IJPSR (2018), Volume 9, Issue 6 **(Research Article)**

INTERNATIONAL JOURNAL OF PHARMACEUTICAL SCIENCES AND RESEARCH

Received on 02 September, 2017; received in revised form, 09 November, 2017; accepted, 12 November, 2017; published 01 June, 2018

SENSITIVE SPECTROPHOTOMETRIC DETERMINATION OF TRACE AMOUNTS OF VANADIUM (IV, V) USING DITHIOLPHENOLS AND HYDROFOB AMINS

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Keywords:

New spectrophotometric reagents, Spectrophotometry, Vanadium (IV,V), Soil, Water, Biological samples

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ABSTRACT: Dithiolphenole (DP) has been synthesized and characterized with IR and NMR spectroscopic methods. A simple and spectrophotometric method has been developed for the determination of trace amounts of vanadium (IV, V). The reagents forms blue coloured insoluble in water complex with vanadium (IV, V) 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-phenantroline (Phen), batophenantroline (BPhen) and dipiridile (Dip) 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, V) at λ_{max} 610 - 630 nm. Vanadium (IV, V) forms 1: 1: 1 complex with DP and Am, stability constant of the complex was found to be 9.58 - 10.95 (pH_{opt} = 6.4 - 7.9). The proposed method was successfully applied to the analysis of vanadium in soil, natural water samples and plant material. 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.

INTRODUCTION: Vanadium - trace mineral that is part of the micro-organisms and is involved in the regulation of carbohydrate metabolism, cardiovascular activity, stimulates growth and cell reproduction. Among the products that contain vanadium, include: rice, beans, potatoes, barley, buckwheat, green salad, *etc*.

QUICK RESPONSE CODE

DOI: 10.13040/IJPSR.0975-8232.9(6).2211-20

Article can be accessed online on: www.ijpsr.com

DOI link: http://dx.doi.org/10.13040/IJPSR.0975-8232.9(6).2211-20

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]. Vanadium is present in abundance in the earth's crust [2]. It is also present in relatively higher concentrations in crude oils and coal [2, 3] and their combustion gives rise to the higher concentrations of vanadium in the atmosphere [2].

Industrial effluent from titanium and uranium processing plants as well as steel industries contain higher concentrations of vanadium [2, 4].

Vanadium is one of the essential trace elements for animals and plants; however, vanadium essentiality for humans has not been established [3]. Nevertheless, 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 toxic than other states [8]. The amount of vanadium in soils and plants has been found to be a critical factor in recent years. The metal 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.

Recently, vanadium has been noticed as the index element in urban environmental pollution, especially air pollution [9]. 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].

Colorimetric and atomic emission or atomic absorption methods are most commonly used for the determination of vanadium. However, colorimetric methods are generally preferred; as they involve less expensive instrumentation and afford better sensitivity when appropriate chromogenic reagents and solvent extraction preconcentration steps are employed. Most of the extractive spectrophotometric methods developed for vanadium are based on reactions with suitable colour producing reagents. However, most of the existing methods suffer from limitations such as longer periods of time for phase separations, weak stability of coloured complexes and interferences from metal ions like tungsten, tin, antimony and anions and various complexing agents. Therefore, a wide variety of spectrophotometric methods for the determination of vanadium have been reported[16 - 26].

In this respect, a very promising reagent is dithiolphenols (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-dithiolphenol (DTP), 2, 6-dithiol-4-methylphenol (DTMP), 2, 6-dithiol-4-ethylphenol (DTEP) and 2, 6-dithiol-4-tertbutylphenol (DTBP) in the presence of hydrophobic amines (Am). As hydrophobic amine phenantroline (Phen), batophenantroline (B. Phen) and dipiridile (Dip) were used. Based on these data, new selective and highly sensitive procedures were developed for the extraction-spectrophotometric determination of trace vanadium in soil, water and biological samples.

Experimental:

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. The process of thermolysis of the compounds was studied using derivatograph system «ShimadzuTGA-50H». 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.

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 $NaVO_3 \cdot 2H_2O$. The working solutions with concentration 0.1 mg/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 [27].

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.

Characterization of the Reagent: DP was synthesized according to the procedure [28]. The reagent was characterized by taking the elemental analysis, NMR and IR spectra **Table 1** [29 - 31].

TABLE 1: THE RESEARCH RESULTS OF IR AND NMR SPECTROSCOPY

Reagent	IR (KBr), см$^{-1}$	^{1}H NMR (300.18 MHz, C_6D_6)
DTP	3470 ν (OH), 3050 ν(CH), 2580 ν(SH), 1580 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)
DTMP	3460 ν (OH), 3050 ν(CH), 2570 ν(SH), 2962 и 2872 ν(-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)
DTEP	3460 ν (OH), 3050 ν(CH), 2575 ν(SH), 2965 и 2874 ν(-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)
DTBP	3458 ν(OH), 2568 ν(SH), 3040 ν(CH), 1535 ν(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--$C(CH_3)_3$)

Procedure:

General Procedure for the Determination of Vanadium (V): Required aliquots of solution containing different amounts (0.2 - 18 μg/ml) of vanadium (V) 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 solution 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 min after the complete separation of the phases, the organic phase was separated from the aqueous phase and the absorbance of the extracts was measured on KFK-2 at room temperature and 590 nm (*l* = 0.5cm).

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 hr. 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 50-60ºC 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.

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 hr. 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.

Preparation of Food Samples: A wet ash method was employed in the preparation of the sample solution. 0.5 g of the sample was dissolved in a 1:1 mixture of nitric acid and perchloric acid. The solution was evaporated to dryness, and the residue was ashed at 300 ºC. The ash was dissolved in 2 mL of 1M sulphuric acid and made up to the volume in a 25 mL standard flask with distilled water.

RESULTS AND DISCUSSION: V(V) 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 identical, *i.e.*, in the interaction with DTMP, V(V) was reduced to V(IV) and VO^{2+} was the complex – producing form. This fact was also confirmed by ESR spectrometry [32]. 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 DTMP, vanadium (V) is reduced to vanadium (IV) by the reagent itself. The results of the studies are presented in **Fig. 1**.

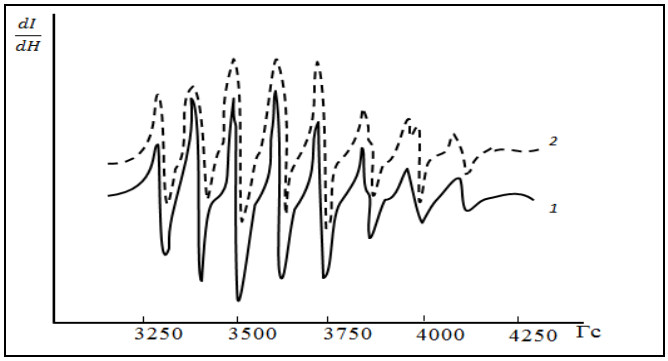

FIG. 1: HYPERFINE SPLITTING OF THE PARA-MAGNETIC RESONANCE LINE IN SOLUTIONS. (1) V (IV)-DTMP-Phen and (2) V(V)-DTMP-Phen.

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 6.4 - 7.9. Hence further analytical investigations were carried out in media of pH 7. With further increase in the acidity of the aqueous phase, the recovery of vanadium (IV, V) decreases. This is because with increasing acidity, the concentration of the anionic reactive form of vanadium (IV, V) decreases. At pH ≥ 9, the extraction of the complex is practically not observed, which is probably because a decrease in the degree of protonation of Am.

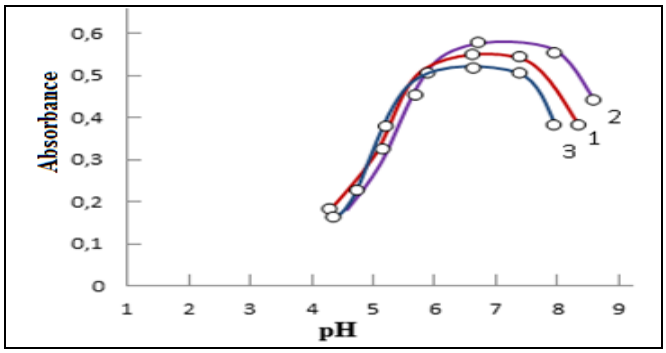

FIG. 2: ABSORBANCE OF MIXED - LIGAND COMPLEXES AS A FUNCTION OF THE PH OF THE AQUEOUS PHASE. 1. V (IV) - DTEP-Phen, 2. V (IV)-DTEP - BPhen, 3. V (IV) - DTEP - Dip**,** $C_V = 3.92 \times 10^{-5}$M, $C_{DP} = 1.0 \times 10^{-3}$M, $C_{Am} = 0.8 \times 10^{-3}$M, КФК-2, λ = 590 nm, λ= 0, 5 см.

Effect of Extractants: V(V) 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, benzene, chlorobenzene, toluene, o-xylene, isobutanol, isoamyl alcohol, cyclohexane, ethyl acetate, *n*-butanol, isoamyl acetate, benzoyl alcohol and their mixes. Extracti-bility 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 comp-lexes 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 [33] after reextraction, and in the aqueous phase, its concentration was found by the differrence.

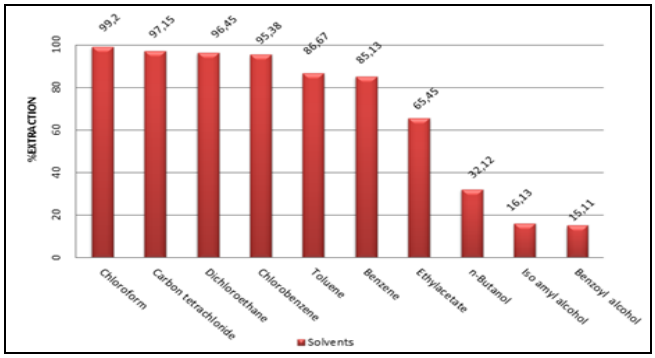

FIG. 3: EFFECT OF SOLVENTS ON EXTRACTION OF V(V) ASV-DTEP-BPEN

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 (2.95-3.85) × 10^4 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.

Effect of Temperature: The V(IV)–DP-Am system attained maximum and constant absorbance at 15 - 60 ºC. All subsequent measurements were done at room temperature (25 ± 1 ºC).

Effect of Reagent Concentration and Incubation Time: 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 0.8 × 10^{-3} M of Am in the solution is required. 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. After mixing thecomponents, the absorbance reaches its maximum within 10 min at room temperature.

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 [34] **Fig. 5**.

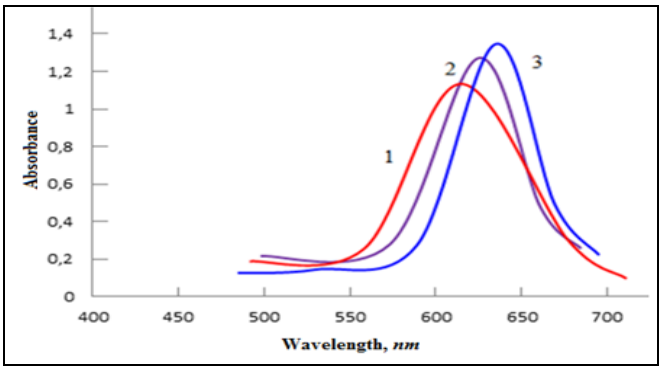

FIG. 4: ABSORPTION OF MIXED - LIGAND COMPLEXES V - DP -AM. V (IV)-DTP-PHEN (1), V(IV) - DTEP-PHEN (2), V(IV)-DTBP-PHEN (3) $C_{V(IV)}$ = 3.92×10^{-5}M, C_{DP} = 1.0 ×10^{-3}M, C_{Am}= 0.8 ×10^{-3}M; Shimadzu 1240, λ=1 см.

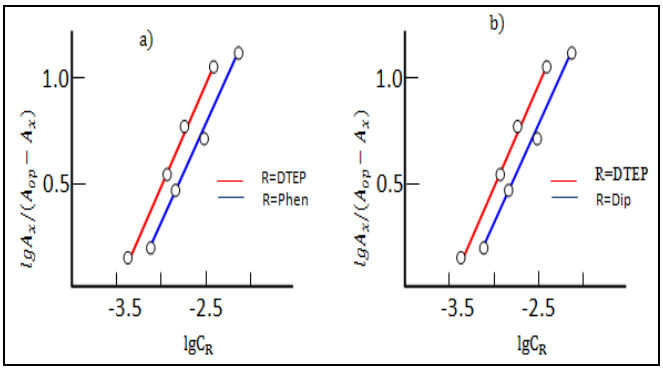

FIG. 5: DETERMINATION OF THE RATIO OF COMPONENTS BY THE EQUILIBRIUM SHIFT METHOD FOR (a) V(IV)-DTMP-Phen AND (b) V(IV)-DTEP-Dip. 1- V: DP; 2- V: Am. C_V = 3.92 × 10^{-5} M. Shimadzu 1240, l = 590 nm, l = 1cm

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 [35, 36].

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 DTMP, 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 [30, 31].

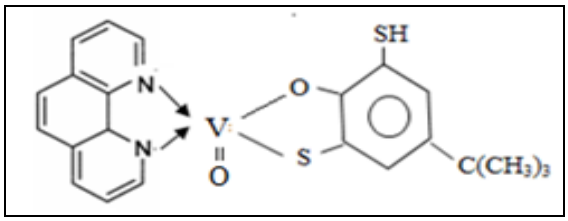

FIG. 6: STRUCTURE OF COMPLEX VO (DTBP) (PHEN)

Thermogravimetric study of the complex V(IV) - DTEP-Phen shows that the rapid expansion of the complex starts at 480 ºC. 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 ºC formed V_2O_5. Proceeding from the obtained data, we propose the following structure for the extracted mixed ligand complex **Fig. 6**.

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 Ke calculated on a formula lgKe = lgD - lg [Am] were presented in **Table 2**.

Additional experiments by the Akhmedly's method [37] 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).

Chemical-analytical parameters pertaining to the proposed methods are given in **Table 2**.

TABLE 2: SOME CHEMICAL-ANALYTICAL PARAMETERS OF V(IV)-DP-AM COMPLEXES

Compound	pH_{opt}	Extraction ratioR	Coefficient of distribution D	λ, nm	Δλ, нм	ε×10 $^{-4}$	Equilibrium constants lgK_e	Constants of stability lgβ	Extraction constants lgK_{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

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 Mo(VI), W(VI), Ti(IV), Zr(IV), Fe(III), Cu(II), Cr(VI), Mn(VII), Nb(V) and Ta(V) form with DTEP 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, Mo(VI), W(VI), Ti(IV), 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. In conclusion the analytical parameters pertaining to the proposed method are given in the **Table 3**. These results reveal that various cations and anions can be tolerated at satisfactory levels.

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 calibration 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 complexes for extractive spectrophotometric determination of V(IV) are listed in **Table 4**.

The sensitivities expressed as molar absorptivity, of the proposed method are compared in **Table 5** with those of published spectrophotometric methods.

TABLE 3: INFLUENCE OF INTERFERING IONS ON THE DETERMINATION OF VANADIUM (IV) AS MLC WITH DP AND AM

Ion	Molar Excess of the Ion	Masking agent	Found V, µg (S_r)		
			DTEP+Phen	DTEP+BPhen	DTEP+Dip
Co(II)	120		30.0(0.05)	29.8(0.04)	29.8(0.04)
Ni(II)	120	NaCN	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	NaF	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	$Na_2S_2O_3$	30.2(0.04)	29.5(0.04)	29.6(0.04)
Hg(II)	10		30.5(0.04)	29.5(0.05)	29.8(0.04)
Ag(I)	20	KI	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(0.03)	29.8(0.04)
Mo(VI)	15	Citrate	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)	29.3(0.05)	30.4(0.06)
Ta(V)	45	NaF	29.6(0.05)	29.6(0.05)	30.4(0.04)
Pt(II)	50		30.0(0.03)	29.4(0.03)	30.0(0.03)
Pd(II)	50	Na_3PO_4	30.2(0.03)	30.5(0.04)	30.2(0.03)
Mn(II)	14		29.6(0.04)	30.0(0.03)	30.6(0.06)
$UO^{2+}{}_2$	60	CH_3COO^-	29.8(0.04)	29.7(0.05)	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)	29.5(0.05)	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)	30.0(0.03)	30.2(0.03)
Iodide	530		29.8(0.04)	29.8(0.05)	29.5(0.04)
Urea	450		29.6(0.04)	29.8(0.03)	29.6(0.04)
Thiocyanate	600		30.2(0.04)	30.5(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)	30.0(0.04)	30.2(0.03)
$Cr_2O_7^{2-}$	80	KSCN	29.5(0.05)	30.6(0.05)	30.5(0.05)
Sulfosalicylic acid	200		29.6(0.05)	29.8(0.03)	29.6(0.05)
Thiourea	350		29.8(0.04)	29.7(0.04)	29.8(0.03)
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)

(30.0 µg V added)

TABLE 4: 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 (ngmL^{-1})	Sandell 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

Analytical Applications: The proposed method has been applied for the determination of vanadium (V) in plants, water and soil samples. The data presented in the **Table 6**, **7** and **8** indicate the accuracy and precision of the proposed method.

TABLE 5: COMPARISON OF SELECTED REAGENTS FOR THE SPECTROPHOTOMETRIC DETERMINATION OF VANADIUM

Reagent	Medium (solvent)	λ, nm	ε×10^{-4}	Linear range (ng mL^{-1})	References
Sulfonitrazo	2.3	522	2.06		32
8 -Mercaptoquinoline	4.0 – 5.5(chloroform, toluene)	412	0,30	0.5-1.5	33,38
8-hydroxyquinoline	3.0 – 5.0(chloroform)	550	3,00	-	33
H_3PO_4+$NaWO_4$	0.25M H_2SO_4(water)	400	0.14	-	1, 33
[VO(DTMP)(Phen)]	7.0-7.7(chloroform)	628	3.61	0.5-16	This work
[VO(DTEP)(Phen)]	6.7-7.5(chloroform)	625	3.71	0.2-18	This work
[VO(DTEP)(BPhen)]	6.9-7.6(chloroform)	615	3.84	0.4-16	This work
[VO(DTBP)(Phen)]	7.0-7.9(chloroform)	630	3.85	0.3-18	This work

TABLE 6: CORRECTNESS AND REPRODUCIBILITY OF DETERMINATION OF VANADIUM LEVELS IN SURFACE SOIL SAMPLES

Soil sample	Procedures	$\bar{X}$, %	S	S_r	$\bar{X} \pm \frac{t_p \cdot S}{\sqrt{n}}$
Marine soil	8-Hydroxyquinoline	1.12·10^{-2}	0.000448	0.042	(1.12±0.047)·10^{-2}
	AAS	1.14 ·10^{-2}	0.000581	0.051	(1.14±0.060) ·10^{-2}
	[VO(DTEP)(BPhen)]	1.15·10^{-2}	0.000391	0.034	(1.15±0.041) ·10^{-2}
	[VO(DTEP)(Dip)]	1.12 ·10^{-2}	0.000358	0.032	(1.12±0.037) ·10^{-2}
	[VO(DTBP)(Phen)]	1.13 ·10^{-2}	0.000429	0.038	(1.12±0.045) ·10^{-2}
Agriculture soil	8-hydroxyquinoline	1.59·10^{-2}	0.000715	0.045	(1.59±0.078)·10^{-2}
	[VO(DTEP)(BPhen)]	1.64 ·10^{-2}	0.000787	0.048	(1.64±0.088) ·10^{-2}
	[VO(DTBP)(Phen)]	1.63·10^{-2}	0.000717	0.044	(1.63±0.078)·10^{-2}
Industrial soil	8-hydroxyquinoline	2.39·10^{-2}	0.000884	0.037	(2.39±0.092)·10^{-2}
	[VO(DTEP)(BPhen)]	2.42·10^{-2}	0.000847	0.035	(2.42±0.089)·10^{-2}
	[VO(DTBP)(Phen)]	2.38·10^{-2}	0.000998	0.042	(2.38±0.105)·10^{-2}
River soils (soils of river floodplains)	8-hydroxyquinoline	1.43·10^{-2}	0.000758	0.053	(1.43±0.079)·10^{-2}
	[VO(DTEP)(BPhen)]	1.45 ·10^{-2}	0.000565	0.039	(1.45±0.059) ·10^{-2}
	[VO(DTBP)(Phen)]	1.39·10^{-2}	0.000583	0.042	(1.39±0.061)·10^{-2}

n = 5, P = 0.95 (Incision depth of 10 - 20 cm) (п = 6, p = 0.95)

TABLE 7: DETERMINATION OF VANADIUM IN PLANTS

Analyzed object	Procedures	$\bar{X}$, mg/kg	*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

n = 5, P = 0.95 (п = 6, p = 0.95)

TABLE 8: DETERMINATION OF VANADIUM LEVELS IN ENVIRONMENTAL WATER SAMPLES WITH DTBP AND PHEN

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

(n = 6, p = 0, 95)

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.

- The results obtained show that the newly developed method in which the reagent dithiolphenols (DP) was used, can be effectively used for quantitative extraction and estimation of V(IV) from aqueous media.
- Mixed-ligand complexes of vanadium (IV) with DP in the presence of Am have been investigated by spectrophotometric method.
- Extraction of mixed ligand complexes is maximal at pH 6.4 - 7.9. The proposed method is quick and requires less volume of organic solvent.
- 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.
- The Beer's law was applicable in the range of 0.2-18µg/ml.
- A simple, rapid and sensitive methods proposed for the determination of trace amounts of vanadium. The method is very precise, faster and simpler than other methods.

ACKNOWLEDGEMENT: Nil

CONFLICT OF INTEREST: Nil

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How to cite this article:
Kuliev KA, Aliev SG, Suleymanova EI, Sultanzade SS, Maharramova LM, Melikova AY and Ismailova RA: Sensitive spectrophotometric determination of trace amounts of Vanadium (IV, V) using dithiolphenols and hydrofob amins. Int J Pharm Sci Res 2018; 9(6): 2211-20. doi: 10.13040/IJPSR.0975-8232.9(6).2211-20.