Application of Heteropoly Compounds for Determination of Chemical Speciations of Arsenic in Natural Waters

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Abstract

The procedure has been developed to determine arsenate, arsenite, monomethylarsonate, and dimethylarsenite ions in water by the capillary electrophoresis method with spectrophotometric registration of detectable forms of arsenic derivatives. Isopolymolybdate has been selected as a reagent for derivatization. The stoichiometry has been studied and the extinction coefficients of the detected heteropoly complexes have been determined. Optimum conditions for their formation and for electrophoretic separation have been selected. Upon concentrating by the electrostacking method, the developed procedure affords the detection limits at a level of 0.01 µg/ml.

INTRODUCTION

In studies of ecosystems of technogenic character, the information on chemical forms of elements that show various toxicity and different migration ways in nature takes on a special significance. Among the known toxicants, the compounds of arsenic represent serious danger. Sweet waters contain salts of arsenic, arsenous, monomethylarsonic (MMA), and dimethylarsinic (DMA) acids [1]. Traditionally, the complex methods that combine separation (liquid or gas chromatography) and element-selective detecting (atomic emission and atomic absorption spectrometry, inductively coupled plasma mass spectrometry, *etc.*) are applied for their determination [2–4]. Weak absorption of the mentioned compounds even in ultraviolet area presents a significant obstacle for application of more simple and affordable schemes on the basis of spectrophotometric detecting. Their transformation into compounds with the large values of molar extinction coefficient, which can be readily registered by means of simple detectors of the flow-through type, is envisioned to be expedient to increase their determination sensitivity.

It is known that for spectrophotometric arsenate determination the use is made of heteropoly compounds (HPC) in the form of arsenotungstates [5], arsenomolybdovanadates [6], arsenomolybdenic heteropoly acid $H_3AsMo_{12}O_{40}$ or heteropoly blue $H_{3+x}AsMo_{12-x}^{VI}Mo_x^{IV}O_{40}$ [6–8]. Application of photocolorimetric reaction for the postcolumn derivatization mode of chromatographic arsenate ion determination with the formation of yellow form of arsenomolybdenic heteropoly acid has been also described [9]. For the postcolumn derivatization mode of DMA determination employing the reaction of arsenomolybdate formation, the variant of its prior oxidation into arsenate under severe conditions is suggested. This circumstance

complicates the analysis scheme [10]. There are also literary data about existence of heteropoly compounds for DMA, MMA, and arsenite ions [11−18]. However, the literature contains no insights into their analytical application.

Within the present research, we have studied the possibility of analytical application of the reactions to form HPC with molybdate for determination of all four chemical speciations of arsenic.

The purpose of this work is to select, to optimize, and to unify the formation conditions for HPC of arsenate, DMA, MMA, and arsenite ions with molybdate ions for their subsequent determination by the capillary electrophoresis method with spectrophotometric detecting.

EXPERIMENTAL

Sodium dimethylarsenite $NaAsO_2(CH_3)_2$ of Aldrich corporation and sodium salt of monomethylarsonic acid that was synthesized by the procedure [19] have been used in the work. Qualification of chloric acid and sodium hydroxide was "extra pure" (os. ch.), and that of the remaining reagents was no less than "analytically pure" (ch. d. a.).

Initial solutions of arsenate, arsenite, MMA, and DMA with arsenic content of 1 mg/ml were prepared by dissolving of sodium arsenate $(Na_3AsO_4) \cdot 12H_2O$, arsenic oxide As_2O_3, sodium monomethylarsonate $Na_2AsO_3CH_3$, and sodium dimethylarsenite $NaAsO_2(CH_3)_2 \cdot 3H_2O$ in water. Arsenic oxide (III) was dissolved in water at heating with addition of a minimum quantity of sodium hydroxide (up to pH 9). The obtained solutions are stable when stored in a refrigerator (T = 5 °C). Working solutions of chemical speciations of arsenic were prepared immediately before use by dilution of initial solutions.

For spectrophotometric measurements, the reagent solutions with molybdate concentration of $4.8 \cdot 10^{-3}$ and $6.4 \cdot 10^{-3}$ M were prepared by dissolving of sodium molybdate $Na_2MoO_4 \cdot 2H_2O$ in water. The values pH 3−5 were provided by the addition of chloric acid. Interaction of arsenic compounds with a reagent was studied when mixing equal volumes of solutions of

chemical speciations of arsenic and molybdate, while keeping pH in an interval of 3−5. The values pH of HPC solutions were monitored by means of I-130 ionomer with an accuracy of ±0.02 units. Electronic absorption spectra were registered in Specord M-40 spectrophotometer.

Determination of chemical speciations of arsenic in model solutions was conducted with a capillary electrophoresis setup "Kapel 104-T" with UV detector (254 nm) and quartz capillary (diameter of 75 µm, the total length of 70 cm, the length from an inlet to the detector was 50 cm). During the course of analysis, the temperature of capillary was maintained at a level (20±0.1) °C. The electrolytes containing 5 mmol/l of sodium molybdate and 10 mmol/l of sodium perchlorate with pH 3, 4, and 5 and also the solutions with 2.5 mmol/l concentration of sodium molybdate and 5 mmol/l of sodium perchlorate (pH 3) were used as an electrophoretic buffer. Water solutions of a mixture of chemical speciations of arsenic were fed by pressure (pneumatic feeding: 30 mbar, 5 s) or under the influence of electric field (electrokinetic feeding: −25 kV, 10 s) without prior addition of a reagent. Running voltage comprised −16 kV.

RESULTS AND DISCUSSION

According to the literary data, structurally characterized heteropolymolybdate ions of various chemical speciations of arsenic show the following composition: $[AsMo_{12}O_{40}]^{3-}$, $[As_2Mo_{18}O_{62}]^{6-}$, $[AsMo_9O_{31}(OH_2)_3]^{3-}$, $[As_2Mo_6O_{26}]^{6-}$, $[As_4Mo_{12}O_{52}H_4]^{4-}$, $[H_4As_4Mo_4O_{26}]^{4-}$ with arsenate ions [13]; $[(CH_3)_2AsMo_4O_{15}H]^{2-}$ with DMA [13]; $[(CH_3AsO_3)_2Mo_6O_{18}]^{4-}$, $[(CH_3AsO_3)Mo_6O_{18}(H_2O)_6]^{2-}$ with MMA [13]; and $[As_3Mo_3O_{15}]^{3-}$ with arsenite ions [18].

Authors [20−24, 15] studied the equilibriums of formation of heteropolymolybdates in water solution from evidence of potentiometric measurements with molar ratios Mo : As, which were close to the stoichiometry of complexes, for arsenic concentrations of no less than 1 mmol/l. However, the results of computation regarding formation of heteropoly molybdates

correlated with spectrophotometric measurements only for arsenate ions [20, 21]. We have investigated the possibility for spectrophotometric detecting of low concentrations of arsenate, DMA, MMA, and arsenite ions with an excess of the reagent of sodium molybdate for the pH in a range of 3—5. Absorption spectra, which have been recorded 2 min, 1 h, and 1 day later than the solutions were prepared, coincided, which bears witness to quick establishment of equilibrium in the system.

$(CH_3)_2AsO_2^-$ ions

It is known that at pH 3—5, dimethylarsenite forms HPC of composition $[(CH_3)_2AsMo_4O_{14}OH]^{2-}$ with absorption maximum at 40 000 cm^{-1} ($\varepsilon \approx 2 \cdot 10^4$) [11—13, 23]. For this complex, which was synthesized by the procedure [11], dependence of the mean
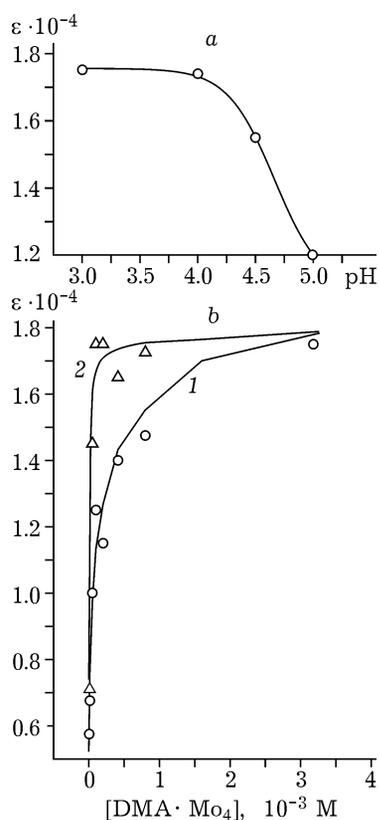
Fig. 1. Dependence of molar extinction coefficient ε of DMA $\cdot$ Mo$_4$ heteropoly complex on pH (*a*) and on $[(CH_3)_2AsMo_4O_{14}OH]^{2-}$ concentration (*b*): *a* − $C_{DMA} = 8 \cdot 10^{-4}$ M, $C_{Mo(VI)} = 3.2 \cdot 10^{-3}$ M; *b* − pH: 4.5 (*1*), 4.0 (*2*).

extinction coefficient ε on pH at $\nu_{max} = 40\ 000\ cm^{-1}$ is given in Fig. 1, *a*. It can be seen that ε decreases with increase in pH from 4 to 5. At pH 4.5, ε drops with a decrease in concentration of complex (see Fig. 1, curve *1*), whereas at pH 4.0, ε is invariable down to the concentration of ~10^{-4} M (see Fig. 1, curve *2*). The acquired data of spectrophotometric measurements bear witness to dissociation of the complex at a concentration less than 10^{-4} M and pH > 4. An excess of molybdate can displace equilibrium of the reaction towards complexation of arsenic.

To make an estimate of the possibility for spectrophotometric DMA determination, complexation with an excess of molybdate was explored under the following conditions: $C_{Mo(VI)} = 3.2 \cdot 10^{-3}$ M, $C_{ДМА} = 5 \cdot 10^{-5}$—$2.4 \cdot 10^{-3}$ M, pH 4.0 and 3.0.

Isopolymolybdates $H_xMo_7O_{24}^{-(6-x)}$ ($x = 0, 1, 2$ or 3) that are present in solution absorb light in UV area. The distinct maximum associated with HPC formation is evidenced at 40 000 cm^{-1} on the background of molybdate absorption (Fig. 2, *a*). For pH 4.0 and 3.0, linear growth of optical density with DMA concentration at 40 000 cm^{-1} is observed up to the ratio Mo : DMA that is equal to 4 (see Fig. 2, *b*). In the regions $\nu > 43\ 300\ cm^{-1}$ and $\nu < 37\ 000\ cm^{-1}$, absorption of solutions decreases with an increase in DMA concentration up to a ratio Mo : DMA equal to 4 (see Fig. 2, *a*, spectra *1—9*). The existence of two isobestic points bears witness to formation of a complex with DMA $\cdot$ Mo$_4$ stoichiometry. Extinction coefficients ε_c of this complex obtained with an excess of molybdate have been calculated from the equation

$$D = \varepsilon_{Mo}(C_{Mo} - 4C_{DMA})l + \varepsilon_c C_{DMA}l$$
$$= C_{DMA}(\varepsilon_c - 4\varepsilon_{Mo})l + C_{Mo}\varepsilon_{Mo}l \qquad (1)$$

under the assumption that DMA is completely bound into the complex. The resulting values ($1.71 \cdot 10^4$ at pH 4.0 and $1.74 \cdot 10^4$ at pH 3.0) coincide with the extinction coefficient, which has been calculated for $[(CH_3)_2AsMo_4O_{14}OH]^{2-}$ complex that was synthesized with stoichiometric proportions between arsenic and molybdate (see Fig. 2), and with literary estimations [12].
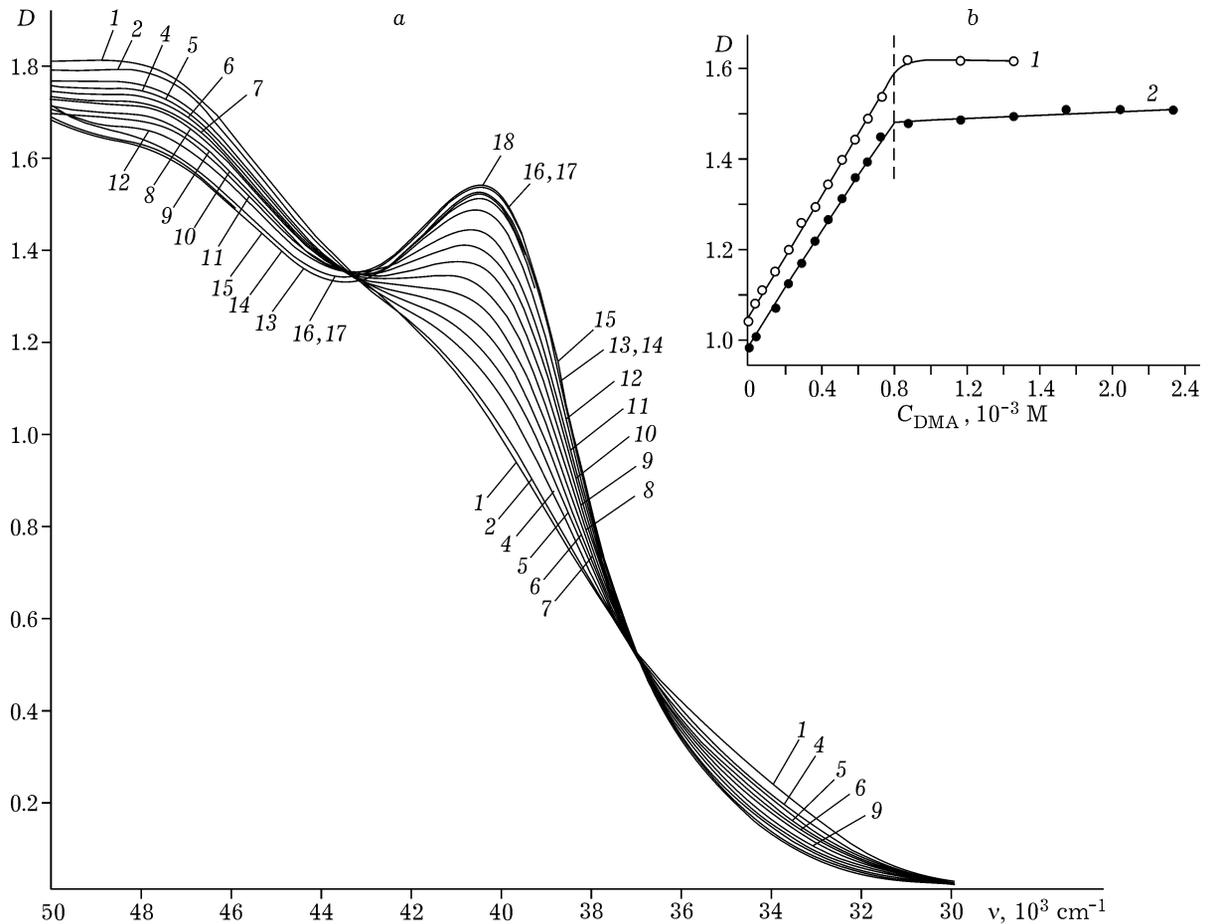
Fig. 2. Absorption spectra of molybdate in the presence of DMA (*a*) and dependence of optical density on DMA concentration (*b*): *a* − $C_{Mo(VI)}$ = 3.2 · 10^{-3} M,　pH 4.0, *l* = 1 mm, C_{DMA}, 10^{-3} M: 0 (*1*),　0.05 (*2*), 0.1 (*3*), 0.2 (*4*), 0.3 (*5*), 0.4 (*6*), 0.5 (*7*), 0.6 (*8*), 0.7 (*9*), 0.8 (*10*), 0.9 (*11*), 1.0 (*12*), 1.2 (*13*), 1.6 (*14*), 2.0 (*15*), 2.4　(*16*), 2.8 (*17*), 3.2 (*18*); *b* − ν = 40 000 cm^{-1}, $C_{Mo(VI)}$ = 3.2 · 10^{-3} M, pH: 3 (*1*),　4 (*2*).

For HPC of arsenate, arsenite, and MMA, the studies were made under conditions optimum for DMA complexation in compliance with the purpose of the work, which consists in selecting the conditions of concurrent formation of HPC of all detectable forms of arsenic for their subsequent separation under the unified scheme of analysis. Thus, applied in all experiments was the reagent with pH 3.0 and 4.0, which contained an excess of molybdate, whereby the optical density did not exceed 2.

$HAsO_4^{2-}$ ions

Absorption spectra of arsenate ions in the presence of molybdate have been investigated under the following conditions: $C_{Mo(VI)}$ = 2.4 · 10^{-3} M, $C_{As(V)}$ = 5 · 10^{-6}–10^{-3} M, pH 4.0 and 3.0.

Absorption spectra are presented in Fig. 3, *a*. At first, growth of absorption of solutions in the entire ultraviolet area (see Fig. 3, *a*, spectra *1*−*7*) is observed with an increase in arsenate concentration. With further increase in the concentration of As(V), a decrease of absorption in the regions 42 000 cm^{-1} and 37 200 cm^{-1} occurs, and a maximum at 40 000 cm^{-1} becomes clearly defined (see Fig. 3, *a*, spectra *8*−*11*). Dependences of optical density on As(V) concentration at ν = 40 000 cm^{-1} (see Fig. 3, *b*) are linear up to the ratio Mo : As ≈ 9. The inflection point of the curves corresponds to the previously considered changes in absorption spectra. Then the second linear segment is evidenced up to the ratio Mo : As ≈ 3.

According to the equation

$$p\text{H}^+ + q\text{MoO}_4^{2-} + r\text{HAsO}_4^{2-}$$
$$= (\text{H}^+)_p(\text{MoO}_4^{2-})_q(\text{HAsO}_4^{2-})_r \qquad (2)$$
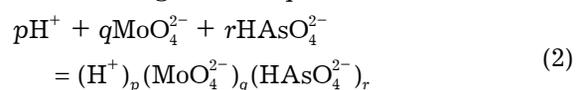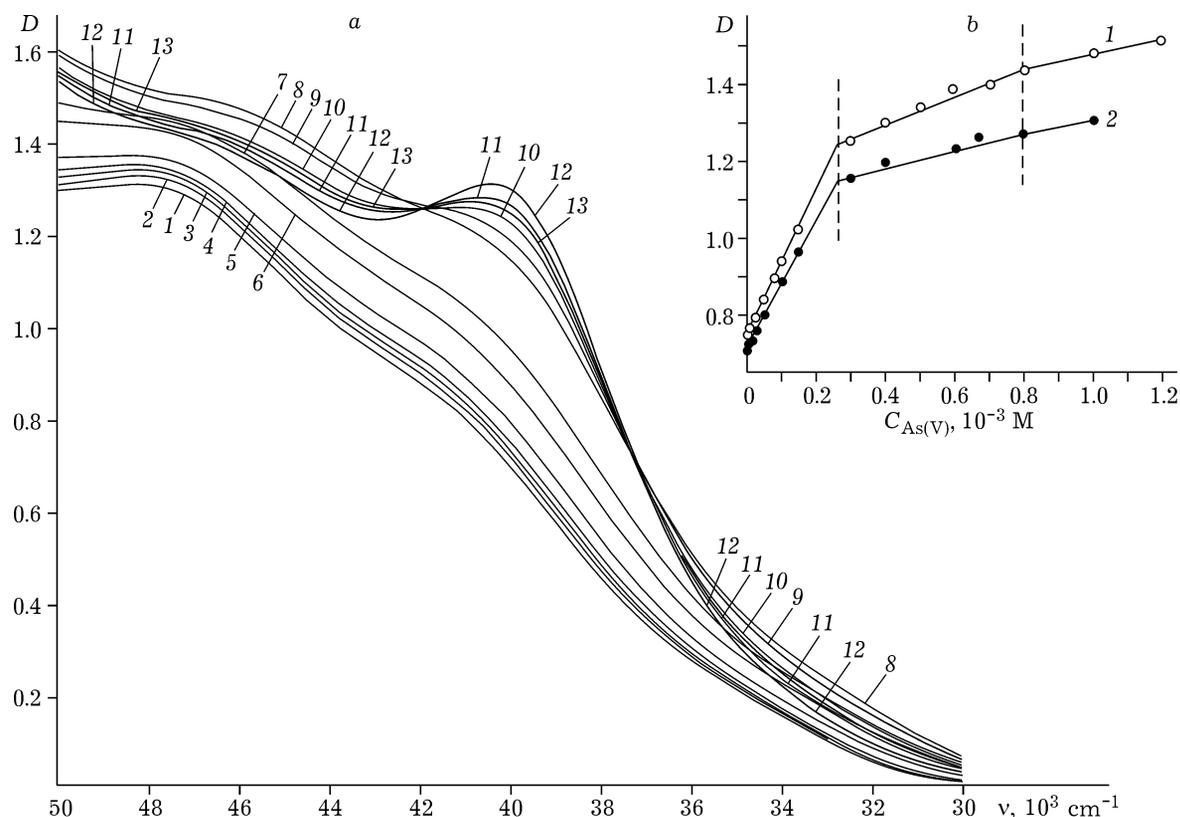
Fig. 3. Absorption spectra of molybdate in the presence of arsenate ion (*a*) and dependence of optical density on concentration of arsenate ions (*b*): $a - C_{Mo(VI)} = 2.4 \cdot 10^{-3}$ M, pH 4.0, $l = 1$ mm, $C_{As(V)}$, 10^{-3} M: 0 (*1*), 0.005 (*2*), 0.010 (*3*), 0.025 (*4*), 0.051 (*5*), 0.010 (*6*), 0.15 (*7*), 0.30 (*8*), 0.40 (*9*), 0.60 (*10*), 0.80 (*11*), 1.0 (*12*), 0.67 (*13*); $b - \nu = 40\,000$ cm^{-1}, $C_{Mo(VI)} = 3.2 \cdot 10^{-3}$ M, pH: 3 (*1*), 4 (*2*).

the work [21] established the fact of formation of (p, q, r) complexes, specifically, $(x, 9, 1)$, $x = 14$, 15, 16 and $(y, 6, 2)$, $y = 10$, 11, 12, in the system $H^+ - MoO_4^{2-} - HAsO_4^{2-}$ depending on the concentration of reagents ([Mo(VI)] = 12 mM and [As(V)] = 1–25 mM) over the region of pH 3–5.

It is reported also about HPC formation with higher molybdenum content at greater excess of molybdate [15]. Our data correspond to formation of AsMo$_9$ complex with an excess of molybdate for low arsenic concentrations and formation of As$_2$Mo$_6$ at higher arsenic concentrations. With an assumption that within the initial linear segment of the curves (see Fig. 3, *b*), As(V) is completely bound into the AsMo$_9$ complex, its extinction coefficient can be calculated:

$$D = \varepsilon_{Mo}(C_{Mo} - 9C_{As(V)})l + \varepsilon_c C_{As(V)}l$$
$$= C_{As(V)} (\varepsilon_c - 9\varepsilon_{Mo})l + C_{Mo}\varepsilon_{Mo}l \qquad (3)$$

The data acquired ($\varepsilon_c = 4.5 \cdot 10^4$ at pH 4.0 and $4.7 \cdot 10^4$ at pH 3.0) are in agreement with the

ε_c values presented in the work [22] that are equal to $((4.8-5) \cdot 10^4)$ for complexes $(p, 9, 1)$ of the same stoichiometry.

$CH_3AsO_3^{2-}$ ions

Absorption spectra of the solutions containing monomethylarsonate and molybdate ions have been studied under the following conditions: $C_{Mo(VI)} = 2.4 \cdot 10^{-3}$ M, $C_{MMA} = 10^{-5}-1.3 \cdot 10^{-3}$ M, pH 4.0 and 3.0.

Absorption of solutions increases with an increase in MMA concentration and forms maximum in the region of 40 000 cm^{-1} (Fig. 4, *a*). Before the ratio Mo : MMA ≈ 6, spectra *1–7* yield an isobestic point at 34 500 cm^{-1}. At higher concentration of MMA, absorption in the region of 34 500 cm^{-1} increases, whereas in the region of 45 000 cm^{-1}, absorption growth becomes weaker (see Fig. 4, *a*, spectra *8–12*) that is suggestive of change in composition of the
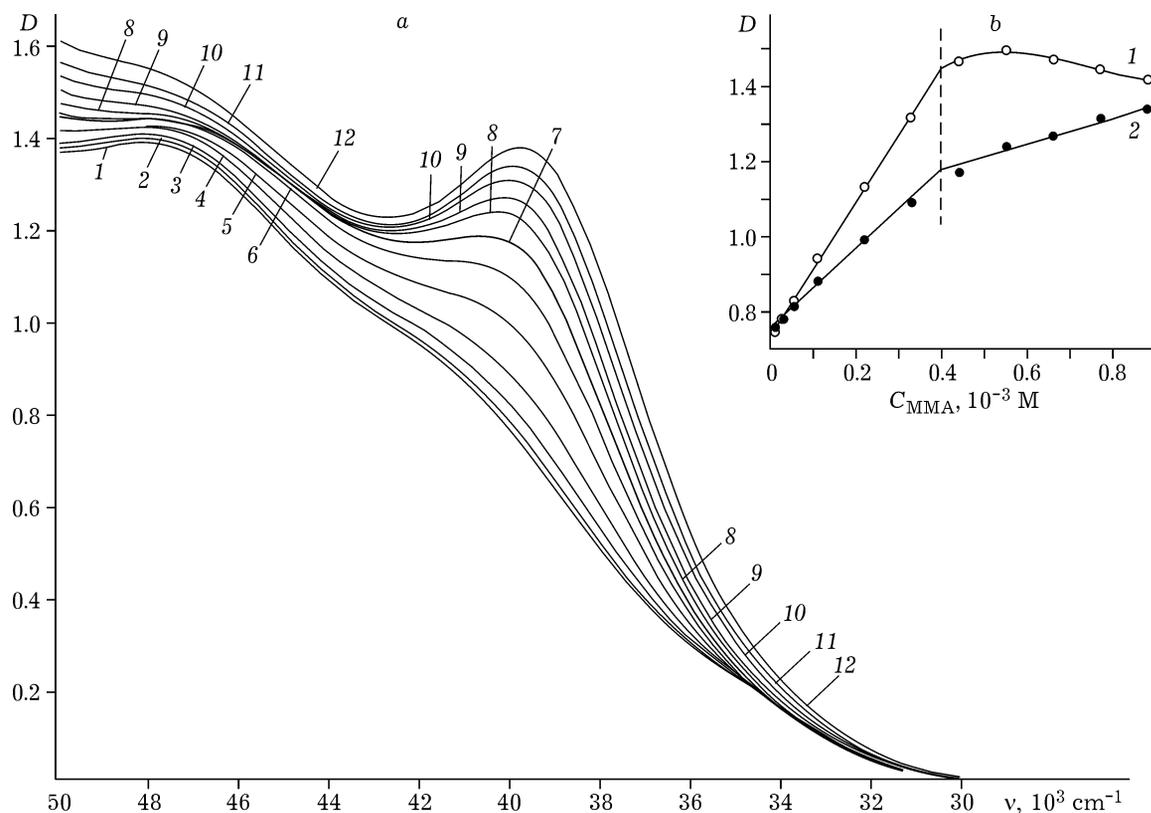
Fig. 4. Absorption spectra of molybdate in the presence of MMA (*a*) and dependence of optical density on MMA concentration (*b*): *a* − $C_{Mo(VI)}$ = 2.4 · 10^{-3} M, pH 4.0, *l* = 1 mm, C_{MMA}, 10^{-3} M: 0.011 (*1*), 0.027 (*2*), 0.055 (*3*), 0.11 (*4*), 0.22 (*5*), 0.33 (*6*), 0.44 (*7*), 0.55 (*8*), 0.66 (*9*), 0.77 (*10*), 0.88 (*11*), 1.1 (*12*); *b* − ν = 40 000 cm^{-1}, $C_{Mo(VI)}$ = 3.2 · 10^{-3} M, pH: 3 (*1*), 4 (*2*).

formed complexes. With an increase in MMA concentration, optical density at ν_{max}= 40 000 cm^{-1} (see Fig. 4, *b*) increases linearly up to the ratio Mo : MMA ≈ 6 and then the linearity is violated.

Based on potentiometric data, authors [24] could not make unambiguous conclusion regarding the composition of MMA complexes with molybdate. According to the adopted computation scheme, they can be represented by the compounds (*p*, 6, 2), (*p*, 6, 1), (*p*, 7, 1), and (*p*, 9, 1). Absorption spectra of MMA compounds with molybdate were not studied previously. Spectrophotometric data we obtained have demonstrated that at pH 4.0 and 3.0 and with substantial excess of molybdate, the complex of composition (MMA)Mo$_6$ prevails.

The values ε_c, specifically, 2.9 · 10^4 at pH 4.0 and 3.7 · 10^4 at pH 3.0, have been calculated for the (MMA)Mo$_6$ complex that is formed with an excess of molybdate, according to

$$D = C_{MMA}(\varepsilon_c - 6\varepsilon_{Mo})l + \varepsilon_{Mo}C_{Mo}l \qquad (4)$$

AsO_2^- ions

Absorption of solutions, which contain arsenite and molybdate ions, increases with concentration of arsenite ions at concentrations $C_{Mo(VI)}$ = 3.2 · 10^{-3} M, $C_{As(III)}$ = 5 · 10^{-5}–3.2 · 10^{-3} M and at pH 3.0 and 4.0, while increases to a lesser degree than with the other speciations of arsenic (Fig. 5). It can be inferred that this absorption is caused by the presence of As(V) that is formed as a result of As(III) oxidation. However, X-ray photoelectronic spectrum of initial As$_2$O$_3$ exhibited a symmetric 3*d* peak at 45.2 eV that is characteristic of As^{3+}, as opposed to 46 eV in As$_2$O$_5$ [25]. Identity of the absorption spectra that were obtained after preparation of solutions in the nitrogen atmosphere and upon their standing for 1 h in oxygen demonstrates that there is no oxidation of As(III) into As(V) by air oxygen in the solutions under investigation.

Absorption of solutions increases with concentration of As(III) (see Fig. 5, *a*). Dependence of optical density on concentration
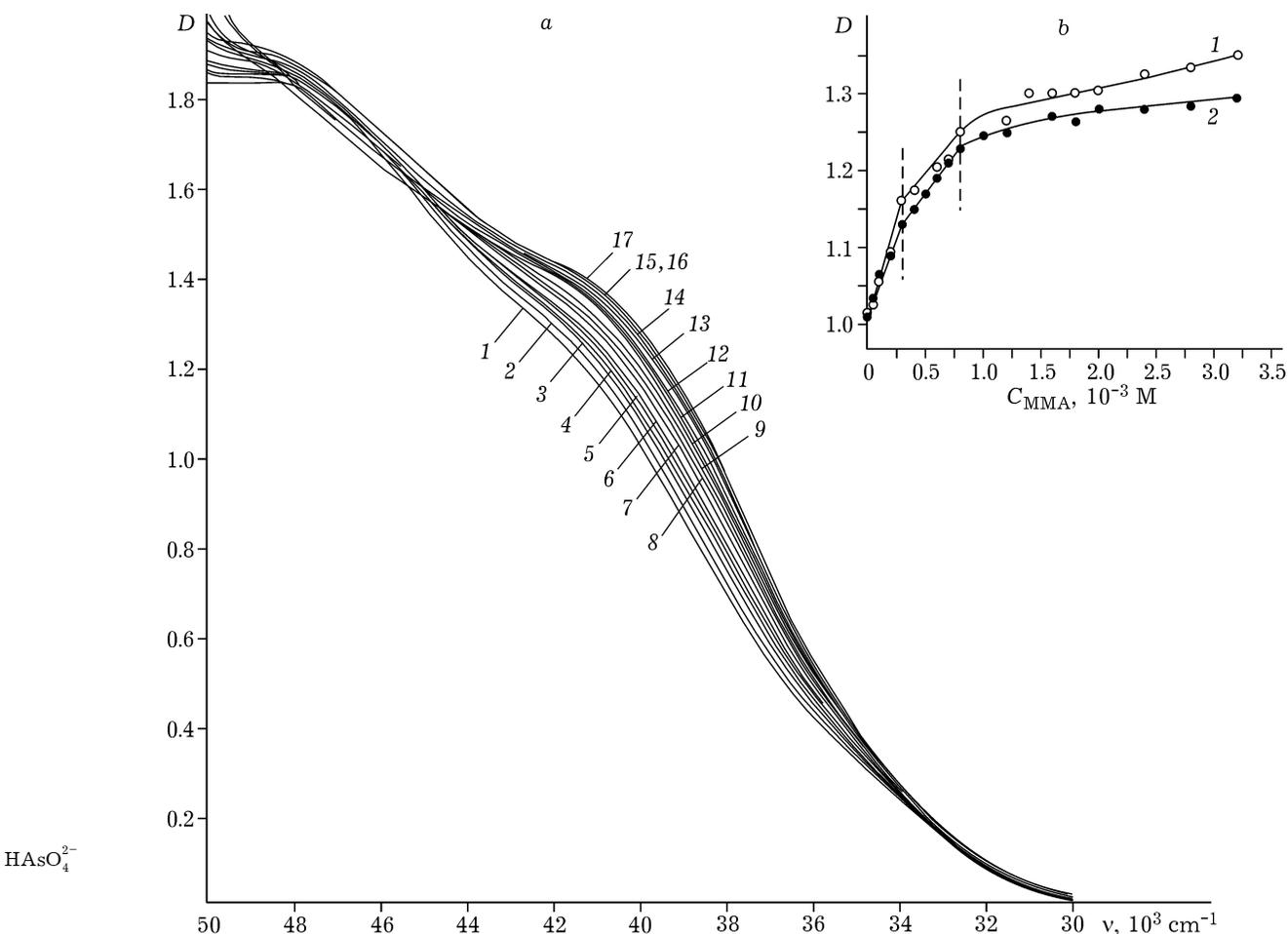
Fig. 5. Absorption spectra of molybdate in the presence of arsenite ion (a) and dependence of optical density on concentration of arsenite ion (b): $a - C_{Mo(VI)} = 3.2 \cdot 10^{-3}$ M, pH 4.0, $l = 1$ mm, $C_{As(III)}$, 10^{-3} M: 0.05 (*1*), 0.1 (*2*), 0.2 (*3*), 0.3 (*4*), 0.4 (*5*), 0.5 (*6*), 0.6 (*7*), 0.7 (*8*), 0.8 (*9*), 1.0 (*10*), 1.2 (*11*), 1.6 (*12*), 1.8 (*13*), 2.0 (*14*), 2.4 (*15*), 2.8 (*16*), 3.2 (*17*); $b - \nu = 40\,000$ cm^{-1}, $C_{Mo(VI)} = 3.2 \cdot 10^{-3}$ M, pH: 3 (*1*), 4 (*2*).

of arsenite ion shows two inflection points that correspond to the ratios Mo : As that are equal to 11 : 1 and 4 : 1 (see Fig. 5, *b*).

Literary data about HPC for As(III) are rather few in number. Compounds of arsenic (III) with molybdenum (VI) have been obtained that show variable composition: nNa$_2$O (or K$_2$O) $\cdot$ As$_2$O$_3$ $\cdot$ mMoO$_3$ $\cdot$ pH$_2$O ($m = 2$, 5, 8), 3(CN$_3$H$_6$)$_2$O $\cdot$ As$_2$O$_3$ $\cdot$ 12MoO$_3$ $\cdot$ 2H$_2$O and 3BaO $\cdot$ 2As$_2$O$_3$ $\cdot$ 8MoO$_3$ $\cdot$ 12H$_2$O [17]. No investigations into the properties of these compounds have been performed up to now. Only one compound of arsenic (III) with molybdate [As$_3$Mo$_3$O$_{15}$]$^{3-}$ has been synthesized and structurally

TABLE 1

Conditions of spectrophotometric determination of arsenic compounds at pH 4 and/or 3

Chemical speciation of arsenic	Concentration of Mo(VI), 10^{-3} M	Analytical speciation of HPC	$\varepsilon_c \cdot 10^{-4}$ at $\lambda = 250$ nm	Range of determinable concentrations of As, 10^{-4} M
	2.4	AsMo$_9$O$_{31}$(OH$_2$)$_3^{3-}$	4.5 (pH 4)	0.05−2.7
			4.7 (pH 3)	
DMA	3.2	(CH$_3$)$_2$AsMo$_4$O$_{14}$OH^{2-}	1.7 (pH 4 и 3)	0.5−8.0
MMA	2.4	CH$_3$AsO$_3$Mo$_6$O$_{18}$(H$_2$O)$_6^{4-}$	2.9 (pH 4)	0.1−4.0
			3.7 (pH 3)	
AsO$_2^-$	3.2	−	−	0.5−3.0

characterized [18]. Therefore, based on the spectrophotometric data we obtained, only assumptions on the stoichiometry of the formed HPC can be suggested.

Table 1 summarizes the results of the performed investigations on the selection of optimum conditions for the formation of HPC of arsenate, arsenite, DMA and MMA ions with molybdate ions. High values of HPC extinction coefficients (at $\lambda = 250$ nm) enable determination of arsenic compounds on the background of an excess of molybdate. The range of the determinable concentrations coincides with the linearity region in the initial segment of the dependence of optical density on the concentration of arsenic.

Determination of chemical speciations of arsenic

The capillary electrophoresis method (CEP) with spectrophotometric detecting ($\lambda = 254$ nm) was applied to determine chemical speciations of arsenic after their transformation to HPC.

Solution of isopolymolybdate with admixture of perchlorate ion that masks silicate ion was used as master electrolyte. Ionic strength, pH of electrolyte, and electrode voltage were varied to optimise the conditions of separation. The running voltage was chosen to be −16 kV, whereby the feasible time of analysis and the least noise of a base line are attained. To displace the reaction equilibrium towards formation of HPC, the maximum concentration of molybdate has been chosen, whereby a minimal drift of the base line occurred. The perchlorate ion concentration matched the molybdate : perchlorate ratio that was equal to 1 : 2. Presented in Fig. 6 are the electrophoregrams of HPC of chemical speciations of arsenic for pH 3, 4, and 5. It can be seen that the best separation is attained at pH 3. The increase in pH yields the increased time of analysis because of growth in the rate of the electroosmotic flow that is in opposition to the movement of ions towards the detector, whereas the mobility of HPC of arsenate and
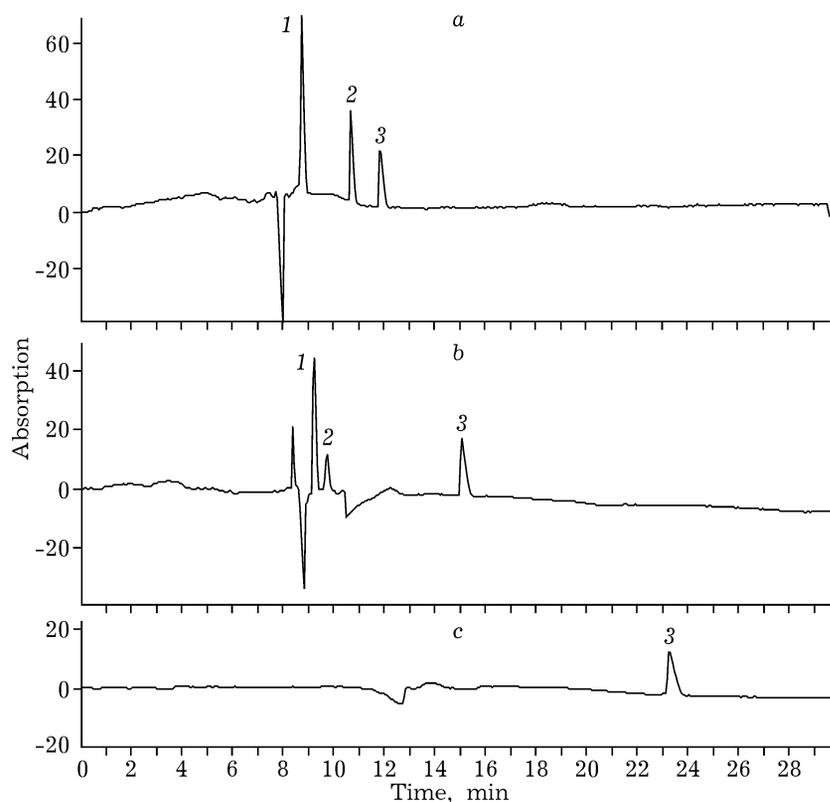
Fig. 6. Separation of chemical speciations of arsenic by the CEP method with application of *in situ* derivatization depending on pH. Electrolyte: 5 mM Na_2MoO_4, 10 mM $NaClO_4$; pneumatic sample feeding: 30 mbar, 5 s; running voltage −16 kV; $C_{As} = 20$ μg/ml. pH values: 3 (*a*), 4 (*b*), 5 (*c*); *1* − arsenate ion, *2* − MMA, *3* − DMA.
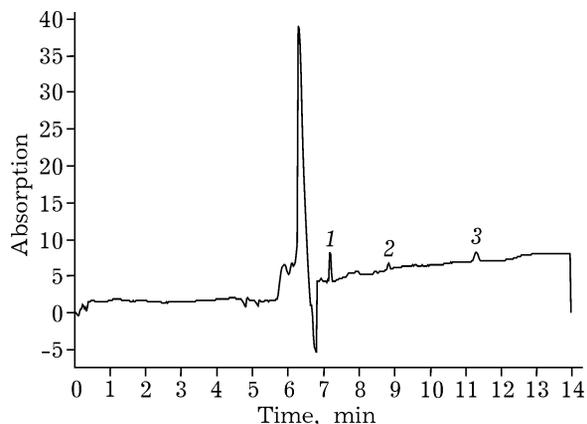
Fig. 7. Separation of chemical speciations of arsenic by the CEP method with application of *in situ* derivatization and electrostacking (electrolyte: 2.5 mM Na_2MoO_4, 5 mM $NaClO_4$, pH 3; electrokinetic feeding of sample from water solution: −25 kV, 10 s; running voltage −16 kV; C_{As} = 0.01 mg/l): *1* − arsenate ion, *2* − MMA, *3* − DMA.

monomethylarsonate ions grows due to an increase in their effective charges. This leads to resolution failure at pH 5 and to coincidence with a negative peak whose origin is caused by the gradient of molybdate concentration. No signal from HPC of arsenite ion was observed under all conditions, although the electronic spectra give evidence for its formation. Seemingly, HPC of arsenite ion is distinguished for its small stability, which leads to its destruction under the effect of electric field in the capillary. Arsenite ion was determined from a difference of arsenate concentrations before and after oxidation of sample with bromine water. With pneumatic sample feeding, calibration plots for all speciations are linear over a range of 0.1−20 µg/ml; at electrokinetic feeding, over a range of 0.01−0.5 µg/ml. Detection limits with pneumatic sample feeding were equal to 0.06−0.12 µg/ml. We succeeded in substantial decrease of detection limits with electrokinetic feeding of sample (electrostacking) from water solution during 10 s under voltage of −25 kV. Under selected conditions, the detection limits for chemical speciations of arsenic were equal to 0.005−0.01 µg/ml. Electrophoregram of the mixture of HPC of chemical speciations of arsenic with 0.01 µg/ml content of each form is presented in Fig. 7.

CONCLUSIONS

Thus, the present work has selected, unified, and optimised the conditions for

concurrent formation of heteropolymolybdates with arsenate, arsenite, monomethylarsonate, and dimethylarsenite ions in solutions. The possibility to apply the reaction of HPC formation for spectrophotometric detecting of arsenic speciations listed above in a combination with electrophoretic separation has been shown.

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