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APPLICATION OF TITAN CHLORIDE AT DETERMINATION ARSENIC AS MOLYBDOARSENATE

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The conditions for recovery arsenate molybdenum by chloride of titanium (III) were determined in the sulfuric environment. Obtained The diagram of stability arsenate molybdenum at depending from correlation of the concentrations «acid – molybdate». The photometric method for determination of arsenic with use chloride of titanium as reducing agent is proposed.

Key words: arsenate molybdenum; recovery; chloride of titanium; stability diagram, determination of arsenic.

Heteropolycomplexs (HPC) are the very difficult in a theoretical relation representatives of co-ordinating connections, their study has both scientific and practical interest. HPC apply for determination of such elements, as silicon, germanium, phosphorus, and arsenic. Arsenic, for example, elemental a harmful admixture, is in materials metallurgical, semiconductor and row of other industries of industry, limiting his maintenance to 10^{-5}-10^{-8} %, that requires application of especially sensible methods of determination of small concentrations of arsenic. It is known that for an analysis use the sensible reaction of renewal of molybdo-complexs of arsenic and phosphorus different reducing materials. Reactions go in identical conditions, complexes must be divided therefore. Such task decides due to application untraditional for HPC of repairer - titan chloride (Ш). It application is based on electoral ability of molybdoaresenate (MA) to be restored by the titan chloride on to the cold, while molybdophosphate (MP), interfering in these conditions with determination, is not restored quite. Titan chloride as a repairer for determination of arsenic did not apply before.

Determination of arsenic, as shown in works [1-4], execute witn use a highly sensitive reaction renewals of molybdoaresenate by ascorbic acid. Renewal goes at heating of solutions in a sulfate environment and accompanied by formation of dark blue product, so-called «heretopolyblue» (GPB). Colouring of complex develops in time, arriving at maximal lightabsorption in the visible area of spectrum at lengths of waves ~ 830 nm. Characteristically, that along with MA, in the same conditions, renewal passes and present person in solution of molybdophosphate, which renders mixing influence on determination of arsenic, and complexes must be divided.

By the authors of work [5] renewal of molybdophosphate is investigated by an untraditional reducing material – titan chloride (III). The conditions of renewal complex are in-process described and it is shown that a reaction passes at heating of solutions with formation of GPB, absorptive light in the visible area of spectrum. In addition, with the purpose of finding out of stability of MP to operating on it reducing material - chloride of titan, research of cross-coupling of concentrations of sulphuric acid and molybdate on renewal is executed. On the basis of the experienced data the area of correlation of concentrations «acid-molybdateis» is got in the limits of which renewal of surplus molybdate is not within.

It is known that for the receipt of recovered HPB of molybdenum a traditional reducing material is ascorbic acid. Being a «soft» reducing material (standard oxidizing potential of the system $E^{o}_{окс/ред}$ = + 0.18 V), it restores the ligand sphere of heteropolyanion without it destruction. However, oxidization of ascorbic acid passes with participation cations of hydrogen on a scheme:

$$C_6H_8O_6 - 2e \Rightarrow C_6H_6O_6 + 2H^+, \quad E^0{}_{\text{окс/ред}} = +\,0{,}18\ \text{V}\,, \tag{1}$$

and it real oxidizing potential depends on a pH environment. So, in the interval of pH from 0,7 to 1,0, which corresponds to the conditions of stability of molybdoarsenate, potential of ascorbic acid changes from – 0.120 V to + 0,326 V. Such dependence of oxidizing potential of $E_{окс/ред}$ from pH does undesirable application of ascorbic acid at a study, for example, of cross-coupling of concentrations of sulphuric acid and molybdate on renewal of MA, as these concentrations change in wide limits.

Such defect the chloride of titan (III) is deprived. The reaction of oxidization of titan goes on a schemet:

$$Ti^{4+} - 1e \Rightarrow Ti^{3+}\ , \quad E^0{}_{\text{окс/ред}} = +\,0{,}18\ \text{V}. \tag{2}$$

Real potential of pair Ti^{4+}/Ti^{3+}, as be obvious from a reaction (2) does not depend on a pH environment, and in the range of pH, characteristic for stability of molybdoarsenate, oxidizing potential takes on a value, numeral equal standard E^0 = + 0.10 V. In addition, found out by us unique ability of titan chloride preferentially to restore molybdoarsenate, at what, a reaction goes at a room temperature. The presence of MP does not interfere with determination, because restored only at heating of solutions. Therefore a titan chloride (III) is an interesting reagent for determination of stability of MA at it renewal.

It is set preliminary experiments, that the concentration of chloride titan (III) solution during a few hours changes insignificantly, therefore solution of repairer was applied without additional cautions. The study of influence for concentration of reducing material showed that at the constant concentrations of other components the absorbancy of the recovered solutions remains unchanging in the interval of concentrations of titan chloride from 3.2 to $12.8 \cdot 10^{-3}$ M. Unlike MP, renewal of MA goes at a room temperature with formation of characteristic product of reaction - HPB. Colouring of complex develops in time, arriving at a maximal value in 20 minutes after mixing of components. The absorbancy of solutions was fixed by means of photocolorimeter FEK-56 and spectrophotometer SP-4A.

It is set that the recovered complex has the expressed maximum at the wavelength ~840 nm, that specifies on individuality of the got compound and, simultaneously, high sensitiveness of reaction, molar coefficient of redemption of which $\varepsilon_{\text{макс}}$ = 2800. However, as appeared, the concentrations of acid and molybdate influence on renewal not separately, and jointly. For proof of this phenomenon influence of concentration of sulphuric acid is studied on a few different concentrations of molybdate (at the permanent concentrations of arsenate and chloride of titan a $8{\cdot}10^{-5}$ M and $5{\cdot}10^{-3}$ M is accordingly).

It is shown the experienced and calculation way, that in the area of most stability MA linear dependence of absorbancy of solutions of An on the concentration of arsenate C_{As}, and the calculated coefficient of correlation R is near to one ($R = 0{,}9998$) is saved. So for an analysis the methods of spectrophotometry determination of arsenic are worked out in a metallic nickel (standard sample 172б). The contents of arsenic in a standard sample was determined on equation of gauge scheme, expected with the use of least-squares method, which looks like:

$$C_{As} = 81{,}43\,A. \qquad (3)$$

A confidence interval for determination of concentration of arsenic corresponds to exactness of determination of arsenic 1.74 % and it testifies at possibilities of application of titan chloride (III), as repairer, for determination of arsenic as recovered molybdoarsenate.

Conclusions. The optimal conditions of renewal of molybdoarsenate by titan chloride (III) a are certain at a room temperature. Conformity to law of joint influence of concentrations for sulphuric acid and molybdate is set on renewal. The diagram of stability of molybdoarsenate is got, titan (III) recovered by a chloride and the area of concentrations, suitable for an analysis, is found. It is worked out and approved on a standard sample methods of determination of arsenic in a nickel with exactness 1.74 %.

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