

A SUPERSENSITIVE SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF URANIUM(VI) WITH ERIOCHROMAZUROL B IN THE PRESENCE OF TENSIDES

Milan PIŠTĚLKA^a, Bohumil STOJEK^b and Josef HAVEL^c

^a Nuclear Power Station Dukovany, 675 50 Dukovany,

^b Odra River Basin, Water Management Enterprise, 701 26 Ostrava and

^c Department of Analytical Chemistry, Purkyně University, 611 37 Brno

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The influence of various tensides on the sensitivity of the reaction of uranyl with chromatographically pure Eriochromazurol B (2'',6''-dichloro-3,3'-dimethyl-4-hydroxyfuchson-5,5'-dicarboxylic acid) was studied and considerable bathochromic and hyperchromic effects were observed. The reaction is most sensitive in the presence of cetyltrimethylammonium or cetylpyridinium bromide. Based on the study of the equilibria and optimization of the conditions, a method is suggested for the determination of uranium traces in waters consisting in the measurement of absorbance at 624 nm at pH 5. With the molar absorptivity value of 136 000, the method ranks among the most sensitive spectrophotometric methods of determination of uranium in general. The uranium traces in waters can conveniently be extracted with tri-n-octylamine and reextracted into an aqueous phase. For 10 ml samples, the detection limit is 0.025 ppm uranium. The results obtained are evaluated statistically.

Hydroxytriphenylmethane dyes containing the salicylic acid functional group such as Chromazurol S (CAS), Eriochromazurol B (CAB), or Eriochromcyanine R (ECR) serve as highly sensitive reagents for the spectrophotometric determination of a number of heavy metals including uranyl ions in aqueous or aqueous-alcoholic solutions¹. This group of organic reagents for analysis in solutions has recently gained importance owing to the application of tensides, which alter the optical properties of the dyes and their chelates with metal ions² as well as the acid-base properties of the metallochromic indicators. The development of tens of novel methods for spectrophotometric determinations in the presence of tensides, featuring increased sensitivity, has revitalized spectrophotometry as an important branch of analytical chemistry in general. Among elements that can be determined with higher sensitivity owing to the use of tensides is also uranium³. This element is usually determined⁴⁻⁶ with CAS; the reaction, in the absence of tenside, has been studied in detail⁷. The addition of tenside brings about a significant improvement in sensitivity; polyvinyl alcohol⁸, cetylpyridinium bromide^{9,10}, cetyltrimethylammonium chloride¹¹, and gelatine¹² have been employed. The effect of a great number of tensides has been investigated by Evtimova¹³. So far the highest sensitivity has been attained with the use of Septo-

nex³. Very sensitive is also the reaction of uranium with ECR in the presence of cetyltrimethylammonium¹⁴. Eriochromazurol B, which in contrast to chromazurol S contains no sulphonic group in its molecule, has been used for the determination of uranium in aqueous-alcoholic solutions^{15,16}. The effect of cetylpyridinium on the determination of uranium with CAS has been investigated by Malaník and Malát¹⁷, who mention the fact that the unsulphonated derivative, CAB, is more sensitive. The purity of CAS, CAB, and ECR has been the concern of a number of authors^{3,18,19}.

The present work is a continuation of our previous study of the effect of tensides on the CAS-uranyl system; the results of that investigation are compared with those obtained now for the reaction of uranyl with CAB using reagent of chromatographic purity. For the CAB-uranyl-cetylpyridinium bromide system the complex equilibria are studied in detail and the reaction conditions are optimized with a view to employing CAB for the determination of traces of uranium in waters, especially after its extraction separation with tri-*n*-octylamine (TOA). Our previous partial results^{20,21} are here summarized. A succinct account of the method in question has been given recently²².

EXPERIMENTAL

Chemicals and Apparatus

Eriochromazurol B (M_r 459.3) was purified similarly as Chromazurol S (ref.³) by repeated precipitation with hydrochloric acid. The supplied chemical (Merck, Darmstadt), which is the sodium or disodium salt, contains various impurities, partly of inorganic nature, which lower its reactivity appreciably. A CAB batch of about 2 g was dissolved in approximately 250 ml of water, the solution was filtered over a dense glass filter (S4), and the free acid, which is very low soluble in solutions of $\text{pH} < 3$, was precipitated slowly from the constantly stirred filtrate. The precipitate was collected on another S4 glass filter, dissolved in a small excess of 0.1M-NH_3 , and CAB was immediately precipitated with dilute (1 : 3) hydrochloric acid. The product was vacuum filtered and washed repeatedly with water acidified with hydrochloric acid ($\text{pH} \approx 3$) and with pure water; the precipitation was repeated three times. The final product was allowed to dry for a week over solid KOH in a desiccator and then in free air to constant weight. The purity of the chemical was checked by determining its carbon content by elemental analysis ($92.49 \pm 0.32\%$ active substance with respect to the anhydrous preparation). The yield was about 50%. The stock solution in a concentration of 1.2 mmol l^{-1} was prepared by dissolving the substance in a small excess of ammonia so that the resulting pH of solution did not exceed pH 9; the solution was steady for at least 3 weeks. The reagent was chromatographically pure^{18,19}.

Solution of uranyl nitrate of reagent grade purity (Lachema, Brno) in 0.1M-HNO_3 was prepared in a concentration of $210.7 \text{ mmol l}^{-1}$ and standardized by precipitation with hydrogen peroxide or 8-hydroxyquinoline²³. The two methods gave results identical to within $\pm 0.5\%$ rel.

Hydrochloric acid and ammonia were purified by isothermal distillation in a desiccator at room temperature²⁰ using redistilled water in a Teflon crucible. High purity substances were thus obtained; the hydrochloric acid exhibited lower blank values than the acid for the manufacture of semiconductors (Lachema, Brno).

Ethanol denatured with 5% methanol and pyridine were purified by distillation. Cetylpyridinium bromide (CPB) pure (Lachema, Brno), $C_{21}H_{38}NBr \cdot H_2O$, was recrystallized twice from water and dried freely in air. Ajatin (benzyltrimethylammonium bromide) was recrystallized three times from water. Septonex (1-ethoxycarbonylpentadecyltrimethylammonium bromide) (Farmakon, Olomouc) and Zephiramin (benzyltrimethylammonium bromide) (Dojindo, Japan) were used without pretreatment, as were cetyltrimethylammonium bromide (CTMAB) pure (Lachema, Brno) and Slovasol O (W. Pieck Chemical Works, Nováky). The tensides were used in alcoholic solutions.

The remaining chemicals were of reagent grade purity. The solutions were made up using redistilled water from a quartz apparatus.

The ionic strength of the solutions was adjusted to $I = 0.1$ ($(H, NH_4)NO_3$) with nitric acid and ammonia. The spectrophotometric measurements were performed on a Superscan 3 spectrophotometer (Varian, Switzerland) interfaced to an HP 9815 A computer (Hewlett-Packard, USA) or on a Spektromom 201 instrument (MOM, Budapest) at $20 \pm 2^\circ C$. The acidity of the solutions was measured on an MV 87 pH-meter (Präcitronic, GDR) fitted with a GK 2302C combined electrode (Radiometer, Copenhagen).

Preparation of Solutions

The components were mixed in volumetric flasks. Because of the low solubility of the reagent, 10% (*v/v*) ethanol was used as solvent. Although the order of the components combined had no appreciable effect on the absorbance, the following order was adhered to: uranyl solution, nitric acid for the ionic strength adjustment, tenside solution, ethanol for making its concentration up to 10% (*v/v*), and reagent solution. The initial pH was invariably about pH 1.1, and the desired value then was adjusted by a slow "titration", *i.e.* by adding dilute ammonia by means of a micro-pipette or microsyringe so that the volume changes could be disregarded. For obtaining the dependences on the concentrations of one of the three components (metal, reagent, tenside), series of samples were prepared; again, the initial pH was 1.1 and the adjustment was made with dilute ammonia. Any pH adjustment was conducted in the direction towards higher pH, by alkalinizing the solution stirred with a magnetic stirrer. In this manner well reproducible results were obtained, whereas acidification of basic solutions led to hysteresis effects and the reproducibility was rather poor.

RESULTS

Absorption Spectra of Uranyl-Eriochromazurol B Solutions in the Presence of Tensides

The complexes of uranyl with CAB are sparingly soluble in aqueous-alcoholic solvents (10% (*v/v*) ethanol); precipitates are usually formed if the uranyl concentration exceeds $5 \mu mol l^{-1}$. The solubility of the dye is also limited, particularly in acid solutions ($pH < 3$). In the presence of surfactants, however, the precipitates and moreover, the absorption maxima are solubilized of the chelates are shifted to higher wavelengths and the colour becomes more intense^{3,9}. The effect of various tensides was examined (Table I), and at the reagent-to-metal molar ratio $c_L/c_M = 2.2$ the reaction of uranyl with CAB was found most sensitive when CPB or CTMAB were

present. In the presence of the former, two marked maxima appear in the spectra at 624 and 650 nm, in the presence of the latter, a maximum is observed at 621 nm and another one can be traced at 655 nm. With the remaining tensides, the uranyl-CAB system exhibits a single maximum in the 630 nm range.

Dependence of Absorbance of Uranyl-Eriochromazurol B-Tenside System on pH

The reaction of uranyl with CAB in the presence of the tensides studied takes place at pH 2.5–8; the absorbance vs pH curves (Fig. 1) indicate that for all of the tensides studied, several complex equilibria establish in this pH region. Superior to the remaining tensides, CPB was chosen for the subsequent experiments. While $10^{-3}M$ solutions of CPB in ethanol are steady for a minimum of two weeks, alcoholic solutions of CTMAB show turbidity in 1–2 days, and aqueous solutions of CTMAB are also unstable, giving rise to turbidity of unknown composition. Zephiramin and Ajatin are least suitable since the determination in their presence is least sensitive and moreover, precipitates separate from solutions of ionic strength higher than 0.1 (NH_4NO_3).

Acid-Base and Optical Properties of Eriochromazurol B in Solutions Containing Cetylpyridinium Bromide

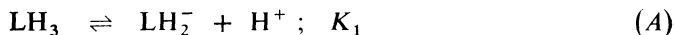
Eriochromazurol B is a triprotic acid, LH_3 , existing, in dependence on pH, in five different dissociation forms, LH_4^+ , LH_3 , LH_2^- , LH^- , and L^{3-} (ref.¹⁹). In view

TABLE I

Effect of tensides on the sensitivity of the reaction of uranyl with Eriochromazurol B. The values of the molar absorptivity ϵ were calculated from the plateaus of the absorbance-pH curves

Tenside	λ_{max} nm	ϵ $10^4 \text{ cm}^2 \text{ mmol}^{-1}$	Optimum pH region
Cetylpyridinium bromide	624	1.36 ₅	4–7
	650	1.10	
Cetyltrimethylammonium bromide	621	1.36	4–7
	655	0.51	
Septonex	634	1.104	5.5–7
Slovasol O	629	0.94 ₄	6–7
Zephiramin	637	0.83 ₁	6.5–7
Ajatin	635	0.80 ₄	6–7

of the fact that the protonation of the molecular species LH_3 to the cation species LH_4^+ only takes place in strongly acid solutions and the dissociation of the LH_2^- species to the L^{3-} anion occurs in strongly basic solutions ($\text{p}K \approx 12$) while the complex equilibria of uranyl with CAB establish within the region $\text{pH } 2.5-8$, only the equilibria



and



were taken into account.

The dissociation constants $\text{p}K_1$ and $\text{p}K_2$ were determined in 10% (*v/v*) ethanol at ionic strength $I = 0.1$ and at various concentrations of reagent and for solutions with excess CPB. In cationactive tenside solutions the values of the dissociation constants of weak acids vary^{23,24} and depend on the tenside concentration; this effect has been described and discussed elsewhere²⁴. In the present work the optical properties of the LH_3 , LH_2^- , and LH^{2-} species and the dissociation constants $\text{p}K_1$ and $\text{p}K_2$ are determined for two concentrations of CPB as used throughout the study. The $A = f(\text{pH})$ dependences were evaluated by the classical graphical and graphical-logarithmic analysis based on the relations²⁵. In addition, a computer matrix analysis of the spectra was carried out by means of the EY608+FA608 program²⁶,

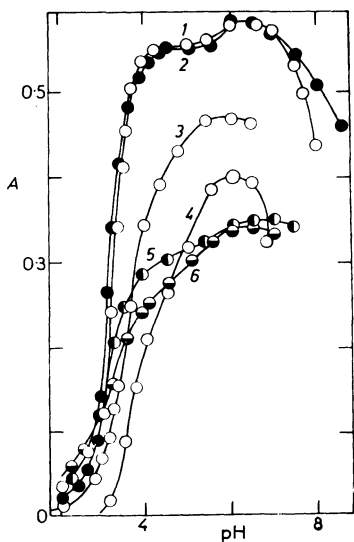


FIG. 1

Absorbance-pH curves for the uranyl-CAB-tenside systems; $c_U = 4.214 \mu\text{mol l}^{-1}$, $c_L = 9.25 \mu\text{mol l}^{-1}$, $c_T = 0.2 \text{ mmol l}^{-1}$, $I 0.1$, 10% (*v/v*) ethanol). Tenside, λ (nm): 1 CPB, 624; 2 CTMAB, 621; 3 Septonex, 634; 4 Slovasol O, 629; 5 Zephiramin, 637; 6 Ajatin, 635

the constants were calculated by this program adapted to the Tesla 200 computer²⁷. The results of analyses of the optical and acid-base properties of CAB are given in Table II. Interestingly enough, the dissociation constants in nitrate and in chloride solutions are different even at the same ionic strength (Fig. 2); this effect of the inert electrolyte can be explained in terms of the different stability of the ionic associates of the cetylpyridinium cation with the salt anion. As a consequence of the more extensive formation of associates with nitrate,



and greater stability of the cetylpyridinium associate with nitrate as compared with chloride, the concentration of free CP^+ cations decreases, whereupon the formation of the associates of the dye, $\{\text{CP}^+, \text{LH}_2^-\}$ and $\{(\text{CP}^+)_2, \text{LH}^{2-}\}$, is suppressed and the

TABLE II

Molar absorptivities and acid-base constants of Eriochromazurol B in cetylpyridinium bromide solutions, $c_T = 1.0 \text{ mmol l}^{-1}$, $c_{\text{EDTA}} = 0.498 \text{ mmol l}^{-1}$, $I = 0.1$, 10% (v/v) ethanol. The upper values were obtained by the FA608+EY608 program^{26,27}, calculation for wavelengths 370 to 660 nm step 10 nm; the lower values were obtained by graphical analysis, pK calculated as average of the graphical and logarithmic analysis for 430 and 510 nm

c_L $\mu\text{mol l}^{-1}$	Ionic strength adjustment	$\epsilon, \text{cm}^2 \text{mmol}^{-1}$			pK
		LH_3 (470 nm)	LH_2^- (510 nm)	LH^{2-} (430 nm)	
5.2	$(\text{NH}_4, \text{H})\text{NO}_3$	20 830	22 345	18 945	pK_2 1.32 ± 0.02
		21 950			1.34
60	$(\text{NH}_4, \text{H})\text{NO}_3$	19 890	20 760	17 960	1.28 ± 0.01
			20 670		1.22
60	$(\text{NH}_4, \text{H})\text{Cl}$	18 760	18 030	21 120	0.92 ± 0.01
			21 190		0.82
5.2	$(\text{NH}_4, \text{H})\text{NO}_3$	20 830	22 350	18 950	pK_3 5.17 ± 0.01
		21 960	18 750		5.18
60	$(\text{NH}_4, \text{H})\text{NO}_3$	19 890	20 760	17 960	5.21 ± 0.01
			20 670	17 880	5.21
60	$(\text{NH}_4, \text{H})\text{Cl}$	18 760	18 030	21 120	4.78 ± 0.01
			20 900	17 930	4.79 ₅

dissociation constants of CAB are altered. These dependences have been evaluated quantitatively and from a general point of view elsewhere²⁴.

Complex Equilibria of Uranyl with Eriochromazurol B in Solutions Containing Excess Cetylpyridinium Bromide

Absorbance-pH curves. In practice the determinations are usually performed using a rather high excess of reagent with respect to the metal analyzed ($p_L = c_L/c_M = 5-20$). In addition to the measurements at $p_L = 2.2$, the spectra of the uranyl-CAB-CPB system were also measured at a higher excess of reagent, $p_L = 5.7$, and the position of the absorption peaks and the spectral patterns were found unaffected by the p_L value²¹. The $A = f(\text{pH})$ curves measured in detail for the absorption maxima using excess of reagent, $p_L = 5.71$ and 14.29 , and excess of tenside, $p_T = c_T/c_M = 95.24$ and 238.1 (Figs 3 and 4), indicate that several complex equilibria establish in the solution in dependence on pH. The pH scale can be divided into four distinct regions, *viz.*, pH 1.7-3.8, pH 3.8-4.5, pH 4.5-6.5, and pH 6.5-8.5. The last range is characterized by a decrease in absorbance due to the gradual hydrolysis of the complexes; the most marked changes, however, are observed in the first pH range. The curves were subjected to graphical analysis, and a 1 : 1 complex was found to be formed with the elimination of two hydrogen ions. A result of the graphical analysis of curve 2 in Fig. 4, for different numbers of split-off hydrogen ions (q), is shown in Fig. 5. The transformation plots are nonlinear for $q = 1$ and 3 (curves 1 and 3 in Fig. 5) and linear for $q = 2$ (curves 2 and 4). Curve 2 in Fig. 5 is the transformation graph for the molar absorbance of the complex, curve 4, for the molar absorbance of the metal. The absorbance intercept of curve 4 is zero, which

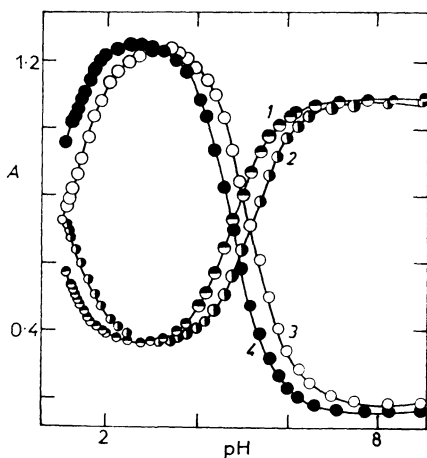
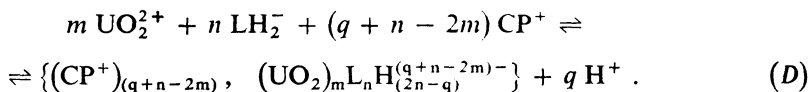


FIG. 2

Absorbance-pH curves for CAB in CPB solutions; $c_L = 60 \mu\text{mol l}^{-1}$, $c_T = 1 \text{ mmol l}^{-1}$, $c_{\text{EDTA}} = 498 \mu\text{mol l}^{-1}$. λ (nm): 1, 2 430, 3, 4 510; I : 1, 4 0.1 (NH_4 , HCl), 2, 3 0.1 (NH_4 , HNO_3)

gives evidence that the complex involves reaction components (UO_2^{2+} and LH_2^-) which themselves do not absorb at 624 nm. The relations employed for the graphical analysis have been published elsewhere^{3,25}. The above facts together with the analogy of the CAS-uranium-Septonex system²⁵ indicate that the complex formed in the first region of the complex equilibrium is an ionic associate described by equilibrium (D) with $q = 2$:



The regions of the second and third complex equilibria were also subjected to graphical analysis, the absorbance changes in the corresponding segments, however, are relatively low and they could not be accounted for satisfactorily enough.

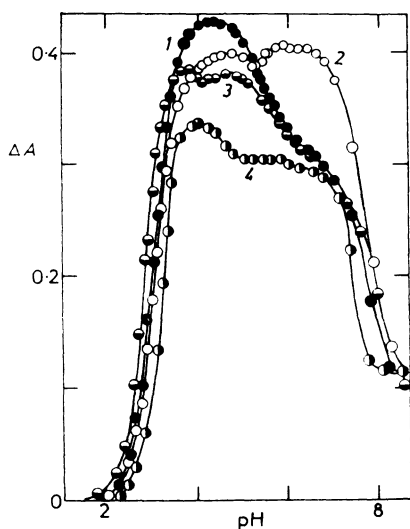


FIG. 3

Absorbance-pH curves for uranyl-CAB-CPB systems with excess reagent; $c_U = 4.2 \mu\text{mol} \cdot \text{l}^{-1}$, $I 0.1$ (NH_4, H) NO_3 , 10% (v/v) ethanol. c_L ($\mu\text{mol} \cdot \text{l}^{-1}$), c_T ($\text{mmol} \cdot \text{l}^{-1}$), λ (nm): 1 60, 1, 515; 2 60, 1, 624; 3 60, 0.4, 615; 4 24, 0.4, 615; ΔA is the absorbance of the solutions from which the absorbance of reagent solution (free of metal) was subtracted

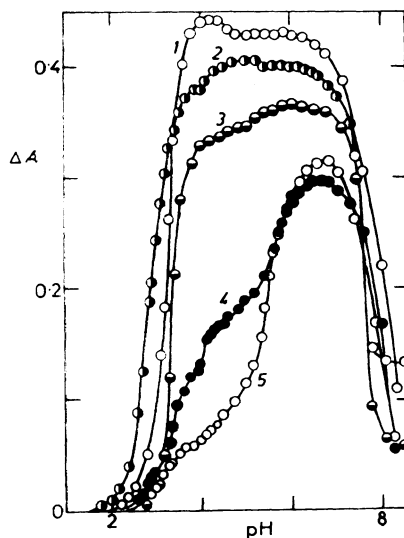
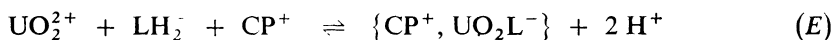


FIG. 4

Absorbance-pH curves for uranyl-CAB-CPB systems with excess reagent; $c_U = 4.2 \mu\text{mol} \cdot \text{l}^{-2}$, $I 0.1$ (NH_4, H) NO_3 , 10% (v/v) ethanol. c_L ($\mu\text{mol} \cdot \text{l}^{-1}$), c_T ($\text{mmol} \cdot \text{l}^{-1}$), λ (nm): 1 24, 0.4, 624; 2 60, 0.4, 624; 4 24, 0.4, 655; 4 60, 0.4, 655; 5 60, 1, 655; ΔA is the absorbance of the solutions from which the absorbance of reagent solution (free of metal) was subtracted

Curves of molar ratios and continuous variations. The molar ratios curves measured at pH 4 and 6.5 demonstrate the formation of complexes with the uranium-to-CAB ratio predominantly 1 : 2 (for 623 and 653 nm, $c_L/c_M = 1.71$ and 2.0, respectively, at pH 4, and 1.90 and 2.0, respectively, at pH 6.5). The region of the first complex equilibrium analyzed in Fig. 5 belongs to the 1 : 1 complex, as confirmed by the continuous variations curves, which at pH 3.70 exhibit the maximum at the 1 : 1 component ratio, whereas at pH 4.5 and pH 6 the component ratio corresponding to the maximum is shifted to 1 : 1.5 and 1 : 2, respectively. The 1 : 1 complex is probably the $\{CP^+, UO_2L^-\}$ associate formed by the equilibrium



This complex then transforms with increasing pH into at least two other complexes with the uranium-to-CAB ratio 1 : 2, the optical constants of which approach each other closely. The 1 : 2 complex in the region of pH 5–6.5 can be utilized for the photometric determination of uranium. The decrease in absorbance accompanying the increasing concentration of reagent (p_L above 3–4) is probably due to the competitive effect of the excess reagent leading to binary ion pairs $\{CP^+, LH_2^-\}$ or $\{(CP^+)_4, UO_2L_4^{4-}\}$, and possibly also $\{(CP^+)_2, UO_2(LH_2)^{2-}\}$. The inclusion of the second molecule of reagent in the LH_2^{2-} or LH_2^{2-} form seems to be more likely than the inclusion of the L^{3-} form because in this manner the only slightly higher molar absorbance of the 1 : 2 complexes as compared with the 1 : 1 complex can be well accounted for.

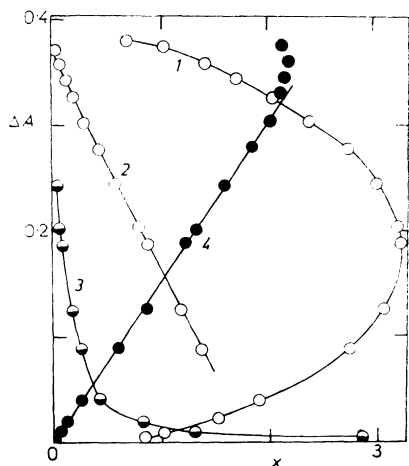


FIG. 5

Graphical analysis of the absorbance-pH curve for the uranyl-CAB-CPB system; $c_U = 4.2 \mu\text{mol l}^{-1}$, $c_L = 60 \mu\text{mol l}^{-1}$, $c_T = 0.4 \text{ mmol l}^{-1}$, $I = 0.1$, $\lambda = 624 \text{ nm}$. q : 1 1, 2 2, 3 3, 4 2. ΔA is the absorbance of the solutions from which the absorbance of reagent was subtracted

Attempts were made to extract the ternary complex of uranium with CPB and CAB into conventional extracting agents, but in fact only the binary associate of reagent with CPB was extracted, which gave evidence of a high stability and extractability of the binary associate. Uranium was not observed to be extracted. The possibility of utilizing the ternary complexes for analytical purposes was therefore examined in aqueous solutions only.

Spectrophotometric Determination of Uranium with Eriochromazurol B in the Presence of Cetylpyridinium Bromide

Cetylpyridinium bromide was chosen as the most suitable tenside for the determination of uranium. The spectra and the absorbance curves in dependence on pH and on the concentrations of reagent and tenside were analyzed, and the optimum conditions for the determination were found as follows: pH 5, $c_L = 24 \mu\text{mol l}^{-1}$, $c_T = 0.4 \text{ mmol l}^{-1}$; 10% (v/v) ethanol; wavelength 624 nm. Under these conditions the absorbance is constant over the pH 4.7–6.2 range. Reagent or tenside concentrations higher than as indicated should be avoided because otherwise a lowered absorbance and, consequently, a lowered sensitivity are obtained. The effect of various substances on the determination of uranium was examined under the above conditions and at the uranium concentration $c_U = 4.2 \mu\text{mol l}^{-1}$. Of buffers, pyridinium, β -picolinium, and hexamethylenetetramine buffers do not interfere up to a concentration of 0.1 mol l^{-1} , whereas phthalate, chloroacetate, acetate, formate, and phosphate buffers interfered considerably. The urotropine buffer, decomposing slowly at pH < 6 to ammonia and formaldehyde and thereby changing its pH value is not very suitable, and the β -picolinium buffer is not in common use. Therefore, the pyridinium buffer was employed and is recommended for use in a concentration of 0.1 mol l^{-1} . The effect of foreign ions and substances was also investigated in this buffer. A foreign substance was considered interfering if, on the concentration level used, it induced an error in the absorbance higher than 2% rel.

The ionic strength (KNO_3) has no effect up to I 0.6, at higher values the sensitivity decreases (–6% at I 1.0 and –7.4% at I 1.5). As to the alcohol content of the solvent, it should not be increased above the optimum 10% (v/v), otherwise the absorbance decreases considerably (–6.2% and –14.3% in 20% and 30% (v/v) ethanol).

Of other surfactants, gelatine does not interfere up to a concentration of 0.1%; in 0.5% gelatine solution the absorbance decreases by 10%. Polyvinyl alcohol (PVA) raises the absorbance slightly (by 5% in 0.64% PVA), whereas CTMAB has no effect up to a concentration of 1.2 mmol l^{-1} .

Interferences from foreign elements were also investigated. For this purpose, the elements were added to the uranium solution before the remaining components. The results of the analyses are given in Table III. Of common cations, Fe(III) inter-

feres even at low concentrations. Be(II), Th(IV), Al(III), and Ti(IV) also interfere. Of anions, oxalates, perchlorates, and EDTA are found to interfere.

Analytical curves for the determination of uranium(VI). The validity of Beer's law was tested for two concentrations of reagent (Fig. 6). The curve, particularly for the higher concentration, consists of two linear parts, the segment at higher concentrations of metal exhibiting a higher slope (a higher molar absorptivity). The segments were treated by the linear regression method (Table IV). In the determination of uranium in pure solutions in the presence of pyridinium buffer, the molar absorptivity was as high as $126\,000\text{ cm}^2\text{ mmol}^{-1}$. The lower sensitivity

TABLE III

Interference from foreign ions in the spectrophotometric determination of uranium(VI) with Eriochromazul B in cetylpyridinium bromide solutions; $c_U = 4.2\ \mu\text{mol l}^{-1}$, $c_L = 24\ \mu\text{mol l}^{-1}$, $c_T = 0.4\ \text{mmol l}^{-1}$, pH 5 (pyridinium buffer), $I\ 0.1$, $\lambda\ 624\ \text{nm}$

Ion (X)	c_X mmol l^{-1}	p_X^a	Interference ^b
NO_3^-	600	142 860	—
SO_4^{2-}	600	142 860	—
Cl^-	300	71 430	—
BO_2^-	50	11 905	—
CO_3^{2-}	0.4	95.2	—
PO_4^{3-}	0.2	47.6	—
ClO_4^-	0.1	23.8	^c
EDTA	0.05	11.9	—
Oxalate	0.002	0.5	—
Zn^{2+}	4.77	1 125	+
Ca^{2+}	12.5	2 971	+
Pb^{2+}	0.482	115	+
Cd^{2+}	0.307	73	+
Cu^{2+}	0.0543	12.9	+
VO_2^+	0.0286	6.8	+
Ti(IV)	0.002	0.48	+
Fe^{3+}	0.001	0.24	+
Be^{2+}	0.0005	0.12	+
Th(IV)	0.0005	0.12	+
Tl^{3+}	0.0005	0.12	+

^a $p_X = c_X/c_U$ is the ratio of the concentrations of the interfering ion and uranyl at which the error of determination is +2% or -2%; ^b sign of the error induced by the interfering ion; ^c formation of precipitate.

at lower uranium concentrations is associated with the relatively higher excess of reagent. The linear segment of higher sensitivity, where the excess of reagents relatively smaller, can be extended by lowering the total analytical concentration of reagent (Fig. 6, curve 2); the analytical curve then is linear over the region of $c_U =$

TABLE IV

Statistical parameters of the analytical curves for the determination of uranium with Eriochrom-azurolo B in cetylpyridinium bromide solutions

Curve	c_L $\mu\text{mol l}^{-1}$	$\epsilon \pm s_\epsilon$ $\text{cm}^2 \text{mmol}^{-1}$	A_L^a	s_{yx}^b	r^c
Curve 1 in Fig. 6, 1st part	60	$87\,500 \pm 390$	0.141 ± 0.002	0.0035	0.9993
Curve 1 in Fig. 6, 2nd part	60	$126\,050 \pm 450$	0.001 ± 0.001	0.002 ₁	0.9999
—	24	$136\,500 \pm 500$	0.001 ± 0.001	0.002	0.9998
Curve 2 in Fig. 6 ^d	24	$123\,000 \pm 250$	0.013 ± 0.001	0.001 ₅	1.0000

^a Absorbance of the blank calculated as the intercept of the regression straight line $A = A_L + \epsilon c_U$ (ref.^{3,2}); ^b standard deviation characterizing the variance about the regression straight line^{3,2}; ^c correlation coefficient of the regression straight line; ^d determination of uranium after its extraction separation.

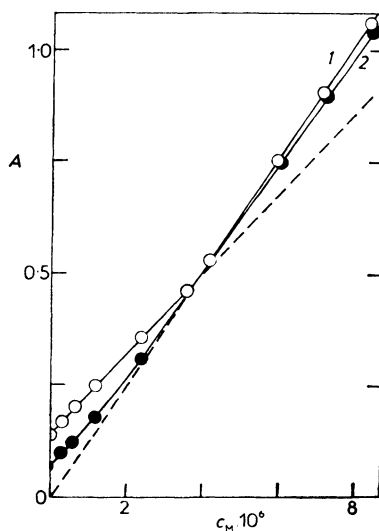


FIG. 6

Analytical curves for the spectrophotometric determination of uranium with CAB in the presence of CPB. 1 determination in pure solutions at $c_L = 60 \mu\text{mol l}^{-1}$, 2 determination after the extraction separation of uranium with TOA at $c_L = 24 \mu\text{mol l}^{-1}$; $c_T = 0.4 \text{ mmol l}^{-1}$, 10% (v/v) ethanol, pH 5 (0.1M pyridinium buffer), λ 624 nm

= $2.5-8.4 \mu\text{mol l}^{-1}$. The curved part of the calibration plot at the lowest uranium concentrations can be eliminated by a constant addition of uranium to a concentration of $2 \mu\text{mol l}^{-1}$.

Procedure for the determination of uranium in pure solutions. Stock solution of CAB (1.2 mmol l^{-1}) is prepared by dissolving 55.1 mg of the purified chemical in 5 ml of 0.5M ammonia and diluting the solution to 100 ml with redistilled water. The working solution is obtained from the stock solution by tenfold dilution. The solutions are steady at least for three weeks. A solution of CPB in a concentration of 4 mmol l^{-1} is obtained by dissolving 161 mg of substance in 100 ml of ethanol, and it is steady at least for a week.

For the determination, 1–10 ml of weakly acid solution of uranium, 2.5 ml of standard solution of uranyl nitrate ($c = 20 \mu\text{mol l}^{-1}$), 2.5 ml of CPB solution, and 5 ml of the working solution of reagent are pipetted into a 25 ml volumetric flask, dilute ($\sim 0.1\text{M}$) ammonia is added dropwise until violet colour appears, 2.5 ml of 1M pyridinium buffer pH 5 is added, and the volume is made up to the mark. In 5 min the absorbance is measured in a 1 cm cell at 624 nm. The colour is steady for a minimum of 4 h. After a time, a blue coating appears on the walls of the cells and vessels; it is recommended to rinse them periodically with dilute hydrochloric acid and ethanol. The analytical curve is linear over the region of 0–38 $\mu\text{g U}$ per 25 ml. The detection limit for 10 ml samples is 0.05 ppm uranium. The sensitivity of the method under given conditions is characterized by the above value of the molar absorptivity, $125\,000 \text{ cm}^2 \text{ mmol}^{-1}$.

*Determination of Uranium with Eriochromazurol B after its Extraction.
Separation from Waters and Heavily Contaminated Solutions*

Because of the interferences from a number of ions encountered in practice (Table III), a suitable uranium separation procedure should be applied prior to the determination. Trioctylphosphine oxide (TOPO) is unsuitable as an extracting agent because it is reextracted into the aqueous phase and interferes with the determination. Of other agents, tri-n-octylamine (TOA) proved most convenient^{28–31}. The conditions given in ref.³² were modified so that the extraction was carried out with 0.1M-TOA in benzene from 4M-HCl in the presence of ascorbic acid; uranium then was reextracted with 0.3M-HCl and determined.

Procedure. A volume of sample, smaller than 13 ml, is placed in a separating funnel and made up to 13 ml with water, and 10 ml of 10M-HCl, 2 ml of 5% ascorbic acid, and 5 ml of 0.1M-TOA in benzene are added and the whole is agitated for 3 min. After the phase separation, the aqueous phase is discarded, the benzene phase is washed twice with 5 ml of 4M-HCl by 1 min shaking, and uranium is reextracted with $2 \times 5 \text{ ml}$ of 0.3M-HCl, the aqueous phase being drawn off always after a 2 min

shaking. The reextracts are combined in a 25 ml volumetric flask, and further proceeded as with pure uranium solutions.

To improve the reproducibility of the determination, an aliquot (*e.g.*, 2.5 ml) of the organic phase, instead of the whole volume, can be reextracted in an extra separating funnel. The amount of uranium treated then is, however, lower. The extraction of uranium with TOA is quantitative, the latter does not interfere with the subsequent analysis of the aqueous reextract, and the shape of the analytical curve is the same as with pure solutions. Within the limits of error, the slope of the linear

TABLE V
Limits of determination of uranium after its extraction separation with tri-*n*-octylamine

Number of determinations	$1 - \alpha^a$	A_{lim}^b	Lowest determinable uranium concentration	
			c_{lim}^c nmol l ⁻¹	q_{lim}^d μg l ⁻¹
2	0.99	0.022 ₈	185	169.2
2	0.95	0.009 ₉	80.5	73.8
5	0.99	0.004 ₉	39.8	36.9
5	0.95	0.003 ₄	27.6	24.6

^a α is the significance level; ^b limiting absorbance value.

TABLE VI
Evaluation of the analyses of model samples of uranium after its extraction separation with tri-*n*-octylamine. The samples contained interfering ions as given in the text

Parameter	Sample A	Sample B
Added, μmol l ⁻¹	4.80	0.59
Found, μmol l ⁻¹	4.82	0.598
	4.78	0.541
	4.76	0.581
	4.74	0.606
	4.79	0.557
Average (\bar{x})	4.78 ± 0.03	0.57 ₇ ± 0.033
Confidence interval for $\alpha = 0.05$	$\bar{x} \pm 1.86 \cdot 10^{-8}$	$\bar{x} \pm 3.1 \cdot 10^{-8}$
	$\bar{x} \pm 0.39\%$	$\bar{x} \pm 5.37\%$

segment of the curve is also identical with that for the direct determination of uranium in pure samples. A statistical evaluation of the two analytical curves is presented in Table IV, the detection limits, for various numbers of determination, are given in Table V. Clearly, uranium can be determined by the extraction procedure in concentrations as low as 0.025 ppm. The high selectivity for uranium is documented by analyses with high concentrations of all the interfering substances, using two levels of uranium concentration, viz. 57.23 and 7.02 μg in 10 ml samples containing also 1 000 μg of Ti(III), 999.8 μg (of Al(III)), 4 235.8 μg of Be(II), 748.5 μg of Ca(II), 11 600 μg of Th(IV), 1 000 μg of Zr(IV), 1 215.3 μg of Mn(II), 1 116.9 μg of Fe(III), 1 150.6 μg of Cu(II), 2 361.5 μg of Zn(II), and 5 000 μg of Pb(II). The results (Table VI) demonstrate that the determination of uranium after its extraction separation is sufficiently accurate even in the presence of a high excess of interfering elements. The confidence intervals for the samples with the higher (57.17 μg) and lower (7.02 μg) uranium contents were $\pm 0.39\%$ rel. and 5.37% rel., respectively.

Owing to the high molar absorptivity, this novel method ranks among the most sensitive methods of photometric determination of uranium in general; also, the method is suitable for the determination of uranium in waters heavily contaminated by other elements, for which it actually has been suggested³³.

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