An improved ion chromatographic method for determination of trace levels of perchlorate in environmental water

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Abstract An improved ion chromatographic (IC) method was developed to determine trace levels of perchlorate in environmental water samples. Perchlorate was separated in the hydroxide selective column IonPac AS16 using NaOH as an eluent with an organic modifier. To eliminate the coelution of perchlorate and 4-chlorobenzene sulfonate (4-CBS), an organic solvent as modifier was added to the eluent. Of four organic solvents studied, acetonitrile proved to be the most efficient based on the retention time of perchlorate and 4-CBS. To improve the method sensitivity, a concentrator column (AG19) was used to concentrate perchlorate online. With the adoption of a preconcentration step, the sensitivity of our method was improved and the method detection limit (MDL) was reduced to 0.1 μg/L. The linear range was from 0.2 μg/L to 200 μg/L with a linear correlation coefficient of 0.9989 and the relative standard deviation (RSD) of peak area for eleven successive injections of 0.5 μg/L perchlorate was 4.2%. The method had been applied to the determination of perchlorate in some real environmental water samples and recovery was between 93% and 113%.

Keywords perchlorate, ion chromatography, environmental water sample

Perchlorate is regarded as a new emerging persistent inorganic contaminant because of some peculiarities such as high water solubility, mobility and stability. It mostly exists in the form of ammonium perchlorate, potassium perchlorate and sodium perchlorate which are used as solid rocket oxidants and ignitable sources in munitions and fireworks or used in roadside flares and air bag inflation systems [1]. Improper treatment and accidental releases can result in the contamination of environmental water and drinking water. Different levels of perchlorate have been detected in food, biological, and environmental water samples [2,3]. In recent years, the analysis and toxicity of perchlorate have received considerable attention. Urbansky [4] indicated that perchlorate can be taken up by the thyroid gland and interfere with iodide uptake because its size is similar to that of iodide. Consequently the production of thyroid hormones is reduced and the thyroid functions are affected, which may result in the improper regulation of metabolism for adults and the development of behavioral problems for infants and children. In some cases, disruptions in thyroid hormone levels can cause thyroid gland tumors. Even minimal uptake of perchlorate can cause thyroid gland tumors [5]. In February 2005, the United States Environmental Protection Agency (US EPA) established an official reference dose (RfD) for drinking water of 24.5 μg/L perchlorate. Perchlorate has also been included in the EPA’s Drinking Water Contaminant Candidate List prepared under the Safe Drinking Water Act (SDWA) [6].

In recent years, many methods such as those based on UV-Vis spectrophotometry [7], fluorimetric analysis [8], electrochemiluminescence [9], surface-enhanced Raman spectroscopy [11–12] and electrochemical methods which employ ion-selective electrodes [10] have been developed for the analysis of perchlorate. Mass spectrometric methods for perchlorate determination are expected to have the highest sensitivity and selectivity. However, there are some disadvantages for the method based on MS detection. For example, when direct ESI-MS is used for the detection of perchlorate, there is ion-suppression due to inadequate chromatographic separation and this can affect the accuracy and precision of perchlorate determination [2,13]. In addition, these techniques are highly sophisticated and the instrumentation is very expensive. IC with conductivity detection is an alternative method for perchlorate determination and it uses a less complex and less expensive system. There are some IC methods developed for the determination of perchlorate in different matrices [3,14–20]. The IC method has been established as US EPA
Method 314.0 [14]. Unfortunately, the IC method does not provide absolute evidence for the presence of perchlorate because the chromatographic retention time is not considered to be a unique identifier. For example, when the perchlorate was determined using AS16 as the separating column, false positive results are obtained in the presence of 4-CBS. Thus, a second confirmatory method is needed (such as the method based on MS detection) when the AS16 is used as separating column.

In this paper an improved IC method with conductivity detection is described for the determination of perchlorate. To enhance the selectivity and the sensitivity, two measures were taken. First, an organic solvent was added to the eluent to improve the resolution of perchlorate and 4-CBS and eliminate the false positives for perchlorate in the presence of 4-CBS. Second, by adopting an online preconcentration step, perchlorate was concentrated in the column and the method sensitivity was improved. Under optimized conditions, the MDL for perchlorate was found to be 0.1 μg/L. This MDL complies with the requirement for the determination of perchlorate in many real environmental samples with complex matrices.

## 1 Experimental

### 1.1 Chemicals and instruments

All solutions were prepared with deionized water further purified by EASY pure LF system (Barnstead, USA). The NaOH eluent was prepared with 50% (W/W) sodium hydroxide solution. All organic solvents used were of chromatography grade. Fluoride, chloride, nitrite, bromide, nitrate, sulfate and phosphate standard solutions (1000 mg/L) were purchased from National Research Center for CRM’s (China). Perchlorate solutions were obtained by dilution of concentrated stock solution prepared by dissolving solid reagent (Analytical grade, Beijing South Shangle Chemical Plant, China) in deionized water. The 4-CBS used was purchased from Sigma Co. (USA).

A Dionex model ICS 2500 ion chromatograph (Sunnyvale, CA, USA) equipped with a GP pump, an IonPac AS16 analytical column (4 mm × 250 mm) and an IonPac AG16 guard column (4 mm × 50 mm) was used throughout. The eluent was made up of 67% eluent A (80% acetonitrile/20% water), 15% eluent B (100 mmol/L NaOH) and 18% eluent C (acetonitrile), which was run in isocratic elution mode at a flow-rate of 1.0 mL/min. The detection was performed using ED50A conductivity detector. Suppression of the eluent was achieved by ASRS-ULTRA suppressor (4 mm) in the autosuppression external water mode. An IonPac AG19 was used as the concentrator column. The DX-300 pump was employed for the concentration of perchlorate. Both instrument control and data collection were performed using Chromeleon chromatography workstation (Chromeleon 6.7).

### 1.2 The preparation of samples

The environmental samples including tap water, ground water, ice and snow were collected from Beijing, the Tibetan Plateau and Macao. The specific information for sample collection is as follows: Tap water was collected from Macao. Ground water was collected from Haidian District in Beijing. Snow samples 1–3 were collected from different residential areas near our laboratory. Ice samples 1 and 2 were collected from the Tibetan Plateau. All samples were stored in a refrigerator at 4°C before analysis.

Before the samples were run on the IC system, they were subjected to a series of processes including filtration using 0.22 μm nylon membrane, elimination of sulphate and chloride using On-Guard Ba and Ag–H column and 20 ml of the sample was concentrated online. In the pre-concentration process the pretreated samples or standards were introduced into the concentrator column (AG19) by DX-300 at a flow-rate of 2.0 mL/min for 10 min. Each sample was injected in triplicate.

## 2 Results and discussion

### 2.1 Optimization of chromatographic parameters

The IonPac AS16 is often used as the separation column for the determination of perchlorate in different matrices. In the EPA 314.0 method, the IonPac AS16 was also selected as the separation column. Because of the presence of 4-CBS in some environmental samples and its coelution with perchlorate in an IonPac AS16 column, 4-CBS can interfere with the determination of perchlorate using EPA 314.0 method which may result in false positives for perchlorate determination. Two methods, changing the eluent or the solid-phase, can be used to solve the problem. In this paper, an eluent with organic modifier was adopted to get a good resolution for perchlorate and 4-CBS.

#### 2.1.1 The effect of the concentration of NaOH in eluent

IonPac AS16 column is a highly hydrophilic and hydroxide-selective column so the main component of the mobile phase is sodium hydroxide. Under the typical isocratic elution condition specified in the EPA 314.0 method where 50 mM NaOH is used as eluent, the determination of perchlorate suffers from the interference of 4-CBS, a coelution compound that exists in some environmental samples. To solve this problem, the first method that we used was to adopt gradient elution. The effects of the