

CHROM. 5327

Separation of the four butyl alcohol isomers on a cation-exchange resin column*

Separation of aliphatic C_1 - C_7 alcohols has been reported using gas chromatography (GC) with different columns¹⁻⁶. Higher alcohols have been derivatized and separated by GC^{7,8}. Alcohol derivatives have been separated and identified by both paper and thin-layer chromatography^{9,10}. An enzyme method¹¹ and a nuclear magnetic resonance method¹² have also been used for alcohol analysis and identification. Alcohol derivatives have also been separated by column chromatography^{13,14}. Solubilization chromatography was used to separate C_5 - C_{12} *n*-aliphatic alcohols in acetic acid solution on Amberlyst 15 and A-26 resins¹⁵. A Dowex 50W X2 column was used for chromatographic separations of diastereoisomers of alcohols after conversion to esters¹⁶.

This report describes a method using Dowex 50W X2 (K^+ form) in a column to separate aqueous solutions of C_1 - C_4 aliphatic alcohols with water as the eluant. A carbon analyzer was used to monitor the fractions, and GC was used for final identification of specific alcohols.

Experimental

Column chromatography. A glass column (2.7×148 cm) having a fritted disc as a support was used. The resin, (2.7×143 cm) 200-400 mesh Dowex 50W X2 (K^+ form), was used in all separations without regeneration. Alcohol mixtures (10 μ l each of methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol and 2-methyl-2-propanol, in 1 ml of water) were applied to the column and were eluted with water. The flow rate of elution was 0.5 ml/min and 2.5-ml fractions were collected. The alcohol content of alternate tubes was determined on 20 μ l of solution by a Beckman Carbon Analyzer.

Gas chromatography. A Varian Aerograph 204-1C gas chromatograph with a hydrogen flame detector was used with a Porapak Q column (stainless steel tube, $d = 1/8$ in., $l = 16 \frac{1}{2}$ ft.). The column temperature, initially 125°, was programmed to increase 4°/min to 225°. Helium was the carrier gas at 25 ml/min. 1 μ l of 1% aqueous solution was used to determine the retention time of each alcohol. 20- μ l fractions were injected for analysis and identification.

Results and discussion

Fig. 1 is a gas chromatogram of a mixture containing 10 μ l of each alcohol. It is clear that the peak heights are different because of differences in the densities of the alcohols and in the detector response. This mixture of alcohols was separated on the ion-exchange column, and fractions were analyzed by the carbon analyzer and identified by GC. The latter showed that the alcohols were eluted from the cation-exchange column in the order 2-methyl-2-propanol, 2-propanol, ethanol, methanol, 1-propanol, 2-butanol, 2-methyl-1-propanol, and 1-butanol. The first major elution peak contained a partially separated mixture of 2-methyl-2-propanol, 2-propanol, ethanol, and metha-

* Reference to a company or product name does not imply approval or recommendation of the product by the U.S. Department of Agriculture to the exclusion of others that may be suitable.

anol. The second major peak contained 1-propanol and 2-butanol. Only 2-methyl-1-propanol and 1-butanol were separated in pure form. It should be possible by increasing the length of the column to achieve complete separation of the component alcohols; SPITZ *et al.*¹⁰ separated diastereoisomers of esters with a 10000-cm column.

Fig. 2 shows an elution diagram obtained with the carbon analyzer of the sepa-

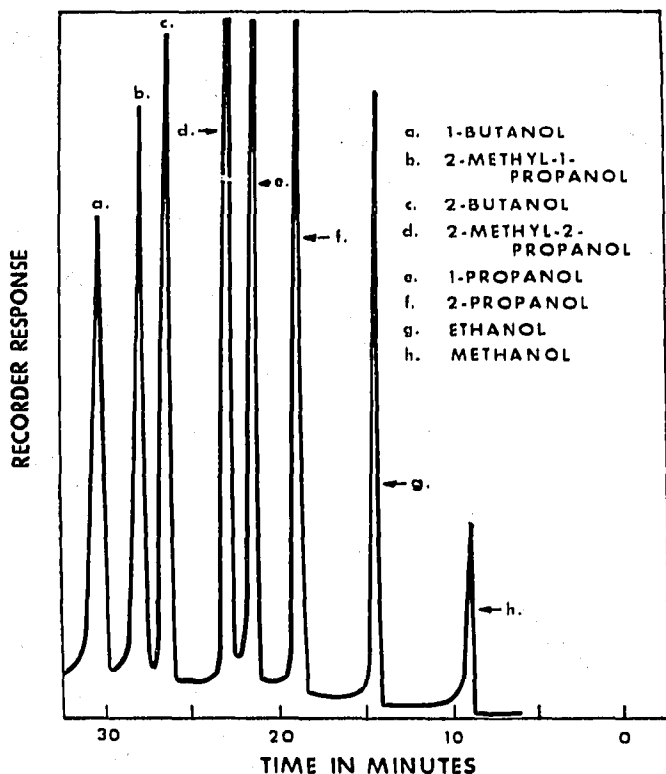


Fig. 1. Gas chromatogram of a mixture of C_1 - C_4 aliphatic alcohols.

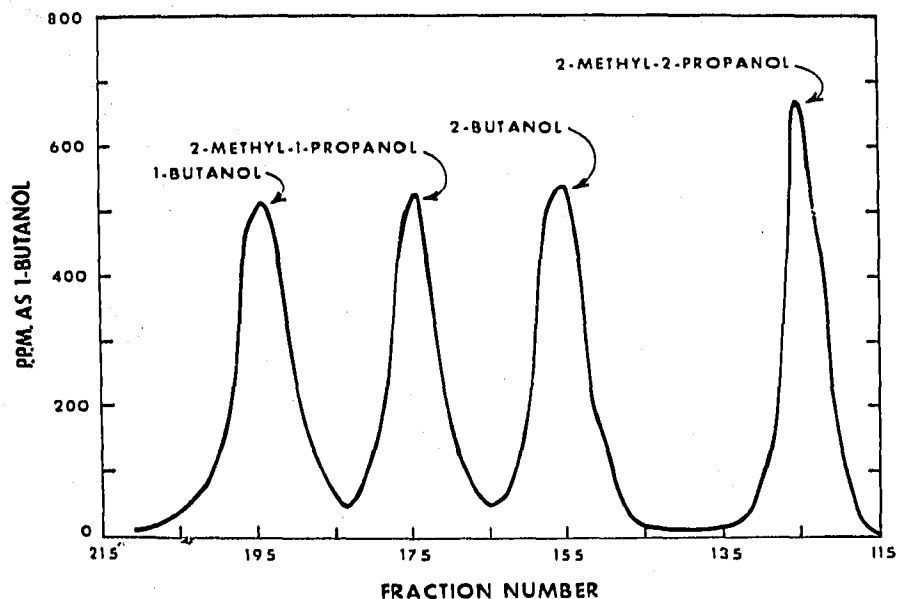


Fig. 2. Elution diagram of the four butyl alcohols separated on a cation-exchange resin column analyzed by a carbon analyzer.

ration on the cation-exchange column of the four butyl alcohol isomers in an aqueous mixture. The four-carbon alcohols (2-methyl-2-propanol, 2-butanol, 2-methyl-1-propanol, and 1-butanol) were eluted and separated quantitatively by column chromatography as described. GC analysis of the fractions showed that separations were complete, and the peaks defined by analysis with a carbon analyzer contained only that particular aqueous alcohol. The baseline regions between the peaks contained no alcohol but had a small carbon content due to atmospheric carbon dioxide in the eluting water. It is noteworthy that the separation of the four-carbon alcohols occurred in the same order on both the GC and the ion-exchange columns.

An explanation of how cation-exchange resins may function to separate non-ionic materials has been described by WALKER AND SAUNDERS¹⁷. For the separation of aliphatic alcohols on a cation-exchange column, at least two factors must be considered — the size and the shape of the hydrated molecule. In the case of the four butyl alcohol isomers, the tertiary alcohol has a size-shape factor such that it diffuses more slowly into the resin pores and consequently passes through the column first, but because 1-butanol passes most easily into the pores, it is the last to be eluted.

In comparison to sugars on this cation-exchange resin column, the aliphatic C₁-C₄ alcohols move more slowly with the result that sharp separations of these aqueous alcohols from pentoses and higher sugars can be made.

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