An extraction-chromogenic system for vanadium(IV,V) based on 2,3-dihydroxynaphtalehne

1 Introduction

Vanadium is a biologically important trace element with many industrial applications. Making up about 0.014% of the Earth’s crust, it is the fifth-most abundant transition metal [1]. Key factors that determine vanadium’s roles in physiological systems are its oxidation-reduction properties (e.g. ability to switch easily between oxidation states V and IV) and flexible stereochemistry [2, 3].

Many methods have been proposed for vanadium determination and speciation [4-6]. Among the most sensitive and cost effective are the extraction-spectrophotometric methods based on ternary complexes involving catecholic ligands [6-9]. However, the mechanism of color development in such methods is disputable since it is not always clear whether the main spectral bands are due to the formation of coordination compounds or products of oxidation and polymerization of the reagent(s) [10].

Several papers [11-14] describe liquid-liquid extraction of V V with 2,3-dihydroxynaphtalehne (DN) – a catechol type ligand of analytical importance [15]. However, the possibility of V V → V IV reduction caused by DN, a phenomenon well documented by Adediran and Pratt [16], is underestimated in these papers. For example, the time dependent absorbance at pH values higher than 5.25 in the V V – DN – iodonitrotetrazolium chloride (INT) system [11] has been attributed solely to a redox reaction between DN and INT, assuming that the tetrazolium salt INT is able to inhibit the reduction of V V to V IV caused by ortho-diphenolic compounds [17]. A convenient way to throw additional light on the mentioned assumption is to compare results obtained with V IV and V V. To the best of our knowledge, such a comparison has not been performed so far and V IV-DN ternary complexes have never been studied.

Here, we report our results for extraction-chromogenic systems containing V IV or V V, DN, 2,3,5-triphenyl-2H-tetrazolium chloride (TTC), water and chloroform. We selected TTC for the present study since it is the simplest commercially available tetrazolium salt. Moreover, TTC has many applications based on ion-association [17-22] and oxidation-reduction [23-25]. Molecular parameters of TTC and some compounds containing its cation TT+ are given in the literature [26, 27].
2 Experimental procedure and theoretical details

2.1 Reagents and Apparatus

Stock $\text{V}^{\text{IV}}$ aqueous solution ($5 \times 10^{-2} \text{ mol dm}^{-3}$) was prepared from $\text{VO}_2^+ \cdot 5\text{H}_2\text{O}$ (Fluka, purum) and standardized by potassium permanganate titration. Working solutions at a concentration of $2 \times 10^{-4} \text{ mol dm}^{-3}$ were prepared daily as described previously [28]. $\text{V}^{\text{V}}$ solution ($2 \times 10^{-4} \text{ mol dm}^{-3}$) was prepared by dissolving $\text{NH}_4\text{VO}_3$ (VEB Laborchemie Apolda, puriss. p.a.) in distilled water. $\text{DN}$ solution ($2 \times 10^{-3} \text{ mol dm}^{-3}$) was prepared daily by dissolving an appropriate amount of the solid reagent (Fluka, purum) in chloroform. The concentration of TTC (from Loba Feinchemie GMBH, p.a.) was $5 \times 10^{-3} \text{ mol dm}^{-3}$ (aqueous solution). The acidity of the aqueous medium was set by the addition of buffer solution, prepared by mixing $2.0 \text{ mol dm}^{-3}$ aqueous solutions of $\text{CH}_3\text{COOH}$ and $\text{NH}_4\text{OH}$. The resulting pH was checked by a Hanna HI 83141 pH meter (manufactured in Romania) calibrated according to manufacturer’s instructions.

A Camspec M508 spectrophotometer (United Kingdom), equipped with 10 mm path-length glass cells, was used for the absorbance measurements. All experiments were performed at room temperature $\sim 23 ^\circ \text{C}$ (air-conditioner).

2.2 Procedure

Aliquots of $\text{V}^{\text{IV}}$ or $\text{V}^{\text{V}}$ solution, buffer solution and TTC solution were transferred into separatory funnels. The resulting solutions were diluted with distilled water to a total volume of 10 cm$^3$. Aliquots of $\text{DN}$ chloroform solutions were added and the organic phase was made up to 10 cm$^3$ with chloroform. The funnels were shaken for extraction for a fixed time (10 – 300 s). After separation of the layers, portions of the chloroform extracts were transferred through filter papers into cells. The absorbances were measured against simultaneously prepared blank solutions (containing all of the reagents with the exception of vanadium) or chloroform.

2.3 Theoretical details

The structures of the anionic chelates were optimized at the BLYP/6-31++G* level of theory. For structure I the charge and the multiplicity were set to –1 and singlet, while for the structures II and III they were –1 and doublet. Subsequent frequency calculations were performed to prove that the found structures lie in minima on the PESs.

The initial structures of the anionic chelates for energy gradient optimizations were constructed relying on experimental data for the molar ratios V-DN and V-TTC. Technically the initial molecular complexes were constructed keeping in mind the positions and the orientations of the electron-accepting and electron-donating centrums as well as our intuition for producing a stable complex. All calculations were performed with the GAUSSIAN 03 program package [29].

2.4 Statistical calculations

All statistical calculations were performed with a spreadsheet program (Microsoft Office Excel 2010) at a probability of 95%.

3 Results and Discussion

3.1 Absorption spectra, composition, formulae and equations

Figure 1 shows the absorption spectra of the chloroform-extracted complexes and their corresponding blanks. Figure 1a represents the results obtained with high $\text{DN}$ concentration ($8.0 \times 10^{-4} \text{ mol dm}^{-3}$). Spectrum 1 (with $\text{V}^{\text{IV}}$) and 2 (with $\text{V}^{\text{V}}$) are practically identical and this is an indication that under the given conditions $\text{V}^{\text{V}}$ is reduced to $\text{V}^{\text{IV}}$. The small differences at wavelengths where the blank (spectrum 3) absorbs intensively, could be regarded as a result of an oxidation-reduction interaction between $\text{V}^{\text{V}}$ and $\text{DN}$, converting a portion of $\text{DN}$ to its oxidation product [16, 30, 31] with different spectral and distribution properties. Another explanation could be the different degree of aggregation of the complexes derived from $\text{V}^{\text{IV}}$ and $\text{V}^{\text{V}}$. The small differences at wavelengths where the blank (spectrum 3) absorbs intensively, could be regarded as a result of an oxidation-reduction interaction between $\text{V}^{\text{V}}$ and $\text{DN}$, converting a portion of $\text{DN}$ to its oxidation product [16, 30, 31] with different spectral and distribution properties. Another explanation could be the different degree of aggregation of the complexes derived from $\text{V}^{\text{IV}}$ and $\text{V}^{\text{V}}$. It is supported by the observation (Figs. 1 and S1) that the main absorption band at 310 – 350 nm for the species obtained with $\text{V}^{\text{IV}}$ is more clearly split into two components (see the blue circle in Fig. 1b). This evidence of aggregation [32] must be related in some way to another type of aggregation, characteristic for the blank samples, whose visible manifestation (spectra 3 in Figs. 1 and S1) is a very narrow peak (at ca. 325 nm) which depends on the $\text{DN}$ concentration (spectra 3 and 3’ in Fig. 1b).

Spectra 1 and 2 in Figs. 1 and S1 are characterized by a main absorption maximum at $\lambda = 333 \text{ nm}$. Another maximum of interest is that at $\lambda = 630 \text{ nm}$.
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A moderate concentration of DN the position of these maxima is not affected by changes in pH and the absorption ratio \(A_{333}/A_{630}\) changes only slightly. However, when the concentration of DN is low (e.g. \(8.0 \times 10^{-5}\) mol dm\(^{-3}\)) the main maximum for the sample with V\(^{V}\) shifts to ca. 340 nm and the absorbance at the second maximum (at 630 nm) becomes very low (Fig. 1b, spectrum 2'); as a result, the \(A_{333}/A_{630}\) ratio increases significantly. The spectral changes accompanying the decrease of the DN concentration could be attributed to retention of the initial fifth oxidation state of vanadium and related differences in the composition of the extracted species.

Fig. 2 illustrates the dependence of the absorbance at 333 nm and 630 nm on the concentration of DN. Note that the shape of the curve 1 (obtained with V\(^{V}\) at \(\lambda = 333\) nm) is normal, while that of curve 2 (obtained with V\(^{V}\) at the same conditions) is complicated due to oxidation-reduction events.

The dependence of the absorbance on the concentration of TTC, when the DN concentration is \(4 \times 10^{-4}\) mol dm\(^{-3}\), is shown in Fig. 3. There are no anomalies in the shape of the curves obtained with V\(^{V}\). One can conclude comparing curves 1 and 2 that saturation is reached more easily when the initial oxidation state of vanadium is V (curve 2). In this case, there is a well-defined plateau (with a constant maximum absorbance in a wide concentration range). When the initial oxidation state of vanadium is IV (curve 1), a gradual increase in the absorbance is observed up to \(C_{TTC}\) close to \(1.2 \times 10^{-3}\) mol dm\(^{-3}\). This is typical for both wavelengths (333 nm and 630 nm) and shows that there might be some difference in the mechanisms of complex formation for V\(^{IV}\) and V\(^{V}\).

To determine the molar ratios in the ternary complexes, we used the mobile equilibrium method [33], the straight-line method of Asmus [34], and the
Job’s method of continuous variations [35]. The results based on the saturation curves shown in Figs. 2 and 3 are given in Figs. 4 – 6 (mobile equilibrium method) and Figs. S2 – S5 (straight-line method of Asmus). Fig. 4 shows that the vanadium:DN molar ratio is 1:2 when the initial oxidation state of vanadium is IV (straight lines 1 and 1’; slopes close to 2). When the initial oxidation state is V (straight lines 2 and 2’), the vanadium:DN molar ratios are different for 333 nm and 630 nm (1:1 and 1:2 respectively). The same result was obtained by the method of Asmus (Fig. S3). It should be noted that the result 1:1 was obtained for relatively low DN concentrations (up to 1×10^{-4} mol dm^{-3}).

When the DN concentration is low, the chance of a fast oxidation-reduction process between the diphenolic compound and V^{IV} is lower [36]. Therefore, V^{IV} can be partially extracted in the organic phase under the form of a ternary complex according to Eq. 1.

\[
\begin{align*}
\text{H}_2\text{VO}_4^{-} (\text{aq}) + \text{H}_2\text{DN} (\text{org}) + \text{TT}^+ (\text{aq}) & \rightarrow \\
(\text{TT}^+)\text{[VVO}_2\text{(DN)}] (\text{org}) + 2\text{H}_2\text{O} (\text{aq})
\end{align*}
\]  

Eq. 1 is constructed in accordance with the established V^{IV}:TTC molar ratio of 1:1 (Fig. 5, line 2; Fig. S5a) and the state of V^{IV} [6] and the tetrazolium salt [17] in the aqueous phase. This reaction involves the formation of an anionic complex [V^{IV}O(DN)]^{−} whose ground-state equilibrium geometry is shown in Fig. 7, structure I. Studies with other catecholic compounds [36] have shown that the formation of the 1:1 (V^{IV}:DN) complex is a fast process favoured by increasing the pH [31]. The fact that there is a serious difference in the shape of the pH curves for \( \lambda = 333 \) nm (Fig. S6, curves 1 and 2) for V^{IV} (maximum at pH 5.5) and V^{V} (maximum at pH 7) shows that eq. 1 is really an important stage in the overall extraction-chromogenic process for the system with V^{IV} (especially for DN concentrations lower than ca 5×10^{-4} mol dm^{-3}).

If we assume that the absorption maximum at 630 nm is due to the formation of a 1:2 V^{IV}-to-DN ternary complex (Fig. 4, lines 1’ and 2’; Figs. S2b and S3b), two formulae are of importance considering that the V:TTC molar ratio is 1:1 at this wavelength (Fig. 5, lines 1’ and 2’; Figs. S4b and S5b): \((TT^+)\text{[V}^{IV}\text{O(HDN)}\text{(DN}^2\text{)N}] (\text{org})\) (Fig. 7, structure II) and \((TT^+)\text{[V}^{IV}\text{(OH)(DN)N}] (\text{org})\) (Fig. 7, structure III). These isomeric structures differ by the position of the hydrogen atom H13. In the structure II, H13 is bonded to the oxygen atom O3 from DN and in the structure III – to the oxygen atom of the V=O group.

Line 1 in Fig. 5, obtained for the complex derived from V^{IV} at 333 nm, has a slope which is statistically different from unity: 1.22 ± 0.03. There are two explanations of this result:

1. Simultaneous extraction [37] of complexes with different TT-to-V ratios: 1:1 and 2:1.
2. Aggregation in the organic phase [19, 38, 39].

The assumption of simultaneous extraction of 1:1 and 2:1 complexes is not consistent with the results presented in Fig. 8. In fact, a symmetrical isomolar curve with a maximum at \( x = 0.5 \) was obtained. On the other hand, the concavities near the ends of this curve are a strong indication for the existence of species of the type M\(_{m}\)L\(_{n}\)
where \( m = n > 1 \) [38-41] and \( M \) and \( L \) are the cation and anion, respectively. As a matter of fact, this is consistent with the assumption made above that some kind of aggregates are formed in the organic phase, especially when the initial oxidation state of vanadium is IV.

The mobile equilibrium method [33] is a useful tool for determining the composition of complex species with \( m = n \) [19, 38, 39]. The results shown in Fig. 6 (slope of 3 for \( n = m = 3 \)) demonstrate that the extracted species can be regarded as aggregates made of three subunits with a \( V^{V} : T T \) molar ratio of 1:1. If we assume that these three subunits are identical, e.g. \((T T^{+})[V O \text{ (HDN}^{-}) (D N_{2}^{-})]_{3} \), one can write the following equation under the optimum conditions for \( V^{V} \) extraction (Table 1):

\[
3 V O(H_{2}O)_{5}^{2+}\ (aq) + 6 H_{2}DN\ (org) + 3 T T^{+}\ (aq) \leftrightarrow \leftrightarrow \left[[(T T^{+})[V O \text{ (HDN}^{-}) (D N_{2}^{-})]]_{3}\ (org) + 6 H_{2}O\ (aq) + 9 H^{+}\ (aq) \right] (2)
\]

A parallel process, which is the main process that occurs in the blank, is the interaction between TTC and ND. Based on our experience with similar systems containing tetrazolium salts and diprotic chromogenic reagents \( H_{2}L \) [42], and the above mentioned indication of aggregation in the blank (a very narrow peak at \( \lambda = 325 \) nm), we can propose the following equation for this process:

\[
x H_{2}DN\ (org) + x T T^{+}\ (aq) \rightarrow \left[(T T^{+})\text{(HDN)}\right]_{x}\ (org) + x H^{+}\ (aq) \quad (3)
\]

It should be mentioned that in contrast to the previously reported system \( V^{V} \)-DN-INT [11] the spectral characteristics of the blank are stable in time (Fig. S9). This indicates that (i) \( x \) can be regarded as a constant for the given reaction conditions and (ii) there is no oxidation-reduction reaction between DN and TTC. Having in mind eq. 3, we can rewrite eq. 2 in the following way:

\[
3 V O(H_{2}O)_{5}^{2+}\ (aq) + 3 H_{2}DN\ (org) + \left[[(T T^{+})\text{(HDN)}\right]_{x}\ (org) \rightarrow \rightarrow \left[(T T^{+})[V O \text{ (HDN}^{-}) (D N_{2}^{-})]]_{y}\ (org) \right] + + \left[[(T T^{+})\text{(HDN)}\right]_{(x-3)}\ (org) + 5 H_{2}O\ (aq) + 6 H^{+}\ (aq) \right. (4)
\]

As noted above, there is a difference in the extraction mechanism when the initial oxidation state of vanadium is \( V \) (and the concentration of the DN is not very high). In this case, the complex formation passes through the formation of an extractable \( V^{V} \) complex \((T T^{+})[V O \text{ (DN)}]\) (step 1). The next step, described by Kustin et al [30] for similar catecholic compounds in aqueous solutions, is the destruction of the complex due to changes in DN which accompany its oxidation by \( V^{V} \) (step 2; rate determining step). The last step 3 is the formation of the final \( V^{V} \)-DN-TT complex. In our conditions, the slow step 2 occurs in the organic phase. Consequently, it can affect the processes of aggregation therein and the formula of the final structure should be \([[(T T^{+})[V O \text{ (HDN}^{-}) (D N_{2}^{-})]]_{y}, with y less than 3.\)

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**Table 1. Extraction-spectrophotometric optimization of the \( V^{V} \)-DN-TTC-water-chloroform system**

| Parameter          | Optimization range | Optimal value | Figures |
|--------------------|--------------------|---------------|---------|
| Wavelength, nm     | 300-1000           | 333           | Fig. 1 and S1 |
| pH                 | 4.0-8.0            | 5.5±0.2       | Fig. S6 |
| Buffer volume, cm³ | 0.5-5.0            | 1.0           | Fig. S7 |
| Concentration of DN, mol dm⁻³ | (0.2-10.0)×10⁻⁴ | 5.0×10⁻³ | Fig. 3 |
| Concentration of TTC, mol dm⁻³ | (0.25-15.0)×10⁻⁴ | 1.0×10⁻³ | Fig. 4 |
| Extraction time, sec. | 10-300          | 120           | Fig. S8 |

**Figure 6:** Determination of the TTC: \( V^{V} \) molar ratio by the mobile equilibrium method for \( \lambda = 333 \) nm and \( m = n \). pH 5.5, \( c_{V(IV)} = 3×10^{-5} \) mol dm⁻³, \( c_{DN} = 4.0×10^{-4} \) mol dm⁻³. Straight line equations \( y = (a ± SD)x + (b ± SD) \): 1) \( y = (1.22 ± 0.03)x + (4.87 ± 0.10) \), \( R^2 = 0.9980 \); 2) \( y = (2.10 ± 0.04)x + (8.83 ± 0.13) \), \( R^2 = 0.9988 \); 3) \( y = (2.98 ± 0.06)x + (12.79 ± 0.21) \), \( R^2 = 0.9984 \); 4) \( y = (3.86 ± 0.09)x + (16.76 ± 0.31) \), \( R^2 = 0.9980 \)
Figure 7: The optimized ground-state geometry of monoanionic chelates of $V^+$ (structure I) and $V^{n-}$ (structures II and III) with DN
3.2 Analytical characteristics

We studied the dependence of the absorbance at $\lambda = 333$ nm on the concentration of $V^{IV}$ under the optimum conditions for the formation of aggregates containing three 1:2:1 ($V^{IV}$:DN:TTC) subunits (Table 1). Good linearity ($R^2 = 0.9994$, $N = 11$) was observed in the concentration range from 0.1 μg cm$^{-3}$ to 3.1 μg cm$^{-3}$ (Fig. 9, line 1). The linear regression equation was $A = 0.405y + 0.011$ where $y$ is the $V^{IV}$ concentration in μg cm$^{-3}$. The molar absorptivity ($\varepsilon$) and Sandell's sensitivity (SS) were $\varepsilon_{333} = 2.1 \times 10^4$ dm$^3$ mol$^{-1}$ cm$^{-1}$ and SS$_{333} = 2.4$ ng cm$^{-2}$. The limits of detection (LOD) and quantitation (LOQ), calculated as 3 and 10 times SD of the intercept divided by the slope, were LOD = 0.03 μg cm$^{-3}$ and LOQ = 0.11 μg cm$^{-3}$.

3.3 Constant of extraction and fraction extracted

We calculated the conditional constant of extraction $K_{ex}$ by the Likussar-Boltz method [43] (Fig. 8) extended by us with equation 5 which is valid for $M_mL_n$ species with $m = n = 3$ (where M and L are the cation and anion, respectively).

$$K_{ex} = 0.001375 \times (6/k)^5 \times y_{max}^{-1} (1-y_{max})^{-6}$$

(5)

The obtained value was Log $K_{ex} = 21.2 \pm 0.2$ (three replicate experiments). It is statistically equivalent to that found by the mobile equilibrium method [33] for $m = n = 3$: Log $K_{ex} = 21.1 \pm 0.2$. Eq. 6 was used for the calculations. In it, $c$ is the vanadium concentration ($c_{V(IV)} = 3 \times 10^{-5}$ mol dm$^{-3}$), $b$ is the intercept of the straight line 3 in Fig. 6 (b = 12.79 ± 0.21), and $A_{max} = 0.671$ (see Fig. 3, curve 1; three replicate experiments).

$$\log K_{ex} = b - \log m - \log(c/A_{max})^{m-1}$$

(6)

The fraction extracted was calculated by the formula $E\% = 100 \times A_1/A_3$, where $A_1$ and $A_3$ are the absorbances measured for single and triple extractions at the optimum conditions (Table 1) in equal final volumes of 25 cm$^3$ as described previously [11]. The value obtained was $E = (98 \pm 2)\%$ (four replicate experiments).

4 Conclusions

Vanadium forms well chloroform-extractable species with DN and TTC. They are stable and intensively colored.

Figure 8: Likussar-Boltz method for the determination of the conditional extraction constant ($K_{ex}$). pH 5.5, $\lambda = 333$ nm, $c_{DN} = 5 \times 10^{-4}$ mol dm$^{-3}$, $k = c_{V(IV)} + c_{TTC} = 1 \times 10^{-4}$ mol dm$^{-3}$.

Figure 9: Absorbance of extracted species vs concentration of vanadium. pH 5.5, $c_{TTC} = 1.0 \times 10^{-3}$ mol dm$^{-3}$, $\lambda = 333$ nm (1 and 2), $630$ nm (1’ and 2’), $c_{V(IV)} = 5.0 \times 10^{-4}$ mol dm$^{-3}$ (1 and 1’) or $4.0 \times 10^{-4}$ mol dm$^{-3}$ (2 and 2’). Line equations: 1) $y = 0.4054x + 0.0106$, $R^2 = 0.9994$; 1’) $y = -0.0131x^2 + 0.1637x - 0.0004$, $R^2 = 0.9992$; 2) $y = -0.0234x^2 + 0.3592x + 0.0109$, $R^2 = 0.9995$; 2’) $y = -0.0135x^2 + 0.1267x + 0.0083$, $R^2 = 0.9975$

When the concentration of DN is high, the oxidation state of vanadium in the final complex is IV independently of the initial oxidation state of vanadium – IV or V. In this case the extracted species are aggregates of three 1:1:2 (TT-$V^{IV}$-DN) complexes. There is a difference in the extraction mechanism for $V^{V}$ and $V^{IV}$ when the DN concentration is low, since $V^{V}$ is quickly extracted under the form of a 1:1:1 complex, (TT’)$[V^{IV}O_2(DN)]$. As a result, the oxidation-reduction process between $V^{V}$ and DN (which is followed
by destruction of this complex) occurs in the organic phase and the degree of aggregation of the final product(s) becomes smaller.

The results described in this paper show that the well-known Likussar-Boltz method can be extended for compounds with a molar ratio of 3:3, provided that other method is used to prove the mentioned molar ratio.

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Supplementary Material: The online version of this article offers supplementary material (Figs.S1-S9).

References

[1] Tracey A.S., Willsky G.R., Takeuchi E.S., Vanadium: chemistry, biochemistry, pharmacology and practical applications, CRC press, Boca Raton – London – New York, 2007.
[2] Michibata H.E., Vanadium: biochemical and molecular biological approaches, Springer, Dordrecht – Heidelberg – London – New York, 2012.
[3] Rehder D., The role of vanadium in biology, Metallomics, 2015, 7, 730-742.
[4] Chen Z.L., Owens G., Trends in speciation analysis of vanadium in environmental samples and biological fluids – a review, Anal. Chim. Acta, 2008, 607, 1-14.
[5] Pyrzyńska K., Recent developments in spectrophotometric methods for determination of vanadium, Microchim Acta, 2005, 149, 159-164.
[6] Taylor M. J. C., Staden J. F., Spectrophotometric determination of vanadium(IV) and vanadium(V) in each other’s presence, Analyst, 1994, 119, 1263-1276.
[7] Agarwal C., Deb M., Mishra, R., Sensitive spectrophotometric determination of vanadium in environmental samples at ppb levels, Anal. Lett., 1990, 23, 2063-2075.
[8] Agrawal C., Patel K.S., Mishra, R.K., Extraction-spectrophotometric determination of vanadium (V) with pyrocatechol and N1-hydroxy-N1,N2-diphenylbenzamidine, Bull. Chem. Soc. Jpn., 1991, 64, 2616-2618.
[9] Prasada Rao T., Reddy M.L.P., Ramalingom Pillai A., Application of ternary and multicomponent complexes to spectrophotometric and spectrodifluorometric analysis of inorganics, Talanta, 1998, 46, 765-813.
[10] Nardillo A.M., Catoggio, I.A., A study of vanadium(IV)-3-methylcatechol-quaternary ammonium systems : its analytical implications, Anal. Chim. Acta, 1975, 74, 85-99.
[11] Simeonova Z., Gavazov K., Alexandrov A., Extraction-spectrophotometric study on the system vanadium(V) – 2,3-dihydroxynaphthalene – iodonitrotetrazolium chloride – water – chloroform and its analytical application, Cent. Eur. J. Chem., 2006, 4, 258-266.
[12] Lekova V., Gavazov K., Dimitrov A., Racheva P., Extraction-spectrophotometric study on the vanadium(V) - 2,3-dihydroxynaphthalene - tetrazolium violet - water - chloroform system, Scientific Researches of the Union of Scientists – Plovdiv, Ser. C, 2007, 6, 171-174.
[13] Mondal R.K., Rathore D.P.S., Tarafder, P.K., Extraction of vanadium as an ion-pair of its 2,3-dihydroxynaphthalene–vanadium(V) anionic complex with cetyltrimethylammonium cation (CTA–), and its sensitive and selective determination in silicate rocks, soil and minerals, In: National Seminar on Significant Advancements in Plasma/Flame/Associated Techniques and their Applications in Chemical Characterization of Atomic Minerals, SAP-2013 (23-24 January 2013, AMD Hyderabad, India) 2013, 83-84.
[14] Mondal R. K., Rathore D.P.S., Tarafder P. K., Determination of vanadium in steel and geological samples by its extraction and spectrophotometry determination using 2,3-dihydroxynaphthalene, Explor. Res. Atomic Miner., 2013, 23, 113-116.
[15] Tarafder P. K., Mondal R. K., A review on the complex forming ability of O,0’ type ligands with transition metals: introducing 2,3-dihydroxynaphthalene as a potential analytical reagent, Rev. Anal. Chem., 2011, 30, 73-81.
[16] Aderian S., Pratt R., Inhibition of serine β-lactamases by vanadate – catechol complexes, Biochemistry, 2008, 47, 9467-9474.
[17] Gavazov K.B., Dimitrov A.N., Lekova V.D., The use of tetrazolium salts in inorganic analysis, Russ. Chem. Rev., 2007, 76, 169-179.
[18] Stefanova T. S., Simitchiev K. K., Gavazov K. B., Liquid–liquid extraction and cloud point extraction for spectrophotometric determination of vanadium using 4-(2-pyridylazo) resorcinol, Chem. Pap., 2015, 69, 495-503.
[19] Kostova D., Triphenyltetrazolium chloride as a new analytical reagent for molybdenum(VI): Application to plant analysis, J. Anal. Chem., 2011, 66, 384-388.
[20] Alexandrov A., Tetrazolium salts for solvent extraction of elements as ion association complexes. Review, Universität des Saarlandes, Saarbrücken, 1984.
[21] Bashammakh A. S., Extractive spectrophotometric determination of bismuth(III) in water using some ion pairing reagents. E.J.Chem., 2011, 8, 1462-1471.
[22] El-Shahawi M., Bashammakh A., Alwael H., Al-Sibaai A., Al-Ariqe H., ICP-OES determination of titanium(VI) in marine and wastewater samples after preconcentration onto unloaded and reagent immobilized polyurethane foams packed columns, J. Chromatograph. Separat. Techniq. 2014, 5, 247, DOI: 10.4172/2157-7064.1000247.
[23] Berridge M.V., Herst P.M., Tan, A.S., Tetrazolium dyes as tools in cell biology: New insights into their cellular reduction, Biotechnol. Annu. Rev., 2005, 11 (Suppl.), 127-152.
[24] Sabnis, R. W., Handbook of biological dyes and stains: synthesis and industrial applications, Wiley, Hoboken, 2010.
[25] Ogata J., Kikura-Hanajiri R., Yoshimatsu K., Kiuchi F., Goda Y., Detection method for the ability of hemp (Cannabis sativa L.) seed germination by the use of 2,3,5-triphenyl-2H-tetrazolium chloride (TTC), Yakugaku zasshi: J. Pharmaceut. Soc. Jpn., 1998, 128, 1707-1711.
[26] Creanga, D., Nadejde, C., Molecular modelling and spectral investigation of some triphenyltetrazolium chloride derivatives, Chem. Pap., 2015, 69, 495-503.
[27] Gavazov K.B., Delchev V.B., Toncheva G.K., Georgieva Z.G., Microcomputer-Assisted Multicomponent Spectrophotometric Analysis. DE GRUYTER OPEN.
An extraction-chromogenic system for vanadium (II) with 4-nitrocatechol and 2,3,5-triphenyl-2H-tetrazolium, Russ. J. Gen. Chem., 2015, 85, 1945-1951.

Genç F., Gavazov K.B., Türkyilmaz, M., Ternary complexes of vanadium(IV) with 4-(2-pyridylazo)-resorcinol (PAR) and ditetrazolium chlorides (DTC), Cent. Eur. J. Chem., 2010, 8, 461-467.

Frisch M.J., Trucks G.W., Schlegel H.B., Scuseria G.E., Robb M.A., Cheeseman, J.R.; et al., Gaussian 03, Revision D.01, (Gaussian, Inc., Wallingford CT, 2004).

Kustin K., Nicolini C., Toppen D.L., Interaction of catechol and catechol derivatives with dioxovanadium (V). II. Kinetics of ligand oxidation, J. Am. Chem. Soc., 1974, 96, 7416-7420.

Ferguson J.H., Kustin K., Interactions between vanadate and 1,2-aromatic diols. Complex formation and oxidation-reduction, Inorg. Chem., 1979, 18, 3349-3357.

Yuzhakov V.I., Association of dye molecules and its spectroscopic manifestation, Russ. Chem. Rev., 1979, 48, 1076-1091.

Zhiming Z., Dongsten M., Cunxiao Y., Mobile equilibrium method for determining composition and stability constant of coordination compounds of the form $M_nR_m$, J. Rare Earths, 1997, 15, 216-219.

Asmus E., Eine neue Methode zur Ermittlung der Zusammensetzung schwacher Komplexe, Fresenius’ J. Anal. Chem., 1960, 178, 104-116, (in German).

Likussar W., Boltz D.F., Theory of continuous variations plots and a new method for spectrophotometric determination of extraction and formation constants, Anal. Chem., 1971, 43, 1265-1272.

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