SHIMADZU

Application News

No.C85

Liquid Chromatography Mass Spectrometry

Analysis of Perchlorate in Water by Non-Suppressed Ion Chromatography-Mass Spectrometry

Perchlorate is a chemical substance that occurs both naturally and as a manufactured compound, and is used in a wide range of applications. It is a common accelerant in rocket engines and an explosive in the pyrotechnics industry. From the standpoint of health, however, it is now suspected to be associated with hypothyroidism. Thus, in 2005, the U.S. Environmental Protection Agency (EPA) set the reference dose (RfD) of perchlorate to 0.0007 mg/kg body weight/day. This reference dose is reflected in the limit of 24.5 ppb in drinking water. In Japan, perchlorate is a required test item as specified in the Waterworks Law.

For perchlorate analysis, the EPA method[1), 2), 3)] specifies that following separation by reversed phase or anion-exchange chromatography, detection must be conducted by mass spectrometry. For anion-exchange chromatography in the non-suppressed mode as specified in Method 331.0, a 100–200 mmol/L volatile salt solution is used as the eluent. Despite its volatility, highly concentrated salt eluent is a source of contamination which can adversely affect ionization efficiency or contaminate an instrument, so the amount used must be kept to a minimum.

Here, we introduce an example of analysis of perchlorate using the Shim-pack IC-A3 (S) anion-exchange column. This column permits the analysis of perchlorate using a low-concentration volatile salt eluent, which is suitable for the mass spectrometer.

We checked the analytical conditions using an eluent consisting of an aqueous solution of 25 mmol/L ammonium acetate containing 20 % acetonitrile, and the perchlorate ion eluted in about 16 minutes. To prevent the anions (F^-, Cl^-, NO_2^-, Br^-, NO_3^-, PO_4^{3-}, SO_4^{2-}), etc. from being introduced into the mass spectrometer before the later eluting perchlorate ion, the portion of the eluate from 0–11.5 minutes was diverted from the column to waste. During that time, a solution with the same composition as the eluent was directed into the mass spectrometer using a separate pump to maintain liquid flow into the source and prevent a shock to the interface due to a sudden change from zero to constant flow.

Analysis of Standard Solution

The perchlorate ion is detected using electrospray ionization (ESI)-LC/MS. The $^{35}ClO_4^-$ *m/z* 99 ion is detected as the base peak of the perchlorate ion spectrum. Fig. 1 shows the selected ion monitoring (SIM) chromatogram of a perchlorate standard solution.

Here, the peak area %RSD (n = 5) of the perchlorate was 4.21. Fig. 2 shows the calibration curve over the concentration range of 0.3125–10 µg/L. Excellent linearity was obtained, with a correlation coefficient (R^2) greater than 0.9999.

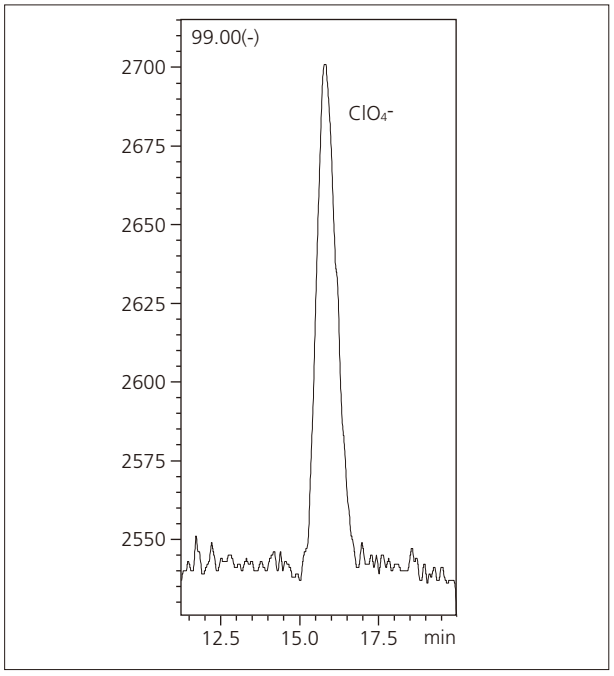

Fig. 1 SIM Chromatogram of ClO_4^- (0.625 µg/L)

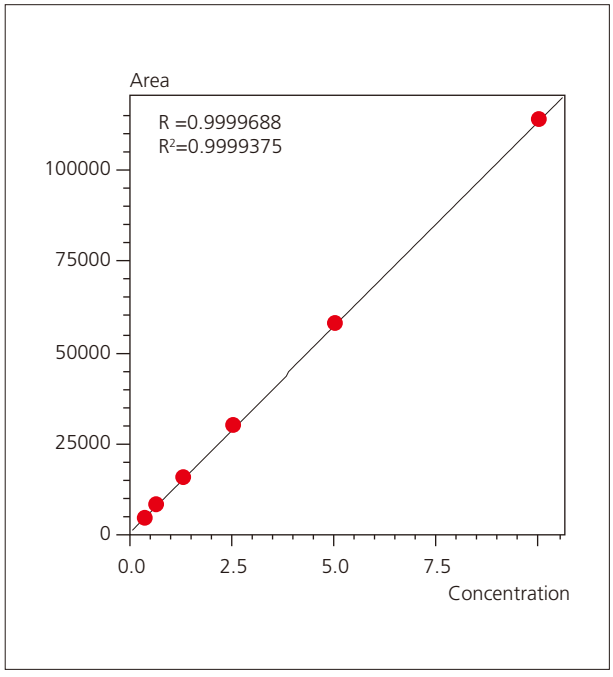

Fig. 2 Calibration Curve (0.3125–10 µg/L)

1) EPA METHOD 331.0 Document #: 815-R-05-007
2) EPA METHOD 332.0 Document #: EPA/600/R-05/049
3) EPA METHOD 6850

Analysis of Environmental Water

Next, we introduce an example of analysis of perchlorate in environmental water. Fig. 3 shows the SIM chromatograms obtained from analysis of tap water, lake water, and river water, respectively, that had been spiked with 1 µg/L ClO_4^-. After adding perchlorate to the lake water and river water, the samples were filtered through a 0.22 µm membrane filter. Excellent recovery was obtained for all samples, with respective recoveries of 107 %, 101 %, and 99 %.

A non-suppressed single LC/MS system (Fig. 4) is a low-cost, easy-to-operate system for monitoring perchlorate in water such as factory wastewater.

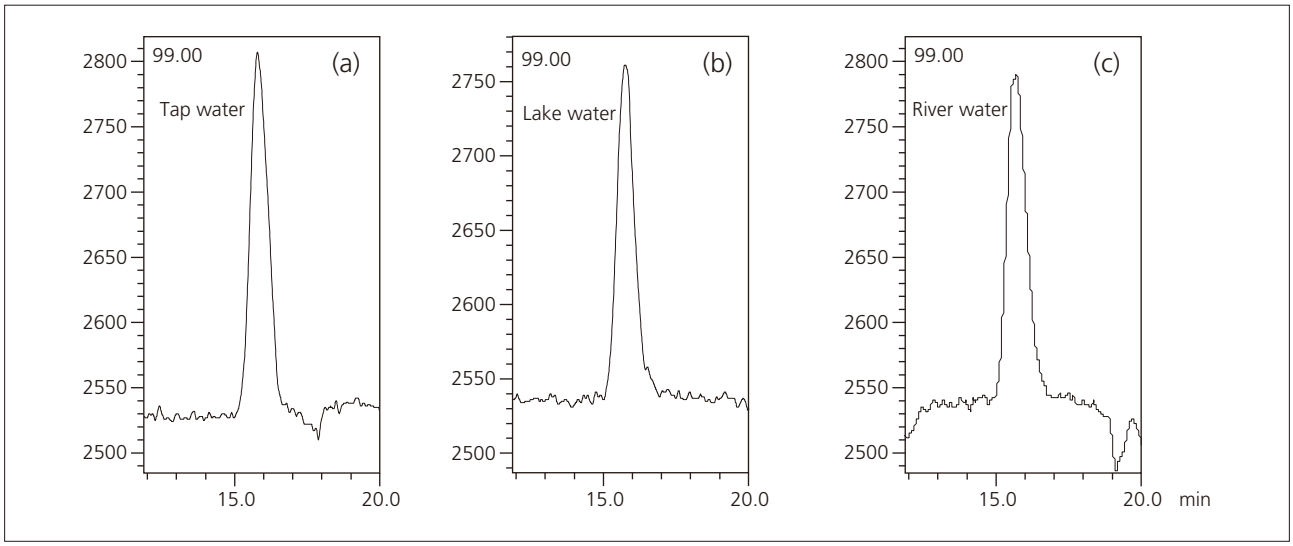

Fig. 3 SIM Chromatograms of ClO_4^- in Tap Water (a), Lake Water (b), and River Water (c)

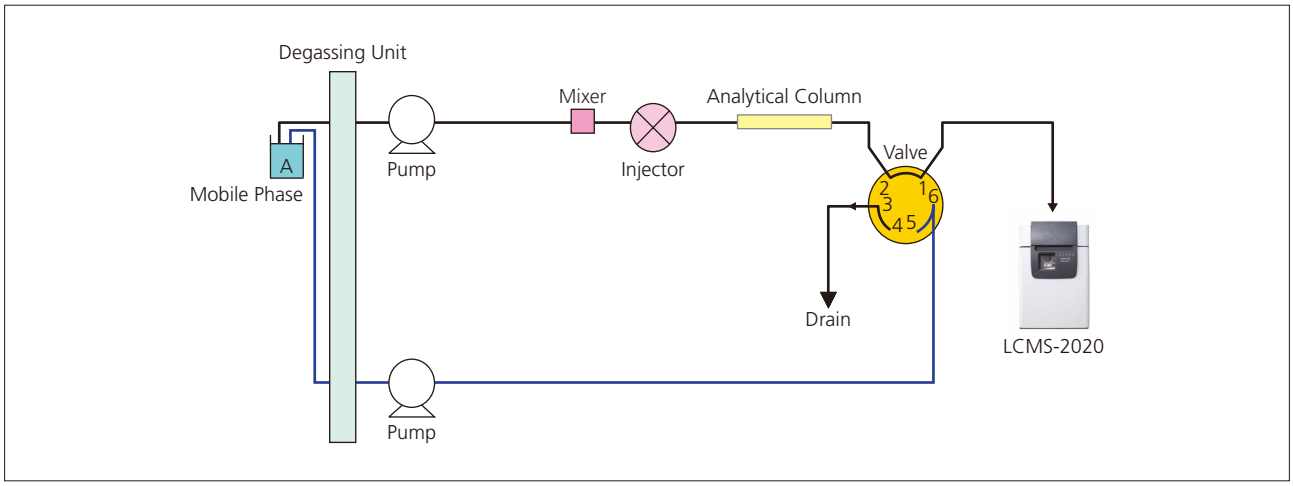

Fig. 4 Flow Diagram of LC/MS System

Table 1 Analytical Conditions

Column	: Shim-pack IC-A3 (S) (150 mmL. × 2 mmI.D.)		
Mobile Phase A	: 25 mmol/L Ammonium acetate-water / Acetonitorile = 80/20		
Flow Rate	: 0.3 mL/min		
Injection Volume	: 50 µL		
Column Temperature	: 40 °C		
Probe Voltage	: -3.5 kV (ESI-negative mode)		
Nebulizing Gas Flow	: 1.5 L/min	Drying Gas Flow	: 1.5 L/min
DL Temperature	: 250 °C	Block Heater Temprature	: 400 °C
DL Voltage / Q-array Voltage	: Using default values		

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