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Trace elemental analysis

Multielement analysis of drinking water samples as per regulations from the Bureau of Indian Standards using ICP-MS

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Keywords

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Goal

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

Introduction

The quality of drinking water refers to its safety, purity, and suitability for human consumption. It is essential that drinking water meets specific standards and guidelines to ensure it does not pose any health risks to individuals who consume it. Drinking waters are regularly monitored for the content of different elements, in particular highly toxic heavy metals such as arsenic, cadmium, mercury, and lead, which are severely detrimental for human and environmental health. The regulations applicable for testing and assuring water quality in India are as follows:

• IS 10500:2012 Drinking water - Specification

• IS 13428:2005 Packaged Natural Mineral Water - Specification

• IS 14543:2004 Packaged Drinking Water - Specification

These regulations specify stringent maximum contaminant levels (MCLs) of different toxic and some nutritional elements in drinking water samples, as listed in Table 1.

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Drinking water samples must be regularly monitored to ensure that they comply with these regulations. Inductively coupled plasma mass spectrometry (ICP-MS) is a powerful technique for analyzing 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. Additionally, a high robustness of the ICP-MS system is also a desired feature because it helps analytical testing laboratories, carrying out analysis of different drinking water samples regularly, to cope with a high sample load and deliver accurate results on time. While drinking water samples are usually low in Total Dissolved Solids (TDS) content, different drinking waters may be fortified with varying amounts of nutrient elements to increase their nutritional values. When analyzing a mix of such different samples, Argon Gas Dilution (AGD) offers a comprehensive solution for effective handling of a variety of sample types including those with high TDS in one analytical run. In addition, AGD helps to avoid off-line liquid sample dilution, which in turn saves associated labor and cost, and minimizes the risk of contamination, while still delivering consistent results with minimum matrix effects.

This application note describes the analysis of different drinking water samples using the iCAP MSX ICP-MS operated with AGD as a tool to facilitate sample dilution directly during sample introduction.

Experimental
Instrument parameters
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 2. 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 function 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 highest reliability, efficiency, and robustness for effective use in the laboratory and seamless delivery of hundreds of samples daily.

Table 1. Specification of maximum contaminant levels (MCLs) of different elements in different drinking waters as per Indian regulations

Element	Drinking water BIS 10500:2012 (mg·kg^{-1})	Packaged natural mineral water IS 13428:2005 (mg·L^{-1})	Packaged drinking water IS 14543:2004 (mg·L^{-1})
Ag	0.1	0.01	0.01
Al	0.03	-	0.03
As	0.01	0.05	0.05
Ba	0.7	1	1
Ca	75	100	75
Cd	0.003	0.003	0.01
Cr	0.05	0.05	0.05
Cu	0.05	1	0.05
Fe	0.3	-	0.1
Hg	0.001	0.001	0.001
Mg	30	50	30
Mn	0.1	2	0.1
Mo	0.07	-	-
Na	0.02	150	200
Ni	0.02	0.02	0.02
Pb	0.01	0.01	0.01
Sb	-	0.005	-
Se	0.01	0.05	0.01
U	0.03	-	-
Zn	5	5	5

The Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software was used to control the full laboratory setup and 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. To ensure consistent operation throughout the entire period of this study, system maintenance was performed based solely on the recommendations of the Thermo Scientific™ HAWK Consumables and Maintenance Assistant, provided as part of the Qtegra ISDS Software. The HAWK Consumables and Maintenance Assistant (CMA) contains a series of preset and fully customizable alerts to schedule maintenance actions for key components of the sample introduction system. An additional component of HAWK is the Instrument Performance monitoring tool within the Dashboard that allows the easy visualization of the instrument performance over time.

Sample preparation

Three different bottled mineral water samples were analyzed in this study. The samples were acidified to contain approximately 2% HNO_3 and 0.5% HCl prior to analysis.

Table 2. 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 temperature (°C)	2.7
Injector	Quartz, 2.5 mm ID
Torch	Quartz torch
Auxiliary flow (L·min^{-1})	0.8
Cool gas flow (L·min^{-1})	14
Nebulizer flow (L·min^{-1})	0.45
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

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 five calibration standards and a calibration blank. The calibration standard 4 was used as a quality control (QC) standard in this study.

Two certified reference materials (CRM) LGC-6026 Hard drinking water – metals and SLRS-6 River water were included in the study and used in combination with each other to verify the accuracy of the analyses.

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.

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

Element	Std 1	Std 2	Std 3	Std 4	Std 5
Concentrations in mg·L^{-1}					
Ca	1	10	50	100	500
Na, Mg	0.2	2	10	20	100
Concentrations in µg·L^{-1}					
Ba	2	20	100	200	1000
Fe, Zn, Mo	0.4	4	20	40	200
Al, Cr, Mn, Ni, Cr, Cu, As, Se, Ag, Cd, Sb, Pb, U	0.2	2	10	20	50
Hg	0.02	0.2	1	2	10

Results and discussion
Linearity and detection limits

A five-point calibration curve with different concentrations of the elements as listed in Table 3 was used to demonstrate the linearity of the instrument. Calibration curves for all analytes, including trace and major elements, were established in the same run using this set of calibration standards. Excellent correlation coefficients (>0.999 or higher) were obtained for all target elements.

Excellent limits of detection (LOD) were obtained across the entire mass range for the different elements, as listed in Table 4. The LODs were determined by analyzing a blank solution 10 times, and the LODs were automatically calculated by the Qtegra ISDS Software using the 3σ criterion, taking into account the standard deviation of the blank measurements. Please note that the automatic 5 times dilution is already factored in the detection limits given in the table.

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})
^{23}Na	0.38	^{95}Mo	0.004
^{24}Mg	0.37	^{107}Ag	0.004
^{27}Al	1.0	^{111}Cd	0.004
^{44}Ca	3.0	^{121}Sb	0.003
^{52}Cr	0.005	^{137}Ba	0.008
^{55}Mn	0.060	^{202}Hg	0.0002
^{56}Fe	0.043	^{207}Pb	0.003
^{60}Ni	0.013	^{238}U	0.004
^{63}Cu	0.020		
^{66}Zn	0.005		
^{75}As	0.040		
^{78}Se	0.450		

Accuracy

The accuracy of the analysis was assessed by analyzing two CRM samples multiple times within the analytical sequence. The concentration data obtained during the analysis was compared to the certified values provided in the CRM certificates to calculate the percent accuracy for each analyte. Very good recoveries within the 80–120% range were obtained for both CRMs. It should be noted that the concentrations for Al, Cu, and Zn in LGC-6026 were outside of the calibrated range for this study and therefore were not reported. Table 5 provides a summary of the analytes, their certified concentration values, and the calculated percent accuracy. The percent accuracy values presented in the table are the averages calculated from five different measurements of each CRM.

Robustness

Different drinking water samples and CRMs were analyzed as a part of a 12-hour sequence, carried out to demonstrate the suitability of the instrument and the method for uninterrupted operation in analytical testing laboratory settings. A typical daily sequence consisted of a calibration block at the beginning of the Qtegra ISDS Software LabBook, including calibration blank and

Table 5. Certified quantity values and measured values for the two certified reference materials (CRM)

Element	CRM SLRS-6 River water n=5 Mass fraction (µg/kg)	Recovery (%)	CRM LGC-6026 Hard drinking water – metals n=5 Mass fraction (µg/kg)	Recovery (%)
Al	33.9 ± 2.2	108.3 ± 5	-	-
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
Cd	-	-	4.98 ± 0.15	112.0 ± 3
Cr	0.252 ± 0.012	104.3 ± 3	50.0 ± 1.9	118.3 ± 3
Cu	24.0 ± 1.8	108.8 ± 3	-	-
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
Mn	2.12 ± 0.10	109.0 ± 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
U	0.0699 ± 0.0034	88.3 ± 5	4.95 ± 0.40	95.8 ± 3
Zn	1.76 ± 0.12	108.3 ± 5	-	-

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
Na	2.770 ± 0.220	93.4 ± 3	24.60 ± 0.79	113.4 ± 2

standards, followed by an initial calibration verification (ICV), and a quality control (QC) check using the Std 4 as a QC standard. After this, a block of 15 unknown water samples followed by one QC check, setup as a continuous calibration verification (CCV), was run. The block of unknown samples and QC was repeated throughout the LabBook. Along with the regular QC checks, the CRM samples were measured five times interspersed in the LabBook and together, these helped ensure accuracy throughout the measurement sequence.

The typical requirement of analytical testing laboratories to obtain internal standards response (and QC checks), within acceptable ranges of the initial calibration blank was easily met in the robustness sequence run in this study (Figure 1). Even after running the ICP-MS continuously for >250 samples, the internal standard response was within 80–120%, demonstrating the robustness of the system for extended period. This means that additional steps like dilution and re-analysis of samples showing higher matrix

suppression are avoided by using automatic AGD Level 5 dilution from within the instrument. The behavior of the internal standards, as displayed within the Qtegra ISDS Software, is shown in Figure 1. The periodic QC checks every 15 unknown samples yielded excellent recoveries well within 90–110% for all analytes, as shown in Figure 2, thus proving that the data obtained over time was consistently accurate and reliable. Based on these results as well as the CRM recoveries (Table 5) within the LabBook, it can be concluded that the system performed reliably and accurately over time.

Elemental concentrations in water samples

The different concentration ranges of the elements, found in the unknown water samples, are displayed in Table 6, expressed as minimum and maximum values that were measured to demonstrate the variability of analyte concentrations in different samples in a summarized way. The different elements were all found well below the maximum thresholds defined in the regulatory specifications.
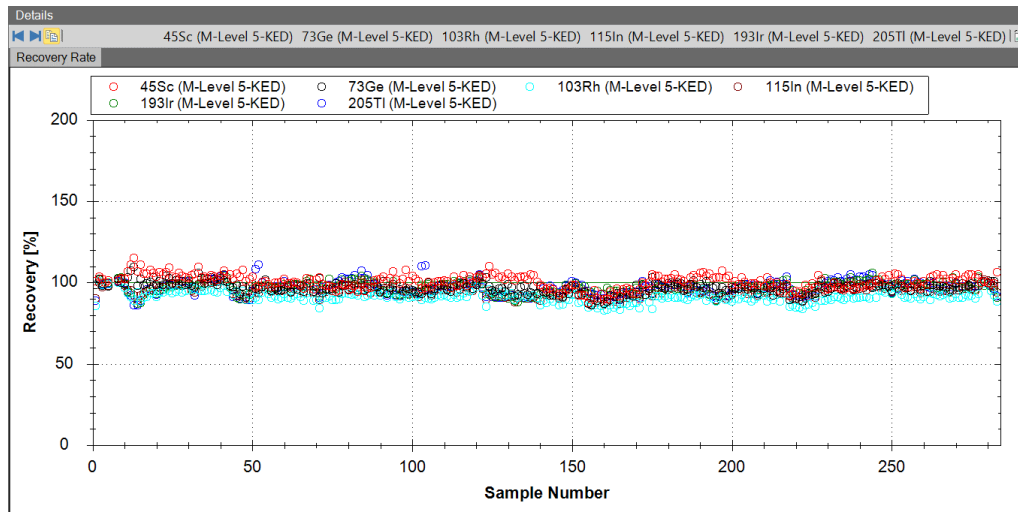

Figure 1. Internal standard recovery plot from the robustness test showed stable recoveries over 12 hours
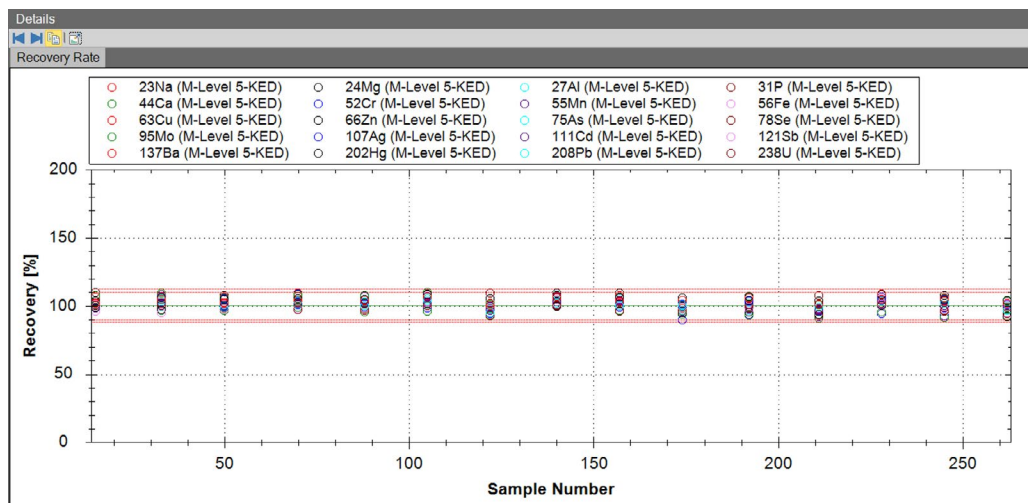

Figure 2. QC recoveries of target analytes between 90–110% for uninterrupted measurement of >250 samples

Table 6. Concentration ranges of different elements in the unknown samples. Numbers shown in blue are in mg·L^{-1}, all others are in µg·L^{-1}.

Analyte	Sample 1	Sample 2	Sample 3
Na	6.73	1.80	5.3
Mg	14.22	5.46	17.6
Al	3.56	7.23	<DL
Ca	73.19	35.69	64.8
Cr	0.09	<DL	0.27
Mn	70.16	<DL	<DL
Fe	11.46	0.73	<DL
Ni	1.06	<DL	0.03
Cu	1.60	0.03	0.04
Zn	5.87	1.96	2.21
As	0.22	0.29	0.07
Se	<DL	<DL	1.45
Ag	0.058	<DL	22.13
Cd	0.010	<DL	<DL
Sb	0.014	0.18	0.075
Ba	49.18	12.50	63.03
Hg	<DL	0.006	<DL
Pb	0.110	<DL	0.007
U	<DL	0.051	0.016

Conclusion

This application note highlights the ease and effectiveness of using the iCAP MSX ICP-MS in combination with the iSC-65 Autosampler for routine monitoring of water quality in terms of elemental composition. The method described involves a 5-fold dilution of all samples using AGD (Argon Gas Dilution) for the sensitive and reliable elemental analysis across different drinking water samples. By utilizing this approach, accurate and precise results can be obtained for routine water quality monitoring. The instrument performance exceeds the requirements of analytical testing laboratories tasked with the analysis of different water and other environmental samples. The main conclusions are summarized below.

- The use of Argon Gas Dilution, the availability of different dilution levels, and accomplishing dilution automatically inside the instrument with no additional sample handling required reduces time and effort spent in preparing samples and helps achieve seamless measurements of drinking water samples.

The AGD features are easy to set up and operate and are fully integrated and supported in the Qtegra ISDS Software.

- Excellent linearity was achieved for all analytes due to the large linear dynamic range of the iCAP MSX ICP-MS, which allows for precise determination of major elements and trace elements with low and high concentrations in one measurement without further sample dilution. The LODs of the different analytes demonstrate that the instrument easily meets and exceeds the sensitivity requirements specified in local regulations pertaining to water analysis.

- Robust and stable analytical performance with exceptional signal stability was demonstrated over a 12-hour uninterrupted sequence.

References
1. IS 10500:2012 Drinking water - Specification
2. IS 13428:2005 Packaged Natural Mineral Water - Specification
3. IS 14543:2004 Packaged Drinking Water - Specification

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