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Surfactant-sensitized post-column reaction with xylenol orange for the determination of lanthanides by ion chromatography

Eduardo A. Gautier*, Raquel T. Gettar, Roberto E. Servant, Daniel A. Batistoni

Unidad de Actividad Química, Comisión Nacional de Energía Atómica, Av. Libertador 8250, (1429) Buenos Aires, Argentina

Abstract

The presence of the cationic surfactants cetylpyridinium chloride and hexadecyltrimethylammonium bromide in an alkaline 40% methanol medium was found to enhance sensitivity when xylenol orange is employed as the post-column reaction reagent for the determination of lanthanides by dynamic ion chromatography. Detection of individual lanthanides was carried out at 618 nm after separation by cation-exchange chromatography with gradient elution on a C_{18} column. The eluent was α -hydroxyisobutyric acid–sodium octanesulfonate, pH 3.8. Sensitivity enhancements by factors of three to six, compared with xylenol orange alone, were achieved at a cationic surfactant concentration of 2.4 mM. The calibration response was linear in the 0.05 to 5 $\mu\text{g ml}^{-1}$ analyte concentration range. Limits of detection below 3 ng were obtained for all the natural lanthanides and lanthanum. No sensitivity enhancement effects were observed with anionic (sodium dodecyl sulfate) and non-ionic (Triton X-100) surfactants under the conditions tested.

Keywords: Derivatization, LC; Detection, LC; Lanthanides; Xylenol orange; Surfactants

1. Introduction

The analysis of lanthanides, including lanthanum, has been widely studied due to its importance in geochemistry and in high technology fields such as the development of superconductor and nuclear materials. Neutron activation analysis, X-ray fluorescence, atomic absorption, inductively coupled plasma (ICP) atomic emission spectrometry, ICP mass spectrometry and chromatography are the most frequently employed techniques for the determination of those elements. Robards et al. [1] have published a complete review covering the most important developments in different fields of chromatography for the simultaneous determination of lanthanides.

The post-column reaction system, based on the formation of a visible absorbing metal complex and

its spectrophotometric detection, has become a well established methodology in ion chromatography (IC), due to enhanced specificity and sensitivity effects in metal analysis. Principles and applications of post-column reaction systems have been discussed by Haddad and Jackson [2].

Elchuk and Cassidy [3] and Knight et al. [4] have reported an excellent chromatographic separation of lanthanides with α -hydroxyisobutyric acid (HIBA) as the eluent, 1-octanesulfonate as the column modifier and Arsenazo III as the post-column reaction reagent.

To improve the post-column detection of metal ions, the presence of a suitable surfactant has been used to increase the absorbance of the metal complexes.

The most common limitations of post-column reactions, i.e. low solubility of the formed complexes and slow reaction rates, can be overcome by addition

*Corresponding author.

of an appropriate surfactant. The use of surfactants can also lead to a lowering of the optimum pH at which the metal–dye complex is quantitatively formed [5]. In addition, increases in molar absorptivities and bathochromic shifts of the wavelength of maximum absorption are frequently observed. The properties of surfactants and their applications in analytical chemistry have been extensively reviewed [5–8]. In this regard, the review presented by McIntire [8] critically analyzes the current status and future potentials of micellar systems.

Xylenol orange (XO) has been investigated, in the presence of micelles, for the spectrophotometric determination of some alkaline earth and transition metals [9], lanthanum [10] and zirconium [11]. The masking effect of some ligands in micellar media allows the determination of the heaviest lanthanides in the presence of the lightest [12]. Relatively few reports on the application of micelles as part of the post-column reaction in IC have been published. XO/cationic surfactant has successfully been applied in microscale cation-exchange chromatography [13]. Xia and Cassidy [14] have studied the effect of different kinds of surfactants on some transition metals. The reaction between La(III) and Arsenazo III is fast enough not to be affected by the presence of sodium dodecyl sulfate (SDS) micelles.

The purpose of this work was to evaluate the potential of micelles from cationic, anionic and non-ionic surfactants for sensitivity enhancement when XO is employed as a post-column reaction reagent for the determination of lanthanides after dynamic ion-exchange separation.

2. Experimental

2.1. Apparatus

A Konik (Barcelona, Spain) KNK-500A liquid chromatograph equipped with a Rheodyne (Cotati, CA, USA) Model 7125 injector, a 100- μ l sample loop and a Vydac 201 TP (Hesperia, CA, USA) silica-based C₁₈ reversed-phase column (15 cm \times 4.6 mm I.D.) was used.

The post-column reaction reagent was supplied by a pneumatic pump Lazar (Los Angeles, CA, USA) to a stainless steel tee connection Valco ZT1 (Houston,

TX, USA) for tube size 1/16 in. (1 in.=2.54 cm), bore 0.75 mm. The eluent–post-column reaction reagent mixed solution was routed through a stainless steel tube (30 cm \times 0.010 in. I.D.) to a Linear (Reno, NV, USA) UVIS 204 variable-wavelength UV–Vis detector. No reaction coil was employed.

Data were transferred to a personal computer via an A/D interface and processed by means of integration software, Konikrom Chromatography Data System V.5 (Barcelona, Spain).

Molecular absorption spectra of the complexes were obtained with a Perkin-Elmer (Norwalk, CT, USA) Model 559A UV–Vis spectrophotometer.

2.2. Reagents

Distilled water, passed through a Nanopure water-purification unit (Sybron/Barnstead, Boston, MA, USA), was used for all solutions. All eluents and samples were filtered through 0.22 μ m membrane filters. Eluents were degassed with helium.

The post-column chromogenic reagent was xylenol orange [3,3'-bis(N,N-di(carboxymethyl)amino-methyl *o*-cresolsulphonphthalein); Aldrich, Milwaukee, WI, USA]. Stock solutions of XO ($5 \cdot 10^{-3}$ M) were prepared in pure methanol.

The surfactants tested and their critical micelle concentrations (CMCs) in aqueous solutions in the absence of additives [7] are: polyoxyethylene-*tert*-octylphenol (Triton X-100, CMC=0.2 mM) as non-ionic surfactant, sodium dodecylsulfate (SDS) (CMC=8.1 mM) as anionic surfactant, cetylpyridinium chloride (CPC; CMC=0.9 mM) and hexadecyltrimethylammonium bromide (CTAB; CMC=0.9 mM) as cationic surfactants. For IC experiments, stock solutions of the ionic surfactants were obtained by dissolution of their salts in a methanol–buffer (40:60, v/v) solution (pH=8.7).

The alkaline buffer solution (pH=8.7) was a 1:1 mixture of 2 M ammonium hydroxide and 4 M ammonium chloride and the acidic buffer (pH=4.9) solution was a 1:1 mixture of 0.2 M potassium acid phthalate and 0.1 M sodium hydroxide.

Stock solutions (1000 μ g ml⁻¹) of the different cations were prepared by acid dissolution of high purity oxides (Aldrich) after appropriate thermal treatment [15] to assure stoichiometry. Standard solutions of individual and mixed lanthanides were

prepared by dilution of stock solutions with 1 mM hydrochloric acid, which were filtered prior to injection into the chromatographic system.

The post-column reaction reagent was pneumatically pumped with nitrogen at a flow-rate of 1.5 ml min⁻¹. The mobile phase was prepared by dissolving appropriate amounts of HIBA (TCI, Tokyo, Japan) and 1-octanesulfonate (Eastman Kodak, Rochester, NY, USA) in water, followed by adjustment of the pH to 3.8 with concentrated ammonium hydroxide. The chromatographic system was operated in a linear gradient program mode with HIBA concentrations ranging from 0.05 to 0.24 M over 10 min at a flow-rate of 1 ml min⁻¹. The 1-octanesulfonate concentration in the eluent was maintained constant at 0.01 M. The operating column temperature was 30°C.

Spectrophotometric batch experiments were carried out in such a way as to simulate the final

composition of the solution in the chromatographic reaction cell at a HIBA concentration of 0.24 M.

3. Results and discussion

3.1. Chromatographic separation

Dynamic ion-exchange chromatography was chosen as the separation method for lanthanides. An existing technique with 1-octanesulfonate as the ion-interaction reagent and a complexing agent (HIBA) as the mobile phase [3,4] was applied with slight modifications.

The advantages of this method are the variable ion-exchange capacity of the column and its efficiency. The latter could be adjusted by varying the 1-octanesulfonate concentration, which is sorbed on the C₁₈ phase.

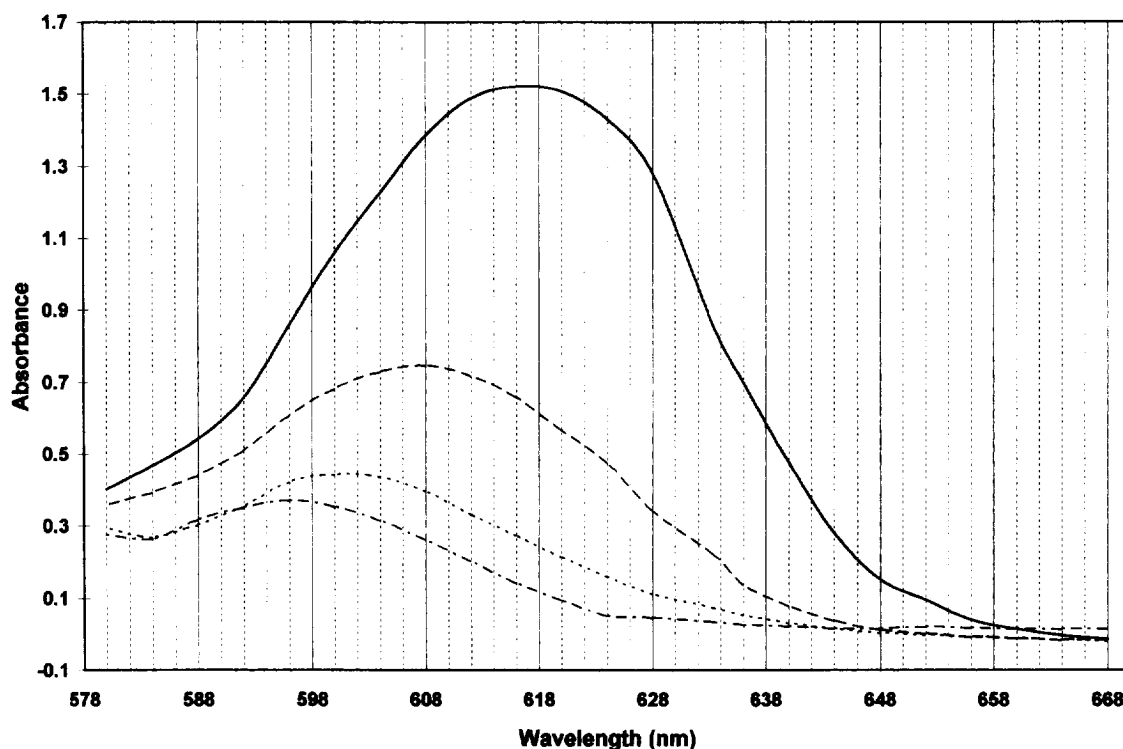


Fig. 1. Effect of CPC on spectra of selected complexes of lanthanides. ···· Nd-XO; — Nd-XO-CPC; - · - · Lu-XO; - - - Lu-XO-CPC; [XO]= $3 \cdot 10^{-5}$ M; [HIBA]= $9.6 \cdot 10^{-2}$ M; [1-octanesulfonate]= $8 \cdot 10^{-3}$ M; [CPC]= $2.4 \cdot 10^{-3}$ M; [lanthanides]= $1.5 \cdot 10^{-5}$ M; methanol concentration=24% and buffer (pH 8.7)=36%.

HIBA is a chelating agent that decreases the effective charge of the trivalent lanthanides, allowing their elution in a reasonable time. The reproducibility of the retention time within the same batch of eluent was 0.1%. However, if special care in the preparation of the eluent solutions is not taken, differences of several minutes could be obtained between different eluent batch solutions. This effect could be due in first place to the fact that small changes in the concentration of the ion-interaction reagent affect the ion-exchange capacity and the efficiency of the column. Secondly, minor variations in the amount of ammonium hydroxide added for pH adjustment could cause changes in the eluent's ionic strength, without modifying the final pH obtained, but affecting the retention times.

3.2. pH selection in the post-column reaction

Changes in pH of the final solution produce different behaviours of the dye in the presence or

absence of cationic surfactants. A similar effect was reported in a spectrophotometric study of some triphenylmethane dyes [16].

In the absence of surfactant, the lanthanides and XO are reported to form a binary complex with a 1:1 molar ratio [17]. The optimum pH of formation is between 4.8 and 5.3. Svoboda and Chromy [10] suggest that the molar ratio is 1:2 and showed that the introduction of a cationic surfactant in alkaline medium made possible an improvement in the spectrophotometric characteristics of the reaction products.

Batch spectrophotometric studies were performed in the presence of the cationic surfactants CPC and CTAB, anionic surfactant (SDS) and non-ionic surfactant (Triton X-100) at concentrations above their CMC in aqueous solutions and at pH values of 4.9 (with the addition of acidic buffer) and 8.7 (with the addition of alkaline buffer). Significant absorbance enhancements were observed only at pH 8.7 with cationic surfactants. A relatively high alkaline

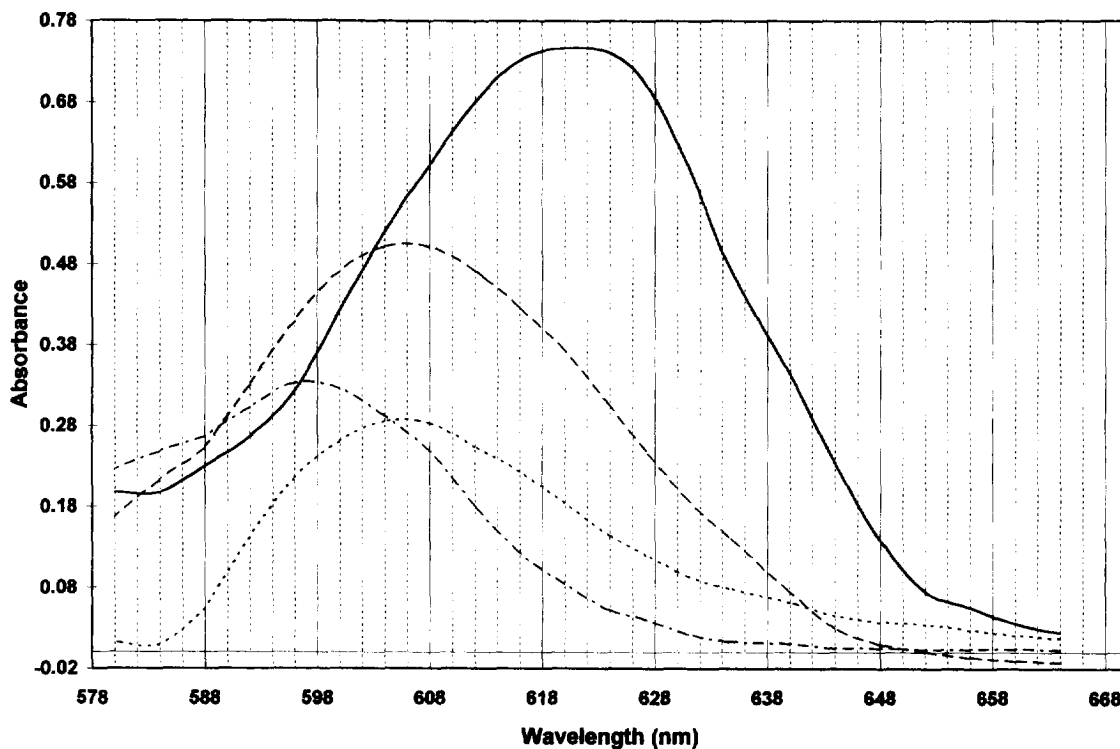


Fig. 2. Effect of CTAB on spectra of selected complexes of lanthanides. \cdots Ce-XO; — Ce-XO-CTAB; $-\cdot-\cdot-$ Er-XO; $-\cdot-\cdot-$ Er-XO-CTAB; $[\text{CTAB}] = 2.4 \cdot 10^{-3} \text{ M}$; $[\text{lanthanides}] = 1.5 \cdot 10^{-5} \text{ M}$. Other conditions were the same as in Fig. 1.

buffer concentration is necessary to warrant a final pH of 8.7 because of the intrinsic buffer capacity of HIBA at a concentration of 0.24 M.

3.3. Wavelength selection

All experiments were performed at a concentration of pumped XO of $5 \cdot 10^{-5}$ M with a final concentration after the mixing tee of $3 \cdot 10^{-5}$ M. Higher amounts of the dye tended to decrease the absorbance, while causing a simultaneous increase in the baseline noise.

Absorption spectra of Lu–XO and Nd–XO complexes (580–670 nm range) in the presence and absence of the micellar agent CPC are depicted in Fig. 1. Fig. 2 shows the effect of CTAB on the XO complexes of Ce and Er. The analytes were chosen as being representative of the light and heavy lanthanide subgroups.

An increase in molar absorptivities and a bathochromic shift is apparent. The purple colour of the complexes changes to blue for Ce and Nd and to

violet for Lu and Er with the addition of CTAB or CPC. The shifts are then higher for Ce and Nd (600 to 618 nm) than for Lu and Er (596 to 606 nm).

The addition of the cationic surfactant to the binary complex XO–lanthanide may result in the formation of a ternary complex with a stoichiometric ratio of lanthanide–XO–CPC=1:2:4 at pH=7.5 [10,17]. Other authors suggest a ratio of 1:1:3 at pH=4 [12]. Cermakova [18] has suggested the existence of micellar effects over the ionization equilibrium of the dyes, rather than the formation of complexes with the surfactant.

Changes in the micro-environment of the chromophore, produced by electrostatic interactions between cationic surfactant micelles and anionic dyes and hydrophobic interactions between adjacent surfactant chains and organic groups of the dye, are proposed as an explanation of the observed spectral shifts [6].

A working wavelength of 618 nm was chosen in order to attain higher sensitivities, in spite of the fact that the baseline peak-to-peak noise is higher than at 630 nm. This wavelength was proposed by Hirose et

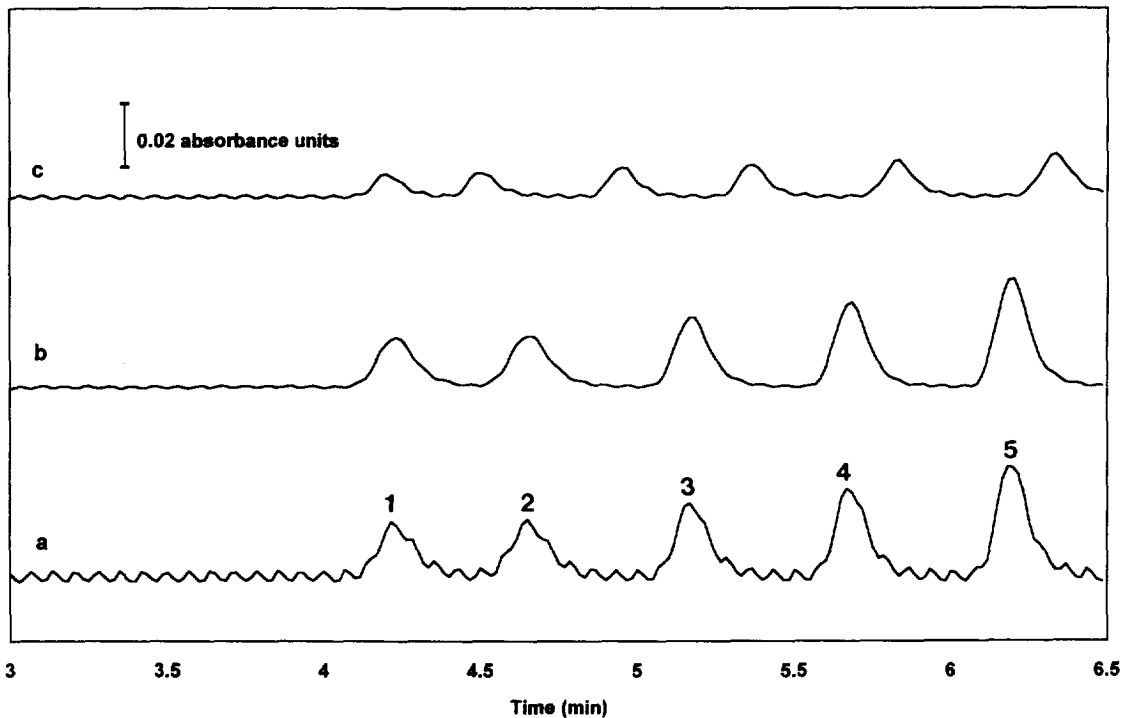


Fig. 3. Partial chromatograms (1=Lu; 2=Yb; 3=Tm; 4=Er; 5=Ho) showing baseline noise. (a) 618 nm; (b) 618 after smoothing and (c) 630 nm. Lanthanide concentration=1 $\mu\text{g ml}^{-1}$. Experimental conditions were as described in the text.

al. [13]. This noise problem could be overcome by further optimising the chromatographic system or by employing a signal smoothing routine. The second alternative was chosen. Fig. 3 shows partial chromatograms at 618 nm before and after applying a nine points Savitzky-Golay algorithm (included in the software package) and at 630 nm (without smoothing). As some examples, signal-to-noise ratios at 630, 618 and at 618 nm with smoothing were, respectively, 7.3, 5.6 and 22.4 for Lu; 7.4, 5.8 and 22.8 for Yb and 9.3, 8.1 and 32.0 for Tm.

3.4. Effect of methanol

Addition of methanol was required to prevent opalescence caused by the ion-pair association between the anionic species in the eluent and the cationic surfactants from the post-column reaction reagent and to obtain complete solubilization.

The optimum concentration after the tee mixing

was in the range of 20–30% methanol. No effects were observed on the absorbance spectra. A concentration of 40% methanol in the post-column reaction reagent was chosen, corresponding to 24% after the tee.

3.5. Effect of cationic surfactant concentration

If the phenomenon of sensitivity enhancement in the presence of surfactant is attributed to the formation of micelles, changes in the physical properties of the solution with increasing concentration of the amphiphile should be observable for a constant concentration of XO. The variations in peak areas for selected lanthanides in the system XO–CPC vs. the CPC concentration are shown in Fig. 4. The concentration of the cationic surfactant was varied from 0 to 40 mM in the post-column reagent. A similar behaviour was observed for CTAB with all of the lanthanides. A concentration of surfactant of 4 mM

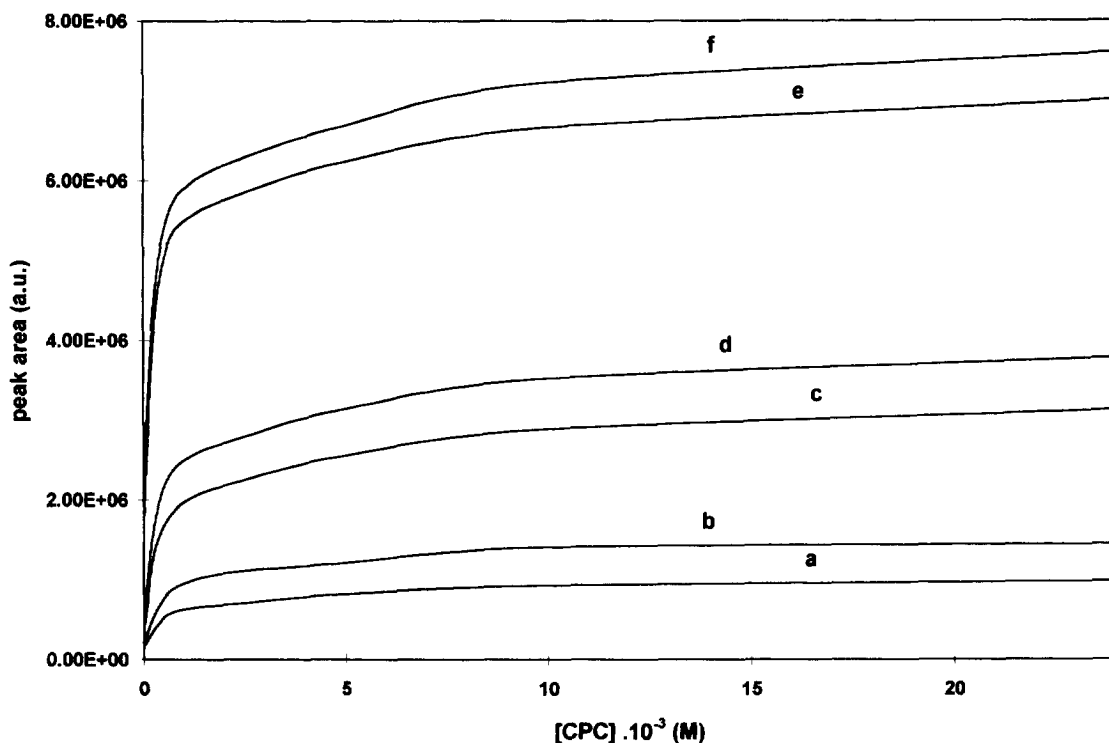


Fig. 4. Peak area vs. CPC concentration after tee mixing of solutions. a, Lu; b, Er; c, Gd; d, Eu; e, Nd; f, Ce. Lanthanide concentration = 5 $\mu\text{g ml}^{-1}$. Experimental conditions were as described in the text.

in the post-column reaction reagent was chosen for practical work (2.4 mM after the tee mixing). Chromatograms with and without the addition of CPC are compared in Fig. 5. The resultant sensitivity enhancement was three- to six-fold, depending upon the element.

3.6. Effect of foreign ions

The effect of the presence of other ions such as: Cd(II), Al(III), Fe(III), Cu(II), Hg(II), Y(III), Mg(II), Ca(II), Sr(II), Ba(II) and U(VI) was examined by injecting $20 \mu\text{g ml}^{-1}$ of each element, simultaneously with a mixture of $1 \mu\text{g ml}^{-1}$ of each lanthanide.

A peak corresponding to Cd(II) appears in the chromatogram between the Pr and Ce peaks, affecting the quantitation of those lanthanides. Y(III) is

eluted at the same time as Dy. The other cations do not interfere at the concentration levels tested.

3.7. Linearity and detection limits

Calibration curves for the determination of the lanthanides were found to be linear over the range $0.05\text{--}5 \mu\text{g ml}^{-1}$. However, quantitative measurements are not limited to the concentration range mentioned.

Calibration results for selected lanthanides when CPC was used as the surfactant are shown in Table 1, as regression data of peak area vs. concentration curves. Similar regression performance was obtained for the remaining lanthanides, with cationic surfactants. Detection limits, estimated on the basis of three times the standard deviation of the baseline noise, are also included. Because changes in baseline noise with increased surfactant concentrations are

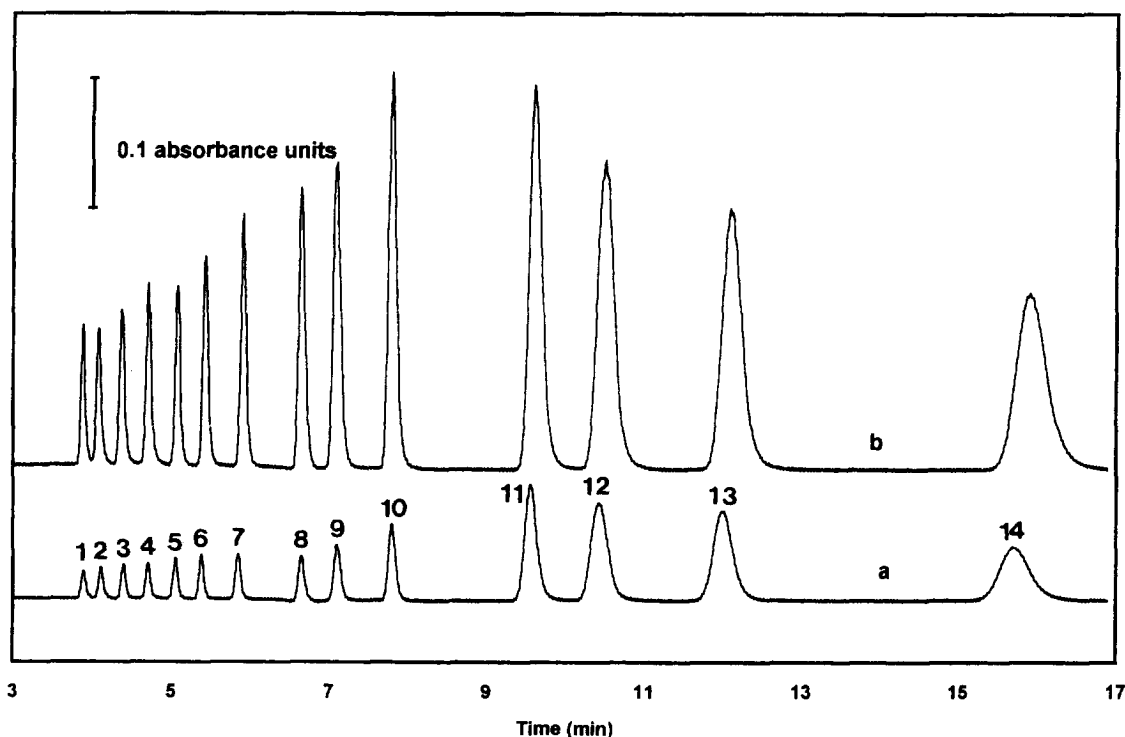


Fig. 5. Chromatograms of lanthanides (a) without CPC and (b) with CPC. Lanthanide concentration = $5 \mu\text{g ml}^{-1}$. [CPC] = $2.4 \cdot 10^{-3} M$. 1, Lu; 2, Yb; 3, Tm; 4, Er; 5, Ho; 6, Dy; 7, Tb; 8, Gd; 9, Eu; 10, Sm; 11, Nd; 12, Pr; 13, Ce; 14, La; Experimental conditions were as described in the text.

Table 1
Regression data of integrated absorbance vs. concentration

Element	$a \times 10^3$	$b \times 10^5$	$SD \times 10^4$	r^a	n^b	DL ^d (ng)
Lu	0.3 (0.6) ^c	0.70 (0.02)	0.13	0.9983	9	6
Er	-0.7 (0.7)	1.07 (0.02)	0.15	0.9992	9	3
Nd	2.2 (6.1)	12.2 (0.1)	1.34	0.9996	10	0.4
Ce	-6.9 (6.7)	12.9 (0.1)	1.46	0.9996	10	0.3

Equation $y = a + bx$ where y = peak area (arbitrary units), x = concentration ($\mu\text{g ml}^{-1}$), a = intercept and b = slope of selected lanthanides with CPC.

^aCorrelation coefficient.

^bNumber of data points.

^cStandard deviations in parentheses.

^dDetection limit.

negligible, limits of detection could be improved by employing higher concentrations of micellar agent (at least up to 24 mM, see Fig. 4).

The detection limits obtained in this work are of the same order of magnitude as those reported for other post-column reagents, such as Arsenazo III [4,19], Chlorophosphonazo III [20] and 4-(2-pyridylazo)-resorcinol (PAR) [21]. It must be mentioned that detection limits depend critically upon the type of eluent, the post-column reagent flow-rates and the pump pulsations.

Precision was estimated by calculating the relative standard deviation of peak areas from ten injections of a standard solution containing $0.5 \mu\text{g ml}^{-1}$ of each lanthanide. Obtained values were: 5% for Gd and Eu, 3% for the heaviest lanthanides (Lu, Yb, Tm, Er, Ho, Dy and Tb) and 1% for the lightest (Sm, Nd, Pr, Ce and La). An unexplained systematic negative peak between Gd and Eu, usually observed at low analyte concentrations, could be the origin of the poor repeatability for those elements.

It can be concluded that in an IC system employing HIBA as the eluent, the addition of cationic surfactants to post-column reaction reagents can be considered an interesting option to improve the determination of lanthanides at trace levels with xylenol orange.

This method could be applied when a different chromatographic system is used to separate rare earths. However, a meticulous study of the influence

of the eluent on the post-column reaction must be considered, due to the possible masking effect of different complexing agents.

Acknowledgments

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