column capacity for high-volume preconcentration of trace elements. Further studies using different matrices, sample loading speeds, and preconcentration factors will further elucidate the performance of the system.

| Preconcentration Factor | Average % Recovery (100 ppt, all REEs, Cd, Pb) |
|---|---|
| 20x | 107.1 |
| 100x | 100.2 |
| 1000x | 100.3 |

## Conclusions

- **Preconcentration and matrix removal is required for determination of ultratrace elemental concentrations or isotope ratios in high matrix samples.**
- **A new system for automatic preconcentration and matrix removal for samples from 10 mL to > 1 L will allow accurate and precise elemental and isotopic ratio determinations, even for ultratrace elements in high matrix samples.**
- **Further work to demonstrate isotope ratio determination in large volume seawater samples is ongoing.**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