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Short communication

Spectrophotometric determination of tungsten based on molybdotungsten isopolyanions in presence of non-ionic surfactant

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Abstract

Simple and sensitive method was developed for the spectrophotometric determination of tungsten. The method was based on the formation of the colour associate of molybdotungsten isopolyanion (IPA) with organic dye malachite green and solubilization in the solution of non-ionic surface-active substance (SAS). Recommended procedure permits tungsten determination in the linear range 10^{-6} to 10^{-5} mol l^{-1} with $\varepsilon = 7.1 \times 10^4$ mol^{-1} l cm^{-1}. More than 100-fold excess of molybdenum do not interfere. The proposed method was applied to the determination of tungsten in cobalt-molybdenum catalyst and in stainless steel with satisfactory results.

Keywords: Tungsten; Molybdotungsten isopolyanion; Surface-active substance; Spectrophotometry

1. Introduction

The spectrophotometric determination of tungsten is often accompanied with the interference of molybdenum because the chemical properties of these elements are very similar [1,2]. A great number of organic reagents and dyes are applied to the extraction-spectrophotometric determination of tungsten, but these methods are not selective and sensitive enough [3–12]. The formation of molybdotungstophosphate heteropolyanions (HPA) was used for the high selective spectrophotometric determination of tungsten or molybdenum in presence of each other [13,14]. These methods are again not sufficiently sensitive. The formation of associate of HPAs with cationic organic dyes is often applied to increase the sensitivity of the determination of elements occupying a central place in HPA [15–17], but very seldom to the determination of ligand metals. Spectrophotometric determination of molybdenum based on charge transfer complex of the molybdotungstophosphate with 3,3,5,5-tetramethylbenzidine in PVA medium was recently reported [18].

In this paper we describe the formation of coloured associate between molybdotungsten IPAs and triphenylmethane dye Malachite Green in presence of non-ionic polyoxyethylene SAS (OP-10, OP-7, sintanol ALM-10) and method of tungsten determination based on this reaction. In comparison with other methods described procedure does not include solvent extraction.

2. Experimental

2.1. Apparatus

Spectrophotometric measurements were carried out by means of a Specord M-40 and SF-46 UV-Vis spectrophotometers. IR-spectra were recorded on a Specord M-80 spectrophotometer as KBr pellets. pH-meter EV-74 was applied to pH-measurements of the solutions.

2.2. Reagents

All chemicals were of analytical grade. A Mo(VI) and W(VI) stock solutions (0.1 mol l^{-1}) were prepared by dissolving of the recrystallized preparates $Na_2MoO_4{\cdot}2H_2O$ and $Na_2WO_4{\cdot}2H_2O$. The purified with method [19,20]

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dye malachite green (MG) was used for preparation 10^{-3} mol l^{-1} solution. 1% solution of non-ionic SAS sintanol ALM-10 was used. TiO_2 (rutile) was provided by the Predmaterials Int. Inc. (particle size <0.6 μm, surface area >6.0 m^2 g^{-1}).

3. Results and discussion

3.1. Absorption spectra and optimization of conditions

In the solid state and in neutral solutions malachite green exists in cationic form R^+. Maximal yield of this form is observed in pH range 3–4. In more acidic solutions the RH^{2+} form is present and at pH <2 R^+ transforms completely to the only slightly coloured form (yellow-brown). Equilibrium is reached very slowly and can be accelerated by means of heating at 35 °C for 30 min.

The presence of non-ionic SAS only slightly changes the MG spectrum (Fig. 1A and B). Small broadening and increasing of the band intensity of basic absorption band at 624 nm are observed. Interaction of MG with molybdotungsten isopolycomplex (MTC) in the presence of non-ionic SAS leads to further changes in spectrum (Fig. 1C). It is strongly broadened, and overlapping band at about 590 nm as well as a shoulder near 700 nm are appeared. Presence of MTC prevents decreasing of the R^+-form intensity due to the formation of ion-association complex. These effects are apparently micellar in nature. The spectrum of the solution of the isopolymolybdate-MG-SAS system has similar character but its intensity is much lower and becomes negligible at pH <2.

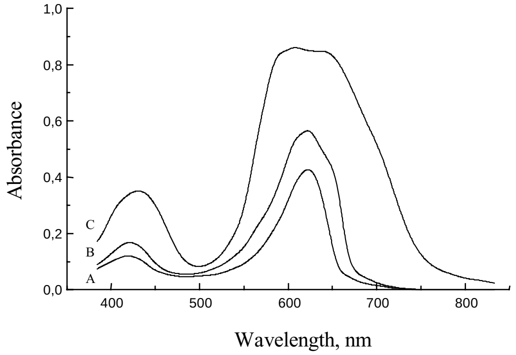

Fig. 1. Absorption spectra of MG (A), MG-SAS system (B), associate MG-MTC-SAS (C). Conditions: (A) 1.2×10^{-5} mol l^{-1} MG, pH 3.0; (B) as A but with 0.16% sintanol; (C) 4.8×10^{-5} mol l^{-1} Na_2MoO_4, 1.3×10^{-5} mol l^{-1} Na_2WO_4, 6.4×10^{-5} mol l^{-1} MG, 0.04% sintanol, pH 2.0.

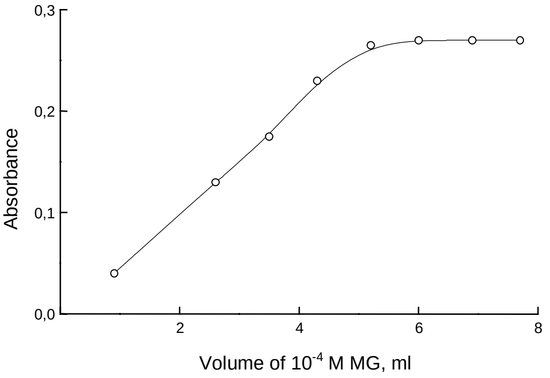

Fig. 2. Effect of MG concentration on the absorbance of MG-MTC associate solution in the presence of sintanol. Conditions: 3.4×10^{-6} mol l^{-1} MTC, 1.0×10^{-4} mol l^{-1} MG, pH 2.0, $\lambda = 620$ nm.

In a study of the effect produced by the variation of the MG concentration on the absorbance of the MG-MTC associate was found that maximum absorbance was obtained with a six-fold molar excess of MG to MTC (Fig. 2). Charge of the isopolyanion may be responsible for such ratio. It is known that isopoyanions with general formula $Mo_xW_{7-x}O_{24}{}^{6-}$ are formed at the $z < 1.17$ ($z = C_H/(C_{Mo} + C_W)$) in acidified solutions containing $MoO_4{}^{2-}$, $WO_4{}^{2-}$ or both anions [22–25]. Formation of the associates between MG and derivatives of heptamolybdotungstate IPAs can be proposed. By using of the aged solutions of MTC intensity of the colour decreases due to the transformation to the derivatives of paratungstate-B $Mo_xW_{12\text{-}x}O_{42}H_2{}^{10-}$ that are not be able to form stable associates with MG. Therefore, we used fresh prepared solutions of MTC. At $z > 1.17$ can be formed other mixed IPAs, e.g. derivatives of a metatungstate IPA with Keggin structure $H_2Mo_xW_{11-x}O_{40}{}^{6-}$ [24,26,27].

This assumption was further confirmed by investigation of the IR spectra of yellow TMA and dark green MG salts that had been precipitated from the solutions having z 1.14 (Fig. 3A) or 1.3 (Fig. 3B). IR spectra of these compounds are characterized by bands that can be attributed to the vibrations of the metal-oxygen bonds of IPA [28].

In spectra MG salts precipitated at z 1.17 dominate bands at 964, 904 and 804 cm^{-1} that in their position and shape are very close to the bands of pseudometatungstates and dodecatungstate-Y β-$H_2W_{12}O_{40}{}^{6-}$ (Fig. 3A) [24].

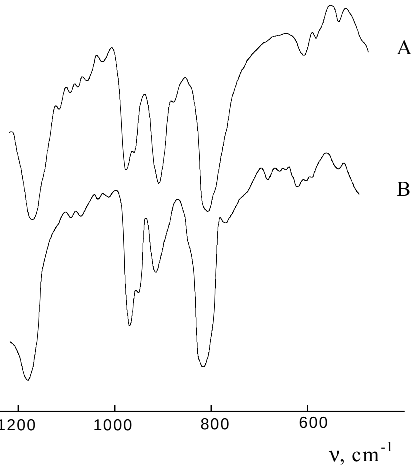

Fig. 3. IR spectra of MG salts of MTC precipitated from solutions with different z. (A) $z = 1.14$, (B) $z = 1.33$.

Second spectrum has bands typical for decatungstate anion $W_{10}O_{32}{}^{4-}$ (Fig. 3B). Salts of heptamolybdotungstate IPA are much more soluble. Therefore, its bands were not expected in IR spectrum. Three most intensive bands of the organic cation are also present (1592, 1370 and 1176 cm^{-1}).

Different non-ionic SAS (OP-10, OP-7, sintanol) can stabilize ion-association complex. The most reproducible results were obtained with sintanol ALM-10. Maximum and constant absorbance was obtained beginning from the concentration of SAS that corresponds to the volume of 1% SAS 0.5–1.0 ml. No further changes are observed once there are sufficient micelles present to solubilize all of the associate (above $\sim 4 \times 10^{-4}$ $mol\,l^{-1}$). Critical micelle concentration for sintanol corresponds well with values given in the literature for the other analogous SAS (Triton X-100: 1×10^{-4} to 3×10^{-4} $mol\,l^{-1}$ [21]).

The excess of free dye is discoloured by addition of 0.5 $mol\,l^{-1}$ H_2SO_4 to pH 1.5–2.0 before diluting and heating of the solution at 35 °C in water bath (10–15 min). At pH <2 the absorbance of the solution of the system Mo-MG-SAS does not exceeds 0.05 in the wide concentration range of molybdate until 0.3 $mol\,l^{-1}$. The addition of tungstate to this solution results in an increasing of the absorbance at 620 nm as a result of formation of ion-association complex MG-MTC.

3.2. Calibration graph

Procedure: In 25 ml flasks add 1.2 ml of 10^{-3} $mol\,l^{-1}$ Na_2MoO_4, 0.25–2.5 ml of 10^{-4} $mol\,l^{-1}$ Na_2WO_4, 1 ml of 1% sintanol, 1.6 ml of 10^{-3} $mol\,l^{-1}$ MG, bring with 0.5 $mol\,l^{-1}$ H_2SO_4 pH to 1.5, dilute to the mark, keep for 10 min at 35 °C in water bath. Measure absorbance after cooling at 620 nm in 1 cm cells against a reagent blank. The calibration graph was found to obey Beer's law in the range 1.0×10^{-6} to 1.0×10^{-5} $mol\,l^{-1}$ W(VI). The fitted equation was $\Delta A = (7.06 \pm 0.43) \times 10^4 \cdot C_W$, where C_W is the concentration of W(VI), $mol\,l^{-1}$. The correlation coefficient was equal to 0.997, and molar absorption coefficient was equal to 7.06×10^4 $mol^{-1}\,l\,cm^{-1}$.

3.3. Effect of foreign ions

The effect of foreign ions on the determination of 10^{-6} $mol\,l^{-1}$ W(VI) was studied. The tolerance limits (within 5% error) of those ions are summarized in Table 1.

Table 1
Tolerance limits (within 5% error) of foreign ions for the determination of 10^{-6} $mol\,l^{-1}$ W(VI)

Tolerance limit [ion]:[W(VI)]	Ion
≥20000	Na^+, K^+, $NH_4{}^+$, $NO_3{}^-$, Cl^-, $SO_4{}^{2-}$, $ClO_4{}^-$, $CO_3{}^{2-}$, EDTA, Ca^{2+}, Mg^{2+}
≥100	Ni^{2+}, Co^{2+}, Mn^{2+}, Zn^{2+}, Cu^{2+}, $MoO_4{}^{2-}$
50	$SiO_4{}^{2-}$
10	Fe^{3+}, Al^{3+}, Ti(IV), $VO_3{}^-$
1	$PO_4{}^{3-}$, $AsO_4{}^{3-}$, Cr^{3+}

In summary, one- and twovalent ions do not interfere to the determination of tungsten. Three and more charged metal ions must be separated before determination. This correlates with known ability of these ions to form stable heteropoly complexes with tungsten(VI) in acidified aqueous solutions [27]. From this viewpoint effect of the $PO_4{}^{3-}$ and $AsO_4{}^{3-}$ ions can be also explained. The interference from the metals ions can be excluded using the adsorption of W(VI) on metal oxides (TiO_2, ZrO_2) [29]. Though Fe(III) can be partly adsorbed its desorption with 9 M NaOH does not take place.

3.4. Application

In order to validate this method, it was applied to the determination of tungsten in molybdo-cobalt catalyst and in stainless steel.

I. *Molybdo-cobalt catalyst:* A pretreatment of the sample was carried out in the following way. A 0.100 g sample was treated with 20 ml of 25% solution of NH_3. This solution was separated and placed in 100 ml flask, remaining precipitate was digested with 20 ml of HNO_3 (1:1) by heating in boiling water bath. Both solutions were combined and diluted to the mark. An aliquot (2.5 ml) of this solution was pipetted and tungsten was determined in it according to the procedure used in the preparation of the calibration graph. The results of the determination and recovery test are shown in Table 2.

II. *Stainless steel:* Weigh a 0.1 g sample of stainless steel. Place it in 125 ml conical beaker, add 5 ml concentrated HNO_3 plus 15 ml concentrated HCl, allow the reaction to proceed, warming on the hot-plate as required, dilute the solution to 25 ml in a graduated flask. Place an aliquot of this solution containing from 30 μg up to 150 μg of

Table 2
Determination of tungsten in Mo-Co catalyst and the results of recovery test

Proposed method					Thiocyanate method [1] W content in sample ($n = 5$, $P = 0.95$) (%)
Added W (μg)	Found W (μg)	Recovery	R.S.D. ($n = 5$) (%)	W content in sample (%)	
0	45.7	–	2.5	1.80	1.83 ± 0.04
18.4	65.2	106			
36.8	81.3	96.7			

Content of some other important elements: Mo = 52%, Co = 6.4%.

W in polyethylene beaker, add 1.0 ml of 1 M NaF, adjust pH to 3.0 with 0.1 M sodium acetate, add 100 mg of TiO_2 (rutile), stir for 10 min for selective adsorption of W(VI), centrifuge. The residue in centrifugal tube wash twice with deionized water, add 3 ml of 9 M NaOH solution (as desorbing agent), stir for 30 min to elute the adsorbed W(VI), then the eluent adjust to pH 0 with 2.4 ml 5 M H_2SO_4. Continue with the determination as in general procedure (part 3.2). The contents of the components in certified reference material (CRM) no. 249a were equal to (in %): C: 0.136, Mn: 0.41, Si: 0.32, P: 0.013, Cr: 13.73, Ni: 3.12, W: 1.87, V: 0.283, Ti: 0.006, Mo: 0.05, Cu: 0.161, B: 0.01. The content for total tungsten obtained in CRM $1.85 \pm 0.07\%$ ($n = 5$, $S_r = 0.04$) agreed well with the certified value.

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