

# Reactions between dyes of the Alizarin Green series and vanadates in the presence of Septonex (carbethoxypentadecyltrimethylammonium bromide)

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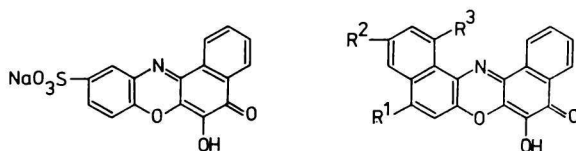
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The coordination properties of three dyes of the Alizarin Green series and vanadates were studied in the presence of Septonex. The defined ternary complexes  $VL_2S_4$  and  $VL_2S_6$  arise in weakly acid medium of pH 2—6.5. The equilibrium constants of the studied complex formation were calculated and a method of photometric determination of vanadium was proposed.

Были исследованы координационные свойства трех красителей очереди ализариновой зелени и ванадатов в присутствии септонекса. В слабокислой среде (рН 2—6,5) возникают в растворе тройные комплексы  $VL_2S_4$  и  $VL_2S_6$ . Были вычислены константы равновесия изученных комплексообразований и был разработан метод фотометрического определения ванадия.

In the presence of cationic tensides, the phenoxazone dyes of the Alizarin Green type give important analytical reactions. These dyes were used as metallochromic indicators for chelatometric determination of vanadium in the presence of cetyltrimethylammonium bromide [1] or they were used as reagents for photometric determination of vanadium [1, 2], iron [3], uranium and cetyltrimethylammonium [4].

The aim of this study was to investigate coordination equilibria of the vanadate ions with a few dyes of the Alizarin Green type, *i.e.* sodium 6-hydroxy-5-benzo(*a*)phenoxazone-10-sulfonate (*I*), sodium 6-hydroxy-5-dibenzo(*a, j*)phenoxazone-9,11-disulfonate (*II*), and sodium 6-hydroxy-5-dibenzo(*a, j*)phenoxazone-11,13-disulfonate (*III*), in the presence of Septonex (*S*) and find out conditions for analytical application of these reactions (Scheme 1).



I

II  $R^1 = R^2 = \text{SO}_3\text{Na}$ ,  $R^3 = \text{H}$

III  $R^1 = \text{H}$ ,  $R^2 = R^3 = \text{SO}_3\text{Na}$

Scheme 1

## Experimental

### Chemicals and instruments

The stock solution of the dyes ( $4 \times 10^{-4}$  M or  $10^{-3}$  M) was prepared by dissolving the requisite amount of their sodium salt in water. The purity of the dyes was checked by paper and thin-layer chromatography [5, 6]. The  $10^{-2}$  M solution of Septonex was prepared by dissolving solid Septonex (Spofa) in water. The content of Septonex was determined by titration with sodium tetraphenylborate according to *Uno* [7] and *Cross* [8]. The  $10^{-2}$  M stock solution of vanadates was made by dissolving  $\text{NH}_4\text{VO}_3$  in equimolar amount of NaOH. The content of vanadates was determined indirectly by titrating the excess of Mohr's salt with a standard solution of potassium bichromate using diphenylamine as indicator [9, 10].

The pH value of solutions was maintained constant by means of 0.1 M-HCl and acetate buffer solutions ( $\text{CH}_3\text{COOH}/\text{NaOH}$ ). The ionic strength  $I$  was adjusted to the value 0.01 by means of 1 M solution of KCl or necessary amount of the buffer solution. All chemicals used were anal. grade reagents.

The absorbance of solutions was measured on instruments Specord UV VIS (Zeiss, Jena) and Unicam SP 1800 (Cambridge, England) in 1, 2, and 5 cm cells. The pH values were measured on a pH-meter PHM 4d (Radiometer, Copenhagen) (reliability of measurement  $\pm 0.02$  pH) with a glass and saturated calomel electrode. The pH-meter was calibrated with 0.05 M solutions of potassium hydrogenphthalate and potassium tetroxalate.

### Evaluation of experimental data

The composition of ternary complexes was ascertained by the method of mole ratios [11], the method of continual variations [12], and the method of tangent ratios [13]. The stability constants of ternary complexes were calculated from the concentration curves (1) or the pH curves (2)

$$A = f(c_v)c_L, c_s, \text{pH} \quad c_s > c_L, c_v \quad (1)$$

$$A = f(\text{pH})c_L, c_v, c_s \quad c_s > c_L, c_v \quad (2)$$

where  $c_L$ ,  $c_v$ , and  $c_s$  denote total analytical concentration of dye, vanadates, and tenside, respectively.

## Results and discussion

None of the investigated dyes gives a characteristic reaction with vanadates. At  $\text{pH} < 3.7$  in the presence of vanadates, an oxidative destruction of the dyes takes place while at  $\text{pH} > 3.7$  this reaction manifests itself in equimolar solutions only by a small change in tint of the dye. In the presence of cationic tenside, blue (*I*) or green (*II*, *III*) ternary complexes arise in solutions in the  $\text{pH}$  region 2—6.5 (in Tables 1—3 the values of  $\lambda_{\text{max}}$  and  $\varepsilon_{\text{max}}$  of these complexes are quoted).

Absorption curves (*I*) of the solutions with constant concentration of dye and tenside and varying concentration of vanadates exhibit single isosbestic point at a certain  $\text{pH}$  and  $c_s$  (Tables 1—3). It has been revealed by the method of mole ratios that a complex of the composition  $\text{V:L} = 1:2$  always arises in the solution.

Table 1

Equilibrium constants of the ternary vanadate—dye *I*—Septonex system

pH	$\log * \beta_{1,2}$	$\log * \beta_{1,2,4}$	$\varepsilon_{\text{max}}(574 \text{ nm})$ $10^4$	$\lambda_{\text{iso}}$ nm	$c_s$ $10^{-4} \text{ M}$	$\text{p}K'_1$	Medium
1.88—2.8 <sup>c</sup>	$4.88 \pm 0.06$	$17.34 \pm 0.06$	2.08	516	6.4	4.63	KCl + HCl
3.80 <sup>a</sup>	4.17	15.43		514	16.0	4.66	} Acetate buffer
3.93 <sup>a</sup>	3.85	16.83	2.08	514	6.4	4.70	
4.17 <sup>b</sup>	3.59	19.08	2.07	513	2.0	5.16	
4.35 <sup>a</sup>	3.67	16.66		510	6.4	4.70	
4.73 <sup>a</sup>	2.96	15.94		506	6.4	4.70	
5.12 <sup>a</sup>	2.52	16.94	2.08	514	3.2	4.83	
5.62 <sup>a</sup>	1.82	14.89		464	6.4	4.70	

Calculation from concentration curves (*I*): *a*)  $c_L = 4 \times 10^{-5} \text{ M}$ ; *b*)  $c_L = 1.6 \times 10^{-5} \text{ M}$ ; *c*) calculation from  $\text{pH}$  curve (*2*):  $c_L = c_V = 1.6 \times 10^{-5} \text{ M}$ , mean of 9 values transformed in logarithmic form, interval of reliability  $\pm 0.06$  determined for 95% level of probability.

10—15 titrations (*I*) in the  $\text{pH}$  range 3.6—5.8 were performed with each dye. The concentration of dyes was  $c_L = (1.6—8) \times 10^{-5} \text{ M}$ . The excess of cationic tenside was equal to  $c_s = (5—100) c_L$ . The concentration of vanadates varied in the range  $c_V = (0—5) c_L$ . Likewise, the method of tangent ratios according to which either the concentration of vanadates varied in the presence of an excess of dye and tenside or the concentration of dye varied in the presence of an excess of vanadates and tenside ( $c_s = 1.6 \times 10^{-3} \text{ M}$ ,  $c_L = 8 \times 10^{-5} \text{ M}$ , resp.  $c_V = 10^{-4} \text{ M}$ ,  $\text{pH}$  3.84 (*I*),  $\text{pH}$  3.96 (*II*);  $c_s = 8 \times 10^{-4} \text{ M}$ ,  $c_L = 8 \times 10^{-5} \text{ M}$ , resp.  $c_V = 10^{-4} \text{ M}$ ,  $\text{pH}$  4.69 (*III*)) indicates formation of a complex in the ratio  $\text{V:L} = 1:2$ . In the presence of excess tenside, the method of continual variations in equimolar solutions of vanadates and

Table 2

Equilibrium constants of the ternary vanadate—dye II—Septonex system

pH	$\log * \beta_{1,2}$	$\log * \beta_{1,2,6}$	$\epsilon_{\max}(626 \text{ nm})$ $10^4$	$\lambda_{\text{iso}}$ nm	$c_s$ $10^{-4} \text{ M}$	pK'	Medium
2.0—2.8 <sup>d</sup>	$4.86 \pm 0.10$	$24.32 \pm 0.10$	2.42	560	6.4	5.01	KCl + HCl
3.59 <sup>b</sup>	4.02	20.36	2.43	560	16	4.84	} Acetate buffer
3.81 <sup>c</sup>	3.16	22.12		562	6.4	5.80	
3.90 <sup>b</sup>	3.47	23.06		561	6.4	5.01	
4.12 <sup>b</sup>	3.29	19.48	2.43	556	16	4.84	
4.14 <sup>a</sup>	3.01	24.87		561	2.0	5.88	
4.33 <sup>b</sup>	3.10	22.70	2.40	559	6.4	5.01	
4.69 <sup>b</sup>	2.75	22.36		556	6.4	5.01	
4.94 <sup>b</sup>	1.59	22.59		560	3.2	6.01	
5.59 <sup>b</sup>	1.80	20.75		541	6.4	5.01	

Calculation from concentration curves (1): a)  $c_L = 1.6 \times 10^{-5} \text{ M}$ ; b)  $c_L = 4 \times 10^{-5} \text{ M}$ ; c)  $c_L = 8 \times 10^{-5} \text{ M}$ ; d) calculation from pH curve (2):  $c_L = c_V = 1.6 \times 10^{-5} \text{ M}$ , mean of 8 values transformed in logarithmic form, interval of reliability  $\pm 0.10$  determined for 95% level of probability.

Table 3

Equilibrium constants of the ternary vanadate—dye III—Septonex system

pH	$\log * \beta_{1,2}$	$\log * \beta_{1,2,6}$	$\epsilon_{\max}(590 \text{ nm})$ $10^4$	$\lambda_{\text{iso}}$ nm	$c_s$ $10^{-4} \text{ M}$	pK'	Medium
2.3—3.0 <sup>c</sup>	$4.01 \pm 0.09$	$26.48 \pm 0.09$	2.29	540	2.5	6.92	KCl + HCl
3.60 <sup>b</sup>	3.67	24.78	2.30	539	4.0	6.98	} Acetate buffer
4.25 <sup>b</sup>	0.99	15.42		538	40.0	6.78	
4.27 <sup>b</sup>	2.00	18.93		538	16.0	6.70	
4.27 <sup>b</sup>	2.72	21.66		539	8.0	6.69	
4.30 <sup>b</sup>	2.94	24.13	2.30	540	4.0	6.98	
4.31 <sup>b</sup>	2.77	25.79		540	2.5	7.20	
4.51 <sup>a</sup>	2.31	21.01		540	8.0	6.68	
4.52 <sup>a</sup>	1.36	17.59		540	20.0	6.71	
4.54 <sup>a</sup>	2.82	23.48		540	4.0	6.76	
4.55 <sup>a</sup>	2.61	24.67		541	2.5	6.92	
5.90 <sup>b</sup>	-0.21	21.15		536	4.0	6.98	

Calculation from concentration curves (1): a)  $c_L = 1.6 \times 10^{-5} \text{ M}$ ; b)  $c_L = 4 \times 10^{-5} \text{ M}$ ; c) calculation from pH curve (2):  $c_L = c_V = 1.6 \times 10^{-5} \text{ M}$ , mean of 8 values transformed in logarithmic form, interval of reliability  $\pm 0.09$  determined for 95% level of probability.

dye ( $c_0 = 4 \times 10^{-5}$  M,  $c_s = 2 \times 10^{-3}$  M, pH 3.84 (I), pH 3.96 (II);  $c_0 = 4 \times 10^{-5}$  M,  $c_s = 4 \times 10^{-4}$  M, pH 4.32 (III)) also gives equal results.

If the solution of vanadates and dye is titrated with the solution of tenside, the absorption curves  $A = f(c_s)_{c_L, c_v, \text{pH}}$  exhibit one isosbestic point for the reactions of dyes I and II  $\lambda_{\text{iso}} = 512$  nm (I) ( $c_L = c_v = 1.6 \times 10^{-5}$  M, pH 5.30) and  $\lambda_{\text{iso}} = 546$  nm (II) ( $c_L = 4 \times 10^{-5}$  M,  $c_v = 1.4 \times 10^{-5}$  M, pH 4.66), but two isosbestic points for the reactions of dye (III)  $\lambda_{\text{iso}} = 561$  nm ( $c_s \leq c_L$ ),  $\lambda_{\text{iso}} = 536$  nm ( $c_L \leq c_s < 3c_L$ ) ( $c_L = c_v = 1.6 \times 10^{-5}$  M, pH 4.70) (Fig. 1). In all cases the absorption curves are not simple, some premicellar and micellar formations which have considerable influence on the form of absorption curves arise with increasing concentration of tenside  $c_s > 2c_L$  (I) or  $c_s > 3c_L$  (II, III) in the solution. A great decrease in absorbance of the solution is to be observed at the wavelengths corresponding to the maximum of the form  $\text{HL}^-$  (I) (478 nm) or  $\text{HL}^{2-}$  (II, III) (510 nm (II), 504 nm (III)) while only a slight increase in absorbance of the solution (Fig. 1) appears at the wavelengths corresponding to the absorption of ternary complexes (a similar course is to be observed with absorption curves of the solutions containing dye I or dye II). By the method of mole ratios, it has been found that the complexes of the composition L:S = 1:2 (I), 1:3 (II), L:S = 1:1 and 1:3 (III) (Fig. 2); V:S = 1:4 (I), 1:6 (II), come into existence in the solution. In titrations, the concentration of dye  $c_L$  was  $c_L = (1.6-8) \times 10^{-5}$  M while the concentration of vanadates was  $c_v < 1/2 c_L$  or  $c_v = (1-5) c_L$ . The concentration of tenside varied in the range  $c_s = (0-50) c_L$ . Six titrations were performed with each dye in the pH range 4.2-5.4.

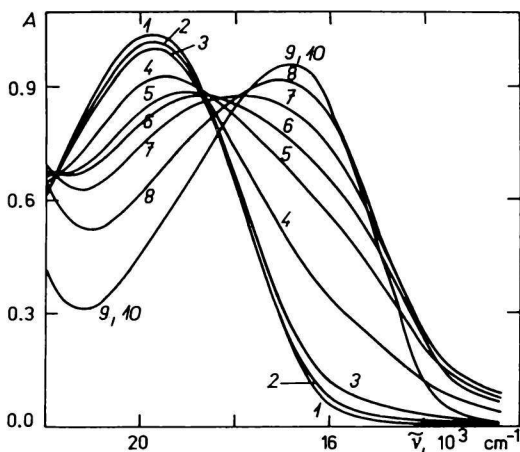


Fig. 1. Absorption curves of the vanadate—dye III—Septonex complexes.

$c_L = 1.6 \times 10^{-5}$  M,  $c_v = 1.6 \times 10^{-5}$  M, pH 4.70, 5 cm cells.

$c_s (10^{-5} \text{ M})$ : 1. 0.0; 2. 0.8; 3. 1.6; 4. 2.88; 5. 4.16; 6. 4.8; 7. 5.6; 8. 8.0; 9. 16; 10. 32.

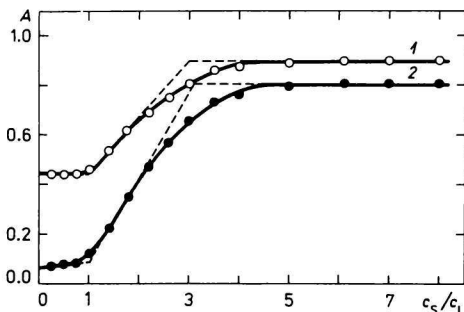


Fig. 2. Curves of the mole ratios  $c_s/c_L$  for the vanadate—dye III—Septonex system.  
 $c_L = 1.6 \times 10^{-5}$  M,  $c_V = 4 \times 10^{-5}$  M, pH 5.29, 5 cm cells.  
 1.  $\lambda = 566$  nm; 2.  $\lambda = 625$  nm.

As both relationships (I) and  $A = f(c_s)_{c_L, c_V, \text{pH}}$  lead to equal value of molar absorption coefficients, it may be concluded that defined complexes  $\text{VL}_2\text{S}_4$  (I) and  $\text{VL}_2\text{S}_6$  (II) are formed in the solution. As to the reaction of dye (III), it may be assumed that the complex  $\text{VL}_2\text{S}_6$  is also formed if the tenside is present in sufficient excess.

The first complex  $\text{L}:\text{S} = 1:1$  (III) exhibits small absorption in the proximity of 590 nm where the absorption maximum of the ternary complex occurs and this absorption is similar to that of the binary  $\text{L}-\text{S}$  complex arisen in a solution of dye (III) and tenside. Therefore we may suppose that this complex is a binary  $\text{L}-\text{S}$  complex in which the tenside is localized on some of the sulfo groups of the dye.

In all ternary complexes  $\text{VL}_2\text{S}_4$  (I) or  $\text{VL}_2\text{S}_6$  (II, III) the number of the bonded molecules of tenside is greater than the number of the sulfo groups in the complex. This fact leads to the assumption that the second (I) or third (II, III) molecule of tenside is bonded to convenient negative or strongly polar parts of the dye (chelate-forming configuration of the phenolic and carbonyl group). The difference in composition of the complexes  $\text{VL}_2\text{S}_4$  (I) and  $\text{VL}_2\text{S}_6$  (II, III) may be explained by the fact that dyes II and III possess one surplus sulfo group with respect to dye I, on which the tenside can be bonded. Similar results have been obtained earlier [1, 3].

The formation of ternary complexes  $\text{VL}_2\text{S}_r$  ( $r = 4$  or  $r = 6$ ) may be described by eqn (A)



which is characterized by equilibrium constant (3) or  $^*\beta_{1,2}$  for the formalism of formation of a binary complex  $\text{VL}_2$

$$^*\beta_{1,2,r} = [\text{VL}_2\text{S}_r][\text{H}^+]^2[\text{V}]^{-1}[\text{HL}]^{-2}[\text{S}]^{-r} \quad (3)$$

By using the equations of mass balance of vanadates, dye, and tenside and those of absorbance (4—7), eqn (3) may be transformed into the form (8) or (8a)

$$c_v = [V] + [VL_2S_r] \quad (4)$$

$$c_L = [L'] + 2[VL_2S_r] \quad (5)$$

$$c_s = [S] + r[VL_2S_r] \quad (6)$$

$$A = \bar{\epsilon}_L[L'] + \epsilon[VL_2S_r] \quad (7)$$

$$*\beta_{1,2,r} = \frac{(A - A_0)(A_{\max} - A_0)^{2+r}[H^+]^2}{[2pA_{\max} - A - (2p - 1)A_0](A_{\max} - A)^2[2qA_{\max} - rA - (2q - r)A_0]^r} \cdot \frac{1}{c_L^{2+r}\{[H^+](K'_a + [H^+])^{-1}\}^2} \quad (8)$$

$$\log \frac{(A - A_0)(A_{\max} - A_0)^{2+r}}{[2pA_{\max} - A - (2p - 1)A_0](A_{\max} - A)^2[2qA_{\max} - rA - (2q - r)A_0]^r} = \\ = \log *\beta_{1,2,r} + 2pH + (2 + r) \log c_L + 2 \log \{[H^+](K'_a + [H^+])^{-1}\} \quad (8a)$$

where  $A_0 = \bar{\epsilon}_L c_L$ ,  $A_{\max} = \epsilon c_L / 2$ ,  $\bar{\epsilon}_L$  and  $\epsilon$  are the mean absorption coefficient of the all forms of dyes and the absorption coefficient of ternary complex,  $p = c_v / c_L > 1/2$ ,  $q = c_s / c_L$ ,  $K'_a$  stands for dissociation constants of the phenolic proton of dyes in the presence of Septonex [14], and  $[L']$  is the conditioned concentration of dye in the presence of Septonex.

The excess cationic tenside ( $c_s = (15-50) c_L$ ), relationship (8a) exhibits linear course with the slopes corresponding to splitting of two protons ( $A$ ) for all dyes in the pH range 2—3. The molar absorption coefficient of the complex  $VL_2S_r$  was read from concentration curves (1) (excess of tenside and dye) and pH curve (2) (excess of vanadates and tensides). The equilibrium constants of reaction ( $A$ ) were calculated numerically from eqn (8) for pH 2—3 (Tables 1—3). At higher pH values, the conditioned constants of stability (9) or the constant  $\beta_{1,2}$  expressing the formalism of formation of the binary complex  $VL_2$ , were calculated from the difference in absorbance according to concentration curves (1) corresponding to the quantitative and to the real reaction [15, 16]. The simultaneous absorbance of complex and free dye was respected. Hence, it holds

$$\beta'_{1,2,r} = [VL_2S_r][V]^{-1}[L']^{-2}[S]^{-r} \quad (9)$$

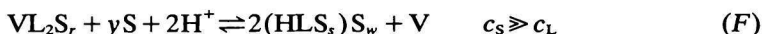
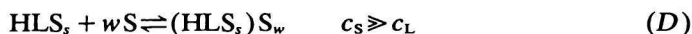
where  $[L']$  is the conditioned concentration of dye in the presence of Septonex. Subsequently, the conditioned constants of stability  $\beta'_{1,2,r}$  and  $\beta'_{1,2}$  were transformed by calculation into the equilibrium constants  $*\beta_{1,2,r}$  and  $*\beta_{1,2}$  (10)

$$*\beta = \beta'([H] + K'_a)^2 \quad (10)$$

These constants are listed in Tables 1—3.

The decrease in  $*\beta$  at higher pH values may be explained by polymerization and varying degree of hydrolysis of vanadates. In an acid medium ( $pH < 3$ ), the

existence of the  $\text{VO}_2^+$  ions may be presumed [17]. The unequal values of  $^*\beta_{1,2,r}$  at different concentrations of Septonex may be interpreted in terms of different degrees of association of Septonex. Furthermore, an increase in the constant  $^*\beta_{1,2}$  is to be observed for the reaction of dye (III) before the concentration of tenside attains the value  $c_s \approx 10c_L$  and subsequently this constant starts to decrease (Table 3). This fact has led us to the assumption that the simultaneous reactions (A—F) take place in the solution



where  $s$  denotes the number of the sulfo groups in dye.

Reactions (A—C) and (E) support the formation of ternary complexes while reactions (D) and (F) inhibit the formation of ternary complexes. The prevalence of one equilibrium over another depends on concentration of tenside and number and position of the sulfo groups in dye. For the reaction of dye III, we may assume that reactions (D) and (F) prevail over the others at a great concentration of tenside and for this reason, a decrease in  $^*\beta_{1,2}$  may be observed in the reaction of this dye. On the contrary, reaction (E) prevails over reactions (D) and (F) with dyes I and II at a great concentration of tenside. Therefore a slight increase in the constant  $^*\beta_{1,2}$  accompanying an increase in concentration of tenside is to be observed in the reactions of these dyes. A negative influence of high concentration of tenside on the formation of ternary complexes was also found and discussed by other authors [18—20].

### Determination of vanadium

In the pH range 3.5—4.5, the stability of the arising ternary complexes derived from dyes II and III is sufficient and enables us to use these dyes as reagents for photometric determination of vanadium in the presence of Septonex. It is sufficient to use a moderate excess of dye for this determination. The determination is reliable and sensitive (Table 4).

The ions of alkali and alkaline earth metals, 100-fold excess of the  $\text{Be}^{2+}$ ,  $\text{Ce}^{3+}$ ,  $\text{Tl}^+$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Mn}^{2+}$ , and  $\text{Cd}^{2+}$  ions, 50-fold excess of the  $\text{La}^{3+}$  and  $\text{Y}^{3+}$  ions, 25-fold excess of the  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Al}^{3+}$ , and  $\text{Cr}^{3+}$  ions, 5-fold excess of the  $\text{Sc}^{3+}$ ,  $\text{CrO}_4^{2-}$ ,  $\text{Ag}^+$ , and  $\text{PtCl}_6^{2-}$  ions, and equimolar amounts of the  $\text{Zr}^{4+}$ ,  $\text{Th}^{4+}$ ,  $\text{Bi}^{3+}$ ,  $\text{Sb}^{3+}$ ,  $\text{Ti}^{4+}$ , and  $\text{Sn}^{4+}$  ions do not prevent the determination. On the other hand, the  $\text{Hg}^{2+}$ ,  $\text{Hg}_2^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{MoO}_4^{2-}$ ,  $\text{WO}_4^{2-}$ ,  $\text{In}^{3+}$ ,  $\text{Ga}^{3+}$ ,  $\text{Pd}^{2+}$ ,  $\text{UO}_2^{2+}$ ,  $\text{Ce}^{4+}$ ,  $\text{Au}^{3+}$ ,  $\text{Sn}^{2+}$ , and  $\text{Ti}^{3+}$  ions interfere with the determination.



Table 4

## Photometric determination of vanadium

Dye	Concentration range μg/ml	λ nm	ε	Sensitivity <sup>a</sup> μg/cm <sup>2</sup>	Relative standard deviation		pH	c <sub>s</sub> 10 <sup>-3</sup> M	c <sub>L</sub> 10 <sup>-4</sup> M
					b	c			
<i>II</i>	0.1—2	630	24 000	0.0023	1.1	0.815	3.83	4	1.4
<i>III</i>	0.09—2	610	22 800	0.0023	1.3	0.72	3.98	1.4	1.4

a) For  $A = 0.001$ ; b)  $v = (s/\bar{x}) \cdot 100\%$ ,  $s = k_n R$ ,  $n = 6$  (95% level of probability); c) ( $v\%$ ) for  $\mu\text{g/ml}$ .

In the presence of cationic tenside, the selectivity of the determination is enhanced while the colour reaction of the Cu(II) ions with the dyes and the hydrolysis of the Zr<sup>4+</sup>, Th<sup>4+</sup>, Bi<sup>3+</sup>, Sb<sup>3+</sup>, Ti<sup>4+</sup>, and Sn<sup>4+</sup> ions are suppressed. The colour of the solutions develops in 15 min and does not change for 24 h. In mixing the solutions, equal ionic strength of all solutions must be preserved. At otherwise equal composition, a solution with ionic strength 0.1 exhibits half absorbance in comparison with a solution having ionic strength equal to 0.01. However, the change in absorbance is very slight in the ionic strength range 0.005—0.015. Because of the tendency to exclude a solid ionic L—S associate from solution, dye *I* is not suited for the photometric determination of vanadium.

## Working procedure

A sample containing 5—100 μg of vanadium is put into a graduated flask (50 ml) holding 7 ml of 10<sup>-3</sup> M dye *II* or *III*, 5 ml of acetate buffer (pH 3.5—4.0), and 20 ml of 10<sup>-2</sup> M Septonex (*II*) or 7 ml of 10<sup>-2</sup> M Septonex (*III*). The flask is filled with water up to the mark and after 15 min the absorbance is measured at 630 nm (*II*) and 615 nm (*III*) with respect to blank sample.

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