

Optimization of ion chromatography

N. GROS and B. GORENC*

Department of Chemistry and Chemical Technology, University of Ljubljana, 61000 Ljubljana (Yugoslavia)

ABSTRACT

The strategy for planning ion chromatographic separations on a Dionex AS4A column was developed on the basis of the examination of the effect of NaHCO_3 , $\text{NaHCO}_3 + \text{Na}_2\text{CO}_3$ and Na_2CO_3 eluents on the retention times of chloride, bromide, sulphate, nitrite, nitrate and hydrogenphosphate. The suppressor limitations of increasing the eluent concentration, the upper eluent concentration limits of conductivity background stabilities, the upper concentration limits above which the anions are no longer well separated and the lower limits at which peaks become too wide or asymmetric were determined. On these bases the separation of other combination of anions can also be optimized.

INTRODUCTION

There are two specific characteristics of the Dionex 4000i ion chromatography system, a column and an anion micromembrane suppressor, both protected by a patent.

The first consequence of these characteristics is that one does not fill the columns with commercially available anion-exchange resins, but buys the column on the basis of the manufacturer's information about anions that can be separated on it and a description of the analytical problems that can be solved. For example, for so-called hydrophilic anions four Dionex columns, AS1, AS2, AS3 and AS4, are available [1], but for anions such as chloride, bromide, sulphate, nitrite, nitrate and hydrogenphosphate present in similar concentration ranges the AS4 column offers the best selectivity [2].

For work on such a column, the manufacturer provides not only a list of suitable eluents [3], but also a specific eluent composition ($[\text{NaHCO}_3 + \text{Na}_2\text{CO}_3] = 1.7 + 1.8 \text{ mmol/l}$) as being the best for the AS4A column. This eluent composition is probably an acceptable solution for many applications, but it is impossible for it to be the best for all of them. There is no doubt that the separation of all six of the mentioned anions is very good under these conditions. However, if the sample contains only three of them, *e.g.*, nitrite, nitrate and sulphate, the situation is different. These anions have very different retention times and there is no reason for the time of analysis to be so long, while the anions are not only well separated at shorter retention times but also their peaks are sharper, better defined and therefore more suitable for quantitative analysis.

Applications of the AS4A column using other eluent compositions have been reported [4–20], but they are of little practical value when we want to optimize the separation of a combination of anions that is not the same as any of those published. From particular applications we can only get an idea of trying another eluent and the only thing we know after each experimental step is the necessity to try another stronger or weaker eluent in the next one. However, solving an analytical problem by trial and error in this way can be very time consuming and there is no progress in problem solving from one combination of anions to another; the starting position remains the same all the time.

The aim of this work was to build up a background for planning the separations of different combinations of anions by establishing the effect of the concentrations of three eluents (NaHCO_3 , $\text{NaHCO}_3 + \text{Na}_2\text{CO}_3$ and Na_2CO_3) of increasing eluting strength on the retention behaviour of chloride, bromide, sulphate, nitrite, nitrate and hydrogenphosphate, which are common constituents of many different aqueous samples, and therefore to make it possible to solve different analytical problems more easily and effectively.

However, in our system not only the column but also the suppressor determines the limits of our examinations. The manufacturer suggests the operating conditions for this also. It is certain that the suppressor cannot compensate for the background conductivity of any eluent composition. The upper eluent concentration limits at which the instabilities of the background conductivity are still of such a magnitude that the chromatographic peaks can be recognized were determined for all three eluents used. From the methodological point of view this offers the possibility of making a decision about the suitability of the AS4A column for the determination of a component not previously examined after only one experimental step under extreme eluting conditions.

EXPERIMENTAL

Apparatus and experimental conditions

The Dionex 4000i ion chromatographic apparatus consisted of an AG4A guard column, an AS4A separation column, an anion micromembrane suppressor, and a conductimetric detector, with an injection volume of 50 μl , eluent flow-rate 2.0 ml/min, regenerant sulphuric acid concentration 12.5 mmol/l and regenerant flow-rate 2.8 ml/min. A Spectra-Physics SP 4290 integrator was used.

Reagents and procedures

All solutions and eluents were prepared from analytical-reagent grade chemicals using deionized water obtained from a Milli-Q water purification system (Millipore, Bedford, MA, U.S.A.). All salts were in the sodium form to avoid any effect of different cations.

Six stock solutions, each with an anion concentration of 1 g/l, were used and all the working solutions listed in Table I were prepared from them.

A comparison was made between the retention times of all six anions obtained with solutions prepared from only one salt and a solution with a mixture of all six anions. No significant differences were found so all subsequent experiments were performed with a mixture of all six anions.

TABLE I
WORKING SOLUTIONS

Solution	Cl ⁻ (mg/l)	Br ⁻ (mg/l)	SO ₄ ²⁻ (mg/l)	NO ₂ ⁻ (mg/l)	NO ₃ ⁻ (mg/l)	HPO ₄ ²⁻ (mg/l)
A	2.5	—	—	—	—	—
B	—	7	—	—	—	—
C	—	—	7	—	—	—
D	—	—	—	4.5	—	—
E	—	—	—	—	6	—
F	—	—	—	—	—	15
G	2.5	7	7	4.5	6	15

Two stock eluent solutions, 100 mmol/l NaHCO₃ and 100 mmol/l Na₂CO₃ were used. All other eluent compositions were prepared in the chromatographic system by mixing these two solutions with deionized water obeying the microprocessor program.

RESULTS AND DISCUSSION

The results of examination of the effects of NaHCO₃, NaHCO₃ + Na₂CO₃ and Na₂CO₃ eluent concentrations on the retention times of chloride, bromide, sulphate, nitrite, nitrate and hydrogenphosphate are presented in Figs. 1–3. It is evident that the retention behaviour of anions is much more alike when Na₂CO₃ or NaHCO₃ + Na₂CO₃ is used, than with NaHCO₃ as the eluent. With the first two eluents the retention times of all six anions are very similar and relatively short after a small increase of eluent concentration, whereas with NaHCO₃ the anions remain well separated at all concentrations. Hence already from the graphical presentation of the results it can be concluded that the usable eluent concentration range is the widest when using NaHCO₃ as eluent, but on the basis of the chromatograms and integrator

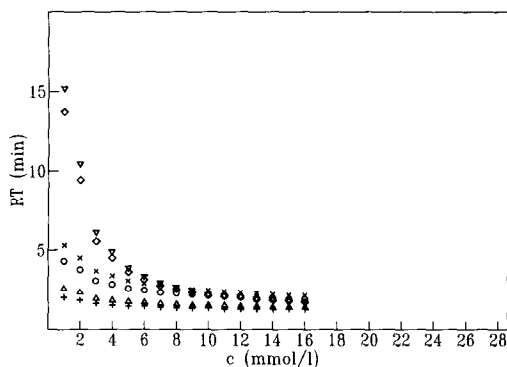


Fig. 1. Effect of Na₂CO₃ eluent concentration on the retention times (RT) of anions. + = Cl⁻; Δ = NO₂⁻; ○ = Br⁻; × = NO₃⁻; ∇ = HPO₄²⁻; ◇ = SO₄²⁻.

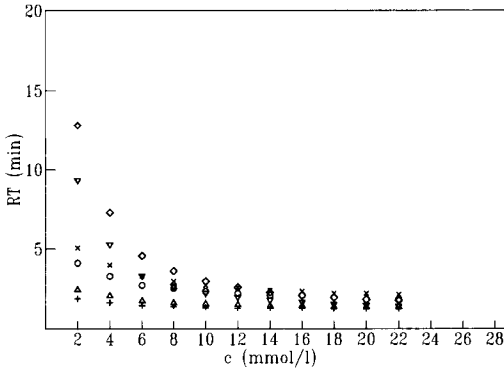


Fig. 2. Effect of $\text{NaHCO}_3 + \text{Na}_2\text{CO}_3$ eluent on the retention times of anions. The concentrations represent the total concentration of the two constituents, which were always present in equal amounts. Symbols as in Fig. 1.

baseline codes fairly specific concentration limits for all three eluents can be determined.

Eluent concentration limits for the separation and determination of all six anions

In the Introduction it was mentioned that the suppressor determines the limit of increase in eluent concentration while above this limit the background conductivity becomes completely unstable, the chromatograms become unrepeatable and peaks can no longer be recognized. However, the concentration limit under which an eluent can be used is also eluent dependent. From Fig. 4, which shows the effect of eluent concentration on the background conductivity, the upper limits of usable concentration ranges for all three eluents can be determined as 16 mmol/l for Na_2CO_3 , 22 mmol/l for $\text{NaHCO}_3 + \text{Na}_2\text{CO}_3$ and 28 mmol/l for NaHCO_3 .

The background conductivity also becomes unstable below these concentrations, but it has no effect on peak recognition; however, it is important because it impedes the accurate determination of anion concentrations. These eluent concentra-

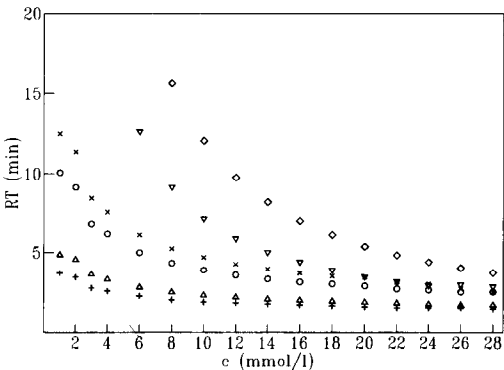


Fig. 3. Effect of NaHCO_3 eluent concentration on the retention times of anions. Symbols as in Fig. 1.

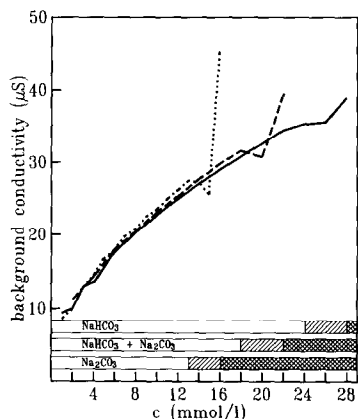


Fig. 4. Dependence of the background conductivity on the concentrations of the three eluents. The bands are divided into three parts. From left to right there is a range of stable background conductivity, a range of small instability and a range of completely unstable background conductivity. Solid line, NaHCO_3 ; dotted line, Na_2CO_3 ; dashed line, $\text{NaHCO}_3 + \text{Na}_2\text{CO}_3$.

tion limits of unstability of the background conductivity which can be seen from Fig. 4 are 13 mmol/l for Na_2CO_3 , 18 mmol/l for $\text{NaHCO}_3 + \text{Na}_2\text{CO}_3$ and 24 mmol/l for NaHCO_3 .

However, for the successful separation of the six anions two eluent concentration limits already mentioned are not very important, because at such high eluent concentrations the anions are no longer well separated. Hence the limit which has to be considered now is not the limit of the available eluent concentration range but the limit of the suitable eluent concentration range. From this point of view it can be seen that Na_2CO_3 is unsuitable for the separation of this mixture as sulphate and hydrogenphosphate are unseparated over the whole eluent concentration range. In contrast, all the anions can be successfully separated using $\text{NaHCO}_3 + \text{Na}_2\text{CO}_3$ below 6 mmol/l and NaHCO_3 below 18 mmol/l.

There is also a lower limit to the eluent concentration because the peaks become too wide or very asymmetric and their determination becomes unreliable. The lower limits of eluent concentrations for different anions and also previously mentioned upper limits of usable eluent concentration ranges are shown in Fig. 5. The results offer the possibility of planning a successful separation and determination of all six anions in mixtures under different conditions.

Possibilities for planning the separations of other combinations of anions

There are generally two cases of other combinations of anions, one when the mixture contains only some of above-mentioned anions and the other when the mixture contains not only some of these anions but also other anions that have not been examined. Before describing the methodology for solving these two types of analytical problems, two approaches that were developed for this purpose should be described. Fig. 6 offers the possibility, for a combination of anions, of answering the question of whether they are separated under selected eluting conditions. Further, on

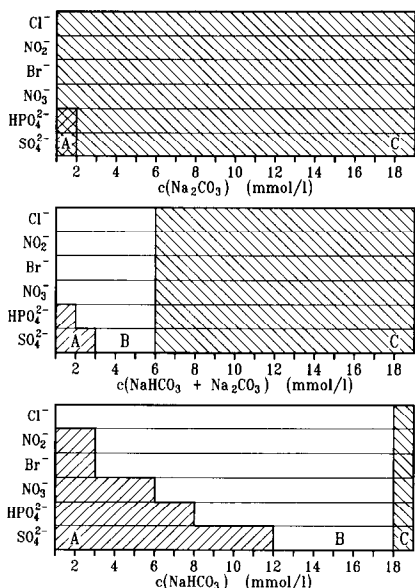


Fig. 5. Usable concentration ranges for the separation of all six anions (B). A, Peaks are too wide or asymmetric; C, not all of the six peaks are separated.

the basis of Fig. 7, the elution sequence of anions under these conditions can be predicted.

On these bases, the separation of any combination of examined anions can easily be optimized and the separation conditions can be simply predicted. Na_2CO_3 will probably be more suitable for the elution of anions with very long or very different retention times. On the other hand, NaHCO_3 will probably offer the best possibilities for the elution of anions with very short or very similar retention times. Because

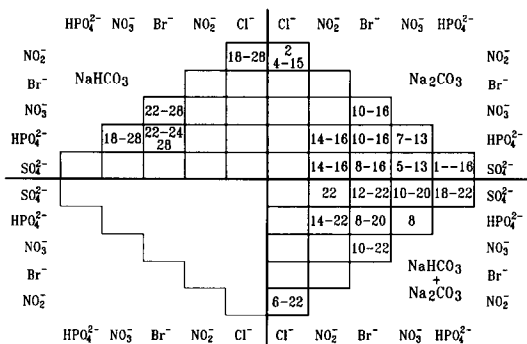


Fig. 6. Eluent concentrations at which the combinations of anions are not separated. Empty boxes represent anions that are well separated over the whole eluent concentration range. Numbers in boxes represent eluent concentrations (mmol/l) at which two ions are not separated. The basis for the decision as to whether ions were separated and not separated were the integrator's baseline codes (BC) present in each chromatographic report (BC : 01 - separated).

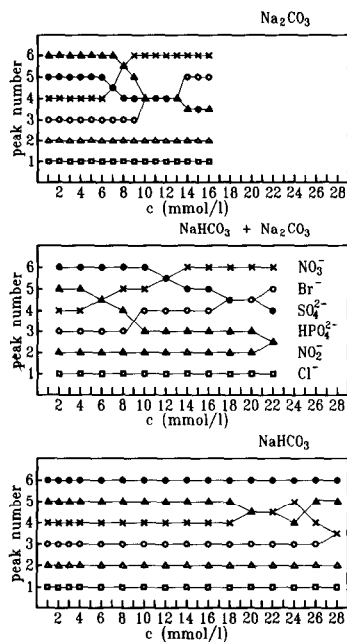


Fig. 7. Effect of eluent concentration on the elution sequence of anions.

of its very wide usable concentration range, it could also be the most suitable for planning gradient elution separations.

The results can also be helpful for the optimization of a mixture that also contains other anions, but some additional experiments would be necessary. First the usability of the AS4A column for the determination of an anion has to be established, suitable eluting conditions for this anion have to be determined and then combined with the optimum separating conditions for other anions.

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