

### A Novel Method of using Ion-Exchange Resins

WHEN considering a chromatographic method for separating a complex mixture, it is desirable to choose an adsorbent which functions through only one type of adsorption mechanism. Most adsorbents in use to-day lack this desirable property, so that the displacement chromatographic technique of Tiselius is not always applicable. It is the purpose of this communication to describe a novel chromatographic method of using ion-exchange resins so that only one of two possible adsorption mechanisms associated with their use can function.

Weak organic electrolytes and, in particular, aromatic organic ions can be adsorbed on an ion-exchange resin by a combination of salt linkages and Van der Waals' adsorption forces, if the electrical charge of the resin has the opposite sign to that of the organic ions. Partridge<sup>1</sup> and Davies<sup>2</sup> have recently discussed the deleterious effects arising from the simultaneous operation of these adsorption mechanisms and have shown that a major limitation of ion-exchange resins to-day is their inability to fractionate mixtures containing aromatic molecules.

It is suggested that these difficulties can be resolved if aromatic molecules are adsorbed on a dissociated ion-exchange resin the electrical charge of which has the same sign as the aromatic ions. Under these conditions only the undissociated aromatic molecules can be adsorbed, since the corresponding ions cannot approach the surface against its repulsive electrostatic forces. Any change in pH which dissociates the adsorbed aromatic molecules will result in their desorption.

The use of ion exchange resins in this manner is illustrated by the following experimental observations. Acid dyestuffs, such as Methyl Orange, Fast Red A (Colour Index No. 176), and Chicago Blue (Colour Index No. 518), are adsorbed by the carboxylic resin 'Amberlite IRC-50' in its undissociated state in acid solutions, whereas no adsorption occurs in alkaline regions where the resin and the dyes are fully ionized. Similarly, the basic dyestuff, Methylene Blue, is adsorbed by the polyamine resin 'Amberlite IR-4B' under alkaline conditions where the resin is unionized; but addition of acid completely desorbs the previously adsorbed dyestuff.

In solutions of high ionic strength and suitable pH, ions as well as their corresponding undissociated molecules may be adsorbed on the undissociated resin by the Van der Waals' forces. This difficulty may be avoided by using a resin which is dissociated during the adsorption and desorption cycles, and this procedure ensures the adsorption of only undissociated molecules. For example, the acid dyestuff Methyl Orange is adsorbed by the sulphonic resin 'Amberlite IR-120', under acid conditions in which the resin, but not the dyestuff, is ionized. Complete desorption occurs upon the addition of alkali, which ionizes the adsorbed dye molecules. Similarly, the basic dyestuff Neutral Red (Colour Index No. 825) is adsorbed by the strongly basic resin 'Amberlite IRA-400' under alkaline conditions in which the resin, but not the dyestuff, is ionized. Complete desorption occurs upon the addition of acid, which ionizes the adsorbed dye molecules.

These principles explain many anomalies in the literature, including the recent work of Abrams and Dickinson<sup>3</sup>, who studied the decolorization of sugar solutions with polyamine resins and with the new

decolorizing 'non-ionic' phenolic-type resin, 'Duolite S-30'. When used for decolorizing sugar solutions, these resins can be regenerated by treatment with a small amount of sodium hydroxide. Desorption results from the ionization of the phenolic groups of these resins and the expulsion of the previously adsorbed colouring matter, which is known to be a mixture of weak organic acids.

The use of ion-exchange resins in the manner outlined here will be considered in greater detail from theoretical and experimental aspects in a publication to appear elsewhere.

D. E. WEISS

Division of Industrial Chemistry,  
Commonwealth Scientific and Industrial  
Research Organisation,  
Melbourne.  
March 2.

<sup>1</sup> Partridge, S. M., *Biochem. J.*, **45**, 459 (1949).

<sup>2</sup> Davies, C. S., *Biochem. J.*, **45**, 38 (1949).

<sup>3</sup> Abrams, I. M., and Dickinson, B. N., *Indust. Eng. Chem.*, **41**, 2521 (1949).

### Separation of Carboxylate Ions on the Paper Chromatogram

THE work of Martin and Synge<sup>1</sup> on the separation of amino-acids by partition chromatography on silica gel has led to the application of this method to the separation of other groups of structurally similar compounds. Lester Smith<sup>2</sup> and Ramsey and Patterson<sup>3,4</sup> have separated by this means the straight-chain fatty acids containing one to ten carbon atoms, and Elsdon<sup>5</sup> has put the procedure on a quantitative basis in the case of acetic, propionic and *n*-butyric acids.

Since paper partition chromatography affords an equally effective and even simpler method of separating mixtures of closely related compounds, we have attempted to apply the latter method to the separation of the lower fatty acids, with the ultimate aim of identifying the acids produced in bacteriological culture media. Lugg and Overell<sup>6</sup> succeeded in separating quantitatively mixtures of citric, malic and tartaric acids, using butanol-acetic acid as the mobile phase. The positions of the acids after development of the chromatogram were detected by spraying the dried paper with Bromophenol Blue or Bromocresol Green. The volatility of the lower fatty acids, however, imposes a severe limitation when applying this method to their separation. An attempt was made by Fink and Fink<sup>7</sup> to overcome this difficulty by chromatographing the potassium hydroxamate derivatives prepared from the corresponding methyl esters, afterwards spraying with ferric chloride to ascertain the positions of the salts.

We find that the volatility of the acids can be more easily overcome by conversion into the corresponding sodium salts and separation of the anions with butanol saturated with 1.5 *N* ammonium hydroxide. After drying at 95° C. for five minutes, the paper is sprayed with a suitable indicator solution. Preliminary work has shown that Bromocresol Green (40 mgm. in 100 ml. of water or alcohol, adjusted to blue with sodium hydroxide) reveals the anions as yellow spots and the cations as deep blue spots on a pale blue background. Bromothymol Blue (40 mgm. in 100 ml. water adjusted to blue with sodium hydroxide) gives rise to yellow spots at the positions of the anions and deep blue spots at the positions of the cations on a green background.