

## ION CHROMATOGRAPHY OF ALKALI, ALKALINE EARTH METAL AND AMMONIUM IONS WITH CONDUCTIVITY DETECTION AND ORGANIC COMPLEXING ACID ELUENT

Jüri IVASK and Jaan PENTCHUK

Tartu Ülikooli Keemilise Füüsika Instituut (Institute of Chemical Physics, University of Tartu), Jakobi 2, EE-2400 Tartu, Eesti (Estonia)

Presented by K. Lääts

Received March 3, 1994; accepted April 21, 1994

**Abstract.** The simultaneous ion chromatography of mono- and divalent cations, with non-suppressed conductivity detection, on the cation-exchange column Katiex K is described. The effect of pyridine-2,6-dicarboxylic acid mixtures with tartaric acid eluent on the retention and separation of cations was studied. The mean efficiency of the chromatographic system evaluated by the HETP value was 0.15 mm. Optimum elution conditions were established by measuring the effect of eluent composition on the resolution of cations. With the combination of 7.5 mM tartaric acid and 0.75 mM pyridine-2,6-dicarboxylic acid as eluent, ions of lithium, sodium, ammonium, potassium, magnesium and calcium could be completely separated within 20 min.

**Key words:** ion chromatography, alkali and alkaline earth metal ions, organic complexing acid eluent.

### INTRODUCTION

Monovalent sodium, ammonium and potassium ions and divalent magnesium and calcium ions are found together in most water samples, and often all these species need to be determined. In ion chromatography (IC), mono- and divalent cations are usually determined under separate elution conditions. Recently, some methods have been proposed for handling mono- and divalent species simultaneously by isocratic elution [1–3]. In the previous paper [4], it has been found that the Katiex K column is applicable for determining monovalent cations in ground water samples. Under these conditions, however, divalent cations are captured in the column and, as a result, the column needs periodical regeneration. In this paper, the mixtures of tartaric acid and pyridine-2,6-dicarboxylic acid (PDCA) were tested in order to find the optimum separation conditions for the simultaneous determination of the most usual mono- and divalent cations in natural waters.

### EXPERIMENTAL

**Instrumentation.** The apparatus used was an IAK-12 analytical chromatograph with conductivity detector (INKROM Ltd., Estonia). The separation column used was an IC cation column Katiex K 3×150 mm (ECOS Ltd., Estonia) with particle size 10 µm.

**Reagents and procedures.** All the reagents used were of analytical grade (Reakhim, Russia). The standard solutions of cations were prepared by dissolving the weighed amounts of inorganic salts in degassed distilled water. The test solution contained 1 ppm lithium, 5 ppm sodium, 5 ppm ammonium, 10 ppm potassium, 10 ppm magnesium, and 10 ppm calcium ions. Eluents used were prepared from tartaric acid and PDCA as well as their mixtures without pH adjustment. All eluents were prepared daily and filtered.

**Chromatographic conditions.** The chromatographic experiment was performed with a flow rate of 1 ml/min. The sample volume used was 50  $\mu$ l. The sensitivity of the conductivity detector was set to 16  $\mu$ S/cm FS. The column, loop injector and the cell of the conductivity detector were maintained at 35°C.

## RESULTS AND DISCUSSION

The metal cation elution ability of tartaric acid is determined by its dissociation and complex stability constants (KML), as well as its concentration. Because of the low values of tartrate complex stability constants (Na:  $\log_{KML}=0.73$ ; K:  $\log_{KML}=0$  [3]), the elution of monovalent cations depends mostly on the  $[H^+]$ -concentration of the eluent. The elution of divalent metal ions with higher  $\log_{KML}$  values for tartrate complexes (Mg:  $\log_{KML}=1.36$ ; Ca:  $\log_{KML}=1.80$  [3]) is more influenced by the ligands of the organic acid. When 1 mM nitric acid eluent [4] is replaced by 7.5 mM tartaric acid eluent, divalent cations are no more captured in the column and all cations of the test solution can be separated in a single run (Fig. 1, A). However, the retention times for magnesium and calcium ions are considerably larger than that of monovalent cations, and the total analysis time is quite long. One way to accelerate the elution of divalent cations is to add a more strong ligand to the tartaric acid eluent: PDCA, for example. PDCA is characterized by the fact that the complex of Ca—PDCA ( $\log_{KML}=4.6$ ) is remarkably more stable than that of Mg—PDCA ( $\log_{KML}=2.32$ ) [3]. When the concentration of PDCA in the 7.5 mM tartaric acid eluent was increased from 0 to 0.75 mM, the retention time of Ca ions decreased more rapidly than that of Mg ions. At the PDCA concentration 0.3 mM, Mg and Ca ions eluted as a single peak, but the concentration 0.75 mM PDCA caused the elution of Ca before Mg ions with good resolution (Fig. 1, B), and the total analysis time decreased to 20 min. This elution sequence could not be achieved by other conventional organic acid eluents. To optimize the eluent composition, resolution values ( $R$ ) for ion peak pair Ca/Mg were plotted vs. PDCA concentration ( $C$ ) in the eluent (Fig. 2). The peaks are completely separated at absolute values  $R>1$ . The corresponding PDCA concentration is below 0.14 mM or above 0.725 mM, the latter being preferable due to shorter analysis time. Further analysis time shortening using more concentrated PDCA modifier in the eluent is limited by the resolution decrease in the group of monovalent cations. The efficiency of the used IC system was evaluated by calculating HETP values [5]. The obtained values for all cations were quite close and ranged from 0.18 mm for sodium to 0.13 mm for calcium, potassium and ammonium.



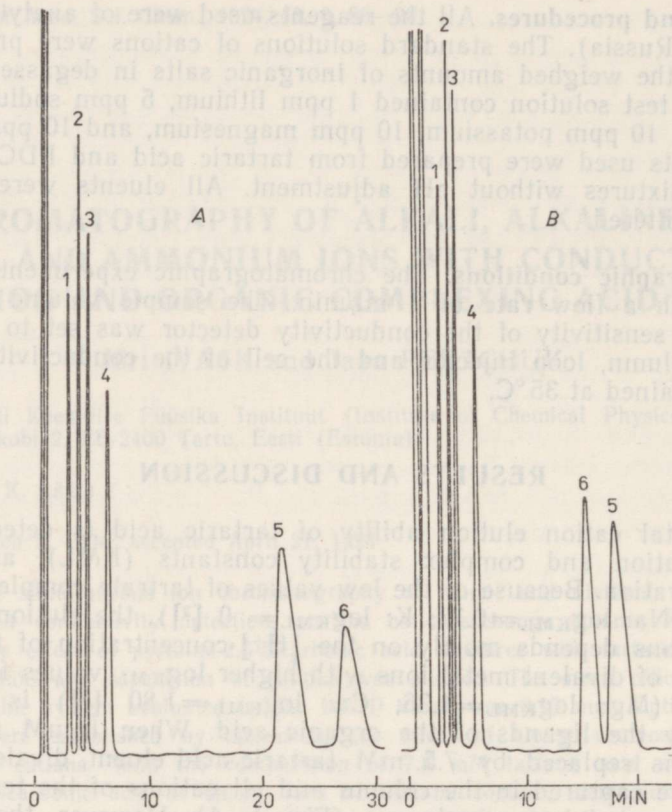


Fig. 1. Separation of cations with 7.5 mM tartaric acid eluent without (A) and with 0.75 mM pyridine-2,6-dicarboxic acid (B). Conditions as in text.

Ions: 1 — lithium, 2 — sodium, 3 — ammonium, 4 — potassium, 5 — magnesium, 6 — calcium.

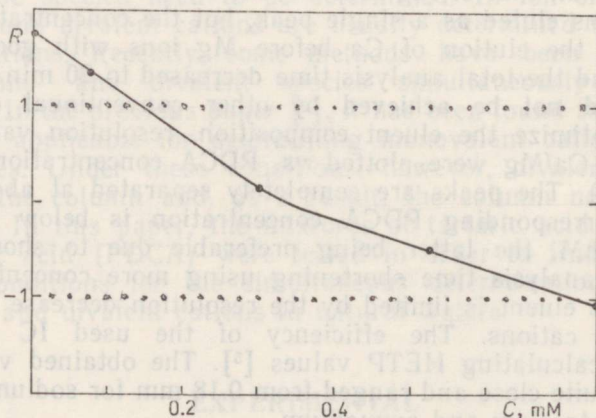


Fig. 2. The effect of pyridine-2,6-dicarboxic acid concentration (C) on the peak pair calcium/magnesium resolution ( $R = (t'_{Ca} - t'_{Mg}) / (\omega_{Ca} + \omega_{Mg})$ , where  $t'$  is the adjusted retention time and  $\omega$  is the peak width at its half height).

## CONCLUSIONS

Non-suppressed IC with Katiex K separation column, using the mixture of tartaric acid and PDCA as eluent with conductivity detection recommends itself, due to its good separation efficiency, for the simultaneous separation of alkali and alkaline earth metal ions. This IC method can compete with other analytical methods, such as flame photometry, titrimetry, ionometry etc., for the analyses of alkali and alkaline earth metals.

## ACKNOWLEDGEMENT

Financial support from the Estonian Innovation Foundation that made possible to obtain chromatographic equipment is gratefully acknowledged.

## REFERENCES

1. Schomburg, G., Kolla, P., Läubli, M. W. Ion chromatography of alkali and alkaline earth metal ions using a silica-based polymer-coated stationary phase. — *Int. Lab.*, 1989, 4, 40—47.
2. Sato, H. Isocratic elution of sodium, ammonium, potassium, magnesium and calcium ions by ion-exchange chromatography. — *J. Chromatogr.*, 1989, 469, 339—349.
3. Yan, D., Schwedt, G. Simultaneous ion chromatography of alkali, alkaline earth and heavy metal ions with conductivity and indirect UV detection: Comparison of eluents containing organic complexing acids and copper sulfate. — *Frese-nius J. Anal. Chem.*, 1990, 338, 149—155.
4. Ivask, J., Penchuk, J. Application of the Katiex K cation-exchange column to determining sodium, ammonium, and potassium ions in ground water samples. — *Proc. Estonian Acad. Sci. Chem.*, 1991, 40, 3, 166—169.
5. Ettre, L. S. The new IUPAC nomenclature for chromatography. — *LC·GC Int.*, 1993, 6, 9, 544—548.

## LEELIS-, LEELISMULDMETALLIDE JA AMMOONIUMIOONIDE IOONKROMATOGRAAFILINE LAHUTAMINE KASUTADES KONDUKTOMEETRILIST DETEKTORIT JA ELUENDINA KOMPLEKSOONHAPPEID

Jüri IVASK, Jaan PENTŠUK

On kirjeldatud ühekolonnistioonkromatograafilist süsteemi ühe- ja kahelaenguliste katioonide lahutamiseks kationiitkolonni Katiex K abil ning uuritud viin- ja püridiin-2,6-dikarboonhappe segudest eluentide mõju katioonide retentsioonile ja lahutumisele. Kromatograafilise süsteemi efektiivsus väljendatuna HETP ühikutes oli keskmiselt 0,15 mm. On leitud optimaalsed eluerimistingimused uurides eluendi koostise mõju katioonide lahutatusele. Kasutades eluendina 7,5 mM viinhappe ja 0,75 mM püridiin-2,6-dikarboonhappe kombinatsiooni, on võimalik 20 minuti jooksul lahutada liitium-, naatrium-, ammonium-, kaalium-, magneesium- ja kaltsiumioonide segu täielikult.



# ИОНОХРОМАТОГРАФИЧЕСКОЕ РАЗДЕЛЕНИЕ ИОНОВ ЩЕЛОЧНЫХ И ЩЕЛОЧНОЗЕМЕЛЬНЫХ МЕТАЛЛОВ И АММОНИЯ С ИСПОЛЬЗОВАНИЕМ КОНДУКТОМЕТРИЧЕСКОГО ДЕТЕКТОРА И КОМПЛЕКСООБРАЗУЮЩИХ ОРГАНИЧЕСКИХ КИСЛОТ В КАЧЕСТВЕ ЭЛЮЕНТА

Юри ИВАСК, Яан ПЕНЧУК

Описан ионохроматографический метод последовательного анализа одно- и двухзарядных катионов на катионообменной колонке «Катиекс К» с использованием кондуктометрического детектора без супрессорной системы. Изучено влияние смесей пиридин-2,6-дикарбоновой кислоты с виннокислым элюентом на удерживание и разделение катионов. Средняя эффективность хроматографической системы, выраженная в единицах ВЭТТ, составляла 0,15 мм. Оптимальные условия элюирования найдены при изучении влияния состава элюента на разделение катионов. Используя в качестве элюента раствор 7,5 мМ винной кислоты и 0,75 мМ пиридин-2,6-дикарбоновой кислоты, можно разделить ионы лития, натрия, аммония, калия, магния и кальция в течение 20 мин.

## REFERENCES

1. Schomburg, D., Kott, P., Jandt, M. W. Ion chromatography of alkali and alkaline earth metal ions using a silica-based polymer-coated stationary phase — *J. Lab. Autom.* 1989, 4, 40—47.
2. Sato, H. Effective elution of sodium, ammonium, potassium, magnesium and calcium ions by ion-exchange chromatography. — *J. Chromatogr.* 1980, 188, 330—340.
3. Van D. Schwell, G. Simultaneous ion chromatography of alkali, alkaline earth and heavy metal ions with conductivity and indirect UV detection. Comparison of eluents containing organic complexing acids and copper sulphate. — *J. Anal. Chem.* 1980, 58, 145—150.
4. Ivask, J., Penck, J. Application of the Katiek K cation-exchange column to determining sodium, ammonium, and potassium ions in ground water samples. — *Proc. Estonian Acad. Sci. Chem.* 1991, 40, 3, 166—169.
5. Eise, L. S. The new IUPAC nomenclature for chromatography. — *J. Chromatogr.* 1993, 6, 2, 541—548.

## LEELIS, LEEJISUMJDMETALIDE JA AMMOONIUMIOONIDE IOONKROMATOGRAAFILISE LAHUTAMISE KASUTAJAES KONDUKTOMETRIKSE DETEKTORIT JA ELUENDINA KOMPLEKSOONHAPPEID

Juri IVASK, Jaan PENČUK

On kirjeldatud järjestikulist ioonkromatograafilist süsteemi ühe- ja kahevalentsete katioonide lahutamiseks kationivaheldelise Katiek K adsorbentiga ja kahe- ja kolmevalentsete katioonide lahutamiseks kationivaheldelise Katiek K adsorbentiga ja piiridin-2,6-dikarboonhappe kompleks moodustavate katioonide lahutamiseks. Kromatograafilise süsteemi keskmine efektiivsus väljendatuna HETP ühikutes oli keskmiselt 0,15 mm. Optimaalsed eluendite koostised uuritud katioonide lahutamiseks leiti kasutades lahutusel 7,5 mM viinhapet ja 0,75 mM piiridin-2,6-dikarboonhappe kompleksiooni, on võimalik 20 minutiga lahutada liitium, naatrium, ammoonium, kalium, magneesium ja kalsiumioonide segu lahendist.