Direct Analysis of Trace Elements in Seawater Using ICP-MS with Versatile Reaction Modes

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1 Introduction

The determination of trace elements in seawater is usually considered to be challenging for 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 compromise the accuracy of elements, such as As, Co, V, Zn, Cu, and Fe, if not corrected for. Even elements like Cd, Sn, and Pb that are less affected by spectral interferences are difficult to determine with good accuracy and precision due to their low ppt concentrations in seawater.

Both the NexION® 2000 ICP-MS and NexION® 5000 Multi-Quadrupole ICP-MS are equipped with Universal Cell Technology (UCT), which allows for samples to be run in Standard, Collision with Kinetic Energy Discrimination (KED), and Reaction with Dynamic Bandpass Tuning (DBT) modes.

While the NexION 2000 possesses a single transmission analyzer quadrupole, the NexION 5000 Multi-Quadrupole ICP-MS is a four quadrupole ICP-MS system that combines tandem mass analyzers (Q1 and Q3) with UCT (Q2) to achieve interference-free analysis.

This work describes the direct analysis of seawater samples where the NexION 2000 ICP-MS was used for the analysis of coastal seawaters and the NexION 5000 ICP-MS used for open ocean waters. Both instruments were equipped with PerkinElmer's All Matrix Solution (AMS) and High Throughput System (HTS).

2 Standards and Sample Preparation

Seawater samples were analyzed directly. A 10X dilution was achieved using a combination of online internal standard addition and online gas dilution by the All Matrix solution (AMS), eliminating the need for offline dilution.

Calibration standards were prepared in 3% ultra-clean NaCl (SeaBlank®, Elemental Scientific Inc.) and acidified to 1% HNO_3.

Table 1. Analytes and corresponding concentrations in the calibration standards

Analytes	Calibration Standards (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 - 100
Hg	0.01 - 10

Table 2. Certified Reference Materials (CRMs) used for method validation

Name	Description	Source
NASS-7	Open-Sea Seawater	National Research Council, Canada
CASS-6	Nearshore Seawater	National Research Council, Canada
MX014	Coastal Seawater	National Measurement Institute, Australia

3 Instrumental Conditions

Sample analysis was performed on both NexION 2000 ICP-MS and NexION 5000 ICP-MS using the instrument configurations and conditions listed in Table 3 in a non-cleanroom, routine laboratory environment.

Table 3. NexION ICP-MS instrument configurations and conditions.

Component/ Conditions	NexION 5000	NexION 2000
Nebulizer	ST-PFA microflow	
Spray Chamber	Quartz cyclonic with AMS matrix port	
Torch	One-piece quartz, 2mm injector	
Cones	Pt sampler and skimmer Ni Hyper-skimmer with OmniRing™ Technology	Ni sampler and skimmer Aluminum hyper-skimmer
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	
RF Power	1600 W	
Plasma Gas	15 L/min	
Auxiliary Gas	1.2 L/min	
Nebulizer Gas	Optimized for <2.5% oxides	
AMS gas	Optimized for ½ intensity for ^{115}In in STD	
Cell gas	O_2: 1.0 mL/min NH_3: 0.6-1.4 mL/min Helium: 5.0 mL/min	

The elements analyzed, their respective isotopes and mode of analysis in this method are listed in Table 4. The NexION 5000 Multi-Quadrupole ICP-MS has both MS/MS and Mass-shifting capabilities, enabling it to isolate the mass of interest in Q1, react this mass in the cell via a controlled reaction with reaction gases and then be transferred to Q3 for mass separation before detection.

Table 4. Isotope and mode of analysis

Element	NexION 2000		NexION 5000	
	Mass	Gas Profile	Mass	Gas Profile
Al	27	Ammonia	27/27	Ammonia
Ti	48	Helium	48/131	Ammonia
V	51	Ammonia	51/51	Ammonia
Cr	52	Ammonia	52/86	Ammonia
Mn	55	Ammonia	55/55	Ammonia
Fe	54	Ammonia	56/90	Ammonia
Co	59	Helium	59/59	Helium
Ni	60	Helium	60/60	Helium
Cu	65	Helium	65/65	Helium
Zn	66	Helium	66/66	Helium
As	91	Oxygen	75/91	Oxygen
Se	94	Oxygen	78/94	Oxygen
Mo	95	Helium	95/127	Oxygen
Ag	107	Helium	107/107	Ammonia
Cd	111	Helium	111/111	Ammonia
Sn	118	Helium	118/118	Ammonia
Sb	121	Helium	121/121	Ammonia
Te	130	Ammonia	128/128	Ammonia
Ba	137	Helium	137/137	Ammonia
Hg	202	STD	202/202	Oxygen
Tl	205	STD	205/205	Ammonia
Pb	208	Helium	208/208	Ammonia
Th	232	STD	232/232	STD
U	238	STD	238/238	STD

4 Results and Discussion

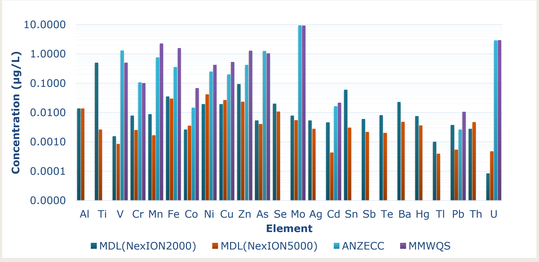

Figure 2. Method detection limits (MDLs) in 3% NaCl compared to ANZECC[1] and MMWQS[2] water guidelines.

MMWQS - Malaysian Marine Water Quality Standards and Index
ANZECCV-Australian and New Zealand Environment and Conservation Council)

MDLs achieved from this work are displayed in Figure 2. The MDLs met the detection requirements for all regulated elements by ANZECC and MMWQS specifications. MDLs were in single-digit ppt to sub-ppt level for most elements except for a few elements that which are known to be ubiquitous in non-cleanroom and routine laboratory environments.

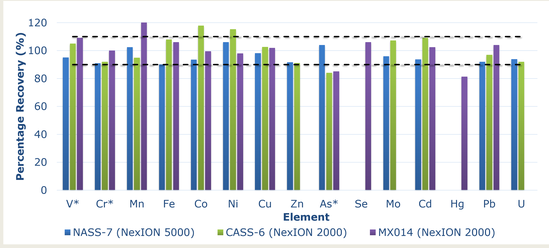

Figure 3. Recoveries for open-sea and coastal certified reference materials (CRMs). "Reference-only" quantity values denoted with an asterisk (*).

The accuracy of the method was validated via the recoveries of the seawater certified reference materials (CRMs). Excellent recoveries within ±10% were achieved for all analytes in open-sea seawater CRM NASS-7 using the NexION 5000. Coastal seawater CRMs CASS-6 and MX014 recoveries were well within ±10% for most elements using NexION 2000, with the exceptions of Mn in MX014 and Co and Ni in CASS-6 which were also within the ±20% range.

Summary

A procedure for the direct analysis of trace elements in seawater samples using the NexION 2000 & 5000 ICP-MS equipped with AMS and HTS was reported. Superior interference removal capability and outstanding sensitivity was demonstrated by the exceptional detection limits and accuracy.

Key features of NexION ICP-MS

- ✓ Superior interference removal capability via UCT with pure reaction gases
- ✓ Exceptional detection limits and accuracy

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