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### Determination of organic anions by ion chromatography using a hollow fiber suppressor

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Ion chromatography is a unique analytical technique for the separation and determination of organic and inorganic anions and cations (ion chromatography is the subject of U.S. Patent No. 3,920,397 and other U.S. patents, exclusively licensed to the Dionex Corporation by The Dow Chemical Company). The technique involves separating the species of interest on an ion-exchange separating column, followed by suppression of the background conductivity of the eluent electrolyte by a suppressor column<sup>1</sup>. However, the suppressor column complicates the analysis because (a) the suppressor column must be periodically regenerated or replaced, (b) the elution time of weak acid ions such as acetate, propionate, etc., vary due to ion exclusion effects<sup>2</sup> in the unexhausted portion of the suppressor column and (c) some band-spreading occurs in the suppressor column.

Recently, a counter-current continuously regenerated hollow fiber ion-exchange suppressor was developed at Dow<sup>3</sup>. The hollow fiber ion-exchange suppressor allows continuous use without periodic regeneration and eliminates ion response and elution time variations which occur when ion-exchange resin bed suppressor columns are used.

This paper describes the use of hollow fiber suppressor for analysis of organic anions.

## EXPERIMENTAL

### *Apparatus*

The ion chromatograph used in this work was a preproduction prototype of the Model 10 available from Dionex Corporation (Sunnyvale, CA, U.S.A.) where the conventional suppressor column was replaced with a hollow fiber ion-exchange suppressor. Aqueous solutions of NaOH, Na<sub>2</sub>CO<sub>3</sub>-NaHCO<sub>3</sub> or Na<sub>2</sub>CO<sub>3</sub>-NaOH were used as eluents. An aqueous solution of 0.02 *N* H<sub>2</sub>SO<sub>4</sub> was used as the hollow fiber regenerant at 2 ml/min flow-rate. (The hollow fiber suppressor is the subject of a patent application and is available from Diotex Corporation which is under license from The Dow Chemical Company).

## RESULTS AND DISCUSSION

The purpose of this work was to investigate conditions under which the conventional ion-exchange resin suppressor column can be replaced with the recently developed hollow fiber ion-exchange suppressor. It is a device which consists of low density sulfonated polyethylene ion-exchange hollow fibers. The theory of operation is shown in Fig. 1.

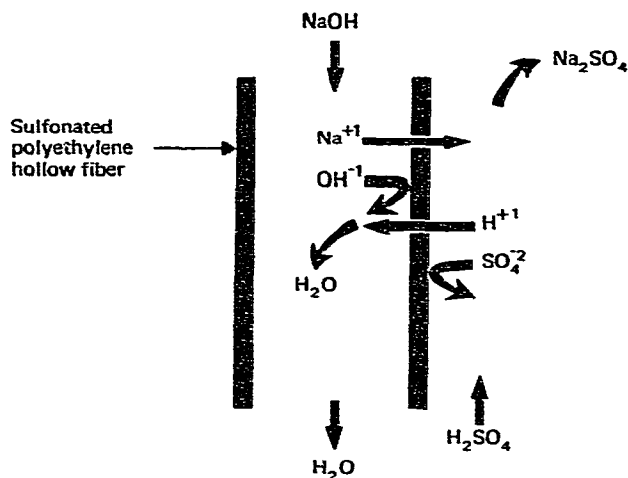


Fig. 1. Theory of operation of a hollow fiber suppressor.

The sulfonated polyethylene allows sodium ion to permeate out and hydrogen ion to permeate in. Hydroxide and sulfate ions tend not to permeate the fiber wall because of Donnan exclusion forces<sup>4</sup>. Thus, a sodium hydroxide eluent is deionized to water in the device. When the eluent contains Na<sub>2</sub>CO<sub>3</sub> or NaHCO<sub>3</sub>, they are converted to H<sub>2</sub>CO<sub>3</sub> in the suppressor.

Many organic acids such as acetic and chloroacetic acids, propionic and chloropropionic acids, glycolic acid, formic acid, oxalic acid, succinic acid, etc., can be determined by ion exclusion chromatography. An analytical column of high-capacity resin such as Aminex 50W-X4 in the H<sup>+</sup> form is used with either water as the eluent and a conductivity detector, or a dilute acid eluent and a UV detector<sup>5</sup>. However, when water is the eluent, the separation of most of the above acids is difficult, and it is more difficult if inorganic anions such as Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, F<sup>-</sup>, etc., are present. The separation of most of these acids is improved if a dilute acid is used as the eluent, but the detection limits are not as good, because most of these acids have relatively low molar absorptivity in the UV region of the spectrum. The high conductivity of the dilute acid eluent prevents the use of a conductivity detector which is generally much more sensitive for these compounds than a UV detector.

The use of ion chromatography was our approach as a solution to these problems. However, it was found that the separation of these organic anions was complicated due to an ion exclusion phenomenon which occurs in the unexhausted portion of the suppressor.

Although the overall physical length of the suppressor column remains steady, the unexhausted portion of the column at any given time is the effective length of the column. Due to ion exclusion effects in the continuously decreasing unexhausted portion of the suppressor, the elution time of the anions vary, and resolution can be lost. Fig. 2 demonstrates the above problem. The use of a hollow fiber suppressor eliminates the problem since it allows not only continuous use of the suppressor without periodic regeneration, but most important, it eliminates elution time variations as a function of suppressor column exhaustion.

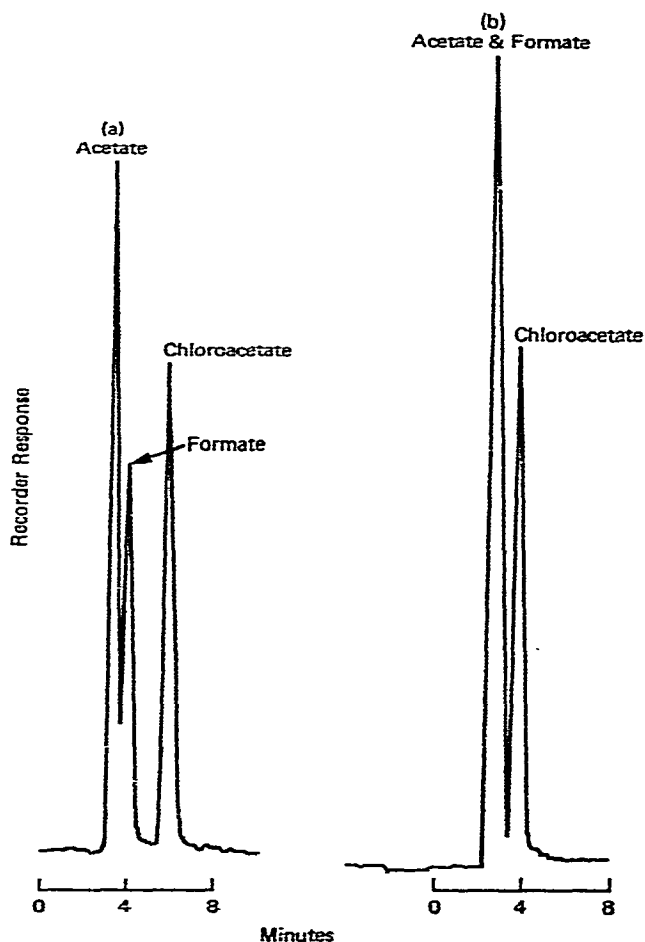


Fig. 2. Degradation of resolution with suppressor column exhaustion. a, Fully regenerated; b, 70% exhausted.

In all experimental work, an anion separator obtained from Dionex Corporation and a hollow fiber ion-exchange suppressor prepared for this experimental work at the Dow Analytical Laboratories were used. Depending on the anions present in the experimental samples, different eluents such as aqueous solutions of  $\text{Na}_2\text{CO}_3\text{-NaHCO}_3$ ,  $\text{Na}_2\text{CO}_3\text{-NaOH}$  or  $\text{NaOH}$  at different concentrations were used.

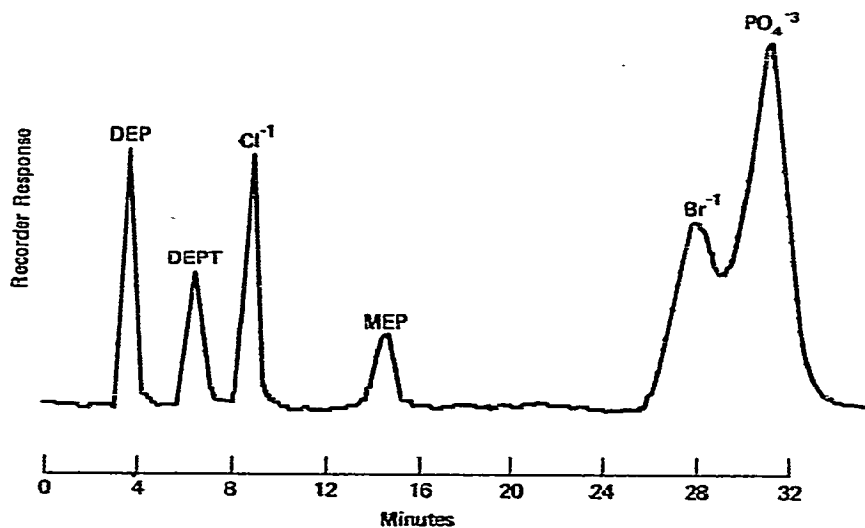


Fig. 3. Separation of organophosphates using a carbonate-bicarbonate eluent.

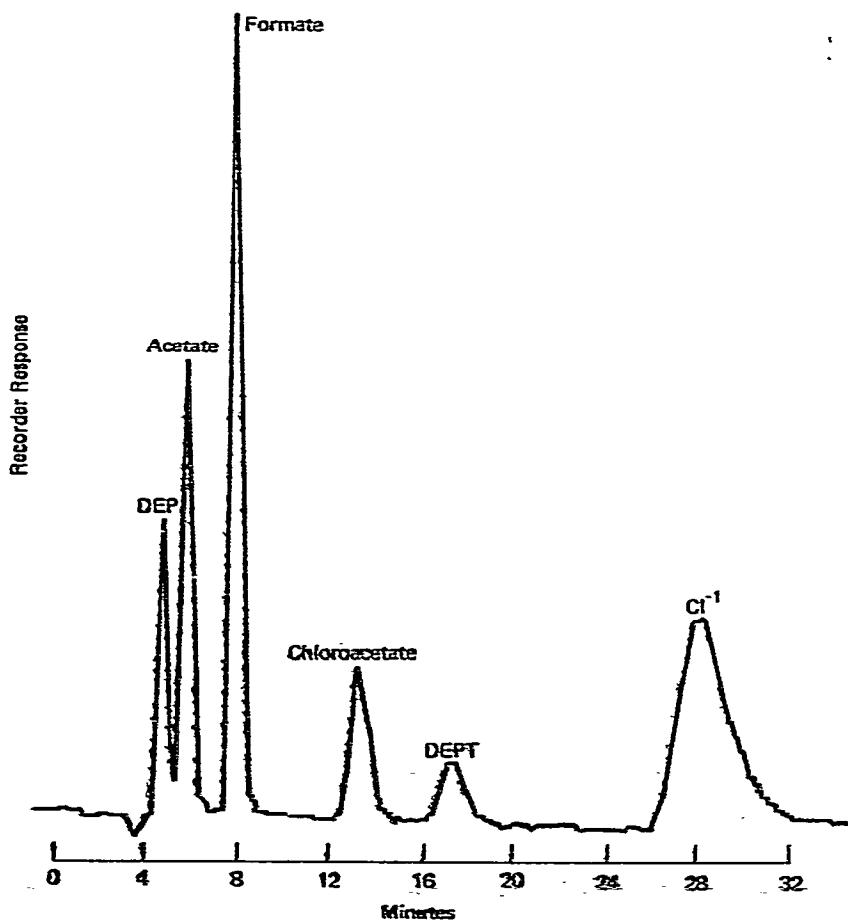


Fig. 4. Separation of organophosphates and carboxylic acids using a sodium hydroxide eluent.

Eluents containing NaOH must be protected from absorbing the  $\text{CO}_2$  found in air. A tube of Ascarite® absorbent was used for this purpose. The selectivity coefficient of  $\text{CO}_3^{2-}$  is greater than  $\text{OH}^-$ , and thus the "strength" of the eluent increases as NaOH absorbs  $\text{CO}_2$ . This increasing strength of the eluent causes the faster elution of the ions of interest and thus a loss of resolution.

Chromatograms of attempted ion chromatographic separations of weak organic anions using a hollow fiber stripper are presented with recommendations of eluents and experimental conditions. However, no attempt was made to optimize the conditions in each case, and probably better separations can be obtained by changing the experimental conditions. Fig. 3-7 show separations of several anions using the same analytical system, but different eluents.

In Fig. 3, the separation of diethyl phosphate (DEP), diethyl phosphorothioate (DEPT) and monoethyl phosphate (MEP) (all  $\text{P-OC}_2\text{H}_5$  compounds) is shown in the presence of phosphate, chloride and bromide ions. The eluent was an aqueous solution of 0.0012 *M*  $\text{Na}_2\text{CO}_3$  and 0.0012 *M*  $\text{NaHCO}_3$  at 1.0 ml/min flow-rate. Fig. 4 shows the

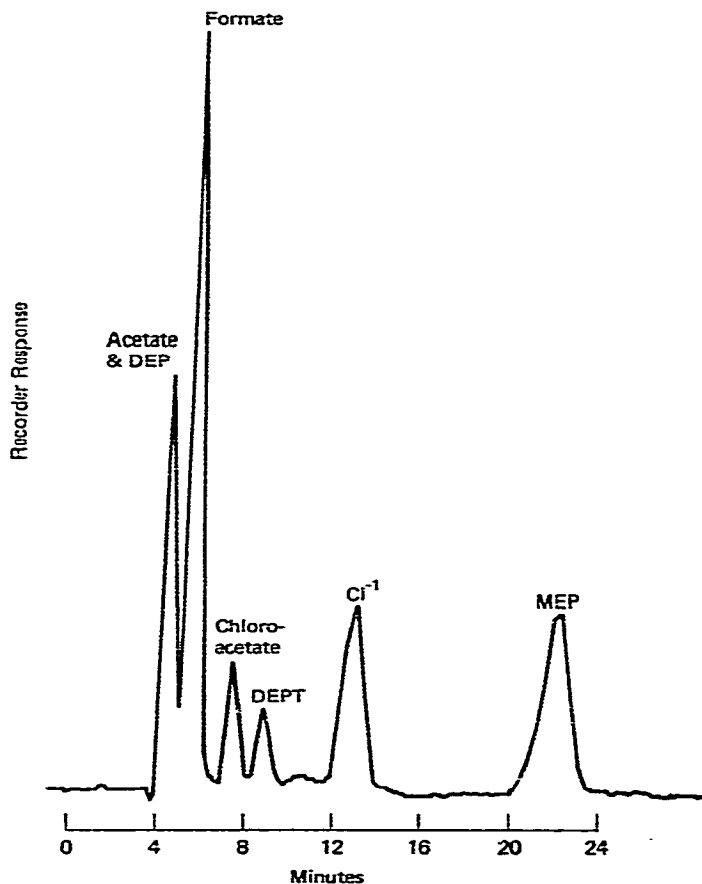


Fig. 5. Separation of organophosphates and carboxylic acids using a sodium hydroxide-sodium carbonate eluent.

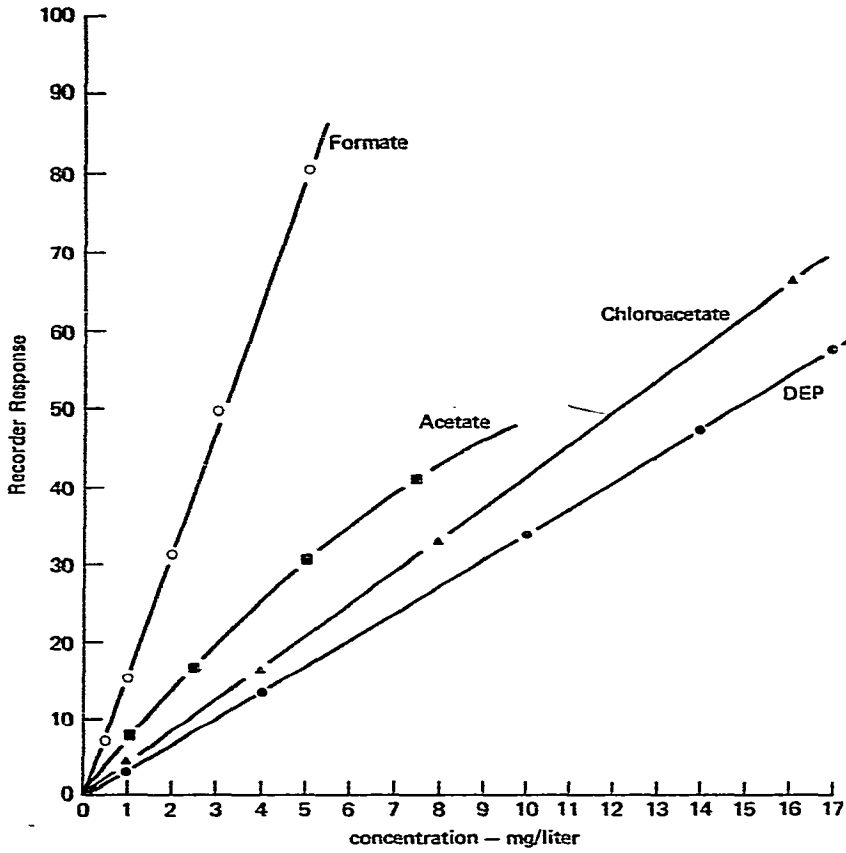


Fig. 6. Linearity of formate, acetate, chloroacetate and diethyl phosphate (DEP).

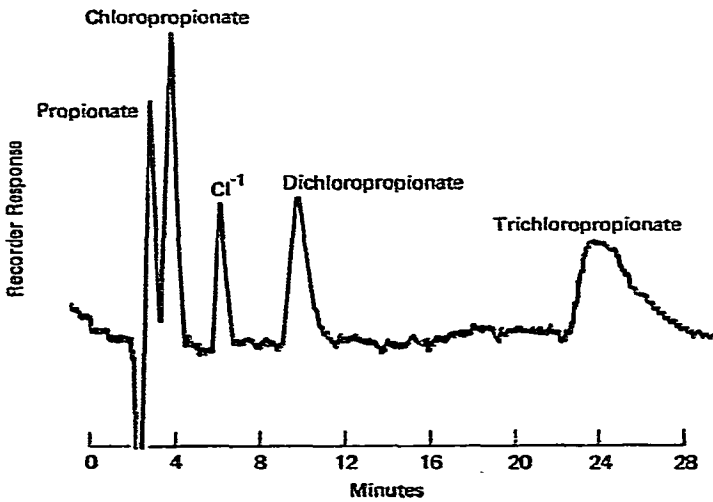


Fig. 7. Separation of propionic and chloropropionic acids using a sodium carbonate-bicarbonate eluent.

separation of the same organophosphoric acids and aliphatic acids such as acetic acid, formic acid and monochloroacetic acid. An aqueous solution of 0.0025 *N* NaOH at 1.3 ml·min flow-rate was used as an eluent. The elution time of the monoethyl phosphate which was present in the sample is too long and is not shown in this chromatogram. However, by using an aqueous solution of 0.0030 *N* NaOH and 0.0005 *M* Na<sub>2</sub>CO<sub>3</sub> as eluent, the MEP elutes after 23 min as Fig. 5 shows.

Fig. 6 shows the standard curves (peak height *versus* concentration) for formic acid, acetic acid, monochloroacetic acid and diethyl phosphate. Excellent linearity over the relatively narrow concentration range tested was observed for formic acid, monochloroacetic acid and diethyl phosphate while the linearity for acetic acid was acceptable.

Hollow fiber suppressor was also successfully used for the ion chromatographic separation of propionic and chloropropionic acids using 0.0012 *M* Na<sub>2</sub>CO<sub>3</sub> and 0.0012 *M* NaHCO<sub>3</sub> at 1.8 ml/min flow-rate as Fig. 7 shows. The hollow fiber suppressor was also used for the analysis of experimental samples containing acetic acid, chloroacetic acid, dichloroacetic acid, trichloroacetic acid and oxalic acid.

## CONCLUSIONS

The data obtained show that a hollow fiber ion-exchange suppressor can be used in ion chromatography for the separation and determination of organic anions without change of ion response or elution time variation of the ions.

## ACKNOWLEDGEMENTS

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