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Note

Separation of mono- and dicarboxylic acids by liquid chromatography

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The separation of carboxylic acids containing two or three carboxyl groups has been the subject of several investigations. Johnson and Samuelson[1] separated various uronic acids on anion-exchange resins, monitoring the eluates by the carbazole method or by reaction with dichromate and determining the unreacted dichromate spectrophotometrically. Bengtsson and Samuelson[2] also employed anion-exchange chromatography in separating acids containing two and three carboxyl groups. The acids were introduced into the column as the sodium salts and eluted with magnesium acetate at controlled pH. The separation of maleic and fumaric acids on cation-exchange resins in the hydrogen form was reported by Patel *et al.*[3]. Using 0.01 *N* hydrochloric acid as eluent, they monitored the eluates by collecting fractions and titrating with standard hydroxide solution. In the present investigation an attempt was made to separate citraconic, fumaric, acrylic and acetic acids as minor components in maleic acid.

EXPERIMENTAL

Reagents and equipment

Analytical grade chemicals of 99% purity or better were used as standards. Dowex 50W-X4 and Aminex 50W-X4 cation resins were obtained from Bio-Rad Labs, Richmond, Calif., U.S.A. The modular liquid chromatograph consisted of a Beckman (Fullerton, Calif., U.S.A.) Model DU ultraviolet (UV) spectrophotometer, a Gilford (Oberlin, Ohio, U.S.A.) Model 222 photometer, a power supply, an elevated cuvette chamber cover (No. 1045) and a Model 203A 10-mm flow-through cell with bubble trap from Gilford.

Column preparation

Two columns were prepared, one 200 × 9.0 mm I.D. with Dowex 50W-X4 (100 μm) cation-exchange resin and the other 230 × 9.0 mm I.D. with Aminex 50W-X4 (30–35 μm) cation-exchange resin. The resins were made into a slurry with water and introduced at the top of the columns, while applying a slight suction to the bottom. They were conditioned by pumping through a solution of 0.1 *N* hydrochloric acid for 2 h followed by water for one hour.

Procedure

An attempt was made to duplicate the work of Patel *et al.* by injecting 50 μl of a solution containing 50 μg/ml maleic and 60 μg/ml fumaric acid into the column of Dowex 50W resin, eluting with 0.01 *N* hydrochloric acid, and monitoring the eluates by UV spectrophotometry at 210 nm. The experiment was carried out under pressure. This was repeated with eluent concentrations of 0.005 *N* and 0.001 *N*. Although the acids are completely separated at the higher eluent concentrations, the retention times are greater, which is partially due to the suppression of the ionization of the acids. A typical chromatogram obtained with 0.001 *N* hydrochloric acid as eluent is shown in Fig. 1.

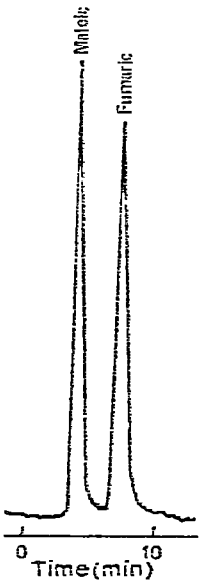

Fig. 1. Separation of maleic and fumaric acids on Dowex 50W-X4 (100 μm). Eluent, 0.001 *N* hydrochloric acid; flow-rate, 1.1 ml/min; UV monitor at 210 nm.

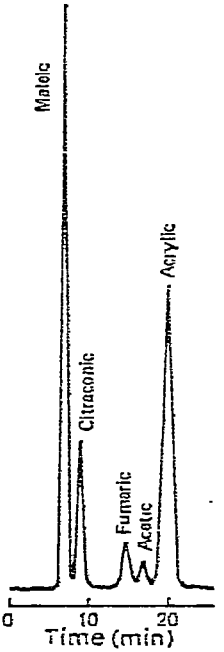

Fig. 2. Separation of maleic, citraconic, fumaric, acetic and acrylic acids on Aminex 50W-X4 (30–35 μm). Eluent, 0.001 *N* hydrochloric acid; flow-rate, 0.8 ml/min; UV monitor at 210 nm.

In order to determine the retention times and sensitivities of the acids of interest, known amounts of each acid were dissolved in water, injected unto the column of Aminex 50W resin and eluted with 0.001 *N* hydrochloric acid with a flow-rate of 0.8 ml/min.

RESULTS

A typical chromatogram of the acids of interest is shown in Fig. 2. Under the conditions of these experiments as low as 1 μg/ml of each component except acetic acid (100 μg/ml) can be determined.

DISCUSSION

The method used in this report for separating maleic and fumaric acid offers a definite advantage over that of Patel *et al.*, and differs from the latter in that pressure instead of gravity-flow was employed, along with a ten-fold dilution of the eluent. The separation was completed in less than 10 min by the present technique while the method of Patel *et al.* required 3 h 45 min. excluding the time required for titrating the various fractions. Also, by UV monitoring, it is possible to determine most of the acids in concentrations as low as 1 μg/ml.

Although the concentration of the eluent had some effect on the retention times of the various acids, it was not necessary to buffer the solutions. Another desirable feature of this technique is the fact that the column does not have to be regenerated, making it easily adaptable to automation for on-stream analyses.

After a month of laboratory operation no loss in resolution or change in retention time was observed, and no back-washing of the column was necessary.

The wavelength (210 nm) was selected for monitoring the acids of interest, because acetic acid which is the weakest UV absorber of the group has its strongest absorptivity in this region.

The only problem encountered was that of air bubbles being trapped in the UV cell. This was eliminated, however, by de-gassing the eluent. In general, the retention times increased with increased concentration of eluent.

ACKNOWLEDGEMENT

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3 D. J. Patel, R. A. Bhatt and S. L. Bafna, *Chem. Ind. (London)*, (1967) 2110.