

Determination of Trace Perchlorate in Drinking Water by Developing Ion Chromatography Coupled with Mass Spectrometry (IC-MS)

Y M Xu¹, H J Guo¹, H Y Ning¹, H W Yuan¹, X Hu¹, J He^{1,2}, P C Pan^{1,2} and H Chen^{2,*}

¹Sichuan West Analytical Testing Co., Ltd., Chengdu, 610101, China

²Sichuan Institute of Atomic Energy, Chengdu, 610101, China

Corresponding author and e-mail: H Chen, haochen@siae.cn

Abstract. Perchlorate (ClO_4^-) in drinking water poses healthy risk for human beings. The routine method of IonPac AS16 polarizable anion analytical column to analyze ClO_4^- in drinking water failed due to the false positive behavior of perchloric acid. Therefore, an ion chromatography coupled with mass spectrometry (IC-MS) method was developed to determine the content of ClO_4^- in drinking water based on IonPac AS20 column, 45 mM KOH eluent and negative ion mode of mass spectrometry. The **results** show that the ClO_4^- concentration displayed an excellent linear performance in the range of 1-20 $\mu\text{g/L}$ using the newly developed method, its method detection limit (MDL) was determined to be 0.47 $\mu\text{g/L}$, and the recoveries of the spiked samples ranged from 92.0% to 101.5%, meeting the relevant requirements of GB/T 6379.6-2009.

1. Introduction

Perchlorate (ClO_4^-) has been widely used in many fields, such as rocket propellants, fireworks manufacturing, arms industry, car airbag, highway safety flash board, etc[1]. Perchlorate is chemical stable and highly soluble in water, so with entering into environment during industrial production and discharge, it goes easily into the underground water, causing water pollution. These contaminated water often harms human health through the food chain or drinking water[2,3]. Recently, overdose of perchlorate has been detected in the Chinese tea exported to Europe. So European Union (EU) is preparing to set more strict standards to limit the importation of high perchlorate-containing Chinese tea, which is causing more concern. In the late 2015, EU required the maximum content of 0.75 mg/kg for the perchlorate in tea in the proposal of Circular on the Standard for Perchlorate and Anthraquinone Content in Tea in the EU. It has been reported[4-6] that the ionic radius of ClO_4^- is very close to that of iodide (I) ions, so it tends to diffuse into the thyroid competed with I ions, hinders the absorption of I ions in thyroid, decreasing the synthesis of thyroid hormone, and resulting in metabolism of human body in disorder. The higher ClO_4^- content even leads to thyroid cancer. Especially, it is more harmful for the growth and development of fetal and infant central nervous system.

Based on the above issues, American Environmental Protection Organization (EPA) has enacted the *Safe Drinking Water Act* in which perchlorate is listed as one of the environmental pollutants, and established a national standard for drinking water[7-8] that the reference dose of perchlorate for human health is 0.7 $\mu\text{g}/\text{kg}$ per day, that is, the concentration of perchlorate in drinking water is less than 24.5 $\mu\text{g}/\text{L}$. Wu et al. [9] conducted a preliminary investigation on the perchlorate content of 300 water samples from 15 sites in 13 provinces in China and found that 86% of the water samples contained perchlorate at a concentration ranging from 0.02 $\mu\text{g}/\text{L}$ to 54.4 $\mu\text{g}/\text{L}$. Perchlorate pollution was found in Liuyang City[10], China's largest fireworks production base. In addition, the perchlorate concentration in the dust of northern China was in the range of 0.132-5300 mg/kg [11]. While in southern India, the perchlorate concentration in groundwater ranged from 0.005 to 7690 $\mu\text{g}/\text{L}$ [12]. Apparently, perchlorate pollution of drinking water has become more and more global, widespread and serious.

Over the years, the rapid development of ion chromatography and high sensitive techniques made the analysis of trace perchlorate more accurate.

EPA has developed ion chromatography as the standard method 314.0[13]. However, with the technological development of analyzing perchlorate[14], it was found that during analyzing some drinking water samples using IonPac AS16 column, the qualitative determination of perchloric acid appeared false positive behavior with the issue of eluting both 4-chlorobenzenesulfonic acid and perchlorate. For this problem, IonPac AS20 column has been improved by modifying the filler structure with a high-capacity, anion-exchange column of hydroxide system. This structure could greatly reduce the adsorption of perchlorate by the stationary phase of 4-chlorobenzenesulfonic acid and eliminate the interference of 4-chlorobenzenesulfonic acid to determining perchlorate content. In the present study, we select IonPac AS20 as the pretreatment separation column to determine trace perchlorate.

2. Experimental

2.1. Instruments and reagents

Thermo Scientific Dionex ICS-5000⁺ Ion Chromatography with EGC Eluent Auto-Generator, Conductivity Detector and ChromeLeon 7 Chromatography workstation;

Thermo Scientific MSQ plus with Electrospray Ion (ESI) source;

Dionex AS20 chromatography column, 250 \times 2 mm;

Dionex AERS500 anion suppressor, 2 mm;

Dionex EGC500 KOH eluent;

Millipore Direct Q-8 Ultrapure water purification system;

Ultrapure water, 18.2 $\text{M}\Omega\cdot\text{cm}$;

Sodium perchlorate standard, 1 mg/L .

2.2. Chromatographic conditions

Eluent: 45 mM KOH, at the same concentration, automatically generated online by the EGC Eluent Auto-Generator;

Flow rate: 0.3 mL/min ;

Injection volume: 150 μL ;

Response signal: 70 mA .

2.3. MS conditions

Spray source temp.: 390 $^{\circ}\text{C}$;

Polarity: negative ion mode;

Spray pressure: 20 psi ;

Probe voltage: -3 kV;
 Declustering voltage: -40 V;
 Probe temp.: 450 °C;
 Selected Ion Monitoring (SIM) channel: 99, 101, and 107 mass/charge ratio (m/z);
 Dwell time: 1 s;
 Sampling time: 200 ms;
 Run time: 18 min.

3. Results and discussion

3.1. Linear range, precision and detection limit

Configure a series of perchlorate standard solutions of 1, 2, 5, 10 and 20 µg/L respectively, inject 150 µL into mass spectrometry and record the peak area of perchlorate. The chromatogram and calibration curve of perchlorate standard solutions are shown in Figure 1. The results show that the method displays a good linearity in the range of 1~20 µg/L of perchlorate solutions, the linear correlation coefficient $r = 0.999$. Table 1 shows the results from 7 replicate injections of 10 µg/L perchlorate solution, and the values were calculated from an external standard calibration curve. The method detection limit (MDL) is determined as 0.47 µg/L and the precision (relative standard deviation, RSD) is 1.48%.

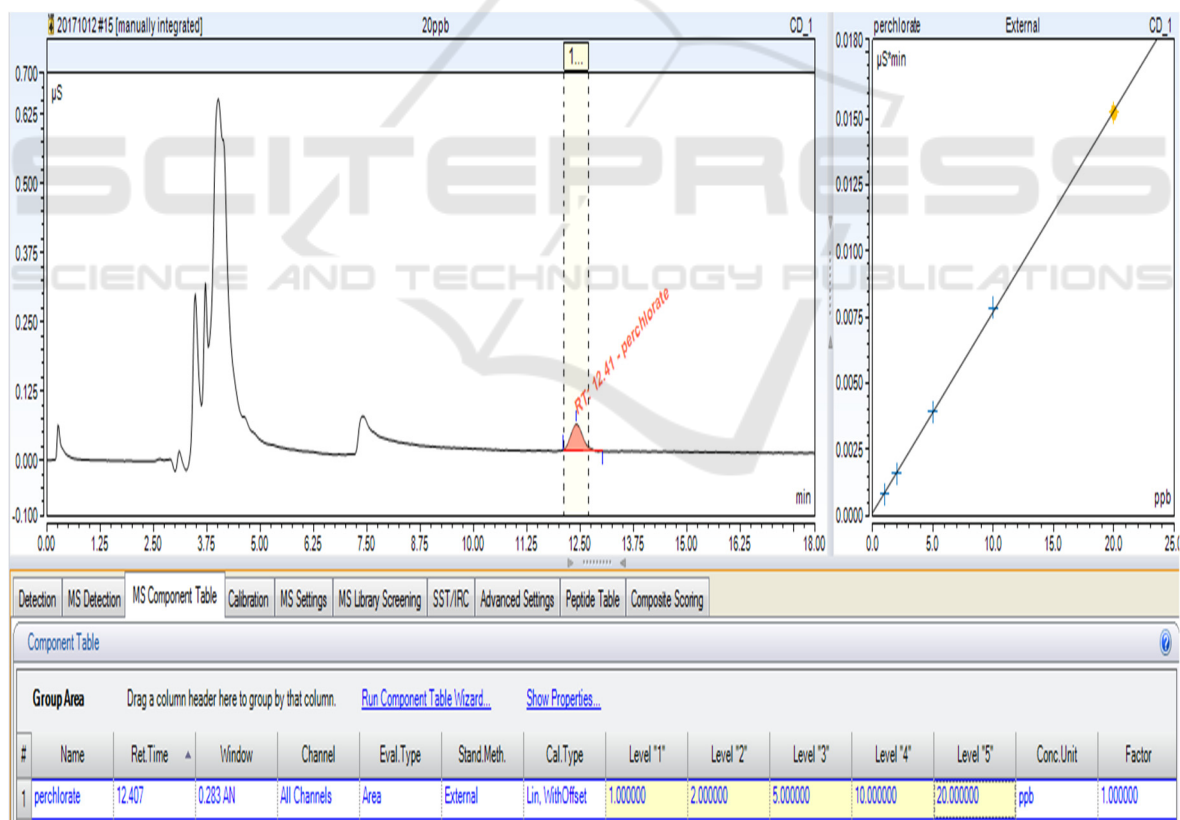


Figure 1. Chromatogram and calibration curve of perchlorate.

Table 1. MDL calculation using 10 µg/L perchlorate.

Replicate	Amount (µg/L)	Average (µg/L)	Standard deviation (s.d., µg/L)	RSD (%)	MDL (3.14 × s.d., µg/L)
1	9.91				
2	9.86				
3	10.24				
4	10.08	10.03	0.15	1.48	0.47
5	10.15				
6	9.95				
7	10.03				

3.2. Sample analysis and spiked sample experiments

Taking tap water and bottled drinking water as samples, the samples were directly filtered through 0.22 µm aqueous membrane filter, and samples were spiked and analyzed respectively, the results are shown in Figure 2 and Table 2. It can be seen that the recoveries of spiked samples are all in the range of 92.0% ~ 101.5%, indicating that the method is accurate, stable and reliable.

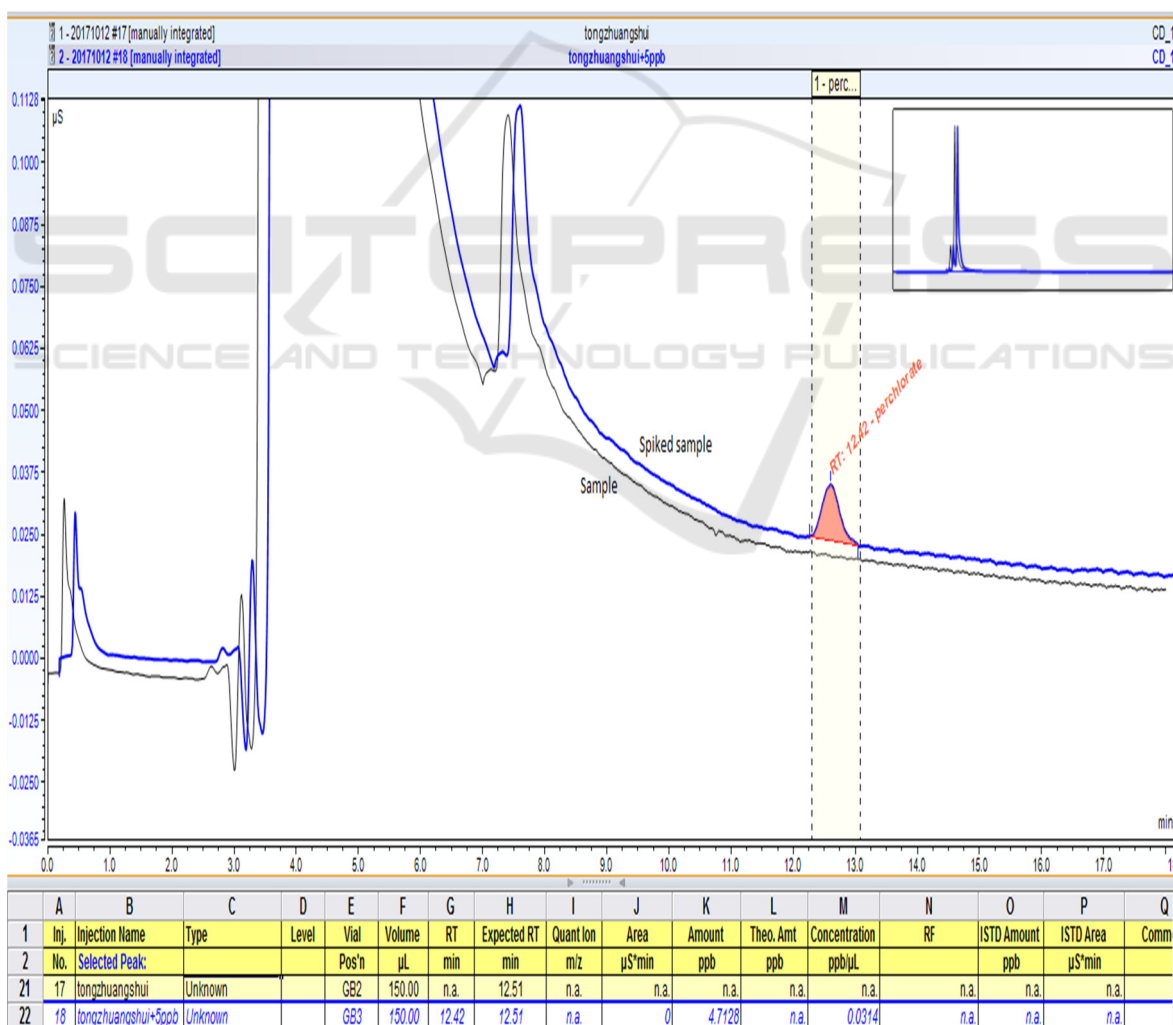


Figure 2. Chromatogram of sample and spiked sample (bottled drinking water).

Table 2. Results of samples and spiked samples.

Samples	Amount (samples, $\mu\text{g/L}$)	Spiked Amount ($\mu\text{g/L}$)	Amount (spiked samples, $\mu\text{g/L}$)	Recoveries (%)
tap water	N.D.	2.0	1.84	92.0
bottled drinking water	N.D.	2.0	2.03	101.5
tap water	N.D.	20.0	18.63	93.1
bottled drinking water	N.D.	20.0	19.54	97.7
tap water	N.D.	50.0	47.27	94.5
bottled drinking water	N.D.	50.0	50.12	100.2

N.D.: Not be detected

4. Conclusions

In this paper, IC-MS method was developed to detect the trace perchlorate in drinking water, and demonstrated low MDL, excellent precision and high accuracy which meet the relevant requirements of GB/T 6379.6-2009 “Accuracy (trueness and precision) of measurement methods and results—Part 6: Use in practice of accuracy values”.

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