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Sensitive spectrophotometric determination of trace amounts of vanadium (iv, v) using 2,6-dithiol-4-propyl-phenole and hydrofob amins

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Abstract

Dithiol-4-propylphenole (DTPP) 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 reagent forms an blue coloured insoluble in water complex with Vanadium (IV, V) in acidic medium (pH 2.75-2.85). In the presence of hydrophobic amins form ternary complexes. Aniline (An) and N-methylaniline (mAn) were used as the hydrophobic amine. The molar absorptivity of coloured species are $(2.75-2.85) \cdot 10^4 \text{ L}\cdot\text{mol}^{-1} \cdot \text{cm}^{-1}$. Beer's law is obeyed in the range 0.05–3.2 µg/ml of Vanadium (IV, V) at λ_{max} 630-634 nm. Vanadium (IV, V) forms 1:2:2 complex with DTPP and Am, stability constant of the complex was found to be 9.7-9.8 ($\text{pH}_{\text{opt}} = 3.3-5.5$). The proposed method was successfully applied to the analysis of vanadium in alloys, natural water samples and plant material. The results obtained were agreed with the reported methods at the 95 % 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: New chromogenic reagent, spectrophotometry, vanadium (IV,V), alloys and biological samples.

1. Introduction

Vanadium is a trace element and is of great industrial, biological and pharmacological importance. Vanadium metal is present in different alloys and is an important element present in steels. Survey of literature reveals that several procedures have been reported for the determination of vanadium. In view of crucial role in different fields, it is necessary to develop sensitive analytical procedures for the determination of trace amounts of vanadium.

The procedures include high performance liquid chromatography, electrochemical, spectrofluorimetry, neutron activation analysis, AAS, ion chromatography inductively coupled plasma optical emission spectrometry, spectrophotometry, chemiluminescence etc. are most frequently used for the determination of vanadium compounds [1-16] are most frequently used for the determination of vanadium compounds.

However, the relatively high instrumental cost and need for preconcentration, chromatographic separation, extraction or coprecipitation are common disadvantages.

Although these techniques are sensitive, inconvenient, expensive and time consuming. Many of these procedures are complicated and involve preliminary isolation and pre-concentration procedures.

In scrutiny of literature reveals that several spectrophotometric methods have been reported for the determination of vanadium in environmental and biological samples. Recently, few authors introduced various reagents for spectrophotometric determination of vanadium in various samples such as 2-(2-quinolyazo)-5-diethylaminophenol [17], variamine blue [18], cryamine R [19], Benzylacetate [20], pyrogallol [21], 2-(8-quinolyazo)-5-dimethylaminopheno [22], 2-hydroxyacetophenone [23], 4-(2-pyridylazo) resorcinol [24], tannic acid [25], 2-(5-chloro-2-pyridylazo)-5-dimethylaminophenol [26] and N, N'-bis (2-hydroxyl-3-sulfopropyl)-tolidine [27], 2,4-Dimethoxybenzaldehydeisonicotinoylhydrazone [16]

The above reagents suffer from low selectivity, interference of a large number of metal ions required for the extraction of special solvent colored species and several other activators necessary for photometric determination of the vanadium catalyst. These shortcomings have led the authors to develop new responses to light, sensitive, accurate and reliable method for.

the de-termination of trace amounts of vanadium in various natural and industrial samples. These types of reactions for the determination of V (V) has not been reported yet.

Oxyphenolate complexes of vanadium (IV, V) are insoluble in chloroform, while mixed-ligand complexes with hydrophobic amines and aminophenols easily dissolve in various organic solvents [28-30]. In this respect, a very promising reagent is 2,6-dithiol-4-propylphenol (DTPP), which contains one hydroxyl and two sulfhydryl groups and is a sulfur-containing analogue of mononuclear polyphenols with two oxygen atoms replaced with sulfur atoms [31-33].

In the present work, simple, rapid, selective and sensitive spectrophotometric method is reported for the micro determination of vanadium (IV, V) by complexing with DTPP. The present study is concerned with the investigation of vanadium (IV, V) interaction with DTPP, resulting in the formation of colored complexes insoluble in nonpolar solvents. When hydrophob amins (Am) were introduced into the system, the extraction of these compounds into the organic phase as a mixed-ligand complex (MLC) was observed. Among hydrophob amins Aniline (An) and N-methylaniline (mAn) were used. Based on these data, new selective and highly sensitive procedures were developed for the extraction-spectrophotometric determination of trace vanadium in alloys, tap water and oil biological samples.

2. Experimental

2.1. Instrumentation

The absorbance of colored solutions was measured at 20 ± 1 °C using a KFK-2 photoelectro-colorimeter and SF-26 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. IR - spectra were recorded on a spectro-photometer UR-20.

2.2. Reagents and solutions.

Stock solutions ($1.96 \cdot 10^{-2}$ M) of V (IV, V) were prepared from chemically pure salts $\text{VOSO}_4 \cdot 3\text{H}_2\text{O}$ and $\text{NaVO}_3 \cdot 2\text{H}_2\text{O}$. 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 [35]. The structure of DTPP was confirmed based upon IR and NMR spectral data.

We used a 0.01 M DTPP 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. Procedure

2.3.1. General procedure for the determination of vanadium (V)

Required aliquots of solution containing different amounts (0.05-3.2 $\mu\text{g}/\text{ml}$) of vanadium (V) were transferred into were calibrated test tubes with ground-glass stoppers (the volume of the organic phase was 5mL). 2.8 mL portion of a 0.01 M solution of DTPP, and a 2.2 mL portion of a 0.01M solution of Am were added and the required value of pH was adjusted by adding 0.1M HCl. The volume of the aqueous phase was increased to 20 mL with distilled water. In 10 minute 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 ($l=0.5\text{cm}$).

2.3.2. Determination of vanadium (V) in tap water

Tap water samples were spiked with known amounts of vanadium (V) and analyzed by the proposed general procedure.

2.3.3. Preparation of sample solutions of plant tissue

The method is based on dry mineralization complete decomposition of organic substances by incineration plant samples (sample mass $m = 10$ g) in a muffle furnace at a controlled temperature regime. Cooled to room temperature, the ash moistened dropwise with nitric acid (1: 1) was evaporated in a water bath, placed into a muffle furnace, its temperature is adjusted to 300 °C and held for 30 minutes. The ash in the crucible is wetted carefully with 1M HCl, then 3 ml of this solution. The interfering effect of iron eliminated by the addition of phosphate ion, copper - by the addition of KI.

2.3.4. Preparation of alloy sample solutions

Accurately weighted amount of the alloy sample was dissolved in a mixture of 2 ml of concentrated hydrochloric acid and 10 ml of concentrated nitric acid. The solution was evaporated to a small volume, 1:1 sulphuric acid was added and the solution was then evaporated to dryness. The residue was dissolved in 15 ml of distilled water and filtered. The filtrate was transferred into a 100 ml standard flask and diluted to the mark with distilled water. This serves as stock solution. The stock solution was appropriately diluted to obtain the metal ion solution in the required concentration range. Vanadium was determined in aliquots of the solution using the procedure proposed by us.

3. Results and Discussion

The present study is concerned with the investigation of V (IV,V) interaction with DTPP, resulting in the formation of colored complexes insoluble in nonpolar solvents. Experiments on electromigration in a U-shaped tube and on sorption on EDE-10P (EDE- ethylenediamine, epichlorohydrin; 10- serial number of the brand: P- means that the matrix has a macroporous structure) anion exchangers have demonstrated the anionic nature of single ligand complexes, in the electromigration study of the complexes, it was found that the blue dithiophenolate complexes of Vanadium (IV, V) moved to the cathode. When the sign of the charge of the single-ligand complexes was determined by ion chromatography, the EDE-10P anion exchanger completely absorbed the colored component of the solution. When hydrophob amins (Am) were introduced into the system, the extraction of these compounds into the organic phase as a mixed-ligand complex (MLC) was observed.

DTPP are weak tribasic acid (H_3R) and depending on the pH of the medium may be in molecular and two anionic forms.

3.1. Effect of pH

The effect of pH on the intensity of the color reaction is shown in the Fig. 3. The absorbance was found to be maximum in the pH range 3.3-4.5. Hence further analytical investigations were carried out in media of pH 4. 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 $\text{pH} \geq 8$, the extraction of the complex is

practically not observed, which is probably because a decrease in the degree of proto-nation of Am. CHCl_3 , CCl_4 , $\text{C}_2\text{H}_2\text{Cl}_2$, C_6H_6 , $\text{C}_6\text{H}_5\text{CH}_3$, isopentanol, *n*-he-xanol, and their mixtures were tested as extractants. CHCl_3 , $\text{C}_2\text{H}_2\text{Cl}_2$, chlorobenzene, and were the best diluents. All the further investigations were carried out with chloroform. In a single extraction with chloroform, 98.7-98.8 % of vanadium (IV, V) is extracted in the form of mixed ligand complex. The concentration of Vanadium (IV, V) in the organic phase was determined photometrically by using 8-hydroxyquinoline [36] after reextraction, and in the aqueous phase, its concentration was found by the difference.

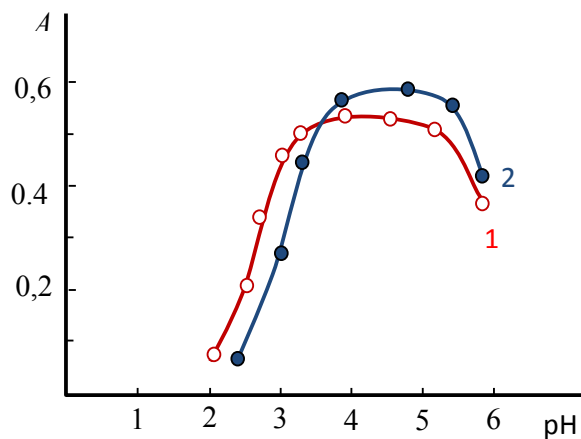


Fig 1: Absorbance of mixed-ligand complexes as a function of the pH of the aqueous phase.

1, V(IV)-DTPP-An; 2, V(IV)-DTPP-mAn.
 $C_V = 3.92 \cdot 10^{-5}$ M, $C_{\text{DTPP}} = 1.2 \cdot 10^{-3}$ M, $C_{\text{Am}} = 1.4 \cdot 10^{-3}$ M, KFK-2, 590 nm, $l = 0.5$ cm.

3.2. Electronic absorption spectra

The proposed method involved the formation of a brownish blue-green color between vanadium (IV,V) and DTPP in a medium of pH 4. The figure revealed that V(IV, V)-DTPP-Am complex has maximum absorbance at 630-634 nm. 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 $(2.75-2.85) \cdot 10^4 \text{ L} \cdot \text{mol}^{-1} \text{ cm}^{-1}$.

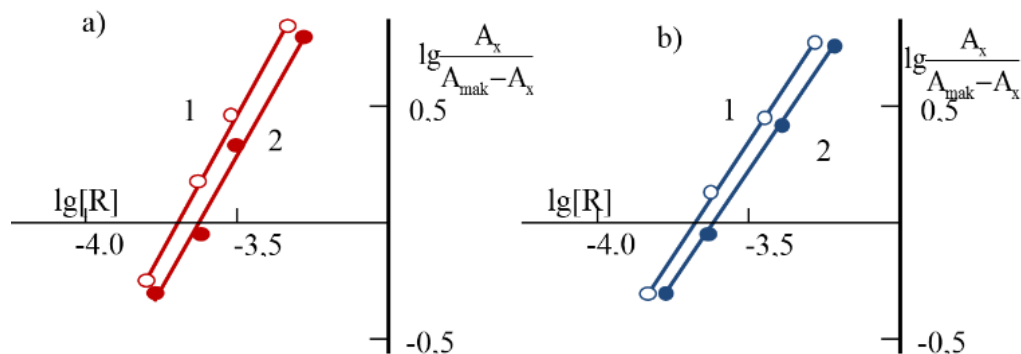


Fig 3: Determination of the ratio of components by the equilibrium shift method for (a) V(IV)-DTPP-An and (b) V(IV)-DTPP-mAn.

1, V:DTPP; 2, V : Am.
 $C_V = 3.92 \cdot 10^{-5}$ M, SF-26, $l = 590$ nm, $l = 1$ cm

It was found that the spectrophotometric characteristics of the MLC of vanadium (IV) and vanadium (V) were identical, i.e., in the interaction with DTPP, V(V) was reduced to V(IV) and

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

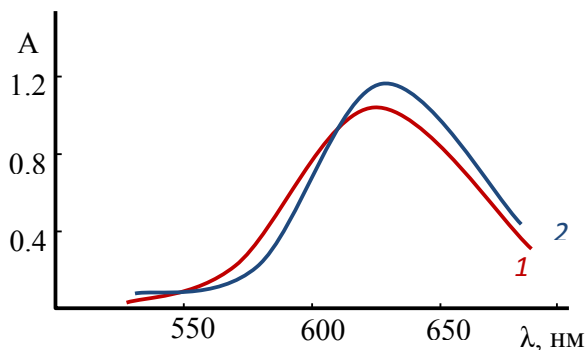


Fig 2: Absorption of mixed-ligand complexes

(1) V(IV)-DTPP-An, (2) V(IV)-DTPP-mAn
 $C_V = 3.92 \cdot 10^{-5}$ M, $C_{\text{DTPP}} = 1.2 \cdot 10^{-3}$ M, $C_{\text{Am}} = 1.4 \cdot 10^{-3}$ M, SF-26, $l = 1$ cm.

3.3. 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)-DTPP-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)-DTPP-Am, the concentration of $1.2 \cdot 10^{-3}$ M of DTPP and $1.4 \cdot 10^{-3}$ M of Am in the solution is required. Unlike single-ligand complexes, mixed-ligand complexes of vanadium (IV, V) with DTPP and Am were stable in aqueous and organic solvents and did not decompose for two days, or over a month after extraction. The required duration of the phase contact was 10 min.

3.4. Stoichiometry of the complexes and the mechanism of complexation

The ratio of components in the complex corresponds to V(IV,V) : DTPP : Am = 1 : 2 : 2; it was determined by the methods of straight line, equilibrium shift, and the relative yield [36] (Fig. 3). 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 DTPP molecule appeared to be one [37, 38].

VO^{2+} was the complex-producing form. This fact was also confirmed by ESR spectrometry [39]. 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 DTPP, vanadium (V) is reduced to vanadium (IV) by the reagent itself.

The results of the studies are presented in fig.4.

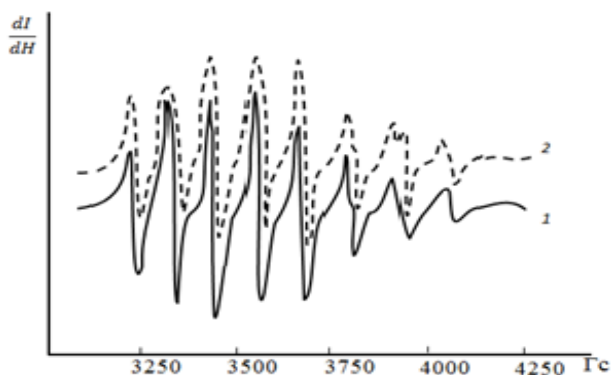
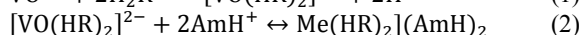
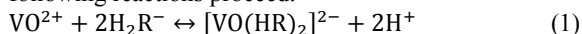


Fig 4: Hyperfine splitting of the paramagnetic resonance line in solutions:

- (1) V(IV)-DTPP-An and (2) V(V)-DTPP-mAn.

Constant of stability of complexes are determined by method of crossing of curves [36].

Given the found component ratio in the complex and an ionic state of vanadium, it was assumed that upon complexation, the following reactions proceed:



From Eqs. (1) and (2), one can judge the reaction mechanism: vanadium (V) is reduced by DTPP in a hydrochloric acid medium to vanadium (IV), and the latter in the form of a VO^{2+} interacts with excess DTPP. The resulting anionic complex $[\text{VO}(\text{HR})_2]^{2-}$ is reacted with Am, which the acidic solution is in the protonated state (AmH^+). Using Eq. (2), the equilibrium constant can be calculated by equation

$$\lg K_e = \lg D - 2 \lg [\text{AmH}^+]$$

The data for calculating $\log K_e$ of the complex are given in Table 1; the average value of the logarithm of the equilibrium constant is 6.6 - 6.7.

Calculation of extent of polymerization of complexes was carried out on the equation [40]. The made calculations showed that MLC in an organic phase won't be polymerized and are in a monomeric form ($\gamma = 1,05-1,12$).

The disappearance of a distinct strip at 2580 cm^{-1} , observed in ranges DTPP and emergence spectrum of complexes of two strips of absorption one of which is displaced towards smaller frequencies, says that one of the sulfhydryl groups participates in formation of a complex. The disappearance of intensity of a strip of absorption in area $3200-3600 \text{ cm}^{-1}$ with a maximum at 3450 cm^{-1} , shows that the hydroxyl group takes part in formation of communication in the ionized state. Detection of strips of absorption at 2380 cm^{-1} indicates availability of the protonated aniline [41, 42]

Structure extractable complexes can be represented as in Figure 5.

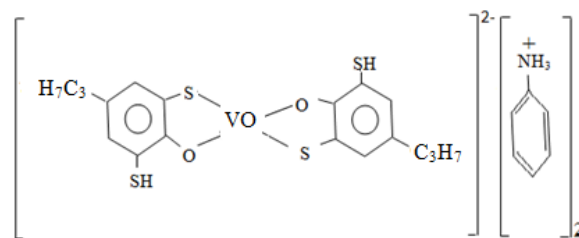


Fig 5: Structure of complex V(IV)-DTPP-An

3.5. Effect of diverse 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. The interference of Fe (III) was eliminated by orthophosphate acid; Cu(II), Cr(VI), and Mn(VII) were masked by thio-urea; Ti(IV), ascorbic acid; and Zr(IV), Nb(V), and Ta(V), by fluoride ions. Ions of Mo(VI), W(VI), Ti(IV), Nb(V), and Ta(V) form with DTPP and Am colored compounds and interfere with the determination of vanadium. However, these elements 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 2. These results reveal that various cations and anions can be tolerated at satisfactory levels.

Table 1: Influence of interfering ions on the determination of vanadium (IV) as MLC with DTPP and Am(30,0 mg V added)

Ion	Molar excess of the ion	Masking agent	Found V, μg	s_r
Co(II)	150		30,0	0,03
Ni(II)	150		30,2	0,03
Al(III)	190		29,8	0,04
Fe(II)	300		29,6	0,04
Fe(III)	50	Na_2HPO_4	30,2	0,04
Cd(II)	210		30,2	0,03
Zr(IV)	75	NaF	30,5	0,05
Cu(II)	50	$\text{SC}(\text{NH}_2)_2$	29,8	0,05
Ti(IV)	25	Ascorbic acid	29,6	0,05
W(VI)	15		29,8	0,04
Mo(VI)	5		30,3	0,05
Cr(III)	80		30,2	0,02
Nb(V)	25	NaF	30,2	0,06
Ta(V)	25	NaF	30,2	0,05
Pt(II)	50		29,2	0,05
Pd(II)	50		30,5	0,06
UO_2^{2+}	55	CH_3COO^-	29,3	0,04
Thiourea	600		29,3	0,04
Nitrate	540		30,4	0,05
Tetra borate	1274		29,5	0,06
Acetate	550		30,5	0,04
Phosphate	600		29,2	0,05
Chloride	365		30,6	0,03
Tartarate	800		29,7	0,05
Iodide	735		30,4	0,06
Urea	444		29,2	0,05
Thiocyanide	612		30,7	0,06
Bromide	769		29,8	0,04
Oxalate	484		29,9	0,03
Fluoride	350		30,5	0,06

Table 2: Physico-chemical and analytical characteristics of V (V)-complex

Characteristics	Value	
	An	mAn
Color	blue-green	blue-green
λ_{\max}	630	634
pH range	2.5-6.0	2.0-6.5
Optimum pH range	3.3-4.3	3.5-4.5
Mole of reagent required per mole of metal ion for full colour development	5 -10(folds)	5-10(folds)
Molar absorptivity (L.mol ⁻¹ cm ⁻¹)	2.75 · 10 ⁴	2.85 · 10 ⁴
Sandal's sensitivity (µg/cm ²)	0.00185	0.00178
Beer's law validity range (µg/ml)	0.05-3.2	0.05-3.2
The equation of calibration curves	0.046+0.51x	0.038+0.55x
Composition of complex (V: DTPP:Am)	1:2:2	1:2:2
Stability constant of the complex	9.70	9.79
lg K _e	6.6	6.7
R (%)	98.7	98.8
Regression coefficient	0.986	0.974

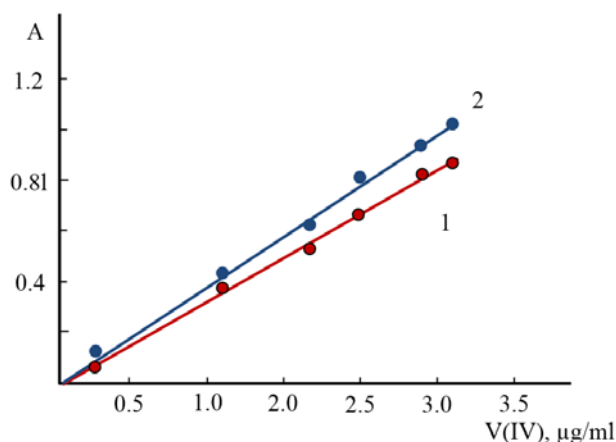
Table 3 demonstrates the data which allow a comparison of the analytical parameters of the procedures for the determination of vanadium with the earlier known procedures [43, 44].

Table 3: Comparative characteristics of the procedures for determining vanadium

Reagent	pH (solvent)	λ , nm	$\epsilon \cdot 10^{-4}$	Beer's law range
Sulfonitrazo	2,3	522	2,06	
8- Mercaptoquinoline	4,0 - 5,5(chloroform, toluene)	412	0,30	0,5-1,5
8 - Hydroxyquinoline	3,0 - 5,0(chloroform)	550	3,00	-
DTPP+An	3,3- 4,3(chloroform)	630	2,75	0,05-3,2
DTPP+mAPn	3,5 - 4,5(chloroform)	634	2,85	0,05-3,2

3.6. Effect of vanadium (IV) concentration

The adherence to Beer's law was studied by measuring the absorbance value of the series of solutions containing different concentrations of the metal ion. A linear calibration graph drawn between absorbance and the metal ion concentration indicates that V(V) may be de-termined in the range 0.05-3.2 µg/ml. The pertaining calibration graph is shown in the Fig. 6.

**Fig 6:** Analytical determination of V (V); $C_{DTPP}=1.2 \cdot 10^{-3}$ M; $C_{Am}=1.4 \cdot 10^{-3}$ M; pH = 3; $\lambda = 590$ nm, $l=0.5$ cm.

3.7. Analytical Applications

The proposed method under the already established optimum conditions was applied for the de-termination of V(V) in tap water, plant tissues and alloys. The proposed procedures for determining vanadium in soils were verified by 8-hydroxyquinoline and formaldoxime methods [8]. The results presented in Table 4-6 indicate the successful applicability of the proposed method to real sample analysis.

Table 4: The results of the vanadium in plants (n = 6, p = 0.95)

Analyzed object	Procedures	\bar{X} , mg/kg	S	S _r	$\bar{X} \pm \frac{t_p \cdot S}{\sqrt{n}}$
Rice	8-Hydroxyquinoline	1,12	0.048	0,043	1,12±0,05
	8- Mercaptoquinoline	1,14	0.068	0,060	1,14±0,07
	DTPP+An	1,15	0.0437	0,038	1,15±0,05
	DTPP+mAn	1,12	0.0504	0,045	1,12±0,05
Potatoes	8- Mercaptoquinoline	6.14	0.304	0,051	6,14±0,32
	8-Hydroxyquinoline	6.10	0.244	0,040	6,10±0,25
	DTPP+An	6.11	0.18	0,029	6,11±0,19
	DTPP+mAn	6.13	0.27	0,045	6,13±0,29
carrot	8-Hydroxyquinoline	1.00	0.033	0,033	1,00±0,034
	DTPP+An	0.98	0.041	0,042	0,98±0,043
	DTPP+mAn	1.02	0.042	0,042	0,98±0,044

Table 5: Determination results of vanadium in standard samples (n = 6, p = 0.95)

Procedures	\bar{X} , %	S	S _r	$\bar{X} \pm \frac{t_p \cdot S}{\sqrt{n}}$
<i>steel-246(0.17%)</i>				
8- Mercaptoquinoline	0.15	0.00525	0.035	0.15±0.0055
8-Hydroxyquinoline	0.19	0.00722	0.038	0.19±0.0076
DTPP+An	0.17	0.00578	0.034	0.17±0.0060
DTPP+mAn	0.16	0.00464	0.029	0.16±0.0048
<i>steel-218 (0.49%)</i>				
8- Mercaptoquinoline	0.47	0.01739	0.037	0.47±0.019
8-Hydroxyquinoline	0.48	0.01728	0.036	0.48±0.018
DTPP+An	0.49	0.01715	0.035	0.49±0.018
DTPP+mAn	0.48	0.01344	0.028	0.48±0.014

Table 6: Determination of Vanadium (V) in water

Vanadium added (5g/ml)	Vanadium found (µg/ml)		Recovery (%)	S	S _r
	Standard Method	Proposed method			
1.0	1.05	1.06±0.031	106.3	0.03	0.028
2.0	2.06	2.07 ± 0.08	107.0	0.08	0.037
3.0	3.05	3.09 ± 0.09	105.4	0.09	0.029

4. Conclusion

The present method using 2,6-Dithiol-4-propylphenole (DTPP) as spectrophotometric reagent for the determination of vanadium (IV,V) in acidic medium is sensitive and simple. The determination of vanadium (IV,V) using DTPP is not laborious and there is no need of heating or extraction of the components.

- Mixed-ligand complexes of vanadium (IV,V) with dithiolphenoles and hydrofob amins have been studied by spectrophotometry.
- Extraction of mixed ligand complexes is maximal at pH 3.3-4.5. The optimal conditions for the formation and extraction of mixed-ligand compounds have been found.
- The molar ratio of the reacting V(IV,V), DTPP and Am species is 1:2:2. The general formula of the ternary complexes is $[VO(DTPP)_2](AmH)_2$. They can be regarded

as ion-associates between doubly charged anionic chelates $[\text{VO}(\text{DTPP})_2]^{2-}$ and protonated Am species.

- A procedure has been developed for extraction-spectrophotometric determination of vanadium in alloys, natural water samples, plant material.

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