

A NOVEL ELUENT FOR SINGLE-COLUMN ION CHROMATOGRAPHY WITH CONDUCTOMETRIC DETECTION

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Abstract. Nitrilotriacetic acid—sodium carbonate mixtures are suggested for the use as eluents in single-column ion chromatography. The respective selectivity coefficients for five common inorganic anions were determined applying three different separator columns.

Key words: ion chromatography, eluent, nitrilotriacetic acid, selectivity coefficients.

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INTRODUCTION

Single-column ion chromatography [1,2] is a widely used technique for the determination of anions in a variety of aqueous matrices. The analytical performance of the technique depends mostly on two criteria, viz. on the choice of an ion-exchanger in the column and that of an appropriate eluent. The mixtures of nitrilotriacetic acid (NTA) and sodium carbonate dissolved in water have been found to be good eluents for single-column ion chromatography with conductometric detection.

EXPERIMENTAL

Model IVK-11 ion chromatograph with a conductometric detector JD-1, both from the Design Office of the Estonian Academy of Sciences, Tallinn, was used. Chromatograms were recorded on a Servogor S recorder (Goerz, Germany). The separator columns used were: (1) column A (4×150 mm) packed with HIKS-1 resin, capacity 0.052 mequiv./cm³; (2) column B (4×150 mm) packed with HIKS-1 resin, capacity 0.019 mequiv./cm³; and (3) column C (4×150 mm) packed with a silica-bonded ion-exchanger CNS-A synthesized in the Institute of Chemistry (Tallinn), capacity 0.019 mequiv./cm³. Eluents were made from reagent grade chemicals, the weighed amounts of NTA and Na₂CO₃ were dissolved in distilled water. At this procedure no CO₂ separation was observed. The concentration of NTA was kept constant in all the eluents (1.0 mM) and the concentration of Na₂CO₃ was varied in the range of 0.5–3.0 mM. The eluent flow rate was 1.6 ml/min.

RESULTS AND DISCUSSION

The eluents with the ratio $a = C_{\text{Na}_2\text{CO}_3}/C_{\text{NTA}} = 0.5 - 3.0$ ($3.7 \leq \text{pH} \leq 9.55$) were tested on three columns, A, B, and C, using a single-column system, see Experimental. The eluents were found to be appropriate for the separation of the anions Cl^- , NO_3^- , and SO_4^{2-} in their mixtures (see Figs. 1 and 2). The capacity factors $k' = (t_R - t_0)/t_0$ for those anions vs. the ratio a are presented in Figs. 3—5. The eluents studied showed only one system peak on the chromatograms if $a \leq 2$. This single system peak was located in the very beginning of the chromatogram before the peak of Cl^- ions. The conductivity background of the eluents tested was acceptable for single-column ion chromatography (see Fig. 6).

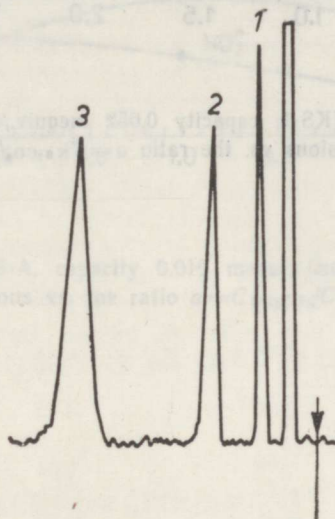


Fig. 1. Chromatogram obtained with column A. Eluent 1.0 mM NTA+1.1 mM Na_2CO_3 , flow rate 1.6 ml/min. Loop volume 221 μl . A conductometric detector was used. Samples: 1 — 23 ppm Cl^- ; 2 — 60 ppm NO_3^- ; and 3 — 120 ppm SO_4^{2-} .

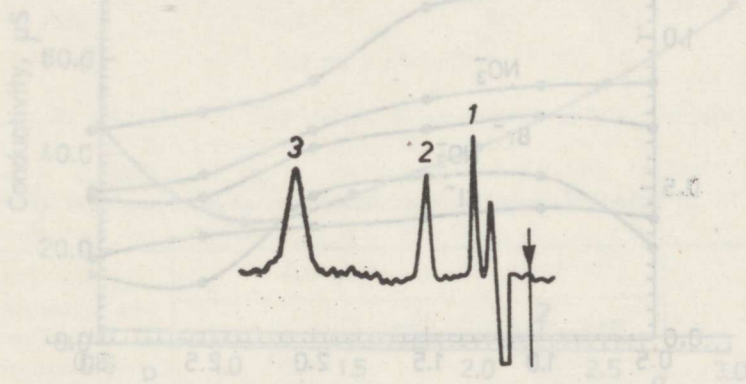


Fig. 2. Chromatogram obtained with column A. Eluent 1.0 mM NTA+1.1 mM Na_2CO_3 , flow rate 1.6 ml/min. Loop volume 221 μl . A conductometric detector was used. Samples: 1 — 7.4 ppm Cl^- ; 2 — 20 ppm NO_3^- ; and 3 — 40 ppm SO_4^{2-} .

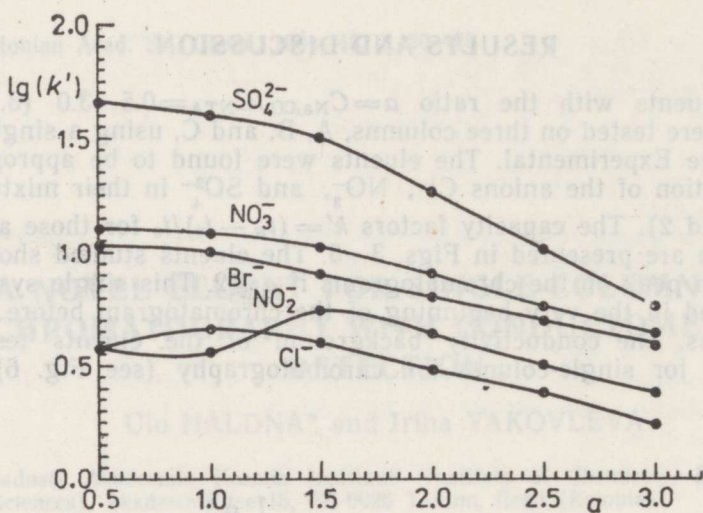


Fig. 3. Column A with HIKS-1, capacity 0.052 mequiv./cm³. The capacity factors k' for anions vs. the ratio $a = C_{Na_2CO_3}/C_{NTA}$.

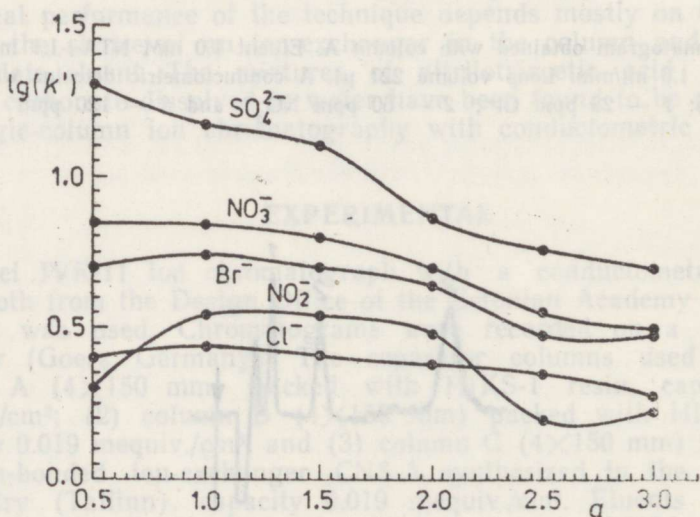


Fig. 4. Column B with HIKS-1, capacity 0.019 mequiv./cm³. The capacity factors k' for anions vs. the ratio $a = C_{Na_2CO_3}/C_{NTA}$.

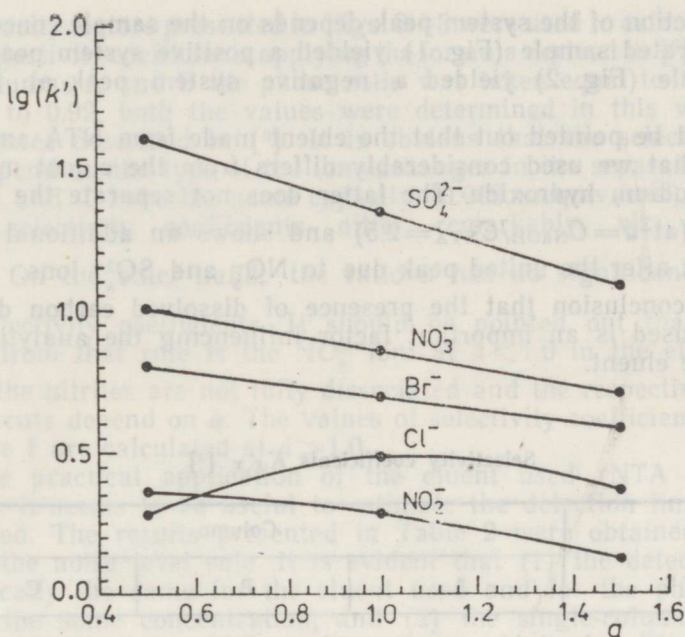


Fig. 5. Column C with CNS-A, capacity 0.019 mequiv./cm². The capacity factors k' for anions vs. the ratio $a = C_{N_2CO_3}/C_{NTA}$.

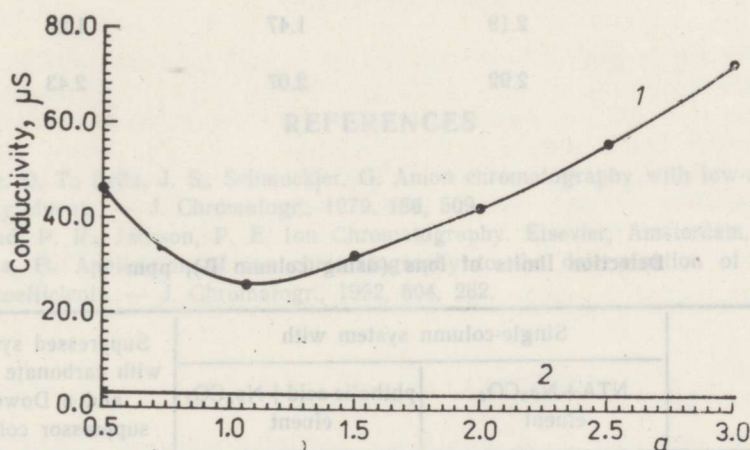


Fig. 6. The background conductivity of the eluents (1) and distilled water (2) vs. the ratio $a = C_{N_2CO_3}/C_{NTA}$. The cell constant used $K = 7.0 \text{ cm}^{-1}$.

The direction of the system peak depends on the sample concentration: the concentrated sample (Fig. 1) yielded a positive system peak but the dilute sample (Fig. 2) yielded a negative system peak at the same location.

It should be pointed out that the eluent made from NTA and sodium carbonate that we used considerably differs from the eluent made from NTA and sodium hydroxide. The latter does not separate the NO_3^- and SO_4^{2-} ions (at $\alpha = C_{\text{NaOH}}/C_{\text{NTA}} = 2.5$) and shows an additional negative system peak after the united peak due to NO_3^- and SO_4^{2-} ions. This fact leads to a conclusion that the presence of dissolved carbon dioxide in the eluent used is an important factor influencing the analytical properties of the eluent.

Table 1

Selectivity coefficients $K_{X,Y}$ [3]

| $K_{X,Y}$ | Column | | |
|---------------------------------------|--------|------|------|
| | A | B | C |
| $K_{\text{Cl}^-, \text{NO}_2^-}$ | 0.64 | 1.00 | 0.82 |
| $K_{\text{Cl}^-, \text{Br}^-}$ | 0.43 | 0.56 | 0.37 |
| $K_{\text{Cl}^-, \text{NO}_3^-}$ | 0.37 | 0.48 | 0.26 |
| $K_{\text{Cl}^-, \text{SO}_4^{2-}}$ | 0.40 | 0.48 | 0.16 |
| $K_{\text{NO}_2^-, \text{Br}^-}$ | 0.68 | 0.62 | 0.60 |
| $K_{\text{NO}_2^-, \text{NO}_3^-}$ | 0.59 | 0.54 | 0.43 |
| $K_{\text{NO}_2^-, \text{SO}_4^{2-}}$ | 0.97 | 0.59 | 0.46 |
| $K_{\text{Br}^-, \text{NO}_3^-}$ | 0.87 | 0.85 | 0.70 |
| $K_{\text{Br}^-, \text{SO}_4^{2-}}$ | 2.19 | 1.47 | 1.20 |
| $K_{\text{NO}_3^-, \text{SO}_4^{2-}}$ | 2.92 | 2.07 | 2.43 |

Table 2

Detection limits of ions (using column B), ppm

| Ion | Single-column system with | | Suppressed system with carbonate eluent and a Dowex suppressor column |
|--------------------|---------------------------------------|---|---|
| | NTA + Na_2CO_3 eluent | phthalic acid + Na_2CO_3 eluent | |
| Cl^- | 0.18 | 0.15 | not measured |
| NO_3^- | 0.65 | 0.6 | 0.02 |
| SO_4^{2-} | 0.8 | 0.7 | 0.03 |

The capacity factors presented in Figs. 3—5 were used to calculate the respective selectivity coefficients applying the formula derived in [3] (see Table 1). For columns A and B the phase ratio was taken equal to 1.1 and for column C to 0.92, both the values were determined in this work using the procedures described in [3]. It is obvious that the selectivity coefficients depend on the type of the ion-exchanger in the separator column: columns B and C have the same capacity (0.019 mequiv./cm³), but some of their selectivity coefficients differ remarkably, viz. $K_{\text{Cl}^-, \text{NO}_2^-}$, $K_{\text{Cl}^-, \text{SO}_4^{2-}}$. On the other hand, the ratio a has no significant influence on the selectivity coefficients. It should be pointed out that the only exception from that rule is the NO_2^- ion: at $a < 1.0$ in the eluents with $\text{pH} < 4.5$, the nitrites are not fully dissociated and the respective selectivity coefficients depend on a . The values of selectivity coefficients presented in Table 1 are calculated at $a > 1.0$.

For the practical application of the eluent used (NTA + sodium carbonate) it seems to be useful to estimate the detection limits for the ions studied. The results presented in Table 2 were obtained applying the twice the noise level rule. It is evident that (1) the detection limits are practically the same for the eluent used and for the phthalic acid eluent of the same concentration, and (2) the single-column detection limits are 20—30 times higher than those obtained with the same apparatus used in a suppressed mode. This result is an expected one [2] because the background conductivity is much higher in a single-column system than in a dual-column system. In the last case the conductivity cell with a constant value of 7.0 cm⁻¹ yielded about 3 μS for the background conductivity, which should be compared to the obtained un-suppressed conductivity of about 30 μS (see Fig. 6).

ACKNOWLEDGEMENT

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UUS ELUENT KONDUKTOMEETRILISE DETEKTEERIMISEGA ÜHEKOLONNILISE IOONIKROMATOGRAAFIA TARVIS

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Nitriilotriäädikhappe ja naatriumkarbonaadi vesilahuse segud on sobivad eluendid ühekolonna ioonikromatograafias. On määratud selektiivsuskoefitsient viie anorgaanilise aniooni korral kasutades kolme erinevat analüütilist kolonni.

НОВЫЙ ЭЛЮЕНТ ДЛЯ ОДНОКОЛОНОЧНОЙ ИОННОЙ ХРОМАТОГРАФИИ С КОНДУКТОМЕТРИЧЕСКИМ ДЕТЕКТИРОВАНИЕМ

Юло ХАЛДНА, Ирина ЯКОВЛЕВА

Смесь водных растворов нитрилотриуксусной кислоты и карбоната натрия предложена в качестве элюента для ионной хроматографии с кондуктометрическим детектированием. Определены значения коэффициентов селективности для пяти неорганических анионов с указанным элюентом, а также с использованием трех разных аналитических колонок.

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| Ion | the mixture used | | selectivity coefficient |
|-------------------------------|---|-----------------------------------|-------------------------|
| | CO ₃ ²⁻ / Na ⁺ | TA ⁻ / Na ⁺ | |
| Cl ⁻ | 0.15 | 0.15 | 0.00 |
| NO ₃ ⁻ | 0.60 | 0.60 | 0.00 |
| SO ₄ ²⁻ | 1.0 | 1.0 | 0.00 |