

Environmental

Reliable analysis of surface and drinking waters following ISO method 17294 using single quadrupole ICP-MS

Author

Jianfeng Cui
Thermo Fisher Scientific,
Bremen, Germany

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Goal

This application note focuses on the analysis of drinking and surface water samples following ISO 17294^{1,2}. In particular, the reliable and consistent performance of the Thermo Scientific™ iCAP™ RQplus ICP-MS over a period of two weeks will be demonstrated. At the same time, the newly developed Thermo Scientific™ Hawk™ Consumables and Maintenance Assistant, which provides laboratory technicians and managers with all the information required to fully leverage the productive time of the instrument, will be presented.

Introduction

Inductively coupled plasma mass spectrometry (ICP-MS) is a widely recognized technique for trace element determination, with excellent detection limits and a very wide dynamic range. One of the key applications, predominantly for single quadrupole ICP-MS instruments, is the monitoring of water samples of different kinds for the content of heavy metals, in particular highly toxic elements such as arsenic, cadmium, mercury, and lead. In Europe, the assurance of water quality is typically assessed by methods such as ISO 17294-1:2004 - Water quality — Application of inductively coupled plasma mass spectrometry (ICP-MS) — Part 1: General guidelines, which provides a framework for the analysis of a wide variety of elements, as well as guidelines for execution of the testing, limits, and applicable quality control tests. The testing itself is performed by analytical testing laboratories that are able to analyze a large number of samples, and provide results with short turnover times. This in turn means that robust and reliable operation of the instrumentation used for the analysis is key to ensure productivity and maintain profitability. Consistent performance day after day is especially important, as interruptions, such 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.

In addition, potential variability of the sample matrices is an important aspect to consider. Drinking water is highly purified, and 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.

The ultimate goal of an analytical testing laboratory is to analyze many different sample types using a single method, irrespective of the nature of the sample. This requires a highly robust system able to tolerate high and variable matrix loads. While off-line liquid sample dilution would be a way to achieve consistent results, this is often not preferred due to the associated labor and cost. Dilution also leads to poorer achievable method detection limits (MDLs) and incurs the risk of contamination, both of which can impact the ability of the method to meet regulatory limits.

This application note describes the analysis of different water samples using the iCAP RQplus ICP-MS operated with argon gas dilution (AGD) as a tool to facilitate sample dilution directly during sample introduction. Different water samples are analyzed following ISO 17294, and reliable performance is demonstrated over 10 working days, allowing the analysis of more than 2,800 samples.

Experimental Instrumentation

An iCAP RQplus ICP-MS was used to analyze different water samples, collected in and around Bremen, Germany (Table 3). To extend the matrix tolerance of the system beyond the often-perceived limit of 0.2% (m/v) total dissolved solids (TDS) (due to constraints imposed by the interface cones on all ICP-MS systems) and to assure consistent results independent of the sample type, the iCAP RQplus ICP-MS offers argon gas dilution (AGD) as a standard solution. 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 can be placed as received onto the autosampler 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) in helium KED mode for all analytes. This facilitates complete removal of polyatomic interferences while maintaining high sensitivity for critical elements.

The instrument parameters used for analyses are shown in Table 1.

Table 1. Instrument parameters

Parameter	Value
Nebulizer	ESI PFA MicroFlow ST, orange cap, 400 $\mu\text{L}\cdot\text{min}^{-1}$
Peristaltic pump tubing	PVC tubing, orange green - orange green, 0.38 mm i.d.
Peristaltic pump speed	25 rpm
Spray chamber	Quartz cyclonic, cooled at 2.7 °C
Torch	Quartz torch
Injector	2.5 mm i.d., Quartz
Interface	Nickel sampler and nickel skimmer cone with high matrix insert
Plasma power	1,550 W
AGD setting	Low
Nebulizer gas	0.39 $\text{L}\cdot\text{min}^{-1}$
Additional gas flow (Ar)	55% (1,000 $\text{mL}\cdot\text{min}^{-1}$ MFC)
CRC gas	Pure helium, 4.12 $\text{mL}\cdot\text{min}^{-1}$
KED	3 V
Scan setting	0.1 s dwell time, 5 sweeps, 3 main runs
Analysis time per sample	Total 2 min 38 s: including uptake and wash out

To automate the analysis, a Thermo Scientific™ iSC-65 Autosampler was used. The iSC-65 Autosampler was specifically designed to meet the needs of analytical testing laboratories and features a series of innovative solutions to facilitate highest reliability and efficient use in the laboratory. This includes not only a visualization of the instrument status by means of an LED panel, but also a step ahead function, allowing analysis of two adjacent samples to be overlapped, ultimately reducing the turnover time per sample. The typical parameters applied for the analysis of water samples are shown in Table 2.

Table 2. Autosampler iSC-65 parameters

Autosampler	iSC-65
Uptake / wash time	55 s / 30 s
Step ahead time	10 s

Samples and sample preparation

One of the main challenges associated with the analysis of water samples is the highly variable matrix load. Whereas drinking water may vary mostly in the concentrations of major analytes, such as the alkaline and alkaline earth elements, surface waters like river, lake, or well water may also contain higher amounts of transition metals, in particular iron. In addition, dissolved organic matter and microorganisms may affect the analysis and lead to increased matrix effects, causing signal suppression and drift. In order to cover a wide variety of potential sample matrices, a total of seven water samples (including one certified reference material) were collected locally and analyzed in this study. An overview of all the samples is shown in Table 3.

Table 3. Seven different water samples analyzed during this work

	Item	Place	Category	Note
1	Tapwater TFS	Bremen West	Tap water	–
2	Tapwater Brinkum	Bremen South	Tap water	–
3	Tapwater Oberneuland	Bremen North	Tap water	–
4	Silbersee Brinkum	Bremen South	Lake	Sampling location is close to a major highway
5	Lake Oberneuland	Bremen North	Lake	Sampling location is close to an area with heavy traffic
6	Wellwater	Bremen North	Well water	Ground water sample, obtained without any additional treatment
7	SLRS-5	Ottawa	River	CRM

Method development

At the beginning of every day of operation (usually Monday through Friday), the instrument was switched on. After an automatic warm-up time of 15 minutes, the instrument's settings and performance were verified. This basic system suitability test comprised a performance report in STD mode to verify that the required signal intensity and stability were obtained, as well as to verify other important plasma parameters, such as oxide ratio ($^{140}\text{Ce}^{16}\text{O}^+ / ^{140}\text{Ce}^+$) and the formation of doubly charged ions ($^{137}\text{Ba}^{++} / ^{137}\text{Ba}^+$). A second performance report was generated with AGD applied. Please note that in general, a single performance report would suffice to prove the system's suitability for analysis. After that, a LabBook was setup using the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software for the analysis of a selection of elements covering the range from ^7Li to ^{238}U .

To assure the selection of isotopes free from isobaric overlaps or abundant spectral interferences, Qtegra ISDS Software contains an automatic selection of a suitable isotope per analyte, so that only the isotope with the least interference and the strongest signal will be automatically measured. Qtegra ISDS Software also contains a dedicated plug-in to control the iSC-65 Autosampler. Within this plug-in, key features of the system can be configured, including actions to be taken upon arriving at an inaccessible sample (for example, an unopened vial), but also the ability to overlap the sampling process of two adjacent samples without interfering with the current measurement. The Step Ahead function allows wash out of the current sample to be started while data acquisition on the sample remaining in the uptake line is still running, so that an additional time saving per sample can be realized. As can be seen from Table 2, the step ahead function was used in this analysis and helped to reduce the sample turnover time by 20 seconds per sample (10 seconds by uptake; 10 seconds by washout), equivalent to 10% of the original analysis time per sample.

Hawk Consumables and Maintenance Assistant

One of the biggest challenges for laboratories monitoring the quality of water samples is the potential of unplanned downtime due to unforeseen maintenance requirements. Especially for operators in charge of a large number of analytical systems, it can be difficult to assess when to perform an inspection of the key components of the sample introduction system, not only to avoid unexpected interruptions due to sudden failure, but also to avoid unnecessary interruptions of the productive time of an instrument. The integrated Hawk Consumables and Maintenance Assistant can provide a full overview on all critical components of the sample introduction system, giving the user timely and accurate information on potential maintenance requirements. Based on this information, even inexperienced operators can easily understand the needs of daily maintenance and replacement of consumables, and act accordingly. This ensures the reliable operation of the instrument and will reduce unplanned interruptions caused by untimely maintenance. Figure 1 provides an overview on how the Hawk system allowed maintenance to be controlled and planned throughout this study. Based on the expected maintenance frequency for the individual components of the sample introduction system, which would ensure an uninterrupted analysis, the Hawk system was reset at the start of the analysis on the first day. With an expected average of 300 samples being analyzed per day, including the required standard solutions, QC checks, and unknown samples, the instrument required a user action (visual inspection of the cones and replacement of the peristaltic pump tubings) at the end of the fourth working day. After the maintenance actions had been executed as required, the individual alerts were reset, leaving a traceable entry in the maintenance log, and the next batch of samples then started.



Figure 1. Detailed maintenance requirements for different parts in the ICP-MS system

Results and discussion

Linearity assessment

The linearity of the instrument was demonstrated using a six-point calibration curve. All calibration curves from trace elements to major elements were established in the same run. All the target elements showed excellent correlation coefficients ($R^2 > 0.999$ or higher). The calibration solutions used for establishing multielement calibration curves and the QC standards for all elements are summarized in Tables 4 and 5.

Calibration standards were prepared in 2% (v/v) nitric acid, with analyte concentrations covering the range expected in the samples. An internal standard solution, containing $100 \mu\text{g}\cdot\text{L}^{-1}$ Sc and Ge, as well as $20 \mu\text{g}\cdot\text{L}^{-1}$ In and Ir in 2% (v/v) nitric acid, was added to all samples online via a T-piece (with a mixing rate between internal standard and samples of 1:1) before entering the spray chamber.

Detection limits

Detection limits (DLs) in solution 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. These calculated DLs are shown in Table 6. For all elements, the detection limits achieved were significantly lower than the required detection limits as per ISO method 17294.

Table 4. Concentration levels for calibration standards. All concentrations are given in $\text{mg}\cdot\text{L}^{-1}$

Elements	Standard concentrations
Ca	1, 10, 40, 100, 500
Na	1, 10, 40, 100, 200
Mg, K	1, 2, 8, 20, 100
Si	0.1, 0.5, 1, 10
P, Ti, Fe, Mn	0.01, 0.1, 1, 10
Al, Zn, Sr	0.02, 0.05, 0.5, 5
Rb	0.01, 0.05, 0.1, 1
Li, B, Be, Ba, V, Cr, Co, Ni, Cu, As, Se, Mo, Cd, Sb, Te, Cs, Tl, Pb, Bi, U	0.001, 0.01, 0.1, 1
Y, Zr, Nb, Ru, Rh, Pd, Sn, Ce, Gd, W, Pt, Hg	0.01, 0.02, 0.08, 0.2
Ag	0.001, 0.01, 0.04, 0.1

Table 5. Concentration levels for QC standard. All concentrations are given in $\text{mg}\cdot\text{L}^{-1}$.

QC standard	Concentration
Zr, W	0.02
Li, V, Cr, Mn, Co, Ni, Cu, Rb, Y, Nb, Mo, Ru, Rh, Pd, Ag, Cd, Sn, Sb, Te, Cs, Ba, Ce, Gd, Pt, Hg, Tl, Pb, Bi, U	0.05
Al	0.25
Be, B, Si, Ti, Fe, Zn, As, Se, Sr	0.5
P	4
Na, Mg, K	30
Ca	40

Table 6. Detection limits achieved

Element	µg·L ⁻¹	Element	µg·L ⁻¹	Element	µg·L ⁻¹
⁷ Li	0.015	⁶⁰ Ni	0.011	¹¹⁸ Sn	0.009
⁹ Be	0.336	⁶³ Cu	0.028	¹²¹ Sb	0.009
¹¹ B	0.611	⁶⁶ Zn	0.041	¹²⁵ Te	0.048
²³ Na	1.152	⁷⁵ As	0.053	¹³³ Cs*	0.009
²⁴ Mg	0.063	⁷⁸ Se	0.079	¹³⁷ Ba	0.013
²⁷ Al	0.183	⁸⁵ Rb	0.004	¹⁴⁰ Ce	0.0003
²⁸ Si	4.517	⁸⁸ Sr	0.003	¹⁵⁷ Gd	0.001
³¹ P	0.335	⁸⁹ Y	0.003	¹⁸² W	0.008
³⁹ K	4.636	⁹⁰ Zr	0.023	¹⁹⁵ Pt	0.002
⁴⁴ Ca	1.426	⁹³ Nb	0.010	²⁰² Hg	0.028
⁴⁸ Ti	0.044	⁹⁵ Mo	0.009	²⁰⁵ Tl	0.002
⁵¹ V	0.003	¹⁰¹ Ru*	0.008	²⁰⁷ Pb	0.001
⁵² Cr	0.003	¹⁰³ Rh	0.001	²⁰⁹ Bi	0.0005
⁵⁵ Mn	0.025	¹⁰⁵ Pd	0.009	²³⁸ U	0.001
⁵⁶ Fe	0.040	¹⁰⁷ Ag	0.003		
⁵⁹ Co	0.001	¹¹¹ Cd	0.005		

*Ru and Cs in ng·L⁻¹

Quality control procedure and results

For reliable analysis in an essential testing laboratory, it is important that the results obtained are also accurate and precise in longer batches comprising different sample types. Commonly, quality control (QC) standards containing a known concentration of all analytes are analyzed periodically during a batch to monitor the analysis performance.

To simulate a high-volume sample analysis, a larger sample batch was scheduled for analysis containing all of the samples collected as well as a certified reference material. The batch was designed to allow for an approximate runtime of 12 hours per day, including a total of 300 samples per day, split into the calibration block and a series of fixed sample sequences. Each sequence in the batch consisted of 20 individual samples and was concluded with a quality control standard (continuing calibration verification, QC sample) before continuing with the next sequence. The same batch was repeatedly analyzed consecutively over 10 working days. This means that a total of over 2800 unknown samples could be analyzed in this period, complemented with 140 CCVs. A full overview of all QC samples that were successfully acquired is shown in Figure 2. All recoveries were within 90% to 120%.

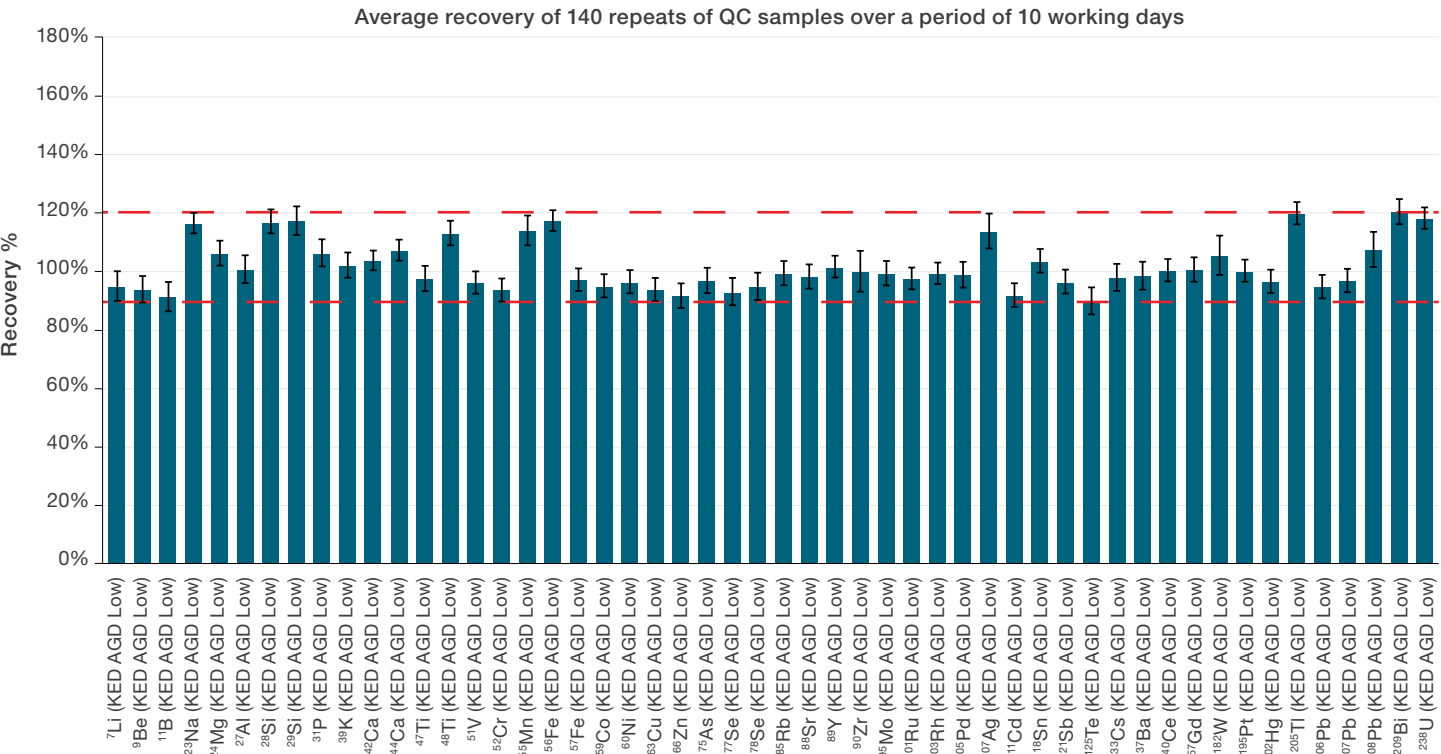


Figure 2. QC samples recovery (90–120%) observed during the full duration of this study

As part of this study, a certified reference material (CRM) sample SLRS-5 (natural river water) was also periodically analyzed through the whole batch. The results obtained for minor and major elements concentrations of SLRS-5 are shown in Table 7.

The results for the river water CRM were also found to be in excellent agreement with the reference values. The recoveries of the CRM sample over a period of two weeks of routine lab analysis are shown in Figure 3.

Table 7. Certified quantity values and measured values for SLRS-5 (river water CRM)

Element	Mass fraction (µg/kg)	Measured values (µg/kg)	Recovery (%)
Al	49.5	50.6	102%
Sb	0.3	0.35	117%
As	0.413	0.478	116%
Ba	14.0	15.2	109%
Cr	0.208	0.216	104%
Co	0.05	0.052	104%
Cu	17.4	18.7	107%
Fe	91.2	91.3	100%
Pb	0.081	0.077	95%
Mn	4.33	4.64	107%
Mo	0.27	0.27	100%

Element	Mass fraction (µg/kg)	Measured values (µg/kg)	Recovery (%)
Ni	0.476	0.525	110%
Sr	53.6	55.9	104%
U	0.093	0.092	99%
V	0.317	0.304	96%
Zn	0.845	0.960	114%

Element	Mass fraction (µg/g)	Measured values (µg/g)	Recovery (%)
Na	5.38	4.89	91%
Mg	2.54	2.45	96%
K	0.839	0.823	98%
Ca	10.5	9.90	94%

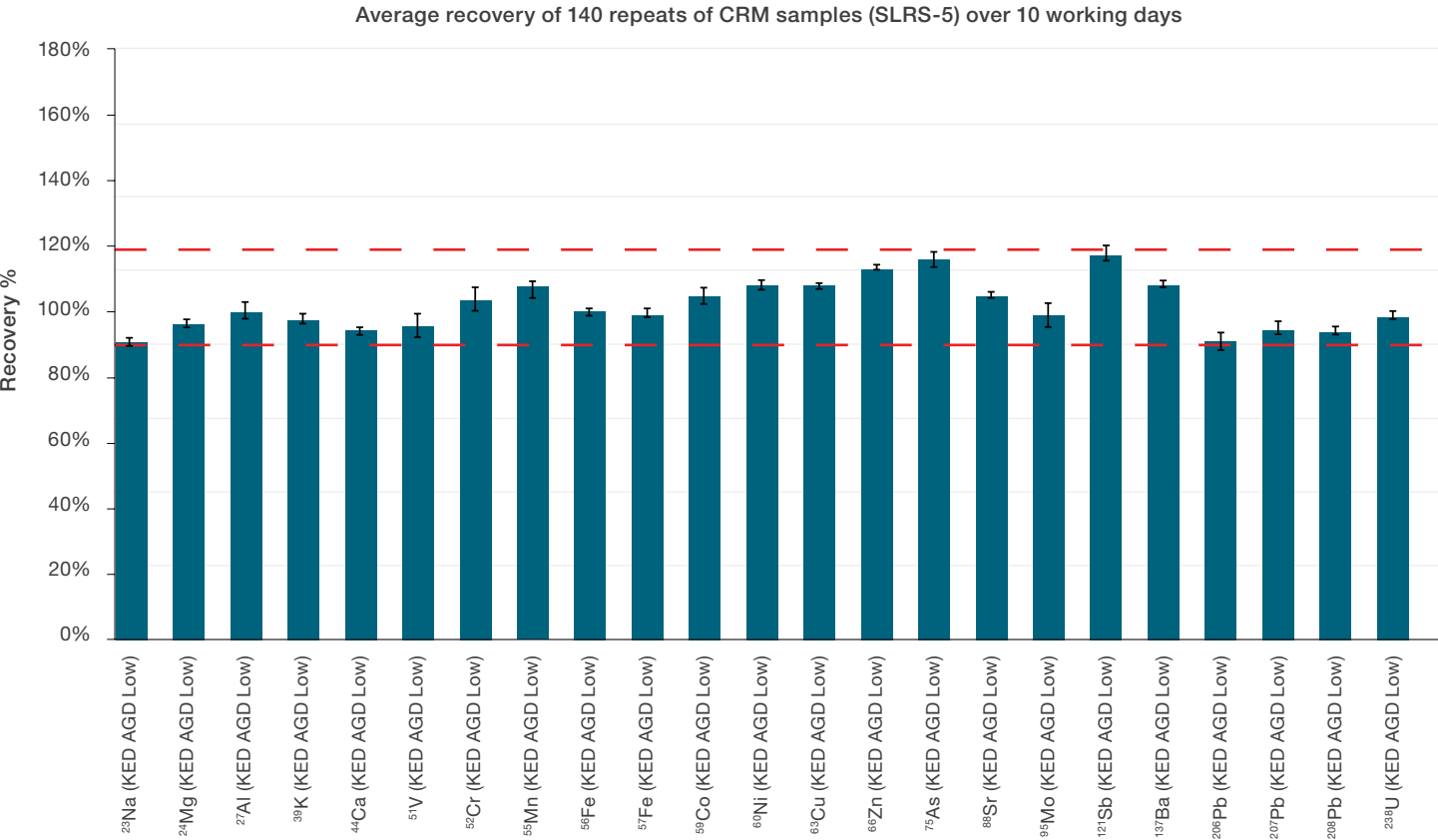


Figure 3. Recovery results for 140 repeats of SLRS-5 CRM samples (90–118%)

Long term stability

To obtain accurate and reliable results on every working day is a key requirement of analytical testing laboratories. This includes not only stable operation and consistent results within a working day, but also flawless operation over extended periods, demonstrated typically by completion of a system suitability test (or performance report). To demonstrate the long-term stability and robustness of the iCAP RQplus ICP-MS system operated using the proposed method, two of the typically applied performance indicators were monitored and will be highlighted in the following. Before starting the analysis of the predefined batch, a performance report was completed to verify the system's sensitivity over the full mass range as well as monitoring other plasma-based parameters (such as oxide ratio or interference removal factor). If any of the required criteria were

not met, the instrument would have been taken out of service for troubleshooting, leading to a delay of the analysis. Figure 4 below contains the cumulative test sample numbers for a typical analysis laboratory, the daily performance check results based on In intensities, as well as the maintenance details required by the system automatically provided by the Hawk system.

The recovery of the internal standards (a real time display generated automatically by the Qtegra ISDS Software) is shown in Figure 5. All isotopes used as internal standards showed excellent recoveries within 90% to 118% over the entire duration of the experiment and in different types of sample matrices. This demonstrates stability and accuracy through the run, with no detectable carryover or other effects from sample matrices (e.g., signal suppression or enhancement).

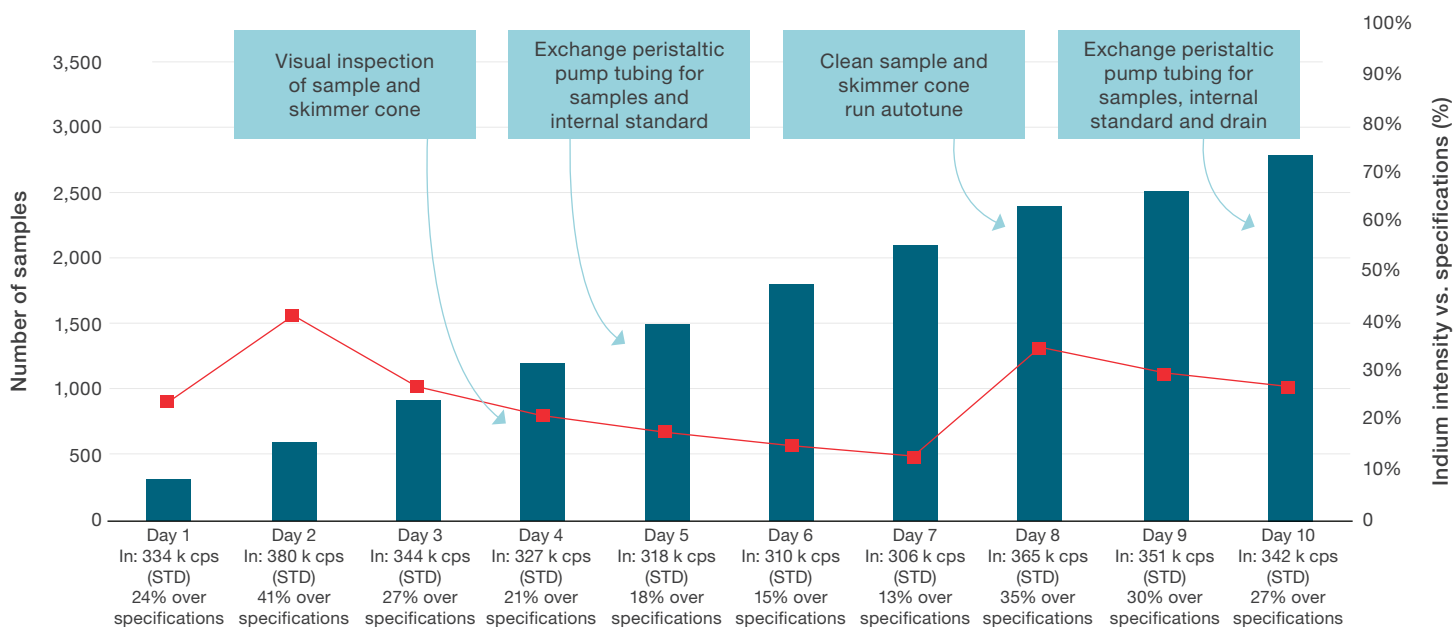


Figure 4. Daily instrument performance check results and maintenance requirements

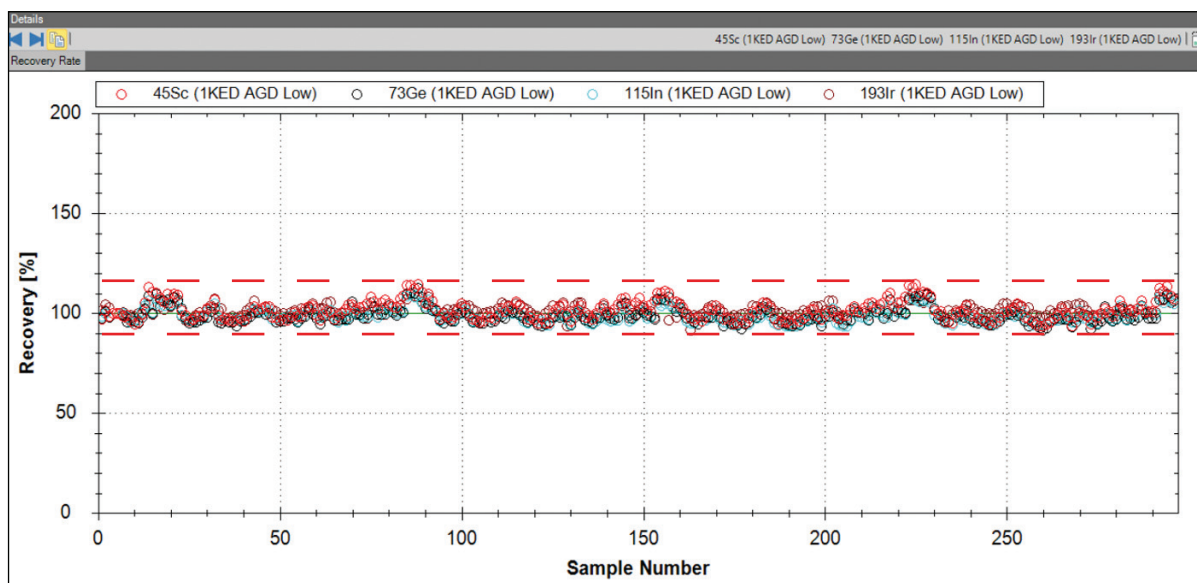


Figure 5. Recoveries of the internal standards from the analysis of 300 samples over 12 hours showing recoveries within 90% to 118%

Conclusion

This application note shows how rapid, accurate, and precise routine monitoring of water quality, with respect to elemental composition, can be effortlessly achieved using the iCAP RQplus ICP-MS combined with the iSC-65 autosampler. The instrument meets the requirements of analytical testing laboratories tasked with the analysis of different water samples, among other sample types. Key takeaways from this study were:

- The iCAP RQplus 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. The use of argon gas dilution is a way to overcome the challenges associated with the analysis of samples with matrix content outside the commonly defined limit of around 0.2% (m/v) TDS. Dilution with argon gas 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 simplified workflow of the Qtegra ISDS Software allows easy method development, implementation of Quality Control protocols, and data evaluation. The Hawk Consumables and Maintenance Assistant provides full visibility of the system's status and potential maintenance requirements, so that unwanted interruptions can be avoided and downtime can be efficiently planned. In case errors occur, the Hawk system provides clear instructions for fast and easy troubleshooting, so that all users can resolve them.

- The large linear dynamic range of the iCAP RQplus ICP-MS of up to 10 orders of magnitude allows for precise determination of major elements and trace elements with low and high concentrations in one measurement without further sample dilution.
- Robust and stable analytical performance was demonstrated over 12 hours of continuous acquisition of 300 potable and surface water samples per day and was repeated over a total of 10 working days, so that a total of close to 3,000 samples were analyzed during this study.

In summary, the iCAP RQplus ICP-MS system together with AGD controlled by Qtegra ISDS Software allows for accurate, fast, sensitive, and robust elemental analysis in different kinds of water samples. In one analysis process, up to 60 elements, from ^7Li to ^{238}U , could be accurately and quantitatively analyzed in one mode. For the analysis of potable and surface water samples, the iCAP RQplus ICP-MS system has been demonstrated to be an instrument that provides outstanding detection limits, effective interference elimination, and excellent stability.

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.

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