Talanta 170 (2017) 9–14

Contents lists available at ScienceDirect

Talanta

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

Headspace single-drop microextraction coupled with microvolume fluorospectrometry for highly sensitive determination of bromide

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ARTICLE INFO

Keywords:
Bromide determination
Fluorospectrometry
Microvolume analysis
Sample preparation
Single-drop microextraction
Water analysis

ABSTRACT

This work reports on the development of a novel methodology for bromide determination by combining headspace single-drop microextraction with microvolume fluorospectrometry. The method lies in the *in situ* generation of bromine, transfer of the volatile to the headspace and trapping/reaction onto a fluorescein-containing aqueous drop exposed to the gas phase. The decrease in the fluorescence intensity enabled the determination of bromide without dilution of the enriched microdrop. Experimental parameters influencing the performance of the method, namely, fluorescence parameters, extractant phase composition, bromine generation conditions and microextraction time, were evaluated and controlled. Under optimal conditions, an enrichment factor of 243 was attained. The limits of detection and quantification achieved under optimal conditions for bromide were found to be 1.4 and 4.4 μg L^{-1}, respectively. The intra-day repeatability, expressed as relative standard deviation, was 4.4% (n=6). Besides, the inter-day reproducibility, performed at four different days, was 7.1%. Finally, the developed method was successfully applied to the determination of bromide in different water samples, showing recovery values in the range of 95–110%, and validated against certified reference material BCR-611 (ground water, Br^- low level). The proposed method represents a highly convenient approach for monitoring of bromide at very low concentrations.

1. Introduction

The biological essentiality of bromide for basement membranes assembly and tissue development has been recently demonstrated [1]. Moreover, several studies have demonstrated its low degree of toxicity and reduced toxicological concern in nutrition [2]. However, it has also been reported in the literature that bromide, which is ubiquitously found in water, is a key matrix component in oxidative water treatment processes as it can promote the formation of undesired compounds [3]. The formation of brominated disinfection by-products (DBPs) of concern has, in fact, motivated a variety of studies regarding mechanisms of DBPs formation and toxicity [4–7]. Generated DBPs show adverse impacts to human health at very low concentrations, so analytical methodologies capable of monitoring bromide at trace levels are required.

Standard methods for determination of bromide in water samples involve ion chromatography, capillary ion electrophoresis with indirect UV detection and UV–vis spectrophotometry [8]. In addition, a number of alternative methodologies involving UV–vis spectrophotometry [9,10], spectrofluorimetry [11], amperometric detection [12], inductively coupled plasma-mass spectrometry [13,14], dielectric barrier discharge-optical emission [15] and total reflexion X-Ray fluorescence [16] have been reported in the literature for bromide determination. It should be noted that flow methods are amply used to on-line monitoring of bromide [9,10,12]. In addition, a microfluidic paper-based analytical device has been recently proposed for on-site detection of high concentrations of bromide in wastewater samples [17]. Development of simple, rapid, sensitive and portable alternatives for determination of bromide at trace level would be highly desirable for *in situ* field monitoring of this halide.

Miniaturization of sample preparation has significantly contributed to the development of improved analytical methodologies. Among other advantages, microextraction techniques enable the achievement of high enrichment factors along with an efficient clean-up of the sample and negligible consumption of solvents. Single-drop microextraction (SDME) is nowadays a well-established liquid-phase microextraction (LPME) technique that exploits the use of a very high sample-to- solvent ratio to achieve the preconcentration of target compounds in a drop of extractant phase, which typically ranges from 1 to 5 μL [18,19]. The headspace mode (HS-SDME) is an excellent approach for the enrichment of volatile analytes or analyte derivatives that also provides increased selectivity, since non-volatile compounds

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http://dx.doi.org/10.1016/j.talanta.2017.03.090
Received 11 January 2017; Received in revised form 21 March 2017; Accepted 28 March 2017
Available online 30 March 2017
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remain in the sample solution and are therefore not extracted.

Some remarkable developments on the combination of HS-SDME with microvolume detection systems have been recently reported towards the automated determination of a variety of analytes [20–22]. However, in spite of the huge potential of miniaturized sample preparation techniques, their coupling with analytical instrumentation is sometimes troublesome. For instance, the development of analytical methodologies based on the combination of LPME with fluorescence spectrometry has been scarcely exploited. In fact, the lack of compatibility between the volumes typically required to carry our microextraction processes and fluorescence measurements forced researchers to use relatively large extractant phase volumes [23] or dilute the enriched extract prior to perform the analysis [24,25]. The current availability of microvolume fluorospectrometers opens up great possibilities for the development of sensitive methodologies in combination with microextraction approaches since dilution is avoided. This fact enables achieving extremely high enrichment factors, as recently demonstrated [26–31].

In this work, we describe a novel methodology for determination of bromide at trace levels by coupling HS-SDME and microvolume fluorospectrometry. The method involves *in situ* bromine generation, transfer of the volatile to the headspace and simultaneous trapping/reaction onto a fluorescein-containing aqueous microdrop. A decrease in the fluorescence intensity is thus produced as a result of the in-drop reaction occurring between bromine and fluorescein to yield the less fluorescent eosin. Fluorescence parameters, vapor bromine generation and transfer conditions, as well as extractant phase composition were fully assessed, and the applicability of the method to the analysis of water samples was demonstrated.

2. Experimental

2.1. Reagents and materials

All chemicals used were of analytical reagent grade. An Ultra Clear™ TWF EDI water purification system (Siemens, Barsbettel, Germany) was used to obtain ultrapure water.

A stock standard solution of bromide (1000 mg L^{-1}) was prepared from potassium bromide (Sigma-Aldrich, St. Louis, MO, USA). Working standards were daily made by dilution of the stock solution with ultrapure water. Potassium bromate (Sigma-Aldrich) and sulfuric acid (Prolabo, Paris, France) were used for bromine generation. Fluorescein (Panreac, Barcelona, Spain) was used for in-drop sensing of vapor bromine, and two water-miscible organic solvents, namely, absolute ethanol (Prolabo) and N,N-dimethylformamide (Merck, Darmstadt, Germany), were evaluated in microextraction experiments.

The following reagents were used to evaluate potential interferences: NaCl, KI, CdO and $FeCl_3 \cdot 6H_2O$ from Sigma-Aldrich; KIO_3 and $CuCl_2 \cdot 2H_2O$ from Merck; $NaNO_2$ and $Ni(NO_3)_2 \cdot 6H_2O$ from Panreac; $NaHCO_3$ and Na_2SO_4 from Carlo Erba (Milan, Italy), NaHClO from Prolabo; and KNO_3 from Probus (Badalona, Spain).

2.2. Apparatus

Fluorescence measurements were carried out with a Thermo Scientific NanoDrop 3300 Fluorospectrometer (Wilmington, DE, USA). Three solid-state light emitting diodes (LEDs) are available as excitation sources, being perpendicularly oriented to the detector. A 2048-element charge-coupled device array detector was connected by an optical fiber to the optical measurement surface. Fluorescence measurements were carried out by a cuvetteless sample retention technology based in surface tension. Fluorescence measurements were carried out at 513 nm by using the blue LED as excitation source (470 nm). The optical pathlength was set at 1 mm.

A 10 μL high precision microsyringe (Hamilton model 1701 RN, 10 AL) was used. Microextraction experiments were performed using 40 mL amber-vials with screw caps of 24 mm (Supelco, Bellefonte, USA) and PTFE-faced septa of 22 mm (Supelco).

2.3. HS-SDME procedure

Blanks, standards or samples (10 mL) made in 0.75 mol L^{-1} H_2SO_4 were placed into a 40-mL amber vial together with a stir bar. After closing the sample vial, 1 mL of a 5 mmol L^{-1} solution of $KBrO_3$ was externally injected to generate vapor bromine. Then, 2 μL of extractant phase (20 μmol L^{-1} fluorescein aqueous solution containing DMF 2% (v/v) and adjusted to pH 10 with NaOH) was exposed to the headspace above a sample stirred at 700 rpm for 10 min. Once the microextraction process was finished, the enriched drop was retracted back into the syringe and subsequently deposited between the sample pedestals of the microvolume fluorospectrometer.

3. Results and discussion

3.1. Evaluation of experimental variables

The method proposed in this work involves chemical conversion of bromide into vapor bromine, its mass transfer to the headspace and subsequent reaction with a fluorescein-containing aqueous microdrop. The chemical reactions involved are as follows:

$$5Br^- + BrO_3^- + 6H^+ \rightarrow 3Br_2 + 3H_2O \quad (1)$$

$$4Br_2 + \text{fluorescein} \rightarrow \text{eosin} + 4Br^- \quad (2)$$

Specifically, bromide is converted into vapor bromine by redox reaction with bromate in acidic media (reaction 1), whereas bromination of fluorescein takes place when the formed volatile reacts with a fluorescein-containing extractant phase, thus yielding tetrabromofluorescein (eosin) (reaction 2). As a result of the in-drop reaction, a decrease in the fluorescence intensity is produced. A number of experimental parameters influencing the microextraction approach have been evaluated for optimal performance, the obtained results being discussed in this section.

3.1.1. Fluorescence parameters

Fluorescence parameters were initially evaluated to achieve the highest sensitivity. Three solid-state light emitting diodes (LEDs), namely UV, blue and white, can be selected as excitation sources in the microvolume fluorospectrometer used in this work, thus covering the range 365–650 nm. The excitation wavelength was evaluated by using the three available LEDs to obtain the fluorescence emission spectra of a 5 μmol L^{-1} fluorescein-containing aqueous drop. As can be observed from Fig. 1, the blue LED (470 ± 10 nm) provided the highest sensitivity for the fluorophore, so it was selected as the optimal excitation source for further experiments. The excitation and emission wavelengths were set at 470 and 513 nm, respectively.

3.1.2. Extractant phase configuration

Selection of the appropriate extractant phase is of utmost importance in HS-SDME. Thus, those experimental parameters influencing the extractability of vapor bromine and its subsequent reaction with fluorescein were evaluated, namely, fluorescein concentration, type and concentration of miscible organic modifiers, and pH of the drop. The concentration of fluorescein in the drop was firstly evaluated in order to ensure the highest linear dynamic range. The fluorescence intensity of fluorescein showed a linear relationship with the fluorescein concentration up to 20 μmol L^{-1} of the fluorophore, so this concentration was set as optimal. Under these conditions, microextraction experiments were carried out to ascertain the effect of the presence of a miscible organic solvent in the drop with the aim of improving the extraction of vapor bromine. Two water-miscible solvents showing different physi-

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