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Short communication

Separation and determination of various elements by cation-exchange chromatography with sodium trimetaphosphate as the eluent

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Abstract

Sodium trimetaphosphate was investigated as a new elution agent for the cation-exchange separation of some metal ions. Cation-exchange equilibrium distribution coefficients with Dowex 50W-X8, 200–400 mesh, a sulfonated polystyrene resin, are presented for twelve elements in different concentration ranges between 0.01 *M* and 0.3 *M* sodium trimetaphosphate. By considering these distribution coefficients, the separation of twelve metal ions has been performed with 0.1 *M* sodium trimetaphosphate at room temperature. It was applied as a small scale (0.5 mg of each element) and large scale (0.5 mmol of each element). It has been seen that this separation can be used for the determination and preparative separation of the metal ions. As an elution agent sodium trimetaphosphate has the following advantages over the other elution agents. The elution peaks are narrow and nearly symmetrical. The tailing effects are very small and separation time is shorter than those of other known methods. Qualitative and quantitative determination of eluted ions were performed by spectrofluorimetry. © 1999 Published by Elsevier Science B.V. All rights reserved.

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1. Introduction

For the separation of various elements, ion-exchange has been used more extensively than any other technique. The separations were performed using cation-exchange or anion-exchange resins. As elution agents, different acid solutions like α -hydroxyisobutyric acid [1], nitric acid and sulfuric acid [2], hydrofluoric acid [3], hydrochloric acid [4,5] were used. Some acid containing organic solvent for example, hydrochloric acid–ethanol [6], hydrochloric acid–acetone [7,8], hydrobromic acid–acetone [9], hydrochloric acid–methanol [10] and it was used some mixtures like hydrobromic–nitric acid [11],

tartaric acid–nitric acid and tartaric acid–ammonium tartarate [12], thiourea–hydrochloric acid [13] solutions were also employed.

In this study, sodium trimetaphosphate was investigated as a new elution agent for the cation-exchange separation of twelve elements. It has been seen that sodium trimetaphosphate has several advantages as an eluent over the other elution agents. Elution curves are narrow and nearly symmetrical comparing to those of the other eluents. The tailing effects are very small and there is no overlapping between adjacent peaks. For this reason elution has been successfully applied to a 6 mg of the mixture of twelve metals for identification and quantitative determination, and to a 240 mg of a mixture of seven metals for preparative separation. Elution was used

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without changing the pH and at room temperature. It is cheaper than other complexing agents. It is possible to precipitate and recover sodium trimetaphosphate by adding ethanol to the eluate.

2. Experimental

2.1. Chemicals

All chemicals used were of analytical reagent grade and at least 99.5% pure. Sodium trimetaphosphate and strongly acidic cation-exchange resin Dowex 50W-X8, 200–400 mesh were supplied by Fluka (Buchs, Switzerland). Other chemicals were provided by Merck (Darmstadt, Germany).

2.2. Equipment

Two different sized glass columns (25 cm×0.5 cm I.D. and 40 cm×1.2 cm length and 1.2 cm I.D.) fitted with fritted glass disks at the bottom were used. The fractions were collected with an automatic fraction collector.

The gradient elution apparatus was designed as in Fig. 1. It is similar to that which was used in CNRS Rare Earths Laboratories in Bellevue, France. As can be seen from the figure there are two flasks for eluting 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 fluorimetric measurements were carried out 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 slit-widths were 10 nm.

2.3. Preparation of the eluting agent and the samples solutions

Sodium trimetaphosphate was used as the elution agent. Firstly, anhydrous sodium trimetaphosphate was prepared from sodium hexametaphosphate [14], then $\text{Na}_3\text{P}_3\text{O}_9 \cdot 6\text{H}_2\text{O}$ was prepared from the anhydrous salt [15].

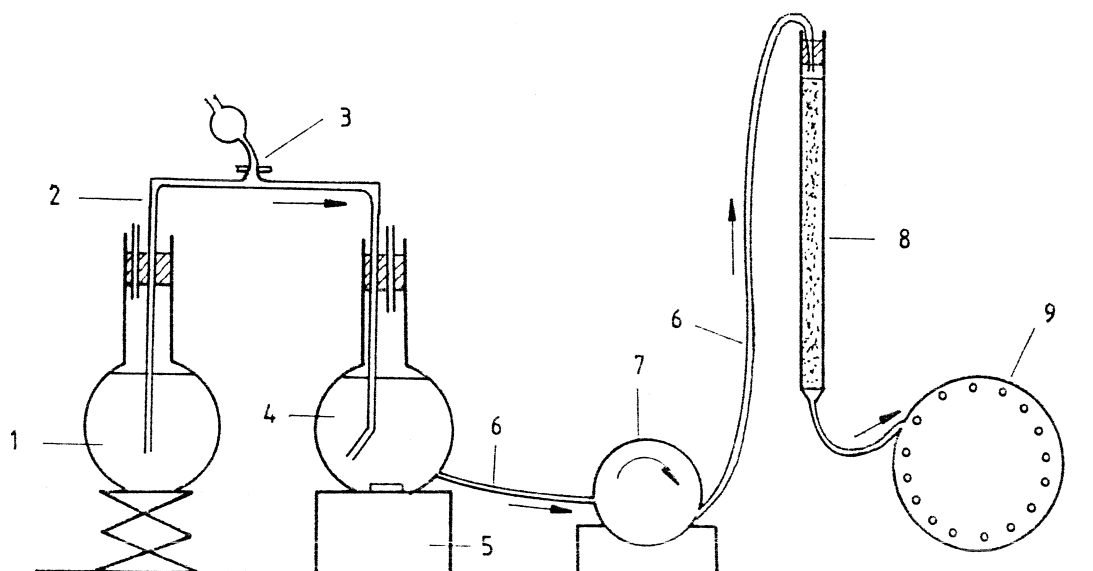


Fig. 1. Gradient elution equipment: 1,4: flask for eluents, 2: glass tubing with three ways tap, 3: rubber bulb, 5: magnetic stirrer, 6: flexible tubing, 7: peristaltic pump, 8: ion-exchange column, 9: fraction collector.

The sample solutions were mainly prepared from the nitrates (Al, Fe, Mn, Ca), the chlorides (Be, Cu), the oxides (Mg, V, Mo, Sn, Th) and the carbonates (Li) of the elements. $\text{Al}(\text{NO}_3)_3$, $\text{Fe}(\text{NO}_3)_3$, $\text{Mn}(\text{NO}_3)_3$, $\text{Ca}(\text{NO}_3)_2$ and CuCl_2 were dissolved in water. MgO , BeCl_2 , Li_2CO_3 and SnO were dissolved in HCl. V_2O_5 and MoO_3 were then reduced with H_2O_2 dissolved in HCl.

2.4. Procedure

2.4.1. Distribution coefficients

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

The portion (0.5 g) of resin (conditioned to the hydrogen form and its mass corrected by being oven dried at 105°C) was equilibrated in a small column with sodium trimetaphosphate solution at the desired concentration. It was transferred into a glass stoppered flask. Then 50 ml of the eluent with a known concentration and containing 1 meq of the cation of the element to be investigated was added. The flask was shaken by a mechanical shaking device for 15 h at room temperature.

The fluorescence measurements with appropriate reagents were carried out before and after equilibrium in the solution. The fluorimetric reagents used for each element are shown in Table 1. The distribution coefficients, K_d , is 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 qualitative identification of individual elements in the fractions of eluate were realised using their appropriate fluorimetric reagents as shown in Table 1.

2.4.3. Elution

Dowex 50W-X8, 200–400 mesh resin was washed several times with distilled water, each time the fine particles were decanted off. The washed resin was kept in water overnight, then it was transferred to the column in a water slurry. Subsequently it was equilibrated by passing elution solution through the column. The sample solution was then carefully added with a small pipette to the top of the resin

Table 1
The fluorimetric reagents used for each element

Element	Reagent	Excitation wavelength (nm)	Emission wavelength (nm)	Limit of detection ($\mu\text{g ml}^{-1}$)	Ref.
Li^+	8-Quinolinol	365	560	0.01	[16]
Be^{2+}	Morin	365	522	$4 \cdot 10^{-4}$ – $1.6 \cdot 10^{-3}$	[17]
Mg^{2+}	Morin	380	436	0.1–0.9	[18]
Al^{3+}	Morin	440	525	10	[19]
Ca^{2+}	8-Hydroxy-quinoline	430	510	10–50	[20]
V^{3+}	Benzoic acid	300	410	0.2	[21]
Mn^{3+}	8-Hydroxy-quinoline-5-sulfonic acid	375	490	0.25–50	[22]
Fe^{3+}	1,2-Phenylenediamine	300	415	0.01	[23]
Cu^{2+}	Morin, Be	390	520	10^{-3} – 10^{-1}	[24]
Mo^{6+}	Rhodamine B, SCN^-	350	578	10^{-1} –1.6	[25]
Sn^{2+}	Morin	420	500	0.1–50	[26]
Th^{4+}	Morin	410	520	0.88	[27]

Table 2
Cation-exchange distribution coefficients in different concentrations of sodium trimetaphosphate solutions

Elements	Molarity of sodium trimetaphosphate			
	0.01 M	0.05 M	0.1 M	0.3 M
Li ⁺	710.7	396.3	78.4	8.42
Be ²⁺	692.3	327.0	75.9	7.64
Mg ²⁺	664.6	301.2	74.4	7.05
Al ³⁺	501.7	246.8	58.8	6.32
Ca ²⁺	463.3	202.6	38.2	4.81
V ³⁺	441.6	196.6	32.0	4.30
Mn ³⁺	430.4	193.0	24.3	4.06
Fe ³⁺	427.4	190.3	21.4	3.97
Cu ²⁺	406.9	181.5	19.0	3.88
Mo ⁶⁺	249.0	141.2	14.6	3.44
Sn ²⁺	195.8	119.7	13.2	3.11
Th ⁴⁺	75.6	36.1	8.04	1.53

column which was previously rinsed with a small amount of water. The absorbed sample in the upper part of the resin column was eluted. Fractions of convenient volume were taken for fluorimetric measurements.

3. Results and discussions

Systematic information on ion-exchange equilibrium distribution coefficients are very useful for planning separations. For this reason, distribution coefficients were determined and are presented in Table 2. As can be seen from this table, there are enough differences between the distribution coefficients for the separations of the elements except in

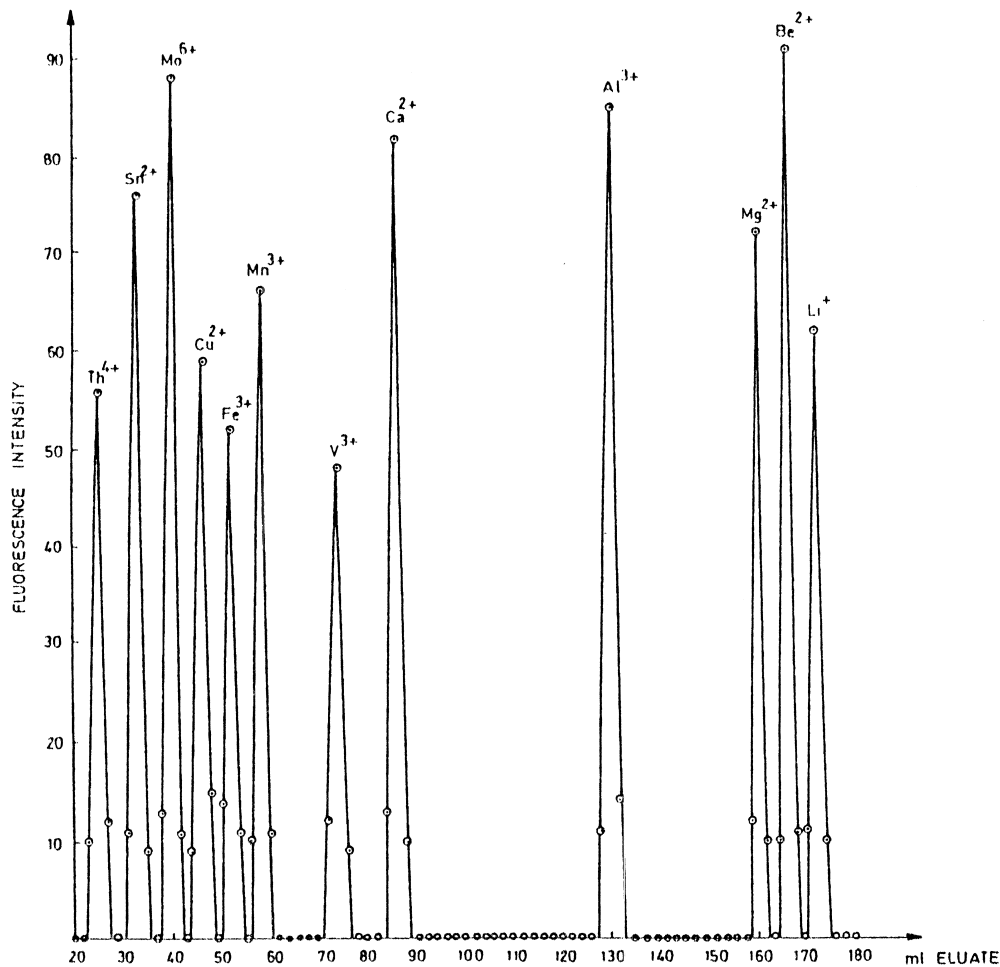


Fig. 2. Elution curves of the elements (0.5 mg of each) with 0.1 M sodium trimetaphosphate; resin bed 23 cm×0.5 cm, flow-rate 2 ml min⁻¹.

case of 0.3 *M*. For separations 0.1 *M* sodium trimetaphosphate is very convenient and 0.3 *M* sodium trimetaphosphate can be used for gradient elutions in order to minimize the elution times.

The following separations were performed by considering these values of distribution coefficients.

3.1. Separation of elements for identification and quantitative determination

Approximately 5 ml solution of synthetic mixture

which contain 0.5 mg of each element was prepared. The sample, as an aqueous solution, was added to the small column containing a resin bed 23 cm in length which was equilibrated, by passing about 250 ml of 0.1 *M* sodium trimetaphosphate solution through it and its top previously rinsed with a small amount of water.

The elements were eluted using 0.1 *M* sodium trimetaphosphate with a flow-rate of 2 ml min⁻¹. Fractions of convenient volumes were collected with an automatic fraction collector. The elution curves

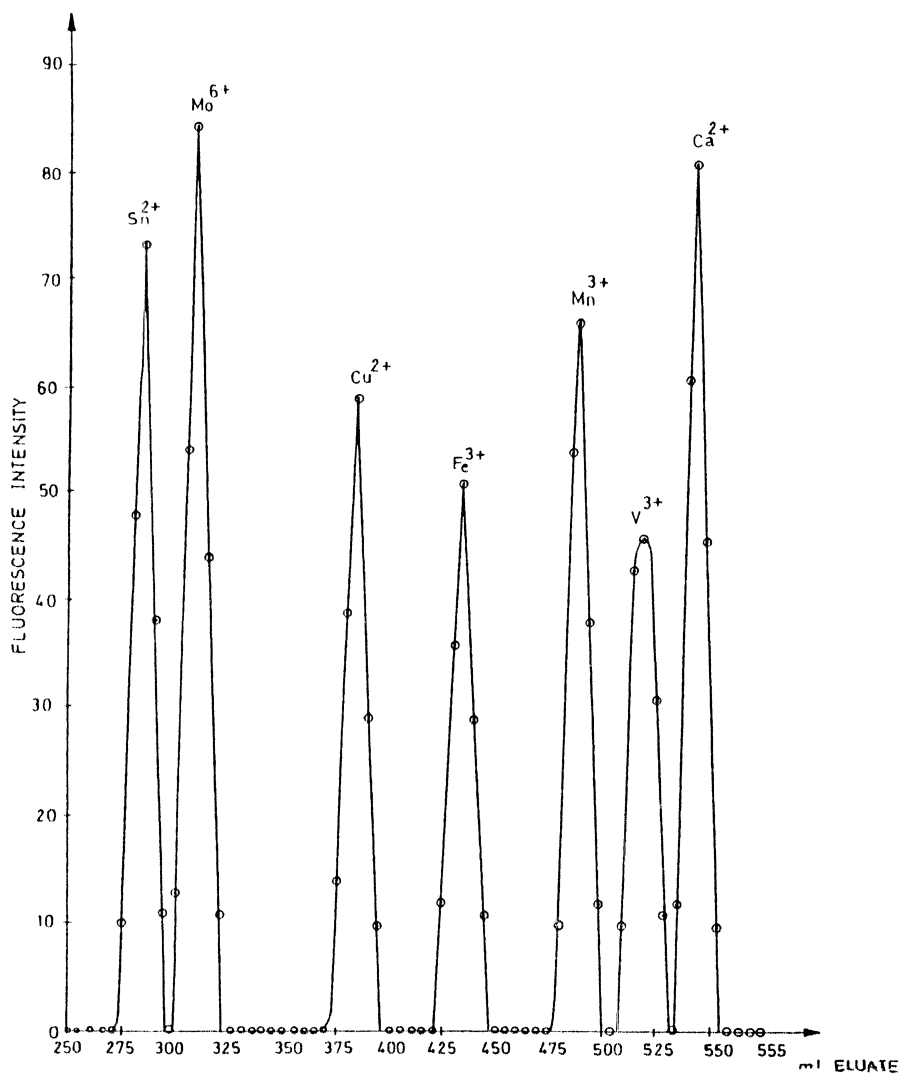


Fig. 3. Elution curves of the elements (0.5 mmol of each) with 0.1 *M* sodium trimetaphosphate for 500 ml eluent, afterwards a 0.3–0.1 *M* concentration gradient of sodium trimetaphosphate was used; resin bed 36 cm × 1.2 cm, flow-rate 2 ml min⁻¹.

are shown in Fig. 2. As can be seen from the figure, all elements were eluted within 175 ml of effluent being collected and they were separated completely from each other.

The qualitative identification of individual elements in the fractions was realised using their appropriate fluorimetric reagents as shown in Table 1.

For quantitative determination, the fractions of each element were collected in a volumetric flask and the amounts of the elements were determined fluorimetrically by preparing calibration graphs with the appropriate reagents.

3.2. Separation of the elements for the preparative purpose

Approximately a 14 ml solution of a synthetic mixture of seven elements which contain 0.5 mmol of each of the elements was prepared. The sample, as an aqueous solution, was added to a large column containing a resin bed 36 cm in length which was equilibrated, by passing about 250 ml of 0.1 M sodium trimetaphosphate solution through it and its top was previously rinsed with a small amount of water. The elements were eluted using 0.1 M sodium trimetaphosphate. In the first part of this elution 500 ml 0.1 M sodium trimetaphosphate was used as the eluent. After manganese was eluted, a 0.3–0.1 M concentration gradient elution was applied. The elution curves are shown in Fig. 3. As can be seen from this figure there is a good separation between each element and, in any case, some of these elements can be easily separated from each other using similar conditions. By using convenient concentration gradient elution, the elution times may be shortened.

4. Conclusion

Sodium trimetaphosphate is a very suitable new elution agent for the separation of some elements. It has the following advantages over the other elution agents. The elution peaks are narrow and nearly symmetrical and the tailing effects are very small. Separation time is shorter than that of other known

methods. It is possible to recover the sodium trimetaphosphate. This method is convenient for the determination and preparative separation of the elements.

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