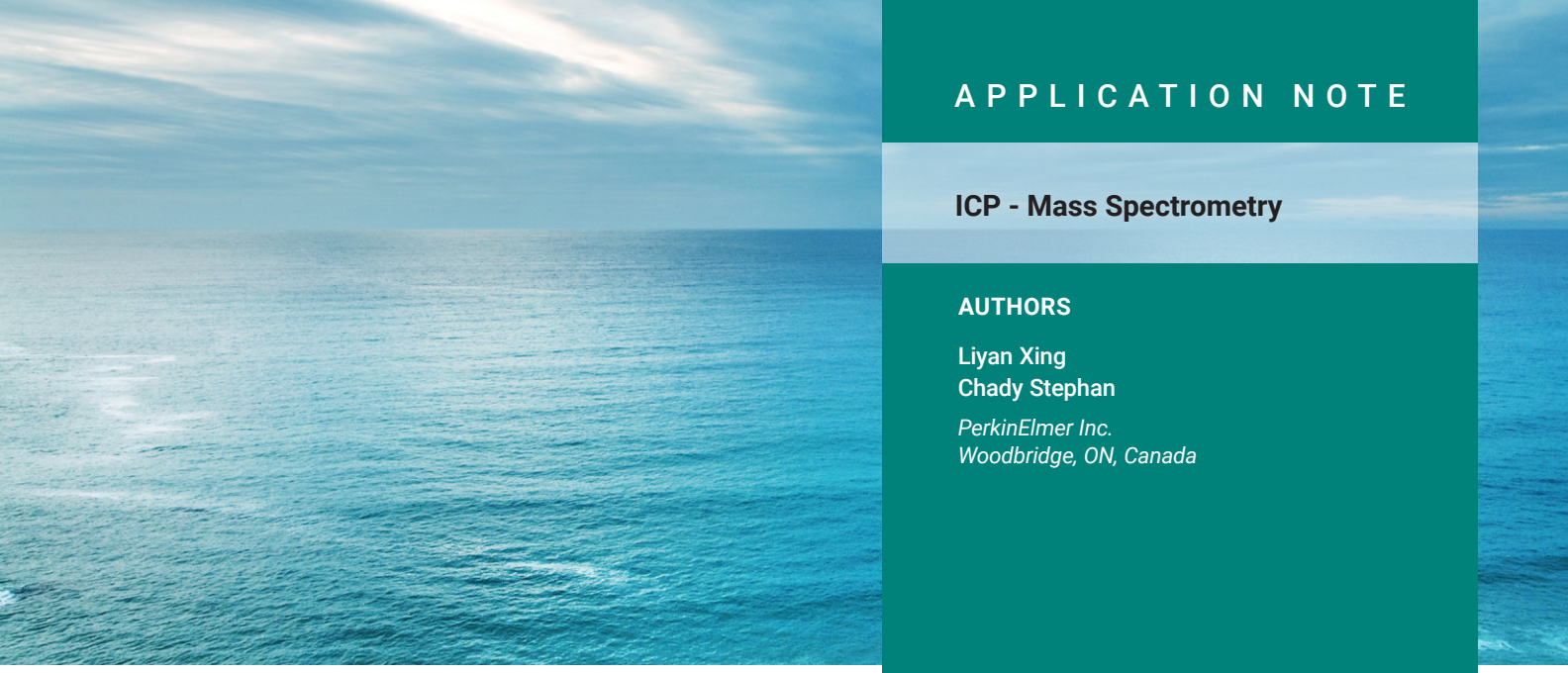

APPLICATION NOTE

ICP - Mass Spectrometry

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Direct Analysis of Trace Elements in Open-Ocean Seawater Using the NexION 5000 ICP-MS

Introduction

The determination of trace elements in seawater is very challenging for inductively coupled plasma mass spectrometry (ICP-MS) due to high total dissolved solids (TDS) in this matrix. The high concentrations of matrix components in seawater, such as sodium, magnesium, and chloride ions, may form polyatomic spectral interferences and complicate the determination of elements, such as arsenic, cobalt, vanadium, zinc, copper, and iron. Even for elements like cadmium, thallium, and lead that are less affected by spectral interferences, the low part-per-trillion (ppt) concentrations in seawater make them difficult to determine with good accuracy and precision.[1]

Recently, we reported a method to analyze trace elements in coastal seawater using the NexION® 2000 ICP-MS[2], which met the specifications to monitor heavy metals in local seawater, as stipulated by MMWQS (Malaysian Marine Water Quality Standards and Index)[3], ANZECC (Australian and New Zealand Environment and Conservation Council)[4] and ARMCANZ (Agriculture and Resource Management Council of Australia and New Zealand, 2000)[4] water guidelines. The concentrations of trace elements in open-ocean seawater are even lower than in coastal areas, thus are more challenging to accurately measure using quadrupole ICP-MS.

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However, the NexION 5000 Multi-Quadrupole ICP-MS is a four-quadrupole system which combines the power of two full-length transmission analyzer quadrupoles (Q1 and Q3) with versatile Universal Cell Technology (UCT, Q2) to achieve interference-free analysis through two basic processes: MS/MS and Mass Shift modes.[5] In MS/MS mode, analyte ions and interfering ions with the same mass are selected by Q1 and enter Q2, where the interferents may react with the cell gas (e.g., NH_3, O_2, CH_4, etc.) and are ejected; examples include $^{35}Cl^{16}O^+$ vs. $^{51}V^+$, $^{39}K^{16}O^+$ vs. $^{55}Mn^+$, $^{40}Ar^{12}C^+$ and $^{40}Ca^{12}C^+$ vs. $^{52}Cr^+$, etc. In Mass Shift mode, the analyte ions react with the cell gas in Q2 to form higher mass ions that are transmitted through to Q3, and interferents are ejected; examples include $^{75}As^+ \rightarrow {}^{91}AsO^+$, $^{78}Se^+ \rightarrow {}^{94}SeO^+$, $^{48}Ti \rightarrow {}^{131}Ti(NH)(NH_3)_4^+$, $^{56}Fe \rightarrow {}^{90}Fe(NH_3)_2^+$, etc. The remaining quadrupole (Q0) is the Quadrupole Ion Deflector (QID) that separates the neutrals and photons from the ion beam, thus minimizing the contamination of the interface region and facilitating long-term stability of the instrument.

As with previous work, direct analysis of seawater using online dilution was adopted in this work. The dilution was performed using the combination of on-line internal standard addition and on-line 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 a discrete amount of sample to the plasma, which is injected during the data acquisition stage. 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 preparations were performed volumetrically. Ultrapure water (Resistivity >18.2 MΩ.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. The 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 (70%, w/v) and concentrated HCl (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 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) in the 3% NaCl solution. The concentrations of the calibration standards used in this application are shown in Table 1. Standard 4 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), 0.5% HCl (v/v) and spiked with 200 µg/L of gold was 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.

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.

Internal Standard (ISTD)

The internal standard solution contained 80 µg/L of Sc, and 4 µg/L each of In, Ir and Rh was prepared by dilution of an internal standard mixed solution (see Consumables Used table) 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.

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)
Ag, Al, As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, Te, Th, Ti, Tl, U, V, Zn	0.1	0.5	1	10	50	100
Hg	0.01	0.05	0.1	1	5	10

QC Samples

Two seawater certified reference materials (CRMs), namely CASS-6 for nearshore seawater, and NASS-7 for open-ocean seawater (both purchased from National Research Council, Ottawa, Ontario, Canada) were used to validate the accuracy of the method.

A spike recovery test was used to validate the method for the uncertified elements. A seawater sample was spiked to the level of Standard 4 (Table 1) using Standard 6 (Table 1) as the stock source.

Instrumentation

All measurements were performed with a NexION 5000 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 5000 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
Cones	Pt sampler and skimmer cones Ni hyper-skimmer cone with OmniRing™ technology
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
AMS gas type	Ar
AMS gas flow	Optimized for ½ Intensity for ^{115}In in STD mode
Cell Gas	**Typical Value**
Oxygen	1.0 mL/min
Ammonia	0.6-1.4 mL/min
Helium	5.0 mL/min

Instrument Optimization

Prior to sample analysis, the instrument was tuned for optimal sensitivity and oxide as well as doubly charged ion ratios, and then optimized in each gas mode. 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 modes of analysis used for each element in this method are listed in Table 3.

Table 3: Isotope and Mode of Analysis for Different Elements.

Element	Mass	Scan Mode	Gas Profile
Al	27/27	MS/MS	Ammonia
Ti	48/131	Mass Shift	Ammonia
V	51/51	MS/MS	Ammonia
Cr	52/86	Mass Shift	Ammonia
Mn	55/55	MS/MS	Ammonia
Fe	56/90	Mass Shift	Ammonia
Co	59/59	MS/MS	Helium
Ni	60/60	MS/MS	Helium
Cu	65/65	MS/MS	Helium
Zn	66/66	MS/MS	Helium
As	75/91	Mass Shift	Oxygen
Se	78/94	Mass Shift	Oxygen
Mo	95/127	Mass Shift	Oxygen
Ag	107/107	MS/MS	Ammonia
Cd	111/111	MS/MS	Ammonia
Sn	118/118	MS/MS	Ammonia
Sb	121/121	MS/MS	Ammonia
Te	128/128	MS/MS	Ammonia
Ba	137/137	MS/MS	Ammonia
Hg	202/202	MS/MS	Oxygen
Tl	205/205	MS/MS	Ammonia
Pb	208/208	MS/MS	Ammonia
Th	232/232	MS/MS	STD
U	238/238	MS/MS	STD

Results and Discussion

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% of the calibration ranges. Selected calibration graphs and the associated residuals graphs are shown in Figure 1. The residual is the deviation of the measured concentration of a standard from the theoretical value. It is a measure of how well a line fits an individual data point. From the residuals, it can be seen that the regression lines also fit well for the lower concentration standards.

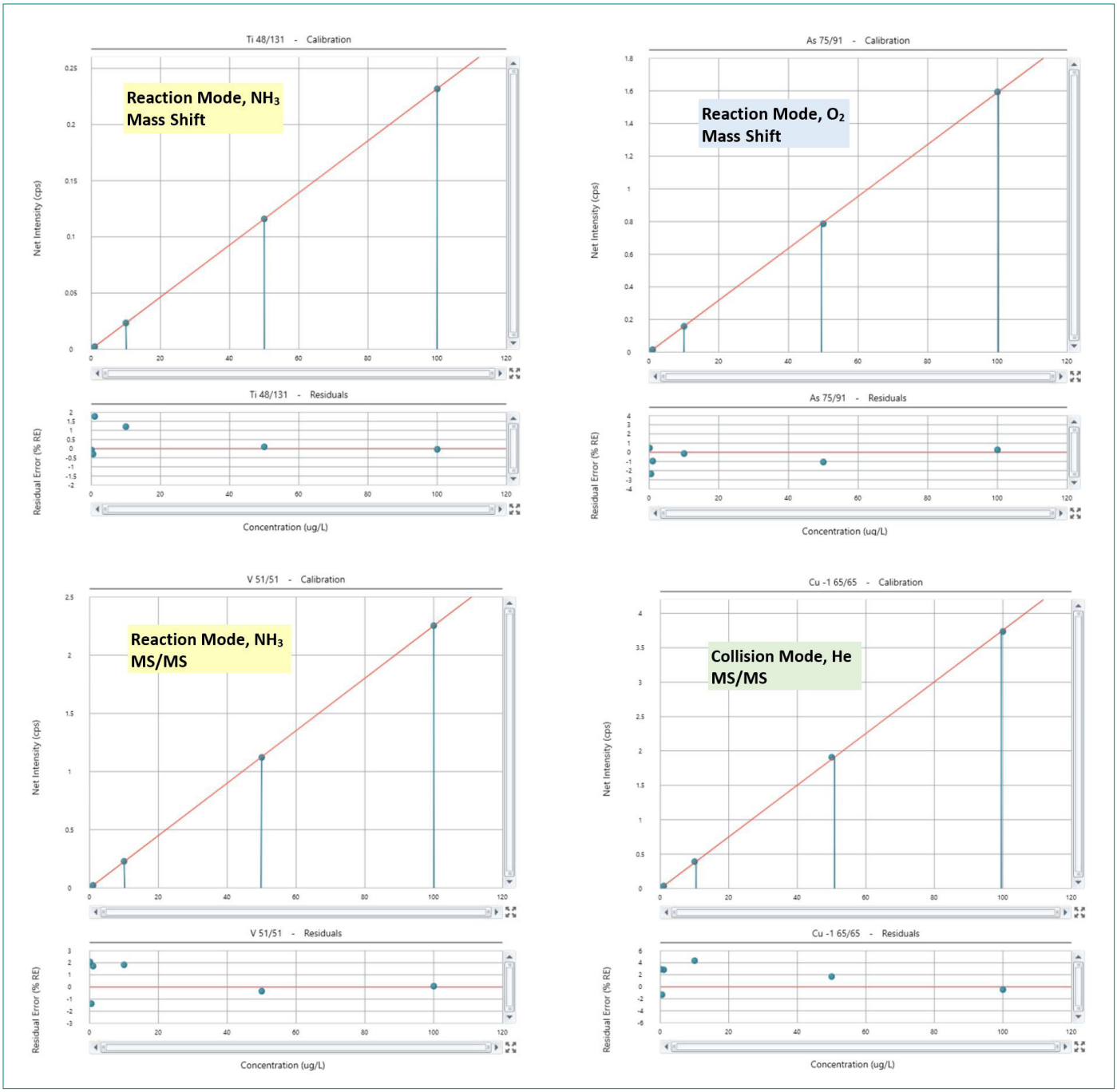

Figure 1: Selected calibration graphs for analysis in 3% NaCl.

Detection Limits

Method detection limits (MDLs) were calculated as three times the standard deviation of ten replicated measurements of the 3% NaCl solution. As shown in Figure 2, the MDLs of this method meet the detection requirements specified by ANZECC and MMWQS for all target elements. MDLs were in single-digit ppt to sub-ppt levels for most elements except for a few elements that were at double-digit levels. These elements, such as Al, Fe, Ni, Cu and Zn, are commonly present in regular laboratory environments. The MDLs for these elements could be further improved in cleanroom settings.

Accuracy

The accuracy of the method was validated via the recoveries of the seawater certified reference materials (CRMs). Each CRM was analyzed five times and the average value was used to calculate the recovery. As shown in Figure 3, excellent recoveries within ±10% were achieved for all analytes in NASS-7 and CASS-6, except for V in CASS-6, which was still within the expanded uncertainty of ±24%, as shown on the CRM certificate.

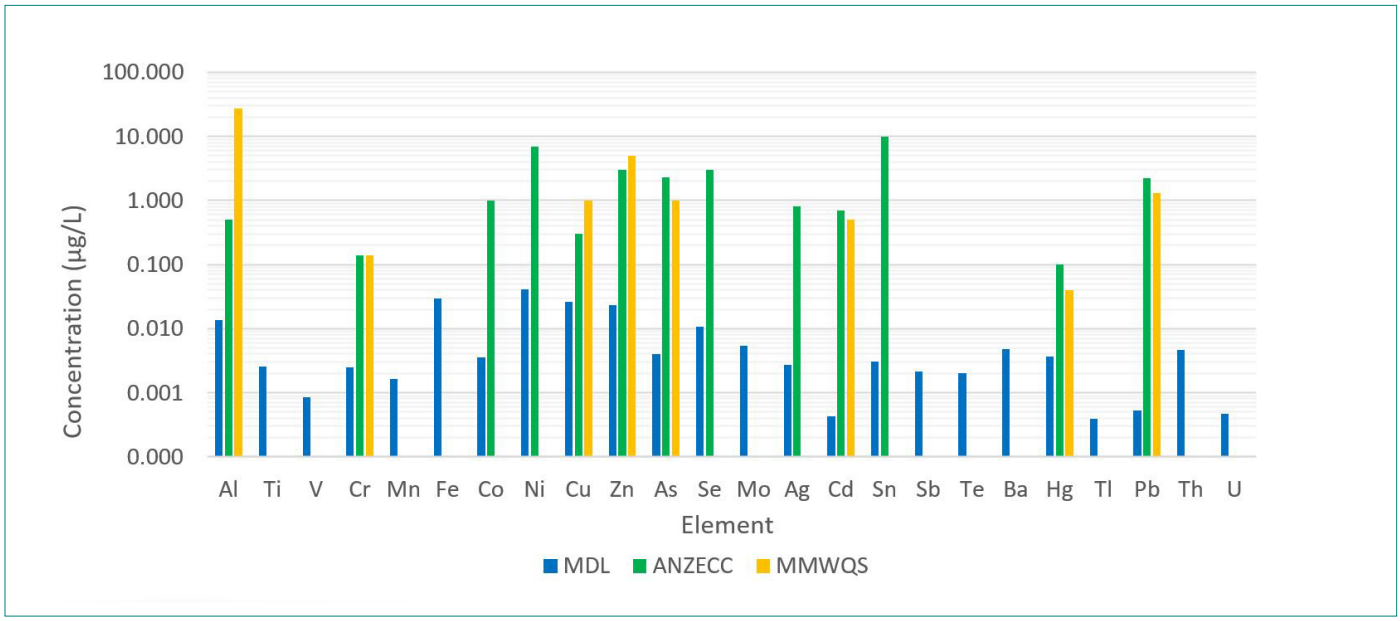

Figure 2: Method detection limits (MDLs) in 3% NaCl compared to ANZECC and MMWQS specifications.

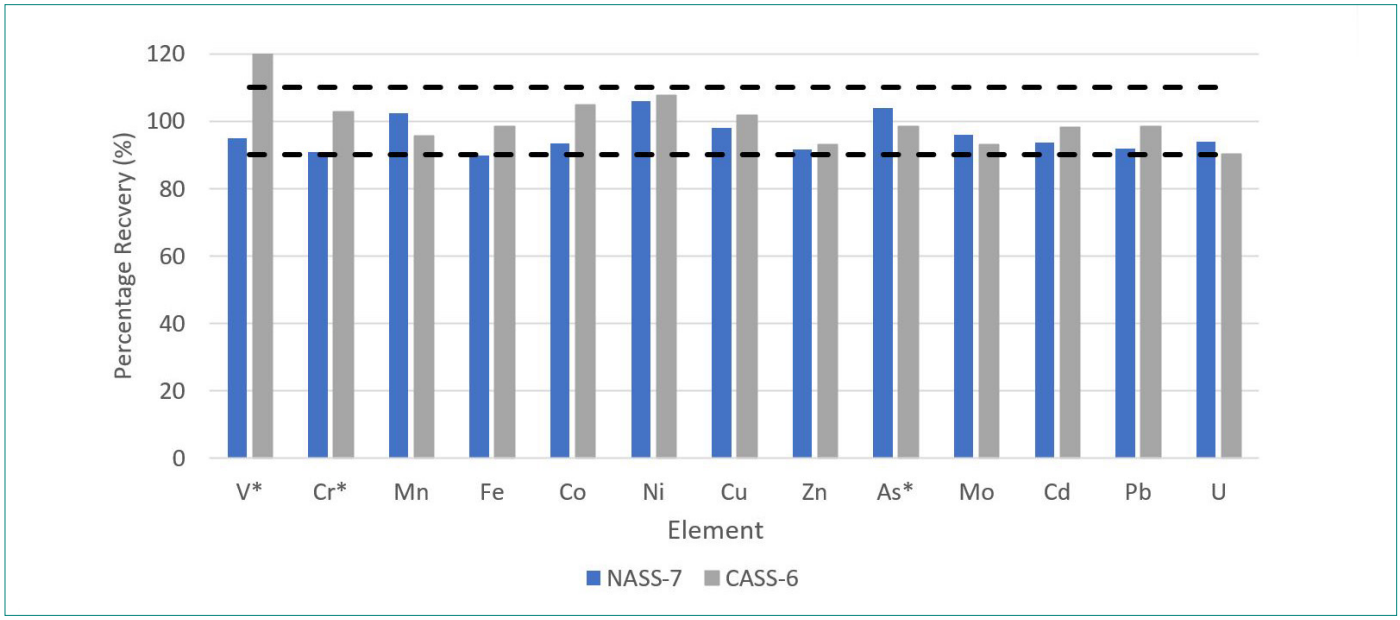

Figure 3: Recoveries for the certified elements in certified reference materials NASS-7 and CASS-6. "Reference-only" quantity values denoted with an asterisk (*).

The accuracy of the method was further validated by spiked recovery tests. The unspiked sample was measured six times and the mean concentration of each analyte was used as the subtrahend to calculate the spiked concentration. Recoveries within ±10% were obtained for all matrix-spiked standards, as shown in Figure 4.

Stability

To validate the long-term stability of the system for this application, seawater samples were measured repeatedly over a period of 10 hours and the CCV recoveries monitored over this period.

All the CCV recoveries were normalized to Standard 4 (Table 1) and were found to be within ±20% of the original reading which is deemed fit for application based upon current literature. As shown in Figure 5, there was no apparent trending throughout the run, demonstrating the validity of the calibration over the 10-hour sample run. This is an important feature for high-throughput laboratories in terms of overall efficiency and productivity by avoiding frequent re-runs of the calibration standards.

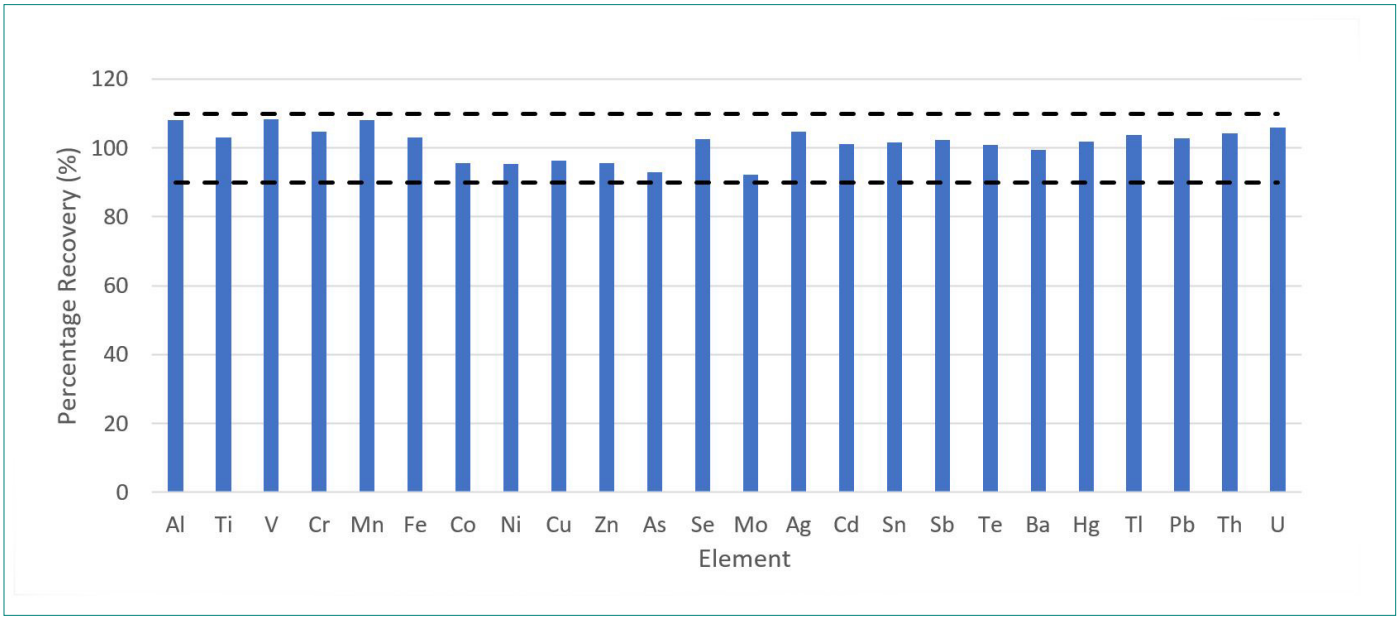

Figure 4: Recoveries for matrix-spiked standards.

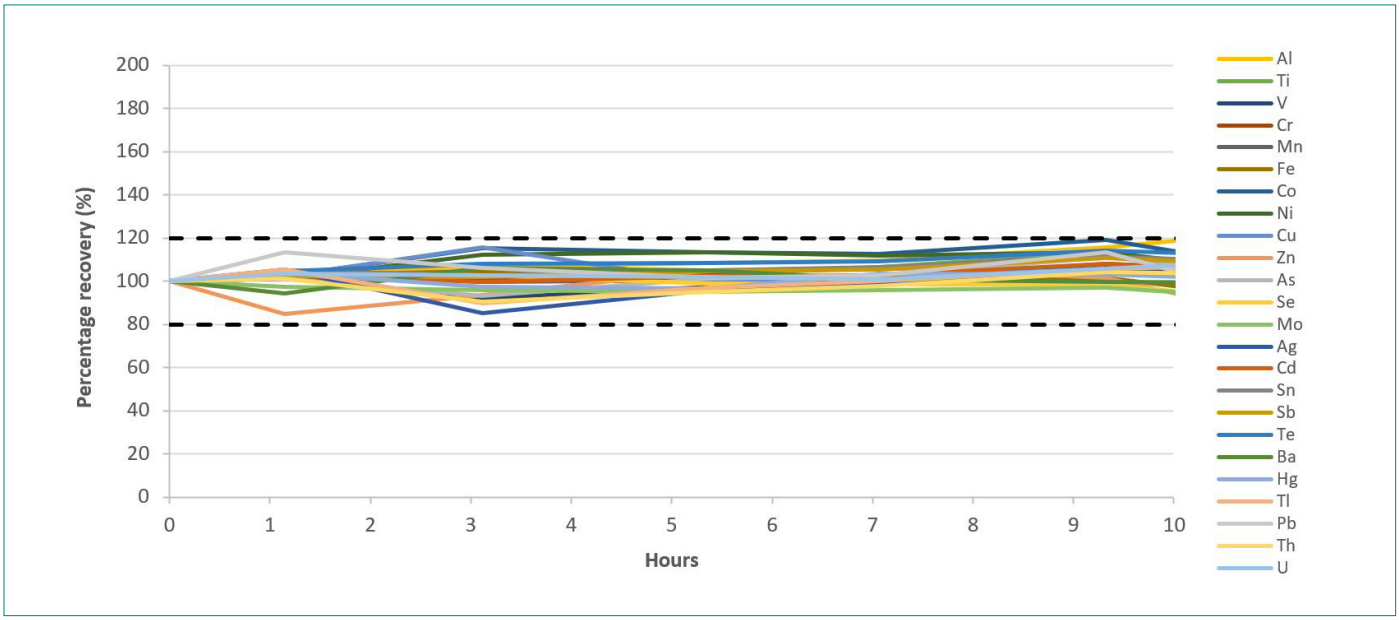

Figure 5: CCV recoveries over a 10-hour sequence of analyses of seawater samples.

Conclusion

This application note reported a procedure for the direct analysis of trace elements in seawater samples using the NexION 5000 Multi-Quadrupole ICP-MS equipped with AMS and HTS. Superior interference removal capability and outstanding sensitivity were demonstrated by the exceptional detection limits, accuracy and long-term stability.

In this analysis, single-digit ppt to sub-ppt level detection limits (DLs) were achieved for most elements except for a few which were at double-digit ppt levels. For all certified elements, the MDLs met the detection requirements specified by the ANZECC and MMWQS guidelines.

The accuracy of this method was validated through the analysis of seawater CRMs. Recoveries within ±10% were found for all certified elements in NASS-7 and CASS-6. The accuracy was further validated by spike recovery tests with ±10% recoveries obtained for all measured elements, including those which did not have certified values.

And last but certainly not least, excellent consistency of the CCV over an impressive 10-hour period demonstrated the outstanding stability of the method and instrumentation used.

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5. "NexION 5000 Multi-Quadrupole ICP Mass Spectrometer", PerkinElmer Brochure, 2020.

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 in 5% HNO_3/trace HCl	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 Te in 10% HNO_3	N9303803
	1000 µg/mL of Au in 10% HCl	N9303759

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