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ION EXCLUSION CHROMATOGRAPHIC DETERMINATION OF WEAK ACIDS USING A CARBONIC ACID SOLUTION AS ELUENT

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By using a carbonic acid solution as eluent which permits conductivity detection of ionic species without a suppressor as a post-column reactor, ion exclusion chromatographic determination of some organic acids was carried out sensitively by means of the conductivity detector.

In recent years, ion exclusion technique1) has become of more interest because of useful in separating strong acids as a class from weak acids and also weak acids from each other. Tanaka et al.2) have described the ion exclusion behavior of a large number of strong and weak acids using water as eluent. Turkelson et al.3) have reported the use of ion exclusion chromatography in separating most of the citric acid cycle acids, demonstrating that ion exclusion can also separate weak acids from each other by the use of a dilute hydrogen chloride solution as eluent.

Further, ion chromatography exclusion (ICE) technique, one of the modes of ion chromatography,4) has been successfully applied to the separation and analysis of organic acids in the various samples having complex matrices, i.e., brine5) and biological samples.6) In this technique using a dilute hydrogen chloride solution as eluent, the separator column is followed by a so-called halide suppressor, which permits sensitive detection of the interest ionic species in a sample solution with the reduction of the background conductivity.

In this communication, we wish to report a new ion exclusion technique using a carbonic acid solution as eluent and conductivity detection without a suppressor as a post-column reactor.

The Dionex Model 10 Ion Chromatograph equipped with conductivity detector was modified. Two Dionex Anion Suppressor7) were used: one (9 i.d.mm x 100 mm) between the pump and the injection valve and another (6 i.d. mm x 60 mm) between the injection valve and the ICE separator.8) There are two reason why we used a superssor before the ICE separator. First, this column will play a role of a so-called guard column for the ICE separator. Secondly, this will neutralize a sample solution and convert sample ions to the corresponding acid forms. Thus, the system can be continually operated for 20 to 30 hours according to the sample matrix and the flow rate without regeneration of columns. In addition, with a view to faster analysis, the separator valve and the suppressor valve were bypassed by connecting the top of the suppressor column directly to the injection valve and the bottom of

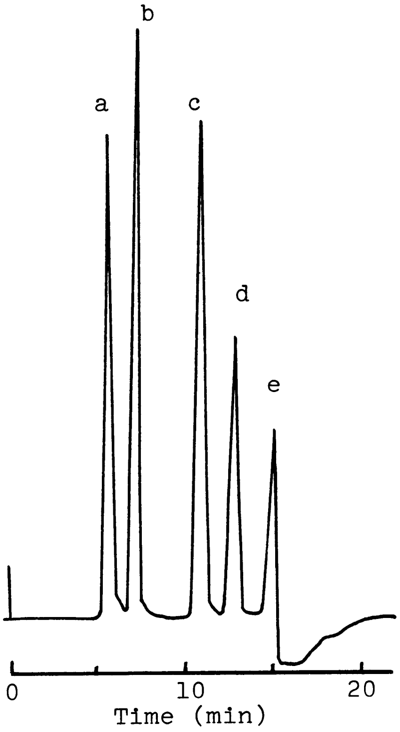

Fig. 1. Chromatogram of a standard mixture.
eluent: 5.4x10^{-3}mol dm^{-3} H_2CO_3
flow rate: 0.88 cm^3 min^{-1}
meter setting: 3 µS.
sample: a- sulfate, b- formate, c- acetate, d- propionate, e- butyrate.

the ICE separator directly to the conductivity cell inlet using a short length of tubings. Eluent reservoir contains a sodium carbonate solution and/or a standard sodium hydrogencarbonate - sodium carbonate solution which is commonly used for anion analysis in ion chromatography.[9)] This solution was converted into a defined concentration of carbonic acid solution by passing it through the suppressor column.

Figure 1 shows a typical chromatogram of standard mixture of four organic acids and sulfate with a good baseline separation. The negative portion of the chromatogram is a peak based on so-called " water dip ", which is generally observed in anion analysis using carbonate eluent.

This technique was applied to the analysis of acetate ion in Klinisalz® B Ringer's solution, which contained NaCl, KCl, CH_3COONa, KH_2PO_4, $MgCl_2$ and xylitol as components. We found that acetate could be analysed with a good precision by this technique without any pretreatment, except for single dilution with distilled water; Taken : 11.81 µg cm^{-3}, Found : 11.85 ± 0.08 µg cm^{-3}(n = 5).

The calibration curve for acetate ion using a peak height showed a good linear relationship from 0.1 µg cm^{-3} to 10 µg cm^{-3} at meter setting 3 µS and from 0.5 µg cm^{-3} to 30 µg cm^{-3} at 10 µS.

Further result will be published in a successive report.

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7) Column packed with 20 - 40 µ Dionex DC-X-8 resin, a microporous strong acid cation exchanger, which consists of an styrene/divinylbenzene copolymer containing sulfonic acid groups.
8) 9 i.d. mm x 200 mm column packed with 9 ± 0.5 µ DC-X-8 resin.
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