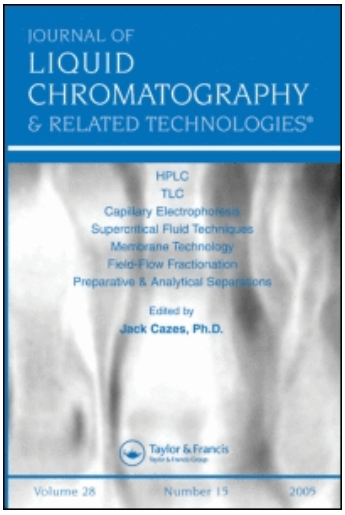

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

RP-IPC with a Lactic Acid Modified Eluent for Separation and Determination of Lanthanide Ions

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To cite this Article Vera-Avila, L. E. and Camacho, E.(1992) 'RP-IPC with a Lactic Acid Modified Eluent for Separation and Determination of Lanthanide Ions', Journal of Liquid Chromatography & Related Technologies, 15: 5, 835 — 850
To link to this Article: DOI: 10.1080/10826079208018838
URL: http://dx.doi.org/10.1080/10826079208018838

JOURNAL OF LIQUID CHROMATOGRAPHY, 15(5), 835-850 (1992)

RP-IPC WITH A LACTIC ACID MODIFIED ELUENT FOR SEPARATION AND DETERMINATION OF LANTHANIDE IONS

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ABSTRACT

A modified method for the separation and determination of Rare Earth Elements in solution was developed. Lanthanide ions were separated by Reversed-Phase Ion Pair Chromatography using a mobile phase gradient of pH and lactic acid concentration. A post-column reaction with 4-(2 pyridyl)azo resorcinol was carried out for the spectrophotometric detection of solutes. The derivatizing reagent composition was optimized for good solute sensitivity and long-term reagent stability. Method limitations due to unadequate instrumentation are presented and discussed.

INTRODUCTION

The separation and analysis of Rare Earth Elements (REE) are important steps in a great variety of research works related to widely different areas. Thus, REE determinations are used in studies on the evolution of igneous rocks[1] in Geochemistry while, in Biochemistry, lanthanide analysis are used in the investigation of the kinetics of cation transport across cell membranes[2].

The traditional methods employed for REE separation and analysis: precipitation, solvent extraction and classical ion exchange, are in general time-consuming, of low selectivity and poor reproducibility. On the other hand, the refined techniques: X-Ray Fluorescence, Neutron Activation Analysis and Mass Spectrometry, have the disadvantage of being expensive and not readily available. In addition, they are not enough specific and/or sensitive[3-6].

In recent years, HPLC has demonstrated its capacity to solve complex inorganic analytical problems[7-10]. The versatility, sensitivity and high resolution power of this technique make it invaluable for the analysis of trace products in complex matrixes. Therefore, the application of HPLC for REE determination has been extensively investigated.

Polymeric or silica-based ion exchangers have been widely used for lanthanide separations[11-13] and Ion Pair Chromatography on reversed-phase columns (RP-IPC) has also been employed[4-6]. Concerning efficiency, resolution and column stability, the best results have been obtained with RP-IPC.

In both systems, REE elution and separation are generally accomplished by means of a complexing agent dissolved in the mobile phase. This compound must be able to form sufficiently strong complexes for the elution of all lanthanides but, at the same time, these complexes must be weak enough to minimize interferences on the detection system. The complexing agent most commonly employed has been α hydroxybutiric acid (HIBA).

REE detection is frequently based on the formation of coloured derivatives at the column exit, followed by spectrophotometrical monitoring of the efluent. The most popular reagents for the post-column reaction are Arsenazo III and PAR [4-(2 pyridylazo) resorcinol] solutions. Detection limits at the ppm level have been reported with both of them. However, it is recommended to use freshly prepared reagents, especially in the case of PAR; because these compounds are slowly degraded in solution[4,5,7].

In this work, we propose a modified method for the determination of lanthanides. The separation is accomplished by RP-IPC with octanesulfonate as pairing ion and lactic acid, instead of HIBA, in the mobile phase. The spectrophotometrical detection of the PAR-lanthanide complexes was further studied in order to find conditions for maximal sensitivity and, at the same time, better stability of the PAR solution.

EXPERIMENTAL

Instrumentation

The LC system used consisted of a Varian 5000 chromatograph with binary gradient elution capacity, a Rheodyne 7125 valve injector with 10 µL loop, a Varian UV-100 variable wavelength detector and a HP 3396 A integrator. The column was thermostated at 28°C by means of a 30 cm heather block. A Beckman 210 A isocratic pump was employed for the addition of the post-column reagent to the column efluent. The mobile phases and the PAR solution were degassed in an ultrasonic bath from Branson Instruments prior to use.

The post-column reactor consisted of a low dead volume tee joint to a capillary teflon tubing (3m x 0.5mm i.d.) tightly coiled around a cartridge to favour the radial mixing of solutions. The reaction was performed at ambient temperature.

The pH of the mobile phases and PAR solutions was carefully adjusted with perchloric acid or sodium hydroxyde solutions using a 2G8N pHmeter from Tacussel, equipped with a combined glass-calomel electrode.

A Sigma 3000 spectrophotometer was employed in the detection studies.

Reagents and Materials

Acetonitrile was HPLC from Merck. The water for the preparation of all solutions and eluents was distilled water

purified in a Nanopure Deionizer (Barnstead Thermolyne Corp.) and thoroughly degassed prior to use. Lactic acid (85% solution from Sigma), 4-(2 pyridyl)azo resorcinol monosodic salt (Aldrich), sodium octanesulfonate (Sigma) and other chemicals were reagent grade. All of them were employed without further purification. Standar solutions of lanthanide nitrates were from Rhône-Poulenc.

A reversed-phase column (25cm x 4.6mm i.d.) packed with Spherosil ODS-2 (Phase Separations) was employed for the separation of lanthanide ions.

Procedures

a) Detection.

In order to find the best conditios for REE detection, two different series of experiments were carried out. First, the pH, PAR concentration and ammonia buffer concentration of PAR-lanthanide solutions were varied and their absorbance was measured at different times over an 8-day period. Then, with the best conditions previously found for the post-column reagent, lanthanide solutions were injected in the chromatographic system without column using various mobile phase compositions and the detector response was registered at different wavelengths. The pH, acetonitrile content, pairing ion and lactic acid concentrations of the eluent were varied during these expriments.

b) Separation.

α hyroxybutiric acid, the compound commonly employed for REE elution in cation exchangers, is not readily available in our country and, indeed, it is relatively expensive. Thus, we searched for a common compoud capable of eluting these ions from the column in the RP-Ion Pair system. We found that simple acids, like perchloric and acetic, at concentrations which did not interfere with the detection system, were too weak for lanthanide elution. Other acids with complexing properties, like citric and tartric, produced extremely wide peaks and/or very short retention times. Finally, lactic acid, a compound with a structure similar to HIBA,

was capable of adequately eluting these metal ions with good efficiency and retention times adjustable by the lactic acid concentration and the pH of the mobile phase.

However, it was observed that retention times continuously changed when lactic acid was present in the mobile phase, indicating a non-equilibrium state in the system. It is known[14] that lactic acid easily reacts in highly concentrated solutions forming a great variety of esters. Thus, in the mobile phases prepared from the commercial 85% solution, the sterified species were slowly hydrolyzed producing a continuos change in the complexing properties of the compound. This phenomenon explains the variations in lanthanide retention times from one injection to the other.

To overcome this problem, a great volume of a 2 M lactic acid solution was heated for 6 hours, without boiling, and stocked in a dark flask. This treatment provokes the hydrolisis of all esters and the autosterification reaction cannot be reproduced in the resulting solution because lactic acid is sufficiently diluted. Mobile phases prepared with this solution gave perfectly reproductible retention times.

The cromatographic conditions finally retained for the separation of lanthanide ions were the following:

Column: 25cm x 4.6mm i.d., packed with 5 μ Spherisorb ODS-2

Column temperature: 28°C Flow: 1 mL/min

Mobile phase: acetonitrile-water 10:90 v/v with sodium octane-sulfonate 0.005 M and

phase A.- lactic acid 0.088 M, pH adjusted to 2.80

phase B.- lactic acid 0.66 M pH adjusted to 3.50.

Gradient

t(min)	0	5	15	25	26	5	36	46
% B	0	1	8	25	100	100	0	0
	separation				column cleaning		equilibrium	

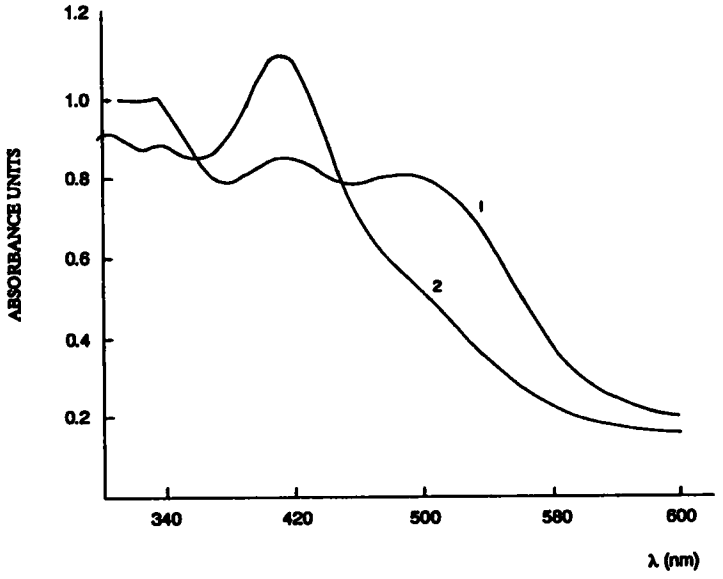

Figure 1. Absorbance Spectra of Par-Praseodimium (1) and PAR (2)

Solutions: 10^{-4} M PAR-Pr or PAR in 2M ammonia buffer (pH=9).
Blank: 2M ammonia buffer (pH=9)

Under these conditions, the most retained solute elutes at 24 minutes but it is necessary to clean the column from accumulated impurities by the passage of 10 mL of the strong mobile phase. Afterwards, the column is re-equilibrated to the initial conditions with only 10 mL of the weak phase.

RESULTS AND DISCUSSION

Detection

Figure 1 shows absorbance spectra of PAR and PAR-Pr solutions, 10^{-4} M each, in 2 M ammonnia buffer at pH = 9 . Absorbance maxima are found at 410 nm and 490 nm respectively. However, at the PAR-Pr maximum, the absorbance of PAR is still too

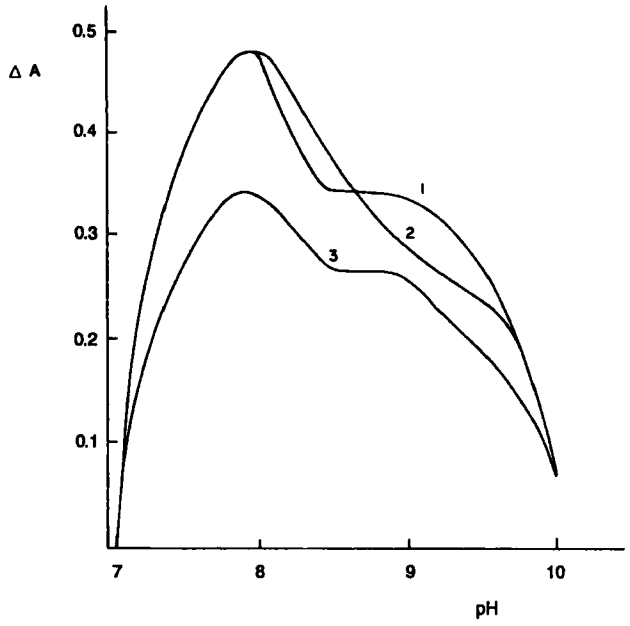

Figure 2. pH Effect on the Absorbance Difference (ΔA) Between the PAR-Pr and the PAR Solutions

Solutions: 10^{-4} M PAR-Pr or PAR in 2 M ammonia, pH adjusted with $HClO_4$ or NaOH.

(1) λ = 520 nm (2) λ = 540 nm (3) λ = 560 nm

high and it is necessary to select higher wavelengths for a good baseline control in the chromatographic expriments.

Figure 2 shows the effect of pH on the absorbance difference (ΔA) between the PAR-Pr and the PAR solutions. For pH<7 the PAR-metal complex is not formed and for pH>10 the lanthanide hydroxydes begin to precipitate.

The ammonia buffer concentration must be higher than 1.5 M to prevent hydroxyde precipitation but lower than 3 M to preserve PAR from degradation. In the range from 1.5 M to 3 M the absorbance of the PAR-Pr solution is practically constant.

The PAR solution is stable for long periods when: the PAR concentration is lower than 10^{-4} M, the ammonia buffer concentration is in the range from 1 M to 3 M and the pH is lower than 11.

To prevent interferences on the detection system, the mobile phase composition must fulfill the following requirements: acetonitrile content <15% v/v, lactic acid concentration <1 M and 2<pH<4 (the high pH limit is due to REE-hydroxyde precipitation).

Considering the precedent results, and the fact that the derivatizing reagent is mixed with the mobile phase at the column exit, the conditions finally selected for detection in the chromatographic experiments were the following:
Solution of PAR $5x10^{-5}$ M in 3 M ammonia buffer at pH 9
Ratio of mobile phase to post-column reagent 1 to 1
Detection wavelength 545 nm

Separation

In RP-IPC systems the hydrophobic pairing ions dissolved in the mobile phase are adsorbed on the suface of the packing transforming the stationary phase into a dynamic ion exchanger. The quantity of adsorbed pairing ion, which determines the column exchange capacity, depends basically on three main parameters: the hydrophobicity of the compound, its concentration in the mobile phase and the content of organic solvent in the eluent[15].

Under our chromatographic conditions, the column is initially equilibrated by the passage of 40 mL of weak mobile phase. On the other hand, during the mobile phase gradient the composition of the stationary phase does not change because the parameters that determine the quantity of adsorbed pairing ion remain constant. Therefore, only a small volume of weak mobile phase (about 5 void volumes) is required to re-equilibrate the column to the initial conditions.

Lanthanide ions are strongly retained on cation exchangers because of their high positive charge density. For their elution and separation, mobile phases of high strength and gradient

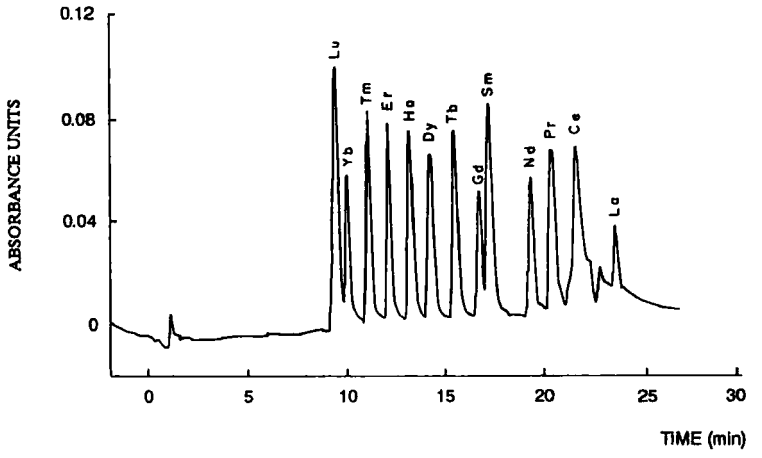

Figure 3. Separation of Lanthanides.

Column: 25cm x 4.6mm i.d. packed with 5 μ Spherosil ODS-2, temperature 28°C. Mobile phase: acetonitrile-water 10:90 v/v with sodium octanesulfonate 0.005 M and lactic acid (eluent A) 0.088 M pH=2.80, (eluent B) 0.66 M pH=3.50 Gradient in text. Flowrate 1 mL/min. Reagent: PAR 0.00005 M in 3M ammonia buffer, pH=9, flowrate 1 mL/min. Detection at 545 nm. Sample: mixture of 13 lanthanides at different concentrations (as in TABLE 4)

elution are required. However, to fasten the column equilibrium at the end of the separation in IPC systems, it is necessary to avoid strong changes in the column exchange capacity during the gradient. This can be achieved by means of a hydrophilic complexing agent dissolved in the weak and strong mobile phases at different concentrations. It has been demonstrated that a ten-fold increment in the concentration of this type of compounds in the eluent does not significatively change the capacity of the dynamic ion exchanger[16].

Lactic acid is a very hydrophilic compound that complexes lanthanide ions forming species of the type ML_n where n = 1, 2

TABLE 1

Separation Repetability.

Element	t_r(min)	Dispersion[1] (%)	Dispersion[2] (%)
Lu	9.3	2.2	3.9
Yb	10.3	1.6	5.2
Tm	11.6	1.9	3.6
Er	12.8	1.2	2.8
Ho	13.8	1.0	2.8
Dy	14.7	0.9	2.8
Tb	15.8	0.7	2.6
Gd	16.9	0.6	2.5
Sm	17.4	0.6	2.5
Nd	19.3	0.5	2.4
Pr	20.4	0.4	1.9
Ce	22.0	0.3	1.5
La	24.1	0.2	1.2

(1) standar sample injected six times.
(2) 6 different samples injected once each.

or 3[17]. These complexes are sufficiently strong to elute all REE but not too strong to prevent the formation of the PAR-metal complexes in the post-column reaction. The advantages of lactic acid compared to HIBA are its accesibility and the low cost of the commercial 85% solution.

Figure 3 shows the separation of lanthanides using a gradient of lactic acid concentration and pH. Under these conditions, 13 lanthanides are well separated, the only case of coelution is Europium-Samarium. The elution order is just the opposite of the lactate-REE complex stability order (increased stability from La to Lu). In fact, Europium and Samarium could not be separated because the stability of their lactate complexes is practically the same. Thus, the disadvantage of lactic acid is the lack of selectivity for this pair of solutes.

Table 1 shows the repetability of the separation assessed by a sextuplicate injection of a standar sample and by the injection

TABLE 2

Interference From Other Metallic Cations

Cation	t_r(min)*	Cation	t_r(min)*
Ba^{2+}	----&	Zn^{2+}	16.5
Sr^{2+}	----&	Ni^{2+}	17.6
Ti^{4+}	----&	Cr^{3+}	20.2
Fe^{3+}	3.3	Cd^{2+}	22.5
Cu^{2+}	8.5	Al^{3+}	24.0

(*) same experimental conditions as for the REE sample
(&) no signal was observed in these cases

of 6 samples with different lanthanide concentrations (differing by a factor of 50 between the two extreme samples). It must be noted that the rigoruos adjustment of the pH of the mobile phases, and especially the pH of the weak phase, is critical for the constancy of retention times.

The detection system based on the post-column reaction with PAR has a good sensitivity but a low selectivity. Several metallic ions also form coloured complexes with this reagent and interfere in REE determinations. Table 2 shows the retention times of several cations injected in the chromatographic system under the same experimental conditions that the lanthanide samples.

The poor selectivity of the derivatizing reaction provokes serious problems in the determination of lanthanides at low concentrations. In these cases, it is absolutely necessary to employ high purity reagents (completely free of trace metals) and to prevent any contact between the metallic parts of the instrument and the mobile phase. The latter is due to the fact that metal traces coming from the apparatus, column or tubing are

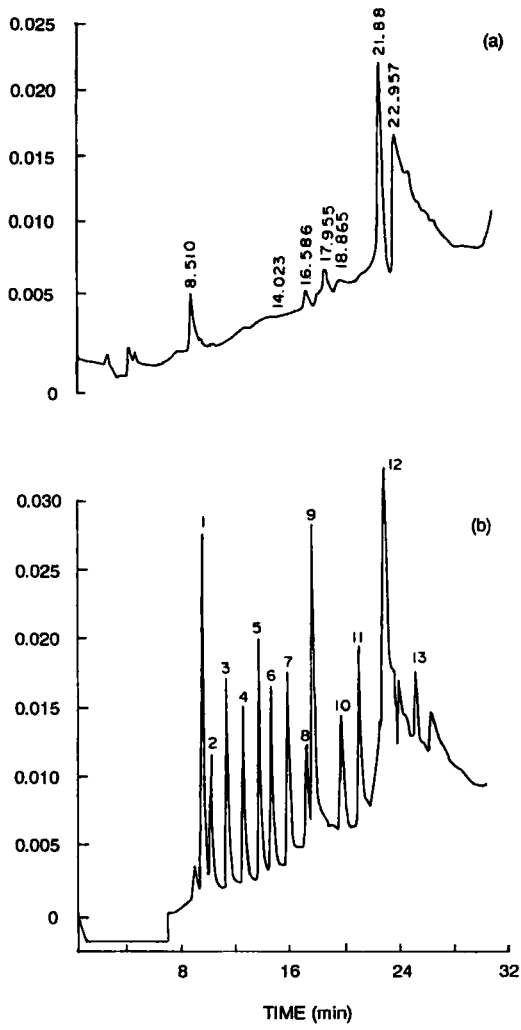

Figure 4. Interference of System Peaks in the Determination of Lanthanides at Low Concentrations.

Conditions as in Figure 3
(a) Blank run, (b) sample: (1) Lu, 2.6ppm (2) Yb, 2.5ppm (3) Tm, 2.4ppm (4) Er, 3.2ppm (5) Ho, 3.7ppm (6) Dy, 3.8ppm (7) Tb, 3.9ppm (8) Gd, 3.1ppm (9) Sm, 8.1 ppm (10) Nd, 5.9 ppm (11) Pr, 10.7ppm (12) Ce, 22ppm (13) La 7.3ppm

TABLE 3

Calibration Curves.
Equation: Y = a x bX where: Y=peak area, X=Concentration (ppm)

REE	Equation[1]		Linear Range[2]		Det.Coeff.	Det.Lim.[3]
	A	B	S.L.	I.L.	r^2	(ppm)
Lu	1.7	9.9	21	1.3	0.9993	0.2
Yb	-1.4	4.6	40	1.2	0.998	0.6
Tm	1.3	6.7	38	1.2	0.9998	0.3
Er	2.9	4.3	51	1.6	0.998	0.4
Ho	1.9	4.3	59	1.8	0.9994	0.4
Dy	1.2	4.1	60	1.9	0.9996	0.4
Tb	1.9	4.2	63	2.0	0.9993	0.4
Gd	3.7	2.3	49	1.5	0.995	0.7
Sm	5.1	2.8	64	4.0	0.9991	0.8
Nd	0.22	2.0	95	3.0	0.9994	0.9
Pr	0.23	1.4	171	5.3	0.990	1.8
La	2.5	0.3	277	8.5	0.998	5.6

(1) $A = a \times 10^{-4}$ $B = b \times 10^{-4}$
(2) S.L. = Superior Limit (ppm) I.L. = Inferior Limit (ppm)
(3) Detection Limit on the basis of 3 times the baseline noise

dissolved by the eluent (especially in acidic media) and transported to the column bed where they accumulate during the equilibrium of the column with the weak phase. Afterwards, they are eluted by the mobile phase gradient giving rise to "ghost" or "system peaks" in the chromatogram[7,11].

Figure 4a shows the chromatogram obtained from a blank gradient run using a high detector sensitivity. Comparison of Figures 4a and 4b indicates that some system peaks strongly interfere with the determination of the last eluting lanthanides, especially Cerium. In fact, under these conditions, Cerium cannot

TABLE 4

Precision of the Determination by Peak Area Measurements. Standar sample injected 6 times.

REE	Conc. (ppm)	C.V. (%)[&]	REE	Conc. (ppm)	C.V. (%)[&]
Lu	10.5	3.8	Gd	12.3	5.4
Yb	9.9	3.3	Sm	32.2	2.6
Tm	9.4	2.5	Nd	23.7	2.3
Er	12.7	3.5	Pr	42.7	3.7
Ho	14.7	4.2	Ce	88.0	5.3
Dy	15.0	4.4	La	58.2	0.9
Tb	15.8	3.3			

& Peak area variation coefficient (relative standar deviation)

be unequivocally detected when its concentration is lower than 40 ppm. Thus, the precise determination of low concentrations of lanthanides in natural samples requires first, a sample pretreatment to eliminate interfering metal ions (especially transition metal ions) and then, the use of adequate apparatus, columns and tubing ("free metal" chromatographic materials) for REE separation.

With our chromatographic system, the detection limits and the precision of peak area or peak height measurements are limited by the background noise provoked by the elution of metal traces accumulated in the column.

Table 3 shows the results of the regression analysis over the linear portion of the curve Peak Area vs Concentration (ppm) for each metal ion, with the exception of Cerium. With a confidence level of 95%, the intercepts are not significatively different from zero except for Samarium which is probably affected by the coelution of a system peak (Fig. 4). The superior limit of the linear range is relatively low because of the low concentration of PAR in the post-column reagent. However, this condition is necessary for a good stability of this compound.

The detection limits, calculated on the basis of 3 times the baseline noise, are lower than the ppm (<10 ng) for the lanthanides that are not affected by coelution of system peaks (see Fig. 4 and Table 3). This means that the detection system has a good sensitivity and, with adequate instrumentation, all the 13 lanthanides could be detected at low nanogramme levels.

Peak area measurements were employed for the calibration curves because they proved to be more precise than height measurements. The peak area variation coefficients, calculated from a sextuplicate injection of a standar sample, are shown in Table 4.

All the experiments reported in Tables 1 to 4 were performed using the same PAR solution for the post-column reaction. A great volume of this solution was prepared and stocked in a dark flask and it was subsequently employed over a period of, approximately, one month with no apparent degradation.

ACKNOWLEDGMENTS

We wish to acknowledge the Rhône-Poulenc Society for kindly providing us with lanthanide standars and "Dirección General de Asuntos del Personal Académico-UNAM" for their aid in the financial support of this work.

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