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Gas-Liquid Chromatography of Fatty Derivatives. III. Analysis of Fatty Amines[1]

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GAS-LIQUID chromatography has been shown to be an effective tool in the analysis of certain fatty derivatives (10,11). Its effectiveness in the analysis of fatty alcohols and amines has been hampered however by unsymmetrical peaks which interfere with area measurements and resolution. The asymmetry which occurs is evidenced by the presence of leading, tailing, or both and is generally encountered with the more highly polar molecules. These deviations from the desired Gaussian, or bell-shaped character, result primarily from some mode of interaction between the components being chromatographed and the liquid stationary phase and/or stationary support.

Knight (9) has shown that highly polar compounds can be chromatographed with a minimum of tailing if the carrier gas is first allowed to become either partially or completely saturated (depending on the analysis) with a volatile component. The polarity and partition isotherm of this component should be somewhat similar to the molecules being analyzed. Peak symmetry and resolution were thus improved. Johns (7) reduced the tailing of certain polar molecules on silicone (DC-550) columns by the addition of small amounts of polar solvents.

James and Martin (5) employed Celite 545, treated with methanolic sodium hydroxide, in the estimation of ammonia and methylamines, and James described the separation of amines containing 1 to 12 carbon atoms (4). Decora and Dineen (2) used a porous inorganic solid prepared from a commercial detergent and treated with potassium hydroxide for the separation of basic nitrogen compounds of pK_a range from 6 to 11 including n-hexylamine.

The procedures reported herein represent an application of the principles described in above techniques. These methods were independently developed in separate laboratories but because of similarity are being combined in one report. The described procedures permit the separation and quantitative determination of saturated fatty amine samples of carbon-chain length ranging from C_8 through C_{22}, using nonpolar liquid substrates on either Chromosorb W or Chromosorb solid supports previously treated to reduce their adsorptivity.

Experimental

Preparation of Solid Support. Procedure A[2]: Chromosorb W, 40–60 mesh, was initially deactivated by washing with concentrated hydrochloric acid and then with water to remove the residue acid, followed by heating at 200°C. for 2 hrs. After screening to 40–60 mesh 15.5 g. of the support were poured into a solution of 1.5 g. of potassium hydroxide in 80 ml. of methanol. After the methanol was removed, the support was again heated at 200°C. for 2 hrs., cooled, and poured into 3.2 g. of Apiezon L, which was dissolved in 60 ml. of methylene chloride. The solvent was removed by evaporation, packing material was screened, and the 40–60 mesh material was heated in a vacuum oven 1 hr. at 60°C. before being used to pack the column.

Procedure B[3]: Chromosorb, 30–60 mesh, was first acid-washed over-night with concentrated hydrochloric acid diluted 1:1 with water. The Chromosorb was then repeatedly washed with distilled water until free of acidity and finally oven-dried at 150°C. over-night. Forty grams of the support were treated with 200 ml. of a 5% solution of potassium hydroxide in methanol for a period of 2.5 hrs. The suspension was transferred to a sintered glass funnel, and the solvent was removed with suction. The support was then rinsed with 200 ml. of fresh methanol and finally with 100 ml. of chloroform. The support was then air-dried.

Twenty grams of Dow-Corning High Vacuum grease were washed, using the pretreatment procedure described by Cropper and Heywood (1). The washed grease was dissolved in sufficient ethyl acetate, and to the solution was added the previously deactivated support. The solvent was slowly removed with continual agitation, and the packing was finally allowed to air-dry. The packing was flushed with nitrogen at 200°C. for 3 hrs. before being used to pack a column.

Instrumental Conditions. Procedure A, using Apiezon L: the gas-liquid chromatographic apparatus used in this work was described previously (10,11). A 2-ft. column (stainless steel, ¼ in. O.D.) was packed with the Apiezon L substrate and equilibrated in the instrument for a few hours at 220°C.

Fatty amines were obtained by careful fractional distillation of commercially available materials.[4] The purified amines in Table I were run at 225°C. both individually and in mixtures using 250 ma. current, 0.002–.005-ml. samples, and a helium flow rate of 55 ml./min.

The symmetry of the peaks, as shown in Figure 1, is as good as that observed for the higher α-olefins

[1] The application of gas chromatography described in this paper was conceived and developed independently and simultaneously in the respective research laboratories of these two companies.

[2] Archer-Daniels-Midland Company procedure.
[3] Atlas Powder Company procedure.
[4] Adogens, Archer-Daniels-Midland Company.

TABLE I

Fatty Amine Standards [a]

Homologue	B.P.,°C.	G L C analysis
n-Octylamine	178–179	99.0% C_8
n-Dodecylamine	139–143/20–21 mm.	99.6% C_{12}
n-Tetradecylamine	96/0.15 mm.	98.0% C_{14}, 2.0% C_{16}
n-Hexadecylamine	157/4 mm.	97.6% C_{16}, 2.4% C_{18}
n-Octadecylamine	139/0.2 mm.	99.0% C_{18}, 1.0% C_{16}
n-Eicosylamine	180/1.5 mm.	89.9% C_{20}, 3.7% C_{22}, 4.8% C_{18} [b]
n-Docosylamine	200/1.5 mm.	85.4% C_{22}, 14.6% C_{20}

[a] Employed for the work, using the Apiezon L column.
[b] Unidentified components accounted for the remainder.

and hydrocarbons (10), indicating negligible absorptivity by the solid support.

Procedure B, using silicone grease: the apparatus employed was a Podbielniak Chromacon, Model 9580. A 48-in. column (copper, ¼ in. O.D.) was packed with the silicone grease substrate, using vibration to insure uniformity within the column.

The purified fatty amines used for this study were supplied to us by the Research Division of Armour and Company. The individual amines were checked for purity by the gas chromatographic technique at 177°C. by using a bridge current of 245 ma. and a helium flow rate of 58 ml./minute. Sample volumes were 0.001 ml.; dilution of the amines with an inert solvent was employed if necessary. Recordings were made with 1 millivolt, full-scale recorder attenuated by a factor

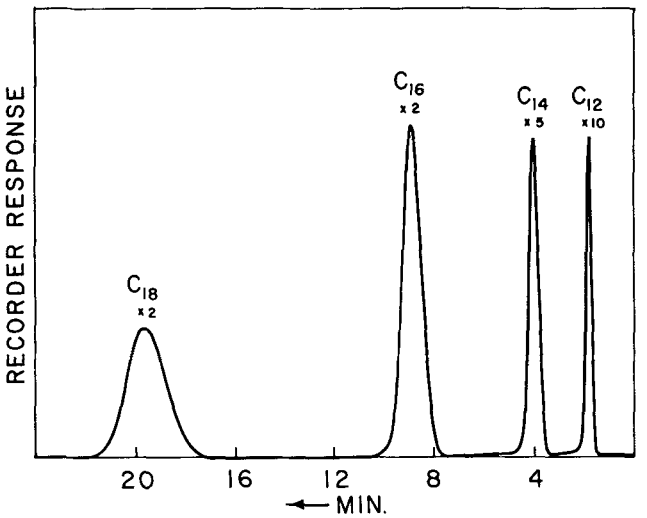

FIG. 1. Chromatogram of fatty amines, Mixture 1, on Apiezon L, using treated Chromosorb W.

of 2x or 5x. Criteria for purity was full-scale deflection for the major component; only trace amounts of other substances were present. With this procedure all amine samples were better than 99% pure.

Figure 2 shows a typical separation of n-alkyl amines ranging from C_8 through C_{18} on silicone grease substrate. A small amount of n-butyl amine was employed to dilute the sample so that column overload would not occur with any individual fatty amine.

Figure 3 shows a typical analytical curve obtained from a commercial hexadecylamine sample. Since no amines lower than C_{12} were anticipated, a 35-in. column was used. The helium flow rate was 40 ml./minute. In addition to the four known amines, trace amounts of at least six other components are seen. This 35-in. column is now being routinely employed for analysis of fatty amine samples of the type shown in Figure 3.

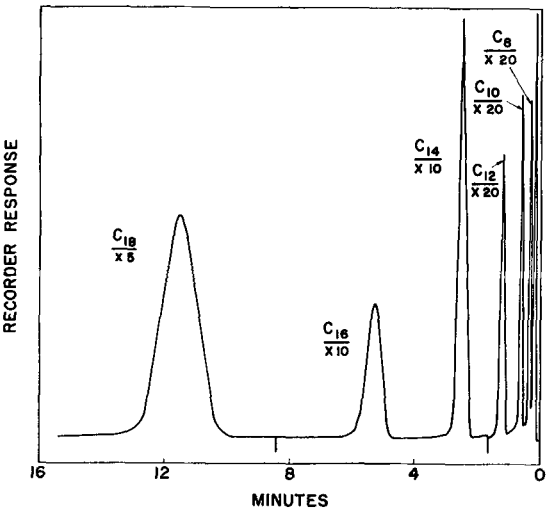

FIG. 2. Chromatogram of fatty amine sample on silicone grease, using treated chromosorb.

Quantitative Analysis of Amine Mixtures. For a quantitative analysis of mixtures, peak area calibration was necessary since it was found that the actual compositions of known mixtures were not exactly represented by peak areas. Relative sensitivity factors ($K^{w/n}$) were determined for C_{12}, C_{14}, C_{16}, and C_{18} amines by determining the area response for separate components on an equal-weight basis and assigning a factor of 1.000 to hexadecylamine. The measured area for each component over the corresponding $K^{w/n}$ value gives the calculated area.

$$\frac{A_1}{K^{w/1}} + - - - - + \frac{A_4}{K^{w/4}} = \text{S.C.A.} \quad (6)$$

The analysis for single components is obtained by

$$\frac{A_1/K_1^w}{\text{S.C.A.}} \times 100 = \text{percentage by weight of component 1, where S.C.A. equals the sum of the calculated areas.}$$

Table II shows the $K^{w/n}$ factors obtained from known amine mixtures on both Apiezon L and on Silicone Grease columns. The data indicate that the relative responses per gram among the fatty amines

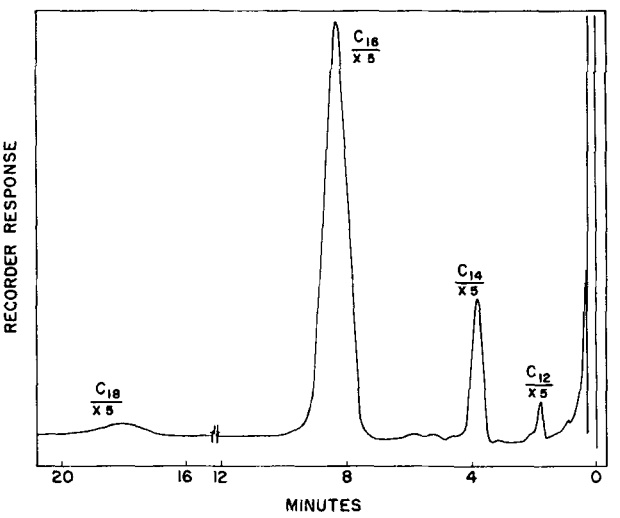

FIG. 3. Typical chromatogram of a commercial hexadecylamine sample on silicone grease, using treated chromosorb.

TABLE II

Relative Sensitivity Factors for Fatty Amines

Amine	Response per gram	
	Apiezon L	Silicone Grease
Octylamine	.....	1.126
Decylamine	.....	1.093
Dodecylamine	1.068	1.063
Tetradecylamine	1.033	1.036
Hexadecylamine	1.000	1.000
Octadecylamine	0.946	0.946

approximates a linear function of molecular weight. This is in agreement with other available data on homologous series of fatty components (3,8).

Results. The results of the analyses of three known mixtures are shown in Table III. Two of the samples were run by employing the Apiezon L column, and one was run by using the Silicone Grease column. In all three mixtures the calculated area percentages are in good agreement with known sample composition.

TABLE III

Analysis of Known Mixtures of Amines

Amine	Mixture 1 [a]		Mixture 2 [a]		Mixture 3 [b]	
	Known wt., %	Determined wt., %	Known wt., %	Determined wt., %	Known wt., %	Determined wt., %
C_{12}	29.3	29.5	21.9	21.8	30.0	30.3
C_{14}	27.2	27.0	28.8	28.8	30.0	29.6
C_{16}	22.7	23.0	24.5	24.8	40.0	40.1
C_{18}	20.8	20.5	24.8	24.6	.....	.....

[a] Apiezon L column.
[b] Silicone Grease column.

Saturated fatty alcohols may also be run on the Apiezon L column under the same conditions as the corresponding fatty amines, and the symmetry of the peaks is comparable. No quantitative data is yet available concerning fatty alcohol mixtures.

The limiting temperatures of the Apiezon L column when used for the separation of both amines and alcohols appears to be 230°C. Above this temperature the liquid substrate deteriorates, but at 225°C. the column is stable for relatively long periods of time.

No deterioration has been observed with the Silicone Grease column when operating at temperatures in the range of 175–180°C. Preliminary data indicate that the life expectancy of a column prepared with silicone grease on treated Chromosorb is shorter than one prepared by using a support phase which is not pretreated to reduce its adsorptivity.

Summary

The separation of fatty amines has been carried out with nonpolar substrates on solid supports of Chromosorb and Chromosorb W, which were previously treated with potassium hydroxide to overcome adsorptivity. In this manner well-resolved symmetrical peaks are obtained. Untreated supports give peaks which trail and prohibit precise quantitative measurements. Both Apiezon L on Chromosorb W and Silicone Grease on Chromosorb have proved effective, the latter at 176°C. and the former at 225°C. Relative detector sensitivity factors have been determined for the amines C_8 to C_{18}, thus permitting accurate analyses. The relative response for primary alkyl fatty amines is a linear function of molecular weight.

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Acidolysis of Vegetable and Marine Oils with Phthalic Acids

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THE CONVERSION of vegetable and marine oils to partial esters by alcoholysis with polyhydric alcohols is a process that is used extensively in the manufacture of oil-modified alkyd resins. Acidolysis is a term that describes a similar alkyd manufacturing process in which oil is heated with a dibasic acid at high temperature to obtain an exchange reaction and liberation of monobasic acids from the oil. Both processes have the same purpose, that is, to change the neutral triglyceride oils into compounds that can be esterified with the other alkyd components to form an homogeneous oil-modified alkyd resin. It is the purpose of this paper to present some data on the reaction of triglyceride oils with the isomeric phthalic acids and the conversion of acidolysis products to alkyd resins. Orthophthalic acid dehydrates to the anhydride when heated, but the other two isomers, isophthalic and terephthalic acids, are heat-stable and readily react with oils at elevated temperatures.

Acidolysis Reaction

Procedures. All experiments were conducted in a 5-liter, four-neck, round-bottom flask equipped with stirrer, thermocouple, nitrogen gas inlet, and reflux condenser. The condenser contained a special baffle-type of packing and was heated with boiling water in the jacket; this arrangement permitted rapid heating without loss of glycerol during esterification. The flask was heated with an electric mantle. Alkyd-grade nonbreak and alkali-refined oils, and commer-