Analytica Chimica Acta 741 (2012) 32–37

Contents lists available at SciVerse ScienceDirect

Analytica Chimica Acta

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

Sensitive and robotic determination of bromate in sea water and drinking deep-sea water by headspace solid-phase micro extraction and gas chromatography–mass spectrometry

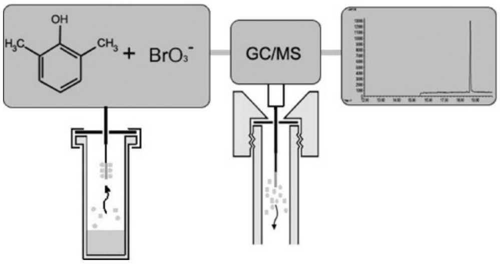
Hyun-Hee Lim[a], Ho-Sang Shin[b,*]

[a] Department of Environmental Science, Kongju National University, Kongju 314-701, Republic of Korea
[b] Department of Environmental Education, Kongju National University, Kongju 314-701, Republic of Korea

HIGHLIGHTS

- This study is the first analysis method with HS SPME GC–MS of bromate.
- Selection of reagent and fibre, reaction temperature/time and pH were optimized.
- The best reagent and fiber is 2,6-DMP and CAR-PDMS.
- LOD and LOQ in sea water were 0.016 and 0.051 $\mu g\,L^{-1}$ and RSD was less than 7.0%.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 16 March 2012
Received in revised form 16 June 2012
Accepted 20 June 2012
Available online 5 July 2012

Keywords:
Bromate
Headspace solid-phase microextraction
Gas chromatography–mass spectrometry
Sea water

ABSTRACT

A robotic method has been established for the determination of bromate in sea water and drinking deep-sea water. Bromate in water was converted into volatile derivative, which was measured with headspace solid-phase micro extraction and gas chromatography–mass spectrometry (HS-SPME GC–MS). Derivatization reagent and the HS-SPME parameters (selection of fibre, extraction/derivatization temperature, heating time and; the morality of HCl) were optimized and selected. Under the established conditions, the detection and the quantification limits were 0.016 $\mu g\,L^{-1}$ and 0.051 $\mu g\,L^{-1}$, respectively, and the intra- and inter-day relative standard deviation was less than 7% at concentrations of 1.0 and 10.0 $\mu g\,L^{-1}$. The calibration curve showed good linearity with $r^2 = 0.9998$. The common ions Cl^-, NO_3^-, SO_4^{2-}, HPO_4^{2-}, $H_2PO_4^-$, K^+, Na^+, NH_4^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, Mn^{4+}, Mn^{2+}, Fe^{3+} and Fe^{2+} did not interfere even when present in 1000-fold excess over the active species. The method was successfully applied to the determination of bromate in sea water and drinking deep-sea water.

1. Introduction

Bromate (BrO_3^-) is not commonly found in water, but it is formed when ozone used to disinfect drinking water reacts with naturally occurring bromide found in source water [1–4]. Bromate is also formed when chlorinated water is exposed to sunlight [5] or when water is treated with concentrated hypochlorite [6].

Bromate is a kind of potential carcinogen, which has been proven by both the U.S. Environmental Protection Agency and the International Agency for Research on Cancer [7,8]. Because of health concerns, the concentration of bromate in drinking water is a major concern among regulatory agencies all over the world [9–12]. Regulatory agencies in the USA [10] and European countries [11] have established a maximum contaminant level of bromate of 10.0 $\mu g\,L^{-1}$ in drinking water, and Korea [12] has established a maximum contaminant level of bromate of same concentration in natural mineral water.

Many methods have been proposed for the determination of bromate in water. Spectrophotometry [13–15], electroanalysis

---

* Corresponding author. Tel.: +82 41 850 8811; fax: +82 41 850 8998.
E-mail address: hshin@kongju.ac.kr (H.-S. Shin).

0003-2670/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.aca.2012.06.046

[16,17], X-ray fluorescence analysis [18], flow-injection analysis [19,20] and electrophoresis [21–24] have been reported as techniques for the determination of bromate, but their sensitivities are not adequate to detect low ng L^{-1}. Also a number of methods have been developed to deal with a variety of water matrices using ion chromatography (IC) [25–50], and most of these methods have been received in standard methods of analysis [42–45]. In fact, bromate quantity can be determined at sub-$\mu g\,L^{-1}$ levels after pre-concentration techniques [28,30]. Alternative and sensitive detection techniques include post-column derivatization [26,44,45] and mass detection [33–41,46–48], but these methods suffer from complex plumbing operations or high costs. Multi dimensional (MD) IC methods were published for the removal of chloride and sulfate ions [49,50]. The methods utilize column-switching whereby a switching-valve is used to selectively divert analytes of interest onto a second or third dimension column, but these were able to determine bromate at levels of 2.5 $\mu g\,L^{-1}$ in the presence of 30 mg L^{-1} chloride.

In recent years, industrial, academic and government bodies have been collaborating in research and development and commercialization activities to release the potential of deep-sea water (DSW). DSW generally refers to sea water that lies in the sea about 200 meters or more in depth where sunlight no more reaches. DSW is characterized by stabilized low temperatures, richness in minerals and purity [51]. Unrefined sea water contain about 5.0% of sodium-chloride and up to 2.0% other minerals (salts) containing bromide (150 mg L^{-1}) [49]. The food industry, medical treatment facilities and drinking water industry have utilized DSW and it has received special attention due to its balance of essential minerals including calcium and magnesium for use in health drink, so called drinking DSW. Although drinking DSW is made by desalinating the high salt water using reverse osmosis process, it can contain the large excess of ions such as bromide, iodide, chloride and sulfate. Because bromate is happened from the disinfection of water containing bromide, the ozonation of drinking DSW is prohibited in Korea. The Korean Environmental Minister adopted 10 $\mu g\,L^{-1}$ as a regulatory concentration of bromate [12] in drinking DSW. Determination of bromate in more complex sample matrices, such as sea water and DSW, presents far greater analytical challenges due to the large excess of matrix interference from ions such as chloride and sulfate.

For the purpose, gas chromatographic mass spectrometric methods (GC–MS) [52,53] following a redox reaction of bromate and extraction have been developed to detect bromate in complex matrices. These methods can analyze bromate with very low detection limits and without chloride interferences, but involve multistep reactions containing removal of free bromide [52] or suffer from interference in chlorinated waters [53]. A previous our work [54] showed that the bromine formed from bromate with acidic conditions reacted with 2,6-dialkylphenols to form 4-bromo-2,6-dialkylphenols, which could be used for the determination of bromate in water by GC–MS. The shortcoming of this method is that the organic derivative must be extracted and concentrated before the injection in GC–MS. Robotic sample treatment is necessary for the routine analysis of a number of samples.

Headspace solid-phase micro extraction (HS-SPME) is a popular technique in the analytical area routinely used automatically to analyze volatile compounds. Headspace is discriminatory in nature since only the volatile compounds in the injection vials can be transferred to the GC system while non-volatile interference will remain in the headspace vials.

In the present study, we report on a HS-SPME GC–MS method designed to automatically determine bromate in sea water and drinking DSW. The objective of our research was to select optimum detivatization reagent for the HS-SPME method, optimize the HS-SPME parameters (selection of fiber, extraction/derivatization temperature, heating time and acidity), and evaluate the feasibility of using the developed method to determine bromate in raw water (i.e. sea water) of drinking DSW and drinking DSW samples.

2. Experimental

2.1. Reagents

Sodium chloride (99.5%), potassium iodide (99.5%), potassium bromide (99%), potassium bromate (99.8%), phenol (PN) (99%), 2,6-difluorophenol (2,6-DFP) (98%), 2,6-dimethylphenol (2,6-DMP) (99.5%), 2,6-dimethylaniline (2,6-DMA) (99%) and 2,4,6-trifluorophenol (2,4,6-TFP) (99%) were of analytical grade and obtained from Sigma (St. Louis, MO, USA). A stock standard solution of bromate was freshly prepared before use by dilution of a 5 mL portion of commercially available bromate standard solution (1000 mg L^{-1}, Sigma, St. Louis, MO, USA) to 100 mL with water. A known volume of this solution was sequentially diluted to give a 1.0 mg L^{-1} bromate standard solution. This solution was used within 1 h of its preparation.

The pure water used in this study was purified by a Milli-Q-Reagent-Grade water system (ZD20) (Millipre, Bedford, MA, USA) and had a resistivity of over 18.2 MΩ.

Commercially available SPME fibers (100-μm polydimethylsiloxane (PDMS), 65-μm polydimethylsiloxane-divinylbenzene (PDMS-DVB), 85-μm polyacrylate (PA), and 85-μm carboxen-polydimethylsiloxane (CAR-PDMS) fused-silica fibers) were purchased from Supelco (Bellefonte, PA, USA).

2.2. Sampling

Five sea-water samples were taken from surface sea water in the East Sea, Korea (38.20°N latitude; 128.60°N longitude) in December 2011. The location is not in relation to drinking DSW brands. Five drinking DSW samples were purchased from several local markets.

2.3. Extraction/derivatization procedures

Water samples of 5.0 mL were placed into 10 mL headspace vials with carried-lined screw caps. After the control to optimum pH with 1 M HCl, 40 μL of 2,4,6-TFP (5 mg L^{-1}), 40 μL of derivatization reagent (10 mg L^{-1}) and 2.0 g of NaCl were added to the sample solutions. A derivatization/adsorption was carried out simultaneously in each headspace vial with continuous shaking, and the derivatives were desorbed in an injection port and passed onto the column for analysis. To study the optimal derivatization conditions, the reaction was performed for various amount of PN, 2,6-DMP, 2,6-DFP, 2,6-DMA (10, 20, 30, 40 and 50 μL of 10 mg L^{-1} standard solution) and SPME adsorption times (40, 50, 60, 70 and 80 min). Derivatization efficiencies were calculated at various temperatures (50, 60, 70, 80 and 90 °C) and acidity (2.0, 5.0, 10.0, 25.0 and 50.0 mM). The acidity of each sample was controlled with 1 M HCl. The optimum conditions for derivatization of bromate were determined by the areas of the formed bromophenols or bromoaniline.

2.4. SPME fibers

PDMS, PDMS-DVB, PA and CAR-PDMS fused-silica fibers were evaluated for the bromate detection. The fiber was initially conditioned according to the instructions of the manufacturer to remove contaminants and to stabilize the solid-phase. Conditioning was carried out in an extra split/splitless port with helium carrier gas prior to each adsorption.