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Application News

High Performance Liquid Chromatography

Perchlorate Quantitation in Drinking Water Using Suppressed Anion Chromatography Coupled with Single Quadrupole MS

■ Introduction

Perchlorate naturally forms in the atmosphere, especially in arid states in the southwestern U.S. It also occurs from the manufacture of a wide variety of industrial compounds. For instance, it is used as an oxidizer in the manufacture of munitions, missiles and fireworks. Perchlorate is considered toxic in that it may cause dysfunction of the thyroid gland and may lead to a reduction of thyroid hormones.

The EPA has established a Lifetime Drinking Water Health Advisory of 15 ppb for perchlorate to reduce health risks. More than 10 states in U.S. have established heath advisory levels for perchlorate in drinking water ranging from 1 to 18 ppb; for example, California and Maryland have proposed standards of 6 ppb and 1 ppb, respectively. A few quantitative methods for perchlorate have been developed by the U.S. EPA. Method 332.0 is one of the most sensitive methods using suppressed anion chromatography coupled with mass spectrometry.

In this study, an IC-MS method was developed using a novel electrolytically regenerated anion suppressor as a part of a modular IC system coupled with a LC-MS 2020 single quadrupole MS to achieve higher sensitivity and selectivity for perchlorate determination in drinking water. Both conductivity detection (CDD) and MS with electrospray ionization are used in the method. The CDD is used to monitor the column effluent, only the perchlorate fraction is directed to MS via a divert valve. Two predominant perchlorate ions are $^{35}Cl^{16}O_4^-$ and $^{37}Cl^{16}O_4^-$ with m/z are 99 and 101, respectively. Selected ion monitoring (SIM) of both ions was used in the method.

According to EPA 332.0, perchlorate is determined using the ions of m/z 101 due to fewer mass spectral interferences. The 3:1 area count ratio of the two ions is used for confirmation of perchlorate in samples.

The system produced a linear response with a correlation coefficient greater than 0.9999 from concentration of 0.25 ppb to 20 ppb. This study demonstrated robust and reliable performance of the novel modular IC-MS for the determination of perchlorate in drinking water.

■ Experimental

Equipment
Experiments were performed using a modular Shimadzu IC system, which consists of the following:

- Shimadzu degasser DGU-20A5R (Part Number: 228-45019-43)
- Shimadzu LC-20Ai pump (Part Number: 228-65010-58)
- Shimadzu autosampler SIL-20AC PEEK with inert kit (Part Number: 228-65106-58; 228-61451-41)
- Shimadzu column oven CTO-20A (Part Number: 228-45009-42)
- Shimadzu Conductivity Detector CDD-10Avp (Part Number: 228-45054-42)
- Shimadzu electrolytic suppressor (Part Number: 228-74006-41)
- Shimadzu LabSolutions chromatography data system software version 5.97 was used for all experiments (Part Number: 223-62701-92)

Materials
Sodium carbonate was obtained from Sigma-Aldrich.

Perchlorate (ClO_4^-) 1000 ppm was purchased from Inorganic Ventures Inc. Standards at different concentration were prepared by diluting from the commercial stock standards using degassed deionized water with resistivity equal or greater than 18.0 MΩ-cm.

Eluent preparation

Preparation of 1 L of 0.18 M stock sodium carbonate; dissolve 19.08 g sodium carbonate (Na_2CO_3) in deionized water and dilute to 1 L. Preparation of 1 L of eluent (6 mM sodium carbonate); pipet 33.3 mL of stock sodium carbonate then dilute to the mark with deionized water.

IC-MS conditions

The method conditions for both IC and MS are shown in Table 1.

Table 1: Method Conditions

IC	
Column	Concise AN1HS 50 mm x 3.0 mm I.D.
Eluent	6 mM sodium carbonate
Flow rate	0.5 mL/min
Column oven	30 °C
Injection volume	500 µL
Detection	Suppressed conductivity; 180 mA in external water mode, water flow rate is 1.0 mL/min
Auxiliary pump	Acetonitrile at 0.5 mL/min
Run time	11 min
MS (LCMS-2020)	
Ionization	ESI
Interface temperature	350 °C
DL temperature	250 °C
Nebulizing gas flow	1.5 L/min
Heat block	400 °C
Drying gas flow	15 L/min
Q-Array DC voltage	0 V (SIM)
Selected ions m/z	99, 101

■ **Results and Discussion**

The schematic diagram of the IC-MS system used in this study is illustrated in Figure 1. Common to anion exchange chromatography, the non-volatile eluent, sodium carbonate (Na_2CO_3) is used to affect the separation. Eluent then passes through an electrolytically regenerated suppressor to remove the sodium ions and any analyte counter cations prior to entering the conductivity detector flow cell and mass spectrometer.

In this method, external fresh water is continuously pumped through the suppressor regeneration channel at a 1 mL/min flow rate using the second pump to affect the electrolysis regeneration of the suppressor and yield a more stable, low noise baseline for the determination of perchlorate at low ppb levels. The conductivity detector is used to monitor column effluent. Only the perchlorate peak fraction is directed to the MS using a divert valve; this protects the MS from a buildup of trace salts from the eluent post-suppressor.

Based on the peak shape and retention time of perchlorate, the divert fraction was set from 5.5 to 10 min to get perchlorate fully recovered. A third pump provided an auxiliary flow of acetonitrile post-suppressor to enhance MS perchlorate response.
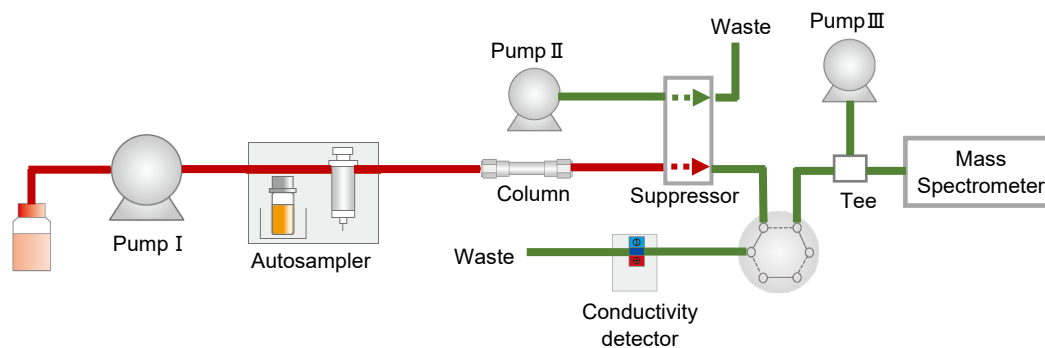

Figure 1: Schematic diagram of IC-MS system for perchlorate analysis.

Linearity and Method Detection Limit
A five-point calibration curve was established across the concentration range of 0.25 to 20 ppb. Correlation coefficients of $r^2 > 0.9999$ were obtained for both ions, m/z 99 and 101, as shown in Figure 2. Figure 3 shows the overlay chromatogram of perchlorate m/z 101 at each calibration level and zoom in perchlorate peak at concentration of 0.5 and 0.25 ppb.

The Method Detection Limit (MDL) is a statistically calculated concentration, defined as the minimum concentration of a compound that can be measured with 99% confidence that the measured concentration is distinguishable from a blank. The MDL was investigated by making seven replicate injections of 0.5 ppb perchlorate standard. The MDL was calculated as (t) x (S), where t is student's t value for 99% confidence level (t = 3.14 for seven replicates) and S is standard deviation from seven injections. The MDL study shows that a level of 50 ppt perchlorate can be determined with 99% confidence using this method.
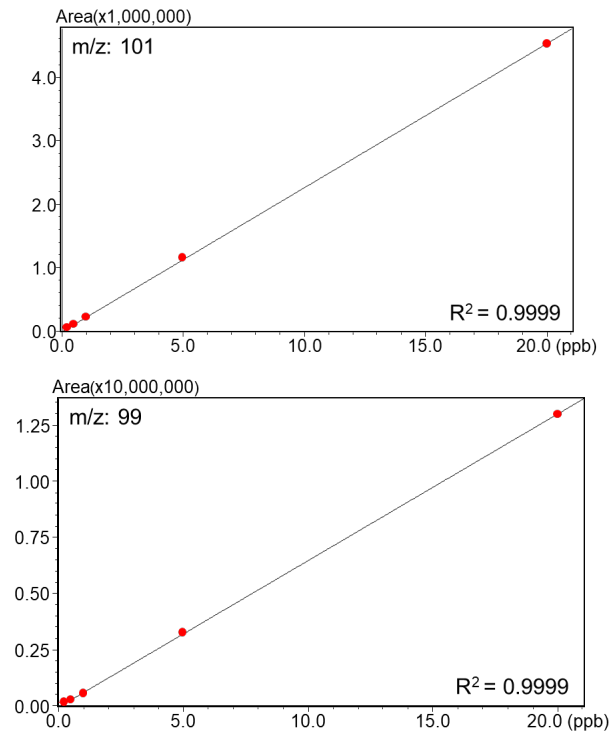

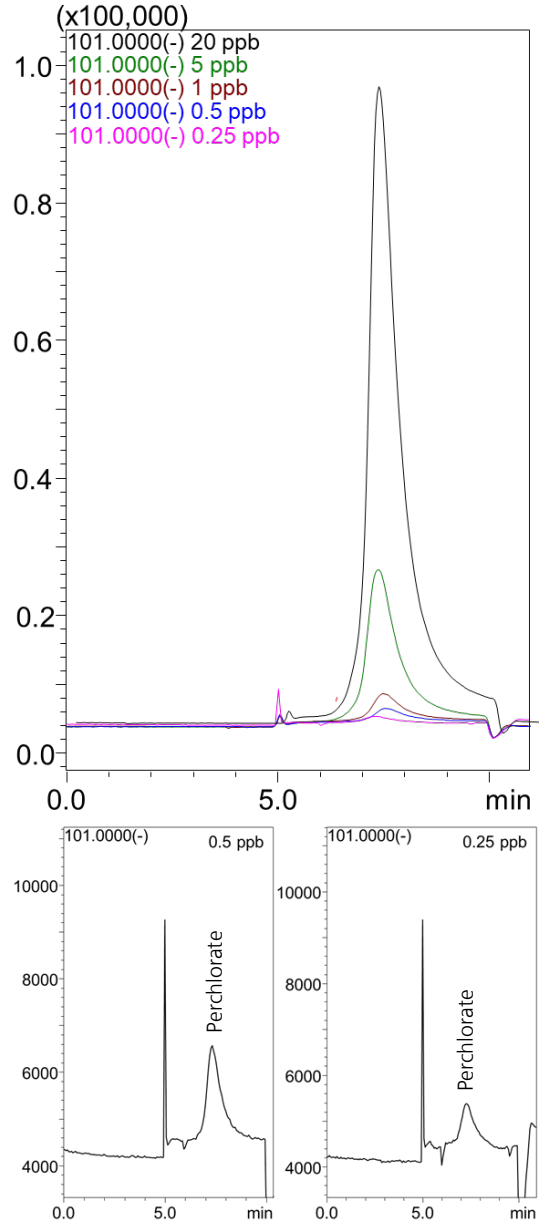**Figure 2**: Standard curves for ions m/z 101 and 99.

Figure 3: Chromatogram of perchlorate m/z 101 at each calibration level.

Reproducibility and Accuracy

Method precision was performed using two perchlorate standards with concentration of 0.5 ppb and 1 ppb, respectively. Table 2 shows retention time precision and peak area precision of m/z 101 from 7 injections for each concentration. As shown in the table, excellent reproducibility was achieved for both retention time and peak area, even for the sample at low concentration of 0.5 ppb. Table 2 also shows the area count ratio of m/z 99 to 101 are 2.74 and 2.65 for 0.5 and 1 ppb perchlorate standard, respectively. The results shown in the table meet the area account ratio requirement for confirmation of perchlorate, which is the range of 2.31-3.85 specified in EPA 332.0.

Table 2: Retention time and peak area reproducibility over 7 injections

ClO_4^- Standard (ppb)	Tr Precision (%RSD)	Area Precision (%RSD)	Area count ratio m/z 99 to 101
0.5	0.25	3.79	2.74
1	0.06	0.92	2.65

The performance and accuracy of the method were investigated by spiking perchlorate standards of 2 ppb and 10 ppb concentration into blank water. 96% recovery was obtained for the first concentration. A recovery of 99.3%% was obtained for the second concentration.

Determination of perchlorate in tap water and bottled water

Figure 4 shows a chromatogram of laboratory tap water using the method developed in this study. Panel A is the chromatogram from the conductivity detector. As shown in the figure, the most common anions in the water including fluoride, chloride, nitrite, bromide, nitrate, phosphate and sulfate were eluted in 4 minutes in the analysis. Divert flow to the MS started at 5.5 minutes, perchlorate was eluted at 7.4 min and detected by MS as shown in panel B. The area count ratio of m/z 99 to 101 in this analysis is 2.74, the value identified perchlorate elution. Perchlorate is quantified using the ions of m/z 101, 0.315 ppb of perchlorate was measured.

Figure 5 is a chromatogram of perchlorate analysis of a bottled water. The measured perchlorate concentration in this bottled water is 0.09 ppb, nevertheless the concentration is out of the calibration range.
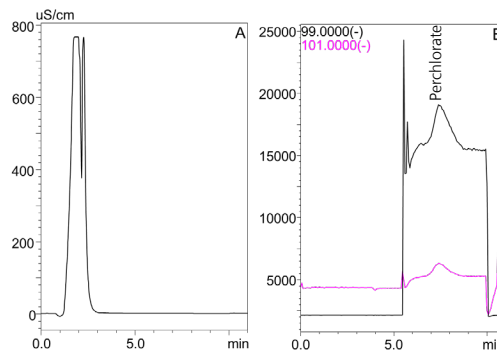

Figure 4: Perchlorate analysis of tap water using IC-MS. Panel A: chromatogram from the conductivity detector, panel B: perchlorate chromatogram from MS.
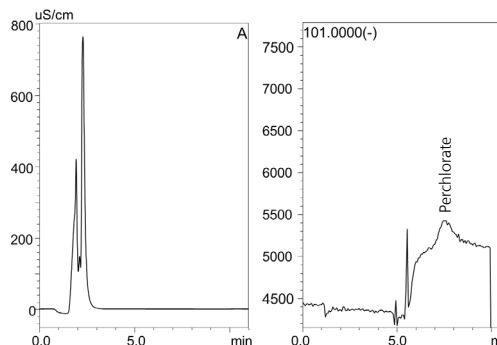

Figure 5: Perchlorate analysis of bottled water using IC-MS. Panel A: chromatogram from the conductivity detector, panel B: perchlorate chromatogram from MS.

■ **Conclusion**

A Shimadzu suppressed anion chromatograph coupled with a single quadruple MS provides sensitive and reliable performance for the determination of perchlorate in drinking water. The method detection limit obtained in this study is 0.05 ppb, and the method precision, accuracy and sample recovery obtained in the method meets the quality criteria outlined by EPA 332.0.

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