

Solid-Phase–Spectrophotometric and Test Determination of Simultaneously Present Phosphorus Forms (Phosphorus Speciation) in Water

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Abstract—Solid-phase–spectrophotometric and test procedures are proposed to determine phosphorus as its ion associate with a quaternary ammonium salt and molybdoantimonophosphoric acid immobilized on silica gel in the concentration range 1.9–124 $\mu\text{g P/L}$. The determination of 4 μmol of phosphorus is not affected by (in μmol) alkali and alkaline-earth metals ($\leq 2 \times 10^4$), NH_4^+ ($\leq 1 \times 10^3$), Co^{2+} (≤ 1.0), Cu^{2+} (≤ 100), Mn^{2+} (≤ 10), Fe^{3+} (≤ 300), NO_3^- and SO_4^{2-} ($\leq 2 \times 10^4$), CO_3^{2-} ($\leq 1 \times 10^4$), As (≤ 20), and Si ($\leq 1 \times 10^3$). The procedure was tested in the determination of various phosphorus forms in natural waters.

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Phosphorus is one of the most important biogenic elements. Its main forms in natural waters are ortho-, meta-, pyro-, and polyphosphates and various phosphorus-containing organic compounds [1]. An increase in the phosphorus concentration in water reservoirs due to various effluents produces an uncontrolled amount of vegetative biomass, which in its turn leads to the reorganization of the aquatic life and to the prevailing of putrefactive processes. Therefore, the determination of phosphorus as both dissolved and suspended compounds in ground, surface, and sewage waters is an essential part of water quality control [1]. For these purposes, a procedure based on the photometric determination of reduced molybdoantimonophosphoric heteropolyacid is used as an international standard procedure (ISO 6878-1) [2]. However, the use of the standard procedure is limited by objects with phosphorus concentrations of $\geq 40 \mu\text{g/L}$ and lower.

Determination sensitivity can be increased by an extraction [3] or adsorption preconcentration of phosphorus on active carbon [4], naphthalene [5], or polyurethane foams (PUFs) [6] either as heteropolyacids (HPAs) and or as their ion associates with basic dyes. Among the proposed adsorbents, PUFs are the most efficient because they contain ester groups that have a high affinity to heteropolycomplexes. Finely dispersed silica gels appear to be even more promising matrices for the adsorption–spectrophotometric determination of phosphorus as HPA, because they exhibit no intrinsic absorption in the visible spectral region and possess better kinetic properties [7]. The use of adsorbents of this type allows the determination of the analytical signal directly in the concentrate, even visually [7], without elution. Unmodified silica gels cannot recover

HPAs from aqueous solutions. It was shown earlier that silica gels modified with macromolecular quaternary ammonium salts (QAS–SG) possess the properties of anion exchangers [8–10]. However, we failed to find in the literature data concerning the use of these adsorbents for the determination of phosphorus. The goal of this work was to develop procedures for solid-phase–spectrophotometric and visual test determination of trace amounts of phosphorus as its ion associate formed on the surface of QAS–SG upon treatment with an aqueous solution of reduced HPA.

EXPERIMENTAL

Reagents. Water was purified as described in [11]. We used chloroform, hexane, tetradecylammonium nitrate, 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. A mixed reagent containing 2.58 mmol of ammonium heptamolybdate, 1.28 mol of sulfuric acid, and 30 mmol of ascorbic acid was prepared immediately before the experiment. A chloroform solution of QAS and an aqueous solution of the corresponding substances were prepared by dissolving weighed portions of the reagents in chloroform or distilled water. SG-60 silica gel with $S_{\text{sur}} = 490 \text{ m}^2/\text{g}$ and $d_{\text{por}} = 6 \text{ nm}$ (Merck) modified with QAS by adsorption from a chloroform–hexane solution of QAS was used (QAS–SG). The adsorbent capacity for QAS was 25 $\mu\text{mol/g}$. Molybdoantimonophosphoric acid was prepared as follows. Three milliliters of the mixed reagent and 0.12 mL of a 3 mmol/L solution of potassium anti-

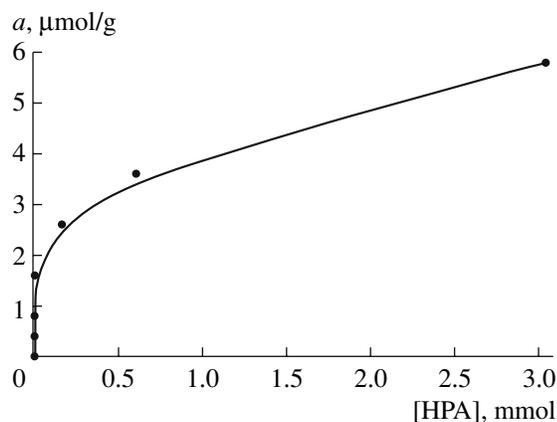


Fig. 1. Adsorption isotherm of HPA on QAS-SG; $a_{\text{QAS}} = 25 \mu\text{mol/g}$, $V/m = 200 \text{ mL/g}$, $c(\text{H}_2\text{SO}_4) = 0.25 \text{ mol}$, $T = 285 \pm 1 \text{ K}$.

mony tartrate were added to an aliquot portion of the solution containing phosphorus; then, the mixture was diluted to 15 mL with distilled water and allowed to stand for 5 min for an equilibrium to be reached.

Apparatus. The absorption spectra of solutions ($l = 1.0 \text{ cm}$) and adsorbents ($l = 0.1 \text{ cm}$) were recorded on an SF-46 spectrophotometer and a KFK-3 photoelectric colorimeter, respectively. The acidity of solutions was measured with an EV-74 universal potentiometer with a glass electrode. An MM-5 magnetic stirrer was used to stir suspensions.

Procedures. We studied the adsorption of HPAs on QAS-SG in a steady-state mode. For this purpose, a portion of an aqueous solution (5–100 mL) with a certain concentration of HPA was stirred with 0.010–0.150 g of QAS-SG for 1–10 min using a magnetic stirrer. The adsorbent was separated by decantation; then, its absorbance was measured in a thin layer ($l = 0.1 \text{ cm}$) or its color was compared with a color scale. The equilibrium concentration of HPA was determined by measuring its intrinsic absorption at 880 nm. The recovery of HPA (Γ , %) and adsorption (a , mol/g) were calculated by the equations $(c - [c]) \times 100/c$ and $a = (c - [c])V/m$, respectively, where c and $[c]$ were the initial and equilibrium concentrations of the adsorbate in solution, mol/L; V was solution volume, L; and m was adsorbent mass, g.

RESULTS AND DISCUSSION

Molybdophosphoric and mixed molybdoantimonophosphoric HPAs are the most commonly used analytical species for determining phosphorus [12, 13]. In developing adsorption-spectrophotometric and visual test procedures, we preferred HPA with a composition of $\text{H}_6\text{PSbMo}_{11}\text{O}_{40}$, whose reduced form formed rapidly (for 5 min) at room temperature. It is also known that mixed HPA is less soluble than $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ [13],

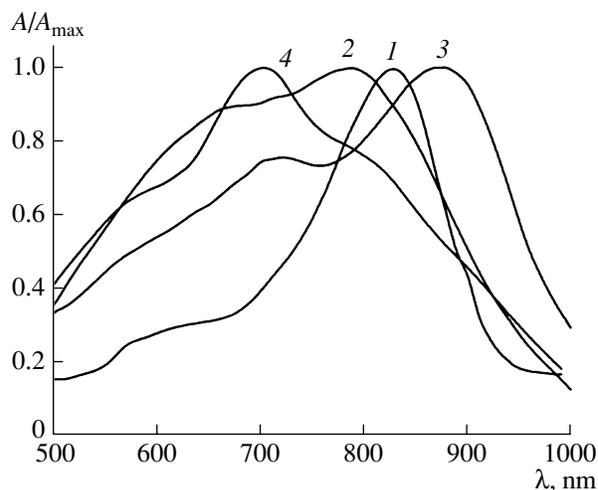
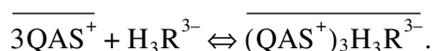


Fig. 2. Normalized absorption spectra of (1 and 2) molybdophosphoric and (3 and 4) molybdoantimonophosphoric HPA obtained (1 and 3) in solution and (2 and 4) on the surface of QAS-SG; c_{HPA} , μmol : (1, 3) 6.0 and (2, 4) 3.0; $a_{\text{QAS}} = 25 \mu\text{mol/g}$; pH 0.3.

which is particularly important in the case of adsorption preconcentration.

Molybdoantimonophosphoric acid was prepared in solution under the optimum conditions of its formation by mixing solutions of phosphate, ammonium molybdate, sulfuric acid, and potassium antimony tartrate followed by reducing the mixture with ascorbic acid.

QAS-SG efficiently recovers HPA from a 0.2–0.4 mol aqueous solution of sulfuric acid, that is, under the optimum conditions of the HPA formation. The triply charged H_3R^{3-} anion dominates in solution at this acidity [12]. The adsorption equilibrium is reached in 4 min. The adsorption isotherm can be attributed to the H-3 type (Fig. 1) [14]. The presence of a region of chemisorption in the isotherm is indicative of the high affinity of HPA to the surface of QAS-SG. In the range of phosphorus concentrations 0.1–3.0 $\mu\text{mol/L}$, the isotherm can be formally linearized on the Langmuir coordinates with a correlation coefficient of 0.989. In this case, the relative capacity of QAS-SG for HPA is 7.6 $\mu\text{mol/g}$, which corresponds to the ratio of immobilized surface groups⁺ : $\text{H}_3\text{R}^{3-} \approx 3 : 1$. The conditional adsorption constant is $9.3 \times 10^5 \text{ L/mol}$. The mechanism of the formation of ion associate on the surface can be described as follows:



The hypsochromic shift in the absorption spectra of adsorbed molybdophosphoric ($\Delta\lambda = 40 \text{ nm}$) and molybdoantimonophosphoric ($\Delta\lambda = 180 \text{ nm}$) HPAs (Fig. 2) and the redistribution of the band intensities confirmed the formation of ion associates on the surface of QAS-SG.

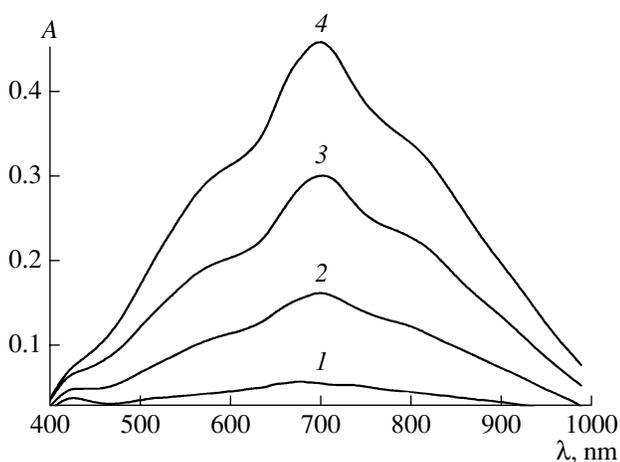


Fig. 3. Absorption spectra of QAS-SG treated by HPA solutions of different concentrations; c_{HPA} , μmol : (1) 0.0, (2) 31.0, (3) 93.0, and (4) 186.0; $a_{\text{QAS}} = 25 \mu\text{mol/g}$; $V/m = 200 \text{ mL/g}$; pH 0.3.

The absorption of the modified adsorbent at 700 nm increased proportionally with the phosphorus concentration in solution (Fig. 3). Under the optimum conditions for the heterogeneous reaction, the calibration equation for the solid-phase-spectrophotometric determination of phosphorus was the following:

$$A_{700} = (0.075 \pm 0.006) + (2.51 \pm 0.08)c \text{ (mg/L)}$$

$$(r = 0.996).$$

The curve was linear in the range of phosphorus concentrations 1.9–124 $\mu\text{g/L}$ with $V/m = 200 \text{ mL/g}$. The study of the effect of the ratio of the solution volume to the adsorbent weight on the recovery and analytical signal proved that adsorption characteristics of HPA remained almost unchanged as V/m was increased to 700 mL/g. The partition coefficient was 6.6 L/g at $V/m = 670 \text{ mL/g}$, and the detection limit of phosphorus calculated by the s test was 1.9 $\mu\text{g P/L}$.

To evaluate the performance characteristics of the proposed adsorption-spectrophotometric procedure for determining phosphorus, reference solutions were analyzed that contained phosphorus in concentrations of 31, 62, and 124 $\mu\text{g/L}$. The found phosphorus concentrations were 32 ± 2 ; 62 ± 3 , and $122 \pm 5 \mu\text{g/L}$, respectively ($n = 3$, $P = 0.95$). The results obtained indicated that the accuracy of the procedure was good.

The study of the effect of the major components of natural waters showed that the determination of 4 $\mu\text{mol/L}$ of phosphorus was not affected by alkali and alkaline-earth metals in the concentrations $\leq 2 \times 10^4$, $\text{NH}_4^+ \leq 1 \times 10^3$, $\text{Co}^{2+} \leq 1$, Cu^{2+} and $\text{Mn}^{2+} \leq 10$, $\text{Fe}^{3+} \leq 300$, NO_3^- and $\text{SO}_4^{2-} \leq 2 \times 10^4$, and $\text{CO}_3^{2-} \leq 1 \times 10^4 \mu\text{mol}$. Arsenic in the concentration $\leq 1.5 \text{ mg/L}$ (30-fold maximum permissible concentration (MPC)) and silicon in the concentration $\leq 28 \text{ mg/L}$ (three-fold MPC) did not affect

the results of phosphorus determination, which allowed us to recommend the proposed procedure for analyzing waters of various types.

An increase in the concentration of HPA in the adsorbent phase was accompanied by the change in the adsorbent color from white to blue. This was used as the basis for the development of a visual test scale for semiquantitative determination of phosphorus in the concentration range 2.2–248 $\mu\text{g/L}$ (at $V/m = 670 \text{ mL/g}$).

Development of the test scale for visual determination of phosphorus. The graduation interval was selected using the colorimetric method [15]. To obtain reference solutions with phosphorus concentrations of 0.0, 6.2, 12.4, 31, 62, 109, 170, and 248 $\mu\text{g/L}$, corresponding aliquot portions of the phosphorus solution were placed in 25-mL volumetric flasks. Then, 5 mL of the mixed reagent solution and 0.2 mL of a 3-mmol solution of potassium antimonyl tartrate were added to each flask, and the mixture was diluted up to the mark with distilled water and stirred. After 5 min, the solution was transferred to a 50-mL beaker; 0.125 g of QAS-SG was added, and the suspension was stirred for 5 min. The adsorbent was separated by decantation and used as a color scale. Such a concentrate was stable for at least three days.

The developed procedures were tested in the determination of orthophosphate in well water and in determining total phosphorus, total polyphosphates, orthophosphate, and phosphoric acid esters after the corresponding treatment [1] in lake water.

Determination of orthophosphate in lake and well water. An aliquot portion of water was placed in a 50-mL beaker; 3 mL of the mixed reagent solution and 0.12 mL of a 3-mmol solution of potassium antimonyl tartrate were added. The mixture was diluted to 15 mL with distilled water and stirred. After 5 min, 0.075 g of QAS-SG was added to the solution, and the suspension was stirred for 5 min. The adsorbent was separated by decantation; then, its absorbance was measured in a thin layer ($l = 0.1 \text{ cm}$) at 700 nm or its color was compared with the color scale. The measurements were performed against unmodified silica gel. The solid-phase-spectrophotometric determination of phosphorus in the sample was performed using the calibration curve on the $A_{700}-c_{\text{P}}$ coordinates.

Determination of total polyphosphates and phosphoric acid esters in water was performed after the acid prehydrolysis of the sample [1]. For this purpose, 2 mL of 4.5 mol sulfuric acid was added to 100 mL of a water sample prefiltered through a fine-porous paper filter, and the mixture was boiled for 30 min. After the solution was cooled to room temperature, the sample was transferred to a 100-mL volumetric flask and diluted to the mark with distilled water. The determination was performed as in the case of orthophosphate.

Determination of total phosphorus in water was performed after the wet oxidation of the sample [1]. In this case, 50 mL of an unfiltered sample was placed in

Table 1. Determination of phosphorus in various forms in lake and well water by the developed (I) solid-phase-spectrophotometric and (II) test procedures and (III) the arbitration procedure [2] ($n = 3$ (I and III) and 10 (II), $P = 0.95$)

Type of water	Phosphorus form	Phosphorus concentration, $\mu\text{g/L}$ (*mg/L)		
		I	II	III
Lake water	Orthophosphate	14.6 ± 0.9	12 ± 3	<42
	Polyphosphates and phosphoric acid esters	39 ± 2	31 ± 6	<42
	Total phosphorus	$170 \pm 10^*$	$160 \pm 40^*$	$167 \pm 9^*$
Well water	Orthophosphate	33 ± 2	31 ± 6	<42

Table 2. Comparison of spectrophotometric (SP), extraction-spectrophotometric (ESP), and adsorption-spectrophotometric (ASP) procedures for determining phosphorus as HPAs

Procedure (adsorbent)	Detection limit, $\mu\text{g P/L}$	Do not interfere, mmol/L	Reference
SP	15	Si (≤ 0.2), As ($\leq 6 \times 10^{-3}$), Fe^{3+} (≤ 0.3), Cu^{2+} (≤ 0.1), F^- (≤ 4)	[2]
ESP	6.1	Si (≤ 0.3), As, Ge (≤ 0.1)	[3]
ASP (naphthalene)	3.1	Si (≤ 0.18), As ($\leq 1 \times 10^{-3}$), alkali and alkaline-earth metals, Cl^- , SO_4^{2-} ($\leq 1 \times 10^{-3}$)	[5]
ASP (PUF)	20	Si (≤ 0.7)	[6]
ASP (QAS-SG)	1.9	Si (≤ 1), As ($\leq 2 \times 10^{-2}$), alkali and alkaline-earth metals ($\leq 2 \times 10^4$), NH_4^+ (≤ 1), Co^{2+} ($\leq 1 \times 10^{-3}$), Cu^{2+} (≤ 0.1), Mn^{2+} ($\leq 1 \times 10^{-2}$), Fe^{3+} (≤ 0.3), NO_3^- (≤ 20), CO_3^{2-} (≤ 10)	Present article

a chemical-resistant beaker; then, 0.3 mL of 30% hydrogen peroxide and 1.0 mL of sulfuric acid (1 : 3) were added. The solution was heated on a sand bath for 6 h and evaporated to dryness. The dry residue was dissolved in 30 mL of distilled water upon heating. The solution obtained was quantitatively transferred to a 100-mL flask, diluted to the mark with distilled water, and analyzed as described above for the determination of orthophosphate. Simultaneously, a blank experiment was performed with distilled water; its result was subtracted from the phosphorus concentration found in the sample.

The results of determining various forms of phosphorus in waters using the developed and the arbitration [2] procedures are given in Table 1 and indicate that the accuracy and precision of the proposed procedure are generally satisfying. The procedure can be used to determine various phosphorus forms in natural waters.

A comparative analysis of the developed procedures and the best analogs known from the literature is presented in Table 2. It is seen that the proposed procedures outperform the known procedures for determining phosphorus as HPAs [2] in sensitivity, including those using extraction [3] and adsorption [5, 6] preconcentration. The high sensitivity and selectivity allow the use of the developed procedures for determining simultaneously present forms of phosphorus in water, in particular, orthophosphate and polyphosphate. The

possibility of determining the phosphate concentration immediately in the course of sampling followed by the refinement of the data in a laboratory by solid-phase spectrophotometry is an important advantage of the proposed visual test. In this case, the transportation of large volumes of water to the laboratory is not needed. The use of the developed solid-phase reagent for determining phosphate concentrations at the place of sampling prevents errors due to the imbalance in the orthophosphate-polyphosphate system because of sample conservation with acids or the use of procedures including heating. The procedures are rapid, simple, and ecologically safe. The time of one experiment is shorter than 15 min; the procedure does not require expensive equipment and highly qualified personnel.

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