

# Robust and sensitive multi-element determination in surface and sea waters using triple quadrupole ICP-MS

Authors: Tomoko Vincent<sup>1</sup>, Naoki Iwayama<sup>2</sup> and Tokutaka Ikemoto<sup>3</sup>

<sup>1</sup>Thermo Fisher Scientific, Germany,

<sup>2</sup>Seikan Kensa Center Inc., Japan,

<sup>3</sup>Thermo Fisher Scientific, Japan

Keywords: Argon gas dilution (AGD), drinking water, environmental analysis, lake water, river water, sea water, sensitivity and robustness, surface waters, TQ-ICP-MS

## Goal

To demonstrate the applicability of the Thermo Scientific™ iCAP™ TQe ICP-MS in combination with argon gas dilution (AGD) for direct analysis of trace elements in complex environmental samples (i.e., sea water, brackish water, lake water, or river water).

## Introduction

The release of toxic substances into the environment as a result of domestic or industrial activities is a major cause of concern, with potential health risks associated with the toxicity of the chemicals discharged.<sup>1</sup> Amongst environmental pollutants, heavy metals are of interest due to their known toxicity combined with their persistence and



bio-accumulative properties.<sup>2</sup> Although heavy metals can originate from natural sources, anthropogenic activities, such as mining, industrial production, and agricultural activities,<sup>3</sup> are typically the main routes of release of these elements into the environment. To protect human health and the environment, strict regulatory measures and guidelines have been established globally and/or specifically for certain countries, with clear maximum allowable concentrations of toxic elements in environmental samples (such as sea water or potable water). As an example, the applicable maximum contaminant levels established by the Ministry of the Environment in Japan for potable, sea, and river waters are summarized in Table 1.

**Table 1. Maximum allowable limits ( $\mu\text{g}\cdot\text{L}^{-1}$ ) of inorganic elements in potable water and environment water in Japan.** Numbers annotated with \* apply to river water only.

Element	Potable water	Sea and river water
Cd	3	3
Se	10	10
Pb	10	10
As	10	10
Cr ( $\text{Cr}^{6+}$ )	20	50
B	1,000	1,000*
Zn	1,000	-
Al	200	-
Fe	300	-
Cu	1,000	-
Na	200,000	-
Mn	50	-
Ca, Mg etc. (Hardness)	300,000	-
Hg	0.5	0.5

In general, Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is the preferred analytical technique for the analysis of metals and related contaminants at low levels. However, the analysis of samples containing higher levels of dissolved solids (typically above 0.5%) is a known challenge in ICP-MS. The complexity of the sample matrix can significantly affect the sensitivity of the instrument, cause intensity fluctuation of the internal standard (suppression and drift), and lead to increased system maintenance with unwanted downtime due to clogging of the interface cone orifices, torch injectors, or nebulizer tips.

To analyze complex samples, such as sea water, dilution must be performed, either using liquid dilution or, alternatively, dilution of the sample aerosol with an inert gas such as argon. Dilution with argon gas is often perceived as beneficial because samples can be placed directly on the autosampler, without the need of a manual, time-consuming dilution step prior to analysis. However, reducing the impact of the matrix by sample dilution is not the only challenge for this analysis. Elements with high first ionization potentials, such as zinc, arsenic, selenium, and cadmium, typically suffer from reduced recovery under the dry plasma conditions observed when using gas dilution. For all elements, the potential occurrence of interferences (predominantly polyatomic species) may lead to false positive results if these are not removed.

This application note describes an optimized analytical method for the analysis of a variety of water samples (sea, lake, river, and potable waters) using the iCAP TQe ICP-MS. To overcome the analytical challenges described above, this instrument was operated using argon gas dilution (AGD) and was equipped with the novel PLUS torch<sup>4</sup>. The PLUS torch is a replacement for the standard torch of the system made from high purity ceramic material.

## Experimental

### Instrumentation

An iCAP TQe ICP-MS system equipped with a standard sample introduction system configuration was used for all analyses. To automate the sample introduction, a Teledyne™ CETAC™ ASX-560 autosampler (Teledyne CETAC Technologies, Omaha, NE, USA) was selected. To remove all potentially occurring interferences, the ICP-MS was operated in SQ KED and TQ-O<sub>2</sub> modes, using the parameters presented in Table 2.

**Table 2. Instrument configuration and operating parameters**

Parameter	Value	
Nebulizer	Borosilicate glass Micromist (Glass Expansion, Australia), 400 $\mu\text{L}\cdot\text{min}^{-1}$ , pumped at 30 rpm	
Pump tubing	Orange – green, 0.38 mm i.d.	
Spray chamber	Quartz cyclonic, cooled at 2.7 °C	
Torch	PLUS torch	
Injector	2.5 mm i.d., quartz	
Interface	Nickel sampler and nickel skimmer cone with High Matrix insert	
Plasma power	1,550 W	
Nebulizer gas	0.30 $\text{L}\cdot\text{min}^{-1}$	
Additional argon gas	0.68 $\text{L}\cdot\text{min}^{-1}$	
QCell setting	TQ-O <sub>2</sub>	SQ KED
Gas flow	100% O <sub>2</sub> , 0.34 $\text{mL}\cdot\text{min}^{-1}$	100% He, 5.5 $\text{mL}\cdot\text{min}^{-1}$
CR bias	-6.3 V	-21 V
Q3 bias	-12 V	-18 V
Scan settings	0.1 s dwell time, 5 sweeps, 3 main runs	
Lens setting	Autotuned	
Sample uptake	60 s	
Wash time	50 s	
Total analysis time	3 min	

The instrument was equipped with the option to use Argon Gas Dilution (AGD) to facilitate the analysis of all types of water samples [including sea water samples with high total dissolved solids (TDS)] without any liquid dilution prior to analysis in a single batch.<sup>5</sup> To accomplish this, the gas flow to the nebulizer is reduced, while an additional flow of argon gas is added to the gas port located at the spray chamber elbow, resulting in a dilution factor of ~10 times applied to the samples (as derived from the difference in intensity observed with AGD compared to the standard tuning of the instrument). Consequently, using AGD, less sample is introduced to the plasma, and the plasma is significantly drier (a reduction of the oxide ratio is typically observed). Overall, the use of AGD leads to more effective decomposition of the sample constituents and hence improved matrix tolerance.

The analysis of samples containing high amounts of TDS can lead to an increased maintenance cycle, predominantly for the interface cones but also for the torch. The deposition of salt residues over time can lead to devitrification, shortening the lifetime of conventional quartz torches.

### Data acquisition and data processing

The Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software was used to create LabBooks for sample analysis, data acquisition, processing, and reporting. The Reaction Finder method development tool automates the selection of optimized collision/reaction gas selection and product ion mass (if applicable) to ensure generation of the best quality data through complete interference removal with minimal user effort. Based on the selection of the element to analyze from the periodic table, Reaction Finder will automatically create a method using optimized analysis settings, including selection of the best isotope for analysis, acquisition mode (SQ vs. TQ), reactive gas, and scan type (mass shift vs. on mass).

### Sample preparation

Polypropylene bottles were used for the preparation of all blanks, calibration standards, and samples. Two certified reference materials (CRM) were used: NASS-7 [sea water, National Research Council Canada (NRC-CNRC)] and SLRS-5 (river water, NRC-CNRC). In addition, three different water samples were collected in and around Bremen, Germany (sea water, lake water, and potable water). All water samples were acidified with 2% v/v HNO<sub>3</sub> (Optima™ grade, Fisher Scientific™) after collection. In addition, the samples were filtered through a 0.45 μm membrane to remove particles. A total of 30 elements were analyzed in all samples. All blanks, calibration standards, and quality control standards (QC) were prepared using a mixed acid diluent [2% v/v HNO<sub>3</sub> and 1% v/v HCl (Optima grade, Fisher Scientific)] and single element standards (SPEX™ CertiPrep, Metuchen, NJ, USA), listed in Table 3.

**Table 3. Summary of the concentration details of the CCV and CCB QC solutions**

	Concentration range in calibration solutions (μg·L <sup>-1</sup> )	CCB	CCV (μg·L <sup>-1</sup> )	Sea water spike level (μg·L <sup>-1</sup> )
Li, Be, Al	2–200	2% HNO <sub>3</sub> and 1% HCl	10	20
Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Mo, Ag, Cd, Sn, Sb, Ba, Hg, Tl, Pb, U	1–50	2% HNO <sub>3</sub> and 1% HCl	10	20
B, Si	50–2,000	2% HNO <sub>3</sub> and 1% HCl	200	200
Mg, K, Ca	10,000–200,000	2% HNO <sub>3</sub> and 1% HCl	40,000	100,000
Sr	2–200	2% HNO <sub>3</sub> and 1% HCl	10	1,000

An internal standard solution, containing 100  $\mu\text{g}\cdot\text{L}^{-1}$  Y, In, and Tb in 2% v/v  $\text{HNO}_3$  and 5% v/v isopropanol (IPA) was added to all samples prior to entry to the spray chamber, via a T-piece with a mixing ratio between the internal standard and the samples of 1:1. The addition of IPA to the plasma enhances the sensitivity of some elements, such as arsenic and selenium, resulting to improved results, as reported previously.<sup>6</sup>

Details of the measurement modes, acquisition parameters, and internal standards used for each element are summarized in Table 4.

For ongoing quality control, Continuing Calibration Verification (CCV) and Continuing Calibration Blank (CCB) solutions were periodically analyzed throughout the entire measurement sequence.

## Results and discussion

### Sensitivity and linearity

Table 4 summarizes the Instrument Detection Limits (IDLs) obtained, together with the coefficient of determination ( $R^2$ ) for all the elements analyzed in this study. The IDLs were calculated as three times the standard deviation of ten replicate measurements of the calibration blank. As no manual dilution was performed prior analysis, these IDLs directly correspond to the method detection limits (MDL). The MDLs obtained were significantly below the maximum limitation of the Japanese Ministry of the Environment regulations (Table 1).

### Accuracy, precision, and robustness

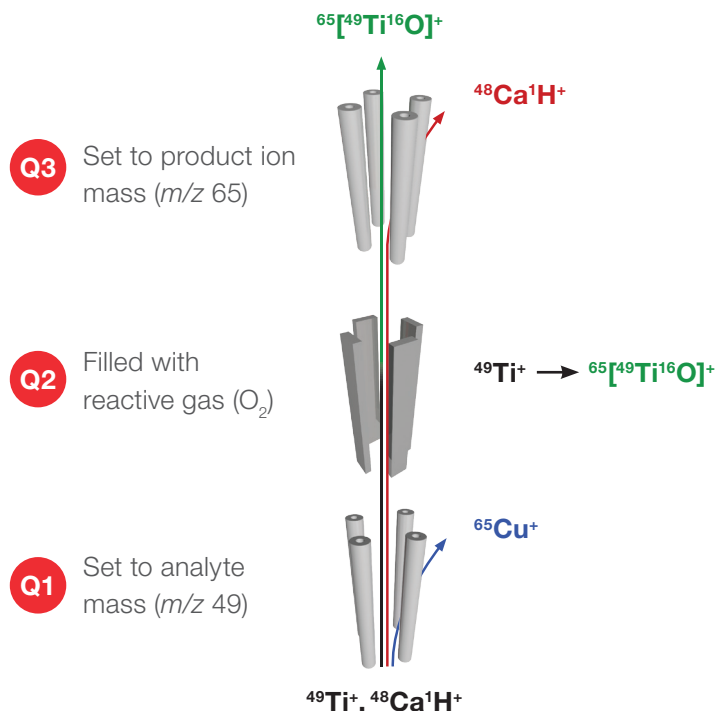
#### Interference removal

In general, determination of the heavy metals of greatest concern (e.g., cadmium, tin, mercury, lead) requires analysis at  $\mu\text{g}\cdot\text{L}^{-1}$  levels or lower. At the same time, typical water samples contain high amounts of Na, K, Ca, and Mg (often in the region of several hundred  $\text{mg}\cdot\text{L}^{-1}$ ). These major elements, together with their corresponding anions, can create intense and complicated interferences on the low concentration analytes. Moreover, unexpected elements, such as the lanthanides, can often cause positive bias on the results for key elements (for example,  $^{150}\text{Nd}^{2+}$  interference on  $^{75}\text{As}$ ) even at relatively low concentrations. Therefore, it is important to ensure complete interference removal to avoid false positive results by using triple quadrupole ICP-MS where appropriate.

**Table 4. Summary of analysis modes, calibration results, and MDLs for all target analytes.** The concentration range for  $R^2$  was shown in Table 3.

Analyte	Mode	Internal standard	Coefficient of determination ( $R^2$ )	MDLs ( $\mu\text{g}\cdot\text{L}^{-1}$ )
$^7\text{Li}$	KED	$^{115}\text{In}$	0.9994	0.340
$^9\text{Be}$	KED	$^{115}\text{In}$	0.9999	0.471
$^{11}\text{B}$	KED	$^{115}\text{In}$	0.9992	0.573
$^{24}\text{Mg}$	KED	$^{115}\text{In}$	0.9999	3.000
$^{27}\text{Al}$	KED	$^{115}\text{In}$	0.9997	0.579
$^{28}\text{Si}$ as $^{28}\text{Si}^{16}\text{O}$ at $m/z$ 44	TQ- $\text{O}_2$	$^{89}\text{Y}$	0.9991	5.200
$^{39}\text{K}$	KED	$^{115}\text{In}$	0.9998	57.174
$^{44}\text{Ca}$	KED	$^{115}\text{In}$	0.9995	25.043
$^{49}\text{Ti}$ as $^{49}\text{Ti}^{16}\text{O}$ at $m/z$ 65	TQ- $\text{O}_2$	$^{89}\text{Y}$	>0.9999	0.043
$^{51}\text{V}$ as $^{51}\text{V}^{16}\text{O}$ at $m/z$ 67	TQ- $\text{O}_2$	$^{89}\text{Y}$	>0.9999	0.034
$^{52}\text{Cr}$	KED	$^{115}\text{In}$	>0.9999	0.162
$^{55}\text{Mn}$	KED	$^{115}\text{In}$	>0.9999	0.016
$^{56}\text{Fe}$	KED	$^{115}\text{In}$	0.9996	0.372
$^{59}\text{Co}$	KED	$^{115}\text{In}$	>0.9999	0.015
$^{60}\text{Ni}$	KED	$^{115}\text{In}$	0.9965	0.067
$^{63}\text{Cu}$	KED	$^{115}\text{In}$	>0.9999	0.048
$^{66}\text{Zn}$	KED	$^{115}\text{In}$	>0.9999	0.105
$^{75}\text{As}$ as $^{75}\text{As}^{16}\text{O}$ at $m/z$ 91	TQ- $\text{O}_2$	$^{115}\text{In}$	>0.9999	0.018
$^{80}\text{Se}$ as $^{80}\text{Se}^{16}\text{O}$ at $m/z$ 96	TQ- $\text{O}_2$	$^{115}\text{In}$	>0.9999	0.029
$^{88}\text{Sr}$ as $^{88}\text{Sr}^{16}\text{O}$ at $m/z$ 104	TQ- $\text{O}_2$	$^{115}\text{In}$	>0.9999	0.053
$^{98}\text{Mo}$ as $^{98}\text{Mo}^{16}\text{O}$ at $m/z$ 114	TQ- $\text{O}_2$	$^{115}\text{In}$	>0.9999	0.016
$^{107}\text{Ag}$	KED	$^{115}\text{In}$	>0.9999	0.011
$^{111}\text{Cd}$ as $^{111}\text{Cd}$ at $m/z$ 111	TQ- $\text{O}_2$	$^{159}\text{Tb}$	>0.9999	0.005
$^{118}\text{Sn}$	KED	$^{159}\text{Tb}$	>0.9999	0.067
$^{121}\text{Sb}$	KED	$^{159}\text{Tb}$	>0.9999	0.047
$^{138}\text{Ba}$	KED	$^{159}\text{Tb}$	>0.9999	0.038
$^{202}\text{Hg}$	KED	$^{159}\text{Tb}$	0.9999	0.010
$^{205}\text{Tl}$	KED	$^{159}\text{Tb}$	>0.9999	0.001
$^{208}\text{Pb}$	KED	$^{159}\text{Tb}$	>0.9999	0.004
$^{238}\text{U}$	KED	$^{159}\text{Tb}$	>0.9999	0.003

As an example, the analysis of titanium is illustrated in Figure 1 and shows how TQ-ICP-MS can help to overcome potential interferences in calcium rich sample matrices. In this case, the most abundant isotope of titanium ( $^{48}\text{Ti}$ ) is affected by isobaric overlap with  $^{48}\text{Ca}$ . Although the use of ammonia is widely recognized as an effective way to remove this potential bias, this reactive gas is not commonly found in laboratories performing analytical testing of water samples due to health and safety restrictions. However, the use of  $\text{O}_2$  as the reaction gas with a different titanium isotope ( $^{49}\text{Ti}$ ) provides an effective alternative approach ( $^{48}\text{Ti}$  cannot be used with an  $\text{O}_2$  cell gas due to reaction between  $^{48}\text{Ca}^+$  and  $\text{O}_2$ ). With Q1 set to transmit  $^{49}\text{Ti}^+$  and Q3 set to transmit the  $^{49}\text{Ti}^{16}\text{O}^+$  product ion, interference from  $^{48}\text{Ca}$  is completely avoided and any  $^{48}\text{Ca}^1\text{H}^+$  interference on  $^{49}\text{Ti}$  is filtered out in the collision / reaction cell (Q2). As a result of mass filtration in the first quadrupole,  $^{65}\text{Cu}^+$ , which would otherwise be a potential interference on the  $^{49}\text{Ti}^{16}\text{O}^+$  product ion, is eliminated before the ion beam enters Q2. Table 5 compares the results between He KED mode and TQ- $\text{O}_2$  mode in sea water and drinking water, respectively. As the sea water analyzed in this study contained  $>400 \text{ mg}\cdot\text{L}^{-1}$  of Ca, full interference removal for  $^{49}\text{Ti}$  could not be accomplished using He KED mode alone. The results in this mode were  $>140$  times higher than those obtained in TQ- $\text{O}_2$  mode. This false positive result mainly originates from unresolved  $^{48}\text{Ca}^1\text{H}^+$  interference, with potential additional interference from  $^{35}\text{Cl}^{14}\text{N}^+$ . In contrast, TQ- $\text{O}_2$  mode allowed significantly lower backgrounds to be obtained and more accurate results compared to He KED mode where false positive results were observed. Similar results were obtained for drinking water, which although containing a lower amount of calcium, was still positively biased in He KED mode.



**Figure 1. Schematic diagram showing the use of TQ- $\text{O}_2$  mode to selectively analyze titanium in the presence of calcium induced interferences**

**Table 5. Comparison of results obtained with He KED and TQ- $\text{O}_2$  modes using AGD when analyzing titanium ( $^{49}\text{Ti}$ ) in samples containing high amounts of calcium**

	Ca amount ( $\mu\text{g}\cdot\text{L}^{-1}$ )	Ti concentration results ( $\mu\text{g}\cdot\text{L}^{-1}$ )	
		He KED at $m/z$ 49	TQ- $\text{O}_2$ at $m/z$ 65 as $^{49}\text{Ti}^{16}\text{O}$
Sea water	$>400,000$	130	0.9
Drinking water	$>40,000$	3	<MDL

As part of this study, two certified reference materials for sea water (NASS-7) and river water (SLRS-5), as well as various water samples, were analyzed to assess the method performance. In total, 171 samples were analyzed (the details are shown in Table 7). The results for both CRMs were in excellent agreement with the reference values (Table 6), except for chromium and iron, for which the concentrations found in the CRM value were close to or below the MDL levels. To ensure accurate and reliable analysis, samples were spiked and the recoveries were determined. (The spike concentrations are shown in Table 3.)

**Table 6. Quantification of multiple elements in several water samples.** All data annotated with \* are known reference values (expected values) and \*\* are indicative (non-certified) values.

Analyte	NASS-7 sea water ( $\mu\text{g}\cdot\text{L}^{-1}$ )			SLRS-5 river water ( $\mu\text{g}\cdot\text{L}^{-1}$ )		Unknown samples ( $\mu\text{g}\cdot\text{L}^{-1}$ )	
	CRM value	Measured (n=5)	Spike recovery (%)	CRM value	Measured (n=15)	Lake water	Potable water
$^7\text{Li}$	-	146 ± 12.8	108	-	0.4 ± 0.05	3.0	6.2
$^9\text{Be}$	-	<MDL	84	0.005*	<MDL	<MDL	<MDL
$^{11}\text{B}$	3,750 ± 120	3856 ± 105 <sup>(a)</sup>	94	-	22.8 ± 3.9	137.5	20
$^{24}\text{Mg}$	-	1,142,000 ± 44 <sup>(a)</sup>	100	2,540 ± 160	2,570 ± 140	6,410	4,160
$^{27}\text{Al}$	-	1.2 ± 0.15	94	49.5 ± 5.0	45.8 ± 1.52	19.8	1.04
$^{28}\text{Si}$ as $^{28}\text{Si}^{16}\text{O}$ at <i>m/z</i> 44	-	171.2 ± 47.6	111	-	1,959 ± 40 <sup>(a)</sup>	717.9	9,740.02 <sup>(a)</sup>
$^{39}\text{K}$	-	347,400 ± 9.3 <sup>(a)</sup>	82	839 ± 36	887 ± 10	10,320	2,540
$^{44}\text{Ca}$	-	397,400 ± 6.4 <sup>(a)</sup>	106	10,500 ± 400	10,935 ± 347	50,500	42,650
$^{49}\text{Ti}$ as $^{49}\text{Ti}^{16}\text{O}$ at <i>m/z</i> 65	-	0.9 ± 0.07	101	-	0.3 ± 0.07	0.4	<MDL
$^{51}\text{V}$ as $^{51}\text{V}^{16}\text{O}$ at <i>m/z</i> 67	1.27 ± 0.08**	1.37 ± 0.12	101	0.317 ± 0.033	0.327 ± 0.004	0.1	0.07
$^{52}\text{Cr}$	0.107 ± 0.016**	<MDL	95	0.208 ± 0.023	0.230 ± 0.032	<MDL	<MDL
$^{55}\text{Mn}$	0.75 ± 0.06	0.8 ± 0.15	90	4.33 ± 0.18	4.22 ± 0.21	89.77	0.06
$^{56}\text{Fe}$	0.351 ± 0.026	<MDL	103	91.2 ± 5.8	93.1 ± 2.9 <sup>(a)</sup>	23.66	2.01
$^{59}\text{Co}$	0.0146 ± 0.0014	<MDL	109	0.05*	0.052 ± 0.003	0.05	0.03
$^{60}\text{Ni}$	0.248 ± 0.018	0.25 ± 0.084	101	0.476 ± 0.064	0.389 ± 0.015	0.5	0.5
$^{63}\text{Cu}$	0.195 ± 0.014	0.182 ± 0.046	99	17.4 ± 1.3	17.5 ± 0.92	1.77	12.9
$^{66}\text{Zn}$	0.42 ± 0.08	0.43 ± 0.18	88	0.845 ± 0.095	0.90 ± 0.036	161.7 <sup>(a)</sup>	12.6
$^{75}\text{As}$ as $^{75}\text{As}^{16}\text{O}$ at <i>m/z</i> 91	1.26 ± 0.02**	1.24 ± 0.09	96%	0.413 ± 0.039	0.39 ± 0.02	0.71	0.07
$^{80}\text{Se}$ as $^{80}\text{Se}^{16}\text{O}$ at <i>m/z</i> 96	-	0.24 ± 0.09	101%	-	0.082 ± 0.003	0.05	0.07
$^{88}\text{Sr}$ as $^{88}\text{Sr}^{16}\text{O}$ at <i>m/z</i> 104	-	6,436 ± 233 <sup>(a)</sup>	102%	53.6 ± 1.3	51.9 ± 0.86	216.5	120.37
$^{98}\text{Mo}$ as $^{98}\text{Mo}^{16}\text{O}$ at <i>m/z</i> 114	9.29 ± 0.4	9.49 ± 0.54	107%	0.5*	0.52 ± 0.03	0.1	0.06
$^{107}\text{Ag}$	-	0.002 ± 0.004	88%	-	<MDL	<MDL	<MDL
$^{111}\text{Cd}$ as $^{111}\text{Cd}$ at <i>m/z</i> 111	0.0161 ± 0.0016	0.0153 ± 0.002	102%	0.0060 ± 0.0014	0.007 ± 0.001	0.01	0.01
$^{118}\text{Sn}$	-	<MDL	84%	-	<MDL	<MDL	<MDL
$^{121}\text{Sb}$	-	0.227 ± 0.009	96%	0.3*	0.33 ± 0.01	0.09	0.01
$^{138}\text{Ba}$	-	5.58 ± 0.055	104%	14.0 ± 0.5	15.0 ± 0.18	232.71 <sup>(a)</sup>	16.81
$^{202}\text{Hg}$	-	0.034 ± 0.047	101%	-	0.03 ± 0.02	0.03	0.03
$^{205}\text{Tl}$	-	0.011 ± 0.008	103%	-	0.003 ± 0.002	0.01	<MDL
$^{208}\text{Pb}$	0.0026 ± 0.0008	0.0025 ± 0.0014	98%	0.081 ± 0.006	0.09 ± 0.002	0.04	0.11
$^{238}\text{U}$	2.92 ± 0.42	3.2 ± 0.264	106%	0.1*	0.097 ± 0.004	0.07	0.01

Results annotated with <sup>(a)</sup> are higher than the maximum calibration standard concentration, but nonetheless show good spike recovery results because of the wide linear range of the detector.



## Robustness

For reliable analysis in high-throughput analytical testing laboratories, it is important that the results obtained are accurate and precise throughout long analytical run sequences consisting of different sample types. Commonly, quality control (QC) standards containing known concentrations of all the analytes of interest are analyzed periodically during each analysis batch to monitor method performance.

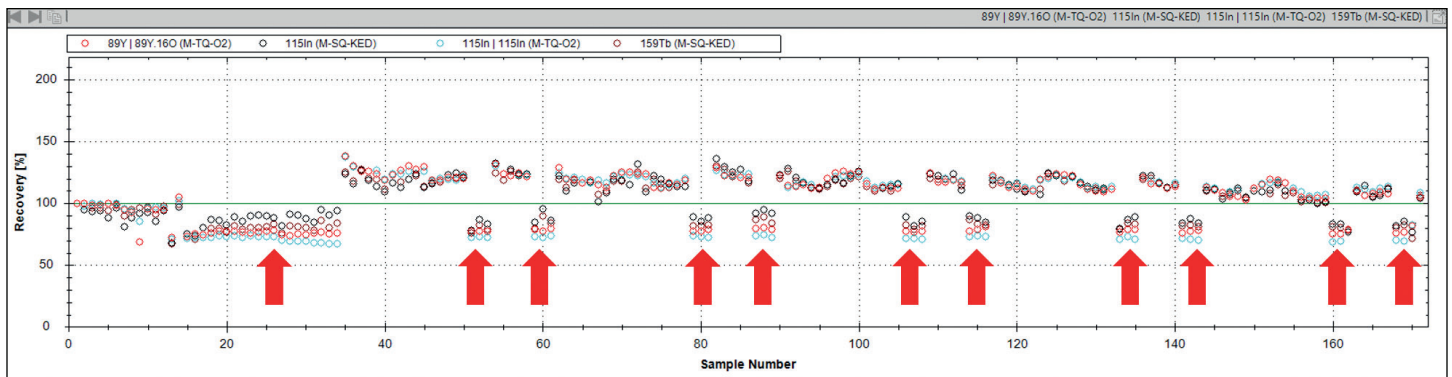
Table 7 shows the analysis procedure for this study. To simulate a high sample volume, a larger sample batch was scheduled for analysis containing all the water samples previously analyzed. The batch contained several blocks of unknown samples and required QC checks, as shown in Table 7. The total number of solutions analyzed was 171 samples (including 120 unknown samples), requiring a total analysis time of approximately 9 hours. The batch was repeated on 12 consecutive working days.

**Table 7. Analysis procedure for a total of 171 samples over 9 hours**

Batch component	Sample detail	Total number of samples
1	Standard calibration solution and ICV	14
2	Sea water and spiked sea water	20
3–8	5 samples each of lake water, river water, drinking water and 3 sea water samples	100
N/A	QC checks (CCB, CCV for different groups of elements)	37

The relative standard deviation of all CCVs ( $n = 5$  per batch) showed excellent recovery (within 92% to 104%) with a relative standard deviation of  $\pm 3.5\%$  within the batch. The response of the internal standards in one selected analysis is shown in Figure 2. All internal standards showed reliable and predictable recovery (within approximately 69% to 122%) over the entire runtime of the batch, demonstrating robust analytical performance. It is important to note that those samples causing a suppression of the internal standard were, in every case, undiluted sea water. Whereas an internal standard recovery of around 70% still allows for accurate correction of matrix effects and potential drift, it is far more important that the signal of the internal standard immediately and reliably returns to expected levels (approximately 110% in this example) when switching back to lower matrix samples (e.g., 2%  $\text{HNO}_3$  for QC checks or less saline water types). This ultimately demonstrates the system's ability to effectively analyze a variety of different sample types with vastly different TDS load in a single batch.

The analysis of samples such as undiluted sea water also has a significant impact on all components of the sample introduction system. While clogging of the cones through deposition of material is greatly reduced by using AGD other components of the system (i.e., the torch and injector) are still in direct contact with the sample. Prolonged analysis of such sample matrices is known to cause devitrification, which ultimately leads to more frequent replacement/exchange of the torch.



**Figure 2. Response of the internal standards in a batch covering about ~9 hours of uninterrupted analysis of 171 samples.** Samples with lower recovery (approx. 70%) correspond to undiluted sea water.

In this study, the iCAP TQe ICP-MS was equipped with the novel PLUS torch, a direct replacement of the standard quartz torch, with identical geometry, made from a high performance ceramic material. This material is frequently used for torches used in ICP-OES and has been proven in the field to last significantly longer when routinely analyzing challenging sample matrices. The use of the PLUS torch also provides a number of additional advantages for analysis using ICP-MS. Due to the opaque color of the material, the plasma temperature is slightly increased, which enables more effective decomposition of the sample matrix. In conjunction with sample dilution using AGD, greater robustness is achieved, which is reflected in improved long term stability of the internal standard signal, as illustrated in Figure 2.

Figure 3 shows an image of the PLUS torch and injector tip after repeating the aforementioned batch analysis over 12 consecutive days. As shown, the torch body and injector are both in perfect condition, with no visible deposition of material. The use of the PLUS torch for such analysis facilitates more consistent system performance with reduced maintenance intervals and less instrument down time, ultimately enabling higher productivity and reduced cost per sample.



**Figure 3. PLUS torch (left) and tip of the injector (right) after the repeated analysis of a mixed batch containing all sample types over 12 consecutive days**

#### References

1. Zhou, J. et al. Mine waste acidic potential and distribution of antimony and arsenic in waters of the Xikuangshan mine, China. *Applied Geochemistry*, **2017**, 77, 52-61.
2. Cabral Pinto, M. et al. Human Health Risk Assessment Due to Agricultural Activities and Crop Consumption in the Surroundings of an Industrial Area. *Exposure and Health*, **2020**, 12, 629-640.
3. Birka, M. et al. Tracing gadolinium-based contrast agents from surface water to drinking water by means of speciation analysis. *Journal of Chromatography A*, **2016**, 1440, 105-111.
4. Thermo Fisher Scientific. Product Spotlight 44485: Thermo Scientific iCAP Qnova Series ICP-MS PLUS Torch for Improved ICP-MS Analysis of Challenging Samples.
5. Thermo Fisher Scientific. Technical Note 43202: Analysis of High Matrix Samples using Argon Gas Dilution with the Thermo Scientific iCAP Q ICP-MS.
6. Thermo Fisher Scientific. Application Note 43250: Dramatically Improved Performance of Arsenic and Selenium Determination using the Thermo Scientific iCAP Q ICP-MS with Methane Addition.

#### Conclusions

The iCAP TQe ICP-MS, equipped with the PLUS torch and operated using AGD, was employed to analyze 30 elements in different environmental water samples, including sea water, without any upfront manual or automated dilution. A suite of major and toxic elements commonly analyzed in water were determined in these samples. The analytical method was rigorously tested for performance, and the results obtained clearly demonstrated the following analytical advantages:

- The iCAP TQe ICP-MS allowed the aspiration of all sample matrices without prior manual dilution and allowed excellent MDLs to be obtained, eliminating the need for labor-intensive manual sample dilution and accelerating the sample throughput.
- Excellent agreement with representative CRMs was achieved. Additionally, spike recovery tests revealed recoveries between 84 to 110%, in line with the expected values in most regulatory methods.
- The TQ-O<sub>2</sub> operating mode allowed for selective and precise determination of multiple elements, including Si, Ti, V, As, Se, Mo, and Cd, in all the samples analyzed.
- Excellent CCV recovery results (92 to 104%) and stable and consistent internal standard response were obtained across a sample batch containing 171 of samples, demonstrating the reliability of the approach.
- The novel PLUS torch allowed consistent analysis of a large number of samples, including high TDS samples such as sea water, over twelve days without any loss of performance or need for maintenance.
- In summary, the iCAP-TQe ICP-MS, operated in TQ-O<sub>2</sub> and SQ KED modes and equipped with the AGD option, represents a viable analytical configuration for analytical testing laboratories where a variety of environmental samples, in high numbers, are required to be analyzed for their elemental content and where instrument uptime and reliable, consistent analytical results are vital.

Find out more at [thermofisher.com/TQ-ICP-MS](https://thermofisher.com/TQ-ICP-MS)

**For Research Use Only. Not for use in diagnostic procedures.** © 2021 Thermo Fisher Scientific Inc. All rights reserved. SPEX is a trademark of CertiPrep. Teledyne CETAC is a trademark of Teledyne Cetac Technologies. All other trademarks are the property of Thermo Fisher Scientific and its subsidiaries. This information is presented as an example of the capabilities of Thermo Fisher Scientific products. It is not intended to encourage use of these products in any manners that might infringe the intellectual property rights of others. Specifications, terms and pricing are subject to change. Not all products are available in all countries. Please consult your local sales representatives for details. **AN44495-EN 0621C**

**ThermoFisher**  
SCIENTIFIC