THE SPECTROPHOTOMETRIC DETERMINATION OF ELEMENTS WITH CHROMAZUROL S IN THE PRESENCE OF CETYLTRIMETHYLAMMONIUM BROMIDE AND TRITON X-100.

I. THE DETERMINATION OF THE SUM OF THE RARE EARTH ELEMENTS

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Received July 28, 1992
Accepted November 22, 1992

The study of the interactions of the rare earth elements (REE) with chromazurol S in the presence of a cationic and nonionic tenside permitted a number of general conclusions to be drawn for the effect of tensides on the chromogenic analytical reaction. The ternary ion associate with chromazurol S and cetyl trimethyl ammonia in the presence of Triton TX-100 is useful for the sensitive spectrophotometric determination of REE in mixtures and in hydroxide concentrates.

Chromazurol S (CAS) as a triphenyl methane dye with a salicylic acid functional group, in the presence of cationic and nonionic tensides, is a sensitive but nonselective reagent for the transition and heavy element cations. Binary and especially ternary Me–CAS–tenside associates are formed, with an elevated molar absorption coefficient, accompanied by a bathochromic shift of the absorption maximum. Their composition and especially structure need not be clear; however, they are usually stabilized in micellar tenside medium. It is important here that the reagent is a polybasic acid, where some of the pK_a values are greatly affected by the formation of the binary associate[1 – 4], e.g. for chromazurol S in the formation of the binary associate with the tenside cation $\{H_2L^{2-}, 2T^+\}$, the pK_a(COOH) value decreases from p$K_a \approx 2.3$ to p$K_a \approx 1.0$ (refs[1,3]).

A number of explanations have been proposed to explain the tenside phenomenon[5 – 7]; however, none sufficiently explains the behaviour of the system.

The interactions of the ions of some lanthanoids, Y and La with CAS and cationic tensides have been studied in the past[8 – 13]. An attempt to reproduce the published results led to ambiguities, time instability, the formation of turbidity and rapid decomposition of the associates under the given conditions.

This work described the determination of optimum conditions for the formation of the ion associates, corresponding to a quaternary system with a nonionic tenside (REE–CAS–cetyltrimethylammonium bromide–Triton X-100) with a critical concentration of cationic tenside in aqueous media. These conditions permit the sensitive spectrophotometric determination of the sum of the REE in mixtures and hydroxide concentrates.

EXPERIMENTAL

Chemicals

CAS – trisodium salt of 2″,6″-dichloro-3″-sulfo-3,3′-dimethyl-4-hydroxyfuchson-5,5′-dicarboxylic acid, $C_{23}H_{13}Cl_2O_9SNa_3$, M_r = 605.3, a product of the Merck, Germany. The product did not contain coloured impurities (chromazurol B and metal chelates of impurities) detectable by TLC on silica gel with a butanol–concentrated acetic acid–water 7 : 1 : 5 mobile phase. The active component content recalculated to the trisodium salt was 60.0%, found by elemental analysis from the carbon content and potentiometric titration with 0.1 M NaOH from the difference between the consumption between the inflection point for the second carboxyl proton and the inflection point for a defined amount of 0.1 M HCl added prior to the titration to an aqueous solution of the dye[14,15]. The weighed amounts were corrected for the active component content.

The stock solution of CAS with a concentration of c_L = 1.25 mmol l^{-1} was prepared by dissolving a precisely weighed amount of substance in redistilled water with addition of two drops of concentrated NH_3 solution, transferred to a 50 ml volumetric flask and filled to the mark. The stock solution was used for two days at most.

Cetyltrimethylammonium bromide (CTMA) – $C_{19}H_{42}BrN$, M_r = 364.46, cetylpyridinium bromide (CP) – $C_{12}H_{38}BrN$, M_r = 384.45, products of Lachema, Brno; 1-ethoxycarbonylpentadecyltrimethyl ammonium bromide (Septonex) – $C_{21}H_{44}O_2BrN$, M_r = 384.45, the product of Spofa, Prague; cetyldimethylbenzylammonium bromide (CDBA) – $C_{24}H_{44}BrN$, M_r = 396.1, product of BDH Chemicals, England. The commercial products were repurified by dissolving about 5 g of the tenside in a small amount of hot ethanol (50 ml) and filtering through an S4 glass frit, followed by precipitation with diethyl ether (500 ml). The crystals formed were separated on an S4 glass frit and dried in the air and in a desiccator above anhydrous $CaCl_2$. Stock solutions were prepared in ethanol with a tenside concentration of 10 – 40 mmol l^{-1}. The stock solutions are stable for at least one month.

Benzyldimethyllaurylammonium bromide (Sterinol) – $C_{21}H_{38}BrN$, M_r = 384.45, the product of the Galenus Co., Poland, was a 10% aqueous solution.

Triton X-100 (TX-100) – octylphenolpolyethyleneglycol ether, $C_{14}H_{21}(OCH_2CH_2)_nOH$, M_r ≈ 650, product of scintillation purity from the Koch–Light Laboratories Ltd., England.

The stock 1% aqueous solutions of the above two tensides were used for one month at the most.

The standard 0.05 M REE solutions were prepared by dissolving defined weights of the nitrates (La, Pr, Nd, Sm, Gd, Tb, Er), oxides (Y, Ho, Lu), carbonates (Dy, Tm, Yb) and chloride (Eu) in HNO_3. The final HNO_3 concentration was 0.1 mol l^{-1}. The chemicals employed were of chemical or spectral purity from Lachema, Brno, Czech Republic; Fluka, Switzerland; Soyuzkhimexport, C.I.S.; and Loba Chemie, Austria.

The contents of the elements in solution was checked by EDTA titration over xylenol orange at pH 5.0 – 5.5.

Hydroxide concentrate of REE 086/85, Minerals Research Institute, Kutná Hora, Czech Republic. Mean values of the contents of the sums of the REE oxides: 98.2% (41.0% Ce, 26.2% La, 18.4% Nd, 5.3% Pr, 7.2% other REE's). The preparation of the concentrate solutions is described below.

Ethanol containing 5% methanol was purified by distillation after addition of EDTA (approx. 2 g l^{-1}). Ethanol must not remain in contact with EDTA for longer than 2 weeks. Redistilled water from an all-quartz apparatus from the Heraeus Co., Germany, was employed.

All the remaining chemicals were of analytical purity or were doubly distilled from aqueous solutions.

Instruments

The spectrophotometric measurements were carried out on a Specord M40 double-beam recording spectrophotometer and Spekol 211 single-beam spectrophotometer (both from Zeiss, Jena, Germany) in quartz cuvettes with a path length of 10 mm.

A digital Radelkis 208/1 pH meter (Radelkis, Hungary) was used with a combined GK 2301 electrode (Radiometer, Copenhagen, Denmark). Calibration was carried out using standard S 1306 (pH 4.01) and S 1336 (pH 9.18) buffers from Radiometer, Copenhagen, Denmark. The electrode was washed daily with hot ethanol to remove adsorbed tensides and associates.

Preparation of Working Solutions

Prior to the measurements, the components were mixed in the order sample (solution of REE cations), 0.1 M HNO_3 to adjust the acidity, tenside solutions and reagent solutions. The final pH adjustment was carried out using an NH_3 solution and a pH meter prior to diluting the final solution to the mark in the volumetric flask with water. It is sometimes useful to add an optimized mixture of reagent and tenside to the acidic solution of REE cations: $c_L = 0.715$ mmol l^{-1}, $c_{CTMA} = 1.56$ mmol l^{-1}, $c_{Triton} = 0.08$ wt.%.

Decomposition of the Hydroxide Concentrate

An amount of 0.25 g of finely ground hydroxide concentrate was dispersed in 3 ml of water in a 50 ml beaker and was decomposed after 15 min by the addition of 2 ml concentrated HCl and 0.5 ml 30% H_2O_2 with heating. After completion of the reaction, the solution was evaporated to dryness, the residue was dampened with 2 ml of concentrated HCl and, after addition of 10 ml of hot water, was heated to complete dissolution. The solution was filtered through medium-density filter paper, the paper was burned in a platinum crucible, the ash was decomposed with heating in a mixture of 1 ml of concentrated $HClO_4$ and 3 ml concentrated HF, the solution was evaporated to dryness and the extract of the residue in 3 ml HCl (1 : 1) was combined with the filtrate. After evaporation of the solution to dryness, 5 ml of 1 M HNO_3 were added and the solution was diluted to 50 ml with water. The working solutions were prepared by diluting this solution one hundredfold. The weighed amount of hydroxide concentrate was corrected for the water content, which was found as the decrease in mass of 0.200 g of concentrate after annealing for half an hour in a platinum crucible.

Evaluation of the Data

The calibration dependence was treated by regression analysis by the STAT-G program[15] on a PC/AT microcomputer on the basis of at least 6 concentration values in the linear part of the dependence and at least 5 blank values. The program includes the Student significance test of intercept q, test of the linearity of the scatter analysis (F-test), Grubbs test of remoteness of values on the calibration curve and the blank, calculation of the molar absorption coefficient ε, intercept q, the deviations of these values and the detection limits.

RESULTS AND DISCUSSION

The CAS–Cationic Tenside T^+ System

As the pH value changes, the binary associates $\{H_2L^{2-}, 2T^+\}$ and $\{HL^{3-}, 3T^+\}$ are gradually formed in solution. The first is more stable and is readily deposited from solution as the tenside concentration approaches the stoichiometric ratio in the associate. The limiting ratio c_{T^+}/c_L required to retain the associate in solution is dependent on the given tenside, pH and ionic strength of the solution.

In the presence of CTMA, turbidity is not formed in solution at pH > 6 even for a ratio $c_{T^+}/c_L = 3$. At pH < 6, with increasing amount of the H_2L^{2-} form and with increasing ionic strength, it is necessary that $c_{T^+}/c_L > 4$. A slight bump appears on the spectrum at 580 – 590 nm and simultaneously the positions of the short-wavelength absorption maxima of H_2L^{2-} and HL^{3-} change. Especially in the presence of micellar concentrations of CTMA, the equilibrium of H_2L^{2-} (λ_{max} = 512 nm) and HL^{3-} (λ_{max} = 415 nm) is shifted in favour of HL^{3-}, where the pK_a change is −0.85 (at c_L = 30.0 μmol l^{-1} and c_{CTMA} = 1 200 μmol l^{-1}). The limiting concentration ratio, c_{T^+}/c_L = 3.1 is analogously valid for CP. Sterinol, CDBA and Septonex form more stable associates at pH < 6. More marked spectral changes, apparently caused by the associate $\{H_2L^{2-}, 2T^+\}$, appear at 580 – 590 nm. The associate is reliably solubilized at micellar tenside concentrations, i.e. at $c_{T^+}/c_L \approx 6$ (Septonex) or $c_{T^+}/c_L \approx 10$ (Sterinol, CDBA). The differences between the conditional pK_a (H_2L^{2-}/HL^{3-}) values found in this work and those published in the literature[3] are a result of the different ionic strength of the solution (I = 0.002 mol l^{-1} ($HNO_3 + NH_3$) in this work).

The effect of the nonionic tenside Triton X-100 on the spectra of CAS and changes in the pK_a value are negligible for I = 0.002 mol l^{-1}, in contrast to earlier observations for I = 0.1 mol l^{-1} (ref.[3]).

The Ce–CAS–Cationic Tenside System

Marked differences between the spectra of the binary and ternary systems can be seen from Figs 1 and 2. It follows from measurements in the Ce–CAS–CTMA system at pH

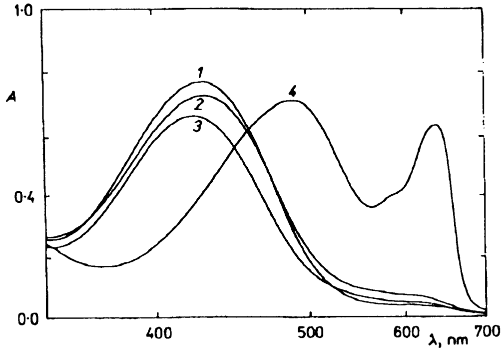

FIG. 1

Absorption spectra in the Ce–CAS–CTMA system. c_{Ce} = 10.33 μmol l^{-1}, c_L = 40.0 μmol l^{-1}, c_{CTMA} = 120 μmol l^{-1}, pH 8.0, I = 0.004 mol l^{-1} ($HNO_3 + NH_3$). *1* CAS; *2* Ce–CAS; *3* CAS–CTMA; *4* Ce–CAS–CTMA

5.8 – 10.2 and in dependence on the concentration of cationic tenside that two ternary associates are probably formed, the first with λ_{max} = 624 nm and the second with λ_{max} = 650 nm, with the latter predominating at pH > 8.5. In the presence of a small excess of tenside versus CAS, at c_{Ce} = 10.33 μmol l^{-1}, c_L = 40.0 μmol l^{-1} and c_{CTMA} = 120 μmol l^{-1}, the absorbance greatly increases in the 600 – 650 nm region, with a simultaneous shift of λ_{max} for HL^{3-} from 426 nm to the 490 – 500 nm region. At a constant ratio c_{T^+}/c_L = 3.14, the optimum pH for the associate with λ_{max} = 624 nm shifts in dependence on the reagent concentration between c_L = 31.8 – 143 μmol l^{-1} from pH 8.0 to pH 9.0. The ion associate with λ_{max} = 650 nm appears in this pH interval at a small reagent excess c_L = 31.8 – 63.6 μmol l^{-1}, corresponding to c_L/c_{Ce} < 6 at pH > 8.5. The absorption maximum of $\{HL^{3-}, 3T^+\}$ at 415 nm is shifted to 490 – 500 nm in the presence of Ce^{3+} and the cationic tenside CTMA at pH 8, i.e. to a value close to λ_{max} = 512 nm for the $\{H_2L^{2-}, 2T^+\}$ form. The absorbance at this maximum increases with increasing c_{Ce} at constant pH and c_L, or with increasing c_L at constant pH and c_{Ce}. However, as the pH increases in the region 6 – 10, the absorbance of the long wavelength absorption maximum of the reagent decreases and its position shifts back to shorter wavelengths (450 nm at pH 10 in solutions with c_{Ce} = 8.26 μmol l^{-1}, c_L = 40.0 μmol l^{-1}, and c_{CTMA} = 120 μmol l^{-1}, see Fig. 2).

The formation of the analytically more useful associate of Ce^{3+} with λ_{max} = 624 nm at pH 8.8 requires at least a sixfold excess of CAS compared to Ce^{3+} at an optimum ratio of c_{CTMA}/c_L ≈ 3.1 to yield maximum solution absorbance (Fig. 3). The formation

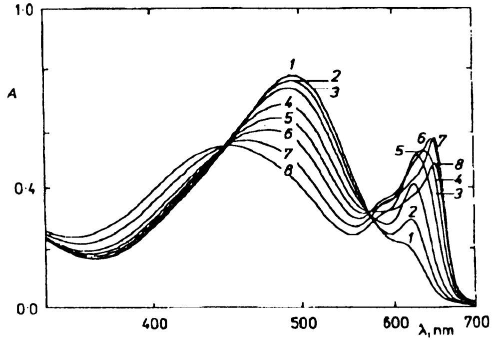

FIG. 2

Absorption spectra in the Ce–CAS–CTMA system in dependence on the pH. c_{Ce} = 8.26 μmol l^{-1}, c_L = 40.0 μmol l^{-1}, c_{CTMA} = 120 μmol l^{-1}, I = 0.004 mol l^{-1} (HNO_3 + NH_3). pH: *1* 5.82; *2* 6.43; *3* 7.04; *4* 7.82; *5* 8.37; *6* 8.91; *7* 9.62; *8* 10.18

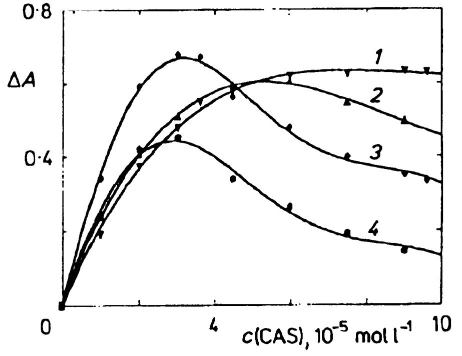

FIG. 3

Dependence of the differential absorbance on the CAS concentration in the Ce–CAS–CTMA system. c_{Ce} = 10.33 μmol l^{-1}, c_{CTMA}/c_L = 3.14, pH: 7.8 (curves *2* and *4*), 8.8 (curves *1* and *3*), I = 0.004 mol l^{-1} (HNO_3 + NH_3). λ (nm): *1*, *2* 624; *3*, *4* 650 of the associate with λ_{max} = 650 nm is greatly suppressed at higher CAS concentrations, preventing its analytical utilization. The absorbance is not completely constant for either of the associates; at pH > 7, the absorbance increases in time with increasing reagent concentration and decreases with increasing pH. For c_{Ce} = 10.33 μmol l^{-1}, $c_L \geq$ 90 μmol l^{-1}, at a ratio of c_{CTMA}/c_L = 3.14 and ethanol content of less than 5 vol.%, the time decrease of the absorbance at 624 nm is better than –0.7 %/min for pH < 8.5 and –1.0 %/min for pH < 9.0. For the associate with λ_{max} = 650 nm, it was not possible to find conditions for which the time decrease in the absorbance would be better than –2 %/min.

The effect of the cationic tenside: the ratio c_{CTMA}/c_L is an independent variable which limits towards the stoichiometric value. For CTMA, the maximum absorbance at 624 nm is attained at a ratio of c_{CTMA}/c_L = 3.0 for c_L = 64 – 143 μmol l^{-1} and at pH 7.9 – 8.9 (see Fig. 4, curves *3*, *4*), the time decrease in the absorbance is better than –1.0 %/min. Turbidity is often formed at the limiting value $c_{CTMA}/c_L \approx$ 2.8, while at c_{CTMA}/c_L > 3.5 the formation of the associate and its time stability dramatically decrease; at c_{CTMA}/c_L > 8 the decomposition is complete after 1 min. At high CAS concentrations, c_L = 143 μmol l^{-1} the decomposition can be observed from $c_{CTMA}/c_L \approx$ 5.

The method of continuous variations indicates that, at $c_0 = c_L + c_{Ce}$ = 30 μmol l^{-1} and constant ratio of c_{CTMA}/c_L = 3.0, the ratio of the components in the associate is Ce : CAS = 1 : 2 at 624 nm and 1 : 3 at 650 nm.

In the presence of CP, the formation of the associate with λ_{max} = 650 nm is suppressed and appears only in the presence of a small excess of reagent (c_L/c_{Ce} < 5). The optimum reagent excess is c_L/c_{Ce} = 7, i.e. c_L = 70 μmol l^{-1} to c_{Ce} = 10 μmol l^{-1}, while concentrations of CAS of c_L = 70 – 150 μmol l^{-1} have no effect on the absorbance but increase the blank value. Once again, the optimum c_{CP}/c_L ratio is close to 3 (see Fig. 4, curve *2*), i.e. $c_{CP}/c_L \approx$ 3.3; at a ratio of less than 3.0, turbidity is formed. The decrease in the absorbance at 624 nm is equal to –1 %/min for optimum conditions,

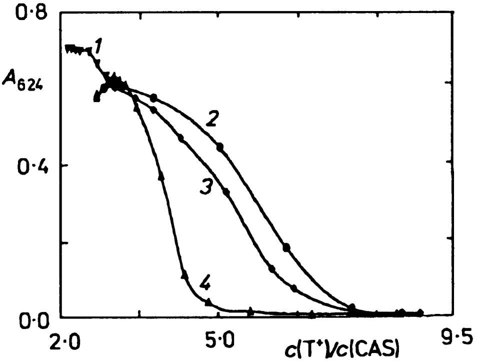

FIG. 4

Dependence of the absorbance at λ = 624 nm on the ratio c_T/c_L in various systems. c_{Ce} = 10.33 μmol l^{-1}, p_{Triton} = 0.016 wt.%, I = 0.004 mol l^{-1}. Curve (system, c_L in μmol l^{-1}, pH): *1* Ce–CAS–CTMA–Triton, 95.4, 9.5; *2* Ce–CAS–CP, 46.6, 8.2; *3* Ce–CAS–CTMA, 63.6, 7.9; *4* Ce–CAS–CTMA, 143, 8.9

pH 8.5, ethanol content of less than 5%, $c_L = 93.3$ μmol l^{-1} and $c_{CP} = 320$ μmol l^{-1}, i.e. $c_{CP}/c_L = 3.43$. At $c_L = 70$ μmol l^{-1}, $c_{Ce} = 10.33$ μmol l^{-1} and $c_{CP}/c_L = 3.43$, the optimum pH 8.1 – 8.5. As the reagent concentration increases, the optimum pH is shifted to higher values, pH 8.9, similarly as for CTMA.

In the presence of Sterinol, CDBA and Septonex, the binary associates with CAS are formed more readily, and thus turbidity appears at $c_{T^+}/c_L \leq 5$ (Septonex) or $c_{T^+}/c_L \leq 10$ (Sterinol, CDBA). At c_{T^+}/c_L ratios above the critical values, the formation of the ternary associate with $\lambda_{max} = 624$ nm is unstable in time or completely suppressed, so that these tensides are not suitable for use in combination with REE and CAS.

The Effect of the Nonionic Tenside

At concentrations of $p_{Triton} = 0.001 - 0.5$ wt.%, the nonionic tenside Triton X-100 (hereafter Triton) does not affect the Ce–CAS binary system. For $c_{Ce} = 10.33$ μmol l^{-1} and $c_L = 40$ μmol l^{-1}, only the low-absorbance associate is formed with $\lambda_{max} = 610$ nm at pH 8 – 11.

However, after the addition of Triton in an amount of $p_{Triton} = 0.010 - 0.025$ wt.% to a solution containing $c_{Ce} = 10.33$ μmol l^{-1}, $c_L = 95.4$ μmol l^{-1} and $c_{CTMA} = 208$ μmol l^{-1}, the ternary associate with $\lambda_{max} = 624$ nm is stabilized in time, the optimum pH is shifted to pH ≈ 10 and the formation of the ion associate with $\lambda_{max} = 650$ nm is sufficiently suppressed for $c_L > 100$ μmol l^{-1}. The ion associate Ce–CAS–CTMA is then not precipitated from solution even for $c_{CTMA}/c_L = 2.1$. The optimum conditions for the formation of the Ce–CAS–CTMA ternary associate with $\lambda_{max} = 624$ nm in the presence of Triton are $c_L = 63.6 - 143$ μmol l^{-1}, $c_{CTMA}/c_L = 2.3 \pm 0.2$ (see Fig. 4, curve *1*), $p_{Triton} = 0.01 - 0.02$ wt.% and pH 9.8 – 10.3. The time stability of the absorbance is then better than −0.5 %/min.

As follows from comparison of the absorption spectra (Figs 2 and 5) and other results, Triton does not participate in the formation of the associate, but only shifts the

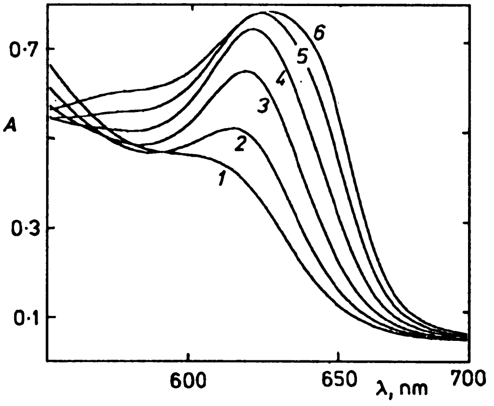

FIG. 5
Absorption spectra in the Ce–CAS–CTMA–Triton system in dependence on the pH. $c_{Ce} = 10.33$ μmol l^{-1}, $c_L = 143$ μmol l^{-1}, $c_{CTMA} = 312$ μmol l^{-1}, $p_{Triton} = 0.016$ wt.%, $I = 0.004$ mol l^{-1} ($HNO_3 + NH_3$). pH: *1* 7.80; *2* 8.40; *3* 9.00; *4* 9.57; *5* 10.08; *6* 10.54

optimum pH from pH ≈ 9 to pH ≈ 10 and protects the associate against decomposition. The CMC for pure Triton at $I \approx 0$ is 330 μmol l^{-1}, i.e. about 0.019 wt.%, and this value decreases slightly with increasing ionic strength of the solution[16,17]. It can thus be concluded that Triton acts simply as a protective colloid for the poorly soluble ternary Ce–CAS–CTMA complex.

The effect of the inert electrolyte: For c_{Ce} = 5.02 μmol l^{-1}, c_L = 143 μmol l^{-1}, c_{CTMA} = 312 μmol l^{-1}, p_{Triton} = 0.016 wt.% and pH 10.2, the effect of the inert salt is negligible. For c_{Ce} = 10.33 μmol l^{-1}, the scatter of the results increases to up to 30% for parallel measurements (solutions) with increasing salt concentration, especially through the pH adjustment with NH_3. The limiting salt concentrations in mol l^{-1} producing a relative deviation from the absorbance of the pure solutions of ±2% are: 0.1 (KNO_3), 0.05 (KCl), 0.005 (K_2SO_4), 0.001 (KH_2PO_4) and 0.05 (NaCl).

Interferences: Table I gives the interfering effects of various ions for optimum conditions and medium concentrations of Ce^{3+} according to the calibration dependences. The considerable interference from Mg^{2+}, Ca^{2+} and Al^{3+} is a disadvantage; Fe^{3+} and Th^{4+} interfere at all concentrations. These elements are usually present as components or impurities in mineral raw materials containing REE. The interference from metal ions, especially Al^{3+} decreases with time and can be decreased if the measurement is carried out 5 min after adjusting the pH.

Calibration dependence: The optimum linear calibration dependence in the ternary Ce–CAS–CTMA system is obtained for 624 nm, c_L = 95.4 μmol l^{-1} and c_{CTMA} = 300 μmol l^{-1}, i.e. c_{CTMA}/c_L = 3.14 (3.0 – 3.3) and pH 8.5 – 9.0. The curvature of the dependence for c_{Ce} > 16 μmol l^{-1}, where there is a small excess of reagent compared to

TABLE I

The effect of some ions and salts in the Ce–CAS–CTMA–Triton system (c_{Ce} = 6.65 μmol l^{-1}, c_L = 143 μmol l^{-1}, c_{CTMA} = 312 μmol l^{-1}, p_{Triton} = 0.016 wt.%, pH 10.2)[a]

Interferent	c, mmol l^{-1}	x	w
Ca^{2+}	4.5	68	20
Mg^{2+}	0.0021	0.32	0.056
Al^{3+}	0.0018	0.27	0.052
NO_3^-	100	15 000	6 600
SO_4^{2-}	8.0	1 200	820
PO_4^{3-}	0.20	30	20
KCl	80	12 000	6 400
NaCl	40	6 000	2 500

[a] x molar fraction, w weight fraction of the interferent compared to Ce^{3+} leading to a change in ΔA_{624} of 2%.

Ce^{3+}, is a consequence of the formation of the associate with λ_{max} = 650 nm. The curvature of the dependence for low concentrations of Ce^{3+}, $c_{Ce} < 2$ μmol l^{-1}, follows from the hypsochromic shift of λ_{max} for the ternary and binary associate with the tenside (cf. curves *3* and *4* in Fig. 1).

In the quaternary Ce–CAS–CTMA–Triton system, the calibration dependences are optimum for λ = 624 nm, c_L = 143 μmol l^{-1}, c_{CTMA} = 312 μmol l^{-1}, i.e. c_{CTMA}/c_L = 2.18 (2.1 – 2.5), p_{Triton} = 0.016 wt.% and pH 10.2. The greatest sensitivity is attained for the linear range c_{Ce} = 1.5 – 16 μmol l^{-1}. The reagent concentration employed is a compromise between suppression of the formation of the associate absorbing at 650 nm and increasing the linear range of the dependence and absorbance of the blank. The absorbance is measured within 1 min of adjusting the pH value. Table II gives the evaluation of the calibration dependences for various tensides.

As the ionic strength of the solution is increased (KNO_3), the molar absorption coefficients and the upper limit of the linear dependence decrease; however, the curvature of the curve in the vicinity of the origin decreases and almost disappears for *I* = 0.1 mol l^{-1}. Table III gives an evaluation of the parameters of the dependences.

Other REE in the Me–CAS–CTMA–Triton System

The other lanthanoids, La and Y behave completely analogously to Ce, as followed from a detailed study of the quaternary system of the Y, La, Pr, Nd or Yb ions with

TABLE II

Evaluation of the linear branch of the calibration dependence of *A* vs c_{Ce} in the Ce–CAS–CTMA–Triton system (c_{CTMA} = 312 μmol l^{-1}, c_{CP} = 320 μ mol l^{-1}, p_{Triton} = 0.016 wt.%)

Tenside	λ, nm	c_L μmol l^{-1}	pH	ε	s_r	*q*	s_q	Linearity range μmol l^{-1}
				10^3 l mol^{-1} cm^{-1}				
CTMA	620	95.4	8.7	67.0	2.0	–0.067	0.02	2.5 – 9
	624			67.7	2.5	–0.086	0.02	3.0 – 13
	628			62.1	2.0	–0.068	0.02	4.0 – 14
CP	620	140	8.2	54.0	0.37	0.018	0.004	3.0 – 13
	624	140		55.4	0.55	0.005	0.005	3.0 – 17
	624	93.3		61.2	0.47	–0.005	0.003	2.0 – 12
CTMA	620	143	10.2	72.3	0.32	0.031	0.003	1.4 – 13
+	624	143		73.3	0.34	0.040	0.003	1.5 – 16
Triton	628	143		74.3	0.39	0.035	0.003	2.0 – 19
	624	95.4		71.3	0.64	0.049	0.005	1.3 – 12

CAS, CTMA and Triton. All the ions form ternary associates with λ_{max} = 624 and 650 nm; optimum conditions are a compromise pH of 10.2, c_L = 143 μmol l^{-1}, c_{CTMA} = 312 μmol l^{-1}, p_{Triton} = 0.016 wt.%. The calibration dependence has the same shape as for Ce^{3+}. Some of its parameters are listed in Table IV.

TABLE III

The effect of the ionic strength (KNO_3) on the calibration dependence in the Ce–CAS–CTMA–Triton system ($c_{Ce} \leq$ 20 μmol l^{-1}, c_L = 143 μmol l^{-1}, c_{CTMA} = 312 μmol l^{-1}, p_{Triton} = 0.016 wt.%, pH 10.2, λ = 624 nm)

$I(KNO_3)$ mol l^{-1}	ε	s_ε	*q*	s_q	*A* (blank)	Linearity range μmol l^{-1}
	10^3 l mol^{-1} cm^{-1}					
0.004	73.3	0.34	0.040	0.0029	0.064	1.5 – 16
0.01	73.4	0.52	0.031	0.0064	0.064	1.5 – 15
0.05	69.3	0.38	0.046	0.0024	0.067	1.0 – 13
0.1	66.7	0.34	0.064	0.0022	0.078	0.5 – 13

TABLE IV

Evaluation of the calibration dependence for the determination of the rare earth elements in the Me–CAS–CTMA–Triton system for optimal conditions[a]

ion	ε	s_ε	*q*	s_q	Optimal pH region	Linearity range μmol l^{-1}
	10^3 l mol^{-1} cm^{-1}					
Y	81.4	0.21	0.020	0.0021	10.2 – 10.7	1.5 – 17
La	73.6	0.67	0.016	0.0058	10.1 – 10.6	1.5 – 17
Ce	73.3	0.34	0.040	0.0029	10.1 – 10.6	1.5 – 16
Pr	75.6	0.64	0.045	0.0056	10.0 – 10.5	1.5 – 15
Nd	74.5	1.22	0.034	0.0010	10.0 – 10.5	1.5 – 15
Sm	75.4	0.51	0.034	0.0040	10.0 – 10.4	1.0 – 14
Eu	76.3	0.53	0.034	0.0046	10.0 – 10.4	1.5 – 15
Gd	77.6	0.57	0.034	0.0050	10.0 – 10.4	1.5 – 16
Tb	79.1	0.29	0.025	0.0029	10.0 – 10.4	1.5 – 16
Dy	79.2	0.28	0.028	0.0029	10.0 – 10.4	1.5 – 16
Ho	80.5	0.60	0.026	0.0048	10.0 – 10.4	1.5 – 18
Er	80.9	0.48	0.025	0.0045	10.0 – 10.4	1.5 – 16
Tm	80.2	0.12	0.047	0.0012	9.8 – 10.3	1.5 – 19
Yb	79.6	0.45	0.013	0.0039	9.9 – 10.3	1.5 – 17
Lu	79.3	0.74	0.034	0.0063	9.9 – 10.3	1.0 – 18

[a] c_L = 143 μmol l^{-1}, c_{CTMA} = 312 μmol l^{-1}, p_{Triton} = 0.016 wt.%, pH 10.2, λ = 624 nm, I = 0.16, A_0 = 0.064, s_0 = 0.002.

The results of our work for the Me–CAS–CTMA (or CP) system are not in conflict with the results given in refs[8,9]. However, no attention was paid in these works to the time course of the reaction and the effect of the tenside concentration, and the measurement was carried out at c_{T^+}/c_L concentrations where turbidity is formed in the solution even at pH > 7, under the conditions recommended in these works. The authors of ref.[10] did not even observe the formation of the associates of Y^{3+} and La^{3+} with CAS in the presence of T^+. The authors of ref.[13] considered the absorption maximum at $\lambda = 505$ nm at pH 7 to be the maximum of the Y–CAS–CTMA ternary associate formed; however, it apparently corresponds only to a shift of the absorption maximum of the HL^{3-} form of the reagent.

The formation of ternary associates of the REE ions with $\lambda_{max} = 624$ or 650 nm is maximal at a ratio of $c_{CTMA}/c_L = 3.0$ and is thus dependent on the existence of the binary associate $\{HL^{3-}, 3T^+\}$ at pH > 5. It follows from the maxima of the Job curves for the Ce–CA–CTMA system that the ratio of the components for the association is Ce : CAS : CTMA = 1 : 2 : 5 – 6 or 1 : 3 : 9. The reaction mechanism given below is then probable, where a proton is split off from the phenolic hydroxyl.

$$Ce^{3+} + 2\,\{HL^{3-}, 3T^+\} \longrightarrow \{CeL_2, 4T^+\}\,T^+ + 2\,H^+ + T^+$$

$$Ce^{3+} + 3\,\{HL^{3-}, 3T^+\} \longrightarrow \{CeL_3, 6T^+\}\,3T^+ + 3\,H^+$$

The results of this work allow us to draw a number of general conclusions for elucidation of the tenside effect. In the interaction of the REE ions with CAS and the cationic tenside, the tenside effect and spectrophotometric sensitization occur only at submicellar tenside concentrations. The low soluble ternary associate formed is stabilized and solubilized by the small excess of cationic tenside over the stoichiometric reagent : tenside ratio or preferably by the presence of micellar concentrations of nonionic tenside (Triton). At an excess of the cationic tenside, the formation of the binary associate with the reagent is preferred over the insufficiently stable ternary ion associate, which is decomposed or not even formed. The ternary associate is not stable in a micellar medium of cationic tenside even in the presence of a more polar solvent (ethanol, methanol). In this respect, the REE differ from UO_2^{2+}, Al^{3+}, Fe^{3+}, Th^{4+}, Sc^{3+}, In^{3+}, Ga^{3+} whose ternary ion associates with cationic tensides are stable in acidic or weakly acidic micellar tenside medium and a considerable increase in the molar absorption coefficient occurs only after attaining the CMC of the cationic tenside (micellar sensitization). Only a much greater excess of tenside decomposes the ternary associate.

Determination of REE in Model Samples and Hydroxide Concentrates

The absorbance at 624 nm was measured for the optimal conditions (c_L = 143 μmol l^{-1}, c_{CTMA} = 312 μmol l^{-1}, p_{Triton} = 0.016 wt.%, pH 10.2) for 8 model mixtures containing La, Ce and Nd as the REE present in the greatest amounts in natural samples and concentrates of these samples, and Er as a representative of the heavy lanthanoids. The contents of the elements in mole %, the sum of the concentrations of the REE ions and deviations of the total concentration of REE ions from the actual values are given in Table V.

The absorbance was read graphically from the calibration dependence for Ce or numerically from the equation of the regression straight line corresponding to the calibration dependences for Ce, La and Nd and the weighed mixtures of lanthanoids. Parameters ε and q of the latter dependence were obtained as the arithmetic average of the ε and q values from the regression lines for Ce, La and Nd with statistical weights 0.5, 0.3 and 0.2, corresponding approximately to the contents of the individual REE in the hydroxide concentrate (see the concentration composition in the section Chemicals).

The summary concentration of REE in the solutions of hydroxide concentrate was calculated as if 98.21% of the oxides of all the REE in the concentrate consisted only

TABLE V
Evaluation of 8 model samples for the determination with CAS in the presence of CTMA and Triton at λ = 624 nm (c_L = 143 μmol l^{-1}, c_{CTMA} = 312 μmol l^{-1}, p_{Triton} = 0.016 wt.%, I = 0.004 mol l^{-1}, pH 10.2)

Concentration	Sample							
	1	2	3	4	5	6	7	8
La[a], %	33	50	–	–	50	–	–	–
Ce[a], %	45	50	50	51	–	20	20	50
Nd[a], %	22	–	50	–	50	80	80	–
Er[a], %	–	–	–	49	–	–	–	50
c(REE)[b]	9.199	10.25	10.21	10.14	10.13	10.13	10.02	4.091
δ(Ce)[d], %	–1.8	–2.8	0.0	–0.2	1.7	0.0	4.1	2.2
δ(Ce)[c], %	0.0	–1.2	1.4	–0.8	0.4	1.9	6.0	4.6
δ(La)[c], %	3.1	1.6	4.2	4.2	3.2	4.7	8.8	11.9
δ(Nd)[c], %	–0.8	–2.0	–0.4	0.4	–0.4	0.9	5.0	4.5
δ(Ln)[c], %	0.7	–0.6	2.0	2.0	1.0	2.4	6.6	6.5

[a] Me^{3+} content in the model sample. [b] Summary REE concentration in μmol l^{-1}. [c] Percentage deviation of the concentration found by calculation according to the calibration dependence for the Me metal ion. [d] Percentage deviation of the concentration found graphically according to the calibration dependence for the Me metal ion.

of CeO_2. This approximation does not lead to any significant error relative to the actual content of oxides.

The deviations found for the sum of the REE from two analyses of the standard hydroxide concentrate for evaluation from the calibration dependence for the main components of the REE mixture are given in Table VI.

For model No. 1 (Table V), whose composition corresponds to the usual contents of REE in the hydroxide concentrate, the optimal evaluation is that carried out according to the calibration dependence for Ce or a mixture of lanthanoids. The summary concentration of REE in the concentrate evaluated from these calibration dependences exhibits a mean deviation of –3.8% or 2.9%, respectively.

TABLE VI
Determination of the sum of the REE in the hydroxide concentrate by CAS in the presence of CTMA and Triton at λ = 624 nm

Corrected sample weight, mg	$c(\text{REE})^a$, μmol l^{-1}	$\delta c'(\text{REE})^b$, %				
		Ce[c]	Ce	La	Nd	Ln
167.9	7.663	–3.7	–3.6	0.4	–4.1	–2.6
164.3	7.499	–4.0	–4.0	0.0	–4.6	–3.1

[a] Actual value of the summary concentration of a 2 500 times diluted solution of the hydroxide concentrate of REE after decomposition. [b] Deviation $c'(\text{REE})$ calculated from the calibration dependence. [c] $c'(\text{REE})$ found graphically.

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Translated by M. Štulíková.