

REACTIONS OF VANADIUM(V, IV) WITH 4-(2-THIAZOLYLAZO)RESORCINOL

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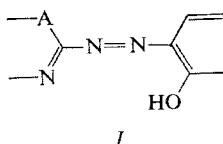
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Complex VO₂LH was detected spectrophotometrically in solutions of vanadium(V) with 4-(2-thiazolylazo)resorcinol (TAR = LH₂) in 30% v/v ethanol in a pH range of 1–2.5; the complex exhibits a principal absorption maximum at 555–560 nm and a side peak at 440 nm; the molar absorption coefficient value is $\epsilon(545 \text{ nm}) = 1.67 \cdot 10^4$. The *p*-hydroxyl group of the ligand in the VO₂LH chelate begins to dissociate at pH ≥ 2.5 during the formation of chelate VO₂L⁻ with λ_{max} 545 nm and $\epsilon(545 \text{ nm}) = 2.65 \cdot 10^4$. The analysis of the absorbance–pH curves and the $A = f(c_1)$ dependences gave the equilibrium constant for chelate VO₂LH, $*k_{11} = [\text{VO}_2\text{LH}][\text{H}]/[\text{VO}_2][\text{LH}_2]$, the approximate value of $\log *k_{11}$ being 1.5, the stability constant, $\beta_1 = [\text{VO}_2\text{LH}]/[\text{VO}_2] \cdot [\text{LH}^*] = *k_{11}/K_{a3}$ (where K_{a3} is the dissociation constant for the *o*-hydroxyl group in TAR), $\log \beta_1 = 12.1$, and the dissociation constant for chelate VO₂LH, $K_{ak} = [\text{VO}_2\text{L}][\text{H}]/[\text{VO}_2\text{LH}]$, $\log K_{ak} = -3.57$ in 30% v/v ethanol at $I = 0.1$ and 25°C. In 30% v/v dimethylformamide, these constants for chelate VO₂LH are $\log *k_{11} = 0.70$, $\log \beta_1 = 11.12$ and $\log K_{ak} = -3.74$. Ternary complex V(LH)(OC₄H₉)₃⁺ with a principal maximum at 575 nm and a side peak at 450 nm and with $\epsilon(575 \text{ nm}) = 1.70 \cdot 10^4$ is quantitatively formed in 30% v/v ethanol in the presence of *n*-butanol, in the range 1M-HNO₃ – pH 2.5. Complex VO₂L⁻ is suitable for the determination of vanadium (V) at a pH of 4.5–5.5 and the ternary complex for a less sensitive but more selective determination in 30% v/v ethanol containing 1.0–0.1M-HNO₃. Vanadium(IV) forms a less stable complex, V(OH)L⁺, at pH ≥ 2.2 , with a single maximum at 545 nm, $\epsilon(545 \text{ nm}) = 2.43 \cdot 10^4$, equilibrium constant $k_{11}^* = [\text{V(OH)L}][\text{H}]/[\text{V(OH)}_2][\text{LH}_2]$, $\log *k_{11} = -0.40$ and $\log \beta_1 = 10.22$ in 30% v/v ethanol at $I = 0.1$ and 25°C.

Reactions of vanadium(V) belong among the analytically important reactions of heterocyclic azo dyes containing the analytical group I



where A = C, S, N

In aqueous or mixed media, red, purple or blue binary and ternary chelates are formed chiefly with pyridylazo and thiazolylazo dyes; some of them are extracted into non-aqueous solvents

as solvates or ion-associates. Vanadium(V) can be sensitively and selectively determined spectrophotometrically with 4-(2-pyridylazo)resorcinol¹⁻¹⁷. Little attention has been paid to complexes of the other valence forms of vanadium with heterocyclic azo dyes^{18,19} and to the reaction of vanadium(V) with thiazolylazo dyes²⁰⁻²².

In the present paper, reactions of vanadium(V) and (IV) with 4-(2-thiazolylazo)-resorcinol (TAR), which is a suitable reagent in this group because of its availability and easy preparation in a pure form, were studied spectrophotometrically in a mixed medium of 30% v/v ethanol, or 30% v/v dimethylformamide. The earlier results for the equilibrium of vanadium(V) with TAR (ref.²²) were made more complete and the procedures for the spectrophotometric determination of vanadium with this reagent were evaluated.

EXPERIMENTAL AND RESULTS

Chemicals and Instruments

A 0.1M solution of vanadium(V) was prepared by dissolving 11.698 g NH_4VO_3 (*p.a.*) in 200 ml of cold H_2SO_4 (1 : 1), adding the substance in portions, and diluting to 1000 ml. 0.05M solutions of vanadium(IV) sulphate and perchlorate were prepared by dissolving a weighed amount of ammonium vanadate in 200 ml H_2SO_4 (1 : 4) or 200 ml HClO_4 (1 : 5) resp., reducing the vanadium with gaseous sulphur dioxide, removing excess reductant by heating on a water bath and diluting with water to 1000 ml. The solution titre was checked manganometrically²³.

4-(2-Thiazolylazo)resorcinol (Pure Chemicals Research Institute, Lachema, Brno), recrystallized from ethanol, was evaluated by elemental analysis, by thin-layer chromatography on silica gel G (ref.²⁴) and by spectrophotometric titration with copper(II) nitrate forming a 1 : 1 chelate in a medium of 20% v/v ethanol, with a final ligand concentration of $c_L = 3.7 \cdot 10^{-5}\text{M}$ at pH 5.8 (0.02M acetate buffer) and λ 540 nm. Solutions of the reagent were prepared by dissolving a weighed amount of the substance in ethanol or dimethylformamide.

95% ethanol, refined, of highest purity, denatured with 5% methanol, was distilled before use; it can contain varying amounts of impurities increasing the absorbance of a V(V) solution containing TAR in 30% v/v ethanol in the acidic region. Consequently, especially during study of the ternary V(V)-TAR-*n*-butanol complex in acid media, spectral pure ethanol for UV measurements was employed. All other solvents were of *p.a.* purity or redistilled.

The acidity of vanadium(V)-TAR solutions was adjusted with nitric acid or sodium hydroxide or ammonia; during the determination of vanadium at pH 4.5-5.5 a pyridine buffer was employed; in concentrations of $\leq 0.1\text{M}$, it does not affect the results.

The ionic strength was adjusted to a value of 1.0 using potassium nitrate.

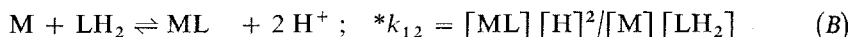
The absorbance of the solutions was measured in the usual way or in an apparatus for continuous measurements using the SF 4A spectrophotometer and 10 mm cuvettes; the acidity of the solutions was measured using the PHK-1 pH-meter with a Radiometer G 202 B glass electrode. The pH values for mixed media were not corrected.

Methods of Studying Complex Equilibria

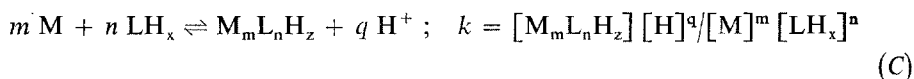
The types of complex equilibria, the molar absorption coefficients and the equilibrium constants of the chelates were determined from the absorbance-pH curves

of solutions with excess metal or reagent and from the $A = f(c_L)$ dependences at a constant metal concentration by pH graphical analysis as described in an earlier paper²⁵. Some of the dependences in 30% v/v dimethylformamide medium were also evaluated using the PRCEK III program (ref.^{26,27}) on the MSP 2A computer. The existence of side equilibria, the hydrolysis of vanadate and the formation of mixtures of vanadium(V)-TAR complexes markedly affected the results.

For direct and logarithmic analysis of the absorbance-pH curves in solutions with excess metal ions, where one of the following equilibria is particularly important,



or further equilibria according to the general equation



and when the metal is non-absorbing, then the equations

$$A = \varepsilon c_L/n - (ZA - \bar{\varepsilon}_L c_L)(n\bar{\varepsilon}_L - \varepsilon Z)^{n-1} [H]^q / (nA - \varepsilon c_L)^{n-1} k n c_M^m \quad (1)$$

$$\begin{aligned} \log [(ZA - \bar{\varepsilon}_L c_L) / (\varepsilon c_L - nA)^n] + (n-1) \log (Z\varepsilon - n\bar{\varepsilon}_L) = \\ = q \text{ pH} + \log k + m \log c_M \end{aligned} \quad (2)$$

are valid. For formation of chelates in solutions with excess ligand, it holds that

$$c_M / (A - A_{0L}) = 1/\varepsilon + [H]^q Z / k \varepsilon c_L^n \quad (3)$$

$$\log [(A - A_{0L}) Z^n / (\varepsilon c_M - A + A_{0L})] = \log k + q \text{ pH} + n \log c_L \quad (4)$$

In analysis of the $A = f(c_L)$ dependence at constant c_M and pH, the equations

$$\begin{aligned} c_M / (A - A_{0L}) = 1/(\varepsilon - n\bar{\varepsilon}_L/Z) + \\ + [H]^q Z^n / [c_L - n(A - A_{0L}) / (\varepsilon - n\bar{\varepsilon}_L/Z)]^n (\varepsilon - n\bar{\varepsilon}_L/Z) k, \end{aligned} \quad (5)$$

$$\begin{aligned} \log \{(A - A_{0L}) / [c_M (\varepsilon - n\bar{\varepsilon}_L/Z) - (A - A_{0L})]\} = \\ = q \text{ pH} + \log k + n \log [c_L - n(A - A_{0L}) / (\varepsilon - n\bar{\varepsilon}_L/Z)] - n \log Z \end{aligned} \quad (6)$$

were employed to describe the complex formation. The limit of transformation (5) was approximately determined graphically using the primary dependence $c_M/\Delta A =$

$= f(1/c_L^n)$ and refined by 2–3 successive approximations until two successive values of the intercept were identical.

The conversion of the quantitatively formed MLH complex into the ML complex by dissociation of the *p*-hydroxyl group of the ligand, *i.e.* the equilibrium



is characterized for the pH curves of solutions with excess metal by the equations

$$c_L/A = n/\varepsilon_2 + (nA - \varepsilon_1 c_L) [\text{H}]^q / A \varepsilon_2 K_{\text{ak}}, \quad (7)$$

$$c_L/A = n/\varepsilon_1 - (\varepsilon_2 c_L - nA) K_{\text{ak}} / A [\text{H}]^q \varepsilon_1, \quad (8)$$

$$\log(A - \varepsilon_1 c_L) / (\varepsilon_2 c_L - A) = q \text{pH} + \log K_{\text{ak}}. \quad (9)$$

Symbols employed: c_M, c_L are the overall concentrations of the metal ions or the ligand, respectively, $\bar{\varepsilon}_L = \varepsilon_{\text{LH}_2} + \varepsilon_{\text{LH}_3} [\text{H}] / K_{\text{a1}}$ where $\varepsilon_{\text{LH}_2}$ and $\varepsilon_{\text{LH}_3}$ are the molar absorption coefficients of the LH_2 and LH_3^+ forms of the reagent and K_{a1} is the dissociation constant of the LH_3^+ form, $Z = 1 + [\text{H}] / K_{\text{a1}}$, ε and k are the molar absorption coefficient and equilibrium constant of the chelate in general, ε_1 and ε_2 are the molar absorption coefficients of the MLH and ML chelates and A_{0L} is the absorbance of the reagent with a concentration of c_L .

Acid-Base Equilibria of 4-(2-Thiazolylazo)resorcinol in 30% v/v Ethanol and 30% v/v Dimethylformamide

The dissociation constants of TAR in 30% v/v ethanol and 30% v/v dimethylformamide have already been determined graphically from the absorbance–pH curves using the equations derived earlier²⁵ or numerically using the PRCEK II program^{26,27}, and are given together with the λ_{max} values for the individual forms in Table I.

Complex Equilibria of Vanadium (V) with TAR in 30% v/v Ethanol

The absorption curves of solutions containing TAR ($c_L = 4.00 \cdot 10^{-5}$), and increasing metal concentrations reflect the formation of a complex with λ_{max} 555 nm and an isosbestic point at 485 nm at pH 1.71 (Fig. 1) and of another complex with λ_{max} 545–550 nm and λ_{iso} 480 nm at pH 4.80 (Fig. 2). The absorption curves of equimolar solutions ($c_M = c_L = 4.00 \cdot 10^{-5} \text{M}$) and of solutions with excess metal ($c_L = 4.00 \cdot 10^{-5} \text{M}$, $c_M = 4.00 \cdot 10^{-3} \text{M}$) at various pH values are analogous.

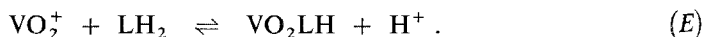
TABLE I
Dissociation Constants and Absorbance Maxima of TAR

Form	Dissociation of group	p <i>K</i> _a		λ _{max} ^a , nm
		30% ethanol ^a	30% DMF ^b	
LH ₃ ⁺	NH ⁺ thiazole	0.68	0.84 ± 0.04	482,410
LH ₂	<i>p</i> -OH	6.48	6.56 ± 0.07	438,415
LH ⁻	<i>o</i> -OH	10.62 ± 0.03	10.42 ± 0.07	480,400
L ²⁻				513,405

^a See ref.²⁸, ^b see ref.²⁹.

The absorbance-pH curves of V(V) solutions with excess reagent ($c_M = 4.00 \cdot 10^{-5}M$, $c_L/c_M = 20$) and of equimolar solutions ($c_M = c_L = 4.00 \cdot 10^{-5}M$) reflect the formation of chelates from pH 1.5–2.0; the pH-curves for solutions with excess metal ($c_L = 4.00 \cdot 10^{-5}M$, $c_M/c_L = 25, 50$ and 100) indicate chelate formation from pH 1 (Fig. 3a, curves 1–5). The inflection on the pH curves for excess metal at pH ~ 2.5 roughly separates the areas corresponding to two different complex equilibria (Fig. 3a, curves 1–3). While the same horizontal part of the pH curves for solutions with excess metal and with excess ligand indicates the probability of the formation of a chelate with V:L = 1:1 in both cases, the pH-curve of equimolar solutions at its highest part does not attain the value of the absorbance or conditional molar absorption coefficient (ϵ (545 nm) = $A/c_L = 16825$) found from curves for an excess of one component (average value $\epsilon = 26514$). On increasing the component concentrations to a value of $c_M = c_L = 6.4 \cdot 10^{-5}M$, the value of molar absorption coefficient is $\epsilon = 18125$. The pH curves of equimolar solutions in dimethylformamide have a similar course (Fig. 3b, curve 4), as have those in water²². The anomalous shape of the pH curves for equimolar solutions is probably a result of the hydrolysis of VO₂⁺ ions to give H₂V₁₀O₂₈⁴⁻ and HV₁₀O₂₈⁵⁻, which predominate in vanadate solutions at pH 2–6 (ref.³⁰) and do not quantitatively depolymerize during reaction with TAR. The HVO₄²⁻ and VO₄³⁻ ions formed in alkaline medium do not form coloured chelates.

The rising part of the absorbance-pH curves in solutions with excess metal or ligand in a pH range of 1–2.5 were graphically analyzed assuming the equilibrium



Dependence (3) for solutions with excess ligand ($c_L/c_M = 20$) is linear, dependences (1) for solutions with excess metal ($c_M/c_L = 25, 50$ and 100) are slightly curved at the

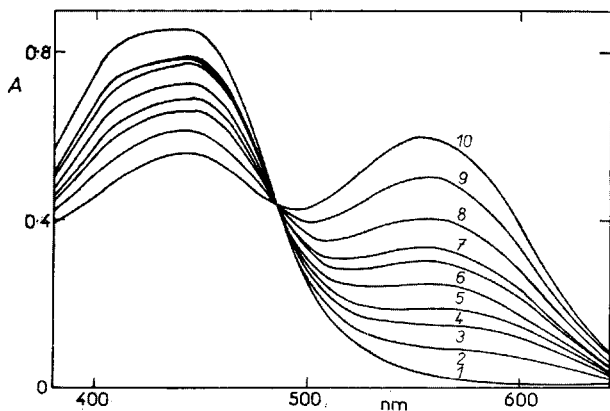


FIG. 1

Absorption Curves of TAR Solutions with Increasing Concentrations of V(V) in 30% v/v Ethanol at pH 1.71

$c_L = 4.00 \cdot 10^{-5} M$, c_M : curve 1 0, 2 $5.00 \cdot 10^{-6} M$, 3 $9.00 \cdot 10^{-6} M$, 4 $4.60 \cdot 10^{-5} M$, 5 $1.92 \cdot 10^{-4} M$, 6 $3.40 \cdot 10^{-4} M$, 7 $4.80 \cdot 10^{-4} M$, 8 $8.00 \cdot 10^{-4} M$, 9 $1.60 \cdot 10^{-3} M$, 10 $4.00 \cdot 10^{-3} M$ (corrected for the absorbance of V(V) at $\lambda \leq 490$ nm).

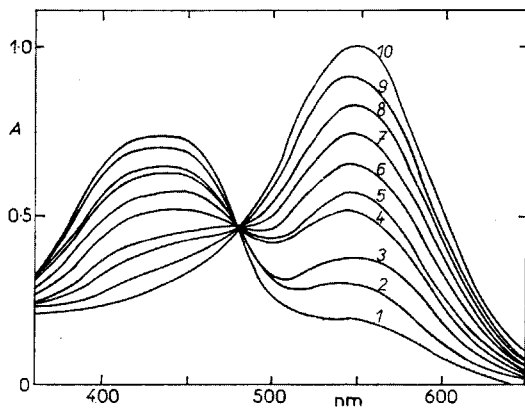


FIG. 2

Absorption Curves of TAR Solutions with Increasing Concentrations of V(V) in 30% Ethanol at pH 4.60

$c_L = 4.00 \cdot 10^{-5} M$, c_M : curve 1 $8.00 \cdot 10^{-6} M$, 2 $1.00 \cdot 10^{-5} M$, 3 $1.60 \cdot 10^{-5} M$, 4 $1.80 \cdot 10^{-5} M$, 5 $2.40 \cdot 10^{-5} M$, 6 $3.20 \cdot 10^{-5} M$, 7 $4.80 \cdot 10^{-5} M$, 8 $8.00 \cdot 10^{-5} M$, 9 $9.60 \cdot 10^{-5} M$, 10 $2.00 \cdot 10^{-4} M$ (corrected for the absorbance of V(V) at $\lambda \leq 410$ nm).

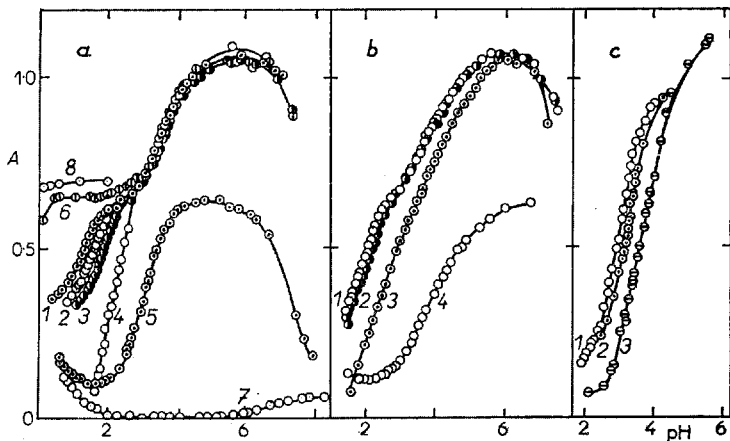


FIG. 3

Absorbance-pH Curves in the TAR-Vanadium(V) System λ 545 nm, I 0.1

a: V(V), 30% v/v ethanol. Curves 1-6 $c_L = 4.00 \cdot 10^{-5} M$, c_M/c_L : 1 100, 2 50, 3 25, 5 1, 7 0, 6 50 (ethanol impure), curves 7 and 8 $c_M = 4.00 \cdot 10^{-5} M$, c_L/c_M : 4 20, 8 10.6 (with 0.2% v/v n-butanol). *b:* V(V), 30% dimethylformamide. Curves 1-3 $c_L = 4.00 \cdot 10^{-5} M$, c_M/c_L : 1 200, 2 100, 4 1, curve 3 $c_M = 4.00 \cdot 10^{-5} M$, $c_L/c_M = 20$. *c:* V(IV), 30% v/v ethanol. Curves 1 and 2 $c_L = 4.00 \cdot 10^{-5} M$, c_M/c_L : 1 100, 2 25, curve 3 $c_M = 4.00 \cdot 10^{-5} M$, $c_L/c_M = 20$.

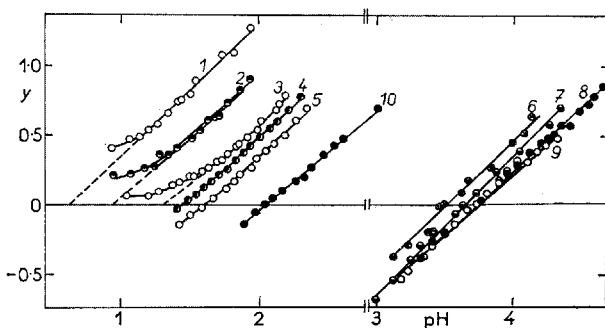


FIG. 4

Logarithmic Analysis of the Absorbance-pH Curves of a TAR Solution Containing V(V) at 545 nm

Curves 4, 5, 8, 9 30% v/v dimethylformamide, otherwise 30% v/v ethanol. Curves 1-5 $y = \log(ZA - \bar{\epsilon}_L c_L)/(e c_L - A)$, 6-9 $y = \log(A - \epsilon_1 c_L)/(\epsilon_2 c_L - A)$. $c_L = 4.00 \cdot 10^{-5} M$, c_M/c_L : curve 1 100, 2 50, 3 25, 4 200, 5 100, 6 100, 7 50, 8 100, 9 200, curve 10 $y = \log(\Delta AZ/\epsilon c_M - \Delta A)$, $c_M = 4.00 \cdot 10^{-5} M$, $c_L/c_M = 20$.

end of the low pH region due to undefined competing equilibria, but are also initially linear (at higher pH values) and provide similar values of the molar absorption coefficient for the VO_2LH chelate (Table II). The dependences of the logarithmic analysis of the pH-curves in the pH region 1–2.5 according to equations (2) and (4) with slope $q = 1.0$ confirm the dissociation of one proton in equilibrium (E). A deformation similar to that during direct analysis complicates the precise determination of the equilibrium constants of the VO_2LH chelate in solutions with excess metal, (Fig. 4, curves 1–3 and 6). The values of the equilibrium constants of the VO_2LH chelate determined by logarithmic analysis under various concentration conditions are given in Table III.

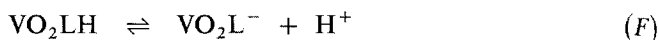
TABLE II

Values of the Molar Absorption Coefficients of Chelates of Vanadium(V) with TAR at 545 nm

Conditions	$\epsilon_{545\text{nm}}, \text{mmol}^{-1} \text{cm}^2$	
	VO_2LH^a	VO_2L^{-b}
30% v/v ethanol		
$c_L = 4.00 \cdot 10^{-5}\text{M}, c_M/c_L = 100$	16 350	27 452
$c_M/c_L = 50$	16 550	26 225
$c_M/c_L = 25$	17 250	26 100
$c_M = 4.00 \cdot 10^{-5}\text{M}, c_L/c_M = 10$	—	26 575
$c_L/c_M = 20$	—	26 250
$c_M = 4.00 \cdot 10^{-5}\text{M}, c_L = (2.9-9.6) \cdot 10^{-4}\text{M}, \text{pH } 2.05$	14 115	—
$c_L = (0.3-3.5) \cdot 10^{-4}\text{M}, \text{pH } 2.30$	15 679	—
$c_L = (1.5-7.6) \cdot 10^{-4}\text{M}, \text{pH } 2.69$	18 832	—
$c_L = (0.1-7.1) \cdot 10^{-4}\text{M}, \text{pH } 3.05$	20 000	—
30% v/v ethanol and $2 \cdot 10^{-3}\text{M}$ n-butanol		
$c_L = 4.00 \cdot 10^{-5}\text{M}, c_M/c_L = 50$	16 250	26 600
30% v/v dimethylformamide		
$c_L = 4.00 \cdot 10^{-5}\text{M}, c_M/c_L = 200$	17 375	24 925
	$16\,607 \pm 191^c$	$24\,830 \pm 38^c$
$c_L = 4.00 \cdot 10^{-5}\text{M}, c_M/c_L = 100$	17 750	25 325
$c_M = 4.00 \cdot 10^{-5}\text{M}, c_L/c_M = 20$	—	26 425
$c_M = c_L = 4.00 \cdot 10^{-5}\text{M}$	—	15 825
water		
$c_L = 4.00 \cdot 10^{-5}\text{M}, c_M/c_L = 50$	—	26 075

^a Direct analysis in the pH region 1.0–2.5, ^b from the horizontal part ($\epsilon = A/c$) at pH ~ 5.5 , ^c computed at 550 nm.

The dissociation of complex VO₂LH, *i.e.* equilibrium (F)



was evaluated by analysis of the second region of the rising part of the pH-curves for solutions with $c_M/c_L = 50$ and 100 in the pH range 3.0–4.5 using transformations (7)–(9) (Fig. 4, curves 6 and 7). The values of the molar absorption coefficient of the VO₂L⁻ chelate are given in Table II and the dissociation constant in Table III.

The concentration dependences $\Delta A = A - A_{0L} = f(c_L)$ at $c_M = 4.00 \cdot 10^{-5} \text{M}$ and c_L increasing in the interval $(0.14 - 9.6) \cdot 10^{-4} \text{M}$ in 30% v/v ethanol at pH 2.05, 2.30, 2.69, 3.05 and 4.86 (Fig. 5, curves 1–5) were interpreted using transformations (5) and (6), whose linear course for $n = 1$ or the average value of the slope of the logarithmic dependence, $n = 1.02$, confirmed the existence of equilibrium (E) in the pH range 2.05–2.69. Dependences (5) for pH 3.05 and 4.86 are almost linear but the values of the molar absorption coefficient determined from them and the results of the logarithmic analysis are markedly affected by the formation of the VO₂L⁻ complex and by hydrolytic equilibria of vanadium(V).

TABLE III
Values of Constants for the VO₂LH Chelate

K	log K	
	30% v/v ethanol	30% v/v dimethylformamide
$*k_{11} = [\text{VO}_2\text{LH}][\text{H}]/[\text{VO}_2][\text{LH}_2]$	1.74 ^c ; 1.74 ^d ; 1.56 ^e ; 1.06 ^f ; 1.33 ^g ; 1.51 ^h ; 1.22 ⁱ ; 1.30 ^j	0.63 ^k ; 0.76 ^c
average	1.53	0.70
$\beta_1^a = [\text{VO}_2\text{LH}]/[\text{VO}_2][\text{LH}]$	12.15	11.12
$\beta_1^b = [\text{VO}_2\text{LH}]/[\text{VO}_2][\text{LH}]$	8.01	7.26
$K_{ak} = [\text{VO}_2\text{L}][\text{H}]/[\text{VO}_2\text{LH}]$	-3.52 ^c ; -3.62 ^d	-3.72 ^k ; -3.71 ^c ; -3.66 ^l ; -3.88 ^m
average	-3.57	-3.74

^a $\beta_1 = *k_{11}/K_{a3}$, where K_{a3} is the dissociation constant of the *o*-hydroxyl group of TAR; ^b $\beta_1 = *k_{11}/K_{a2}$, K_{a2} is the dissociation constant of the *p*-hydroxyl group of TAR; ^c $c_L = 4.00 \cdot 10^{-5} \text{M}$, $c_M/c_L = 100$, ^d $c_L = 4.00 \cdot 10^{-5} \text{M}$, $c_M/c_L = 50$; ^e $c_L = 4.00 \cdot 10^{-5} \text{M}$, $c_M/c_L = 25$; ^f $c_M = 4.00 \cdot 10^{-5} \text{M}$, $c_L/c_M = 20$ (mixture of chelates VO₂LH and VO₂L), ^g $c_M = 4.00 \cdot 10^{-5} \text{M}$, $c_L = (2.9 - 9.6) \cdot 10^{-4} \text{M}$, pH 2.05; ^h $c_M = 4.00 \cdot 10^{-5} \text{M}$, $c_L = (0.3 - 3.6) \cdot 10^{-4} \text{M}$, pH 2.30, ⁱ $c_M = 4.00 \cdot 10^{-5} \text{M}$, $c_L = (1.5 - 7.6) \cdot 10^{-4} \text{M}$, pH 2.69; ^j $c_M = 4.00 \cdot 10^{-5} \text{M}$, $c_L = (0.1 - 7.1) \cdot 10^{-4} \text{M}$, pH 3.05; ^k $c_L = 4.00 \cdot 10^{-5} \text{M}$, $c_M/c_L = 200$; ^l $c_L = 4.00 \cdot 10^{-5} \text{M}$, $c_M/c_L = 200$ — by computer; ^m $c_L = 4.00 \cdot 10^{-5} \text{M}$, $c_M/c_L = 100$ — by computer.

Job plots for equimolar solutions with $c_M + c_L = 6.40 \cdot 10^{-4} \text{M}$ at pH 2.87, 4.44, 5.27 (0.05M pyridine buffer) and 7.27 (0.05M tris-(hydroxymethyl)aminomethane buffer) in the range λ 545–590 nm also confirmed the component ratio V : TAR = = 1 : 1 in complexes of vanadium with TAR in 30% v/v ethanol.

Complex Equilibria of Vanadium (V) with TAR in 30% v/v Dimethylformamide

The absorbance–pH curves for TAR solutions containing excess metal ($c_L = 4.00 \cdot 10^{-5} \text{M}$, $c_M/c_L = 100$ and 200), solutions with excess ligand ($c_M = 4.00 \cdot 10^{-5} \text{M}$, $c_L/c_M = 20$) and equimolar solutions ($c_M = c_L = 4.00 \cdot 10^{-5} \text{M}$) have a similar course to the curves for 30% v/v ethanol, differing only in a slight shift to higher pH values (Fig. 3a, b). By analysis of the pH-curves for solutions with excess metal in the pH range 1.4–2.6 using transformations (1) and (2) and the adapted PRCEK II program²⁶, the formation of the VO_2LH complex according to equation (E) was demonstrated (Fig. 4, curves 4 and 5). Equilibrium (F) was evaluated by analysis of a further section in the pH range 3–5 (Fig. 4, curves 8 and 9). The values of the molar absorption coefficients for the two chelates and the equilibrium and dissociation constants of the VO_2LH chelate in 30% v/v dimethylformamide are given in Tables II and III.

The Effect of Organic Solvents

In solutions containing $2.8 \cdot 10^{-5} \text{M-V(V)}$ and $6.0 \cdot 10^{-4} \text{M-TAR}$ at pH 4.5, other organic solvents in a concentration of 30% v/v, such as methanol, dimethylformamide,

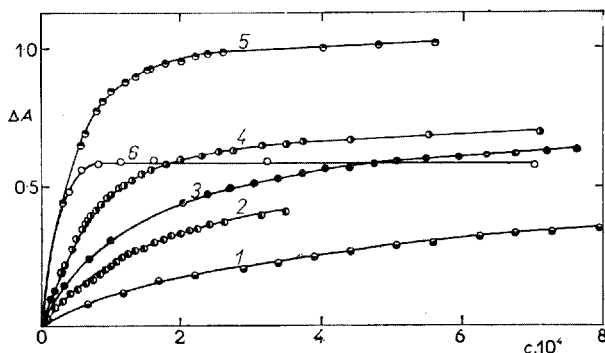


FIG. 5

The $A - A_{0L} = f(c_L)$ Dependence in Solutions of TAR Containing V(V) in 30% v/v Ethanol
 1 0.1. Curves 1–5 545 nm, 6 575 nm. pH: curve 1 2.05, 2 2.30, 3 2.69, 4 3.05, 5 4.86 (0.05M pyridine buffer), 6 0.5M- HNO_3 , 0.2% v/v n-butanol, $c_M = 3.52 \cdot 10^{-5} \text{M}$.

dimethyl sulphoxide, acetone and also the addition of 0.2% polyvinyl alcohol or cetylpyridinium bromide, have the same effect on the absorbance of the complex as 30% v/v ethanol. At 75% v/v concentrations of the solvents, the absorbance values are lower for ethanol (-13%), methanol (-29%) and acetone (-19%) and higher for dimethylformamide (+9%) and dimethyl sulphoxide (+5%).

In acid media at pH 2.5, small amounts of isopropanol, n-butanol, isoamylol and acetaldehyde increase the absorbance of the solutions. The dependences of the absorbance of vanadium(V) solutions containing TAR on the concentration of active solvent attain a horizontal section at 570 nm in the presence of 0.072% v/v n-butanol ($\epsilon = 1.63 \cdot 10^4$), 0.37% v/v acetaldehyde ($\epsilon = 1.57 \cdot 10^4$) and 1.2% v/v isopropanol ($\epsilon = 1.64 \cdot 10^4$). Similarly, a plateau is formed on the absorbance-pH curve of a solution containing $c_M = 4.00 \cdot 10^{-5} \text{M}$ and $c_L = 4.24 \cdot 10^{-4} \text{M}$ in 30% v/v ethanol in the presence of 0.2% v/v butanol at $\text{pH} \leq 2$ (at 570 nm, $\epsilon 1.75 \cdot 10^4$) (Fig. 3a, curve 8). Commercial refined ethanol, distilled before use, sometimes contains the substances mentioned above as impurities in amounts sufficient to cause deformation of the pH-curves or even the appearance of a plateau at $\text{pH} \leq 2.5$ (Fig. 3a, curve 6).

Complex Equilibria in the System V(V)-TAR-n-Butanol

The absorption curves of solutions of $4.00 \cdot 10^{-5} \text{M}$ TAR with excess vanadium(V), $c_M/c_L = 25$ and with 1% v/v n-butanol demonstrate the quantitative formation of a complex with a principal maximum at 570–575 nm and an additional maximum at 450–455 nm in the range 1.4M-HNO₃-pH 2.16 in 30% v/v ethanol and the conversion of this complex at $\text{pH} > 2.16$ into another complex with $\lambda_{\text{max}} 545 \text{ nm}$ and isosbestic points at 473 and 590 nm (Fig. 6).

The composition of the complex formed at $\text{pH} < 2.5$ in 30% v/v ethanol with the participation of n-butanol was determined by the continuous variation method in the ternary system V(V)-TAR-n-butanol for each combination of two components in the presence of a sufficient constant excess of the third component. The Job plot for the TAR-V(V) system ($c_0 = 8.00 \cdot 10^{-5} \text{M}$) in the presence of 0.03M n-butanol and 0.1M-HNO₃ confirms the component ratio in the complex $\text{V} : \text{TAR} = 1 : 1$ in the range 540–600 nm (Fig. 7, curve 1). The maximum of the variation curve for TAR-n-butanol ($c_0 = 8.00 \cdot 10^{-5} \text{M}$) in the presence of excess vanadium at the same acidity ($c_M = 8.00 \cdot 10^{-4} \text{M}$) in the range 540–600 nm gives the ratio $\text{TAR} : \text{n-butanol} = 1 : 3$ (Fig. 7, curve 2) and similarly a curve for V(V)-n-butanol ($c_0 = 8.00 \cdot 10^{-5} \text{M}$) in the presence of excess TAR ($c_L = 8.00 \cdot 10^{-4} \text{M}$) in the range 560–600 nm confirms the ratio $\text{V(V)} : \text{n-butanol} = 1 : 3$ (Fig. 7, curve 3). During the construction of this curve, the overall absorbance value at each point was diminished by the value under a line joining the initial point (absorbance of $8.00 \cdot 10^{-4} \text{M-TAR}$, no vanadium) and the final point ($8.00 \cdot 10^{-4} \text{M-TAR}$, $8.00 \cdot 10^{-5} \text{M}$

$-V(V))$ of the curve. In the remaining cases the absorbance at the initial point was zero and the curves were constructed in the usual way after subtracting the corresponding value for TAR alone. The measurement of the variation curve for components TAR-n-butanol ($c_0 = 1.6 \cdot 10^{-4}M$) in solutions containing $1.5 \cdot 10^{-2}M-V(V)$ and $0.5M-HNO_3$ in the interval 570–600 nm (Fig. 7, curve 4) was complicated by the slow formation of the ternary complex and partial decomposition of TAR.

The small dependence of the complex equilibrium in the presence of n-butanol on the acidity and the formation of the complex in $2M-HNO_3$ does not exclude the

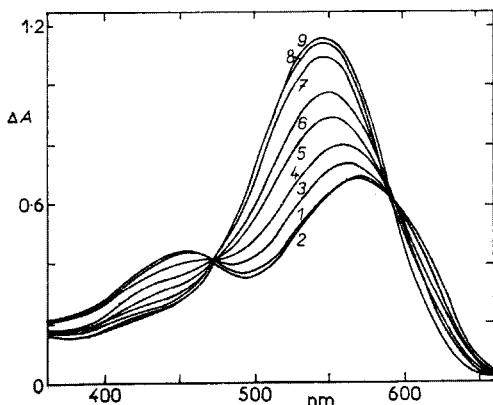


FIG. 6

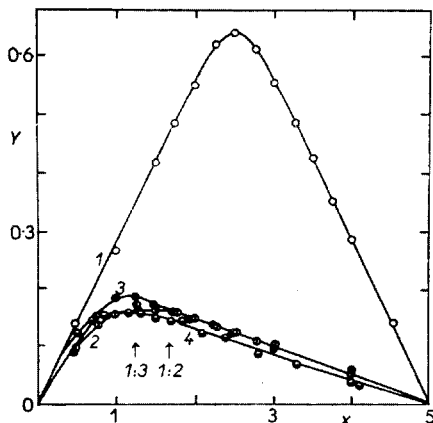
Absorption Curves of a Solution of TAR Containing V(V) at Various pH Values in 30% v/v Ethanol in the Presence of 1% v/v n-Butanol

$c_L = 4.00 \cdot 10^{-5}M$, $c_L = 1.00 \cdot 10^{-3}M$. Results corrected for the absorbance of V(V). pH: curve 1 1.42M- HNO_3 , 2 2.16, 3 3.21, 4 3.93, 5 4.22, 6 4.80, 7 5.36, 8 6.03, 9 6.48.

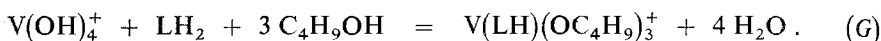
FIG. 7

The Variation Method for the V(V)-TAR-n-butanol System in 30% v/v Ethanol

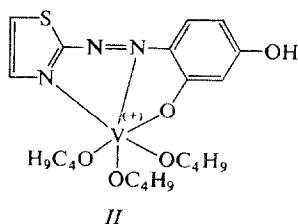
λ 575 nm. Curves 1–3: $c_0 = 8.00 \cdot 10^{-5}M$, $0.1M-HNO_3$, 4: $c_0 = 1.60 \cdot 10^{-4}M$, $0.5M-HNO_3$. Curve 1 $x = ml$ TAR, $(5-x) ml$ V(V), $0.03M$ n-butanol; 2 $x = ml$ TAR, $(5-x) ml$ n-butanol, $8.00 \cdot 10^{-4}M-V(V)$; 3 $x = ml$ n-butanol, $8.00 \cdot 10^{-4}M-TAR$; 4 $x = ml$ TAR, $(5-x) ml$ n-butanol, $1.5 \cdot 10^{-2}M-V(V)$.



reaction of the hydrated $V(OH)_4^+$ ion with TAR and n-butanol without splitting of hydrogen ions according to equilibrium (G)



The complex formed probably has the structure II



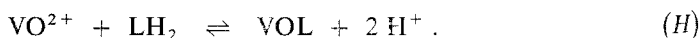
At $pH > 2.5$, the participation of n-butanol in the complex equilibria of vanadium(V) with TAR in 30% v/v ethanol cannot be excluded; however, it is not obvious from the absorbance-pH curves.

Complex Equilibria of Vanadium(IV) with TAR in 30% v/v Ethanol

The absorbance curves of solutions of vanadium(IV) with TAR ($c_L = 4.00 \cdot 10^{-5} M$, $c_M = 1.00 \cdot 10^{-3} M$) in 30% v/v ethanol with increasing pH in the interval 2.11–4.54 characterize the formation of a complex with λ_{max} 545–550 nm and λ_{iso} 481 nm. Most of these curves correspond to solutions containing free reagent with λ_{max} 438 nm in a mixture with the complex, so that the formation of a protonated complex of the type MLH with an undissociated *p*-hydroxyl group on the bound ligand cannot be demonstrated on the basis of the existence of an additional maximum. Curves at $pH > 3.6$ without an additional maximum are typical for unprotonated complexes of the ML type (Fig. 8).

The absorbance-pH curves of solutions of TAR with excess vanadyl ions ($c_L = 4.00 \cdot 10^{-5} M$, $c_M/c_L = 25$ and 100) and the curve for excess reagent ($c_M = 4.00 \cdot 10^{-5} M$, $c_L/c_M = 25$) in 30% v/v ethanol demonstrate the formation of a chelate from $pH \geq 2$ which is considerably affected by hydrolysis of the vanadium(IV) at $pH 4.5-5.5$ (Fig. 3c).

Graphical analysis of the absorbance-pH curves did not prove the existence of the most probable equilibrium



Transformations (1)–(4) for dissociation of two protons do not yield linear dependences (Fig. 9, curves 4–6). On the contrary, a complex equilibrium involving dissociation of only one proton was unambiguously demonstrated (Fig. 9, curves 1–3). The formation of a protonated complex with dissociation of one proton according to the usual type of equilibrium

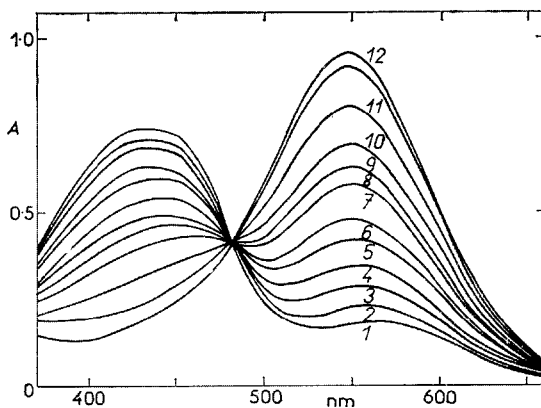
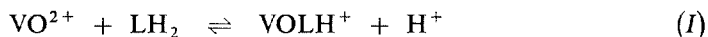


FIG. 8

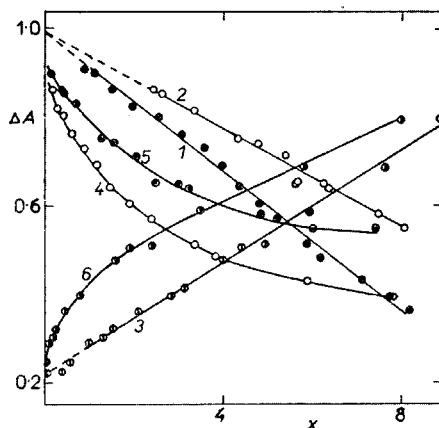
Absorption Curves for Solutions of V(IV) Containing TAR in 30% v/v Ethanol at Various pH Values

10^{-1} , $c_L = 4.00 \cdot 10^{-5} \text{M}$, $c_M = 1.00 \cdot 10^{-3} \text{M}$. pH: 1 2.11, 2 2.40, 3 2.61, 4 2.79, 5 2.91, 6 3.04, 7 3.19, 8 3.25, 9 3.39, 10 3.66, 11 4.08, 12 4.54.

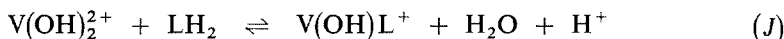
FIG. 9

Direct Analysis of the Absorbance–pH Curves of Solutions of V(IV) Containing TAR in 30% v/v Ethanol

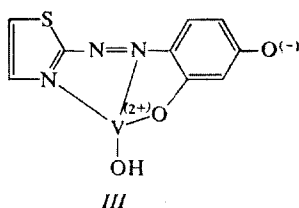
λ 545 nm, $a = (A - \bar{\epsilon}_L c_L)$. Curves 1–3: $q = 1$, 4–6: $q = 2$. Curves 1, 2, 4, 5: $c_L = 4.00 \cdot 10^{-5} \text{M}$, $y = A$; 3 and 6: $c_M = 4.00 \cdot 10^{-5} \text{M}$, $y = 5 \cdot 10^3 c_M / \Delta A$. Curve 1 $c_M / c_L = 100$, $x = 10^4 a[\text{H}]$; 2 $c_M / c_L = 50$, $x = 2 \cdot 10^4 a[\text{H}]$; 3 $c_L / c_M = 20$, $x = 10^4 [\text{H}]$; 4 $c_M / c_L = 100$, $x = 5 \cdot 10^6 a[\text{H}]^2$; 5 $c_M / c_L = 50$, $x = 2 \cdot 10^7 a[\text{H}]^2$; 6 $c_L / c_M = 20$, $x = 10^7 [\text{H}]^2$.



is, however, contrary to the colour properties of the studied chelate (existence of a single maximum on the absorbance curve in the visible region and the relatively high value of the molar absorption coefficient estimated from the absorbance curves and pH-curves ($\epsilon \sim 2.4 \cdot 10^4$ at 545 nm), which are typical for unprotonated complexes). The given data agree best with equilibrium (J)



involving reaction of the hydrated V(OH)_2^{2+} ion (ref.³¹) and dissociation of one proton as a result of the increasing acidity of the *p*-hydroxyl group on bonding of vanadium(IV). The assumed structure of the chelate III is



The values of the molar absorption coefficient and the equilibrium constant of the V(OH)L^+ chelate, determined using transformations (1)–(4) are given in Table IV.

The complex composition $\text{V(IV)} : \text{TAR} = 1 : 1$ was also confirmed by the continuous variation method for solutions with $c_0 = 8.00 \cdot 10^{-5} \text{M}$ in 30% v/v ethanol at pH 4.04, 5.70 and 7.95 (0.005M tetraborate buffer) in the range λ 545–580 nm.

The V(OH)L^+ complex of 4-(2-thiazolylazo)resorcinol is not very promising for analytical applications because of its lower stability compared with the complexes of vanadium(V), also found for the complexes of vanadium(IV) with PAR (ref.¹⁸) and affected by hydrolytic equilibria³¹.

The Spectrophotometric Determination of Vanadium(V) at pH 4.5–5.5

The optimal conditions for the determination of vanadium(V) as the VO_2L^- complex in 30% v/v ethanol are given at pH 4.5–5.5 in the presence of a pyridine buffer in a concentration of $\leq 0.1 \text{M}$ (Fig. 3a, curve 7), the reagent concentration of $c_L = 6.0 \cdot 10^{-4} \text{M}$ (Fig. 5, curve 5), ionic strength of 1.0 (KNO₃) and λ 550 nm. The calibration curves in a concentration range of 0.3–3.4 $\mu\text{g V/ml}$ for several pH values in the range pH 4.05–5.56 were evaluated by the least squares method using a computer. Some characteristic values are given in Table V.

SO_4^{2-} , NO_3^- , Cl^- , ClO_4^- , H_2PO_4^- , acetate, tartrate, sulphosalicylate, NH_4^+ , hexamethylenetetramine and pyridine do not interfere in concentrations up to $6.0 \cdot 10^{-3} \text{M}$; large excess of Mg^{2+} , Ca^{2+} and the alkali metal ions also do not inter-

TABLE IV

Values of the Molar Absorption Coefficient and Equilibrium Constant of the $V(OH)L^+$ Chelate in 30% v/v Ethanol

Conditions	ϵ 545 nm $\text{mmol}^{-1} \text{cm}^2$	$\log *k_{11}^a$
$c_L = 4.00 \cdot 10^{-5} \text{M}$, $c_M/c_L = 100$	24 650	-0.46
$c_L = 4.00 \cdot 10^{-5} \text{M}$, $c_M/c_L = 50$	24 800	-0.35
$c_M = 4.00 \cdot 10^{-5} \text{M}$, $c_L/c_M = 20$	22 989	-0.38

^a Values of $*k_{11} = [V(OH)L^+][H]/[V(OH)_2^{2+}][LH_2]$ found by logarithmic analysis, stability constant $\beta_1 = [V(OH)L^+]/[V(OH)_2^{2+}][L^{2-}] = *k_{11}/K_{a3}$, $\log \beta_1 = 10.22$.

TABLE V

Some Characteristics of the Spectrophotometric Analytical Curves for the Determination of Vanadium(V) with TAR in Weakly Acidic Media

pH	λ , nm	ϵ^a $\text{mmol}^{-1} \text{cm}^2$	q^b	s^c $\mu\text{g/ml}$	m^d $\mu\text{g/ml}$	sens. ^e $\mu\text{g/cm}^2$	r_k^f	$U \cdot 10^{4g}$
4.10	550	23 810 ± 78	0.046 ± 0.002	0.0062	0.0187	0.0214	0.99995	0.85
	560	23 172 ± 84	0.024 ± 0.002	0.0069	0.0208	0.0220	0.99993	0.92
4.52	550	25 644 ± 87	0.059 ± 0.002	0.0081	0.0242	0.0199	0.99993	1.99
	560	24 839 ± 76	0.029 ± 0.002	0.0073	0.0220	0.0205	0.99994	1.53
4.95	550	25 917 ± 72	0.084 ± 0.002	0.0067	0.0201	0.0197	0.99996	1.39
	560	25 123 ± 52	0.042 ± 0.001	0.0050	0.0149	0.0203	0.99997	0.72
5.56	550	26 062 ± 124	0.136 ± 0.003	0.0114	0.0341	0.0195	0.99986	4.07
	560	25 292 ± 91	0.064 ± 0.002	0.0087	0.0260	0.0201	0.99992	2.22
4.95 ^h	550	25 076 ± 59	0.080 ± 0.001	0.0057	0.0169	0.0203	0.99997	0.92
	560	24 343 ± 69	0.039 ± 0.002	0.0068	0.0205	0.0209	0.99996	1.17
5.51 ^h	550	25 393 ± 124	0.162 ± 0.003	0.0117	0.0350	0.0201	0.99986	4.06
	560	24 701 ± 106	0.083 ± 0.003	0.0103	0.0309	0.0206	0.99989	2.99

^a Molar absorption coefficient values for 545 nm are lower than the values for 550 nm; ^b absorbance of the blank; ^c standard deviation of one determination $s = \sqrt{U/(n-2)} \cdot 1000$ at wt./ ϵ , number of experimental points $n = 14$; ^d determination limit³³ $m = 3$ s; ^e sensitivity index according to Sandell³² for $A = 0.010$; ^f correlation coefficient³³; ^g $U = \sum (A_{i(\text{calc})} - A_i)^2$; ^h in the presence of 0.01M-CaCDA.

fere. The calcium salt of CDTA, which proved useful for masking a number of metals during the determination of vanadium(V) with 4-(2-pyridylazo)resorcinol^{3,5,7} was used here in a concentration of 0.01M (Table IV); it decreases the absorbance of solution when present in higher concentrations. EDTA and its calcium or magnesium chelates and oxalate and heavy metal ions such as Fe³⁺ (even in the presence of F⁻), Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺ and Cd²⁺ interfere. The interfering effects of some ions at pH 4.9 are summarized in Table VI.

The Spectrophotometric Determination of Vanadium(V) with TAR and n-Butanol in 1M-0.1M-HNO₃

For the determination of vanadium(V) as the ternary complex V(LH)(C₄H₉O)₃⁺, a medium of 0.1-1.0M-HNO₃ (Fig. 3a, curve 8), containing 0.2% v/v n-butanol and a final reagent concentration of c_L = 6.0 · 10⁻⁴M (Fig. 5, curve 6), is most suitable. In the given acidity range, the absorbance of the reagent is not constant because of protonization; consequently, the same conditions must be maintained in the sample and reference solutions as those employed for the calibration curve. The acidity was adjusted using nitric acid with a concentration of 5M or less. Final acid concentrations >1M are not suitable due to the possibility of esterification. The absorbance of the solution does not depend on the order in which the components are mixed and is constant for at least 32 hours. The calibration curves for the determination of 0.1-2.7 µg V/ml in 30% v/v ethanol with 6.0 · 10⁻⁴M TAR and 0.2% v/v n-butanol in the range 1M-0.1M-HNO₃ at λ 570-580 nm were evaluated

TABLE VI

The Effect of Some Ions on the Determination of Vanadium (V) with TAR in 30% v/v Ethanol at pH 4.9

Ion	µg/ml ^a	ion/V ^b	Ion	µg/ml ^a	ion/V ^b
Ni ²⁺	6.48	4.52	WO ₄ ²⁻	6.12	4.28
Be ²⁺	6.84	4.76	MoO ₄ ²⁻	76.0	53.2
Al ³⁺	10.8	7.56	Mn ²⁺	105	73.2
Zr(IV)	12.2	8.56	Cd ²⁺	108	75.2
Cr ³⁺	14.6	10.2	F ⁻	45.6	31.6
Co ²⁺	17.2	12.0	oxalate	1.40	1.06
Zn ²⁺	34.4	24.0	citrate	3.04	2.12
Pb ²⁺	66.4	46.4			

^a Concentration of ions at which deviation error of ±2% rel. is not exceeded at the given V(V) content; ^b weight ratio.

by the least squares method by a computer. Some characteristic parameters are given in Table VII.

The determination of vanadium(V) under the given conditions is not disturbed by Cl^- (0.8M), NO_3^- (0.45M), ClO_4^- (0.6M), SO_4^{2-} (0.1M), Pb^{2+} (11171 $\mu\text{g/ml}$), Zn^{2+} (53400 $\mu\text{g/ml}$), Cd^{2+} (22142 $\mu\text{g/ml}$), Mn^{2+} (12600 $\mu\text{g/ml}$). The interference of a num-

TABLE VII

Some Characteristics of the Spectrophotometric Analytical Curves for the Determination of Vanadium (V) with TAR in the Presence of n-Butanol in Acidic Media

Meaning of symbols as in Table V.

Molarity of HNO_3	λ , nm	ϵ , $\text{mmol}^{-1} \text{cm}^2$	q	s , $\mu\text{g/ml}$	m , $\mu\text{g/ml}$	Sensitivity, $\mu\text{g/cm}^2$	r_k	$U \cdot 10^4$
1.0	570	$16\,517 \pm 112$	0.449 ± 0.003	0.005	0.0502	0.0308	0.99975	3.23
	575	$16\,694 \pm 78$	0.343 ± 0.002	0.016	0.0472	0.0305	0.99985	3.72
	580	$16\,485 \pm 95$	0.231 ± 0.003	0.019	0.0583	0.0309	0.99977	5.54
0.5	570	$16\,828 \pm 65$	0.420 ± 0.002	0.011	0.0319	0.0303	0.99991	1.48
	575	$17\,048 \pm 51$	0.287 ± 0.002	0.010	0.0304	0.0299	0.99994	1.61
	580	$16\,804 \pm 58$	0.192 ± 0.002	0.012	0.0351	0.0303	0.99992	2.09
0.1	570	$17\,371 \pm 51$	0.175 ± 0.002	0.012	0.0358	0.0293	0.99993	2.66
	575	$17\,332 \pm 53$	0.122 ± 0.002	0.012	0.0370	0.0294	0.99992	2.83
	580	$17\,050 \pm 35$	0.082 ± 0.001	0.008	0.0249	0.0299	0.99997	1.23

TABLE VIII

The Effect of Some Ions on the Determination of Vanadium (V) with Tar in 30% v/v Ethanol and 0.2% n-Butanol in 1M- HNO_3

Ion	$\mu\text{g/ml}^a$	Ion/V ^b	Ion	$\mu\text{g/ml}^a$	Ion/V ^b
Cu^{2+}	10.2 ^c	6.67	Co^{2+}	316	206
MoO_4^{2-}	18.5 ^d	12.1	UO_2^{2+}	542	354
WO_4^{2-}	27.6 ^{d,e}	18.0	Ni^{2+}	892	583
Cr^{3+}	39.0	25.5	Al^{3+}	1 229	803
Zr(IV)	61.3 ^c	40.1	Fe^{3+}	27 500 ^d	17 900

^a Concentration of ions at which a deviation of $\pm 2\%$ rel. is not overstepped at the given V(V) concentration; ^b weight ratio; ^c in the presence of 0.02M-EDTA; ^d in the presence of 0.4M- H_3PO_4 ; ^e from 1800 $\mu\text{g/ml}$ cloudy due to the presence of tungstic acid.

ber of other metals can be suppressed using EDTA, which does not affect the absorbance of the vanadium complex at a concentration of 0.02M. The presence of 0.4M- H_3PO_4 decreases the interference from MoO_4^{2-} and WO_4^{2-} ions. Limiting concentrations of some interfering ions in the determination of 1.53 $\mu\text{g V/ml}$ in 1M- HNO_3 at λ 580 nm are given in Table VIII.

Compared with other heterocyclic azo-dyes, primarily with 4-(2-pyridylazo)resorcinol (PAR) and 2-(2-pyridylazo)-5-diethylaminophenol, TAR is a less sensitive reagent (Table IX); advantages, however, lie in its availability and the relatively easy preparation of the pure reagent and its stability towards oxidation.

The selectivity of the determination of vanadium(V) increases for the ternary complexes in acid media, V-TAR-n-butanol, V-PAR- H_2O_2 ¹⁰ and V-PAR- NH_2OH ¹⁷, and after extraction of ion associates of the chelates of vanadium with tetraphenylphosphonium or tetraphenylarsonium cations¹⁴ or with quinine⁹ into chloroform.

TABLE IX

A Survey of Heterocyclic Azodyes Proposed for the Spectrophotometric Determination of Vanadium(V)

Reagent	$\epsilon \cdot 10^{-4}$ of the VO_2L chelate (nm)	Optimum pH	Reference
4-(2-Thiazolylazo)resorcinol (TAR)	2.65 (545)	5.0—5.5	this work
1-(2-Pyridylazo)-2-naphthol (PAN)	1.69 (615) ^a	3.5	34
4-(2-Pyridylazo)resorcinol (PAR)	2.6—3.6 (540—50)	5—7	1,2,5,6,8,9,10,17
2-(2-Pyridylazo)-5-diethyl- - <i>m</i> -aminophenol (PAAF)	5.25 (570)	3—4	35
5-Bromo-PAAF	4 (580)	3—4	35
3,5-Dibromo-PAAF	5 (590)	3—4	35
5-(2-Pyridylazo)-2-monoethyl- amino- <i>p</i> -cresol (PAAC)	3.8 (560) ^b	2—5	36
3-Bromo-PAAC	3.66 (580) ^a	2.0—3.5	36
3,5-Dibromo-PAAC	4.05 (600) ^b	2.4—4.5	36
TAR — n-Butanol	1.70 (575)	0.1M- HNO_3 pH 1	this work
PAR- H_2O_2	1.65 (540)	0.5—3	10
PAR — NH_2OH	1.72 (550)	0.4N- H_2SO_4	11,17
PAR — tetraphenylphosphonium (arsonium) cation	3.9 (560) ^c	5.5	14
PAR — quinine	3.7 (560) ^a	5	9

^a Extraction into chloroform; ^b extraction into dichloroethane; ^c extraction into a mixture of chloroform-acetone (5 : 1); other determinations in aqueous medium.

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