Talanta 79 (2009) 442–445

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Determination of perchlorate in river by ion-pair hollow-fiber liquid-phase microextraction coupled with electrospray ionization tandem mass spectrometry

Hsin-Chang Chen, Wen-Tsen Chen, Wang-Hsien Ding*

Department of Chemistry, National Central University, Chung-Li 320, Taiwan

ARTICLE INFO

Article history:
Received 18 February 2009
Received in revised form 2 April 2009
Accepted 2 April 2009
Available online 10 April 2009

Keywords:
Perchlorate
Hollow-fiber liquid-phase microextraction
Electrospray tandem mass spectrometry
Water analysis

ABSTRACT

This paper describes the analysis of perchlorate (ClO_4^-) in surface water samples by a rapid and reliable ion-pair hollow-fiber liquid-phase microextraction (HF-LPME) method coupled with flow-injection electrospray ionization tandem mass spectrometry (ESI-MS–MS) technique. The effects of the type and concentration of ion-pairing reagents, extraction time, temperature and pH value on the quantitative extraction of perchlorate by ion-pair HF-LPME were investigated and optimized. Di-*n*-hexyl ammonium acetate (DHAA) was employed to form an extractable ion-pair complex with aqueous perchlorate. The characteristic ions $[ClO_4\text{-}ClO_4\text{-}DHA]^-$ at *m/z* 384.6 and 386.7 were observed in the ESI negative-ionization mode. The predominant product ions $[ClO_4]^-$ at *m/z* 99 and 101 were used for quantitation and to maximize the detection selectivity and sensitivity. The limit of detection (LOD) was 0.5 μg/L. The reliability and precision of the standard addition method of ion-pair HF-LPME for the determination of trace levels of perchlorate in surface water were demonstrated.

1. Introduction

Perchlorate (ClO_4^-) gained a great amount of attention as an environmental contaminant after it was detected in abnormally high concentrations in drinking water supplies in the western United States in 1997. Nowadays, detection of perchlorate contamination in the environment and in foodstuffs continues to increase, especially in groundwater, drinking water, milk, vegetables and even in bottled water [1–10]. The presence of perchlorate in drinking water, agricultural irrigation sources, and food supplies is of great concern because it can have an adverse impact on human health through interfering with iodide uptake by the thyroid [11]. A relationship exists between fireworks display and the environmental occurrence of perchlorate, for example, the concentration of perchlorate in a municipal lake was found to have increased dramatically within 14 h after a fireworks display [8]. This relationship stimulated our interest to investigate the content and distribution of perchlorate in Taiwan, where fireworks use is widespread in festivals, wedding celebrations and religion activities. Furthermore, many unlicensed fireworks factories exist in suburban or rural areas in Taiwan may threaten not only the environment but also the safety of the residents of those areas.

The determination of perchlorate in environmental water samples is most often performed using (i) suppressed ion chromatography (IC) coupled with conductivity detection (CD) [1–3], and (ii) electrospray ionization mass spectrometry (ESI-MS) or ESI-tandem mass spectrometry (ESI-MS–MS) with IC, liquid chromatography (LC) [4–8], or flow-injection analysis (FIA) [9,10]. ESI-MS and ESI-MS–MS techniques have been applied widely to the analysis of perchlorate in environmental samples because of their high sensitivity and specificity. Several sample preparation techniques have been applied for perchlorate analysis in various water samples, including standard addition [9], ion-pair liquid–liquid extraction (ion-pair LLE) [10], or sample pretreatment with ion-exchange cartridges [1,4,6,7]. Currently, liquid-phase microextraction (LPME), a simple and cost-efficient technique, has emerged as an attractive alternative for sample preparation (see Refs. [12–14] and reference therein). Hollow-fiber-protected LPME (HF-LPME) coupled with GC–MS or LC–MS has been applied successfully to the determination of various organic contaminants in environmental, biological and food samples (see Refs. [12–16] and reference therein). However, combination of HF-LPME with tandem mass spectrometry to analyze anionic analytes (e.g., perchlorate) in complex environmental samples has not been reported.

In this study, the effects of various operating parameters on the extraction of perchlorate from aqueous samples by ion-pair HF-LPME were evaluated. Di-*n*-hexylammonium acetate (DHAA) was applied in this ion-pair HF-LPME coupled with ESI-MS–MS analysis because of its volatility, its weak signal suppressing effect, and the relatively low abundances of its Na^+, K^+ adducts, which simplify the mass spectra interpretation [17]. Moreover, this developed method

* Corresponding author. Tel.: +886 3 4227151x65905; fax: +886 3 4227664.
E-mail address: wanghsiending@gmail.com (W.-H. Ding).

0039-9140/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2009.04.002

was applied for the first time to extract perchlorate directly from complex environmental samples at a trace-level.

2. Experimental

2.1. Reagents and materials

HPLC-grade methanol was purchased from Merck (Darmstadt, Germany). Reagent-grade 1-octanol was used as received from Fluka (Buchs, Switzerland). The reagent-grade ion-pair reagents: di-*n*-propylammonium acetate (DPAA), di-*n*-butyl ammonium acetate (DBAA), di-*n*-amylammonium acetate (DAAA), di-*n*-hexylammonium acetate (DHAA) and decyltrimethylammonium bromide (DeTMA-Br) were purchased from TCI (Tokyo, Japan). Sodium perchlorate (used as the standard) was obtained from Sigma–Aldrich (St. Louis, USA). All other chemicals were of analytical grade and used as received. Deionized water was further purified using a Millipore water purification device (Millipore, Bedford, USA). A stock solution of perchlorate standard (1000 μg/mL) was prepared in deionized water. The Accurel Q3/2 polypropylene hollow fiber membrane (600-μm I.D., 200-μm wall thickness, 0.2-μm pore size) for HF-LPME was obtained from Membrana (Wuppertal, Germany). The hollow fiber (30-cm in length) was cleaned ultrasonically in acetone for 20 min and air-dried prior to use. A 100-μL syringe equipped with a conical needle tip (SGE, Sydney, Australia) was used for LPME experiments.

2.2. Sample collection

Water samples were collected on November 7, 2007, 6 days after an explosion at a firework factory in Miao-Li County, Taiwan. Sample-A (specific conductance 370 μS/cm) was collected in a ditch, 20 m from the point of explosion. Sample-B (specific conductance 500 μS/cm) was collected from Ho-Long River at the location of the ditch exit. The third water sample (Sample-C, specific conductance 390 μS/cm) was also collected from Ho-Long River, but 20 km downstream from the site of the explosion. The pH of each sample was ca. 7.1. Upon arrival at laboratory, the samples were immediately passed through a 0.45-μm membrane filter, and then subjected to the ion-pair HF-LPME procedures using the standard addition method for quantitation.

2.3. Ion-pair HF-LPME

The LPME device and the basic principle of Hollow-fiber-protected LPME involving ion-pair formation have been described elsewhere [15]. The hollow fiber (30-cm in length) was firstly dipped for 8 min in 1-octanol. Subsequently, 100 μL of 1-octanol was injected into the lumen of the hollow fiber, and then the fiber was placed in a 40-mL sample-vial with 40 mL of sample solution containing 4 mM DHAA. For optimal extraction (see Section 3.2), a water bath's temperature was controlled at 30 °C using a remote probe, and the sample was stirred at 300 rpm (100 rpm = 10.47 rad/s) for 40 min. After extraction, the 1-octanol was retracted into a 100-μL micro-vial, and then an aliquot of 60-μL was injected by flow-injection into ESI-MS–MS system. Each piece of fiber was employed only once to avoid any possibility carryover.

2.4. Flow-injection ESI-MS–MS

A mixture of methanol and dichloromethane (70:30, v/v) was used as the carrier liquid of the flow-injection system and the flow-rate was 0.1 mL/min. No LC column was required for this analysis. Perchlorate was detected using an Agilent LC-MSD Trap SL mass spectrometer (Palo Alto, USA) equipped with an ESI in negative-ionization mode. The detection parameters were optimized by estimating the signal intensity through a series of continuous-infusion experiments. Mass spectra were collected in the scan range *m*/*z* 80–450. The optimized ESI parameters (see Section 3.1 and Table 1) were applied. The helium background gas was maintained at a pressure of 6×10^{-6} Torr during the MS–MS measurements. Quantitation of perchlorate was performed through product ion scans recording two transitions.

Table 1
Experimental optimized conditions.

Ion-pair LPME	
Fiber length	30 cm
Ion-pairing reagent	4 mM DHAA
Extraction solvent	1-octanol
Stirring rate	300 rpm
Extraction time	40 min
Extraction temperature	30 °C
pH	7.0
Flow injection	
Carrier liquid	MeOH: CH_2Cl_2 (70:30, v/v)
Injection volume	60 μL
Flow-rate	0.1 mL/min
Negative ESI-MS–MS	
Capillary voltage	4000 V
Drying gas temperature	325 °C
Drying gas flow-rate	3.5 L/min
Nebulizing gas pressure	22 psi
Fragmentation amplitude	0.25 V
Precursor ions	*m*/*z* 384.6 and 386.7 $[ClO_4\text{-}ClO_4\text{-DHA}]^-$
Product ions	*m*/*z* 99 $[^{35}ClO_4]^-$ and *m*/*z* 101 $[^{37}ClO_4]^-$

3. Results and discussion

3.1. Optimization of ESI-MS–MS

A mixture of methanol and dichloromethane (70:30, v/v) as the carrier liquid to transport the ion-paired perchlorate complex into ESI-MS–MS system was applied to obtain the highest ionization signal, which has been described by Magnuson et al. [10]. The effect of several parameters were evaluated to optimize the ESI ionization efficiency and thereby obtain the highest and most stable signal-to-noise (S/N) ratio for the intensity of the flow-injection peak under MS–MS conditions. Fig. 1 displays that the capillary voltage was optimized at 4000 V (tested between 1000 and 6000 V); the drying gas temperature and drying gas flow-rate were optimized at 325 °C (tested between 300 and 400 °C) and 3.5 L/min (tested between 2 and 8 L/min), respectively; and the nebulizing gas pressure was optimized at 22 psi (tested between 10 and 50 psi) (Table 1). Under ESI-MS conditions, a stable and predominant complex featuring one DHA cation and two perchlorate anions ($[ClO_4\text{-}ClO_4\text{-DHA}]^-$) at *m*/*z* 384.6 and 386.7 were detected. Similar complexes formed through ion pairing between a cation and perchlorate ions have been reported previously [10]. Under the optimized MS–MS conditions, the predominant product ions $[ClO_4]^-$ at *m*/*z* 99.1 and 101.2 were observed as a result of the loss of the DHA cation and one perchlorate anion. These predominant product ions as quantitation ions were used to maximize the detection selectivity and sensitivity.

3.2. Ion-pair HF-LPME

Table 1 also lists the optimized conditions of the ion-pair HF-LPME technique. The extraction solvent in HF-LPME should be compatible with the fiber and have low volatility. According to previously reports [12–16,18], 1-octanol has been employed in the extraction of various organic compounds with satisfied extraction efficiency. Therefore, 1-octanol was selected as the extraction solvent for the study.