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ARTICLES

Determination of Volatile Low-Molecular-Weight Amines in Water by Capillary Electrophoresis after Headspace Microextraction

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Abstract—A method for the simultaneous determination of ammonium and seven volatile alkylamines (methylamine, dimethylamine, trimethylamine, ethylamine, *n*-propylamine, isopropylamine, and diethylamine) in aqueous media by capillary electrophoresis after headspace microextraction into a 5-μL drop of a 0.01 M solution of H_3PO_4 was developed. A solution containing 2 mM acridine, 20 mM acetic acid, and 0.05% Tween 20 was chosen as a background electrolyte for indirect photometric detection. Hydrodynamic sample injection was used. The method was tested using the samples of drinking water with the addition of ammonium and alkylamines. The accuracy of the results was confirmed by a standard addition method. The method developed provides an analytical range from 0.003 to 20 mg/L.

Keywords: capillary electrophoresis, alkylamines, headspace microextraction

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Short-chain aliphatic amines widely occur in aquatic environments because of their widespread use as intermediates in the chemical and pharmaceutical industries [1]. These compounds are formed in the production of plastics, dyes, medicines, oxidation inhibitors, and explosives [2] and in the petrochemical industry [3]. In addition, aliphatic amines are common components of biological systems as the decomposition products of organic materials, such as amino acids and proteins. In addition to the problems of hygiene, these compounds are dangerous to human life due to a strong odor because they are irritating to the skin, eyes, mucous membranes, and respiratory tract. Alkylamines can react with certain nitrogen-containing compounds to form nitrosamines, which are carcinogenic. Thus, there is a need to determine aliphatic amines in various matrices [4]. The concentrations of a number of organic amines in drinking water from centralized drinking water supply systems and in fishery water bodies are regulated in accordance with sanitary standards [5, 6].

In most cases, chromatographic methods are used to determine aliphatic amines in water. In particular, a number of methods for the determination of amines using gas chromatography (GC) [7, 8] and liquid chromatography (LC) [9, 10] have been described. A common feature of these methods is time-consuming sample preparation. In LC, derivatization is often used to increase sensitivity because aliphatic amines do not have high UV absorption or fluorescent properties. Chromatographic methods usually include a stage of preconcentration and separation of analytes from the matrix. The preconcentration of aliphatic amines is difficult to perform because of their high polarity and solubility in water [11–14].

Liquid–liquid extraction [15, 16], solid-phase extraction [17, 18], ion-pair extraction [19], etc., are used as sample preparation methods. Most of these methods are time-consuming, and they require the use of significant amounts of expensive and toxic reagents, in particular, organic solvents, such as toluene, carbon tetrachloride, and methylene chloride [12, 20].

Capillary electrophoresis (CE) is an alternative method for the determination of amines, which allows to overcome the above limitations. Its advantages include low consumption of reagents and no need for the derivatization of analytes having low absorption in the UV region due to the use of indirect photometric detection. Malinina with coauthors [21, 22] proposed an approach that allowed them to substantially increase the sensitivity of indirect photometric detection of amines in their determination by capillary electrophoresis.

A combination of CE with sample preparation methods that do not include the use of toxic solvents and reagents is promising. Thus, Kamentsev et al. [23] described the determination of a number of amines in samples with a complex matrix by capillary electro-

phoresis after steam distillation. The limitation of this approach is a high limit of determination (0.25 mg/L).

The use of currently available sample preparation methods such as headspace microextraction will make it possible to completely implement the advantages of CE in the determination of amines in samples with complex matrices. The miniaturization of a liquid–liquid extraction method due to a significant decrease in a volume ratio between the solvent and the aqueous phase led to the development of microextraction methods. A special feature of the microextraction methods is that only small portions of analytes are extracted or preconcentrated for the subsequent determination [24]. Headspace microextraction can be performed using simple devices, in particular, a usual microsyringe [25]. Water and aqueous solutions can also serve as extractants for the preconcentration of volatile and water-soluble analytes, such as alkylamines [26]. Headspace microextraction is the most attractive method because of a wide range of environmentally friendly polar solvents for extraction.

For the determination of volatile analytes, an appropriate solvent microdroplet is placed in the headspace above the sample solution [27, 28] or in a sample vapor flow [29–31]. Headspace microextraction is also suitable for the extraction of volatile compounds from samples with a complex matrix [32, 33]. For example, Kaykhaii et al. [34] proposed the simultaneous determination of ethylamine, isopropylamine, propylamine, diethylamine, and butylamine by GC after headspace microextraction into a drop of benzyl alcohol.

The aim of this work was to study the simultaneous determination of the trace concentrations of a number of low-molecular-weight alkylamines in aqueous media by capillary electrophoresis after headspace microextraction.

EXPERIMENTAL

Reagents and equipment. The solutions of alkylamines were prepared by diluting the stock solutions of alkylamines with a concentration of 1 g/L with water. The calibration curves were constructed using the aqueous solutions of alkylamines and ammonium in a concentration range from 0.01 to 1 mg/L. All reagents were of chemically pure grade or higher. Twice-distilled water was used for the preparation of all of the solutions.

The experiments were performed on a Capel-104T capillary electrophoresis instrument (Lumex) with photometric detection at 254 nm. An unmodified quartz capillary was used (inner diameter, 75 μm; total length, 60 cm; and effective length, 50 cm). Separation was performed at a voltage of 20 kV and a temperature of 20°C with hydrodynamic sample injection at 30 mbar for 10 s. A solution containing 2 mM acridine, 20 mM acetic acid, and 0.05% Tween 20 was used as a background electrolyte [21, 22].

At the beginning and at the end of a working day, the capillary was successively washed for 5 min with water, 1 M HCl, water, a 0.5 M solution of NaOH, and water. Before each analysis, the capillary was washed with running electrolyte for 3 min. The separation was carried out with a positive polarity. The electroosmotic flow was directed toward the cathode.

Headspace microextraction method . A solution of Na_2SO_4 with a concentration of 0.3 g/mL was added to a 2-mL aliquot portion of the sample; the resulting solution was placed in a 10-mL glass vial equipped with a septum and rendered alkaline with 1 mL of a 0.1 M NaOH solution. The vial was placed in an ultrasonic bath; the septum was punctured with a needle of a chromatographic syringe, and a 5-μL drop of a 0.01 M solution of H_3PO_4 was squeezed out. Extraction was carried out for 60 min at 70°C. After the completion of headspace microextraction, the absorbent drop (5 μL) was transferred into an Eppendorf tube and diluted to 100 μL with twice-distilled water, and the resulting solution was analyzed by capillary electrophoresis.

RESULTS AND DISCUSSION

We studied the possibility of the simultaneous determination of ammonium and seven volatile alkylamines (methylamine, dimethylamine, trimethylamine, ethylamine, propylamine, isopropylamine, and diethylamine) in drinking water samples, including samples with the addition of ammonium and alkylamines, by CE after headspace microextraction.

The effects of time, temperature, absorbent droplet volume, and the concentrations of NaOH and H_3PO_4 solutions on the headspace microextraction were investigated. First, we studied the effects of the concentration of NaOH solutions (0.01–1 M), which are necessary for converting the ammonium ion and alkylamines into volatile species, and the concentration of H_3PO_4 (0.01–1 M) in the absorbent solution. The concentrations of 0.1 M NaOH and 0.01 M H_3PO_4 were chosen as optimal. Further increase in the concentration of the NaOH solution did not increase the extraction of analytes into the drop. With an increase in the concentration of H_3PO_4, the absorbent solution containing analytes became strongly acidic to negatively affect the results of the CE analysis without an increase in the extraction of analytes.

Ultrasonic mixing was chosen as an optimal method for mixing the solution in the course of headspace microextraction. The effects of temperature in a range from 30 to 70°C and the duration of headspace extraction (15–60 min) were also studied. The mixing of sample solution in an ultrasonic bath at 70°C for 60 min was chosen as an optimum.

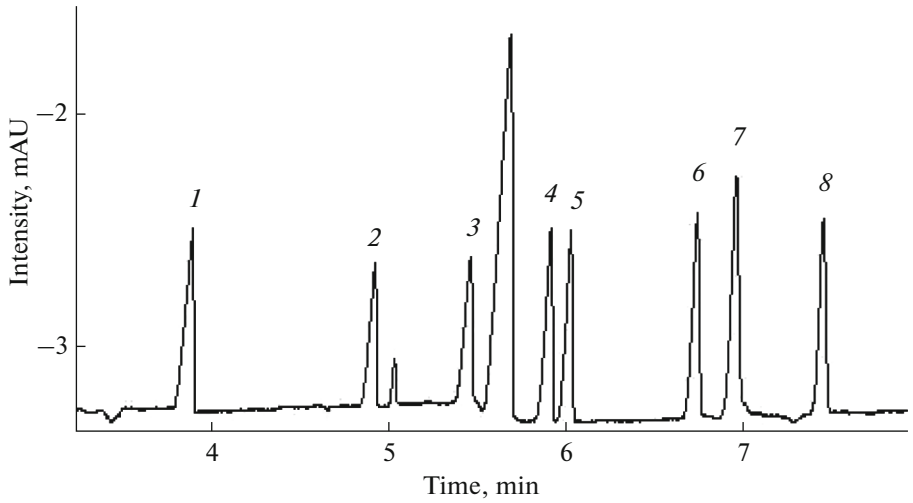

Fig. 1. Electropherogram of a drinking water sample with the addition of ammonium and alkylamines after headspace microextraction. Background electrolyte composition: 2 mM acridine, 20 mM acetic acid, and 0.05% Tween 20. Sample injection: 30 mbar for 10 s. The detection wavelength was 254 nm: (*1*) ammonium, (*2*) methylamine, (*3*) dimethylamine, (*4*) trimethylamine, (*5*) ethylamine, (*6*) *n*-propylamine, (*7*) isopropylamine, and (*8*) diethylamine.

It was established that the analytical signal increased with the droplet volume. However, droplets with a volume of greater than 5 μL are unstable and detach from the syringe needle tip during headspace microextraction. Thus, a drop volume of 5 μL was chosen as optimal.

The effect of the addition of Na_2SO_4 solution on the salting out of analytes was investigated [35, 36]. It was found that the extraction of analytes increased by 15% at a 0.3 g/mL concentration of Na_2SO_4 solution, and the extraction remained unchanged at a higher concentration of Na_2SO_4; therefore, we used the addition of Na_2SO_4 solution with a concentration of 0.3 g/mL in the subsequent experiments.

In the CE of a sample after headspace extraction, the peaks of all analytes were separated, but the peaks of some analytes were broadened, possibly, due to interactions between amines and the capillary walls. The peak broadening was almost the same for all the amines. It is well known that the nonionic surfactant Tween 20 reduces the adsorption of analytes on the capillary surface [37, 38]; therefore, Tween 20 was introduced into the background electrolyte. Figure 1 shows that no peak broadening was observed after the addition of the nonionic surfactant to the electrolyte solution.

The linearity range of calibration curves for ammonium, methylamine, dimethylamine, trimethylamine, ethylamine, *n*-propylamine, isopropylamine, and diethylamine was from 0.01 to 1 mg/L. The analytical ranges for all of the analytes were 0.003–20 mg/L with consideration for their preconcentration by headspace microextraction. As can be seen in Table 1, the determination limits (calculated at a signal-to-noise ratio of 10 : 1) were lower than the maximum permissible concentrations (MPCs) of the analytes in drinking water and in fishery water bodies in all cases. As can be seen in Table 1, the determination limits provide an opportunity to determine the majority of the aforementioned alkylamines in drinking water and fishery water at a level of 1/2MPC.

The method developed was tested in the analysis of drinking water samples and model solutions. This method can also be used for the determination of the ammonium ion and alkylamines in natural water and wastewater. Figure 1 shows a typical electropherogram of a drinking water sample with the addition of ana-

Table 1. Maximum permissible concentrations of aliphatic amines in drinking water and fishery water

Analyte	MPC, mg/L	
	I*	II*
Ammonium	–	0.5
Methylamine	1.0	0.05
Dimethylamine	0.1	0.005
Trimethylamine	2.0	0.01
Ethylamine	0.5	–
n-Propylamine	0.5	–
Isopropylamine	2.0	–
Diethylamine	2.0	0.05

* I is MPC in drinking water according to *SanPin 2.1.4.1074-01* [5].
** II is MPC in fishery water bodies [6].

Table 2. Results of the determination of alkylamines in tap water samples ($n = 5$, $P = 0.95$)

Analyte	Found, mg/L	
	I*	II**
Ammonium	0.11 ± 0.02	1.2 ± 0.2
Methylamine	0.105 ± 0.007	1.1 ± 0.2
Dimethylamine	0.097 ± 0.008	0.96 ± 0.09
Trimethylamine	0.09 ± 0.01	1.0 ± 0.1
Ethylamine	0.09 ± 0.01	1.0± 0.1
n-Propylamine	0.08 ± 0.02	0.9 ± 0.2
Isopropylamine	0.09 ± 0.01	0.9 ± 0.2
Diethylamine	0.09 ± 0.01	0.9 ± 0.2

* Added, 0.10 ± 0.01 mg/L of an analyte.
** Added, 1.0 ± 0.1 mg/L of an analyte.

lytes after headspace microextraction. The accuracy of the results was evaluated using the standard addition method. A known volume of a standard solution of a mixture of ammonium and seven alkylamines was introduced into the test water samples, and the electrophoresis analysis of the resulting solution was performed after headspace microextraction. The results of the determination of alkylamines without additives and with the addition of standard solutions (Table 2) indicate the accuracy of the method.

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