Spectrophotometric determination of lanthanoides and yttrium by flow injection analysis, using Chrome Azurol S in the presence of cationic surfactants

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In alkaline 0.1 M solution of ammonia buffer, having a pH of 9.4 ± 0.2, and containing hexadecyltrimethylammonium bromide (CTMAB) (c = 0.1—0.2 mmol dm^{-3}) or hexadecylpyridinium bromide (CPB) (c = 0.2—0.4 mmol dm^{-3}), Chrome Azurol S forms stable products with rare earth and yttrium ions. These products have an absorption maximum at λ = 620 nm and molar absorption coefficients ε = 6.3—7.1 m^2 mmol^{-1} for CTMAB and ε = 6.8—8.2 m^2 mmol^{-1} for CPB. In the presence of CTMAB (c = 0.10—0.15 mmol dm^{-3}) and at pH ≈ 10 a less stable product is formed, with an absorption maximum at λ = 650 nm and ε = 9.2 m^2 mmol^{-1}. Poorly selective reactions of lanthanoides and yttrium possess high sensitivity with a detection limit DL = 0.3—0.6 μmol dm^3 for CPB and DL = 0.5—0.9 μmol dm^{-3} for CTMAB, respectively, and with high colour contrast $\Delta\lambda$ = 200—230 nm. Optimal conditions for analysis depend on the reagent and surfactant concentration and to some extent on the concentration of lanthanoide and of the inert salt as well. The reaction has been utilized for the determination of Ln(III) and Y(III) by means of flow injection analysis at λ = 620 nm or 650 nm in the concentration range of 2—20 μmol dm^{-3} of Ln(III), DL = 2—3 μmol dm^{-3} of Ln(III). The determination was preceded by the separation of lanthanoides. The reaction can also be applied for postcolumn derivatization of lanthanoides after HPLC or IEC separation chromatography.

В присутствии 0,1—0,2 ммоль дм$^{-3}$ бромида гексадецилтриметиламмония (CTMAB) или 0,2—0,4 ммоль дм$^{-3}$ бромида гексадецилпиридиния (CPB) Хромазурол S (CAS) в щелочной среде 0,1 моль дм$^{-3}$ аммиачного буферного раствора с pH 9,4 ± 0,2 образует с ионами редкоземельных элементов и иттрия стабильные продукты с максимумом поглощения при λ = 620 нм и молярными коэффициентами поглощения ε = 6,3—7,1 м^2 ммоль$^{-1}$ для CTMAB или ε = 6,8—8,2 м^2 ммоль$^{-1}$ для CPB. В присутствии 0,10—0,15 ммоль дм$^{-3}$ CTMAB при pH ≈ 10 образуется менее устойчивый продукт с максимумом поглощения при λ = 650 нм и молярным коэффициентом поглощения

9,2 м^2 ммоль$^{-1}$. Слабо избирательные реакции лантанидов и иттрия характеризуются высокой чувствительностью с пределом определения DL = 0,3—0,6 мкмоль дм$^{-3}$ для CPB и DL = 0,5—0,9 мкмоль дм$^{-3}$ для CTMAB с сильным цветовым контрастом $\Delta\lambda$ = 200—230 нм. Оптимальные условия определения зависят от концентраций реагента и ПАВ, а отчасти и от концентрации лантанидов и инертных солей. Данная реакция была использована для определения содержания Ln(III) и Y(III) посредством проточно-инъекционного анализа при λ = 620 нм или 650 нм в интервале концентраций 2—20 мкмоль дм$^{-3}$ Ln(III) с пределом определения DL = 2—3 мкмоль дм$^{-3}$ Ln(III) после предварительного отделения лантанидов. Реакцию можно также использовать для постколонной дериватизации лантанидов после их разделения ионообменной хроматографией или высокоэффективной жидкостной хроматографией.

Ternary systems consisting of metal ion—triphenylmethane dye—surfactant have found widespread use in analytical chemistry in determinations of trace concentrations of certain elements [1—4]. The popularity of such systems is due to both high sensitivity and colour contrast. The price to be paid for such assets is a rather low selectivity. Molar absorptivities can be dramatically increased by the presence of cationic or nonionic surfactants, with the concomitant bathochromic shift of absorption maxima, compared to those of the binary systems. There are cases where molar absorption coefficients ε attain values 15—20 m^2 mmol^{-1} and colour contrast is higher than 100 nm [1—5].

One of the early systems used for spectrophotometric determination of lanthanoides consisted of triphenylmethane dye (Xylenol Orange, Methylthymol Blue, Glycinecresol Red, and others) in the presence of CTMAB or CPB [6—11]. In addition, reagents such as Chrome Azurol S [12, 13], Eriochrome Azurol B [14], Bromopyrogallol Red [15], and Eriochrome Cyanine R have been used. When a cationic surfactant is present, absorption maxima appear in the region of λ = 610—650 nm, having ε = 4—5 m^2 mmol^{-1}. Another special feature of the reaction is the narrow interval of surfactant and reagent concentrations in which the reaction works. Not surprisingly some authors, disregarding that fact, have found Chrome Azurol S and its analogues unsuitable for determination of lanthanoides in the presence of surfactants [16]. The whole problem is both complex and extensive, interactions between lanthanoides and hydroxytriphenylmethane dyes are far from being understood.

Aiming at their application in flow injection analysis of separated samples and for postcolumn derivatization of lanthanoides after HPLC or IEC chromatography, we have studied interactions of lanthanoides and yttrium with Chrome Azurol S in the presence of cationic surfactants CTMAB, CPB, and Septonex.

Experimental

Stock solutions of 0.01 M lanthanoides and yttrium were prepared by dissolving samples of nitrates (La, Ce, Pr, Nd, Tb, Ho), oxides (Sm, Er, Y) or carbonates (Eu, Gd, Dy, Yb) having analytical purity grade (Reakhim, USSR), in the calculated volume of 1 M-HNO_3 and diluting with water to 0.1 M-HNO_3. Such solutions were standardized by chelatometric titration in the presence of Xylenol Orange. For use, stock solutions were diluted by 0.1 M-HNO_3 to concentrations of 0.01—1 mmol dm^{-3}.

Chromatographically pure preparations of the Chrome Azurol S (2″,6″-dichloro-3″--sulfo-3,3′-dimethyl-4-hydroxyfuchson-5,5′-dicarboxylic acid (CAS in further text) were used after purification [17] of the commercial product (Merck, Darmstadt). The content of active substance was checked by potentiometric titration of samples of solid CAS by carbonate-free 0.1 M-NaOH. Samples contained 70.6 and 85.0 % of active substance after correction to anhydrous acid. Additional parameters that have been checked were values of molar absorption coefficients of 4×10^{-5} M-CAS solutions in pH regions, where LH_3^- (pH = 1.1) and LH^{3-} (pH = 8.0) acidobasic forms prevailed. The values $\varepsilon = 2.44\ m^2\ mmol^{-1}$ (at $\lambda = 470$ nm) and $\varepsilon = 2.21\ m^2\ mmol^{-1}$ (at $\lambda = 430$ nm) differed only by 7 % from those published in the literature [17, 18]. Commercial reagent contained 35—40 % of active substance only. Stock solution of CAS ($c = 5$ mmol dm^{-3}) was prepared by dissolving solid reagent in few cm^3 of water, containing 10—15 drops of concentrated ammonia solution and after the sample dissolved completely it was diluted to final concentration with water.

In flow injection analysis (FIA) and in other measurements in stationary conditions a "mixed" reagent, containing the required CAS concentration, cationic surfactant, and buffer with pH = 9.4 ± 0.2, was directly injected to the flow stream of the acidic solution of lanthanoides.

Anal. grade quality samples (Lachema, Brno) of CPB were purified before making 0.01 M standard stock solution in diluted ethanol ($\varphi = 20$ vol. %). Similarly 0.01 M stock solutions of CTMAB in water were prepared. Aqueous solution (0.005 M) of Septonex (SPX, 1-ethoxycarbonylpentadecyltrimethylammonium bromide) was prepared using pharmaceutical purity samples of SPX (Slovakofarma, Hlohovec).

Ethanol containing 4.5 vol. % of water and 5 vol. % of methanol was distilled with an addition of EDTA ($\varrho = 1$ g dm^{-3}). Water used in solutions was redistilled from quartz apparatus Bi-18 Destamat (Heraeus Quarzschmelze, GFR). Other chemicals supplied by Lachema, Brno were of either anal. grade or MOS purity. Ionic strength of solutions was maintained at $I = 0.1$ mol dm^{-3} by HNO_3 and $NH_3 \cdot H_2O$ or NaOH.

Acidity of solutions was determined by OP 208/1 pH-meter equipped with OP 0808 combined electrode (Radelkis, Budapest). Regular calibrations were performed, utilizing a set of standard buffers K21 and K71, having pH 2.18 and 7.00, respectively, supplied by Radelkis. All spectrophotometric measurements were performed on a digital double--beam spectrophotometer Specord M 40 (Zeiss, Jena) in quartz cuvettes with 1 cm path length, at constant temperature 24 ± 1 °C. For FIA measurements in dynamic conditions an experimental set-up, consisting of a home-made PTFE loop-valve injector with total volume variable from 8—100 mm^3, spectrophotometric detector with variable wavelength in the range of 335—800 nm and flow cell with 18 mm^3 volume, adapted from

a single-beam spectrophotometer Spekol 21, and the K 201 recorder (Zeiss, Jena) was used.

Carrier stream of either acidic lanthanoide and yttrium solution or alkaline solution of the mixed reagent was propelled by gravity at the flow rate of 0.5—3 $cm^3 min^{-1}$ since neither peristaltic nor membrane pumps could perform with satisfactory reproducibility and high precision (0.1—1.0 % for piston pump or gravity propelled stream, 1—5 % for commercial peristaltic or membrane pumps). Components of the FIA system, shown in Fig. 1, were connected with Teflon tubing of internal diameter 0.6 mm, in order to avoid secondary contamination of solutions as well as the effect of sorption at the surface of capillary system made from other plastic materials.

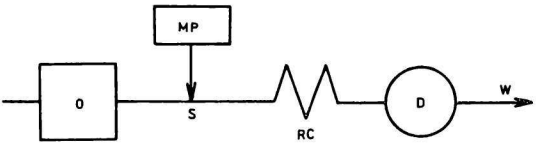

Fig. 1. Block scheme of the FIA analyzer.
O — stream flow, MP — membrane pump, S — sampler, RC — reaction coil, D — detector, W — waste.

Tuned to optimal conditions the FIA system worked with a flow rate of approximately 1 $cm^3 min^{-1}$, the distance between injection and detection site being $l = 40$ cm at dispersion $D = c_0/c_m = 7$ (c_0 — signal at zero dispersion of the zone, c_m — signal at the peak maximum), and with 30 mm^3 injection volume. Such experimental conditions gave maximal yield of the reaction and the highest peak absorbances.

Results and discussion

In the ternary system consisting of Ln(III)—CAS—surfactant where Ln(III) represents lanthanoide ions and those of lanthanum and yttrium the total absorbance and the rate of product formation depends beside other factors on the order in which the components are mixed. The fastest way to reach equilibrium is to add the mixed reagent (CAS + surfactant + buffer) to the acidic (pH = 1—3) solution of Ln(III) or alternatively by adding mixture of acidic solution of Ln(III) or CAS (pH = 1—2, HNO_3), surfactant and either ammonia or buffer solution to the acidic CAS or Ln(III) solution. Both addition of Ln(III) to the mixed reagent and the reversed process elicited equilibrium in 7—10 min. In the case when the acidic Ln(III) solution having pH 1—2, surfactant and either ammonia or buffer solution were consecutively added to the aqueous solution of CAS the equilibrium was reached in 30—40 min. Absorbance of the reaction product was stable for at least 12 h.

Sometimes recommended optimal pH interval of 5.2—6.7 [12—14, 16] was

found unsuitable owing to the acid-base equilibrium LH_2^{2-}/LH^{3-} of CAS and to high absorption of LH_2^{2-} form at $\lambda \approx 550\,\text{nm}$ ($\varepsilon \approx 1.5\,\text{m}^2\,\text{mmol}^{-1}$ at $\lambda = 550\,\text{nm}$). Therefore neutral and basic solution with pH ≥ 7 were studied, in which CAS existed exclusively in the yellow LH^{3-} form with absorption maximum at $\lambda = 420\,\text{nm}$ and with negligible absorbance in the long-wavelength region of the spectrum ($\varepsilon = 0.04$—$0.08\,\text{m}^2\,\text{mmol}^{-1}$ at $\lambda = 590$—$620\,\text{nm}$), despite the marked decline of the selectivity.

As model ions, representing the whole lanthanoide group, served La(III), Yb(III), Gd(III), Y(III), for which detailed measurements were carried out. For the rest of the group only basic data were determined.

Analyzing the absorption spectra of solutions containing La(III), CAS, and CTMAB (Fig. 2) we could infer that under given experimental conditions (c_L(CAS) = 74.6 μmol dm^{-3}, c_M(La(III)) = 10 μmol dm^{-3}, c_T(CTMAB) = = 0.2 mmol dm^{-3} at pH = 7—11) at least two reaction products were formed, having absorption maxima at $\lambda = 620$ and 650 nm, respectively.

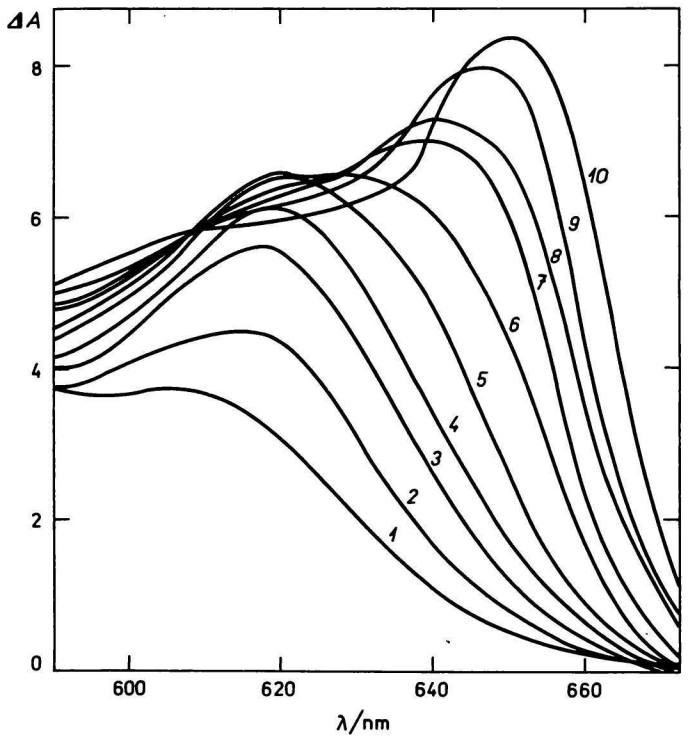

Fig. 2. Absorption spectra of La(III)—CAS—CTMAB solutions.
The curve for pH: *1.* 7.18; *2.* 7.63; *3.* 8.10; *4.* 8.41; *5.* 8.73; *6.* 9.14; *7.* 9.47; *8.* 9.61; *9.* 9.93; *10.* 10.11.

Absorbance *vs.* pH plots ($\Delta A = f(\mathrm{pH})$) for the absorption maximum at $\lambda = 620$ nm displayed a near flat curve at pH = 8.8—9.6, with less than 3 % of ΔA. For the absorption maximum at $\lambda = 650$ nm similar curve showed a flat part at pH = 9.8—10.2. The latter maximum had higher molar absorptivity ($\varepsilon = 9.2\,\mathrm{m^2\,mmol^{-1}}$) than that at $\lambda = 620$ nm ($\varepsilon = 6.3\,\mathrm{m^2\,mmol^{-1}}$) in the pH interval 9.2 ± 0.4.

Absorbance *vs.* pH curves for various CTMAB concentrations in the range of 0.05—0.5 mmol dm^{-3} (other parameters as above) show that the reaction product with absorption maximum at $\lambda = 620$ nm forms quantitatively in the narrow interval of c_T(CTMAB) = 0.1—0.2 mmol dm^{-3}. At both higher and lower CTMAB concentrations its formation is suppressed (Fig. 3). The reaction product with the absorption maximum at $\lambda = 650$ nm is formed in still narrower range of CTMAB concentration (c_T(CTMAB) = 0.1—0.15 mmol dm^{-3}).

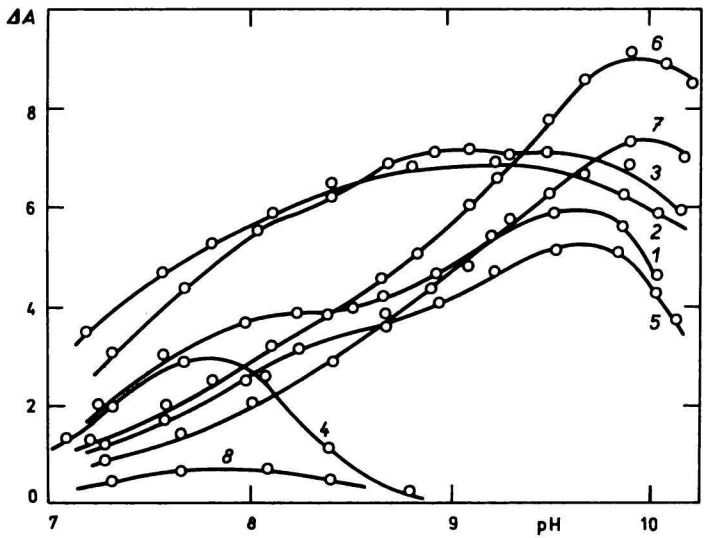

Fig. 3. Absorbance *vs.* pH curves for the La(III)—CAS—CTMAB system at $\lambda = 620$ nm or $\lambda = 650$ nm (curves *1*—*4* and *5*—*8*, respectively).
The curve for c_T(CTMAB)/(mmol dm^{-3}): *1*. 0.05; *2*. 0.1; *3*. 0.2; *4*. 0.4; *5*. 0.05; *6*. 0.1; *7*. 0.2; *8*. 0.4.

The optimal range of CTMAB concentrations can be influenced by changing the CAS/CTMAB concentration ratio. Thus for c_M(La(III)) = 0.01 mmol dm^{-3} and c_L(CAS) = 0.15 mmol dm^{-3} optimal concentration range of CTMAB was, for product with the absorption maximum at $\lambda = 620$ nm ($\varepsilon = 6.0\,\mathrm{m^2\,mmol^{-1}}$), 0.4—0.5 mmol dm^{-3} in the pH interval of 9.2—9.6. The formation of the second

product with the absorption maximum at $\lambda = 650$ nm was under such conditions strongly suppressed (Fig. 4). At optimal CTMAB but half CAS concentrations the solutions of the ternary system La(III)—CAS—CTMAB became turbid and simultaneously with the rising CTMAB concentration the optimal pH interval was shifted to lower values.

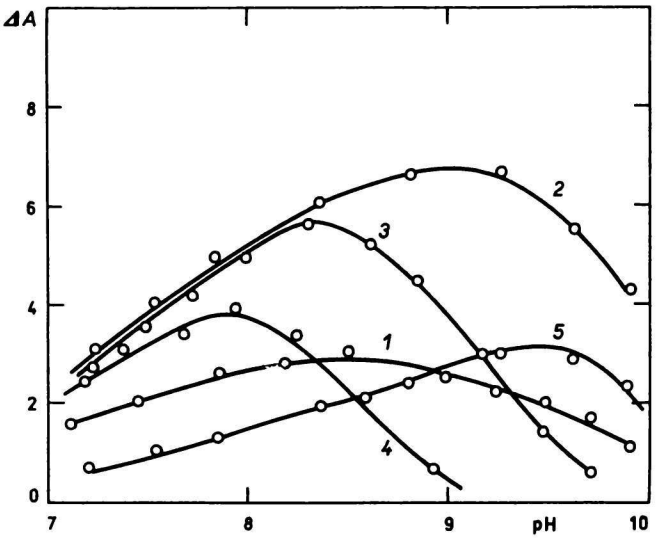

Fig. 4. Absorbance *vs.* pH curves for the La(III)—CAS—CTMAB system at $\lambda = 620$ nm (curves *1*—*4*) and $\lambda = 650$ nm (curve *5*).
The curve for c_T(CTMAB)/(mmol dm^{-3}): *1.* 0.05; *2.* 0.4; *3.* 0.8; *4.* 1.0; *5.* 0.05.

The dependence of the absorbance on CAS concentration, shown in Fig. 5 illustrates that at c_T(CTMAB) = 0.1 mmol dm^{-3} and c_M(La(III)) = 0.01 mmol · dm^{-3} both reaction products, at $\lambda = 620$ nm (pH = 9.2—9.6) and at $\lambda = 650$ nm (pH ≈ 10), are formed quantitatively for c_L(CAS) = 0.04—0.08 mmol dm^{-3}. At higher CTMAB concentrations quantitative formation of both products requires higher CAS concentrations. For other experiments the following concentrations were selected as optimal: c_L(CAS) = 0.08 mmol dm^{-3}, c_T(CTMAB) = 0.2 mmol dm^{-3} in the pH interval 9.4 ± 0.2 for the reaction product with the absorption maximum at $\lambda = 620$ nm and c_T(CTMAB) = = 0.1 mmol dm^{-3} at pH ≈ 10 for the reaction product with the absorption maximum at $\lambda = 650$ nm.

The dependence of absorbance of CAS and CTMAB solutions on La(III) concentration, measured at $\lambda = 650$ nm ($\Delta A = f(c_M)$), was quite nonlinear at low La(III) concentrations, due to changes of spectral properties (Fig. 6) of the second reaction product ($\lambda_{max} = 650$ nm) at c_M(La(III)) < 2 μmol dm^{-3}. In con-

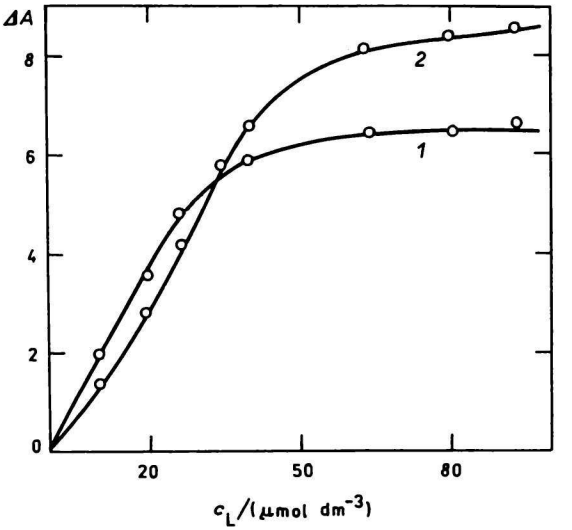

Fig. 5. Concentration dependence $\Delta A = f(c_L)$ for the La(III)—CAS—CTMAB system at $\lambda = 620$ nm or $\lambda = 650$ nm (curves *1* and *2*).
The curve for pH: *1.* 9.4; *2.* 9.9.

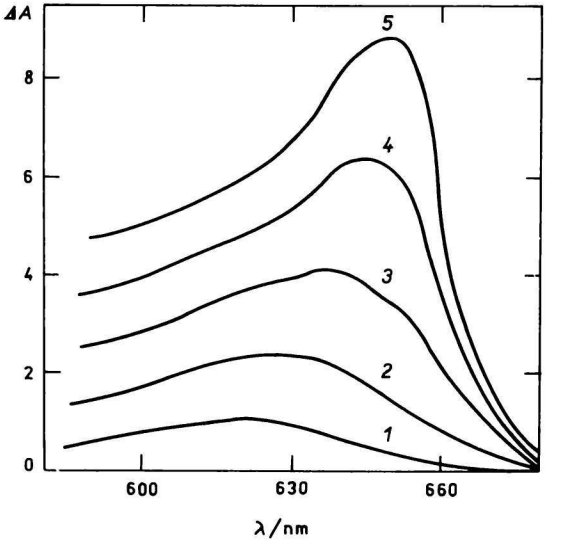

Fig. 6. Absorption spectra of the La(III)—CAS—CTMAB system, taken at variable concentration of La(III) ions.
c_L(CAS) = 74.6 μmol dm^{-3}; c_T(CTMAB) = 0.1 mmol dm^{-3}; pH = 9.6.
The curve for c_M(La)/(μmol dm^{-3}): *1.* 2.0; *2.* 4.0; *3.* 6.0; *4.* 8.0; *5.* 10.0.

ditions optimal for the formation of the second product decreasing La(III) concentration elicited a hypsochromic shift of the 650 nm maximum to 620 nm. This is probably due to lower stability of the product with the maximum at $\lambda = 650$ nm at lower La(III) concentrations, when it is transformed to the more stable product with the absorption maximum at $\lambda = 620$ nm.

Unfortunately we could not find conditions suitable for the quantitative formation of more absorbing reaction product ($\varepsilon = 9.0\,\mathrm{m^2\,mmol^{-1}}$ at $\lambda = 650$ nm). Hence for the analytical determination of other lanthanoides the more stable reaction product with a maximum at $\lambda = 620$ nm under the above-mentioned conditions was selected, in spite of its inferior optical characteristics.

ΔA *vs.* pH plots of 1×10^{-5} M-Gd(III) and -Yb(III) solutions at the selected optimal CAS concentrations and c_T(CTMAB) = 0.05—1 mmol dm^{-3} were quite analogous to those measured for the La(III)—CAS—CTMAB system. Maximal absorbances were reached at c_T(CTMAB) = 0.2—0.4 mmol dm^{-3} for Gd(III) and at c_T(CTMAB) = 0.1—0.4 mmol dm^{-3} for Yb(III), always in the pH interval of 9.0—9.6.

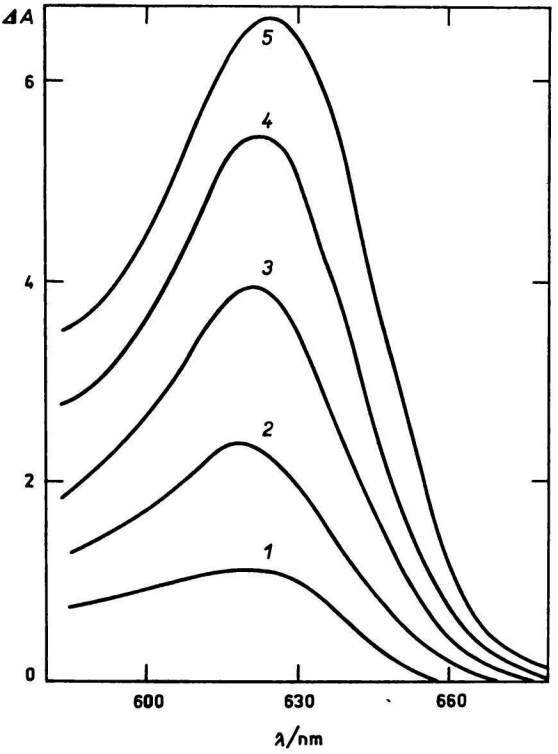

Fig. 7. Absorption spectra of the La(III)—CAS—CPB system, taken at variable concentration of La(III) ions.
c_T(CPB) = 0.2 mmol dm^{-3}; pH = 9.4; $\varphi(C_2H_5OH)$ = 10 %, other parameters as in Fig. 6.

Optimal experimental conditions were found adequate both for determination of La(III) and Gd(III) or Yb(III). It can be safely assumed that they would do for other lanthanoides and yttrium as well. Assuming this, calibration curves $\Delta A = f(c_M)$ at $\lambda = 620$ nm in 0.1 M ammonia buffer with pH = 9.4 were measured for all lanthanoides and yttrium.

In contrast to the ternary system La(III)—CAS—CTMAB in the system La(III)—CAS—CPB the formation of the product with the absorption maximum at $\lambda = 650$ nm was suppressed, as can be seen from the absorption spectra of solutions, containing La(III), CAS, and CPB (Fig. 8) as well as from ΔA *vs.* pH plots at c_T(CPB) = 0.05—1 mmol dm^{-3} and under conditions, given in Figs. 7 and 8.

At CAS concentration 0.08 mmol dm^{-3} optimal CPB concentration was 0.2—0.4 mmol dm^{-3} and molar absorption coefficient reached values of 6.7 m^2 mmol^{-1} in the pH interval of 9.2—9.4. At higher CAS concentrations

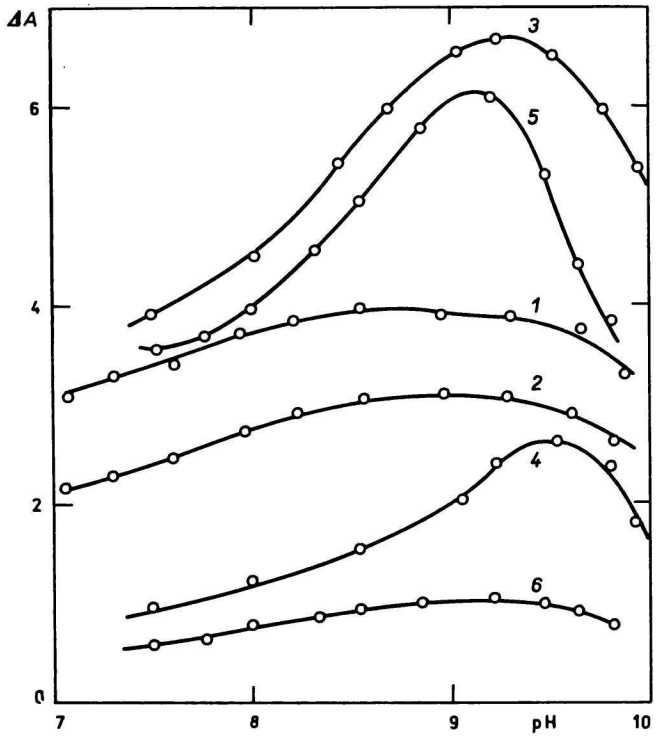

Fig. 8. Absorbance *vs.* pH curves $\Delta A = f$(pH) for the La(III)—CAS—CPB system at $\lambda = 620$ nm or $\lambda = 650$ nm (curves *1*—*3* and *4*—*6*, respectively).
c_M(La(III)) = 10 μmol dm^{-3}; c_L(CAS) = 162 μmol dm^{-3}; $\varphi(C_2H_5OH)$ = 10 %.
The curve for c_T(CPB)/(mmol dm^{-3}): *1*. 0.05; *2*. 0.05; *3*. 0.2; *4*. 0.2; *5*. 0.5; *6*. 0.5.

optimal CPB concentrations shifted to higher c_T(CPB) values. Thus at c_L(CAS) = 0.242 mmol dm^{-3} the optimal concentration of CPB was 0.4—0.6 mmol dm^{-3}, whereby the ε value increased to 6.8—6.9 m^2 mmol^{-1}, compared with solutions, in which c_L = 74.6 μmol dm^{-3}. In order to ensure maximum reaction yield for all studied lanthanoides, further measurements were performed under the following experimental conditions: $c_M \geq 2$ μmol dm^{-3}, c_L(CAS) = 0.08 mmol dm^{-3}, c_T(CPB) = 0.2 mmol dm^{-3}, in 0.1 M ammonia buffer (pH = 9.4).

When it comes to analytical applications, the system La(III)—CAS—SPX is of little interest, since at SPX concentrations 0.1—0.3 mmol dm^{-3} and c_M(La(III)) = 0.01 mmol dm^{-3} and c_L(CAS) = 0.08 mmol dm^{-3} the solution becomes turbid and at both higher and lower SPX concentrations the formation of products with absorption maxima at 620 nm and 650 nm is strongly suppressed. When the CAS concentration is increased to 0.15 mmol dm^{-3} the turbidity region encompasses the entire SPX concentration range 0.08—0.5 mmol dm^{-3}.

Calibration curves $\Delta A = f(c_M)$ were measured for all lanthanoides and yttrium under optimal experimental conditions and for the systems Ln(III)—CAS—CTMAB and Ln(III)—CAS—CPB. To the 25 cm^3 calibrated flasks 0.0—2.5 cm^3 of 0.0001 M acidic Ln(III) and Y(III) solutions and 5 cm^3 of reagent, having pH 9.4 (see above) were given. After dilution to 25 cm^3, mixing and 5 min delay, the absorbance at λ = 620 nm was measured against blank.

Experimental data were subjected to linear least-square analysis by standard routine software and its results are given in Table 1.

The values of molar absorption coefficients are for both cationic surfactants as well as for all lanthanoides and yttrium practically identical and occupy a narrow interval of values, 6.3—7.05 (for CTMAB) and 6.8 to 8.2 (for CPB), respectively. All calibration curves gave high correlation coefficients r_{xy} = 0.9963—0.9995 and negligible A_0 intercept. The value of t-criterion, equal to $|A_0|/s_a$ was usually lower than the critical value (t_c = 2.57) for the 0.95 level of confidence and $n - 2 = 4$ degrees of freedom. The standard deviation s_0 reached 0.01—0.02, *i.e.* values only 2—4 times higher than the declared precision of absorbance measurement on Specord M 40.

Detection limit of the lanthanoide determination, given as $3s_0$ criterion (DL = $3s_0/\varepsilon$) is only marginally better for CPB over CTMAB (DL = 0.36—0.63 and 0.49—0.90 μmol dm^{-3}, respectively, path length l = 10 mm).

Out of routinely used complexing reagents, used for elution of lanthanoides in HPLC or IEC chromatography tartrates do not interfere up to concentrations of 0.01 mol dm^{-3}, glycine and α-hydroxybutyric acid (HIBA) up to 0.2 mol dm^{-3}. Conversely, at concentrations exceeding 0.001 mol dm^{-3} EDTA, NTA, IDA, citric acid as well as other complexing reagents disturb the elution by interfering with the product formation.

Table 1

Statistical parameters of calibration curves $\Delta A = f(c_M)$ of lanthanoides and of yttrium with Chrome Azurol S and with either CPB or CTMAB $c_L(\text{CAS}) = 0.08\ \text{mmol dm}^{-3}$; $c_T(\text{CPB or CTMAB}) = 0.2\ \text{mmol dm}^{-3}$; $c_M(\text{La(III)}) = 2\text{—}20\ \mu\text{mol dm}^{-3}$; 0.1 M solution of ammonia buffer at pH = 9.4, $\lambda = 620$ nm, the curve constructed of $n = 6$ points

Ion	CTMAB				CPB			
	$-100a$	ε / $\text{m}^2\ \text{mmol}^{-1}$	$100s_0$	DL / $\mu\text{mol dm}^{-3}$	$-100a$	ε / $\text{m}^2\ \text{mmol}^{-1}$	$100s_0$	DL / $\mu\text{mol dm}^{-3}$
La^{3+}	2.2 ± 1.5	6.33 ± 0.20	1.9	0.90	1.4 ± 0.9	6.81 ± 0.14	1.2	0.53
Ce	1.5 ± 0.9	6.58 ± 0.12	1.1	0.50	1.5 ± 1.0	6.95 ± 0.18	1.4	0.60
Pr	2.6 ± 1.2	6.64 ± 0.22	1.6	0.72	1.2 ± 1.2	7.58 ± 0.22	1.6	0.63
Nd	2.4 ± 1.1	6.88 ± 0.18	1.5	0.65	1.6 ± 0.8	7.57 ± 0.13	1.3	0.52
Sm	2.7 ± 1.3	6.70 ± 0.17	1.4	0.63	1.7 ± 0.9	7.29 ± 0.11	1.2	0.49
Eu	2.5 ± 1.2	6.66 ± 0.19	1.5	0.68	1.2 ± 1.1	7.58 ± 0.20	1.4	0.55
Gd	2.4 ± 1.0	6.85 ± 0.17	1.3	0.57	1.4 ± 0.9	7.87 ± 0.15	1.3	0.50
Tb	2.6 ± 1.2	6.61 ± 0.16	1.4	0.64	0.9 ± 0.9	7.71 ± 0.09	1.2	0.47
Dy	2.5 ± 1.4	6.96 ± 0.15	1.2	0.52	1.2 ± 1.2	7.67 ± 0.24	1.3	0.51
Ho	2.0 ± 1.1	6.90 ± 0.19	1.3	0.57	1.3 ± 0.9	7.98 ± 0.11	1.1	0.41
Er	1.1 ± 0.8	6.75 ± 0.13	1.1	0.49	1.0 ± 1.2	7.83 ± 0.29	1.3	0.50
Yb	1.8 ± 1.0	7.05 ± 0.18	1.2	0.51	1.5 ± 0.9	7.85 ± 0.15	1.0	0.36
Y	2.3 ± 1.0	7.01 ± 0.17	1.4	0.60	1.7 ± 0.8	8.17 ± 0.13	1.1	0.40

a — y-intercept.

The reaction of CAS with Ln(III) and Y(III) in the presence of CTMAB or CPB was utilized for spectrophotometric determination by flow injection method, following the chromatographic separation. To the stream of the mixed reagent (see above) with the constant flow rate 1 $cm^3 min^{-1}$ 30 mm^3 of acidic Ln(III) or Y(III) solution, having the starting concentration 1—20 $\mu mol\, dm^{-3}$, was injected. The absorbance of the reaction product was registered as a sharp peak, belonging to the reaction zone flowing through the 18 mm^3 flow cell. The peak hight at optimal flow rate 1 $cm^3 min^{-1}$ and optimal length of reaction capillary $l = 40$ cm was a linear function of the Ln(III) or Y(III) concentration of the injected sample volume in the entire interval $c_M = 2$—20 $\mu mol\, dm^{-3}$, with the corresponding statistical parameters of a line, expressed by the equation $y = ax + b$

$$A_{620} = -0.19 + 3.76 \times 10^6 c_M$$

$$A_{650} = -1.77 + 5.16 \times 10^6 c_M$$

for wavelength $\lambda = 620$ nm ($s_a = 1.87$, $s_b = 0.23 \times 10^6$, $s_0 = 2.80$) or for $\lambda = 650$ nm ($s_a = 2.77$, $s_b = 0.25 \times 10^6$, $s_0 = 4.49$).

Detection limit, defined as above, was 2.3 $\mu mol\, dm^{-3}$ at $\lambda = 620$ nm and 2.6 $\mu mol\, dm^{-3}$ at $\lambda = 650$ nm, allowing one to determine 10—12 ng of La(III) in the injected 30 mm^3 sample volume. The corresponding standard deviation of the measurement of analytical signal depends on La(III) concentration in the sample and equals 0.05 and 0.13 at $\lambda = 620$ nm, and 0.04 and 0.11 at $\lambda = 650$ nm at the respective 20 and 2 $\mu mol\, dm^{-3}$ La(III) concentrations.

In the same manner other lanthanoides and yttrium can be determined, the detection limit being similar, 2.5 $\mu mol\, dm^{-3}$ for Gd(III), 3.1 $\mu mol\, dm^{-3}$ for Yb(III), and 2.3 $\mu mol\, dm^{-3}$ for Y(III).

From the above given results it is clear that the Ln(III)—CAS—CTMAB and Ln(III)—CAS—CPB systems are suitable for highly sensitive analysis of separate lanthanoide and yttrium ions as well as for the determination of their total content. The found values of molar absorption coefficients are marginally higher than those measured for the so far most sensitive reaction with Arzenazo III [19] or its analogues. The reaction of Ln(III) with CAS in the presence of CPB is slightly more sensitive than in the presence of CTMAB, but both reactions are poorly selective [1—5, 19]. Under the conditions used for the determination of lanthanoides many other ions of elements give analogous reaction products often with much higher molar absorption coefficients [19]. Therefore the reaction can be utilized effectively for determination of the total lanthanoide content, if it is preceded by efficient separation of ions of transition metals on ion exchangers, as well as for highly sensitive postcolumn detection of lanthanoide ions in the visible region following their separation by various HPLC or IEC chromatographic methods.

References

1. Pılipenko, A. T. and Tananaiko, M. M., *Raznoligandnye i raznometallnye kompleksy i ikh primenenie v analiticheskoi khimii.* P. 101. Khimiya, Moscow, 1983.
2. Tikhonov, V. N., *Zh. Anal. Khim. 32,* 1435 (1977).
3. Savvin, S. B., *CRC Crit. Rev. Anal. Chem. 8,* 55 (1979).
4. Marczenko, Z., *CRC Crit. Rev. Anal. Chem. 11,* 195 (1981).
5. Savvin, S. B., Chernova, R. K., and Kudryavtseva, L. M., *Zh. Anal. Khim. 34,* 66 (1979).
6. Chernova, R. K., *Zh. Anal. Khim. 32,* 1477 (1977).
7. Chernova, R. K., *Zh. Anal. Khim. 33,* 1934 (1978).
8. Kirillov, A. I., Makarenko, O. P., Poluektov, N. S., Lauer, R. S., and Shaulina, L. P., *Zh. Anal. Khim. 28,* 1618 (1973).
9. Verkhande, C. and Munshi, K. N., *J. Indian Chem. Soc. 52,* 939 (1975).
10. Belousova, V. V., Chernova, R. K., and Sukhova, L. K., *Zavod. Lab. 44,* 390 (1978).
11. Poluektov, N. S., Ovchar, L. A., and Lauer, R. S., *Zh. Anal. Khim. 28,* 1958 (1973).
12. Verkhande, C. and Munshi, K. N., *Indian J. Chem. 14A,* 189 (1976).
13. Klopf, G. J. and Cook, K. D., *Anal. Chim. Acta 162,* 293 (1984).
14. Verkhande, C. and Munshi, K. N., *Microchem. J. 23,* 28 (1978).
15. Němcová, I., Plocková, P., and Tran Hong Con, *Collect. Czechoslov. Chem. Commun. 47,* 503 (1982).
16. Jarosz, M. and Marczenko, Z., *Anal. Chim. Acta 159,* 309 (1984).
17. Pollaková-Mouková, N., Gotzmannová, D., Kubáň, V., and Sommer, L., *Collect. Czechoslov. Chem. Commun. 46,* 354 (1981).
18. Baldwin, W. G. and Stranks, D. R., *Aust. J. Chem. 21,* 603 (1968).
19. Savvin, S. B., *Organicheskie reagenty gruppy Arzenazo III.* Atomizdat, Moscow, 1971.

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