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ION CHROMATOGRAPHY WITH AN ION-EXCHANGE MEMBRANE SUPPRESSOR

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SUMMARY

Suppressor and separator column packings for ion chromatography are described. The suppressor consists of fine cation-exchange membrane tubing and an outer plastic tubing, which allow continuous operation with minimum peak broadening without peak height changes or varying water-dip interference.

The separator packing uses small-anion latex-bonded styrene–divinylbenzene copolymer, which gives a high resolution because of a thin superficial macroporous construction. It is also mechanically rigid and chemically extremely stable.

INTRODUCTION

Ion chromatography, first introduced in 1975 by Small *et al.*[1], is a unique combination of a separator with low ion-exchange capacity, a suppressor to remove most of the background conductance of the eluent, and a conductivity detector to locate the peaks. Since its introduction, ion chromatography has become popular and is widely used for the analysis of inorganic anions (and certain cations), because of its fine resolution and high sensitivity.

Although the adoption of a suppressor column enables superior ion-chromatographic performance, it also causes the following problems.

(1) The suppressor column must be regenerated periodically to remove the accumulated ions from the eluent stream. As the separated species are re-mixed in the void volume of the suppressor, a loss of resolution (peak broadening) occurs. The suppressor volume is always a compromise between regeneration frequency and chromatogram resolution.

(2) Owing to interaction with the suppressor column, the peak height of the nitrite drastically changes as a function of suppressor exhaustion[2]. Retention time of "water dip" also changes accordingly.

For the reasons mentioned above, Gjerde *et al.*[3] proposed to eliminate the suppressor by using an anion-exchange resin of very low capacity, and by adopting an eluent having a very low conductivity. This approach is of limited use, however, because of its low sensitivity and narrow useful concentration range[2].

This paper describes a new type of ion-chromatographic system for the separa-

tion and quantitative determination of anions. Instead of a suppressor column filled with cation-exchange resin, a new type of suppressor using a cation-exchange membrane tubing was developed, which enables an uninterrupted analysis and lessens the band broadening effect. For the separator column packing, a small-anion latex was bonded to styrene–divinylbenzene copolymer. With this separator and suppressor combination, very sharp anion separations could be achieved and changes of nitrite peak heights proved to be minimal.

EXPERIMENTAL

Suppressor

A diagrammatic view of a suppressor is presented in Fig. 1. It consists of two coaxial tubes. The inner tube is made of perfluorosulphonic acid cation-exchange membrane (Dupont Nafion type 811X), which was heated to 150°C, and stretched to lengthen it 3.75 times to make a fine tubing of 0.4 mm I.D. and 0.55 mm O.D. A 5-m length of this resultant tubing was inserted coaxially into a PTFE tube of 1.0 mm I.D.

Eluent and separated ionic species flow inside the inner tubing while a so-called scavenger (aqueous acid) flows outside. As the cation-exchange membrane is per-
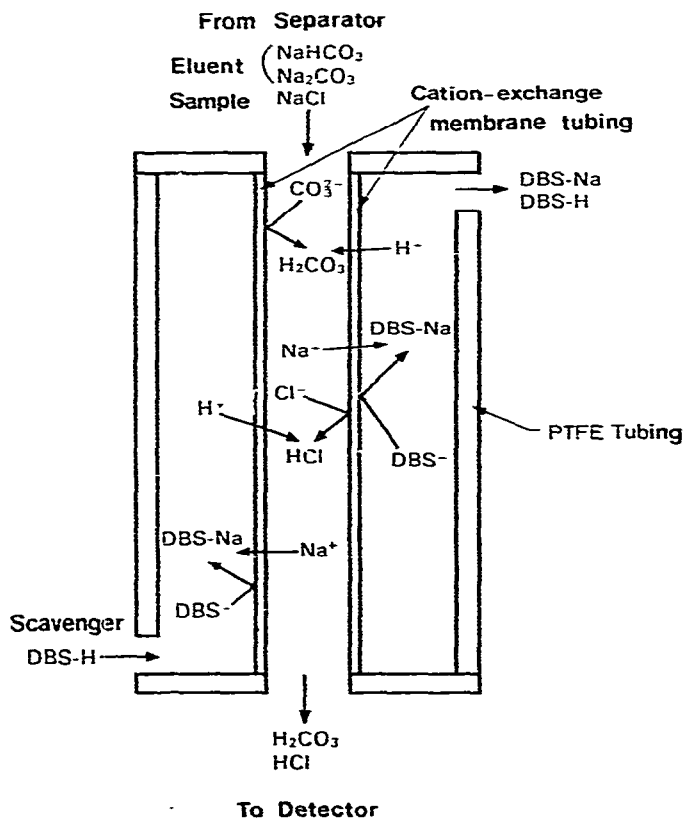

Fig. 1. Theory of operation of a cation-exchange membrane tubing suppressor. DBS-H = dodecylbenzenesulfonic acid; DBS-Na = sodium dodecylbenzenesulphonate.

meable to cations but is impermeable to anions, cations in the eluent and samples are exchanged with hydrogen ions in the scavenger.

Separator resin

A strong base anion-exchange resin AG 1-X8 (200–400 mesh, chloride form, Bio-Rad) was ground and a 0.6 g fraction was suspended in 300 ml of methanol and centrifuged. The resultant ion-exchange resin latex was added to 5 g of styrene–divinylbenzene copolymer MCIGEL CHP-3C (10 μm, Mitsubishi), and the methanol was evaporated in a 60°C hot bath. Just before all the methanol had evaporated, 0.25 g of a mixture of chloromethylstyrene and divinylbenzene (95:5) with 1 % of α,α'-azobis-isobutyronitrile as a catalyst was added and stirred thoroughly. Polymerization then proceeded for an hour in a 80°C drying oven followed by cooling at room temperature. After the beads had been separated, they were aminated with trimethylamine.

The final product was washed with methanol, water, 1 M HCl, and water.

Flow system

The chromatographic system used is shown in Fig. 2. The separator, suppressor and detector are enclosed in a temperature-controlled oven at 40°C to prevent temperature fluctuations.
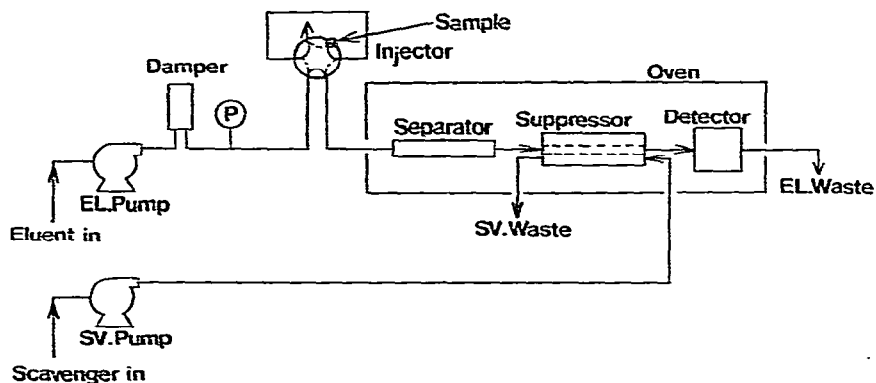

Fig. 2. Flow diagram. Eluent pump, LDC Model 396 Minipump; damper, Waters low-pressure filter; injector, rheodyne 7125; scavenger pump, Iwaki EP diaphragm pump; detector, YEW conductivity detector; oven temperature, 40°C.

Unless otherwise noted, the eluent used is 0.004 M Na_2CO_3 and 0.004 M $NaHCO_3$, and the scavenger is 0.05 M dodecylbenzenesulphonic acid (DBS). The flow-rate is 2 ml/min for both eluent and scavenger.

Standard sample solutions were prepared from reagent grade sodium salts containing 5 ppm fluoride, 10 ppm chloride, 15 ppm nitrite, 30 ppm phosphate, 10 ppm bromide, 30 ppm nitrate, and 40 ppm sulphate.

A conventional Dionex 30829 (100 × 9 mm I.D.) suppressor column packed with cation-exchange resin was used for comparison.

RESULTS AND DISCUSSION

Suppressor

The effect of the suppressor was examined without a separator column by injecting 100 μl of 200 ppm chloride ion, first with water flowing instead of scavenger and then with 0.05 M DBS as scavenger. Background conductance decreased significantly from 1.5 mS/cm to 30 μS/cm as soon as the scavenger was used, because sodium carbonate and sodium bicarbonate were converted into carbonic acid which has low conductivity. At the same time, the peak height of the chloride ion increased 2.5 times because sodium chloride was transformed into hydrochloric acid (see Fig. 3).
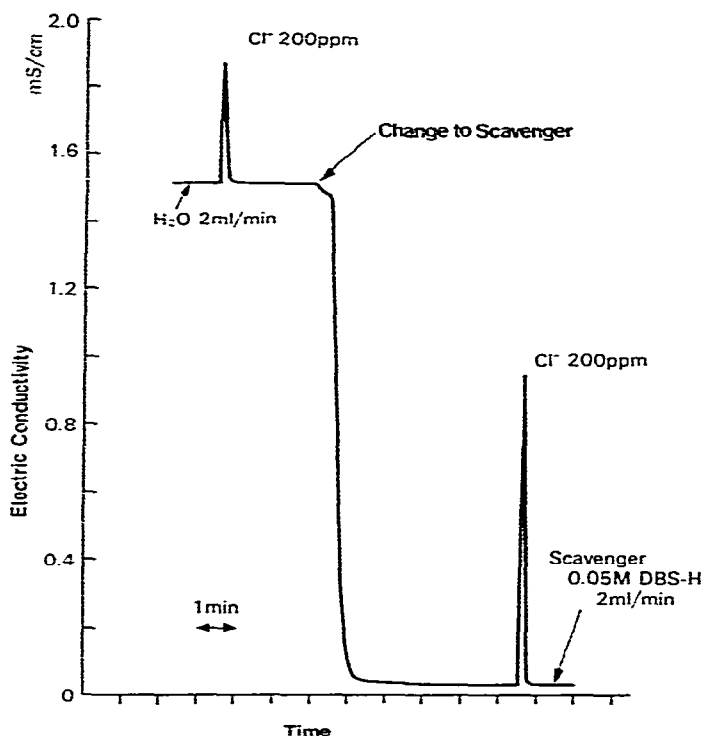
Fig. 3. Effect of the tubing suppressor.

The dependence of the peak height on the tubing length was investigated by injecting 100 μl of 10 ppm chloride ion with a scavenber flow-rate of 2 ml/min. The results (Fig. 4) reveal that 5 m of tubing are sufficient for an eluent with a flow-rate of 2 ml/min and that peak broadening occurs with longer tubing lengths. For an eluent with higher flow-rate or higher concentration, the flow-rate of the scavenger should be changed accordingly.

The scavenger used can be any aqueous acid as long as an ideal cation-exchange membrane is used. But, in practice, the leakage of scavenger into the eluent is inevitable, and therefore the molecular weight of the scavenger should be as large as possible. At the same time, it should not be corrosive, toxic, or dangerous.
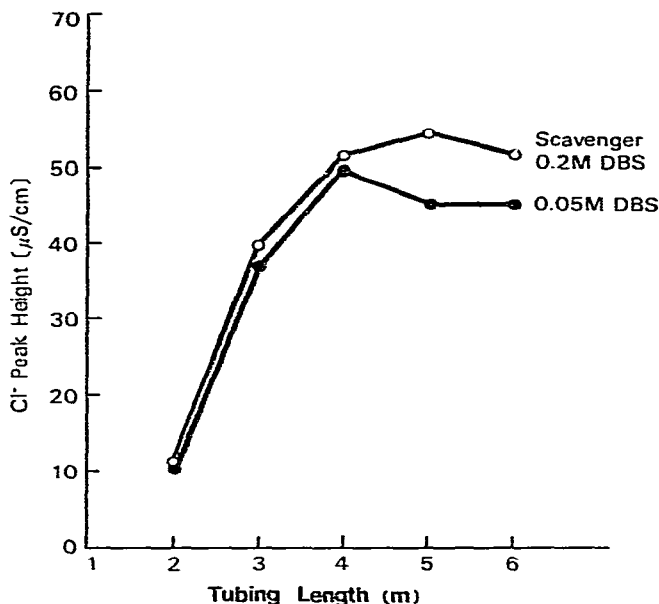
Fig. 4. Relationship of peak height to tubing length following injection of 100 μl of 10 ppm chloride.

DBS and nitric acid were compared as scavengers in regard to background conductance and peak height by injecting 100 μl of 10 ppm chloride ion. Fig. 5 illustrates the changes in peak height and background conductance as a function of scavenger concentration. For the same concentration level, nitric acid has higher background conductance than DBS. Another experiment showed that hydrochloric acid acts the same as nitric acid as a scavenger.

Separator

The ion-exchange capacity of the separator resin was found to be 0.035 mequiv./g. This can be easily adjusted by changing the amount of latex. The resin was washed several times with 1 M HCl, 1 M NaOH, methanol, and acetone, but no change in ion-exchange capacity was found. The resin was packed into a column and then removed. The procedure was repeated three times but no change in ion-exchange capacity was observed. Thus, the packing resin for a separator column proved to be chemically stable and mechanically rigid.

The resin was packed into a stainless steel column (250 × 4.6 mm I.D.) with a dynamic packing technique. A chromatogram combining the separator and suppressor is shown in Fig. 6. The seven anions were separated within 10 min. Theoretical plate numbers including suppressor, are 1800 for chloride and 1100 for sulphate. Fig. 7 illustrates the relationship between HETP and eluent flow-rate. The HETP value includes the suppressor for experimental and practical reasons. The HETP change of the sulphate when the eluent flow-rate changes from 2 to 4 ml/min is *ca.* 25 %. This enables fast analysis (7 anions within 5 min) with minimum chromatogram deterioration.

Fig. 8 illustrates a chromatogram for seven anions at low concentrations. The
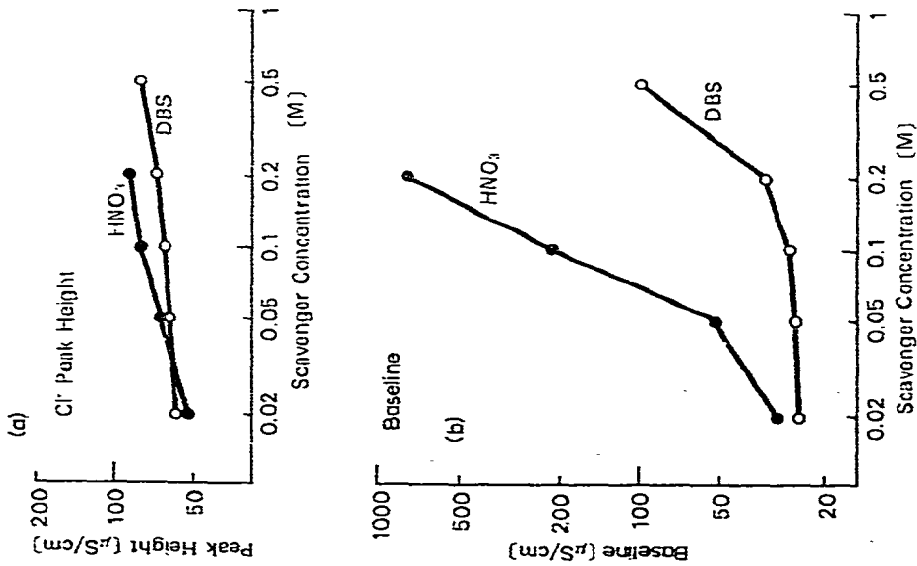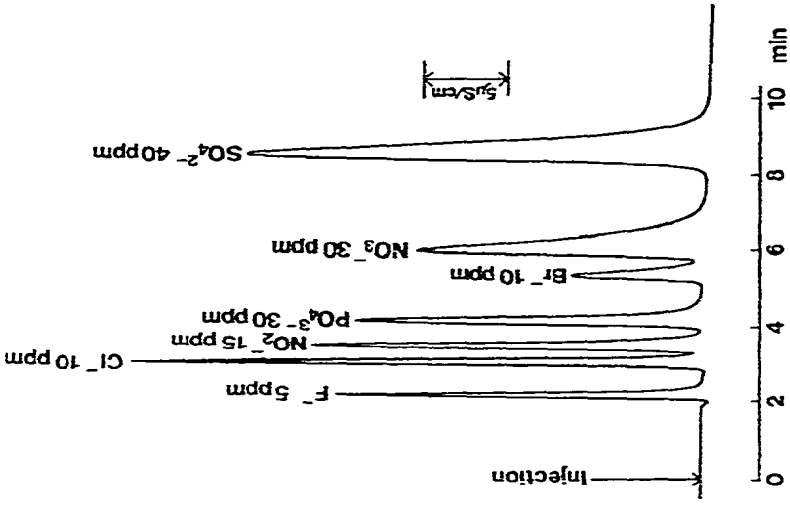
Fig. 5. (a) Change of peak height as a function of scavenger and concentration. (b) Background conductivity as a function of scavenger and concentration.

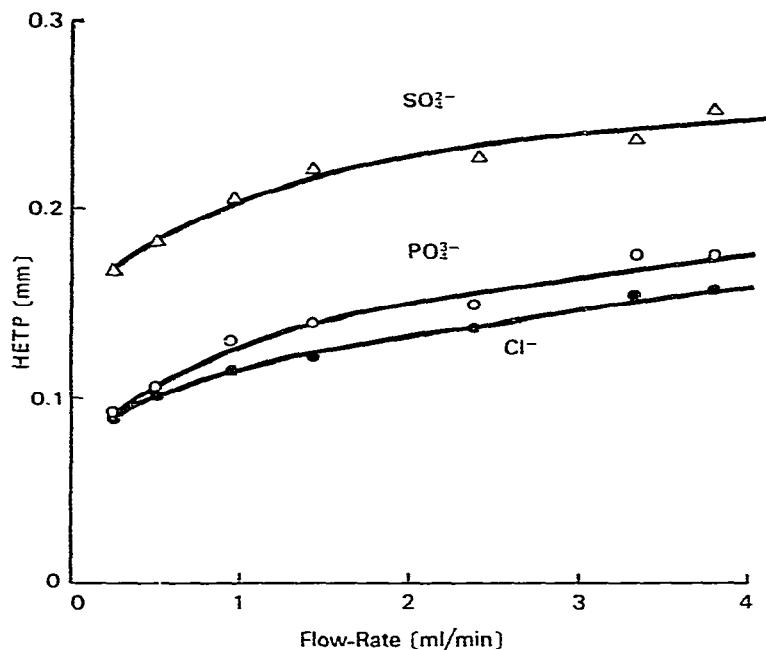Fig. 6. Chromatogram of seven anions using a tubing suppressor. Injection volume, 100 μl.

Fig. 7. Relationships between height equivalent to a theoretical plate (HETP) and eluent flow-rate. Measurements include tubing suppressor.
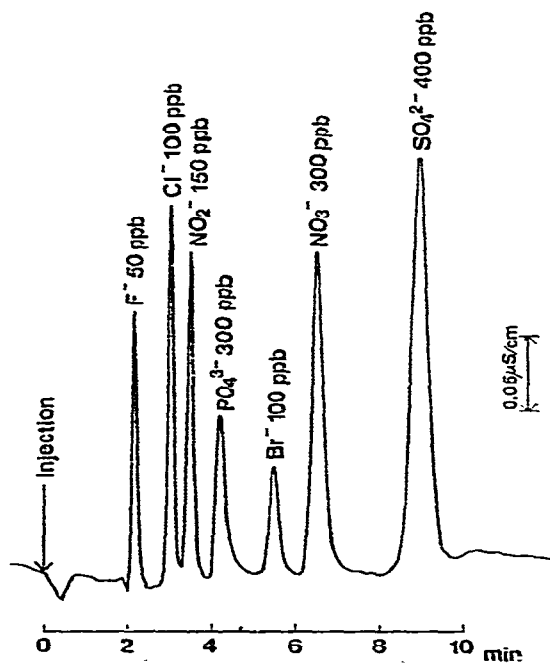

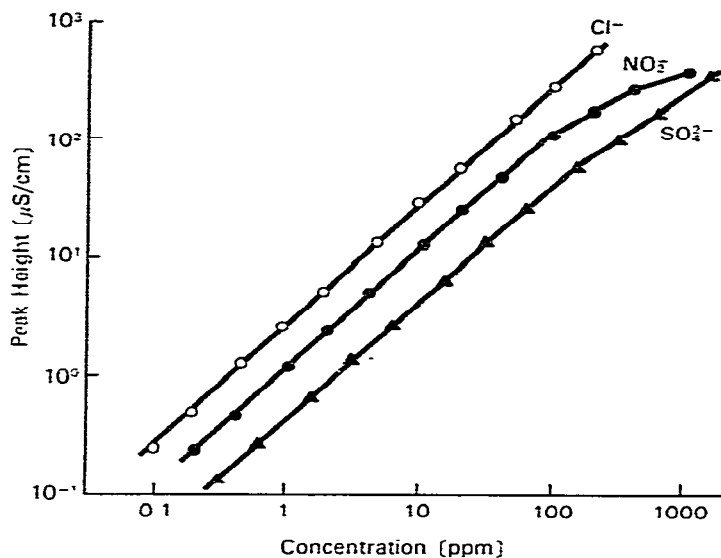Fig. 8. Chromatogram with low concentrations of anions. Injection volume, 100 μl.

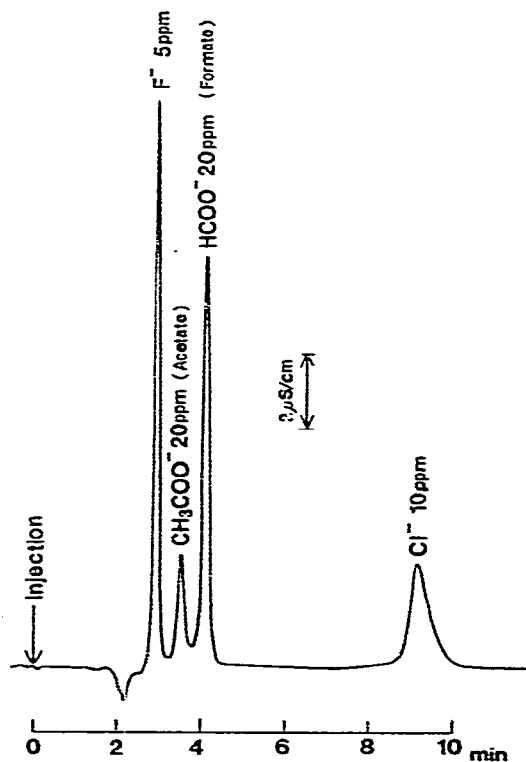Fig. 9. Calibration curves for chloride, nitrite, and sulphate. Injection volume, 100 μl.

Fig. 10. Chromatogram for acetate and formate. Eluent, 0.015 M Ba$_2$B$_4$O$_7$; flow-rate 2 ml/min; injection volume, 100 μl.
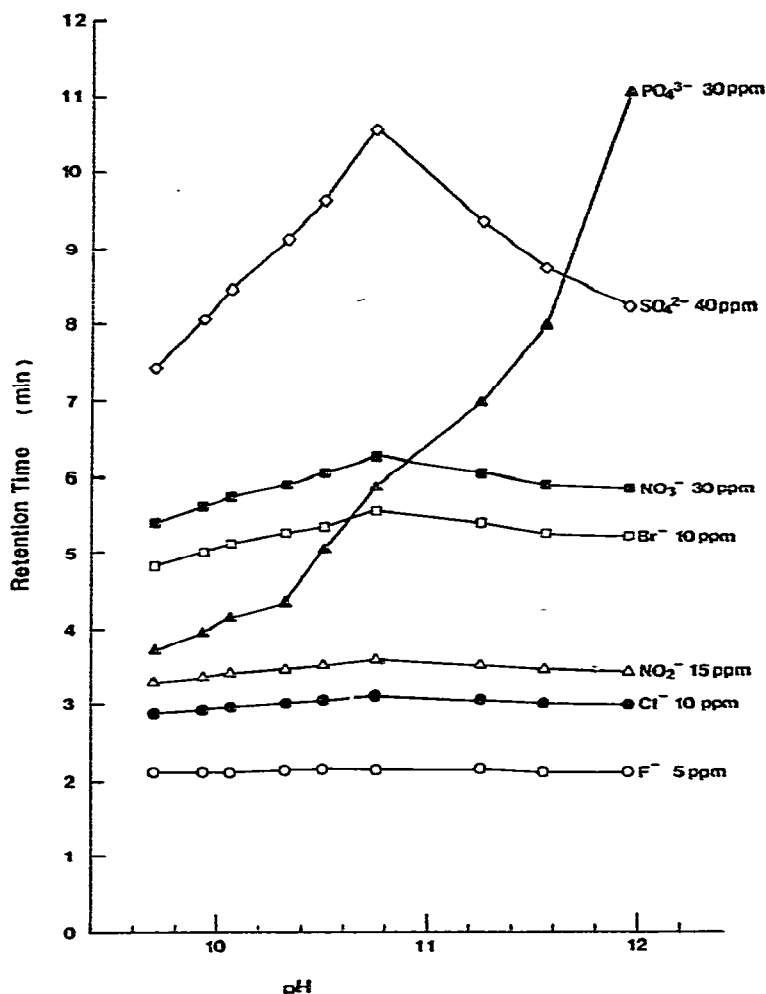
Fig. 11. Change of retention times with eluent pH. The pH of the eluent was adjusted by adding sodium bicarbonate or sodium hydroxide to 0.004 M Na_2CO_3.

sample was diluted with an eluent to avoid a "water dip". Detection limits are 5 ppb* for chloride and 20 ppb for sulphate, when the signal-to-noise ratio is set to 2. Fig. 9 shows the linearity and dynamic range of some typical anions.

Eluents

Eluent with 0.004 M Na_2CO_3 and 0.004 M $NaHCO_3$ was used under standard conditions because of its intermediate affinity for the separator resin and safety aspects. For species with high affinity such as chromate or iodide, the eluent concentration was increased by a factor between 2 and 10 with increased scavenger flow-rate. Organic anions with low affinity that elute between fluoride and chloride can be

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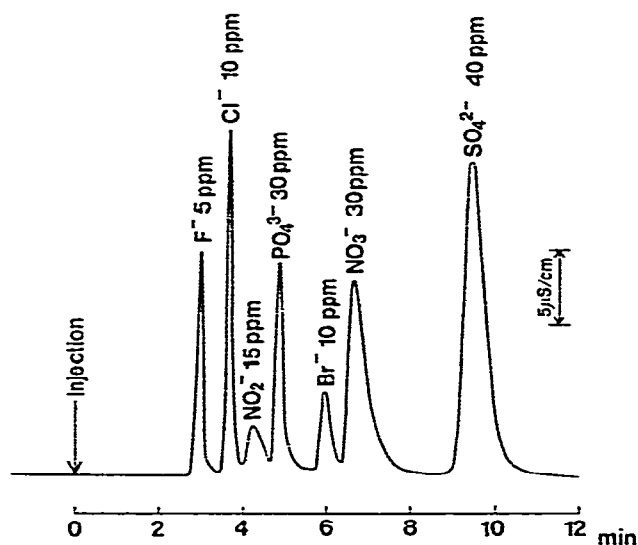* Throughout this article, the American billion (10^9) is meant.

Fig. 12. Chromatogram of seven anions using a conventional packed suppressor just after regeneration. Conditions are the same as Fig. 6 except the suppressor.
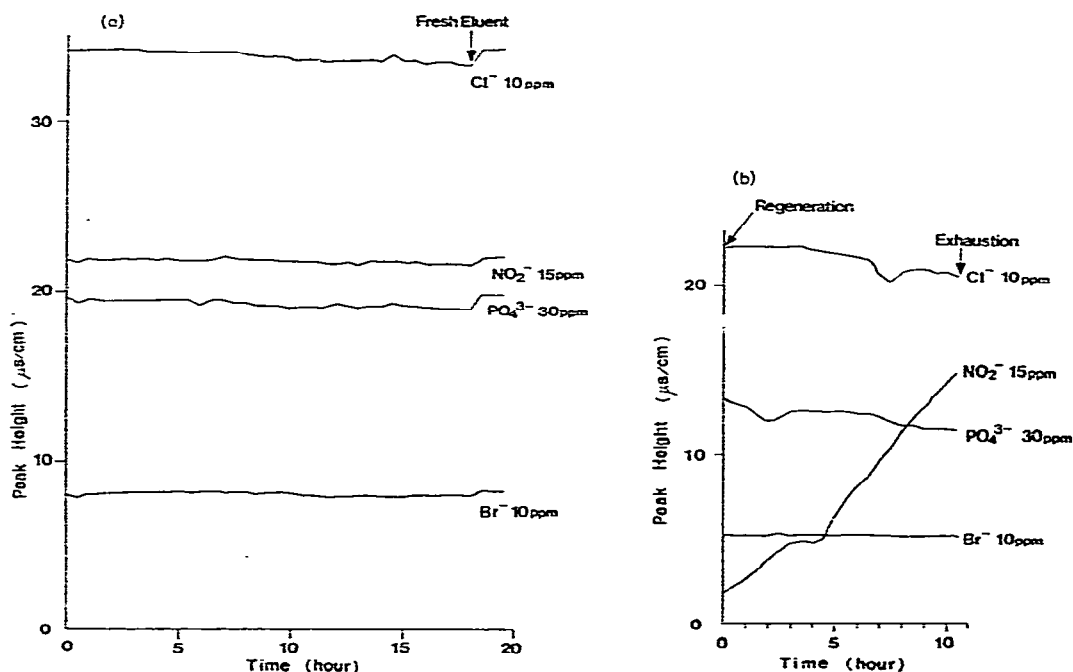

Fig. 13. (a) Changes of peak heights of chloride, nitrite, phosphate, and sulphate with the tubing suppressor. Injection volume, 100 μl. (b) Changes of peak heights of the same four anions with a conventional suppressor from regeneration to full exhaustion. (Full exhaustion occurs only with the conventional suppressor.)

separated with eluents of low eluting power. Fig. 10 shows the separation of acetate and formate using 0.015 M $Na_2B_4O_7$ as an eluent.

The effect of retention time changes were investigated by varying the pH of the eluent (Fig. 11). The pH was adjusted using NaOH and $NaHCO_3$ while the concentration of Na_2CO_3 was held constant.

Comparison with conventional suppressor

A comparison was made between an ion-exchange membrane tubing suppressor and a conventional suppressor packed with cation-exchange resin, while using the same separator, eluent, standard sample solution, and flow system. Chromatograms are shown in Fig. 6 for a tubing suppressor and in Fig. 12 for a conventional packed suppressor. Note that peak broadening with a tubing suppressor is minimal while peak heights showed a 50 % increase.

Fig. 13 illustrates the change in peak heights for each suppressor under identical conditions. The change of nitrite peak with a conventional packed suppressor is so large that it is almost impossible to quantify the nitrite ions. This phenomenon is due to interaction of the sample with cation-exchange resin in the unexhausted portion of the suppressor column. This interaction is a function of suppressor exhaustion. In a tubing suppressor, equilibrium between exhaustion and regeneration is established and peak heights remain resonably constant for a considerable time.

Changes in retention time of the water dip (negative peak against a baseline of carbonic acid) are plotted in Fig. 14 for a conventional and a tubing suppressor. With a conventional suppressor, the water dip moves and interfere with nitrite, chloride and fluoride peaks as a function of suppressor exhaustion. This upsets the quantification of those ions especially when the concentration is low. In a tubing suppressor the water dip interferes with the fluoride peak but this interference remains constant. In both cases, the water dip can be avoided by adding the same amount of sodium bicarbonate and sodium carbonate as eluent to the sample solution.
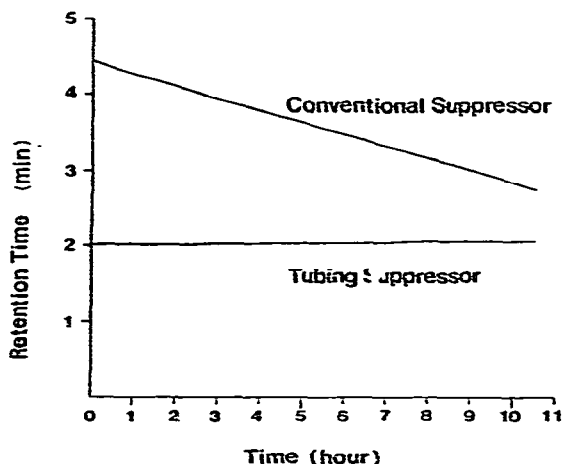

Fig. 14. Change of conventional suppressor water-dip retention time in relation to tubing suppressor.

CONCLUSION

An ion-exchange membrane suppressor enables continuous chromatogram operation. Wide choice of eluent, eluent concentration and eluent flow-rate become possible without the annoying problems related to regeneration such as time dependence of water dip and nitrite peak height changes.

The thin superficial macroporous packing resin combined with a tubing suppressor allows fast analysis.

An anion suppressor for cation analysis is now under development.

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3 D. T. Gjerde, J. S. Fritz and G. Schmuckler, *J. Chromatogr.*, 186 (1979) 509.