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RAPID SEPARATION OF LANTHANIDES BY REVERSED PHASE HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

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RAPID SEPARATION OF LANTHANIDES BY REVERSED PHASE HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

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ABSTRACT

Dynamically modified high performance liquid chromatography was used for the separation of lanthanides. The separations were carried out on a C_{18} column dynamically converted into a cation exchanger by the sorption of hydrophobic anions like n-octane sulphonate. α-hydroxy isobutyric acid was employed as an eluent. The separated lanthanide ions were monitored spectrophotometrically after post-column reaction with Arsenazo (III), used as a chromogenic reagent. The effect of different chromatographic parameters such as concentrations of eluent and modifier, mobile phase pH, presence of methanol in the mobile phase etc. were studied and the optimum separation conditions were established. It has been possible to separate fourteen lanthanide elements in less than 5 minutes by elution with α-hydroxy isobutyric acid in the concentration gradient mode. Quantitative determination was performed for La and Nd using internal standards like Ce and Er.

1. INTRODUCTION

Separation of lanthanides is an example of one of the most complex types of chemical separations in view of their similar electronic configuration and nearly same ionic radii. The 14 elements between La and Hf are completing one of their inner levels - 4f, while the outer levels remain unchanged. The valency 3+ is fairly typical for all these elements (with exceptions e.g. Ce, Eu). Separation and determination of lanthanides is of great importance in environmental sciences, geochemistry, in nuclear technology for the burn-up determination of fuels etc. In the modern society, rare-earth elements (REEs) are widely used in applications such as ceramics, semi-conductors, magnets, fertilizers and so forth [1]. Thus large amounts of REEs are emitted in to the environment, which may lead to substantial exposure to humans. In this context, analytical methods for the determination of REEs in environmental samples should be established to elucidate their environmental and physiological role [2]. The chemistry of REEs makes them particularly useful in studies of marine geology [3,4]. The ability to detect low levels of REEs in aqueous samples is particularly important in the study of the mobility of REEs during water-rock interactions. Because REEs serve as analogue for the actinide elements (Am, Cm), the accurate determination of REEs is also important for predicting the behavior of the radioactive actinides in the future radioactive repositories [5]. The use of Sm-Nd couple in geochronology is very well known and is commonly used for dating of different types of rocks[20].

In nuclear technology, separation and quantification of individual lanthanides is a challenging task, since it should be done in a short time and in a simple way. A number of methods have been reported in the past but these methods require long separation times or give only partial resolution between the neighbouring lanthanides. Before 1940s, the task of separating lanthanides was accomplished only with great efforts, using classical chemical processes. The chemical separations like fluoride, oxalate, phosphate and hydroxide precipitations, partial decomposition, dissolution etc. are time consuming, require significant sample size and suffer from the possibility of lanthanides losses [6,7].

Developments in different areas of science and technology have prompted scientists to depend upon separation method for lanthanides using classical ion-exchange methods employing complexing agents as eluents. The introduction of the use of complexing eluents in the ion exchanger made possible the repetition of the same chemical reaction many thousands of time, amplifying the slight difference in the stability constants of the Ln-eluent complexes and this led to better separation methods. But these methods have poor resolution and are time consuming with respect to elution and quantification [8].

Modern analytical techniques which are available for lanthanides determination have also got many drawbacks. For example, neutron activation analysis provides suitable sensitivity but is complicated, depends upon the availability of a reactor and involves complicated experimental procedures [9]. It also requires chemical group separation of the element of interest from the interfering element [10] and cannot be used in matrices containing U, Pu etc.

Isotope Dilution-Thermal Ionisation Mass Spectrometry (ID-TIMS) usually provides precise and accurate results but it can not be used for four lanthanides viz. Pr, Tb, Ho & Tm. Also the technique is prone to isobaric interferences in the case of certain lanthanides. Though AAS allows accurate and precise determination [11], the technique offers poor sensitivity and is a single element analysis technique [12].

Application of HPLC with on-line detection has reduced the analysis time from days to a few minutes because of its speed, high sensitivity and multi-elemental analysis capability using single injection. HPLC can give rapid, high resolution and sensitive detection for many metal ion species including lanthanides [13].

There are two approaches for the separation of metal ions using HPLC viz. (i) using bonded phase ion-exchangers [14,15] and (ii) using dynamically modified reversed phase column [16]. Studies have shown that dynamic ion exchangers give superior resolution for the metal ion separations and greater flexibility with regard to choice of separation conditions than bonded ion-exchangers [17-19]. Dynamic exchangers are formed when ionic hydrophobic modifiers are sorbed onto the hydrophobic surface of the reversed phase to produce a charged layer at the surface where ion exchange can occur. The detection of the lanthanides was done by post-column reaction where, the eluted lanthanide ions form a fast and strong complex with certain chromogenic reagents to give complexes of high molar absorbance. This report gives the results of detailed investigations carried out for the separation and quantification of lanthanides using HPLC.

Initially, experiments were focused on establishing the conditions necessary for isocratically separating and quantifying lanthanides on a modified reversed phase column. Later on, parameters like mobile phase composition, concentration of the post-column reagent, pH, optimum monitoring wavelength for observing the eluting lanthanides, use of internal standards for quantification etc. were studied for obtaining fast and efficient separation of lanthanides.

2. EXPERIMENTAL

2.1. Apparatus

A schematic of the HPLC system used in the present work is given in Fig.1. It consisted of a L-7100 (Merck Hitachi) gradient pump, a Rheodyne sampling valve (Model 7725I) with 20μL sample loop, a 1cm guard column and a 15cm analytical column (Supelcosil LC_{18}) (both the columns packed with C-18 reversed phase material) and a Diode Array Detector (DAD) L-7450A (Merck Hitachi). The eluted ions were monitored after a post-column reaction with a metallochromic reagent. Post-Column Reagent (PCR) was added with a piston pump (Hurst, Princeton

Ind.) into the low dead volume mixing tee (Valco) via a pulse dampner. The signal from the detector was processed by HSM D-7000 software package and the chromatograms were monitored on PC. The HPLC system was computer controlled through interface D-7000 (Merck Hitachi).

2.2. Reagents and Materials

Freshly deionised water (18.2 MΩ cm) purified through a Milli Q system (Gradient-Millipore) was used for all dissolutions and dilutions. α-Hydroxy IsoButyric Acid (α-HIBA) (Fluka) was used as an eluent. Camphor-10-sulphonic acid (Fluka) and sodium salt of n-octane sulphonic acid monohydrate (Sigma-Aldrich) were tested as the cationic modifiers. The lanthanides were obtained in the form of their oxides from Indian Rare Earths Ltd. (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy and Yb) and Fluka (Ho, Er, Tu and Lu) having chemical purity greater than 99.99% and were of natural isotopic composition. These oxides were dissolved in nitric acid, evaporated to near dryness and stock solutions were made in dilute nitric acid (0.01M). Arsenazo (III) (Fluka) was used as the PCR. All HPLC mobile phases were filtered through 0.45μm Millipore membrane filters.

2.3. Procedure

Appropriate quantities of α-HIBA and modifiers camphor-10-sulphonic acid and sodium n-octane sulphonate were dissolved in water and made to 0.5M and 0.1M, respectively. pH of both the solutions was adjusted using ammonium hydroxide and nitric acid. All experiments were conducted at ambient temperature (25^0C). Eluent was pumped through the column until a constant pH of the effluent was observed, serving as an evidence for equilibrium conditions in the column. The eluted ions were monitored after a post-column reaction with the metallochromic reagent, Arsenazo(III).

3. RESULTS AND DISCUSSION

Preliminary work was concentrated on establishing the conditions necessary for isocratically separating lanthanides on a 15cm Supelcosil C_{18} column. A synthetic mixture of 14 Lns (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) of 5ppm (w/v) each, injected through a 20 μL loop, could be separated in the isocratic mode in 50 minutes using a mobile phase consisting of 0.1M α-HIBA and

0.003 M sodium n-octane sulphonate (Fig.2). However, the heavier lanthanides showed poor resolution while broad peaks were observed for lighter lanthanides.

The various parameters discussed below were studied with an aim to achieve the separation of lanthanides in short time.

3.1. Wavelength

The detection of the Ln-Arsenazo(III) complex was done by the UV-Visible detector with photodiode array as transducers for the absorbance measurements. After passing through the sample and the solvent in the flow cell, the light from the deuterium lamp is focused onto the prism and the dispersed light is reflected onto the photodiode array, for conversion into electrical signals. Selection of the detector wavelength is an important factor in the attainment of high sensitivity. λ corresponding to a high molar absorptivity of the Ln-Arsenazo(III) would provide a large change in absorbance. Another important factor was the base-line noise generated by the piston pump used to deliver PCR. Under the experimental conditions, λ_{max} of the Ln-Arsenazo(III) complex and that of the reagent blank are not much different and hence the base line noise increases as the molar absorption of the complex increases. In practice, base line noise was the limiting factor in the selection of a suitable λ and we found that 645nm gave the best value for signal to noise (S/N) ratio (Fig.3).

3.2. Effect of Modifier

The effect of changes in the composition of the mobile phase was studied in detail. An increase in the concentration of the modifier was found to increase the ion exchange capacity of the column. This proportionately increased the adsorption of positively charged Ln-α-HIBA complex on the negative hydrophobic bed in column and hence the retention time of the lanthanides (Fig. 4). Studies were carried out using camphor-10-sulphonic acid as well as sodium n-octane sulphonate as two modifiers in independent experiments and the latter was found to be more effective for separation of lanthanides. However, a larger percentage of the modifier was observed to lead to excessive peak broadening and prolonged elution times.

3.3. Effect of Eluent

It was decided to use α-HIBA, as it has been shown by the previous workers to be one of the best complexing reagents for the ion-exchange separation of lanthanides [15,22 & 23]. It was observed that an increase in the concentration of α-

HIBA in the mobile phase reduced the retention time and hence degraded the resolution. This can be attributed to increased interaction of α-HIBA with the adsorbed Ln-α-HIBA complex on the ion-exchanger bed (Fig. 5).

3.4. Effect of Methanol

It was observed that the lanthanide ions elute faster from the column when methanol is added to the mobile phase (Fig. 6). A small amount (1-3%) of methanol reduced the elution time of the lanthanides without effecting the resolution. Thus the introduction of small amount of methanol in the mobile phase can be used to reduce time required for separation. However, peak merging was observed when methanol content in the mobile phase was more than 3%.

3.5. Effect of pH

When silica based reversed phase columns are used, it is necessary to maintain the eluent pH in the range 2-8 to prevent the rapid column deterioration. At pH higher than 8, dissolution of silica occurs and hydroxides of lanthanides precipitate, whereas the lower limit is set by the deterioration of the C_{18} material of the column. Effect of mobile phase pH on the retention time and the resolution of the eluting lanthanides was studied by carrying out the separation of a mixture consisting of La, Nd, Er and Lu with α-HIBA of varying pH from 3 to 5 in increments of 0.5. It was observed that retention time decreases with the increase in pH (Fig.7). This behaviour can be explained on the basis of increased ionisation of α-HIBA, which is a weak acid, with increase in high pH value and thus enhancing its complexation with lanthanide ions. Mobile phase pH was chosen to be 4.0 as it brought about the separation in minimum time with desired resolution. Higher pH values led to merging of the peaks whereas lower pH values resulted in prolonged elution time.

3.6. Post Column Reagent

Arsenazo (III), a specific complexing agent for lanthanides was used as the PCR [20, 21]. A single piston pump, after its calibration for flow rate, was used for delivering the PCR. The pH, flow rate and composition of the complexing agent were varied and optimised to yield the best absorbance of Ln-Arsenazo (III) complex. Lowering the pH caused a shift in the λ_{max} of Arsenazo(III) towards shorter wavelength due to protonation of Arsenazo(III). Best results were obtained with 1.5×10^{-4}M Arsenazo(III) in 0.01M urea and 0.1M HNO_3 solution, at a flow rate of

0.3mL/min and using a wavelength 645nm for monitoring. Urea was introduced in the Arsenazo(III) solution to prevent its oxidation in presence of nitric acid [18].

3.7. Gradient Elution Mode

The data obtained from the studies on the effect of changes in concentration of modifier and eluent, discussed above, were used to program the gradient profile. The gradient elution was found to overcome the limitations of the isocratic elution in terms of peak shape and elution time.

With the gradient condition, it was possible to carry out the separation of 14 lanthanides in less than 9 min (Fig. 8). By increasing the flow rate to 2 mL/min and with some modification in the gradient profile, the separation of the same mixture could be accomplished in less than 5 min without degrading the resolution (minimum resolution 1.2 for Lns pair) (Fig.9). Further increase in the flow rate did not cause any appreciable reduction in the elution time. It is expected that the separation time may be reduced further by choosing a column of lesser dead volume.

3.8. Calibration of Method

Different parameters viz. introduction of internal standard, stirring of post column reagent, injection of sample etc. which were contributing to better reproducibility were carefully studied and were optimised. Changes in spectral parameters like reducing spectral bandwidth to 2nm and increasing spectral interval to 3.2s led to significant improvement in the base line. Calibration and linearity checking of method was done for La and Nd (burn-up monitors) using 200ng of each of two internal standards Ce and Er (Table1). Ce was found to be a better internal standard (reproducibility 1 to 3%) for La and Nd, due to its proximity with La and Nd peaks. The use of Er as an internal standard gave reproducibility from 1 to 10% for La and Nd quantification. This can be attributed to the large difference in the elution time of Er as compared to that of La and Nd. Linearity was observed in the 50-300ng range for La and Nd with correlation coefficient $r^2 \geq 0.986$ (Figs.10 and 11).

4. CONCLUSION

Dynamically modified reversed phase HPLC coupled with post-column derivatisation is attractive for separating lanthanides in a short time. The method discussed will be useful for rapid separation of individual rare-earths from a mixture of lanthanides.

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Table 1

RSD for Lanthanum and Neodymium determination by HPLC with Er and Ce as internal standard

Amount of La , Nd (ng)	Lanthanum		Neodymium	
	Using Er as internal standard	Using Ce as internal standard	Using Er as internal standard	Using Ce as internal standard
50	9.2	3.8	10.2	2.8
100	2.7	2.1	5.2	3.0
150	5.4	1.7	4.1	0.6
200	2.5	1.5	3.1	1.0
250	1.4	0.7	1.5	1.1
300	0.1	0.1	1.2	0.9

Note:

1. Relative Standard Deviation (RSD) obtained from 5 replicate injections
2. Amount of Er added in each case = 200ng
3. Amount of Ce added in each case = 200ng

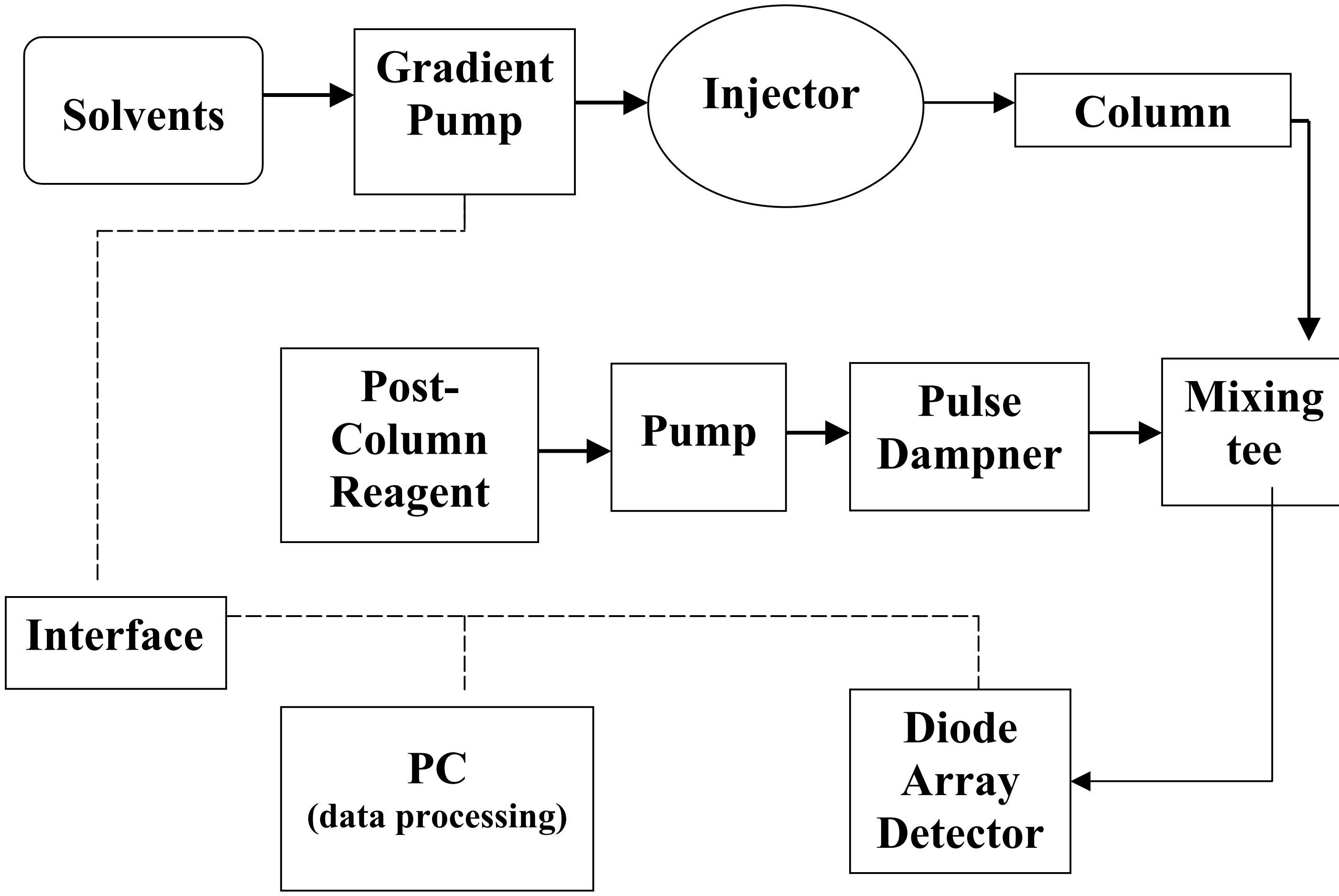

Fig. 1 Schematic of HPLC system used for the separation and determination of lanthanides

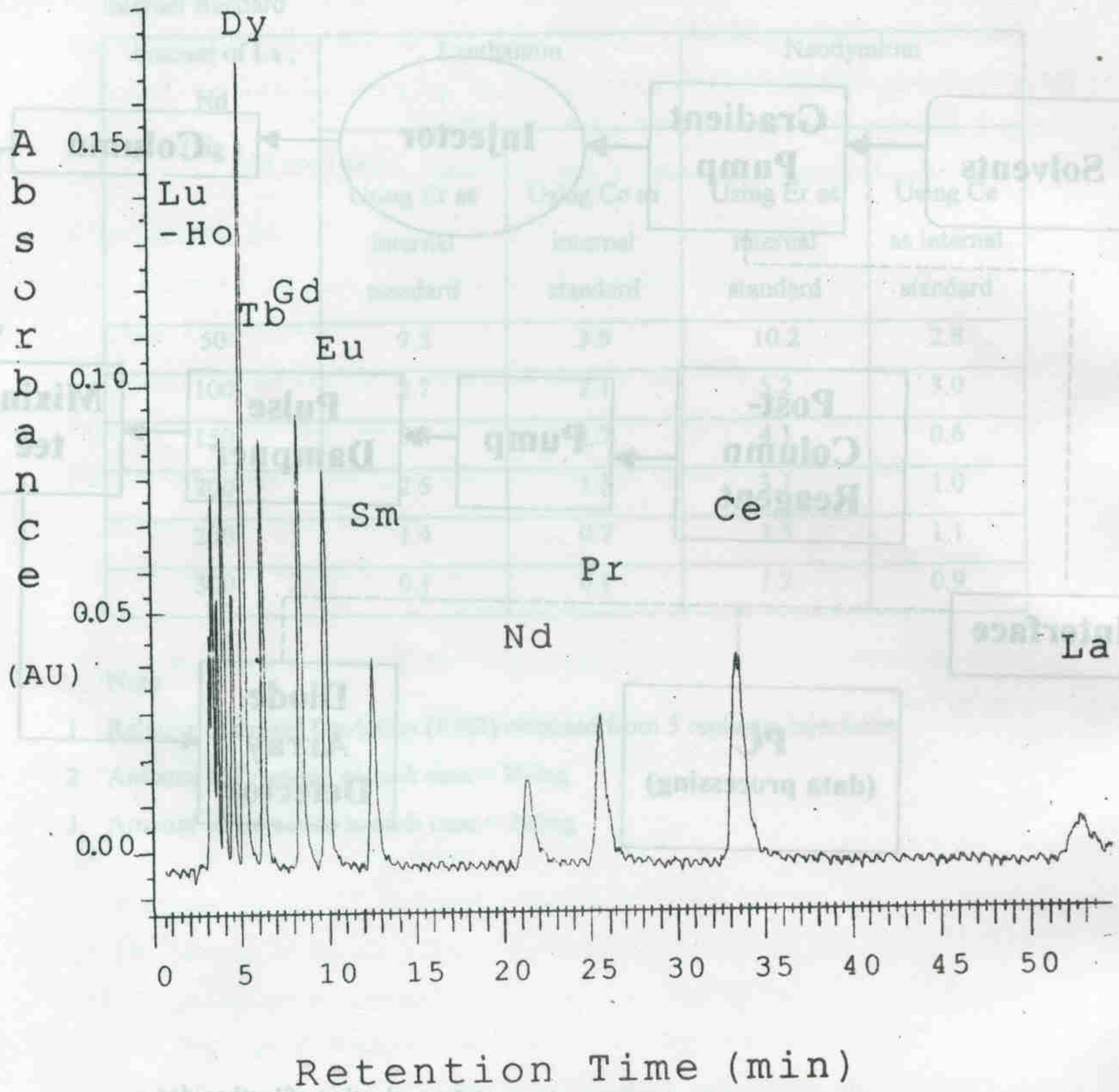

Fig.2 Isocratic separation of lanthanides

Chromatographic conditions: 0.1M α-HIBA (pH 4.0); sodium n-octane sulphonate; flowrate: 1mL/min

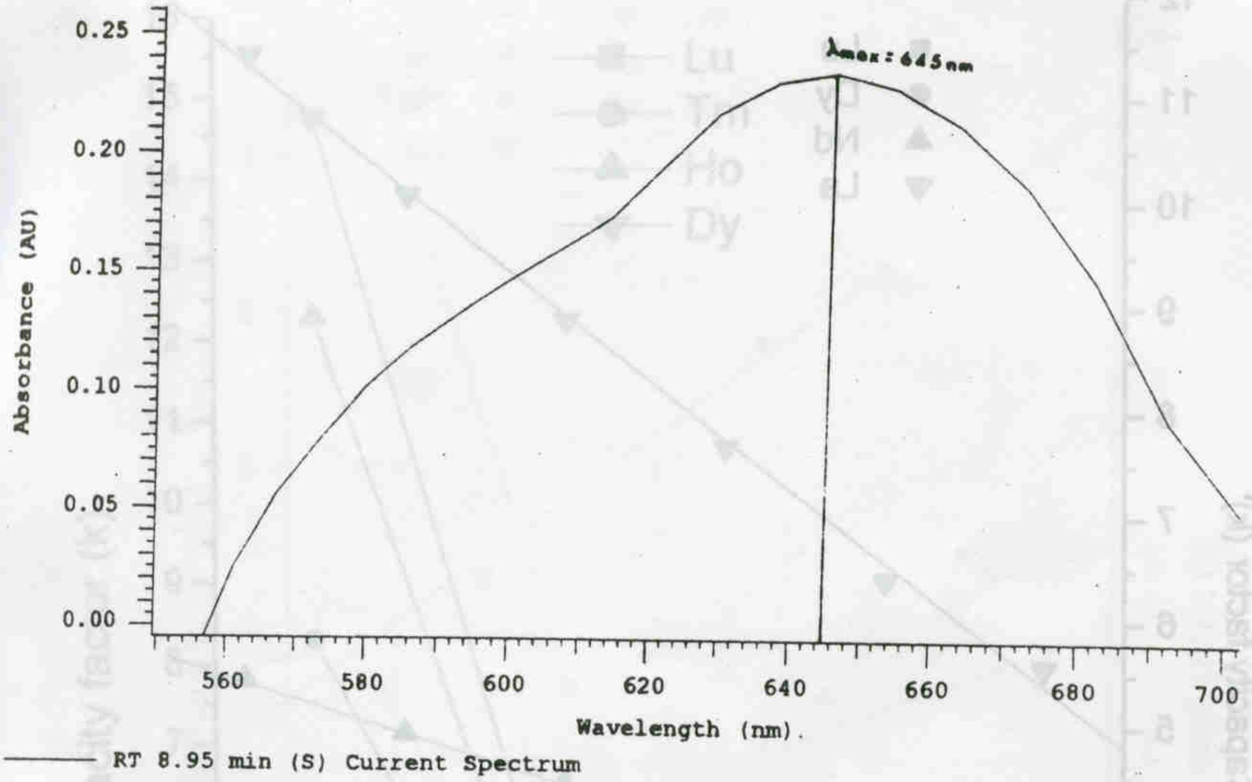

Fig.3 DAD scan showing the response of La-Arsenazo(III) complex as a function of wavelength in the range 550 to 700nm

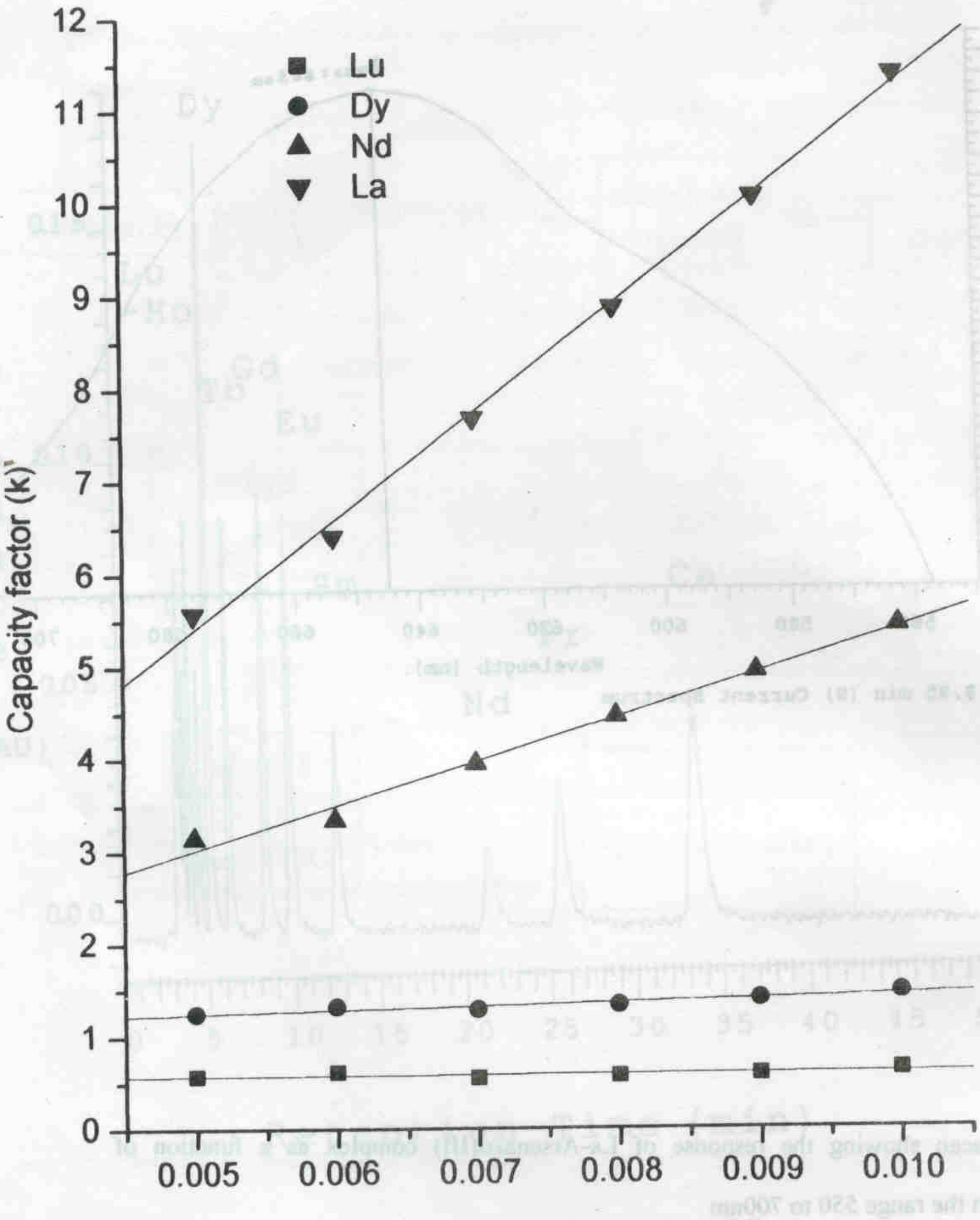

Fig. 4 Effect of concentration of modifier on k of lanthanides

Chromatographic conditions: 0.1M α-HIBA (pH 3.5)

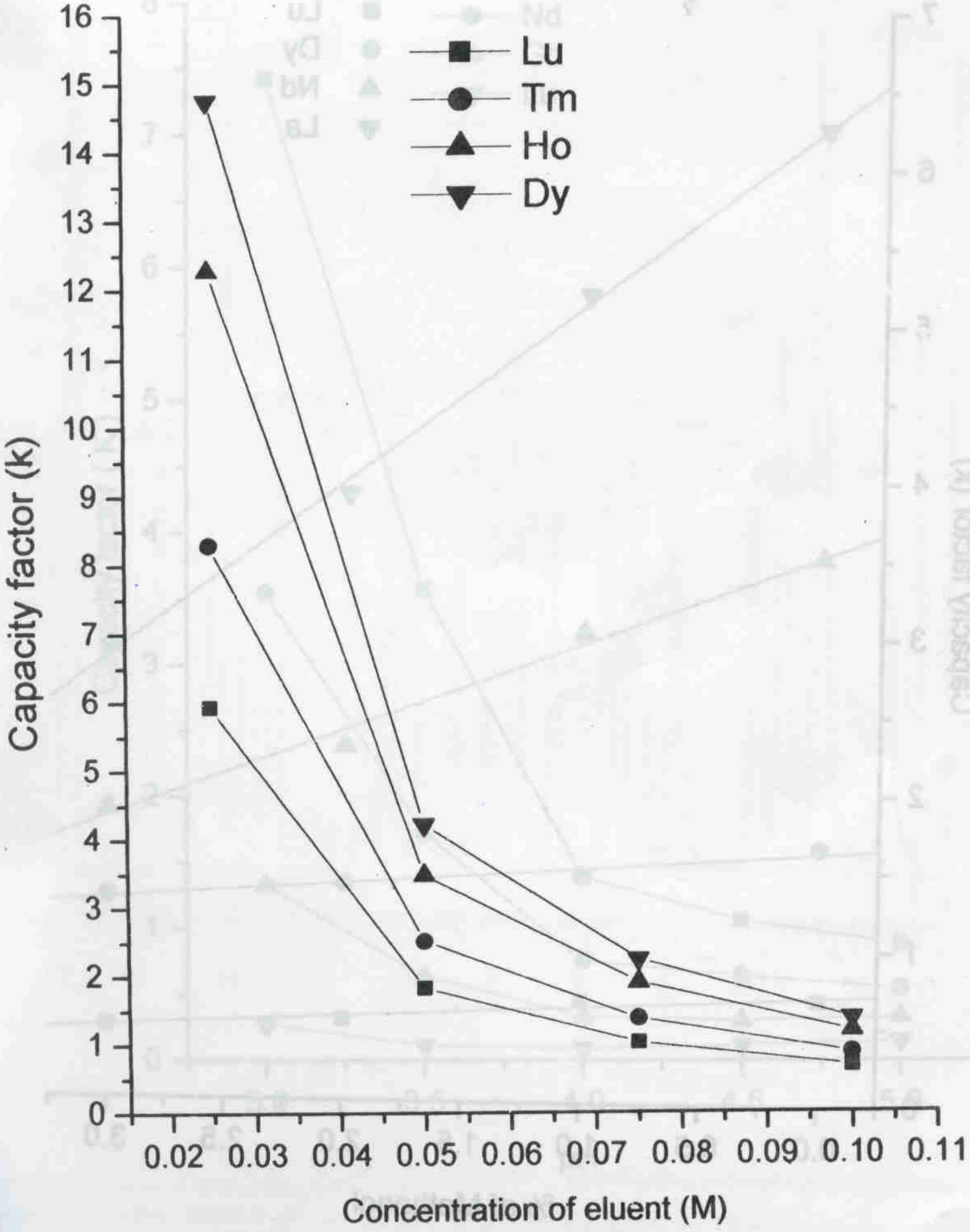

Fig.5 Effect of concentration of eluent on k of lanthanides

Chromatographic conditions: 0.002M sodium n-octane sulphonate (pH 3.5)

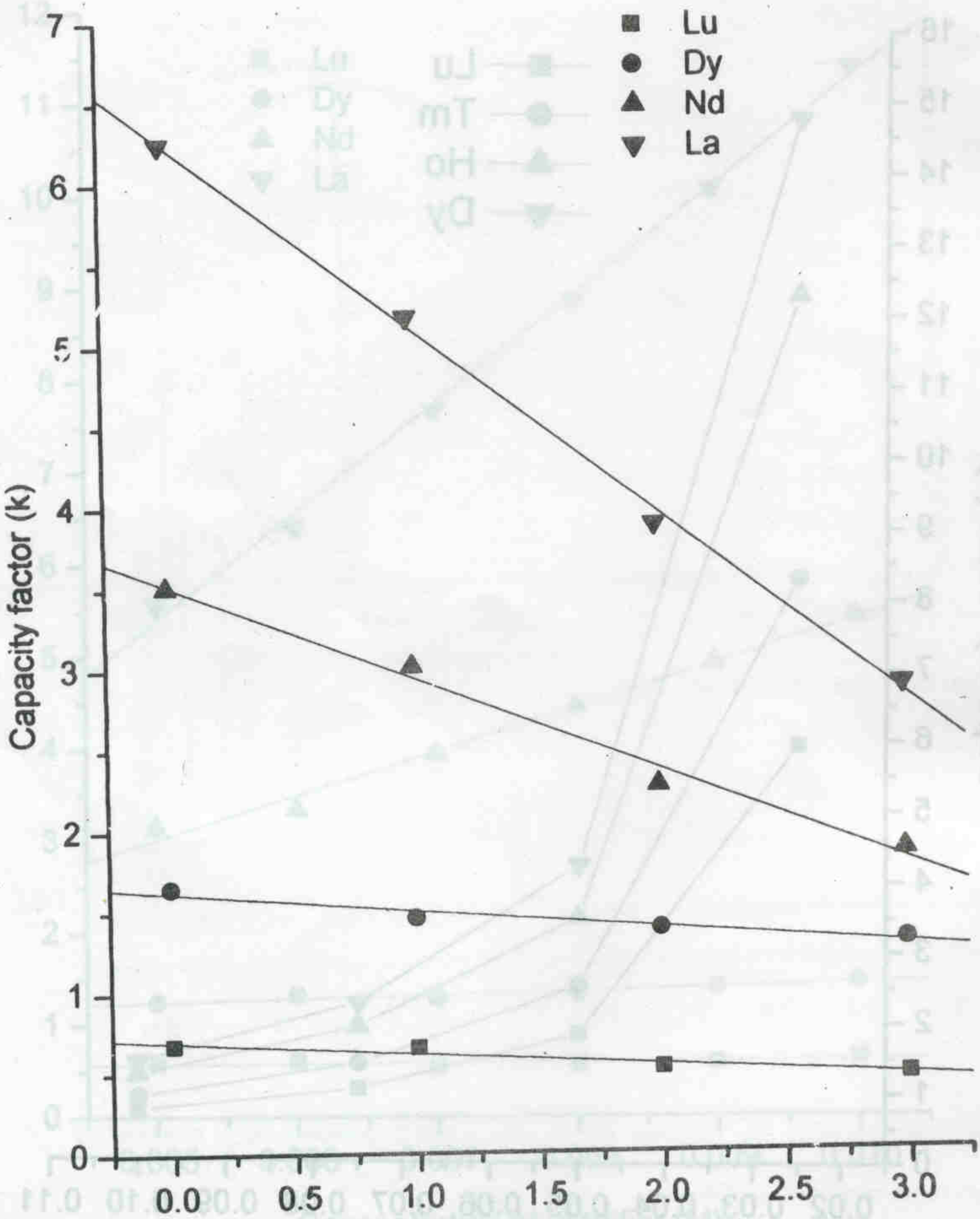

Fig.6 Effect of percentage of methanol in the mobile phase on the k of lanthanides

Chromatographic conditions: 0.1M α-HIBA and 0.005M sodium n-octane sulphonate (pH 3.5)

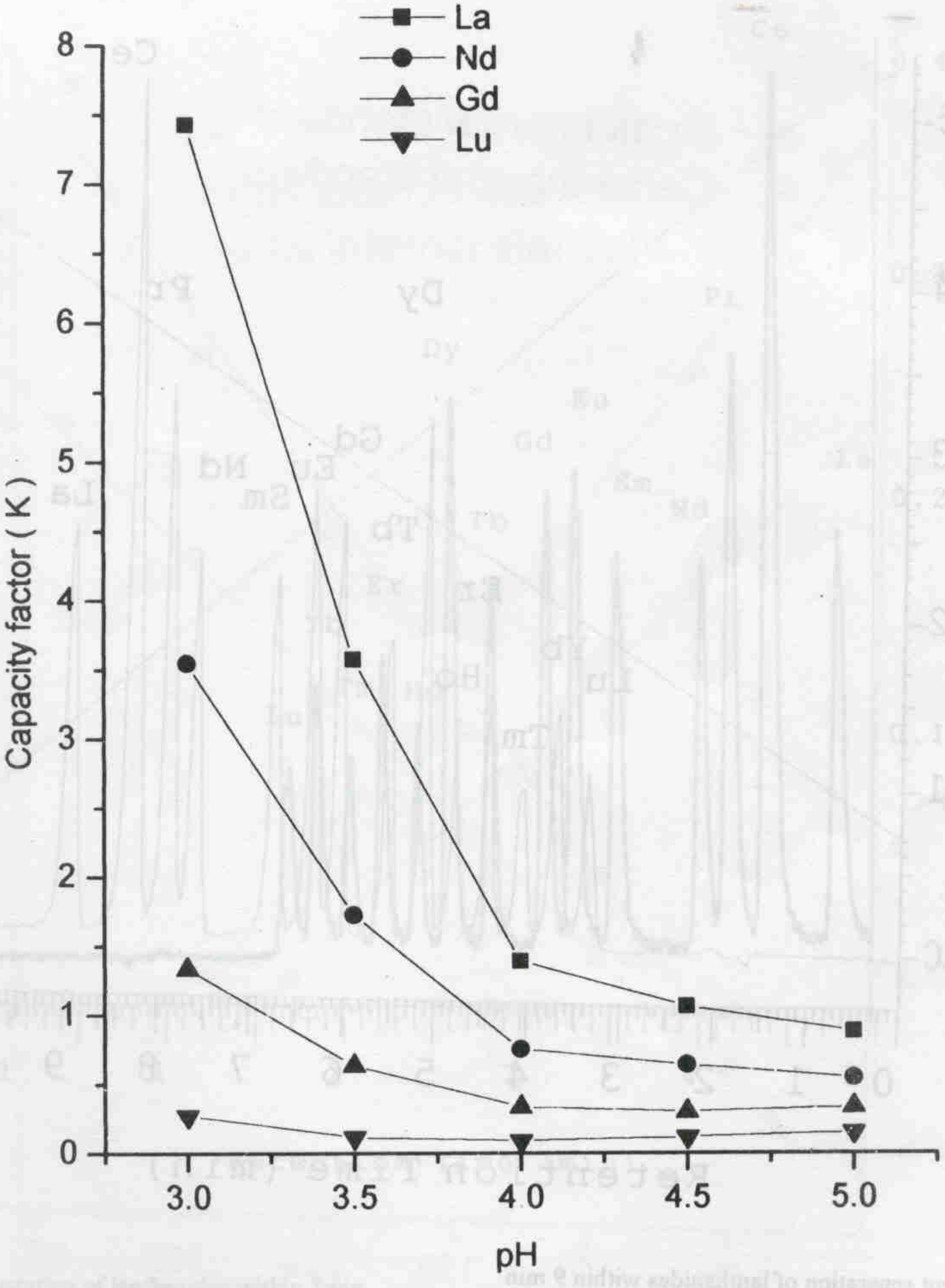

Fig.7 Effect of pH of eluent on the k of lanthanides

Mobile phase: 0.25M α-HIBA and 0.002M sodium n-octane sulphonate

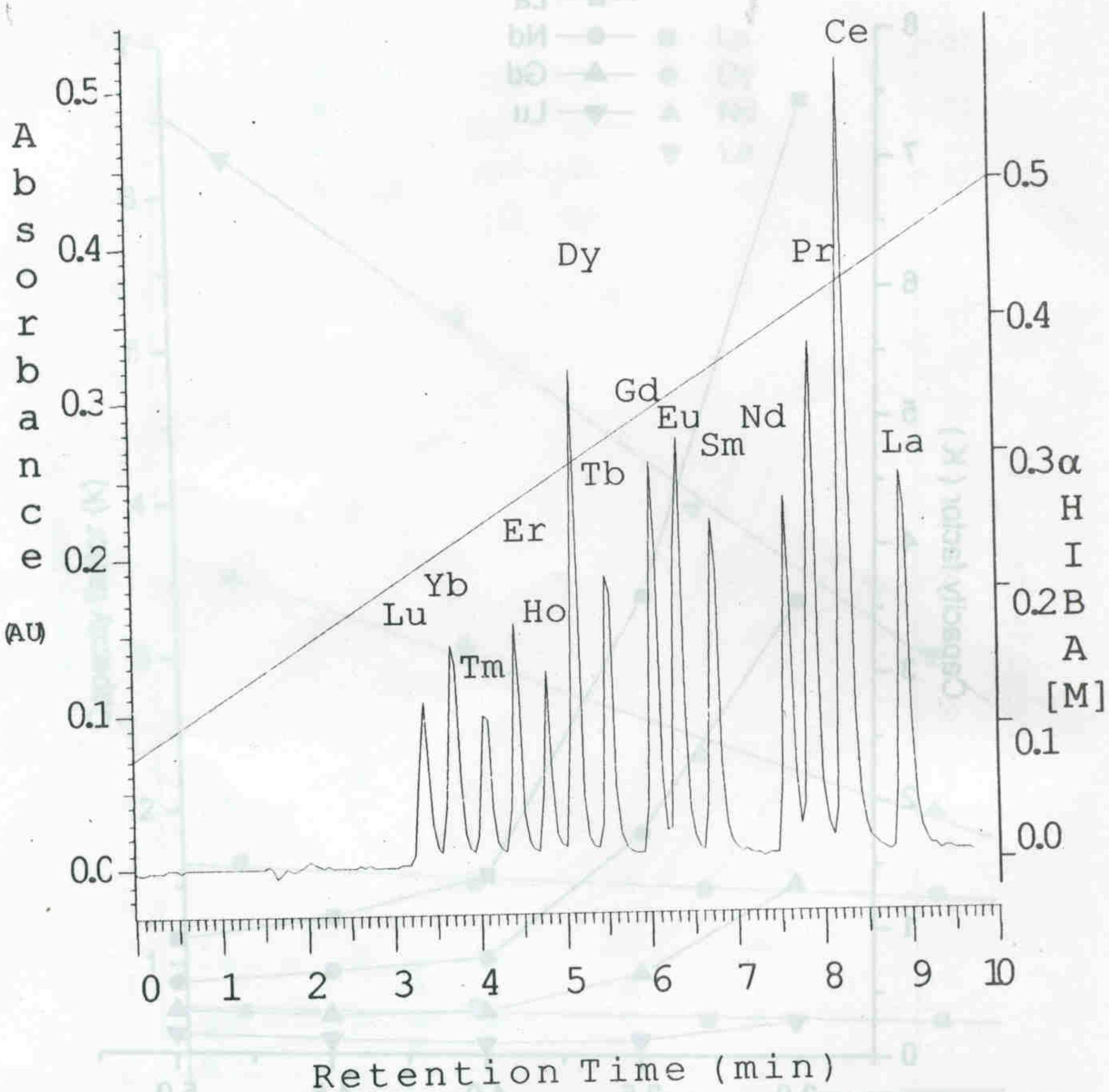

Fig. 8 Gradient separation of lanthanides within 9 min

Chromatographic conditions: 0.07 to 0.5M α-HIBA (pH 4.0) in 10min; 0.003M sodium n- octane sulphonate; flow rate: 1mL/min

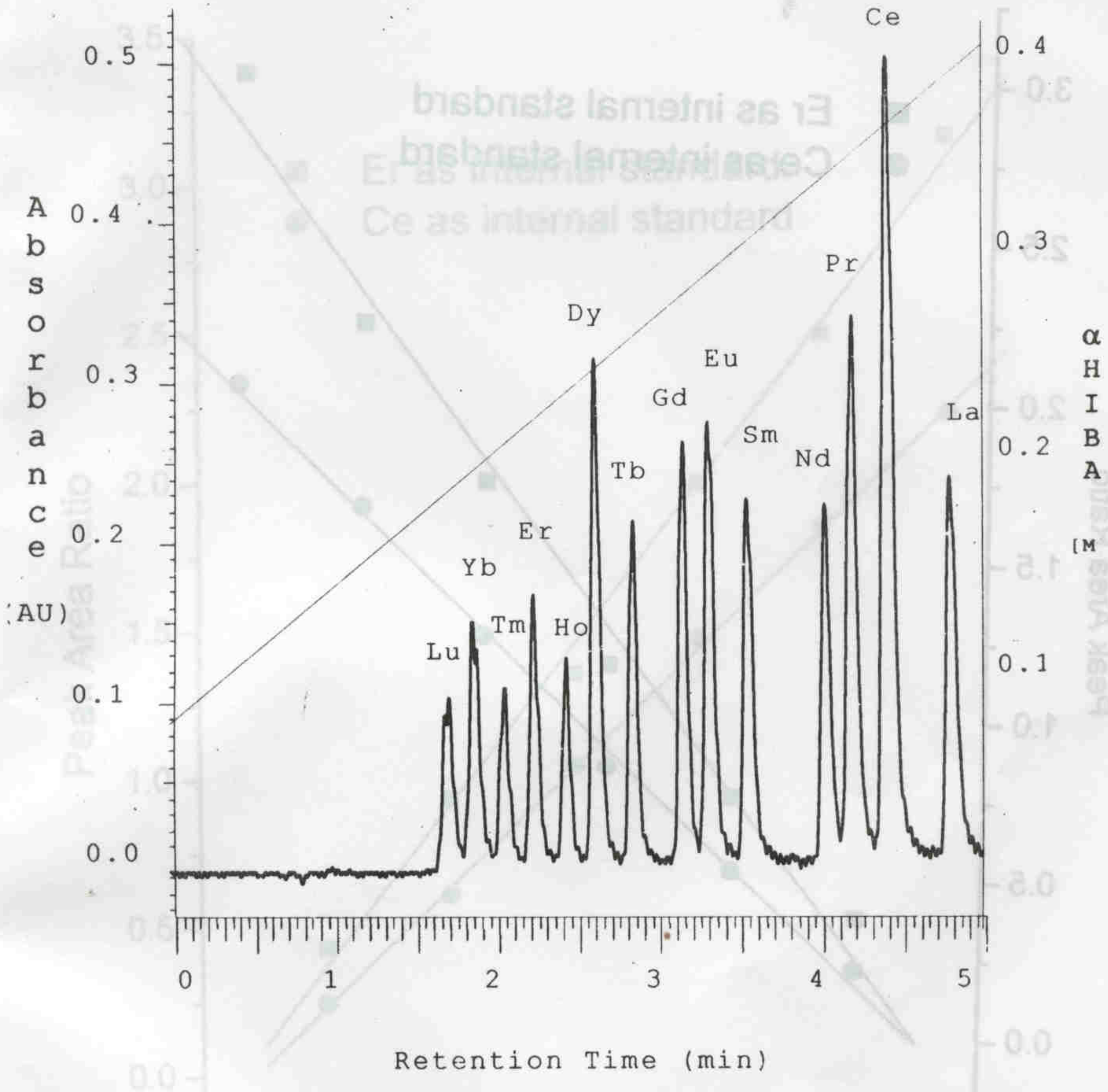

Fig.9 Gradient separation of lanthanides within 5min

Chromatographic conditions:0.07 to 0.4M α-HIBA (pH 4.0) in 5 min; 0.003M sodium n-

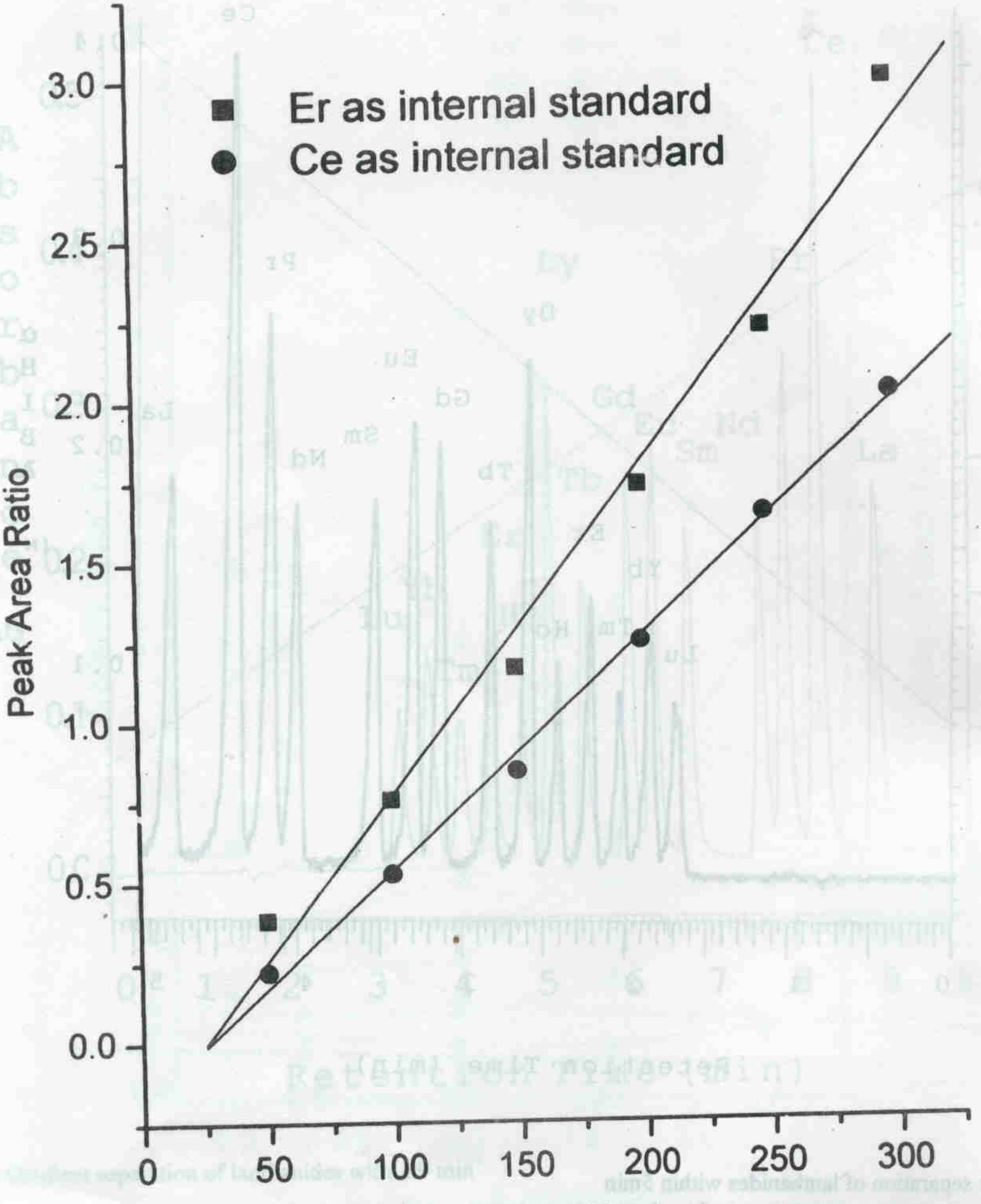

Fig.10 Calibration plot of La in the range 50-300 ng using Er and Ce as the internal standards. Correlation coefficient (r^2): 0.986 (w.r.t. Er) and 0.996 (w.r.t.Ce)

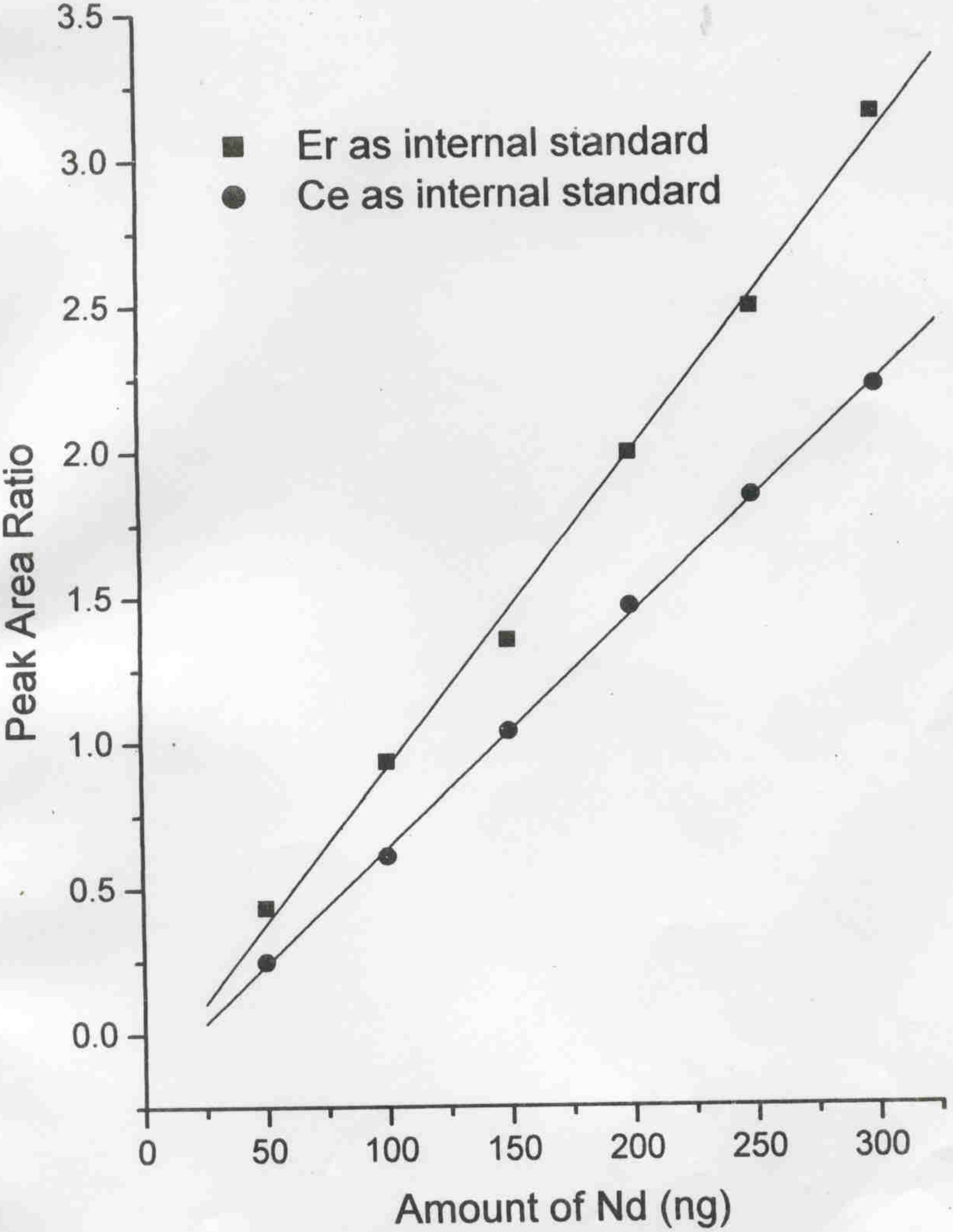

Fig.11 Calibration plot of Nd in the range 50-300 ng using Er and Ce as the internal standards

Correlation coefficient (r^2) : 0.994 (w.r.t. Er) and 0.998 (w.r.t.Ce)