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New elution agent, sodium trimetaphosphate, for the separation and determination of rare earths by anion-exchange chromatography

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Abstract

In this study, sodium trimetaphosphate was investigated as a new elution agent for anion-exchange separations of the rare earth elements and thorium. Distribution coefficients of these elements have been determined regarding four different concentrations of sodium trimetaphosphate ($3 \cdot 10^{-3}$; $5 \cdot 10^{-3}$; $7 \cdot 10^{-3}$ and $0.01 M$) on the strongly basic anion exchanger Dowex 1-X4, 200–400 mesh. The separation of the rare earths and thorium obtained from an Australian monazite has been studied by means of elution with sodium trimetaphosphate concentration gradient on a Dowex 1-X4 ion-exchange column. It was applied to the 5 and 250 mg samples. In a small scale separation, all rare earths and thorium were separated in 26 min with concentration gradient elution of sodium trimetaphosphate. Qualitative and quantitative determinations were realized by spectrofluorimetry. In this method the elution peaks are narrow, tailing effects are very small, Dy and Y are well separated. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Anion-exchange elution for the separation of the rare earths has been employed for many years. Danon separated thorium and praseodymium in nitric acid media by anion exchange [1]. Marcus and Nelson separated six rare earth elements in 7 h with concentration gradient elution of lithium nitrate solutions. The elements eluted in reasonably sharp bands though with some overlapping [2]. The anion-exchange behaviour of the rare earths and some other elements (U, Th) in aliphatic alcohols containing nitric acid was investigated by Korkish et al. [3]. Cha et al. used an anion-exchange method for separating six rare earth elements in monazite with EDTA. But

each element was not completely separated due to adjacent elements overlapping some parts [4]. Usuda and Magara separated five rare earth elements in 2.5 h in nitric acid–methanol media by anion exchange [5]. Al-Shawi and Dahl managed to separate La, Ce, Pr and Nd in magnesium alloys in 14 min with α -hydroxyisobutyric acid (α -HIBA) using ion chromatography coupled to a post-column detection system [6].

In this study, sodium trimetaphosphate was investigated as a new complexing agent for the anion-exchange separation of the 14 rare earth elements and thorium. It has been seen that it has also some important advantages over the other eluting agents; like good separations without overlapping, symmetrical elution curves without tailing, shorter elution time and operating without pH change. It has a lower cost than other complexing agents and elution is

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performed at room temperature. Furthermore, in these elutions studying very low concentrations of sodium trimetaphosphate also plays an important role. In addition, it is possible to recover the sodium trimetaphosphate from the eluate by adding ethanol to the solutions.

2. Experimental

2.1. Chemicals

The rare earth solutions were prepared by dissolving the appropriate amount of the oxides. The oxides were used 99.9% pure. Other chemicals were of analytical-reagent grade and at least 99.5% pure. All chemicals were obtained from Merck (Darmstadt, Germany) and Fluka (Buchs, Switzerland). The strongly basic anion exchanger Dowex 1-X4 (200–400 mesh; chloride form) marketed by Bio-Rad Labs. (Richmond, CA, USA) was used. Distilled water was used to prepare the solutions.

2.2. Equipment

The gradient elution apparatus was designed as

shown in Fig. 1. It is similar to that used in CNRS Rare Earths Laboratories, Bellevue, France [7]. As can be seen from the figure there are two flasks for elution solutions. The second flask was equipped with a magnetic stirrer. The two flasks were connected by a tube with a three-way tap and a bulb. In order to adjust the flow-rate a peristaltic pump was placed between the second flask and the resin column.

The fluorometric measurements were made on a Perkin-Elmer 204 fluorescence spectrophotometer (Norwalk, CT, USA) with a 150 W xenon arc lamp. The fluorescence intensities of solutions were measured in 10 mm quartz cells. The excitation and emission slitwidths were 10 nm.

In this study, two different sizes of glass columns (40×1.2 cm I.D. and 25×0.5 cm I.D.) fitted with fritted glass disks in the bottom were used.

2.3. Preparation of eluting agent and rare earth elements

Sodium trimetaphosphate solutions were prepared by dissolving $\text{Na}_3\text{P}_3\text{O}_9 \cdot 6\text{H}_2\text{O}$. Anhydrous sodium trimetaphosphate ($\text{Na}_3\text{P}_3\text{O}_9$) was prepared by heating sodium hexametaphosphate for 8–12 h at 500°C

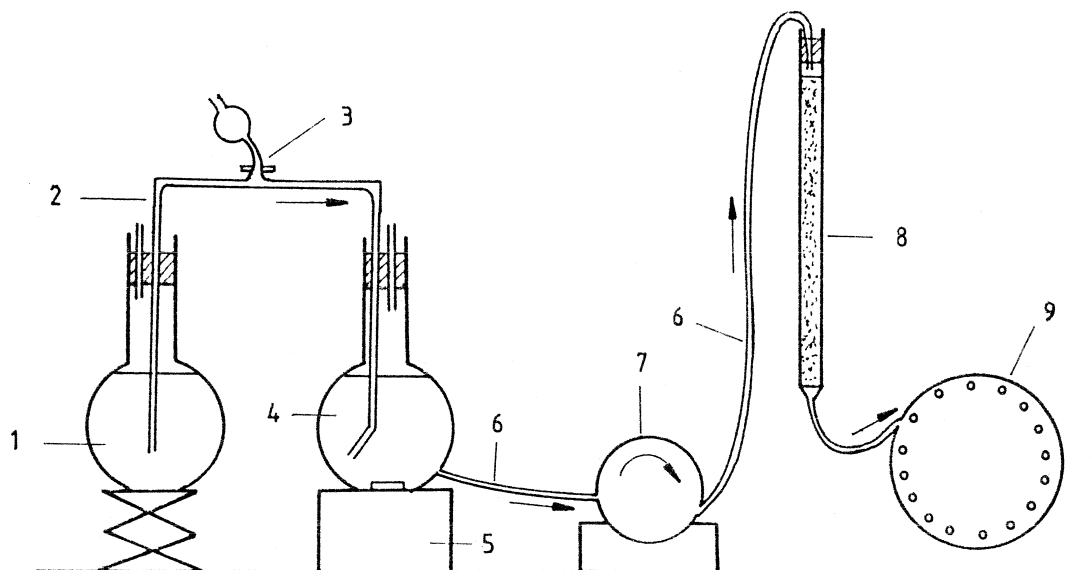


Fig. 1. Gradient elution equipment: 1,4: flask for eluents, 2: glass tubing with three way tap, 3: rubber bulb, 5: magnetic stirrer, 6: flexible tubing, 7: peristaltic pump, 8: ion-exchange column, 9: fraction collector.

[8]. The 6-hydrate, $\text{Na}_3\text{P}_3\text{O}_9 \cdot 6\text{H}_2\text{O}$, was prepared in the following manner: a 51-g amount of anhydrous sodium trimetaphosphate was dissolved in 160 ml of water at room temperature. A 45-ml volume saturated solution of sodium chloride was added and the mixture agitated for 4 h. The crystalline product was filtered and dried in air [9].

For the decomposition of the ores and minerals containing rare earths there are different methods in the literature, like concentrated sulfuric acid, perchloric acid, hydrochloric acid, hydrofluoric acid, fusion with sodium peroxide, fusion with alkali carbonates, fusion with sodium pyrosulfate [10]. There are also different methods for the separation of the rare earth oxides from monazite like H_2SO_4 digestion and NaOH extraction [11]. In this study, rare earth elements were separated from an Australian monazite concentrate as the mixture of their oxides by the conventional benzoic acid method [10]. But Th was not separated from rare earths by precipitation. Because, as can be seen from distribution coefficients, it is possible to separate all rare earth elements and thorium with anion-exchange elution in sodium trimetaphosphate media.

2.4. Procedure

2.4.1. Distribution coefficients

The resin was conditioned to the chloride form by passing 2 M HCl, 2 M NaOH and 2 M HCl, respectively through the resin column and each time the resin was washed by passing distilled water, finally it was dried in air.

The portion (0.5 g) of this resin (its mass corrected as the oven dried resin at 105°C) was equilibrated in a small column with sodium trimetaphosphate solution in the desired concentration until equilibration. It was transferred into a glass stoppered flask. Then, 50 ml of eluent at known concentration and containing 1 mequiv. of the cation was added. The flask was shaken for 15 h in a mechanical shaker at room temperature.

The fluorescence intensities of solutions were measured before and after equilibrium. The distribution coefficients K_d are calculated by the following equation:

$$K_d = \frac{I_0 - I}{I} \cdot \frac{\text{ml of solution}}{\text{g of dry resin}}$$

where I_0 and I are the fluorescence intensities of the solution before and after equilibration with the resin.

2.4.2. Identification

The elements in the eluted fractions were defined by spectrofluorometry using morin [12]. The qualitative identification of individual rare earth elements were realized using appropriate fluorimetric reagents. Since the appropriate fluorimetric reagent was not found for Nd, Ho, Er and Yb, they were precipitated from the eluate with oxalic acid. The rare earth oxides were obtained by ignition of these oxalate precipitates and the elements were identified from the color of their oxides.

The quantitative determination of each element in the fractions were also realized with appropriate fluorimetric reagents using calibration curves.

2.4.3. Elutions

The strongly basic anion-exchange resin Dowex 1-X4, 200–400 mesh, was washed several times with distilled water for removal of fine particles. The resin in water was left for a few minutes until the large particles have settled and then the turbid supernatant liquid was poured off. The washed resin was transferred to the column in a water slurry after it was kept in water overnight. Subsequently it was equilibrated by passing the elution solution through the column. Then the sample solution was added to the top of the resin column. The adsorbed sample in the upper part of the resin column was eluted. Convenient volumes of fractions were collected with an automatic fraction collector.

3. Results and discussion

The experimental distribution coefficients are presented in Table 1. The use of strongly complexing agents, results in the formation of anionic complexes of the lanthanide metals. Under these conditions, the lanthanide series may be separated by anion exchange.

Table 1
Anion-exchange distribution coefficients in different concentrations of sodium trimetaphosphate solutions

Rare earth elements	Concentration of sodium trimetaphosphate			
	$3 \cdot 10^{-3} M$	$5 \cdot 10^{-3} M$	$7 \cdot 10^{-3} M$	0.01 M
Th	192.3	123.1	77.2	6.44
Lu	171.7	112.0	66.6	5.78
Yb	149.1	103.4	57.9	5.30
Tm	133.4	82.8	50.6	5.09
Er	119.9	71.2	45.2	4.77
Ho	93.1	61.8	34.1	4.16
Dy	72.0	55.1	26.8	3.97
Y	64.2	43.9	20.9	3.22
Tb	50.2	34.6	15.7	2.88
Gd	43.8	24.7	12.5	2.34
Eu	35.2	18.9	9.07	2.16
Sm	31.3	16.9	7.39	1.98
Nd	28.5	14.1	5.79	1.72
Pr	26.7	11.9	3.79	1.44
Ce	23.4	10.5	2.91	1.08
La	18.8	9.16	2.03	0.96

3.1. Separation of rare earth elements

In the first part of the study, 5 mg of the mixture of rare earth oxides which was prepared from the Australian monazite were taken and dissolved in dilute HNO_3 by heating. Cerium was reduced with H_2O_2 . The solution was then evaporated almost to the dryness. Afterwards it was reevaporated twice in the same manner following the addition of 0.5 ml concentrated HCl. The sample was dissolved in 3 ml $3 \cdot 10^{-3} M$ sodium trimetaphosphate solution and this was transferred to the top of the small column containing a resin bed 23 cm in length which was equilibrated before with 250 ml of $7 \cdot 10^{-3} M$ sodium trimetaphosphate solution and its top previously rinsed with a small amount of water.

The results obtained from distribution coefficients were examined. In the first part of elution, a $7 \cdot 10^{-3} M$ sodium trimetaphosphate solution was used. After 21 ml effluent was eluted, the elution was performed using a concentration gradient of $7 \cdot 10^{-3}$ –0.01 M sodium trimetaphosphate. A flow-rate of 2 ml min^{-1} was used. The elution curves are shown in Fig. 2. In order to obtain shorter elution time, by considering the distribution coefficients, another elution was carried out. The same amount of sample was taken and it was dissolved and prepared as described above. In this elution, a concentration gradient was

used ($7 \cdot 10^{-3}$ –0.01 M sodium trimetaphosphate) from the beginning to the end of the elution procedure. The elution curves are represented in Fig. 3. As can be seen from Fig. 3, La, Ce and Pr were overlapping in some parts. Another elution was performed for better distribution of peaks. The same amount of sample was taken again. In the first part of this elution, $7 \cdot 10^{-3} M$ sodium trimetaphosphate was used. After 12 ml effluent was taken, the elution was performed using a concentration gradient of $7 \cdot 10^{-3}$ –0.01 M sodium trimetaphosphate. The elution curves are represented in Fig. 4. This elution was completed in 53 ml of eluent at a flow-rate of 2 ml min^{-1} and there was no overlapping. The separations were carried out very well. Yttrium is located between terbium and dysprosium and it also was well separated from dysprosium. The thorium was eluted after lutetium.

In the second part of this study, 250 mg of the mixture of rare earth oxides prepared from the Australian monazite was taken. It was dissolved and prepared as described above. But the sample solution was transferred to the top of the large column containing a resin bed 36 cm in length which was equilibrated before with 250 ml of $7 \cdot 10^{-3} M$ sodium trimetaphosphate solution and its top previously rinsed with a small amount of water. In the first part of this elution, $7 \cdot 10^{-3} M$ sodium trimetaphosphate

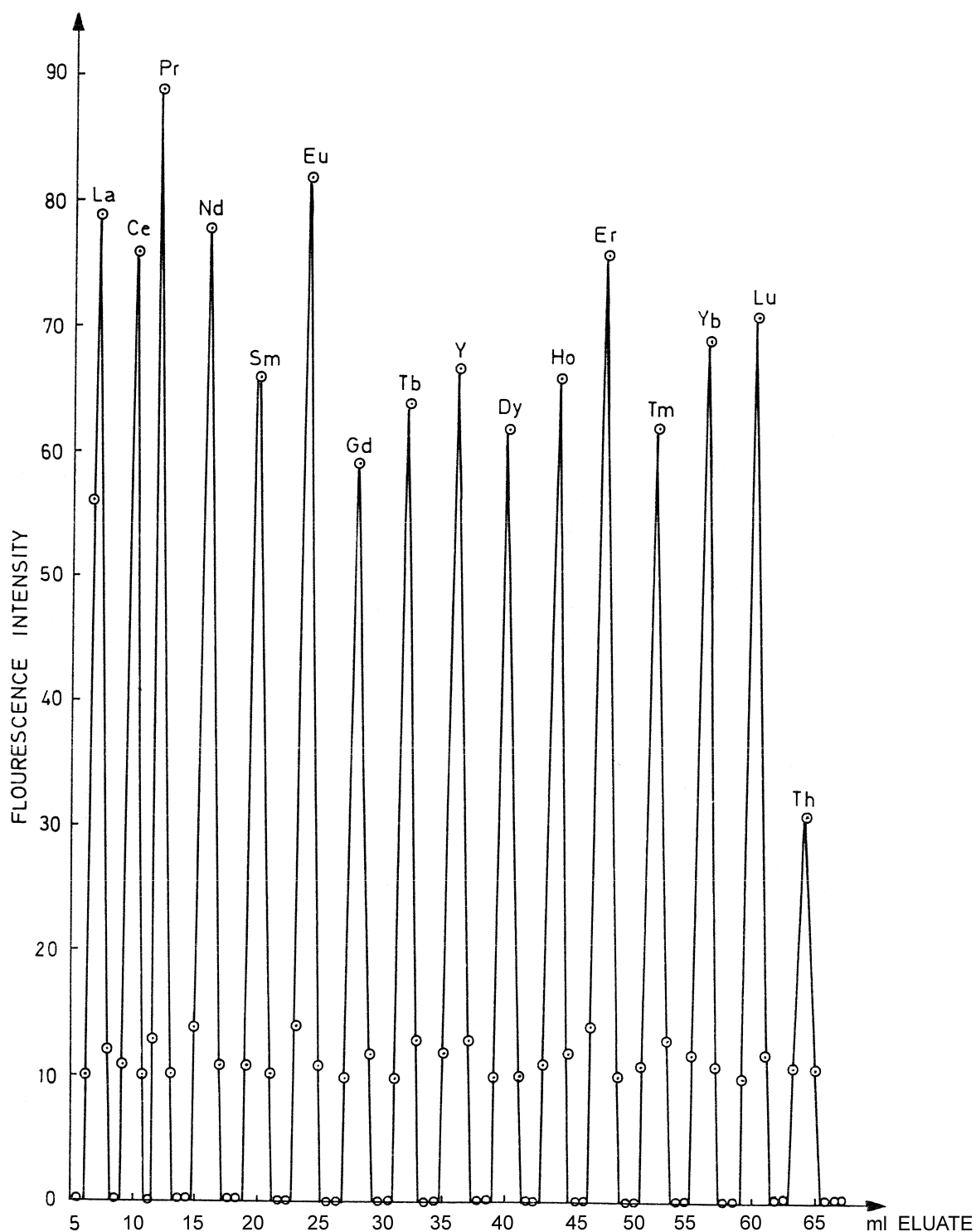


Fig. 2. Elution curves of the elements (in 5 mg of rare earth oxides obtained from monazite) with first, 21 ml $7 \cdot 10^{-3} M$ and then a $7 \cdot 10^{-3} - 0.01 M$ concentration gradient of sodium trimetaphosphate; resin bed 0.5 cm diameter; 23 cm length; flow-rate 2 ml min^{-1} .

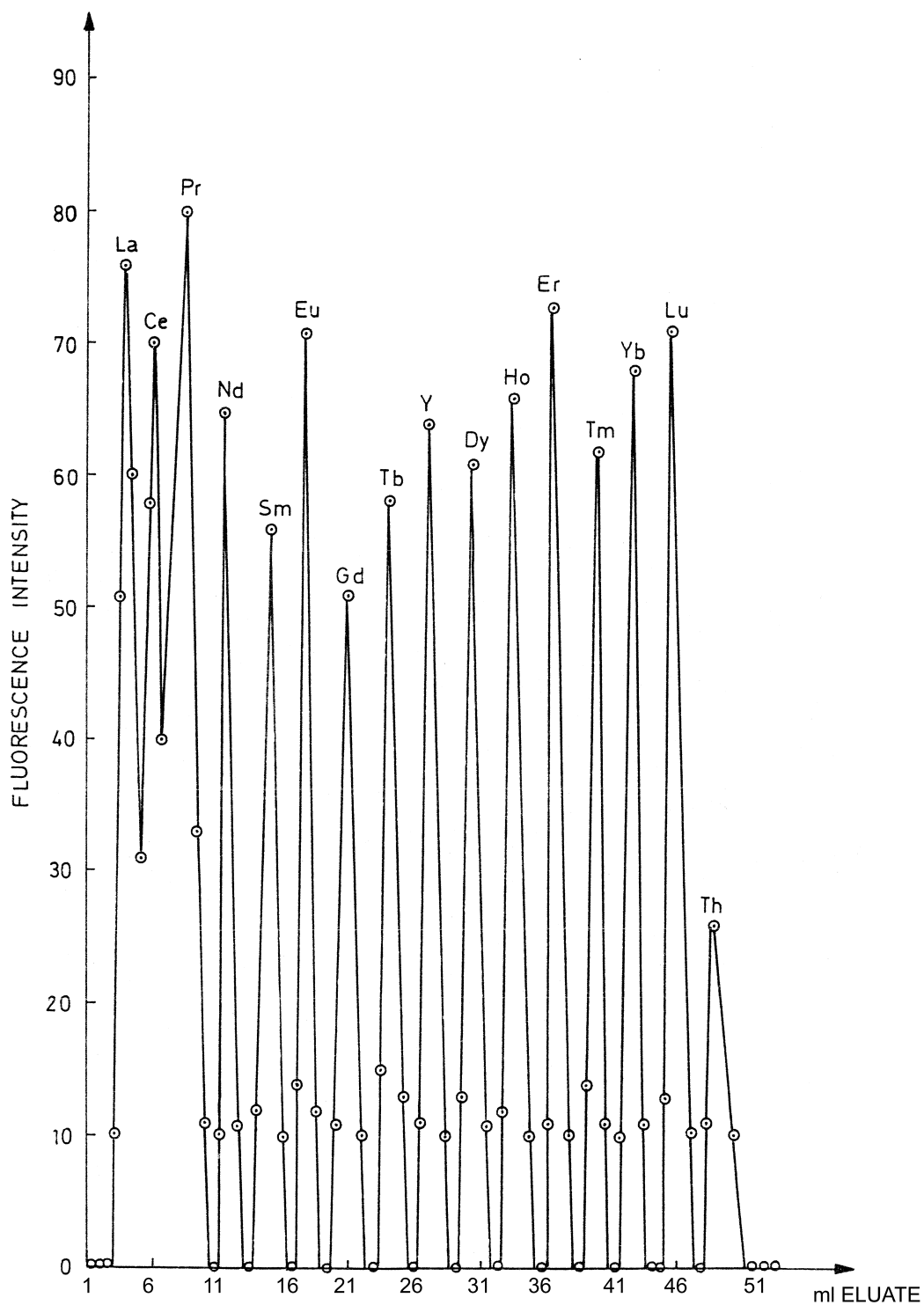


Fig. 3. Elution curves of the elements (in 5 mg of rare earth oxides obtained from monazite) with a $7 \cdot 10^{-3}$ – 0.01 M concentration gradient of sodium trimetaphosphate; resin bed 0.5 cm diameter, 23 cm length; flow-rate 2 ml min^{-1} .

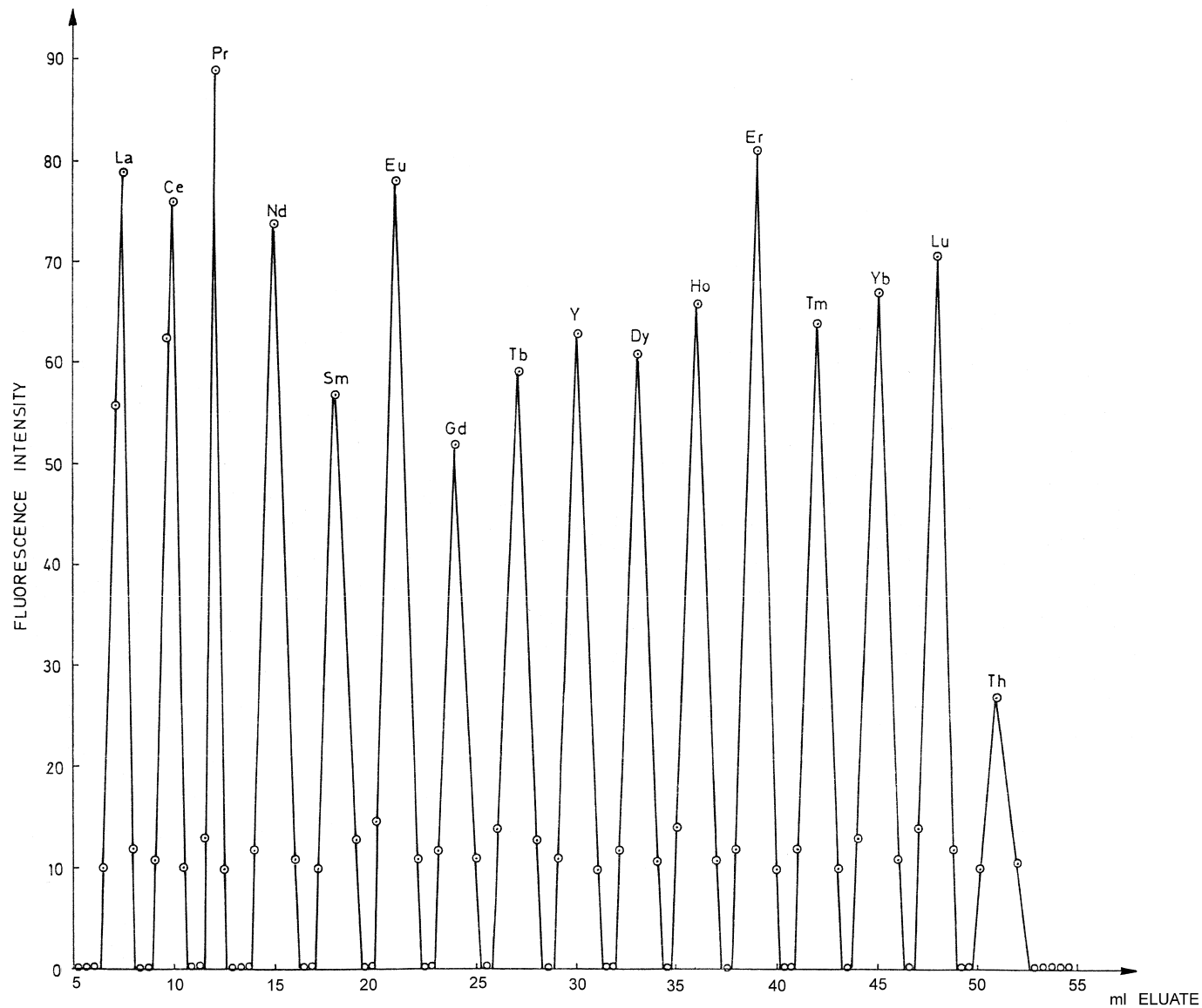


Fig. 4. Elution curves of the elements (in 5 mg of rare earth oxides obtained from monazite) with first, 12 ml $7 \cdot 10^{-3}$ M and then a $7 \cdot 10^{-3}$ –0.01 M concentration gradient of sodium trimetaphosphate; resin bed 0.5 cm diameter, 23 cm length; flow-rate 2 ml min^{-1} .

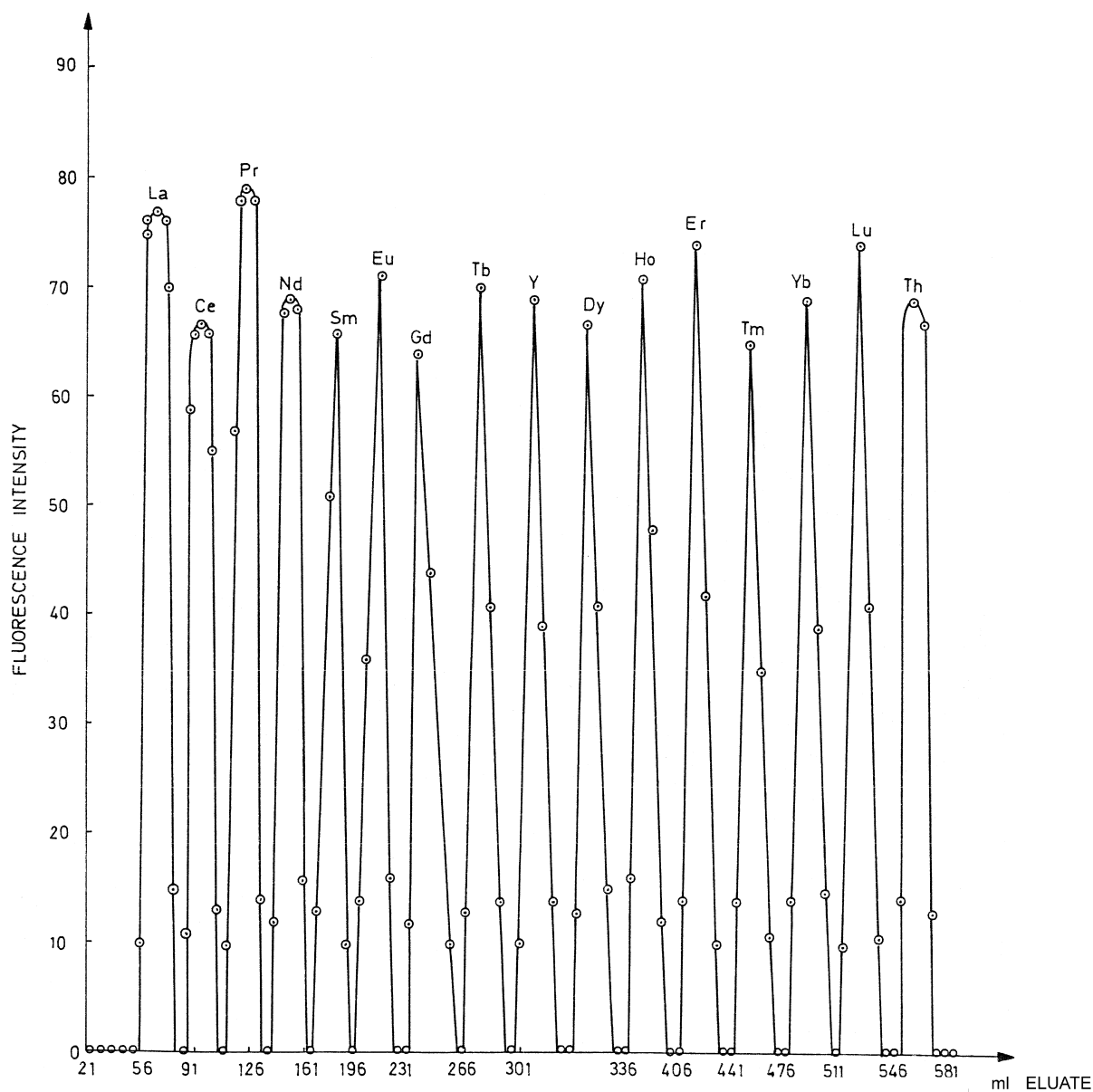


Fig. 5. Elution curves of the elements (in 250 mg of the rare earth oxides obtained from monazite) with first, 196 ml $7 \cdot 10^{-3}$ M and then a $7 \cdot 10^{-3}$ –0.01 M concentration gradient of sodium trimetaphosphate; resin bed 1.12 cm diameter, 36 cm length, flow-rate 2 ml min^{-1} .

was used. After 196 ml effluent was taken, the elution was performed using a concentration gradient of $7 \cdot 10^{-3}$ –0.01 M sodium trimetaphosphate. The elution curves are represented in Fig. 5. All the rare earth elements, yttrium and thorium were eluted within 567 ml effluent and they were separated completely from each other.

4. Conclusion

In this study, it has been demonstrated that sodium trimetaphosphate is a very suitable new elution agent for the separation of rare earths and thorium on strongly basic-anion exchange resins at room temperature. Very good separations were obtained using

a concentration gradient of elution. It was seen that these separations can be applied successfully to the different rare earth mixtures for the determination and for preparative purposes.

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