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Research Article

Extraction-atomic-absorption determination of titanium (IV) with azoderivative para-tret-butylphenol

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Abstract

The complexation of titanium (IV) with 2-hydroxy-5-tret-butylphenol-4'-methoxyazobenzene was studied using atomic-absorption and spectrophotometric methods. Optimum conditions were found for the formation of a complex and its extraction with chloroform and n-butanol which provide necessary fixation efficiency of titanium ions. Stability constants of the complex β_K *= 9,02±0,01, as well as equilibrium constant of complexation reaction (3,52·10^4) were calculated using Komar method. Molar absorption coefficient equals to ((3,2-4,1) 10^4. Calibration curve is linear at concentrations of 1-10 mcg/ml. Extraction-atomic adsorption determination of titanium was developed.*

Keywords*: Titanium, complexation, extraction, atomic-absorption technique.*

Introduction

Analytical chemistry of titanium has reached considerable successes. However, the determination of its low concentrations is a promising task. Physical-chemical methods of analysis, particularly, atomic-absorption method is prospective for its solution. Direct atomic-absorption determination of low contents of titanium in complex objects is not always possible due to the influence of accompanying elements, as well as insufficient sensitivity. A number of works have been done on the determination of titanium in different objects of atomic-absorption concentrating (N.Perruza, *et all*, 1998), (R.A.Aliyeva, *et all*, 2007), (Y.A.Zolotov, *et all*, 1971), (I.P.Kharlamov, *et all*, 1982), (V. Price, *et all*, 1976), (S.A.Denisova, *et all*, 1998). One of the prospective techniques of increasing selectivity and sensitivity of atomic-absorption method is combination with extraction (A.M. Pashajanov, 2006), (A.M.Pashajanov, 2015), (A.M.Pashajanov, 2005), (A.M.Pashajanov, 2006), (A.M.Pashajanov, 2005).

In the present work the complexation of titanium with HR, as well as conditions of extraction concentrating and atomic-absorption determination in alloys and steels were studied.

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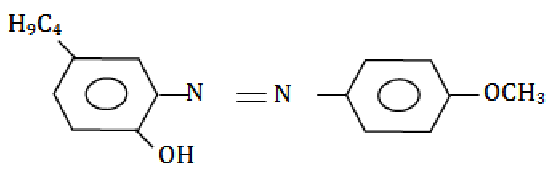
Experimental part

Reagents and instruments

Standard solution of titanium with concentration of 1,0 ·10^{-4}M was prepared from metallic titanium using the technique (P.P.Korostelev, 1964). HCl, 1 and CH_3COOH and NH_4OH were used for necessary acidity of solutions. Ionic strength of solutions (μ=0,1) were kept constant with KNO_3. Chloroform, dichloroethane, carbon tetrachloride, benzene, toluene, hexane, n-butanol and butylacetate were used as organic solvents. 3,5·10^{-4}M solution of HR was prepared by dissolution of accurate weight in ethanol. 2-hydroxy-5-tret-butylphenol-4'-methoxyazobenzene was synthesized using the technique (A.A.Mejidov, *et all*, (1981). The reagent is a monoacid and has a general structural formula:



The content and structure of the reagent was determined by elemental analysis, as well as IR- and UV-spectroscopy. IR-spectrum 3450 cm^{-1}(O-H arom.); 2960cm^{-1} (C-H from CH_3), 3030cm^{-1}(C-H arom.); 1592, 1496cm^{-1}(C=C arom.); 1408 cm^{-1}(N=N), 1168 cm^{-1}(C-C), 1264cm^{-1} (C-N), 1136, 1104cm^{-1}(arom. O-C).

Instruments

Optical density of solutions was measured with spectrophotometer SPh-46 and photoelectrocolorimeter KFK-2.

Atomic absorption of titanium was measured on atomic-absorption spectrophotometer AAS-1N.
As light sources standard hollow cathode lamps of the same firm and the lamp LSP-1 were used. Acidity of solutions was monitored by universal ionomer EV-74. Optimum measurement conditions are listed in Table 1.

Table 1 Conditions of atomic-absorption determination of titanium

Wavelength, nm	Slot width, mm	Lamp current, мA	Acetylene flow, l/h	Consumption of nitrogen oxide, l/h
364,3	0.5	20	200	180

Technique

A certain amount of standard solution of titanium, 10 ml of buffer solution with certain pH, 1.0 ml HR were poured into a separatory funnel and stoppered tubes, diluted with distilled water till 25 ml, and resulting compound of 10 ml n-butanol was extracted and mixed a minute. After complete separation of phases extract was sprayed into the acetylene-nitrogen oxide and atomic-absorption of titanium was measured.

Results and discussion

Spectrophotometric study of the reaction

Study of dependence of complexation on acidity of the medium showed that maximum yield of the complex $Ti(OH)_2R_2$ is observed at pH 3-6. pH 3-4 limit is optimum for complete complexation of titanium (Fig. 1).

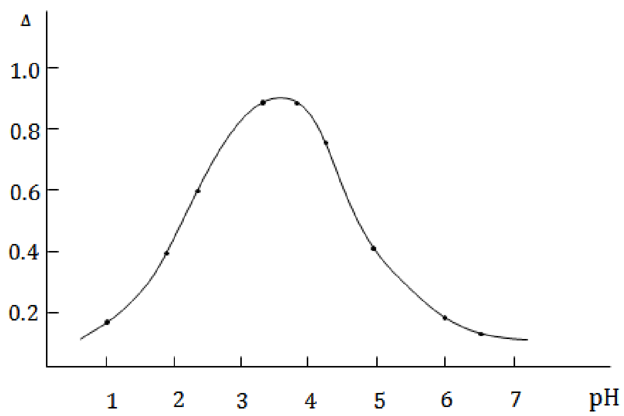


Fig.1 Influence of pH on complexation of Ti (IV). C_{HR}=3,6·10^{-4}M, C_{Ti}=1,0·10^{-3}M, λ=470nm, $V_{org.}$=10ml, l=0,5 cm, KFK-2, SPh-46

Effect of concentration of reagent

A series of experiments with constant concentrations of titanium and variable concentration of reagent HR were made to study the impact of reagent concentration on complexation. At high amount of HR up to (3,5-5,0)·10^{-4}M the extraction of titanium increases, and further increase of reagent concentration does not influence on the extraction of titanium. (3,5-5,0)10^{-4}M HR is necessary for complexation of titanium.

Absorption spectrum of the complex

Under optimum conditions maximum absorption spectrum of the complex is observed at 460-470 nm, but reagent – 360-370 nm, thus complexation is followed by bathochromic shift (Fig.2). Absorption spectrum points to the formation of one complex.

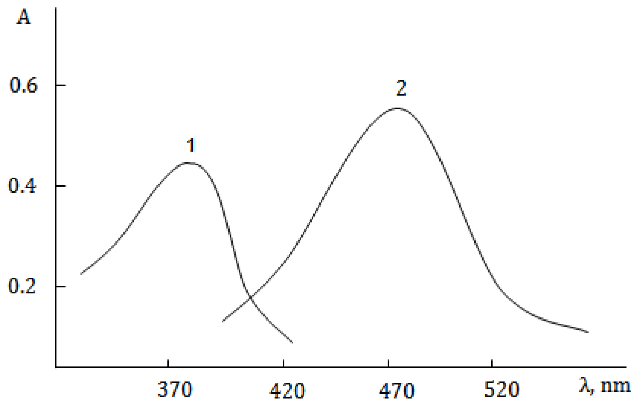


Fig.2. Absorption spectrum of extracts of reagent (1) and complex Ti (IV); C_{HR}=3,5·10^{-4}M, C_{Ti}=1,0·10^{-3}M, $V_{org.}$=10ml, l=0,1 cm, KFK-2, SPh-46.

Composition and physical-chemical properties of the complex

Using the techniques of molar ratio and equilibrium shift it was established that the complex with titanium ratio to HR 1:2 is formed under optimum conditions of extraction (A.M.Pashajanov, 2005). Knowing the ratio of components in titanium complex (IV) with HR, as well as considering the condition of components of the system the formation reaction and extraction of homogeneous ligand complex of titanium can be written as

$$Ti(OH)_4 + 2HR \rightarrow Ti(OH)_2R_2 + 2H_sO$$

Complexes of titanium are formed immediately after mixing the components. Molar absorption coefficients of the complex were calculated from saturation curves (M.I.Bulatov, *et all,* 1986). Concentration intervals where Beer's law is observed are established (Table 2). Calibration curve is linear at concentrations of titanium 1÷10 mg/ml.

Stability constants of homogeneous complex of titanium (IV) lgβ=9,01±0,01 were calculated using the method of curve crossing (M.I.Bulatov, *et all,* 1986), (Table 2).

Influence of foreign ions

Selectivity of extraction-atomic absorption determination of titanium with HR was studied. It was established that large amounts of alkali and alkali-earth elements and rare earth elements do not interfere the determination of titanium.

Table 2 Effect of accompanying ions on the results of determining titanium (introduced 5 mkg/ml Ti)

Accompanying ion	Allowed amount of accompanying ion, mg	Accompanying ion	Allowed amount of accompanying ion, mg
Na(I)	250		
K(I)	200	Pb^{+2}	100
Ca(II)	100		
Mg(II)	100	V(V)	50
Ba(II)	100	W(VI)	50
Cd(II)	50	Cl^-	5
Zn(II)	100	Br^-	5
Cr(II)	100	J^-	10
Ni(II)	50	SO_4^{-2}	10
Co(II)	50	PO_4^{-3}	10
Fe(III)	50	NO_3^-	5
Al(III)	100	CO_3^{-2}	10
Cu(II)	100		

Extraction of the complex

Chloroform, dichloroethane, carbon tetrachloride, benzene, toluene, xylene, hexane and n-butanol were tested for extraction of the complex from organic solvents. Organic solvent must be combustible in direct spraying of extract into burner flame.

Experiments show that atomic absorption of titanium decreases when using halogen containing solvents. n-butanol was found to be the most suitable for atomic-absorption analysis. It does not change combustion mode of flame and does not create background in analytical line of titanium. n-butanol supports flame stability which allows determining titanium in direct spraying of extracts into flame. Extractability of the complex was evaluated by distribution coefficient and extraction degree. Equilibrium concentration of titanium in aqueous phase was determined using atomic-absorption technique. The content of titanium in organic phase was found in difference. Degree of homogeneous extraction of titanium complex with n-butanol equals to 96-98%.

Table 2 Bases of photometric characteristics of titanium (IV) complex

Reagent	pH	λ_{Max}, nm	Ratio of components	ε_{Max}	lgβ	Interval of obedience of Beer's law , mg/ml
HR	4	470	1:2	$3{,}2\cdot10^4$	9,02±0,01	1-10

Extraction-atomic-absorption determination technique of microgram amounts of titanium in aluminum alloys was developed on the basis of experiments.

Determination

0.5 g of a sample weight is placed into 100 ml of beaker. 20 ml of chlorohydric acid (1:1) is added into a beaker. After the completion of the reaction beaker is cooled and 3 ml of hydrogen peroxide is added. Solution is evaporated to 10 ml, cooled, filtered off and quantitatively transferred to 100 ml of measuring flask. Solution volume is brought to the label with distilled water. Aliquot part (10ml) of solution is placed into separatory funnel. Then it follows as written in the technique. The content of titanium is found by calibration curve. Accuracy of technique was tested on standard samples in aluminum alloys AC 12M2 (A 2034x) and VAL 10(A186).

Table 3 Results of extraction-atomic-absorption determination of titanium in standard samples on the basis of aluminum (n = 5, p=0,95)

Standard sample	Content, Ti %		S_r
	Nameplate	found	
AC 12M2 A2034x	0,22	0,21+0,001	0,020
VAL10 A186 (1864)	0,020	0,021±0,001	0,012
1865	0,091	0.091±0,002	0,016

Conclusions

Complexation of Ti (IV) with 2-hydroxy-5-t-butylphenol-4'-methoxyazobenzene (HR) was studied. Optimum conditions of complexing and its extraction with chloroform and n-butanol were found. Molar absorption coefficient equals to $(3{,}2\text{-}4{,}1)\cdot10^4$. Stability constant of titanium in butanol β_K = 9,02±0,01. Beer's law is obeyed in concentrations of 1-10 mkg/ml titanium. Determination technique of titanium in alloys was developed.

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