

Flow-Injection Photometric Determination of Arsenic Microconcentrations in Water Media with Chromatomembrane-Cell Preconcentration by Extraction

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Abstract

The procedure for flow-injection photometric determination of arsenic microconcentrations in water media was developed. The determination limit is 1 µg/L. The range of determined contents is 10 µg/L to 120 µg/L. Such small value of determined contents is achieved due to the original scheme of sample pretreatment including the chromatomembrane reactionary gaseous extraction of arsenic as arsine form and its subsequent liquid-absorbing extraction from a gas phase into solution of reagent in a chromatographic column. The second factor provided lower concentrations was the use of new reagent for arsenic: 5-(1,3-benzodioxol-5-yl)-3-(4-iodophenyl)-2-phenyl-3H-1,2,3,4-tetraazol-2-ium chloride in an admixture of solvents water – butanol-1 – dimethyl sulfoxide (10:3:12).

Keywords Determination of arsenic, chromatomembrane cell

Introduction

Arsenic belongs to a number of the rather abundant pollutants of natural water which connected with wide application of its compounds in industry and agriculture. The compounds of arsenic are capable to be bioaccumulated by different aqueous organisms leading in the end link of alimentary chain to the human danger. Maximum permissible concentration (MPC) of arsenic in water according to the existing standards is 50 µg/L [1], so that requires special corresponding methods of its determination in water.

The determination of arsenic content in water at the MPC level is not accessible by using the most widely known direct photometric method based on measuring the absorbance of the reduced form of molybdenum-arsenic acid in aqueous or organic media [2]. It does not follow the way they should be realised under: the stationary or flow-injection scheme of analysis. Methods of arsenic contents determination proposed in recent years based on the extraction of arsenic in volatile hydride form and the subsequent absorption of arsine by the solutions of tetrazolium salts [3] have designated the for determination of arsenic microconcentrations. However, in this case, the methods of analysis developed up to now do not solve the problems of ecological monitoring neither on a detection limit nor on selectivity [4].

The purpose of the present study is the development of the most effective scheme of sample pretreatment for flow-injection photometric determination of arsenic with tetrazolium salts and searching for a new reagents on arsenic among compounds of this class.

Experimental

The working solutions of arsenic were prepared by a sequential dilution of aliquot parts of common starting solution with concentration of arsenic 0.5 g/L obtained by dissolving Na₃AsO₄·12H₂O in deionized water and standardized by iodometric titration [2]. Deionized water used for preparing all solutions was obtained by passing the distilled water through an ion-exchange column with a mixed layer of an anionite Dowex 50W-X8 and cationite Dowex 1X-8 in OH⁻ and H⁺ forms, respectively. Auxiliary solutions of sodium borohydride with concentrations 0.1; 0.3; 0.5; 0.7; 0.9; 1.0; 1.1 % in 0.1 mol/L solution of sodium hydroxide, and also 6 and 8 mol/L hydrochloric acid were prepared. Dimethyl sulfoxide and butanol-1 were rectified by distillation. The following tetrazolium salts were studied as reagents for arsenic: 2,3,5-triphenyltetrazolium chloride, 5-(1,3-benzodioxol-5-yl)-3-(4-iodophenyl)-2-phenyl-3H-1,2,3,4-tetraazol-2-ium chloride and 3-(2-methylphenyl)-2,5-diphenyl-3H-1,2,3,4-tetraazol-2-ium chloride. Reagents were synthesized in St. Petersburg State Institute of Technology according to method described elsewhere [5]. The working solutions with concentration of 2×10⁻³ mol/L were prepared by dissolving a shot of the corresponding reagent in a mixture of solvents: 0.3 mol/L of solution of sodium hydroxide in water, butanol-1 and dimethyl sulfoxide in a ratio 10:3:12 v/v, correspondingly. The solutions of the reagent are stable for one month in dark glass flasks.

A method of the determination of arsenic microamounts in water was developed by the flow-injection analyzer (FIA) with the photometric detector. The gaseous extraction of arsenic as arsine form took place inside the chromatomembrane cell (CMC) of cylindrical shape with the dimensions of mass-exchange layer: diameter 18 mm, height 10 mm [6]. The process of gaseous extraction was carried out in two ways: in a flow of nitrogen through the CMC from external source in a flow of hydrogen generated by acidification of a sample by

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hydrochloric acid. Arsine was absorbed from a gas-extractant flow to the solution of a reagent in a gas-liquid chromatographic column filled with fiberglass as a carrier of the fixed liquid phase. The dimensions of a column are: 25 mm length and 10 mm diameter. The disturbing action of antimony hydride was eliminated using the known method of its decomposition by a passage through a column with ascarite [4] which represents the alloy of sodium hydroxide with asbestos. Length of the column is 10 mm, diameter is 5 mm.

Results and discussion

The development of the scheme of sample pretreatment for effective arsenic determination using tetrazolium salts followed the choice of photometric reagent for arsenic from several compounds of this class which were at our disposal. We compared the spectrophotometric characteristics of products of reaction between arsine and tetrazolium salts (formazanes). The comparison showed that the product of reaction of arsine with 5-(1,3-benzodioxol-5-yl)-3-(4-iodophenyl)-2-phenyl-3H-1,2,3,4-tetraazol-2-ium chloride has the most high coefficient of molar absorption and the most stable optical density among other formazanes. The absorption spectra of reaction products in the chosen mixture of solvents are shown in Fig. 1. The coefficients of molar absorption of formazanes are given in Table 1.

The data obtained allowed to choose from studied tetrazolium salts as a reagent on arsenic 5-(1,3-benzodioxol-5-yl)-3-(4-iodophenyl)-2-phenyl-3H-1,2,3,4-tetraazol-2-ium chloride conditionally called "arsol". All further research devoted to the development of method for the determination of arsenic microconcentrations in water were carried out using it as a photometric reagent.

The next step of the study was the development of the common procedure of sample pretreatment for arsenic determination with the chosen reagent. The selected scheme (see Fig. 2) included chromatomembrane gaseous extraction of arsenic as arsine form with subsequent gas-liquid chromatographic extraction into solution of the chosen reagent.

The development of scheme was followed by the selection of solvent composition in which the liquid absorption of arsine with a subsequent interaction with "arsol" (chosen as the reagent) occurs. Additional requirements to the solvent are possibility to solve the product of reaction between arsine and the above mentioned reagent and lack of low-boiling components which prevent from using it as a fixed phase in the gas-liquid column at liquid absorption of arsine. The procedure of trial-and-error selection of components allowed to choose the following mixture as a solvent: water – butanol-1 – dimethyl sulfoxide (10:3:12). The found solvent composition allowed to implement the scheme of gas-liquid chromatographic extraction of arsine.

The comparison of silica gel and fiberglass as carrier of a fixed phase in the absorption chromatographic column was investigated. By using fiberglass, the colored product of reaction formed in a fixed phase successfully quickly and quantitatively eluted together with was fixed phase by the solution of identical composition. Simultaneously regeneration of a fixed phase in the column takes place. In case of silica gel as a carrier, formazanes from the column are not eluted by the mixture of solvents used as a fixed phase. The achievement of their quantitative extraction from the column is possible only by flushing it with alcohol that complicates the scheme of FIA.

The optimal concentrations of other reagents in auxiliary solutions were chosen according to the peak value of analytical

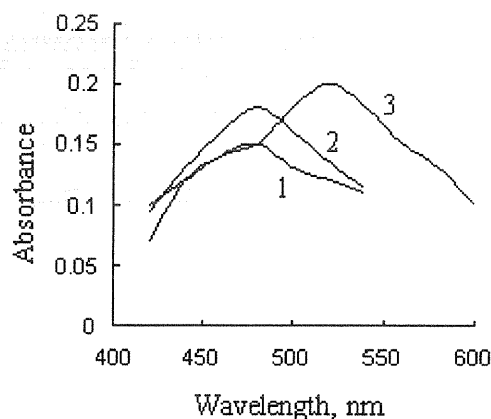


Fig. 1. Absorption spectra of interaction products (in solutions) of arsine with the following reagents 1: 2,3,5-triphenyltetrazolium chloride; 2: 3-(2-methylphenyl)-2,5-diphenyl-3H-1,2,3,4-tetraazol-2-ium chloride; 3: 5-(1,3-benzodioxol-5-yl)-3-(4-iodophenyl)-2-phenyl-3H-1,2,3,4-tetraazol-2-ium chloride.

signal as a function of their concentration under other conditions being equal.

In the preliminary experiment for the selection of optimal concentration of sodium borohydride, the scheme of chromatomembrane gaseous extraction was used. This traditional procedure involves continuous injection of gas-extractant in mass-exchange layer of the CMC with simultaneous injection of aqueous solution [7]. In the developed procedure of arsenic extraction as arsine form, the formation of hydrogen in significant volumes takes place, thus it can be used as gas-extractant without supply from the outward source. Evidently in this case, the completeness of arsenic extraction depends besides the rate of nitrogen expenditure on the volume of formed hydrogen. The volume itself depends on sodium borohydride concentration in solution dosed into the sample and on the concentration of hydrochloric acid used for neutralization of sample in the mixed solution. Therefore the influence of sodium borohydride concentration on completeness of arsine extraction was studied with as well as without injection of gas-extractant from outward source to the CMC. The concentration of sodium borohydride in 0.1 mol/L sodium hydroxide solution dosed into the sample varied from 0.1 to 1.1% (Fig. 3). Under the chosen concentration of sodium borohydride the values of the analytical signal obtained with and without injection of gas-extractant in the CMC from outward source coincide. This fact evidences that forming amount of hydrogen is sufficient for the realization of effective chromatomembrane gaseous extraction of arsine from aqueous phase that allows to give up an outward source of gas-extractant at the stage of arsenic extraction.

The results of investigation of the hydrochloric acid concentration influence on gaseous extraction of arsenic are presented in Fig. 4. According to the data the maximal value of detector signal is achieved at the concentration of hydrochloric acid 1.5 mol/L in terms of solution obtained after admixture of currents. The minimal acid concentration in sample necessary to provide the maximal completeness of arsine extraction – 1.5 mol/L was chosen for further experiments.

For elimination of the disturbing action of antimony which also forms in presence of sodium borohydrides the volatile hydride capable to react with the tetrazolium salts, it was separated from the current of a gaseous phase in the absorbing column filled with ascarite [4]. In the column used up to 2 mg of antimony can be caught.

According to the found conditions of extraction and absorption of arsenic, the following scheme for the flow-injection determination of its microconcentrations in water (Fig. 2) was chosen. The currents are commuted using two-running switching tap. In the first position (absorption phase) corresponding to full lines in Fig. 2, arsine is absorbed in chromatographic column (11). The duration of the absorption phase is 300 sec (increasing the time of absorption does not lead to change of the analytical signal as seen from Fig. 5). The flow of the sample solution (3) (standard solution of arsenic) pumped (5) the with rate of 5 ml/min is sequentially mixed with the following solutions: 6 mol/L hydrochloric acid (2) and 0.5 % sodium borohydride (1) in a ratio 5:2:1 accordingly and is directed to the CMC (7) through a mixing spiral (6) and further to outlet (9). From the CMC (7) arsine is transferred by gas-extragent (hydrogen) to the chromatographic column (11) through the column with ascarite (8). Eluent (4) is pumped through the flow photometric detector (13) with the rate of 2 ml/min. The line of a background signal corresponding to «zero» concentration of arsenic in eluent is registered on FIA display.

In the second position of the switching tap (elution phase) (10) corresponding to the dotted lines in Fig. 4 arsine from the

CMC (7) is directed to outlet (12) with the current of gas-extragent. The duration of elution phase is 120 s (optical density of eluate reaches the level of background signal as shown in Fig. 6 and formazane is completely eluated from chromatographic column). Eluent (4) is directed to the chromatographic column (11), thus eluate arrives the detector (13), simultaneously fixed phase is deposited on fiberglass in the chromatographic column (11). Colored formazane presented in the eluate causes the modification in optical density of solution which is registered by detector (13) as peak of eluation.

For analysis the regular procedure of FIA graduating by standard solution of arsenic in the selected analysis conditions of was used.

The determination limit is 1 µg/L. The range of determined contents is 10 µg/L to 120 µg/L. The duration of one analysis process is 7 min.

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Table 1. Spectrophotometric characteristics of compounds formed in the reactions of arsine with different tetrazolium salts in medium water – butanol-1– dimethyl sulfoxide(10:3:12)

Reagent	λ_{max} , nm	$\epsilon \cdot 10^4$, L/mol-cm at the moment of formazane formation	$\epsilon \cdot 10^4$, L/mol-cm trough 10 min after formazane formation
2,3,5-triphenyltetrazolium chloride	480	2.5	0.9
5-(1,3-benzodioxol-5-yl)-3-(4-iodophenyl)-2-phenyl-3H-1,2,3,4-tetraazol-2-ium chloride	520	3.5	3.4
3-(2-methylphenyl)-2,5-diphenyl-3H-1,2,3,4-tetraazol-2-ium chloride	480	2.6	1.0

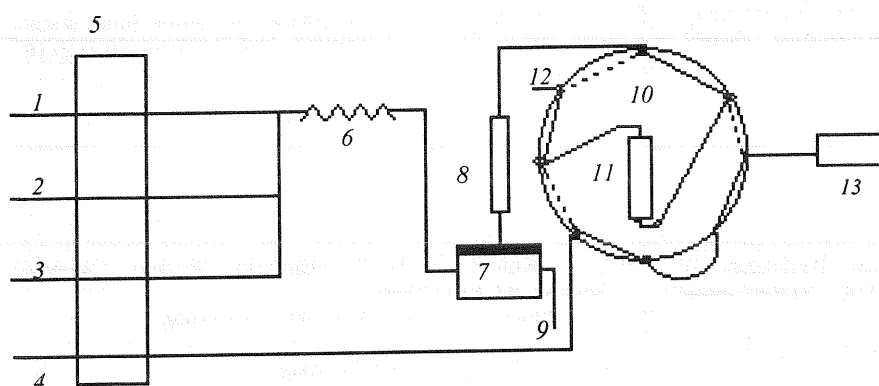


Fig. 2. The scheme for flow-injection determination of arsenic microconcentrations: 1,2,3,4: flows of solution of sodium borohydride; hydrochloric acid; sample and tetrazolium salt reagent, respectively; 5: peristaltic pump; 6: mixing spiral; 7: CMC; 8: column with ascarite; 9: sample outlet; 10: two-position switching tap; 11: chromatographic; 12: gas phase outlet; 13: detector.

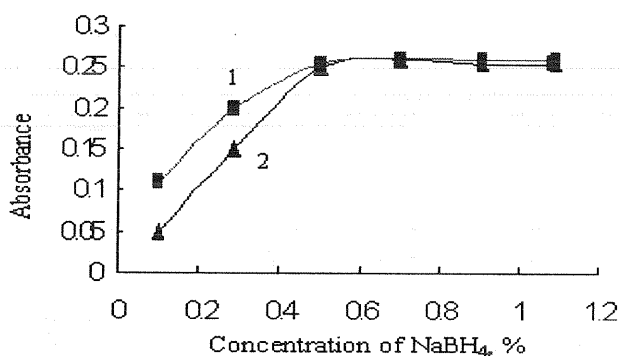


Fig. 3. The influence of sodium borohydride concentration in 0.1 mol/L sodium hydride solution at fixed hydrochloric acid concentration 1.5 mol/L, arsenic concentration 30 $\mu\text{g/L}$: 1 – with injection of gas-extragent to the CMC from outward source (expenditure rate of nitrogen 12 ml/min); 2 – without injection of gas-extragent from outward source; arsol concentration 2×10^{-3} mol/L

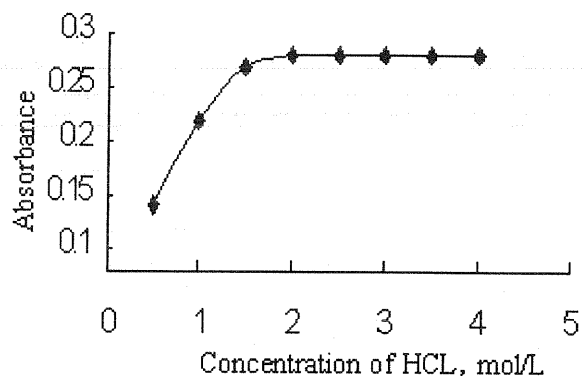


Fig. 4. The influence of hydrochloric acid concentration in the solution introduced for neutralization of admixed solution of sample and sodium borohydride concentration, concentration of arsenic is 30 $\mu\text{g/L}$, arsol concentration 2×10^{-3} mol/L

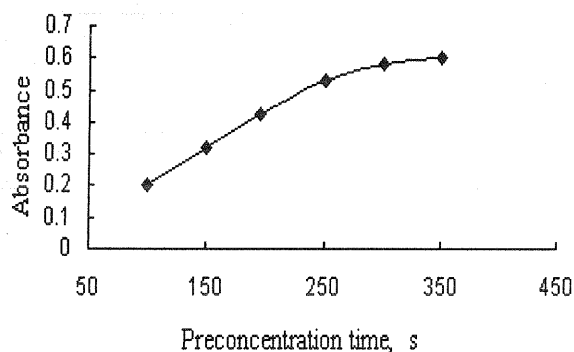


Fig. 5. Analytical signal as a function of preconcentration time, arsenic concentration 100 $\mu\text{g/L}$, arsol concentration 2×10^{-3} mol/L.

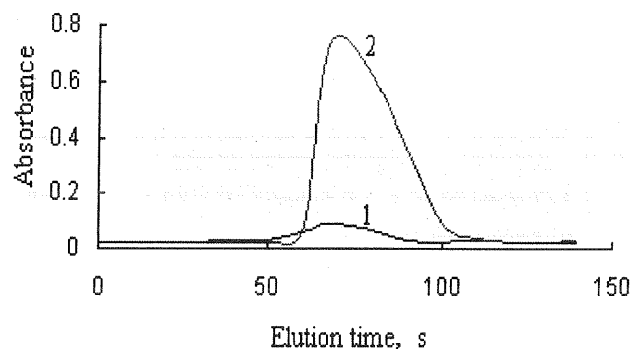


Fig. 6. Analytical signal as a function of elution time, arsenic concentration 1: 10 $\mu\text{g/L}$, 2: 120 $\mu\text{g/L}$, arsol concentration 2×10^{-3} mol/L.

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