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Journal of Chromatography A, 789 (1997) 135–139

JOURNAL OF
CHROMATOGRAPHY A

Ion chromatographic separation of metallic ions on a bonded poly- β -diketone-type non-cyclic crown ether stationary phase

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Abstract

Tetra(oxydimethyl) poly- β -diketone-type non-cyclic crown ether ion chromatographic stationary phase was prepared by grafting non-cyclic crown ether on silica gel modified previously with γ -aminopropyltriethoxysilane. The chromatographic behavior of this stationary phase was studied. Very good separation was obtained for alkali, alkaline earth and transition metals on this stationary phase using methanol and water of various proportions as mobile phase. © 1997 Elsevier Science B.V.

Keywords: Stationary phases, LC; Crown ether stationary phases; Metals; Chloride; Nitrate

1. Introduction

Ordinarily used ion chromatographic stationary phases are of resinic type [1,2] and chemically bonded type [3]. Ion-exchange is their common separation mechanism, a certain amount of acid, base or salt has to be added in the mobile phase making the operation tedious and causing serious corrosion of the instrument. The newly developed bonded crown ether ion chromatographic stationary phases [4,5] can overcome the above shortcoming. Using only water or an aqueous solution containing a certain amount of organic solvent as the mobile phase, good separation effects can be accomplished on these stationary phases. The mobile phase is simplified and can also match the conductivity detector commonly used in ion chromatography. However, the synthesis of these crown ethers is rather difficult, their cost price is high, thus their application is limited. The non-cyclic crown ether also possesses selective complexation ability with

ionic substances but is easier to synthesize, so it is a ion chromatographic stationary phase of broad prospect. The authors have studied mono-, di- and tri(oxydimethyl) poly- β -diketone-type non-cyclic crown ether stationary phases [6], and have found that the ability of separating inorganic ions increases with the increase of oxydimethyl group in the stationary phase. The tetra(oxydimethyl) poly- β -diketone-type non-cyclic crown ether ion chromatographic stationary phase is synthesized [7] and its chromatographic behavior studied.

2. Experimental

2.1. Instrumentation

The ion chromatograph used for this work was composed of a Waters 6000 pump, a DDJ-01 conductivity detector (Sichuan Analytical Instrument Plant, China), a Rheodyne 7125 injector (10 μ l), a stainless-steel column (150 \times 4.6 mm I.D.) and a XWT-200 recorder (Shanghai Dahua Instrument and

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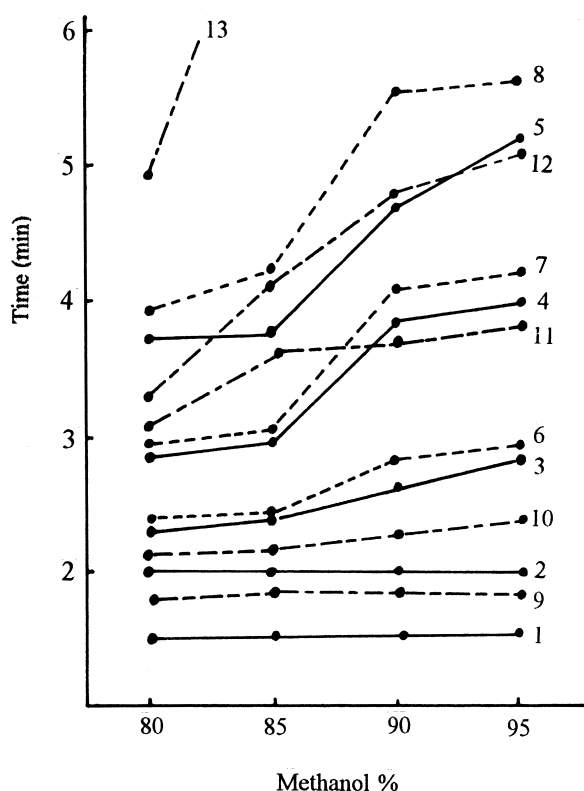


Fig. 1. Retention time of alkali metal salts versus mobile phase of different methanol content. 1. LiCl, LiNO₃; 2. NH₄Cl, NH₄NO₃; 3. NaCl; 4. CsCl; 5. KCl; 6. NaNO₃; 7. CsNO₃; 8. KNO₃; 9. LiSO₄; 10. (NH₄)₂SO₄; 11. Na₂SO₄; 12. CsSO₄; 13. K₂SO₄.

3.2. Chromatographic behavior of the stationary phase

Fig. 1 shows the retention times of a few common alkali metal salts, with mobile phases of various methanol content used. It can be seen that in mobile phases of different methanol content the Li⁺, NH₄⁺, Na⁺, Cs⁺ and K⁺ salts of the same acid have distinctly different retention times. Therefore it is very easy to separate these metal ions when crown ether phase is used. Besides, other than the chloride and nitrate of Li and ammonium, in the same mobile phase the salts of sodium, cesium and potassium show increasing retention times when the salt is changed from chloride, nitrate to sulfate. That is, the salt type of same alkali metal can be easily judged.

It can also be seen from Fig. 1 that along with the increase of methanol content in mobile phase, the retention times of all alkali metal salts increases, although in different degrees. Therefore the optimum separation can be reached through adjustment of their retention times by variation of mobile phase composition. On the other hand the grafted phase retains alkali earth and transition metal salts more strongly than alkali metal salts, the three group metal salts can well be separated in a short time by adjustment of methanol content in mobile phase (see Fig. 2). This characteristic is different from the crown ether stationary phase reported in the literature

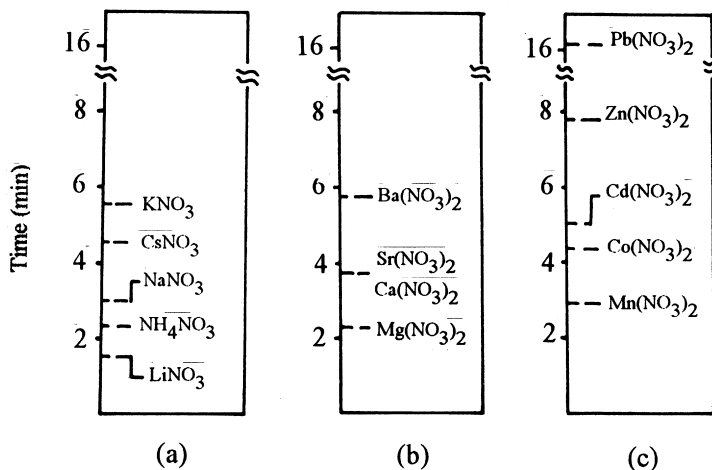


Fig. 2. Selectivity of stationary phase. Mobile phase: (a) methanol–water (95:5); (b) methanol–water (30:70); (c) 100% water.

[4,5]. On those phases, the retention of some alkali metal salts is stronger than that of alkali earth metal salts, so that the elutions of mono- and divalent metal salts are mingled with each other. But on this β -diketone-type non-cyclic crown ether stationary phase the retention order is alkali metal < alkali earth metal < transition metal, this characteristic makes it more convenient in chromatographic application.

3.3. Chromatographic separation

3.3.1. Separation of alkali metals

By using methanol–water (95:5, v/v) as mobile phase the separation of chlorides, nitrates and sulfonate of Li^+ , NH_4^+ , Na^+ , Cs^+ and K^+ can all be accomplished within 6–9 min. This phase has special selectivity to K^+ and NH_4^+ , whose separation on ion-exchange stationary phase is rather difficult. Fig. 3 shows the chromatogram of alkali chlorides.

3.3.2. Separation of alkali earth metals

The chlorides and nitrates of alkali earth metals have been separated. Using methanol–water (30:70, v/v) as mobile phase, all salts, except Ca and Sr pair,

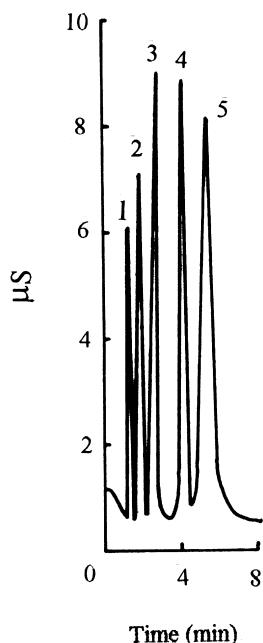


Fig. 3. Separation of alkali metals. 1. LiCl ; 2. NH_4Cl ; 3. NaCl ; 4. CsCl ; 5. KCl .

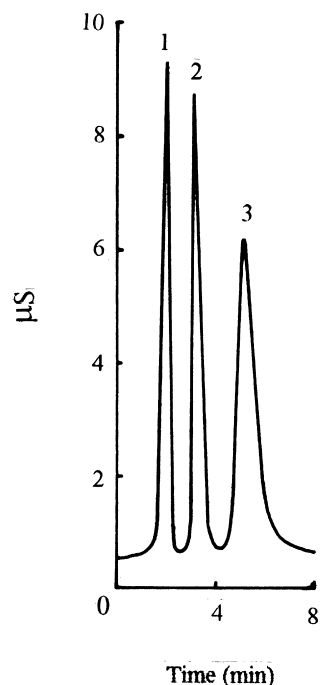


Fig. 4. Separation of alkaline earth metals. 1. $\text{Mg}(\text{NO}_3)_2$; 2. $\text{Ca}(\text{NO}_3)_2$; $\text{Sr}(\text{NO}_3)_2$; 3. $\text{Ba}(\text{NO}_3)_2$.

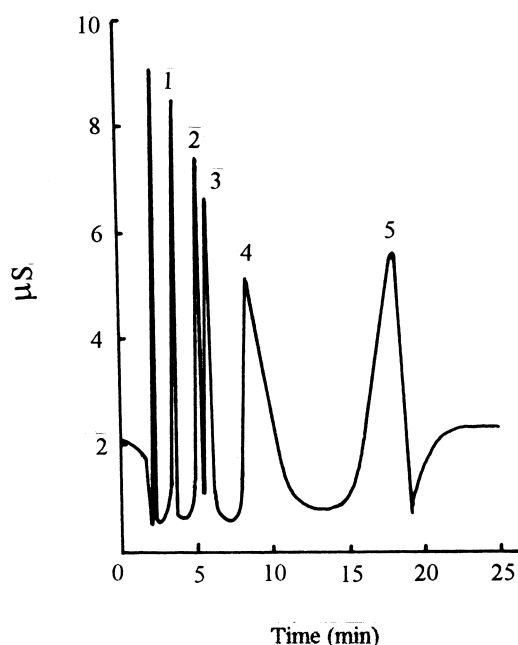


Fig. 5. Separation of transition metals. 1. $\text{Mg}(\text{NO}_3)_2$; 2. $\text{Co}(\text{NO}_3)_2$; 3. $\text{Cd}(\text{NO}_3)_2$; 3. $\text{Zn}(\text{NO}_3)_2$; 5. $\text{Pb}(\text{NO}_3)_2$.

can accomplish baseline separation within 6 min. Fig. 4 shows the chromatogram of the nitrates of alkali earth metals.

3.3.3. Separation of transition metals

Fig. 5 shows the chromatogram of transition metals. Using only water as mobile phase the separation of nitrates of five transition metals, Mn, Co, Cd, Zn and Pb, is completely reached within 16 min.

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