

Environmental

Analysis of drinking water in compliance with the U.S. EPA Method 200.8, Revision 5.4 using the Thermo Scientific iCAP MSX ICP-MS

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Keywords

ICP-MS, iCAP MSX ICP-MS, U.S. EPA Method 200.8, Revision 5.4, 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, ground waters and drinking waters, in accordance with U.S. EPA Method 200.8, Revision 5.4

Introduction

Analytical laboratories conducting routine water analysis often experience high sample workloads that demand quick turnaround and reporting of accurate results based on requirements that adhere to local, state, and federal regulations, as applicable. Compliance with comprehensive quality control protocols and detection limits requirements ensures accurate results and data quality in such laboratories. In the U.S., the approved analytical method for drinking water compliance monitoring by inductively coupled plasma mass spectrometry (ICP-MS) is U.S. EPA Method 200.8, Revision 5.4, which includes procedures for the analysis of dissolved elements in ground waters, surface waters, and drinking water samples, as well as total recoverable elements in these types of waters and in wastewater, soils, and sludges.

This application note describes an analytical workflow developed using the iCAP MSX ICP-MS that enables laboratories to perform uninterrupted analysis of water samples for extended periods. The iCAP MSX ICP-MS 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 using Argon Gas Dilution (AGD). This entails the automatic and reproducible online addition of argon gas, using a dedicated mass flow controller, to the sample aerosol, enhancing robustness and reliability to consistently deliver accurate and precise results. ICP-MS instrumentation must be capable of analyzing varying sample types (e.g., drinking water, seawater, wastewater, soils), which include samples with high TDS. This approach of sample dilution using argon gas reduces the deposition of matrix on the interface cones and assures consistent readouts for QC checks, as well as reliable long-term robustness with minimal downtime.

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

Table 1. Instrument configuration and typical operating parameters

| Parameter | Value |
|--|---|
| Nebulizer | iCAP MX Series ICP-MS 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) | 0.447 |
| CRC conditions | Not used as per U.S. EPA Method 200.8 v5.4 requirements |
| AGD setting, argon flow (L·min ⁻¹) | AGD Level 5, 0.50 |
| RF power (W) | 1,550 |
| Sampling depth (mm) | 8 |
| Number of replicates | 3 |
| Spray chamber temp. (°C) | 2.7 |
| Dwell time | 0.05 s |
| Sweeps | 5 |

water samples. A standard aqueous sample introduction system was used, along with integrated argon gas dilution and typical instrument parameters, as listed in Table 1. The 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. The method was set up as a template in the software to ensure easy generation of data files in daily analysis, where the entire workflow meets the quality control requirements described in U.S. EPA Method 200.8.

Optimized instrument conditions were obtained using the autotune routines included with the Qtegra ISDS Software to ensure that analytical robustness and detection sensitivity are achieved during analysis.

The ICP-MS was operated in standard mode, as the use of traditional correction equations (Table 2) is mandated for the mitigation of isobaric and polyatomic interferences when U.S. EPA Method 200.8 is used for drinking water compliance monitoring under the Safe Drinking Water Act and the National Primary Drinking Water Regulations (NPDWR) 40 CFR Part 141. The use of a collision/reaction cell (CRC) is not permitted. Internal standardization was employed to monitor and compensate for physical interferences, instrument drift, and signal suppression or enhancement caused by the sample matrix.

Table 2. Summary of correction equations used for the target analytes

| Analytes | Correction equation |
|----------|--|
| As | $3.127 [(^{77}\text{Se} - 0.815 \times ^{82}\text{Se})]$ |
| Cd | $1.073 [(^{108}\text{Cd} - 0.712 \times ^{106}\text{Cd})]$ |
| Pb | $[^{206}\text{Pb} + ^{207}\text{Pb} + ^{208}\text{Pb}]$ |
| Mo | $[0.146 \times ^{99}\text{Ru}]$ |
| V | $3.127 [(^{53}\text{Cr} - 0.113 \times ^{52}\text{Cr})]$ |

Calibration standards

Calibration curves were generated for 21 analytes using six calibration standards and a calibration blank. Multi-element stock standards were prepared from single element standards of each target analyte (1,000 mg·L⁻¹, SPEX™ CertiPrep™, Metuchen, NJ, USA). Two different stock solutions were prepared at a concentration level of 2 mg·L⁻¹ to accommodate analytes with different concentrations and chemical compatibility. The stock solutions were then diluted gravimetrically using 1% (v/v) nitric acid as a diluent to result in the concentrations specified in Table 3. An internal standard solution containing 20 µg·L⁻¹ of ⁶Li, Sc, Y, Tb, and Bi was added on-line continuously during the analysis. All solutions used for analysis consisted of 1% (v/v) HNO₃ in ultrapure water containing 100 µg·L⁻¹ Au as a stabilizer for Hg.

Table 3. List of target analytes and their concentrations ($\mu\text{g}\cdot\text{L}^{-1}$) in calibration standards

| Analytes | STD 1 | STD 2 | STD 3 | STD 4 | STD 5 | STD 6 | STD 7 |
|--|-------|-------|-------|-------|-------|-------|-------|
| Hg | 0 | 0.01 | 0.1 | 0.25 | 1 | 2 | 5 |
| Al, Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, Se, Ag, Tl, Th, U, V, Zn | 0 | 1 | 5 | 25 | 100 | 200 | 500 |

Please note that the concentration of selenium used in this study was 5 times lower compared to the requirements of EPA Method 200.8, Rev. 5.4

Table 4. List of analytes and their MCLs in drinking waters allowed by NPDWR and NSDWR

| MCL | | SMCL | |
|---------|---------------------------------------|---------|---------------------------------------|
| Analyte | MCL ($\text{mg}\cdot\text{L}^{-1}$) | Analyte | MCL ($\text{mg}\cdot\text{L}^{-1}$) |
| Sb | 0.006 | Al | 0.05 to 0.2 |
| As | 0.010 | Ag | 0.1 |
| Ba | 2.0 | Cu | 1.0 |
| Be | 0.004 | Mn | 0.05 |
| Cd | 0.005 | Zn | 5 |
| Cr | 0.1 | | |
| Pb | 0.015 | | |
| Hg | 0.002 | | |
| Se | 0.05 | | |
| Tl | 0.002 | | |

Sample preparation

In total, five different water samples, collected locally, including tap water (typical TDS level $100\text{--}300\text{ mg}\cdot\text{L}^{-1}$), ground water (typical TDS level $500\text{--}700\text{ mg}\cdot\text{L}^{-1}$), and surface water (typical TDS level up to $1,000\text{ mg}\cdot\text{L}^{-1}$) were analyzed for the determination of dissolved elements. The samples were filtered using $0.45\text{ }\mu\text{m}$ pore size membrane filters followed by acidification using nitric acid to adjust the nitric acid concentration of the samples to approximately 1%. Multiple aliquots of these samples (equally split between ground water, surface water, and tap water) were then analyzed to assess accuracy and precision, performance of duplicate measurements, and robustness over a 16-hour analysis. A certified reference material (CRM) SLRS-5 (natural river water) was included in the analysis as an additional verification of accuracy.

Results and discussion

Detection limits and linearity

The detection limits of the method must be below the standards for inorganic contaminants in drinking waters set by the National Primary Drinking Water Regulations (NSDWR) and the National Secondary Drinking Water Regulations (NSDWR) (Table 4) with the maximum contaminant level (MCL) and secondary maximum contaminant level (SMCL) for each inorganic contaminant or analyte in this study. Here, the method detection limits (MDLs) for all analytes were calculated following the guidance provided in U.S. EPA Method 200.8, Revision 5.4. Seven replicate aliquots of fortified calibration blank (fortified at 2–5 times the concentration level of the expected detection limits) were analyzed, and the standard deviation of these measurements was multiplied by the Student's *t* value, which is 3.14 for seven replicate measurements. The results are summarized in Table 5. The MDLs achieved for all analytes were below the requirement of the regulations, suggesting that the developed method enables sensitive determination of all target analytes, meeting or exceeding the requirements. The correlation coefficients (R^2) obtained for all analytes were greater than 0.999, which suggests excellent linear response for the established concentration range for each analyte. The analytes, with their mass-to-charge ratio (m/z) and calibration R^2 are also summarized in Table 5.

Table 5. List of analytes, m/z, correlation coefficients, and MDLs

| Analyte | m/z | R ² | MDL (µg·L ⁻¹) |
|---------|-------------|----------------|---------------------------|
| Ag | 107 | 0.9995 | 0.052 |
| Al | 27 | 0.9992 | 0.228 |
| As | 75 | 0.9995 | 0.046 |
| Ba | 137 | 0.9998 | 0.025 |
| Be | 9 | 0.9996 | 0.022 |
| Cd | 111 | 0.9998 | 0.022 |
| Co | 59 | 0.9994 | 0.010 |
| Cr | 52 | 0.9992 | 0.045 |
| Cu | 63 | 0.9995 | 0.061 |
| Hg | 202 | 0.9993 | 0.005 |
| Mn | 55 | 0.9990 | 0.026 |
| Mo | 98 | >0.9999 | 0.018 |
| Ni | 60 | >0.9999 | 0.037 |
| Pb | 206+207+208 | 0.9996 | 0.010 |
| Sb | 123 | 0.9994 | 0.020 |
| Se | 82 | 0.9998 | 0.193 |
| Th | 232 | 0.9991 | 0.046 |
| Tl | 205 | 0.9996 | 0.013 |
| U | 238 | 0.9993 | 0.024 |
| V | 51 | 0.9996 | 0.038 |
| Zn | 66 | 0.9995 | 0.122 |

Quality Control (QC) checks

Laboratory Reagent Blank (LRB) – LRB sample was prepared from 1% (v/v) HNO₃ in ultrapure water, which was treated similarly as real samples by exposing it to the filtration through a 0.45 µm pore diameter membrane filter. The LRB sample was analyzed every 15 samples, and resulting concentrations of all analytes were monitored. The concentrations of all analytes in subsequent LRB samples were found to be within the acceptable range as specified in U.S. EPA Method 200.8.

Laboratory Fortified Blank (LFB) – An aliquot of LRB was spiked with stock solutions to yield the final concentration of 75 µg·L⁻¹ for all analytes (except for Hg, which spiked at a concentration level of 0.75 µg·L⁻¹). The recovery of each analyte was calculated automatically within the Qtegra LabBook using a recovery test available in the comprehensive QC toolkit. The recovery values for all analytes were found to be within the range of 85–115%, which suggests that the acceptance criteria were met, and analysis could be continued.

Quality Control Sample (QCS) – QCS solution was prepared by spiking an aliquot of the LRB using independent analyte stock solutions (different from the stock solutions used for preparation of calibration standards) to yield analyte concentrations at 50 µg·L⁻¹ level (except for Hg, which was spiked at 0.5 µg·L⁻¹ concentration level). The QCS was used to confirm the initial validity of calibration standards as well as to confirm the ongoing instrument performance during the measurement of more than 16 hours. The QCS was analyzed every 10 samples, with the percent accuracy for all analytes in each QCS found to be well within the acceptable range of ±10% (equivalent to 90–110%) of the true concentration.

Accuracy

Laboratory Fortified Matrix (LFM) – To assess and demonstrate method accuracy and precision, one of the water samples was spiked in duplicate at a concentration level of 50 µg·L⁻¹ for all analytes (except for Hg, which was spiked at a concentration level of 0.5 µg·L⁻¹). The percent recovery of each analyte was calculated automatically within Qtegra ISDS Software based on the measured concentration for the unspiked and spiked replicates of the LFM. The average percent recovery for all analytes was found to be within the range of 85–115%, against the acceptable range of 70–130%, with relative percent difference of less than 5% between duplicate spike measurements. Table 6 lists the analytes and their average percent recovery calculated from duplicate measurements of spiked water sample.

Analysis of Certified Reference Material (CRM) and

observed accuracy – To further demonstrate method accuracy, a certified reference material (SLRS-5, natural river water) was analyzed three times during a long-term analysis of more than 16 hours. 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 SLRS-5 CRM. Table 7 summarizes the list of analytes, their certified concentration values, and calculated percent accuracy. The percent accuracy values given are the average calculated from three different measurements of SLRS-5 CRM.

Table 6. Average percent recovery calculated from the duplicate measurement of spiked water sample (spike levels 0.5 µg·L⁻¹ for Hg and 50 µg·L⁻¹ for other analytes)

| Analyte | Concentration in unspiked water sample (µg·L ⁻¹) | Measured spike concentration (µg·L ⁻¹) | Spike recovery (%), n=2 |
|---------|--|--|-------------------------|
| Ag | 2.4 | 54.1 | 108.2 |
| Al | 15.5 | 48.9 | 97.8 |
| As | 0.015 | 52.4 | 104.9 |
| Ba | 14.3 | 51.1 | 102.3 |
| Be | 0.036 | 52.5 | 105.1 |
| Cd | 0.032 | 51.0 | 102.1 |
| Co | 0.087 | 51.0 | 102.0 |
| Cr | 0.084 | 51.0 | 102.0 |
| Cu | 89.9 | 52.2 | 104.4 |
| Fe | 91.3 | 52.0 | 104.0 |
| Hg | 0.019 | 0.52 | 104.9 |
| Mn | 0.011 | 51.9 | 103.9 |
| Mo | 0.312 | 52.3 | 104.6 |
| Ni | 5.4 | 46.8 | 93.6 |
| Pb | 0.304 | 54.0 | 108.0 |
| Sb | 0.024 | 54.8 | 109.6 |
| Se | 0.122 | 49.5 | 99.1 |
| Th | 0.095 | 55.2 | 110.3 |
| Tl | 0.158 | 54.0 | 107.9 |
| U | 0.055 | 55.1 | 110.3 |
| V | <DL | 51.6 | 103.3 |
| Zn | 79.3 | 49.9 | 99.7 |

Table 7. List of analytes, certified concentrations and accuracy (as percent) of the certified reference material (CRM) SLRS-5

| Analyte | Certified concentration (µg·L ⁻¹) | Accuracy (%), n=3 |
|---------|---|-------------------|
| Al | 49.5 ± 5.0 | 95.2 ± 5 |
| As | 0.413 ± 0.039 | 94.2 ± 7 |
| Ba | 14.0 ± 0.5 | 112.1 ± 3 |
| Be | 0.005* | 100.0 ± 3 |
| Co | 0.05* | 106.8 ± 3 |
| Cr | 0.208 ± 0.023 | 93.8 ± 6 |
| Cu | 17.4 ± 1.3 | 94.4 ± 2 |
| Fe | 91.2 ± 5.8 | 105.1 ± 6 |
| Mn | 4.33 ± 0.18 | 104.2 ± 4 |
| Mo | 0.27 ± 0.04 | 103.4 ± 5 |
| Ni | 0.476 ± 0.064 | 91.6 ± 1 |
| Pb | 0.081 ± 0.006 | 97.3 ± 2 |
| Sb | 0.3* | 86.2 ± 4 |
| U | 0.093 ± 0.006 | 93.0 ± 7 |
| V | 0.317 ± 0.033 | 101.3 ± 2 |
| Zn | 0.845 ± 0.095 | 97.4 ± 3 |

*Information values, as per CRM certificate of analysis

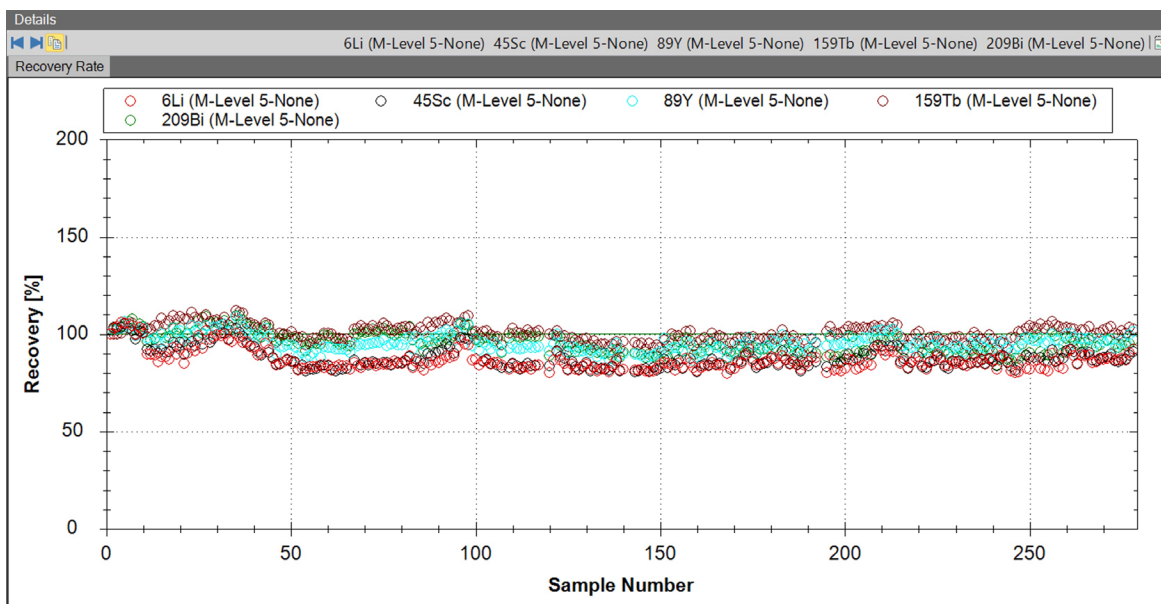


Figure 1. Internal standard recovery plot from a Qtegra LabBook, highlighting the consistent recovery of internal standards within 80–112% throughout the 16-hour continuous analysis

Method robustness

A robust instrument and optimized method are key requirements when analyzing varying sample matrices within an analytical run. Instrument drift and physical interferences due to the sample matrices can cause signal enhancement or suppression and must be corrected for. In addition, U.S. EPA Method 200.8 includes specific guidelines and requirements, such as internal standardization, to monitor and correct for instrument drift and physical interferences. An internal standard must be added to all standards and samples in the run sequence and must not deviate outside of the acceptable range of 60–125% compared to the response observed in the calibration blank.

As previously mentioned, an internal standard solution containing $20 \mu\text{g}\cdot\text{L}^{-1}$ of ${}^6\text{Li}$, Sc, Y, Tb, and Bi was added online during the analysis. Figure 1 shows a plot of the internal standards recovery against the calibration blank throughout the 16-hour analysis. As shown, all internal standards recoveries were within the range of 80–112%, well within the acceptance criteria of U.S. EPA Method 200.8. These results demonstrate the robustness of the method and instrument setup that included online sample dilution.

Conclusions

The quality of analytical data obtained during this study indicates that the iCAP MSX ICP-MS, equipped with a built-in AGD system for controlled and automatic dilution of the sample aerosol, is a powerful solution for the analysis of varying sample matrices within a single run sequence. Some of the important outcomes of this study are highlighted here.

- The MDLs achieved comfortably meet the requirements of the method and were below the regulations for inorganic contaminants in drinking water. This indicates that the instrument setup, with optimized sample dilution, provides the sensitivity and robustness for the analysis of a variety of water samples in a single, extended analysis.
- The accuracy and precision obtained from the analysis of the LFM and SLRS-5 CRM indicate that the developed method and instrument setup were optimized for the variety of samples analyzed. Furthermore, the ease of instrument tuning, operation, and LabBook set up through the Qtegra ISDS Software allows routine analysis of varying environmental samples with minimal effort while improving productivity.
- The accurate results obtained from the analyses of the QCS samples demonstrate on-going instrument performance and calibration over the extended analysis of varying sample matrices.
- The internal standard recoveries of 80–112% observed during the 16-hour analysis demonstrate robustness of the instrument and that the dilution applied to each sample was helpful in minimizing the effects of physical interferences.
- The QC toolkit included within the Qtegra ISDS Software enables easy set up and compliance with the comprehensive QC protocol of U.S. EPA Method 200.8. Customizable report templates are available to provide all data required for audit and regulatory purposes. The use of the flags and limits features within the software helps highlight and call out data falling outside the acceptable concentration ranges and provides easy visualization and review of data.

References

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