A NEW METHOD FOR THE DETERMINATION OF PHOSPHATE IONS IN NATURAL AND TREATED WASTEWATERS

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ABSTRACT

A new indirect method for the determination of phosphate ions in natural and waste waters after purification is proposed. The method is based on the formation of a molybdophosphate complex (MPhC), its separation from the excess of unbound molybdate by extraction with isoamyl acetate, reextraction of MPhC into a weakly alkaline aqueous phase, and determination of the amount of molybdenum after the destruction of MPhC by the sulfonitrazo DAP reagent. The method has been tested on model solutions, natural and treated waste waters. The method allows to determine from 0.02 to 0.43 mg/dm^3 of phosphate ion (in terms of phosphorus), regression equation A = 0,032±0,035 + (1,15±0,05)C(P), correlation coefficient r = 0,995, C$_{min}$ = 0,01 mg/dm^3.

Key words: orthophosphate ions, molybdophosphate complex, spectrophotometry, sulfonitrazo DAPH reagent, natural and waste waters.

INTRODUCTION

Determination of small amounts of phosphate ions in low-concentration solutions is of great importance for various industries, environmental, agrochemical and biological research. This applies primarily to natural and treated wastewater, because the determination of the phosphate content allows to control the process of pollution of water bodies with nutrients.

The concentration of phosphorus in waters varies from 0.02 to 5.4 mg/dm^3 (in terms of phosphorus), that is, the upper limit significantly exceeds the maximum allowable concentrations that do not cause eutrophication. There are many catchment areas in Ukraine, the economic activity of which has entered the zone of ecological risk. These are, first of all, the main rivers of Ukraine − Dnieper, Danube, Dniester, Southern Bug, which make the main contribution to the inflow of water with high content of phosphorus compounds in the Ukrainian coastal waters of the Black Sea − 0.57 km^3/year (70.5%) at an average phosphate concentration of 0.15 mg/dm^3 [1,2]. The accumulation of phosphorus compounds in the waters of small rivers of the Crimea, Odessa and Mykolayiv regions and the Ingul River is 0.086 thousand tons/year. Analysis of the average annual concentrations of phosphates for 2010 − 2020 shows an increase in their content in the water of the Dnieper in 2… 2.5 times [3,4]. As a result of eutrophication, the oxygen content decreases, fish die, and large amounts of biomass make water treatment much more difficult.

It is known, that eutrophication is limited only, when the phosphorus concentration in reservoirs decreases below 0.5 mg/dm^3, and at a concentration below 0.05 mg /dm^3 it almost completely stops [1−3]. Given the importance of quantifying orthophosphates in natural objects, this problem is highlighted in a separate section of analytical chemistry [5].

The main source of phosphate ion in urban wastewater is synthetic detergents. A large number of detergents contain as an alkaline agent with a large buffer capacity of trisodium phosphate Na$_3$PO$_4$. A characteristic property of the phosphate ion is the ability to form condensed systems − polyphosphate, metaphosphate ions and so on. These compounds are

formed during the polymerization of the orthophosphate ion and consist of two or more PO_4^{3-} groups. Some of them are also used in industry and everyday life as emollients and may be present in wastewater. These include, for example, sodium pyrophosphate ($Na_4P_2O_7$), sodium tripolyphosphate ($Na_5P_3O_{10}$), sodium hexametaphosphate ($Na_6P_6O_{12}$), and others. Polyphosphate ions in water undergo stepwise hydrolysis, turning into orthophosphate ions. The rate of hydrolysis is strongly influenced by pH, temperature and salt composition of water. Organophosphorus compounds are widely used in the national economy as active insecticides, acaricides, defoliants, herbicides and others. These include carbophos, chlorophos, phosphamide, trichlorometaphos. By their chemical structure, they are derivatives of phosphorus, phosphonic, and others phosphoric acids, esters of thio- and dithiophosphoric acids. All these compounds are unstable in the environment, but their time in the water may be sufficient for a significant deterioration in the quality of natural waters, often undecomposed drugs fall into water treatment plants.

The main conversion reactions of almost all of these compounds are hydrolysis and oxidation. The vast majority of phosphorus-containing compounds in water are almost completely hydrolyzed and the end product of these processes are acidic phosphates. The rate of hydrolysis is influenced by pH, temperature and salt composition of water. The presence of bacteria accelerates the hydrolysis process [6]. The total (gross) phosphorus content in the water sample is determined after the conversion of all phosphorus-containing compounds into orthophosphate ions [5,7].

The content of phosphorus-containing compounds is regulated depending on the nature and purpose of the waters. Thus, the maximum permissible concentration of phosphate ions in water, water for domestic needs and fisheries in Ukraine is 3.5 mg PO_4^{3-}/dm^3 (1.14 mg P/dm^3).

Constant monitoring of the phosphate content in water bodies and drinking water by different methods makes it possible to assess the degree of risk for aquatic ecosystems, especially for organisms living in the aquatic environment, and a person who uses water resources [8,9].

Among the large number of proposed methods for the determination of phosphorus in these objects, spectrophotometric methods with extraction or sorption concentration are most often used. In many methods, the main form of phosphorus (V) determination is heteropoly acids − molybdophosphate complex (MPhC). The color, intensity and color stability of these compounds depend on the quantitative and qualitative composition, their structure, as well as on the use of reducing agents with a certain redox potential in the system [5,7].

To determine the phosphorus content, the reaction of formation of a yellow (unreduced) heteropoly acid − $H_3[P(Mo_3O_{10})_4]$, ($\lambda_{max} = 310$ nm, $\varepsilon_{310} = 1.2 \cdot 10^4$) is often used in the interaction of phosphate ions and sodium or ammonium molybdate [9]. In the studied solutions, according to the experimental conditions, there is always an excess of molybdate ions, the maximum light absorption of which is also in the UV region of the spectrum; therefore, phosphate ions can be determined only at wavelengths greater than 345 nm, at which the sensitivity is much lowerMethods using reduced forms of blue MPhC are more common. The molar absorption coefficients of the reduced and mixed complexes are much higher and allow a greater sensitivity to be achieved than using the yellow MPhC. For example, for molybdophosphate blue, $\varepsilon_{665} = 2.2 \cdot 10^4$ [8]. The process of MPhC formation occurs when an excess of ammonium or sodium molybdate solution is added to an acidic solution containing orthophosphate ions. As reducing agents are used ascorbic acid, stanum (II) chloride, hydrazine sulfate, etc. [10, 11]. Ascorbic acid is a mild oxidizing agent and does not reduce the excess of molybdate ions; the use of the reducing agent stanum (II) chloride increases the rate of reduction.

Methods for determining phosphorus based on the formation of MPhC have a number of disadvantages. For the yellow complex, this is work in the UV region, low sensitivity and selectivity − a number of cations and anions interfere with the determination of phosphorus − arsenate, tungstate, dichromate, nitrite and thiosulfate anions, cations Al^{3+}, Cu^{2+}, Fe^{3+}.

Methods for the determination of orthophosphate ions with the formation of a blue heteropoly acid after the reduction of MPhC in the aqueous or organic phase are more sensitive.

However, they all have low reproducibility, which is due to the unstable ratio of valence forms of molybdenum Mo(V) /Mo(VI), which depends on the acidity of the solution and the nature of the reducing agent. The intensity of the color changes with time and influence of temperature, therefore, it is necessary to strictly observe the conditions of the experiments, which complicates the analysis as a whole [13].

For the purpose of concentrating the phosphate ion, separating it from interfering ions and excess molybdate ion and increasing the sensitivity of determination, the extraction of MPhC with organic reagents in the form of a yellow or blue complex is used. Usually, the yellow complex is extracted and the reduction is carried out in the organic phase, but techniques are known using the reduction in the aqueous phase. Extracts of reduced and unreduced MPhC retain the color inherent in their aqueous solutions. The general view of the spectra is identical, but the absorption maxima of this compounds in organic solvents, as a rule, are slightly shifted to the short-wavelength region. Reduced MPhC are extracted better than unreduced ones.

Alcohols, ketones, ethers, petroleum ether, carbon tetrachloride, chloroform and some others were studied as extractants. Among aliphatic alcohols, alcohols with 4-8 carbon atoms have the best extraction properties; alcohols with a smaller number of carbon atoms extract MPhC from solutions non-quantitatively, while those with a larger amount form stable emulsions at the phase boundary. During extraction with octanol, the excess molybdic acid practically does not pass into the organic layer.

The most suitable extractants were found to be a 20% solution of butan-1-ol in chloroform (extract 98.9% of MPhC), butyl acetate (99.9%), cyclohexanone (99.9%), and quinoline (95.7%). For complete extraction, it is necessary that the ratio of Mo : P in an aqueous solution be greater than 42 [14,15].

In the case of butanol, the determination of less than 50 mg P is not interfered with by 4 mg of As, Si, and up to 1 mg of Ge. In addition, the extraction removes a significant part of the excess molybdate ion, which also absorbs in the ultraviolet region of the spectrum. Butanol is used for the extraction of trace amounts of phosphate ion in the form of MPhC from wastewater.

In [16], a sequential selective extraction of heteropoly complexes of arsenic (MAC), silicon (MSC), and phosphorus (MPhC) using various extractants was proposed. At pH 1.8, MPhC is extracted with diethyl ether, then, by changing the acidity, MSC and methyl isobutyl ketone MAC are extracted with butanol.

It was found that during extraction with butyl acetate, molybdic acid is practically not recovered. The acidity of the medium and the concentration of the molybdate ion have little effect on the extraction, but it is better to carry out it from 0.5 N HCl in the presence of 0.5 % sodium or ammonium molybdate solution. The composition of the complex, extracted with butylacetate, corresponds to the ratio P: Mo = 1: 12. For other extractants, this ratio may be different [9]. The extract is characterized by an absorption maximum at 320 nm, $\varepsilon = 2.3 \cdot 10^3$. It has been shown that the presence of salts (NaCl, NaNO$_3$, Na$_2$SO$_4$ etc.) in a solution in small concentrations (1−3 %) does not have a noticeable effect on the extraction, which is important for determining the phosphate-ion in waters [10].

In addition to the methods for determining the phosphate ion in the form of MPhC, methods with the formation of ternary complexes are often used. The quality of the third component in these complexes are present ions V (V), Bi (III) or Sb (III). Molar absorption coefficients these compounds allowing to reach greater sensitivity, then MPhC. . So, for the yellow ternary complex of molybdovanadophosphate acid $\varepsilon = 1.7 \cdot 10^4$ [10, 11], for molybdobismuthphosphate blue $\varepsilon_{720} = 1.66 \cdot 10^4$ [10,14].

The most sensitive group of methods for determining the phosphate ion are methods with the formation of ionic associates of MPhC with basic dyes. These methods were developed by Babko and Pilipenko and their staffes [10]. They are also convenient in that silicon does not form such compounds and does not interfere with the determination. The molar extinction coefficients of the dyes themselves are high and often reach 10^5, and 1 molecule of the MPhC can attach 3 or more molecules of the main dye, which leads to a sharp increase in

the detection sensitivity. The following basic dyes were used: crystal violet, malachite green, iodine green, brilliant green, safranin, etc.

Intensely colored associates are found in solutions in the form of colloids or suspensions. In practice, the determination of the phosphate ion in the form of MPhC associates with basic dyes is carried out in three versions: with the extraction separation of colored compounds and photometry of extracts, with separation of the solid phase by centrifugation, its subsequent dissolution in suitable solvents and photometry of the solution, and with the stabilization of the solid phase in aqueous solutions. Various surfactants are used as stabilizers, in particular, nonionic ones, for example, OP-10. The use of associates and surfactants makes it possible to determine $1–200$ mcg/dm^3 of phosphate ion. However, these methods require careful observance of the analytical conditions, especially the acidity of the medium, removal or destruction of excess dyes, since the latter often absorb in the same spectral region as the associate. The methods are characterized by low reproducibility and analysis duration due to the need to separate, stabilize, and dissolve the formed colored compounds [17−19].

Some sources propose the determination of phosphate ions by an indirect method using the multiplication reaction. The principle of this method is that the formed MPhC with a strict stoichiometric ratio of the amounts of molybdenum and phosphorus is destroyed and the content of molybdenum is determined, and then recalculated to the content of phosphorus. For example, in [13, 17], the reduced blue MPhC was separated from the excess of molybdate ions by extraction, the complex was reextracted into a weakly alkaline aqueous phase, decomposed, and the content of molybdenum with the reagent 2,3,7-trioxyfluorone was determined in the presence of neonol.

In [20, 21], the yellow MPhC was separated from the excess of molybdate ions by extraction, its aqueous phase was transferred, the complex was destroyed, and the amount of molybdenum in the final solution was photometrically determined, which is equivalent to the amount of phosphorus in the MPhC, by the sulfonitrazo E reagent. The advantage of using unreduced heteropolyoxoacid $H_3[P(Mo_3O_{10})_4]$ is the preparation of a compound with a strictly stoichiometric composition, in which the ratio P: Mo = 1:12, therefore the multiplication factor in this reaction is 12, and the detection sensitivity depends on the sensitivity of the reaction to molybdenum.

The aim of this work was to improve the method for the indirect determination of phosphate ions using a sensitive and selective reagent for molybdenum − sulfonitrazo DAPh (SN DAPh) and to develop a new sensitive and selective method for the determination of small amounts of phosphate ions in natural and purified wastewaters.

EXPERIMENTAL PART

MATERIALS AND METHODS OF RESEARCH

The following reagents were used: potassium dihydrogen phosphate KH_2PO_4; sodium molybdate dihydrate $Na_2MoO_4·2H_2O$; hydrochloric acid HCl, saturated, 38%; ammonium hydroxide NH_4OH, 25%, $\rho = 0.91$ g/dm^3; reagent sulfonitrazo DAPh; isoamyl acetate $CH_3−CH(CH_3)−CH_2−CH_2−OCO−CH_3$; potassium hydrogen phthalate $HOOC−C_6H_4−COOK$, c.

To register the optical density, we used a photoelectric photometer KFK-3-01-"ZOMZ".

A pH meter/MV/ISE/Temp ADWA AD1200 PBX was used to control the pH.

The following solutions were used for the studies.

1. Standard solutions of phosphate ion [10]:

1.1. Phosphate ion standard solution № 1. A portion of potassium dihydrogen phosphate weighing 0.4394 g was dissolved in distilled water and diluted in a 1 dm^3 volumetric flask with water to the mark. C(P) = 0.1 g P/dm^3 (100 mg P/dm^3).

1.2. Phosphate ion standard solution № 2. A solution of № 1 with a volume of 10 cm^3 was transferred to a volumetric flask with a capacity of 100 cm^3 and made up to the mark with water. C(P) = 0.01 g P/dm^3 (10mg P/dm^3).

1.3. Phosphate ion standard solution № 3. A solution of № 2 with a volume of 10 cm^3 was transferred to a volumetric flask with a capacity of 100 cm^3 and made up to the mark with water. C(P) = 0.001 g P/dm^3 (1 mg P/dm^3).

2. Standard solutions of molybdate ion [22]:

2.1. Molybdate ion standard solution № 1. A portion of sodium molybdate dihydrate weighing 2.5219 g was dissolved in a small amount of hot distilled water, 1 cm^3 of saturated HCl was added, cooled, quantitatively transferred to a 1 dm^3 volumetric flask and diluted with water to reflux. C(Mo) = 1 g Mo/dm^3.

2.2. Molybdate ion standard solution № 2. A solution of № 1 with a volume of 10 cm^3 was transferred to a volumetric flask with a capacity of 100 cm^3 and made up to the mark with water. C(Mo) = 0.1 g Mo/dm^3.

3. Sodium molybdate solution, 10%.

4. Hydrochloric acid solutions: saturated, 5% and 0.1 N.

5. A solution of ammonium hydroxide, 0.1%.

6. Isoamyl acetate.

7. Phthalate buffer solution. To a 200 cm^3 volumetric flask was added 15.7 cm^3 of 0.1 N hydrochloric acid solution, 50 cm^3 of 0.2 M potassium hydrogen phthalate solution and made up to the mark with water; pH = 3.5 [23].

8. Aqueous solution of SN DAPh, 0.05%.

RESULTS AND DISCUSSION
## STUDY OF EXTRACTION AND REEXTRACTION OF MPhC

After receiving the yellow complex of MPhC, it was extracted to separate from the excess of molybdate ions. The best extractants for MPhC are ethers (the separation coefficient of molybdenum heteropoly- and isopolycomplexes, equal to the ratio of their distribution coefficients > 1000). After twice washing the extract with acidic solutions, the minimum value of the light absorption of the blank experiment is reached [13].

Investigated the extraction of MPhC with butyl acetate, amyl acetate, and isoamyl acetate in an acidic medium. In the case of using amyl and isoamyl acetate, there is no foaming and fast phase separation is achieved. Under these conditions, practically all of the unbound molybdate ion remains in the aqueous phase together with the ions that interfere, which significantly increases the selectivity of the method. It was found that the complex is more fully reextracted if the volumes of the organic and aqueous phases are approximately the same.

The process of interaction of molybdate ions with SN DAPh after reextraction of the molybdophosphate complex into the aqueous phase was studied separately. In this case, in a weakly alkaline medium, there is a course of competing complexation reactions between the MPhC and the SN DAPh complex. The alkaline environment causes the destruction of MPhC. But at pH 9.5 ... 10 this process slows down and the complex begins to break down, so it is necessary to strictly observe the pH value of the solution in the range of 8 ... 9. To do this, it is advisable to use a dilute 0.1% solution of ammonium hydroxide.

INVESTIGATION OF THE INTERACTION OF MOLYBDATE IONS WITH SULFONITRASO DAPH

Among the o,o'-dioxyazocompounds, the sensitive and contrast reagent for the molybdate ion is SN DAPh − 3-sulfo-5-nitro-4'-diethylamino-2,2'-dioxyazobenzene [24].
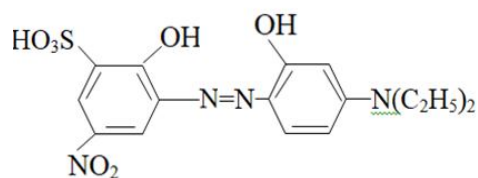
The study of the use of the reaction of molybdate ion with SN DAPh for indirect determination of phosphate ions was not performed.
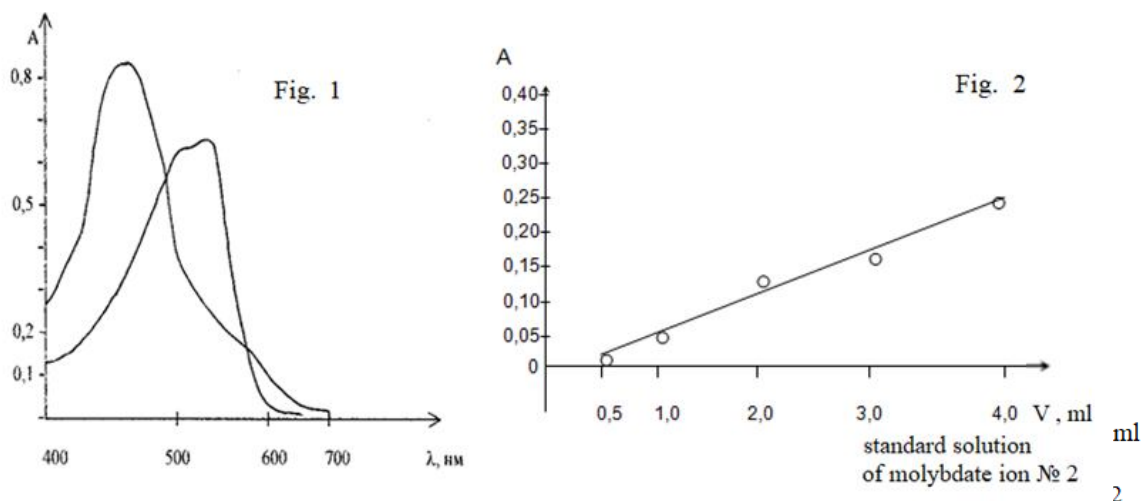

Fig. 1. Spectra of the reagent SN DAPh (1) and its complex with modibdate (2) $(C_R = C_{comp} = 3{,}6 \cdot 10{-}6$ mol/25 ml solution)

Fig. 2. Calibration graph for determining the range of optimal concentrations of molybdate ion when determining it with sulfonitrazo DAF reagent ($\lambda = 560$ nm)

The MoO_4^{2-} ion reacts with SN DAPh at pH = 3.5 in phthalate buffer medium.

The formation of the complex occurs immediately after the addition of the reagent. The color intensity of the newly formed complex with the reagent SN DAPh is stable over time and does not change during the day. The molar ratio of the components in the complex with an excess of reagent is 1:1, λ_{max}(reagent) = 460 nm, λ_{max}(complex) = 560 nm. The color of the reagent solution is orange, and the color of the complex with molybdate ions is intensely crimson. The difference between the light absorption λ_{max} is 100 nm, i.e., the reagent is sufficiently contrast and almost does not absorb at 560 nm, which distinguishes it from the reagent sulfonitrazo E. The molar light absorption coefficient of this complex with SN DAPh is $\varepsilon = 1.3 \cdot 10^4$.

To clarify the interval of concentrations, reproduction and testing of the method of determining the amount of molybdate ion, a graph № 1 of the dependence of the optical density on the concentration of molybdate ions − A = f(C_{Mo}) was constructed.

To do this, in eight volumetric flasks of 25 cm³ consistently made, respectively, 0; 0.2; 0.5; 1.0; 1.5; 2.0; 3.0 and 4.0 cm³ of a standard solution of molybdate ion № 2, then to each was added 3 cm³ of phthalate buffer and 2 cm³ of 0.05% solution of SN DAPh reagent, the contents of each flask were adjusted to the mark with water. After 5 min, the optical density was determined at $\lambda = 560$ nm in a cuvette 2 cm thick.

The regression equation of the graduated graph $A = 0.029\pm0{,}03 + (1.05\pm0{,}05)C(Mo)$, correlation coefficient $r = 0{,}990$.

The experiment showed that the range of concentrations that can be determined is from 0.75 to 16 mg Mo /dm³ ($0.84 \cdot 10^{-5} \ldots 16.8 \cdot 10^{-5}$ mol Mo/m³).

DEVELOPMENT OF METHODS FOR INDIRECT DETERMINATION OF PHOSPHATE IONS WITH SULFONITRAZO DAPH REAGENT

1. Construction of a graduated graph № 2 to determine the concentrations of molybdate ion after reextraction and destruction of the MPhC complex.

Based on the analysis of the composition of the MPhC complex $H_3[P(Mo_3O_{10})_4]$, the calculated range of concentrations of phosphate ions, which can be determined by the developed method, is from $C(P)_{min} = 0.02$ mg P /dm^3 to $C(P)_{max} = 0.43$ mg P/dm^3.

Based on these data, the volumes of standard solutions of phosphate ions were determined to build a graduated graph for determining the content of these ions in the studied objects.

1.1. To the separating funnel per 100 cm^3 was made separately for each experiment, respectively, 0; 0.5; 1.0; 2.0; 3.5; 5.0; 7.5; 10.0 and 12.5 cm^3 of a standard solution of phosphate ion № 3, then 0.5 cm^3 of a 10% solution of sodium molybdate, 1 cm^3 of HCl saturated and 30 cm^3 of distilled water. Within 1 min, MPhC is formed in the solutions, so the solution becomes yellowish.

1.2. Isoamyl acetate, 10 cm^3, is added to the separating funnel with the MPhC solution and shaken for one minute. The formed MPhC passes into an organic phase. The aqueous phase is poured into the second funnel, to which is added 5 cm^3 of isoamyl acetate. Shake for one minute. The organic phase after the second extraction turns yellow. Both extracts (~15 cm^3) are poured into one separatory funnel and washed twice with portions of 5% HCl of 10 cm^3 each, the washings are discarded.

1.3. The organic phase, 15 cm^3 of water and 0.5 cm^3 of 0.1% ammonium hydroxide solution (pH of the solution 8… 9), shake for 1… 2 min. The complex in the slightly alkaline medium is reextracted to the aqueous phase. After stratification, the aqueous phase containing MPhC is placed into a 25 cm^3 volumetric flask, 3 cm^3 of phthalate buffer solution, 2 cm^3 of SN DAPh reagent solution are added, heated in a water bath and boiled for 3 minutes. The last operation is performed for the complete destruction of the MPhC complex. After cooling, the solution is made up to the mark with water, stirred and photometered at 560 nm in a cuvette with l = 2 cm relative to the comparison solution (3 cm^3 of phthalate buffer, 2 cm^3 of SN DAPh reagent solution, water to the mark in a 25 cm^3 flask).

Construct a graduated graph of the dependence A = f (m (P) based on the recalculation of $m(P) = \dfrac{m(Mo) \cdot 30,97}{95,94 \cdot 12}$ mg.
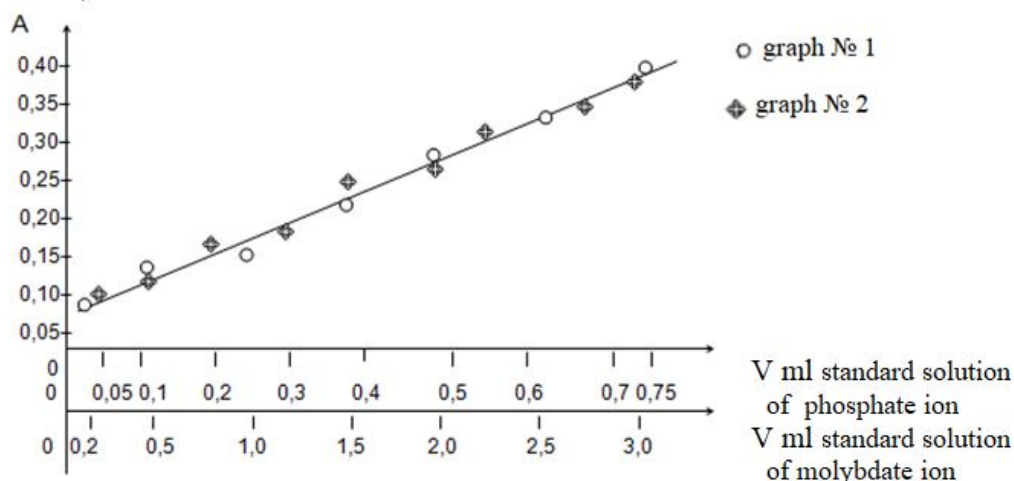

Fig.3. Calibration graphs for determining the content of phosphate ion in a solution by the amount of molybdate ion.

Regression equation of the obtained graduated graph A = 0,032±0,035 + (1,15±0,05)C(P), correlation coefficient r = 0,995. So, that is, the slope and range of the determined

concentrations of phosphate ions by the definition of these ions through the molybdophosphate complex and the direct determination of molybdate ions are almost the same. This means that the processes of extraction and reextraction allow to almost completely separate the MPhC from the excess molybdate ions, quantitatively translate it first into the organic, then into the inorganic phase, and then − quantitatively translate it into a complex with SN DAPh.

The range of phosphate ion concentrations to be determined is 0.02… 0.43 mg P /dm^3.

DETERMINATION OF PHOSPHATE ION CONCENTRATION IN MODEL SOLUTIONS AND IN INVESTIGATED WATERS

The method was tested on model solutions by the method of "taken-found" and on samples of tap, wastewater and natural water.

The test water up to 20 cm^3 was added to a 25 cm^3 volumetric flask, 0.5 cm^3 of 10 % sodium molybdate solution, 0.5 cm^3 of HCl saturated and water were added to the mark. MPhC is formed in the solution within 1 min. Further analysis was performed according to items 1.2 and 1.3.

Model solutions were prepared from distilled water by adding the calculated volumes of standard phosphate ion solution.

Sampling was performed in the summer according to GOST R 51593-2000 on the day of determination. Samples of test waters, based on the results of previous studies, were pre-diluted four times: to 5 cm^3 of water was added 15 cm^3 of distilled water.

The content of phosphate ions in terms of phosphorus was determined by the formula:

$$C(\text{P}) = \frac{m(\text{P}) \cdot 1000}{V_{\text{samp}}} \text{ mg P/dm}^3,$$

where m(P) is the mass of phosphorus, determined on the sample, V_{samp} is the volume of water under study.

The research results are presented in the tables.

Table 1. The results of determination of phosphate ions in in model aqueous solutions (n = 5, P = 0.95))

Sample	Taken P, mg /dm^3	Found P, mg /dm^3	RSD (%)
1	0,025	0,024±0,0008	0,1
2	0,05	0,05±0,002	0,4
3	0,10	0,11±0,004	0,9
4	0,20	0,21±0,006	0,8
5	0,40	0,40±0,014	1,6

Table 2. Results of determination of phosphate ion (in terms of phosphorus) in tap, river and waste waters (n = 5, P = 0.95)

Sample	Found P, mg /dm^3	RSD (%)
Tap water	0,08 ± 0,0025	2,5
Wastewater is treated after the machine-building plant PTZ	0,38 ± 0,015	1,8
Annual water (Yzh. Bug river)	0,31 ± 0,012	1,4
Artesian water (gardening well "Southern Bug")	<0,02	

The results of the analysis of the given types of waters presented in the table show satisfactory reproducibility and correctness of the offered technique.

CONCLUSIONS

An indirect method for the determination of phosphate ions in natural and treated wastewater is proposed, which is based on the formation of molybdophosphate heteropoly acid, its extraction with isoamyl acetate in order to separate from the excess molybdate ion and other ions in the water, determining the equivalent amount of molybdate ions with the reagent sulfonitrazo DAF. The range of determined concentrations of phosphate ion (in terms of phosphorus) is 0.02… 0.43 mg/dm^3, regression equation A = 0,032±0,035 + (1,15±0,05)C(P), correlation coefficient r = 0,995, C_{min} = 0,01 mg/dm^3. This method allows to assess the contamination of water with phosphates at the level necessary to control eutrophication processes in lowconcentrated natural and treated wastewater.

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