STUDY OF THE REACTIONS OF DYES OF THE ALIZARIN GREEN SERIES WITH UO_2^{2+} IONS IN THE PRESENCE OF CETYLTRIMETHYLAMMONIUM CATION

Nguyen TRUONG SON[a], Eduard RUŽIČKA[a] and Jan LASOVSKÝ[b]

[a] *Department of Analytical and Organic Chemistry and*
[b] *Department of Inorganic and Physical Chemistry, Palacký University, 771 46 Olomouc*

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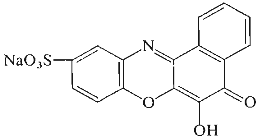
The reactions of four dyes of the alizarin green series with UO_2^{2+} ions in the presence of cetyltrimethylammonium cation (CTA^+, S) were studied. At lower tenside concentrations than the critical micelle concentration (cmc), defined ternary $UO_2L_2S_4$ or $UO_2L_2S_2$ complexes are formed in the solution. The stability constants of the complexes formed were determined and a procedure for the photometric determination of uranium and cetyltrimethylammonium was proposed.

Phenoxazone dyes of the alizarin green type (*I*)–(*IV*) undergo important analytical reactions in the presence of cationoid tensides. In the presence of cetyltrimethylammonium (CTA^+) cation, these dyes were used as metallochromic indicators for the chelometric determination of vanadium[1] or as reagents in the photometric determination of vanadium[1,2] and iron[3].

This work was carried out in order to study the coordination equilibria of UO_2^{2+} ions with dyes (*I*)–(*IV*) in the presence of CTA^+. Dye *II* was proposed as a reagent for the photometric determination of uranium and cetyltrimethylammonium.



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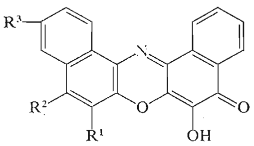

II; $R^1 = R^2 = H$, $R^3 = SO_3Na$
III; $R^2 = H$, $R^1 = R^3 = SO_3Na$
IV; $R^1 = H$, $R^2 = R^3 = SO_3Na$

EXPERIMENTAL

Chemicals and Instruments

The stock solutions of the dyes ($4 . 10^{-4}$M or $1 . 10^{-3}$M) were prepared by dissolving the required amounts of their sodium salts in water. The dye purity was controlled by elemental analysis, paper chromatography and thin-layer chromatography[4,5]. A 10^{-2}M-CTA$^+$ solution was prepared by dissolving solid cetyltrimethylammonium bromide (*p.a.*, Lachema) in water. The CTA$^+$ concentration was determined by titration of sodium tetraphenylborate using the method described by Cross[6] and Uno[7]. The stock solution of 10^{-2}M-UO_2^{2+} ions was determined gravimetrically as the oxinate[8].

The pH of the solution was maintained with 0·1M-HCl and acetate buffer (CH_3COOH–NaOH system). The ionic strength I was adjusted to a value of 0·1 with 0·1M-KCl solution or with a suitable buffer concentration. All the chemicals employed were of *p.a.* purity.

The solution absorbances were measured using Specord UV-VIS (Zeiss, Jena) and Unicam SP 1800 (Cambridge, England) instruments with 1, 2 and 5 cm cuvettes. The pH measurements were carried out on a PHM 4d pH meter (Radiometer, Copenhagen) (reliability of measurement ±0·02 pH unit) with glass and saturated calomel electrodes. The pH meter was calibrated with NBS solutions (0·05M potassium hydrogen phthalate and 0·05M potassium tetraoxalate).

Evaluation of Experimental Data

The composition of the ternary complexes was found by the molar ratio method[9], by the method of continuous variations[10] and by the tangent ratio method[11]. The stability constants of the ternary complexes were found from concentration curves *1* and *2* and from the pH curves *3*. The composition and conditional stability constants of the binary UO_2–L complexes were found by transformations analogous to the Ketelarr transformation[12] of dependence (*4*).

$$A = f(c_{UO_2})_{c_L, c_S, pH}\,, \quad c_S > c_L, c_{UO_2} \tag{1}$$

$$A = f(c_S)_{c_L\, c_{UO_2}, pH} \tag{2}$$

$$A = f(pH)_{c_L, c_{UO_2}, c_S}\,, \quad c_S > c_L, c_{UO_2} \tag{3}$$

$$A = f(c_{UO_2})_{c_L, pH}\,, \tag{4}$$

where c_{UO_2}, c_L, c_S are the overall analytical concentrations of UO_2^{2+} ions, dye and tenside, respectively.

RESULTS AND DISCUSSION

In weakly acid medium (pH 3–6·5) the studied dyes and UO_2^{2+} ions form stable blue-purple (*I*) to blue (*III*) and (*IV*) complexes, except for the blue UO_2-L(*II*) complexes which change in dependence on time. For the reactions of dyes (*I*), (*III*) and (*IV*), absorption curves *4* with constant dye concentration (c_L $4 . 10^{-5}$M or $8 . 10^{-5}$M) varying concentration of UO_2^{2+} ions ($c_{UO_2} = (0-50)\, c_L$) have a single isosbestic point λ_{iso} at 510 nm (pH 4·66, *I*), 550 nm (pH 4·48, *III*) and 559 nm (pH 3·98, *IV*). As the complexes formed are not very stable, Ketelaar transformations were employed for determining their compositions and conditional stability constants. It is assumed that the following reaction occurs in solution:

$$a\,UO_2^{2+} + b\,HL \rightleftharpoons (UO_2)_aL_b + b\,H^+ \qquad (A)$$

which is characterized by the conditional stability constant

$$\beta'_{a,b} = [(UO_2)_aL'_b][UO'_2]^{-a}[L']^{-b}\,. \qquad (5)$$

Equation (5) can be transformed to give the form

$$\frac{c_L}{\Delta A} = \frac{b}{\Delta\varepsilon} + \frac{1}{(\beta'_{a,b}\,\Delta\varepsilon)^{1/b}\left(c_{UO_2} - a\,\dfrac{\Delta A}{\Delta\varepsilon}\right)^{a/b}\Delta A^{(b-1)/b}}\,, \qquad (6)$$

where $\Delta A = A - \bar{\varepsilon}_L\,.\,c_L$, $\Delta\varepsilon = \varepsilon_c - b\,.\,\bar{\varepsilon}_L$; $\bar{\varepsilon}_L$ is the average molar absorption coefficient of acid–base forms of the dye and ε_c is the molar absorption coefficient of the complex.

For the reaction of dyes (*I*), (*III*) and (*IV*) it was found that linear equation (*6*) is valid only for $a = b = 1$ (Fig. 1). (The dependence for dyes (*III*) and (*IV*) is similar). Consequently, a complex with composition $UO_2 : L = 1 : 1$ is formed in the solution. The molar absorption coefficient for the complex formed was found graphically from transformation (*6*) and the conditional stability constant (*5*) was calculated numerically (Table I).

In the presence of CTA^+, absorption curves *1* with various concentrations of dye and tenside ($c_L = (1{\cdot}5-8)\,.\,10^{-5}$M, $c_S = (2-40)\,.\,10^{-4}$M, pH 3·84–4·7) and changing concentration of UO_2^{2+} ions ($c_{UO_2} = (0-5)\,c_L$) exhibit a single isosbestic point at λ_{iso} 526 nm (pH 4·20, *I*); 570 nm (pH 4·21, *II*); 566 nm (pH 4·09, *III*); 569 nm (pH 3·98, *IV*). It was found by the molar ratio method that a complex with composition $UO_2 : L = 1 : 2$ is formed in the solution in all cases. During titrations (*1*), the dye concentration c_L had a value of $(1{\cdot}5-8)\,.\,10^{-5}$M. The tenside excess was approximately $(10-50)\,c_L$. The UO_2^{2+} ion concentration was varied over the range $(0-5)\,c_L$. For each dye 6–8 titrations were carried out over the pH range 3·84 to 4·70. Similarly, the tangent ratio method, with excess tenside and dye and varying concentration of UO_2^{2+} ions or in excess UO_2^{2+} ions and tenside and varying concentration of dye (c_L 8 . 10^{-4}M, c_L 8 . 10^{-5}M or c_{UO_2} $(1-2)\,.\,10^{-4}$M, pH 4·20 (*I*), pH 4·70 (*II*), pH 4·43 (*III*), pH 4·57 (*IV*)) indicated formation of a complex with a ratio of $UO_2 : L = 1 : 2$.

In titration of dye and uranyl solutions with tenside solutions (*2*) ($c_L = (1{\cdot}5-8)\,.\,10^{-5}$M, $c_{UO_2} = (1-6)\,c_L$) the absorption curves exhibit a single isosbestic point

TABLE I

Conditional Stability Constants for the Binary UO_2–Dye Complex and Absorption Maximum of the First Long Wavelength Band

Dye	pH	$\log \beta'_{1,1}{}^a$	λ_{max}, nm	ε_{max}
	4·66	3·02 ± 0·01		7 250
I	5·55	3·53 ± 0·06	582	6 900
	5·97	3·39 ± 0·06		6 760
	4·48	3·44 ± 0·05		5 780
III	5·07	3·95 ± 0·05	614	5 800
	5·86	4·06 ± 0·03		5 300
IV	3·98	3·11 ± 0·04	625	6 260
	4·71	4·51 ± 0·06		6 050

[a] Calculated from concentration curves *4* (c_L 4·10^{-5}M) for transformation *6*, average of 6—8 values transferred to logarithmic scale (confidence limits found for 95% probability).

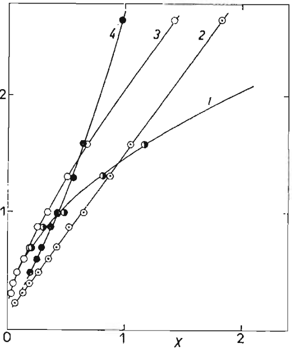

FIG. 1

Dependence of Transformation (*6*)

c_L 4 . 10^{-5}M, pH 4·66, 1 cm cuvettes; $Y = 10^4 c_L/\Delta A$; $X = 1/\Delta A^{(b-1)/b} . (c_{UO_2} - a(\Delta A/\Delta\varepsilon)^{a/b}$, *1* $b = 1$, $a = 2$, $X . 10^8$; *2* $b = a = 1$, $X . 10^{-4}$; *3* $b = a = 2$, $X . 10^{-5}$; *4* $b = 2$, $a = 1$, $X . 10^{-3}$.

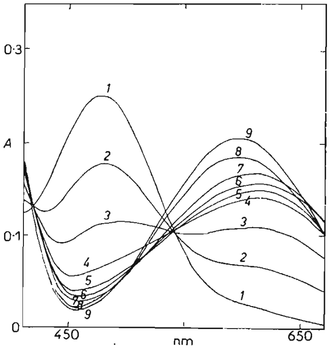

FIG. 2

Absorption Curves for the Ternary UO_2–Dye *I*–CTA^+ System

c_L 1·5 . 10^{-5}M, c_{UO_2} . 10^{-4}M, pH 4·70, 2 cm cuvettes; c_S (10^{-5}M): *1* 0·0; *2* 0·48; *3* 0·96; *4* 1·44; *5* 1·92; *6* 2·4; *7* 4·0; *8* 8·0; *9* 23·2.

for the reaction of dyes (*III*) and (*IV*) λ_{iso} (*III*) 556 nm (pH 4·59); λ_{iso} (*IV*) 576 nm (pH 4·16) and two isosbestic points for the reactions of dyes (*I*) and (*II*) λ_{iso} (*I*) 541 and 526 nm (pH 4·70) (Fig. 2), λ_{iso} (*II*) 576 and 554 nm (pH 4·25) (Fig. 3). It was found by the molar ratio method that, in the reactions of dyes (*III*) and (*IV*), a single complex is formed with a ratio of L : S = 1 : 2, while for reaction of dyes (*I*) and (*II*) two complexes are formed stepwise with ratios of L : S = 1 : 1 and 1 : 2. For the reaction of dye (*II*) the method of continuous variations for dye and tenside in the presence of excess UO_2^{2+} ions (c_0 2·4 . 10^{-5}M, c_{UO_2} 4 . 10^{-5}M, 10^{-4}M, pH 4·64 and 4·76) yield identical results (L : S = 1 : 1 and 1 : 2). The tangent ratio method with excess tenside and uranyl and varying concentration of dye and in excess dye and uranyl and varying tenside concentration (c_{UO_2} 10^{-4}M, c_S 8 . 10^{-4}M or c_L 8 . 10^{-5}M, pH 4·43, λ 630 nm (*III*); pH 4·57, λ 650 nm (*IV*) indicated that a complex with ratio L : S = 1 : 2 (*III*) (*IV*) is formed in the solution. For titration of solutions of dye and uranyl with a tenside solution (c_L 4 . 10^{-5}M or 8 . 10^{-5}M, $c_{UO_2} < c_L/2$, pH 4·43, 4·57, 4·66, 4·76 and 5·10) it was found that complexes with ratios of $UO_2 : S = 1 : 2$ (*I*) and 1 : 4 (*II*, *III*, *IV*) are formed.

The results obtained indicate that in the presence of cationic tenside the coordination number of UO_2^{2+} ions is increased[13–15] as a result of dehydration of UO_2^{2+} ions and dye by the tenside and thus the sensitivity of the UO_2^{2+}-dye reaction is increased; ternary $UO_2L_2S_2$ (*I*, *II*) and $UO_2L_2S_4$ (*III*, *IV*) complexes are formed in solution and, in a sufficient excess of tenside, also the $UO_2L_2S_4$ (*I*, *II*) complex. At higher tenside concentrations, $c_S > 2c_L$, protomicelle and micelle species are formed in solution (the cmc for CTA^+ has a value of 9·2 . 10^{-4}M (ref.[16])), which have a marked effect

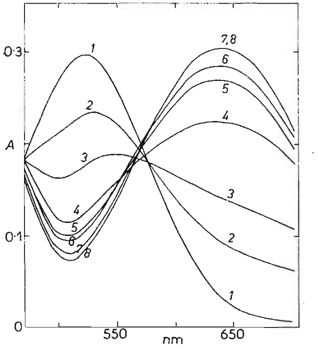

FIG. 3

Absorption Curves of the Ternary UO_2–Dye *II*–CTA^+ System

c_L 1·6 . 10^{-5}M, c_{UO_2} . 10^{-4}M, pH 4·25, 2 cm cuvettes; c_S [10^{-5}M]: *1* 0·0; *2* 0·48; *3* 0·96; *4* 1·92; *5* 2·88; *6* 3·36; *7* 6·4; *8* 8·0.

on the ternary UO_2–L–S (*I*) complex. A hypsochromic shift in the absorption maximum ($\Delta\lambda$ 20 nm) and an increase in the molar absorption coefficient (Fig. 2) can be observed for this complex. The effect of protomicelle and micelle species on the complexes of the other dyes is negligible and the absorption coefficients and maxima of the complexes practically do not change. In the photometric determination of uranyl it is preferable to employ a large excess of CTA^+, to eliminate the precipitation of solid ion associates in solution.

Complex formation can be written as

$$UO_2^{2+} + 2HL + rS \rightleftharpoons UO_2L_2S_r + 2\,H^+ \qquad (B)$$

(where $r = 2$ or 4), which is characterized by the equilibrium constant

$$^*\beta_{1,2,r} = [UO_2L_2S_r][H]^2[UO_2]^{-1}[HL]^{-2}[S]^{-r}\,. \qquad (7)$$

Equilibrium constant (7) can be rearranged to forms (*8*) and (*8a*)

$$^*\beta_{1,2,r} = \frac{(A - A_0)(A_{max} - A_0)^2\,.\,[H]^2}{[2pA_{max} - A - (2p - 1)A_0]\,.\,(A_{max} - A)^2\,[2sA_{max} - rA - (2s - r)A_0]^r}\,.$$

$$.\,\frac{1}{[[H]/(K'_a - [H])]^2\,c_L^{2+r}}\,. \qquad (8)$$

$$.\log\frac{(A - A_0)(A_{max} - A_0)^2}{[2pA_{max} - A - (2p - 1)A_0](A_{max} - A)^2\,[2sA_{max} - rA - (2s - r)A_0]^r} =$$

$$= \log {}^*\beta_{1,2,r} + 2\,pH + (r + 2)\log c_L + 2\log[[H]/(K'_a + [H])]\,, \qquad (8a)$$

where $A = \bar{\varepsilon}_L[L'] + \varepsilon_c[UO_2L_2S_r]$, $A_0 = \bar{\varepsilon}_L\,.\,c_L$, $A_{max} = \varepsilon_c\,.\,c_L/2$, $\bar{\varepsilon}_L$ is the average absorption coefficient of acid–base form of the dye, ε_c is the molar absorption coefficient of the ternary complex, $p = c_{UO_2}/c_L$ ($p \geqq 1/2$), $s = c_S/c_L$ and K'_a is the dissociation constant of the dye in the presence of CTA^+ (ref.[17]); $[L']$ is the conditional concentration of the dye.

It excess cationoid tenside ($c_S = 50c_L$), dependence (*8a*) for dyes (*I*) and (*II*) is linear in the pH range 3·5–4·5 with a slope corresponding to dissociation of two protons (*B*). The molar absorption coefficient of the $UO_2L_2S_4$ complex was found from concentration curves *1* (excess tenside) and from pH curves *3* (excess uranyl and tenside). The equilibrium constants for reaction (*B*) were calculated from equation (*8*) (Tables II and III).

The equilibrium constants $^*\beta'_{1,2,r}$ and $^*\beta'_{1,2}$ ($r = 0$) were also calculated from the conditional stability constants $\beta'_{1,2,r}$ and $\beta'_{1,2}$, which can readily be found from

TABLE II

Equilibrium Constants for the Ternary UO_2–Dye *I*–CTA^+ System

pH	log $^*\beta_{1,2}$	log $^*\beta_{1,2,2}$	log $^*\beta_{1,2,4}$	ε_{max}
		$\lambda_{max} = 590$ nm		
3·5—4·5[a]	1·77 ± 0·09	—	14·23 ± 0·09	1·75 . 10^4
3·83[b]	1·80	—	13·96	—
3·98[c]	1·78	—	12·70	1·76 . 10^4
4·25[b]	1·76	—	13·92	1·73 . 10^4
		$\lambda_{max} = 610$ nm		
4·20[d]	1·22	12·49	—	—
4·70[d]	0·48	11·91	—	1·08 , 10^4

[a] Calculated from pH curves *3* $c_L = c_{UO_2} = 1{\cdot}6 . 10^{-5}$M, c_S $8{\cdot}10^{-4}$M, pK_a' 4·48, average of 9 values transferred to logarithmic scale (confidence limits ±0·09, 95% probability). [b] Calculated from concentration curves *1*, c_L 1·5 . 10^{-5}M, c• 10^{-3}M, pK_a' 4·48. [c] Calculated from concentration curves *1*, c_L 6 . 10^{-6}M, c_S 2 . 10^{-3}M, pK_a' 4·55. [d] Calculated from concentration curves 2, c_L 1·6 . 10^{-5}M, c_{UO_2} 10^{-4}M.

TABLE III

Equilibrium Constants for the Ternary UO_2–Dye *II*–CTA^+ System

pH	log $^*\beta_{1,2}$	log $^*\beta_{1,2,4}$	ε_{max} (650 nm)
3·6—4·5[a]	2·65 ± 0·10	15·17 ± 0·10	2·15 , 10^4
3·84[b]	2·94	15·12	—
4·20[c]	2·92	15·10	2·14 . 10^4
4·20[c]	2·90	15·35	2·05 . 10^4
4·55[b]	2·63	14·81	—
4·25[d]	—	—	2·05 , 10^4

[a] Calculated from pH-curves *3* $c_L = c_{UO_2} = 1{\cdot}6 . 10^{-5}$M, c_S 8 . 10^{-5}M, pK_a' 4·75, average of 8 values transferred to logarithmic scale (confidence limits ±0·10, 95% probability). [b] Calculated from concentration curves *1* c_L 4 . 10^{-5}M, c_S 10^{-3}M, pK_a' 4·75. [c] Calculated from concentration curves *1* c_L 1·6 . 10^{-5}M, c_S 8 . 10^{-5}M, pK_a' 4·75. [d] Calculated from concentration curves 2, c_L 1·6 . 10^{-5}M, c_{UO_2} 10^{-4}M.

concentration curves *1* and 2 from the absorption differences between the quantitative and actual reactions[18,19] considering simultaneous absorbance by the dye and complex. Then constants $\beta'_{1,2,r}$ and $\beta'_{1,2}$ were recalculated to the corresponding equilibrium constants $^*\beta_{1,2,r}$ and $^*\beta_{1,2}$ from equation (*10*) (Tables II – V).

$$\beta'_{1,2,r} = [UO_2L_2S_r][UO_2]^{-1}[L']^{-2}[S]^{-r} \qquad (9)$$

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

TABLE IV

Equilibrium Constants of the Ternary UO_2–Dye *III*–CTA^+ System

pH	log $^*\beta_{1,2}$	log $^*\beta_{1,2,4}$	ε_{max} (630 nm)
4·09[a]	2·13	11·81	1·73 . 10^4
4·43[b]	2·17	15·01	—
4·38[c]	1·22	20·45	1·71 . 10^4
4·59[d]	0·40	19·64	—
4·96[d]	—0·83	17·54	—

[a] Calculated from concentration curves *1* c_L 8 . 10^{-5}M, c_S 4 . 10^{-3}M, pK'_a 4·88. [b] Calculated from concentration curves *1*, c_L 1·6 . 10^{-5}M, c_S 8 . 10^{-4}M, pK'_a 4·71. [c] Calculated from concentration curves 2 c_L 8 . 10^{-5}M, c_{UO_2} 10^{-4}M. [d] Calculated from concentration curves 2, c_L 8 . 10^{-5}M, c_{UO_2} 2 . 10^{-4}M.

TABLE V

Equilibrium Constants of the Ternary UO_2–Dye *IV*–CTA^+ System

pH	log $^*\beta_{1,2}$	log $^*\beta_{1,2,4}$	ε_{max} (650 nm)
3·98[a]	2·15	11·83	1·77 . 10^4
4·36[b]	2·01	14·45	—
4·58[b]	1·76	14·20	1·77 . 10^4
4·16[c]	1·82	23·34	1·76 . 10^4
4·70[c]	1·28	23·65	—

[a] Calculated from concentration curves *1* c_L 8 . 10^{-5}M, c_S 4 . 10^{-3}M, pK'_a 4·81. [b] Calculated from concentration curves *1*, c_L 1·6 . 10^{-5}M, c_S 8 . 10^{-4}M, pK'_a 4·76, [c] Calculated from concentration curves 2, c_L 1·6 . 10^{-5}M, c_{UO_2} 10^{-4}M.

The decrease in $^*\beta$ at higher pH values or the different values of $^*\beta_{1,2,r}$ at various CTA^+ concentrations can be explained by different degrees of hydrolysis of UO_2^{2+} ions and of the complex or by dissociation of CTA^+.

Determination of Uranium and Cetyltrimethylammonium

The stability of the $UO_2L_2S_4$ (*II*) complex is sufficient to allow direct photometric determination of uranium in a small excess of dye and tenside. In weakly acid media of pH 4·2–4·5 and at I 0·01 using 2 . 10^{-4}M dye (*II*), 0·50–11·5 μg U/ml can be reliably determined (λ 650 nm, ε 21500). The standard deviation of the blank (A) for 6 parallel determinations has a value of ±0·001. The detection limit* (c_{min}) is 0·096 μg U/ml. The relative standard deviation for 6 parallel determinations has a value of 0·75% (7·14 μg/ml). The determination is not disturbed by alkali metal ions, alkaline earth ions, a 50-fold excess of Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Tl^+ or Mn^{2+} ions, a 25-fold excess of Y^{3+}, Sc^{3+}, La^{3+} or $3e^{3+}$ ions, a 5-fold excess of Ag^+, $PtCl_6^{2-}$, Cu^{2+}, Al^{3+} or Cr^{3+} ions or an equimolar amount of Zr(IV), Th(IV), Bi(III), Sb(III) or Ti(IV) ions. The following ions interfere in the determination: Hg_2^{2+}, Hg^{2+}, Au^{3+}, Pd^{2+}, Ce^{4+}, Sn^{2+}, Fe^{2+}, Fe^{3+}, In^{3+}, Ga^{3+}, WO_4^{2-}, MoO_4^{2-} and VO_3^-. The selectivity of the determination is increased in the presence of CTA^+. Hydrolysis of Zr(IV), Th(IV), Bi(III), Sb(III) and Ti(IV) ions is suppressed. The colour formation takes 10 minutes and is constant for 2 hours.

Determination Procedure

An amount of 10 ml of 10^{-2}M-CTA^+ is added to a 50 ml volumetric flask containing 10 ml of 10^{-3}M dye *II*, 5 ml of acetate buffer (0·1M) of pH 4·3 and 25—500 μg of uranium. The flask is filled to the mark and after 10 minutes the absorbance is measured against a blank at 650 nm.

In weakly acidic media (pH 4·5–5·0), the stability of the $UO_2L_2S_2$ (*II*) complex in a small excess of dye and uranyl permits direct photometric determination of cetyltrimethylammonium. Using 1·6 . 10^{-4}M dye (*II*), 2 . 10^{-4}M uranyl and I 0·01, 3·6 to 28·8 μg CTA^+/ml can be reliably determined (λ 650 nm, ε 10250). The standard deviation of the blank (A) for 6 parallel determinations has a value of ±0·001. The detection limit is 0·258 μg CTA^+/ml. The relative standard deviation for 6 parallel determinations has a value of 1·01% (17·3 μg CTA^+/ml). The determination is not disturbed by a 30-fold excess of Na_2SO_4, a 10-fold excess of $NaHCO_3$, a five-fold excess of tripolyphosphate and equivalent amounts of carboxymethylcellulose. This method is almost as sensitive as the method employing pyrocatechol violet and UO_2^{2+} ions (ε 1·2 . 10^4), but is not complicated by photochemical oxidation of the complex[20]. In comparison with the method employing VO_3^- and dye *III* (ε 4·4 . 10^3),

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* The detection limit was found from the relationship $x = \bar{x}_0 + 6s_{x_0}$, where x is the smallest measurable value of the absorbance[21,22] and x_0 is the blank value.

this method is more sensitive and more suitable with respect to the time stability of the complex. The solution colouration is constant for 40 minutes.

Determination Procedure

A sample containing 0·018—1·44 mg CTA^+ is added to a 50 ml volumetric flask containing 8 ml of 10^{-3}M dye *II*, 5 ml of acetate buffer (0·1M) of pH 4·6 and 1 ml of 10^{-2}M-UO_2^{2+} ions. The solution is diluted to the mark and the absorbance is measured after 5 minutes against a blank at 650 nm.

The remaining dyes are not suitable for photometric determination of uranium and CTA^+. The $UO_2L_2S_4$ (*III*, *IV*) complexes for $c_{UO_2} < c_L/2$ are not stable and the ternary complexes decompose with time. The UO_2 — dye *I* — CTA^+ reaction is also not suitable because of precipitation of L—S associates in solution. Dyes *I*, *III* and *IV* are not suitable for the determination of CTA^+ because of their low sensitivity (λ 610 nm, ε 5040 (*I*); λ 630 nm, ε 4300 (*III*); λ 650 nm, ε 4400 (*IV*)). It is necessary in preparation of solutions to maintain the ionic strength constant in all samples. The absorbance of a solution of ionic strength 0·1 is half that of a solution with identical composition but with an ionic strength of 0·01. The change in the absorbance on a change in the ionic strength from 0·001 to 0·015 is, however, negligible.

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REFERENCES

1. Nguyen Truong Son, Lasovský J., Ružička E., Šimek J., Szotkowská J.: This Journal, in press.
2. Lasovský J., Ružička E.: This Journal *42*, 1941 (1977).
3. Ružička E., Nguyen Truong Son: This Journal *43*, 1885 (1978).
4. Sedláčková J.: *Thesis*. Palacký University, Olomouc 1975.
5. Juřina J., Ružička E.: Unpublished results.
6. Cross J. T.: Analyst (London) *90*, 315 (1965).
7. Uno T., Miyajima K., Tsukatani H.: Yakugaku Zasshi *80*, 153 (1960).
8. Patrovský V.: *Analytická chemie vzácných prvků*, p. 126. Published by SNTL, Prague 1956.
9. Yoe J. A., Jones A. L.: Ind. Eng. Chem., Anal. Ed. *16*, 41 (1944).
10. Job P.: Ann. Chim. (Paris) *9*, 113 (1928).
11. Harving A. E., Manning D. L.: J. Amer. Chem. Soc. *72*, 4488 (1950).
12. Ketelaar A. A. J., van de Stople C., Goudsmit A., Dzcubar V.: Rec. Trav. Chim. Pays-Bas *71*, 1104 (1952).
13. Pilipenko A. T., Tananaiko M. M.: Talanta *21*, 501 (1974).
14. Noriki Sh: Anal. Chim. Acta *76*, 215 (1975).
15. Kawamato H., Akaiwa H.: Japan Analyst *24*, 127 (1975).
16. Fendler E., Fendler J.: *Advances in Physical Organic Chemistry*, Vol. 8, p. 271. Academic Press, London, New York 1970.
17. Nguyen Truong Son, Lasovský J., Ružička E.: Unpublished results.

18. Somer L., Jin Tsin-Jao: Chem. Listy *55*, 574 (1961).
19. Nomura T.: Bull. Chem. Soc. Jap. *41*, 2803 (1968).
20. Lasovský J., Ružička E., Nguyen Truong Son in the book: *Analytika, chemie a technologie tensidů a detergentů*, p. 135. The House of Technology ČVTS, Ostrava 1976.
21. Eckschlager K.: *Chyby chemických rozborů*, 2nd Edition, p. 163. Published by SNTL, Prague 1971.
22. Svoboda V., Gerbatsch R.: Z. Anal. Chem. *242*, 1 (1968).

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