



Vanadium (IV and V) speciation with a catechol derivative and tetrazolium salt

Petya Racheva, Kiril Blazhev Gavazov^{*}, Vanya Dimitrova Lekova, Atanas Nikolov Dimitrov

Department of General and Inorganic Chemistry, University of Plovdiv, Plovdiv, Bulgaria

Received 15 June 2008; received in revised form 4 December 2008; accepted 10 December 2008

Abstract

The possibility of application of 4-nitrocatechol (4-NC) - tetrazolium salt - organic solvent systems for liquid-liquid extraction-spectrophotometric vanadium (IV and V) speciation was studied. Six commercially available tetrazolium salts (2,3,5-triphenyltetrazolium chloride (TTC), 3-(2-naphtyl)-2,5-diphenyltetrazolium chloride (Tetrazolium Violet, TV); 3-(4,5-dimethyl-2-thiazol)-2,5-diphenyltetrazolium bromide (Thiazolyl Blue Tetrazolium, MTT), 2-(4-iodophenyl)-3-(4-nitrophenyl)-5-phenyltetrazolium chloride (INT), 3,3'-(4,4'-biphenylene)bis(2,5-diphenyltetrazolium) chloride (Neotetrazolium chloride, NTC) and 3,3'-[3,3'-Dimethoxy(1,1'-biphenyl)-4,4'-diyl]bis(2,5-diphenyltetrazolium) chloride (Blue Tetrazolium chloride, BTC)) and three organic solvents (chloroform, 1,2-dichloroethane, 1-butanol) were tested in this study. The best results were obtained with MTT and chloroform. A direct, very simple, fast and sensitive procedure for vanadium (IV and V) speciation based on the spectral differences of the extracted ternary complexes of V(IV) and V(V) was developed. It was found that the optimization of the MTT to 4-NC ratio has a key role in the speciation results. At deficiency of 4-NC towards MTT the vanadium(IV) complex absorbed light at 390 and 570 nm, while the V(V) complex absorbed only at 390 nm. The corresponding molar absorptivities were calculated to be $\varepsilon_{V(IV)390} = 3.6 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$, $\varepsilon_{V(IV)570} = 1.7 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $\varepsilon_{V(V)390} = 3.1 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$. The method was applied for vanadium (IV and V) speciation in industrial samples with low Fe and Al content (catalyst for oxidation of SO₂) and good results were obtained in terms of precision and accuracy.

Keywords: Vanadium, Speciation, Nitrocatechol, Thiazolyl blue tetrazolium, Extraction, Determination, Spectrophotometric

1. Introduction

The two most common vanadium forms encountered in environmental, biological and industrial systems are vanadium (V) and vanadium(IV). These forms have different toxic, nutritional, catalytic and other properties. That is why the methods for vanadium determination should provide information on speciation [1-5].

^{*}Corresponding author. Tel.: +359 32261420; fax: +359 32261352.
E-mail address: kgavazov@abv.bg (K.B. Gavazov)

Many methods have been used for vanadium (IV/V) speciation, including anion-exchange chromatography with inductively coupled plasma mass spectrometry (ICP-MS) [6], high performance liquid chromatography (HPLC) with ICP-MS [7], chromatography with inductively coupled plasma optical emission spectrometry (ICP-OES) [8,9], liquid chromatography with UV detection [10], electrothermal atomic absorption spectrometry (ETAAS) [11], ion-exchange chromatography with graphite-furnace atomic absorption spectrometry (GFAAS) [12], solid phase extraction (SPE)-ICP-OES with ultrasonic nebulization [13], SPE-ETAAS [14,15], capillary electrophoresis with spectrophotometry [16], volumetry [17], SPE with spectrophotometry [18,19], flow injection analysis [20,21], flotation with spectrophotometry [22], liquid-liquid extraction (LLE) with spectrophotometry [23-29], and spectrophotometry (including catalytic kinetic spectrophotometry) [4,5, 30-32].

The methods involving spectrophotometry are rather popular due to their simplicity, low-cost instrumentation and easy automation. However, most of the spectrophotometric procedures reported for vanadium (IV/V) speciation are indirect [4, 18-21, 23,26, 28-30, 32], reagent and time consumptive [24,26,27,30], low-sensitive [16, 24-26, 30,31] or demand stringent reaction conditions [5,16]. It is known that vanadium (V) reacts with catechol derivatives and auxiliary reagents to form colored ternary complexes which could be used for LLE-spectrophotometric determination of vanadium [33-39]. The oxidation state of vanadium in these complexes most probably is +4. Vanadium (V) as a strong oxidant is able to oxidize the catechol derivative to quinoid products being reduced to vanadium (IV) which later reacts with the excess of the catechol derivative [40-42]. The investigations [39,43] on ternary ion-association complexes with participation of tetrazolium cations, however, showed that the tetrazolium salts may inhibit the reduction of vanadium(V) to vanadium(IV) in the course of complex formation with ortho-polyphenolic compounds. In the presence of tetrazolium salts vanadium (V) and vanadium (IV) may save their initial oxidation states which allows correct determination of these valence species [28,29,39].

The goal of this work was to develop a direct, simple, sensitive, and fast LLE-spectrophotometric procedure for vanadium (IV and V) speciation based on the spectral differences of the ternary complexes of vanadium (IV) and vanadium (V) with a catechol derivative and a tetrazolium cation. Preliminary investigations and the literature [34,38,39, 42-45] showed that 4-nitrocatechol is more sensitive and more stable to oxidation reagent than catechol, pyrogallol, 3-methylcatechol, gallic acid, tannic acid, 2,3-dihydroxynaphtalene and other ortho-polyphenolic compounds. That is why for the present study we selected 4-NC along with six commercially available and widely used [39] tetrazolium salts: 2,3,5-triphenyltetrazolium chloride (TTC), 3-(2-naphtyl)-2,5-diphenyltetrazolium chloride (Tetrazolium Violet, TV); 3-(4,5-dimethyl-2-thiazol)-2,5-diphenyltetrazolium bromide (Thiazolyl Blue Tetrazolium, MTT), 2-(4-iodophenyl)-3-(4-nitrophenyl)-5-phenyltetrazolium chloride (INT), 3,3'-(4,4'-biphenylene)bis(2,5-diphenyltetrazolium) chloride (Neotetrazolium chloride, NTC) and 3,3'-[3,3'-Dimethoxy(1,1'-biphenyl)-4,4'-diyl]bis(2,5-diphenyltetrazolium) chloride (Blue Tetrazolium chloride, BTC).

2. Experimental

2.1. Reagents

The following reagents were used: NH_4VO_3 from VEB Laborchemie Apolda, purissimum. A 250-mL volume of stock solution ($5 \times 10^{-3} \text{ mol L}^{-1}$) of pentavalent vanadium was prepared by dissolving 0.1462 g of the salt in distilled water with warming. Working solutions ($2 \times 10^{-4} \text{ mol L}^{-1}$) were prepared by dilution. $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ from Fluka, purum, as a $5 \times 10^{-2} \text{ mol L}^{-1}$ stock aqueous solution. The concentration was checked by titration with a standard solution of potassium permanganate. The working $2 \times 10^{-4} \text{ mol L}^{-1}$ solutions were prepared every day.

4-nitrocatechol (4-NC) from Fluka, pro analysis, as a 2×10^{-3} mol L⁻¹ aqueous solution. Tetrazolium salts: TTC, TV, MTT and INT from Loba Feinchemie AG, pro analysis, and NTC and BTC from Fluka, for microscopy, as 2×10^{-3} mol L⁻¹ aqueous solutions. Acetate buffer solutions were prepared by mixing of appropriate volumes of 0.1 mol L⁻¹ aqueous solutions of CH₃COOH and CH₃COONa.

2.2. Apparatus

A Specol-11 spectrophotometer (Carl Zeiss, Germany) equipped with 1.0 cm-in-width cells was employed for reading the absorbance. The pH measurements were made with a HI 83140 pH meter (Italy) with a combined plastic electrode.

2.3. General procedure

Aliquots of vanadium (IV) or/and vanadium (V) solution, acetate buffer solution, tetrazolium salt solution and 4-NC solution were introduced into 100-mL separatory funnels. The resulting solutions were diluted with distilled water to a total volume of 10 mL. Then 5 mL of organic solvent were added and the funnels were shaken for several minutes. A portion of the organic layer was filtered through a filter paper into a cell and the absorbance was read against a simultaneously prepared reagent blank.

2.4. Procedure for determination of vanadium (IV) and vanadium (V) in catalysts

50-500 mg of powdered catalyst sample was placed in a 100 mL beaker. 25 mL of H₃PO₄ (1:1) were added and the contents were heated for about 30-40 min in inert atmosphere (N₂, CO₂). The resulting mixture was diluted to 100 mL and filtered through a filter paper at a medium speed. The precipitate of silicic acid was carefully washed. The filtrate and the liquid fraction obtained after washing were transferred into a 1000 mL volumetric flask and the contents were diluted with distilled water up to the mark [28, 29].

An aliquot of the obtained solution corresponding to 1.6-17 µg vanadium was transferred to a 100-mL separatory funnel. pH was adjusted to 4.0 ± 0.3 by adding dropwise preliminary determined amount of 5% ammonia solution. Then, 3 mL of acetate buffer solution (pH 4.66; CH₃COOH to CH₃COONa v/v ratio = 55:45), 0.8 mL of 2.0×10^{-3} mol L⁻¹ MTT solution and 1 mL of 3.6×10^{-4} mol L⁻¹ 4-NC solution were added. The volume was made up to 10 mL with distilled water, and after that 5 mL of chloroform were added. The contents were shaken well for 3 min and a portion of organic layer was transferred through a filter paper into 1-cm path-length cell. Absorbance was measured at 390 nm and 570 nm against a simultaneously prepared reagent blank.

3. Results and discussion

3.1. The choice of an extraction system

The following parameters were of importance when we studied the possibility to apply 4-NC and TS for vanadium (IV and V) speciation: the concentration of TS and 4-NC, pH, the sequence of reagents addition, the extraction time and the phase separation time. To prevent the reduction of V(V) to V(IV) by 4-NC the concentration of 4-NC had to be kept low and TS had to be introduced to the vanadium aliquot before 4-NC. From the other side, in order to prevent the oxidation of V(IV) to V(V) by the air oxygen pH had to be kept below 5.6 [2]. That is why the pH of analyzed solution had to be adjusted carefully (e.g. by adding dropwise preliminary determined amount of dilute ammonia solution). In addition, to limit the possibility for changes

of the initial oxidation state of vanadium the waiting time before extraction, the extraction time and the phase separation time had to be as short as possible [29].

The choice of the organic solvent was dictated by the individual properties of the TS and pH. 1,2-dichloroethane formed stable emulsions after the extraction at pH values lower than 5 and hence 6-15 min waiting time was necessary for clear phase separation. n-Butanol ensured faster extraction process in comparison with chloroform and dichloroethane, but drying with anhydrous ammonium sulfate was needed [43], the sensitivity was low, and the spectral differences between the complexes of vanadium (IV) and vanadium (V) were small. The use of mixed solvent n-butanol + chloroform gave some advantages in comparison with pure n-butanol, but the blank absorbed significantly and the distillation of the mixture was difficult. It should be mentioned that the vanadium (IV and V) speciation with NTC was possible only with this mixed solvent, because the formed complexes were slightly soluble in pure chloroform or dichloroethane.

The extraction systems which could be used for vanadium (IV and V) speciation are shown in Table 1. The 4-NC – MTT – chloroform system was found to be the best. This system was not plagued by disadvantages such as long extraction time, long phase separation time and high absorbance of the blank. In addition, MTT ensured highest sensitivity of determination.

Table 1

Extraction systems for vanadium (IV and V) speciation

Extraction system for V (IV / V)	Disadvantages
4-NC - TTC - chloroform	low sensitivity, long extraction time (10-15 min)
4-NC - MTT - chloroform	-
4-NC - MTT - dichloroethane	long phase separation time (7-12 min)
4-NC - TV - chloroform	high absorbance of the blank, long extraction time, incomplete extraction
4-NC - INT - chloroform	small spectral differences for V(V) and V(IV)
4-NC - NTC – n-butanol + chloroform (7:3 v/v ratio)	high absorbance of the blank, long extraction time (15-20 min)
4-NC - BTC - chloroform	long extraction time, incomplete extraction

3.2. Optimal conditions for vanadium (IV and V) speciation, analytical characteristics and calculations

The optimal operating conditions for vanadium (IV and V) speciation with 4-NC and MTT are systematized in Table 2. The spectra of the complexes recorded at these conditions are shown in Fig. 1. It can be seen that the absorbance of vanadium (V) at 570 nm is close to zero ($\epsilon_{570V(V)} = 650 \text{ L mol}^{-1} \text{ cm}^{-1}$) what allows to calculate the concentration of vanadium (V) and vanadium (IV) by equations 1 and 2 [46].

$$C_{V(V)} = \frac{\epsilon_{V(IV)570} \times \frac{A_{390}}{l} - \epsilon_{V(IV)390} \times \frac{A_{570}}{l}}{\epsilon_{V(V)390} \times \epsilon_{V(IV)570}} \quad (1)$$

$$C_{V(IV)} = \frac{A_{570}}{\epsilon_{V(IV)570} \times l} \quad (2)$$

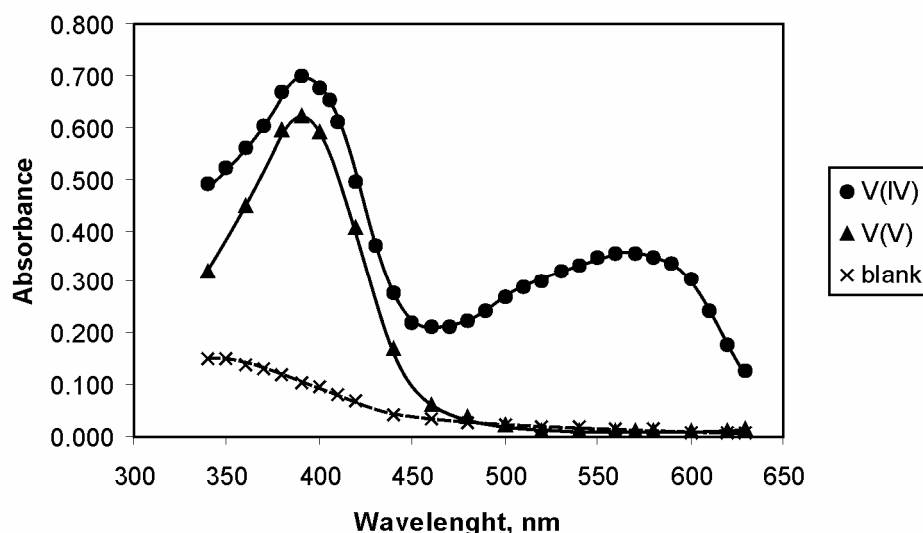


Fig. 1 Spectra of the V(IV) - 4-NC - MTT complex, the V(V) - 4-NC - MTT complex and the blank (4-NC - MTT) in chloroform. $C_{V(V)} = C_{V(IV)} = 2 \times 10^{-5} \text{ mol L}^{-1}$, $C_{4\text{-NC}} = 3.6 \times 10^{-5} \text{ mol L}^{-1}$, $C_{\text{MTT}} = 1.6 \times 10^{-4} \text{ mol L}^{-1}$, $l = 1 \text{ cm}$.

In these equations A_{390} and A_{570} are the absorbance values measured (against a blank) at 390 and 570 nm, respectively, l is the cell path-length, and ϵ_{390} and ϵ_{570} are the molar absorptivities calculated from the calibration plots at 390 and 570 nm (Table 2), respectively. Since the absorption of the blank at 390 nm (Fig. 1) depends to some extent on both concentration of the reagents and pH a special attention should be paid to the similarity of the conditions of preparation of the sample and blank.

Table 2

Optimal conditions and analytical characteristics of the extractive-spectrophotometric vanadium (IV and V) speciation with 4-NC and MTT

Optimal conditions for V(IV,V) speciation	Analytical characteristics
pH 4.5-4.8 (acetate buffer)	$\epsilon_{390V(IV)} = 3.6 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$
C_{MTT} (aqueous phase) – $1.6 \times 10^{-4} \text{ mol L}^{-1}$	$\epsilon_{570V(IV)} = 1.7 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$
$C_{4\text{-NC}}$ (aqueous phase) – $3.6 \times 10^{-5} \text{ mol L}^{-1}$	$\epsilon_{390V(V)} = 3.1 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$
Volume of the aqueous phase – 10 mL	$\epsilon_{570V(V)} \approx 0$
Volume of the organic phase – 5 mL	Beer's law range – up to $1.7 \mu\text{g mL}^{-1}$ V(IV,V)
Organic solvent – chloroform	LOQ ₃₉₀ – $0.15 \mu\text{g mL}^{-1}$ V(V)
Extraction time – 3 min	LOQ ₃₉₀ – $0.13 \mu\text{g mL}^{-1}$ V(IV)
Cell path-length – 1.0 cm	LOQ ₅₇₀ – $0.15 \mu\text{g mL}^{-1}$ V(IV)
Wavelengths – 390 nm (V(V)+V(IV))	Standard deviation (V(V)) – 0.008-0.010
570 nm (V(IV))	Standard deviation (V(IV)) – 0.001-0.016

The correlation between the measured sample absorptions and the concentration of vanadium (IV and V) was estimated using regression analysis. Apparently, the method was linear up to the vanadium(IV) or vanadium(V) concentration of $1.7 \mu\text{g mL}^{-1}$, what could be attributed to deficiency of 4-NC at higher vanadium concentrations. The linear equations for vanadium (IV) and vanadium (V) could be expressed as $A_{V(IV)390} = 0.702 \times 10^4 C + 0.004$, $A_{V(IV)570} = 0.334 \times 10^4 C + 0.002$ and $A_{V(V)390} = 0.601 \times 10^4 C + 0.006$ respectively, where C is concentration in $\mu\text{g mL}^{-1}$. The corresponding correlation coefficients were calculated to be 0.9995, 0.9994 and 0.9995. The limits of detection ($\text{LOD}_{V(IV)390} = 0.040 \mu\text{g mL}^{-1}$, $\text{LOD}_{V(IV)570} =$

0.045 $\mu\text{g mL}^{-1}$, $\text{LOD}_{\text{V(V)}_{390}} = 0.044 \mu\text{g mL}^{-1}$) and the limits of quantification (LOQ) (Table 2) were calculated as 3 times and 10 times the standard deviation $\text{SD}(y)$, respectively. The Sandell's sensitivities of $1.4 \times 10^{-3} \mu\text{g cm}^{-2}$ (V(IV)_{390}), $3.0 \times 10^{-3} \mu\text{g cm}^{-2}$ (V(IV)_{570}) and $1.7 \times 10^{-3} \mu\text{g cm}^{-2}$ (V(V)_{390}) were estimated as well.

3.3. Determination in binary mixtures of vanadium (V) and vanadium (IV)

Binary mixtures of vanadium (V) and vanadium (IV) in different proportions were prepared and analyzed by the proposed procedure. The results are shown in Table 3. It can be concluded that the method gives satisfactory results for vanadium (V), vanadium (IV) and for the total vanadium.

Table 3

Determination in binary mixtures of V(IV) and V(V)

Added (μg)		V(IV) to V(V) ratio added	Found (μg) *		V(IV) to V(V) ratio found
V(IV)	V(V)		V(IV)	V(V)	
0.0	10.2	0.00	0.3	9.9	0.03
0.5	9.7	0.05	0.6	9.5	0.06
1.0	9.2	0.11	1.1	9.1	0.12
2.0	8.2	0.24	2.1	8.1	0.26
3.1	7.1	0.44	3.1	7.1	0.44
4.1	6.1	0.67	4.1	6.0	0.68
5.1	5.1	1.00	5.1	5.1	1.00
6.1	4.1	1.50	6.2	4.0	1.50
7.1	3.1	2.30	7.2	3.1	2.30
8.2	2.0	4.10	8.0	2.2	3.60
9.2	1.0	9.20	9.0	1.1	8.20
9.7	0.5	19.40	9.6	0.6	16.00
10.2	0.0	∞	10.2	0.0	∞

* Mean of three determinations

3.4. Interference studies

The selectivity of the method was investigated by determination of 6 μg of vanadium (V) or vanadium (IV) in the presence of various ions (Table 4). The foreign ions (FI) were considered to interfere if the absorbance reading differed from the value measured for sample with vanadium complex only by more than $\pm 3\%$. The determination of both vanadium (IV) and vanadium (V) was not affected by high amounts of alkaline ions, Co^{2+} , Ni^{2+} , Zn^{2+} , Mg^{2+} , Cd^{2+} and Mn^{2+} , and moderate amounts of Ce^{3+} , F^- and Cr^{3+} . Mo(VI) , Fe^{2+} , Fe^{3+} , U(VI) , Cr(VI) , NO_3^- , W(VI) , Al^{3+} , Re(VII) and Cu^{2+} , however, interfered seriously at 1:1 FI-to-vanadium(IV and V) ratio. The preliminary studies indicated that the choice of masking agents in case of vanadium (IV and V) speciation is quite limited. CDTA was found to be an effective masking agent for Al^{3+} , Fe^{3+} , Cu^{2+} and Re(VII) , but masked partially V(IV). Citrate, in its turn, disturbed the vanadium (IV)-vanadium (V) equilibrium and also was unsuitable for masking. Fluoride and tartrate at concentrations which did not affect the determination of vanadium had small masking effect.

In order to outline the ability of application of the proposed speciation method without masking we investigated the binary mixtures of vanadium (IV and V) (10 μg) and FI at a FI-to-vanadium m/m ratio smaller than 1 (see Table 4). The results show that the proposed method could be quite suitable for analysis of industrial samples, including some kind of catalysts for oxidation of SO_2 during the production of sulphuric acid [47].

Table 4

The effect of diverse ions on the determination of 6 µg or 10 µg* vanadium

Foreign ion (FI)	Tolerable FI to V ratio (390 nm)		Tolerable FI to V(IV) ratio (570 nm)	Tolerable FI to V ratio for V(IV,V) speciation
	V(V)	V(IV)		
K ⁺ , Na ⁺	3000	3000	3000	3000
Mg ²⁺	3000	400	400	400
Ni ²⁺	1200	1000	750	750
Co ²⁺	1000	1100	1000	1000
Ce(III)	500	300	100	100
Zn ²⁺	500	1500	1000	500
Cd ²⁺	500	500	1000	500
Mn ²⁺	300	2000	2000	300
F ⁻	50	100	300	50
Cr ³⁺	7.5	5	10	5
Br ⁻	4	4	3	3
Cu ²⁺	1	0.75	1	0.75
Re(VII)	1	0.5	4	0.5
Al ³⁺	1	0.5	0.75	0.5
W(VI)	1*	0.5*	3*	0.5*
NO ₃ ⁻	0.5	0.5	0.5	0.5
Cr(VI)	0.5*	0.5*	0.25*	0.25*
U(VI)	0.5*	0.5*	5*	0.5*
Fe ³⁺	0.25*	0.25*	0.3*	0.25*
Fe ²⁺	0.25*	0.25*	0.4*	0.25*
Mo(VI)	0.1*	0.1*	1*	0.1*

3.5. Analytical application

The last step of this study was to apply the described method for analysis of real samples and to compare the results with those obtained by another method. The LP-120 used catalyst samples (Monsanto) which are characterized with low Fe and Al content were developed. The results (P=95%) are shown in Table 5. It can be concluded that the new method gives satisfactory results and could compete successfully with the known spectrophotometric and LLE-spectrophotometric methods for vanadium (IV and V) speciation in terms of sensitivity, simplicity, rapidity, repeatability, precision and accuracy.

Table 5

Determination of vanadium (IV) and vanadium (V) in the catalyst samples *

Sample	4-NC - MTT method			PAR - MTT - CDTA method [28]		
	V(V) (%)	V(IV) (%)	V _{tot} = V(IV)+V(V) (%)	V(V) (%)	V(IV) = V(V)-V _{tot} (%)	V _{tot} (%)
Catalyst 1	1.94±0.01	0.597±0.001	2.54±0.01	1.93±0.01	0.60±0.03	2.53±0.02
Catalyst 2	1.71±0.01	0.68±0.02	2.39±0.03	1.71±0.02	0.69±0.04	2.40±0.02

* Mean of five determinations

4-(2-pyridylazo)-resorcinol (PAR), 1,2-Diamino-cyclohexane-N,N,N',N'-tetraacetic acid (CDTA)

4. Conclusions

A direct, very simple, sensitive, fast and precise liquid-liquid extraction-spectrophotometric procedure for vanadium (IV and V) speciation with 4-nitrocatechol and thiazolyl blue tetrazolium was developed. The method was successfully applied for determination of vanadium (IV) and vanadium (V) in industrial samples with low Fe and Al content.

Acknowledgment

This work was supported by the Research Fund of the University of Plovdiv "Paisii Khilendarski".

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