

GAS CHROMATOGRAPHIC SEPARATION OF C₁ TO C₅ ALCOHOLS

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ABSTRACT

A gas chromatographic method for the separation of C₁ to C₅ alcohols using Tide as the column packing is offered.

The method is rapid, reproducible and shows a high degree of specificity for the alcohols studied. It is shown that complex alcohol mixtures can be readily separated and that quantitative analysis of these mixtures should be possible.

Tide should also be useful for the separation of similar materials and for use as a solid support for many liquid substrates.

Mixtures of short chain alcohols are usually determined by infrared spectrophotometric methods. The results obtained are subject to the usual restrictions associated with mixtures of three or more constituents. That is, the analytical absorption bands used must be resolvable and the mixture must be free of interfering materials. In addition, the absorption calculations can be cumbersome and assume increasing complexity as the number of components increases. Finally, comparatively large samples are required for the analysis. For these reasons, a more direct method is preferable.

Recently, Porcaro and Johnston used a gas chromatographic method for the identification of primary amyl alcohols. For a stationary phase they used the commercial detergent Tide, which can best be described as a mixture of alkylary sulfonates. The development to be discussed here involves an extension of their work to other alcohols of short chain length.

EXPERIMENTAL

Apparatus: A Model 8200 Dynatronics Instrument Corporation chromatograph, coupled to a General Electric, 0 - 1 millivolt, 1 second full-scale response recorder was used.

Column Preparation: Tide was heated in a vented drying oven at 110°C for 12 hours to evaporate the moisture and drive off the perfume. A 40/60 mesh sample of this material was packed in 1/4 inch O. D. copper tubing, 8 feet in length and the column was conditioned at 200°C with the carrier gas flowing for a period of five hours.

Selection of Column Operating Conditions: The operational parameters for the separation were optimized, using nitrogen as the carrier gas, by measuring the retention times as a function of the linear carrier gas velocity μ_g at several temperatures. The number

of theoretical plates (N) and the Height equivalent to a theoretical plate (H.E.T.P.) for each combination of temperature and carrier gas velocity were calculated using equations (1) and (2) respectively.

$$\text{Equation 1: } N = k \left[\frac{t_x}{P_w} \right]^2$$

$$\text{Equation 2: } \text{H.E.T.P.} = \frac{L}{N}$$

Where:

- k = constant depending on the column length, packing etc.
- t_x = time, in minutes, from the air peak to sample peak.
- P_w = sample peak width at the base line.
- L = the column length in inches.

The H.E.T.P. was plotted as a function of μ_g for each temperature used and the optimum μ_g were ascertained from these plots.

Figure 2-a depicts typical plots in which carrier gas velocities of 75 and 102 inches per second were selected as the optimum for the respective temperatures indicated. Subsequently, the H.E.T.P. at the optimum μ_g for each temperature was plotted versus the temperature to ascertain the best operating temperature.

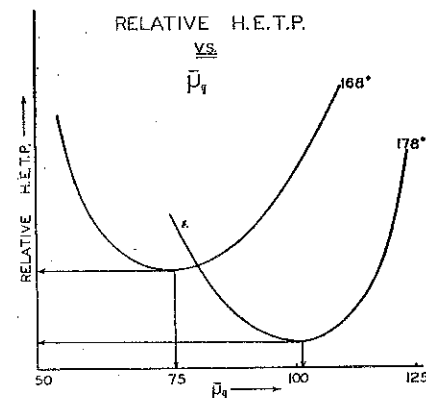


FIGURE 2-a.

Figure 2-b is illustrative of a typical result for selection of the optimum temperature. For these particular separations the optimum temperature was found to be 162°C.

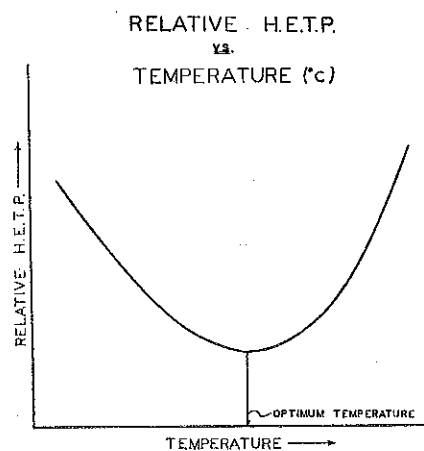


FIGURE 2-b.

The general instrument parameters used were selected on the basis of these experiments and are listed.

Temperatures—162°C

Gas Flow—52 cc/min at the outlet.

Sample Sizes—0.5 μ l

Chart Speed—1 inch/minute

Detector Current—145 milliamps

Detectors—Tungsten filaments.

RESULTS

Reagent grade alcohols were used for calibrating the elution times for the C₁ to C₆ alcohol series studied. In addition, several equivolume synthetic mixtures of these alcohols were prepared to further test the utility of the separative procedure.

Table 1 tabulates the relative retention times for the series using the retention time of tertiary butyl alcohol as the reference. It is interesting to note that only methyl and n-propyl alcohol exhibit qualitative interference under the conditions used. In other instances, there is some quantitative interference but none that cannot be obviated by the usual corrective methods.

TABLE I
RELATIVE RETENTION TIMES FOR C₁ TO C₆ ALCOHOLS
(Tertiary Butyl Alcohol as Reference)

Alcohol	Relative Retention Time	Interference
Methyl	1.40	n-Propyl
Ethyl	1.31	
Isopropyl	1.06	
n-Propyl	1.40	Methyl
n-Butyl	1.76	
sec-Butyl	1.35	
tert-Butyl	1.00	
Isobutyl	1.67	
n-Amyl	2.79	
Isoamyl	2.61	
sec-amyl	1.84	
tert-amyl	1.51	

Figures 5 through 8 illustrate the degree of separation observed for several of the equivolume synthetic mixtures.

Subsequent experiments have shown that better resolution can be obtained by reduction of the sample size with a corresponding increase in the amplifier gain. The limiting factor here is the noise-level that can be tolerated.

DISCUSSION

Tide as a stationary phase offers a rapid and reliable means for the gas chromatographic identification of short chain alcohols. The chromatograms obtained indicate that quantitative determinations are feasible in many of the instances studied. It is likely that Tide will also be useful for the separation of many other materials. In fact, it has been used for the separation of both hydrocarbons and sulfur compounds by Desty and Harbourn² and for pyridines by Decora and Dinneen³. Its comparatively low cost and the fact that it should be readily usable as the solid support for many liquid substrates should be inducements to investigate its utility for other separations.

LITERATURE CITED

1. Porcaro, P. J., Johnston, V. D., *Anal. Chem.* **33**, 361 (1961).
2. Desty, D. H., Darbourn, C. L. A., *Anal. Chem.* **31**, 1965 (1959).
3. Decora, A. W., Dinneen, G. J., *Anal. Chem.* **32**, 164 (1960).

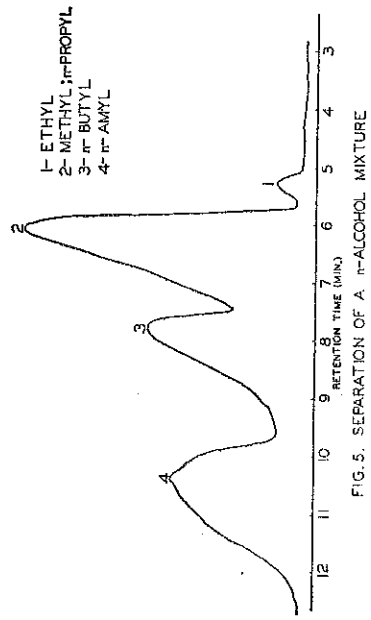
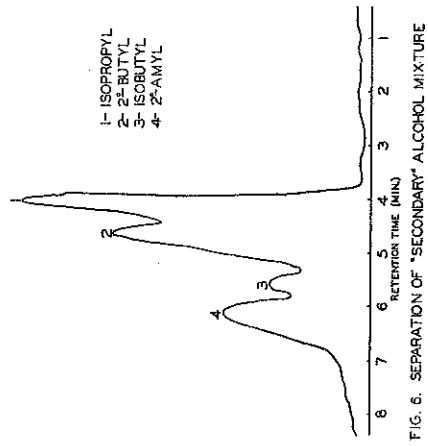
FIG. 5. SEPARATION OF A *n*-ALCOHOL MIXTURE

FIG. 6. SEPARATION OF "SECONDARY" ALCOHOL MIXTURE

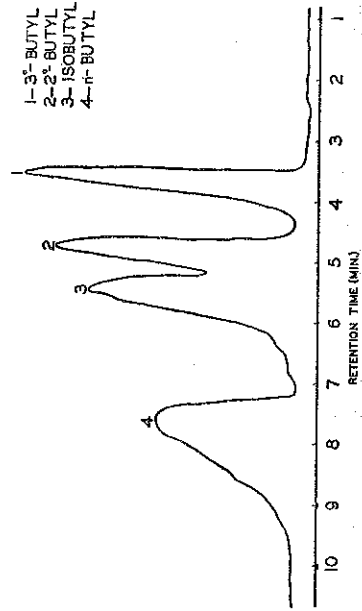


FIG. 7. SEPARATION OF BUTYL ALCOHOLS

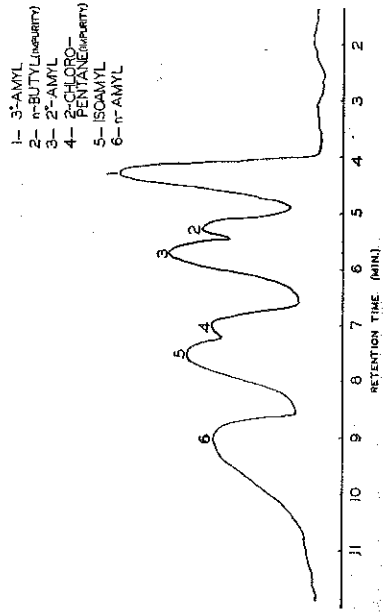


FIG. 8. SEPARATION OF AMYL ALCOHOLS