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Determination of Perchlorate in Drinking Water using Suppressed Anion Chromatography Coupled with Single Quadrupole MS

Hui Guo, PhD; Ruth Marfil-Vega, PhD
Shimadzu Scientific Instruments, Inc.

1. Introduction

Perchlorate is considered toxic in that it may cause dysfunction of the thyroid gland and may lead to a reduction of thyroid hormones. Despite current lack of regulation at federal level, there are several states where perchlorate needs to be monitored in drinking water to ensure compliance with the corresponding Maximum Contaminant Levels. A few perchlorate determination methods have been developed by the U.S. Environmental Protection Agency (EPA). EPA Method 332.0 is one of the most sensitive methods using suppressed ion 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 (ESI) 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. The system produced linear response with coefficient of determination greater than 0.9999 from concentration of 0.25 ppb to 20 ppb. This study demonstrated the robust and reliable performance of the novel modular IC-MS for the determination of perchlorate in drinking water.

2. Experimental

Experiments were performed using a modular Shimadzu Prominence IC system with built-in electrolytically regenerated suppressor and a single quadrupole mass spectrometer detector (LCMS-2020) with ESI interface.
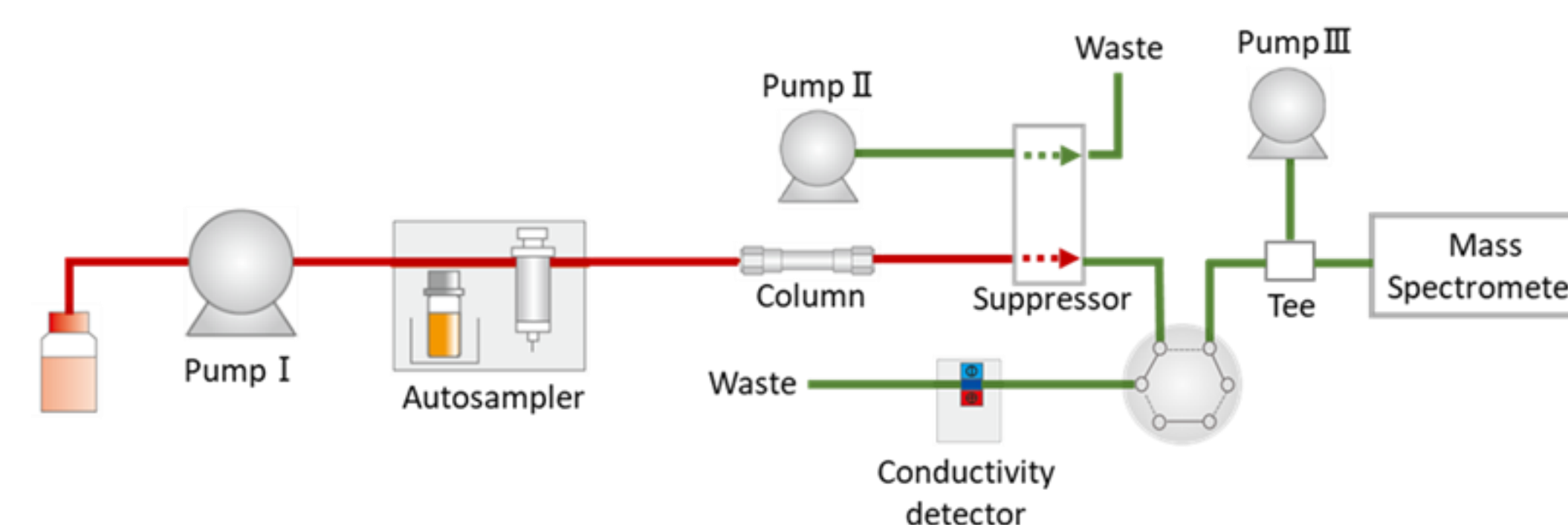
Prominence IC and LCMS-2020

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

The schematic diagram of the IC-MS system used in this study is illustrated in Figure 1. 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 CDD 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. A third pump provided an auxiliary flow of acetonitrile post-suppressor to enhance MS perchlorate response. Method conditions are listed in Table 1.

Table 1 Method conditions

IC (Prominence)	
Column	Concise AN1HS 50mm 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 ºC
Drying gas flow	15 L/min
Selected ions m/z	99, 101

3. Results and Discussion

A five-point calibration curve was established across the concentration range of 0.25 to 20 ppb as shown in figure 2. Correlation coefficients of $r^2 > 0.9999$ were obtained for both ions, m/z 99 and 101, and excellent accuracy (between 93.8% and 102.3%) was achieved for m/z 101.
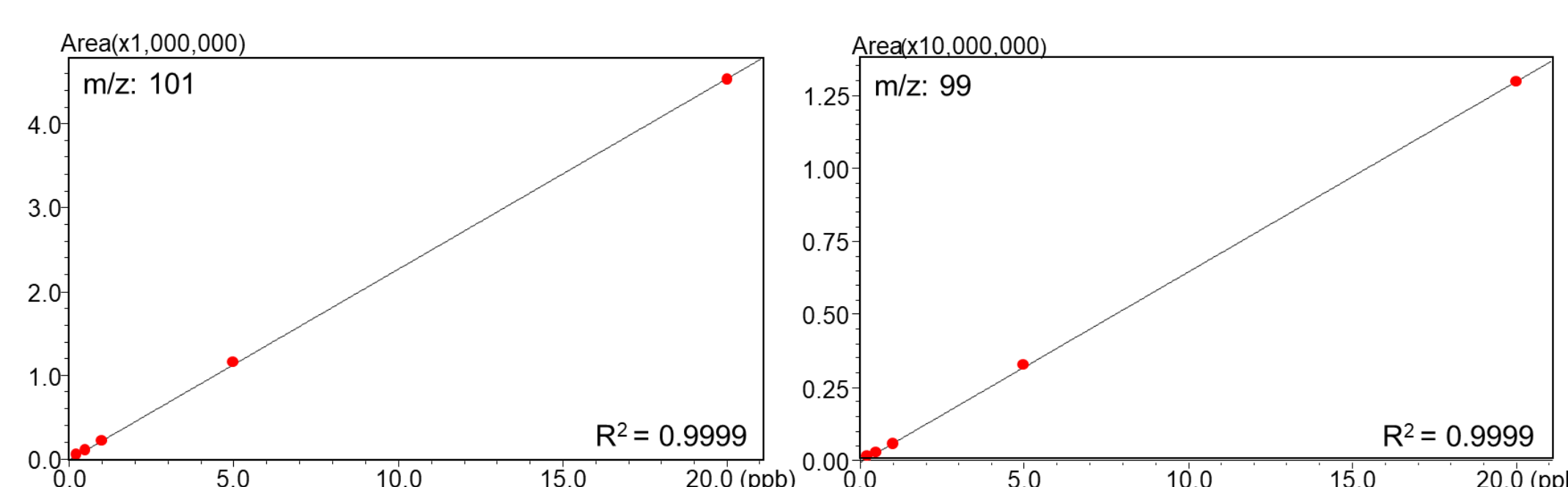

Fig. 2 Standard curves for ions m/z 101 and 99.

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.

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 count ratio requirement for confirmation of perchlorate outlined in EPA 332.0 (range: 2.31- 3.85). 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 from spiking 2 ppb standard. A recovery of 99.3% was obtained from spiking 10 ppb standard.

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

Figure 3 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 panel A, the most common anions in the water including fluoride, chloride, nitrite, bromide, nitrate, phosphate and sulfate quickly coeluted 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 presence of perchlorate (m/z 99 and 101) ions were monitored as shown in panel C. The area count ratio of m/z 99 to 101 in this analysis is 2.74, the value confirmed perchlorate elution. Perchlorate m/z 101 is used for the quantitative analysis. The concentration of perchlorate quantified in the laboratory water was 0.315 ppb.
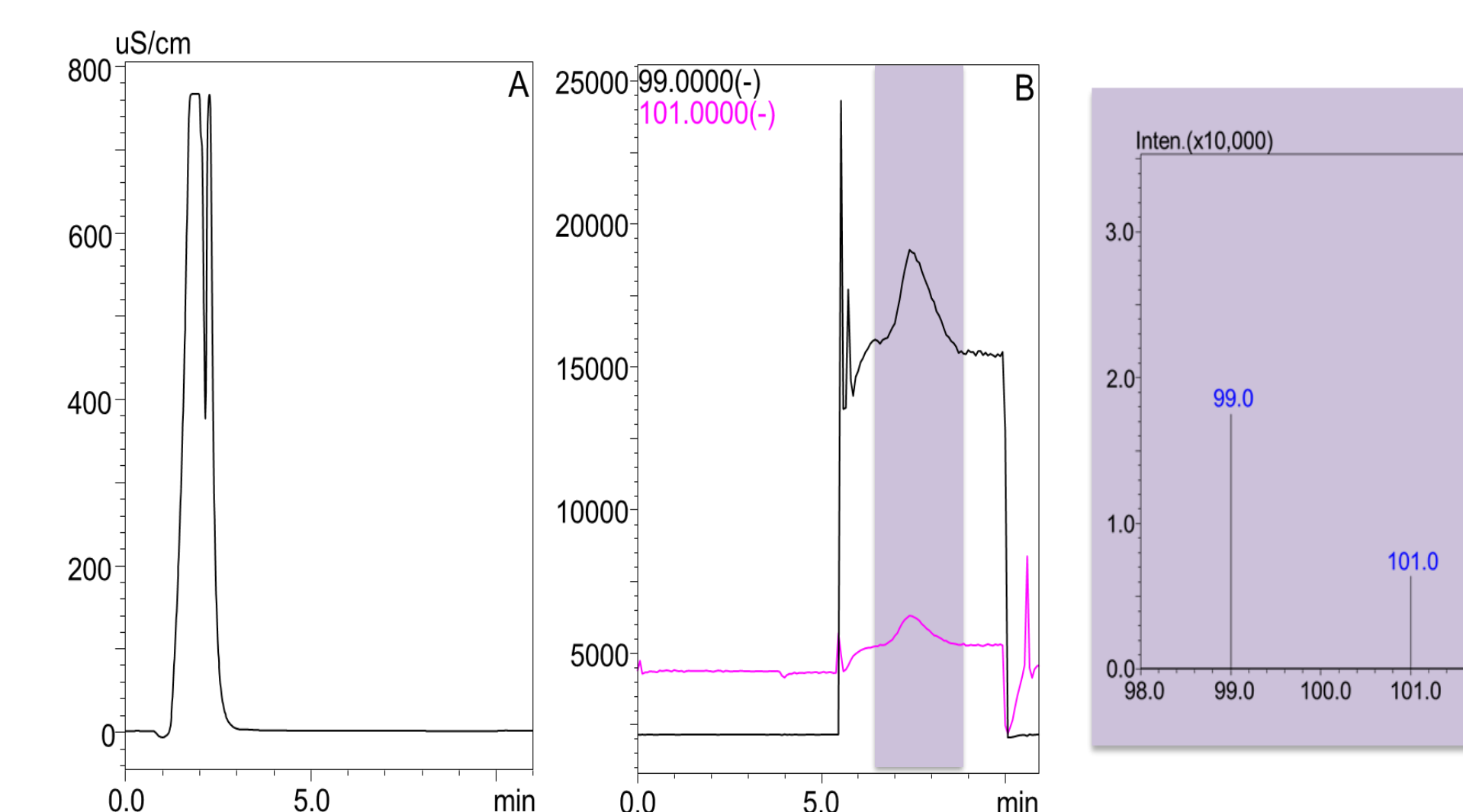

Fig. 3 Perchlorate analysis of tap water using IC-MS. Panel A: chromatogram from the conductivity detector, panel B: perchlorate chromatogram from MS, panel C: perchlorate (m/z 99 and 101) ions were found in mass spectra.

4. Conclusion

A Shimadzu Prominence IC coupled with LCMS-2020 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.