

Application Note

Use of the SPR-IDA Reagent for the Determination of Trace Metals in a Coastal Seawater Reference Material

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The direct introduction of seawater to an Inductively Coupled Plasma Mass Spectrometer (ICP-MS) can cause a number of serious problems. The high dissolved solids content (approx. 3.5%) of seawater can suppress analyte signal, cause interelement interferences, and clog the interface sampler and skimmer cones.

The seawater sample can be diluted (often 1:10), but at the expense of detectability, as some elements of interest are in the 5 to 50 ppt (ng/L) range. In addition, certain matrix-based interferences can still be significant. An alternative is a sample preparation method that can selectively preconcentrate trace metals of interest while having much less affinity for major matrix components such as Na, Ca, and Mg.

A chelating polymer resin called SPR-IDA (Suspended Particulate Reagent – Iminodiacetate) can be used for pre-concentration / matrix elimination of seawater. The reagent consists of 10 micron diameter polymer beads derivatized with the chelating agent iminodiacetate. The beads are supplied as a 10% suspension in deionized water, and can be easily pipetted into a sample.

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.

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 100 μ L aliquot of a 10% suspension of SPR-IDA reagent beads was then pipetted directly into the sample. The tube was covered with parafilm and the contents well mixed.



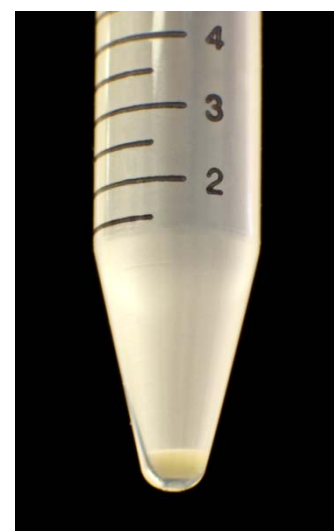
10% w/v SPR-IDA



Seawater



Seawater + 100 μ L
10% SPR-IDA



SPR-IDA Bead Pellet

The sample was then spiked with 0.5 μ g/L yttrium. Yttrium functions as an internal standard, helping to correct for any volume differences 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 (NH₄OH, 29%, Ashland Chemicals, Columbus, OH) was added in two steps (25 µL + 20 µL) to adjust the pH to approximately eight. Note that the sample was well mixed after each addition of NH₄OH.

The SPR-IDA beads were then allowed to settle for approximately one hour. The sample was then placed in a centrifuge and spun at 2000 rpm for 10 minutes. The supernatant liquid was then carefully poured off to minimize any loss of beads. The beads were mostly 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% v/v absolute high-purity nitric acid (SCP Science Plasma Pure Plus, Quebec Canada) was then added to the bead residue to extract any bound metal ions. The extract was then 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 were spiked at 0.25, 0.50 and 1.0 µg/L prior to the addition of the SPR-IDA reagent beads. The procedure above was then used to process the sample spikes as well as a reagent blank.

ICP-MS OPERATING CONDITIONS

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

ICP Power: 1500 W

Nebulizer Gas: 0.81 L/min

Nebulizer: Cross-flow with Rytan Scott 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

EXPERIMENTAL RESULTS

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 original values were measured by ICP-OES (PerkinElmer Optima 5300DV) after a 200x dilution with 2% HNO₃.

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

Table 1: CASS-4 Matrix

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 elements. For this reason the ⁶²Ni isotope was measured due to a high background at m/z = 60, most likely from ⁴⁴Ca¹⁶O⁺.

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

Element	m/z	Certified ($\mu\text{g/L}$)	Found ($\mu\text{g/L}$)
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 +/- 0.155	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

Table 2: CASS-4 Nearshore Seawater

Note: Uncertainty is based upon a 95% confidence limit; the value of 3.0 $\mu\text{g/L}$ given for Uranium is a reference value.



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