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APPLICATION OF A CHLORIDE ION-SELECTIVE ELECTRODE AS A DETECTOR IN GEL CHROMATOGRAPHY

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SUMMARY

Sodium salts of some anions were eluted with sodium chloride solution on a Sephadex G-15 column and the elution curve of chloride ions added as a background electrolyte was recorded automatically with a chloride ion-selective electrode. From the resulting elution curve, the elution volume and the amount of each anion in the sample could be determined.

INTRODUCTION

For the detection of inorganic compounds in liquid chromatography, many instrumental methods have been applied, such as absorption spectrophotometry^{1,2}, radiometry³, differential refractometry⁴, thermometry⁵, atomic-absorption spectrophotometry^{6,7}, and several electrochemical methods^{8–10}. Also, several attempts to use ion-selective electrodes have been published¹¹, but the number of species detectable by a particular electrode was limited to two or three.

In a previous paper¹², we demonstrated that the behaviour of anions in a sample solution can be followed by determining the concentration distribution of sodium chloride as a background electrolyte by argentimetry. This suggests that it might be possible to automate the procedure by selectively determining the anion of the background electrolyte, *e.g.*, with an ion-selective electrode.

In this work, an attempt was made to record automatically the concentration distribution of chloride ions of the background electrolyte (sodium chloride) by using a chloride ion-selective electrode with a flow-through cell. The separation and indirect determination of anions in a sample solution on a Sephadex G-15 column were carried out by measuring the concentration distribution of chloride ions in the effluent.

EXPERIMENTAL

Sample solution

All reagents used were of guaranteed grade. Sample solutions of acetate, bromide, citrate, fluoride, iodide, nitrate, oxalate, sulphate and thiocyanate ions were

prepared from their sodium salts. Each sample solution contained sodium chloride at the same concentration as that of the eluent.

Eluent

The eluent used was 0.01 *M* sodium chloride.

Column

Sephadex G-15 (Pharmacia, Uppsala, Sweden; dry particle size 40–120 μm) was used as the bed material. The dry powder was suspended in the eluent and allowed to swell for 2 days, then a slurry of the resulting gel was poured into a 50 \times 1.5 cm glass tube with a porous polystyrene disc at the bottom. A small disc of filter-paper served to reduce disturbances at the top of the gel bed. After packing, 500 ml of the eluent were passed through the column in order to settle the gel bed.

Apparatus

The chromatographic flow system used is shown in Fig. 1, in which E is the flow-through cell equipped with a chloride ion-selective electrode and a reference electrode. As shown in Fig. 2, the cell is composed of two pieces of silicone gum stoppers. Three holes were bored in the upper stopper to insert the ion-selective electrode, the reference electrode and the effluent outlet (diameter 1 mm). The lower stopper had a hollow, deep enough for the tips of the two electrodes mounted in the holes of the upper stopper to be dipped in, and a hole for the effluent inlet (diameter 1 mm). These two pieces of the stoppers were maintained in close contact with each other in a glass tube and used as a detector. The volume of liquid in the detector cell was about 1 ml.

A TOA CL-125B chloride ion-selective electrode (Toa Denpa, Tokyo, Japan) was used. The reference electrode was a Double-junction type HC-305D (Toa Denpa); the inner cylinder solution was saturated potassium chloride solution and outer cylinder solution was saturated potassium nitrate solution.

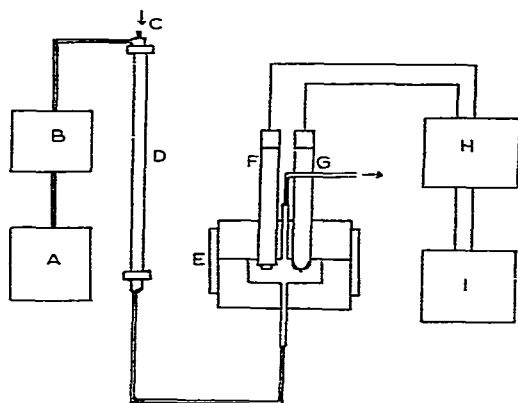


Fig. 1. Schematic diagram of the chromatographic system. A, Eluent reservoir; B, pump; C, sample injector; D, gel column; E, flow-through cell; F, chloride ion-selective electrode; G, reference electrode; H, potentiometer; I, recorder.

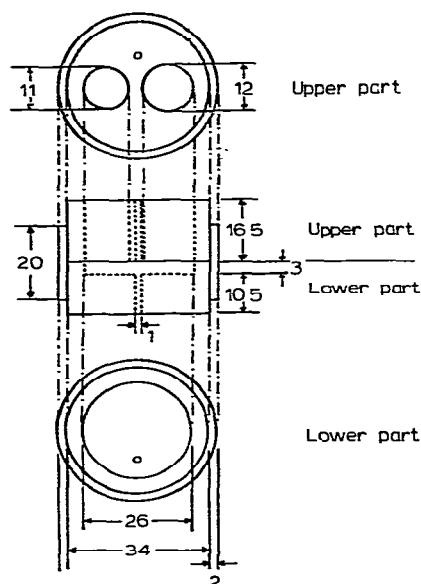


Fig. 2. Flow-through cell for ion-selective electrode and reference electrode. Dimensions in millimetres.

A TOA Ion Meter 1M-1B potentiometer (TOA Denpa), a Hitachi 056 recorder (Hitachi Seisakusho, Tokyo, Japan) and a Sibata SP-C-200 micro-pump (Sibata Chemical, Tokyo, Japan) were used.

Procedure

A 1.00–0.25-ml volume of the sample solution was eluted in the usual manner. The electrode response was measured with an ion meter (output ± 30 mV full-scale) and a strip-chart recorder (input 1 or 2 mV full-scale).

RESULTS AND DISCUSSION

Identification of peaks on elution curves

A chromatogram of 1 ml of 0.005 *M* sodium sulphate solution is shown in Fig. 3C. Figs. 3A and 3B show the chromatograms of 0.5 ml of 0.05 *M* sodium sulphate solution eluted with 0.1 *M* sodium chloride solution, determined by photometry and argentimetry, respectively (*cf.*, Fig. 1 in ref. 12). The two elution profiles in B and C are remarkably similar. The negative peaks on the curves correspond to the respective sample bands due to sodium sulphate, and the positive peaks correspond to the elution positions of chloride ions excluded by the sample zones. The elution profiles of oxalate, acetate and fluoride ions (Fig. 4) obtained by this method was also similar to those obtained by argentimetry^{12,13}. Iodide and thiocyanate ions showed two positive peaks, as in the elution profile obtained by argentimetry^{12,13}. The second positive peaks corresponded to the respective sample bands. The mechanism of the appearance of these second positive peaks for the sample bands would be due to the higher

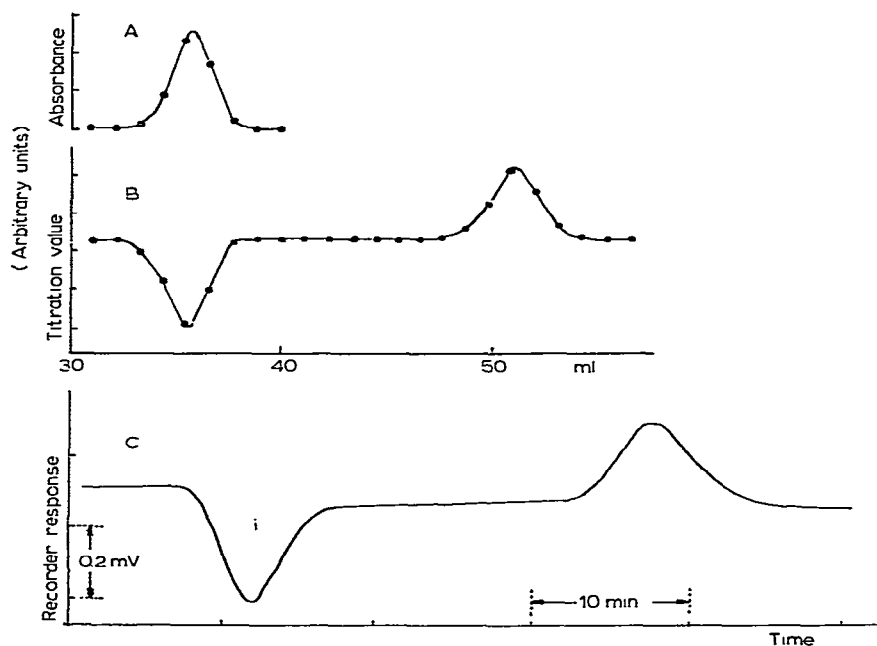


Fig. 3. Elution curves for sulphate ions: (A) photometry¹²; (B) argentimetry¹²; (C) recorder response with the chloride ion-selective electrode. Column: 42.0×1.5 cm. Eluent: (A) and (B) $0.1 M$ NaCl (*cf.*, ref. 12); (C) $0.01 M$ NaCl. Flow-rate: 40 ml/h . Sample: (A) and (B) 0.5 ml of $0.05 M$ Na_2SO_4 in $0.1 M$ NaCl (*cf.*, ref. 12); (C) 1.0 ml of $0.005 M$ Na_2SO_4 in $0.01 M$ NaCl.

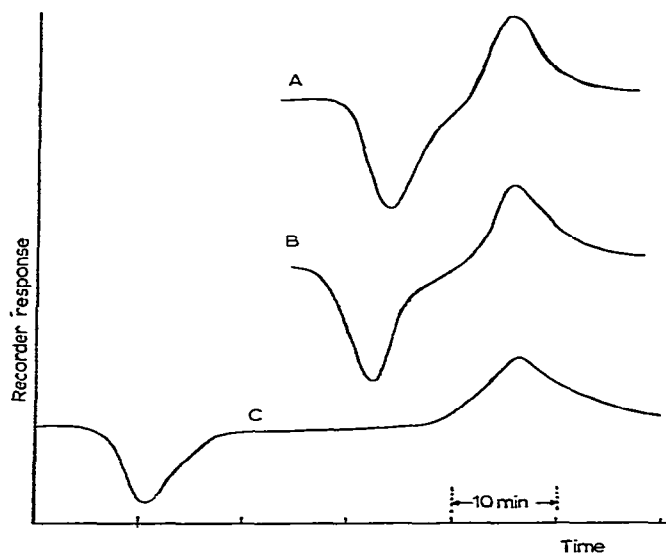


Fig. 4. Elution curves for acetate, fluoride and oxalate ions. Column: 42.0×1.5 cm. Eluent: $0.01 M$ NaCl. Flow-rate: 41.3 ml/h . Sample: (A) 1.0 ml of $0.01 M$ CH_3COONa in $0.01 M$ NaCl; (B) 1.0 ml of $0.01 M$ NaF in $0.01 M$ NaCl; (C) 1.0 ml of $0.01 M$ $\text{C}_2\text{O}_4\text{Na}_2$ in $0.01 M$ NaCl.

selectivity constants¹⁴ of iodide and thiocyanate ions for the chloride ion-selective electrode used here.

Effect of flow-rate on HETP

Fig. 5 shows the relationship between the height equivalent to a theoretical plate (HETP) and the flow-rate for sulphate ions. The results indicate that flow-rates in the range of about 30–40 ml/h give the smallest HETP values. The flow-rate in this work was kept in this optimal range, unless otherwise stated.

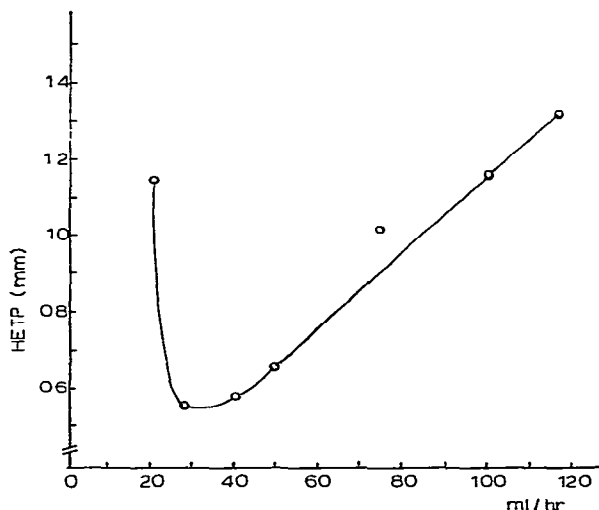


Fig. 5. Relationship between HETP and flow-rate. Column: 42.0×1.5 cm. Eluent: 0.01 M NaCl. Sample: 1.0 ml of 0.005 M Na_2SO_4 in 0.01 M NaCl. Chart speed: 5 mm/min.

Separation and determination of some anions

The separation and detection of some anionic components in a mixed solution could be performed by utilizing the differences in their elution volumes, and typical examples are illustrated in Figs. 6–8. The results show that up to seven components can be separated and detected by one elution process.

The relationships between the peak areas and the sample concentrations of citrate, sulphate, acetate, oxalate and fluoride ions are shown in Fig. 9, and can be seen to be linear, within experimental error.

When sodium nitrate was used as the sample solution, as shown in Fig. 8, a positive peak was observed for the nitrate zone, but the elution curve for the nitrate zone obtained by argentimetry indicated a negative peak (*cf.*, Fig. 2 in ref. 12). The reason for this discrepancy in these two elution curves has not yet been fully explored, but may be partly due to the interfacial potentials that could be caused between the outer cylinder solution of potassium nitrate in the reference electrode and the sample solution of sodium nitrate. When nitrate ions were used as a sample, the content of this component could not be determined from its peak area owing to the positive response of this ion.

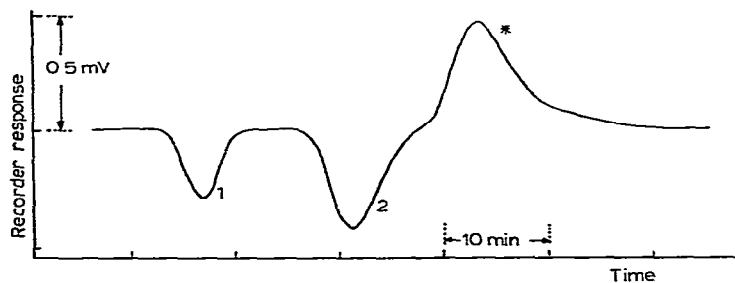


Fig. 6. Chromatographic separation. Column: 42.0×1.5 cm. Eluent: $0.01 M$ NaCl. Sample: 1.0 ml of a mixture containing $0.003 M$ $C_6H_5O_7Na_3$ (1) and $0.01 M$ NaF (2) in $0.01 M$ NaCl solution. Flow-rate: 40.8 ml/h. * This peak is the Cl^- peak caused by the exclusion of the eluting agent from the sample zones.

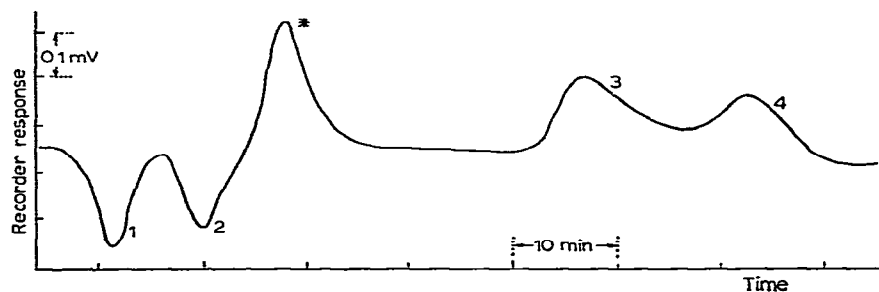


Fig. 7. Chromatographic separation. Column: 42.0×1.5 cm. Eluent: $0.01 M$ NaCl. Sample: 0.6 ml of a mixture containing $0.005 M$ Na_2SO_4 (1), $0.01 M$ CH_3COONa (2), $3.3 \cdot 10^{-6} M$ NaI (3) and $7.5 \cdot 10^{-5} M$ NaSCN (4) in $0.01 M$ NaCl. Flow-rate: 64.0 ml/h. * This peak is the Cl^- peak caused by the exclusion of the eluting agent from the sample zones.

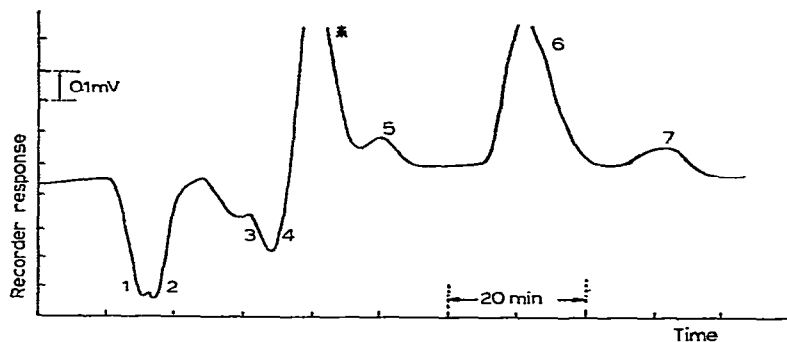


Fig. 8. Chromatographic separation. Column: 42.0×1.5 cm. Eluent: $0.01 M$ NaCl. Sample: 0.25 ml of a mixture containing $6 \cdot 10^{-3} M$ $C_6H_5O_7Na_3$ (1), $3 \cdot 10^{-3} M$ $C_2O_4Na_2$ (2), $2 \cdot 10^{-3} M$ CH_3COONa (3), $6 \cdot 10^{-3} M$ $NaBrO_3$ (4), $2 \cdot 10^{-2} M$ $NaNO_3$ (5), $2 \cdot 10^{-5} M$ NaI (6) and $3 \cdot 10^{-4} M$ NaSCN (7) in $0.01 M$ NaCl. Flow-rate: 33.0 ml/h. * This peak is the Cl^- peak caused by the exclusion of the eluting agent from the sample zones.

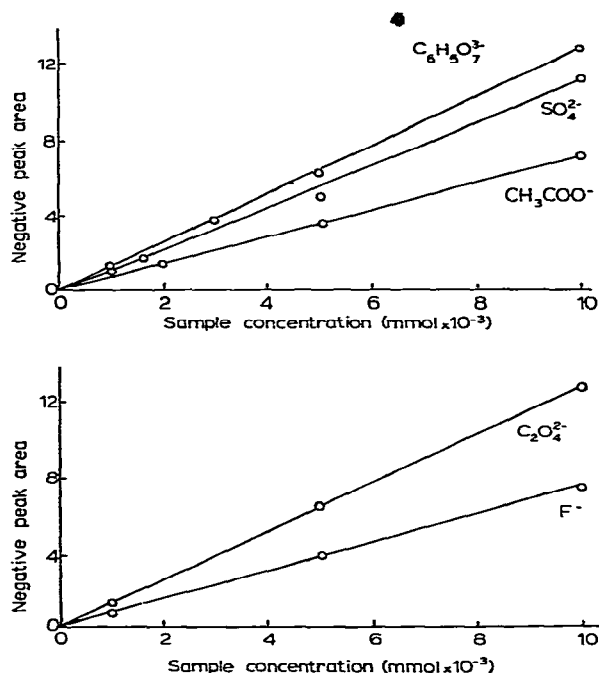


Fig. 9. Calibration graphs for the anions based on negative peak area measurement.

Of the negative peaks, the peaks of the anions located close to the positive peak of chloride ions, due to exclusion of the eluting agent from the sample zone, were omitted because of the difficulty in measuring accurately the areas of their peaks.

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