ThermoFisher
SCIENTIFIC

Environmental

Comprehensive analysis of water samples in alignment with EN ISO Method 17294 using ICP-MS

Authors

Sukanya Sengupta[1], Adrián Vicent Claramunt[2], Rasheed Ishola[2], Daniel Kutscher[1]

[1]Thermo Fisher Scientific, Bremen, Germany

[2]Thermo Fisher Scientific, Vilnius, Lithuania

Keywords

ICP-MS, iCAP MSX ICP-MS, ISO Method 17294-2, robustness, matrix tolerance, Argon Gas Dilution, quality control, regulatory compliance

Goal

To demonstrate the performance of the Thermo Scientific™ iCAP™ MSX ICP-MS for the analysis of a variety of water samples including surface waters, groundwaters and drinking waters

Introduction

The monitoring of drinking and surface water for the content of different elements, in particular highly toxic heavy metals such as arsenic, cadmium, mercury, and lead, is crucial for human and environmental health and safety. In Europe, the ISO 17294-1:2004 method[1] is applicable for testing and assuring water quality. The method specifies the use of inductively coupled plasma mass spectrometry (ICP-MS) for the measurement of trace elements in different water types and provides guidelines for the analytical method. ICP-MS is a powerful technique for the analysis of a wide range of analytes in given samples, providing superior sensitivity that enables the reliable detection of very low concentrations of analytes in water samples. However, potential variability of the sample matrices is an important aspect to consider. While drinking water is significantly cleaner than other water samples, like river or well water, may vary in their matrix composition (i.e., major elements or other substance classes), leading to both physical and spectral interferences. Analytical testing laboratories often perform the testing of water samples on behalf of water providers, companies, and government authorities, and therefore need to provide accurate and reliable results for many different sample types. To cope with a high sample load, ideally a single method can be used across different kinds of

thermo scientific

samples, irrespective of their nature. This requires a sensitive and highly robust ICP-MS system that is able to tolerate variable matrix loads.

This application note describes the analysis of different water samples using the Thermo Scientific™ iCAP™ MSX ICP-MS operated with Argon Gas Dilution (AGD) as a tool to facilitate sample dilution directly during sample introduction. AGD offers a comprehensive solution for effective handling of a variety of sample types including those with high Total Dissolved Solids (TDS) in one analytical run. Different water samples are analyzed following ISO 17294-1:2004, and reliable performance is demonstrated over four weeks of analysis, allowing the analysis of more than 5,000 unknown samples. This application note demonstrates how the use of AGD helps avoid off-line liquid sample dilution, which in turn saves associated labor and costs, and minimizes the risk of contamination, while still delivering consistent results with minimum matrix effects.

Experimental

Instrument parameters

In this application note an iCAP MSX ICP-MS was operated in conjunction with a Thermo Scientific™ iSC-65 Autosampler for the accurate and reliable analysis of drinking and surface water samples. The standard configuration of the sample introduction system was used, and typical instrument parameters (including AGD settings) are listed in Table 1. The use of argon gas, provided directly from the instrument itself, is an attractive way to dilute the sample online at no additional cost. Water samples (previously acidified) can be placed onto the autosampler as received and analyzed directly, with the dilution carried out inside the instrument. To overcome interferences, the instrument was operated using the QCell collision/reaction cell (CRC) with helium in kinetic energy discrimination (KED) mode for all analytes. The use of KED, in conjunction with the automatically applied low mass cut off offered through the unique design of the QCell CRC facilitates the complete removal of polyatomic interferences while maintaining high sensitivity for critical elements without the need to switch measurement modes during a run.

The iSC-65 Autosampler, specifically designed to meet the needs of analytical testing laboratories, features innovative solutions to facilitate the highest reliability, efficiency, and robustness for effective use in the laboratory and seamless delivery of hundreds of samples daily.

The Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software was used to control the full laboratory setup, to generate, process, and report analytical data. The integrated functions for quality control checks, internal standards response check, etc. provide the ability to quickly assess data quality and report correct data.

Table 1. Instrument configuration and typical operating parameters

Parameter	Value
Nebulizer	iCAP MX Series nebulizer
Interface cones	Ni-tipped sample and skimmer
Spray chamber	Cyclonic quartz
Spray chamber temp. (°C)	2.7
Injector	Quartz, 2.5 mm i.d.
Torch	Quartz torch
Auxiliary flow (L·min^{-1})	0.8
Cool gas flow (L·min^{-1})	14
Nebulizer flow (L·min^{-1})	0.447
CRC gas	Pure helium, 4.6 mL·min^{-1}
KED	3 V
AGD setting	AGD Level 5
RF power (W)	1,550
Sampling depth (mm)	8
Number of replicates	3
Dwell time per isotope (s)	0.05

Sample preparation

To cover a wide variety of typical sample matrices, a total of 19 different water samples, collected locally, were analyzed in this study. An overview of all the samples is shown in Table 2. The samples belonged to six different categories— tap, bottled mineral, well, lake, and river water, and snow. The samples were filtered using 0.45 µm pore size membrane filters followed by acidification to approximately 2% HNO_3 and 0.5% HCl concentrations. In addition, fresh snow was collected and prepared in the same way for analysis.

Table 2. List of water samples analyzed in this study with approximation of the TDS range as the sum of Na, Mg, K, and Ca

Category	Samples	Approx. TDS [mg·L^{-1}]
Tap water	Tap waters from 11 different locations around Lithuania	4–300
Bottled mineral water	Two different commercially available bottled drinking water samples fortified with minerals	40–90
Well water	Well water collected from 2 different locations in Lithuania	90–150
River water	River water collected from 2 rivers in Lithuania	50–100
Lake water	Lake water collected from a lake close to Vilnius	10–20
Snow	Clean snow collected after strong snowfall in the Vilnius area	<5

Standards

Multi-element stock standards were prepared from single element standards of each target analyte (1,000 mg·L^{-1}, SPEX™ CertiPrep, Metuchen, NJ, USA) which were then diluted gravimetrically using 2% (v/v) HNO_3 and 0.5% HCl as a diluent to result in the concentrations specified in Table 3. Calibration curves were generated for the analytes using six calibration standards and a calibration blank. The calibration standard 4 was used as a quality control (QC) standard throughout the experiments.

Two certified reference materials (CRM) LGC-6026 Hard drinking water – metals and SLRS-6 River water were included in the study to verify the accuracy of the analyses. Using these two reference materials in combination with each other, the accuracy of the method could be demonstrated for 24 elements.

An internal standard solution containing 20 µg·L^{-1} of Sc, Ge, Rh, In, Ir, and Tl was added on-line continuously during the analysis. All solutions used for analysis consisted of 2% (v/v) HNO_3 in ultrapure water containing 100 µg·L^{-1} gold as a stabilizer for mercury.

Experimental design

The instrument was operated over a period of four weeks for water analysis on every working day. Dedicated autotunes, suitable for different operation modes and dilution levels, are provided within the Qtegra ISDS Software of the iCAP MSX ICP-MS and were used to automatically tune the instrument at the beginning of the study. On each day of operation, the ignition of the plasma, an automatic warm-up of 15 minutes, and system suitability check (by means of a Performance Report) were carried out using the Get Ready feature inside the Qtegra ISDS Software. The Get Ready process can also be scheduled for automatic execution on a specific day/time so that the instrument is ready for analysis while the operator can complete other tasks (i.e., related to sample preparation). The system performance was checked in high matrix mode, with and without the use of AGD, to ensure the required signal intensity and required stability.

At the same time, other important plasma parameters, such as oxide ratio (^{140}Ce.^{16}O$^+$/^{140}Ce$^+$) and the formation of doubly charged ions (^{137}Ba^{++}/^{137}Ba$^+$) were checked. Please note that in general, a single Performance Report would suffice to prove the system's suitability for analysis.

Each day, a LabBook was set up and run for uninterrupted sequences of >10–12 hours. A wide selection of elements covering the range from ^{7}Li to ^{238}U were analyzed in every sample, calibration standards, and CRMs. A typical daily sequence consisted of a calibration block at the very beginning of the LabBooks, comprising calibration blank and standards, followed by an initial calibration verification (ICV) quality control (QC) check using the Std 4 as a QC standard. Following the initial calibration and calibration check, a block of 15 unknown water samples were analyzed followed by another QC check setup as a continuous calibration verification (CCV). The block of unknown samples followed by a QC were repeated throughout the LabBook. CRM samples were measured at least thrice in each LabBook, and along with the regular quality control checks, this ensured high data quality over the entire duration of the analysis.

Results and discussion
Linearity and detection limits

The linearity of the instrument was demonstrated using a six-point calibration curve with different concentrations of the elements as listed in Table 3. All calibration curves from trace elements to major elements were established in the same run. All the target elements showed excellent correlation coefficients (>0.999 or higher).

Excellent limits of detection (LOD) were obtained across the entire mass range for the different elements, as listed in Table 4. The LODs were established by measuring a reagent blank solution, which was prepared in parallel to the samples. This solution was analyzed 10 times, with the resulting instrumental detection limits being calculated by Qtegra ISDS Software automatically using the 3σ criterion.

Table 3. List of target analytes and their concentrations in calibration standards

Element	Concentrations in mg·L^{-1}				
	Std 1	Std 2	Std 3	Std 4	Std 5
Ca	1	10	50	100	500
Na, Mg, K, P	0.2	2	10	20	100
Element	**Concentrations in µg·L^{-1}**				
Ba, Sr, B	2	20	100	200	1,000
B, Fe, Zn, Mo	0.4	4	20	40	200
Li, Be, Al, Ti, V, Cr, Mn, Ni, Co, Cu, As, Se, Rb, Zr, Ru, Pd, Ag, Cd, Sn, Sb, Te, Cs, W, Re, Pt, Pb, Bi, Th, U	0.2	2	10	20	100
La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hg	0.02	0.2	1	2	10

Table 4. List of analytes and the respective limits of detection (LOD) obtained for each

Analyte	LODs (µg·L⁻¹)	Analyte	LODs (µg·L⁻¹)
^{7}Li	0.13	^{111}Cd	0.004
^{9}Be	0.22	^{118}Sn	0.001
^{11}B	1.04	^{121}Sb	0.003
^{23}Na	0.38	^{125}Te	0.060
^{24}Mg	0.37	^{133}Cs	0.001
^{27}Al	1.0	^{137}Ba	0.008
^{31}P	11.6	^{139}La	0.002
^{39}K	5.7	^{140}Ce	0.001
^{44}Ca	3.0	^{141}Pr	0.001
^{47}Ti	0.15	^{146}Nd	0.0003
^{51}V	0.005	^{147}Sm	0.001
^{52}Cr	0.005	^{153}Eu	0.0002
^{55}Mn	0.060	^{157}Gd	0.0008
^{56}Fe	0.043	^{159}Tb	0.0007
^{59}Co	0.001	^{163}Dy	<0.00001
^{60}Ni	0.013	^{165}Ho	0.0007
^{63}Cu	0.02	^{166}Er	<0.00001
^{66}Zn	0.005	^{169}Tm	0.0003
^{71}Ga	0.008	^{172}Yb	0.003
^{75}As	0.04	^{175}Lu	0.001
^{78}Se	0.45	^{182}W	0.018
^{85}Rb	0.003	^{185}Re	0.001
^{88}Sr	0.015	^{195}Pt	0.004
^{90}Zr	0.006	^{202}Hg	0.0002
^{95}Mo	0.004	^{207}Pb	0.003
^{101}Ru	0.001	^{209}Bi	0.003
^{105}Pd	0.002	^{232}Th	0.002
^{107}Ag	0.004	^{238}U	0.004

Accuracy

The accuracy of the analysis was demonstrated by analyzing two CRM samples several times within the analytical sequence. The percent accuracy of each analyte was calculated based on the concentration data obtained during the analysis and the certified values given for each analyte in the CRM certificates. The concentrations for Al, B, Cu, and Zn in LGC-6026 were outside of the calibrated range for this study and are therefore not reported. Very good recoveries within the 80–120% range were obtained for the remaining elements in both CRMs. Table 5 summarizes the list of analytes, their certified concentration values, and calculated percent accuracy. The percent accuracy values given are the average calculated from 40 different measurements of each of the two CRMs over the four weeks of analysis.

Long term stability

Different drinking and surface water samples were analyzed daily over a period of four weeks as a part of a sequence as described previously. During analysis, analytical testing laboratories specifically monitor the response of the internal standards (in addition to the mandatory QC checks), which needs to fall within the range of 80–120% of the initial calibration blank. Samples that show suppression or enhancement of the internal standard response would normally be diluted and re-analyzed, meaning a significant additional effort before a result can be reported. Excellent stability was observed, with minimal matrix suppression from different kinds of surface water samples, ranging from snow and clean drinking water to river water containing higher TDS. The observed TDS range was between 35 mg·kg⁻¹ and 300 mg·kg⁻¹, and using an automatic 5 times dilution with AGD enabled analysis of these different matrices within a single method. The validity of the calibration block was monitored throughout the measurement sequence by running periodic QC checks every 15 unknown samples and the recoveries were well within 80–120% for all analytes, thus proving that the data obtained over time was consistently accurate and reliable.

Based on the results of the internal standard response, QC checks, and CRM recoveries within the LabBooks, it can be concluded that the system performed reliably and accurately over time. An example of the behavior of the internal standards, as displayed within the Qtegra ISDS Software, is shown in Figure 1.

Analytical testing laboratories rely on robust and reliable operation of the instrumentation used for the analysis, as this is key to ensure productivity and maintain profitability. Consistent performance day after day is especially important, as unplanned downtime for maintenance or failure of the quality control checks leads to delays and increased workload on lab personnel to make up for the gap. The Thermo Scientific™ HAWK Consumables and Maintenance Assistant (CMA) provided as part of Qtegra ISDS Software comes with a series of alerts to schedule maintenance actions for key components of the sample introduction system. An additional component of Qtegra ISDS Software is the Instrument Performance Monitoring tool within the Dashboard, that allows the easy visualization of the instrument performance over time.

To ensure consistent operation throughout the entire period of this study, system maintenance was performed based solely on the recommendations of the HAWK Consumables and Maintenance Assistant. A visual inspection of the sample cone, carried out occasionally, indicated no cone degradation or blockage throughout the entire duration of this long-term study.

Table 5. Certified quantity values and measured values for two CRM samples

| Element	CRM SLRS-6 River water n=40		CRM LGC-6026 Hard drinking water – metals n=40	
	Mass fraction (µg/kg)	Recovery (%)	Mass fraction (µg/kg)	Recovery (%)
Al	33.9 ± 2.2	108.3 ± 5	199.9 ± 6.1	Outside calibration range
Sb	0.3372 ± 0.0058	103.8 ± 4	4.99 ± 0.17	105.0 ± 3
As	0.57 ± 0.08	109.6 ± 9	10.00 ± 0.31	109.2 ± 2
Ba	14.3 ± 0.48	100.5 ± 4	116.1 ± 3.5	104.8 ± 3
Be			5.08 ± 0.26	101.6 ± 9
Cd			4.98 ± 0.15	112.0 ± 3
Cr	0.252 ± 0.012	118.9 ± 3	50.0 ± 1.9	118.3 ± 3
Co	0.053 ± 0.012	113.5 ± 3	4.88 ± 0.17	116.2 ± 3
Cu	24.0 ± 1.8	108.8 ± 3	2017 ± 56	Outside calibration range
Fe	84.5 ± 3.6	87.7 ± 2	198.4 ± 5.5	91.4 ± 3
Pb	0.170 ± 0.026	89.1 ± 3	9.98* ± 0.14	90.6 ± 5
Li			11.24 ± 0.58	112.5 ± 5
Mn	2.12 ± 0.10	113.8 ± 4	48.4 ± 1.5	119.0 ± 2
Mo	0.215 ± 0.018	83.8 ± 6	4.77 ± 0.25	98.7 ± 6
Ni	0.617 ± 0.022	89.1 ± 6	19.00 ± 0.72	90.6 ± 3
Se			10.19 ± 0.59	86.6 ± 3
Sr	40.72 ± 0.32	100.0 ± 3	491 ± 20	107.5 ± 5
U	0.0699 ± 0.0034	88.3 ± 5	4.95 ± 0.40	95.8 ± 3
V	0.352 ± 0.006	88.5 ± 3	4.96 ± 0.15	111.1 ± 3
Zn	1.76 ± 0.12	108.3 ± 5	621 ± 19	Outside calibration range
Element	Mass fraction (µg/g)	Recovery (%)	Mass fraction (µg/g)	Recovery (%)
Ca	8.770 ± 0.200	106.9 ± 3	77.1 ± 2.2	116.8 ± 1
Mg	2.137 ± 0.058	106.0 ± 3	18.50 ± 0.76	116.7 ± 2
K	0.652 ± 0.054	90.9 ± 2	5.30 ± 0.15	102.9 ± 2
Na	2.770 ± 0.220	93.4 ± 3	24.60 ± 0.79	113.4 ± 2
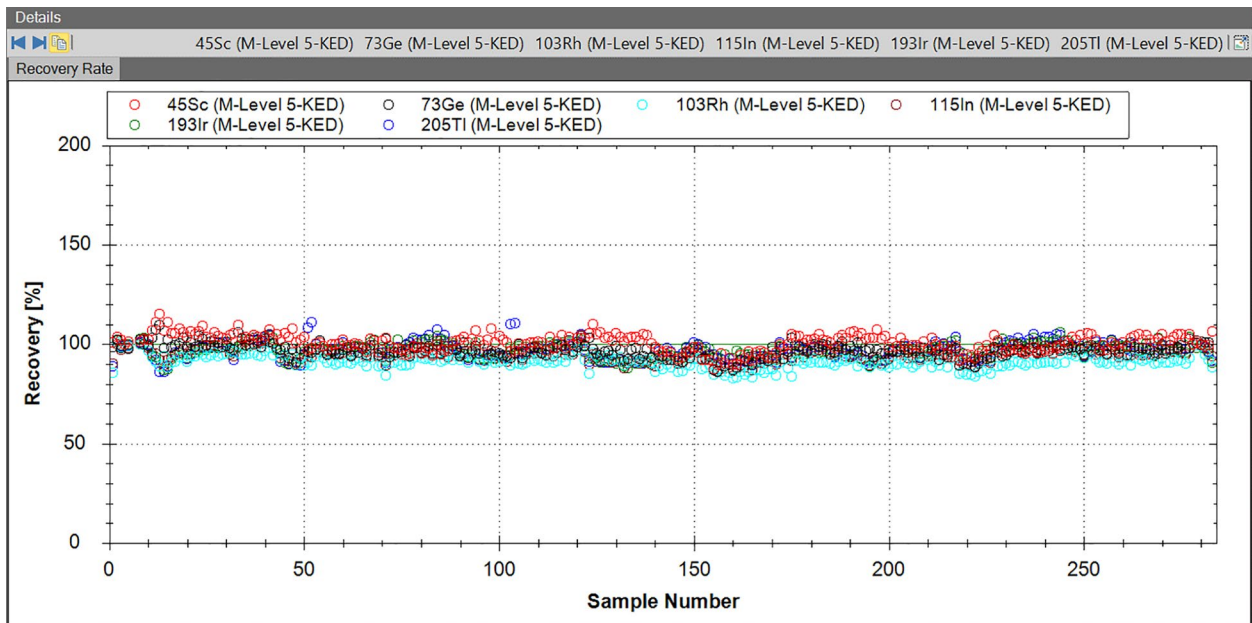
Figure 1. Representative internal standard recovery plot from a LabBook showing stable recoveries over 12 hours

The same was also confirmed by the successful daily Performance Reports. As a preventative measure only, the cones were cleaned once at the end of three weeks, but no maintenance requirement was indicated by change in sensitivity or stability of the analyte signals. Over the period of four weeks of analysis, including >5,000 different surface water samples and QC standards, the matrix load encountered by the instrument daily did not result in any significant sensitivity drop or fluctuation.

Elemental concentrations in water samples

The concentration ranges observed in the analysis of all samples are displayed in Table 6. To summarize the amount of data, only the lowest and highest concentrations measured for each of the sample types investigated are displayed here. However, beyond the variation in hardness, it becomes obvious that some elements can be present in vastly different concentrations within a group of similar samples. One example is Fe in tap water, which was found to be non-detectable in some tap water samples; whereas in others, it was found in concentrations of more than 50 µg·L^{-1}. Similar findings were obtained for Zn, which was found in concentrations between around 2 µg·L^{-1} and up to more than 300 µg·L^{-1} across multiple sample types. This again highlights that for comprehensive analysis of different water types, an instrument must be capable of handling wide concentration ranges appropriately.

Table 6. Ranges of elements and REEs in the different sample groups. Numbers shown in blue are in mg·L^{-1}, all others in µg·L^{-1}.

	Tap water		Lake water		Snow		Bottled mineral water		Well water		River water	
	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max
Li	0.45	6.13	<DL	0.19	<DL	0.80	1.60	2.23	1.50	2.17	0.83	2.37
Be	<DL	1.41	<DL	0.24	<DL	0.32	<DL	<DL	<DL	0.31	<DL	<DL
Na	1.83	178.6	0.15	0.3	1.35	2.2	1.80	5.3	4.00	6.1	3.51	3.7
Mg	0.44	22.2	0.19	0.3	1.58	2.3	5.46	17.6	18.23	22.3	8.39	15.6
Al	<DL	14.11	<DL	4.48	73.34	124.76	<DL	7.23	<DL	9.15	1.13	27.30
K	0.50	6.2	0.23	0.3	0.57	0.6	0.44	1.7	0.49	6.6	1.96	5.7
Ca	1.80	90.0	2.71	3.3	13.20	18.0	35.69	64.8	72.28	101.9	43.20	67.2
Ti	0.33	14.70	0.45	0.54	2.51	3.03	5.85	11.74	13.19	18.95	7.11	12.37
V	0.01	1.21	0.02	0.06	0.15	0.18	0.03	0.08	0.08	1.24	0.18	1.03
Cr	<DL	0.55	0.09	0.12	0.29	0.37	<DL	0.27	0.12	0.55	0.17	0.46
Mn	<DL	70.16	<DL	<DL	1.38	1.66	<DL	0.01	<DL	<DL	<DL	0.11
Fe	<DL	58.52	<DL	1.58	80.42	102.93	<DL	0.73	1.03	5.36	0.29	108.08
Co	<DL	1.44	<DL	0.01	0.18	0.21	<DL	0.02	0.05	0.51	0.06	0.41
Ni	0.04	3.21	0.02	0.04	0.38	0.47	0.03	0.03	0.28	3.42	0.53	2.44
Cu	0.04	100.3	0.19	0.31	4.28	5.18	0.03	0.04	1.46	118.07	1.38	93.82
Zn	1.90	200.3	2.79	3.80	16.43	22.02	1.96	2.21	25.70	415.42	2.36	312.72
As	<DL	0.93	<DL	0.10	0.08	0.12	0.07	0.29	0.07	0.99	0.43	0.70
Se	<DL	1.09	<DL	<DL	<DL	<DL	<DL	1.45	<DL	1.00	<DL	<DL
Sr	4.66	273.28	2.95	3.59	13.56	16.44	44.92	131.86	126.77	173.80	53.53	135.63
Mo	0.20	1.11	<DL	0.06	<DL	0.06	0.27	0.32	0.10	1.18	0.22	1.00
Pd	<DL	0.03	<DL	0.01	<DL	<DL	<DL	<DL	<DL	<DL	<DL	0.01
Ag	<DL	0.11	<DL	0.05	<DL	0.03	<DL	22.13	<DL	<DL	<DL	<DL
Sb	<DL	0.21	<DL	0.02	0.02	0.03	0.07	0.18	0.02	0.23	0.04	0.19
Ba	0.94	131.31	1.40	1.51	3.33	4.87	12.50	63.03	23.65	29.95	25.69	29.76
Pt	<DL	0.014	<DL	0.011	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Th	0.010	1.054	<DL	0.361	0.010	0.300	0.009	0.018	0.010	0.030	<DL	0.005
Cd	<DL	0.066	<DL	0.008	0.025	0.045	<DL	<DL	<DL	0.019	<DL	0.032
Sn	<DL	0.159	<DL	0.059	0.016	0.019	<DL	0.009	<DL	0.019	<DL	0.007
ΣREE	<DL	0.028	0.009	0.019	0.707	0.846	0.001	0.002	0.011	0.026	0.016	0.107
Hg	<DL	0.087	<DL	0.015	0.001	0.040	0.001	0.006	0.001	0.001	<DL	0.002
Pb	<DL	6.037	0.040	0.053	0.871	1.029	<DL	0.007	0.055	0.691	0.038	0.570
U	0.058	3.099	0.011	0.021	0.027	0.035	0.016	0.051	1.113	2.321	0.806	1.884

Conclusion

This application note shows how accurate and precise routine monitoring of water quality, with respect to elemental composition, can be effortlessly achieved using the iCAP MSX ICP-MS combined with the iSC-65 Autosampler. The method, based on a 5-fold dilution of all samples using AGD for fast, sensitive, and robust elemental analysis in different kinds of water samples. In one analytical method, more than 55 elements, from ^{7}Li to ^{238}U, could be accurately and quantitatively analyzed in one mode, which helps to realize productivity and cost savings. The instrument meets the requirements of analytical testing laboratories tasked with the analysis of different water samples, amongst other sample types. The main conclusions are summarized below.

- The use of Argon Gas Dilution and the availability of different dilution levels is a way to overcome the challenges associated with high and moreover variable matrix content. Dilution is accomplished automatically inside the instrument with no additional sample handling required. AGD is fully integrated and supported in the Qtegra ISDS Software, so that it is easy to set up and operate.

- The large linear dynamic range of the iCAP MSX ICP-MS allows for precise determination of major elements and trace elements with low and high concentrations in one measurement without further sample dilution. Excellent sensitivity was achieved for all analytes, easily meeting the requirements specified in local and regional regulations pertaining to water analysis. In addition, effective interference elimination and excellent stability were also demonstrated over four weeks.

- Robust and stable analytical performance was demonstrated over 12 hours each working day over the duration of four weeks, with >5,000 samples and QC checks run during this study.

- The iCAP MSX ICP-MS was designed to allow robust and reliable analysis while being easy to maintain. The key components that operators handle most, such as the nebulizer, spray chamber, and interface, can be easily accessed and disassembled for effortless maintenance and minimal downtime. Leveraging the HAWK Consumables and Maintenance Assistant, performance of the correct maintenance action at the right time allows to effectively prevent interruptions and reduces unplanned downtime significantly.

References

1. ISO 17294-1:2004 – Water quality – Application of inductively coupled plasma mass spectrometry (ICP-MS) – Part 1: General guidelines.
2. ISO 17294-2:2016 – Water quality – Application of inductively coupled plasma mass spectrometry (ICP-MS) – Part 2: Determination of selected elements including uranium isotopes.

Learn more at **thermofisher.com/icp-ms**

thermo scientific