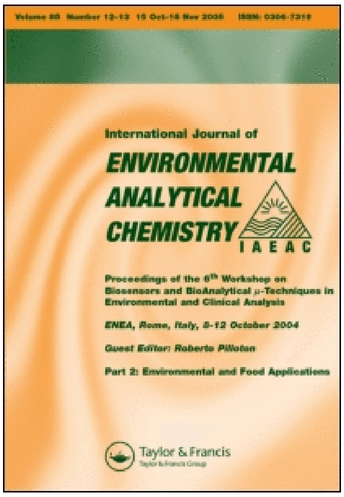

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Simultaneous Ion Chromatographic Determination of Weakly and Strongly Retained Inorganic Anions using Aminoacids as Eluents

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Dedicated to Professor W. Haerdi on the occasion of his 60th birthday

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At present eluents that are most widely used in ion chromatography of inorganic anions are salts with carbonate and hydroxyl eluting ions. But these eluents appear to be of no efficiency when samples containing both weakly and strongly retained inorganic anions are to be analyzed. In this case, one should use either expensive and complicated gradient elution technique or double injection with different eluents separately for weakly and strongly retained anions.

In this work, the simultaneous ion chromatographic determination of weakly and strongly retained inorganic anions without gradient elution is considered. The most common eluent for ion chromatography of anions, carbonate and aminoacids are compared. Dependence of the chromatographic behaviour of the strongly retained inorganic anions upon the concentration of the organic components in the eluent is shown.

KEY WORDS: Ion chromatography, anion determination, aminoacids.

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INTRODUCTION

At present strongly retained inorganic anions (which have retention time longer than sulphate) are often determined using gradient elution,[1,2] but this requires a special technique. Separation of these anions on the silica-based sorbents has been described,[3] however such sorbents are not always available. The determination of these ions on styrene-divinylbenzene sorbents utilizing eluents most common in ion chromatography of anions (carbonate, hydroxyl and phthalate eluting ions) shows no good results. Retention times are too long,[1,4] chromatographic peaks are broad and are not separated quantitatively.[2] Besides, simultaneous determination of weakly and strongly retained inorganic anions is of importance when samples of unknown composition are to be analyzed. Usually this problem is solved only by using gradient elution.[1,2,4]

The aim of our investigation was to work out the procedures for simultaneous determination of weakly and strongly retained inorganic anions on the sorbent HIKS-1 synthesized in the Institute of Chemistry of Estonian Academy of Sciences, Tallin. To raise the efficiency of separation, aminoacids have been used as eluents. Utilizing aminoacids as eluents has been proposed earlier.[5,6] Their main advantages are the detection on the background signal of deionized water, which ensures an increase of determination sensitivity, and elimination of so called “water” and “carbonate” peaks that affect determination of weakly retained anions.

The problem of interest has also been the comparison of the elution strength of aminoacids and carbonate eluents and the consideration of the action of different organic modificators in the eluent.

EXPERIMENTAL

Technique

BIOTRONIK IC-1000 ion chromatograph (FRG) has been used. Separator glass columns utilized have been: 3 × 50, 3 × 100 and 3 × 250 mm packed with HIKS-1 (functional groups—quaternary ammonium bases, specific capacity 0.03–0.06 meqv/ml). Suppressor column: 6 × 150 mm, Dowex-1. Injected volume—100 μl. Conductometric detection has been used, retention times and area of the peaks have been measured by SHIMADZU C-R3A integrator.

Reagents

Solutions of eluents and samples have been prepared by dissolving acids and salts (reagent grade) in deionized water (the background conductivity 2.3 μS).

RESULTS AND DISCUSSION

Preliminary experiments showed that monobased aminoacids Leucine and Glycine did not ensure sufficient efficiency of separation, even when solutions of high concentration (5 mM) were used as eluents. Hence further work was carried out with dibased aminoacids possessing greater eluting strength.

L-Glutamic acid appeared to show good efficiency as an eluent, but retention time of anions was greatly affected by their concentration in the sample. This prevented qualitative determination, therefore experiments were continued with another aminoacid D-Tyrosine. In this case the dependence of the retention time upon the sample concentration has not been observed in broad interval: 0.01–1 ppm (0.01–100 ppm for NO_3^-). Figure 1 shows the chromatogram of strongly retained anions using Tyrosine. Figure 2 presents simultaneous determination of weakly and strongly retained anions.

Calibration curves are linear from 0.01 to 250 ppm. Detection limits are on the 10 ppb level. Further decrease of detection limits is possible but deionized water of higher purity is to be used in this case because salts in deionized water influence determination of sample components under high sensitivities of the detector. The method is characterized by high reproducibility (relative standard deviation does not exceed 0.02). The reliability of the method was checked by the comparison of ion chromatography with direct potentiometric detection with ion-selective electrodes. Table 1 shows results of the determination of chloride and nitrate in samples of waste water done by these two methods. One can see that the results are in good agreement.

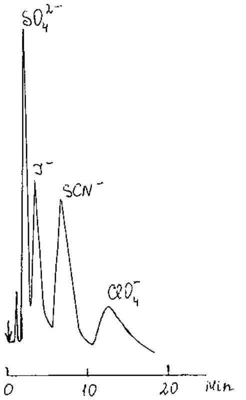

Figure 1 Chromatogram of mixture of strongly retained anions (50 ppm each). Column: 3 × 50 mm (0.06 meqv/ml). Eluent: Tyrosine, 2 mM (pH 11.0). Flow rate: 1.8 ml/min.

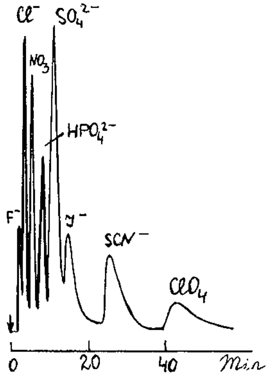

Figure 2 Chromatogram of mixture of weakly and strongly retained anions (ppm: 1 F^-; 2 Cl^-; 8 NO_3^-; 17 HPO_4^-; 17 SO_4^{2-}; 17 I^-; 17 SCN^-; 17 ClO_4^-). Column: 3 × 250 mm (0.03 meqv/ml). Eluent: Tyrosine, 1 mM (pH 10.8). Flow rate: 1.8 ml/min.

Table 1 Results of determination of chloride and nitrate in waste water (ppm)

Anion	*Ion chromatography*	*Ion-selective electrode*
Cl^-	18.4 ± 0.9	19.5 ± 1.0
NO_3^-	3.17 ± 0.16	3.22 ± 0.16

Figures 1 and 2 show that dependent on the aims of the study chromatographic conditions can be changed. For instance, if the determination of only strongly retained components is needed one can increase pH and eluent concentration and decrease the length of the separator column. If the sample of an unknown composition is to be analyzed then a long separator column and low eluent concentration are suitable.

The eluent which is most often used in ion chromatography of anions is carbonate eluent. That is why a problem of interest for us was the comparison of the elution action of carbonate eluent and Tyrosine. Figure 3 shows the chromatogram of the mixture of inorganic anions obtained in the same conditions as in Figure 2, but carbonate eluent was used in this case. Comparison of the two figures proves that Tyrosine is of greater eluting strength than carbonate eluent especially if strongly retained anions are concerned. To get chromatograms with similar retention times we increased carbonate eluent concentration more than three-fold relative to Tyrosine. Sensitivity of determination using Tyrosine is higher because detection is carried out relative to the background signal of deionized water, but not the carbonic acid. Besides, the concentration of cations in Tyrosine eluent is less than in carbonate eluent hence the working time of the suppressor column rises considerably.

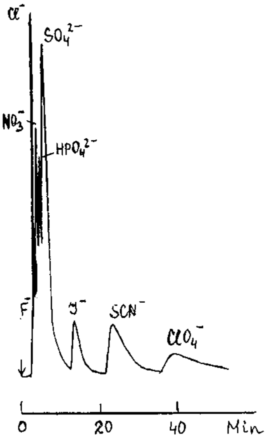

Figure 3 Conditions see Figure 2. Eluent: Na_2CO_3–$NaHCO_3$, 3 mM each (pH 10.5).

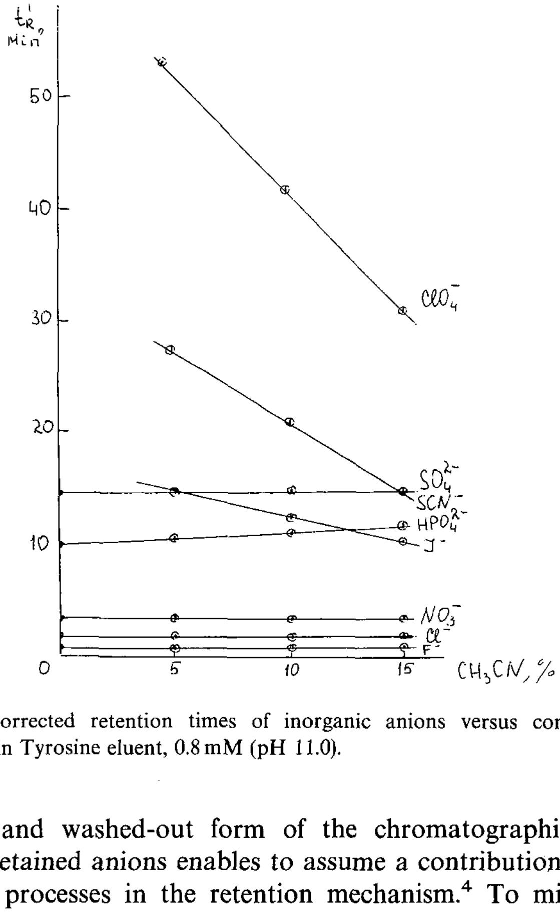

Figure 4 Corrected retention times of inorganic anions versus concentration of acetonitrile in Tyrosine eluent, 0.8 mM (pH 11.0).

Broad and washed-out form of the chromatographic peaks of strongly retained anions enables to assume a contribution of non-ion exchange processes in the retention mechanism.[4] To minimize this contribution we studied a number of organic modifications in the eluent: benzene alcohol, 1,4-Dioxane and acetonitrile. Dioxane and acetonitrile were effective in decreasing retention times of strongly retained anions, but when dioxane was used the pressure in the system increased markedly. Therefore experiments were carried out using acetonitrile as a modificator. Figure 4 presents the dependence of the retention times of inorganic anions on the acetonitrile concentration in the Tyrosine eluent. The same dependence is observed when using carbonate eluent. The curves show that acetonitrile influences retention time of only strongly retained anions. It could be due to the ability of acetonitrile itself to sorb according to non-ion exchange mechanism. It screens the sorption sites for strongly retained anions and thus prevents their sorption according to the same mechanism. It could be also due to the specific interaction between acetonitrile and strongly retained anions (for example, dipole–dipole interaction).

Tyrosine with acetonitrile was used for the analysis of samples of river and waste water.

CONCLUSIONS

The possibility of rapid and selective simultaneous determination of weakly and strongly retained inorganic anions is shown. Detection limits are at the 10 ppb level measured on the background signal of deionized water (2.3 μS). Relative standard deviation does not exceed 0.02. Tyrosine appears to be a more effective and stronger eluent than the most often used carbonate eluent. Dependence of the retention times of inorganic anions upon the concentration of different organic modificators in the eluent is shown.

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