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INCREASING THE SELECTIVITY IN THE ION CHROMATOGRAPHIC DETERMINATION OF SODIUM, AMMONIUM, AND POTASSIUM IONS. THE EFFECT OF THE ELUENT POLYETHYLENE GLYCOLIC MODIFIER

Jüri IVASK, Jaan PENTSUK, Ülo HALDNA. SELEKTIIVSUSE SUURENDAMINE NAATRIUMI, AMMOONIUMI JA KAALIUMI IOONIDE IOONKROMATOGRAAFILISEL MÄÄRAMISEL. ELUENDI POLÜETÜLEENGLÜKOOLSE MODIFIKAATORI MÕJU

Юри ИВАСК, Яан ПЕНЧУК, Юло ХАЛДНА. УЛУЧШЕНИЕ СЕЛЕКТИВНОСТИ ПРИ ИОНОХРОМАТОГРАФИЧЕСКОМ ОПРЕДЕЛЕНИИ СОДЕРЖАНИЯ ИОНОВ НАТРИЯ, АММОНИЯ И КАЛИЯ. ДЕЙСТВИЕ ЭЛЮЕНТНОГО ПОЛИЭТИЛЕНГЛИКОЛЕВОГО МОДИФИКАТОРА

Introduction

In ion chromatographic determination of ammonium ions in the presence of large amounts of sodium and potassium ions it is desirable to increase the selectivity of the separation for these ion peaks. This can usually be achieved by adding amino acidic [1] or alcoholic [2] modifiers to the eluent. In this paper the effect of polyethylene glycol (PEG) as an eluent modifier in increasing the separation selectivity of these cations is evaluated.

Experimental

The experiment was carried out using an ion chromatographic system equipped with a conductivity detector (Design Office of the Estonian Academy of Sciences) and column Katieks K (3.3×150 mm; methacrylic cation exchange resin with carboxylic groups; "ECOS", Estonia). All the reagents used were of analytical grade ("Reakhim", USSR). The nitric acid eluent concentration was 1.0 mM and flow rate 1.0 ml/min. The concentration of the PEG (MW=300) modifier in the eluent was varied in the range 0—10 vol%. Triethylene glycol (TEG) as an eluent modifier was also used under the same conditions. The experiment was

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repeated with the column BT IV KA (3.3×100 mm; polystyrenedivinylbenzene cation exchange resin with sulpho groups; "Biotronik", Germany). The optimum conditions found were checked using the methacrylic cation exchange resin with sulpho groups (synthesized by the authors and denoted as SS-4B in the following text). The cation test solution contained 5 ppm sodium, 5 ppm ammonium, and 10 ppm potassium ions. The relative retention values ($\alpha_A^B = t_{R,B} - t_0 / t_{R,A} - t_0$, where A and B is a pair of ions) were calculated (according to [3]) for each eluent applied.

Results and Discussion

In the case of the Katieks K column, an increase in the PEG modifier concentration in the nitric acid eluent had only a slight effect on the relative retention of NH_4^+/Na^+ ions (Table). The effect on the relative retention of K^+/NH_4^+ ions was more significant (Table). This is explained by an interaction between the PEG modifier and K^+ ions [4].

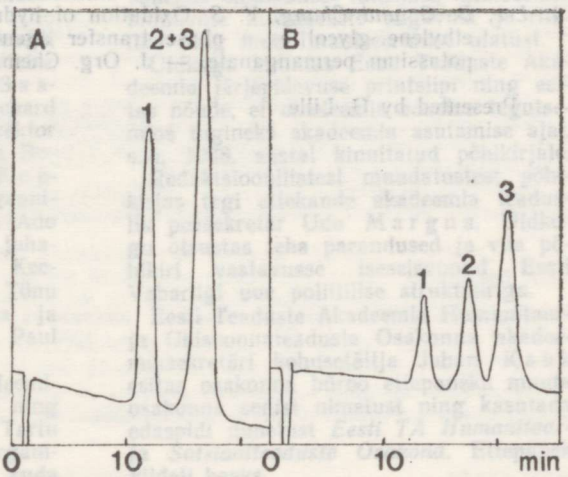
Under the same conditions, the application of TEG as the eluent modifier caused only a slight effect ($\alpha_{NH_4^+}^{K^+}$ increased from 1.45 to 1.51; $\alpha_{Na^+}^{NH_4^+}$ remained constant at 1.19).

Thus, ammonium and potassium are a well-separated pair of peaks on the cation exchange resin with carboxylic groups. It is interesting to evaluate the effect of both the modifiers studied on the cation exchange resin containing sulpho groups. It should be noted that the pair K^+/NH_4^+ is less separated on the resins with sulpho groups than the pair NH_4^+/Na^+. The results obtained with BT IV KA column showed that the effect of the PEG and TEG on the retention of the test solution cations was nonselective. The relative retention of both ion peak pairs decreased ($\alpha_{Na^+}^{NH_4^+}$ from 1.46 to 1.19 and $\alpha_{NH_4^+}^{K^+}$ from 1.30 to 1.06) when the concentration of PEG increased. The effect of TEG was insignificant.

The results obtained with both columns indicate that the resin matrix plays an important role and the effect of the PEG modifier is most useful on the methacrylic cation exchange resin with sulpho groups (SS-4B; Fig.).

The effect of the eluent PEG modifier concentration (C) on the relative retention (α) of ion peak pairs on the column Katieks K

C_{PEG}, vol %	$\alpha_{Na^+}^{NH_4^+}$	$\alpha_{NH_4^+}^{K^+}$
0.0	1.19	1.45
2.5	1.23	1.54
5.0	1.25	1.65
7.5	1.29	1.82
10.0	1.27	1.87



The effect of the PEG modifier in the nitric acid eluent. Column: 3.3×150 mm, experimental methacrylic cation exchanger with sulpho groups (SS-4B); sample loop 0.1 ml. Ions: *1* — sodium; *2* — ammonium; *3* — potassium. **A** — eluent 1 mM nitric acid; 1 ml/min. **B** — eluent 1 mM nitric acid + 10 vol% PEG; 1 ml/min.

A drawback in using the PEG eluent modifier is a decrease in sensitivity; the peak heights with the eluent containing 10 vol% PEG are approximately 15% of those obtained when a pure nitric acid eluent was used. Comparing amino acidic eluent modifiers, PEG produced a somewhat better effect. The simple alcoholic modifiers should have a concentration of about 50 vol% to produce the same effect as 7.5 vol% PEG.

Conclusions

1. The PEG modifier in the eluent is applicable to improve the separation of ammonium and potassium ions using cation exchange resins based on the methacrylic matrix. This is related to both resins Katieks K and SS-4B (the latter synthesized in our laboratory).
2. On the methacrylic resin with sulpho groups (SS-4B), the achieved effect is useful for enhancing the separation of ammonium and potassium ions which without the modifier are insufficiently separated on this resin.
3. When the column BT IV KA was applied, the PEG eluent modifier did not show any useful effect: all the cations were less retained but not separated better.

REFERENCES

1. *Ivask, J. and Pentchuk, J.* Increasing the selectivity in the ion chromatographic determination of sodium, ammonium, and potassium ions. The effect of the eluent amino acidic modifier. — Proc. Estonian Acad. Sci. Chem., 1992, **41**, 1, 33—35.
2. *Hradil, J., Švec, F., Aratskova, A., Belyakova, L., and Orlov, V.* Ion chromatography on methacrylate ion exchangers. — J. Chromatogr., 1989, **475**, 209—217.
3. *Snyder, L. R. and Kirkland, J. J.* Introduction to Modern Liquid Chromatography. John Wiley & Sons, New York; Chichester, 1979, 22—31.
4. *Lee, D. G. and Chang, V. S.* Oxidation of hydrocarbons. 8. Use of dimethyl polyethylene glycol as a phase transfer agent for the oxidations of alkenes by potassium permanganate. — J. Org. Chem., 1979, **43**, 8, 1532—1536.

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