

SPECTROPHOTOMETRIC STUDY OF THE REACTION OF URANIUM(VI) WITH BROMOPYROGALLOL RED AND DETERMINATION OF URANIUM(VI)

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Three different complexes with a stoichiometric ratio of $\text{UO}_2 : \text{L} = 1 : 1$ and a complex with $\text{UO}_2 : \text{L} = 2 : 1$ are formed in the system of bromopyrogallol red (BPGR)- $\text{UO}_2(\text{II})$ -aqueous ethanol in dependence on the pH and the component concentrations. In the presence of quarternary base cations, especially cetylpyridinium bromide or *n*-butyltriphenylphosphonium bromide, ternary complexes with substantially higher absorption coefficients are formed. Three procedures for the spectrophotometric determination of uranium with BPGR were evaluated under the optimum reaction conditions in the binary system and in ternary system with *n*-butyltriphenylphosphonium bromide, cetylpyridinium bromide and polyvinyl alcohol, at pH 6–7 in a pyridine medium.

Bromopyrogallol red (5,5'-dibromopyrogallolsulphonephthalein, BPGR) refs^{1–6} is an outstanding metallochromic indicator for many metal ions and a sensitive spectrophotometric reagent. Its selectivity is not high but can sometimes be considerably improved in the presence of suitable masking agents^{7,8}. The reaction of UO_2^{2+} is of analytical importance^{6,9}; however, detailed study of the complex-forming reaction of UO_2^{2+} with BPGR in solution and of the conditions for spectrophotometric determination of uranium with this reagent is not available.

In the present paper, a method for the spectrophotometric determination of uranium(VI) with BPGR in a pyridine buffer medium or in the presence of butyltriphenylphosphonium bromide and polyvinyl alcohol is proposed on the basis of a study of the complexation equilibria. A method for the spectrophotometric determination of uranium with BPGR in the presence of cetyltrimethylammonium bromide was published after this work had been finished¹⁰.

EXPERIMENTAL AND RESULTS

A 0.2107M standard solution of uranyl nitrate (Lachema, Brno) in 0.1M- HNO_3 was standardized gravimetrically with 8-hydroxyquinoline and hydrogen peroxide. The results of the two methods agreed within $\pm 0.5\%$ rel. On diluting the standard solution the acidity did not decrease below 0.1M- HNO_3 .

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Bromopyrogallol red (BPGR), Lachema, Brno, was purified chromatographically on a polyamide powder (Lachema, Brno) column pre-washed with HCl (1 : 4). The reagent was dissolved in methanol adding a 1% hydrazine hydrate solution; after adsorption of the polyamide column, a yellow impurity was first eluted by HCl (1 : 4) and then a red product identified as pyrogallol red. The column was finally washed with water and pure BPGR was eluted by ammonia (1 : 8) containing 1% hydrazine hydrate. BPGR acid was immediately precipitated in the eluate using HCl (1 : 1). The preparation was redissolved in dilute ammonia containing 1% hydrazine hydrate and reprecipitated with HCl (1 : 1); the solution with the precipitate was rapidly heated to 80°C and cooled with ice. The precipitate was filtered off, washed with a small amount of cold water and dried over KOH and silica gel. The preparation purity was checked using thin-layer chromatography on microcrystalline cellulose Merck in butanol-acetic acid-water (4 : 1 : 5), n-propanol-water (1 : 1) and methanol-water (1 : 1) systems. While the original substance yielded several spots and contained c. 25% pyrogallol red, the purified preparation was chromatographically pure and was standardized by potentiometric titration with a 0.05M-KOH solution after dissolving the sample in 50% (v/v) methanol.

Polyvinyl alcohol, Moviol 50/88 (Farbwerke Höchst, A.G.), hydrazine hydrate 85% (Erba, Italy), tetraphenylarsonium chloride (Schuchhart, Munich), n-butyltriphenylphosphonium bromide (Lachema, Brno), tetra-n-hexylammonium bromide (Kodak, USA) and cetylpyridinium bromide (Lachema, Brno) and the other chemicals employed were of *p.a.* purity or were recrystallized.

Water was distilled twice in a quartz apparatus and ethanol was distilled and contained 4.1% methanol and 4.3% water.

The ionic strength was adjusted to 1.0 or 2.0 with potassium nitrate, which was recrystallized twice from water, or with sodium perchlorate recrystallized according to Biedermann¹¹. The absorbance was measured on SP-500 and SP-700 spectrophotometers (Unicam, England) and the pH was determined using PHM-3k and PHM-4d instruments (Radiometer, Copenhagen) with a G 202B glass electrode calibrated by a phosphate buffer aqueous solution (pH 6.53). The pH values for aqueous-ethanolic solutions were not corrected. In some cases the solutions were prepared and the absorbance measured using the device for continuous spectrophotometric measurements described by Havel¹².

Methods of the Study of Complexation Equilibria in Solution

Direct graphical and logarithmic analysis of the absorbance pH-curves and of the curves for the absorbance dependence on the concentration of some of the components at a constant pH was employed, in solutions with an excess of one component or in equimolar solutions. For curve interpretation, the slope-intercept type transformations of the expressions for equilibrium constants or conditional stability constants, which were derived and discussed earlier^{13,14}, were employed. The common methods of continuous variations and molar ratios were also used. Computations were performed using the PRCEK type programs¹⁵⁻¹⁷ in the algol or fortran versions.

For computation of the absorbance in a system of multicomponent mixtures from known values of the molar absorption coefficients and the equilibrium constants, the HALTAFALL SPEFO program was used and adapted for the MINSK 22 computer¹⁸.

The analytical calibration curves, $A = f(c_M)_{pH, c_L = const.}$, were evaluated by linear regression using the least-squares method on an MSP-2A computer¹⁹.

The detection limit of a spectrophotometric method, m_s , for a selected probability of 99.73% is defined by the relationships,

$$m_s = 3s_{xy} \quad (\text{in absorbance units});$$

$$m_s = 3s_{xy}/\epsilon \quad (\text{in concentration units}),$$

where s_{xy} is the standard deviation for the scatter around the regression straight line.

Reagent Stability and Solution Preparation

BPGR is poorly soluble in water; it readily dissolves in alkaline media, but then has limited stability and is readily oxidized²⁰. The recommended addition of sodium hydroxide for the reagent dissolution in water²⁰ was found to be unsuitable, as the absorbance pH-curves of reagent solutions thus prepared exhibit hysteresis on change from acidic solutions to alkaline and back. The recommended addition of ascorbic acid for stabilization of reagent solutions²⁰ was also inconvenient for the purposes of the present work, as relatively stable complexes with UO_2^{2+} were formed²¹. Hydrazine hydrate was most suitable for stabilization of BPGR alkaline solutions. Reagent stock solutions with concentrations of c. $10^{-3}M$ in the presence of 0.01% dimethylformamide, 50% (v/v) ethanol and 0.1% (v/v) hydrazine hydrate are stable for at least 150 hours. An accurately weighed amount of BPGR is dissolved in a small amount of dimethylformamide, ethanol and hydrazine hydrate are added, the mixture is diluted with water and acidified with dilute HNO_3 to a resultant concentration of 0.001M.

Acid-Base Properties of BPGR

BPGR yields six variously coloured acid-base forms: H_5L^+ , H_4L , H_3L^- , H_2L^{2-} , HL^{3-} and L^{4-} (ref.²⁰). In 30% (v/v) ethanol at pH 0.35–1.5 there is a pronounced transition from orange form H_4L to red form H_3L^- and at pH 3.20–6.97 red form H_3L^- is converted to purple H_2L^{2-} . It has been spectrophotometrically determined for the working pH region of the solutions and 30% (v/v) ethanol that $pK_{a1}(H_3L^- : H_4L^0) = 0.24$ (I 2.0) and $pK_{a2}(H_2L^{2-}/H_3L^-) = 4.78 \pm 0.03$ (I 0.1). Suk²⁰ gives $pK_{a1} = 0.16 \pm 0.02$ and $pK_{a2} = 4.39 \pm 0.01$ at $I = 0.2$ for an aqueous medium. The λ_{max} and ϵ values are, respectively, 465 nm, $\epsilon = 21\,000$ (440 nm) for H_4L^0 ; 437 nm and $\epsilon = 16\,000$ (440 nm) for H_3L^- ; 565 nm and $\epsilon = 51\,300$ for H_2L^{2-} ; 565 nm and $\epsilon = 17\,500$ for HL^{3-} .

The determination of the first dissociation constant was rather difficult because of the poor stability of BPGR in strongly acidic solutions. Absorbance values extrapolated to time $t = 0$ were employed for the calculation.

Complexation Equilibria of Uranyl with BPGR in Solutions of 30% (v/v) Ethanol

In solutions with excess uranyl the absorption curves indicate the presence of three complexes, at pH 1.5, in a pH region of 1.5–3.9 and at pH > 4.7 (Fig. 1).

A gradual formation of at least two complexes is confirmed by absorbance pH-curves measured under analogous conditions (Figs 2–4). The absorbance pH-curve were analyzed in the region of the first complexation equilibrium, *i.e.* at pH < 1.8, using transformations (1) and (2),

$$A = \frac{\varepsilon c_L}{n} - \frac{(AZ - \bar{\varepsilon}_L c_L)(n\bar{\varepsilon}_L - Z\varepsilon)^{n-1} [H^+]^n}{(\varepsilon c_L - nA)^{n-1} c_M^n *K_{mn}} \quad (1)$$

$$\log \frac{ZA - \bar{\varepsilon}_L c_L}{(\varepsilon c_L - nA)^n} = q \text{ pH} + m \log c_M - (n-1) \log (n\bar{\varepsilon}_L - Z\varepsilon) + \log *K_{mn} \quad (2)$$

where $Z = 1 + ([H^+]/K_{ax})^{-1}$, $\bar{\varepsilon}_L = \varepsilon_{Lx} + \varepsilon_{L(x-1)}([H^+]/K_{ax})^{-1}$,

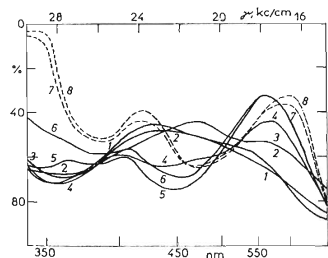


FIG. 1

Absorption Curves of BPGR Solutions Containing Excess UO_2^{2+}

$c_L = 2.00 \cdot 10^{-5} M$, $c_M/c_L = 200$, $I 0.1$, 30% (v/v) ethanol; pH: 1.50, 2.1.95, 3.2.27, 4.2.68, 5.3.28, 6.3.93, 7.4.66, 8.5.00.

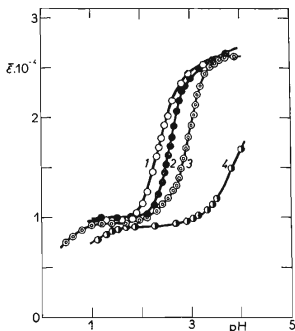
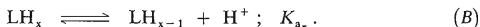
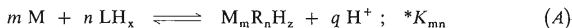


FIG. 2

Dependence of $\bar{\varepsilon} = (A - A_L)/c_L$ on the pH for Solutions Containing Excess UO_2^{2+}

565 nm, $I 0.1$, 30% (v/v) ethanol. Curves:
 1 $c_M = 1.58 \cdot 10^{-3} M$, $c_L = 2.88 \cdot 10^{-5} M$;
 2 $c_M = 6.32 \cdot 10^{-3} M$, $c_L = 2.62 \cdot 10^{-5} M$;
 3 $c_M = 3.16 \cdot 10^{-2} M$, $c_L = 2.34 \cdot 10^{-5} M$;
 4 $c_M = 0$, $c_L = 3.24 \cdot 10^{-5} M$.

A being the absorbance, c_M and c_L the overall analytical concentrations of the metal and the reagent, respectively, and indices m , n and q being the coefficients in the equation of the assumed complexation equilibrium, (A). These transformations are further valid on condition that, during complexation equilibrium (A), the reagent dissociates according to equilibrium (B), i.e. that two more absorbing species are present in the solution in addition to the coloured complex, $M_mR_nH_z$ with molar absorbance ϵ , namely, LH_x and LH_{x-1} with molar absorbances ϵ_{L_x} and $\epsilon_{L_{x-1}}$, respectively.



It was found that transformation (I) is linear for values $m = n = q = 1$, i.e. that a 1 : 1 complex is formed according to equilibrium (C):

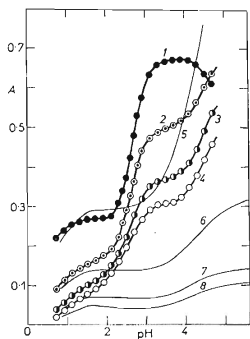
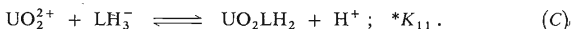


FIG. 3

Absorbance pH-Curves for BPRG Solutions Containing Excess UO_2^{2+}

$c_L = 2.62 \cdot 10^{-5} M$, $I = 0.1$, 30% ethanol.

Curves 1-4: $c_M = 6.32 \cdot 10^{-4} M$; 5-8: $c_M = 0$. Curves 1 5565 nm; 2 6600 nm; 3 7620 nm; 4 8630 nm.

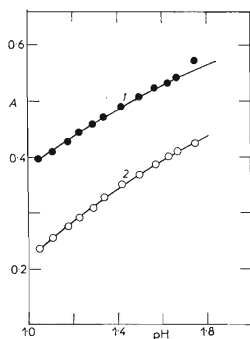


FIG. 4

Absorbance pH-Curves for Solutions with Excess UO_2^{2+} in the Region of the First Complexation Equilibrium (C)

$c_L = 9.49 \cdot 10^{-5} M$, $c_M = 1.896 \cdot 10^{-2} M$, $I = 2.0(NaClO_4)$; 30% (v/v) ethanol. Curves 1 600 nm, 2 620 nm.

The coordination of a single uranyl was independently confirmed by the analysis of the $A = f(c_M)$ dependence at pH 1.20 and λ 600 and 620 nm, using transformation (3),

$$A = \varepsilon c_L - \frac{(ZA - \bar{\varepsilon}_L c_L)[H^+]^q}{*K_1 c_M^m} \quad (3)$$

Linear dependences were obtained for $m = 1$.

The other part of the absorbance pH-curves in solutions with excess uranyl at pH 1.9–3 was analyzed using transformations for conversion of a mononuclear complex into a polynuclear complex, as the curves are shifted to lower pH values with increasing uranyl excesses and the reagent structure permits bonding of another uranyl.

For the assumed general equilibrium, (D), the transformations employed have form (4) or (5):



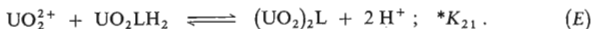
$$A = \varepsilon_2 c_L / n - \frac{(bA - \varepsilon_1 c_L)^d (b\varepsilon_2 - n\varepsilon_1)^{v-d} [H^+]^q}{(\varepsilon_2 c_L - nA)^{v-1} c_M^r *K} \quad (4)$$

$$A = \varepsilon_1 c_L / b + \frac{(\varepsilon_2 c_L - nA)^v c_M^r *K}{(bA - \varepsilon_1 c_L)^{d-1} (b\varepsilon_2 - n\varepsilon_1)^{v-a} [H^+]^q} \quad (5)$$

As the composition of the initial complex is known ($a = b = 1$) and the reagent does not dissociate in the given region, the relationships are considerably simplified. The transformations were linear for values $v = d = r = 1$ and $q = 2$. The equilibrium constant values were determined from transformation (6),

$$\log \frac{\varepsilon_1 c_L - A}{A - \varepsilon_1 c_L} = \log *K + q \text{ pH} + r \log c_M \quad (6)$$

As the interpretation of the absorbance pH-curve using Eqs (4)–(6) yields only the number of dissociating hydrogen ions during the complexation equilibrium, the concentration dependence, $A = f(c_M)$, at pH 3.17 was analyzed. Transformations (4) and (5) were linear for $r = 1$ and the same value for r was found from Eq. (6). The combined analysis of the pH-curve and of the concentration dependence then confirmed coordination of another uranyl to the reagent molecule according to equilibrium (E), with formation of a complex with $UO_2 : L = 2 : 1$ (λ_{\max} 565 nm).



The values of the molar absorption coefficients for complexes UO_2LH_2 and $(\text{UO}_2)_2\text{L}$ are in a good agreement for both types of absorbance dependence and are given in Table I.

In equimolar solutions, the continuous variation curves at pH 3.70 and 4.60 ($c_0 = 1.264 \cdot 10^{-4}\text{M}$) exhibit a maximum for a component molar ratio of $\text{UO}_2 : \text{L} = 1 : 1$ at all wavelengths (620–640 nm). The molar ratio method also indicated the formation of a 1 : 1 complex at pH 4.50.

The absorbance pH-curves of equimolar solutions exhibit a single wave at pH 2.5 to 7.0 (Fig. 5). As a 1 : 1 complex was indicated by the continuous variation and molar ratio curves, transformations with $m = n$ were considered for formation of complex $\text{M}_m\text{L}_n\text{H}_x$ during the curve interpretation. The interpretation was carried out assuming the reaction of UO_2^{2+} with LH_3^- according to Eqs (7) and (8):

$$A = \varepsilon c_L/n - \left\{ \frac{(ZA - \bar{\varepsilon}_L c_L)(Z - n\bar{\varepsilon}_L)^{2n-1} [\text{H}^+]^q}{n^{2n} Z^n K} \right\}^{1/2n}, \quad (7)$$

$$\log \frac{ZA - \bar{\varepsilon}_L c_L}{(\varepsilon c_L - nA)^{2n} Z^n} = q \text{ pH} + \log K - (2n - 1) \log (Z\varepsilon - n\bar{\varepsilon}_L). \quad (8)$$

TABLE I

Survey of the Molar Absorption Coefficients for Various complexes of UO_2^{2+} with BPGR in Solution

	$\varepsilon \cdot 10^{-3}$
UO_2LH_2	6.6; 6.8 ^a ; 6.3 ^b (600 nm); 6.5 ^b ; 7.0 ^b (600 nm); 5.5 ^a ; 5.7 ^a ; 5.1 ^b (620 nm); 9.1 ^b ; 8.4 ^b (565 nm)
$(\text{UO}_2)_2\text{L}$	25.1 ^a ; 25.7 ^a (565 nm); 19.4 ^a ; 18.8 ^a ; 19.8 ^c ; 19.5 ^c (600 nm) 14.0 ^c ; 13.9 ^c (620 nm)
$\text{UO}_2(\text{LH}_{(3-x)})(\text{OH})_y$ $x + y = 3$	12.3 ^d (620 nm); 9.50 ^d (630 nm); 7.9 ^d (640 nm)
$\text{UO}_2(\text{LH}_2)^*$	11.1 ^e (630 nm); 9.3 ^e ; 9.1 ^f (640 nm); 7.9 ^e ; 7.8 ^f (650 nm)

^a $A = f(\text{pH})$ in solutions with excess c_M using Eq. (1); ^b $A = f(c_M)$ at pH 1.20 according to (3); ^c $A = f(c_M)$ at pH 3.70 according to (4.5); ^d $A = f(\text{pH})$ for solutions with $c_M = c_L$ according to (7); ^e $A = f(\text{pH})$ for solutions with excess ligand according to (10); ^f $A = f(c_L)$ at pH 3.56 according to (10).

Since the molar absorption coefficients for the forms LH_3^- and LH_2^{2-} are very close at $\lambda = 620-640$ nm, the values of A_{0L} are almost constant (Fig. 5), simplifying relationships (7) and (8). ε_L/Z and $A_{0L}/c_L = \text{const.}$ and thus expressions $(\varepsilon - \bar{\varepsilon}_L/Z)^{1/2}$ and $(\varepsilon - \bar{\varepsilon}_L/Z)^{3/4}$ for formation of the monomer with $m = n = 1$ and the dimer with $m = n = 2$ are also constant. Among all the equilibrium types considered

FIG. 5

Absorbance pH-Curves in Equimolar Solutions

1.0:1, 30% (v/v) ethanol, 0.01% hydrazine hydrate, after 20 min. Curves: 1, 3 $c_M = c_L = 6.32 \cdot 10^{-5}$ M; 5, 7 $c_M = c_L = 1.264 \cdot 10^{-4}$ M; 2, 4 $c_M = 0$, $c_L = 6.32 \cdot 10^{-5}$ M; 6, 8 $c_M = 0$, $c_L = 1.26 \cdot 10^{-4}$ M. Curves 1-4: $Y = A$; 5-8 $A/2 = Y$; Curves 1, 2, 5, 6 620 nm, 7, 8 630 nm; 3, 4 640 nm.

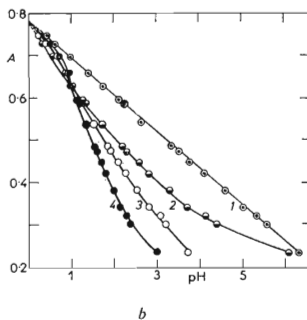
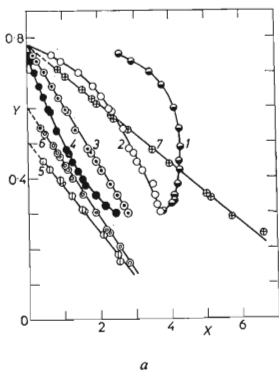
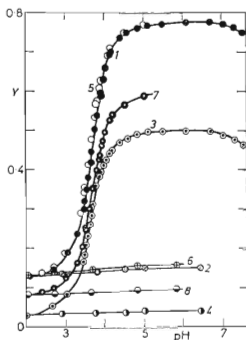
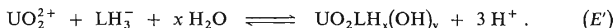


FIG. 6

Graphical Analysis of the Absorbance pH-Curves for Equimolar Solutions

a Curves 1-5 $c_M = c_L = 6.32 \cdot 10^{-5}$ M; 6, 7 $c_M = c_L = 1.26 \cdot 10^{-4}$ M. Curve 1 $X = B/2 \cdot 10^3 [\text{H}]^{1/2}$; 2 $X = B/4 \cdot 10^5 [\text{H}]^{2/2}$; 3, 5, 6 $X = B \cdot 10^6 [\text{H}]^{3/2}$; 4 $X = B/2 \cdot 10^8 [\text{H}]^{4/2}$; 7 $X = B \cdot 2 \cdot 10^6 [\text{H}]^{3/2}$. $B = Z^{1/2}(A - A_L)^{1/2}$. Curves 1-5 $Y = A$; 6, 7 $Y = A/2$; 1-4, 7 620 nm; 6 630 nm; 5 640 nm. b $c_M = c_L = 6.32 \cdot 10^{-5}$ M, 620 nm; Curves 1 $X = (A - A_L)^{1/2} Z^{1/2} [\text{H}]^{3/2} \cdot 10^6$; 2-4 $X = (A - A_L)^{1/4} Z^{1/2} [\text{H}]^{3/4} = B [\text{H}]^{3/4}$; 2 $X = B \cdot 10^6 [\text{H}]^{6/4}$; 3 $X = B \cdot 10^5 \cdot [\text{H}]^{5/4}$; 4 $X = B \cdot 10^4 [\text{H}]^{4/4}$.

(Fig. 6a,b), the dependence is linear only for $m = n = 1$ and $q = 3$, which corresponds to reaction (E')



Equilibria for the formation of monomer ML (dissociation of 3 protons) and dimer M_2L_2 (with dissociation of 6 protons) were also differentiated by comparing the normalized experimental absorbance curve, $Y = f(\text{pH})$, for equimolar solutions with normalized $Y = f(\text{pH})$ curves calculated for both cases.

Normalized function Y is given by

$$Y = \frac{A - \varepsilon_1 c_L}{\varepsilon_2 c_L - \varepsilon_1 c_L} \quad (9)$$

assuming that the absorbing reagent is converted into an absorbing complex, where $A_{01} = \varepsilon_1 c_L$ and $A_{02} = \varepsilon_2 c_L$ are the corresponding lower and upper branches of function $Y = f(\text{pH})$. The value of function Y was computed for both equilibria using the HALTAFALL SPEFO program¹⁸ with iteratively selected values of constants κ_1 (formation of complex ML with dissociation of three protons) ($\log \kappa_1 = -3$) and κ_2 (formation of complex M_2L_2 with dissociation of 6 protons) ($\log \kappa_2 = -6$). The values of the conditional constants thus selected have no effect on the shape of the $Y = f(\text{pH})$ curves and only determine their position in the $y(Y)$ and $x(\text{pH})$ coordinate system. The computed $Y = f(\text{pH})$ curves were then suitably shifted along the pH-axis and compared over the whole range with the experimental points normalized with respect to Y . The number of protons dissociated basically affects the slope of these curves, which increases with the number of protons dissociated, so that it is sufficiently different for the two cases tested.

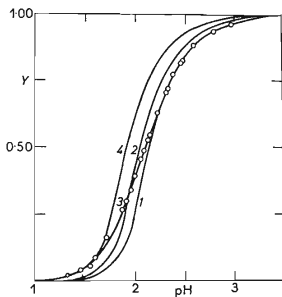


FIG. 7

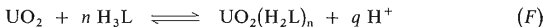
Comparison of the Normalized Calculated $Y = f(\text{pH})$ Curves with the Normalized Experimental $Y = f(\text{pH})$ Curve

$Y = (A - A_{01}) / (A_{02} - A_{01})$. Curves 1, 2, 4 calculated for equilibrium: $2\text{M} + 2 \text{LH}_x \rightleftharpoons \text{M}_2\text{L}_2\text{H}_x + 6 \text{H}^+$; Curve 3 calculated for equilibrium $\text{M} + \text{LH}_x \rightleftharpoons \text{MLH}_x + 3 \text{H}^+$; \circ — experimental points.

It is clear from Fig. 7 that the experimental $Y = f(\text{pH})$ curve has a shape and slope identical over the whole range with the theoretical curve computed for equilibrium (D) (formation of a complex with $M : L = 1 : 1$), which excludes the presence of the dimer.

In solutions containing excess ligand ($c_L/c_M = 5$ and 20), strong reagent absorption interferes, especially that of form LH_2^{2-} at $565 - 620 \text{ nm}$ and $\text{pH} > 4$, since the UO_2 -complex formed has λ_{max} at 625 nm in this medium. A pronounced absorbance transition can be seen at $640 - 680 \text{ nm}$ and $\text{pH} 2 - 5$ on the difference absorbance pH-curves (Fig. 8).

The common equilibrium, (F), was tested first:



using transformations (10)–(12)

$$A - A_L = \Delta A = \varepsilon_1 c_M - \Delta A [\text{H}]^q Z^n c_L^{-n} k^{-1} \quad (10)$$

$$c_M/\Delta A = 1/\varepsilon + [\text{H}] Z/c_L k \varepsilon \quad (10a)$$

$$\Delta A = \varepsilon_1 c_M + \text{const.} (A_0 - \Delta A) [\text{H}]^{-q} \quad (11)$$

$$\log(\Delta A Z)/(\varepsilon_1 c_M - A) = q \text{pH} + n \log c_L = \log k, \quad (12)$$

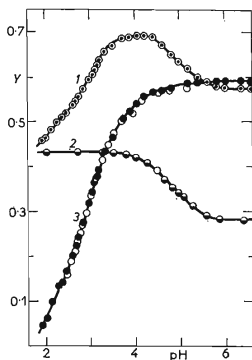
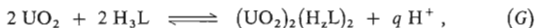


FIG. 8

Absorbance pH-Curves for UO_2^{2+} Solutions Containing Excess Ligand

$c_M = 6.321 \cdot 10^{-5} \text{ M}$, $c_L/c_M = 20$, 640 nm , 0.01% (v/v) hydrazine hydrate. Curve 1 $Y = A/2$; 2 $Y = A/2$, $c_M = 0$; 3 $\bullet Y = A - A_L$, $c_L = 1.264 \cdot 10^{-3} \text{ M}$; $\circ Y = A - A_L$, $c_L = 1.251 \cdot 10^{-3}$.

where $Z = 1 + K_a/[H]$, $K_a = 10^{-4.78}$ and A_0 is the absorbance on the plateau of the absorbance curve. Transformation (10) and (10a) were linear only for $q = 1$, i.e. the dissociation of a single proton (Fig. 9, curve 6). This value was exactly confirmed in the logarithmic analysis according to Eq. (12). Transition between two complexes is excluded in this medium (curve 5 in Fig. 9 is a straight line passing exactly through the origin; $A_{01} = \epsilon_1 c_M = 0$ in transformation (11) for transition between two complexes). The analysis of the concentration dependence, $\Delta A = f(c_L)$, at pH 3.56 and 640, 650 nm according to Eqs (10), (10a), confirms the coordination of a single reagent particle. The spectrophotometric study thus formally verifies equilibrium (C) in solutions with excess ligand, but it is noteworthy that the optical properties of the 1 : 1 complex formed in solutions with excess ligand are different from those of the 1 : 1 complex formed in solutions with excess cation (see the molar absorption coefficients in Table I). The graphical analysis of the absorbance pH-curve in Fig. 8 using transformations (13), (14) (ref.²²) at 640 and 630 nm does not confirm the presence of a dimer with $UO_2 : L = 2 : 2$ even at pH > 3 according to possible equilibrium (G)



where 4 to 6 protons would have to be dissociated. Dependence $c_M/\Delta A = f(X)$ according to Eq. (13) are non-linear even assuming dissociation of $2H^+$ and $4H^+$ (see Fig. 9, curves 7, 8) and the slope of logarithmic transformation (14) yields only slope $q = 1.7-1.8$ for the extrapolated molar absorption coefficient of the dimer assumed from (13) and (10A) at pH > 3.

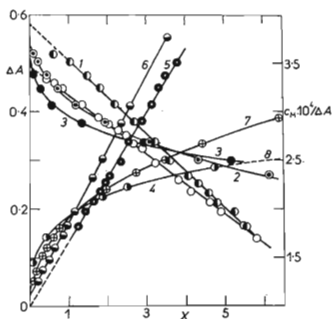


FIG. 9

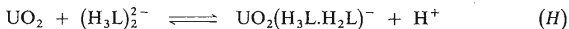
Graphical Analysis of the Absorbance pH-Curves for Solutions with Excess Ligand

$c_M = 6.32 \cdot 10^{-5} M$; Curve 1, 4 $X = \Delta A \cdot [H] \cdot 10^4$; 2 $X = \Delta A [H]^2 \cdot 10^7$; 3 $X = \Delta A [H]^3 \cdot 10^{10}$; 5 $(\epsilon c_M - A)/[H] \cdot 10^{-2}$; 6 $Y = c_M \cdot 10^4 / \Delta A$, $X = [H] \cdot Z \cdot 10^3$; 7 $Y = c_M \cdot 10^4 / \Delta A$, $X = [H]^2 Z^2 \cdot 10^6 / (2A_0 - 2\Delta A)$; 8 $Y = c_M \cdot 10^4 / \Delta A$, $X = [H]^4 Z^2 \cdot 10^{12} / (2A_0 - 2\Delta A)$; Curves 1-3, 5 640 nm, $c_L = 1.25 \cdot 10^{-3} M$; 4 650 nm, $c_L = 1.26 \cdot 10^{-3} M$.

$$c_M/\Delta A = 2/\varepsilon + \frac{[H]^q Z^2}{c_L^2(\varepsilon c_M - 2 \Delta A) \kappa} \quad (13)$$

$$\log \frac{\Delta A Z^2}{(\varepsilon c_M - 2 \Delta A)^2} = q \text{ pH} + 2 \log c_L + \log \kappa - \log \varepsilon. \quad (14)$$

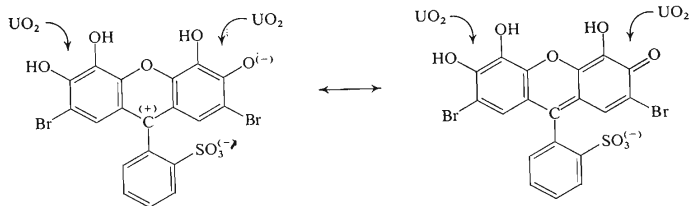
Dimerization of some ligand form should also be considered in solutions with excess ligand at $\text{pH} \geq 4$. This possibility is indicated by greater differences in the ligand $\text{p}K_{a2}$ values for various concentrations and wavelengths. Then with assumed reaction (H),



only one proton is dissociated, the reagent dimer then appears as a single species in transformation (10) for concentration dependence $\Delta A = f(c_L)$, $n = 1$ and the 1 : 1 complex formed has optical properties different from those of the complex in solution containing excess cation (cf e.g. the effect of dimerization on the molar absorption coefficient with methylene blue^{23,24} or 2,2'-dihydroxyazo dyes²⁵).

Concluding Remarks on the Complexation Equilibria

From the structural point of view, neither of the two donor atom groups in the dye is preferred for bonding to the metal:



The symmetrical form of the reagent supports the stepwise formation of complexes UO_2LH_2^+ ($\text{pH} 0.9-1.8$, 30% (v/v) ethanol) and $(\text{UO}_2)_2\text{L}$ ($\text{pH} 1.9-3.5$, 30% (v/v) ethanol) in solutions containing excess UO_2^{2+} . The different character of the 1 : 1 complex in equimolar solutions of UO_2^{2+} and BPGR at $\text{pH} 4.6-7.0$ is caused by simultaneous hydrolysis. From the measured data it follows that the most probable composition is $[\text{UO}_2\text{LH}_2(\text{OH})_2]^{2-}$. The 1 : 1 complex formed in solutions with excess ligand must have a different structure than the analogous complex formed in solutions with excess metal cation. The equilibrium constants were cal-

culated only for equilibrium (C) in solutions with excess uranyl: $\log *K_{11} = -0.56 \pm 0.02$ (average of six values), I 2.0 (calculated from Eq. (2) at 600 and 620 nm); for equilibrium (E): $\log *K_{21} = 3.18 \pm 0.05$ (average of 10 values for I 0.1, calculated from Eq. (6) at 565, 600 and 620 nm); for equilibrium (C) in solutions with excess ligand, $\log *K_{11} = 0.02$ (calculated from Eq. (12), I 0.1 at 640 and 630 nm).

Determination of Uranium(VI) with Bromopyrogallol Red

The absorbance of the 1 : 1 complex is constant at pH 5.0–7.0 even with a small ligand excess ($c_L/c_M \geq 5$). Calibration curves $\Delta A = f(c_M)$ are linear for concentrations $< 21 \mu\text{g U/ml}$ at 385–680 nm, pH 6.05 and $c_L = 3.16 \cdot 10^{-4} \text{M}$. The measuring results were evaluated by regression analysis on a computer¹⁹ and are summarized in Table II.

TABLE II

Characteristic Data for Methods A, B and C for the Determination of Uranium with BPGR Obtained from the Regression Analysis of the Calibration Curves

Values	A		E		C	
λ	385 nm	630 nm	640 nm	650 nm	630 nm	630 nm
r_k^a	0.9999	1.0000	0.9999	0.9998	0.9998	1.0000
$\varepsilon \pm \sigma_\varepsilon^b$	$7\,000 \pm 20$	$12\,150 \pm 20$	$10\,600 \pm 30$	$8\,900 \pm 10$	$36\,400 \pm 90$	$31\,600 \pm 60$
s_{xy}^c	$1.6 \cdot 10^{-3}$	$1.89 \cdot 10^{-3}$	$2.28 \cdot 10^{-3}$	$3.32 \cdot 10^{-3}$	$3.10 \cdot 10^{-3}$	$1.99 \cdot 10^{-3}$
m_A^d	0.005	0.006	0.007	0.010	0.006	0.006
$m_c, \mu\text{M l}^{-1e}$	0.687	0.468	0.647	1.122	0.165	0.189
$m_c, \mu\text{g U/ml}^f$	0.164	0.111	0.154	0.267	0.039	0.045
$\text{M l}^{-1}, \text{U}^g$						
for $A = 0.01$	$1.43 \cdot 10^{-6}$	$0.82 \cdot 10^{-6}$	$0.95 \cdot 10^{-6}$	$1.13 \cdot 10^{-6}$	$0.27 \cdot 10^{-6}$	$0.32 \cdot 10^{-6}$
U^h	$0.506 \cdot 10^{-4}$	$0.709 \cdot 10^{-4}$	$0.102 \cdot 10^{-3}$	$0.218 \cdot 10^{-3}$	$0.190 \cdot 10^{-3}$	$0.122 \cdot 10^{-3}$

^a Correlation coefficient, ^b molar absorption coefficient and its $3s_\varepsilon$, ^c standard deviation for one determination, ^d determination limit, $A = 3s_{xy}$, ^e determination limit in $\mu\text{M l}^{-1}$, ^f determination limit in $\mu\text{g U/ml}$, ^g sensitivity index, ^h $\text{U} = \Sigma(A_{\text{meas}} - A_{\text{calc}})^2$. Method A: pH 6.05, 0.1M pyridine buffer, $c_L = 3.160 \cdot 10^{-4} \text{M}$, $c_{\text{hydrazine hydrate}} = 0.01\%$. Method B: $c_L = 3.16 \cdot 10^{-5} \text{M}$, 0.1M pyridine buffer, 0.2% polyvinyl alcohol, pH 6.13, $2.5 \cdot 10^{-3} \text{M}$ -butyltriphenylphosphonium bromide, 30% (v/v) ethanol. Method C: Reagent, polyvinyl alcohol, buffer as with method B, $2.5 \cdot 10^{-3} \text{M}$ pyridinium bromide, pH 5.89.

The effect of other substances and ions: The interference from some substances and ions is summarized in Table III. No interference is encountered with ClO_4^- , SO_4^{2-} , Cl^- , NO_3^- and Na^+ , K^+ and NH_4^+ even with a more than 1000fold excess (c_X/c_M in $\text{M} \cdot 1^{-1}$). Ions CO_3^{2-} , PO_4H^{2-} , F^- , MoO_4^{2-} and WO_4^{2-} strongly interfere,

TABLE III

Effect of Other Substances and Ions on the Determination of Uranium with BPGR^a (the deviation of the solution absorbance does not exceed $\pm 2\%$)

Substance or ion	c_X/c_M $\text{M} \cdot 1^{-1}$	mg X/ml	Substance or ion	c_X/c_M $\text{M} \cdot 1^{-1}$	mg X/ml
ClO_4^-	1 580	9.9	$\text{NH}_4(\text{I})$	2 777	3.060
SO_4^{2-}	3 322	20.2	$\text{Ca}(\text{II})$	(+) 250	0.320
NO_3^-	2 848	11.2	$\text{Mg}(\text{II})$	(+) 62	0.050
Cl^-	1 898	4.25	$\text{Cu}(\text{II})$	(-) 0.57	0.0012
F^-	(+) 272.1	0.327		(+) 3.99 ^b	0.080 ^b
CO_3^{2-}	(-) 19.0	0.072	$\text{Zn}(\text{II})$	(+) 0.210	0.0005
HPO_4^{2-}	(-) 39.6	0.237		6.3 ^b	0.013 ^b
MoO_4^{2-}	(-) 0.32	0.0017	$\text{Fe}(\text{II})$	(+) 0.13	0.0002
WO_4^{2-}	(-) 0.33	0.0027		10.1 ^b	0.017 ^b
Acetate	(+) 488.8	1.823	$\text{Mn}(\text{II})$	(+) 0.480	0.0008
Oxalate	(-) 3.87	0.022	$\text{Ni}(\text{III})$	(+) 1.090	0.002
Tartrate	(+) 158.2	1.48		(-) 13.2 ^b	0.025 ^b
H_3BO_3	(-) 595	1.18	$\text{Al}(\text{III})$	(-) 0.040	0.00003
Ascorbis acid	(+) 59.7	0.34		1.33 ^b	0.0010 ^b
5-Sulphosalicylic acid	(+) 9.70	0.134	$\text{Cr}(\text{III})$	(+) 0.470	0.0008
CDTA	(+) 193.0	4.225	$\text{Fe}(\text{III})$	(-) 0.022	0.0004
EDTA	(-) 17.7	0.417		0.80 ^b	0.0015 ^b
$\text{Ca}(\text{EDTA})$	(-) 50.0	0.710	$\text{La}(\text{III})$	(+) 3.210	0.028
$\text{Mg}(\text{EDTA})$	(-) 29.4	0.410	$\text{Sc}(\text{III})$	(+) 0.0290	0.001
$\text{Na}(\text{I})$	6 644	9.660	$\text{Y}(\text{III})$	(-) 0.430	0.003
$\text{K}(\text{I})$	2 848	7.020	$\text{Ti}(\text{IV})$	(-) 0.900	0.0014
Pyridine buffer			$\text{V}(\text{V})$	(-) 1.950	0.0062
(pH 6.05)	5 850 ^c	29.2 ^c	Triethanolamine buffer		
Tris(hydroxymethyl- aminoethane) (pH 6.10)	5 850 ^c	70.7	(pH 6.10)	(+) 157 ^c	1.460
Tetraborate buffer					
(pH 6.10)	(-) 17.3 ^c	0.210			
Citrate buffer					
(pH 6.10)	(-) 21.7 ^c	0.180 ^c			

^a $c_L = 3.1605 \cdot 10^{-4} \text{M}$, $c_U = 3.160 \cdot 10^{-5} \text{M}$, pH 6.05, 0.1M pyridine buffer, 0.01% (v/v) hydrazine hydrate, 630 nm; measured after 10 min, ^b in the presence of masking mixture $\text{Ca}(\text{EDTA}) + 5\text{-sulphosalicylic acid} + \text{tartrate}$, ^c concentration related to the buffer base.

while EDTA, CDTA, the Ca-chelate of EDTA and tartrate interfere only to a low degree at pH 6, so that they can be employed for masking some interfering cations, e.g. EDTA for masking Sc^{3+} , La^{3+} and Y^{3+} . A suitable masking mixture contains 50 ml $4 \cdot 10^{-2}\text{M}$ - $\text{Ca}(\text{NO}_3)_2$, 45 ml $4 \cdot 10^{-2}\text{M}$ -EDTA, disodium salt, 1 ml 0.1M-5-sulphosalicylic acid and 4 ml 0.1M-sodium-potassium tartrate. It was employed for masking Cu(II), Fe(III), Zn(II) and Al(III), with resultant concentrations of $1.8 \cdot 10^{-3}\text{M}$ -Ca-EDTA, 10^{-4}M -5-sulphosalicylic acid and $4 \cdot 10^{-4}\text{M}$ -sodium-potassium tartrate. Only a 0.3% negative deviation of the absorbance at 650 nm is caused in this way, compared with a UO_2^{2+} solution without the masking mixture. The $\Delta A = f(c_M)$ dependence is linear up to 21 $\mu\text{g U/ml}$ ($\epsilon = 8330$ for 650 nm).

The effect of buffers: At pH 5.0–7.0 a pyridine buffer (pH 6.05) or a tris(hydroxymethyl)aminomethane buffer (pH 6.10) can be employed, as they do not interfere even in an excess of $c_X/c_M = 850$. Buffers based on phosphate, tetraborate, citrate and triethanolamine strongly interfere (the latter interferes when present in concentration greater than $c_X/c_M = 157$). The pyridine buffer with pH 6.05 and a resultant concentration of 0.1M with respect to the base gave the best results.

The effect of ethanol: Ethanol affects neither the absorbance of the complex solutions nor the complex stability in time at concentrations from 5 to 30% (v/v).

The effect of the solution ionic strength: The solution absorbance increases with increasing salt concentration. However, this effect is negligible within $I = 0-0.5$ (KNO_3); above $I 0.5$ the absorbance increases sharply (by up to 17% at $I 1.5$ and 640 nm).

Procedure: To a weakly acidic solution of U(VI) containing less than 1 mg U in the form of the $\text{UO}_2(\text{II})$ nitrate, chloride or sulphate are added 5 ml 0.5% dye solution, 5 ml of the masking mixture and 5 ml 1M pyridine buffer with pH 6.0–7.0; the solution is diluted to 50 ml with water. The absorbance is measured after 10 min at 630–680 nm.

Reagent solution: An accurately weighed amount of 0.5 g of the dye is dissolved in 1 ml dimethylformamide, 52 ml 96% (v/v) ethanol, 10 ml 0.01M- HNO_3 and 10 ml 1% aqueous hydrazine hydrate are added and the solution is diluted to 100 ml with redistilled water.

This procedure is analogous to that of Lukyanov and Duderova⁹, but the molar absorption coefficient of the system is higher ($\epsilon = 12300$ at 620 nm) than the value given by these authors ($\epsilon = 8800$ at 620 nm). The authors' lower value is probably caused by too high an EDTA concentration, which decreases the absorbance of $\text{UO}_2(\text{II})$ complex solutions if $c_X/c_M \geq 18$.

The effect of tensides: Precipitate is formed in solutions with $c_L/c_M > 5$, $c_M = 3.16 \cdot 10^{-5}\text{M}$ and pH 6.13 (0.1M pyridine buffer) on addition of cationogenic tensides. Their formation can, however, be prevented by adding polyvinyl alcohol. The solution absorbance in a region of 630–680 nm increases. Even polyvinyl

alcohol alone (0.2%) increases the absorbance of solutions of the $\text{UO}_2(\text{II})$ chelate with BPGR 2.4 times. The effect of various onium cations on the absorption coefficient of the system is shown in Table IV.

Determination of Uranium with BPGR in the Presence of Butyltriphenylphosphonium Bromide and Polyvinyl Alcohol

The λ_{max} for the UO_2 -chelate with BPGR shifts only minutely in the presence of butyltriphenylphosphonium bromide (λ_{max} 615 nm), but the molar absorption coefficients in this region increase substantially. The optimum conditions for the determination involve $c_L = 1.5 \cdot 10^{-4} \text{M}$, $c_{\text{BTTP}} = 5 \cdot 10^{-3} \text{M}$, $c_{\text{PVA}} = 0.2\%$, pH 6.13 (0.1M pyridine buffer) and 10% (v/v) ethanol. The $\Delta A = f(c_M)$ dependence is linear down to 7.5 $\mu\text{g U/ml}$. The results of the computed linear regression are given in Table II.

Procedure: To a weakly acid uranium solution containing less than 375 $\mu\text{g U}$ are added 5 ml 0.1% reagent solution in 50% (v/v) ethanol, 5 ml 1M pyridine buffer (pH 6–7), 5 ml 2% PVA solution in water and 10 ml $2.5 \cdot 10^{-2} \text{M}$ butyltriphenylphosphonium bromide in 25% ethanol and the solution is diluted to 25 ml with redistilled water. The absorbance is measured after 10 min at 650 nm against water; the blank absorbance is subtracted. The solutions are stable at least 24 h in the presence of PVA.

TABLE IV

Conditional Molar Absorption Coefficients in the $\text{UO}_2(\text{II})$ -BPGR-Quarternary Base System^a

In the presence of tetraalkylammonium iodides, the ternary complex separates from the solution within a short time.

Base	$c_B \cdot 10^3$	% (v/v) ethanol	630	$\epsilon \cdot 10^3$ 640	650 nm
Without base	—	10	11.11	9.25	7.8
Cetylpyridinium bromide ^b	8.0	15	31.6	30.4	28.7
Tetra-n-hexylammonium iodide ^c	1.25	10	30.6	25.8	21.2
Tetra-n-butylammonium iodide ^b	2.0	20	21.1	19.0	15.8
Tetra-n-propylammonium iodide ^b	2.5	20	23.8	21.3	17.1
Tetraphenylarsonium chloride ^b	2.0	10	24.0	20.2	16.8
n-Butyltriphenylphosphonium bromide ^b	5.0	10	30.6	26.6	22.1

^a $c_M = 3.161 \cdot 10^{-5} \text{M}$, $c_L/c_M = 5$, 0.2% polyvinyl alcohol, pH 6.13 (0.1M pyridinium buffer); measured after 10 min, ^b Procedure: BPGR + $\text{UO}_2(\text{II})$ + pyridine buffer + polyvinyl alcohol + base, ^c procedure: polyvinyl alcohol + base + $\text{UO}_2(\text{II})$ + BPGR + pyridine buffer, ^b procedure: BPGR + base + polyvinyl alcohol + pyridine buffer + $\text{UO}_2(\text{II})$.

Determination of Uranium with BPGR in the Presence of Cetylpyridinium Bromide and Polyvinyl Alcohol

In the presence of cetylpyridinium bromide, the λ_{\max} of the UO_2 -chelate with BPGR lies at 625 nm, *i.e.* is the same as that in the solution without the onium cation. The solution absorbance is stable for at least 4 hours and the optimum conditions for the determination are as follows: $c_L = 1.58 \cdot 10^{-4}\text{M}$, $c_{\text{CP}} = 2.5 \cdot 10^{-3}\text{M}$, 0.1M-pyridine buffer (pH 5.89), 0.2% PVA and 15% (v/v) ethanol. The $\Delta A = f(c_M)$ dependence is linear down to $7.5 \mu\text{g U/ml}$ at 630–680 nm. The results of the computed linear regression are given in Table II.

Procedure: To a 50 ml volumetric flask are gradually added 5 ml 0.1% reagent solution in 50% (v/v) ethanol, 10 ml $6 \cdot 10^{-2}\text{M}$ cetylpyridinium bromide solution in 50% (v/v) ethanol, 5 ml 2% PVA in water, 5 ml 1M-pyridine buffer (pH 5.9) and a weakly acidic uranium sample solution containing at most $375 \mu\text{g U}$. The solution is diluted to the mark with redistilled water and the absorbance is measured after 10 min at 630–680 nm against water; the blank absorbance is subtracted.

The sensitivity parameters for procedures A, B and C for the determination of uranium in pure solutions are compared in Table V. The procedures in the presence of butyltriphenylammonium bromide or cetylpyridinium bromide showed higher sensitivities (Table IV) than that specified by Kirillov and coworkers¹⁰ for the procedure in the presence of cetyltrimethylammonium bromide [$(25.88 \pm 0.05) \cdot 10^3$ at 635 nm].

TABLE V

Sensitivity Parameters for Three Procedure (A, B, C) of the Determination of Uranium with BPGR

nm	Molar absorption coefficients		
	A	B	C
630	$12\,150 \pm 20$	$36\,400 \pm 90$	$31\,600 \pm 60$
640	$10\,560 \pm 30$	$31\,670 \pm 90$	$30\,500 \pm 60$
680	$4\,800 \pm 30$	$15\,045 \pm 60$	$25\,000 \pm 50$
Sensitivity index ($\mu\text{g U/cm}^2$ for $A = 0.010$)			
630	0.196	0.065	0.075
640	0.225	0.075	0.078
680	0.494	0.158	0.095

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