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Extraction concentrating of tungsten (VI) in complex form with 2-Hydroxy-5-Tret-Butylphenol-4′-Methyl-Azobenzene and Its determination by atomic-absorption spectrometry

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Abstract

Complexation of tungsten (VI) with azo-compound synthesized with para-tret-butylphenol (2-hydroxy-5-tret-butylphenol-4′-methyl-azobenzene) was studied by using spectrophotometric method. Spectrophotometric characteristics of the complex were calculated, composition of the complex was determined by different techniques. Stability constant of the complex ($lgK_{уст}$=4.2·10^{10}), as well as equilibrium constant of the complexation reaction (3.2·10^4) were calculated by using Komar method. Molar absorption coefficient equals to (2.1±0.1)·10^4. Calibration curve is linear at concentrations of tungsten 1.0–10 mkg/ml.

Keywords: Tungsten, atomic-absorption method, extraction, complexation

Introduction

Atomic-absorption determination of tungsten has not been widely used yet. Direct atomic-absorption method is often used for determination of 1.0–10% tungsten. Direct atomic-absorption determination of lower contents of tungsten in complex objects is not always possible due to the effect of accompanying elments on analytical signal. One of the promising methods to enhance selectivity and sensitivity of atomic-absorption method is its use in combination with extraction [1, 3].

A number of reagents were proposed for extraction concetrating of tungsten: bromine pyrogallol red, cetylpyridinium chloride, rhodamine B dithiol [4, 6].

In the present work extraction conditions of tungsten 2-hydroxy-5-tret-butylphenol-4′-methylazobenzene (HR) were studied and extraction-atomic-absorption method for determining tungsten in different objects was developed.

Experimental Part

Reagents and instruments: Initial solution of tungsten (VI) was prepared by dissolution of Na_2WO_4 to 0.5M NaOH. Solutions with lower content of tungsten were prepared by diluting initial solution. Concentrated HCl, 1n of CH_3COOH and NH_4OH were used for creating necessary acidity. 1M KCl was used to create ionic power of solution.

Chloroform, dichloroethane, carbo tetrachloride, benzene, toluene, hexane, n-butanol and butyl acetate were used as organic solvents.

Reagent (2-hydroxy-5-tret-butylphenol-4′-methylazobenzene) was synthesized by the method [7].
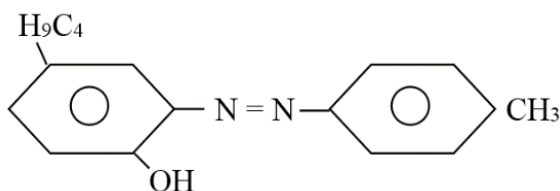
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Fig 1: Reagent is a monoacid which has a general structural formula

Additional treatment of the reagent was performed by recrystallization from ethyl alcohol. Composition and structure of the reagent were established with elemental analysis, IR-, UV-spectroscopy. IR-spectra 3450 cm^{-1} (O–H arom.); 2960 cm^{-1} (C–H from CH$_3$), 3030 cm^{-1} (C–H arom.); 1592, 1496 cm^{-1} (C=C arom), 1408 cm^{-1} (N=N). 1168 cm-1 (C–C), 1264 cm^{-1} (C–N), 1136 cm^{-1}, 1104 cm^{-1} (arom. O–C). 4.2·10^{-4} M of reagent solution was prepared by dissolution of weighed samples in ethanol.

Instruments: Optical density was measured with spectrophotometer SF-46 and photoelectron calorimeter KFK-2.pH value was controlled by universal ionomer EV-74.

Atomic absorption of tungsten was measured on atomic-absorption spectrophotometer AAS-1N (Germany). As light sources standard hollow cathode lamps were used. Optimum measurement conditions are listed in Table 1.

Table 1: Atomic-absorption determination of tungsten

Wavelength, nm	Slot width, nm	Lamp current, mA	Consumption of acetylene, l/hr	Consumption of nitrogen oxide, l/hr
255.1	0.5	25	200	180

Technique: A certain amount of standard solution of tungsten, necessary amount of HCl, 0.5 ml of HR were poured into a separatory funnel, shaken and aqueous phase was diluted with distilled water to 20 ml. After 1-2 minutes 10 ml of n-butanol was added and extracted 1 minute. After complete separation of phases extract was sprayed into the acetylene-nitrogen oxide flame and atomic absorption of tungsten was measured under optimum conditions.

Results and Discussion

Spectrophotometric study of the reaction: The effect of acidity on complexation of tungsten is given in Figure 1. In acidic medium tungsten with HR forms colored complex. Influence of HCl and H$_2$ SO$_4$ on complexation of tungsten with HR is not the same. For full extraction of the complex the use of 1.5–2.5 ml 0.8 M of HCl or 0.5–0.8 ml 0.4 M of H$_2$SO$_4$ is necessary. pH of these solutions is found to be 1.5–2.0. At lower acidity optical density decreases, that is probably related to the formation of wolframic acid.
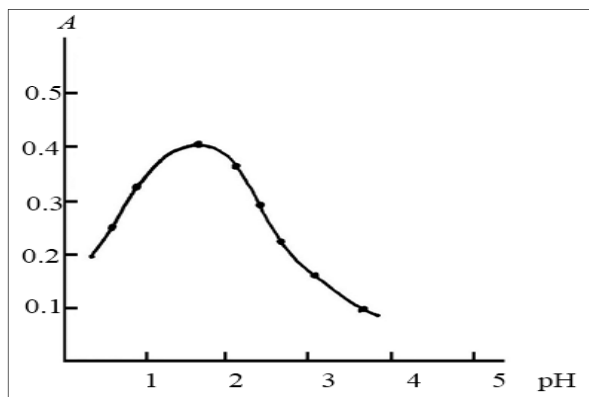

Fig.1. Effect of pH on complexation of tungsten (VI). C_W =3.2·10^{-5} M; C_{HR}=4.210^{-4}M, λ = 420 nm.

Extraction of the complex: Chloroform, dichloroethane, carbo tetrachloride, benzene, toluene, xylene, hexane and n-butanol were used to extract the complex from organic solutions.

Organic solvent must be combustible in direct atomization of extracts to burner flame.

The highest recovery of tungsten (96%) was obtained during extraction with chloroform and n-butanol. Studies show that atomic absorption of tungsten decreases with the use of halogen-containing solvents. n-butanol is found to be most suitable for atomic-absorption analysis. It does not change combustion mode of flame and does not form a background in analytical line of tungsten. n-butanol supports stable burning

flame which allows us to determine tungsten in direct spraying the extract into flame. Extractability of the complex was evaluated by diffusion coefficient and degree of extraction. Equilibrium densities of tungsten in aqueous phase were determined by using atomic-absorption method. Amount of tungsten in organic phase was found by the difference. Degree of single extraction of tungsten complex with n-butanol equals to 96–98%.

The effect of aqueous phase volume and hold time on formation and completeness of extraction of tungsten complex was studied. The increase of the aqueous phase volume up to 20 ml does not significantly influence on optical density of butanol extract. When holding colored complex of tungsten with HR for 2 minutes maximum optical density of solvent is achieved. The complex was stable for two days.

Effect of reagent concentration

A series of experiments with constant concentrations of tungsten and variable concentrations of HR reagent were carried out to study the influence of HR on formation of the complex. When concentration of HR increases up to 0.8 ml (4.2·10^{-4}M) extraction of tungsten increases and further increase of its concentration does not influence on extraction of tungsten. 4.2·10^{-4}M HR is needed for the formation of the complex W-R.

Absorption spectrum of complex

Under optimum conditions light absorbance spectrum was taken, maximum was observed in the range of 420–440 nm, reagent maximally absorbs in the range of 360–380 nm. Complexation is accompanied by bathochromic shift (Fig.2).
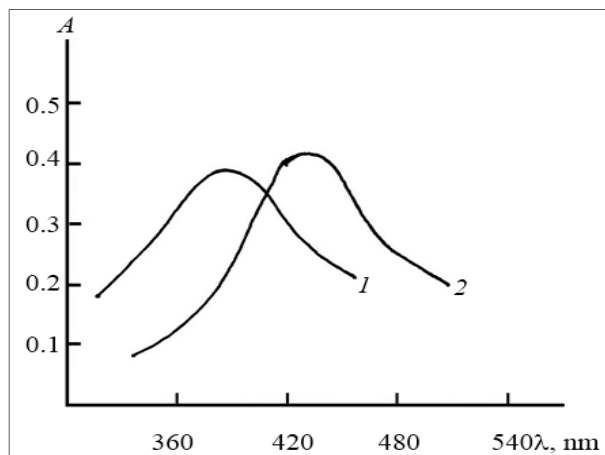

Fig 2. Absorption spectrum of reagent extracts (1) and complex W; C_W=3,2·10^{-5}M, C_{HR}=4,2·10^{-4} M; $V_{org.}$=5 ml; l=0,5 cm; KFK-2.

Composition and physical-chemical properties of the complex.

Ratio of components in the complex equals to W(VI):HR=1:2 under optimum conditions found by method of equilibrium shift and straight-line method of Asmus [8].

Stability constant in ionic associate in chloroform is found to be $4{,}3 \cdot 10^{12}$ and equilibrium constant of complexation reaction ($3{,}2 \cdot 10^4$ at pH 2.0) was calculated by spectrophotometric data for chloroform solvent with using dependence of light absorbance of solutions on pH. Molar absorption coefficient of tungsten calculated by Tolmachev method [8] equals to $(2.1\pm0{,}1)10^4$. Calibration curve is linear at concentrations of tungsten 1–10 mkg/ml. By Nazarenko method [9] it was established that complex forming form is $WO(OH)^{2+}$.

Influence of foreign ions.

Selectivity of extraction-atomic –absorption determination of tungsten with HR was studied. It was established that large amounts of alkali, alkali-earth elements and rare earth elements do not interfere with the determination of tungsten. Under optimum conditions up to 100 mkg of Co, Ni, No, Nb, Ta do not interfere with the determination of tungsten. Since tungsten forms complexes in more acidic medium than vanadium, determination of tungsten in the presence of less amounts of vanadium is possible. Effect of V and Mo was eliminated by the change of pH and oxalate-ions correspondingly. Interfering effect of the basis (iron) is eliminated by adding ascorbic acid. According to the studies of extraction-atomic-absorption method for determining microgram amounts of tungsten in steel was developed.

Determination of tungsten in steel: Weighed sample of alloy (0.2 g) is dissolved at heating in 150 ml of H_2SO_4 (1:4). 3−5 ml of mixture (1:3) HNO_3 and HCl is added and heated till release of nitrogen oxide. Nonsoluble residue is filtered and filtrate is moved to 100 ml of measuring flask. After cooling the solution is diluted with water up to the mark. Aliquot part of solution is moved to separatory funnel, 2,0 ml of 0.8 M HCl, and 0.5 ml of HR are added, is diluted with water up to 25 ml and 10 ml of n-butanol is extracted 1 minute. Organic phase is separated and sprayed into acetylene-nitrogen oxide flame, atomic absorption of tungsten is measured under optimum conditions.

Table 2. Results of extraction-atomic-absorption determination of tungsten (VI) in steel (n=5; P=0.95)

Standard sample	Content, W%		Sr
	By specification	found	
EI-69	0.40	0.39	0.012
EI-415	0.55	0.51	0.014

Amount of tungsten was found by calibration curve.
Validity of results was confirmed by determination data of tungsten and standard sample of steel.

References
1. Price V. Analytical Atomic-Absorption Spectroscopy. M. Mir. 1976, 341.
2. Kharlamov IP, Eremina GV. Atomic-Absorption analysis in ferrous metallurgy. M. Metallurgy. 1982, 165.
3. Zolotov YA, Kuzmin NM. Concentrating of microelements M. Chemistry. 1982, 371.
4. Busev AI, Ivanov VM, Sokolov TA. Analytical chemistry of tungsten M. Nauka, 1976, 238.
5. Savvin SB, Chernova RK, Beloloptseva TN, Jour Analt. chem. 1980; 35(6):1128.
6. Umland F, Jansen A, Tearing D, Wyunsch G. Complex compound in analytical chemistry. M., Mir. 1975, 531.
7. Gasimov VT, Mejidov AA. Coordination chemistry. 1990; 16(10):1355-1359.
8. Bulatov MI, Kalinkin IP. Practical guidance on photocolorimetric and spectrophotometric methods of analysis L., Chemistry. 190.
9. Nazarenko VM, Lebedeva NV, Biryuk EA, Shustova MV. Journal inorganic chemistry. 1962; 7(12):2731.