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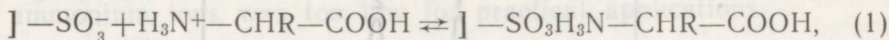
INCREASING THE SELECTIVITY IN THE ION CHROMATOGRAPHIC DETERMINATION OF SODIUM, AMMONIUM, AND POTASSIUM IONS.

THE EFFECT OF THE ELUENT AMINO ACIDIC MODIFIER

Jüri IVASK, Jaan PENTCHUK. SELEKTIIVSUSE SUURENDAMINE NAATRIUM-, AMMOONIUM- JA KAALIUMIOONIDE IOONKROMATOGRAAFILISEL MÄÄRAMISEL. ELUENDI AMINOHAPPELISE MODIFIKAATORI MÕJU

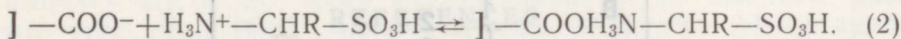
Юри ИВАСК, Яан ПЕНЧУК, УЛУЧШЕНИЕ СЕЛЕКТИВНОСТИ ПРИ ИОНОХРОМАТОГРАФИЧЕСКОМ ОПРЕДЕЛЕНИИ СОДЕРЖАНИЯ ИОНОВ НАТРИЯ, АММОНИЯ И КАЛИЯ. ДЕЙСТВИЕ ЭЛЮЭНТНОГО АМИНОКИСЛОТНОГО МОДИФИКАТОРА

Recently, ion chromatography has become a widely used analytical method for the determination of sodium, ammonium, and potassium ions in a wide range of samples [1]. The commercially available cation exchange materials demonstrate different selectivity for the separation of these cations. In the cases of ammonium determination in the presence of large amounts of sodium and potassium, it is important to increase the selectivity of the separation for these ion peaks. It has been demonstrated that when glycine or β -alanine is added to the mineral acid eluent, the selectivity of the separation for ammonium is better than in case of a pure mineral acid eluent [2]. The aim of the present paper is to check the presumption that amino acid (glycine, β -alanine, etc.) added to the eluent will be adsorbed on the cation exchanger with sulpho groups by its amino group:



where J— is the resin matrix, R is a substituent, and the carboxylic group of the amino acid will take part in the ion exchange of the sample's cations, changing the selectivity of their separation.

This principle should be equally applicable to a cation exchanger with carboxylic groups using an aminosulphoacid (taurine, aminomethanesulphonic acid, etc.) modifier in the eluent:



Experimental

The experiment was carried out using an ion chromatographic system equipped with a conductivity detector (Special Design Office of the Estonian Academy of Sciences) and columns Katiüks K (cation exchanger with carboxylic groups; "ECOS", Estonia) and BT IV KA (cation exchanger with sulpho groups; "Biotronik", Germany). All the reagents used were of analytical grade ("Reakhim", USSR). When the

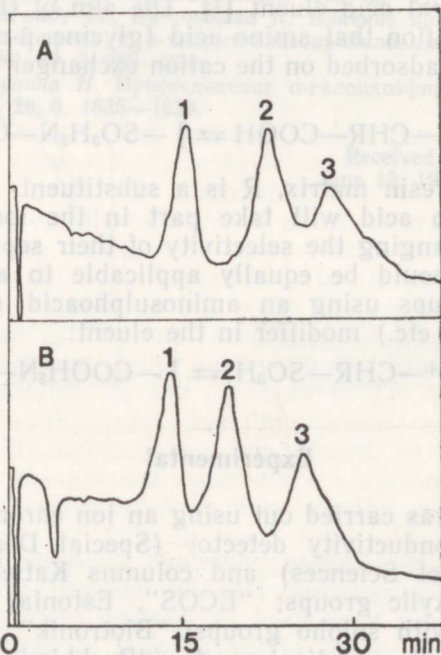
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Katiex K column was used, the eluent flow rate was 1.0 ml/min and the nitric acid concentration was 1 mM. The concentration of the modifier (taurine) was varied in the range 0—5.0 mM. For the BT IV KA column, the respective values were 1.5 ml/min and 1.5 mM, and the concentration of the modifier (β -alanine) was varied in the range 0—1.2 mM. The glycine modifier was assayed on the experimental cation exchanger with sulpho groups (synthesized in the Institute of Chemistry of the Estonian Academy of Sciences). The cation test solution contained 5 ppm sodium, 5 ppm ammonium, and 10 ppm potassium. The relative retention values (α) for critical peak pairs were calculated (according to [3]) for each eluent used.

The effect of the eluent aminoacidic modifier concentration (C) on the relative retention (α) of ammonium and potassium on the cation exchanger with sulpho groups

$C_{\beta\text{-alanine}}$, mM	eluent pH	$\alpha_{\text{NH}_4^+}^{\text{K}^+}$
0.0	2.86	1.36
0.2	2.90	1.39
0.5	2.99	1.41
0.8	3.09	1.47
1.2	3.22	1.52



The effect of the glycine modifier in the nitric acid eluent. Column 3×150 mm, experimental cation exchanger with sulpho groups; sample loop 0.1 ml. Ions: 1— sodium; 2 — ammonium; 3 — potassium.

A — eluent 2.5 mM nitric acid, 2.0 ml/min. B — eluent 2.0 mM nitric acid plus 2.0 mM glycine, 2.5 ml/min.

The taurine concentration increase in the 1 mM nitric acid eluent in case a cation exchanger with carboxylic groups was used caused only a slight increase in the relative retention of ammonium and sodium ions. This was probably due to the fact that at the eluent pH value 3.05 used, only 3% of the taurine molecules exist as cations while 97% is in the form of zwitter ion (calculated using Henderson-Hasselbach equation cited in [4]). The zwitter ion evidently passed the separation column without any alteration by sorbent ionogenic groups and sample cations. To increase the concentration of the cationic form of taurine, a more concentrated nitric acid eluent (up to 0.1 M) is required; this complicates the analytical process essentially.

The effect of the β -alanine concentration in the 1.5 mM nitric acid eluent using a cation exchanger with sulpho groups on the relative retention of potassium and ammonium ions was more significant (Table). At the achieved pH values of the eluent, the majority of the β -alanine molecules exist as cations which took part in the ion exchange processes of the sample cations' elution. In order to elucidate the achieved increase in the relative retention of ammonium and potassium cations, one must take into consideration that when the concentration of β -alanine in the eluent is increased, the pH of the eluent rises. However, at higher pH values, the role of the cationic form of the β -alanine decreases (from 83.4% at pH 2.90 to 70.5% at pH 3.22), which reduces the influence of the growth of β -alanine content.

The effect of the glycine modifier is illustrated in the Figure.

Conclusion

In conclusion, the amino acid modifier in the mineral acid eluent on a cation exchanger with sulpho groups is applicable for increasing the separation of ammonium and potassium ions. For a carboxyl cation exchanger, the effect of taurine on increasing the separation of sodium and ammonium ions was too low for practical applications.

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