

Analysis of Ultra-trace Level Elements in Seawaters by XSERIES 2 ICP-MS with 3rd Generation Collision Cell Technology

Key Words

- Collision Cell
- Environmental / Geochemical
- ICP-MS
- Kinetic Energy Discrimination
- Seawater/Brine

Introduction

The trace and ultra-trace composition of seawater and other natural saline waters is of interest for both geological studies and environmental monitoring purposes. Furthermore, in regions where fresh water supplies are scarce, saline waters form the feedstock for desalination plants. These use filtration and reverse osmosis processes to desalinate water on a massive scale. The product is used for domestic water supply and consequently, the analysis of the saline feedstock quality is a key factor in the process. Analysis of various process waste streams is also important.

The analysis of natural saline waters has long been a challenge for ICP-MS, particularly for determination of the ultra-trace level elements of interest. The challenges arise from the complex and highly concentrated ionic matrix components found in seawater. The composition of seawater is largely the same worldwide, the principal variations being the ratio of water to total salt content. Total dissolved solids (TDS) vary from as low as approximately 8000 ppm (mg/L) in the Baltic Sea to as high as 60,000 ppm in bay areas of the Arabian Gulf. The "nominal" dissolved solids, upon which formulae for artificial seawater are based, is about 34,500 ppm, of which about 25,000 ppm is taken to be sodium chloride. A typical seawater composition, showing major salt constituents, is given in Table 1.

COMPONENT	CONCENTRATION (MG/L)	% OF TOTAL SALT
Chloride	18,980	55.04
Bromide	65	0.19
Sulfate	2,649	7.68
Bicarbonate	140	0.41
Fluoride	1	0.00
Boric acid	26	0.07
Magnesium	1,272	3.69
Calcium	400	1.16
Strontium	13	0.04
Potassium	380	1.10
Sodium	10,556	30.61
Total	34,482	99.99

Table 1: Composition of Typical Seawater

The complex and concentrated composition causes analytical problems in the form of physical and polyatomic interferences. Due to the very high TDS levels found in typical seawaters (~3.5 %), dilution is required in order to obtain acceptable stability and reasonable suppression

characteristics, but exacerbates the problem of confident determination of the typically exceedingly low concentrations of analytes of interest. Solid phase chelation (SPC) has been used to selectively separate the metals of interest from the matrix constituents, allowing removal of the interferences and pre-concentration. This can lead to lower detection limits and improved accuracy. However, solid phase chelation is somewhat prone to contamination and is labour intensive and rather slow, hence a direct analysis method is extremely desirable.

Even after dilution, polyatomic interferences remain and can severely hamper accurate determination of many analytes. Table 2 lists some of the polyatomic species arising from the matrix components. The use of collision/reaction cell can be applied to this analysis, improving or eliminating many interference situations.

ANALYTE	PROBLEM MATRIX COMPONENT	MATRIX-BASED POLYATOMIC INTERFERENCES	GAS-BASED POLYATOMIC INTERFERENCES
⁵¹ V	Cl, boric acid, K, sulphate	ClO, ClN, ArB, KC, SOH	
⁵² Cr	Carbonate, Cl, Ca, K, sulphate	ArC, ClO, ClOH, CaC, KC, SO	ArO, ArN
⁵⁵ Mn	K, Ca, carbonate, F	KO, KN, CaC, CaN, ArF	ArN
⁵⁶ Fe	Ca, K, carbonate	CaO, KOH, CaC, CaN	ArO
⁵⁹ Co	F, Ca, Na	ArF, CaOH, CaO, NaAr	ArOH
⁶⁰ Ni	Ca, Mg, carbonate	CaO, MgAr, CaC, CaOH	
⁶³ Cu	Na	NaAr	
⁶⁵ Cu	Mg, Ca, sulphate	MgAr, CaOH, SO ₂ , SO ₂ H	
⁶⁶ Zn	Mg, sulphate	MgAr, SO ₂ , SO ₂ H, SO ₂ H ₂	
⁷⁵ As	Cl, K	ArCl, KAr	
⁷⁸ Se			Kr, Ar ₂
⁸⁰ Se	Ca, Br	CaAr, BrH	Kr, Ar ₂
⁸² Se	Br	BrH	Kr
¹¹¹ Cd	Cl	Ar ₂ Cl	
¹¹⁴ Cd			
²⁰⁸ Pb			

Table 2: Some Possible Interferences Arising from Seawater Matrix and Plasma Gas for Selected Analytes

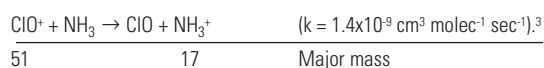
Cell Operation Approaches

In recent years two distinct cell operation approaches have become well documented:

- 1) reactive interference removal (or shifting of the analyte to an alternative mass through reaction); and
- 2) removal by kinetic energy discrimination (KED).

1) Reactive Removal

This approach utilizes ion-molecule reactions between the polyatomic interference species and a reaction gas flowing into the cell. The aim is for the reactions to result in a change of mass-to-charge ratio of the interfering species so that it no longer coincides with the mass of interest, or to promote the loss of charge from the interfering species to prevent its observation. An example is the overlap of $^{35}\text{Cl}^{16}\text{O}^+$ with $^{51}\text{V}^+$. Ammonia has been used as a reaction gas to efficiently remove the chlorate ion.² The primary reaction is an electron transfer between ammonia and the chlorate ion:

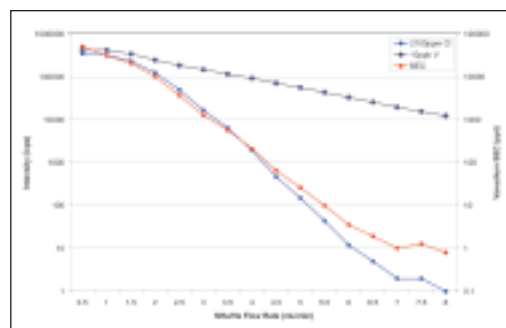


Graph 1 shows a gas optimization plot for 1 % NH_3 in He used as a reaction gas for the removal of ClO^+ . Under optimum cell conditions a blank equivalent concentration (BEC) of 1 ppt was obtained for 51V in 2100ppm chloride (the approximate chloride concentration of a 1+9 dilution of open ocean seawater). This is a significant improvement over the BEC of 73,000 ppt for the same matrix in standard mode. Graph 3 shows the calibration plot for this result.

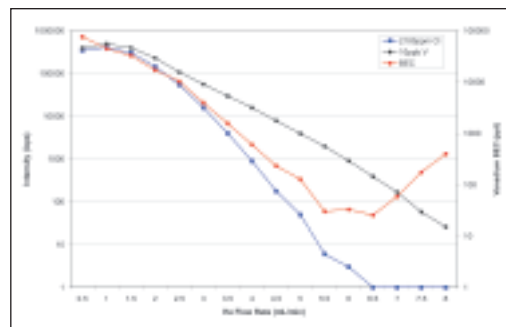
The drawback of this technique is that the performance is strongly dependant on the reactivity of the target polyatomic species with the reagent gas selected. For example, hydrogen has been shown to be highly effective at reactive removal of argon-based polyatomic species.⁴ However, if hydrogen is selected as a reagent gas there will be no reactive removal of ClO^+ since reaction between these species does not proceed:



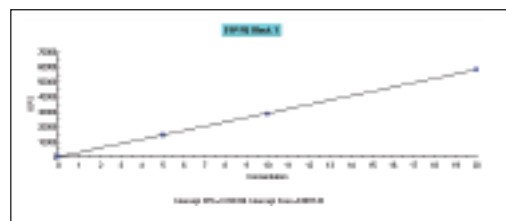
The consequence of this is that a different reaction gas must be selected in order to obtain the optimum interference removal efficiency for each interferent, obtaining the best performance for each analyte. Although there are suggestions, databases and “cookbooks” available in order to assist with the selection of the ideal reagent gas, this still results in considerable complexity in method development and instrument set-up. Furthermore, each polyatomic may require its own optimum cell gas flow rate, resulting in multiple settings for the complete multi-element analysis. Each new setting, or new gas used, requires a gas flow stabilization delay prior to analysis, adding time and complexity to the analytical cycle.



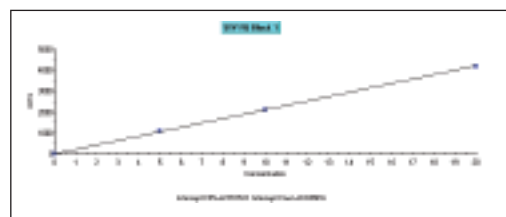
Graph 1: Gas Optimization Plot for 1% NH_3 (in He), Reactive Mode



Graph 2: Gas Optimization Plot for He, Kinetic Energy Discrimination Mode



Graph 3: Vanadium Calibration Plot using 1% NH_3 (in He), Reactive Mode



Graph 4: Vanadium Calibration Plot using He Kinetic Energy Discrimination Mode

2) Kinetic Energy Discrimination (KED)

This approach often utilizes an inert gas such as helium. It discriminates the plasma-based polyatomic ions from the analyte ions by taking advantage of ion kinetic energy differences attributed to differing collision frequencies along the cell path-length caused by the larger ionic radii of the polyatomic ions. The transmission of the lower energy polyatomic species can be discriminated against by the use of a stopping potential between the cell multipole and the analyzer quadrupole. The example of the $^{35}\text{Cl}^{16}\text{O}^+$ overlap on $^{51}\text{V}^+$ can be used again. Figure 1 shows how the chlorate ion, which has a larger ionic radius ($\sim 230 \text{ pm}$)⁶, collides more frequently along a given path-length of the pressurised cell than vanadium (ionic radius $\sim 135 \text{ pm}$) due to its larger size. Consequently it loses more kinetic energy and is not accepted into the analyzer

quadrupole when an appropriate differentiating stopping potential is applied. Graph 2 shows a gas optimization plot for He used as a collision gas for the removal of ClO⁺ with a +2V stopping potential. Under these cell conditions a blank equivalent concentration (BEC) of 31 ppt was obtained for ⁵¹V in 2100 ppm chloride. Again, this is a significant improvement over the BEC in standard mode (73,000 ppt) and is good enough to be used in most analytical situations. Graph 4 shows the calibration plot for this result.

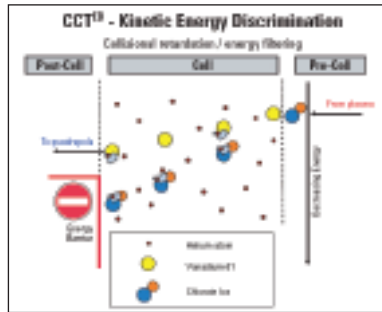


Figure 1: How Kinetic Energy Discrimination Works

Although reactive removal of polyatomics can often be more effective than kinetic energy discrimination alone, the Thermo Scientific XSERIES 2 ICP-MS from has the ability to utilize a hybrid reactive mode with *kinetic energy discrimination*. This mode has the advantage of using the effectiveness of reactive removal for species that undergo chemistry with the reagent gas, but also producing superb interference removal performance (using KED) for polyatomics that do not have reactive chemistry with the reagent gas. In addition, this mode of operation offers extremely simple setup since a single set of conditions can be used for all analytes. This in turn produces the fastest speed of analysis for a collision/reaction cell system since no gas change stabilization delays are required. Since many of the polyatomic species of concern in this application have reactive chemistry with hydrogen (species shown in red in Table 2), this mode of operation with our patented use of a hydrogen-based cell gas is ideal.⁷ For those species without chemistry with hydrogen, removal by KED with the same gas is extremely effective. A mixture of 8 % hydrogen in helium was found to be an excellent gas composition for this mode.

Instrument Configuration

PARAMETER	CONFIGURATION USED
Nebuliser	Glass Concentric
Spraychamber	Glass Conical Impact Bead
Torch	1-Piece, 1.5 mm injector diameter, with PlasmaScreen ^{Plus}
Interface option	Xt
RF power	1400 W
Sample uptake rate	0.4 mL/min, approx., pumped
Infinity ^{II} lens	Autotuned once prior to analysis
Quadrupole resolution	Standard resolution mode: peak width 0.70 amu at 5 % height
CCT gas	8 % Hydrogen in Helium (N5 grade), purified via a gas purification cartridge
CCT mode	+2V Kinetic Energy Discrimination

Table 3: Instrument Configuration

PARAMETER	SETTING
Internal standard isotopes	⁷¹ Ga, ¹¹⁵ In, interpolated response
Number of replicates per sample	3
Scan mode	Peak jumping
Sample uptake time	15 seconds
Wash delay	35 seconds
Total time per sample	3 minutes, 5 seconds

Table 4: Analytical Parameters

CALIBRATION STANDARD	CALIBRATION CONCENTRATION (NG/L)*
Blank	0
Std1	50
Std2	100
Std3	200
Std4	500

Table 5: Calibration Details

*Spiked into open 1:10 dilution of open ocean seawater to negate differences in matrix effects between calibration and samples.

Results

ANALYTE	BEC (PPT)
⁵¹ V	0.2
⁵² Cr	0.2
⁵⁵ Mn	0.2
⁵⁹ Co	0.2
⁶⁰ Ni	0.5
⁶⁵ Cu	0.5
⁶⁶ Zn	4
⁷⁵ As	2
⁷⁸ Se	5
¹¹¹ Cd	0.1
²⁰⁸ Pb	1

Table 6: Blank Equivalent Concentrations in Trace Nitric Acid

ANALYTE	NASS-5 1:10			
	MEASURED PPT	KNOWN PPT	REC %	100PPT SPIKE REC %
⁵¹ V	146.2	120	122	94
⁵² Cr	13.43	11	122	98
⁵⁵ Mn	93.72	91.9	102	102
⁵⁶ Fe	60.88	20.7	294	98
⁵⁹ Co	1.923	1.1	175	100
⁶⁰ Ni	25.09	25.3	99	103
⁶⁵ Cu	33.03	29.7	111	93
⁶⁶ Zn	9.898	10.2	97	110
⁷⁵ As	162.2	127	128	97
⁷⁸ Se	1.927	1.8	108	84
¹¹¹ Cd	1.686	2.3	73	107
¹¹⁴ Cd	2.55	2.3	111	99
²⁰⁸ Pb	1.291	0.8	161	99

Table 7: Results of NASS-5 (Open Ocean Seawater), 1:10 Diluted

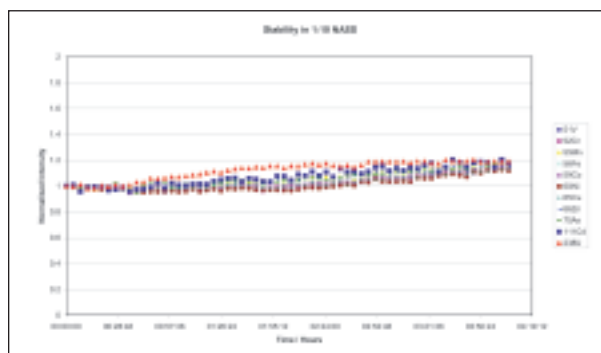
CASS-4 1:10				
ANALYTE	MEASURED	KNOWN	REC %	100PPT SPIKE REC %
⁵¹ V	139.5	118	118	106
⁵² Cr	14.36	14.4	100	94
⁵⁵ Mn	282.1	278	101	102
⁵⁶ Fe	119.7	71.3	168	107
⁵⁸ Co	3.008	2.6	116	109
⁶⁰ Ni	31.02	31.4	99	108
⁶⁵ Cu	62.43	59.2	105	104
⁶⁶ Zn	42.69	38.1	112	110
⁷⁵ As	146.9	111	132	104
⁷⁸ Se	8.874	-	-	113
¹¹¹ Cd	2.318	2.6	89	98
¹¹⁴ Cd	2.186	2.6	84	99
²⁰⁸ Pb	1.69	0.98	172	91

Table 8: Results of CASS-4 (Nearshore Seawater), 1:10 Diluted

SLEW-3 1:5				
ANALYTE	MEASURED	KNOWN	REC %	500PPT* SPIKE REC %
⁵¹ V	581.5	514	113	96
⁵² Cr	39.61	36.6	108	100
⁵⁵ Mn	323.5	322	100	101
⁵⁶ Fe	161.8	113.6	142	103
⁵⁸ Co	9.048	8.4	108	111
⁶⁰ Ni	257.9	246	105	98
⁶⁵ Cu	325.9	310	105	101
⁶⁶ Zn	35.36	40.2	88	103
⁷⁵ As	361.9	272	133	89
⁷⁸ Se	23.91	-	-	96
¹¹¹ Cd	9.736	9.6	101	100
¹¹⁴ Cd	9.642	9.6	100	101
²⁰⁸ Pb	2.275	1.8	126	96

Table 9: Results of SLEW-3 (Estuarine Water), 1:5 Diluted

* 500ppt spike due to higher analyte concentrations.



Graph 5: Four-Hour Stability of 100 ng/L Spike of Selected Elements in 1:10 NASS

Conclusion

The XSERIES 2 ICP-MS incorporates an improved matrix tolerant interface design: the Xt interface. This is even more resistant to the matrix-induced drift often associated with the deposition of matrix-based materials in the interface. It works reducing the thermal conductivity of the skimmer cone to burn off deposition as it occurs.

The XSERIES 2 lens design features a Protective Ion (π) extraction system (see TN40717) that only transmits ions of favourable energy to the collision cell. The optics produce the lowest continuum background ever for a quadrupole ICP-MS (typically ~ 0.1 cps). Combined with improved cell and analyser multipole drive electronics and an improved post-cell optical design for enhanced analyte transmission in KED mode, the system gives optimal cell performance in both reactive and kinetic energy discrimination modes making the XSERIES 2 the ultimate CCT instrument.

All polyatomic interferences of concern in seawater are removed with a single set of analytical conditions (hydrogen/helium kinetic energy discrimination mode). These would normally include chloride interferences, such as $^{35}\text{Cl}^{16}\text{O}^+$ and $^{40}\text{Ar}^{35}\text{Cl}^+$ (interfering with ^{51}V and ^{75}As , respectively), sodium interferences such as $^{23}\text{Na}^{40}\text{Ar}^+$ on ^{63}Cu , and calcium interferences such as $^{44}\text{Ca}^{16}\text{O}^+$ on ^{60}Ni . In each case, the interference is effectively removed with our non-specific, reactive kinetic energy discrimination approach, giving excellent confidence in the results regardless of sample matrix. This is shown by the excellent recoveries at ppt levels for NASS-5, CASS-4 and SLEW-3 (see Tables 8-10) and the very low background equivalent concentrations (BECs) (Table 7). Although this analysis was performed in our Class 10,000 clean room and care was taken in all handling steps, a few analytes show slight deviations from the expected values in the reference materials due to the presence of tiny amounts of contamination at the low ppt levels required. The ability of the system to accurately and confidently make ppt level determinations in seawater matrices is confirmed by the quantitative recovery of ppt level spike additions (Tables 8-10).

The new Xt interface design allows aspiration of high matrix concentration samples, such as seawaters for prolonged periods without significant drift and loss of sensitivity which is normally associated with this type of sample (Graph 5). This results in extended times between maintenance on the cones, fewer QC failures and no compromise in detection limits with time. These developments give the highest possible productivity and confidence in results.

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- 5) As Ref 3.
- 6) Inferred from data separately published by Allen, Alcock and Shannon.
- 7) US patent numbers 5,767,512 and 6,259,091

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