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Study Of The Interaction Of Vanadium(IV) With Dimercaptophenols In The Presence Of Heterocyclic Diamines

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***Abstract*—A simple and spectrophotometric methods has been developed for the determination of trace amounts of vanadium (IV). Dimercaptophenole (DP) has been synthesized and characterized with IR and NMR spectroscopic methods. The reagents forms an blue coloured insoluble in water complex with vanadium(IV) in a weakly acidic and slightly alkaline medium (pH 2.5-8.5). In the presence of hydrophobic amines (Am) form ternary complexes. As hydrophobic amine 1,10-phenantroline (Phen), batophenantroline (BPhen), dipiridile (Dip) and o-aminopyridine (o-AmPy) were used. The molar absorptivity of coloured species are (2.95-3.85)×10^4 L.mol^{-1} cm^{-1}. Beer's law is obeyed in the range 0.2-18 µg/ml of vanadium (IV) at λ_{max} 610-630 nm. Vanadium (IV) forms 1:1:1 complex with DP and Am, stability constant of the complex was found to be 9.58-10.95 (pH$_{opt}$ 5.0-7.9). The proposed methods was successfully applied to the analysis of vanadium in oil and its refined products. The results obtainned were agreed with the reported methods at the 98 % confidence level. The optimum reaction conditions and other analytical parameters were investigated to enhance the sensitivity of the present method. The detailed study of various interferences made the method more selective.**

Keywords—1,10-phenantroline, batophenantroline, dipiridile, o-aminopyridine spectrophotometry, vanadi-um(IV,V).

1. Introduction

Vanadium and its compounds are toxic at excessive entry into the body (respiratory irritation, asthma, nervous disorders, changes in blood counts) their content is subject to control in assessing the quality of food products, raw materials and drinking water [1]. In addition, vanadium - trace mineral that is part of the microorganisms and is involved in the regulation of carbohydrate meta-bolism, cardiovascular activity, stimulates growth and cell reproduction.

Vanadium also present in relatively higher concentrations in crude oils and coal and their combustion gives rise to the higher concentrations of vanadium in the atomphere. Indsutrial effluent from titanium and uranium processing plants as well as steel indusrties contain higher concentrations of vanadium [2,3,4]. Inorganic elements are found in crude oil in trace amounts, mainly in the form of organic complex compounds. Some metals are indicative of the quality and perfor-mance of the oil. Information on the content of metals in oil and oil products is very important not only for oil refining, but also for environmental monitoring and geological research.

Vanadium in higher concentrations is toxic to humans [5] and its toxicity includes respiratory illness [6] and a number of disorders including interference with a number of essential enzyme systems [7]. The toxicity of vanadium is determined by its oxidation state, which ranges from -1 to +5, amongst which oxidation states 2 to 5 are the most stable in solution, V(V) followed by V(IV) [3]. However, vanadium with an oxidation state V(V) is more toixc than other states [8].

The vanadium is an important alloying element and is present as minor constituent in many industrially important materials. Even small amounts cause tremendous increase in hardness and strength. The increasing use of the metal necessitates development of rapid and sensitive methods for the determination of minute quantities of the metal. Vanadium belongs to the III class of hazards and its content is subject to control in the assessment of the quality of food products, raw materials and drinking water. These properties make it necessary to monitor the compounds of vanadium in the environment. Recently, vanadium has been noticed as the index element in urban environmental pollution, especially air pollution [9]. Therefore, the development of new sensivity, selective and accessible methods for determining the trace amounts of vanadium in various objects is an urgent task.

Various instrumental techniques, such as inductively coupled plasma atomic emission spectrometry (ICP-AES) [10], mass spectrometry (ICP-MS) [11] and atomic absorption spectrometry (AAS) [12] have been used for the determination of total vanadium, but for the nanogram (ng) or lower amounts, these methods can be applied only after preliminary isolation and preconcentration, and costly instruments are required [13,14,15]. However, spectrophotometric methods are ge-nerally preferred; as they involve less expensive instrumentation and afford better sensitivity when appropriate chromogenic reagents and solvent extraction preconcentration steps are employed. The-refore, a wide variety of spectrophotometric methods for the determination of vanadium have been reported [16- 26].

The spectrophotometric method is still an attractive method for determining metal ions in va-rious objects, since it is simple, inexpensive and easily accessible. Oxyphenolate and dimerkap-toophenolate complexes of Co(II), Nb(V), V(IV) and Mo(V) insoluble in chloroform, while mixed-ligand complexes with hydrophobic amines and aminophenols easily dissolve in various organic solvents [27-32]. In this respect, a very promising reagent is dimercaptophenols (DP), which contains one hydroxyl and two sulphohydryl groups and is a sulfur-containing analogue of mononuclear polyphenols with two oxygen atoms replaced with sulfur atoms. The real work is devoted to studying of reaction of a complex formation of vanadium(IV) with 2,6-dimercaptophenol (DMP), 2,6-dimercapto-4-methylphenol (DMMP), 2,6-mercapto-4-ethylphenol (DMEP) and 2,6-dimer-capto-4-tertbutylphenol (DMBP) in the presence of hydrophobic amines (Am). As hydrophobic amine 1,10-phenantroline (Phen), batophenantroline (BPhen), dipiridile (Dip) and *o*-aminopyridine (*o*-AmPy) were used.

2. EXPERIMENTAL

2.1.Instrumentation

The absorbance of colored solutions was measured at 20 ± 1°C using a KFK-2 photoelectro-colorimeter and Shimadzu UV1240 spectrophotometer in cells 0.5 and 1.0 cm in thickness, respectively. The equilibrium value of the pH of aqueous phase was measured using a I-120.2 potentiometer with a glass electrode. ESR spectra of solutions of mixed-ligand complexes were registered on a JEOS-JES-PE-3X spectrometer (Japan) with working a frequency of 9400 MHz. Muffle furnace was used for dissolution of the samples. IR spectra were recorded on a spectrophotometer "Specord M 80" (Germany). ^{1}H-NMR spectra were recorded on "Bruker" Fourier Transform (300.18 MHz) in C_6D_6. The process of thermolysis of the compounds was studied using derivatograph system «Shimadzu TGA-50H». Elemental analysis was performed using a TruSpec elemental analyzer (Leco).

2.2.Reagents and solutions

Stock solutions (1.96×10^{-2}M) of V(IV,V) were prepared from chemically pure salts $VOSO_4\cdot 3H_2O$ and $NaVO_3\cdot2H_2O$. The working solutions with concentration 0.1mg/mL were prepared by appropriate dilution of the stock solutions. The concentration of solutions of V(V) and V(IV) was determined by titration with iron(II) salts and potassium permanganate, respectively [33].

We used a 0.01 M DP and Am solution in chloroform. An optimum acidity was created by means of 0.01 M HCl or an ammonium acetate buffer solution. Chloroform was purified by washing with conc. H_2SO_4 and shaking with distilled water followed by washing with a 5% solution of NaOH.

2.3. Characterization of the reagent

DP were synthesized according to the procedure [34]. The reagent was characterized by taking the elemental analysis, NMR and IR spectra (table 1) [35-37].

Table 1. The research results of IR and NMR spectroscopy

Reagent	IR (KBr), см$^{-1}$	^{1}H NMR (300.18 MHz, C_6D_6)
DMP	3470 v(OH), 3050 v(CH), 2580 v(SH), 1580 v(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 v (OH), 3050 v(CH), 2570 v(SH), 2962 and 2872 v(-CH_3), 1555 δ(C_6H_5), 1390 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 v(OH), 3050 v(CH), 2575 v(SH), 2965 and 2874 v(-CH_3), 1555 δ(C_6H_5), 1460 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 v(OH), 2568 v(SH), 3040 v(CH), 1535 v(C_6H_5), 1395 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--$C(CH_3)_3$).

2.4. General procedure for the determination of vanadium

Required aliquots of solution containing different amounts (0.2-18μg/ml) of vanadium (IV) were transferred into were calibrated test tubes with ground-glass stoppers (the volume of the organic phase was 5 mL). 2.5 mL portion of a 0.01 M solution of DP, and a 2.0 mL portion of a 0.01M soluti-on of Am were added and the required value of pH was adjusted by adding 1M HCl (the volume of the organic phase was 5 mL). The volume of the aqueous phase was increased to 20 mL with distilled water. In 10 minnute after the complete separation of the phases, the organic phase was separated from the aqu-eous phase and the absorbance of the extracts was measured on KFK-2 at room temperature and 590 nm (*l*=0.5cm).

2.5. Determination of vanadium in soils

A 0.5-1.0 g weight was finely ground in an agate mortar and calcined in muffle furnace for 3 h. After cooling, the sample was treated and dissolved in a graphite cup in a mixture of 16 mL of HF (conc.), 5 mL of HNO_3 (conc.), and 15 mL of HCl (conc.) at 50-60 ^oC to remove excess hydrogen fluoride. A further 8 mL portion of HNO_3 (conc.) was added triply to the solution that was each time evaporated to 5-6 mL. After that, the solution was transferred into a 100 mL volumetric flask and its volume was brought to the mark with distilled water. Vanadium was determined in aliquots of the solution using the procedure proposed by us.

2.6. Preparation of environmental water samples

The water samples were filtered through Whatman No. 40 filter paper then 100 mL of each filtered water sample was accurately transferred into a 250 mL round bottom flask, and 10 mL of a mixture consisting of HNO_3 and H_2O_2 (1: 9, v/v) were added. These samples were digested by heating under reflux for 1.5 h. The cooled samples were transferred into 100 mL volumetric flask and made up to the mark. With deionized distilled water, mixed well, then subsequently analysed by the proposed spectrophotometric methods.

2.7. Preparation of food samples

A 1 g sample of a plant product is transferred into a porcelain crucible and placed in a muffle furnace for 2 hours at a temperature of about 400 ° C. The precipitate is treated with 40 ml of NaOH, concentration 1 mol / L with heating, then filtered on a paper filter, the solution is neutral-lized with 8 ml of chloride acid, concentration 4 mol / L. The test solution is transferred into a 50 ml flask and made up to the mark with distilled water. The vanadium content is determined by a calibration curve constructed under similar conditions.

3. RESULTS AND DISCUSSION

V(IV) reacts with DP gives a bluish green colored complexes. These complexes are insoluble in non-polar solvents. When hidrophob amins (Am) were introduced into the system, the extraction of these compounds into the organic phase as a mixed-ligand complex (MLC) was observed. DP are weak tribasic acid (H_3R) and depending on the pH of the medium may be in molecular and tree anionic forms.

It was found that the spectrophotometric characteristics of the MLC of vanadium(IV) and vanadium(V) were identica, i.e., in the interaction with DMMP, V(V) was reduced to V(IV) and VO^{2+} was the complexproducing form. This fact was also confirmed by ESR spectrometry [38]. Vanadium [V] does not have unpaired electrons and is diamagnetic, while vanadium(IV) has one d electron and exhibits electron paramagnetic absorption. According to the value of the nuclear spin j=7/2, the ESR spectra of vanadium(IV) consisted of eight lines with the hyperfine structure associated with the interaction of the magnetic moment of an unpaired electron with the magnetic moment of the ^{51}V nucleus. Hyperfine structure consisting of 8 lines was observed in the ESR spectra of chloroform extracts of MLC from aqueous solutions of V(IV) and V(V) salts. Hence, in the complex formation with DMMP, vanadium(V) is reduced to vanadium(IV) by the reagent itself. The results of the studies are presented in fig.1.

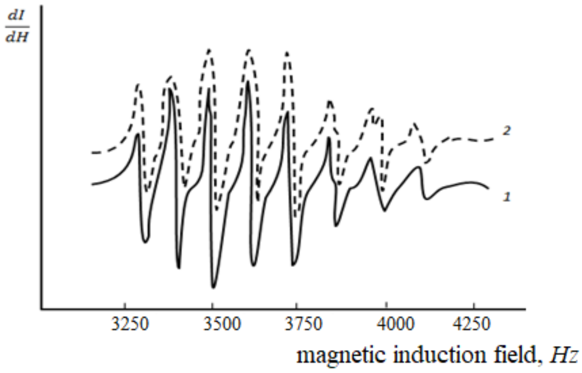

Fig.1: Hyperfine splitting of the paramagnetic resonance line in solutions:

(1) V(IV)-DMMP-Phen and (2) V(V)-DMMP-Phen.

3.1. Effect of pH

The effect of pH on the intensity of the color reaction is shown in the Fig.2. The absorbance was found to be maximum in the pH range 5.0-7.9. Hence further analytical investigations were carried out in media of pH 7. The acidity of the aqueous medium was set by the addition of buffer solution, prepared by mixing 2 mol l^{-1} aqueous solutions of CH_3COOH and NH_4OH. With further increase in the acidity of the aqueous phase, the recovery of vanadium (IV) decreases. This is because with increasing acidity, the concentration of the anionic reactive form of vanadium (IV) decreases. with an increase in the pH of the aqueous phase, the concentration of HR^{2-} and R^{3-}

increases, which leads to the formation of non-extractable complexes $[V(DP)_2]^{4-}$

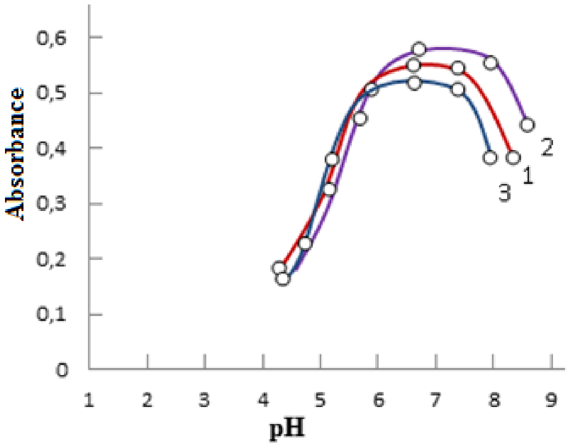

Fig. 2. Absorbance of mixed-ligand complexes as a function of the ph of the aqueous phase

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

$C_V = 3.92\times10^{-5}$M, $C_{DP} = 1.0 \times10^{-3}$ M, $C_{Am} = 8.0\times10^{-4}$ M, КФК-2, λ = 590 nm, ℓ =0,5 cm.

3.2. Effect of extractants

V(IV) reacts with DP and gives a blue colored complexes. These complexes are insoluble in non-polar solvents. When hidrophob amins (Am) were introduced into the system, the extraction of these compounds into the organic phase as a mixed-ligand complex (MLC) was observed.

The extraction of the complex has been tried with several solvents: chloroform, 1,2-dichloroethane, tetrachloromethane, chlorobenzene, benzene, toluene, *o*-xylene, isobutanol, isoamyl alcohol, cyclohexane, ethyl acetate, *n*-butanol, isoamyl acetate,benzoyl alcohol and their mixes. Extractibility of complexes was estimated in coefficient of distribution and extent of extraction. Thus basicity of amines has no noticeable impact on conditions and extraction of complexes. Fast division of layers and the maximum value of molar coefficient of absorption were received at extraction of complexes by chloroform. Organic solvents used for extraction of V(V) can be arranged on the basis of their extraction coefficient values as chloroform > carbon tetrachloride > dichlorethane > chlorbenzene > toluene > benzene > ethyl acetate > n-butanol > iso amyl alcohol> benzoyl alcohol (fig.3). Chloroform was found to be the best extracting solvent hence; it was selected for the extraction throughout the work. After a single extraction with chloroform, 98.6-99.5% of vanadium was extracted as an mixed-ligand complex (in a case the dichloroethane and carbon tetrachloride was removed 95.8-97.5 % of vanadium). The concentration of vanadium(IV) in the organic phase was determined photometrically by using 8-hydroxyquinoline [39] after reextraction, and in the aqueous phase, its concentration was found by the differrence.

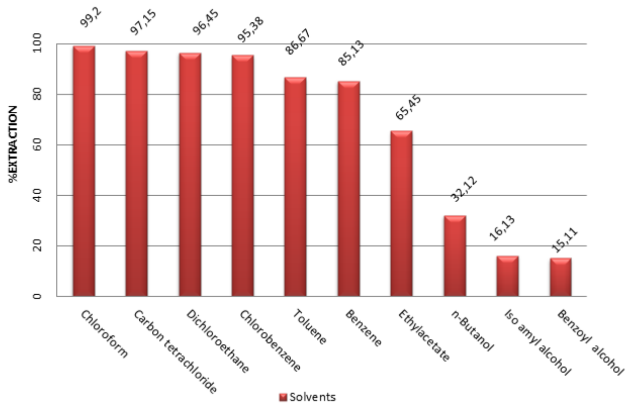

Fig. 3. Effect of solvents on extraction of V(IV) as V-DMEP-BPen

3.3. Electronic absorption spectra

The proposed method involved the formation of a blue-green color between vanadium(IV) and DP in a medium of pH 6.4-7.9. The figure revealed that V(IV)-DP-Am complex has maximum absorbance at 610-630 nm (fig 4). Neither the metal ion nor the reagent has appreciable absorbance at specified wavelengths. Hence further studies were carried out at 590 nm. The molar coefficient of light absorption is $(2.95\text{-}3.85)\times10^4$ L mol^{-1} cm^{-1}.

The color reaction was instantaneous and the absorbance of the complex solution was found to remain constant for at least five hours.

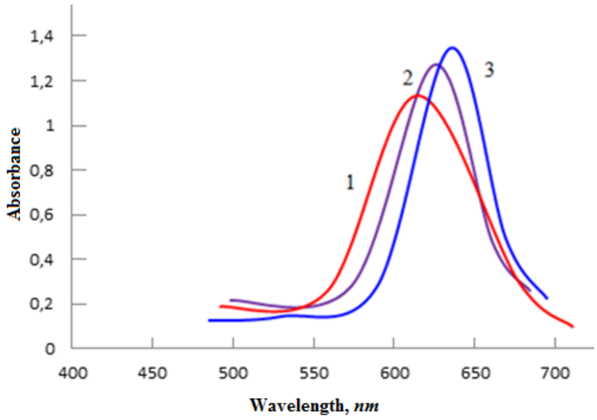

Fig 4. Absorption of mixed-ligand complexes V(IV)-DP-Am.

1) V(IV)-DMP-Phen, 2) V(IV)-DMEP-Phen, 3)-V(IV)-DMBP-Phen

$C_{V(IV)} = 3.92\times10^{-5}$M, $C_{DP} = 1.0 \times10^{-3}$ M, $C_{Am} = 8.0 \times10^{-4}$ M; Shimadzu 1240, ℓ=1 см.

3.4. Effect of temperature

The impact of temperature on the absorption of V(IV)-DP-Am complex has been studied in the range of 25-80 °C. MLC attained maximum and constant absorbance at 15-70 °C (fig 5). All subsequent measurements were done at room temperature (25±1 ^{o}C).

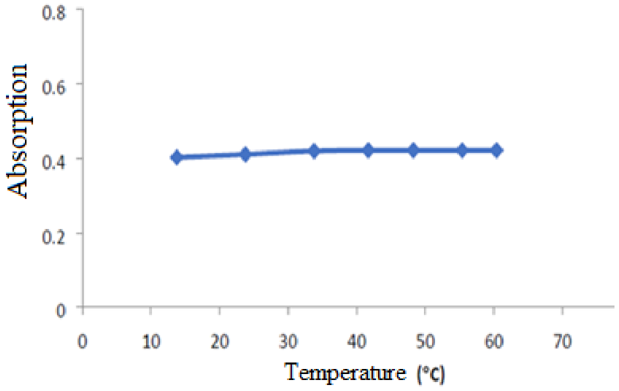

Fig.5.Effect of temperature on the absorbance of V-DMEP-Phen

3.5. Effect of reagents concentration

The studies on effect of various concentrations of the reagent on the color reaction reveal that, a reagent excess of 5-10 fold was required for the V(IV,V)-DP-Am color reaction. However it was found that the presence of excess of the reagent solution does not alter the absorbance of the color reaction. For the formation of mixed-ligand complex V(IV,V)-DP-Am, the concentration of 1.0 ×10^{-3} M of DP and 8.0×10^{-4} M of Am in the solution is required. It is known that π-reverse ligands facilitate the attachment of other ligands.

3.6.Effect of Time

Unlike single-ligand complexes, mixed-ligand complexes of vanadium(IV,V) with DP and Am were stable in aqueous and organic solvents and did not decompose for 48 hours, or over a month after extraction. The results show that for V(IV,V)-DP-Am complex the optimum time of 10 min for full color development is determined as shown in Fig.6.

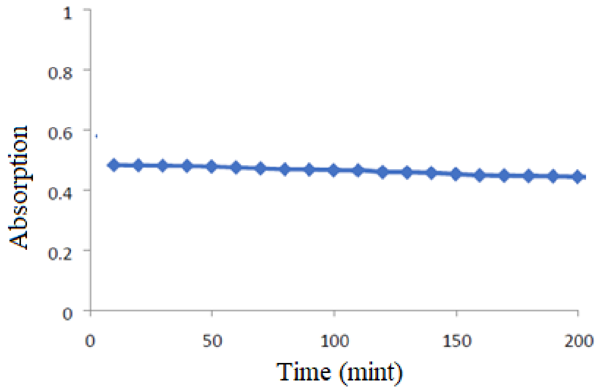

Fig. 6. Effect of time on the absorbance of V-DMEP-Phen

3.7. Stoichiometry of the complexes and the mechanism of complexation

The ratio of components in the complex corresponds to V(IV) : DP : Am = 1:1:1; it was determined by the methods of straight line, equilibrium shift, and the relative yield [40] (Fig.7). It was found using the Nazarenko method that V(IV) in the complexes was present in the form of VO^{2+}. The number of protons replaced by vanadium in one DP molecule appeared to be one [41, 42].

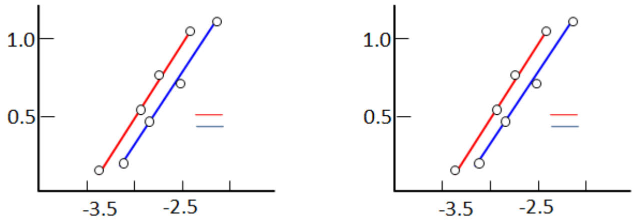

Fig. 7: Determination of the ratio of components by the equilibrium shift method for (a) V(IV)-DMMP-Phen and (b) V(IV)-DMEP-Dip. 1- V:DP; 2- V : Am.

C_V=3.92×10^{-5} M. Shimadzu 1240, l=590 nm, *l*=1cm

Infrared Spectral Studies. The IR spectra of the metal complexes were recorded for KBr discs over the range 4000–400 cm^{-1}. The disappearance of the pronounced absorption bands in the 3250-3620 cm^{-1} with a maximum at 3475 cm^{-1} observed in the spectrum of DMMP, says that the -OH group is involved in the formation of the complex. The observed decrease in the intensity, absorption bands in the area 2570 sm^{-1} shows that one of the -SH groups involved in the formation of coordination bond in the ionized state. Detection of the absorption bands at 1380 cm^{-1} indicates the presence of a coordinated phenantroline [36, 37]. The intense absorption band at 980 cm^{-1} is due to the stretching vibration of the VO^{2+} group. In addition, in the spectra of these compounds are present bands at 1610–1566 and 1498-1409 cm^{-1}, corresponding to $\nu_{C=C}$ and $\nu_{C=N}$ heterocyclic ligand.

Thermogravimetric study of the complex V(IV)-DMEP-Phen shows that the rapid expansion of the complex starts at 480^{o}C. wherein the mass loss of 49.1% (calculated 49.7 %), which corresponds to the removal phenanthroline. At 510-650 °C stands DMEP mass loss of 39.1% (calculated 39.7%). Further, when heated to 675^{o}C formed V_2O_5 (Fig. 8). .

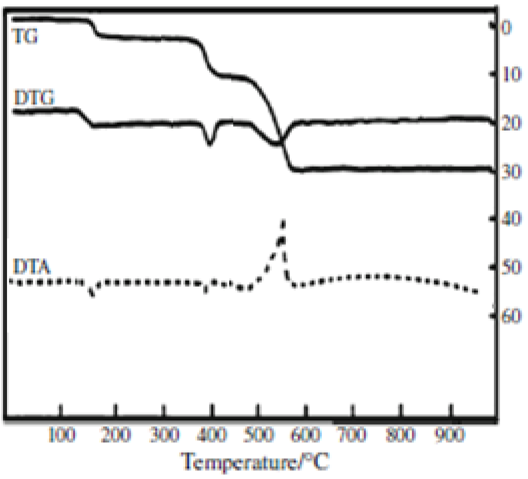

Fig. 9. Thermogram of the complex V(IV) -DMEP-Phen

Proceeding from the obtained data, we propose the following structure for the extracted mixed ligand complex (Fig. 9).

Elemental analysis was performed using a TruSpec elemental analyzer (Leco) (table 2).

Table 2. Elemental analysis results for mixed ligand complexes

Compound	%	M	S	C	N	H	O
[VO(DMEP)(Phen)]	Found	8.79	10.90	65.98	4.73	4.19	5.41
	Calculated	8.75	10.97	65.90	4.80	4.12	5.49
[VO(DMEP)(BPhen)]	Found	12.59	15.63	53.11	6.92	3.85	7.90
	Calculated	12.52	15.71	53.04	6.88	3.92	7.85
[VO(DMEP)(Dip)]	Found	14.71	18.59	45.30	8.05	4.68	8.94
	Calculated	14.69	18.53	45.36	8.15	4.67	8.90

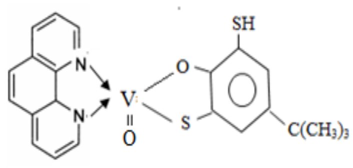

Fig. 9: Structure of complex VO(DTBP)(Phen)

The stability constant of V(IV)-DP-Am complexes was calculated by method of crossing of curves [34] and found to be lgβ = 9.58-10.95 at room temperature.

The sizes of equilibrium constant K ecalculated on a formula lgKe= lgD - lg[Am] were presented in Table 3. Mixed-igand complexes are more stable than homogeneous ligands due to the presence of π-interaction between ligands.

Additional experiments by the Akhmedly's method [43] showed that the complex exists in monomeric form in the organic phase (the obtained coefficient of polymerization γ was equal to 1.05 - 1.18). Sandell's sensitivity: 1.3-1.7 ng cm^{-2}.

Chemical-analytical parameters pertaining to the proposed methods are given in Table 3.

Table 3. Some chemical-analytical parameters of V(IV)-DP-Am complexes

Compound	pH_{opt}	Extraction ratio R	Coefficient of distribution D	□, nm	Δλ, nм	□$\times10^{-4}$	Equilibrium constants lgK_e	Constants of stability lgβ	Extraction constants lgK_{ex}
[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	344	3.62	5.54	10.12	12.70
VO(DMEP))(o-AmPy)]	5.0-6.6	98.7	304	620	244	3.05	5.35	10.04	12.53
[VO(DMBP)(Phen)]	7.0-7.9	99.5	796	630	350	3.85	5.50	10.83	12.91

3.7. Effect of foreign ions

The selectivity for the spectrophotometric determination of vanadium in the form of the complex described above is presented in Table 1. It is determined that Large amounts of alkali and alkaline-earth metals and REE do not interfere with the determination of vanadium. Ions of Ti(IV), Zr(IV), Fe(III), Cu(II), Cr(VI), Mn(VII), Mo(VI), W(VI), Nb(V) and Ta(V) form with DP and Am colored compounds and interfere with the determination of vanadium. The ions which show interference in the spectrophotometric determination of vanadium were overcome by using appropriate masking agents. The interference of Fe(III) was eliminated by orthophosphoric acid; Cu(II), Cr(VI), and Mn(VII) were masked by thiourea; Ti(IV)- ascorbic acid; and Zr(IV), Nb(V), and Ta(V) by fluoride ions. However, Nb(V) and Ta(V) form complexes in more acidic medium. Tartrate masks the milligram quantities of Ta, Ti, W and Mo. Zr fluorides should mask, and copper - thiourea. The influence of Mo, Co, Nb, Al, Zr was also eliminated with sodium citrate.

In conclusion the analytical parameters pertaining to the proposed method are given in the Table 4. These results reveal that various cations and anions can be tolerated at satisfactory levels.

Table 4: Influence of interfering ions on the determination of vanadium (IV) as MLC with DP and Am (30,0 μg V added)

Ion	*Molar Excess of the Ion*	*Masking agent*	Found V, μg (S_r)		
			DMP+Phen	DMMP +Phen	DMBP +Phen
Co(II)	120		29.8(0.04)	30.0(0.03)	30.0(0.03)
Ni(II)	120	NaCN	29.7(0.05)	30.2(0.03)	30.0(0.03)
Al(III)	100		30.2(0.04)	30.2(0.04)	30.2(0.03)

Fe(II)	45		30.2(0.03)	30.2(0.03)	30.2(0.04)
Fe(III)	50	NaF	30.5(0.05)	29.6(0.04)	30.2(0.03)
Cd(II)	65		29.6(0.06)	30.2(0.04)	29.6(0.04)
Zr(IV)	75	NaF	30.2(0.03)	29.7(0.05)	29.6(0.04)
Zn(II)	15		30.8(0.04)	30.2(0.04)	30.2(0.04)
Cu(II)	25	$Na_2S_2O_3$	29.6(0.04)	30.2(0.03)	30.2(0.03)
Hg(II)	10		30.0(0.03)	30.5(0.05)	30.5(0.05)
Ag(I)	20	KI	30.2(0.03)	29.6(0.06)	30.8(0.04)
Ti(IV)	20	Ascorbic acid	30.8(0.04)	29.7(0.05)	29.6(0.04)
Bi(III)	130		30.2(0.04)	30.2(0.04)	30.0(0.03)
W(VI)	20		30.2(0.03)	30.2(0.03)	30.2(0.03)
Mo(VI)	15	Citrate	30.2(0.04)	30.2(0.03)	30.8(0.04)
Cr(III)	90		30.2(0.03)	30.5(0.05)	30.2(0.04)
Nb(V)	45	NaF	30.2(0.04)	29.6(0.06)	29.6(0.04)
Ta(V)	50	NaF	30.2(0.03)	30.2(0.03)	30.2(0.04)
Pt(II)	50		29.6(0.04)	30.8(0.04)	30.2(0.03)
Pd(II)	50	Na_3PO_4	30.2(0.04)	29.6(0.04)	30.5(0.05)
Mn(II)	14		30.2(0.03)	30.2(0.03)	29.6(0.04)
UO_2^{2+}	50	CH_3COO^-	30.5(0.05)	30.5(0.05)	30.2(0.04)
Nitrate	400		29.6(0.04)	29.6(0.06)	30.2(0.03)
Tetraborate	1000		30.2(0.04)	30.2(0.03)	30.5(0.05)
Acetate	550		29.8(0.04)	30.0(0.03)	30.0(0.03)
Phosphate	650		29.7(0.05)	30.2(0.03)	30.0(0.03)
Chloride	370		30.2(0.04)	30.2(0.04)	30.2(0.03)
Tartrate	800		30.2(0.03)	30.2(0.03)	30.2(0.04)
Iodide	530		30.5(0.05)	29.6(0.04)	30.2(0.03)
Urea	450		29.6(0.06)	30.2(0.04)	29.6(0.04)
Thiocyanate	600		30.2(0.03)	29.7(0.05)	29.6(0.04)
Bromide	170		30.8(0.04)	30.2(0.04)	30.2(0.04)
Oxalate	480		29.6(0.04)	30.2(0.03)	30.2(0.03)
Fluoride	240		30.0(0.03)	30.5(0.05)	30.5(0.05)
MnO_4^-	100		30.2(0.03)	29.6(0.06)	30.8(0.04)
$Cr_2O_7^{2-}$	80	KSCN	30.8(0.05)	29.7(0.04)	29.6(0.04)
Sulfosalicylic acid	200		30.2(0.04)	30.2(0.04)	30.0(0.03)
Thiourea	360		30.2(0.03)	30.2(0.03)	30.2(0.03)
Citric acid	450		30.2(0.04)	30.2(0.03)	30.8(0.04)
Ascorbic acid	350		30.5(0.03)	30.5(0.04)	30.4(0.04)

3.8. Characteristics of the analytical method

A series of solutions containing different amounts of the metal ion were prepared as per the general experimental procedure. The absorbance of the solutions was measured at 590 nm. A calib-ration graph drawn between absorbance and the metal ion concentration indicates that V(IV) can be determined in the concentration range 0.2 to 18.0 μg mL^{-1}. The equations of the obtained straight lines and some important characteristics concerning the application of the ternary comp-lexes for extractive-spectrophotometric determination of V(IV) are listed in Table 5.

Table 5. Analytical features of the proposed method for determination of vanadium with DP and Am

Compound	Beer's law range(μg·ml^{-1})	The equation of calibration curves	Detection limits (ng mL^{-1})	Quantification limits (ng mL^{-1})	Sandell sensi-tivity (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(DMEP))(o-AmPy)]	0.2-16	0.039+0.0561x	11	35	1.67
[VO(DMBP)(Phen)]	0.3-18	0.053-0.0715x	9	30	1.32

The sensitivities expressed as molar absorptivity, of the proposed method are compared in Table 6 with those of published spectrophotometric methods.

Table 6. Comparison of selected reagents for the spectrophotometric determination of vanadium

Reagent	Medium (solvent)	λ, nm	$\varepsilon\times10^{-4}$	Linear range (ng mL^{-1})	References
Sulfonitrazo	2.3	522	2.06		39
8 -Mercaptoquinoline	4.0 – 5.5 (chloroform, toluene)	412	0,30	0.5-1.5	39,44
8-hydroxyquinoline	3.0 – 5.0 (chloroform)	550	3,00	-	39
H_3PO_4+$NaWO_4$	0.25M H_2SO_4 (water)	400	0.14	-	1, 39
2,4-dinitro phenyl hydrazine +*N*-(1-naphthalene-1-yl)ethane -1,2-diamine-dihydrochloride	8.0	495	2.22	0.02 - 8.0	45
3-hydroxy-2-[3-(4-methoxyphenyl)-1-phenyl4-pyrazolyl]-4-oxo-4H-1-benzopyran	0.02-0.12 M CH_3COOH (carbon tetrachloride)	415	2.74	0-2.2	46
[VO(DMMP)(Phen)]	7.0-7.7(chloroform)	628	3.61	0.5-16	This work
[VO(DMEP)(Phen)]	6.7-7.5(chloroform)	625	3.71	0.2-18	This work
[VO(DMEP)(BPhen)]	6.9-7.6(chloroform)	615	3.84	0.4-16	This work
[VO(DMEP))(o-AmPy)]	5.0-6.6(chloroform)	620	3.05	0.4-14	This work
[VO(DMBP)(Phen)]	7.0-7.9(chloroform)	630	3.85	0.3-18	This work

3.9. Analytical Applications

The proposed method has been applied for the determination of vanadium(IV) in plants, water and soil samples. The data presented in the Table 7, 8 and 9 indicate the accuracy and precision of the proposed method.

Table 7. Correctness and reproducibility of determination of vanadium levels in surface soil samples. n=5, P=0.95 *(Incision depth of 10 - 20 cm)* (*n* = 6, *p* = 0.95)

Soil sample	Procedures	$\bar{X}$,%	S	S_r	$\bar{X} \pm \frac{t_P \cdot S}{\sqrt{n}}$
Marine soil	8-Hydroxyquinoline	$1.12\cdot10^{-2}$	0.000448	0.042	$(1.12\pm0.047)\cdot10^{-2}$
	AAS	$1.14\cdot10^{-2}$	0.000581	0.051	$(1.14\pm0.060)\cdot10^{-2}$
	[VO(DTEP)(BPhen)]	$1.15\cdot10^{-2}$	0.000391	0.034	$(1.15\pm0.041)\cdot10^{-2}$
	[VO(DTEP)(Dip)]	$1.12\cdot10^{-2}$	0.000358	0.032	$(1.12\pm0.037)\cdot10^{-2}$
	[VO(DTBP)(Phen)]	$1.13\cdot10^{-2}$	0.000429	0.038	$(1.12\pm0.045)\cdot10^{-2}$
Agriculture soil	8-hydroxyquinoline	$1.59\cdot10^{-2}$	0.000715	0.045	$(1.59\pm0.078)\cdot10^{-2}$
	[VO(DTEP)(BPhen)]	$1.64\cdot10^{-2}$	0.000787	0.048	$(1.64\pm0.088)\cdot10^{-2}$
	[VO(DTBP)(Phen)]	$1.63\cdot10^{-2}$	0.000717	0.044	$(1.63\pm0.078)\cdot10^{-2}$
Industrial soil	8-hydroxyquinoline	$2.39\cdot10^{-2}$	0.000884	0.037	$(2.39\pm0.092)\cdot10^{-2}$
	[VO(DTEP)(BPhen)]	$2.42\cdot10^{-2}$	0.000847	0.035	$(2.42\pm0.089)\cdot10^{-2}$
	[VO(DTBP)(Phen)]	$2.38\cdot10^{-2}$	0.000998	0.042	$(2.38\pm0.105)\cdot10^{-2}$
River soils (soils of river floodplains)	8-hydroxyquinoline	$1.43\cdot10^{-2}$	0.000758	0.053	$(1.43\pm0.079)\cdot10^{-2}$
	[VO(DTEP)(BPhen)]	$1.45\cdot10^{-2}$	0.000565	0.039	$(1.45\pm0.059)\cdot10^{-2}$
	[VO(DTBP)(Phen)]	$1.39\cdot10^{-2}$	0.000583	0.042	$(1.39\pm0.061)\cdot10^{-2}$

Table 8. Determination of vanadium in plants, n=5, P=0.95 (*n*= 6, *p*=0.95)

Analyzed object	Procedures	$\bar{X}$, *mg/кg*	*S*	S_r	$\bar{X} \pm \frac{t_P \cdot S}{\sqrt{n}}$
Rice	8-hydroxyquinoline	1.12	0.048	0.043	1.12±0.051
	AAS	1.14	0.068	0.060	1.14±0.070
	DTP+Phen	1.15	0.049	0.043	1.15±0.052
	DTP+Dip	1.12	0.050	0.045	1.12±0.052
	DTMP+Phen	1.12	0.054	0.048	1.12±0.060
Potatoes	8-hydroxyquinoline	6.14	0.304	0.051	6.14±0.32
	Formaldoksim	6.10	0.244	0.040	6.10±0.25
	DTP+Phen	6.12	0.182	0.029	6.12±0.21

	DTP+Dip	6.13	0.272	0.045	6.13□0.29
	DTMP+Phen	6.08	0.225	0.038	6.05□0.25
	DTBP+Phen	6.10	0.150	0.025	6.10□0.16
Carrot	8-hydroxyquinoline	1.00	0.033	0.033	1.00□0.034
	DTMP+Phen	0.98	0.041	0.042	0.98□0.043
	DTBP+Phen	1.02	0.042	0.042	1.02□0.044
Beans	8-hydroxyquinoline	1.82	0.071	0.039	1.82□0.075
	DTMP+Phen	1.85	0.068	0.037	1.82□0.072
Barley	8-hydroxyquinoline	1.69	0.046	0.027	1.69□0.048
	DTMP+Phen	1.71	0.058	0.035	1.71□0.069
Radish	8-hydroxyquinoline	1.73	0.050	0.035	1.73□0.052
	DTEP+BPhen	1.75	0.047	0.027	1.75□0.049
Beet	8-hydroxyquinoline	0.81	0.036	0.045	0.81□0.038
	DTEP+BPhen	0.77	0.025	0.033	0.77□0.027

Table 9. Determination of vanadium levels in environmental water samples with DTBP and Phen (*n*= 6, *p*=0,95)

Added V (mg L^{-1})	Found V (mg L^{-1})		S	S$_r$	$\overline{X} \pm \frac{t_P \cdot S}{\sqrt{n}}$
	Standard Method	Present method			
River water					
1.0	1.006	1.0058	0.000168	0.028	0.0058□0.000175
2.0	2.006	2.0061	0.000259	0.037	0.0061□0.000272
3.0	3.008	3.0059	0.000171	0.029	0.0059□0.000170
Sea water					
2.0	2.0030	2.0029	0.00010	0.036	0.0029□0.000105
3.0	3.0025	3.0034	0.00012	0.035	0.0034□0.000125
Well water					
2.0	2.0015	2.0013	0.000056	0.043	0.0013□0.000059
3.0	3.0010	3.0011	0.000052	0.047	0.0011□0.000054
Tap water					
2.0	2.0020	2.017	0.000065	0.038	0.0017□0.000067
3.0	3.0018	3.018	0.000072	0.040	0.0018□0.000076

4. Conclusion

The proposed method has been applied to determine vanadium in natural waters, soil and food samples with good results. The proposed method is simple and more sensitive than other methods commonly used at microgram level, in addition to lower tolerance limits.

1. The results obtained show that the newly developed method in which the reagent dimercap-tophenols (DP) was used, can be effectively used for quantitative extraction and estimation of V(IV) from aqueous media.
2. Mixed-ligand complexes of vanadium(IV) with DP in the presence of Am have been investigated by spectrophotometric method.
3. Extraction of mixed ligand complexes is maximal at pH 5.0-7.9. The proposed method is quick and requires less volume of organic solvent.
4. The optimal conditions for the formation and extraction of mixed-ligand compounds have been found and the ratios of components in the complexes have been determined.
5. The Beer's law was applicable in the range of 0.2-18 µg/ml.
6. The calculated equilibrium constants and analytical characteristics (constant of extraction, constant of association, constant of distribution, recovery factor, molar absorptivity, Sandell's sen-sitivity, limit of detection and limit of quantification) show that the studied in the present work extraction-chromogenic system could compete successfully with similar systems used for deter-mination of vanadium.
7. A simple, rapid and sensitive methods proposed for the determination of trace amounts of vana-dium in in plants, water and soil samples. The methods is very precise, faster and simpler than other methods.

References

1. Muzgin V. N., Khamzina L.B., Zolotavin V. L., Bezrukov I. Y. Analiticheskaya khimiya vanadiya. M.: Nauka, 1981. 216 s.
2. Beusen J-M and Neven B. Toxicity of vanadium to different freshwater organisms. Bull Environ Contam Toxicol. 1987. 39. 2. pp. 194.
3. Amorim F.A.C., Welz B., Costa A.C.S., Lepri F. G., Vale M.G.R. ,Ferreira S. L.C. Determination of vanadium in petroleum and petroleum products using atomic spectrometric techniques. Talanta, 2007. 72. 2. pp. 349.
4. Akl M.A., El-Asmy A. A., Yossef W.M. Separation via flotation, spectrophotometric speciati-on, and determination of vanadium(IV) in wastes of power stations. Anal Sci, 2005. 21. 11. pp. 1325.

5. Pyrzynska K.,Wierzbicki T. Determination of vanadium species in environmental samples. Talanta. 2004. V. 64. No 4. pp. 823.

6. Woodin M. A., Liu Y., Neuberg D., Hauser R., Smith T. J., Christiani D. C. Acute respiratory symptoms in workers exposed to vanadium-rich fuel-oil ash. Am. J. Ind. Med. 2000. V. 37. No 4. pp. 353

7. Mukherjee B., Patra B., Mahapatra S., Banerjee P., Tiwari A.,Chatterjee M. Vanadium - an element of atypical biological significance. Toxicol Lett. 2004. 150. 2. p.135.

8. Patel B., Henderson G. E., Haswell S. J., Grzeskowiak R. Speciation of vanadium present in a model yeast system. Analyst.1990. V.15. No 8. pp. 1063.

9. Langard S., Norseth T., in: L. Friberg, G. F. Nordberg,V. B. Vouk (Eds.). Handbook on the Toxicology of Metals, Elsevier, Amsterdam. 1986.

10. Da Silva W.G.P., Campos R.C. Miekeley N. A simple digestion procedure for the determination of cadmium, copper, molybdenium and vanadium in plants by graphite furnace atomic absorption spectrometry and mass inductively coupled plasma spectrometry. Anal Lett. 1998. V.31. No 6. pp.1061.

11. Al-Swaidan H.M. Determination of vanadium and nickel in oil products from Saudi Arabia by inductively coupled plasma mass spectrometry (ICP/MS). Anal Lett.1993. V.26. No 1. p.141.

12. Adachi A., Asai K., Koyama Y., Matsumoto Y., Okano T. Determination of vanadium in cigarettes by atomic absorption spectrophotometry. Anal Lett.1998. V.31. No 10. pp. 1769.

13. Mohamed A. A. and El-Shahat M. F. A spectrophotometric determination of chromium and vanadium. Anal Sci. 2000. V.16. No 2. pp. 151

14. Gao J., Zhang X., Yang W., Zhao B., Hou J., Kang J. Kinetic-spectrophotometric determination of trace amounts of vanadium. Talanta. 2000. V. 51. No 3. p.447.

15. Safavi A., Sedghy H.R., Shams E. Kinetic spectrophotometric determination of trace amounts of selenium and vanadium. Fresen J. Anal. Chem.1999. 365. 6. p. 504.

16. Hu, Q., Yang, G., Huang, Z.,Yin, J. Study on Solid Phase Extraction and Spectrophotometric Determination of vanadium with 2-(2-quinolylazo)-5-diethylaminophenol. Bull. Korean Chem. Soc. 2004. V.25. No.2. pp. 263-266

17. Kumar Reddy K.V., Yamini P., Kumar R.K. Venkateswarlu P. Spectrophotometric method for determination of vanadium and its application to environmenttal and biological samples. International Journal of Chemical Engineering and Applied Sciences 2012. V. 2.No 1. pp. 1-5

18. Rana P., Lokhande R., Pitale S., Janwadkar S. Yadav D. Spectrophotometric determination of vanadium with acetophenone 2’,4’-dihydroxy thiosemicarbazone. International Journal of ChemTech Research. 2014. V.6, No.4. pp. 2295-2299

19. Priya B.K., Subrahmanyam P., Kumar J. D., Chiranjeevi P. Simple Sensitive Spectrophotometric Determination of Vanadium in Biological and Environmental Samples. E-Journal of Chemistry. 2006. V. 3. No.4. pp. 286-297.

20. Mastoi G.M.,Khuhawar M.Y. Kinetic spectrophotometric determination of vanadium(V) using ponceau S. Eurasian Journal of Analytical Chemistry. V. No 2, 2007. pp. 68-77.

21. Kiran Kumar T.N., Revanasiddappa H.D. Spectrophotometric determination of vanadium using variamine blue and its application to synthetic, environmental and biological samples. Iranian J. Chem. Soc, 2005, 2, pp. 161.

22. Bosque-Sendra J.M., Valencia L.C., Boudra S. Speciation of vanadium(IV) and vanadium(V) with Eriochrome Cyanine R in natural waters by solid phase spectrophotometry. Fresenius’J. Anal. Chem, 1998. 360. 31.

23. Shigenori N., Tanaka E., Mizutani Y. Flow-injection spectrophotometry of vanadium by catalysis of the bromate oxidation of N,N′-bis(2-hydroxyl-3-sulfopropyl)-tolidine. Talanta. 2003. 61. pp.203.

24. Kuliev K. A. Extraction-spectrophotometric determination of vanadium 2,6-dithiol-4-*tert*-butyl phenol and aminophenol. Journal of Analytical Chemistry. 2011. No1. pp. 1159-1164.

25. Viswanatha C., Praveen Kumar M.D., Ramakrishna Reddy K., Devanna N. Sensitive spectrophotometric determination of trace amounts of vanadium (V) in alloys and biological samples. International Journal of Inorganic and Bioinorganic Chemistry. 2012. V.2. No3. pp. 27-30.

26. Kuliev K.A., Aliev S.G., Suleymanova E.I., Sultanzade S.S., Maharramova L.M.,Melikova A.Y, Ismailova R.A. Sensitive spectrophotometric determination of trace amounts of vanadium (IV,V) using dithiolphenols and hydrofob amins. International Journal of Pharmaceutical Sciences and Research, **9**, 6, p.2211 (2018).

27. Kuliev K.A., Verdizade N.A., Aliev S.G., Abasquliyeva U.B., Efendieva N.N. Anaytical application of ion associates of molybdenum with dithiolphenols and aminophenols. Journal of Materials Science and Chemical Engineering, **7**, No 4, p. 1 (2019).

28. Kuliev K.A., Verdizadeh N.A., Suleymanova G.S. Spectrophotometric Determination of Cobalt(II) with 2,6-Dimercaptophenol and Its Derivatives in the Presence of Hydrophobic Amines, American Journal of Chemistry, 6, №4, p. 95 (2016).

29. Kuliev K.A., Verdizade N.A., Mamedova Sh.A. Development of extractive spectrophotometric methods for the determination of iron(III) with dimercaptophenole and heterocyclic diamines. *Journal of the Chemical Society of Pakistan*, **41**, p.993 (2019).

30. Kuliev K.A., Zalov A.Z., Verdezade N.A., G.S.Suleymanova. Study of Uranium(VI) Complexation with Dithiolphenols and Hydrophobic Amines. *Russian Journal of Inorganic Chemistry,* **64**, p.1522 (2019).

31. Zalov A.Z., Amanullayeva G.I. Spectrophotometric determination of cobalt(II) in a liquid-liquid extraction system containing 2-hydroxy-5-iodothiophenol and diphenylguanidine. *IJRDO-Journal Of Applied Science*, **2,** 7, p. 217 (2016).

32. Kuliev K.A., Verdizadeh N. A., Suleymanova G. S., Efendiyeva N.N.Solvent extraction of cobalt(II) with 2, 6-dithiolphenol and its derivatives in the presence of hydrophobic amines. Journal of the Chemical Society of Pakistan, 2020. V. 42, No. 02,pp.253-262

33. Korostelev P. P. Preparation of Solutions for Chemical Analysis Works. Publishing House of Academy of Sciences of the USSR. 1964.

34. Kuliev A.M., Aliev, S. R., Mamedov, F. N., Movsumzade, M. Synthesis of aminomethyl derivatives of 2-hydroxy-5-tert-alkylthiophenols and their cleavage by thiols. Zh. Org. Khim. 1976. V.12. No2, pp. 426-431.

35. Shrayner R., F'yuzon R., Kortin D., Morrill T. Identifikatsiya organicheskikh soyedineniy: Per. s angl. - M.: Mir, 1983. (In Russian)

36. Bellami L. Infrakrasnie spectri slojnikh molecule (The Infra-Red Spectra of Complex Molecules). Moscow, Mir, 1991.

37. Nakamoto K. (IK-spectr KR neorqaniceskikh i koordinatsionnikh soedineniy (Infrared and Raman Spectra of Inorganic and Coordination Compounds). Moscow, Mir. 1991.

38. Al'tshuler S. A., Kozyrev B. M., Elektronnyi paramagnitnyi rezonans soedinenii promezhutochnykh grupp (Electron Paramagnetic Resonance of the Compounds of Intermediate Groups), Moscow: Nauka, 1972.

39. Marczenko Z., Balcerzak, M. Metod'y spektrofotometrii v UF i vidimoj oblastyakh v neorganicheskom analize. Moskow, Binom. Laboratoriya znanij. 2007.

40. Bulatov M.I.,Kalinkin, I.P. Prakticheskoe rukovodstvo po fotokolorimetricheskim i spektrofotometricheskim metodam analiza (Practical guide on photocolorimetric and spectrophotometric methods of analysis). Moscow, Khimiya. 1972.

41. Nazarenko V.A. Tr. Komis. po analit. khimii Akad. Nauk SSSR. In: Proc. Comission on Analytical Chemistry of the USSR's Academy of Sciences. Moscow, Nauka.1969. 17. p. 22-27.

42. Nazarenko V.A., Biryuk E.A. A study of the chemistry of reactions of multi-valent element ions with organic reagents. Zh. Anal. Khim., 1967. V. 22. No1. pp. 57-64.

43. Akhmedly M. K., Kly'gin A.E., Ivanova L. I., Bashirov E. A. On the chemistry of interaction of gallium ions with a number of sulphophtaleins. Zhurnal Neorganicheskoi Khimii.1974. V.19. No 8. pp. 2007-2012.

44. Umland, F., Janssen, A., Thierig, D., Wünsch, G. Theorie und praktische anwendung von complexbildnern. Frankfurt am Main, Akademische Verlagsgesellschaft. 1971.

45. Priya B.K., Subrahmanyam P., Kumar J.D. [et al.] Simple sensitive spectrophotometric determination of vanadium in biological and environmental samples. E - Journal of Chemistry, -2006. V.3, №4, pp.286-297.

46. Agnihotri R., Agnihotri N., Kumar V. , Kamal R. Synthesis and application of 3-hydroxy-2-[3-(4-methoxyphenyl)-1-phenyl4-pyrazolyl]-4-oxo-4H-1-benzopyran for extractive spectrophotometric determination of vanadium (V). Der Chemica Sinica, 2017, V.8, № 1, pp.158-165.