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Solid-phase spectrophotometric and test determination of silicate in natural water

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ABSTRACT

Quaternary ammonium salts (QAS) of aliphatic (tetradecylammonium nitrate) and heterocyclic (lucigenine) nature immobilized onto silica surface have been proposed as effective anion-exchangers for the adsorptional extraction of silicate in the form of the reduced molybdo-silicic heteropoly anion for the successive determination in the solid phase by using spectrophotometric and visual test techniques. The interface interaction has been investigated. On the basis of the results obtained the new solid-phase spectrophotometric and visual test techniques for the direct silicon determination in the rage of its concentrations 14–400 $\mu g\,L^{-1}$ have been proposed. The tolerance limits of the major components in natural waters and other ions capable of producing heteropoly anions in the silicate determination have been reported. The techniques have been successfully applied for the silicate determination in natural waters.

1. Introduction

It is well known that silicon is a major component of various natural minerals. That is why dissolved silicon is presented in almost all types of natural waters.

The concentration of silicate in the river and lake water usually varies in the range of 1–10 $mg\,L^{-1}$ [1,2]. At the same time, the silicate content in sea water does not exceed 0.5 $mg\,L^{-1}$ [1]. Silicon can be present in natural waters in the form of water-soluble ortho- and polysilicates, as well as in the form of colloid particles $x\mathrm{SiO_2}\cdot y\mathrm{H_2O}$ which are predominant, as a rule [1]. It depends on mineral composition of natural water and the pH value. The silicate content is one of the main characteristics of the quality of drinking and natural water [3,4]. Moreover, trace amounts of silicon are certainly to be controlled in superhigh-purity waters used in semiconductor industry, in the pure reagents production, etc. [5].

The basis of the overwhelming majority of the methods used for the silicate determination is the ability of the silicate to interact with molybdates, tungstates, or vanadates forming heteropoly complexes. The spectrophotometric detection of the more stable reduced “blue form” of molybdo-silicate is the most common way for the SiO_3^{2-} determination [3,4]. The main disadvantages of such a technique are insufficient reproducibility of the results because of the colloid state of the analytical form and relatively low sensitivity, in some cases [2,4]. This is usually caused by a considerable effect of the solution acidity, temperature, duration of the analysis, and the purity of the reagents.

The spectroscopic flow injection method of the silicate detection in the form of oxidized [6] or reduced [7] molybdo-silicic heteropoly acid (HPA) was successfully applied to reduce the time span of the analysis. However, the sensitivity and reproducibility of the methods is not satisfactory.

The extraction-spectroscopic methods based on the extraction of the silicate in the form of the ion associate with cationic dyes are known to be more sensitive in comparison with the spectrophotometric ones [2,8]. At the same time, these techniques show insufficient selectivity as to considerable amounts of anions usually present in the natural samples. Moreover, liquid extraction techniques require toxic organic solvents and are time-consuming [9].

Application of the voltametric method for the silicate determination is mainly limited by the molybdate, tungstate or vanadate mutual interference [10–13]. Moreover, the procedure of the analysis is quite complicated, and is characterized by the poor reproducibility of the results.

The ion-pair reversed phase high performance liquid chromatography (HPLC) method was applied for the silicon determination in the presence of other elements forming ligands of HPA

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[14,15]. However, a wide application of this technique for routine analyses has a few limitations because the procedure appears to be quite complex and rather expensive [16,17].

At the same time, the hyphenated methods based on the molybdo-silicic HPA adsorption followed by the spectroscopic detection of silicium have a number of advantages [18]. High sensitivity and selectivity of the analyte detection can easily be achieved due to the silicon preconcentration followed by the direct detection in the concentrate phase by using either visual or spectroscopic methods [18,19]. Besides, the adsorption method has a number of other advantages, such as high concentration coefficients and environmental safety. In addition, the hyphenated adsorption techniques are known to be successfully applied to carry out the on-site analyses.

Earlier, the solid-phase reagents on the basis of the silica gel modified with quaternary ammonium salt (QAS) of different nature have been proposed for the extraction of a number of elements in the form of anions which then can be detected by using visual and spectroscopic methods [20,21]. In particular, sensitive hyphenated spectroscopic techniques were developed for P and As determination [22,23]. The procedure involved their extraction in the form of reduced HPA from aqueous solution using the silica modified with QAS. The aim of this work is to develop the solid-phase spectrophotometric and visual test methods for the silicate determination.

2. Material and methods

2.1. Reagents and apparatus

Chloroform and hexane suitable for liquid chromatography (Merck) were used. Tetradecylammonium nitrate ($[N(C_{10}H_{21})_4]NO_3$, TDAN) 99% purity was consumed to prepare 1×10^{-2} mol L^{-1} solution in chloroform and hexane (1:16). Lucigenine ($C_{28}H_{22}N_4O_6$, Lc) was used to prepare $1 \times \cdot 10^{-3}$ mol L^{-1} solutions in distilled water. Sodium silicate and potassium antimonyl tartrate of analytical grade; potassium dihydrophosphate, sulfuric acid and sodium arsenate of high-purity grade; ammonium heptamolybdate of reagent grade; and ascorbic acid of pharmaceutical grade were employed to prepare aqueous solutions of the reagents. Aqueous solution of sodium silicate containing 68 mmol L^{-1} of silicon was standardized as described in Ref. [1].

The ammonium molybdate acidic aqueous solution (a mixed reagent) was prepared by dissolving 8.00 g of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in 10 mL of concentrated sulphuric acid. Then, the mixture was diluted with the deionized water to the volume of 100 mL.

The aqueous solutions of the reduced molybdo-silicic acid were prepared as follows: 1.6 mL of sulphuric acid (0.1 mol L^{-1}) and 1.0 mL of the mixed reagent were added to an aliquot portion of the solution containing silicate. The mixture was diluted to the volume 10 mL and left for 30 min. Then, 2.0 mL of 4 mol L^{-1} sulphuric acid and 1.0 mL of 30 mmol L^{-1} ascorbic acid were added to this mixture. The equilibrium of the reaction was reached within 20 min.

Silica gel SG 60 (Merck) with the specific surface area of 490 m^2 g^{-1} and the pores diameter of 6 nm was used without any pre-treatment. The silica gel modified with TDAN by adsorption from the chloroform–hexane (1:16) mixture (TDAN-SG) and another silica gel modified with Lc by adsorption from the aqueous solution (Lc-SG) were used. The adsorbents capacities for TDAN-SG and Lc-SG were 25 and 6 μmol g^{-1}, respectively.

The absorption spectra of the solutions and the sorbents were registered with UV/vis spectrophotometer UNICO UV-2800 and KFK-3 photoelectric colorimeter (Zagorsk, Russia), respectively. The pH-meter Checker (China) was used for pH measurements. The adsorption was facilitated by the use of a magnetic stirrer. The batch technique was applied to study the HPA adsorption onto the adsorbents modified.

2.2. Adsorption study

The batch technique was employed to study the adsorption of HPA onto TDAN-SG and Lc-SG. The weighed amount (0.010–0.150 g) of the modified adsorbent was stirred with 5.0–50.0 mL of HPA solutions containing tartaric acid (0.1 mol L^{-1}) for 1–20 min. The sorbents were separated and then washed with distilled water.

The residue of molybdo-silicic HPA in the solution was controlled spectrophotometrically by its own light absorbance at 810 nm and employing the calibration graphs. The amount of the HPA adsorbed (a, mol g^{-1}), the recovery (R, %) and the distribution coefficient of HPA (D, L g^{-1}) were calculated according to the equations: $a = (c_0 - c_e)Vm^{-1}$; $R = (c_0 - c_e)c_0^{-1} \times 100$; $D = R(100 - R)^{-1}Vm^{-1}$; where c_0 and c_e were the initial and the equilibrium concentrations of the adsorbate in the solution in mol L^{-1}; V was the volume of the solution in L; m was the mass of a sorbent in grams.

2.3. Measurement of the adsorbent light absorbance

Adsorbents light absorbance was then measured in a thin layer ($\ell = 1.0$ mm) with the minimized distance between the cell and the detector window. Non-modified sorbent was referred to as a blank one. Analytical response (ΔA) was calculated by the method of heterochromatic extrapolation ($\Delta A = A_{max} - A_{996}$, where A_{max} and A_{996} was the light absorbance of the sorbent at the maximum of the spectrum and at 996 nm). This way is known to be the most effective [24–26]. Absorbance spectra of the sorbents were chosen to calculate the chromaticity function (chromaticity coordinates A and B in the CIELAB [27] system; total color difference ΔE, luminosity ΔL, color tint ΔT and saturation of color ΔS) according to Ref. [28].

2.4. Interference study

To check the selectivity of the techniques proposed the influence of foreign ions onto silicate determination was investigated. For this purpose a number of solutions containing different proportions of the silicate and a foreign component were prepared. Then, necessary reagents and the weighed portion of the adsorbent were added to the solution. The mixture was mixed as described in Section 2.2 and the light absorbance was measured as described in Section 2.3. Selectivity coefficient was calculated as the ratio between the concentration of the foreign component (c, mol L^{-1}) and that of the silicate ($c(SiO_3^{2-})$, mol L^{-1}) where c was the concentration at which the value of the analytical signal can differ within the range of 5% of that for the silicate itself.

3. Results and discussion

3.1. Adsorption of HPA onto modified adsorbents

In order to develop the solid phase reagents for the silicate determination the silica gels modified with quaternary ammonium salts (QAS) of different nature were studied. High molecular mass aliphatic QAS (TDAN) and heterocyclic ones (Lc) were selected as silica surface modifiers. Aliphatic QAS was chosen because it could effectively be extracted from the chloroform–hexane mixture. Moreover, it appeared to be tightly bound to the silica surface and did not show obvious absorbance in the visible part of the spectra [22]. In contrast to TDAN, water soluble Lc can be immobilized onto silica from the aqueous solution [29]. In addition, two quaternary nitrogen atoms of the reagent molecule can facilitate the absorption of HPA onto the silica gel modified with Lc. A yellow color of the immobilized Lc can easily be contrasted visually: a

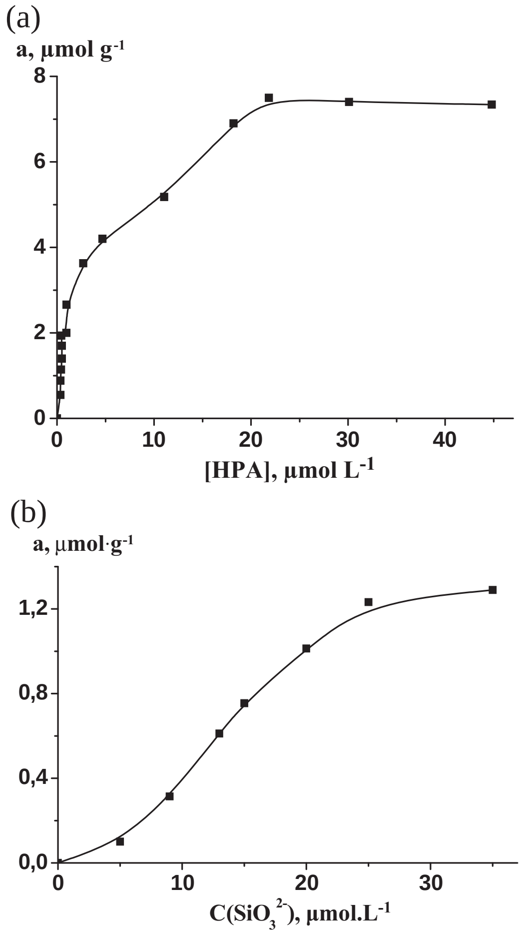

Fig. 1. The isotherm of HPA adsorption onto TDAN-SG (a) and the adsorption of HPA onto Lc-SG as a function of the initial silicate concentration in solution (b); $a(\text{TDAN}) = 25\,\mu\text{mol g}^{-1}$ (a), $a_{\text{Lc}} = 6.0\,\mu\text{mol g}^{-1}$ (b); $C(\text{H}_2\text{SO}_4) = 0.25\,\text{mol L}^{-1}$, $V\text{m}^{-1}$, mL g^{-1}: 130 (a), 100 (b); $T = 291 \pm 1$ K.

yellow color changes for the green one in the case of Lc, and the white one changes for the blue one in the case of TDAN.

The adsorption of silicate from aqueous solutions onto TDAN-SG and Lc-SG was studied in the form of the reduced (blue) molybdo-silicic anion. There were several reasons for that. Firstly, both the oxidized and reduced HPA have a deep color in contrast to silicate. Secondly, the reduced HPA is much more stable in comparison with the oxidized one and has several intensive bands in a long-wave region of the light adsorption spectrum.

It was found that TDAN-SG could completely extract the "blue" HPA from the aqueous solution under the optimal conditions of its formation ($0.15–0.2\,\text{mol L}^{-1}$ sulphuric acid). The kinetic experiments have shown that the adsorption equilibrium for molybdo-silicic HPA can be attained within 20 and 15 min for TDAN-SG and Lc-SG, respectively.

The isotherm of the HPA adsorption onto TDAN-SG (Fig. 1a) can be referred to the H-type [30], which lends support to the high affinity of the heteropolyanion to the silica surface. The adsorption isotherm can formally be linearized in Langmuir coordinates ($R^2 = 0.998$) (in the concentration range of the silicate in solution from 3 to $12\,\mu\text{mol L}^{-1}$) with the affinity constant $K = 3.7 \times 10^5\,\text{L mol}^{-1}$ and maximum adsorption capacity $a_{\max} = 8.3\,\mu\text{mol g}^{-1}$.

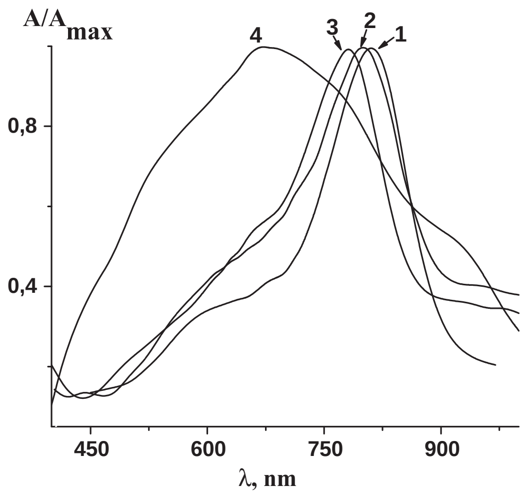

Fig. 2. Standardized absorbance spectra of molybdo-silicic HPA in aqueous solution (1), isobutyl alcohol extract (2), adsorbed onto TDAN-SG (4) and chloroform extract of IA $(\text{TDAN}^+)_3\text{HPA}^{3-}$ (3). $c(\text{Si}) = 7.0\,\text{mmol L}^{-1}$, $C(\text{H}_2\text{SO}_4) = 0.4\,\text{mol L}^{-1}$, $V\text{m}^{-1} = 130\,\text{mL g}^{-1}$, $a(\text{TDAN}) = 25\,\mu\text{mol g}^{-1}$.

3.2. Interaction of HPA with QAS immobilized onto SG

The interaction of HPA anions with the modified surface was investigated by using the adsorption method and solid-phase spectroscopy. The presence of the chemisorption region on the adsorption isotherms of HPA (Fig. 1a) can be referred to the formation of the ion associates on the surface. The maximum adsorption capacity of TDAN-SG was found to be $8.3\,\mu\text{mol g}^{-1}$ for HPA at $a(\text{QAS}) = 25\,\mu\text{mol g}^{-1}$. This supports the supposition of the formation of ion associates with stoichiometry QAS:HPA = 3:1. Taking into account the predominance of the anion form of molybdo-silicic HPA in the solution under these conditions [31] we suggested the formation of the ion associate on the surface according to the following equation:

$$3(\overline{\text{TDAN}^+\text{NO}_3{}^-}) + \text{H}_x\text{SiMo}^{\text{V}}{}_x\text{Mo}^{\text{VI}}{}_{12-x}\text{O}_{40}{}^{3-}$$
$$= \overline{(\text{TDAN}^+)_3\text{H}_x\text{SiMo}^{\text{V}}{}_x\text{Mo}^{\text{VI}}{}_{12-x}\text{O}_{40}{}^{3-}} + 3\text{NO}_3{}^-,$$

where x is the number of molybdenum atoms reduced and it can be equal either 2 or 4 [2].

The attachment of HPA to TDAN-SG results in a short-wave shift of the maximum ($\Delta\lambda = 140$ nm) in the spectrum of HPA with respect to the spectrum of HPA in the solution (Fig. 2, curves 1, 4). This effect cannot be explained only by the formation of the ion associate on the surface. The data presented in Fig. 2 (curves 1 and 3) testifies that the formation of IA between HPA and TDAN is accompanied with a slight short-wave shift of the maximum in the spectrum of HPA (less than 30 nm) which can be explained as the solvent effect [2]. A significant short-wave shift of the maximum ($\geq$60 nm) in the spectrum of HPA after the adsorption onto the surface of polyurethane foam (PUF) was earlier reported [18] and can be caused by the interaction between the adsorbate and the polyetheric fragments of the polyurethane foam. We suppose that significant changes in the spectrum of HPA after the adsorption onto TDAN-SG can be caused by the interaction of HPA with free surface groups of the silica due to the formation of hydrogen bonds between the heteropoly anion and OH-groups on the surface. Such an assumption agrees well with the results reported earlier [32,33]. Such interactions provide for the strong attachment of the HPA onto the surface of SG.

The recovery of the reduced HPA with Lc-SG from aqueous solution in the presence of $0.25–0.40\,\text{mol L}^{-1}$ of sulphuric acid was accompanied by the partial desorption of the reagent from the

Table 1
Parameters of the calibration curves for the silicate determination by sorption-spectroscopic method $Y = (a \pm \Delta a) + (b \pm \Delta b)c(SiO_3^{2-})$, mg L^{-1}.

Adsorbent	Y	$a \pm \Delta a$	$b \pm \Delta b$	R^2	V m^{-1} (mL g^{-1})	LOD (mg L^{-1})	Range of linearity (mg L^{-1})
TDAN-SG	ΔE	25 ± 1	26 ± 2	0.982	130	0.12	0.4–1.1
	ΔS	10 ± 1	19 ± 2	0.953		0.16	0.4–1.1
	ΔL	13 ± 2	20 ± 2	0.976		0.32	0.4–1.1
	ΔA_{680}	0.064 ± 0.004	0.167 ± 0.005	0.998		0.07	0.1–1.1
	ΔA_{680}	0.065 ± 0.004	1.119 ± 0.005	0.998	670	0.014	0.01–0.16
Lc-SG	ΔA_{800}	−0.010 ± 0.006	0.128 ± 0.006	0.996	100	0.14	0.2–2.0
	ΔE	31 ± 7	39 ± 4	0.963		0.54	0.4–2.6
	ΔS	−24 ± 2	−30 ± 2	0.990		0.20	0.4–2.0
	ΔL	14 ± 3	23 ± 2	0.972		0.41	0.4–2.6

surface and formation of ion associate which is slightly soluble in water and could be extracted onto unmodified SG. The interface interaction can apparently be depicted by the scheme shown below:

(i) Formation of the ion associate on the surface of the sorbent:

$$\overline{3Lc^{2+}(NO_3^-)_2} + 2H_xSiMo^{V}{}_xMo^{VI}{}_{12-x}O_{40}{}^{3-} \leftrightarrow \overline{(Lc^{2+})_3(H_xSiMo^{V}{}_xMo^{VI}{}_{12-x}O_{40}{}^{3-})_2} + 2NO_3^-;$$

(ii) Extraction of IA onto unmodified surface of SG:

$$(Lc^{2+})_3(H_xSiMo^{V}{}_xMo^{VI}{}_{12-x}O_{40}{}^{3-})_2 \leftrightarrow \overline{(Lc^{2+})_3(H_xSiMo^{V}{}_xMo^{VI}{}_{12-x}O_{40}{}^{3-})_2},$$

where x can be equal either 2 or 4. Such a scheme of the interface interaction was proved by the appearance of Lc yellow color in the solution when the phases were brought into contact. Later on, in the process of adsorption, this color was getting weaker whereas the color of the adsorbent became more intensive. Moreover, the adsorption of HPA grows as the concentration of HPA in the solution increases (Fig. 1b). So, the data obtained confirm the supposition about complicated schema of HPA adsorption onto Lc-SG.

The light absorbance of the adsorbents (at 680 nm for TDAN-SG and at 800 nm for Lc-SG) varies directly with the concentration of silicate in the solution (Fig. 3). Under the optimal conditions of the interface reaction the calibration curves for the solid-phase spectrophotometric determination of silicate can be described as the equations that are listed in Table 1. The technique based on TDAN-SG was found to be more sensitive than the one based on Lc-SG.

In order to optimize the procedure of the sorption-spectrophotometric method of the silicate determination, the effect of the ratio volume of the solution/adsorbent mass onto the extraction percentage and the analytical signal value were studied. It was shown that the parameters of the HPA extraction using TDAN-SG and the analytical signal in the spectra of the adsorbents do not change up to Vm^{-1} = 670 mL g^{-1}. Maximum distribution coefficient for HPA was found to be 3.3×10^4 mL g^{-1}. So, TDAN-SG can be used for the pre-concentration of silicate in the form of HPA from a diluted solution. As the analytical signal for the silicate determination other colorimetric functions, such as ΔE, ΔL, ΔT and ΔS can be used (Table 1). The limit of SiO_3^{2-} detection calculated by using 3s-criterion was found to be 14 µg L^{-1} in the case of ΔA_{680} as the analytical signal (Table 1).

To check the selectivity of the techniques, the effect of some other ions and the major components in natural water on the silicate determination was investigated. The results are summarized in Table 2. The effect of arsenate ions up to 4.5 mg L^{-1} As(V) (90 MPC, where MPC is maximum permissible concentration) can be eliminated by the addition of citric acid (c = 4.0 mmol L^{-1}). Phosphate ions did not affect the SiO_3^{2-} determination by using of sorption-spectrophotometric technique up to the concentration of 13 mg L^{-1} that is four times more than using "classical" spectrophotometric methods [34].

The increase in HPA content in the adsorbent phase was accompanied by the change in the adsorbent color from white to blue for TDAN-SG and from light-yellow to deep-green for Lc-SG. This fact has been used to develop color scales for the semiquantitative visual test determination of silicates. Operating concentration ranges for the scales proposed were found to be 0.1–4.6 mg L^{-1} (TDAN-SG) and 0.2–2.1 mg L^{-1} (Lc-SG). The main advantage of the

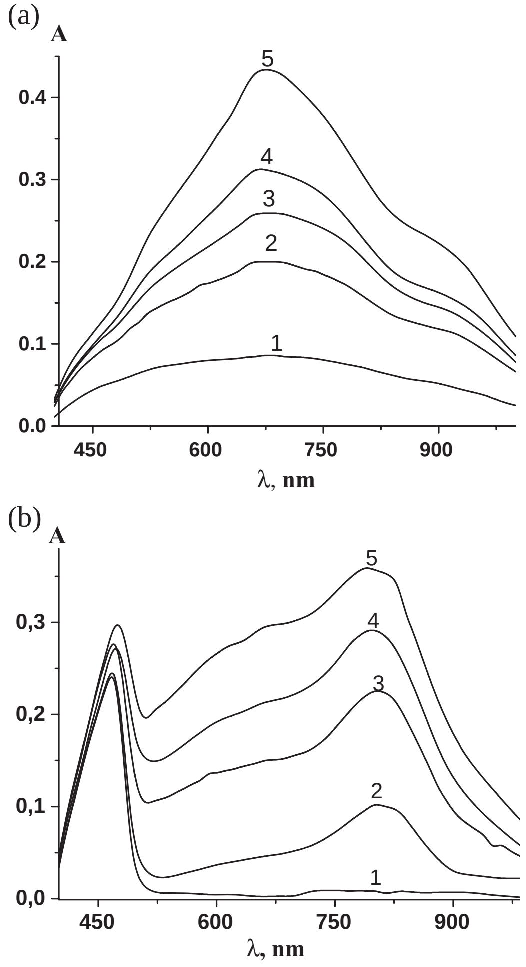

Fig. 3. Absorption spectra of TDAN-SG (a) and Lc-SG (b) treated by HPA solutions at different concentrations; $c(SiO_3^{2-})$, µmol L^{-1}: 0 (1*a*, 1*b*), 5.0 (2*a*), 9.0 (3*a*), 11 (4*a*), 13 (2*b*), 20 (3*b*), 25 (4*b*), 30 (5*a*), 35 (5*b*); a_{QAS} = 25 µmol g^{-1}; Vm^{-1}, mL g^{-1}: 130 (a) 100 (b); pH 0.3, ℓ = 10 mm.

Table 2
Effect of foreign ions onto sorption-spectrophotometric and visual-test determination of 6 μmol L^{-1} silicate.

Ion or substance	Selectivity coefficient	c/MPC (c/c_{max})
AE and AEE	2×10^5	(4)
NH_4^+	167	10
Co(II)	0.3	1
Cu(II)	17	60
Fe(III)	50	33
Mn(II)	3	1
As(V)	3	30
P(V)	33	13
Sb(III)	50	600
CO_3^{2-}	2×10^3	(2.6)
Cl^-	2×10^5	(500)
NO_3^-	3×10^3	100
Humic acids	1[a]	(0.25)

AE and AEE – cations of alkali and alkaline-earth elements; c_{max} – maximal component contents in natural waters, mol L^{-1}; MPC – maximum permissible concentration, mol L^{-1} [1].

[a] Selectivity coefficient in this case was calculated as the ratio of c(humic acids), mg L^{-1} to $c(SiO_3^{2-})$, mg L^{-1}.

scale based on Lc-SG is a high degree contrast and the simplicity of the preparation (no organic solvents needed). Although the color scale based on QAS-SG appeared to be more sensitive. So, both adsorbents can be employed to determine silicate in natural waters.

The results of the silicate determination in different types of natural water (two drinking mineral water and one taken from the lake) using the developed and the alternative [2] procedures are listed in Table 3. The results obtained confirm good accuracy for all the techniques developed. Moreover, one can see that the visual test technique based on Lc-SG proved to be more accurate than the one based on TDAN-SG. This fact can be explained by a small distance between the measuring marcs of the scale. This is caused by a contrasting color blend (a two-color change: "yellow–green") of the adsorbents with the increase in HPA contents on the surface of Lc-SG. As a result, the relative standard deviation (RSD) for the visual test determination of silicate using the color scale based on Lc-SG did not exceed 0.06, that is much less than for the conventional procedure (0.25).

The proposed visual test techniques can easily be applied for the semi-quantitative silicate on-site determination. The procedure of the analysis is simple and do not require highly skilled personnel. The concentrates obtained are stable and can easily be transported to a stationary laboratory for the subsequent quantitative silicate determination by using the sorption-spectrophotometric technique. There is no longer need to transport large amounts of natural waters to a stationary laboratory. The analysis can be performed on-site using a portable equipment. In this way the procedure of the analysis becomes more cost-effective.

3.3. *Test scale preparation*

The test color scales were made according to Ref. [28] using the results of the correlation $\Delta E = f(c)$, where ΔE is the total color difference and c is the concentration of the silicate in the solution. Taking into account that the optimal visual color change can be receptive when $\Delta E \geq 10$ for the adjacent points of the scale, the following silicate concentrations have been chosen (mg L^{-1}): 0; 0.09; 0.20; 0.30; 0.60; 1.00; 2.30 and 4.60 (for TDAN-SG, $\Delta E = 10$) and 0; 0.20; 0.50; 0.70; 1.00; 1.20; 1.70; 2.10 (for Lc-SG, $\Delta E \geq 15$).

It was found that the recovery of HPA with silica in acidic solution is accompanied by silica traces passing into the solution from the surface. As a result, a small quantity of the reduced molybdosilicic HPA can be formed within the time of the phase contact. This process does not influence the results of the silica detection by solid-phase spectrophotometric method. However, the subsidiary reaction leads to the background absorbancy in the visible part of the spectrum. It can be easily eliminated by the addition of tartaric acid before the sorption begins. That is why, the test color scales for the silica determination were produced in the presence of tartaric acid.

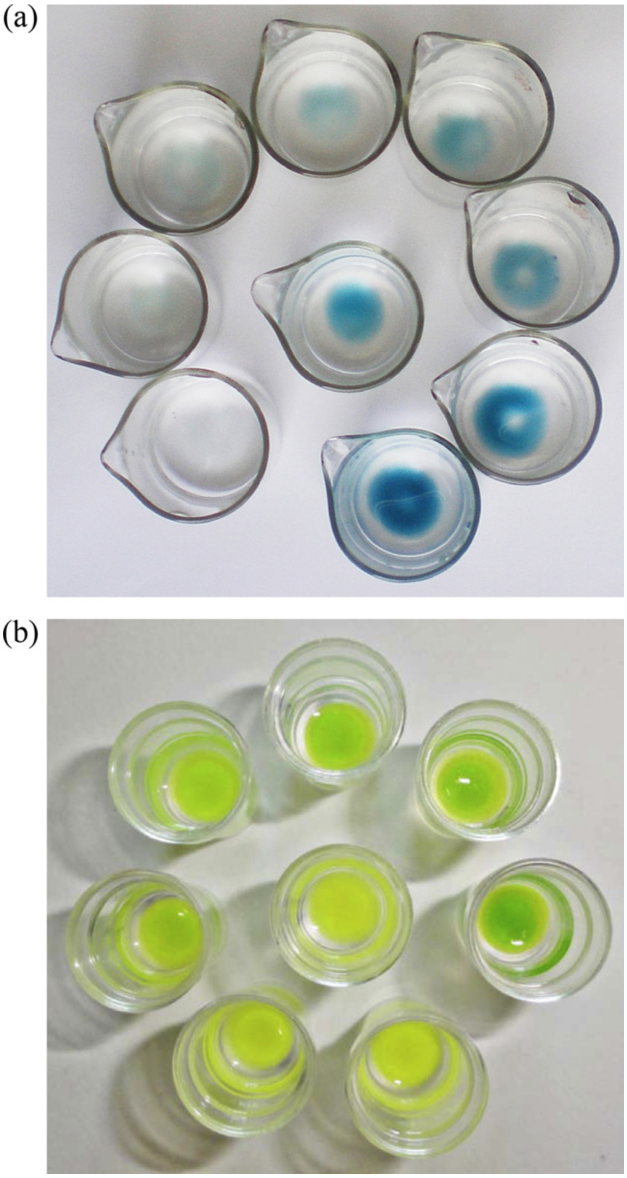

Fig. 4. The color scales based on TDAN-SG (a) and Lc-SG (b) for the visual-test determination of silicate. The concentration of the silicate increases clockwise from white to deep-blue color (mg L^{-1}): 0; 0.09; 0.20; 0.30; 0.60; 1.00; 2.30 and 4.60 (a) and from yellow to green color (mg L^{-1}): 0; 0.50; 0.70; 1.00; 1.20; 1.70; 2.10 (b). The central projection shows the content of the silicate in Mineral water "Znamenivska" (a) and "Morshinska" (b). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

The reduced HPA in the solution was obtained according to the procedure described above in Section 2.1. Then, the portion of TDAN-SG or Lc-SG (0.100 g) was placed into each solution, and the suspensions were stirred for 20 or 15 min respectively.

The adsorbents were separated by decantation; washed with distilled water for several times. The adsorbents obtained in such a way were photographed and then used for the preparation of a computer model of the color scales. Such adsorbents were stable at least for 30 days. The photos of the color scales obtained by using TDAN-SG and Lc-SG are represented on Fig. 4.

Table 3
The result of the silicate determination in natural waters using the developed sorption-spectrophotometric, visual test techniques using (I) TDAN-SG and (II) Lc-SG, and the arbitration spectrophotometric [2] method ($n = 3$, (VT) 10; $P = 0.95$).

Type of water	Aliquot value (mL)	Silicate concentration (mg L^{-1}) (RSD)				
		SSPh		VT		SPh
		I	II	I	II	
Mineral water "Znamenivska" (Ukraine)[a]	0.20	69 ± 3 (0.05)	68 ± 3 (0.05)	70 ± 3 (0.24)	68 ± 8 (0.04)	70 ± 4 (0.05)
Mineral water "Morshinska" (Ukraine)[b]	0.50	39 ± 1 (0.06)	37 ± 2 (0.06)	40 ± 6 (0.17)	38 ± 2 (0.6)	38 ± 1 (0.01)
Lake water (Kiev)	3.50	4.9 ± 0.1 (0.02)	5.0 ± 0.2 (0.03)	4.9 ± 0.2 (0.12)	5.03 ± 0.02 (0.05)	5.4 ± 0.3 (0.03)

SSPh–Sorption-spectrophotometric method, VT–Visual test method; SPh–Spectrophotometric method.

[a] Chemical composition (mg L^{-1}): SiO_3^{2-} (45–65), HCO_3^- (50–250), SO_4^{2-} (<50), Cl^- (50–250), Ca^{2+} (<25), Mg^{2+} (<50), Na^+, K^+ (50–250).

[b] Chemical composition (mg L^{-1}): Na^+, K^+ (<70), Ca^{2+} (5–80), Mg^{2+} (<50), SO_4^{2-} (<100), Cl^- (<60), HCO_3^- (30–200). Total salt content 0.1–0.4 g L^{-1}.

3.4. *Determination of silicate in lake and mineral water*

The procedures developed were tested for the determination of silicate in natural waters. In particular, lake water and two types of mineral water "Znamenyvs' ka" (SJSC "Erlan", Ukraine) and "Morshinska" (OJSC "Oskar, Morshinskij zavod mineralnyh vod", Ukraine) were analyzed by using both the sorption-spectroscopic and visual test techniques.

The detailed procedure of the analysis is provided below. The aliquot of the lake or mineral water together with 0.8 mL of sulphuric acid (0.1 mol L^{-1}) and 0.5 mL of the mixed reagent solutions were placed into a 50 mL beaker. The mixture was diluted to 5 mL with distilled water and stirred. In 20 min 1.0 mL of sulphuric acid (4.0 mol L^{-1}) and 0.5 mL of ascorbic acid (30 mmol L^{-1}) solutions were added to the mixtures. In 15 min 3.5 mL of 0.06 mol L^{-1} tartaric acid solution was added to the solution containing the reduced HPA. Then, the portion of TDAN-SG or Lc-SG (0.100 g) was added to the solution and than the suspension was stirred for 20 or 15 min, respectively. Further on the adsorbent was separated via decantation and washed with a small portion of distilled water for several times.

The adsorbent light absorbance was measured in a thin layer ($l = 0.1$ cm) at 680 nm (TDAN-SG) or 800 nm (Lc-SG) and 995 nm. The measurements were performed against the unmodified silica gel. The sorption-spectrophotometric determination of silicate in a sample was performed by using the calibration curve in $\Delta A_{680} - c(SiO_3^{2-})$ or $\Delta A_{800} - c(SiO_3^{2-})$ coordinates for both methods using TDAN-SG and Lc-SG respectively. Visual-test determination of silicate in the sample was realized by comparing of adsorbent color with the color scales.

4. Conclusion

The sorption-spectrophotometric methods proposed for the silicate determination in the form of the ion associate immobilized onto silica have some important advantage before the liquid extraction methods [2,8,35]. They are simple to perform and environmentally safe.

The sensitivity of the sorption-spectrophotometric method based on TDAN-SG is twice and three times higher than for the sorption-spectroscopic method based on PUF [18] and the sorption-X-ray fluorescent method using cellulose filters [19], respectively because of the higher coefficient of the HPA distribution in the case of TDAN-SG.

The selectivity of the silicate determination in the presence of phosphate ions using the techniques proposed is 4 and 37 times higher than for the spectrophotometric [2] and sorption-spectroscopic method [18], respectively.

Moreover, the tight binding of HPA to the silica surface in the form of the ion associate with TDAN or Lc and its stabilization provides better reproducibility of the results of the silicate determination. The procedures proposed are simple, cost-effective and can be easily applied to the visual on-site testing.

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