

Environmental

Robust analysis of a variety of water, wastewater, and soil samples according to U.S. EPA Method 6020B (SW-846)

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Keywords

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Goal

To evaluate and demonstrate performance of the Thermo Scientific™ iCAP™ MSX ICP-MS for robust analysis of a variety of water, wastewater, and soil samples according to the requirements of U.S. EPA Method 6020B.

Introduction

As a result of industrialization and manufacturing, agriculture and farming, and population growth, various types of solid and liquid wastes are introduced or released into the environment that could be hazardous to humans and the ecosystem. Although there are laws, regulations, and measures in place to minimize and control disposal and release into the environment, wastes reduction from anthropogenic sources will continue to be a challenge. The United States Environmental Protection Agency's (EPA) Office of Land Management and Emergency Response (OLEM) includes the Office of Resource Conservation and Recovery (ORCR) which implements the Resource Conservation and Recovery Act (RCRA). The RCRA gives the EPA the authority to control the generation, transportation, treatment, storage, and disposal of hazardous waste. To do this, the EPA developed regulations, guidelines, and policies for proper and safe management and cleanup of hazardous wastes and programs for pollution prevention and recycling:

- Conserve energy and natural resources by recycling and recovery
- Reduce or eliminate waste
- Clean up waste that may have spilled, leaked, or was disposed of improperly

The EPA developed various test methods for the analysis of contaminants in environmental samples, which can be found in the publication “Test Methods for Evaluating Solid Waste: Physical/Chemical Methods,” also known as SW-846. This is the EPA’s official compendium of analytical and sampling methods that have been evaluated and approved for use by waste management programs to comply with RCRA regulations. The SW-846 compendium functions primarily as a guidance document setting forth acceptable, although not required, methods for the regulated and regulatory communities to use in response to RCRA-related sampling and analysis requirements. SW-846 is a multi-volume document that changes over time as new information and data are developed. This application note will discuss the workflow developed for the analysis of different types of water, wastewater, and digested soil samples using the iCAP MSX ICP-MS, which offers a comprehensive solution for effective and reliable analysis of high dissolved solid containing samples. Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software was used to control the ICP-MS instrument and to generate, process and report analytical data, ensuring that the entire workflow meets the requirements specified in EPA Method 6020B, including quality control samples. To verify the consistent performance of the instrument over time, a sequence of 240 samples was repeated over two consecutive days resulting in a total of 480 samples analyzed.

Experimental

Instrument parameters and experimental conditions

The iCAP MSX ICP-MS instrument used in this study includes a full toolset to allow direct analysis of samples with increased levels of dissolved solids without dilution. The unique features of the instrument include the High Matrix operation mode, as well as Argon Gas Dilution to further increase the system’s robustness to high matrix. In addition, the iCAP MSX ICP-MS offers the new intelligent matrix handling feature to decrease the amount of sample matrix introduced into the system. When activated, it reduces the nebulizer flow during uptake and wash, so that plasma and interface cones are less exposed to the matrix, ultimately improving in-sequence stability and reducing maintenance cycles. To allow for unattended operation, the system was operated in conjunction with a Thermo Scientific™ iSC-65 Autosampler. The sample introduction system was configured using components that are summarized in Table 1.

The iCAP MSX ICP-MS was automatically tuned using the built-in tune sequences to optimize all critical parameters. This readily available tune set helps all analysts in a laboratory to set up and operate the instrument easily and to achieve the required sensitivity and matrix tolerance.

Prior to analysis, the instrument’s performance was verified using the automated performance check available within Qtegra ISDS Software. In this test, the sensitivity across the mass range is checked for ^7Li , ^{59}Co , ^{115}In , and ^{209}Bi . Other plasma-related performance parameters, such as oxide formation and doubly charged ion formation rates, were also checked using the $^{140}\text{Ce}^{16}\text{O}^+ / ^{140}\text{Ce}^+$ and $^{137}\text{Ba}^{++} / ^{137}\text{Ba}^+$ ratios, respectively.

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
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)	0.279
AGD dilution	Level 25
AGD flow, argon (L·min ⁻¹)	0.65
RF power (W)	1550
Sampling depth (mm)	10
Number of replicates	3
Spray chamber temp. (° C)	2.7
KED settings (gas flow rate in mL·min ⁻¹)	4.2 (with a 3 V kinetic energy barrier)
Number of sweeps	10
Sample and drain tube	Orange/Green, 0.381 mm ID

Standard and sample preparation

Diluent and calibration blank matrix: The diluent and calibration blank used was a mixture of 2% (v/v) nitric acid and 0.5% (v/v) hydrochloric acid in ultrapure water.

Preparation of soil samples: Four different soil samples were collected locally for analysis during this study. The sample collection and preparation were performed following the instructions outlined in SW-846 Test Method 3010A. An accurately weighed soil sample of about 1 g was digested on a hot plate using a combination of nitric acid and hydrogen peroxide. The digested sample was then diluted to 50 mL using de-ionized water as a diluent. The final soil sample solutions analyzed in this experiment contained total dissolved solids (TDS) content in the range of 0.1 to 0.7%.

Preparation of wastewater samples: The wastewater samples were prepared to simulate the typical composition of ground water, surface water, and brackish waters with varying concentrations of typically observed elements such as Na, Mg, K, Ca, and Fe and different anions. The commercially available 10,000 mg·L⁻¹ standard solutions and inorganic salts of these elements were used to prepare simulated samples. The anion concentrations were calculated based on the information available in individual certificates. All prepared solutions were analyzed directly without dilution. All solutions were diluted automatically using integrated argon gas dilution with a dilution level of 25. The TDS content of analyzed water samples was in the range of 0.1 to 1.7% as a representative of typically analyzed samples in the environmental laboratories.

Calibration standards

To determine analytical figures of merit, such as instrument detection limits (IDLs), linear dynamic range, and correlation coefficients, calibration curves were generated for 24 analytes by analyzing seven calibration standards and a calibration blank. Multi-element calibration standards were prepared from aqueous single element solutions of each target analyte (1,000 mg·L⁻¹, SPEX™ CertiPrep, Metuchen, NJ, USA). Three different stock solutions were prepared to accommodate analytes with different concentrations and chemical compatibility. The stock solutions were then diluted gravimetrically using diluent to result in the concentrations specified in Table 2. An internal standard solution containing 1,000 µg·L⁻¹ of ⁶Li, 200 µg·L⁻¹ of Sc, and 20 µg·L⁻¹ of Y, Rh, In, Tb, Ho, and Bi was added on-line continuously through the duration of the analysis. All 32 analytes (including the internal standards) were measured using Kinetic Energy Discrimination (KED) mode, with pure helium used as the collision cell gas.

Quality control standards (ICB, CCB, ICV and CCV)

The calibration blank containing a mixture of 2% (v/v) nitric acid and 0.5% (v/v) hydrochloric acid in ultrapure water was used for the Initial Calibration Blank (ICB) and the Continuing Calibration Blank (CCB) during the analytical sequence. The Initial Calibration Verification (ICV) and Continuing Calibration Verification (CCV) were prepared according to EPA Method 6020B. The solution used for ICV was prepared using an independent stock solution, whereas the CCV was prepared using the same stock solutions used in the preparation of the initial calibration solutions. The concentrations of all analytes in both ICV and CCV QC standard solutions were adjusted as per the requirement outlined in EPA Method 6020B. Table 2 summarizes the list of analytes and their concentrations (given in µg·L⁻¹) in the different calibration solutions and ICV and CCV QC standard solutions.

Table 2. List of target analytes and concentrations in calibration standards, ICV and CCV QC standards (µg·L⁻¹)

Analytes	STD 1	STD 2	STD 3	STD 4	STD 5	STD 6	STD 7	STD 8	ICV-QC	CCV-QC
Ag	0	0.1	1	5	10	20	100	250	7.5	10
Be, Ba, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Sb, Tl, Pb, Ti	0	1	10	50	100	500	1,000	5,000	75	100
Na, Mg, K, Ca, Fe, Al	0	50	500	2,500	5,000	10,000	50,000	250,000	3,750	5,000
Hg	0	0.1	0.5	1	5	-	-	-	0.5	1

Results and discussion

Linearity, instrument detection limits, LLOQ, and linear range

Instrumental detection limits (IDLs) for all analytes were calculated following the guidance provided in section 9.3 of EPA Method 6020B. The calibration blank was analyzed ten times, treating it as an individual sample each time. Subsequently, IDLs were calculated based on three times the standard deviation of the ten replicate measurements. The correlation coefficients (R^2) obtained for all analytes were found to be greater than 0.9992, which suggests excellent linear response for the established concentration range for each analyte. The measured analytes, together with their masses (m/z), calibration correlation coefficients (R^2), and IDLs are summarized in Table 3.

The analyte concentration in the lowest concentration calibration standard (Std 2 in Table 2) is the Lower Limit of Quantitation established for this study. As outlined in section 9.6 of EPA Method 6020B, the linear range for all analytes was determined by analyzing standard solutions at concentrations above the highest point of the calibration. The concentration of each analyte was measured against the calibration range (Table 2). The concentration of all analytes in these standards read back within $\pm 10\%$ of the true value establishing the linear ranges. Table 4 summarizes the LLOQ concentrations and the linear range determined for the target analytes.

Quality control (QC)

EPA Method 6020B is a performance-based method that includes a QC protocol requiring the analysis of specific QC standards and samples in the same analytical run as the unknown samples to ensure accuracy, precision, robustness, reproducibility, and reliability of the analytical data. The QC standards and samples analyzed in this study are summarized in the following sections.

Interference Check Sample solutions (ICSA and ICSAB)

To test the effectiveness of the interference correction technique applied and help ensure accurate results, the ICSA and ICSAB solutions were prepared and analyzed in this study as required by the method. The concentration of the ICSA and ICSAB solutions analyzed align with EPA Contract Testing Laboratory Program (CLP) specifications. The ICSA solution contains interfering elements: 100 mg·L⁻¹ Al, Ca, Fe, Mg, K, Na, P, and S; 200 mg·L⁻¹ of C; 1,000 mg·L⁻¹ of Cl; and 2 mg·L⁻¹ of Mo and Ti. The ICSAB solution contains the interferents at concentrations as stated and the analytes: 20 µg·L⁻¹ Ag, As, Ba, Be, Cd, Co, Sb, Se, Tl, and V; 40 µg·L⁻¹ Cr; 25 µg·L⁻¹ Cu, Ni, Pb; and 30 µg·L⁻¹ Mn and Zn.

The percent recovery for all analytes, including interferents in the ICSAB solution and percent recovery of only the interferents in the ICSA solution, was calculated automatically within the Qtegra ISDS Software using the comprehensive quality control function.

Table 3. List of analytes, m/z , correlation coefficients, and instrumental detection limits (IDLs)

Analyte	m/z	R^2	IDL ($\mu\text{g}\cdot\text{L}^{-1}$)	Analyte	m/z	R^2	IDL ($\mu\text{g}\cdot\text{L}^{-1}$)
Ag	107	0.9998	0.011	Mg	24	>0.9999	1.42
Al	27	>0.9999	1.741	Mn	55	>0.9999	0.035
As	75	0.9998	0.180	Mo	95	0.9999	0.04
Ba	137	>0.9999	0.059	Na	23	>0.9999	4.874
Be	9	>0.9999	0.024	Ni	61	0.9997	0.025
Ca	44	>0.9999	7.41	Pb	208	>0.9999	0.012
Cd	111	0.9999	0.013	Sb	121	>0.9999	0.014
Co	59	0.9996	0.006	Se	78	0.9995	0.521
Cr	52	0.9997	0.046	Ti	48	0.9998	0.008
Cu	63	0.9994	0.079	Tl	205	>0.9999	0.008
Fe	54	0.9997	1.43	V	51	0.9999	0.044
Hg	202	0.9996	0.045	Zn	66	0.9996	0.147
K	39	>0.9999	17.53				

Table 4. List of analytes and their established LLOQ concentrations and linear range

Analyte	LLOQ ($\mu\text{g}\cdot\text{L}^{-1}$)	Linear range ($\text{mg}\cdot\text{L}^{-1}$)
Ag, Hg	0.1	2
Be, Ba, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Sb, Tl, Pb, Ti	1	20
Na, Mg, K, Ca, Fe, Al	50	1,000

Table 5. Percent recoveries (% R) obtained for all analytes in the ICSA and ICSAB solutions on day 1

Analytes	% Recovery		Analytes	% Recovery	
	ICSA	ICSAB		ICSA	ICSAB
Ag	NA	88.9	Se	NA	99.4
As	NA	103.0	Tl	NA	101.0
Ba	NA	107.0	V	NA	91.0
Be	NA	108.2	Zn	NA	91.1
Cd	NA	106.3	Al	98.0	104.0
Co	NA	104.0	Ca	100.0	105.0
Cr	NA	98.7	Fe	100.6	106.1
Cu	NA	92.8	Mg	106.0	108.0
Mn	NA	91.8	K	100.0	105.1
Ni	NA	93.7	Na	103.0	106.0
Pb	NA	104.0	Mo	97.3	101.4
Sb	NA	100.7	Ti	96.2	101.1

The percent recovery (% R) values obtained for all analytes in both the ICSA and ICSAB solutions were found to be in the range of 90–110%, which is well within the acceptance criteria of $\pm 20\%$ (equivalent to 80–120%) of the true value. Table 5 presents analytes including interferents and their respective percent recoveries obtained in ICSA and ICSAB solutions.

Initial Calibration Blank (ICB)

A calibration blank solution containing a mixture of 2% (v/v) nitric acid and 0.5% (v/v) hydrochloric acid in ultrapure water was analyzed immediately after the initial calibration to monitor the analyte concentrations to ensure that there is no carryover between samples at levels above the acceptance criteria. As per the acceptance criteria given in section 10.5.4 of EPA Method 6020B, the ICB must not contain any analyte at a concentration above half the LLOQ. The measured concentration of all analytes in the ICB solution were found to meet the acceptance criteria required in the method.

Continuing Calibration Blank (CCB)

For continuous verification of the calibration curve, and to monitor carryover, the CCB and Continuing Calibration Verification (CCV) standards must be analyzed after every 10 samples and at the end of the analytical run sequence. The concentrations of all analytes in the CCB standards measured over two days were found to be well below the LLOQ established for each analyte.

Initial Calibration Verification (ICV)

The ICV standard was prepared using independent stock solutions to yield concentrations of all analytes as per the guidance provided in section 7.24 of EPA Method 6020B and analyzed after calibration to confirm the accuracy of the calibration curve. The concentrations of all the analytes in the ICV solution were found to meet the acceptance criteria of 90–110% of the true value of each analyte given in Table 2. Figure 1 presents the accuracy results obtained for all the analytes in the ICV standard measured during analysis of unknown samples on day 1.

Continuing Calibration Verification (CCV)

As mentioned, a CCV standard was analyzed after every 10 samples to verify the validity of the calibration. Concentrations of all analytes in the CCV standard are shown in Table 2. The concentrations obtained for all analytes in the CCV solution were found to meet the acceptance criteria of 90–110% of the true value of each analyte. Figure 2 shows the accuracy obtained for the analytes in the CCV solution.

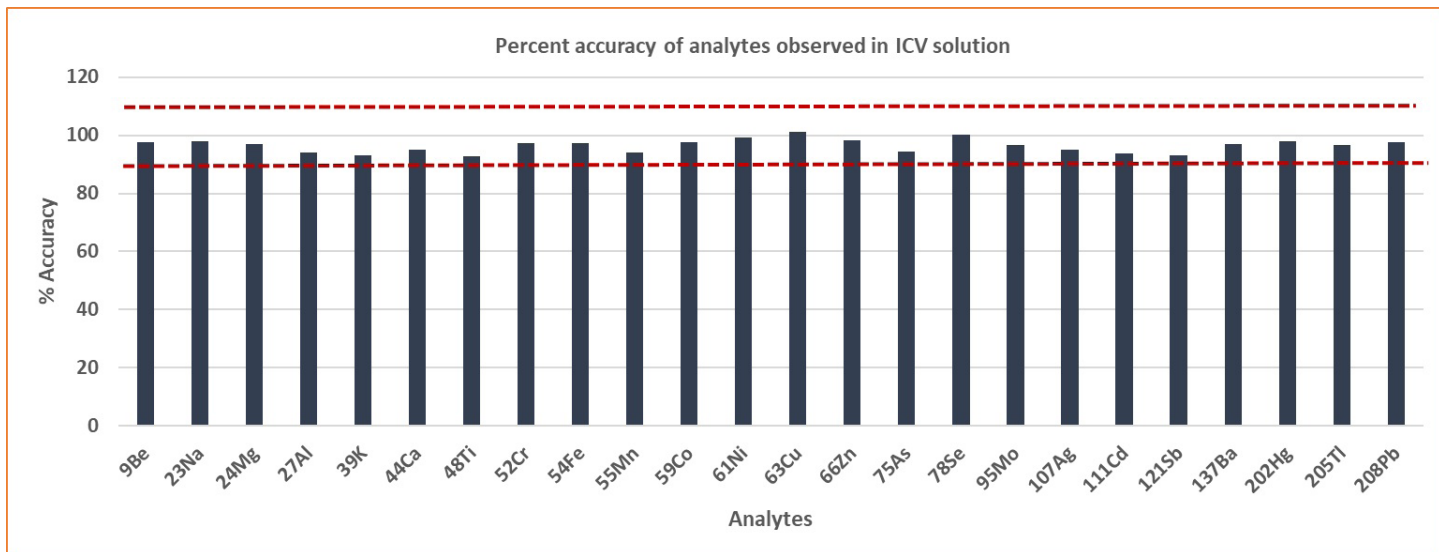


Figure 1. Percent accuracy of all analytes observed in the ICV standard analyzed on day 1

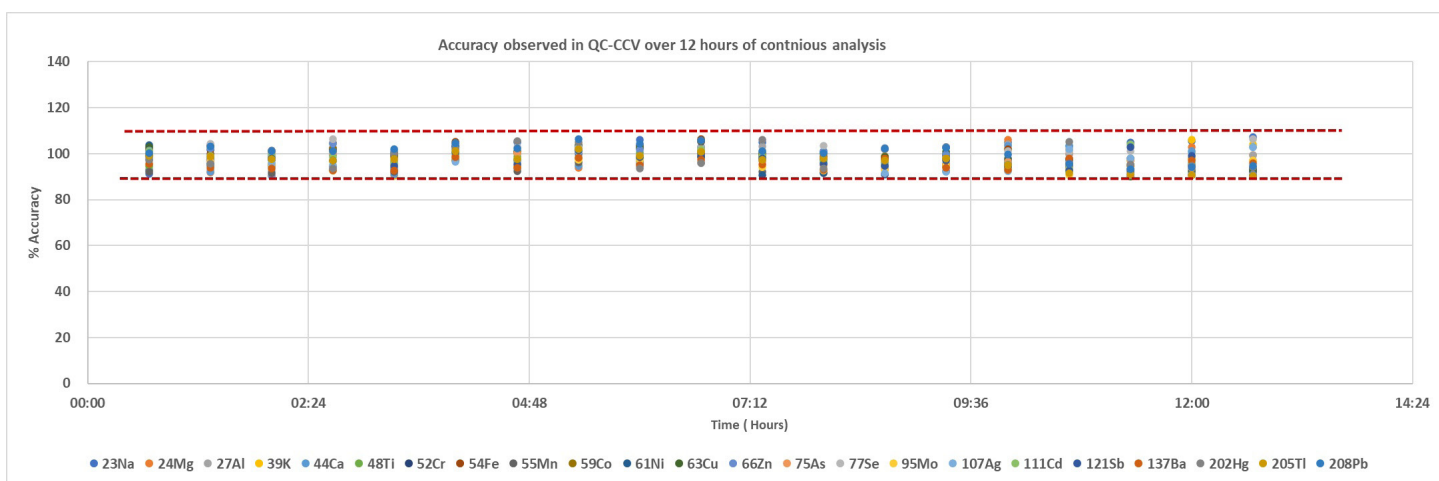


Figure 2. Percent accuracy of CCV standard analyzed over a period of 12 hours of continuous analysis

Matrix spike and duplicate measurement

To evaluate matrix effects and ensure accuracy and precision of the analytical measurement, representative wastewater and soil samples were analyzed in duplicate to investigate any bias and assess the precision of the measurement. For analytes that are above the LLOQ level, the results of the two measurements were used to assess the relative percent difference (RPD) to describe precision. For elements that were found to be present below the LLOQ level, a spike recovery study was performed and the relative percent difference was calculated based on these values. The data obtained in this experiment suggested that the acceptance criteria mentioned in EPA Method 6020B for percent recovery and relative percent difference (RPD) of $\pm 25\%$ and $< 20\%$, respectively, were met successfully in both

sample types. The percent accuracy values obtained during measurement of both matrix spike and duplicate samples were calculated automatically using the QC functions MXS (Matrix Spike) and DUP (Duplicate) available in Qtegra ISDS Software.

Method robustness – ensuring reliable analysis on consecutive days without any maintenance or downtime

Analysis of samples containing high amounts of total dissolved solids (TDS) leads to adverse effects in ICP-MS analysis, such as matrix deposition on the interface cones, signal drift over time, suppression in the response of the internal standards, QC failures, and more frequent maintenance of the instrument. All these challenges result in increased downtime and sample reruns causing a negative impact on laboratory productivity. Some of the indicators of instrument robustness over an extended analysis are

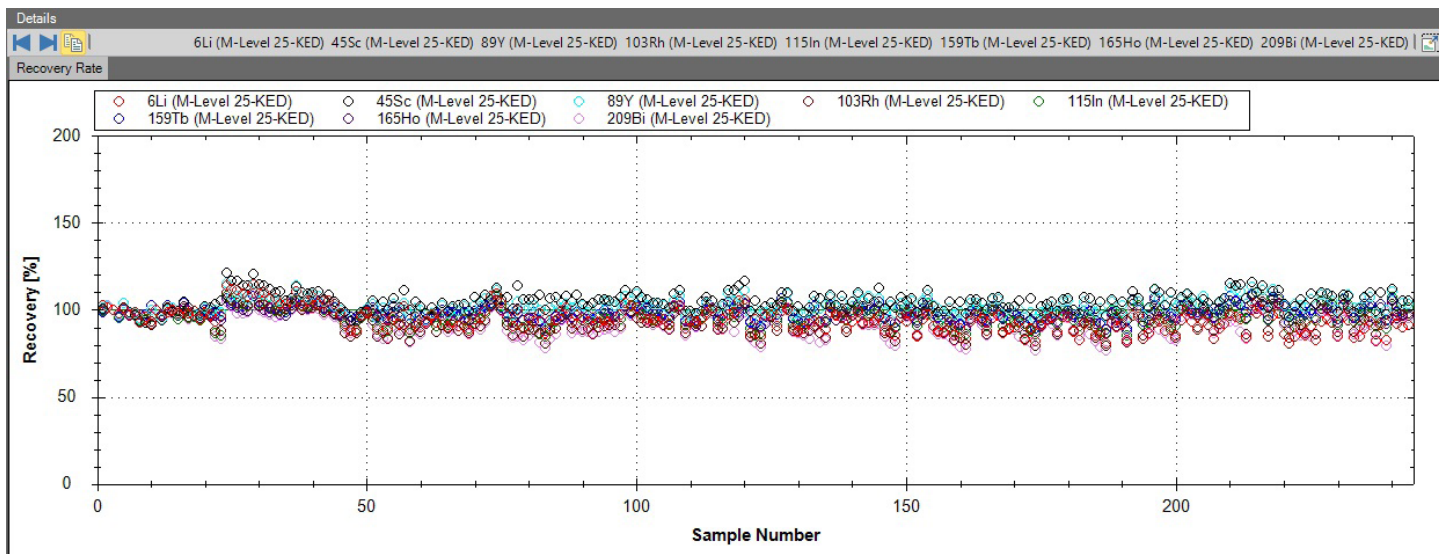


Figure 3. Internal standards response obtained over a period of 12 hours of continuous measurements

consistency and minimum suppression in the internal standards response. In this study, an internal standard solution containing Li, Sc, Y, Rh, In, Tb, Ho, and Bi was continuously added on-line using a Y-connector, and the response of the internal standards relative to the calibration blank was monitored. Figure 3 shows the response of all internal standards monitored in analytical batch containing variety of waters, wastewaters, and soil samples for 12 hours. The samples analyzed in this batch contained TDS ranging from 0.02 to 1.7% and were a mix of 20% water samples, 40% wastewater, and 40% soil digests. As can be seen, all internal standards read-back in a range between 80 to 120%, which is well within the acceptable range of $\pm 30\%$ described in EPA Method 6020B.

Summary

The iCAP MSX ICP-MS was extensively tested for compliance with EPA Method 6020B. The quality of the analytical data obtained over two consecutive days of measurements demonstrated that the built-in Argon Gas Dilution system for controlled and automatic dilution of the sample aerosol is a powerful solution for laboratories analyzing demanding samples, such as soil digests or wastewater, under high-throughput conditions. The overall performance of the instrument suggests that reliable analysis of these types of samples can be performed without need of any maintenance and with no instrument downtime over three or more days of analytical work. Some of the important outcomes of this study are summarized below:

- All the requirements of EPA Method 6020B were met during the test period of two days, enabling the analysis of a total of 480 samples.
- The instrument detection limits (IDLs) and lower limits of quantification (LLOQs) achieved met and exceeded the

requirements given in the method, which suggests that the employed methodology, with its optimized argon gas sample dilution, is suitable for achieving the required robustness and instrument sensitivity for these types of samples.

- Results observed during analysis of ICB and CCB QC standards indicate that the proposed method ensures minimum carryover between samples, enabling trouble-free measurement of high matrix samples across the full calibrated concentration range.
- The accuracy obtained for ICV and CCV standard solutions ensures the reliability and consistency of instrument performance while analyzing challenging high TDS containing samples such as wastewater and solid waste digests.
- The analytical data obtained during analysis of interference check solutions (ICSA and ICSAB) highlight the effectiveness of single KED mode using helium as collision gas in removing potential polyatomic interferences on each analyte, ensuring interference-free analysis every time.
- The data obtained during analysis of matrix spiked and duplicate measurements demonstrate that minimal or no matrix effect was encountered when analyzing complex matrices such as wastewater.
- The observed behavior of the internal standards on two consecutive days of analysis highlights the robustness and consistency of the instrument performance. The consistent internal standard readback within the range of 80–120% suggests that the developed methodology is a reliable solution for effective handling of high TDS containing samples with no impact from the matrix content.
- Qtegra ISDS Software provides all the necessary tools, including different QC functions, automatic calculations and limit and flag functionality, to ensure that the analysis is performed as per the compliance requirements of EPA Method 6020B.

References

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