

A Batch-Mode Chelating Reagent for Seawater Analysis with Quadrupole ICP-MS

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Abstract:

The measurement of trace elements in seawater by quadrupole inductively coupled plasma mass spectrometry (ICP-MS) can present a number of problems. The higher dissolved solids content (~3.5%) of seawater can suppress analyte signal, cause interelement interferences, and clog the ICP-MS interface sampler and skimmer cones.

The seawater sample can be diluted, but at the expense of analyte detectability, as some elements of interest are in the 5 to 50 ppt (ng/L) concentration range. An alternative is a sample preparation method that can selectively preconcentrate analytes while having much less affinity for seawater matrix components such as Na, Ca, and Mg.

A chelating polymer resin called SPR-IDA (suspended particulate reagent – iminodiacetate) can be used for analyte preconcentration / matrix elimination of seawater. The reagent consists of 10 micron diameter polymer beads derivatized with the chelating agent iminodiacetate. The beads are suspended in water and can be pipetted into a sample in a batch mode.

Gravity or centrifugation can be used to separate the beads with any bound analytes from the sample matrix. After washing the beads, nitric acid is added to release the analytes and the concentrate analyzed by ICP-MS.

This paper will give method details and results for a certified reference seawater.



Seawater Reference Material

The seawater sample material used was the CASS-4 Nearshore Seawater Reference Material for Trace Metals available from the National Research Council Canada (Ottawa, Ontario Canada).

General Sample Preparation Procedure

A 15-mL sample of the CASS-4 seawater was added directly to the 15-mL mark of a pre-cleaned 15-mL volume polypropylene centrifuge tube (Corning, Corning NY). A 100µL aliquot of a 10% suspension of SPR-IDA reagent beads was then pipetted directly into the sample. The tube was covered with a laboratory film (Parafilm® M Pechiney Plastic Packaging, Chicago, IL) and the contents well mixed.

The sample was then spiked with 0.5 mg/L yttrium. Yttrium functions as an internal standard, helping to correct for any volume variations in the blank, sample, and spiked samples.

The CASS-4 seawater is preserved with high-purity nitric acid at a pH of 1.6; the SPR-IDA reagent chelates trace metals at neutral to basic pH. High-purity ammonium hydroxide (29%, Ashland Chemicals, Columbus, OH) was added in two steps (25µL + 20µL) to adjust the pH to approximately 8. Note that the sample was well mixed after the first addition of NH₄OH and after the second addition.

The SPR-IDA beads were allowed to settle for approximately 1 hour. The sample tube was then placed in a centrifuge (Jouan MR1812, St.Nazaire, France) and spun at 2000 rpm for 10 minutes. The supernatant liquid was carefully poured off to minimize any loss of beads. Most of the beads were compacted at the bottom of the tube.

A solution of deionized water adjusted to pH 8 with high-purity NH₄OH was then added to the 15-mL mark of the sample tube and the contents well mixed. The beads were again allowed to settle, centrifuged, and the resulting supernatant liquid carefully poured off to waste.

A 0.5-mL aliquot of 7% absolute high-purity nitric acid (SCP Science Plasma Pure Plus, Montreal, Quebec Canada) was added to the bead residue to extract any bound metal ions. The extract was diluted to 3 mL with deionized water and analyzed by ICP-MS.

Sample Quantitation

Sample quantitation was performed by standard additions. Three additional sample aliquots were prepared and spiked at 0.25, 0.50, and 1.0 µg/L prior to the addition of the SPR-IDA reagent beads. The preceding procedure was used to process the sample spikes as well as a reagent blank.

ICP-MS Operating Conditions

Quadrupole ICP-MS: PerkinElmer ELAN 9000 (no reaction cell)

ICP Power: 1500W
Nebulizer gas: 0.81 L/min
Nebulizer: Cross-flow with Rytan Scott-style spray chamber
Sample uptake rate: 1.1 mL/min (pumped)

Data Acquisition:

Sweeps/Reading: 3
Readings/Replicate: 1
Replicates: 5
Points/peak: 1
Dwell time: 333 ms
Total integration time: 999 ms

Sample Matrix

The residual concentrations of Na, Mg, and Ca were also measured in the sample extracts and compared to original values in the CASS-4 seawater. These values were measured by ICP-AES (PerkinElmer Optima 5300DV) after a 200x dilution with 2% nitric acid.

CASS-4 Matrix

Element	Wavelength (nm)	CASS-4 (mg/L)	Extract (mg/L)	Reduction Factor
Na	330.237	9428 ± 130	18.7 ± 0.2	500
Mg	279.077	1148 ± 10	70.5 ± 0.4	16
Ca	317.933	341 ± 4	56.0 ± 0.3	6

The major matrix component Na is considerably reduced in the final extract, while significant levels of Mg and Ca remain as the SPR-IDA does have affinity for the latter. For this reason the ⁶²Ni isotope was measured due to a high background at m/z = 60, most likely from ⁴⁴Ca¹⁶O⁺.

Experimental Results

Eight metals were measured in the CASS-4 seawater using the SPR-IDA reagent beads followed by ICP-MS detection; excellent agreement was observed versus certified and reference values.

CASS-4 Nearshore Seawater

Element	m/z	Certified (µg/L)	Found (µg/L)
Mn	55	2.78 ± 0.19	2.74 ± 0.14
Co	59	0.026 ± 0.003	0.043 ± 0.002
Ni	62	0.314 ± 0.030	0.314 ± 0.025
Cu	65	0.592 ± 0.055	0.621 ± 0.016
Zn	66	0.381 ± 0.057	0.393 ± 0.011
Cd	111	0.026 ± 0.003	0.026 ± 0.002
Pb	208	0.0098 ± 0.0036	0.011 ± 0.001
U	238	3.0	2.57 ± 0.06

Note: Uncertainty is based upon a 95% confidence limit; the value of 3.0 mg/L given for uranium is a reference value.

