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LOW-COST RAPID SEPARATION AND DETERMINATION OF IONIC SPECIES BY SINGLE-COLUMN ION CHROMATOGRAPHY*

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SUMMARY

Inorganic anions can be determined in natural waters using high-performance ion-exchange chromatography. Single-column ion chromatography has been used to minimize the instrumentation, total time and cost requirements of such analyses. The analysis speed can be enhanced through the use of shorter columns without significant losses in efficiency. Anions has been analysed using an "Ion-Guard" cartridge (30 mm × 4.6 mm) which is normally employed as a guard column of sample preconcentrator. Utilization of such cartridges is recommended for high-speed analysis of anions in relatively uncomplicated aqueous samples.

INTRODUCTION

The determination of inorganic anions in natural waters often requires sensitive tools because the ions are present at trace levels. Single-commmn ion chromatography (SCIC) which combines ion-exchange chromatography and direct conductivity detection is particularly well adapted to the analysis of these anions[1-6]. This technique, which necessitates a low-capacity exchange support and a low-conductivity eluent, has been used to minimize the instrumentation, total time and cost requirements of such analyses. It is thus possible easily to detect inorganic anions in rainwater, various mineral waters, domestic water supply, lake and sediment interstitial waters[7].

The development of this technique is now focused on the reduction of the total analysis time. This can be done by using smaller columns or most simply by increasing the elution flow-rate.

The "Ion-Guard" cartridges, which are normally used as guard columns or sample preconcentrators, have been used in SCIC to separate chloride, nitrate and sulphate ions within 3 min[8,9]. These columns can be employed when high sensitivity

is not required or when the sample is not to complex; in such cases the traditional 250-mm column is always used. Nevertheless, it is possible to enrich or to "clean-up" the sample before analysis on the Ion-Guard cartridge. The pre-concentration or clean-up is done simply with a cartridge packed with an appropriate ion exchanger in place of the sample loop in the standard six-port switching valve[10-12].

This work tries to demonstrate the utilization of a small column instead of a long analytical column for separation of anions in water. It also demonstrates that low cost and a reduced analysis time results from the use of an Ion-Guard cartridge.

EXPERIMENTAL

Apparatus

Chromatographic studies were performed with an HPLC pump Model 64 (Knauer, Berlin, F.R.G.) in combination with a six-port switching valve Model 7125 (Rheodyne, Berkeley, CA, U.S.A.), two low-capacity anion-exchange columns, an electrical conductivity detector (Wescan, Santa Clara, CA, U.S.A.) connected with an integrator Model 3390 A (Hewlett-Packard, Palo Alto, CA, U.S.A.). The two columns were obtained from Wescan: standard anion column 269-001 (250 mm × 4.6 mm) and Ion-Guard-anion cartridge 269-003 (30 mm × 4.6 mm). The system used is shown in Fig. 1.

Reagents and solvents

All ionic solutions were prepared with products obtained from Fluka (Buchs, Switzerland) and with doubly distilled, deionized water. The eluent solutions were phthalate buffers obtained from phthalic acid and sodium hydroxide adjusted to the appropriate pH.

Solutions and eluents were filtered on a 0.22-μm filter and degassed in a filtration system (Millipore, Bedford, MA, U.S.A.).
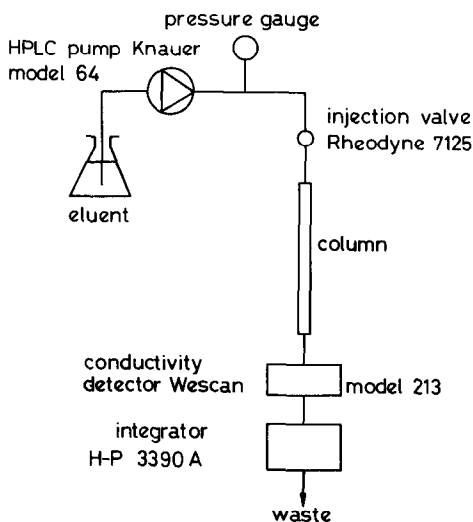

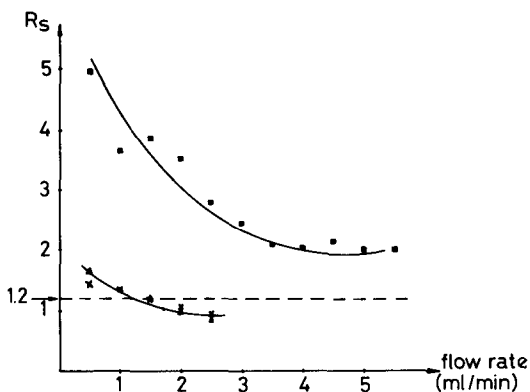Fig. 1. Schematic diagram of the apparatus for SCIC.

Fig. 2. Resolution, R_s, as a function of the ionic strength and the flow-rate of the eluent. Column: 250 mm × 4.6 mm. Concentrations of sodium hydrogen phthalate (pH 4.0): ■, 4; ×, 6; ▲, 8 mM.

RESULTS AND DISCUSSION

Influence of pH

We have already demonstrated[7] that the pH of the eluent has a strong influence on retention times of anions; when the pH increases, the retention times decrease and the separation becomes insufficient. The best conditions involved the use of a small analytical column at pH 4.0. Furthermore, at this pH, the eluent conductance is minimal because phthalic acid is weakly conductive, hence the sensitivity will be maximal.

Chromatography on a "long" column (250 mm × 4.6 mm)

It is possible to modify the ionic strength of the phthalate buffer or the flow-rate to enhance the analysis speed. We have made a study of the influence of both parameters on the separation of chloride and bromide ions. The resolution, R_s =
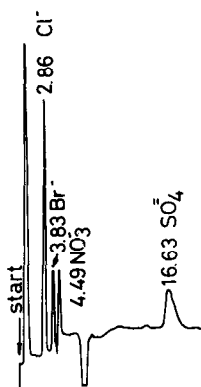

Fig. 3. Chromatogram of 0.2 ml of an aqueous solution containing Cl⁻ (10 ppm) and Br⁻, NO₃⁻ and SO₄²⁻ (each 20 ppm). Eluent: 4 mM sodium hydrogenphthalate pH 4.0. Flow-rate: 3.5 ml min⁻¹. Column: Wescan anion (250 mm × 4.6 mm).
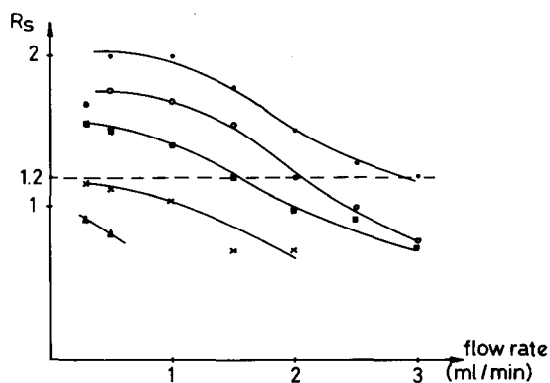
Fig. 4. Resolution, R_s, as a function of the ionic strength and the flow-rate of the eluent. Column 30 mm × 4.6 mm. Concentrations of sodium hydrogenphthalate pH 4.0: ●, 2; ○, 3; ■, 4; ×, 6; ▲, 8 mM.

$2[t_R(Br^-) - t_R(Cl^-)]/[W(Cl^-) + W(Br^-)]$ (where W is the baseline bandwidth) of these two ions as a function of the above parameters is shown in Fig. 2. This factor must be larger than or equal to 1.2 in order to obtain an 100% separation of the two ions.

The optimum concentration of sodium hydrogenphthalate solution is $4 \cdot 10^{-3}$ M. Under this condition the separation is quite good at all flow-rates tested. In practice, nevertheless, back-pressure limitations prohibit the utilization of high flow-rates; for this reason, a flow-rate of 3.5 ml min^{-1} was chosen as optimal. The separation of chloride, bromide, nitrate and sulphate ions takes 17 min under these conditions, as shown in Fig. 3.

The detection limit of this method is of the order of 0.1–0.2 ppm for the four anions tested (injection volume = 0.2 ml). The linearity of the peak area *versus* the amount of anions injected is quite satisfactory in the range of 0.1–30 ppm.

Chromatography on the Ion-Guard cartridge (30 mm × 4.6 mm)

Reduction of the column length is another possibile way to enhance the speed of analysis. As shown above, the separation is a function of the flow-rate and ionic
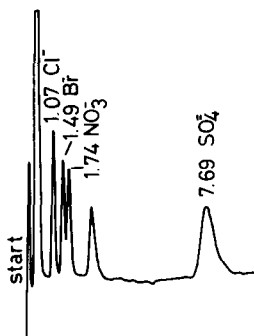

Fig. 5. Chromatogram of 20 μl of the same aqueous solution as in Fig. 3. Eluent: 3 mM sodium hydrogenphthalate pH 4.0. Flow-rate: 1.5 ml min^{-1}. Column: Ion-Guard anion (30 mm × 4.6 mm).

strength of the eluent. Fig. 4 shows the variation of R_s for the separation of chloride and bromide ions as a function of both parameters. In this case, the eluent concentration must be lower than $4 \cdot 10^{-3}$ M, otherwise the separation is not possible, even at low flow-rates. The optimum conditions with this column are $3 \cdot 10^{-3}$ M and 1.5 ml min^{-1} in order to obtain the same chromatographic efficiency as was obtained with the "long" column. An example of anion separation is shown in Fig. 5. In this case, the injection volume (20 μl) was reduced by a factor of ten. This smaller injection volume is necessary with the "ion-guard" column in order to avoid a significant loss in efficiency. Indeed, we have demonstrated that up to 50 μl the efficiency remains constant. For 200 μl, the efficiency decreases by a factor of two.

The detection limits under these conditions are of the order of 1 ppm for the four anions. As for the "long column", the quantitative analysis is quite satisfactory in the range of 1–100 ppm. It is possible to use higher flow-rates with this cartridge, if the conductivity detector is modified so as to reduce the output response time. In this case, the separation of chloride, nitrate and sulphate ions takes 1 min at a flow-rate of 4 ml min^{-1} [8].

Comparison between the two columns

Chromatograms obtained for the two columns tested (Figs. 3 and 5) show that the quality of the separation (efficiency) of four anions under the same optimum conditions is of the same order. The total time is reduced by a factor of two or more with the cartridge as the analytical column. This cartridge allows the use of low elution flow-rates with a resulting low back pressure. In addition, the cost of the cartridge is six times lower than that of a classical analytical column.

For these reasons, the utilization of the Ion-Guard cartridge can be recommended.

CONCLUSIONS

SCIC is a method of choice for rapid analysis of anions in water with simple instrumentation. We have demonstrated that the speed of analysis can be enhanced through the use of a shorter column (30 mm × 4.6 mm) without significant losses in efficiency in comparison with the classical column (250 mm × 4.6 mm). The total time was reduced by a factor of two and the cost by a factor of six with the Ion-Guard column.

The use of this cartridge has been tested with uncomplicated aqueous samples. For waste or industrial waters it is necessary to have a clean-up procedure before analysis. Work in progress concerns pre-concentration and clean-up on-line to ion chromatography.

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