Direct analysis of environmental samples using ICP-MS with argon gas dilution (AGD)

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Goal

To demonstrate the applicability of the Thermo Scientific™ iCAP™ RQ ICP-MS with Argon Gas Dilution (AGD) for performing direct, high-throughput analysis of relevant trace elements in complex environmental samples (sea water, waste water, or drinking water).

Introduction

Analyzing high matrix samples for their trace elements content is a known challenge in ICP-MS. The complexity of the sample matrix can significantly affect system sensitivity, cause intense fluctuation of the internal standard signals, and lead to increased system maintenance with unwanted downtime due to clogging the orifice of the interface cones or tip of the nebulizers.

A typical environmental sample that is often analyzed for trace elements content is sea water (with average salinity of 3.5%), which contains high amounts of Na, K, Ca, Mg, S, and Cl. In order to analyze such complex samples, dilution has to be performed, either using liquid dilution or, alternatively, using an inert gas such as argon. However, reducing the impact of the matrix by sample dilution is not the only challenge for this analysis. In addition, the different composing elements in the matrix can cause significant interferences (mostly polyatomic in nature), leading to potentially false positive results. A comprehensive list of interferences and key contaminants is shown in Table 1. As the concentration of most common contaminants in sea water is at trace or even ultratrace level (below 10 µg·L^{-1}), a high sensitivity ICP-MS system with powerful and effective interference removal capabilities is required in order to obtain accurate results.

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In this application note, the analytical performance of the iCAP RQ ICP-MS for the analysis of complex environmental samples was assessed. In order to effectively reduce the impact of the sample matrix and thus facilitate the direct analysis of all samples without any prior manual or automated liquid dilution, the iCAP RQ ICP-MS was operated using argon gas dilution (AGD). The occurring spectral interferences were eliminated using kinetic energy discrimination (KED) with pure helium as collision gas.

Table 1. Typical target isotopes with commonly observed interferences in complex samples such as sea water

Isotope	Matrix-based interferences example
^{51}V	$^{35}Cl^{16}O$
^{52}Cr	$^{35}Cl^{16}O^1H^+$, $^{37}Cl^{16}O^+$, $^{34}S^{18}O^+$
^{55}Mn	$^{32}S^{23}Na^+$
^{56}Fe	$^{23}Na^{33}S^+$, $^{40}Ar^{16}O^+$, $^{40}Ca^{16}O^+$
^{63}Cu	$^{40}Ar^{23}Na^+$
^{64}Zn	$^{40}Ar^{24}Mg^+$
^{75}As	$^{40}Ar^{35}Cl^+$, $^{40}Ca^{35}Cl^+$
^{78}Se	$^{40}Ar^{37}Cl^1H^+$, $^{40}Ca^{37}Cl^1H^+$

Experimental

Instrumentation

An iCAP RQ ICP-MS fitted with the AGD option was used for all analyses (see Figure 1). As part of this kit, a *pergo* argon humidifier (Elemental Scientific, Omaha, NE, USA) is used to humidify an additional flow of argon added into the sample aerosol before it enters the plasma. The humidifier employs a special tubing that has the ability to permeate water vapor through its membrane, humidifying the argon gas used for dilution of the sample.
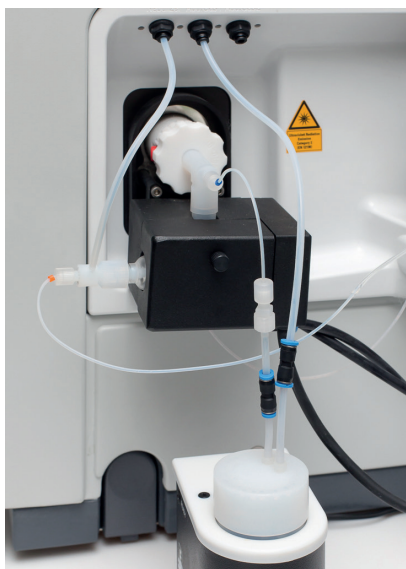

Figure 1. Argon gas dilution, AGD, on the iCAP RQ ICP-MS

The sample introduction system consisted of a Peltier cooled (at 2.7 °C), baffled cyclonic spraychamber, borosilicate nebulizer, and quartz torch with a 2.5 mm i.d. removable quartz injector. The instrument was operated using KED with pure He as the collision gas in the collision/reaction cell (CRC) and hot plasma mode (standard operation mode, STD). The measurement mode switching time between KED and STD was less than 10 seconds. To automate the sampling process, a Teledyne CETAC ASX-560 autosampler (Omaha, NE, USA) was used. Table 2 summarizes the instrument configuration and analytical parameters. Measurement modes were optimized using the default autotune procedures available through the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software.

Table 2. Instrument configuration and operating parameters

Parameter	Value
Nebulizer	Borosilicate glass micromist 400 µL·min^{-1}, pumped at 20 rpm
Spraychamber	Quartz cyclonic, cooled at 2.7 °C
Injector	2.5 mm i.d., quartz
Interface	Nickel sampler and nickel skimmer cone with high matrix insert
Plasma power	1550 W
Nebulizer gas	0.25 L·min^{-1}
Additional gas flow (Ar)	0.65 L·min^{-1}
CRC gas	He, 4.8 mL·min^{-1}
KED	3 V
Analysis time per sample	Total 2 min 10 s: uptake 45 s + wash out 30 s + acquisition time 55 s

Sample preparation

Precleaned polypropylene bottles were used for the preparation of all blanks, standards, and samples. The bottles were rinsed with ultrapure water (18.2 MΩ·cm) and left to dry in a laminar flow clean hood before use.

To test the system performance with relevant sample matrices, certified reference material samples (CASS-5 Nearshore sea water, National Research Council of Canada (NRC-CNRC)) as well as drinking water samples collected from a local Thermo Fisher Scientific facility (Bremen, Germany) were filled in the sample bottles without any sample preparation. Similarly, blanks, calibration standards, and quality control (QC) were prepared using the same procedure, replacing the certified reference material with single element standards (SPEX CertiPrep, Metuchen, NJ, USA). The details of the measurement modes, acquisition parameters, and internal standards used for each element are shown in Table 3.

An internal standard solution, containing 100 µg·L^{-1} Co, Rh, In, Ir, and Bi in 2% v/v HNO_3 and 5% v/v isopropanol (IPA), was added to all samples via a T-piece (mixing rate between internal standard and samples 2:1) used for online dilution before entering the spray chamber. The addition of carbon to the plasma significantly improves the results obtained for elements with higher 1st ionization potential, such as arsenic or selenium, as has been reported previously[1,2].

The use of AGD has been shown to allow the successful analysis of samples containing sea water without any liquid dilution prior to analysis[3]. In order to perform basic validation of the proposed method, both sample matrices were spiked with a known amount of all analytes and analyzed repeatedly in order to determine accuracy and precision. A continuing calibration verification test (CCV) was periodically conducted throughout the entire analysis sequence. The concentrations for CCV and spike recovery tests are summarized in Table 4.

Table 3. Measurement modes (STD or KED) and internal standards used for each element with corresponding target isotopes and dwell times

	Measurement mode	Isotope (m/z)	Dwell time (s)	Internal standard
Be	STD	9	0.1	[59]Co
Al	STD	27	0.1	[59]Co
V	KED	51	0.1	[59]Co
Cr	KED	52	0.1	[59]Co
Mn	KED	55	0.1	[59]Co
Fe	KED	56	0.1	[115]In
Ni	KED	60	0.1	[115]In
Cu	KED	65	0.1	[115]In
Zn	KED	66	0.1	[115]In
As	KED	75	0.2	[115]In
Se	KED	78	0.3	[115]In
Cd	STD	111	0.1	[115]In
Sb	STD	121	0.1	[115]In
Pb	STD	208	0.1	[209]Bi

Table 4. Concentrations of all QC tests (CCV and spike recovery)

		Be	Al	V	Cr	Mn	Fe	Ni	Cu	Zn	As	Se	Cd	Sb	Pb
QC	CCV [µg·L^{-1}]	5	5	-	5	5	5	2.5	2.5	6	5	1	2	2	1
Spike concentration	Sea water [µg·L^{-1}]	5	5	-	5	5	5	2.5	2.5	6	5	1	2	2	1
	Drinking water [µg·L^{-1}]	5	20	-	2.5	5	20	2	20	10	1	1	0.5	1	0.5

Software

Instrument control (tuning, calibration, etc.) as well as data acquisition, processing and reporting was carried out using the Qtegra ISDS Software. Qtegra ISDS Software provides a wide range of features, including a comprehensive feature set for quality control testing, and enables both new and experienced users to leverage the full potential of the instrument. The data is stored in LabBooks, offering a complete record and full traceability of all data sets created over time. Qtegra ISDS Software is a cross platform software and allows easy switching between different users and the use of different evaluation methods and hardware configurations.

Results and discussion

Method development

The use of AGD will ultimately lead to a lower detection sensitivity as compared to standard operation conditions of the system. However, as manual liquid dilution before analysis is obsolete, method detection limits (MDL) often turn out to be not affected.

Initial experiments focused on testing the linearity of target elements and assessment of the detection power of the method. As an example, calibration curves for iron, arsenic and lead were obtained by running the respective standard solutions over a range of 0.5–10 µg·L^{-1} and the results of these experiments are shown in Figures 2, 3, and 4, respectively. As demonstrated, all calibration curves showed excellent linearity with R^2 values better than 0.999. The attainable detection limits were found to be comparable to the theoretical method detection limits resulting in a 10-fold manual dilution of each sample prior to analysis. Table 5 shows the resulting detection limits (LOD) and Background Equivalent Concentration (BEC). As can be seen, excellent LODs are achievable for a range of analytes measured by this method despite the impact on sensitivity caused by using AGD. LODs were calculated as 3x standard deviation of the calibration blank.
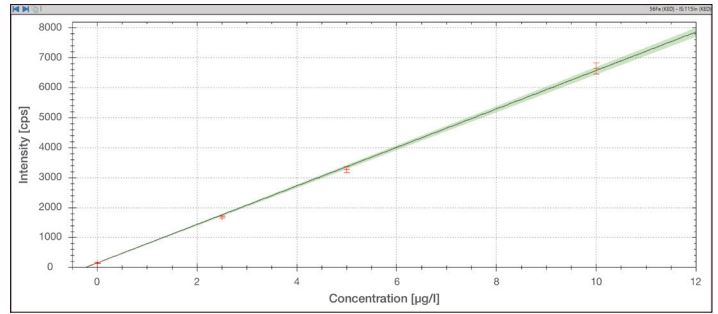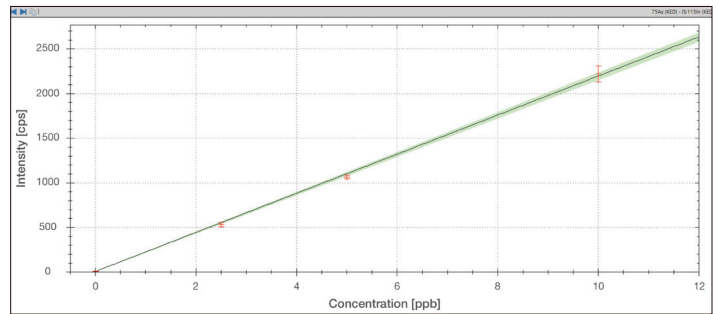

Figure 2. Calibration curve for ^{56}Fe in He KED mode
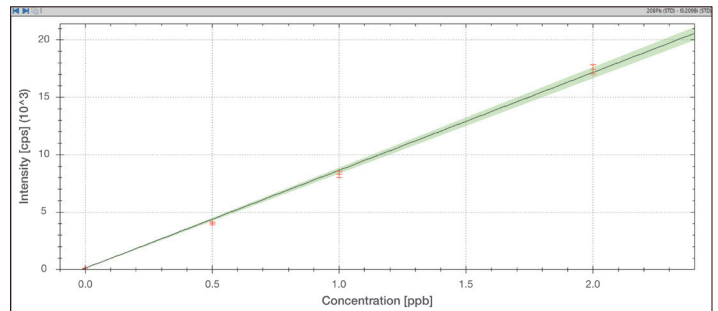

Figure 3. Calibration curve for ^{75}As in He KED mode

Figure 4. Calibration curve for ^{208}Pb in STD mode

Table 5. Results for the CASS-5 sea water and drinking water samples. Analytes concentration are reported as µg·L⁻¹.

	LOD	BEC	CASS-5 sea water reference		Spiked recovery (%)	
			Measured (n=24)	Reported value	Sea water (n=24)	Drinking water (n=24)
Be	0.004	0.001	0.004 ± 0.003	-	98%	102%
Al	0.233	2.800	2.12 ± 0.42	-	115%	97%
V	0.034	0.044	1.50 ± 0.24	1.32 ± 0.14	-	-
Cr	0.055	0.211	0.145 ± 0.072	0.106 ± 0.013	106%	96%
Mn	0.022	0.011	2.72 ± 0.15	2.62 ± 0.20	102%	94%
Fe	0.072	0.240	1.67 ± 0.12	1.44 ± 0.11	107%	98%
Ni	0.054	0.112	0.315 ± 0.03	0.33 ± 0.023	102%	94%
Cu	0.061	0.163	0.381 ± 0.04	0.38 ± 0.028	100%	97%
Zn	0.023	0.033	0.624 ± 0.04	0.719 ± 0.068	105%	97%
As	0.025	0.032	1.62 ± 0.12	1.24 ± 0.09	106%	94%
Se	0.143	0.084	<LOD	-	103%	91%
Cd	0.006	0.002	0.020 ± 0.01	0.0215 ± 0.0018	93%	99%
Sb	0.009	0.008	0.46 ± 0.03	-	98%	98%
Pb	0.007	0.013	0.011 ± 0.002	0.011 ± 0.002	101%	105%

Method validation

As part of this study, the CASS-5 sea water reference material was repeatedly analyzed. In total, 24 independent measurements of separate aliquots of sea water reference material were analyzed in order to assess the repeatability of the method. The results of this test show that the calculated concentrations of the target elements matched closely the respective reported values in the CRM. In addition, both sample matrices under test in this study were spiked with all analytes at relevant concentrations and tested for quantitative recovery.

Recovery values of target elements were calculated from both the CRM sea water sample and the drinking water samples. All results are summarized in Table 5. The recovery results for both samples were between 91% and 115%, indicating excellent method performance.

To simulate a typical routine sample analysis, >150 samples were analyzed in ~6 h. For routine sample analysis, assessing the stability of response is critical and as a consequence, quality control samples were interposed. This feature is enabled in Qtegra ISDS Software as CCVs, which were performed periodically throughout the analytical run.

Using Qtegra ISDS Software, the assessment of both CCVs and spiked sea water samples, intermittently analyzed throughout the analytical run, indicated that good agreement to the expected levels was obtained and demonstrated the suitability of the method for routine use. Figure 5 shows the average (n=8) concentration of the CCV standard and the relative error for selected trace level analytes.
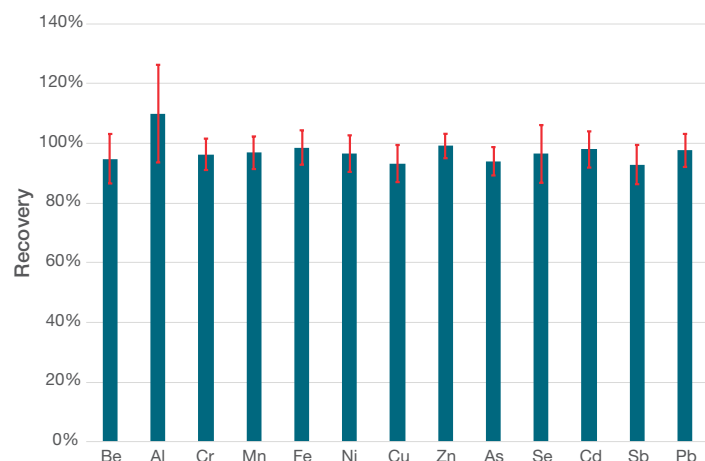

Figure 5. QC continuing calibration verification results. Error bars indicate standard deviation calculated from n=8 repeat measurements.

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Conclusion

The experiment performed demonstrates that the iCAP RQ ICP-MS system equipped with AGD and operated in STD and KED modes enables routine analysis of ultratrace multi-elements in complex samples such as sea water.

- Moreover, using this analytical setup the instrument downtime is minimized and the polyatomic interferences from the matrix components are eliminated.

- The total run time/sample of just 2 min 10 s allows for fully quantitative measurement of 14 elements, including sample uptake and washout, enabling a significant boost in laboratory throughput.

- Ultimately, by using the He KED and STD acquisition modes, comprehensive, ultratrace multi-element analysis, including beryllium, is achieved without sacrificing sensitivity or robustness of the system, making this analytical setup a viable option for environmental sample analysis.

References

1. Larsen et al., J. Anal. At. Spectrom., 1994, 9, 1099-1105.
2. Application Note 43250: Dramatically Improved Performance of Arsenic and Selenium Determination using the Thermo Scientific iCAP Q ICP-MS with Methane Addition.
3. Technical Note 43202: Analysis of High Matrix Samples using Argon Gas Dilution with the Thermo Scientific iCAP Q ICP-MS.

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