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Research Article

Spectroscopic Study of Mixed-Ligand Complexes of Vanadium with Dimercaptophenols and Heterocyclic Diamines

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Abstract

The complex formation of vanadium (IV) with dimercaptophenols (2,6-dimercaptophenol, 2,6- dimercapto-4-methylphenol, 2,6-dimercapto-4-ethylphenol, 2,6-dimercapto-4-tert-butylphenol) and hydrophobic amines. Heterocyclic diamines 1,10-phenanthroline, 2,2/-dipyridyl, and 4,7- diphenyl-1,10-phenanthroline were used as hydrophobic amines. The optimal conditions for the formation and extraction of mixed-ligand compounds were found, and the ratios of components in the complexes were established. Photometric methods for determining vanadium in various objects were developed. The proposed methods are characterized by good reproducibility and low detection limits.

Keywords: Vanadium; Dimercaptophenols; Hydrophobic Amines; Extraction-Photometric Method

Introduction

Vanadium is a trace element that is part of microorganisms and participates in the regulation of carbohydrate metabolism and cardiovascular activity, stimulating cell growth and reproduction. Foods that contain vanadium include rice, beans, potatoes, barley, buckwheat, green salad, etc. Vanadium and its compounds are toxic when consumed in excess (irritation of the respiratory tract, asthma, nervous disorders, changes in blood count), and their content must be monitored when assessing the quality of food products, raw materials, and drinking water.

It is precisely these properties that necessitate the monitoring of vanadium compounds in environmental objects. Analytical control of their content must be carried out using sufficiently reliable methods. Therefore, the development of new sensitive, selective, and accessible methods for determining microquantities of this metal in various objects (atmospheric precipitation, soils, waters, bottom sediments, plants) is a pressing task. Modern requirements for the analysis of environmental objects and food products call for the development of new highly sensitive and rapid methods for determining toxic metals. The multicomponent nature of the objects of analysis and the low concentrations of metal contaminants necessitate the use of combined analysis methods, including a concentration stage. One of the promising methods for determining metals in objects that are complex in nature is spectrophotometric analysis [1,2].

Spectrophotometric reagents have been proposed for determining vanadium in certain environmental and biological objects:

2-(2-quinolylazo)-5-diethylaminophenol e [3], varamine blue [4], eriochrome cyanine R [5], benzyl acetate [6], pyrogallol [7], 2-(8-quinolylazo)-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-hydroxy-3-sulfo- propyl)-tolidine [13], 2,6-dithiol-4-propylphenol [14]. Most of these methods are not sensitive enough or take a long time to develop intense color.

The aim of this work is to study the content of vanadium in plant-based foods, water, and soils. For this purpose, we used mixed-ligand complexes (MLC) with dimercaptophenols (DP) {2,6- dimercaptophenol (DMP), 2,6-dimercapto-4-methylphenol (DMMP), 2,6-dimercapto-4-ethylphenol (DMEP), and 2,6-dimercapto-4-tert-butylphenol (DMBP)} and hydrophobic amines (Am). The hydrophobic amines used were phenanthroline (Phen), batofenanthroline (BPhen), and dipyridyl (Dip).

Materials and Methods

Reagents and solutions

The initial solution (1.96×10^{-2} *M)* V(IV) was prepared from chemically pure $VOSO_4 \cdot 3H_2O$ salt. The concentration of the V(IV) solution was determined by titration with potassium permanganate solution [14]. Solutions with lower concentrations were obtained by diluting the initial solution with distilled water immediately before the experiment.

The study used 0.01 M solutions of DP and Am in chloroform. DF was purified by reprecipitation from ethanol solutions with the addition of water and then distillation. Purified chloroform was used as the extractant.

The ionic strength of the solutions, equal to μ = 0.1, was maintained by the constant addition of the calculated amount of KCl. A 1 M KOH solution and an acetate buffer solution were used to create the required acidity of the solutions. All reagents used were of analytical grade or chemical grade.

Apparatus

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

Methodology

0.1-1.0 ml of the initial solution V(IV) was added to graduated test tubes with ground stoppers at intervals of 0.1 ml, 1.5-2.0 ml of 0.01 M DP solution and 2.0-2.5 ml of 0.01 M Am solution. The required pH value was adjusted by adding 1 M KOH solution or acetate buffer solution. The volume of the organic phase was brought to 5 ml with chloroform, and the aqueous phase to 20 ml with distilled water. After 10 minutes, the organic layer was separated and its optical density was measured at room temperature on a KFK-2 at 590 nm.

Determination of vanadium in soils

The developed methods for determining vanadium were used to determine its content in light brown soil taken from the Caspian zone. A finely ground sample (0.5 g) in an agate mortar is calcined in a muffle furnace for 3 hours. After cooling, the melt is dissolved in a graphite cup at a temperature of 50-60 °C, treating it with a mixture of 16 ml of conc. HF, 5 ml of conc. HNO_3 and 15 ml of conc. HCl. To remove excess hydrogen fluoride, 8 ml of conc. HNO_3 is added to the solution three times and evaporated each time to 5-6 ml. After that, the solution is transferred to a 100 ml volumetric flask and diluted to the mark with distilled water. Vanadium is determined in aliquots of the solution using established methods.

Determination of vanadium in plants

The dry mineralization method is based on the complete decomposition of organic substances by burning plant samples (sample mass m = 10 g) in a muffle furnace at a controlled temperature [26]. The ash cooled to room temperature is moistened drop by drop 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 carefully moistened with 1M HCl, then 3 ml of this solution is added. The interfering effect of iron is eliminated by adding orthophosphate ions, and that of copper by adding KI. The accuracy of the results according to the method was verified using the addition method.

Determination of vanadium in drinking water

Tap water is settled for two days. A 1 L sample is acidified with 3.0 mL of concentrated 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. Take an aliquot of this solution in a separating funnel and determine the vanadium content.

Results and Discussion

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

Table 1: Results of IR and NMR spectroscopy studies.

Reagent	IR (KBr)	^{1}H 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 and 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 and 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).

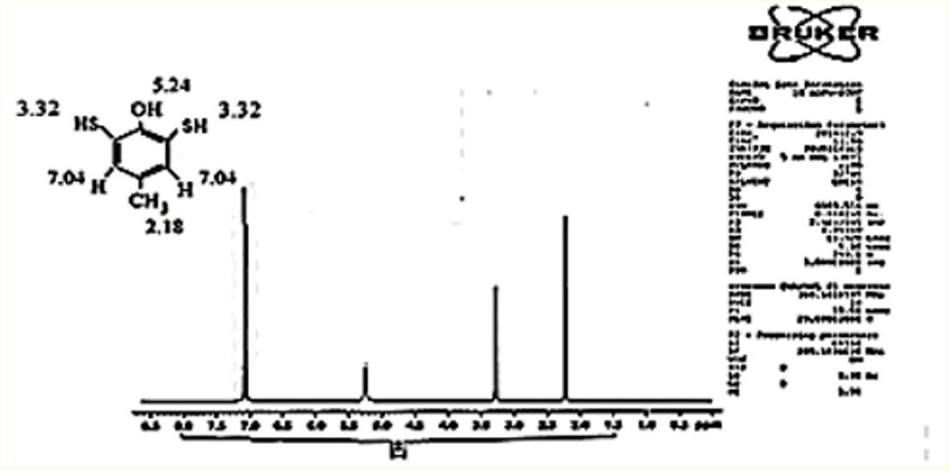


Figure 1: NMR spectra of DMMP.

The best extractants were dichloroethane, chloroform, and carbon tetrachloride. A single extraction with chloroform yields 98.6-99.5% of vanadium (IV) in the form of a complex. It was found that when using 0.4-0.5 M NH_4OH (or pH 8.0-8.5), the degree of re-extraction reaches 95.8-97.5%.

Vanadium (IV) complexes are extracted into chloroform in the pH range of 6.5-7.9. Extraction decreases both when the pH of the aqueous phase decreases and when it increases. The yield of the complex is maximum at a concentration of 8.0×10^{-4} mol/L DP and 8.0×10^{-4} mol/L Am.

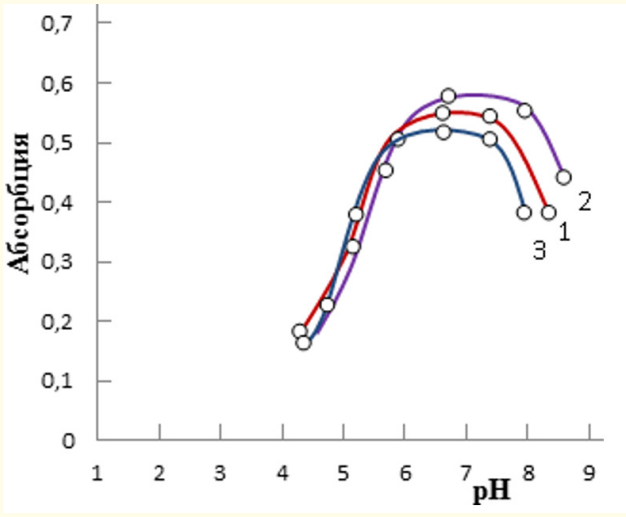


Figure 2: Dependence of the optical density of vanadium(II,IV) complexes with DMEP and Am on the pH of the aqueous phase. 1. V(IV)-DMEP-Phen, 2. V(IV)-DMEP-BPhen, 3. V(IV)-DMEP-Dip; CV = 3.92×10-5 M, CDP = 1.2 ×10-3M, Cam = 8.0 ×10-4 M, KFK-2, λ = 590 nm, ℓ = 0.5 cm.

Vanadium(IV) complexes with DP and Am are stable in aqueous and organic solvents and do not decompose for two days, and after extraction - for more than a month. Maximum optical density is reached within 5 minutes (Figure 3). The complexes are stable when heated to 80°C.

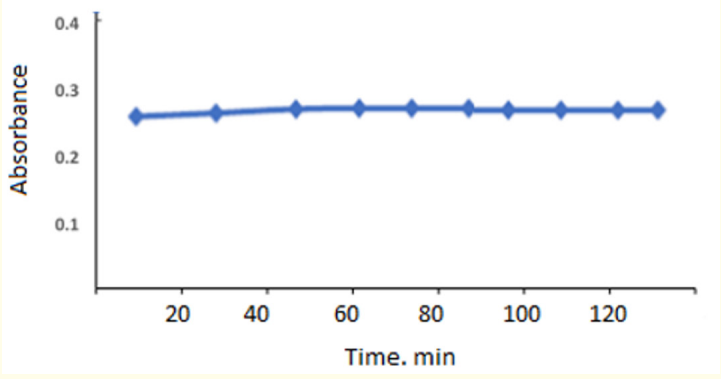


Figure 3: Plot of true absorbance of the V-DMEP-Dip complex versus time. CV = 3.92×10-5M, CDP = 1.2 ×10-3M, CAm = 0.8 ×10-3M, KFK-2, λ = 590 nm, ℓ = 0.5 cm.

The maximum analytical signal during complex formation of V(IV) with DP and Am is observed at 610-630 nm. DP absorbs maximally at 270-280 nm (Figure 4). The bathochromic shift is 340-360 nm. A comparison of the analytical capabilities of the studied 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)×10^4.

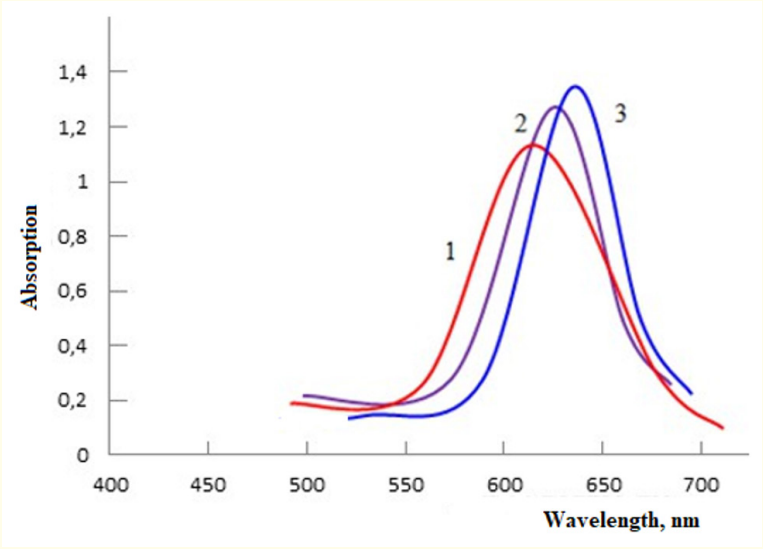


Figure 4: Light absorption of mixed-ligand complexes V(IV)-DMP-Phen (1), V(IV)-DMEP-Phen(2), V(IV)-DMBP-Phen (3). CV(IV) = 3.92×10-5 M, CDP = 1.2 ×10-3 M, CAm = 8 ×10-4 M; SF-26, ℓ = 1 cm.

It was established that the complex-forming form of vanadium is VO^{2+} [19,20]. At the same time, the number of hydrogen atoms displaced by it from one DF molecule turned out to be equal to 1.

The stoichiometry of the complexes under study was determined using the equilibrium shift method and confirmed by Starik Barbane's relative yield and straight line methods [21]. All methods showed that the ratio of components in the complexes is 1:1:1 (Figure 5). The composition of the complexes was determined by the curve intersection method [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].

In the IR spectra of the V(IV)-DMP-Phen complex at 980 cm^{-1}, an intense absorption band appears, caused by 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 towards lower frequencies, indicates that one of the –SH groups participates in the formation of the complex. The observed disappearance of the absorption band in the 3600-3200 cm^{-1} region with a maximum at 3460 cm^{-1} indicates that -OH participates in the formation of a bond with the metal [17,18].

Intense absorption bands in the IR spectra of the complex in the 1569-1550 cm^{-1} region indicate the participation of a cyclic nitro-

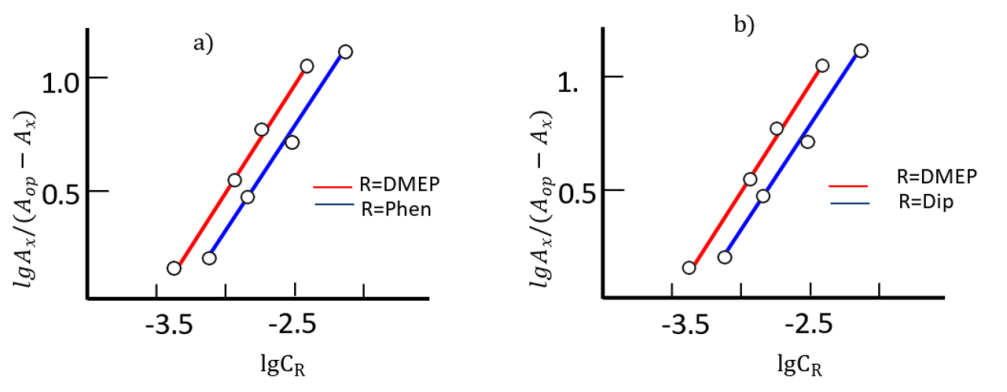


Figure 5: Determination of the ratio of components in the MLC using the equilibrium shift method for V(IV)-DMMP-Phen (a) and V(IV)-DMEP-Dip (b).

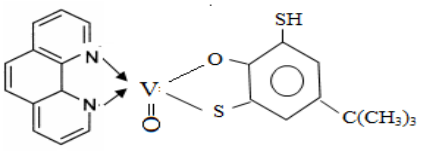
Compound	pHopt	R	D	λ, nm	Δλ, nm	$e \cdot 10^4$	lgKp	lgβ	lgKext
[VO(DMP)(Phen)]	6.5-7.6	98.8	329	610	340	3.12	5.43	9.89	12.39
[VO(DMP)(Dip)]	6.4-7.2	98.6	282	615	345	2.95	5.35	9.58	12.03
[VO(DMMP)(Phen)]	7.0-7.7	99.5	796	628	354	3.61	5.51	10.95	13.54
[VO(DMEP)(Phen)]	6.7-7.5	98.6	282	625	349	3.71	5.49	10.55	12.86
[VO(DMEP)(BPhen)]	6.9-7.6	99.2	496	615	339	3.84	5.62	10.73	13.42
[VO(DMEP)(Dip)]	6.6-7.4	98.8	329	620	342	3.62	5.54	10.12	12.70
[VO(DMBP)(Phen)]	7.0-7.9	99.5	796	630	350	3.85	5.50	10.83	12.91

Table 2: Some chemical and analytical properties of MLC of vanadium (IV) DP and Am.

gen atom in coordination. It is known that the criterion for the coordination of a cyclic nitrogen atom in pyridines and pyrimidines is a shift in the high- frequency region of the bands of valence vibrations of C-C and C-N bonds, or a sharp increase in the intensity of the bands of these bonds. In the IR spectra of the complex, absorption bands are observed at 445 and 600 cm^{-1}, corresponding to ν(V-S) and ν(V-N).

Thermogravimetric study of the V(IV)-DMEP-Phen complex shows that rapid decomposition of the complex begins at 480 ° C, with a mass loss of 49.1% (calculated 49.7%), which corresponds to the removal of phenanthroline. At 510-650° C, DMEP is released, with a mass loss of 39.1% (calculated 39.7%). Further heating to 675 (°) C results in the formation of V_2O_5.

Taking into account the ratio of components in the complexes formed, the number of protons displaced during the reaction, the ionic form of vanadium(IV) and reagents, as well as data from IR spectroscopy and thermogravimetric studies, the following most probable structure of the MLC can be presented, using the example of V(IV)-DMBP-Phen:



Large amounts of alkali metals, alkaline earth metals, and rare earth elements (REE) 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) – by thiourea; Ti(IV) – by ascorbic acid; Zr(IV), Nb(V), and Ta(V) – by 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 amounts of Fe(III) ions do not interfere if they are pre-masked with thioglycolic acid. The interfering effect of small amounts of Fe^{3+}can be eliminated by adding H_3PO_4. Ti(IV) is masked with sodium fluoride. The presence of ten times the amount of iron(III) increases the results by 10%. The influence of Mo, Co, Nb, Al, and Zr was eliminated by sodium citrate. The influence of copper is eliminated by thiourea.

The presence of F^-, Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-} ions as well as thioglycolic, tartaric, citric and ascorbic acids, does not interfere with the determination of vanadium. Oxalic acid gradually destroys the vanadium compound with DP and Am. The possibility of the presence of such active masking agents in the analyzed solution made it possible to achieve good selectivity in the determination of vanadium in the presence of many elements. The selectivity of the photometric determination of vanadium using DP and Am is presented in Table 3.

Table 3: Effect of extraneous ions on the determination of vanadium(IV) in the form of MLC with DP and heterocyclic diamines (30.0 μg V added).

Ion	Molar excess of ion	Masking reagent	V found, μg (S_r)		
			DTF+Fen	DTF+Bphen	DTF+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	$SC(NH_2)_2$	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)
Tetrabromide	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)
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)

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

Co(II) and Ni(II) form colored complexes with DP at high pH values, and even large amounts of these ions do not interfere with the determination of V(IV) with DP and amines. Nb(V), Ta(V), Ti(IV), and Hg(II) ions form complexes with DP and Am in a more acidic environment 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 environment.

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

Table 5 shows data that allows comparison of the analytical characteristics of methods for determining vanadium (IV) with some already known methods [24,25].

Thus, the properties of the complexes formed depend on the acid-base properties of the 2- mercapto group of FAG reagents. Moreover, with the introduction of electron-donating substituents into the structure, i.e., with a decrease in the acidic properties of the FAG reagent, the strength of the complexes increases, and pH_{opt} and pH_{50} shift to the weakly acidic region.

Table 4: Analytical characteristics for triple complexes V(IV)-DP-Am.

Compound	Linear range of calibration curves, μg/ml	Equation of calibration curves	Limit of detection ng ·mL^{-1}	Limit of quantification: ng ·mL^{-1}	Sensitivity, ng/cm^2
[VO(DMP)(Phen)]	0.8-14	0.045+0.0563x	12	39	1.63
[VO(DMP)(Dip)]	0.8-14	0.043+0.0527x	13	42	1.73
[VO(DMMP)(Phen)]	0.5-16	0.045+0.0702x	11	35	1.41
[VO(DMEP)(Phen)]	0.2-18	0.056+0.0674x	10	32	1.30
[VO(DMEP)(Bphen)]	0.4-16	0.053+0.0717x	9	30	1.32
[VO(DMEP)(Dip)]	0.2-16	0.059+0.0651x	10	32	1.30
[VO(DMBP)(Phen)]	0.3-18	0.053-0.0715x	9	30	1.32

Table 5: Comparative characteristics of methods for determining vanadium.

Reagent	Medium (solvent)	λ, nm	e×10^{-4}	Area of compliance with Beer's law (μg/ml)
Sulfonitrazole	2.3	522	2.06	
8-mercaptopyrimidine	4.0 - 5.5 (chloroform, toluene)	412	0.30	0.5–1.5
8-hydroxyquinoline/	3.0–5.0 (chloroform)	550	3.0	-
H_3PO_4 +Na2WO4	0.25M H_2SO_4 (water)	400	0.14	-
[VO(DMMP)(Phen)]	7.0-7.7 (chloroform)	628	3.61	0.5-16
[VO(DMEP)(Phen)]	6.7-7.5 (chloroform)	625	3.71	0.2-18
[VO(DMEP)(Bphen)]	6.9-7.6 (chloroform)	615	3.84	0.4-16
[VO(DMBP)(Phen)]	7.0-7.9 (chloroform)	630	3.85	0.3-18

Analytical application

The developed methods were applied to determine vanadium in soils, plants and water. The developed methods for determining the vanadium content in soils were controlled by the 8- hydroxyquinoline and formaldehyde methods [8]. The results of the determination are presented in Table 6-8.

Table 6: Results of vanadium determination in soil (section depth 10–20 cm) (n = 6, p = 0.95).

Methods	$\bar{X}$, %	S	Sr	$\bar{X} \pm \frac{t_P \cdot S}{\sqrt{n}}$
Soil				
8-hydroxyquinoline	$1.12 \cdot 10^{-2}$	0.000448	0.042	$(1.12 \pm 0.47) \cdot 10^{-2}$
Formaldhoxime	$1.14 \cdot 10^{-2}$	0.000581	0.051	$(1.14 \pm 0.60) \cdot 10^{-2}$
[VO(DMEP)(BPhen)]	$1.14 \cdot 10^{-2}$	0.000402	0.034	$(1.14 \pm 0.44) \cdot 10^{-2}$
[VO(DMEP)(Dip)]	$1.12 \cdot 10^{-2}$	0.000365	0.035	$(1.12 \pm 0.38) \cdot 10^{-2}$
[VO(DMBP)(Phen)]	$1.13 \cdot 10^{-2}$	0.000429	0.038	$(1.13 \pm 0.45) \cdot 10^{-2}$

	Methods	$\bar{X}$, mg/kg	S	Sr	$\bar{X} \pm \frac{t_P \cdot S}{\sqrt{n}}$
Rice	8-hydroxyquinoline	1.12	0.048	0.043	1.12 ± 0.051
	Formaldoxime	1.14	0.068	0.060	1.14 ± 0.070
	DMP+Phen	1.15	0.049	0.043	1.15 ± 0.052
	DMP+Dip	1.12	0.050	0.045	1.12 ± 0.052
	DMMP+Phen	1.12	0.054	0.048	1.12 ± 0.060
Potatoes	8-hydroxyquinoline	6.14	0.304	0.051	6.14 ± 0.32
	Formaldoxime	6.10	0.244	0.040	6.10 ± 0.25
	Phosphorus tungsten	6.15	0.234	0.038	6.15 ± 0.24
	DMP+Phen	6.12	0.182	0.029	6.12 ± 0.21
	DMP+Dip	6.13	0.272	0.045	6.13 ± 0.29
	DMMP+Phen	6.08	0.225	0.038	6.05 ± 0.25
	DMBP+Phen	6.10	0.15	0.025	6.10 ± 0.16
Carrot	8-hydroxyquinoline	1.00	0.033	0.033	1.00 ± 0.034
	DMMP+Phen	0.98	0.041	0.042	0.98 ± 0.043
	DMBP+Phen	1.02	0.042	0.042	1.02 ± 0.044
Beans	8-hydroxyquinoline	1.82	0.071	0.039	1.82 ± 0.075
	DMMP+Phen	1.85	0.068	0.037	1.82 ± 0.072
Barley	8-hydroxyquinoline	1.69	0.046	0.027	1.69 ± 0.048
	DMMP+Phen	1.71	0.058	0.035	1.71 ± 0.069

Table 7: Results of vanadium determination in plants (n = 6, p = 0.95).

Table 8: Results of vanadium determination in water with DMBP and Phen (n = 6, p = 0.95).

Added V, (μg/ml)	Found V, (μg/ml)		S	Sr	$\bar{X} \pm \frac{t_P \cdot S}{\sqrt{n}}$
	Known 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, spectrophotometric methods were used to study the complexation reactions of vanadium(IV) with dimercaptophenols (2,6-dimercaptophenol, 2,6-dimercapto-4-methylphenol, 2,6- dimercapto-4-ethylphenol, and 2,6-dimercapto-4-tert-butylphenol) and hydrophobic amines were studied using spectrophotometric methods. Heterocyclic diamines 1,10-phenanthroline, 2,2/- dipyridyl, and 4,7-diphenyl-1,10-phenanthroline were used as hydrophobic amines. The conditions for the formation, extraction, composition, physicochemical, and analytical properties of the complexes were determined. The structure of the complexes was determined by IR spectroscopy and thermogravimetry. Sensitive and selective methods for the extraction and spectrophotometric determination of vanadium were developed. The methods were applied to determine vanadium in soils, plants, and water. The data obtained were statistically processed.

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