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MICRO COLUMN ION CHROMATOGRAPHY WITH A HOLLOW FIBRE SUPPRESSOR

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SUMMARY

Two novel liquid chromatographic techniques, a hollow fibre suppressor and a micro column, have been coupled to give a micro column ion chromatograph. The column comprised a newly developed low-capacity anion-exchange resin for ion chromatography packed in a fused-silica capillary tubing (190 μm I.D.). The micro suppressor system was constructed from sulphonated hollow fibre tubing (10 × 0.2 mm I.D.). Excellent separations of inorganic anions and carboxylic acids were achieved with this system.

INTRODUCTION

Introduction of the hollow fibre suppressor system into ion chromatography resulted in significant improvements[1]. The sulphonate hollow fibre tubing Nafion is an excellent material for the suppressor, however the smallest size available is about 0.8 mm I.D., which is too large for the present purpose. Therefore the dead volume of the tubing was reduced to minimize band broadening by filling the tubing with beads[2] or drawing out to narrower bores[3].

In a previous study[4], carboxylic acids and keto acids were chromatographed with a hollow fibre suppressor system using a dual detector system comprised of a UV and a conductivity detector.

Micro column liquid chromatography[5,6] only requires very small amounts of packing materials, eluent and samples. Recently, flexible fused-silica tubings were applied to micro column liquid chromatography by Takeuchi and Ishii[7]. Besides their flexibility, these materials are also mechanically stable and chemically inert.

In this work we investigated the applicability and performance of micro column ion chromatography with a hollow fibre micro suppressor system.

MATERIALS AND METHODS

The instrument used was a preproduction prototype of ion chromatographic analyzer Model IC 100 (Yokogawa Electric Co., Tokyo, Japan), with some modifications. A block diagram of the system is shown in Fig. 1. The packing material was

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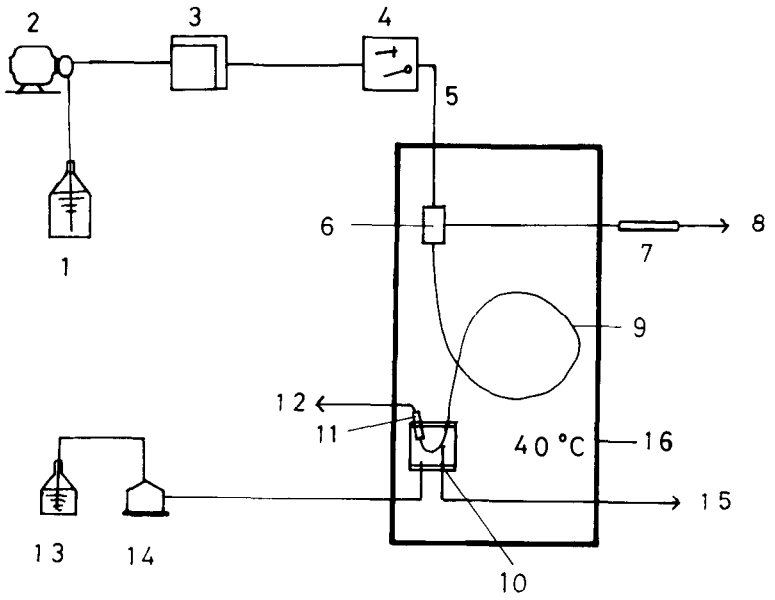

Fig. 1. Block diagram of the microbore packed column ion chromatograph. 1 = Eluent reservoir; 2, 13 = pump; 3 = dumper and pressure gauge; 4 = sample injector; 5 = coonnecting tube (75 μm I.D.); 6 = splitter "T"; 7 = resistor tube (50 μm I.D.); 8, 12, 15 = drain; 9 = column; 10 = suppressor; 11 = conductivity cell; 14 = scavenger reservoir.

the surface agglomerated and bonded strong anion-exchange resin YEW AX-1[3] (particle diameter 10 μm, Yokogawa Electric Co.) whose ion-exchange capacity was 25 μequiv./g. The column and the suppressor system were thermostatted at 40°C.

Fused-silica tubings were obtained from Scientific Glass (North Melbourne, Australia). Dodecylbenzenesulphonic acid was obtained from Tokyo Chemical Industries (Tokyo, Japan) and other chemicals were purchased from Nakarai Chemicals (Kyoto, Japan). A Nafion 811 X tubing (hollow fibre perfluorosulphonic acid cation-exchange membrane; Du Pont, Wilmington, DE, U.S.A.) was drawn out to 0.2 mm I.D. by Yokogawa Electric Co.

The sample solution was injected using a Waters Model U6K injector placed before the splitter. The splitting ratio of the eluent was controlled by adjusting the size of the resistor tube (1.6 mm O.D., stainless steel) inside which a fused-silica tubing of 50 μm I.D. was inserted; the space between the two tubings was filled with epoxy resin. The injector and the splitter "T" was connected to 75 μm I.D. tubing in the same way.

A schematic diagram of a micro packed column, a micro hollow fibre suppressor and a conductivity cell is shown in Fig. 2. A porous PTFE frit was pushed in one end of a 190 μm I.D. fused-silica tubing and a short narrow bore tubing was inserted and glued with an epoxy resin to fix the frit. The tube was covered with two stainless-steel tubes (5 cm × 0.7 mm O.D.) at both ends and the spaces between the inner and the outer tubes were filled with epoxy resin. A slurry of the ion-exchange resin in the eluent was placed in a small column packer one end of which was connected to the fused-silica tube using a Vespel (Du Pont) ferrule. The packing pressure

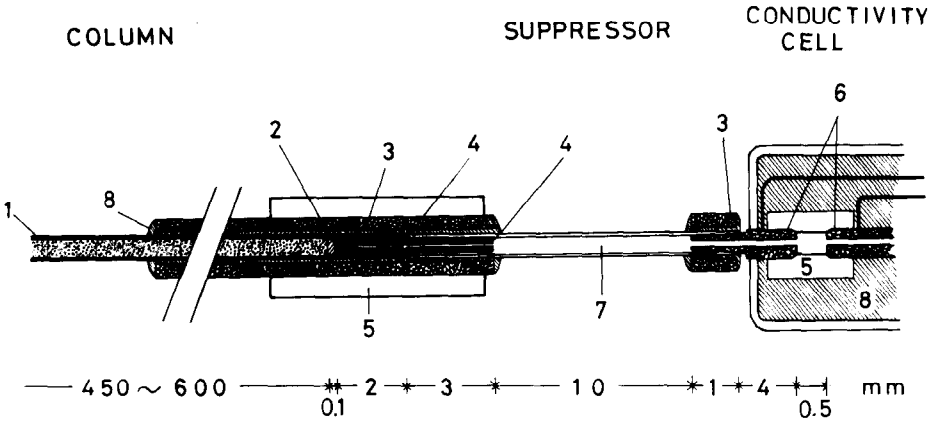

Fig. 2. Schematic diagram of column, suppressor and conductivity cell. 1 = Fused-silica tube (190 μm I.D.); 2 = porous PTFE filter; 3 = stainless-steel tube; 4 = fused-silica tube (25 μm I.D.); 5 = PTFE tube; 6 = electrode; 7 = Nafion tube (0.2 mm I.D.); 8 = epoxy resin.

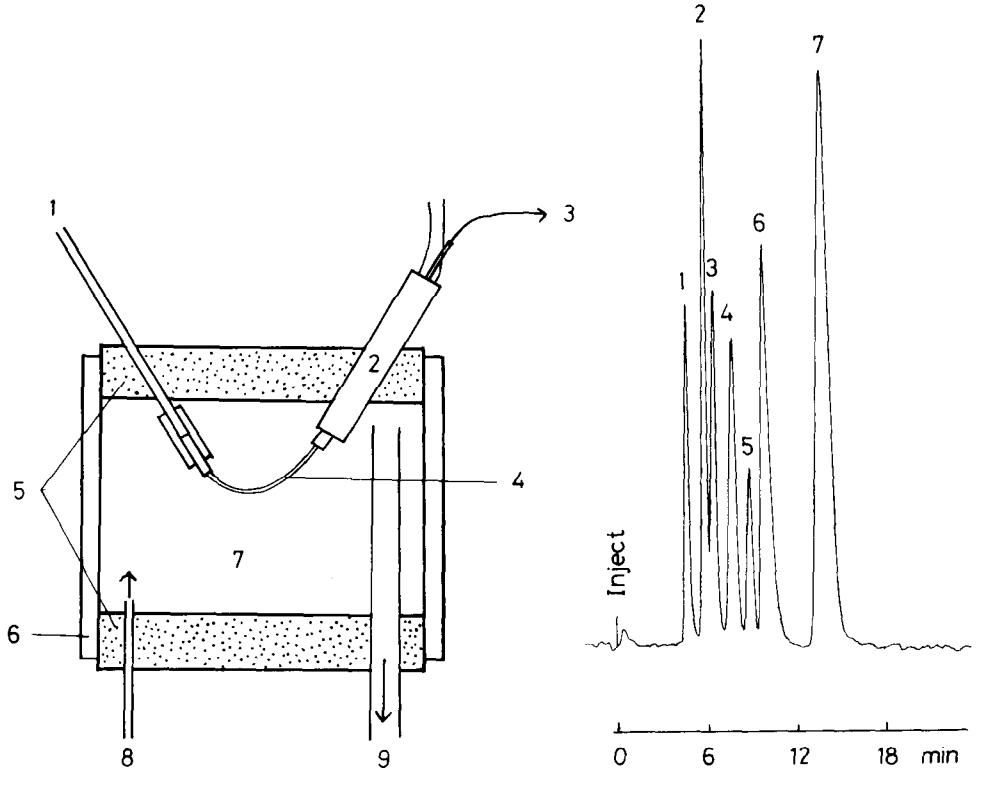

Fig. 3. Schematic diagram of hollow fibre micro suppressor. 1 = Column; 2 = conductivity cell; 3, 9 = drain; 4 = Nafion tube; 5 = silicon rubber stopper; 6 = glass tube; 7 = scavenger; 8 = scavenger inlet.

Fig. 4. Chromatogram of inorganic anions. Column: 190 μm × 47 cm, YEW AX-1 resin. Eluent: 4 mM Na_2CO_3 and 4 mM $NaHCO_3$ (pH 10.2). Temperature: 40°C. Flow-rate: 1.9 μl/min. Pressure: 48 kg/cm^2. Splitting ratio: 70:1. Sample size: 20 μl. Peaks: 1 = F^- (1.4 ng); 2 = Cl^- (2.8 ng); 3 = NO_2^- (4.2 ng); 4 = PO_4^{3-} (8.4 ng); 5 = Br^- (2.8 ng); 6 = NO_3^- (8.4 ng); 7 = SO_4^{2-} (11.2 ng).

was gradually increased from 20 to 250 kg/cm^2 with the aid of a JASCO A 700 pump (Japan Spectroscopy Co., Tokyo, Japan).

The micro hollow fibre tube suppressor was constructed from a Nafion 811 X tubing drawn out to 0.2 mm I.D. On the outside of both ends of the hollow fibre tubing were fixed short stainless-steel tubes for connecting to a column and a conductivity cell. The effective length of the suppressor tube was approximately 10 mm.

The whole suppressor system including hollow fibre tube and connections to the column and to the cell was placed in a glass container with silicon rubber stoppers as shown in Fig. 3. The container was filled with 0.05 *M* dodecylbenzenesulphonic acid solution as a scavenger. The latter was continuously renewed by pumping at a flow-rate of about 0.3 ml/min.

The conductivity cell was made of stainless-steel tubings of 0.5 mm I.D. and 0.36 mm O.D., the distance between the two electrodes being about 0.5 mm. The cell constants for the micro flow cells were about 300 S/cm.

RESULTS AND DISCUSSION

A chromatogram obtained from mixture of seven inorganic anions is shown in Fig. 4. The eluent was 4 m*M* sodium carbonate and 4 m*M* sodium bicarbonate

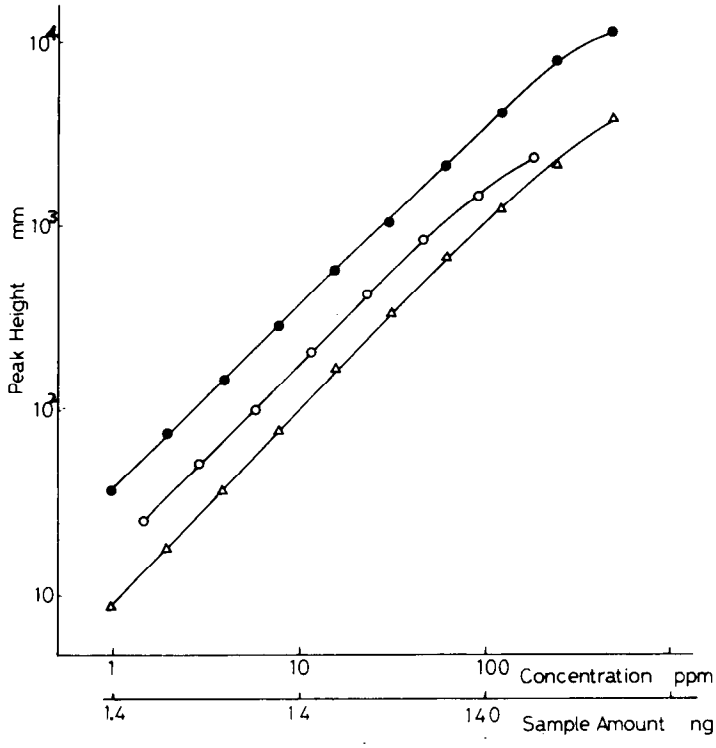

Fig. 5. Relationship between peak height and sample concentration for NO_2^- (○—○), NO_3^- (●—●), and Br^- (△—△). The sample amount was calculated from the sample concentration and the splitting ratio.

solution (pH 10.2) which was pumped through a Milton Royu Mini pump. The splitting ratio was adjusted to 70:1 and the flow-rate was 1.9 μl/min. The amounts of the anions analyzed on the column were calculated from the amounts injected and the splitting ratio.

Calibration curves for 10-μl injections of solutions of NO_2^-, NO_3^- and Br^- shown in Fig. 5. Linear relations were obtained between peak height and sample concentration or amount over approximately two orders of magnitude.

Carboxylic acids were also detected by the conductivity detector with high sensitivity. A mixture of mono- and dicarboxylic acids were applied on a 60 cm × 190 μm anion-exchange column and eluted with the carbonate buffer. The chromatogram and the amount separated on the column are depicted in Fig. 6.

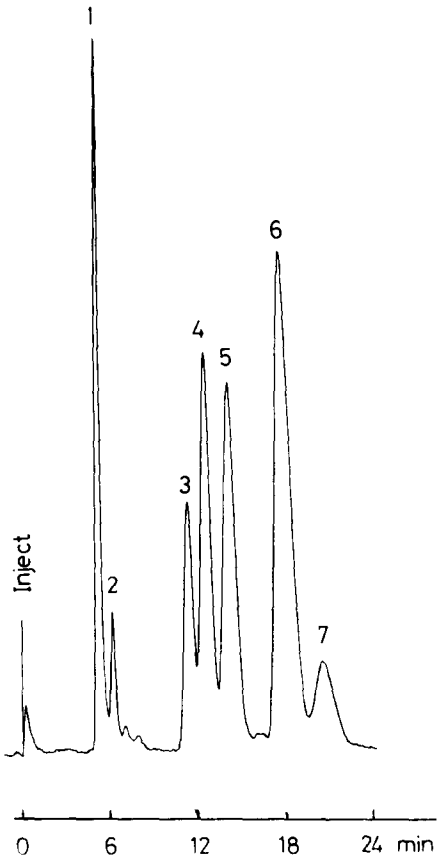

Fig. 6. Chromatogram of carboxylic acids. Column: 60 cm × 190 μm, YEW AX-1 resin. Eluent: 4 m*M* Na_2CO_3 and 4 m*M* $NaHCO_3$ (pH 10.2). Temperature: 40°C. Flow-rate: 2.65 μl/min. Pressure: 65 kg/cm². Splitting ratio: 130:1. Sample size: 3 μl. Peaks: 1 = lactic acid and acetic acid; 2 = oxalacetic acid; 3 = succinic acid (1.55 nmol); 4 = malonic acid (1.55 nmol); 5 = tartaric acid (1.55 nmol); 6 = oxalic acid (1.55 nmol); 7 = fumaric acid (0.76 nmol).

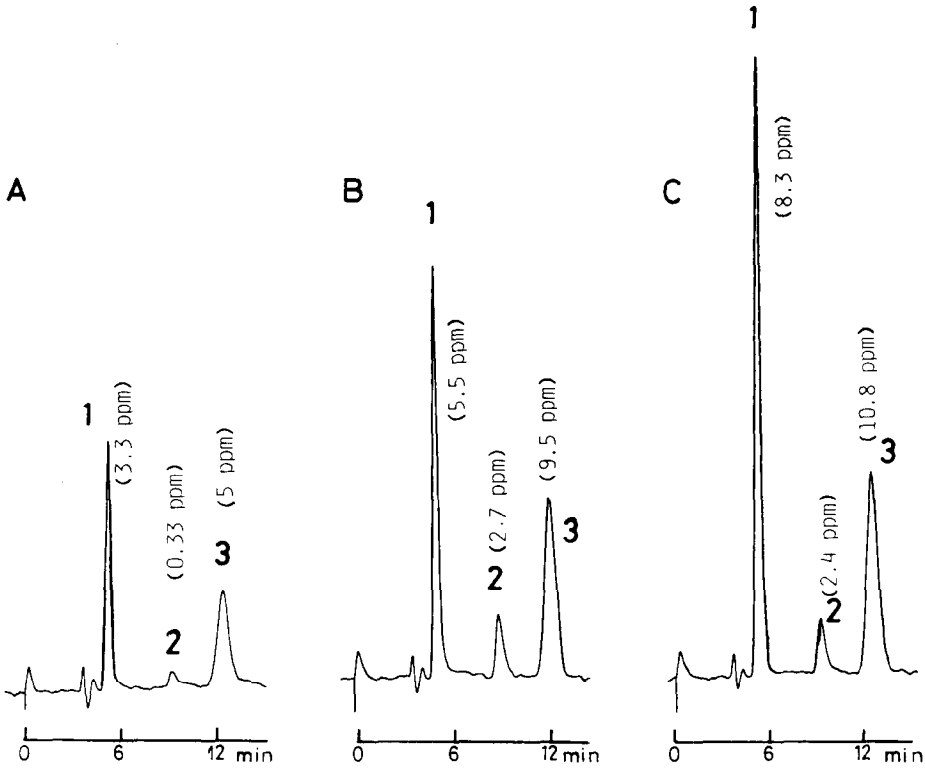

Fig. 7. Chromatograms of river-water. Samples taken at the origin (A), the residential section (B) and downtown (C). Flow-rate: 2.15 μl/min. Pressure: 50 kg/cm^2. Splitting ratio: 120:1. Sample size: 25 μl. Other conditions as in Fig. 4. Peaks: 1 = Cl^-; 2 = NO_3^-; 3 = SO_4^{2-}.

Fig. 7 shows the analysis of river-water samples. The samples were taken at several points from the source to the end of the Kamo-gawa river which flows through Kyoto city. The river-water samples are directly injected on the column. Three anions, Cl^-,NO_3^- andSO_4^{2-}, were observed and their amounts increased with increasing distance from the source.

Fresh fruits were squeezed and the juices were filtered and applied (3 μl) directly on the column. Individual peaks have not yet been identified, however, each juice gave a characteristic chromatographic pattern as shown in Fig. 8.

The present system has more band broadening and this resulted in slightly poorer resolution than a conventional system with a hollow fibre suppressor[3,4]; in the latter a pre-column (5 cm × 4.6 mm I.D.) and a 25-cm analytical column were employed, due to relatively large extra-column dead volumes both before and after the column. Peak shapes became narrower with a shorter hollow fibre suppressor tube; however, the efficiency of the suppressor decreased when its length was less than about 7 mm and the background increased. The dead volume in the detector cell should also be decreased to reduce peak broadening.

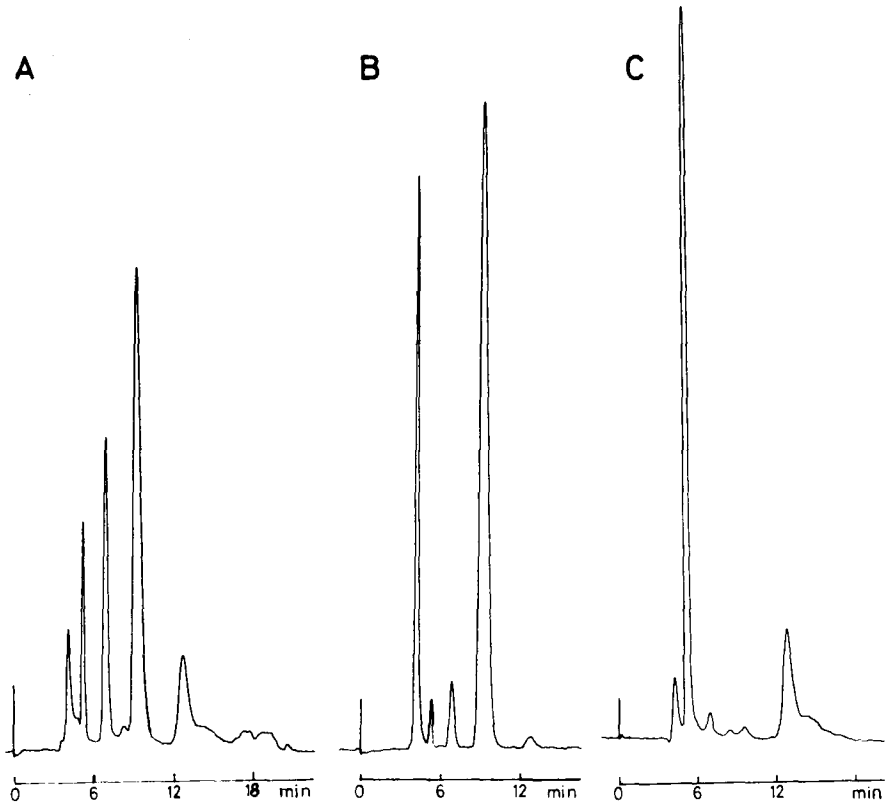

Fig. 8. Chromatograms of orange juice (A), peach juice (B) and papaya juice (C). Flow-rate: 3.4 μl/min. Pressure: 80 kg/cm^2. Splitting ratio: 120:1. Sample size: 3 μl. Other conditions as in Fig. 6.

The cross-sectional area of the micro packed column is about 1/570 of a conventional column; this means that the present column requires only about 0.4% of the packing materials, and this amount should be reduced further when improvements in the micro packed column system are made to attain higher performance.

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