

Extraction-Spectrophotometric Determination of Vanadium in Natural Objects

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Abstract

The complexation of vanadium (IV) with dimercaptophenols (2, 6-dimercaptophenol, 2,6-dimercapto-4-methyl phenol, 2,6-dimercapto-4-ethylphenol and 2,6-dimercapto- 4-tert-butyl phenol) and hydrophobic amines. As the hydrophobic amine, heterocyclic diamines-1,10-phenanthroline, 2,2'-dipyridyl and 4,7-diphenyl-1,10-phenanthroline were used. Optimum conditions for the formation and extraction of mixed ligand compounds were found and the ratios of the components in the complexes were established. Photometric methods for the determination of vanadium in various objects have been developed. The proposed methods are characterized by good reproducibility and low detection limits.

Key words: vanadium, dimercaptophenols, hydrophobic amines, extraction-photometric method

Introduction

Vanadium is a microelement that is a part of microorganisms and takes part in regulation of hydrocarbon metabolism, cardiovascular activity, stimulates growth and reproduction of cells. Among the products that contain vanadium are rice, beans, potatoes, barley, buckwheat, green salad, etc. Vanadium and its compounds are toxic if they are excessively ingested (respiratory tract irritation, asthma, nervous disorders, changes in the blood formula), their content is subject to control when assessing the quality of food, raw materials and drinking water.

It is these properties that necessitate the monitoring of vanadium compounds in environmental objects. Analytical control over their content should be carried out by fairly reliable methods. Therefore, the development of new sensitive, selective and accessible methods for determining the microquantities of this metal in different objects (atmospheric precipitation, soils, waters, bottom sediments, plants) is an urgent task. Modern requirements for the analysis of environmental objects and foodstuffs require the development of new highly sensitive and rapid methods for the determination of toxic metals. The multicomponent nature of the objects of analysis and the low concentration of metallic pollutants necessitate the use of combined analytical methods, including the concentration stage. One of the promising methods for determining metals in complex objects is the spectrophotometric methods of analysis [1, 2].

To determine vanadium in some ecological and biological objects, spectrophotometric reagents have been proposed: 2-(2-quinolyazo)-5-diethylaminophenol [3], blue variants [4], eriochrome cyanine R [5], benzyl acetate [6], pyrogallol [7], 2-(8-quinolyazo)-5-dimethylaminophenol [8], 2-hydroxyacetophenone [9], 4-(2-pyridylazo) resorcinol [10], tannic acid [11], 2-(5-chloro-2-pyridylazo)-5-dimethylaminophenol [12], N, N'-bis (2-hydroxyl-3-sulfopropyl)-tolidin [13], 2,6-dithiol-4-propylphenol [14]. Most of these techniques are not sensitive enough, or it takes a long time to develop color.

The purpose of this work was to study the vanadium content in food products of vegetable origin, water and soils. For this, multiligand complexes (MLC) with

dimercaptophenols (DP) {2,6-dimercaptolphenol (DMP), 2,6-dimercapto-4-methylphenol (DMMP), 2,6-dimercapto-4-ethylphenol (DMEP) and 2,6-dimercapto-4-t-butylphenol (DMBP)} and hydrophobic amines (Am). Of the hydrophobic amines, phenanthroline (Phen), batofenantroline (BPhen), and dipyrindyl (Dip) were used.

Materials and methods of research

Reagents and solutions. The stock solution (1.96×10^{-2} M) V(IV) was prepared from the chemically pure $\text{VOSO}_4 \cdot 3\text{H}_2\text{O}$ salt. The concentration of the solution V(IV) was established by titration with a solution of potassium permanganate [14]. Solutions with a lower concentration were obtained by diluting the stock solution with distilled water just before the experiment.

In the work, 0.01 M solutions of DP and Am in chloroform were used. DF was purified by reprecipitation from ethanol solutions by addition of water and then by distillation. As an extractant, purified chloroform was used.

The ionic strength of the solutions, equal to $\mu = 0.1$, was maintained by the constant introduction of the calculated amount of KCl. To create the necessary acidity of the solutions, a 1 M KOH solution and an acetate buffer solution were applied. All reagents used were qualified analytically pure or chemically pure.

Instruments. The optical density of the organic phase was measured in KFK-2. Spectrophotometric studies of stained reagents were carried out using a "Shimadzu 1240" spectrophotometer. The pH of the solutions was monitored with an I-130 ionomer with a glass electrode. IR spectra were recorded on a Specord M 80 spectrophotometer. The process of thermolysis of compounds was studied using the Shimadzu TGA-50H derivatograph in air in the range of 20-1000 °C, the heating rate was 10 deg / min.

General procedure for the determination of vanadium. In the graduated test tubes with ground stoppers, 0.1-1.0 ml of the initial solution of V (IV) (with an interval of 0.1 ml), 1.5-2.0 ml of 0.01 M DP solution and 2.0-2.0 ml, 5 ml of a 0.01 M solution of Am. The necessary pH was established by adding 1M KOH solution or with an acetate buffer solution. The volume of the organic phase was adjusted to 5 ml with chloroform, and the aqueous phase - up to 20 ml with distilled water. After 10 minutes, the organic layer was separated and its optical density was measured at room temperature on KFK-2 at 590 nm.

Determination of vanadium in soils. The developed methods for the determination of vanadium are used to determine it in light chestnut-colored soil taken from the Caspian region.

Finely ground in an agate mortar a sample (0.5 g) is calcined in a muffle furnace for 3 hours. After cooling, the melt is dissolved in a graphite dish at a temperature of 50-60 ° C, treated with a mixture of 16 ml of conc. HF, 5 mL conc. HNO_3 and 15 mL conc. HCl. To remove excess hydrogen fluoride, add 8 ml of conc. HNO_3 and evaporated each time to 5-6 ml. After this, the solution is transferred to a 100 ml volumetric flask and diluted to the mark with distilled water. In the aliquots of the solution, vanadium is determined by the developed procedures.

Determination of vanadium in plants. The method of dry mineralization is based on the complete decomposition of organic substances by burning plant samples (sample mass $m = 10$ g) in a muffle furnace under controlled temperature conditions. Chilled to room temperature, the ash is wetted dropwise with nitric acid (1: 1), evaporated in a water bath, placed in a muffle furnace, brought to a temperature of 300 ° C and held for 30 minutes. The ash in the crucible is gently moistened with 1 M HCl, then 3 ml of this solution are added. The interfering effect of iron is eliminated by adding ion orthophosphate, copper by adding KI. In the aliquots of the solution, vanadium is determined by the developed procedures.

Determination of vanadium in drinking water. Tap water is defended for two days. A 1 L sample was acidified with 3.0 mL of conc. H_2SO_4 and concentrated by

evaporation to 20 ml. After cooling, filter into a 50 ml flask and dilute to the mark with distilled water. An aliquot of this solution is taken into a separatory funnel and the content of vanadium is determined.

Results and its discussion

Complexing reagents (DMP, DMMP, DMEP and DMBP) are a tribasic weak acid (H_3R) and, depending on the pH of the medium, can exist in molecular and two anionic forms. The reagents were synthesized according to a known method [15] and characterized by physicochemical methods: IR and NMR spectroscopy [16, 17, 18] (Table 1).

Table 1 Results of studies of IR and NMR spectroscopy

Reagents	IR (KBr)	1H NMR (300,18 MHz, C_6D_6)
DMP	3470 cm^{-1} ν (OH), 3050 cm^{-1} ν (CH), 2580 cm^{-1} ν (SH), 1580 cm^{-1} ν (C_6H_5).	δ 5,48 (s, 1H - OH), δ 3,57 (s, 2H - 2SH), δ 7,28 (s, 2H Ar-H), δ 6,95 (s, 1H - Ar-H).
DMMP	3460 cm^{-1} ν (OH), 3050 cm^{-1} ν (CH), 2570 cm^{-1} ν (SH), 2962 и 2872 cm^{-1} ν ($-CH_3$), 1555 cm^{-1} δ (C_6H_5), 1390 cm^{-1} δ_{as} ($-CH_3$).	δ 5,24 (s, 1H- OH), δ 3,32(s, 2H - 2SH), δ 7,11 (s, 2H Ar-H), δ 2,38 (s, 3H $-CH_3$).
DMEP	3460 cm^{-1} ν (OH), 3050 cm^{-1} ν (CH), 2575 cm^{-1} ν (SH), 2965 и 2874 cm^{-1} ν ($-CH_3$), 1555 cm^{-1} δ (C_6H_5), 1460 cm^{-1} δ_{as} ($-CH_2-CH_3$).	δ 5,29 (s, 1H- OH), δ 3,38(s, 2H - 2SH), δ 7,15 (s, 2H Ar-H), δ 2,59 (s, 2H $-CH_2-$), δ 1,22 (s, 3H $-CH_3$).
DMBP	3458 cm^{-1} ν (OH), 2568 cm^{-1} ν (SH), 3040 cm^{-1} ν (CH), 1535 cm^{-1} ν (C_6H_5), 1395 cm^{-1} δ ($-C(CH_3)_3$).	δ 5,15 (s, 1H- OH), δ 3,28 (s, 2H- 2SH), δ 7,05 (s, 2H Ar-H), δ 1,42 (s, 9H $-C(CH_3)_3$).

The best extractants were dichloroethane, chloroform and carbon tetrachloride. With a single extraction with chloroform, 98.6-99.5% of vanadium (IV) is recovered as a complex (Fig. 1). It was found that when using 0.4-0.5 M NH_4OH (or pH 8.0-8.5), the degree of reextraction reaches 95.8-97.5%.

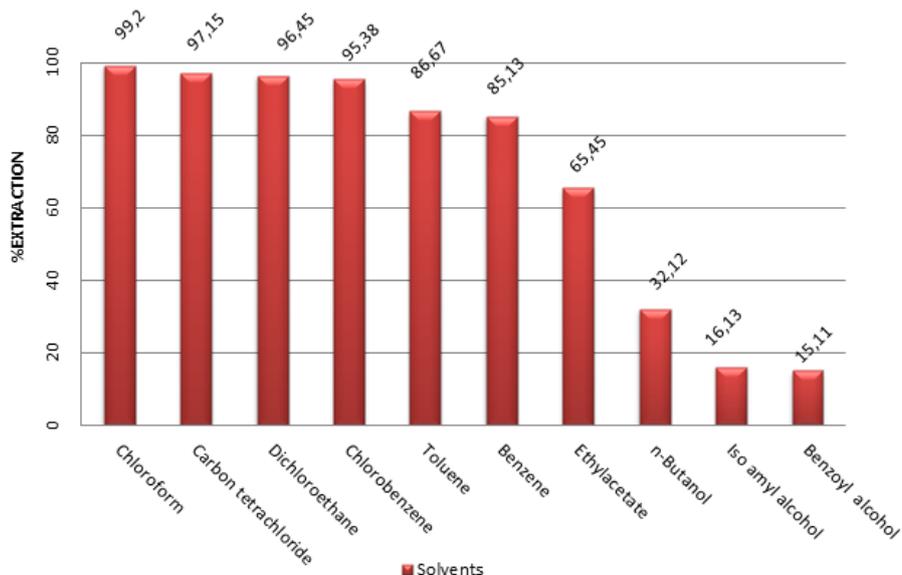


Fig. 1. Effect of solvents on extraction of V(V) as V-DTEP-Phen

Complexes of vanadium(IV) are extracted into chloroform in the pH range 6.5-7.9. Extraction decreases both with decreasing and with increasing pH of the aqueous phase (Fig.

2). The yield of the complexes is maximal at a concentration of 8.0×10^{-4} mol / L DP and 8.0×10^{-4} mol / L Am.

The complexes of vanadium(IV) with DF and Am are stable in aqueous and organic solvents and do not decompose for two days, and after extraction, more than a month. The maximum optical density is reached within 5 minutes. Complexes are stable when heated to 80°C .

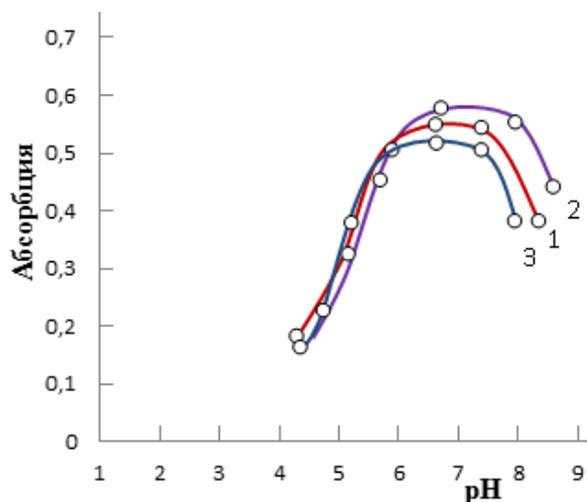


Fig. 2. Dependence of the optical density of the DLC of vanadium (II, IV) with DMEP and Am on the pH of the aqueous phase.

1. V(IV)-DMEP-Phen, 2. V(IV)-DMEP-BPhen, 3. V(IV)-DMEP-Dip

$C_V = 3.92 \times 10^{-5} \text{ M}$, $C_{DP} = 1.2 \times 10^{-3} \text{ M}$, $C_{Am} = 0.8 \times 10^{-3} \text{ M}$, KFK-2, $\lambda = 590 \text{ nm}$, $\ell = 0.5 \text{ cm}$.

The maximum analytical signal for the complexation of V(IV) with DP and Am is observed at 610-630 nm. DP maximally absorbs at 270-280 nm (Figure 3). The bathochromic shift is 340-360 nm. A comparison of the analytical capabilities of the investigated reagents and hydrophobic amines shows that the contrast and sensitivity of the reaction decreases in the series DMBP-DMEP-DMMP-DMP. The molar absorption coefficients of the complexes are $(2.95-3.85) \times 10^4$.

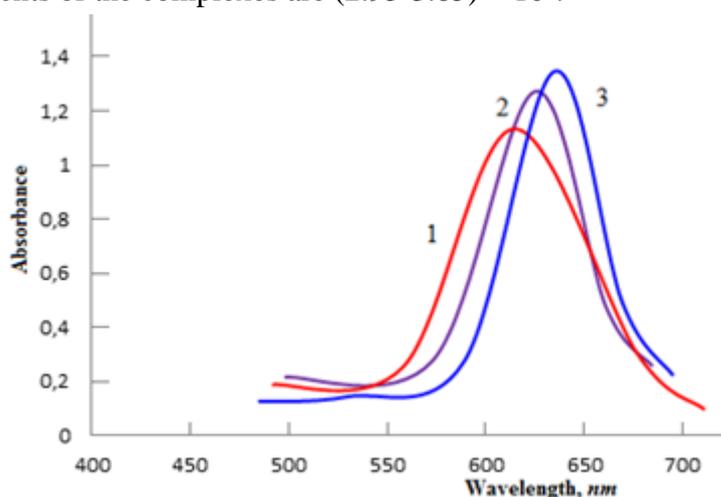


Fig. 3. Absorbance of the multiligand complexes V(IV)-DMP-Phen (1), V(IV)-DMEP-Phen (2), V(IV)-DMBF-Phen (3)

$C_{V(IV)} = 3.92 \times 10^{-5} \text{ M}$, $C_{DP} = 1.2 \times 10^{-3} \text{ M}$, $C_{Am} = 0.8 \times 10^{-3} \text{ M}$; Shimadzu 1240, $\ell = 1 \text{ cm}$.

It was established by Nazarenko's method that the complexing form of vanadium is VO^{2+} [19, 20]. At the same time, the number of hydrogen atoms displaced from one DF molecule turned out to be 1.

The stoichiometry of the complexes studied was established by the method of equilibrium shift, confirmed by the methods of relative yield and a straight line [21]. All methods have shown that the ratio of components in the complexes is 1: 1: 1 (Figure 4). The composition of the complexes was determined by the method of intersection of the curves [21] and their stability constants were calculated (Table 2). The calculations showed that the complexes in the organic phase do not polymerize and are in monomeric form [22].

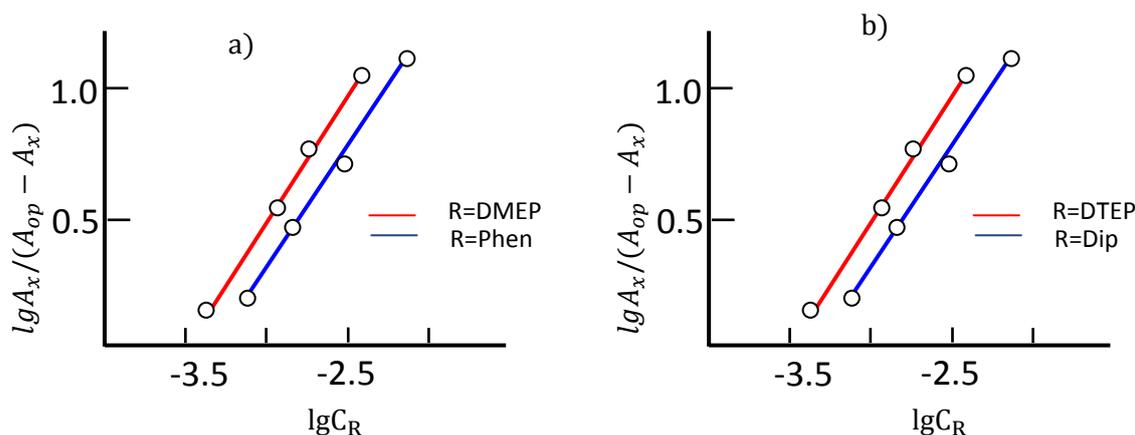


Fig. 4. Determination of the ratio of components in the MLC by the equilibrium shift method for V (IV)-DTMP-Phen (a) and V (IV) -DTEP-Dip (b).

Table 2

Some chemical-analytical properties of the RLC of vanadium (IV) DP and Am

Compound	pH _{opt}	R	D	λ , nm	$\Delta\lambda$, nm	$\epsilon \cdot 10^{-4}$	$\lg K_e$	$\lg \beta$	$\lg K_{ex}$
[VO(DTP)(Phen)]	6,5-7,6	98,8	329	610	340	3,12	5,43	9,89	12,39
[VO(DTP)(Dip)]	6,4-7,2	98,6	282	615	345	2,95	5,35	9,58	12,03
[VO(DTMP)(Phen)]	7,0-7,7	99,5	796	628	354	3,61	5,51	10,95	13,54
[VO(DTEP)(Phen)]	6,7-7,5	98,6	282	625	349	3,71	5,49	10,55	12,86
[VO(DTEP)(BPhen)]	6,9-7,6	99,2	496	615	339	3,84	5,62	10,73	13,42
[VO(DTEP)(Dip)]	6,6-7,4	98,8	329	620	342	3,62	5,54	10,12	12,70
[VO(DTBP)(Phen)]	7,0-7,9	99,5	796	630	350	3,85	5,50	10,83	12,91

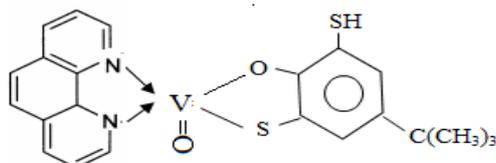
In the IR spectra of the complex V(IV)-DMMP-Phen at 980 cm^{-1} , an intense absorption band appears due to the valence vibration of the VO^{2+} group. The disappearance of a pronounced band at 2580 cm^{-1} , observed in the DMMP spectrum, and the appearance of two absorption bands in the complex spectra, one of which is shifted toward smaller frequencies, indicates that one of the -SH groups participates in the formation of the complex. The observed disappearance of the absorption band in the $3600\text{-}3200 \text{ cm}^{-1}$ region with a maximum at 3460 cm^{-1} shows that -OH participates in the formation of a bond with the metal [17, 18].

Intensive absorption bands in the IR spectra of the complex in the $1569\text{-}1550 \text{ cm}^{-1}$ region indicate the participation of the cyclic nitrogen atom in coordination. It is known that the criterion for coordination of the cyclic nitrogen atom in pyridines and pyrimidines is the shift of bands, stretching vibrations of C-C and C-N bonds to the high-frequency region, or a

sharp increase in the intensity of the bands of these bonds. In the IR spectra of the complex, absorption bands at 445 and 600 cm^{-1} , corresponding to $\nu_{\text{V-S}}$ and $\nu_{\text{V-N}}$, are observed.

The thermogravimetric study of the V(IV)-DMEP-Phen complex shows that the rapid decomposition of the complex begins at 480 °C, with a mass loss of 49.1% (49.7% calculated), which corresponds to the removal of phenanthroline. At 510-650 °C, the DMEP is allocated, the mass loss is 39.1% (39.7% are calculated). Further, when heated to 675 °C, V_2O_5 forms.

Taking into account the ratio of the components in the complexes formed, the number of protons displaced during the reaction, the ionic form of vanadium(IV) and the reagents, as well as the IR spectroscopic and thermogravimetric studies, one can imagine the following most probable structure of the RLC, for example, V (IV)-DMBP-Phen:



Influence of foreign ions. Large amounts of alkali, alkaline earth metals and rare earth elements do not interfere with the determination of vanadium. The interfering effect of Fe (III) was eliminated by thioglycolic acid; Cu(II), Cr(VI) and Mn(VII) - thiourea; Ti(IV) - ascorbic acid, Zr(IV), Nb(V) and Ta(V) - fluoride ions. Mo(VI), W(VI), Ti(IV), Nb(V) and Ta(V) ions with DP and Am form colored compounds and interfere with the determination of vanadium. However, these elements form complexes in a more acidic environment.

Any quantities of Fe(III) ions do not interfere if they are preliminarily masked with thioglycolic acid. The interfering effect of small amounts of Fe^{3+} can be eliminated by the addition of H_3PO_4 . Ti(IV) is masked with sodium fluoride. The presence of tenfold amounts of iron(III) overestimates the results by 10%. The effect of Mo, Co, Nb, Al, Zr was eliminated by sodium citrate. The effect of copper is eliminated by thiourea.

The ions F^- , Cl^- , NO_3^- , SO_4^{2-} and PO_4^{3-} , as well as thioglycolic, tartaric, citric and ascorbic acids do not interfere with the determination of vanadium. Oxalic acid gradually destroys the vanadium compound with DP and Am. In the presence of masking agents, the selectivity of the determination of vanadium in the presence of many elements increases. The selectivity of the photometric determination of vanadium by means of DP and Am is shown in Table. 3.

Table 3

The influence of extraneous ions on the determination of vanadium(IV) in the form of RLA with DF and heterocyclic diamines (30.0 μg V introduced)

Ion	Molar Excess of the Ion	Masking agent	Found V, μg (S_r)		
			DMEP+Phen	DMEP+BPhen	DMEP+Dip
Co(II)	120		30.0(0.05)	29.8(0.04)	29.8(0.04)
Ni(II)	120		30,5(0,03)	29,5(0,04)	29,6(0,04)
Al(III)	100		29,8(0,04)	30,6(0,06)	29,8(0,04)
Fe(II)	45		30,6(0,04)	30,2(0,04)	29,6(0,04)
Fe(III)	50	Na_2HPO_4	30,2(0,04)	30,2(0,03)	30,2(0,04)
Cd(II)	65		30,4(0,03)	30,5(0,04)	29,8(0,04)
Zr(IV)	75	NaF	29,5(0,05)	30,4(0,06)	29,6(0,04)
Zn(II)	15		30,0(0,03)	29,8(0,04)	29,8(0,04)
Cu(II)	25	$\text{SC}(\text{NH}_2)_2$	30,2(0,04)	29,5(0,04)	29,6(0,04)
Hg(II)	10				29,8(0,04)
Ag(I)	20		29,8(0,04)	29,8(0,04)	29,6(0,04)
Ti(IV)	30	Ascorbic acid	29,6(0,04)	29,5(0,04)	29,8(0,04)
Bi(III)	130		29,6(0,04)	30,6(0,06)	29,6(0,04)
W(VI)	15		30,2(0,04)	30,2(0,04)	29,8(0,04)
Mo(VI)	15		30,2(0,03)	30,2(0,03)	29,6(0,04)
Cr(III)	80		29,3(0,05)	30,5(0,04)	29,8(0,04)

Nb(V)	45	NaF	30,4(0,06)	30,4(0,06)	30,4(0,06)
Ta(V)	45	NaF	29,6(0,05)	29,6(0,05)	29,6(0,05)
Pt(II)	50		30,0(0,03)	30,0(0,03)	30,0(0,03)
Pd(II)	50	Sodium orthophosphate	30,2(0,03)	30,2(0,03)	30,2(0,03)
Mn(II)	14		29,6(0,04)	30,0(0,03)	30,6(0,06)
UO ₂ ²⁺	60	CH ₃ COO ⁻	29,8(0,04)	29,8(0,04)	29,8(0,04)
Nitrate	300		29,7(0,04)	29,6(0,03)	29,6(0,04)
Tetraborate	1100		30,3(0,04)	30,2(0,05)	30,4(0,04)
Acetate	550		30,2(0,03)	30,2(0,03)	30,2(0,03)
Phosphate	650		30,5(0,05)	30,3(0,03)	30,5(0,05)
Chloride	370		30,0(0,03)	29,0(0,04)	30,0(0,03)
Tartrate	800		30,2(0,03)	30,2(0,03)	30,2(0,03)
Iodide	530		29,8(0,04)	29,8(0,04)	29,8(0,04)
Urea	450		29,6(0,04)	29,8(0,03)	29,6(0,04)
Thiocyanate	600		30,2(0,04)	30,2(0,04)	30,2(0,04)
Bromide	170		30,2(0,03)	30,6(0,06)	30,2(0,03)
Oxalate	480		30,5(0,05)	30,4(0,06)	30,5(0,05)
Fluoride	240		30,0(0,03)	29,5(0,04)	30,0(0,03)
MnO ₄ ⁻	100		30,2(0,03)	30,2(0,03)	30,2(0,03)
Cr ₂ O ₇ ²⁻	80	Potassium thiocyanate	30,5(0,05)	30,5(0,05)	30,5(0,05)
Sulfosalicylic acid	200		29,6(0,05)	29,6(0,05)	29,6(0,05)
Thiourea	350		29,8(0,04)	29,8(0,04)	29,8(0,04)
Citric acid	450		30,2(0,05)	29,6(0,05)	30,2(0,02)
Ascorbic acid	340		29,2(0,05)	30,2(0,03)	30,2(0,03)

Measurement of the optical density at 670 nm completely excludes the influence of Nb, W, Ti and Bi, which form yellow complexes with reagents. Fe(III) and Mo are masked by thioglycolic acid, W-tartrate, Zr-fluoride.

Co(II) and Ni(II) with DP form complexes at high pH values and even large amounts of these ions do not interfere with the determination of V(IV) with DP and amines. The Nb(V), Ta(V), Ti(IV), and Hg (II) ions form complexes with DP and Am in a more acidic medium than V(IV). Therefore, it is possible to determine V(IV) in the presence of small amounts of these ions by adjusting the pH of the medium.

The linearity region of the calibration curve for chloroform extracts of the complexes is preserved in the range of vanadium concentrations 0.2-20 µg / ml (Table 4). The equation of the calibration dependence for spectrophotometric indication of the signal is given in Table. 4. Based on the equations of the calibration graphs, the limits of photometric detection and the limits of the quantitative determination of vanadium in the form of mixed ligand complexes were calculated [23].

Table 4

Analytical characteristics for ternary complexes V(IV)-DP-Am

Compound	Linear range of calibration graphs, µg / ml	Equation of calibration graphs	Detection limits (ng mL ⁻¹)	Quantification limits (ng mL ⁻¹)	Sensitivity, ng/ cm ²
[VO(DTP)(Phen)]	0,8-14	0,045+0,0563x	12	39	1,63
[VO(DTP)(Dip)]	0,8-14	0,043+0,0527x	13	42	1,73
[VO(DTMP)(Phen)]	0,5-16	0,045+0,0702x	11	35	1,41
[VO(DTEP)(Phen)]	0,2-18	0,056+0,0674x	10	32	1,30
[VO(DTEP)(BPhen)]	0,4-16	0,053+0,0717x	9	30	1,32
[VO(DTEP)(Dip)]	0,2-16	0,059+0,0651x	10	32	1,30
[VO(DTBP)(Phen)]	0,3-18	0,053-0,0715x	9	30	1,32

In Table. 5 shows the data allowing to compare the analytical characteristics of the methods for determining vanadium(IV) with some already known [24, 25].

Table 5

Comparative characteristics of the methods for determination of vanadium

Reagent	Medium (solvent)	λ , nm	$\varepsilon \times 10^{-4}$	Linear range ($\mu\text{g} / \text{ml}$)
Sulfonitrazo	2,3	522	2.06	
8-hydroxyquinoline	4.0-5.5(chloroform, toluene)	412	0.30	0.5-1.5
8-hydroxyquinoline	3,0-5,0(chloroform)	550	3.00	-
$\text{H}_3\text{PO}_4 + \text{NaWO}_4$	0,25M H_2SO_4 (water)	400	0.14	-
[VO(ДТМФ)(Фен)]	7,0-7,7(chloroform)	628	3.61	0.5-16
[VO(ДТЭФ)(Фен)]	6,7-7,5(chloroform)	625	3.71	0.2-18
[VO(ДТЭФ)(Бфен)]	6,9-7,6(chloroform)	615	3.84	0.4-16
[VO(ДТБФ)(Фен)]	7,0-7,9(chloroform)	630	3.85	0.3-18

Thus, the properties of the complexes formed depend on the acid-base properties of the reagents. Moreover, with the introduction of electrodonor substituents into the structures, i.e. with a decrease in the acid properties of the reagent, the strength of the complexes increases, and the pH_{opt} and pH_{50} shift into the weakly acidic region.

Analytical Applications

The proposed method has been applied for the determination of vanadium(V) in plants, water and soil samples. The developed methods for determining the content of vanadium in the soils were controlled by 8-hydroxyquinoline and formaldoxime methods, as well as by the additive method. The data presented in the Table 6 and 7 indicate the accuracy and precision of the proposed method.

Table 6

The results of determination of vanadium in soil (depth of section 10-20 cm) and in plants ($n = 6$, $p = 0.95$)

Analyzed object	Procedures	\bar{X} , mg / kg	S	S_r	$\bar{X} \pm \frac{t_p \cdot S}{\sqrt{n}}$
Soil	8-hydroxyquinoline	$1,12 \cdot 10^{-2}$	0,000448	0,042	$(1,12 \pm 0,47) \cdot 10^{-2}$
	Formaldoxime	$1,14 \cdot 10^{-2}$	0,000581	0,051	$(1,14 \pm 0,60) \cdot 10^{-2}$
	[VO(ДТЭФ)(Бфен)]	$1,14 \cdot 10^{-2}$	0,000402	0,034	$(1,14 \pm 0,44) \cdot 10^{-2}$
	[VO(ДТЭФ)(Дип)]	$1,12 \cdot 10^{-2}$	0,000365	0,035	$(1,12 \pm 0,38) \cdot 10^{-2}$
	[VO(ДТБФ)(Фен)]	$1,13 \cdot 10^{-2}$	0,000429	0,038	$(1,13 \pm 0,45) \cdot 10^{-2}$
Rice	8-hydroxyquinoline	1,12	0,048	0,043	$1,12 \pm 0,051$
	Formaldoxime	1,14	0,068	0,060	$1,14 \pm 0,070$
	ДМФ+Фен	1,15	0,049	0,043	$1,15 \pm 0,052$
	ДМФ+Дип	1,12	0,050	0,045	$1,12 \pm 0,052$
	ДММФ+Фен	1,12	0,054	0,048	$1,12 \pm 0,060$
Potatoes	8-hydroxyquinoline	6,14	0,304	0,051	$6,14 \pm 0,32$
	Formaldoxime	6,10	0,244	0,040	$6,10 \pm 0,25$
	ДМФ+Фен	6,12	0,182	0,029	$6,12 \pm 0,21$
	ДМФ+Дип	6,13	0,272	0,045	$6,13 \pm 0,29$
	ДММФ+Фен	6,08	0,225	0,038	$6,05 \pm 0,25$
	ДМБФ+Фен	6,10	0,150	0,025	$6,10 \pm 0,16$
Carrot	8-hydroxyquinoline	1,00	0,033	0,033	$1,00 \pm 0,034$
	ДММФ+Фен	0,98	0,041	0,042	$0,98 \pm 0,043$
	ДМБФ+Фен	1,02	0,042	0,042	$1,02 \pm 0,044$
Beans	8-hydroxyquinoline	1,82	0,071	0,039	$1,82 \pm 0,075$

	ДММФ+Фен	1,85	0,068	0,037	1,82±0,072
Barley	8-hydroxyquinoline	1,69	0,046	0,027	1,69±0,048
	ДММФ+Фен	1,71	0,058	0,035	1,71±0,069

Table 7

The results of the determination of vanadium in water with DMBP and Phen (n = 6, p = 0.95)

Added V, (µg / ml)	Found V, (µg / ml)		S	S _r	$\bar{X} \pm \frac{t_p \cdot S}{\sqrt{n}}$
	Standard Method	Proposed Method			
1,0	1,06	1,06	0,00168	0,028	0,06±0,00175
2,0	2,06	2,07	0,00259	0,037	0,07±0,00272
3,0	3,08	3,09	0,00261	0,029	0,09±0,00275

Conclusion

Thus, the reactions of complex formation of vanadium (IV) with dithiolphenols (2,6-dimercaptophenol, 2,6-dimercapto-4-methylphenol, 2,6-dimercapto-4-ethylphenol and 2,6-dimercapto-4-tert-butylphenol) and hydrophobic amines. As the hydrophobic amine, heterocyclic diamines-1,10-phenanthroline, 2,2'-dipyridyl and 4,7-diphenyl-1,10-phenanthroline were used. Conditions of formation and extraction, composition, physico-chemical and analytical properties of complexes were revealed. The structure of complexes was established by means of IR spectroscopy and thermogravimetry. Sensitive and selective methods for the extraction-spectrophotometric determination of vanadium have been developed. The techniques are used to determine vanadium in soils, plants and water. The data obtained were statistically processed.

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