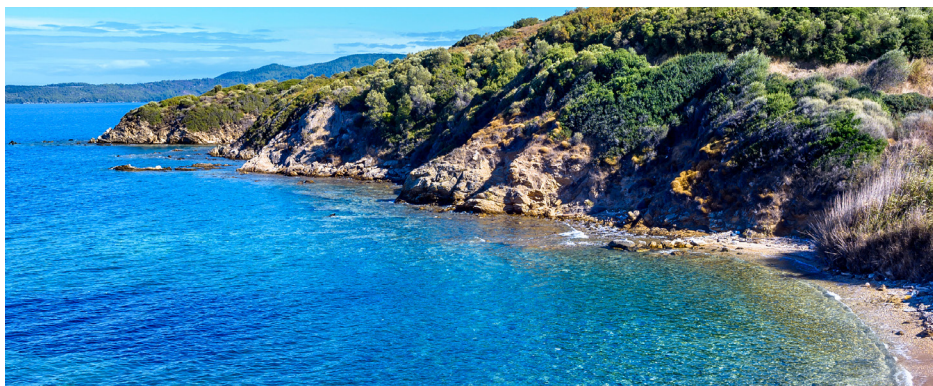


# Direct Analysis of Seawater Using ICP-QQQ and Integrated Advanced Valve System

Fast, robust environmental analyses using an Agilent 9500 ICP-QQQ with AVS MS



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## Introduction

Trace elements in seawater play a vital role in marine biogeochemical cycles, influencing ocean productivity, ecosystem health, and global climate regulation.<sup>1,2</sup> Although present at extremely low concentrations, many trace elements are essential for biological processes, while others, including heavy metals, serve as indicators of contamination from industrial activities and coastal development. Accurate determination of a wide range of elements is therefore critical for environmental monitoring, oceanographic research, and regulatory compliance. EPA Method 200.8 provides a widely adopted quality control (QC) framework for trace metal analysis in natural waters.<sup>3</sup> However, seawater's high salinity and major components such as Na, Mg, Cl, and S create analytical challenges for conventional ICP-MS analysis, including ionization suppression and polyatomic interferences, such as  $\text{ArCl}^+$  on As,  $\text{ArNa}^+$  on Cu,  $\text{SO}_2^+$  on Zn. Overcoming these issues requires advanced interference removal techniques and high sensitivity. Triple quadrupole ICP-MS (ICP-QQQ) addresses these limitations through its MS/MS configuration.

Agilent ICP-MS/MS methods precisely control reaction chemistry and eliminate interferences, ensuring accurate quantification in complex saline matrices.

The Agilent 9500 Triple Quadrupole ICP-MS with its unique Dual-Cell System (DCS) enables accurate, efficient seawater analysis using enhanced collision/reaction cell (CRC) technologies. Its performance is primarily driven by Advanced Helium Mode (AHM). This advanced collision mode delivers exceptional on-mass interference removal using a combination of Kinetic Energy Discrimination (KED) and Collision Induced Dissociation (CID), ensuring precise quantification even in highly saline and complex matrices.<sup>4</sup> Additionally, Air cell mode enables fast, effective mass-shift reactions, adding flexibility for overcoming challenging interferences.<sup>5</sup> By seamlessly integrating AHM with Air cell mode, the 9500 simplifies workflows and delivers reliable results for trace analysis of multiple elements in seawater.

In this study, a 9500 ICP-QQQ fitted with the AVS MS was used to quantify 26 elements in two seawater certified reference materials (CRMs) and a sample collected in Singapore, employing an online reverse-dilution approach. The method was assessed following the performance requirements of EPA Method 200.8.

## Experimental

### Samples and standards

Two seawater CRMs—NIMJ CRM 7204-a (National Metrology Institute of Japan) and NIMA MX014 (National Measurement Institute of Australia)—were analyzed to verify method accuracy. A matrix spike recovery test was also performed on real seawater samples collected in Singapore, which were acidified with concentrated nitric acid (HNO<sub>3</sub>) before analysis.

Calibration standards were prepared from Agilent multi-element and single-element standards (ranges shown in Table 1) using a solution of 2% HNO<sub>3</sub> and 0.5% hydrochloric acid (HCl, v/v). This same solution was used as the diluent, carrier, and to prepare the internal standard (ISTD) mix. The Agilent ISTD mix, containing 10 ppm each of <sup>6</sup>Li, Sc, Ge, Y, In, Tb, and Bi, was diluted to 5 ppb and introduced online during analysis.

**Table 1.** Elements and calibration range.

Element	Calibration Range (ppb)
Be, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, As, Se, Zr, Mo, Ag, Cd, Sn, Sb, Te, Cs, Ba, Tl, Pb, Th, U	0, 0.1, 0.2, 0.5, 1, 2, 5, 10, 50
Fe	0, 1, 2, 5, 10, 50, 100
Hg	0, 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1

### Instrumentation

All analyses were conducted using an Agilent 9500 ICP-QQQ equipped with an integrated Agilent Advanced Valve System for ICP-MS (AVS MS, sample loop = 0.25 mL) and connected to an Agilent SPS 4 autosampler. For this study, AHM and Air cell mode were optimized using autotune to achieve high sensitivity and interference-free determination of trace elements during the direct analysis of seawater.

The standard sample introduction system comprised a u-lens, glass concentric nebulizer, quartz spray chamber and torch, a nickel-plated Ni/Cu sampler cone, and a nickel skimmer cone.

To maintain plasma stability, General Purpose plasma conditions were used. UHMI was not employed in this study to reduce consumption of valuable CRMs. Also, the integrated AVS MS valve system was configured for online reverse dilution, resulting in approximately 15× dilution of the solution introduced into the plasma. This dilution was accomplished by selecting narrower tubing for the sample line (blue/orange) and wider tubing for the ISTD line (white/white).

The integrated online reverse dilution method simplifies workflows by reducing tuning and sample preparation, boosting productivity for high-volume analysis. The system also delivers robust stability over hundreds of undiluted seawater injections, making it ideal for extended runs of challenging saline matrices. The 9500 ICP-QQQ operating conditions are summarized in Table 2.

**Table 2.** Operating conditions of the Agilent 9500 ICP-QQQ.

Parameter	AHM	Air Cell
Plasma Mode	General Purpose	
RF Power (W)	1550	
Sampling Depth (mm)	12	
Nebulizer Gas Flow Rate (L/min)	1.15	
Makeup Gas Flow Rate (L/min)	0	
Dilution Gas Flow Rate (L/min)	0	
Cell Gas Flow Rate (mL/min)	14	0.4
KED (V)	+10	-5

## Results and discussion

### AHM and Air cell mode

Seawater analysis poses significant challenges for ICP-QQQ due to its high salt content, which generates numerous polyatomic interferences originating from the Ar plasma, chloride content, and matrix elements. For example,  $^{35}\text{Cl}^{16}\text{O}^+$  interferes with V at  $m/z$  51;  $^{43}\text{Ca}^{16}\text{O}^+$  with Co at  $m/z$  59; and  $^{40}\text{Ar}^{35}\text{Cl}^+$  with As at  $m/z$  75.

To address these interferences, the 9500 ICP-QQQ quantified all elements in either AHM or Air cell modes, as detailed in Table 3. AHM, which uses a default He flow rate of 14 mL/min, was used for the analysis of most analytes, as it effectively reduces many polyatomic interferences via KED and CID. MDLs below 1 ppt were obtained for all elements analyzed in AHM, including  $^9\text{Be}$  and  $^{238}\text{U}$ , demonstrating uncompromised sensitivity for both low- and high-mass elements. For elements such as Cu, V, Zn, Se, and As, Air cell mode was used. Air was introduced into the cell at 0.4 mL/min, enabling precise MS/MS on-mass and mass-shift strategies.

With these capabilities, the 9500 ICP-QQQ ensures effective interference removal and excellent MDLs for trace elements in complex seawater matrices.

**Table 3.** Agilent 9500 ICP-QQQ method parameters and MDLs.

Analyte	Cell Mode	Q1 Mass	Q2 Mass	Integration Time (s)	MDL (ppb)
Be	AHM	–	9	0.3	0.0000
Cr	AHM	–	52	0.3	0.006
Mn	AHM	–	55	0.3	0.008
Fe	AHM	–	56	0.3	0.003
Co	AHM	–	59	0.3	0.003
Ni	AHM	–	60	0.3	0.001
Cu	Air	63	63	1	0.005
V	Air	51	67	1	0.001
Zn	Air	66	66	1	0.037
Ga	AHM	–	71	0.3	0.0002
Se	Air	78	78	1	0.012
Zr	AHM	–	90	0.3	0.003
As	Air	75	91	1	0.006
Mo	AHM	–	95	0.3	0.002
Ag	AHM	–	107	0.3	0.002
Cd	AHM	–	111	0.3	0.0001
Sn	AHM	–	118	0.3	0.008
Sb	AHM	–	121	0.3	0.002
Te	AHM	–	128	0.3	0.005
Cs	AHM	–	133	0.3	0.004
Ba	AHM	–	138	0.3	0.002
Hg	AHM	–	201	0.3	0.009
Tl	AHM	–	205	0.3	0.0002
*Pb	AHM	–	208	0.3	0.001
Th	AHM	–	232	0.3	0.002
U	AHM	–	238	0.3	0.0001

\*Pb =  $^{206}\text{Pb}$  +  $^{207}\text{Pb}$  +  $^{208}\text{Pb}$

### Seawater CRMs and actual seawater sample analysis results

Two CRMs—NIMJ CRM 7204-a and NIMA MX014—and a seawater sample from Singapore were analyzed to evaluate the accuracy of the method for trace elements in a high-salt matrix. Duplicate aliquots of each CRM were measured, and mean concentrations and recoveries were calculated. For the seawater sample, all analytes were spiked at 5 ppb (0.2 ppb for Hg) to assess recovery. In addition, non-certified elements were added to the CRMs to extend the accuracy evaluation.

Table 4 shows the quantitative results and recoveries for the CRMs (certified and spikes of non-certified elements) and spiked seawater sample. Recoveries for all analytes ranged from 90 to 110%, confirming the reliability of the 9500 ICP-QQQ for the direct analysis of seawater using AHM and Air cell mode.

**Table 4.** Quantitative analysis results for seawater and recoveries for CRM certified elements and spikes.

Analyte	Real Seawater Sample		NMIJ CRM 7204-a: Trace Elements in Seawater		NMIA MX014: Trace Elements in Seawater	
	Measured Conc. (µg/kg)	Spike Recovery (%)	Certified Value (µg/kg)	Recovery** (%)	Certified Value (µg/kg)	Recovery** (%)
Be	< MDL	102	NA	101	NA	108
Cr	0.100	99	9.4 ± 0.5	100	2.613 ± 0.075	99
Mn	0.328	97	9.3 ± 0.4	98	1.48 ± 0.16	100
Fe	2.366	100	9.7 ± 0.6	94	21.7 ± 0.32	96
Co	0.009	98	NA	98	2.864 ± 0.068	100
Ni	< MDL	99	9.8 ± 0.8	100	3.66 ± 0.10	99
Cu	0.570	96	9.6 ± 0.7	99	2.9 ± 0.25	101
V	0.991	107	NA	99	4.76 ± 0.12	99
Zn	1.276	98	12.6 ± 1.7	98	NA	94
Ga	0.012	96	NA	93	NA	95
Se	0.125	102	9.7 ± 0.9	98	3.06 ± 0.26	102
Zr	0.024	105	NA	100	NA	108
As	1.312	104	10.9 ± 0.9	104	2.96 ± 0.26	103
Mo	7.275	106	NA	103	NA	107
Ag	0.191	94	NA	91	NA	92
Cd	0.010	103	3.1 ± 0.2	99	1.318 ± 0.034	99
Sn	< MDL	103	NA	103	NA	100
Sb	0.161	107	NA	102	NA	109
Te	< MDL	102	NA	101	NA	106
Cs	0.216	100	NA	98	NA	104
Ba	7.075	102	NA	95	NA	104
Hg	< MDL	100	NA	91	0.433 ± 0.010	97
Tl	0.012	104	NA	99	NA	106
*Pb	0.011	99	9.4 ± 0.5	99	2.467 ± 0.065	106
Th	0.019	105	NA	109	NA	110
U	2.258	107	NA	107	NA	107

\*Pb = <sup>206</sup>Pb + <sup>207</sup>Pb + <sup>208</sup>Pb

\*\*Recovery of certified elements and spikes of non-certified elements.

## Stability

One major challenge in seawater analysis by ICP QQQ is maintaining long term instrument stability. The high salinity and total dissolved solids (TDS) in seawater promote salt deposition on the sample introduction system, cones, and ion optics, which leads to signal drift, reduced sensitivity, and elevated background noise. As this buildup accumulates, calibration becomes less reliable during extended runs. Although frequent cleaning and optimized rinsing can mitigate these effects, they also increase downtime. Instrument stability is therefore essential for high throughput analysis.

In this study, the 9500 ICP-QQQ was tested for stability over 100 continuous injections of undiluted seawater. Internal standards (5 ppb) were added online, and their recovery was monitored throughout the run. A CCV standard (2 ppb for most analytes, 0.2 ppb for Hg) was measured every 10 samples.

Figure 1 shows ISTD recoveries (Li, Sc, Ge, Y, In, Bi) across AHM and Air cell modes during a full batch run. All recoveries remained within 80–120%, indicating minimal drift over seven hours.

Figure 2 shows CCV recoveries within ±10%, meeting EPA 200.8 criteria. These results demonstrate that the 9500 ICP-QQQ provides excellent matrix tolerance and reliable quantification for long runs of undiluted seawater samples.

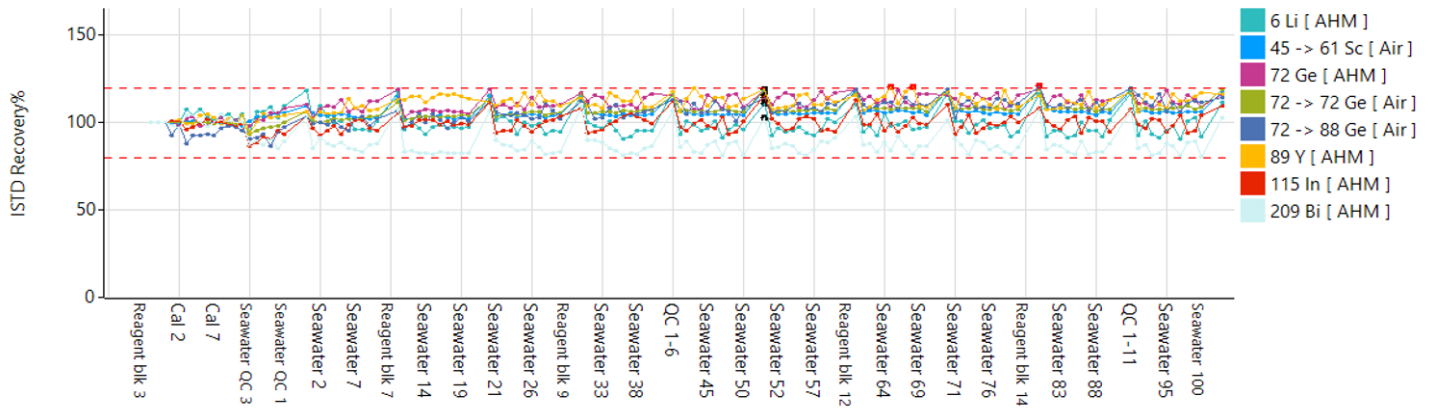


Figure 1. ISTD stability over 100 injections of undiluted seawater samples.

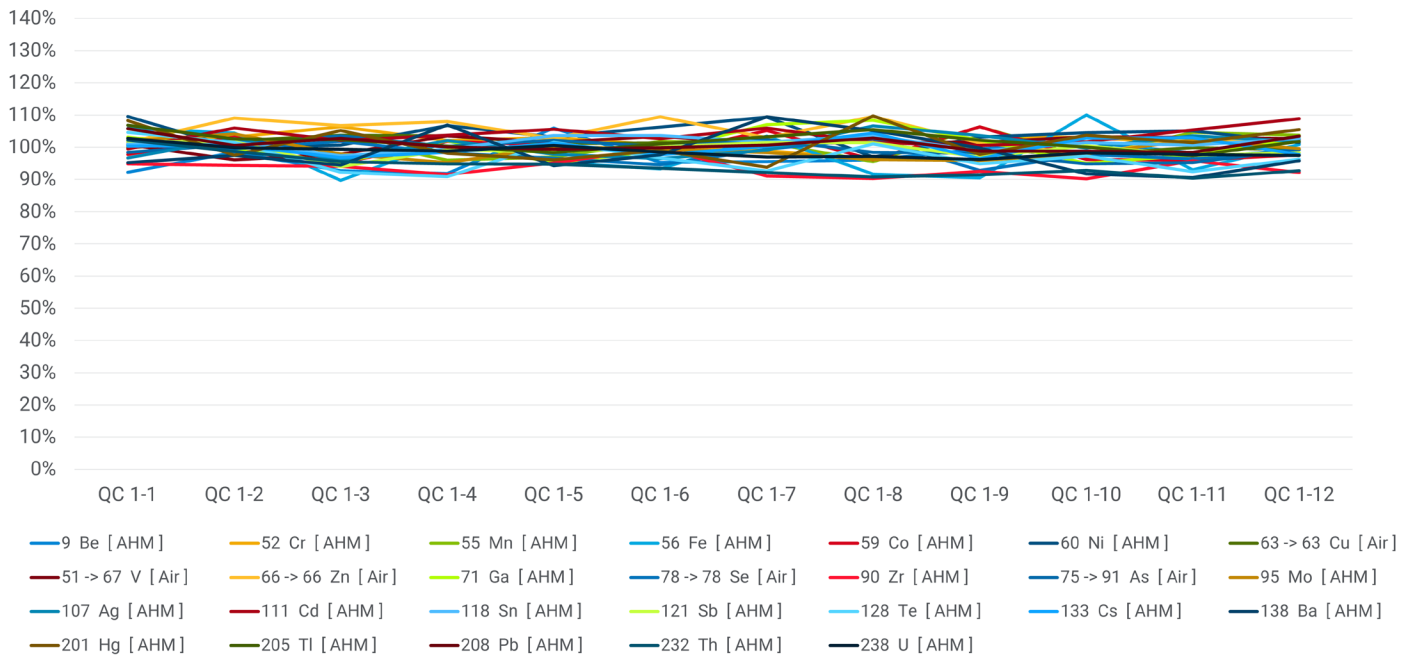


Figure 2. CCV recoveries over 100 continuous measurements of real seawater samples.

## Conclusion

Traditional seawater analysis by ICP-MS often requires extensive sample preparation, such as dilution and matrix separation, to address high salinity and complex matrix effects. These additional steps increase both turnaround time and contamination risk. The method developed here enables direct seawater analysis using an online reverse-dilution approach, eliminating manual preparation and enabling rapid, high-throughput processing. Using the Agilent 9500 ICP-QQQ with AVS MS in online dilution mode, the workflow achieved ppt-level MDLs for 26 elements, excellent accuracy (90–110% recoveries for CRMs and spiked samples), and long-term stability across more than 130 analyses, meeting EPA Method 200.8 QC requirements.

Key advantages of the 9500 ICP-QQQ method:

- Effective interference removal: Advanced gas modes (AHM and Air cell mode) controlled polyatomic species originating from the high-salinity matrices.
- High throughput: Automated online dilution and seamless gas-switching enabled complete analysis in 140 seconds per sample.
- Robust stability: Optimized rinse protocols ensured consistent ISTD recovery and instrument performance over a seven-hour run comprising 100 injections of undiluted seawater samples.

This workflow delivers fast, reliable, and high-quality seawater analysis, making it ideal for environmental monitoring and marine research laboratories seeking maximum efficiency without compromising data integrity.

## References

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3. U.S. EPA. 1994. Method 200.8: Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma-Mass Spectrometry, Revision 5.4. Cincinnati, OH, <https://www.epa.gov/esam/epa-method-2008-determination-trace-elements-waters-and-wastes-inductively-coupled-plasma-mass> (accessed April 2026)
4. Dual-Cell System (DCS) and Advanced Helium Mode (AHM), Agilent publication, [5994-8985EN](#)
5. Air Cell Mode of the Agilent 9500 ICP-QQQ with Dual-Cell System, Agilent publication, [5994-8987EN](#)

## Products used in this application

### Agilent products

Product Type	Description	Part Number
Sample Introduction System	Quartz sample introduction system for 9500 ICP-MS	<a href="#">M5150-67107</a>
	MicroMist nebulizer for 9500 ICP-MS	<a href="#">M5150-67024</a>
Interface	ICP-MS sampler cone for 9500 ICP-MS, Ni tip with Cu base	<a href="#">M5150-67000</a>
	Nickel skimmer cone for 9500 ICP-MS with u-lens	<a href="#">M5150-67005</a>
	Extraction-Omega lens assembly, u-lens, stainless steel base	<a href="#">M5150-67022</a>
Tubing Kits	Easy-fit peristaltic-pump tubing, PVC, white/white, 1.02 mm id, for internal standard	<a href="#">5005-0020</a>
	Easy-fit peristaltic-pump tubing, PVC, blue/orange, 0.25 mm id, for sample	<a href="#">5005-0021</a>
	Easy-fit peristaltic-pump tubing, beige thermoplastic, yellow/blue, 1.52 mm id, for drain	<a href="#">5005-0022</a>
	Sample loop for ADS 2/AVS MS, 0.25 mL, 1.00 mm id	<a href="#">5005-0420</a>
	AVS MS preconfigured tubing kit for 9500 ICP-MS	<a href="#">M5171-67001</a>
Bottle Kits	Diluent/carrier 6 L bottle kit, includes a 6 L can, GL45 StaySafe cap, fittings, and venting valve	<a href="#">5005-0435</a>
	Diluent 2 L PFA bottle kit for ICP-MS, includes 2 L PFA bottle, GL45 StaySafe cap, fittings, and venting valve	<a href="#">5005-0436</a>
	Waste container kit, includes a 10 L waste can, S60 StaySafe cap, fittings, and acid vapor filter	<a href="#">5005-0437</a>
Chemical Standards	Internal standard mix	<a href="#">5183-4681</a>
	Multi-element calibration standard 2A	<a href="#">8500-6940</a>
	Zirconium (Zr) single element standard, 1000 µg/mL	<a href="#">ICP-040</a>
	Molybdenum (Mo) single element standard, 1000 µg/mL	<a href="#">ICP-042</a>
	Tin (Sn) single element standard, 1000 µg/mL	<a href="#">ICP-050</a>
	Antimony (Sb) single element standard, 1000 µg/mL	<a href="#">5190-8244</a>
	Tellurium (Te) single element standard, 1000 µg/mL	<a href="#">5190-8533</a>
	Thorium (Th) single element standard, 1000 µg/mL	<a href="#">5190-8539</a>

[www.agilent.com/chem/9500icpqqq](http://www.agilent.com/chem/9500icpqqq)

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