Combination of Precipitation Preconcentration and Chemical Amplification of the Signal in Flow-Injection Determination of Nanogram Amounts of Phosphorus

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Abstract—Cocprecipitation of ion pairs of quadruply charged molybdovanadophosphoric heteropoly anions and cations of Brilliant Green with the ion pairs of the same dye and paramolybdate ions was used for determining nanogram amounts of phosphorus present as orthophosphates. Filtering of the sol through a column with a filter made of fibrous polypropylene provides on-line preconcentration of phosphorus, eliminates the effect of collector, and makes it possible to elute the concentrate for subsequently measuring the signal in the flow mode. A combination of this technique with chemical amplification of the analytical signal lowers the limit of detection to 0.05 ng of phosphorus in 2 mL.

A wide acceptance of flow-injection analysis (FIA) in studying environmental samples usually requires its combination with preconcentration methods [1]. The combination of the automated FIA method with coprecipitation is the most difficult problem. This method is usually used for the determination of metals; nonmetals are determined much less frequently. Because of the biogenic importance of phosphorus, its determination is one of the topical analytical problems [2, 3]. It is known that phosphorus is required for the survival of living organisms in water bodies; however, the excess of phosphorous leads to undesirable consequences as the eutrophication of water bodies, etc. Extra amounts of phosphates come to natural waters from anthropogenic sources: with agrochemical, industrial, or urban wastes. As a rule, phosphorus occurs in natural waters as orthophosphates. If the determination procedure does not include any pretreatment, the result is the "reactive" phosphorus, namely, the concentration of orthophosphates plus a small amount of polyphosphates hydrolyzed in the course of determination [4].

The oceanographic data [3] testify that the concentration of dissolved phosphorus (mainly of orthophosphates) in seawater is 1–3 ng/mL. This imposes certain requirements on the procedure of flow-injection analysis. These procedures are usually based on the formation of molydbosphates in highly acidic solutions [5–10]; the most sensitive procedures are based on the formation of intensely colored ion pairs of heteropoly anions with cations of triphenylmethane dyes. For instance, a procedure with Malachite Green was described. It should be noted that the concentrate was separated manually by filtration: a nitrocellulose filter with the precipitate was dissolved in methyl cellosolve, and the absorbance of the concentrate was measured using FIA. Although the title of this study contains the keyword “On-line Preconcentration...,” the methodology and the technique used in [9] can hardly be a good combination of microfiltration with FIA.

The aim of this work was to develop a flow-injection procedure for determining nanogram amounts of phosphorus as ion pairs of molybdovanadophosphates with dye cations using a combination of coprecipitation preconcentration, chemical amplification of the signal, and FIA.

EXPERIMENTAL

Apparatus, reagents, and procedures. A flow-injection analyzer designed in our laboratory complemented by extra units (Fig. 1) was used throughout. The manifold includes three peristaltic pumps, connecting tubes made of polyethylene tubing 0.1 cm in inner diameter, a flow cell of the volume ≈20 μL, and path-length 14 mm placed in a Spekol-21 spectrophotometer (former GDR). The volume flow rate of the carrier solution was varied in the range 1–3 mL/min. The transition signals were plotted using a KSP-4 recording potentiometer with a 1-mV scale. The filtering column was made of Teflon (height 3 cm, inner diameter 0.8 cm) and packed with roll filter made of porous high-pressure polypropylene (Mₕ ≈ 2.8 × 10⁵) with an average pore size of ≈50 μm. Alternating work of pumps was controlled using an electronic timer, which provided the regulation of the times of filtering, washing, and elution within the range 1–3 min.
Solutions of KH₂PO₄, Na₆Mo₇O₂₄ · 4H₂O, and NH₄VO₃ (0.01 mol/L) were prepared from reagents of chemically pure grade; 1.25 M HNO₃ was prepared from concentrated acid of reagent grade; and 1 × 10⁻³ M solutions of Brilliant Green, Rhodamine C, and Methylen Blue were prepared from the reagents of pharmacopoeia grade. In the solutions prepared, dyes were converted to their chlorides by passing the solutions through a column filled with an AV-17 anion exchanger in the Cl-form. Dimethylsulfoxide (pharmacopoeia grade) and its less viscous mixture (1 : 1 v/v) with acetonitrile (chromatography grade) were used throughout.

In the course of analysis, 0.5–5 mL of a test solution containing 0.5–10 ng of phosphorus was transferred to a 20-mL Erlenmeyer flask and mixed with 5 mL of 1.25 M HNO₃, 3 mL of a 0.01 M solution of Na₆Mo₇O₂₄ · 4H₂O, and 0.5 mL of a 0.01 M solution of NH₄VO₃. After 15 min, a 1-mL portion of a 5 × 10⁻⁴ M dye solution was added. After the next 10 min, the timer turned on pump a (Fig. 1) for 2 min. The sol obtained (Fig. 1, 1) was filtered in the fixed-time mode (volume flow rate 2 mL/min). Simultaneously, pump c was turned on to fill the washing loop 4 with isopropanol. Next, pumps a and c were turned off, and pump b was turned on for 2 min. The precipitate on the filter was washed with isopropanol 5, which was displaced from the washing loop 4 with solvent 6 (Fig. 1). After the automated washing and the displacement of isopropanol from the washing loop, the concentrate was dissolved in a mixture of dimethylsulfoxide and acetonitrile, which was pumped with pump b. The concentrate dissolved in a moment, and the colored zone formed was pumped to the flow cell of the spectrophotometer. The absorbance was measured at the wave length corresponding to the absorption maximum of the ion pair, and the transition signal was measured as a peak. The peak height was assumed to be directly proportional to the phosphorus concentration in the sample. Note that the electronic circuit of the spectrophotometer can memorize the optical zero of the system. Usually, this was done at the stage of preliminary justification of the analyzer using a flow cell filled with a mixture of dimethylsulfoxide and acetonitrile.

RESULTS AND DISCUSSION

Usually, molybdophosphates PMo₁₅O₄₀²⁻ serve as a typical xanthene and triphenylmethane dyes, the charge stability in solution; these compounds form relatively rapidly [12, 13]. From the viewpoint of coordination chemistry, the structure of α and β isomers of heteropoly anions can be classified to the T₃₁ symmetry; the primary PO₄ tetrahedron in this structure is surrounded with 12 Mo₇O₆ octahedrons, which, in turn, are organized in four octahedral groups Mo₇O₁₃ with triangular faces; the ionic radius is 12 Å [13, p. 23]. The Mo₇O₆⁻ ion forms a ribbon-like structure of the C₂ᵥ symmetry [13, p. 22]. The hydration energy of large ions is not high; thus, the reaction of both [PMo₁₁VO₄₀]⁴⁺ and, to a considerably lesser degree, Mo₇O₆⁻ ions and its protonated species with the dye cations results in the formation of neutral compounds, which are poorly soluble in water. The similarity between the forming hydrophobic ion pairs is responsible for the almost complete coprecipitation of ion pairs of molybdovanadophosphoric heteropoly acid and the dye cation with the ion pairs of the same dye cation and Mo₇O₆⁻ ions. A slight difference in the polarity of the forming ion pairs (because of a difference in the symmetry) manifests itself as a slight dependence of their solubility on the nature of the organic solvent. Both phenomena were used in the online preconcentration and the removal of the collector.

Reactions of molybdophosphates and molybdovanadophosphates with dye cations. The data on the efficiency of dye cations of various types commonly used for determining phosphorus by the method under study were compared with the results of calculations of their molecular diagrams by the PM3 method with due regard to the solution by 10–12 water molecules. In the discussion, we used the results of calculations for which the coincidence of the predicted absorbance maximum with the experimental value was the best. The results are shown in Fig. 2. It can be seen that in typical xanthene and triphenylmethane dyes, the charge