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Eriochrome Black T as a post-column reagent for the ion chromatographic determination of rare earths ☆

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Abstract

The use of Eriochrome Black T in an alkaline, 40% methanol solution was found to be appropriate as post-column reagent for the determination of rare earths by ion chromatography. Detection of individual lanthanides and lanthanum was carried out at 512 nm and 650 nm after separation by dynamic cation exchange chromatography with gradient elution on C_{18} column and employing a solution containing α-hydroxyisobutiric acid/sodium octanesulfonate at pH 3.8 as eluent. The effect of the presence of micelles in the post-column reagent was studied. Sensitivities obtained by the addition of the cationic surfactants cetylpyridinium chloride (CPC) and hexadecyltrimethylammonium bromide (CTAB) were lower than those measured without surfactant addition. In some cases, the signal was totally suppressed. No change in sensitivity was observed with non-ionic (Triton X-100) or anionic (sodium dodecylsulphate, SDS) surfactants but a slight improvement in the baseline noise was observed with the SDS. An evaluation of the influence of chemical and operational variables on the post column reaction (PCR) reagent was carried out either by spectrophotometric tests or by chromatographic experiments. A comparison was performed between three PCR reagents: Eriochrome Black T and xylenol orange in the presence of a cationic surfactant and arsenazo III. Calibration response was linear up to an analyte concentration of 5.0 μg ml^{-1}. Absolute detection limits lower than 7 and 17 ng were obtained at the detection wavelengths of 650 nm and 512 nm respectively, for all the natural lanthanides and lanthanum.

Keywords: Eriochrome Black T; Rare earth ions; Lanthanides

1. Introduction

The characterization of lanthanide containing materials is of great importance in several technological and scientific fields, such as the nuclear industry, the development of superconducting materials, geochemistry and metallurgy. Dynamic ion-exchange chromatography (i.e. the use of an organic reagent present in the eluent as in situ column modifier) has been widely employed for the separation of lanthanides since the early works carried out by Cassidy and co-workers [1–3]. Detection has been performed by employing different post-column reagents, such as arsenazo III [2,3], PAR [1,3,4], xylenol orange [5,6] and others [1,2].

Eriochrome black T (EBT) is a well known colorimetric reagent. It has two ionizable phenolic hydrogen atoms and exists as three different coloured

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species in solution ($pK_1=6.3$, $pK_2=11.5$). A solution of the dye is violet at pH below 6, blue between 8 and 12 and orange above pH 13. As for most metal cations, an EBT:lanthanide ratio of 1:1 has been proposed for the complexes [7,8]. Ratios of 2:1 or 3:1 for Ca^{2+} and Mg^{2+} [9] and for the trivalent metals Al^{3+}, Ga^{3+} and In^{3+} [10] have also been suggested. In spite of its wide application as metalochromic indicator in EDTA titrations and in spectrophotometric determinations, EBT has scarcely been applied as post-column reagent in ion chromatography [11,12]. The aim of this work was to evaluate the analytical performance of the Eriochrome black T as a non-specific colorimetric reagent for post-column detection of lanthanides.

2. Experimental

2.1. Apparatus

All experiments were conducted with a Konik (Barcelona, Spain), Model KNK-500A liquid chromatograph equipped with a Rheodyne (Cotati, CA, USA) Model 7125 injector and a 100 μl sample loop. A Spherisorb (Norwalk, CT, USA) silica based C_{18} reverse phase column (25 cm×4.6 mm I.D.) was used as analytical column. The PCR reagent was delivered under nitrogen pressure using a pneumatic pump Lazar (Los Angeles, CA, USA) to a stainless steel T-shaped connector Valco ZT1 (Houston, TX, USA) for tube size 1/16'', bore 0.75 mm. The eluent/PCR reagent mixed solution was routed through a stainless steel tube (30 cm length; 0.010'' ID) to a Linear (Reno, NV, USA), Model UVIS 204 variable wavelength spectrophotometric detector. No reaction coil was employed. Data acquisition and integration of chromatograms were performed by means of a AT-386 type, 25 Mhz computer, coupled to an A/D interface board. A standard integration software, Konikrom Chromatography Data System V. 5.2, Konik (Barcelona, Spain), was employed for data processing. Molecular absorption spectra of the studied complexes were obtained with a Perkin-Elmer (Norwalk, CT, USA) Model 559A UV–Vis spectrophotometer.

2.2. Reagents

Purified water (18.3 MΩ) obtained from a Nanopure system (Sybron/Barnstead, Boston, MA, USA) was employed. All eluent and sample solutions were filtered through 0.22 μm filters. Eluents were degassed with helium. The mobile phase was prepared by dissolving in water appropriate amounts of analytical reagent grade α-hydroxyisobutiric acid (TCI, Tokyo, Japan) and sodium octanesulfonate (Eastman Kodak Co., Rochester, NY, USA), followed by adjustment at pH=3.8 with aqueous ammonia. The post-column chromogenic reagent was Eriochrome Black T, sodium 1-(1-hydroxy-2-naphthylazo)-6 nitro-2-naphthol-sulfonate, (Merck KGaA, Darmstadt, Germany). Stock solutions of 10^{-2} *M* Eriochrome Black T were daily prepared in pure methanol. The EBT solutions were prepared by dilution with 60% of buffer/40% methanol solution. EBT concentrations between 10^{-5} and 10^{-3} *M* were evaluated to optimize the signal-to-noise ratio. Finally, a concentration of 2 10^{-4} *M* was chosen for all the subsequent experiments. The alkaline buffer solution (pH=8.7) was a 1:1 mixture of 2 *M* aqueous ammonia and 4 *M* ammonium chloride. The tested surfactants and their critical micelle concentrations (cmc) in aqueous solutions in the absence of additives [13] were: polyoxyethylene-t-octylphenol (Triton X-100, cmc=0.2 m*M*), non-ionic surfactant; sodium dodecylsulfate (SDS, cmc=8.1 m*M*) anionic surfactant; cetylpyridinium chloride (CPC, cmc=0.9 m*M*) and hexadecyltrimethylammonium bromide (CTAB, cmc=0.9 m*M*) both cationic surfactants. Stock solutions of the ionic surfactants were obtained by dissolution with 40% methanol–60% buffer solution (pH=8.7). Stock solutions (1000 μg ml^{-1}) of the different cations were prepared as indicated elsewhere [6].

The PCR reagent was delivered at a flow-rate of 0.9 ml min^{-1}. Batch spectrophotometric experiments were carried out by simulating the final composition of the solution in the chromatographic reaction cell for a HIBA concentration of 0.24 *M*.

Analysis of a rare earth alloy was performed as follows: 0.100 g sample was dissolved in 5 ml of aqua regia and diluted to 100 ml with water. A 100 fold diluted sample solution was injected onto the column.

3. Results and discussion

3.1. Chromatographic separation

The selected method for the lanthanide separation was a well known technique, dynamic ion-exchange chromatography on a C_{18} column, with 1-octanesulfonate as ion-interaction reagent and a complexing agent (HIBA) as mobile phase. The advantages of this technique, as well as the factors affecting reproducibility of retention time and efficiency have been discussed [1–3].

The chromatographic system was operated in a linear gradient program mode with the HIBA concentration varying from 0.05 *M* to 0.24 *M* over 10 min at a mobile phase flow-rate of 1 ml min^{-1}. The operating column temperature was 30°C. After each run the initial equilibrium conditions are reached after 7 min of an isocratic flow of the eluent with 0.05 *M* of HIBA. The 1-octanesulfonate concentration in the eluent was maintained constant at 0.01 *M*. Lanthanides form complexes with HIBA that lower the affinity of the lanthanides for the cation exchange sites. Because lutetium forms the most stable complex with HIBA, it will elute first, con-

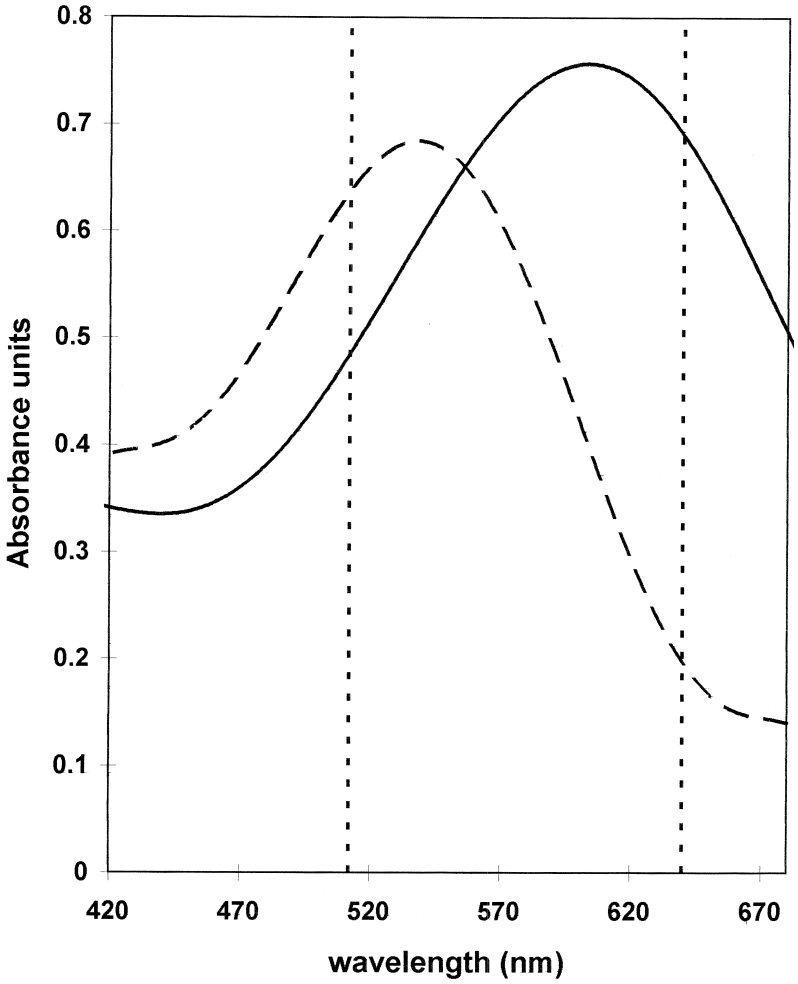

Fig. 1. Absorption spectra of EBT (–); Nd-EBT (---) complex vs. water.

versely, lanthanum, which forms a weaker complex with HIBA, will elute later.

3.2. Wavelength selection

Absorption spectra of the EBT reagent and all lanthanide-EBT complexes in the presence of the components of the eluent and the PCR were obtained using water as reference. Absorption curves of EBT and the Nd-EBT complex are depicted in Fig. 1. That element was considered as representative of the group. Similar spectra were obtained for the remaining lanthanides.

The measurement of Lanthanide-EBT complexes can be carried out successfully at wavelength where the maximum difference between the free EBT and the lanthanide-EBT complex absorbances is found. By observing the curves in Fig. 1, it may be concluded that direct molecular absorption can be applied at 512 nm and indirect detection mode at 640 nm.

3.3. Selection of pH in the PCR reagent

Changes in pH are expected to affect the EBT complexing capacity for the lanthanides, and consequently, the relative absorbance of the lanthanide-EBT complex vs. free EBT. To optimize pH con-

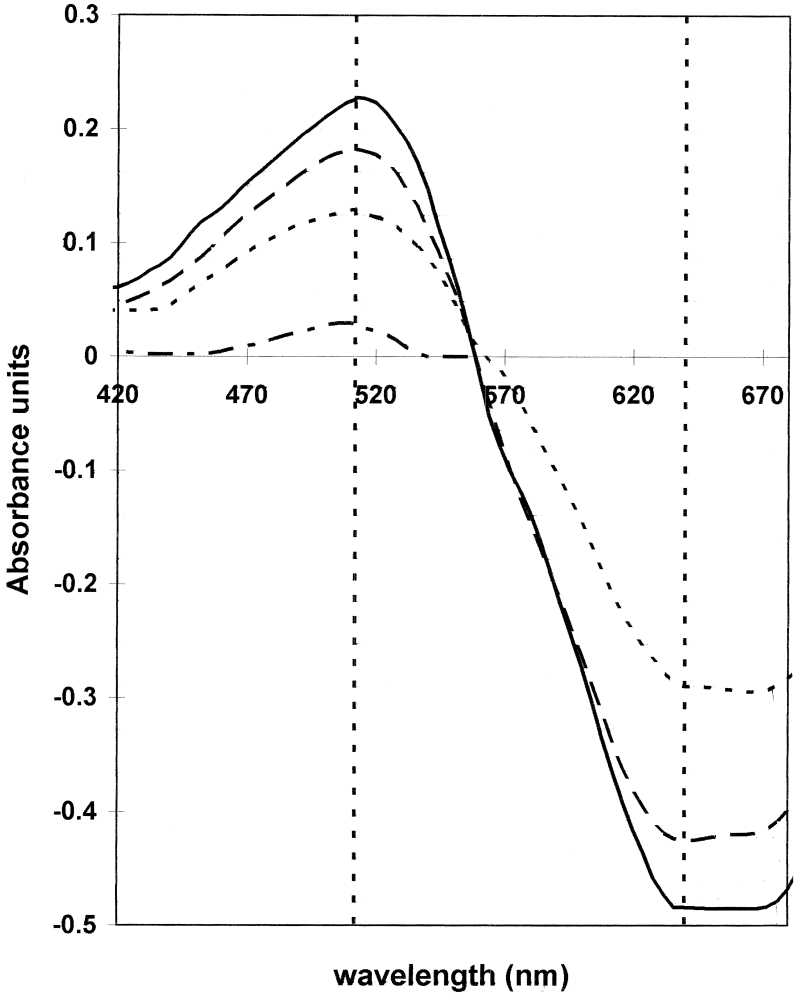

Fig. 2. Absorption spectra of Nd-EBT complex vs. EBT at different pH values. Where -·- is pH=7; --- pH=8; –– pH=9; — pH=10.

ditions for the PCR reagent, we prepared solutions matching the reagent concentrations found at the detector after the tee connection outlet (with the exception of the buffer solution). For each solution, pH was adjusted with 1*M* sodium hydroxide solution. Absorbance vs. wavelength curves recorded for pH values between 7 and 10 using EBT as reference are shown in Fig. 2. Sensitivities increases with pH. Selected working wavelengths (512 and 640 nm) are indicated on the plot. Due to the intrinsic buffer capacity of 0.24 *M* HIBA solution, a relatively high concentration of the alkaline buffer should be required to increase the pH in the PCR reagent. Therefore, a compromise value of pH 8.7 was employed for chromatographic operation.

Although acceptable spectrophotometric sensitivities were obtained at the chosen wavelengths the baseline noise arising from pulses from the pump was relatively high, particularly at 640 nm (indirect mode). Two possibilities may be selected to overcome this problem. A pulse damper may be added to the line, which results in a decrease of the peak to peak noise by a factor of about nine. Alternatively, a smoothing routine can be applied to the raw chromatographic peaks. The second alternative was chosen. A standard software routine based in the

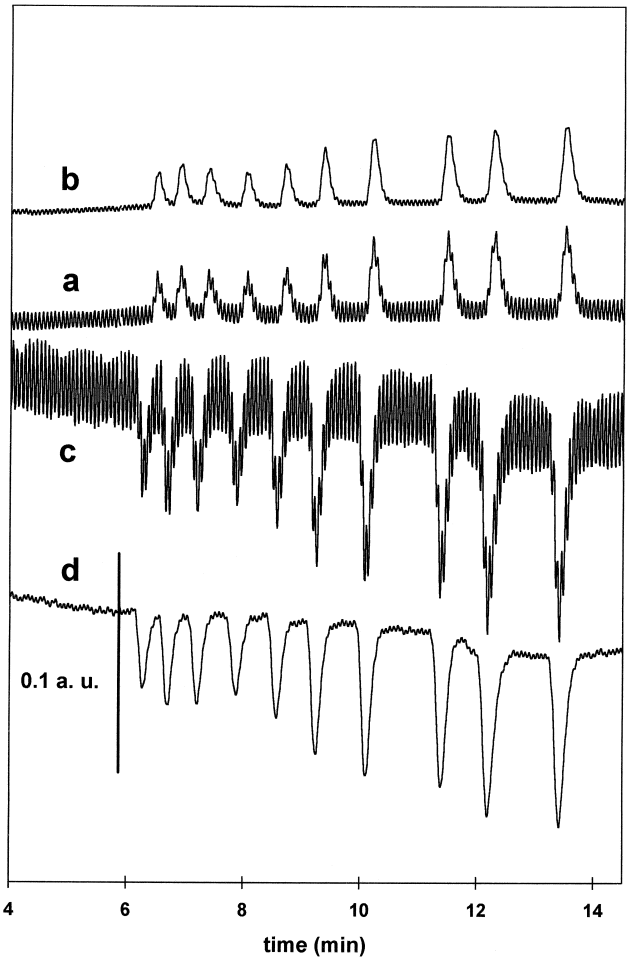

Fig. 3. Chromatograms of 1 $\mu g.ml^{-1}$ of ten lanthanides. (a) Original chromatogram at 512 nm; (b): Idem after one smoothing process; (c) Original chromatogram at 650 nm; (d) Idem after two smoothing processes. Experimental conditions were as described in the text.

Savitzky-Golay algorithm [14] was applied once on peaks measured at 512 nm and twice on signal recorded at 640 nm. A five fold and ten fold decrease in noise respectively, was observed. Fig. 3 shows raw and smoothed chromatograms obtained at both wavelengths for ten successively eluted rare earths (1 $\mu g\ ml^{-1}$ each).

3.4. Effect of surfactants

The addition of surfactants to some dye produce sensitivity enhancements that can be attributed to different processes: micelle or ternary complexes formation. A sensitivity improvement has been reported for the addition of cationic surfactants when xylenol orange was employed as post-column reagent [6].

In the present study, no changes in sensitivity were observed with anionic surfactant (sodium dodecylsulphate, SDS), but the baseline noise is lower. With non-ionic surfactant (Triton X-100) an increase in baseline drift appears at 512 nm, as gradient advances. Sensitivities obtained with the addition of cationic surfactants such as cetylpyridinium chloride (CPC) and hexadecyltrimethyl ammonium bromide (CTAB) were lower.

It is worth mentioning that cationic surfactants cause dye aggregates to be retained by the filter of the pump driving the PCR reagents. It is possible that the addition of surfactant favours the aggregation of EBT dye, preventing the reaction with the REE.

3.5. Effect of foreign ions

As many polyvalent cations are able to change the absorbance of EBT in basic solutions, the effect of the presence of Mg(II), Al(III), Cr(III), Fe(II), Fe(III), Ni(II), Cu(II), Zn(II), Y(III), Cd(II), Hg(II), Ba(II), Th(IV) and U(VI) was examined by adding

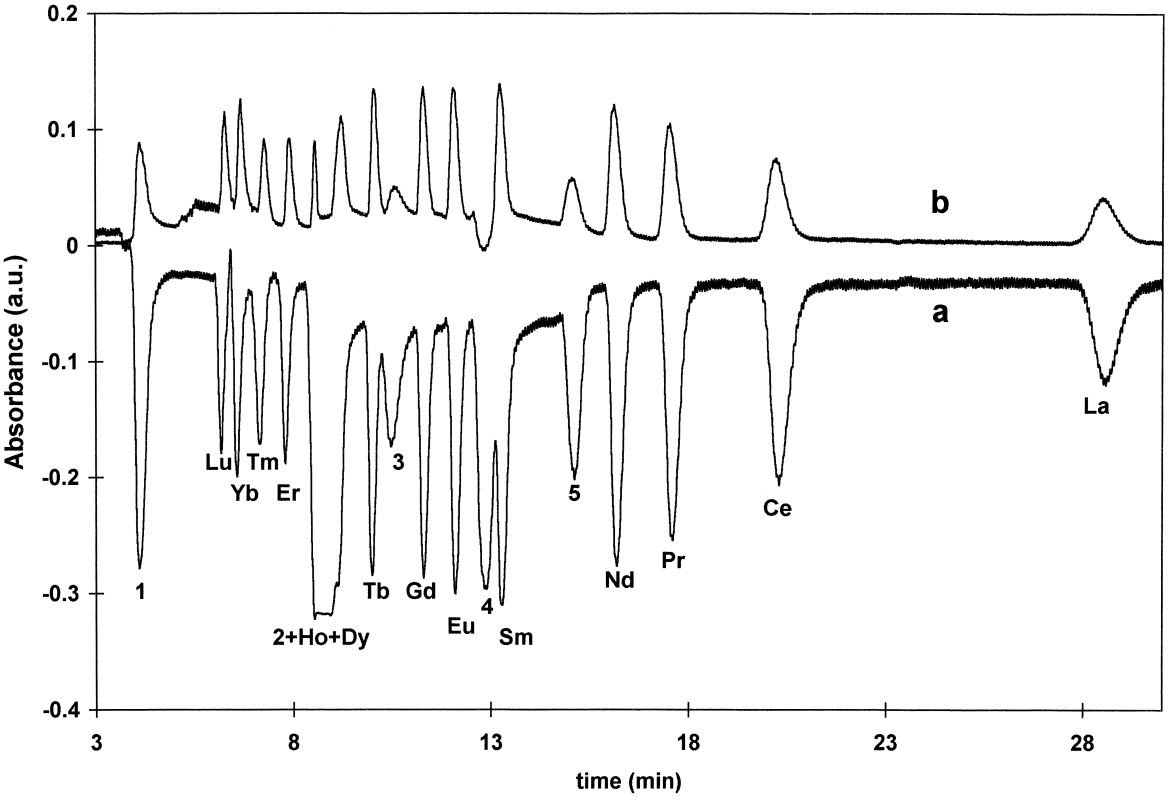

Fig. 4. (a) Chromatogram of 5 $\mu g.ml^{-1}$ of each lanthanide with 40 $\mu g.ml^{-1}$ of the interferences: 1: Fe(III); 2: Cu(II)+Y(III); 3: U(VI); 4: Ni(II); 5: Fe(II). Wavelength detection at 650 nm. (b) Idem at 512 nm. Experimental conditions were as described in the text.

40 μg ml^{-1} of each foreign ion to a solution containing 5 μg ml^{-1} of each lanthanide. Peaks corresponding to: Fe(II), Fe(III), Ni(II), Cu(II), Zn(II), Y(III), Th(IV) and U(VI) were detected. These elements constitute potential interferences for the system studied and should be considered for the determination of lanthanides in complex samples.

The effect of some of the concomitant element peaks on the separation and detection of the 14 rare earths, at 512 and 650 nm is shown in Fig. 4. Differences in sensitivities at both wavelengths are clearly observed.

3.6. Linearity, detection limits and precision

Calibration curves were linear in the tested range of 0.1 to 5.0 μg ml^{-1} of each lanthanide. Detection limits were estimated from three times the measured standard deviation of the baseline noise after one smoothing process of the signal at 512 nm and two smoothing processes at 650 nm. Regression data and detection limits are summarized in Tables 1 and 2.

Precision was estimated by calculating the relative standard deviation of peak areas at 512 nm, from ten injections of a standard solution of 1 μg ml^{-1} of each lanthanide. Obtained values were about 6% for the heaviest lanthanides (Lu, Yb, Tm, Er, Ho, Dy and Tb) and about 3% for the lightest (Gd, Eu, Sm, Nd, Pr, Ce and La).

Table 2
Regression data of integrated absorbance (650 nm) vs. concentration: equation $y=a+bx$, where y=peak area (arbitrary units), x=analyte concentration (μg ml^{-1}), No. of data points=6

Element	a×10^4	b×10^5	SD×10^4	r[a]	DL/ng[b]
Lu	4.7 (2.5)[c]	3.00 (0.08)	3.3	0.9984	7
Yb	2.5 (3.2)	3.8 (0.1)	4.2	0.9985	6
Tm	1.3 (2.2)	4.01(0.07)	2.1	0.9993	6
Er	0.0 (3.0)	3.9(0.1)	2.9	0.9987	6
Ho	6.3 (3.6)	4.4(0.1)	3.9	0.9986	5
Dy	4.4 (10.9)	5.7 (0.4)	4.6	0.9923	4
Tb	11.1 (9.5)	6.6(0.3)	14	0.9955	3
Gd	20.5 (9.4)	6.8(0.3)	12.3	0.9958	3
Eu	27.8 (7.5)	7.5 (0.2)	12.1	0.9979	3
Sm	10.4 (18.5)	8.9(0.6)	9.6	0.9907	3
Nd	11.9 (9.8)	10.1 (0.3)	23.7	0.9980	2
Pr	11.7 (3.2)	10.4 (0.1)	12.6	0.9998	2
Ce	5.4 (13.4)	11.7 (0.4)	17.2	0.9972	2
La	4.0 (13.6)	7.9 (0.4)	17.5	0.9935	3

[a] Correlation coefficient.
[b] Detection limit.
[c] Standard deviation in parentheses.

3.7. Comparison with other PCR detection methods

Linearity and detection limits achieved with the proposed procedure were compared with those obtained by employing two different post-column reagents under optimized conditions. The systems selected for comparison were detection with arsenazo

Table 1
Regression data of integrated absorbance (512 nm) vs. concentration: equation $y=a+bx$, where y=peak area (arbitrary units), x=analyte concentration (μg ml^{-1}). No. of data points=5

Element	a×10^4	b×10^5	SD×10^4	r[a]	DL/ng[b]
Lu	4.6 (1.5)[c]	1.12 (0.05)	1.5	0.9974	17
Yb	8.2 (3.5)	1.3 (0.1)	3.3	0.9906	14
Tm	9.9 (2.2)	1.06 (0.07)	2.1	0.9943	16
Er	6.6 (1.8)	1.19 (0.06)	1.8	0.9968	16
Ho	7.4 (2.1)	1.44 (0.06)	2.0	0.9972	13
Dy	10.8 (3.1)	1.89 (0.09)	3.0	0.9963	10
Tb	12.1 (2.6)	2.32 (0.08)	2.4	0.9984	8
Gd	12.1 (3.0)	2.69 (0.09)	2.9	0.9983	7
Eu	14.8 (3.8)	2.9 (0.1)	3.6	0.9977	7
Sm	15.5 (5.8)	3.2 (0.2)	5.5	0.9955	6
Nd	6.9 (2.9)	3.89 (0.09)	2.8	0.9992	5
Pr	3.6 (1.9)	4.11 (0.06)	1.8	0.9997	5
Ce	−6.1 (3.3)	3.96 (0.09)	3.1	0.9991	6
La	−9.0 (7.4)	3.2 (0.2)	7.1	0.9927	8

[a] Correlation coefficient.
[b] Detection limit.
[c] Standard deviation in parentheses.

Table 3
Comparison with other PCR systems, using optimized experimental conditions for each system

Element	Arsenazo III (658 nm)		Xylenol Orange (618 nm)		EBT (650 nm)		EBT (512 nm)	
	r^a	DL/ng[b]	r^a	DL/ng[b]	r^a	DL/ng[b]	r^a	DL/ng[b]
Lu	0.9997	1.4	0.9983	6	0.9984	7	0.9974	17
Er	0.9998	0.5	0.9992	3	0.9987	6	0.9968	16
Nd	0.9999	0.2	0.9996	0.4	0.9980	2	0.9992	5
Ce	0.9999	0.2	0.9996	0.3	0.9972	2	0.9991	6

[a] Correlation coefficient.
[b] Detection limit.

III (658 nm) [15] and with xylenol orange/CPC (618 nm) [6]. Tests were performed for all lanthanides. Results are included in Table 3 where Nd and Ce were chosen as representative of the low atomic weight rare earths, and Lu and Er as representative of the heaviest elements.

Two comparative chromatograms with different post-column dyes are shown in Fig. 5. The top chromatogram is the separation and detection of a standard solution of 1 μg ml^{-1} of each rare earth, with xylenol orange (with CPC) as PCR reagent [6], while the lower chromatogram shows the separation of the same standard solution detected with eriochrome black T at 512 nm.

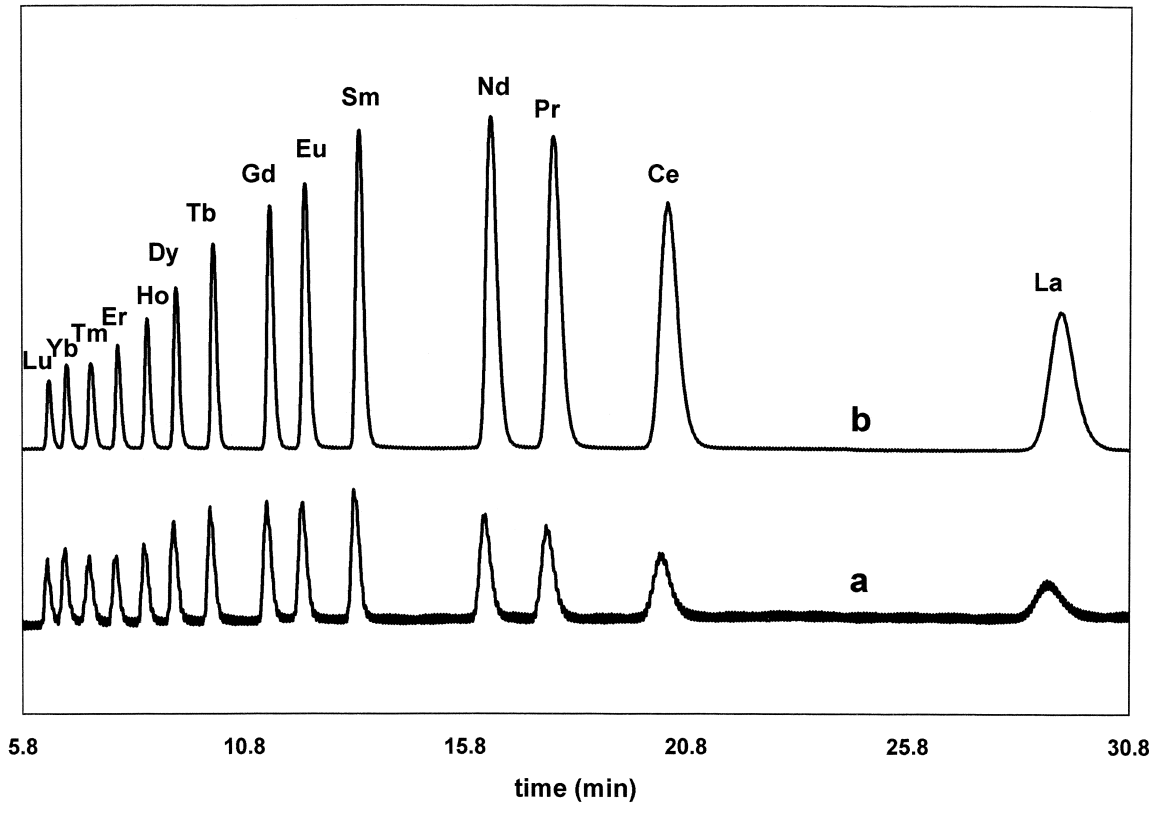

Fig. 5. Comparison of chromatograms with two different PCR reagents. (a) [EBT]=2 10^{-4} M; flow-rate: 0.9 ml. min^{-1} at 512 nm; (b) [XO]=5.10^{-5} *M*, [CPC]=2.4.10^{-3} M; flow-rate: 1.5 ml min^{-1} at 618 nm. Eluent conditions of both experiments was the same and it was described in the text.

Table 4
Percentage composition of a rare earth alloy, obtained with the mentioned methodolgy with two different PCR reagents

Element	Arsenazo III	EBT
Nd	9.8±0.2	9.5±0.4
Pr	3.8±0.7	3.4±0.4
Ce	54±2	51±2
La	27.7±0.3	28.3±0.3

3.8. Analytical application

The applicability of the developed procedure was tested for the characterization of a rare earth alloy employed as oxygen scavenger in the industrial processing of metal alloys. Arsenazo III and eriochrome black T as PCR reagents were compared. Results are included in Table 4.

Eriochorme black T as post-column reagent can be considered as an interesting alternative for the ion chromatography determination of the lanthanides using HIBA as eluent. The method could be applied to different REE separation schemes, but a study of the influence of the eluent and possible interferences by other elements would be required. Sensitivities were lower that those achieved with arsenazo III and xylenol orange, but being the EBT a non specific reagent, it could be conveniently applied to the simultaneous detection of rare earth elements and other polyvalent cations.

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