# GLYCINE-SODIUM CARBONATE ELUENTS FOR ION CHROMATOGRAPHY

Ülo HALDNA and Irina YAKOVLEVA

Eesti Teaduste Akadeemia Keemia Instituut (Institute of Chemistry, Estonian Academy of Sciences), Akadeemia tee 15, EE-0026 Tallinn, Eesti (Estonia)

**Abstract.** The use of aqueous solutions containing glycine and sodium carbonate as eluents in suppressed ion chromatography is suggested. The respective selectivity coefficients for six common inorganic anions were determined applying HIKS-1 analytical columns with different capacities.

**Key words:** ion chromatography, glycine, eluent, detection limits.

## INTRODUCTION

Suppressed ion chromatography [1] is a technique widely applied to the determination of anions in a variety of aqueous matrices. Amino acids have been recommended to be used as eluents in ion chromatography [2]. The analytical performance of determination depends on the match of the analytical column for the eluent used. In this work we report the application of a glycine—sodium carbonate eluent to the analytical column packed with methacrylic resin pellicularly coated with an $[-CH_2-\overset{|}{CH}-C_6H_4-CH_2\overset{+}{N}(CH_3)_3]_n$ ion exchanger (HIKS-1 resin from Khimifil, Tallinn).

## EXPERIMENTAL

A 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 analytical columns were (1) column A (4×150 mm) packed with HIKS-1 resin, capacity 0.019 mequiv./cm³, and (2) column B (4×250 mm) packed with HIKS-1 resin, capacity 0.068 mequiv./cm³. In both cases the suppressor column (4×250 mm) was packed with Dowex 50 WX16 20—50 mesh (Serva). The eluents were made from reagent grade chemicals: the weighed amounts of glycine (Gl) and $Na_2CO_3$ were dissolved in distilled water. In this procedure no $CO_2$ separation was observed. Gl was previously crystallized using hot water. The concentration of Gl was kept constant in all the eluents (3.0 mM) and the concentration of $Na_2CO_3$ was varied in the range of 1.25—3.0 mM. The eluent flow rate was 1.7 ml/min and the loop volume 0.43 ml.

*Table 1*

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

| X, Y | Calculated in this work | | Literature data | | |
|---|---|---|---|---|---|
| | Column A | Column B | [3] b | [4] c | [5] d |
| Cl⁻, NO₂⁻ | 0.80±0.19 | 0.76±0.22 | 1.00 | — | — |
| Cl⁻, Br⁻ | 0.46±0.08 | 0.43±0.11 | 0.56 | — | — |
| Cl⁻, NO₃⁻ | 0.41±0.07 | 0.39±0.10 | 0.48 | 0.39 | 0.33 |
| Cl⁻, HPO₄²⁻ | 0.44±0.11 | 0.53±0.24 | — | 0.44 | 0.29 |
| Cl⁻, SO₄²⁻ | 0.16±0.05 | 0.21±0.03 | 0.48 | 0.21 | 0.17 |
| NO₂⁻, Br⁻ | 0.58±0.05 | 0.57±0.05 | 0.62 | — | — |
| NO₂⁻, NO₃⁻ | 0.51±0.05 | 0.51±0.05 | 0.54 | — | — |
| NO₂⁻, HPO₄²⁻ | 0.70±0.21 | 1.01±0.21 | — | — | — |
| NO₂⁻, SO₄²⁻ | 0.25±0.06 | 0.40±0.09 | 0.59 | — | — |
| Br⁻, NO₃⁻ | 0.87±0.02 | 0.90±0.05 | 0.85 | — | — |
| Br⁻, HPO₄²⁻ | 2.06±0.36 | 3.03±0.13 | — | — | — |
| Br⁻, SO₄²⁻ | 0.73±0.14 | 1.21±0.45 | 1.47 | — | — |
| NO₃⁻, HPO₄²⁻ | 2.70±0.50 | 3.76±0.71 | — | 2.88 | 2.65 |
| NO₃⁻, SO₄²⁻ | 0.96±0.23 | 0.40±0.09 | 2.07 | 1.38 | 1.56 |
| HPO₄²⁻, SO₄²⁻ | 0.13±0.05 | 0.16±0.12 | — | 0.25 | 0.35 |

a The phase ratio $P = V_r/V_m$ used in the calculations of $K_{X, Y}$ [3] was found to be 1.1. The $K_{X, Y}$ values are presented at the confidence level of 0.95.
b Obtained using the single-column system [4] and the nitrilotriacetic acid—sodium carbonate eluent. The column (4×150 mm) was packed with HIKS-1 resin and has a capacity of 0.019 mequiv./cm³.
c Obtained using the suppressed system [3, 4] and carbonate eluents. The column (3×200 mm) was packed with HIKS-1 resin and has a capacity of 0.022 mequiv./cm³ [6].
d Calculated in [3] using the $K_{X, CO_3^{2-}}$ and $K_{Y, CO_3^{2-}}$ values from [5]. The analytical column (3×200 mm) in the suppressed system was packed with HIKS-1 resin and has a capacity of 0.022 mequiv./cm³ [6]. Carbonate eluents were used [6].
— data not available.

## RESULTS AND DISCUSSION

A typical chromatogram obtained using the NH₂CH₂COOH/Na₂CO₃ eluent is presented in Fig. 1. The same set of columns as in case of a classical carbonate eluent (analytical column and the suppressor, see Experimental) was used to record the chromatogram shown in Fig. 2. It should be mentioned that the 3.0 mM Na₂CO₃ eluent has approximately the same eluting power as the standard carbonate eluent (3.0 mM NaHCO₃/2.4 mM Na₂CO₃) [6]. Another circumstance worth stressing is that Na₂CO₃ concentrations at running the chromatograms considered (Figs. 1 and 2) are the same (3.0 mM Na₂CO₃). Comparing Figs. 1 and 2 we can see that (a) the sequence of ions eluted with the standard carbonate eluent and sodium carbonate—glycine eluents is the same, and (b) the addition of Gl (3.0 mM) to the 3.0 mM Na₂CO₃ eluent causes an increase in the retention times by a factor of 1.23—1.9. The lowest increase in the retention time has been obtained for chloride ions

(1.23 times) and the highest for sulphate ions (1.9 times). No considerable changes in the separation of the pair $NO_3^-/Br^-$ were observed, but that of the pair $NO_2^-/Cl^-$ seems to be better when Gl has been added to the eluent used (see Figs. 1 and 2). The eluents glycine + sodium carbonate and glycine + sodium hydroxide yield different retention times on the same analytical columns tested. Comparing these two eluents with the same values of $C_{Na^+}$=6.0 mM and $C_{Gl}$=3.0 mM, we observed that the eluent made with sodium hydroxide showed longer retention times (1.63 times longer for $Cl^-$ and 1.85 times for $NO_3^-$).

It must be pointed out that the eluents with the ratio $a=C_{Na_2CO_3}/C_{Gl}<$ $<0.42$ show too long retention times for $SO_4^{2-}$ and $HPO_4^{2-}$ ions and are therefore practically not applicable.



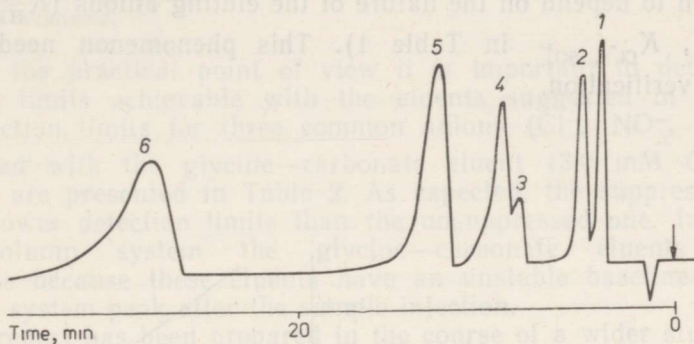Fig. 1. Chromatogram of 5 ppm $Cl^-$ (1), 10 ppm $NO_2^-$ (2), 10 ppm $Br^-$ (3), 20 ppm $NO_3^-$ (4), 50 ppm $HPO_4^{2-}$ (5), and 40 ppm $SO_4^{2-}$ (6). Experimental conditions: eluent 3.0 mM glycine + 3.0 mM $Na_2CO_3$, flow rate 1.5 ml/min, resin used in analytical column HIKS-1 (4×250 mm) 0.068 mequiv./cm³. Suppressor column 4×250 mm with Dowex WX50. Detection range 0.1 mS×20.
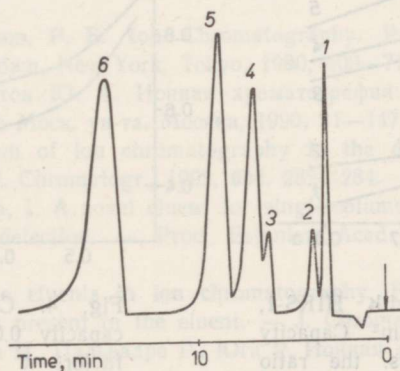


Fig. 2. Chromatogram of the same mixture of ions as in Fig. 1. The eluent used was 3.0 mM $Na_2CO_3$; the resin capacity was 0.019 mequiv./cm³. All the other settings were as in Fig. 1.

The eluents with the ratio $a = 0.42—1.0$ were tested on two columns, A and B, using a dual-column system (see Experimental). The eluents were found to be appropriate for the separation of the anions $Cl^-$, $NO_3^-$, $HPO_4^{2-}$, and $SO_4^{2-}$ in their mixtures (see Fig. 1). The capacity factors $k' = (t_R - t_0 - t_{0, out})/t_0$ for anions studied vs. the ratio $a$ are presented in Figs. 3 and 4. It should be pointed out that in case of using the suppressed system, the capacity factor should be calculated taking into account the time $t_{0, out}$ due to the mobile phase outside the separation column, as shown in [3]. The measured sum $t_0 + t_{0, out}$ [3] was divided into $t_0$ and $t_{0, out}$, applying the procedure described in [3]. For calculating the selectivity coefficients the respective method was used [3] (see Table 1).

Comparing the values of the selectivity coefficients $K_{X, Y}$ for the same resin type (HIKS-1) but determined with different eluents (see Table 1), we can observe that the agreement between the $K_{X, Y}$ values is remarkably good as far as single charged anions are concerned. But when double charged anions $HPO_4^{2-}$ and $SO_4^{2-}$ are involved, the $K_{X, Y}$ values seem to depend on the nature of the eluting anions ($K_{HPO_4^{2-}, SO_4^{2-}}$, $K_{NO_3^-, SO_4^{2-}}$, $K_{Cl^-, SO_4^{2-}}$ in Table 1). This phenomenon needs further study and verification.
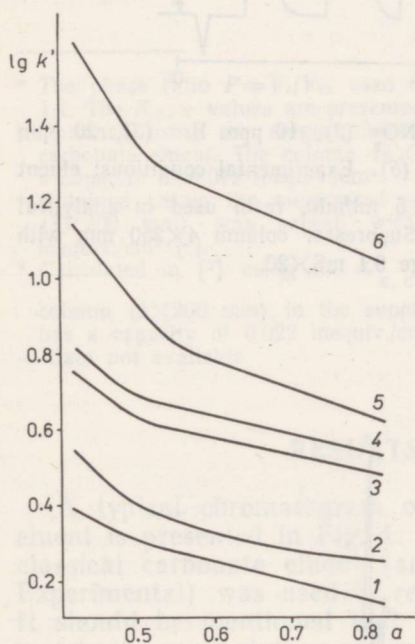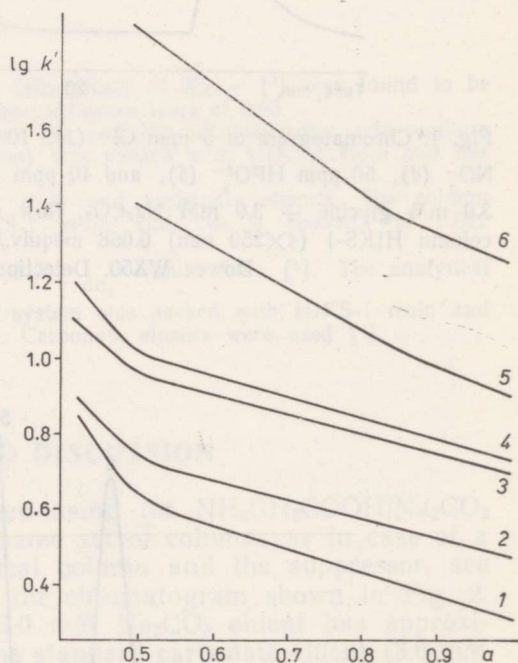


Fig. 3. Column A with HIKS-1, capacity 0.068 mequiv./cm³. Capacity factors $k'$ for anions vs. the ratio $a = C_{Na_2CO_3}/C_{Gl}$. $1$ — $Cl^-$, $2$ — $NO_2^-$, $3$ — $Br^-$, $4$ — $NO_3^-$, $5$ — $HPO_4^{2-}$, and $6$ — $SO_4^{2-}$.

Fig. 4. Column B with HIKS-1, capacity 0.019 mequiv./cm³. Capacity factors $k'$ for anions vs. the ratio $a = C_{Na_2CO_3}/C_{Gl}$. See the caption of Fig. 3 for the designation of ions.

*Table 2*

### Detection limits of ions

| Reference. Column parameters | Detection limit, ppm | | |
|---|---|---|---|
| | $Cl^-$ | $NO_3^-$ | $SO_4^{2-}$ |
| Determined in this study using column B. Loop volume 0.43 ml | 0.0003 | — | 0.18 |
| Determined in [7][a]. Loop volume 0.15 ml | 0.047 | 0.04 | 0.65 |
| Single-column system in [4]. Loop volume 0.15 ml [b] | 0.11 | 0.03 | 0.80 |

[a] The suppressed system was used. The eluent applied was 4 mM $Na_2CO_3$. The equipment used was the same as in the present study.
[b] The eluent used was a mixture of nitrilotriacetic acid (NTA) and $Na_2CO_3$ with a ratio $C_{Na_2CO_3}/C_{NTA} = 1.46$.
— data not available.

From the practical point of view it is important to determine the detection limits achievable with the eluents suggested in this study. The detection limits for three common anions ($Cl^-$, $NO_3^-$, and $SO_4^{2-}$) determined with the glycine—carbonate eluent (3.0 mM Gl 3.0 mM $Na_2CO_3$) are presented in Table 2. As expected, the suppressed system yielded lower detection limits than the unsuppressed one. In the latter (single-column system the glycine—carbonate eluents are not applicable because these eluents have an unstable baseline with more than one system peak after the sample injection.

This report has been prepared in the course of a wider study devoted to the investigation of compounds $NH_{3-n}(CH_2COOH)_n$ as eluents in ion chromatography.

## ACKNOWLEDGEMENT

## REFERENCES

1. Haddad, P. R., Jackson, P. E. Ion Chromatography. Principles and Application. Elsevier, Amsterdam, New York, Tokyo, 1990, 409—716.
2. Шпигун О. А., Золотов Ю. А. Ионная хроматография и ее применение в анализе вод. Изд-во Моск. ун-та, Москва, 1990, 21—147.
3. Haldna, Ü. Application of ion chromatography to the determination of selectivity coefficients. — J. Chromatogr., 1992, 604, 282—284.
4. Haldna, Ü., Yakovleva, I. A novel eluent for single-column ion chromatography with conductometric detection. — Proc. Estonian Acad. Sci. Chem., 1994, 43, 1, 20—26.
5. Haldna, Ü. Carbonate eluents in ion chromatography. Fractions of resin capacity linked to anions present in the eluent. — J. Chromatogr., 1992, 589, 197—199.
6. Халдна Ю., Яковлева И., Пальвадре Р., Юга Р. Ионная хроматография с карбонатными элюентами: описание времен удерживания методом главных компонент. — Изв. АН Эстонии. Хим., 1990, 39, 1, 44—48.
7. Халдна Ю. Л. Сравнение двух кондуктометрических детекторов для ионной хроматографии. — Ж. анал. хим. (In press).

# NAATRIUMKARBONAADI JA GLÜTSIINI SEGUDE LAHUSED ELUENTIDENA IOONKROMATOGRAAFIAS

Ülo HALDNA, Irina JAKOVLEVA

On uuritud võimalusi kasutada naatriumkarbonaadi ja glütsiini segude vesilahuseid eluentidena kahekolonnilises ioonkromatograafias. On leitud, et nende eluentide ja HIKS-1 tüüpi analüütiliste kolonnide korral on ioonide elueerimise järjekord sama, mis standardse karbonaatse eluendi korral. Töös on määratud mõningate anorgaaniliste anioonide alumised detekteerimispiirid ülalnimetatud eluentide kasutamisel. Katseandmetest on arvutatud selektiivsuskoefitsiendi väärtused, kui uuritavas proovis esinevad paarsed kombinatsioonid järgmistest ioonidest: $Cl^-$, $NO_2^-$, $Br^-$, $NO_3^-$, $HPO_4^{2-}$ ja $SO_4^{2-}$.

# СМЕСИ ГЛИЦИНА И КАРБОНАТА НАТРИЯ В КАЧЕСТВЕ ЭЛЮЕНТОВ ДЛЯ ИОННОЙ ХРОМАТОГРАФИИ

Юло ХАЛДНА, Ирина ЯКОВЛЕВА

Исследованы возможности использования смесей водных растворов глицина и карбоната натрия в качестве элюентов для двухколоночной ионной хроматографии (аналитические колонки типа ХИКС-1). Установлено, что порядок элюирования ионов такой же, как и, в случае применения стандартных карбонатных элюентов. Определены пределы обнаружения ионов $Cl^-$, $NO_2^-$, $Br^-$, $NO_3^-$, $HPO_4^{2-}$ и $SO_4^{2-}$ в исследованных пробах, а также рассчитаны по данным хроматограмм коэффициенты селективности для комбинаций указанных ионов.