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A Capillary Gas Chromatographic Method for the Characterization of Linear Fatty Alcohols

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A capillary gas chromatography (GC) method for the analysis of fatty alcohols is described. The method can separate fatty alcohols, fatty acids, hydrocarbons and fatty acid methyl esters containing 6 to 22 carbons, as well as fatty-fatty esters to 40 or more carbons. The precision of the method is better than 2% (rsd); accuracy, based on analyses of a standard mixture and a spiking/recovery experiment, is better than 3% (relative difference between known and measured). A calculated hydroxyl value based upon the GC data agrees well with the titrimetric hydroxyl value.

Gas chromatography is undoubtedly the most important analytical technique for the characterization of fatty alcohols (C_6 to C_{18} alkanols). The technique provides chain length and purity information, and hydroxyl value and compositional data, all at the same time. However, most published methods for the GC analysis of fatty alcohols utilize packed columns which do not provide sufficient resolution for many applications. Some of the liquid phases which have been reported include silicones such as SE-30 (1,2); OV-1 (3); OV-7 (2); OV-17 (3,4); OV-225 (3,4); Silar-10C (2,4); Silar 5-CP (2,5), and glycols such as PEG 4000 (6) and PEGS (7). In many cases the sample is analyzed as an ester or silyl ether derivative (5). The method in the U.S. Pharmacopeia/National Formulary (8) for cetostearyl alcohol uses a methyl silicone gum.

None of these methods provides the high resolution of a modern programmed temperature capillary column technique. The benefits of such an approach include separation of alcohols, methyl esters, hydrocarbons and related fatty materials. Korhaven (9,10) has demonstrated the separation of alcohols and several kinds of esters using SE-30 and OV-351 wall-coated open tubular capillary columns.

We report here a capillary GC method for industrially important linear fatty alcohols which resolves most of the compounds likely to be found in such materials. As an added benefit the method can be used to calculate the hydroxyl value.

EXPERIMENTAL

Instrumentation and operating conditions. GC conditions are summarized in Table 1. Three different GC's were used during the course of this work; results were comparable. The DB-1 capillary column had about 50,000 theoretical plates based on the "peak width at half height" approximation (11).

To establish maximum sensitivity of the flame ionization detectors, injections of octadecanol were made at different hydrogen to air ratios. Air levels of 300–500 ml/min at 50 ml/min in 5 ml/min increments were tested while the hydrogen was varied from 25 ml/min to 45 ml/min in 5 ml/min increments. Maximum peak area for the octadecanol sample was obtained at the gas flows listed in Table 1.

Virtually identical results were obtained with either helium or nitrogen as carrier gas.

The injection port temperature initially was set at 360 C to ensure the vaporization of high molecular weight species such as the fatty-fatty or wax esters (e.g. stearylstearate). Subsequent experiments demonstrated equally good results with a lower injection temperature (280 C). In fact, at 360 C there appeared to be some

TABLE 1

GC Conditions Used for the Analysis of Fatty Alcohols

Instruments	P-E 910 (Perkin-Elmer, Norwalk, Connecticut) H-P 5840, H-P 5880 (Hewlett-Packard, Avondale, Pennsylvania)
Injection port temperature	280 C
Flame ionization detector (FID) temperature	360 C
Column oven temperature	From 75 C to 300 C at 10 C/min, then 300 C for 5 min
Air flow to FID	400 ml/min
Hydrogen flow to FID	30 ml/min
Carrier gas flow	1 ml/min
Split ratio	100:1
Carrier gas	Helium or Nitrogen
Column	15 m × 0.24 mm ID fused silica with 0.25 micron coating of DB-1 (J&W Scientific, Rancho Cordova, California)
Attenuation	16

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degradation of the silylethers of the alcohols to unknown species.

Sample preparation. Pure standards of alcohols, hydrocarbons, etc., were purchased from Polyscience Corp. (Niles, Illinois) and NuChek Prep (Elysian, Minnesota). Chloroform was from Fisher Scientific (Fairlawn, New Jersey). Purity of the standards was determined by chromatographing each one individually at the maximum level consistent with instrument linearity (found experimentally to be 30 mg/ml). The standards were between 97.5% and 99.5% pure. The calculation was in area percent assuming a unity response factor for all peaks. In subsequent calibration work the above determined purities were used for each alcohol. The responses of hexanol, dodecanol, hexadecanol and octadecanol also were checked versus an internal standard, alphahydroxypalmitate. The response of each was 0.77. This figure was used later to confirm that area percent calculations using a unity response for all fatty alcohols were valid.

The split ratio of 100:1 was selected along with a 1 μl injection. At an attenuation of 16 and a sample weight of 30 mg/ml this split afforded an optimum chromatogram as far as sensitivity and linearity were concerned.

Hexanol was used to determine the starting temperature of the oven program. The highest starting oven temperature that allowed baseline separation of hexanol from chloroform was found to be 75 C under the above conditions. No initial temperature hold time was necessary. Temperature program rates of 8, 10 and 15 C/min were tested after establishing the initial temperature. All three rates provided excellent separation of C_6 through C_{20} alcohols. However, 10 C/min was selected because some hydrocarbons, methyl esters and fatty acids were not separated from the alcohols at a 15 C/min program. The 8 C/min rate program offered no separation advantage over the 10 C/min rate. Under the above GC conditions the C_{20} fatty alcohol eluted at approximately 250 C, but we extended the final temperature to 300 C to ensure complete elution of all the fatty-fatty esters. A final temperature hold time of five min allowed the elution of C_{40} fatty-fatty ester.

Hydroxyl value (HV). The wet hydroxyl value method used was similar to those of U.S.P./N.F. (8) and AOCS (12) except that we used acetyl chloride instead of acetic anhydride. That change permitted incubation at 60 C for 20 min rather than one hr at reflux temperatures and gave identical results.

The hydroxyl value also was calculated from the capillary GC results by multiplying the theoretical HV for each chain length by its respective area percent, summing, and dividing by 100. This approach was similar to calculating a weighted average of theoretical HV's.

RESULTS AND DISCUSSION

Resolution. Figure 1 is a chromatogram of a mixture of alcohols, methyl esters, hydrocarbons, fatty acids and fatty-fatty esters prepared from the standards. Baseline separation was obtained in practically all cases for all the

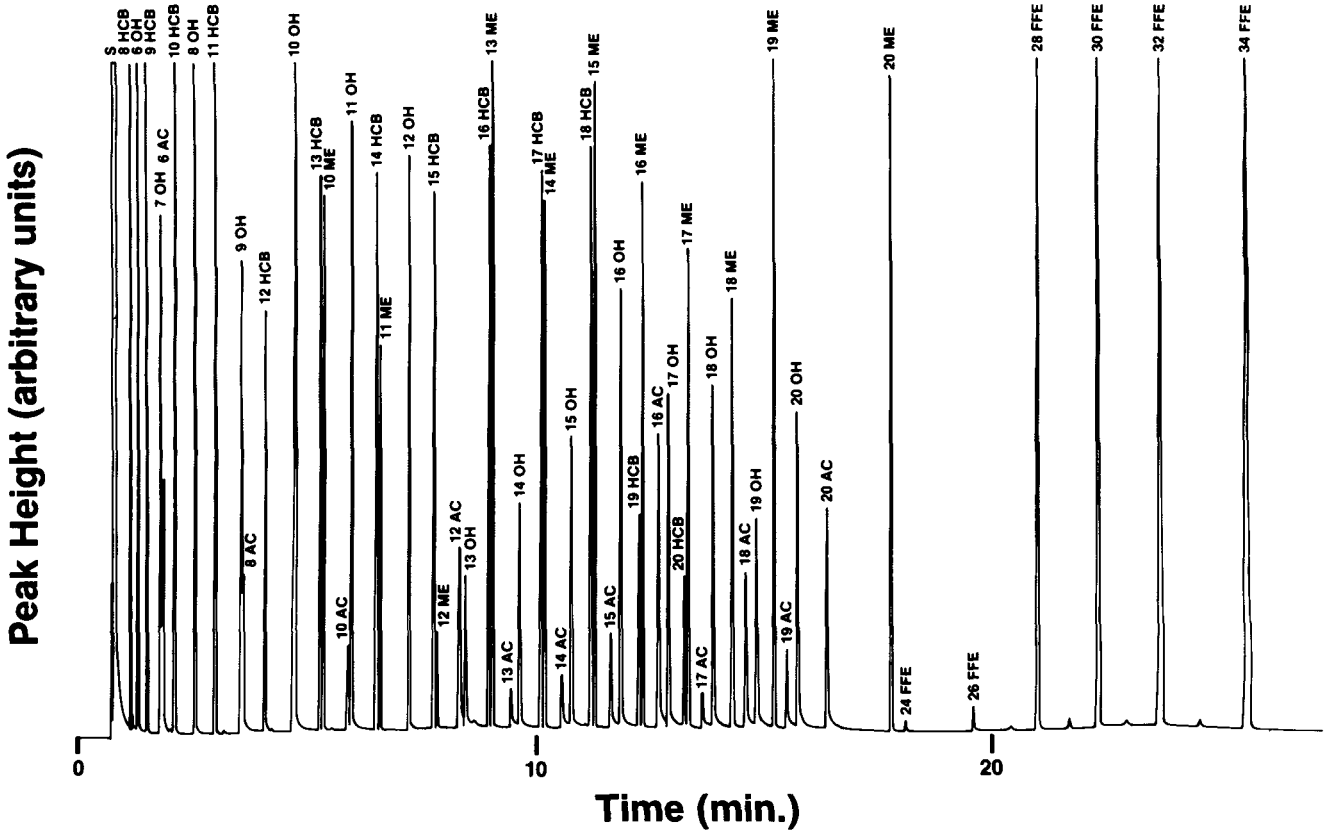

FIG. 1. Capillary chromatogram showing the separation of C-8 to 20 hydrocarbons (HCB), C-6 to 20 alcohols (OH), C-6 to 20 fatty acids (AC), C-10 to 20 fatty acid methyl esters (ME) and C-24 to 34 fatty-fatty esters (FFE) in chloroform (solvent, S). For conditions used, see Table 1 and text.

TABLE 2

Accuracy and Precision of Capillary GC Method

A. Standard Mix

Alcohol	Actual (weight %)	Mean of 6 injections (area %)	Standard deviation (area %)	Relative S.D. (%)	Difference between actual and measured (%)
Lauryl	25.51	24.87	0.39	1.6	0.64
Myristyl	24.65	24.91	0.04	0.2	−0.26
Cetyl	24.44	25.23	0.18	0.7	−0.79
Stearyl	25.34	25.00	0.21	0.8	0.34

B. Recovery of Octadecanol Added to a Coconut Alcohol

Stearyl alcohol added (wt%)	Mean stearyl alcohol concentration (wt%)	Range of measurements (wt%)	Standard deviation (wt%)	Relative SD (wt%)
65.5	64.8	63.0 to 66.4	1.2	1.8

TABLE 3

Comparison of Calculated and Wet Hydroxyl Values for Several Industrially Important Alcohols[a]

Alcohol type	Calculated value[b]	Wet value[b]	Difference
Coconut	285	285	0
Tallow	211	210	1
Stearyl	207	205	2
Cetyl	220	221	−1

[a]Results in this table were selected randomly from 30 data points and were typical of all data points. The "t" test for paired measurements (95% confidence level) did not reject the hypothesis that the results were the same.

[b]Results are to the nearest whole number.

species. However, there are some limitations to this method.

Peak shapes of the fatty acids are poor unless they are converted to either trimethylsilyl ethers or methyl esters. Unsaturated acids such as oleic, linoleic and linolenic do not give good separation on this column and are possible interferences in the analysis of fatty alcohols.

Baseline separation of methyl oleate, methyl linoleate and methyl linolenate is not possible unless the method's temperature program rate is lowered. Under the conditions of the method these unsaturated methyl esters are not baseline resolved from C_{17} alcohol.

Unsaturated alcohols are not well separated from the corresponding chainlength saturated alcohol.

Accuracy and precision. Accuracy and precision data for this method are summarized in Table 2. Part A of the table is data for the replicate analysis of a standard mix of alcohols. The average relative standard deviation across the chainlengths is 0.8%; the average difference between the actual and measured percents is −0.02. Part B of Table 2 shows data for the replicate analysis of a commercial coconut-derived (12 to 16 carbon) alcohol to which stearyl alcohol has been added. The recovery of the added alcohol is 98.9%. Stated differently, because the difference between the percents added and found (0.7%) is less than the standard deviation of the analysis (1.2% in this experiment), we may conclude that the method has acceptable accuracy. This is further proof that response factors for the alcohols are the same.

Hydroxyl value. One of the benefits of this capillary GC method is that one can calculate the hydroxyl value from the chromatogram and get a value equivalent to the titrimetric procedure, another measure of the method's accuracy (see Table 3). This eliminates the need to perform the titrimetric hydroxyl value determination for those laboratories which normally use HV as a product or raw material specification.

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