Determination of perchlorate in the Gum-River surface water by LC-ESI-MS/MS

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금강 지표수에서 LC-ESI-MS/MS에 의한
과염소산이온의 극미량 분석

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Abstract: A liquid chromatography-electrospray ionization-tandem mass spectrometry method (LC-ESI-MS/MS) was used for determining perchlorate in the Gum-River surface water. Sample was directly injected into LC-ESI-MS/MS after the filtrations using PTFE filter paper. The coefficient of variation of perchlorate was less than 3% and the limit of quantification was 0.17 µg/L. Water samples were collected from thirty-five basins of Gum-River on February, April and June 2012, respectively. As a result, perchlorate was detected in the concentration range of 0.23-3.73 µg/L (mean 0.20 µg/L) in the frequency of 15% in general surface water and in the concentration range of 0.36-25.10 µg/L (mean 1.69 µg/L) in the frequency of 36% in surface water samples near industry area.

요 약: 지표수 중에 과염소산이온을 LC-ESI-MS/MS을 사용하여 분석하였다. 시료는 단지 PTFE 필터를 사용하여 거른 후 LC-ESI-MS/MS 시스템에 직접 주입하여 분석하였다. 이 방법은 3% 이내의 정밀도를 보였고 정량한계는 0.17 µg/L이었다. 시료는 금강물 35 개 유역에서 2, 4, 6월에 각각 시료를 채취하였다. 그 결과 일반 하천수에서는 과염소산이온이 0.23-3.73 µg/L (평균 0.20 µg/L) 농도범위로 15% 빈도로 검출되었고 공단 근처의 지표수에서는 0.36-25.10 µg/L (평균 1.69 µg/L)로 36%의 빈도로 검출되었다.

Key words: LC-ESI-MS/MS, perchlorate, surface water, trace analysis

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1. Introduction

Perchlorate (ClO_4^-) is an extremely soluble and stable salt derived from perchloric acid.[1] Perchlorate has been used in manufacturing rocket fuel, explosives, and fireworks for decades.[2,3] It has also been used as an additive in lubricating oils, tanning, finished leather, fabric fixers, dyes, electroplating, aluminum refining, rubber manufacture, paint and enamel production, cattle feeds, and magnesium batteries.[4] The production, storage and improper disposal of wastes containing perchlorate have resulted in the contamination of environment. The water-soluble perchlorate anion moves rapidly into groundwater and surface waters. Nowadays, the detection of perchlorate contamination in the environment continues to increase, especially in groundwater, drinking water, surface water and even in bottled water.[5-14]

Due to the similarity in ionic radius, perchlorate has been reported to inhibit the iodide intake in the thyroid gland and therefore decrease the production of thyroid hormones.[15-17] The US Environmental Protectional Agency found that perchlorate may have an adverse effect on the health of persons and is known to occur in public water systems with a frequency and at levels that it presents a public health concern. The agency puts perchlorate on the final third Contamination Candidate List (CCL3), which recommends an interim health advisory level of 15 µg/L and a health reference level of 15 µg/L for perchlorate.[18-21]

In order to quantify trace perchlorate in environmental water, many methods based on different principles have been proposed. Spectrophotometry has been widely employed for the determination of hydrazine in water through the use of many kinds of ion pairing.[22-26] Electrochemical method,[27] fluorescence analysis,[28] electrophoresis,[29-32] have also been reported as techniques for the determination of perchlorate and ion chromatography (IC) methods were conventionally used to analyze perchlorate in environmental water.[5,33-40] But the sensitivities of these methods are not adequate to detect low µg/L in environmental water. IC coupled with mass spectrometry (IC-MS) methods[41-46] and

liquid chromatography mass spectrometry (LC-MS) using an ion exchange column[47,49] were commonly utilized to quantify trace perchlorate in aqueous media such as drinking water. But this method has disadvantages of the use of online solid phase extraction (SPE) for the sample clean-up.

This study aimed to detect perchlorate in the Gum-River by a simple LC-MS/MS method without the extraction procedure. The method sensitivity, accuracy and precision were investigated.

2. Experimental

2.1. Materials

HPLC-grade methanol (MeOH) and acetonitrile were purchased from Mallinckrodt Baker, Inc. (Paris, KY, USA). Deionized water was obtained from a Milli-Q Integral 5 water purification system (Millipore, Bedford, MA, USA). Ammonium hydroxide (NH_4OH) and acetic acid were from J.T. Baker (Phillipsburg, NJ, USA) and Fluka (Steinheim, Germany), respectively. The stock solutions (1000 g/mL) of perchlorate (ClO_4) and other anion standards were purchased from AccuStandard Inc. (New Haven, CT, USA).

2.2. Water sampling and injection

Surface water samples were collected from thirty-five basins in the Gum River, which contain thirteen surface water samples near industry area. The sampling sites were selected to uniformly represent all streams of the River and the sampling time was on February, April and June 2012.
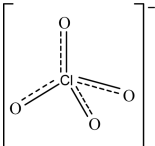
The samples were filtered (PTFE, 0.22 µm) and a 10 µL sample of the solution was injected into the LC-MS/MS system.

2.3. Liquid chromatography-mass spectrometry

The liquid chromatography was an Agilent 1200 series (Agilent, Palo Alto, CA, USA) equipped with a binary pump, online vacuum degassing system, and autosampler.

The analytes were separated using a 50 × 2.0 mm Dionex IonPac AG16 column (Dionex, USA) with a

Table 1. Structure, mass, precursor ion, product ions, fragment voltage and collision energies of perchlorate

Full name	Structure	Molecular formula	Exact mass (*m/z*)	Ion mode	Precursor ion (*m/z*)	Product ions (*m/z*)	Fragment voltage (V)	Collision energy (eV)
Perchlorate		ClO_4^-	98.9490	Negative	99.1 ([M]$^-$)	83.1([M]$^-$-O)	135	20
						67.1([M]$^-$-O$_2$)	135	7

flow rate of 0.7 mL/min was used. Mobile phase A and B were water and 50 mM ammonium hydroxide in water, respectively. The isocratic was used with the composition of mobile phase A 90% and mobile phase B 10%. All of the compounds were eluted within 9.0 min.

The MS-MS detection was performed on a Quattro micro triple quadruple instrument (Agilent, Palo Alto, CA) equipped with an atmospheric pressure ionization (API) interface. The mass spectrometer was operated with electrospray ionization in the negative ion mode (ESI-). The capillary voltage was set to 3.2 kV. The source temperature was 120 °C and the desolvation temperature was 450 °C. Nitrogen was used as desolvation gas (flow 500 L/h) and argon was used as collision gas at a pressure of 3×10^{-3} mbar. Detection was performed in a multiple reaction monitoring (MRM) mode. The fragment voltage and the collision energy were optimized for the different analytes (*Table* 1).

2.4. Calibration and quantification

Calibration curve was established after adding 0.01, 0.05, 0.1, 0.5, 1.0, 2.5, 5.0 and 10.0 µg of the standard in 100 mL blank surface water, in which perchlorate was not detected.

The lowest limit of detection (LOD) and limit of quantification (LOQ) were determined as the lowest concentration of the standard solution resulting in a signal-to-noise ratio of 3:1 and 10:1. Precision and accuracy experiments were performed from water samples spiked with 0.1 and 2.5 µg/L of the analyte in the blank surface water.

3. Results and discussion

3.1. LC-MS/MS optimization

ESI full scan and tandem mass spectra in both polarity modes are measured for perchlorate. As the objective of this work was to detect a very small amount of perchlorate residue in the samples, the MRM mode was chosen. To carry out analysis in MRM, the precursor ion with higher abundance was chosen to achieve more sensitivity and that with higher *m/z* ratio was chosen to achieve more specificity. MS/MS spectra of the precursor ion showed a notable number of product ions optimized different collision energies.

Fig. 1 shows the LC-MS chromatogram of the spiked standard in pure water and the real sample. The discrimination by ion selection was very good. In order to improve the sensitivity of the proposed method, separation of the baseline resolution from the target compounds was performed using a isocratic mobile phase.

3.2. Detection limits

LOD and LOQ were calculated as described in calibration and quantification and estimated to 0.05 and 0.17 µg/L, respectively. Although there is no clean-up or concentration procedure, the its high sensitivity by LC-MS/MS permits the detection of perchlorate at concentration similar or below those reported previously.

The US EPA has established a health reference level of 15 µg/L for perchlorate.[18-21] In Korea, water quality criteria (WQC) for the perchlorate has not yet
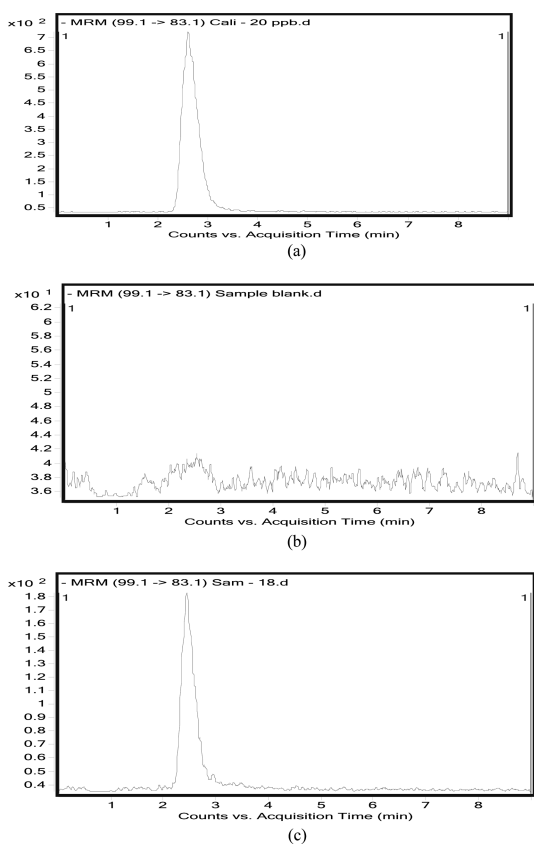
Fig. 1. LC-MS/MS chromatogram of (a) the sample spiked in a concentration of perchlorate (20 µg/L), (b) blank sample and (c) and real samples detected as the concentration of 3.73 µg/L.

been established, but they may be necessary to review water quality criteria after enough monitoring and risk assessment have been completed. Establishing water quality criteria for human health through the monitoring, requires a sensitive analytical method with more low detection limit than the water quality criteria or reference level established in other nations, that is 1.5 µg/L. Therefore, the LOQ of perchlorate in this study meets 0.1 times lower concentration than the water quality criteria or reference value for perchlorate established by the US EPA.

3.3. Calibration curve and linearity

Examination of typical standard curve by computing a regression line of peak area ratios of perchlorate on concentration using a least-squares fit demonstrated

a linear relationship with correlation coefficients of 0.9999. The line of best fits for perchlorate is y = 572.01χ - 31.53.

3.4. Interference

This method did not use an extraction, clean-up or concentration procedure for the determination of under µg/L levels of perchlorate in water. No interference peak was observed in the chromatograms near the retention time of analyte.

3.5. Precision and accuracy

The reproducibility of the assay was very good. For five independent determinations in the concentration of 1.0 and 25 µg/L, the accuracy and the precision were within 104.5% and 7.2%, respectively.

3.6. Water analysis

We used the proposed method to analyze perchlorate in thirty-five surface water samples, which contain thirteen surface water samples near industry area. Water samples were collected in thirty-five basins of the Gum-River on February, April and June 2012, respectively. As a result, perchlorate was detected in the concentration range of 0.23-3.73 µg/L (mean 0.20 µg/L) in the frequency of 15% in general surface water, otherwise in the concentration range of 0.36-25.10 µg/L (mean 1.69 µg/L) in the frequency of 36% in surface water samples near industry area

A similar study was conducted in the Han-River and the Nakdong-River, in which perchlorate was detected in the concentration of nd-18.30 µg/L[49] and nd-278.4 µg/L[50]. The concentration of perchlorate in surface water reported in other countries was in the concentration range of nd-0.33 µg/L (in the Great Lakes of Canada),[48] 1.5-8 µg/L (in the Colorado River of USA),[51] and 0.09-2,300 µg/L (in the Tone River in the near of Japanese industry complex).[52] The concentrations of perchlorate in surface water of the Gum-River were similar to those obtained from the Han-River of Korea and the Colorado River of USA Sea of German, and lower than those found in the Nakdong-River of Korea and in the Tone River of Japan.

4. Conclusions

In this paper, we examined the analytical parameters critical to the perchlorate LC-MS/MS characteristics.

The peak of the perchlorate showed good chromatographic properties using an ion-pair column and a sensitive response for the LC-ESI-MS/MS. The LOQ of perchlorate was 0.17 µg/L. The method was used to analyze water samples from various regions of the Gum-River. The samples revealed perchlorate concentrations in the range of 0.23-25.10 µg/L. The perchlorate concentrations in surface water were similar to those obtained from Great Lakes of Canada and Colorado River of USA, and very lower than those found in the Tone River of Japan. The method may be valuable for the national monitoring project of perchlorate in surface water, waste water, ground water and tap water.

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