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RESEARCH ARTICLE

Yali SHI, Ping ZHANG, Yaqi CAI, Shifen MOU

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

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

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Yali SHI, Ping ZHANG, Yaqi CAI (✉), Shifen MOU
State Key Laboratory of Environmental Chemistry and Ecotoxicity, Research Center for Eco-environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China
E-mail: caiyaqi@rcees.ac.cn

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. Flouride, 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 regent (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% acetonitriel/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 preconcentration 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

concentration of NaOH on retention time of both perchlorate and 4-CBS were studied. It was found that the retention time of perchlorate and 4-CBS with NaOH as eluent were so similar that they could not be separated only by changing the concentration of NaOH. To improve the selectivity using the same column, IonPac AS16, the most convenient method usually is to add a suitable organic solvent modifier into the eluent. Organic solvent modifiers can adjust the hydrophobicity or hydrophilicity of mobile phases thus, change the retention behavior of some ions. This method is very effective in improving the separation of ions with different hydrophobicities or hydrophilicities and it is assumed that the resolution of perchlorate and 4-CBS can be improved using this method because they have different hydrophobicities.

2.1.2 The effect of organic solvents in eluent

Typical organic solvents used in ion chromatography are acetonitrile, methanol, ethanol and isopropanol. The effects of these four organic solvents on the retention of perchlorate and 4-CBS were studied when the concentration of NaOH was fixed at 20 mmol/L in the eluent. In order to ensure complete mixing of the organic solvent and NaOH solution without producing bubbles, the organic solvent was pre-mixed with some water to make eluent C (80% solvent/20% water). The effect of organic solvent on retention time is shown in Fig. 1. It was found that the resolution of perchlorate and 4-CBS changed when an organic solvent is added. When the percentage of the organic solvent in the eluent was greater than 10%, the perchlorate and 4-CBS could be separated completely but when the analysis time was taken into account, the acetonitrile was undoubtedly the best of the four organic solvents used. Furthermore, the system with acetonitrile modifier exhibited the least noise in the 2–5 ns range. Thus, the acetonitrile was selected as organic improver. Finally, the percentage of eluent C (80% acetonitrile) added was set at 18%. We prepared the mobile phase used for the separation of perchlorate and other anions in isocratic elution mode by mixing 62% eluent A, 20% eluent B and 18% eluent C.

The interference of some common anions on the determination of perchlorate was also examined. A standard solution containing 11 anions was run under the selected chromatographic condition. The result showed that phosphate was coeluted with perchlorate so the concentration of NaOH in the eluent was readjusted to 15 mmol/L. Thus, in this paper, the eluent used was a mixture containing 67% eluent A, 15% eluent B and 18% eluent C which was run in isocratic elution mode at a flow-rate of 1.0 mL/min. Using this eluent, neither 4-CBS nor the other anions interfered with the determination of perchlorate. The entire analysis took 30 minutes. The chromatogram of the standard solution containing the 11 anions is shown in Fig. 2.

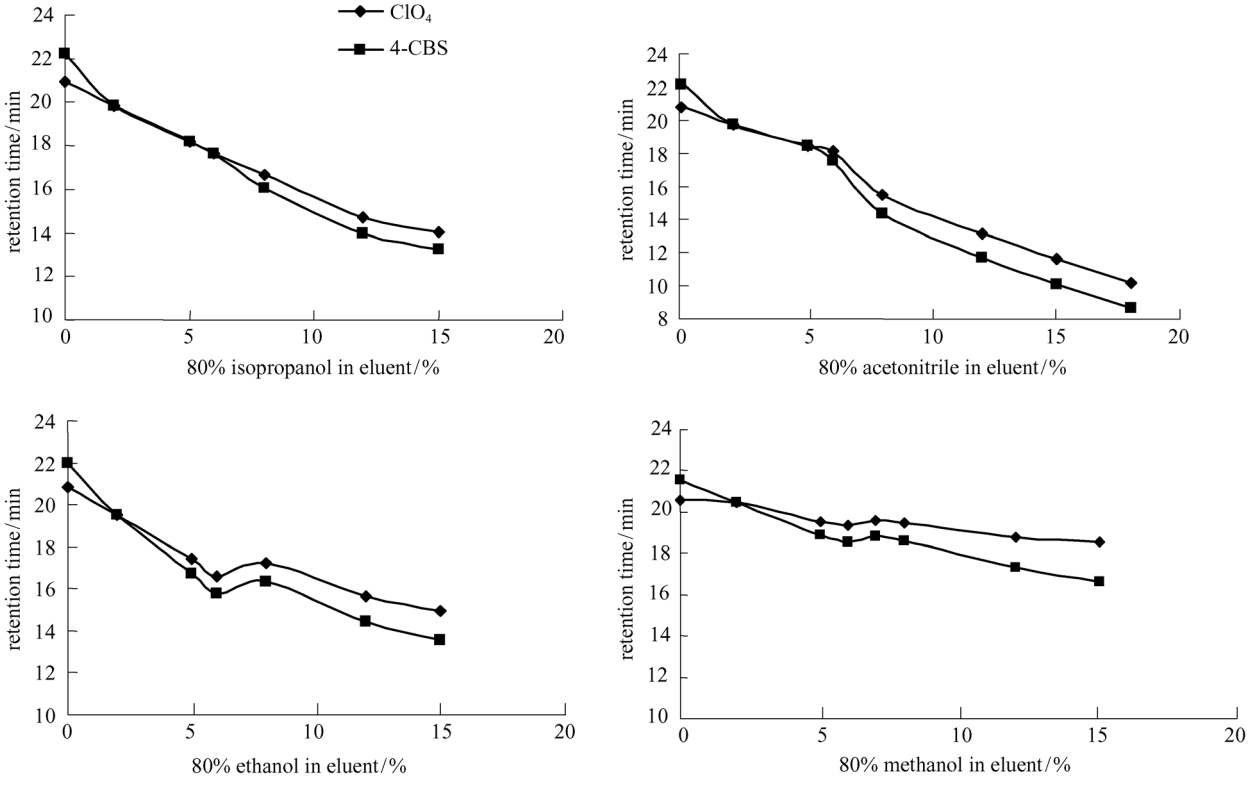

Fig. 1 The effect of organic solvent on the retention time of perchlorate and 4-CBS

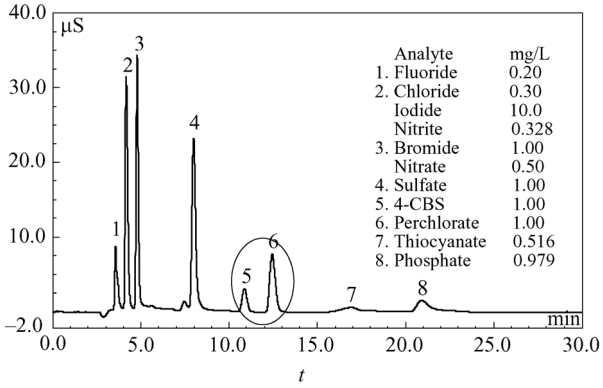

Fig. 2 The chromatogram of eleven anions in standard solution

2.2 The study on the concentration efficiency of perchlorate

The second challenge involved in the determination of perchlorate in many complex matrix samples is the very low concentration levels of perchlorate and high background levels of other compounds in samples. To improve the method sensitivity, a concentrator column was used. The concentrator column was set in the loop position and the standard solution was introduced into the concentrator column using an external pump. Due to perchlorate's hydrophobicity and its strong affinity for the stationary phase of column, an anion guard column, IonPac AG19, was selected as a concentrator column for the preconcentration of perchlorate. The effect of concentration volume on the peak area of perchlorate and the concentration efficiency of perchlorate were investigated.

To evaluate the performance of the preconcentration system, perchlorate at 50 μg/L was determined after it was concentrated using different volumes (5, 10, 15, 20 mL). The preconcentration volume was controlled precisely by the flow rate of the external pump and the preconcentration time. A good linear relationship between the peak area of perchlorate and preconcentration volume was observed. The linear correlation coefficient was 0.9968. To obtain a high sensitivity and shorter preconcentration time, 20 mL was used as preconcentration volume. The flow rate of the solutions introduced into the concentrator column may have some influences on the preconcentration. However, when the flow rate was in the range of 0.2–2.5 mL/min, the influence of the flow rate could be ignored so the standard and sample solution were introduced into the concentrator column at a flow rate of 2.0 mL/min for 10 min.

After the preconcentration volume was determined, we evaluated the preconcentration efficiencies of perchlorate on the AG19 column. Perchlorate standards at concentrations of 0.5–100 μg/L were introduced into the concentrator column and then run in the chromatographic system. One ml of the perchlorate standards at concentrations of 10–2000 μg/L were also injected directly without preconcentration. All peak areas were recorded by the Chromeleon software. The preconcentration efficiencies were calculated by comparing peak areas and the results are presented in Table 1. It was found that good preconcentration efficiencies (in the range of 82.0%–98.5%) were obtained with the IonPac AG19 as concentrator column proving that the IonPac AG19 could be used to concentrate perchlorate.

2.3 Analytical performance

In order to validate the method for the analysis of perchlorate at μg/L levels, a calibration curve was generated with the concentrator column. A perchlorate standard series (0.2, 0.5, 1.0, 2.0, 5.0, 10.0, 50.0, 100, 200 μg/L) was introduced into the concentrator column and then run in the chromatographic system. The result showed that the method had a wide linear range (0.2–200 μg/L) and a fairly good linear relationship between the peak area and concentration of perchlorate was observed. The linear correlation coefficient was 0.9989. The RSD of the peak area for the eleven successive injections of 0.5 μg/L perchlorate was 4.2%. The MDL for perchlorate was 0.1 μg/L (S/N = 3) with the concentrator column used. The described method exhibits better sensitivity than the EPA 314.0 method.

2.4 Analysis of perchlorate in environmental water sample

The described method was applied to the determination of perchlorate in some environmental water samples. The samples must be filtered using a 0.22 μm nylon membrane then passed through an On-Guard Ba and Ag–H column before they can be run in the IC system. On-Guard Ba and Ag were used to remove sulphate and chloride, respectively, in the environmental water samples. Sulphate and chloride in samples can result to poor preconcentration

Table 1 The concentration efficiency for perchlorate on the concentrator column

ρ (perchlorate)/(μg·L^{-1})[a]	peak area of perchlorate[a]	ρ(perchlorate)/(μg·L^{-1})[b]	peak area of perchlorate[b]	concentration efficiencies (%)[c]
10.0	0.0228	0.5	0.0187	82.0
20.0	0.0478	1.0	0.0397	83.1
100.0	0.2594	5.0	0.2343	90.3
200.0	0.5274	10.0	0.4992	94.7
1000.0	2.9303	50.0	2.8842	98.4
2000.0	5.9416	100.0	5.8497	98.5

[a]With 1 mL direct injection; [b]With 20 mL preconcentration; [c]concentration efficiencies = peak area of perchlorate[b]/peak area of perchlorate[a]

Table 2 Perchlorate in environmental water sample and spiked sample

sample	concentration detected by present method/μg·L^{-1}	spiked/μg·L^{-1}	found/μg·L^{-1}	recovery/%	concentration detected bt IonPac AS20/μg·L^{-1}
ground water (Beijing)	0.79	1.00	1.86	106.5	0.77
Tap water (Macao)	3.16	2.00	5.13	98.9	3.27
snow water 1# (Beijing)	85.99	20.00	108.5	112.6	87.08
snow water 2# (Beijing)	15.72	10.00	25.34	96.2	14.68
snow water 3# (Beijing)	7.01	10.00	16.31	93.0	7.39
ice 1# (the Tibetan Plateau)	ND*	2.00	2.08	104.0	ND
ice 2# (the Tibetan Plateau)	ND	1.00	0.95	95.0	ND

Not detected

efficiency of perchlorate. On-Guard H was used to remove the silver that leaches from On-Guard Ag. The results show that different concentrations of perchlorate were found in all samples except for the two ice samples collected from the Tibetan Plateau. The concentration of perchlorate is highest (85.99 μg/L) in snow water 1#. Snow samples 1–3# were collected after the Spring Festival which is why the concentrations of perchlorate are relatively high. Fireworks set off during the Spring Festival could have been the source of perchlorate in the samples. Recovery experiments were carried out by spiking the original samples with different concentrations of perchlorate. The method showed good recovery with values ranging from 93% to 113% (Table 2). Chromatograms of the ground water sample and the same sample spiked with 1.0 μg/L of perchlorate are shown in Fig. 3.

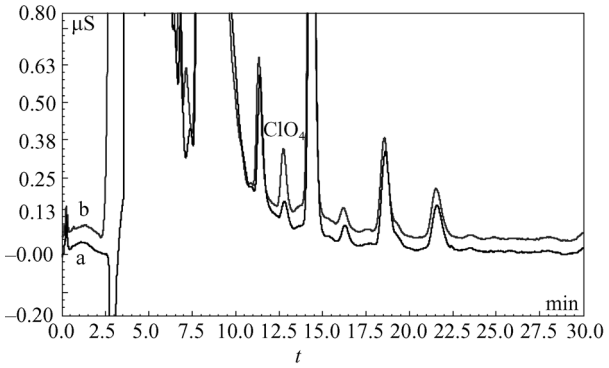

Fig. 3 The chromatogram of ground water and ground water spiked with 1 μg/L perchlorate
a) original sample (with 0.79 μg/L perchlorate); b) spiked sample (spiked with 1.0 μg/L perchlorate)

In order to validate accuracy of the method described in this paper, the sample analysis results were compared with the one obtained using a different column, IonPac AS20. As shown in Table 2, the results are consistent.

3 Conclusions

In this paper, a simple and sensitive ion chromatographic method for the determination of trace levels of perchlorate in environmental samples was developed. By adding a suitable amount of acetonitrile into the eluent as organic modifier, the resolution of perchlorate and 4-CBS and other common anions was enhanced greatly and eliminated the coelution of perchlorate and 4-CBS in the EPA 314.0 method based on IonPac AS16 and conductivity detection. The sensitivity of our method was improved by the adoption of a preconcentration technique. The MDL was reduced to 0.1 μg/L and the linear range was from 0.2 μg/L to 200 μg/L. These values comply with the requirements for perchlorate analysis of ordinary environmental samples.

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