

COMPARISON OF THE REACTIONS OF BERYLLIUM(II) IONS
WITH HYDROXYTRIPHENYLMETHANE DYES IN THE PRESENCE
OF CATIONIC AND NONIONIC TENSIDES.
A RAPID SPECTROPHOTOMETRIC METHOD
FOR DETERMINING Be(II) ION WITH ERIOCHROMCYANINE R
IN THE PRESENCE OF SEPTONEX

Irena BUREŠOVÁ, Vlastimil KUBÁŇ and Lumír SOMMER

*Department of Analytical Chemistry,
J. E. Purkyně University, 611 37 Brno*

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Spectrophotometric methods for determining Be(II) with Chromazurol S, Eriochromcyanine R and Eriochromazurol B in the presence of cationic and nonionic tensides were compared using the basic optical and statistical parameters. A rapid and sensitive method was developed for determining Be(II) using the Be(II)-Eriochromcyanine R-Septonex system in 0.1M pyridine or urotropine buffer of $\text{pH} = 6.0 \pm 0.1$ with a molar absorption coefficient of $8.3 \cdot 10^4 \text{ mmol}^{-1} \cdot \text{cm}^2$ at 590 nm.

The importance of the analytical chemistry of beryllium is increasing with increasing technological importance of metallic beryllium and its alloys with copper, aluminium, magnesium and other elements¹. The determination of the beryllium content in treated materials, in waste waters and primarily in the atmosphere from factories is among the most pressing problems in analytical chemistry, as beryllium is a highly toxic inorganic pollutant with very strict standards for permissible concentrations of beryllium in the factory and surrounding atmosphere. Analytical procedures must be rapid and very sensitive and precise.

In spite of the ever increasing importance of the determination of beryllium by atomic absorption, molecular absorption spectrophotometry in the visible and ultraviolet regions remains an important method in many analytical laboratories. The group of hydroxytriphenylmethane dyes with salicylic acid functional group, especially Chromazurol S, Eriochromazurol B and Eriochromcyanine R, have been found to be among the best spectrophotometric reagents. The binary chelates of these dyes with beryllium exhibit molar absorption coefficients in the range $(0.4-2.3) \cdot 10^4 \text{ mmol}^{-1} \text{ cm}^2$, depending on the experimental conditions. The sensitivity and colour contrast of the reactions are greatly increased in the presence of cationic and nonionic tensides²⁻²⁵, where the molar absorption coefficient values attain values of $(5.0-11.0) \cdot 10^4 \text{ mmol}^{-1} \text{ cm}^2$. Most ternary Be(II)-hydroxytriphenylmethane dye-tenside complexes are formed very slowly and maximum absorbance is attained, depending on the experimental conditions, after 1-3 hours, which is a substantial disadvantage in their use for the development of a rapid spectrophotometric method.

In this work, the reactions of beryllium with Chromazurol S, with its unsulphonated analogue Eriochromazurol B and with Eriochromcyanine R in the presence of cetyltrimethylammonium bromide, cetylpyridinium bromide, Zephiramine, Septonex,

Triton X-100 and Brij 35 were compared from the points of view of the time stability of the ternary species, and sensitivity, precision and colour contrast of the reaction. A rapid and sensitive spectrophotometric method of determining beryllium with Eriochromcyanine R in $2 \cdot 10^{-4} \text{ mol l}^{-1}$ Septonex (1-ethoxycarbonylpentadecyltrimethylammonium bromide) medium was developed.

EXPERIMENTAL

Chemicals and Instruments

The stock solution of $4.88 \cdot 10^{-2} \text{ mol l}^{-1}$ $(\text{Be}(\text{NO}_3)_2$ in 1.0 mol l^{-1} HNO_3 was prepared by dissolving spectral pure beryllium oxide (Johnson Matthey, London, Great Britain) in semi-conductor purity nitric acid and was standardized gravimetrically as BeO. The working solutions were prepared by diluting the stock solution to the required concentration of beryllium with a final concentration of HNO_3 of 0.10 mol l^{-1} .

Chromazurol S (3"-sulpho-2",6"-dichloro-3,3'-dimethyl-4-hydroxyfuchson-5,5'-dicarboxylic acid, further CAS), Eriochromazurol B (2",6"-dichloro-3,3'-dimethyl-4-hydroxyfuchson-5,5'-dicarboxylic acid, further CAB) and Eriochromcyanine R (2"-sulpho-3,3'-dimethyl-4-hydroxyfuchson-5,5'-dicarboxylic acid, further ECR) were purified by a combination of precipitation and extraction methods^{26,27} using commercial substances from the firm Geigy (Basle, Switzerland) or ICN Pharmaceuticals Inc. (New York, USA). The content of the active component was found by elemental analysis and spectrophotometrically^{26,27}.

Zephiramine (benzyltrimethyltetradecylammonium chloride ($\text{C}_{23}\text{H}_{42}\text{NCl}$; $M_r = 368.04$, further ZPA), product of the firm Dojindo Co., Japan. Cetylpyridinium bromide ($\text{C}_{21}\text{H}_{38}\text{NBr}$, $M_r = 384.44$, further CPB) and cetyltrimethylammonium bromide ($\text{C}_{19}\text{H}_{42}\text{NBr}$, $M_r = 364.45$, further CTMA) were the products of Lachema, Brno, Czechoslovakia. Septonex (1-ethoxycarbonylpentadecyltrimethylammonium bromide, $\text{C}_{21}\text{H}_{44}\text{O}_2\text{NBr}$, $M_r = 422.5$, further SPX) was the product of Slovafarma, Hlohovec, Czechoslovakia. The solutions were prepared by dissolving a weighed amount of the tenside in 5 ml of ethanol immediately before use. Triton X-100 (octylphenolpolyethyleneglycol ether, $n \sim 10$, analytical grade, further TX) was a product of Koch-Light Lab. Ltd., Great Britain and Brij 35 (polyoxyethylenemonolauryl ether, $n \sim 20$, $M_r \sim 900$) was a product of Merck, GFR. The stock solutions contained 2% w/v in water.

The remaining chemicals, instruments used and method of measuring and treating the individual absorbance curves were described in earlier works²⁶⁻²⁸.

RESULTS AND DISCUSSION

The absorbance of a solution containing the ternary metal ion-hydroxytriphenylmethane dye-tenside system depends in general, in addition to the experimental conditions, also on the order in which the individual components of the reaction mixture are combined. Of the combinations of mixing procedures tested²⁹, a procedure in which the required volumes of the components are added to the volumetric flask in the order, tenside solution, reagent, acid for adjusting the ionic strength, the acidic solution of Be(II), 50-60% of the total water volume and pH adjustment, proved to be the best. The rate of attaining chemical equilibrium does not, however,

depend on the manner and order of mixing the individual components. Using the other tested procedures, in study of the reaction of unsulphonated Eriochromazurol B, the molecular form of the reagent LH_3^0 or a poorly soluble chelate with beryllium ions is precipitated after acidification of the solution.

All the measurements were carried out at an ionic strength of 0.01 in a chloride or nitrate ion medium, as studies of the binary Chromazurol S and Eriochromazurol B systems with cationic and nonionic tensides²⁹ indicated that the most stable ion associates of the reagent with the tensides is formed in the presence of Cl^- , SO_4^{2-} ($c_x < 0.5 \text{ mol l}^{-1}$) and low concentrations of NO_3^- ($c_x < 0.01 \text{ mol l}^{-1}$) ions. The formation of the binary reagent-tenside species and thus also the ternary metal ion-reagent-tenside species depends on the overall concentration and type of inorganic acid anion because of the varying stability of the ion associates of tensides with these ions, which decreases in the order $\text{ClO}_4^- > \text{NO}_3^- > \text{SO}_4^{2-} \sim \text{Cl}^-$ (ref.²⁹).

Reaction of Be(II) with Chromazurol S

Equilibrium is established in the presence of a 0.1% solution of nonionic Triton X-100 in the Be(II)-CAS-Triton X-100 system within 45–60 min. after solution preparation ($\text{pH} = 6.2\text{--}4.9$, $c_L = 2.5 \cdot 10^{-5} \text{ mol l}^{-1}$, $c_{\text{Be}} = 5 \cdot 10^{-6} \text{ mol l}^{-1}$). The absorbance is stable for up to 120 min and then rapidly decreases in the whole pH interval. At the given pH value, the absorption maximum shifts from 585–600 nm to 602–620 nm, in dependence on time, corresponding to the transition from the binary reagent-tenside species to the ternary Be(II)-CAS-tenside species. Decomposition of this species after a longer time is reflected in a decrease in the absorbance in the wavelength region 600–640 nm with simultaneous shift of the absorption maximum to shorter wavelengths. The dependence of the absorption spectra on the acidity confirms the conversion of the binary reagent-tenside species ($\text{pH} < 3.5$) with absorption maxima at 510 and 585 nm to the ternary species with a marked absorption maximum at 613–617 nm at pH 4.5. The optimal acidity for formation of this species lies in the pH intervals 5.6–5.9 and 6.3–6.9 at an optimal Triton X-100 concentration ($c_L = 3.75 \cdot 10^{-5} \text{ mol l}^{-1}$, $c_{\text{Be}} = 7.5 \cdot 10^{-6} \text{ mol l}^{-1}$, $c_T = 0.10\%$), found from the dependence of the absorbance on the concentration of tenside in the whole pH interval, pH 5.65–6.75. At higher Triton X-100 concentrations, the absorption maximum of the ternary species is shifted to shorter wavelengths (from 617 to 590 nm) and the absorbance decreases. The values of the molar absorption coefficient found under optimal experimental conditions ($c_L = 3.75 \cdot 10^{-5} \text{ mol l}^{-1}$, $c_{\text{Be}} = 7.5 \cdot 10^{-6} \text{ mol l}^{-1}$, 0.1% m/v Triton X-100, pH 5.7) vary in the interval $7.9\text{--}8.1 \cdot 10^4 \text{ mmol}^{-1} \text{ cm}^2$.

In the presence of the cationic tensides, cetyltrimethylammonium bromide and cetylpyridinium bromide, under the same conditions, the equilibrium is established over 1–4 h in dependence on the acidity of the medium ($\text{pH} = 3\text{--}7$) and tenside

concentration ($c_T = 1 \cdot 10^{-4} - 6 \cdot 10^{-2} \text{ mol l}^{-1}$) for CTMA and over 3–4 h for CPB (Table I, Fig. 1). The absorption maximum shifts with time from 595–613 nm (pH 5.2 or 6.1, $\tau \sim 5$ min.) to 618–620 nm for CPB and from 597–607 nm (pH 5.55 to 6.2, $\tau \sim 5$ min) to 616–618 nm for $c_T = 2 \cdot 10^{-4} \text{ mol l}^{-1}$ CTMA or from 589 to 601 nm (pH 5.1–6.2, $\tau \sim 5$ min) to 617–620 nm for $c_T = 2 \cdot 10^{-3} \text{ mol l}^{-1}$ CTMA. A similar shift of the absorption maximum on the absorption spectra in dependence on the acidity of the medium indicates the existence of the binary reagent–tenside species at pH < 3.5 with absorption maxima at 510 and 585 nm and their gradual conversion to the ternary Be(II)–CAS–tenside species with absorption maxima at 618 to 620 nm for CPB (pH 4.8–6.5) or 616–620 nm for CTMA (pH 5.0–6.7). The differential absorbance–pH curves ($c_L = 3.75 \cdot 10^{-5} \text{ mol l}^{-1}$, $c_{Be} = 7.5 \cdot 10^{-6} \text{ mol}$

TABLE I

Survey of the important characteristics of the ternary complexes of Be(II) with Chromazurol S, Eriochromazurol B and Eriochromcyanine R in the presence of tensides. $c_M = 7.50 \cdot 10^{-6} \text{ mol} \cdot \text{l}^{-1}$, $c_L = 3.75 \cdot 10^{-5} \text{ mol l}^{-1}$, $c_T = 2 \cdot 10^{-4} \text{ mol l}^{-1}$, 5% ethanol, $I = 0.01$ (HNO₃ + NaOH) $t = 25^\circ\text{C}$, $l = 10 \text{ mm}$

System	pH interval	pH opt.	λ_{max}^a	$10^4 \cdot \epsilon^b$	τ^c
Be–CAS–TX ^d	5.6–5.9	5.7	613	8.10	120 ^f
Be–CAS–BRIJ ^d	5.6–5.8	5.7	614	7.92	150 ^f
Be–CAS–CPB	4.8–5.2	5.0	618	8.33	180 ^f
Be–CAS–CTMA	5.4–5.7	5.5	613	7.67	60 ^f
Be–CAS–SPX	5.0–5.2	5.1	619	7.70	300
Be–CAS–SPX ^e	5.8–6.0	5.9	619	7.90	300
Be–CAB–ZPA	5.0–5.8	5.4	616	10.60	150 ^g
Be–CAB–CPB	4.6–4.8	4.7	619	8.00	120
Be–CAB–CTMA	4.8–5.1	5.0	618	7.07	60
Be–CAB–SPX	4.7–4.9	4.8	614	7.50	120
Be–CAB–ZPA	4.7–4.9	4.8	615	9.30	90
Be–ECR–TX ^d	5.6–5.8	5.7	583	6.30	70
Be–ECR–CPB	5.0–5.2	5.2	588	8.00	70
Be–ECR–CTMA	5.6–5.8	5.7	587	7.50	70
Be–ECR–ZPA	5.2–5.8	5.4	587	8.90	90
Be–ECR–SPX	5.6–6.1	5.9	590	8.43	5

^a Absorption maximum, nm; ^b molar absorption coefficient, $\text{mmol}^{-1} \text{ cm}^2$; ^c time required for attaining maximum absorption, minutes; ^d $c_T = 0.1\%$ (TX = Triton X-100, BRIJ 35); ^e $c_T = 2 \cdot 10^{-3} \text{ mol l}^{-1}$; ^f for concentration $c_T = 2 \cdot 10^{-3} \text{ mol l}^{-1}$, the equilibrium time is 60–120 min. longer; ^g at $c_T = 2 \cdot 10^{-3} \text{ mol l}^{-1}$, a precipitate is formed in solution.

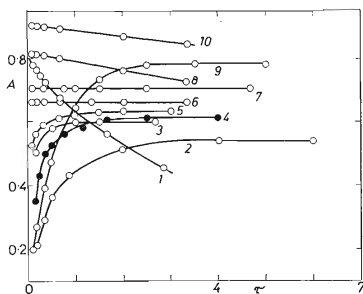
$\cdot l^{-1}$, $c_T = 2 \cdot 10^{-4} \text{ mol l}^{-1}$ CTMA or CPB) and the corresponding dependences of the absorbance on the tenside concentration at a constant pH value confirm the optimum pH interval, $\text{pH} = 5.0 \pm 0.2$ for CPB and $\text{pH} = 5.4 \pm 0.3$ for CTMA and the above most suitable tenside concentration, $c_T = 2 \cdot 10^{-4} \text{ mol l}^{-1}$. The molar absorption coefficients determined under optimal experimental conditions attain values of $8.3 \cdot 10^4$ or $7.7 \cdot 10^5 \text{ mmol}^{-1} \text{ cm}^2$ for CPB and CTMA, respectively. The behaviour of both ternary systems is completely analogous in 0.1 mol l^{-1} chloride and nitrate media.

The presence of frequently used Zephiramine leads to equilibrium establishment in the ternary system after 150 min ($c_T = 2 \cdot 10^{-4}$ or $2 \cdot 10^{-3} \text{ mol l}^{-1}$). The absorption maxima for both Zephiramine concentrations shift in dependence on time and on the acidity of the medium from the region of maximum absorbance of the binary reagent-tenside species (510 and 585 nm) or reagent-metal ion species (580 nm) to 612–616 nm in the optimal pH region, $\text{pH} = 5.4 \pm 0.4$. Under these conditions, the molar absorption coefficient attains a value of $10.6 \cdot 10^5 \text{ mmol}^{-1} \text{ cm}^2$.

Equilibrium is not established in the ternary Be(II)–CAS–Septonex system until after 5 h for both the SPX concentrations in the whole pH interval, $\text{pH} 5.1\text{--}6.3$. The absorption maximum on the absorption spectra is shifted with time and with increasing acidity to longer wavelengths and the absorption maximum of the ternary species lies at 609–619 nm ($\text{pH} 4.8\text{--}6.4$). At $\text{pH} 5.1 \pm 0.1$, an SPX concentration of $c_T = 4 \cdot 10^{-4} \text{ mol l}^{-1}$ SPX is preferable and for $\text{pH} 6.9 \pm 0.1$, a concentration of $2 \cdot 10^{-3} \text{ mol l}^{-1}$. Under the above experimental conditions, the molar absorption

FIG. 1

The dependence of the absorbance on time (h) in the binary Eriochromcyanine R–Septonex system (curves 1, 6, 8 and 10) and in some ternary systems (curves 2–5, 7, 9). $c_L = 3.75 \cdot 10^{-5} \text{ mol l}^{-1}$, $c_{\text{Be}} = 7.5 \cdot 10^{-6} \text{ mol} \cdot \text{l}^{-1}$ (curves 2–5, 7, 9), $c_T = 1 \cdot 10^{-3} \text{ mol} \cdot \text{l}^{-1}$ (curve 2), otherwise $2 \cdot 10^{-4} \text{ mol l}^{-1}$, $I = 0.01$ ($\text{HNO}_3 + \text{NaOH}$), $t = 25^\circ\text{C}$. Reagent-tenside-pH- λ (nm): Curve 1 ECR–SPX–1.00–457; 2 CAS–SPX–6.40–619; 3 ECR–CTMA–7.10–596; 4 ECR–CPB–7.15–598; 5 ECR–Zephiramine–7.10–594; 6 ECR–SPX–8.00–430; 7 ECR–SPX–6.50–586; 8 ECR–SPX–5.20–505; 9 CAS–Zephiramine–5.10–612; 10 ECR–SPX–3.30–505



coefficient attains a value of 7.7 or 7.9 · 10⁴ mmol⁻¹ cm². This fact is probably connected with formation of two different ternary species, as was observed for the Fe(III)-CAS-CPB ternary system²⁹ for various tenside concentrations.

The Reaction of Be(II) with Eriochromazurol B

In the presence of cationic tensides, the behaviour of the ternary Be(II)-CAB-tenside system is similar to the behaviour of the system containing CAS. The reaction equilibrium is established, depending on the type of tenside, in 60 (CTMA), 90 (Zephiramine) or 120 (SPX, CPB) minutes under similar experimental conditions. The absorption spectra exhibit a similar shift of the maximum absorption to longer wavelengths in dependence on the pH and time and the existence of the ternary species is indicated by a sharp absorption maximum at 614 (SPX), 615 (Zephiramine), 618 (CTMA) or 621 (CPB) nm. The optimum tenside concentration was found from the dependence of the solution absorbance on the tenside concentration in the pH intervals 4.6–4.8 (CPB), 4.8–5.1 (CTMA) for all the ternary systems and equals $c_T = 2 \cdot 10^{-4}$ mol l⁻¹. The molar absorption coefficient values determined under optimal conditions, 9.3 · 10⁴ (Zephiramine), 7.5 · 10⁴ (SPX), 8.0 · 10⁴ (CPB) and 7.1 · 10⁴ (CTMA) mmol⁻¹ cm² are generally lower than the corresponding values for Chromazurol S. Thus the reagent has no advantages over sulphonated Chromazurol S.

The Reaction with Eriochromcyanine R

The reagent decomposes slowly, probably with formation of the colourless sultone form, in aqueous solutions of Eriochromcyanine R in the pH interval 3–6.5. This transition is blocked in this pH interval by the presence of tenside^{27,28}. On the other hand, the presence of the tenside hastens the decomposition in the acid region and thus the dependence of the absorbance on time was measured for selected pH values in the interval 1.0–9.0. The $A = f(\tau)$ curves confirm that the reagent is stable in weakly acidic to alkaline media for at least two hours, while at pH < 3 irreversible conversion to the colourless form of the reagent occurs. The rate of the conversion increases with decreasing pH of the solution, so that ECR is unsuitable for determinations in this region (Fig. 1).

The absorption spectra of the binary ECR-tenside system exhibit only slight deformation of the absorption band of the acid-base form LH₂²⁻ in the region around 570–580 nm. The acid-base characteristics of the reagent exhibit similar changes as those described for both the above reagents (CAS, CAB) in the presence of tenside²⁸.

Equilibrium is established in the ternary Be(II)-ECR-tenside system under corresponding experimental conditions much faster than for CAS and CAB. Depending

on the type of tenside, equilibrium is established immediately after solution preparation (SPX) or after 60–70 (Triton X-100, CTMA, CPB) to 90 (Zephiramine) minutes after solution preparation. The molar absorption coefficient values for the individual systems are $6.3 \cdot 10^4$ (Triton X 100), $7.5 \cdot 10^4$ (CTMA), $8.0 \cdot 10^4$ (CPB), $8.9 \cdot 10^4$ (Zephiramine) and $8.4 \cdot 10^4$ (SPX) $\text{mmol}^{-1} \text{cm}^2$. Because of the rapid equilibrium establishment in the Be(II)–ECR–SPX system, the high sensitivity of the reaction and the ready availability of both reagents, this system was chosen for development of a rapid spectrophotometric method of determining beryllium.

Determination of Beryllium with Eriochromcyanine R in the Presence of Septonex

The dependence of the absorption spectrum on time ($c_{\text{Be}} = 7.50 \cdot 10^{-6} \text{ mol l}^{-1}$, $c_{\text{L}} = 3.75 \cdot 10^{-5} \text{ mol l}^{-1}$, $c_{\text{T}} = 2 \cdot 10^{-4} \text{ mol l}^{-1}$, $l = 0.01$) under optimum acidity conditions for formation of the ternary species (pH 5.0–6.5) exhibits a shift of the absorption maxima by 5–8 nm to longer wavelengths, while the intensity of the spectral bands does not change. In the given pH interval, the reaction equilibrium is established within 5–10 min from solution preparation.

The dependence of the absorption spectra on the acidity of the medium (Fig. 3) confirms the gradual transition of the binary reagent–tenside species with absorption maxima at 505 and 570 nm to the ternary species with absorption maxima at 585 to 590 nm with simultaneous conversion of the reagent to the yellow acid–base form LH^{3-} with absorption maximum at 430 nm (see curves 7–11 in Fig. 3). In the weakly alkaline medium (pH \sim 8), the ternary species decomposes, reflected in a marked decrease in the absorbance in the region around 580 nm.

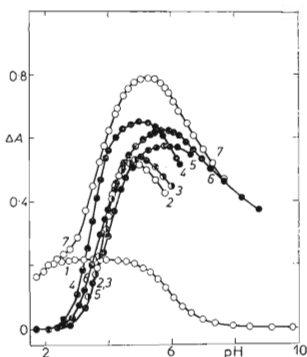


FIG. 2

Differential $\Delta A = A - A_{\text{L}} = f(\text{pH})$ curves for some ternary Be(II)–reagent–tenside systems. For the experimental conditions, see Fig. 1. Reagent–tenside– λ (nm): Curve 1 ECR–SPX–580; 2 CAB–CTMA–617; 3 CAB–CPB–618; 4 CAS–CTMA–613; 5 CAS–CPB–618; 6 ECR–SPX–580; 7 ECR–SPX–580 ($A = f(\text{pH})$)

The dependences of the absorbance on the reagent and tenside concentrations in the above pH interval ($c_T = 1 \cdot 10^{-4} - 4 \cdot 10^{-3} \text{ mol l}^{-1}$ or $c_L = 7 \cdot 5 \cdot 10^{-6}$ to $7 \cdot 5 \cdot 10^{-5} \text{ mol l}^{-1}$) confirm that the ternary species is best formed in roughly a 5-fold concentration excess of the reagent and at a Septonex concentration of $c_T = 2 \cdot 10^{-4} \text{ mol l}^{-1}$. At higher Septonex concentrations, the ternary species decomposes to form the binary ECR-SPX species or the classical chelate Be-ECR is formed.

The absorbance-pH curves of the ternary system under the above experimental conditions exhibit a single formation branch in the pH interval 2-6 with maximum absorbance values in the pH interval 5.7-6.1. The molar absorption coefficients determined from the absorbance of the system at $\text{pH} = 5.9 \pm 0.05$ attain values of $(8.4 \pm 0.1) \cdot 10^4 \text{ mmol}^{-1} \text{ cm}^2$.

The following buffers were tested for acidity adjustment in the above optimal pH interval: pyridine, acetate, HMT and tris-hydroxymethylaminomethane in concentrations of $0.01 - 0.5 \text{ mol l}^{-1}$. Of these, pyridine and HMT buffers with a final concentration of 0.1 mol l^{-1} were found to be most suitable; in concentrations up to 0.2 mol l^{-1} , these buffers do not affect the parameters of the ternary species found in unbuffered aqueous solutions in the whole pH interval. Pyridine buffer with $\text{pH} = 5.90$ was chosen for the actual determination of beryllium with ECR in the presence of SPX; somewhat lower blank values were measured for this buffer (Table II). The dependences of the absorbance on the concentrations of the reagent and Septonex confirmed the above optimal concentration ratios of c_L/c_M and c_T/c_L in the presence of the buffers.

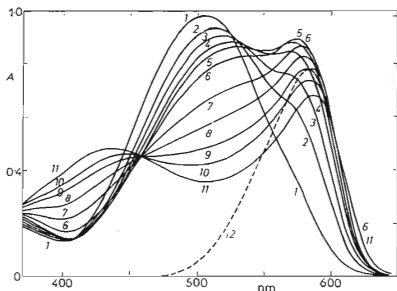


FIG. 3

The absorption spectra of the ternary Be(II)-ECR-SPX system in dependence on the acidity of the medium. For the experimental conditions, see Fig. 1, time 5 min. pH: curve 1 2.90; 2 3.70; 3 4.10; 4 4.31; 5 4.69; 6 5.00; 7 5.69; 8 5.90; 9 6.23; 10 6.48; 11 6.70; 12 5.69, differential curve

The calibration curves are linear in the concentration interval $c_{\text{Be}} = 0.4 - 7.5 \cdot 10^{-6} \text{ mol l}^{-1}$ in 0.1 mol l^{-1} pyridine and HMT buffer media. The results of statistical treatment of the curves by the least squares method using the STAT program are given in Table II. The results reflect the high sensitivity and precision of the determination of beryllium with Eriochromcyanine R in the presence of Septonex, as the estimate of the relative standard deviation of the determination of Be(II) in 10 independent samples was not greater than $\pm 2\%$ (Table II).

It follows from comparison of the basic parameters of the spectrophotometric methods for the determination of beryllium with Chromazurol S, Eriochromcyanine R and Eriochromazurol B in the presence of cationic and nonionic tensides (Triton X-100, BRIJ 35, CTMA, CPB, ZPA, SPX) that, from the point of view of the sensitivity of the determination with the individual reagents, Chromazurol S is most useful in practice. Using this reagent, the molar absorption coefficient at a wavelength of 610–620 nm attains a value of $(0.8 - 1.06) \cdot 10^5 \text{ mmol}^{-1} \text{ cm}^2$. The unsulphonated derivative of Chromazurol S – Eriochromazurol B – has a somewhat less sensitive reaction and thus has no marked advantages for the development of a method of determining beryllium. Of the studied reagents, Eriochromcyanine R is the least sensitive for practically all the tested tensides (Fig. 2).

TABLE II

Statistical parameters of the calibration curves for the ternary Be(II)–Eriochromcyanine R–Septonex system. $c_{\text{L}} = 3.75 \cdot 10^{-5} \text{ mol l}^{-1}$, $c_{\text{T}} = 2 \cdot 10^{-4} \text{ mol l}^{-1}$, $c_{\text{M}} = 0.40 - 7.50 \cdot 10^{-6} \text{ mol l}^{-1}$, pH 5.90, 0.10 mol l^{-1} pyridine buffer, 5% ethanol, 590 nm, = 5 min

Quantity	Value	Note
$\varepsilon \pm d(\varepsilon), \text{ mmol}^{-1} \text{ cm}^2$	$82\,628 \pm 3\,099$	$d(\varepsilon) = 3s_{xy}(\sum x_i^2 - (\sum x_i)^2/n)^{1/2}$
$A_0 \pm d(A_0)$	0.198 ± 0.0097	$d(A_0) = d(\varepsilon) \cdot (\sum x_i/n)^{1/2}$
$S_{A(x,y)} \cdot 10^2$	6.31	$(\sum (A_{\text{exp}} - A_{\text{calc}})^2 / (n - 2))^{1/2}$
Detection limit, pp ^b	6.88	$8 \cdot s_{A(xy)} \cdot 1\,000 \cdot M_r/\varepsilon$
Sensitivity index for $A = 0.010, \text{ pp}^b$	1.09	$10 \cdot M_r/\varepsilon$
Reproducibility, %	$1.95^a, 1.80^b$	$(\sum (A_i - \bar{A})^2 / (n - 1))^{1/2}$

^a Calculated for $c_{\text{M}} = 3 \cdot 10^{-6} \text{ mol l}^{-1}$, $n = 10$; ^b calculated for $c_{\text{M}} = 5 \cdot 10^{-7} \text{ mol l}^{-1}$, $n = 10$, A_0 blank absorbance, calculated from the regression straight line, A_{calc} , A_{exp} calculated theoretically and experimentally determined absorbance values for the individual points on the calibration curve, x_i, c_{M} values for the individual points on the calibration curve, $n =$ number of measurements, M_r relative atomic (molecular) weight of the analyte.

TABLE III

Survey of the important parameters of the spectrophotometric methods for the determination of Be(II) with hydroxytriphenylmethane dyes in the presence of tensides

System	pH	λ_{\max} , nm	$10^{-4} \cdot \epsilon^d$	τ , min ^b	Buffer	$c_{\text{Be(II)}}^c$	Masking agent	Note	Ref.
CAS-ZPA	5.1	610	9.9	> 15	HMT	4–120	Na ₃ PO ₄		2, 3
CAS-PVA	6.5 ± 0.4	615	5.2	> 20–30	HMT, TRIS	5–130	CaEDTA	0.8% PVA	4
CAS-ZPA	5.2	610	10.9	> 30	NaAc	4–80	EDTA	0.5% ZPA, ML ₂ T ₂	7
CAS-CTMA	5.3–5.6	612, 619	9.1	?		6–60	ML ₂		8
CAS-HDTMA	6.6–7.0	596	5.85			< 70		extrn.	9
CAS-POEDA	4.2–4.9; 4.5	605	9.0	> 15	NaAc	< 80	EDTA	not interfere	11
CAS-CTMA	5.0 ± 0.2	615	10.1; 9.45 ^d	90	HMT	< 100	EDTA	ClO ₄ ⁻ , NO ₃ ⁻	12
CAS-BDHA	6.65 ± 0.05	610		120	HMT	non lin.		ML ₂	13, 14
POEDA-CAS	4.4–5.0	605	10.0	15				ML ₂	16
CAS-T ^o	6–7	610		> 30		5–180		ML ₂ T	17
CAS-R ₄ P ⁺	5.8–6.2; 6.2	615	6.47		NaAc	< 126		extrn.	23
CAS-Bip.	5.0	610	5.4; 4.6 ^d	≥ 5		2–200	EDTA	ML ₂ T	30
ECR-BDMTDA	6.7–7.2	592		> 30 ^e		18–55		ML ₂	20
ECR-CTMA	6.7–7.3; 7.0	590	8.65	> 150	boate	< 100	EDTA	15' at 60°C	21
ECR-CTMA	8.2–8.3	600	8.50	> 15–20	NH ₃		EDTA	ML ₃ T ₃	22
ECR-SPX	5.7–6.4	602		> 300		10–155	EDTA	15' at 60°C	24

^a mmol⁻¹ cm²; ^b time required to attain equilibrium; ^c Be(II) concentration range for a linear calibration curve, ng/ml; ^d values in the presence of EDTA; ^e data at 60–70°C; ^f ascorbic acid, 1,10-phenanthroline. PVA polyvinyl alcohol, HCTMA hexadecyltrimethylammonium chloride, POEDA polyoxyethylenedodecylamine (N,N-bis-(polyethylene glycol-dodecylamine), BDHDA benzylidimethylhexadecylammonium chloride, BDMTDA benzylidimethyltetradecylammonium chloride (Zephiramine), T^o various types of polyoxyethylenealkylphenols, R₄P⁺ polyvinylbenzyltriphenylphosphonium chloride, Bip 2,2'-bipyridyl.

For the individual reagents, the most sensitive reactions with beryllium occur in the presence of cationic tenside, primarily Zephiramine and cetylpyridinium bromide. The differences in the sensitivity of the reactions of beryllium with the hydroxytriphenylmethane dyes in the presence of cationic and nonionic tensides are not as marked as for cations of higher valency, Fe(III), Al(III), *etc.*²⁹⁻³¹.

The high sensitivity of the spectrophotometric method of determining beryllium (Table I and II) is in very good agreement with the sensitivity given in the literature (Table III). The high molar absorption coefficient values for the reaction of Be(II) with Chromazurol S in the presence of some nonionic tensides, $\epsilon = (1.2-1.8) \cdot 10^5 \text{ mmol}^{-1} \text{ cm}^2$ are probably a result of the higher impurity content in the tensides used (ref.¹⁹).

The colour contrast of the reactions varies in the interval 60–190 nm and is best for Chromazurol S and Eriochromazurol B with cationic tensides, while the colour contrast for the reaction with Eriochromcyanine R is much lower ($\Delta\lambda_{\text{max}} = \lambda_{\text{max(MLT)}} - \lambda_{\text{max(LT)}} = 70-180 \text{ nm}$), corresponding to the splitting of the absorption band of the LH_2^- acid-base form in the presence of tenside²⁹.

TABLE IV

The effect of interfering ions and masking agents on the spectrophotometric determination of beryllium with Eriochromcyanine R in the presence of Septonex. $c_L = 3.75 \cdot 10^{-5} \text{ mol l}^{-1}$, $c_M = 2.0 \cdot 10^{-6} \text{ mol l}^{-1}$ or $4.0 \cdot 10^{-6} \text{ mol l}^{-1}$, $c_T = 2 \cdot 10^{-4} \text{ mol l}^{-1}$, 5% v/v ethanol, 0.10 mol l⁻¹ pyridine buffer, pH 5.90, $t = 25^\circ\text{C}$, $l = 10 \text{ mm}$, 590 nm, $\tau \sim 5 \text{ min}$

Ion	$c_X/c_M, M^a$	Reagent	$c_X/c_M, M^a$
Cu(II)	1 : 2, 10 : 1 ^b	EDTA	1 : 2
Zn(II)	10 : 1	CaEDTA	5 : 1
Mg(II)	100 : 1	MgEDTA	5 : 1
Ni(II)	10 : 1	NTA	5 : 1
Fe(III)	1 : 70	CDTA	5 : 1
Co(II)	10 : 1	thiourea	2 500 : 1
Al(III)	1 : 80	PO_4^{3-}	1 : 1
Cl^-	5 000 : 1	CH_3COO^-	500 : 1
SO_4^{2-}	5 000 : 1		
ClO_4^-	15 : 1		
NO_3^-	5 000 : 1		
NH_4^+	5 000 : 1		

^a Concentration ratio of the interfering ion (masking agent) related to the beryllium concentration, $c_M = 2.0 \cdot 10^{-6} \text{ mol l}^{-1}$ and $c_M = 4.0 \cdot 10^{-6} \text{ mol l}^{-1}$, leading to a relative absorbance change of $\Delta A = 2\%$; ^b value at $c_{\text{EDTA}} = 1 \cdot 10^{-5} \text{ mol l}^{-1}$.

The reactions of beryllium with hydroxytriphenylmethane dyes in the presence of the individual tensides occur very slowly, except for the reaction of beryllium with Eriochromcyanine R in the presence of Septonex. The maximum absorbance value is attained during 1–3 h; only for the above Be(II)–ECR–SPX system is equilibrium established in 5–10 min. The slow reaction in the ternary systems renders the use of these reactions for the development of a spectrophotometric method for the determination of beryllium less suitable. The equilibrium establishment in the reactions of Eriochromcyanine R can be hastened by heating the solutions to 50–60°C, while increasing the temperature during the reactions of Chromazurol S and Eriochromazurol B leads to precipitation of the binary reagent–tenside species of Be(II) – reagent species (see also ref.¹²). Data on the time dependence of the reaction in the literature are very varied, not only for the various ternary systems, but also for identical systems, as a number of factors affect the course of the reaction (Table III). In addition to the experimental conditions (concentration of the individual components), the slow formation of the binary chelate of beryllium with the individual hydroxytriphenylmethane dyes probably plays an important role^{4,32}.

The reactions of beryllium with the individual reagents in the presence of tenside occur in weakly acid or neutral media (Table II and III), where almost all masking agents (EDT, NTA, tartrate, citrate, etc) strongly interfere. Similarly, displacement equilibria using calcium or magnesium salts of EDTA are less useful than for the corresponding binary systems⁴. The use of these masking agents leads to a considerable decrease in the sensitivity of the determination method^{12,30}. In the actual determination of beryllium, prior separation of it from other ions in the sample on an ion-exchanger or using some other suitable separation method¹ is usually preferable. Masking agents could not be used in the analysis of beryllium bronzes with high copper contents (95–78%) as it was impossible to eliminate the interfering effect of high concentration excesses of copper (Table IV). Separation of copper by electrolysis was found to be most useful here¹.

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