

IC-MS Analysis of Perchlorate in Drinking Water

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Abstract

An ion chromatography-mass spectrometry (IC-MS) method was developed for looking at trace levels of perchlorate in drinking water using a Metrohm ion chromatograph paired with an Agilent InfinityLab LC/MSD iQ. Agilent OpenLab CDS software provided a single software solution for both instrument control and data analysis. The developed method follows the protocols described in U.S. EPA Method 332.0. Typical recoveries were 80 to 120% at the 0.5 and 1 µg/L level in synthetic drinking, ground, and surface water samples within a method detection limit (MDL) of less than 100 ppt.

Introduction

Perchlorate (ClO_4^-) is commonly used as an oxidant in solid fuel propellants for rockets and missiles, and it is also used in the manufacture of fireworks. Previous studies have demonstrated that perchlorate exposure can cause hypothyroidism. Therefore, an assessment of the presence of perchlorate in drinking water is necessary to assess human risk.

Recently, perchlorate contamination was found in many U.S. aquifers associated with the Colorado River in California. Other sites were also identified, but the widest contamination problem was found to be in California, Nevada, and Arizona. Perchlorate was also found at elevated levels in crops that used contaminated water for irrigation.

Ion chromatography (IC) is commonly used for the sensitive and selective analysis of ions and polar species in environmental sample matrices. Conductivity detectors are most common, but IC can also be amenable to UV-Vis, amperometric, and mass spectrometric detection. IC with conductivity detection can be used to measure perchlorate levels in drinking and wastewaters (as per EPA Method 314.0 enhanced). The method can reliably measure 1 to 5 $\mu\text{g}/\text{L}$ in drinking water, but sensitivity decreases dramatically as the complexity of the matrix is increased (such as in surface and wastewaters). Both false positive and false negative results may occur due to matrix effects and coeluting substances detected by conductivity detection.

Lower detection limits for perchlorate are needed as the EPA and state environmental agencies are looking to target levels in the 1 to 14 $\mu\text{g}/\text{L}$ range. Reliability of the measurement in heavy matrix samples is also important. Mass spectrometry (MS) pairs well with IC, as it offers lower detection limits, superior analyte identification, and better extraction from an interfering sample matrix. As per the EPA Unregulated Contaminant Monitoring Rule, detection of perchlorate by MS is more acceptable in a court of law due to its specificity and selectivity.

This application note demonstrates a method for the determination of perchlorate anions at sub-ppb ($\mu\text{g}/\text{L}$) levels in drinking water using IC-MS, following the IC-MS protocol described in the EPA Method 332.0. In this study, a Metrohm IC was paired with an Agilent InfinityLab LC/MSD iQ. Also described is the validation and integration of Metrohm IC drivers in Agilent OpenLab CDS software.

Experimental

Samples

EPA Method 332.0 was developed for perchlorate analysis for various types of water (drinking, surface, ground, and wastewater). One of the requirements of this method is to analyze 1 ppb of perchlorate in the presence of 3,000 ppm total dissolved solids (TDS), which is equal to 1,000 ppm each of chloride, bicarbonate, and sulfate.

Calibration standards were prepared in reagent water (RW).

Instruments, software, and accessories

The following instrumentation, software, and accessories were used in this application note.

Agilent instrumentation, software, and accessories:

- Agilent InfinityLab LC/MSD iQ (G6160A)
- Agilent OpenLab CDS software, version 2.6 (part number M8413-64001)
- Agilent electrospray ionization source (ESI) (G1948B)

Metrohm instrumentation, software, and accessories:

- 940 Professional IC Flex Oven/SeS/PP/Deg
- MSM-HC Rotor A
- IC conductivity detector
- 858 Professional Sample Processor – Pump
- Sample rack (148 vials)
- Metrosep ASUPP19 – 150/4.0
- Metrosep ASUPP19 Guard
- Remote box
- Remote Cable Professional IC to MS Agilent
- IC drivers for Agilent OpenLab CDS

Reagents

The following reagents were used in this study:

- Ultrapure water (ASTM D1193)
- Sodium carbonate anhydrous (Merck)
- Sodium bicarbonate (Sigma-Aldrich)
- Nitric acid

Solutions

The solutions used in this study are listed in Table 1.

Table 1. Solutions.

| Parameter | Value |
|-----------------------|--|
| Eluent | 8 mM Na ₂ CO ₃ + 0.25 mM NaHCO ₃ + 50% acetonitrile |
| Suppressor Regenerant | 1 M Nitric acid |
| Suppressor Rinsing | External water |

Standard solutions

The standard solutions were prepared in ultrapure water as shown in Table 2.

Table 2. Standard solutions.

| Standard | 1 | 2 | 3 | 4 | 5 | 6 |
|--|-----|------|-----|-----|-----|-----|
| ClO ₄ ⁻ (µg/L) | 0.1 | 0.25 | 0.5 | 1.0 | 2.5 | 5.0 |
| NaCl ¹⁸ O ₄ (µg/L) | 5 | 5 | 5 | 5 | 5 | 5 |

Sample preparation

Preparation of sodium perchlorate stock solution

(1,000 mg/L): Sodium perchlorate was weighed out at 1.230 g per 1 L of ultrapure water. Appropriate dilutions were prepared to make 10 mg/L, 1 mg/L, and 100 µg/L working standards for perchlorate.

Preparation of calibration standards: Using appropriate working standards, calibration standards were prepared as follows. The calibration curve is shown in Figure 1.

Preparation of stock matrix solution: For the stock matrix solution, 2,500 mg/L each of Cl⁻, HCO₃⁻, and SO₄²⁻ were prepared. The following were weighed out accurately in a 250 mL volumetric flask: 10.2875 g of ultrapure sodium chloride, 9.2419 g of ultrapure sodium sulfate anhydrous, and 8.6063 g of ultrapure sodium bicarbonate. Water was added to completely dissolve the salts, bringing the volume to the mark. This stock solution was used to prepare simulated matrix samples.

Preparation of stock internal standard solution: A 1,000 mg solution of Cl¹⁸O₄⁻ was prepared by dissolving 0.0131 g of NaCl¹⁸O₄ in 10 mL of RW. The anhydrous NaClO₄ salt was stored in a desiccator to minimize absorption of water from the atmosphere. The internal standard solution (ISTD) was stored in a 30 mL low-density polyethylene (LDPE) screw-cap bottle at 4 °C when not in use. A dilution of ISTD was analyzed periodically by IC-ESI-MS to monitor for oxygen exchange (i.e., replacement of ¹⁸O in the ISTD with ¹⁶O from the water).

Note: No peaks should be observed at m/z 99 or 101. If peaks at these masses are observed, prepare a fresh ISTD.

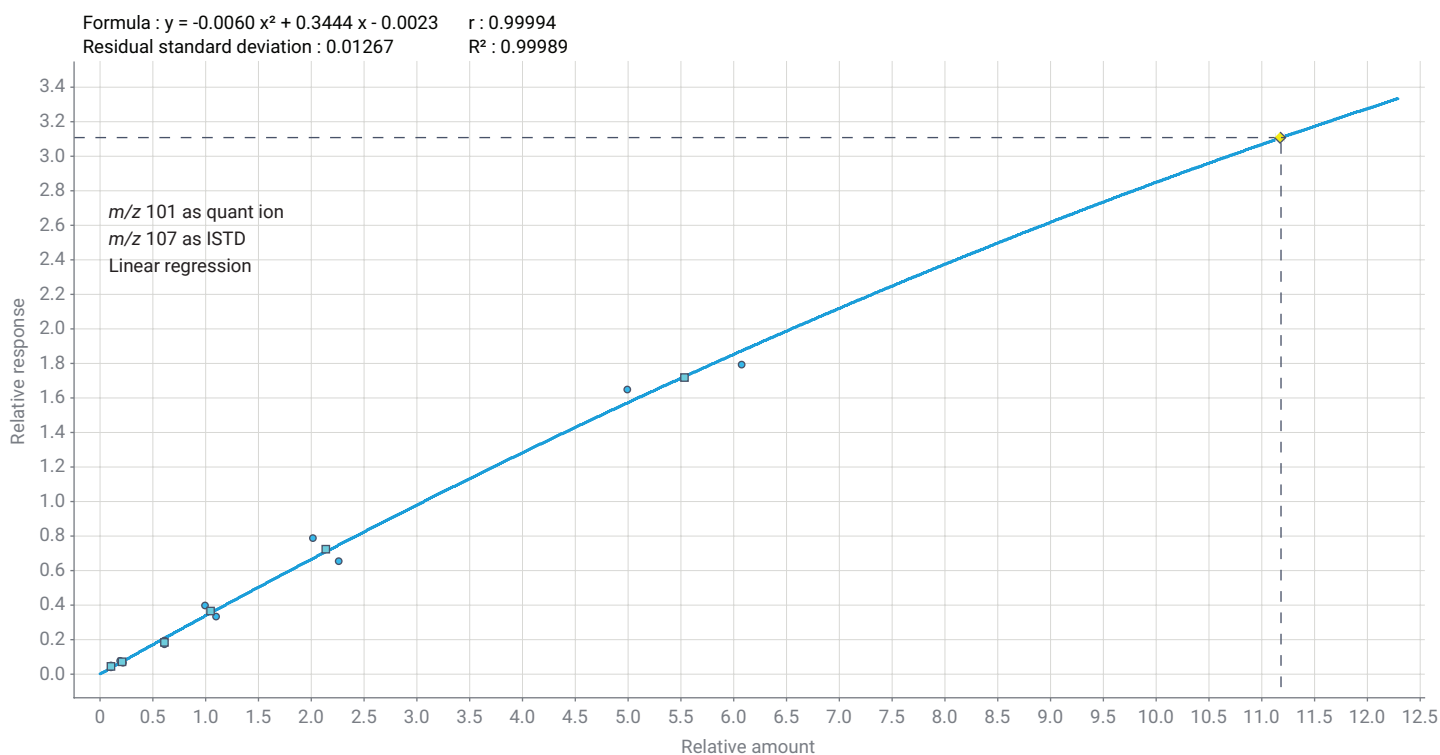


Figure 1. Calibration curve with calibration range 0.5 to 25 µg/L.

Preparation of internal standard primary dilution standard:

The internal standard primary dilution standard (IS-PDS) was prepared by adding 0.1 mL (100 μ L) of the ISTD to 99.9 mL of RW in a 125 mL LDPE storage bottle. The dilution can alternatively be performed by weight using an analytical balance with + 0.1 mg accuracy. The IS-PDS was stored in a 125 mL LDPE screw-cap bottle at 4 °C when not in use. A dilution of IS-PDS was analyzed periodically to monitor for oxygen exchange (i.e., ^{18}O for ^{16}O in the water) that would result in ClO_4^- peaks at m/z 99 or 101.

Preparation of simulated matrix sample fortified

with perchlorate: For RW fortified with 0.5 and 5 $\mu\text{g/L}$ perchlorate, 0.5 and 5 mL, respectively, of 100 $\mu\text{g/L}$ perchlorate standard were measured in 100 mL of ultrapure water. For the matrix (1,000 ppm each of Cl^- , HCO_3^- , and SO_4^{2-} = 3,000 mg/L TDS) fortified with 0.5 $\mu\text{g/L}$ perchlorate, 0.5 mL of 100 $\mu\text{g/L}$ perchlorate standard and 4 mL stock matrix standard were measured in 100 mL of ultrapure water.

Analysis

Samples were directly injected into the IC using an autosampler. **Note:** Optional inline cross-flow ultrafiltration may be used. The parameters for the IC and MS are shown in Tables 3 and 4, respectively.

Table 3. IC parameters.

| Parameter | Value |
|-------------------------|--|
| Eluent Flow Rate | 0.5 mL/min |
| Column Temperature | 32 °C |
| Sample Volume | 100 μL |
| Recording Time | 30.0 min |
| Analysis Time | 28.5 min |
| Suppression | Sequential |
| Suppressor Regeneration | Peristaltic pump; rate 1; MSM step interval 10 min |
| Detection | Conductivity |
| Polarity | Positive |
| Temperature Coefficient | 2.3%/°C |
| Calibration Curve Type | Linear |

Table 4. MS parameters.

| Parameter | Value |
|------------------------|---------------|
| Gas | Nitrogen |
| Gas Flow | 10 L/min |
| Gas Temperature | 325 °C |
| Electrospray Interface | Negative mode |
| Quadrupole Temperature | 100 °C |
| MSD Recording Time | 29.5 min |
| Capillary Voltage | -2,000 V |
| Fragmentor Voltage | 110 V |
| Nebulizer Pressure | 35 psig |

Calculation

Automatic integration using peak area for all components was achieved using Agilent OpenLab CDS software, version 2.6. The quant ion used was m/z 101.

Results and discussion

Example spectra

The chromatograms for 0.5 and 25 $\mu\text{g/L}$ perchlorate with 5 $\mu\text{g/L}$ ISTD are displayed in Figures 2 and 3, respectively.

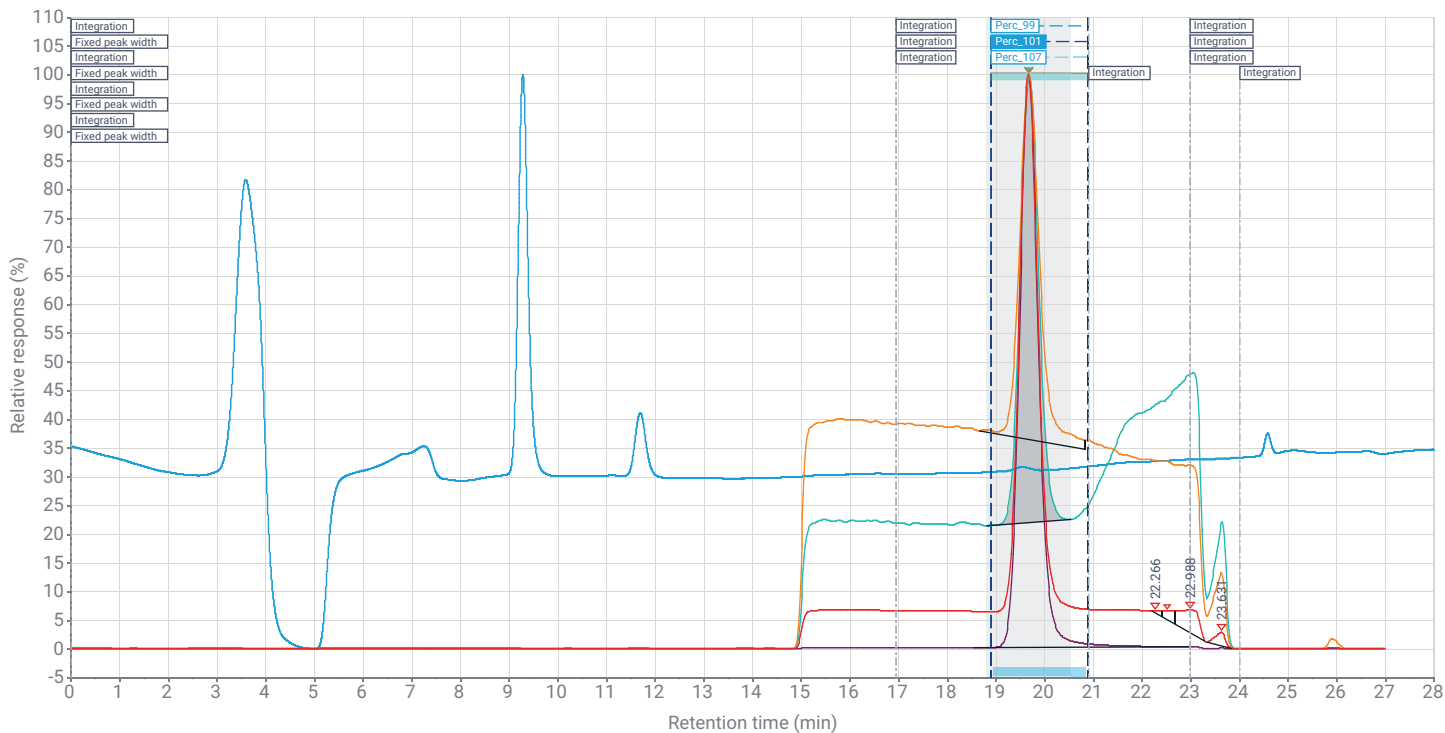


Figure 2. Chromatograms for 0.5 µg/L perchlorate + 5 µg/L ISTD.

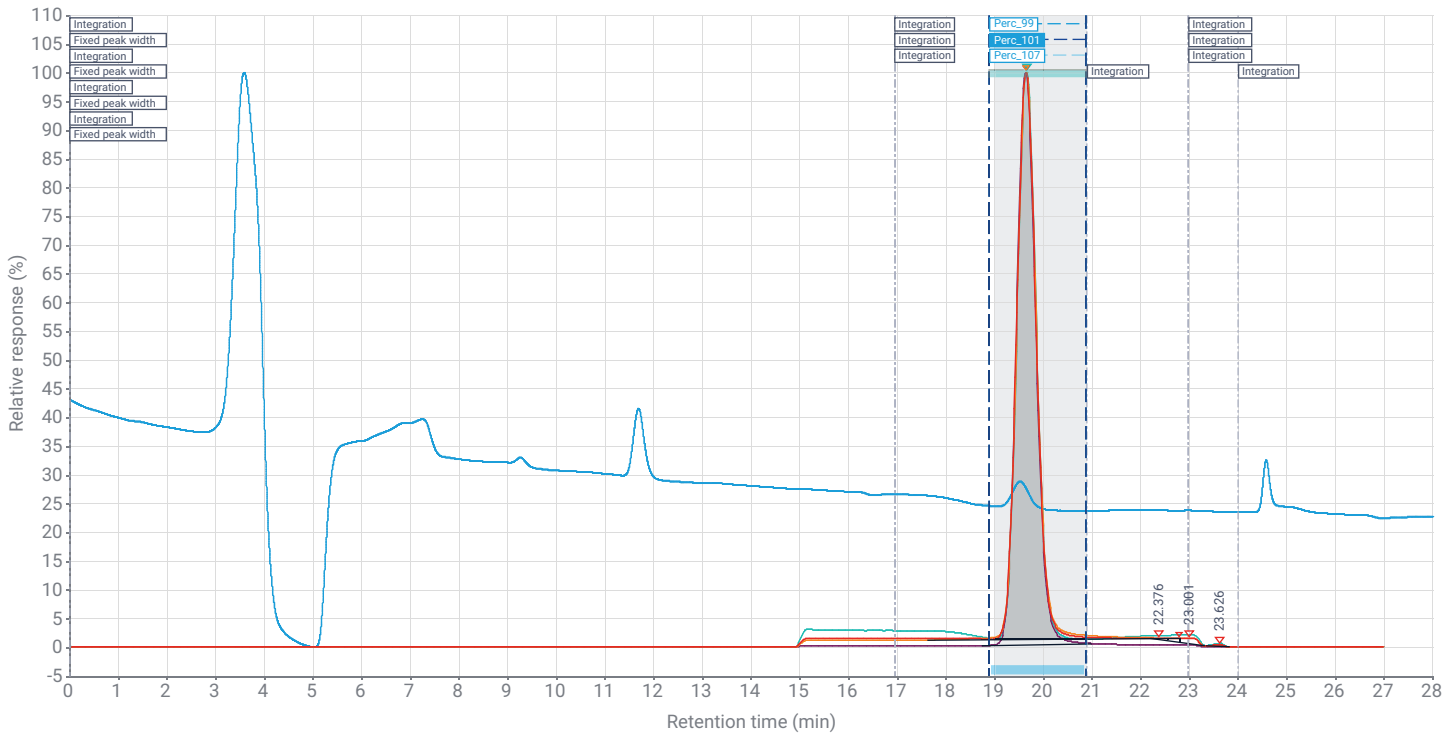


Figure 3. Chromatograms for 25 µg/L perchlorate + 5 µg/L ISTD.

The chromatogram for 3,000 ppm matrix with 1.0 µg/L perchlorate and 5 µg/L ISTD is shown in Figure 4, and demonstrates excellent resolution between matrix and analyte ion.

The chromatogram for ground water with 1 µg/L perchlorate and 5 µg/L ISTD is shown in Figure 5.

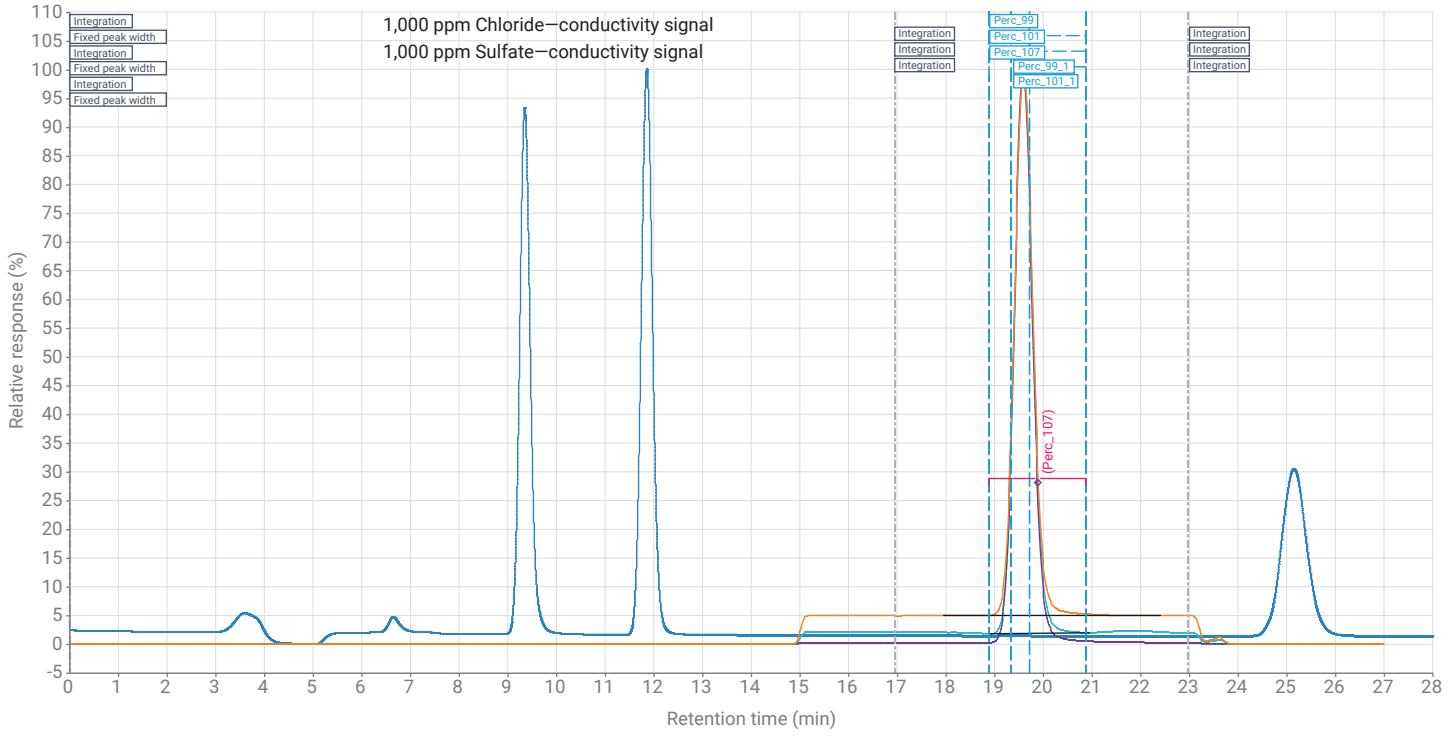


Figure 4. 3,000 ppm matrix (1,000 ppm each of Cl⁻, HCO₃⁻, and SO₄²⁻) + 1 µg/L perchlorate + 5 µg/L ISTD.

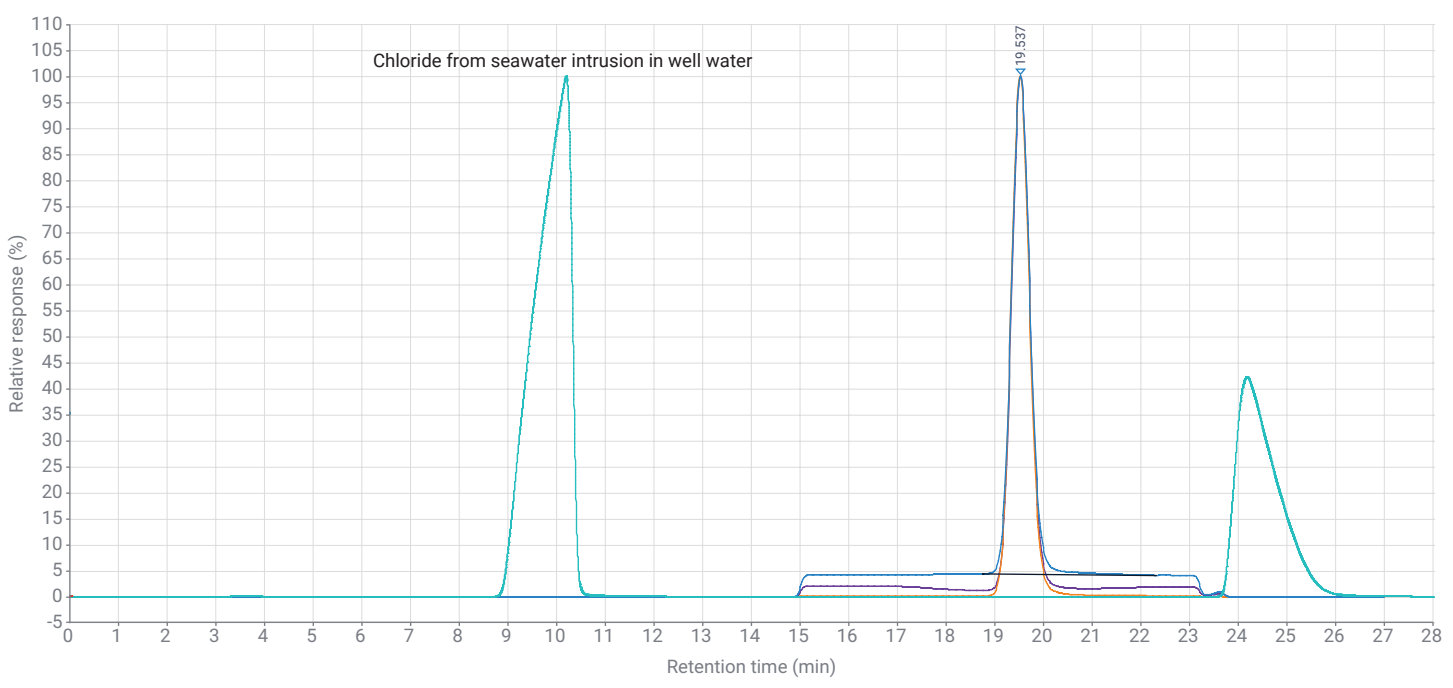


Figure 5. Ground water + 1 µg/L perchlorate + 5 µg/L ISTD.

The figure for blank de-ionized water with 5 µg/L ISTD is shown in Figure 6, and demonstrates that there is no evidence of ¹⁸O degradation to ¹⁶O, even after two years of ISTD preparation.

Maximum conductivity threshold study for perchlorate

A maximum conductivity threshold (MCT) study is required for all EPA methods for perchlorate analysis. This study must demonstrate the resolution of interfering ions from perchlorate and prove the stability of retention times (Table 5).

Table 5. MCT for perchlorate.

| Sample ID | m/z 99 | m/z 101 |
|------------------------------|----------------|----------------|
| 0.5 µg/L Standard | 0.475 | 0.448 |
| 0.5 µg/L Standard | 0.468 | 0.472 |
| 0.5 µg/L Standard | 0.459 | 0.506 |
| 0.5 µg/L Standard | 0.463 | 0.483 |
| 0.5 µg/L Standard | 0.473 | 0.483 |
| 0.5 µg/L Standard | 0.475 | 0.495 |
| 0.5 µg/L Standard | 0.486 | 0.495 |
| Average | 0.4713 | 0.4831 |
| Standard Deviation | 0.01784 | 0.01899 |
| Calculated MDL (µg/L) | 0.056 | 0.060 |

Table 6 shows the reproducibility of matrix suppression effects on 1 µg/L ClO₄⁻.

Table 6. Matrix suppression effects on 1 µg/L ClO₄⁻ (repeat injections).

| Sample ID | m/z 99 | m/z 101 |
|---|----------------|----------------|
| 3,000 ppm Matrix + 1 µg/L ClO ₄ ⁻ | 0.96 | 1.08 |
| 3,000 ppm Matrix + 1 µg/L ClO ₄ ⁻ | 1.01 | 0.98 |
| 3,000 ppm Matrix + 1 µg/L ClO ₄ ⁻ | 1.01 | 0.99 |
| 3,000 ppm Matrix + 1 µg/L ClO ₄ ⁻ | 0.93 | 0.95 |
| 3,000 ppm Matrix + 1 µg/L ClO ₄ ⁻ | 1.08 | 0.96 |
| 3,000 ppm Matrix + 1 µg/L ClO ₄ ⁻ | 1.02 | 0.98 |
| 3,000 ppm Matrix + 1 µg/L ClO ₄ ⁻ | 0.97 | 0.92 |
| Average | 0.9971 | 0.9800 |
| Standard Deviation | 0.04889 | 0.05000 |
| Calculated MDL (µg/L) | 0.154 | 0.157 |

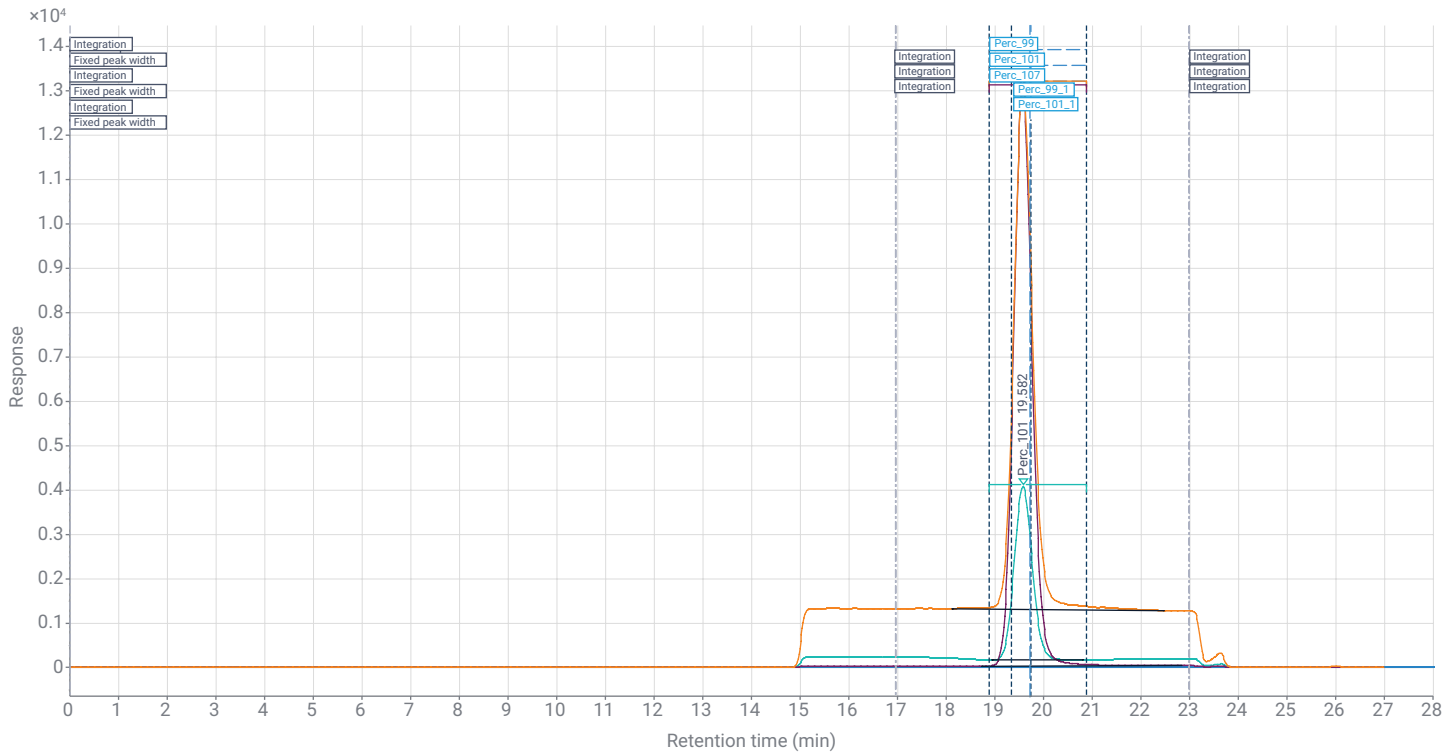


Figure 6. Blank de-ionized water with 5 µg/L ISTD.

The trend for ISTD area counts is shown in Figure 7. For any LC/MS application, "ion suppression" in electrospray is a common phenomenon. However, for this work, the instrument was in operation for more than 35 hours to analyze various samples with varying matrices. The trend line indicates and demonstrates the "ionic suppression," and indicates that there was no significant loss of performance of ESI. There was less than 15% ion suppression observed during this experiment. The ISTD does help to correct for an "ion suppression."

Calibration results

Perchlorate (m/z 101) had an RSD of 0.99994 and an R^2 of 0.999988.

Instrumental parameters for the analysis of perchlorate by IC-MS were initially chosen to reduce or eliminate suppression due to coelution of matrix and analyte ions, and to reduce the effective concentration of matrix in the electrospray interface. Choosing operating conditions in this way increased reliability and stability of the system, but at the cost of potential sensitivity. To reduce matrix suppression, a 4 mm id column was chosen over a 2 mm id column. The larger-diameter column reduced the effective concentration of matrix in the system by dilution effects. The larger column also for increased capacity and column temperature, resulting

in improved peak shape of any matrix or high-concentration materials and reduced tailing into the analyte peak. All these factors ensure that most of the matrix was well separated from the analyte for reduction or elimination of suppression effects.

In addition to the ion exchange column used for the separation, a suppression module was also used to eliminate any sodium and calcium in the sample matrix. The Metrohm IC uses a combination of three micropacked cation resin beds for suppression, which can be changed during an analysis to ensure that any one suppressor does not become saturated with cations. While one suppressor is in operation, another is reconditioning, and the third is rinsing with ultrapure water.

While not a direct problem with the detection of analyte, the presence of involatile cations could accumulate in the interface from the mobile phase. When high-TDS samples are analyzed, this could interfere with the long-term stability of the system. Complete removal of the metal cations also decreases the risk of suppression by ensuring that only protonated anions enter the MS interface. The InfinityLab LC/MSD iQ ESI interface performs best at low flow but does not show the same increase in sensitivity at higher flow as observed with other interfaces.

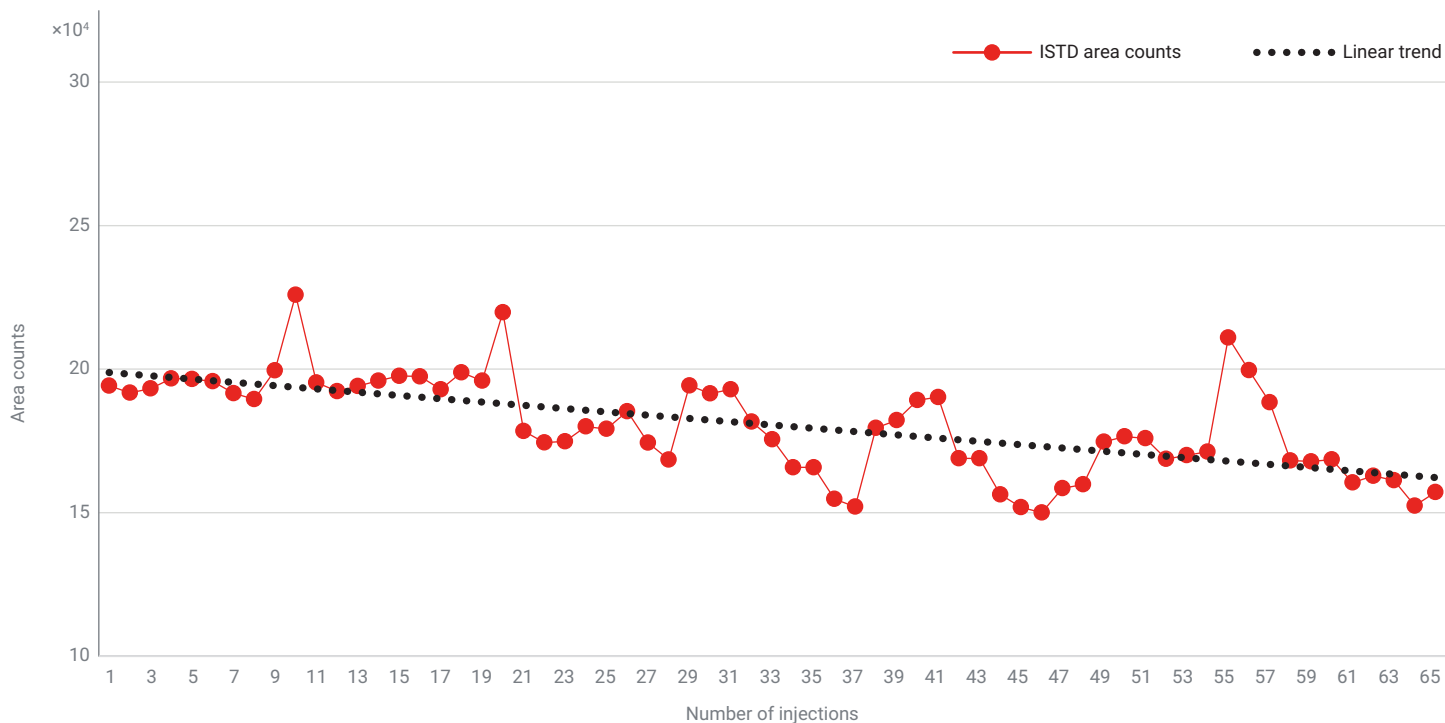


Figure 7. Trend for ISTD area counts "ion suppression" (65 repeat injections).

MS as a detector for perchlorate

The use of an MS as a detector for perchlorate at much lower detection limits (50 to 100 ppt) has shown promise, but reliability issues and problems related to suppression of the ESI signals in typical matrices are well-documented phenomena. The key to reducing suppression is to ensure that the analyte and high concentrations of matrix are well separated and do not enter the ion source at the same time, creating interference. Because of this, the use of the ISTD ^{18}O -enriched perchlorate is mandated.

In addition to ion suppression in the source, the m/z attributed to perchlorate anions (99 and 101) have isobaric interferences, which can be attributed to minor sulfate isotopes and from organic material that can be present and bleed from the column used for IC and the associated suppressor. The selection of separation column and suppressor is critical for reduction of sample bleed and for efficient separation of high levels of interfering ions, particularly sulfate.

Precautions peculiar to ion IC-MS

The use of nonvolatile buffer systems is usually avoided when performing ESI or with any atmospheric pressure ionization (API) technique. Some IC mobile phase reagents (such as strong inorganic acids) are not suited for direct introduction into API sources. The operator must be certain to avoid mobile phases that are not compatible with the stainless-steel parts of the MS. To avoid inorganic salt buildup, it is essential that a suppressor, unique to the IC technique, be employed. The suppressor removes cations from the eluent stream, after the separation column, and replaces them with a proton.

Accumulation in the API source of salts from the mobile phase and any dissolved solids in the sample are eliminated. During system equilibration, before adding the suppressor to the flow path, it is important that the effluent from the IC be diverted by the integral valve of the InfinityLab LC/MSD iQ and not directed to the ESI source. This eliminates the possibility of any sodium carbonate/bicarbonate or other mobile phase constituent from entering the source. Should a contaminating solution be introduced to the source, the MS system should be vented and surfaces up to and including the glass capillary should be cleaned. This will recover the performance lost due to eluent introduction.

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Conclusion

The results showed this IC-MS platform can successfully implement U.S. EPA Method 332.0 for the determination of perchlorate in drinking water. This study demonstrated great sensitivity, precision and accuracy, and exceptional ruggedness while all conditions were met, along with passing all other quality control requirements defined in EPA Method 332.0. The Metrohm IC coupled to the Agilent InfinityLab LC/MSD iQ accurately and precisely determined perchlorate and other oxyhalide ions while conforming to EPA Method 332.0.