AUTHORS

Liyan Xing

Chady Stephan

PerkinElmer Inc.
Woodbridge, ON, Canada

Direct Analysis of Trace Elements in Coastal Seawater Using the NexION 2000 ICP-MS

Introduction

Coastal oceans are some of the most biodiverse places on earth and are the homes to most of the world's seafood resources. With rising global populations and the increasing industrialization of both land and sea, the contamination of coastal seawater by metals and metalloids is of increasing concern. This does not only have an adverse effect on the biological communities which live within these waters but can also have a direct impact on the human communities who rely on local seafood as a form of sustenance. Consequently, many countries run programs to monitor heavy metals in local seawater, such as MMWQS (Malaysian Marine Water Quality Standards and Index)[1], ANZECC (Australian and New Zealand Environment and Conservation Council)[2] and ARMCANZ (Agriculture and Resource Management Council of Australia and New Zealand, 2000)[2] water guidelines.

Due to high total dissolved solids (TDS) in this matrix, seawater is often considered to be one of the most difficult sample types to analyze for the presence of heavy metals and other trace elements. As the technology of choice for trace elemental analysis in seawater, ICP-MS has the advantage of multi-element analysis capability, high sensitivity, low detection limits, wide linear dynamic range, and easy automation. However, like all analytical techniques, ICP-MS analysis is subject to interferences. The high concentrations of matrix components in seawater, such as sodium, magnesium and chloride ions, may form polyatomic spectral interferences making the determination of elements, such as arsenic, cobalt, vanadium, and iron, challenging. Even for elements like cadmium, thallium, and lead, where spectral interferences are less problematic, low part-per-trillion (ppt) concentrations in seawater may be difficult to determine with accuracy and precision[3].

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Collision mode with kinetic energy discrimination (KED) and Reaction mode with dynamic bandpass tuning (DBT) are the two most commonly used techniques to tackle spectral interferences in ICP-MS analysis. In Collision mode with KED, a chemically inert gas, usually helium, collides with analytes and interferences. Since polyatomic interferences have larger cross-sectional diameters than elemental ions at the same mass (i.e., $^{40}Ar^{35}Cl^+$ is larger than $^{75}As^+$), they undergo more collisions and lose more energy than the analyte ion. As a consequence, they cannot make it past the energy barrier at the exit of the cell. In Reaction mode with DBT, a chemically active gas reacts either with the target analyte or the interferent(s), either moving the target analyte to a new mass (i.e., As^+ reacts with O_2 to form AsO^+) or converting the interference to a new species that does not interfere with the target analyte (i.e., $^{51}ClO^+$ reacts with NH_3 to create neutral ClO, while $^{51}V^+$ does not). Following this, the analyte is mass separated in the analyzer quadrupole which follows the cell and is thereafter detected free of interferences. The NexION® 2000 ICP-MS is equipped with Universal Cell Technology (UCT) which allows for samples to be run in Standard, Collision with KED, and Reaction with DBT modes, and three gas channels allow for versatile solutions to mitigate/eliminate spectral interferences.

A few tactics have been developed to dilute the high TDS matrix of seawater, such as liquid dilution, gas dilution, matrix separation, analyte preconcentration, flow injection, reductive precipitation, and hydride generation techniques[3].

In this work, we report the direct analysis of coastal seawater using online dilution. The dilution takes place using a combination of online internal standard addition and online gas dilution in the form of PerkinElmer's All Matrix Solution (AMS). The overall matrix load is further reduced by using PerkinElmer's High Throughput System (HTS), which uses flow-injection technology that delivers the sample to the plasma during the data acquisition stage and diverts the sample to the waste for the rest of the run. Additionally, operated under vacuum, HTS can quickly draw and deliver the sample to the plasma and can perform wash procedures more efficiently and effectively than conventional sample introduction systems.

Experimental

Samples and Standard Preparation

All sample and calibration solution preparation was performed volumetrically. Ultrapure water (resistivity >18.2MΩ.cm), high-purity acids HNO_3 (55% w/v, Tama Chemicals, Moses Lake, Washington, USA) and HCl (20% w/v, Tama Chemicals) were used for all samples, blanks, standards, and wash solutions unless otherwise specified. Diluted acid solutions were prepared via the dilution of the concentrated acid(s) with ultrapure water. Isopropanol (IPA) used in internal standard and washout solutions was electronic-grade for trace metals (99.999% trace metals basis, Sigma-Aldrich, Oakville, Ontario, Canada). The concentrations of the diluted acid solutions were based on concentrated HNO_3 with 70% (w/v) and concentrated HCl with 37% (w/v).

Method Blank

Pure NaCl (3%) was used as the method blank to match the seawater matrix. It was prepared by dilution of seaBlank (10-11%, ultra-clean NaCl purchased from Elemental Scientific, Omaha, Nebraska, USA) and acidified to 1% HNO_3. The method blank was also used as the calibration blank and the diluent to prepare working calibration standards and the continuing calibration blank (CCB).

Calibration Standards

Calibration standards were prepared by diluting commercial multi-element and single-element standards (see Consumables Used table on page 5) in the 3% NaCl solution. The concentrations of the calibration standards used in this application are shown in Table 1 on page 5. Standard 6 in this standard set was used as the continuing calibration verification (CCV) standard. The CCBs and CCVs were measured periodically throughout the sequence.

Carrier Solution

A solution made up of 2% HNO_3 (v/v) and 0.5% HCl (v/v) was spiked with 200 µg/L of gold and used as the carrier solution. Gold was added as a Hg stabilizer and to improve Hg washout. The carrier solution was also used to prepare the internal standard.

Table 1: List of the concentrations of analytes in the calibration standards.

Analytes	Standard 1 (µg/L)	Standard 2 (µg/L)	Standard 3 (µg/L)	Standard 4 (µg/L)	Standard 5 (µg/L)	Standard 6 (µg/L)	Standard 7 (µg/L)	Standard 8 (µg/L)
Hg	0.01	0.025	0.05	0.1	0.5	1	5	10
Li	1	5	10	20	100	200	1000	2000
B	10	25	50	100	500	1000	5000	10000
P	10	25	50	100	500	1000	5000	10000
Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, Te, Th, U, V, Zn	0.1	0.25	0.5	1	5	10	50	100

Wash Solution

The wash solution consisted of 1.5% HCl (v/v) and 0.5% HNO_3 (v/v) spiked with 200 µg/L gold and 5% IPA. IPA was used to facilitate the washout of organic materials from the sample probe and sample loop.

Internal Standard (ISTD)

The internal standard solution contained 200 µg/L of Sc, 20 µg/L of Ga, and 10 µg/L each of In, Ir, Rh, Tm and Bi; and was prepared by dilution of an internal standard mixed solution and Bi single-element standard (see Consumables Used table on page 5) in a solution with the same composition as the carrier solution. Isopropanol (0.1%) was added to address carbon enhancement effects on As and Se. The internal standard was introduced into the designated port of the HTS valve and mixed online with the sample.

QC Samples

Two certified reference materials (CRMs) for coastal seawater, namely CASS-6 (National Research Council, Ottawa, Ontario, Canada) and MX014 (Australian Government National Measurement Institute, North Ryde, New South Wales, Australia) were used to validate the accuracy of the method.

Instrumentation

All measurements were performed with a NexION 2000 ICP-MS (PerkinElmer Inc., Shelton, Connecticut, USA) equipped with HTS and an S20 series autosampler. The instrument components/parameters are shown in Table 2.

Table 2: NexION ICP-MS instrument components and operating conditions.

Instrument Component	Type/Value
Nebulizer	ST-PFA MicroFlow
Spray chamber	Quartz cyclonic with AMS matrix port
Torch	One-piece quartz torch, 2 mm injector
Interface	Nickel sampler and skimmer cones Aluminum hyper-skimmer cone
Peristaltic pump tubing	Carrier: orange/red (0.19 mm i.d.) ISTD: orange/yellow (0.51 mm i.d.) Waste: gray/gray Santoprene (1.30 mm i.d.)
Sample uptake rate	40 µL/min
Operating Conditions	**Type/Value**
RF power	1600 W
Plasma gas flow	15 L/min
Auxiliary gas flow	1.2 L/min
Nebulizer gas flow	Optimized for <2.5% oxides
Cell gas	O_2, NH_3, Pre-mixed H_2/helium (7%)
AMS gas type	Ar
AMS gas flow	Optimized for ½ Intensity for ^{115}In in STD mode

Instrument Optimization

Prior to sample analysis, the instrument was tuned for optimal sensitivity and oxide as well as doubly charged ion ratios. It should be noted that new or newly cleaned cones need to be conditioned before optimization. In this method, the cones were conditioned by aspirating seawater and monitoring the internal standards until the signals stabilized. The elements analyzed, their respective isotopes, and mode of analysis used for each element in this method are listed in Table 3.

Table 3: Isotopes and modes of analysis for different elements.

Analyte	Mass	Mode
Li	7	STD
Be	9	STD
B	10	STD
Al	27	Ammonia DRC
P	47	Oxygen DRC
V	51	Ammonia DRC
Cr	52	Ammonia DRC
Fe	54	Ammonia DRC
Mn	55	Ammonia DRC
Co	59	Helium KED
Ni	60	Helium KED
Cu	63	Helium KED
Zn	66	Helium KED
Sr	87	Helium KED
AsO	91	Oxygen DRC
SeO	94	Oxygen DRC
Mo	95	Helium KED
Ag	107	Helium KED
Cd	111	Helium KED
Sn	118	Helium KED
Sb	121	Helium KED
Te	130	Ammonia DRC
Ba	137	Helium KED
Hg	202	STD
Pb	208	Helium KED
Th	232	STD
U	238	STD
Se-2	78	Hydrogen DRC

Results and Discussion

Detection Limits

The limits of quantification (LOQs) were calculated as 10 times the standard deviation of 10 replicate measurements of the method blank. The LOQs of this method meet the detection requirements for all target elements for ANZECC and MMWQS specifications, as shown in Figure 1. Selenium was also measured using Reaction mode with H_2/He with no mass shift. As expected, a lower detection limit was achieved in Reaction mode with oxygen than with H_2/He. However, for laboratories which do not allow the use of oxygen, H_2/He is still able to achieve LOQs below the regulatory levels and is therefore an attractive alternative in such cases.

Linearity

Calibration curves were plotted following internal standard correction and blank subtraction. A correlation coefficient (R) higher than 0.9995 was obtained for all elements in the calibrated ranges. Recoveries of the calibration standards for all analytes were within ±10% in the calibration ranges.

Accuracy

The accuracy of the method was validated via the recoveries of the CRMs. Each CRM was measured three times and the measurements spread randomly in the sequence. Excellent recoveries within ±10% were achieved for all analytes in MX014 and CASS-6, with the exception of a few elements which had recoveries within ±20%.

Stability

To test long-term stability, 3% seaBlank was analyzed repeatedly over an extended period of 12 hours. The internal standard recoveries were normalized to the calibration blank and plotted. Internal standard recoveries within ±20% were observed for all internal standards (Figure 3) over the entire 12-hour period, validating the long-term stability and robustness of the methodology and instrumentation.
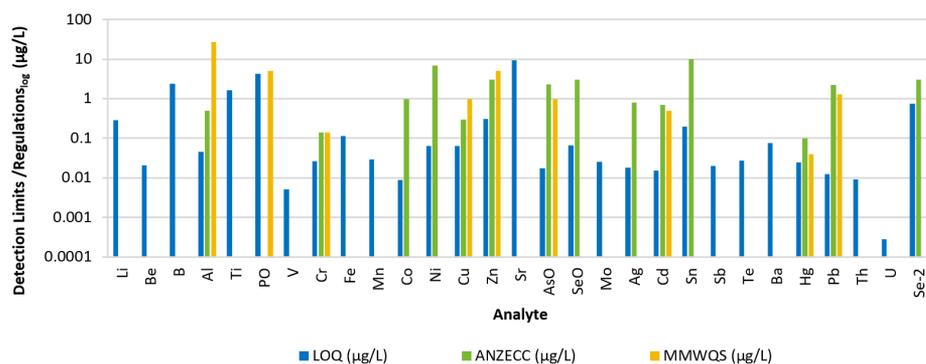
Figure 1: LOQs of this method compared to ANZECC and MMWQS specifications.
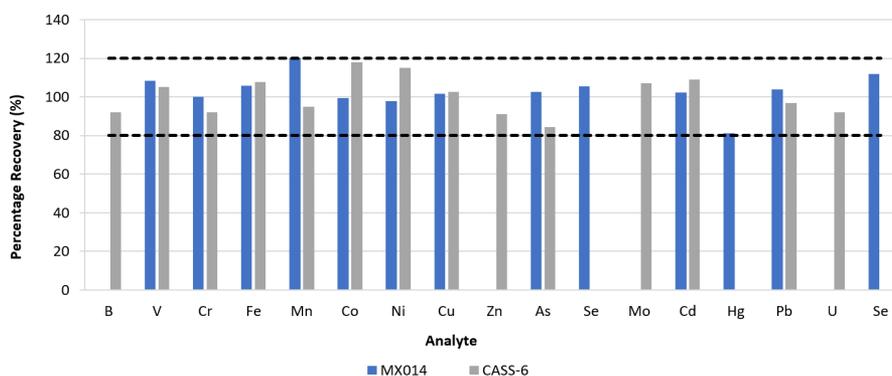
Figure 2: Recoveries for the certified elements in certified reference materials MX014 and CASS-6.
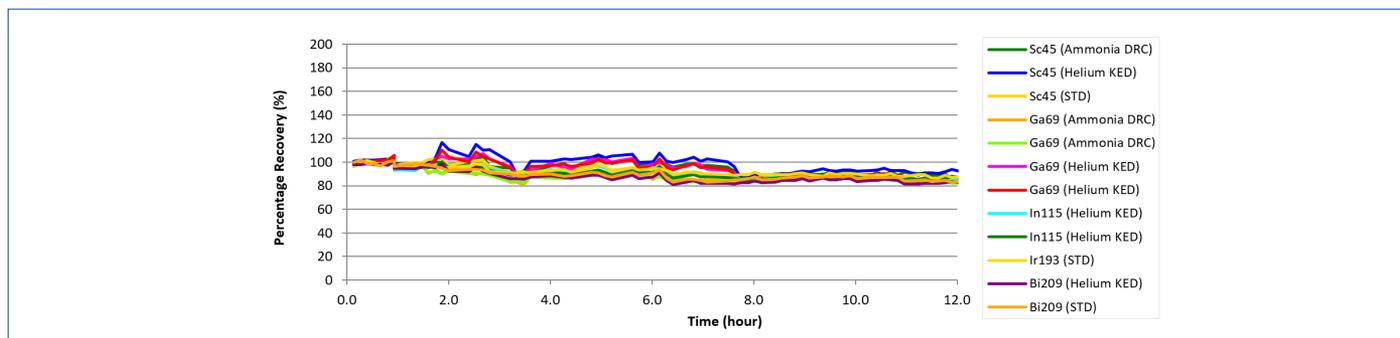
Figure 3: ISTD recoveries during a 12-hour sequence of analysis of seawater samples and 3% seaBlank samples.

Conclusions

This application note reported a procedure for the direct analysis of trace elements in coastal seawater using the NexION 2000 ICP-MS with AMS and HTS. Here, three scan modes were used to resolve interferences and achieve the best analytical performance.

In this analysis, the LOQs were found to be below the specifications set by MMWQS and ANZECC for all regulated elements. The accuracy of this method was validated through the analysis of coastal seawater CRMs and was found to have recoveries within ±10% for all certified elements in coastal seawater CRM MX014 and CASS-6, with the exception of Mn, Hg and Se in MX014 and Co, Ni and As in CASS-6, all of which still fell within ±20% of the certified limits. In all cases, the concentrations were above LOQs.

And last but certainly not least, excellent consistency of the internal standards over an impressive 12-hour period demonstrated the robustness and stability of the method and instrumentation used.

References

1. https://www.doe.gov.my/portalv1/wp-content/uploads/2019/04/BOOKLET-BI.pdf

2. https://www.waterquality.gov.au/sites/default/files/documents/anzecc-armcanz-2000-guidelines-vol1.pdf

3. Pruszkowski E. and Saetveit N., "Benefits of the NexION 300/350 ICP-MS Coupled with a seaFAST 3 Sampling System for Automated High Throughput Analysis of Seawater Samples", – PerkinElmer Application Note, 2013.

Consumables Used

Component	Description	Part Number
Peripump Tubing	ISTD: Orange/Yellow (0.51 mm i.d.)	N8152404
	Carrier: Orange/Red (0.19 mm i.d.)	N8152401
	Waste: Gray/Gray Santoprene (1.30 mm i.d.)	N8152415
Internal Standard Mix	200 mg/L of Sc, 20 mg/L of Ga, 10 mg/L of In, Ir, Rh, Tm	N9307738
Multi-element Standard	100 µg/mL of Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, V, Zn in 5% HNO_3/trace HF	N9301721
	10 µg/mL of B, Th, U in 2% HNO_3	N9307807
Single-element Standard	1000 µg/mL of Hg in 10% HNO_3	N9303740
	1000 µg/mL of B in water	N9303760
	1000 µg/mL of P in water	N9303788
	1000 µg/mL of Li in 2% HNO_3	N9303781
	1000 µg/mL of Te in 10% HNO_3	N9303803
	1000 µg/mL of Bi in 10% HNO_3	N9303731
	1000 µg/mL of Au in 10% HCl	N9303759

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