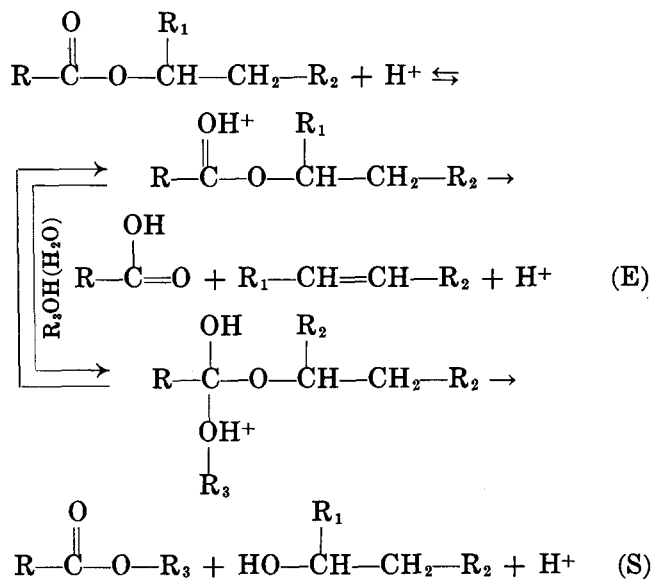


tionary phase per foot of column length (0.01 in. I.D. columns).



Stabilization of polyester stationary phases for gas-liquid chromatography

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► The selection of stationary phases for gas-liquid chromatography at high temperature operation poses many problems. These problems center on the necessity for low vapor pressure, thermal stability, and a high separation factor of the stationary phases. With katharometer detectors the instability of the stationary phase frequently shows itself by the appearance of droplets ("bleed") from the column outlet or, more commonly, by the falling off of column efficiency. With the introduction of very sensitive ionization detectors (1, 2) the bleed is detected long before any physical signs from the column are noticeable. The manifestations are uncontrollable base line drifts and the development of "noise" at a level high enough to mask any peak and render further column operation impractical. Capillary columns (3) with ionization detectors are even more susceptible to stationary phase instability. This is because of their much greater sensitivity and the fact that there is only about 0.1 mg. of sta-

The development of polyester packings (4, 5, 6) has permitted the excellent fractionation of fatty acid methyl esters. However, different batches behave quite variably as regards stability (7). These esters could be expected to have free terminal hydroxyl groups or carboxyl groups. Generally, the residual condensing catalyst, i.e., *p*-toluenesulfonic acid, is also present. With hydrogen ions arising from either the catalyst present or the free carboxyl groups, it seems reasonable that acid-catalyzed ester interchange of the stationary phase within itself, solvolysis (S) with small amounts of water or alcohols in samples or elimination reactions (E) could occur. These reactions would split the polymer and eventually give rise to low-boiling products.

To test the idea that hydrogen ions may be responsible for degeneration of the polymer, alcoholic solutions were treated on an ion exchange resin, Duolite A-4,¹ a weak base. Three hundred g. of polymer (6) prepared from succinic acid, diethylene glycol, and diglycerol (*p*-toluenesulfonic acid as catalyst) was dissolved in 3 l. of 70 per cent ethanol and passed through a Duolite A-4 ion exchange resin in a column 7.5 cm. × 70 cm. About 10 l. of 70 per cent alcohol was used to wash the resin from the column. The alcohol was removed *in vacuo* and the residual oil heated at 50° C and 5 μ. pressure overnight. Columns

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¹ Mention of specific products does not imply endorsement by the U.S. Department of Agriculture over others of similar nature not mentioned.

packed with this material showed very little bleeding and column life was extended markedly.

Columns prepared from stationary phases which were similarly treated, except for passage through the ion exchange resin, showed the instability otherwise regularly observed. However, when a column begins to show deterioration (excessive noise level of the background) it is damaged beyond recovery and should be repacked.

Care should also be taken to remove the acid from packing supports where they are used. It is customary to treat the Celite or C₂₂ brick dust with hydrochloric acid, wash with water, and dry. Some improvement in the supports can be obtained by an aqueous ammonia treatment rather than aqueous sodium hydroxide (8) following the acid and water wash. Afterward the support is carefully washed and dried.

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