NEW WAYS OF ATOMIC ABSORPTION DETERMINATION OF SOME ELEMENTS WITH USE OF HETEROPOLYCOMPLEXES

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Abstract.

The reaction of 11-tungstophosphate with cobalt(II) has been used for indirect spectrophotometric and atomic absorption determination of phosphorus. Excess of cobalt is separated from mixed heteropolyanion with use of cation ion-exchange resin KU-2 in Na^+-form. Cobalt can be determined after destruction of a heteropolyanion or as a complex with α-nitroso-β-naphtol, or on measuring of absorption of cobalt atoms using flame air-acetylene (λ=240,7 nm). The perspectives of this method has been shown for increasing of sensitivity and expansion of number of elements, which can be determined.

Key words: ***Determination of phosphorus, heteropolycomplex, indirect atomic absorption determination, ion-exchange separation.***

1. Introduction

The formation of heteropolymolybdic acids has been widely used as the basis for indirect determination of the hetero-atom. These reactions are perspective in view of high sensitivity. Hetero-atoms indirectly determined earlier more often on atoms of molybdenum [1-3]. But this method has not received wide application probably in view of a low limit of detection of phosphorus. Recently indirect methods were offered which use mixed heteropolycomplexes (HPC) [4,5].

Heteropolyanions of the type $H_hZ^{z+}O_6X^{x+}O_4M_{11}O_{30}{}^{(14-x-z-n)-}$ (M=Mo,W), in which one tungsten atom of an anion $X^{x+}M_{12}O_{40}{}^{(8-n)-}$ having the Keggin structure has been replaced by an atom Z (usually of the first transition series), were first described by Baker and his co-workers [6,7]. It was indicated that a wide variety of metal ions might function as octahedrally coordinated Z^{z+}, and a wide variety of nonmetals and transition metals could function as X^{x+}.

Formation of mixed HPC was most efficient for determination of phosphorus by atomic-absorption spectroscopy. Phosphorus can be determined in this case on the analytical lines of metals (Mo, V, Sb, Bi, Fe). The certain excess of reagents is necessary for complete formation of mixed HPA. After that it is very important to separate excess of an ion of metal. A usual method for separation is the use of extraction [3]. But it has many disadvantages. Full extraction is possible only at high concentration of acid. In these conditions the mixed HPC can not be formed. Only molybdic HPC can be extracted. It is known, that HPC of P, As, Si and Ge are well extracted mainly. Only for phosphorus are found oxygen-containing solvents which can fully extract mixed HPC.

At use of mixed HPC is typical that heteropolyanion (HPA) and metal ion are charged opposite. Therefore separation can be easy made at passing of solution through cation ion-exchange resin. Excess of free metal remain on resin while mixed HPA is passing through resin completely.

At application of the considered approach the number of mixedligand HPA can be very much extended, other elements except for phosphorus can be indirectly determined. Considered method allow to select too most convenient metals for atomic-absorption determination.

2. Experimental

The spectropohotometric measurements were made using Carl Ceiss SPECORD M-40 and LOMO SF-26 spectrophotometers. The atomic absorption measurements were made using C-115 (Sumy, Ukraine) atomic absorption spectrophotometer (AAS) with a hollow-cathode cobalt lamp. The absorption of the cobalt at 240,7 nm was measured under the optimum operating conditions of the instrument, using an air-acetylene flame. Solutions of mixed HPA of phosphorus with cobalt and tungsten can be direct aspirated into the flame.

Ion-exchange separation. For separation was used cation ion-exchange resin KU-2 in Na^+-form. For determination of phosphate in the concentration range $1\text{-}8\bullet10^{-5}$ mol/l in a standard 25-ml conical flasks were placed 0,25-2 ml 0,001 M KH_2PO_4, 2,2 ml 0,1 M Na_2WO_4. Adjust the pH to 3,0-4,5 with 0,1 M H_2SO_4, add further 0,8 ml 0,1 M $CoSO_4$ and dilute to the mark with distilled water. Pass this solution through resin (height 15 cm, thickness 2 cm). Time of passing is about 15 minutes. Pass further water so that general volume of a solution became equal 50 ml.

Determination of cobalt. Visible spectrophotometric method. Add 8 ml 2% NH_3, 2 ml 1 M citric acid, 1,0 ml 0,2% α-nitroso-β-naphtol solution to 35 ml of the prepared above solution, dilute to the mark. Measure the absorbance at 470 nm in a 3,0-cm cell using a reagent blank solution in the matched reference cell. Refer absorbance reading to a calibration graph obtained using standard cobalt solutions.

Atomic absorption spectrometric method. Aspirate standard and unknown solutions. Prepare a calibration graph and determine concentration of unknown samples.

3. Results and discussion

General procedure of indirect determination of phosphorus on cobalt consist in the following. At first should be prepared 'unsaturated' heteropolyanion with the 'Keggin' structure[7]:

$$H_2PO_4^- + 11WO_4^{2-} + 16H^+ = PW_{11}O_{39}^{7-} + 9H_2O$$

The undecatungstophosphate quickly reacts at room temperature with certain hydrated cations, for example, Co(II), to form very stable in the range of pH 2-6 derivatives [8].

$$PW_{11}O_{39}^{7-} + Co^{2+} = PCoW_{11}O_{39}^{5-}$$

HPA can be completely prepared only in this way.

Many complexes of phosphorus are known, but at pH<1 and C_W to C_P ratio more as 12:1 prevail $PW_{12}O_{40}^{3-}$, and at pH 2-7 $PW_{11}O_{39}^{7-}$. Cobalt can be placed in the center of the anion ($(Co(II)W_{12}O_{40}^{6-}$ or $CoO_5CoO_4W_{11}O_{30}^{7-}$ HPAs [9]) or on the periphery (mixed HPA). It is shown that Co in the described procedure forms only mixed HPA. Such complexes as a $CoW_{12}O_{40}^{5-}$ can not be formed, as their formation needs long heating. When studying of sorption of different HPAs ($GaMo_6O_{24}H_6^{3-}$, $PMo(W)_{12}O_{40}^{3-}$, $CrMo_6O_{24}H_6^{3-}$, $NiMo_6O_{24}H_6^{4-}$, $CoW_{12}O_{40}^{5-}$, $PCoW_{11}O_{39}^{5-}$) on the cation ion-exchange resin KU-2 in Na^+-form was shown that all these anions passes fully.

It is found that is required 10-15-fold excess of cobalt or wolframat ions to ensure the complete formation of mixed HPA (Fig. 1). The dependence in Fig. 1 shows that as the cobalt concentration is increased (fig 1a), absorbance is increased constantly only for an initial solution. At the same time after passing of a solution through resin absorbance is constant in the case of the mixed HPA of cobalt (fig. 1b) and too for other complex forming between

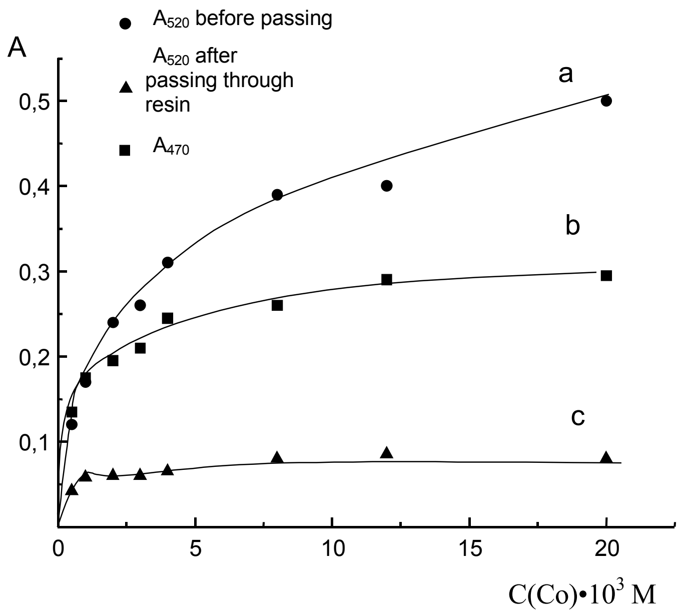

Fig. 1. Influence of excess of cobalt ions on the formation of mixed HPA. C(P)=5•10^{-4} M

cobalt and α-nitroso-β-naphtol (fig 3c). The maximal optical density is in good accordance with theory (ε=72 for $PCoW_{11}O_{39}^{5-}$ [8]).

The sensitivity of determination of phosphorus depends only on a limit of detection of cobalt and thus from the chosen method of determination of this element. It is found that linear dependence of absorbance of cobalt from phosphate concentration is kept in two studied cases in the same range of concentrations – 1-8•10^{-5} mol/l. The reproducibility of a atomic-absorption method is higher than spectrophotometric.

It is necessary to notice that exist possibility further to increase sensitivity of the method if to use other metals such as zinc which have better detection limit [10]. Besides there is a possible indirect atomic-absorption determination with use of derivatives of 'unsaturated' HPAs of such elements as B, Ga, As and many others.

4. Conclusions.

On an example of indirect atomic-absorption and spectrophotometric determination of phosphorus on cobalt as $PCoW_{11}O_{39}^{7-}$ the possibility of expansion of sphere of application of heteropolycomplexes under condition of ion-exchange separation of excess of metal ions is shown.

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