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The Determination of Alcohol and Ether Sulfates and Their Respective Alkyl Carbon Distributions in Detergent Formulations by Gas Chromatography

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ABSTRACT

Four fractions, isolated by the procedure presented in a previous paper, are analyzed by gas chromatography to obtain additional information about the formulation. The alkyl homolog distribution of ethoxylated alcohol nonionic is determined by the gas chromatography (GC) analysis of the resultant alkyl iodides (RI-FNI) produced by the previously reported procedure. The relative ratio of alcohol sulfate to ethoxylated alcohol sulfate is determined by the GC analysis of the combined acid-hydrolyzed products of these two active ingredients. The alkyl homolog distributions of the alcohol sulfate (AS) and ethoxylated alcohol sulfate are then individually calculated after GC analysis of the resultant alkyl iodides produced from the two ingredients by the previous procedure. The source of the original alcohol reactants can often be identified by the characteristic alkyl homologs which are produced by the presented techniques.

INTRODUCTION

In a previous paper (1) Hoyt described the isolation of up to four fractions from a single detergent formulation. This paper describes the subsequent gas chromatographic analyses of the following fractions (Fig. 1): *Free Nonionic (FNI)* contains all ethoxylated alcohols (nonionic) and any unsulfated alcohols and/or ethoxylated alcohol-free oils which were present in the neutral form in the detergent; *Acid-Hydrolyzed Nonionic (AHNI)* contains all alcohols and ethoxylated alcohols which were present in the original detergent as alcohol sulfate (AS) and alcohol ether sulfate (AES) salts; *Alkyl Iodide (RI-FNI)* contains the alkyl groups from the alcohols and/or ethoxylated alcohols present in the FNI fraction, converted to their corresponding iodides by *Hydroiodic Acid* (HI) cleavage during the ethylene oxide (EO) determination; *Alkyl Iodide (RI-AHNI)* contains the alkyl groups from the alcohols and/or ethoxylated alcohols present in the AHNI fraction, also converted to the corresponding iodides by HI cleavage during the ethylene oxide determination.

Analyses of these fractions by gas chromatography (GC) can provide the following information about the components of the formulation: (a) the carbon-number distribution and average molecular weight of the alcohol portion of the nonionic; (b) the ratio of AS to AES; (c) the carbon number distribution and average molecular weight of the AS; (d) the carbon number distribution and average molecular weight of the alcohol portion of the AES; (e) the amount of free, nonethoxylated alcohol present in the nonionic (NI) blendstock and the amount of AS present in the AES blendstock can often be estimated; (f) the amount of free oils present in the anionic blendstocks (AS and AES) can often be estimated.

These data plus the information obtained in the previous paper present a rather detailed analysis of the detergent formulation.

EXPERIMENTAL

Outline of Method

The FNI fraction must contain only free oils, alcohols and/or ethoxylated alcohols with no water, solvent, or other contaminants present. A weighed portion of the fraction is blended with a suitable internal standard (often n-decanol), and the mixture is converted to the trimethylsilyl ether (TMSE) derivative by the reagent Tri-Sil (trimethylchlorosilane and catalysts in pyridine from Pierce Chemical Company). The resulting solution is analyzed by gas chromatography using thermal conductivity detection (TCD) to determine any free alcohol (ROH) and to characterize any free ethoxylated alcohols (NI).

The AHNI fraction must likewise be only alcohol or ethoxylated alcohol – free from any water, solvent, salts, etc. This fraction is also blended with an internal standard, derivatized with Tri-Sil, and analyzed by GC.

The RI-FNI fraction is analyzed as isolated by GC using TCD. The alkyl groups may then be identified by carbon number and, to a lesser degree, by isomers, if present. The relative concentration of each resolved alkyl group may be calculated on a weight-percent basis as the corresponding alcohol by use of the appropriate response factors. The RI-AHNI fraction is composed of the same components as the RI-FNI fraction and is analyzed by the identical procedure.

Experimental Procedure

The two free hydroxyl fractions, the FNI and the AHNI, are prepared for GC analyses by the following procedure. (a) a portion of the dried sample ($\sim$100 mg) is placed in a tared vial and weighed; (b) a known volume ($\sim$10 $\mu\ell$) of a suitable internal standard is delivered to the vial with a microsyringe (weigh until a quantitative delivery technique is developed); (c) add 1.0 cc of Tri-Sil reagent to the vial and cap with a polyethylene- or Teflon-lined cap; (d) mix the sample vigorously and allow to set at room temperature at least 5 min before analyzing. The two alkyliodide fractions are analyzed by GC as received after HI cleavage.

All four types of samples were analyzed by the same GC conditions using a Bendix Model 2300 gas chromatograph equipped with thermal conductivity detectors. The column was prepared as 10% SE-30 on 80-100 mesh Chromosorb W packed in a 2 m x 2.2 mm I.D. stainless steel tube. The column oven was programmed from 150 to 325 at 10 C minute. The injection port had steel liners at 325 C. Integration and calculations were performed by a Varian Model 620 L System V data system.

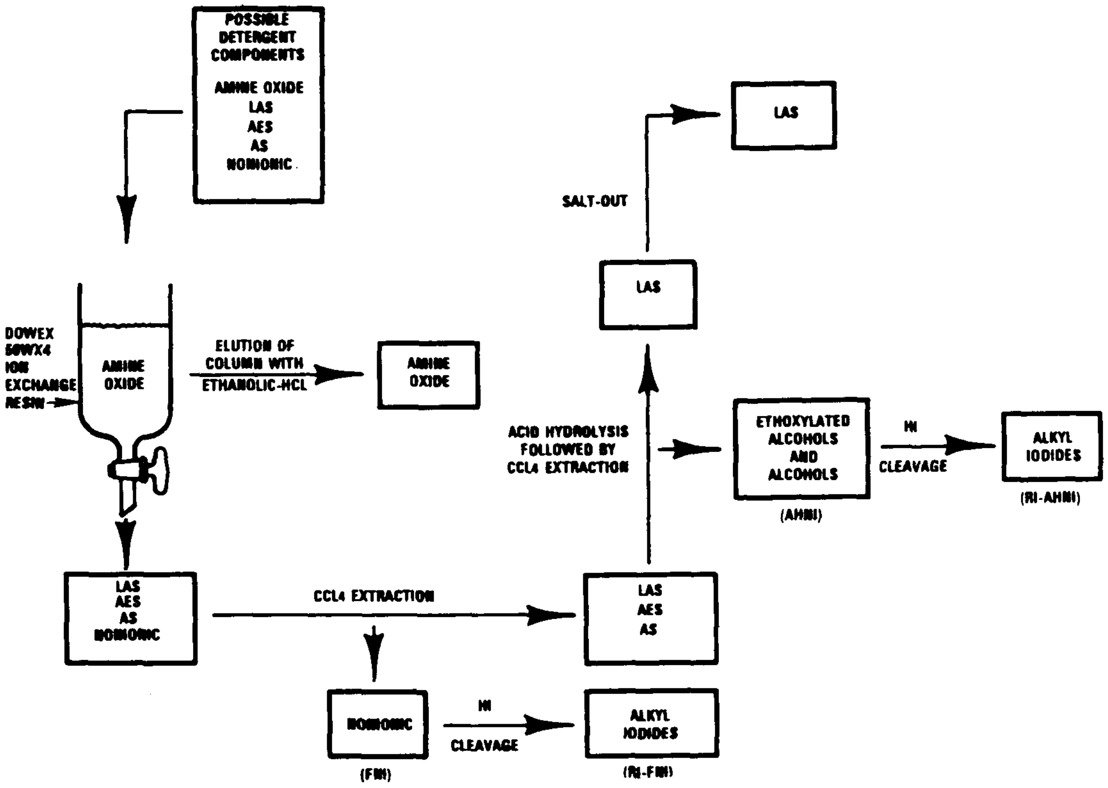

FIG. 1. Flow chart showing the isolation procedure for various detergent fractions.

Determination of Known Blends

To verify the quantitative possibilities of this approach, known blends of alcohol sulfate and alcohol ether sulfates were prepared using various blending materials. Table I gives the analytical data on the three AS blendstocks. These sulfates were prepared from known alcohol blends by laboratory sulfation with chlorosulfonic acid. The alkyl distributions were determined by GC analyses of the reactant alcohols. The active determinations were by the BCG technique (1).

Table II gives similar analytical data on the two alcohol ethoxylate sulfate blending materials. The 1412 AES was prepared by laboratory-scale ethoxylation and sulfation of a known alcohol blend. The 1215 AES was a commercial sample. The alkyl distribution of the latter AES was determined by GC of the resulting alkyl iodides produced by acid hydrolysis and HI cleavage; and, therefore, it is not an independent check of the accuracy of this method. The free (nonethoxylated) alcohol contents in these AES samples were also determined by GC on the AHNI products.

TABLE I

Alcohol Sulfate Blendstocks Data

	1618 As	1415 AS	1218 AS
Active, %w	29.54	27.57	27.08
Cation	Na^+	Na^+	Na+
M.W. of salt	354	319	336
M.W. of alcohol	252	217	234
Alkyl dist. as %w ROH			
C_{10}	---	---	0.3
C_{11}	—	0.1	—
C_{12}	0.2	0.6	19.4
C_{13}	—	6.5	—
C_{14}	1.3	63.3	17.0
C_{15}	—	29.4	—
C_{16}	61.9	0.1	37.8
C_{17}	—	—	—
C_{18}	35.9	—	24.2
C_{19}	—	—	—
C_{20}	0.7	—	1.3

Four blends were prepared from the five blendstocks. The various "known" data on these four blends are given in Table III, with all values obtained by calculations from the data on the blendstocks. Two columns are given under each sample: the "As blended" column gives the "business areas' analysis," which assumed the AES added was pure AES. The "Corrected" column gives the "true analysis" with corrections made for the AS in the AES blendstock. This latter type of values is actually obtained by this procedure while the former type may be of more interest to formulators.

The actual experimental data obtained from these blends are summarized in Table IV. The gas chromatograms of the AHNI fractions of the blends are shown in Figures 2 to 5.

Calculations of GC Data

The first step is to identify and mark the peaks in the AHNI-fraction chromatogram. Using Figure 2 as an example, the ROH-TMSE and the internal standard peaks are identified, and the relative areas attributed to each peak (Column I of Table V) are then corrected by use of the appropriate gravimetric factors (given in Column II) to convert the relative areas of the trimethylsilyl ether derivatives to the relative areas for the corresponding alcohols. These corrected areas in Column III are then used in normal internal standard calculations to determine the concentration of each alcohol component in the AHNI fraction on a weight-percent basis (as approximated by TCD response). These values are in Column IV. The sum of these concentrations represents all alcohols which were produced from the AS (added as AS and/or AS in AES) in the detergent sample. These concentrations can then be normalized to 100% to give the distribution of the alcohol sulfate on a weight-percent-alcohol basis, given in Column V.

Next the ethoxylated alcohol-TMSE peaks are identified, and each homologous series containing the same number of

TABLE II

Alcohol Ethoxylate Sulfate Blendstocks Data

	1412 AES		1215 AES	
Active, % w	29.94		57.70	
Cation	Na^+		NH_4^+	
M.W. of salt	436		415	
M.W. of ether	334		318	
M.W. of alcohol	204		204	
EO content of ether, % w	39.1		35.9	
Free alcohol in AHNI, % w	14.6		11.9	
Alkyl distribution as % w ROH	Free alcohol	Total sample	Free alcohol	Total sample
C_{10}	—	0.3	—	0.2
C_{11}	—	—	1.0	0.7
C_{12}	38.0	37.2	26.0	19.2
C_{13}	—	—	35.0	41.1
C_{14}	62.0	62.1	25.0	26.7
C_{15}	—	—	13.0	11.8
C_{16}	—	0.4	—	0.3

TABLE III

Calculated Values for Known Blends

	Sample No. 49		Sample No. 50		Sample No. 51		Sample No. 52	
AS Type	1218 AS		1218 AS		1618 AS		1415 AS	
AES Type	1215 AES		1412 AES		1215 AES		1215 AES	
EO in AHNI, % w	26.35		24.23		21.42		23.08	
	As blended	Corrected[a]	As blended	Corrected[a]	As blended	Corrected[a]	As blended	Corrected[a]
AS, % w active basis	28.5	37.8	40.3	49.6	42.1	49.5	38.5	46.4
AES, % w active basis	71.5	62.2	59.7	50.4	57.9	50.5	61.5	53.6
Total ROH in AHNI, % w	26.6	35.3	37.8	47.1	37.5	47.4	32.9	43.4
ROH Conc. in AHNI, $ w ROH								
C_{10}	0.07	0.08	0.11	0.11	—	—	—	—
C_{11}	—	0.09	—	—	—	0.07	0.03	0.11
C_{12}	4.71	7.43	7.33	10.82	0.07	1.93	0.20	2.20
C_{13}	—	3.06	—	—	—	2.48	2.14	5.00
C_{14}	4.13	6.70	6.42	12.09	0.49	2.29	20.82	24.51
C_{15}	—	1.13	—	—	—	0.92	9.67	11.50
C_{16}	9.15	10.03	14.25	14.34	23.21	24.97	0.03	0.03
C_{18}	5.87	6.44	9.15	9.21	13.46	14.48	—	—
C_{20}	0.31	0.35	0.49	0.49	0.26	0.28	—	—
AS Dist. as % w ROH								
C_{10}	0.3	0.2	0.3	0.2	—	—	—	—
C_{11}	—	0.3	—	—	—	0.1	0.1	0.2
C_{12}	19.4	21.0	19.4	23.0	0.2	4.1	0.6	5.1
C_{13}	—	8.7	—	—	—	5.2	6.5	11.5
C_{14}	17.0	19.0	17.0	25.7	1.3	4.8	63.3	56.5
C_{15}	—	3.2	—	—	—	1.9	29.4	26.5
C_{16}	37.8	28.4	37.8	30.5	61.9	52.8	0.1	0.1
C_{18}	24.2	18.2	24.2	19.6	35.9	30.5	—	—
C_{20}	1.3	1.0	1.3	1.0	0.7	0.6	—	—
AES Dist. as % w ROH								
C_{10}	0.2	0.1	0.3	0.4	0.2	—	0.2	—
C_{11}	0.7	0.6	—	—	0.7	0.6	0.7	0.7
C_{12}	19.2	17.6	37.2	36.9	19.2	17.6	19.2	17.6
C_{13}	41.1	42.5	—	—	41.1	42.5	41.1	42.6
C_{14}	26.7	27.1	62.1	62.1	26.7	27.2	26.7	27.1
C_{15}	11.8	11.7	—	—	11.8	11.6	11.8	11.6
C_{16}	0.3	0.4	0.4	0.5	0.3	0.5	0.3	0.4

[a] Values corrected for free alcohol sulfate present in AES blendstock.

EO adducts is marked together (refer to Fig. 2). One or two of the series which contain four or fewer EO adducts, show minimum interference, and appear to be representative of the NI, are selected. In this example the series with three and the series with four EO adducts are chosen, as the first two appear to have interfering peaks. The areas for these two series of chosen peaks are listed in Column I of Table VI. The gravimetric factors in column II correct the NI-TMSE areas to the areas for the corresponding alcohols, given in Column III. Direct normalization of these two sets of values to 100% (given in Column IV) yields two approximations of the alkyl distribution of the AES. This AES calculation is referred to as "Method A."

The chromatogram of the RI-AHNI fraction from the formulation is examined next (example in Fig. 6). The iodoalkanes are identified, and their respective areas are tabulated in Column I of Table VII. The gravimetric factors that convert the areas of the iodides to the corresponding alcohol areas in Column III are in Column III. Column III represents the combined alkyls from both the AS and AES expressed as the alcohols. From the EO determination of the AHNI fraction, these combined alcohols should represent 73.6% of the AHNI sample (100%-26.4). Column III is normalized to 73.6% to give Column IV. The contribution of the AS only to the AHNI sample was calculated in Column IV of Table V (repeated in Column V of Table VII). That amount can be subtracted from each alcohol in Column IV to yield the amount of alcohol from AES, as

TABLE IV

Experimental Values for Known Blends

	Sample No. 49		Sample No. 50		Sample No. 51		Sample No. 52
	Run A	Run B	Run A	Run B	Run A	Run B	
AS, %w active basis	35.5	32.6	46.2	51.8	49.2	39.9	42.0
AES, % w active basis	64.5	67.4	53.8	48.2	50.8	68.1	58.0
EO in AHNI, % w	26.4		24.3		21.3		23.1
Total ROH in AHNI, % w ROH	33.13	30.3	43.6	49.1	47.2	37.1	38.8
ROH Conc. in AHNI, % w ROH							
C_{10}	0.07	—	0.15	—	—	—	0.01
C_{11}	0.08	—	—	—	0.06	—	0.08
C_{12}	7.01	6.19	10.08	11.37	1.88	1.58	2.21
C_{13}	3.10	2.64	—	—	2.42	1.94	3.97
C_{14}	6.24	5.84	11.13	12.54	2.11	1.60	22.18
C_{15}	1.44	1.09	—	—	1.00	0.67	10.29
C_{16}	9.53	8.92	13.39	15.33	25.13	29.70	0.02
C_{18}	5.66	5.61	8.84	9.91	14.60	11.62	
C_{20}	—	—	—	—	—	—	
AS Dist. as % w ROH							
C_{10}	0.2	—	0.3		—	—	—
C_{11}	0.2	—			0.1	—	0.2
C_{12}	21.2	20.4	23.1	23.2	4.0	4.3	5.7
C_{13}	9.4	8.7			5.1	5.2	10.3
C_{14}	18.8	19.3	25.5	25.5	4.5	4.3	57.2
C_{15}	4.3	3.6			2.1	1.8	26.5
C_{16}	28.8	29.5	30.8	31.2	53.2	53.1	0.1
C_{18}	17.1	18.5	20.3	20.1	31.0	31.3	—
C_{20}	—	—	—	—	—	—	—
AES Dist. as % w ROH (Method A)							
C_{12}	16	16	39	33	12	19	18
C_{13}	40	41	—	—	45	41	39
C_{14}	26	26	61	67	28	26	24
C_{15}	18	17	—	—	15	14	19
AES Dist. as % w ROH (Method B)							
C_{10}	—	—	—	—	0.3	—	0.3
C_{11}	0.6	0.7	—	—	0.6	0.8	0.5
C_{12}	12.8	20.4	33.1	37.2	14.9	11.1	14.7
C_{13}	35.3	37.7	—	—	36.1	29.0	39.4
C_{14}	26.4	25.5	58.9	61.8	22.5	18.9	31.7
C_{15}	9.9	9.0	—	—	9.8	8.6	13.0
C_{16}	8.9	4.5	6.2	1.0	9.7	21.3	0.4
C_{18}	6.1	2.2	1.8	—	6.1	10.3	—
C_{20}	—	—	—	—	—	—	—
AES Dist. as % w ROH (Method C)							
C_{11}	0.7	0.8	—	—	0.7	1.3	N.A.[a]
C_{12}	9.1	20.4	34.1	36.5	17.5	15.2	N.A.
C_{13}	47.5	42.8	—	—	43.4	43.2	N.A.
C_{14}	30.1	26.0	62.1	59.2	26.7	27.7	N.A.
C_{15}	12.6	10.0	—	—	11.7	12.6	N.A.
C_{16}	—	—	3.8	4.3	—	—	N.A.

[a] Not applicable.

given in Column VI. These values can then be normalized to 100% to give the distribution of the AES, expressed in weight percent as alcohols in Column VII. This AES calculation is referred to as "Method B."

A third calculation procedure is often available to calculate the AES distribution when it is apparent that one major alcohol is a component of the AS, but not the AES. In this example in Figure 2, $C_{16}OH$ and $C_{18}OH$ are present in the AHNI, but ethoxylates of either are not visible. For the first example of "Method C," the $C_{16}OH$ peak was chosen to relate the AHNI and RI-AHNI chromatograms. It is assumes, based on Figure 2, that all C_{16} alkyl in the RI fraction was derived from C_{16} alcohol sulfate. Therefore, Column VI of Table V, repeated as Column II of Table VIII, can be multiplied by 1.214 to yield a revised distribution of the AS, given in Column III, with the $C_{16}OH$ equal to its value in the combined alcohols, 10.83 (given in Column I as repeated from Column IV of Table VII). Subtraction of the AS distribution yields the AES contribution in Column IV which is then normalized to 100% to give Column V, the distribution of the AES by Method C. The same procedure is repeated using the $C_{18}OH$ peak to relate the distributions in the lower portion of Table VIII.

From the distribution of the AS (Column V, Table V), the average molecular weights of the alcohol and its sodium sulfate salt may be calculated (226 and 328, respectively, for this example). From the distributions of the AES by any one of the three methods, the average molecular weight of the original alcohol may be calculated (for this example, 203, using data in Column V, Table VIII). As the total ethoxylated alcohol portion of the AHNI fraction was found to be 69.7% (100%-% free alcohol) and the EO is 26.4%, the original alcohol portion of the ethoxylate is 43.3%. These values allow calculation of the average molecular weight of the ethoxylated alcohol as 327. The average molecular weight of the ammonium sulfate salt is therefore 424. Using these molecular weights, the ratio of alcohol to ethoxylated alcohol in the AHNI fraction (30.3: 69.7 in this example) may be converted to yield the ratio of AS to AES in the formulation (33:67).

Interpretations of Other Chromatograms

Figure 7 shows the AHNI fraction of a formulation which contained no significant FNI fraction. A series of

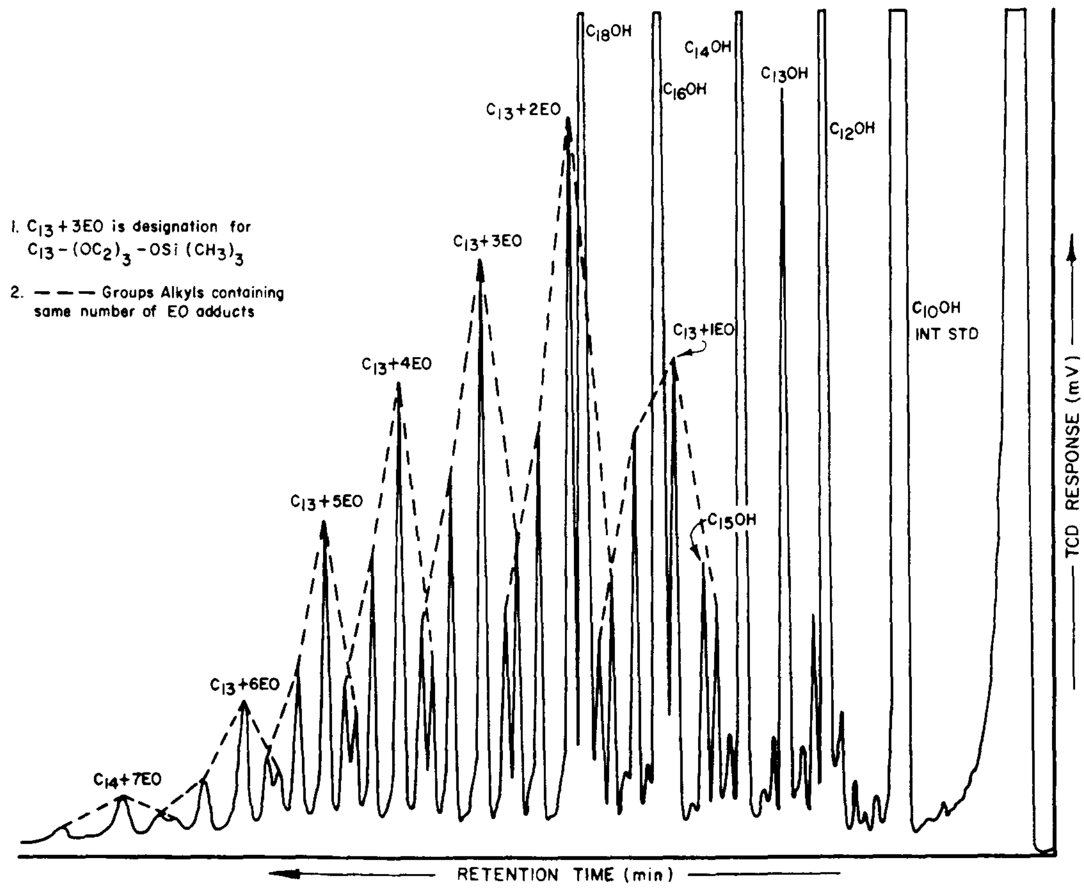

FIG. 2. AHNI of No. 49 blend TMSE from a 12-18 AS and a 12-15 AES.

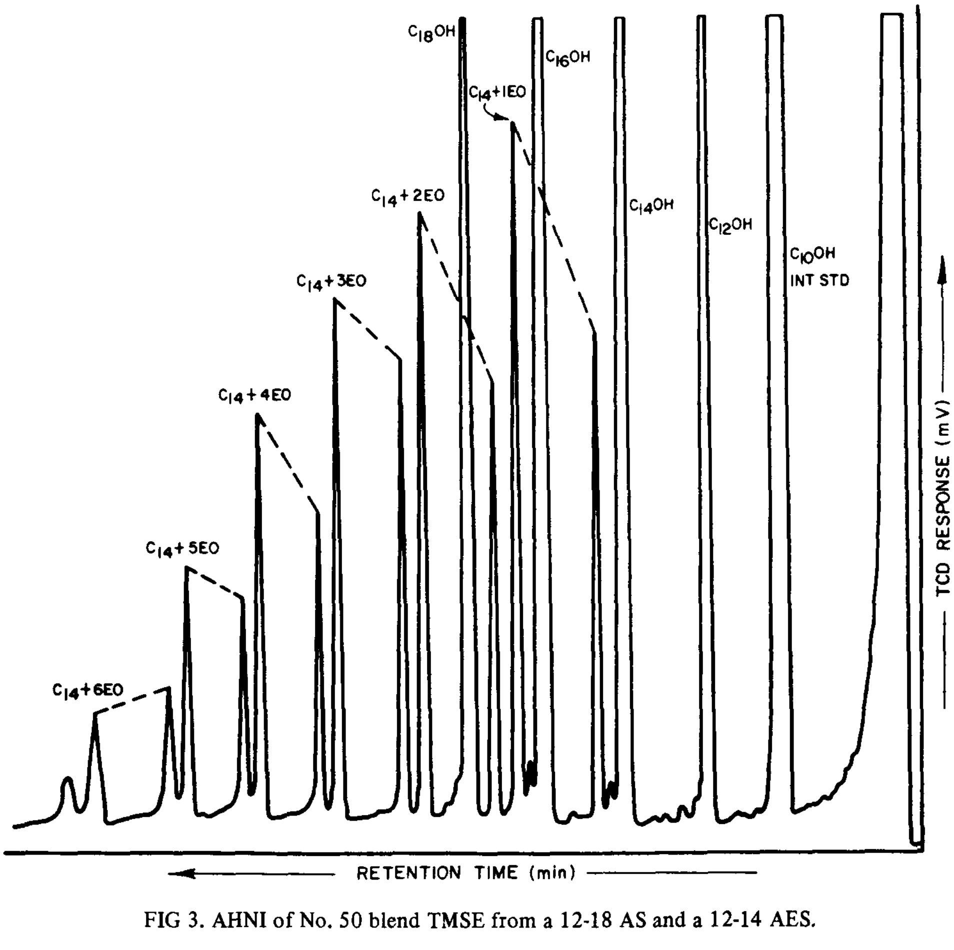

FIG 3. AHNI of No. 50 blend TMSE from a 12-18 AS and a 12-14 AES.

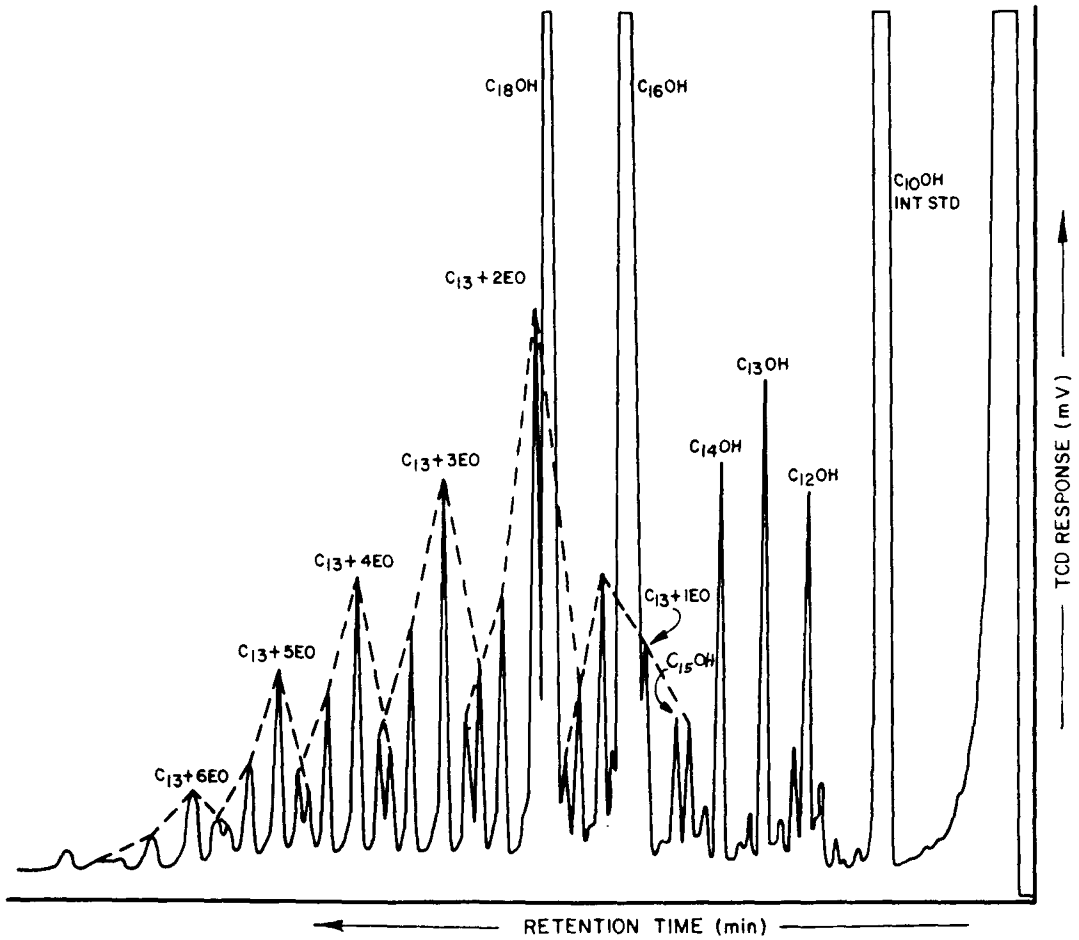

FIG. 4. AHNI of No. 51 blend TMSE from a 16-18 AS and a 12-15 AES.

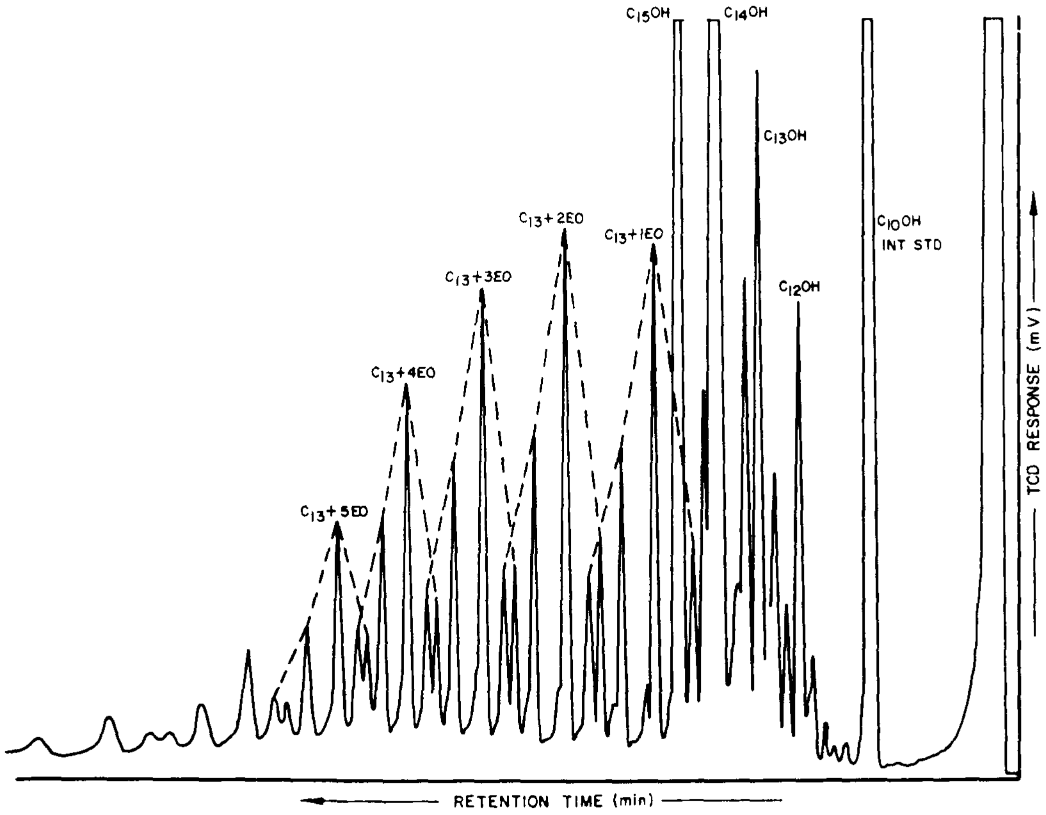

FIG. 5. AHNI of No. 52 blend TMSE from a 14-15 AS and a 12-15 AES.

TABLE V

Calculations of AS Distributions

Compound	I Relative peak area	II Gravimetric correction factor	III Relative area as ROH	IV Alcohol conc. (% w) in AHNI	V AS distribution as % w ROH
C_{10} TMSE	31.817	0.687	21.86	(Int. Std.)	--
C_{12} TMSE	6.895	0.721	4.97	6.19	20.4
C_{13} TMSE	2.882	0.735	2.12	2.64	8.7
C_{14} TMSE	6.250	0.748	4.68	5.84	19.3
C_{15} TMSE	1.149	0.760	0.87	1.09	3.6
C_{16} TMSE	9.290	0.771	7.16	8.92	29.5
C_{18} TMSE	5.646	0.789	4.45	5.61	18.5

TABLE VI

Calculations of AES Distribution by Method A

Compound	I Relative peak area	II Gravimetric correction factor	III Relative area as ROH	IV AES distribution as % w ROH
$C_{12}O(EO)_3$ TMSE	1.328	0.476	0.632	16
$C_{13}O(EO)_3$ TMSE	3.237	0.495	1.602	41
$C_{14}O(EO)_3$ TMSE	1.951	0.512	0.999	26
$C_{15}O(EO)_3$ TMSE	1.242	0.528	0.656	17
$C_{12}O(EO)_4$ TMSE	0.857	0.428	0.367	13
$C_{13}O(EO)_4$ TMSE	2.694	0.446	1.202	42
$C_{14}O(EO)_4$ TMSE	1.649	0.463	0.763	27
$C_{15}O(EO)_4$ TMSE	1.055	0.479	0.505	18

trimethylsilyl ethers of the C_{11}, C_{12}, C_{13}, C_{14} and C_{15} alcohols is readily observed. In addition, a nonionic homologous series of the ethoxylates of those same carbon numbers is also present in the TMSE form. The alkyl chain distributions of the ROH-TMSE series and the NI-TMSE series appear similar. The alkyl distribution of the resulting alkyl iodides from this fraction (Fig. 8) appears also to be similar. By use of an internal standard (n-nonanol) in the AHNI, it was concluded that the formulation included an ionic component of 20% AS and 80% AES with a relatively low EO content. The subjective conclusion was also made that the AS was present in the AES blendstock and was not added as a separate ingredient. (The pattern of free alcohols to their EO-adducts appeared to match the ratios in a common commercial product containing 35-40% EO – 35.9% actually found.)

The interpretation of an FNI fraction from a formulation containing no AHNI fraction was similar to the above illustration. The chromatogram shown in Figure 9 has the same ROH-TMSE series and the same NI-TMSE series as were shown in Figure 7. The conclusion was drawn that this formulation was prepared from a higher-EO-content, alcohol-ethoxylate nonionic which contained 4.6% free alcohol.

In Figure 10, a more complex AHNI fraction from a commercial sample, the TMS ethers of three alcohols are readily observed – $C_{14}OH$, $C_{16}OH$, and $C_{18}OH$. In addition, an NI-TMSE homologous series is also present, composed of C_{14}, C_{16}, and C_{18} alkyls. The 14:16:18 alkyl ratio of the alcohols is ca. 1:6:12 while the 14:16:18 alkyl ratio of the ethoxylates is ca. 2:2:1. This difference in ratios indicates that formulation contains an AS component and a separate AES component. With the addition of a noninterfering internal standard such as n-decanol, the amount of free alcohols in the AHNI fraction and the approximate distribution of the AES were determined. The chromatogram of the RI-AHNI fraction of this sample is shown in Figure 11. The major alkyls in the RI-AHNI were the expected C_{14}, C_{16} and C_{18} iodides. With the alkyl contribution from the AS of each component having been determined by the quantitative analysis of the AHNI fraction and the EO content of the AHNI fraction previously determined, the distribution of the AES can be calculated by "Method B." That AES distribution closely approximated the 14:16:18 ratio which was independently estimated in the AHNI analysis. With the analysis of the AHNI fraction being made, the interpretation of the FNI fraction, if present, should follow. In Figure 12 the chromatogram of the FNI fraction of the sample closely resembles the AHNI fraction. The distributions of the ROH-

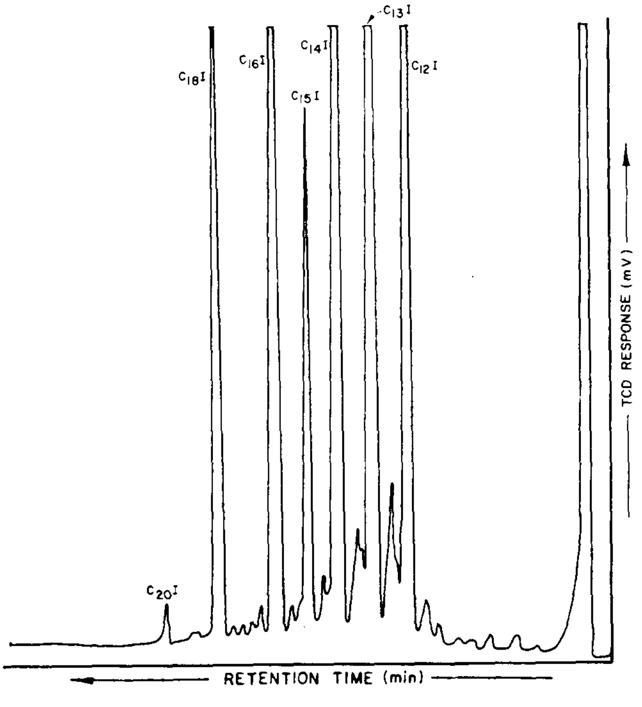

FIG. 6. RI-AHNI of No. 49 blend alkyl iodides from 12-18 AS and a 12-15 AES.

TABLE VII

Calculations of AES Distribution by Method B

Compound	I Relative peak area	II Gravimetric correction factor	III Relative area as ROH	IV ROH area normalized to 73.6%	V ROH from AS	VI ROH from AES	VII AES distribution as % w ROH
$C_{11}I$	0.39	0.610	0.24	0.30	.00	0.30	0.7
$C_{12}I$	19.12	0.628	12.01	14.83	6.19	8.64	20.4
$C_{13}I$	23.32	0.645	15.04	18.58	2.64	15.94	37.7
$C_{14}I$	20.36	0.661	13.46	16.63	5.84	10.79	25.5
$C_{15}I$	5.88	0.675	3.97	4.90	1.09	3.81	9.0
$C_{16}I$	12.39	0.708	8.77	10.83	8.92	1.91	4.5
$C_{18}I$	7.55	0.702	5.30	6.55	5.61	0.94	2.2
$C_{20}I$	0.38	0.730	0.28	0.21	(0.21)	—	—

TABLE VIII

Calculations of AES Distribution by Method C

Compound	I Total ROH area to 73.6%	II ROH from AS in % w	III AS ROH set to $C_{16}OH = 10.83$	IV ROH from AES	V AES distribution as % w ROH
$C_{11}OH$	0.30	0.00	0.00	0.3	0.8
$C_{12}OH$	14.83	6.19	7.51	7.32	20.4
$C_{13}OH$	18.58	2.64	3.20	15.38	42.8
$C_{14}OH$	16.63	5.84	7.09	9.34	26.0
$C_{15}OH$	4.90	1.09	1.32	3.58	10.0
$C_{16}OH$	10.83	8.92	10.83	0.00	0.0
$C_{18}OH$	6.55	5.61	6.81	(0.00)	—
$C_{20}OH$	0.21	—	(0.21)	(0.00)	—
			$C_{18}OH = 6.55$		
$C_{11}OH$	0.30	0.00	—	0.30	0.8
$C_{12}OH$	14.83	6.19	7.23	7.60	20.4
$C_{13}OH$	18.58	2.64	3.08	15.50	41.6
$C_{14}OH$	16.63	5.84	6.82	9.81	26.3
$C_{15}OH$	4.90	1.09	1.27	3.63	9.7
$C_{16}OH$	10.83	8.92	10.41	0.42	1.1
$C_{18}OH$	6.55	5.61	6.55	0.00	—
$C_{20}OH$	0.21	—	(0.21)	(0.00)	—

TMSE series and the NI-TMSE series are quite similar. With the total amount of FNI compared to the total amount of anionic being relatively low (data previously determined) and the alkyl distributions being the same, it was concluded that this formulation contained no added nonionic as such. The nonionic fraction was due to unsulfated components present in the AS and AES blending materials. The AS was only a 16-18 type with the $C_{12}OH$ and $C_{14}OH$ in the AHNI being introduced in the 14-18 type AES.

The AHNI fraction from another commercial formulation is shown in Figure 13. The ROH-TMSE components are primarily C_{14}, C_{15}, C_{16} and C_{18} alkyl chains in a 4:1:8:15 ratio. The NI-TMSE components are C_{14}, C_{15} and C_{16} alkyl chains in an unusual 12:3:4 ratio. Further study of the other three fractions of this formulation led to the conclusion that the sample contained 80% 16-18 AS (the $C_{14}OH$-TMSE and $C_{15}OH$-TMSE peaks were due entirely to unethoxylated alcohols in the AES materials) and 20% of a 50:50 blend of C_{14} and C_{16} AES and C_{14} and C_{15} AES.

DISCUSSION

Results of Analyses of Known Blends

The accuracies of the various analyses of the blends are highly variable as can be seen by comparing the "corrected" columns of Table III with the data in Table IV.

The determinations of the total ROH in the AHNI were highly variable and result directly in errors in the AS/AES ratios and indirectly in the AES distributions by Method B. The distributions of the AS are quite accurate, however, indicating the variation in the total is due to problems relating to the application of the internal standard technique. The errors may be in either weight determination, the area measurement of the IS peak, interferences with the internal standard peak, and/or quantitative reaction of the IS to the TMSE derivative.

The distributions of the AES are also highly variable. No single calculation method consistently gave more accurate distributions. For Sample No. 49, Method C on Run B yielded the best fit; for No. 50 all methods were good with Method B on Run B the best; for No. 51 Method C on Run A was the best; and for No. 52 Method B was a mediocre best.

Interferences and Sources of Errors

As stated earlier, the purity of the AHNI fraction is critical. Any water, solvent, etc., will result in a low AS value while excessive drying of the sample can easily change the distribution of the alcohols by preferential evaporation. The gas chromatogram of the AHNI often has co-eluting peaks due to the complexity. (This particular GC system co-elutes $C_{20}OTMS$ and $C_{12}(OC_2)_3OTMS$ components.) Any fatty acid salts in the formulation will also be isolated in the AHNI fraction, primarily as mixed esters from esterification in the acid-hydrolysis procedure. The weights and area measurement of the IS component are very critical to the total accuracy of the procedure.

The two alkyl iodide fractions may contain excess hexane solvent with no problem and often contain salts which likewise present no interference. The usual components contain no critical GC separation problems. The

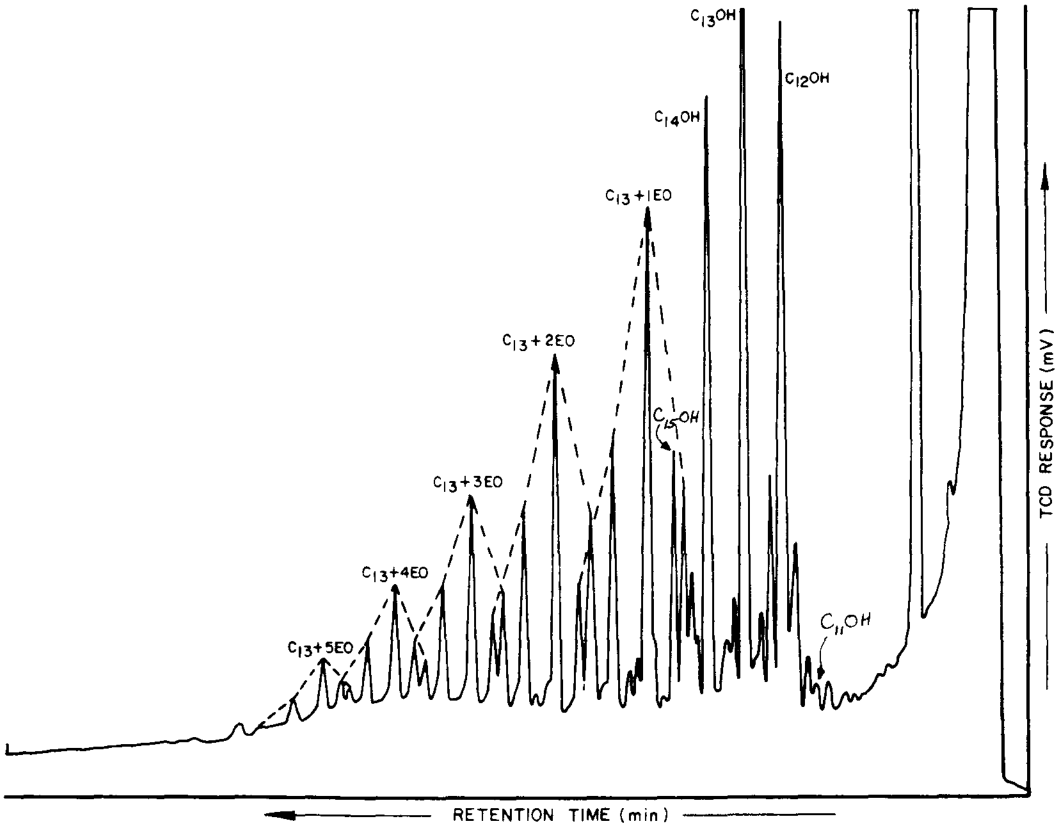

FIG. 7. AHNI of No. 12 sample TMSE from 12-15 AES.

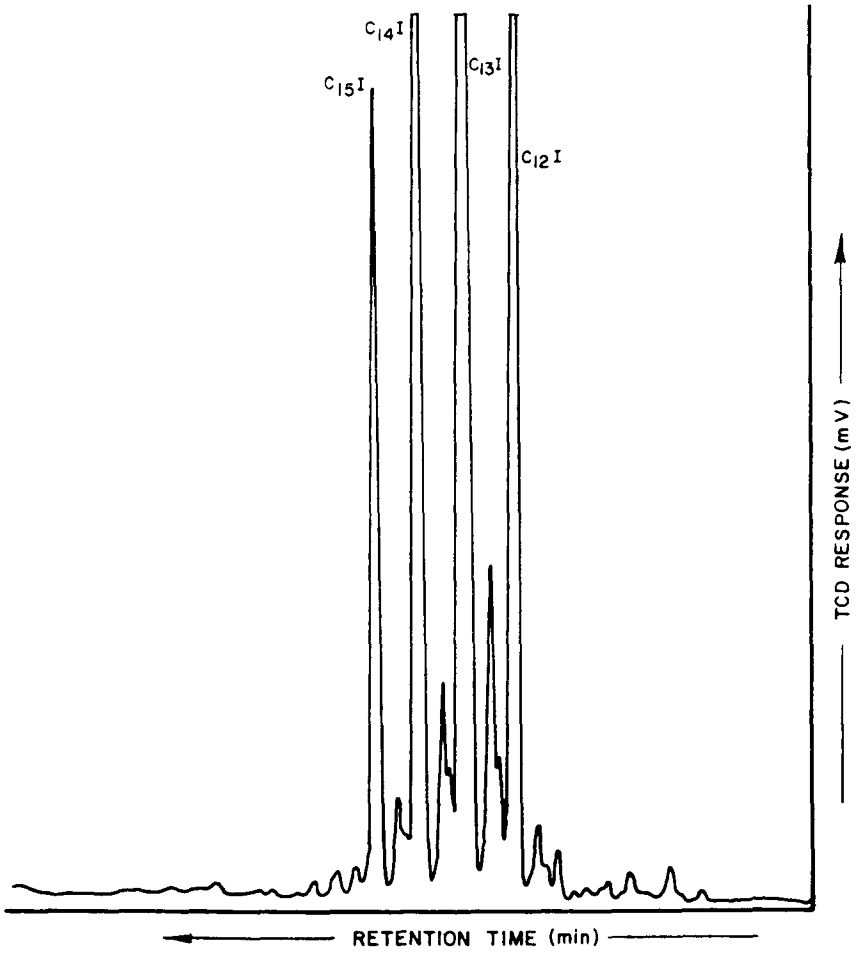

FIG. 8. RI-AHNI of No. 12 sample alkyl iodides from 12-15 AES.

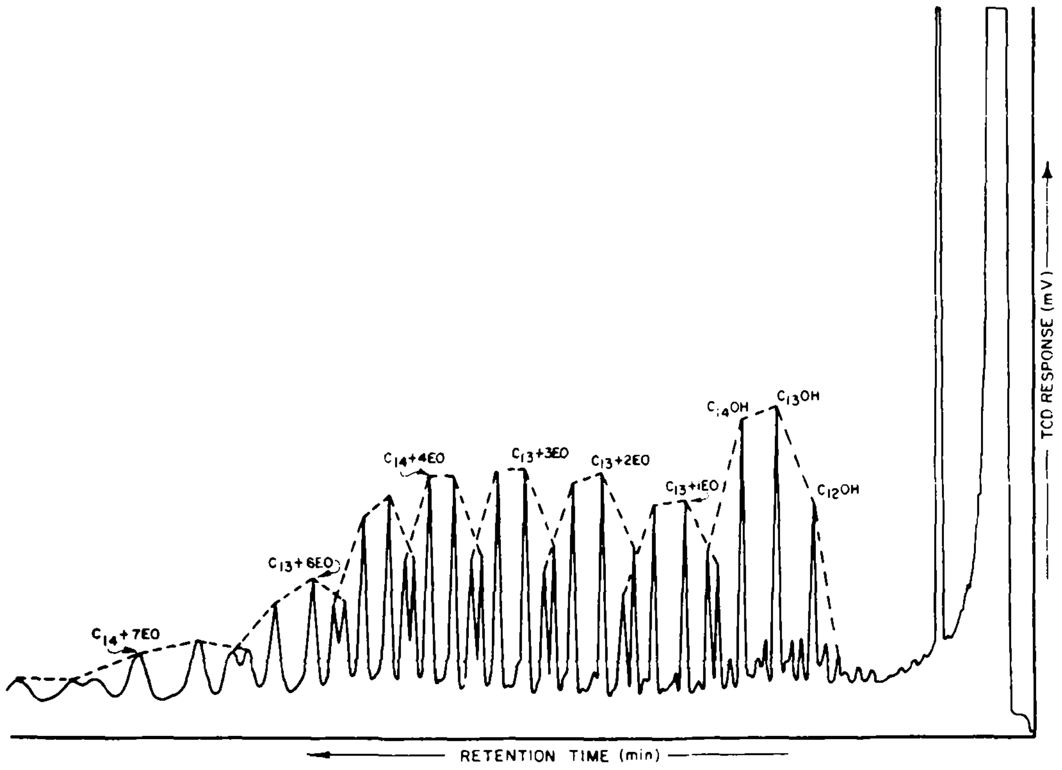

FIG. 9. FNI of No. 11 sample TMSE from a 12-15 nonionic.

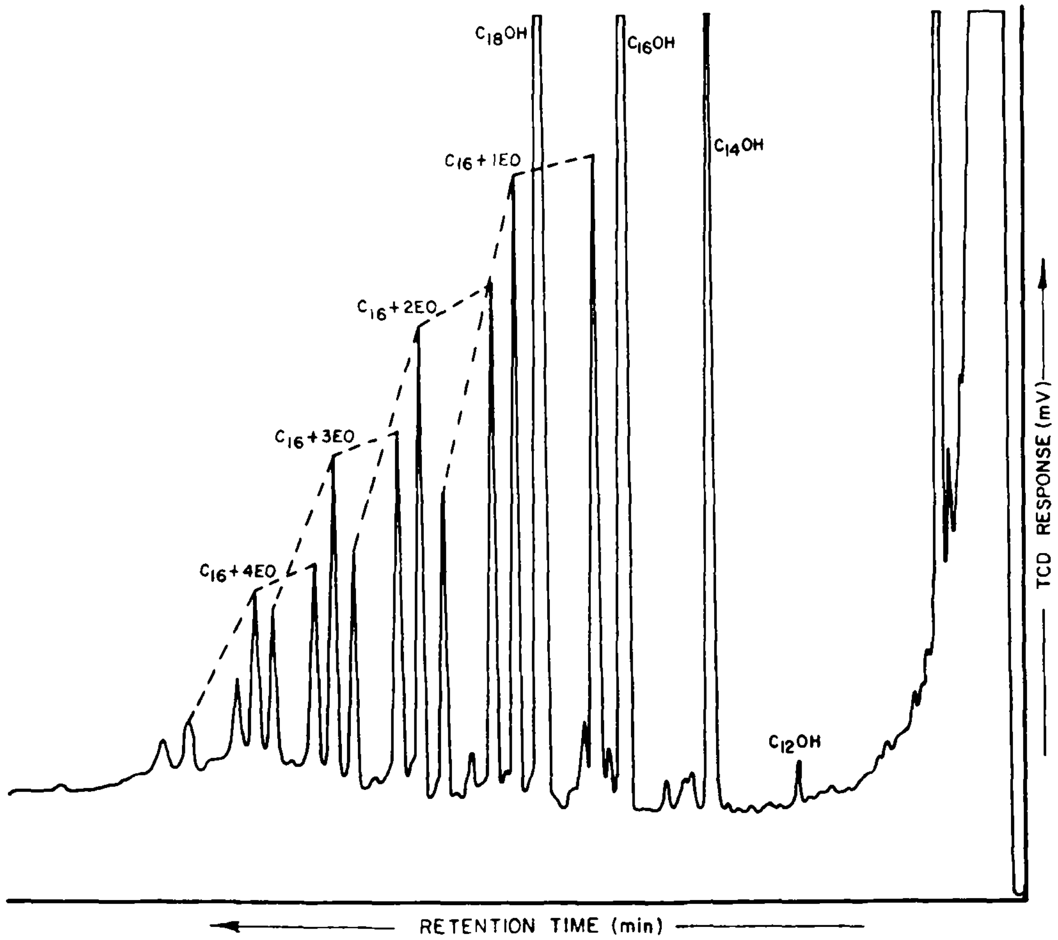

FIG 10. AHNI of No. 160 sample TMSE from a 16-18 AS and a 14-18 AES.

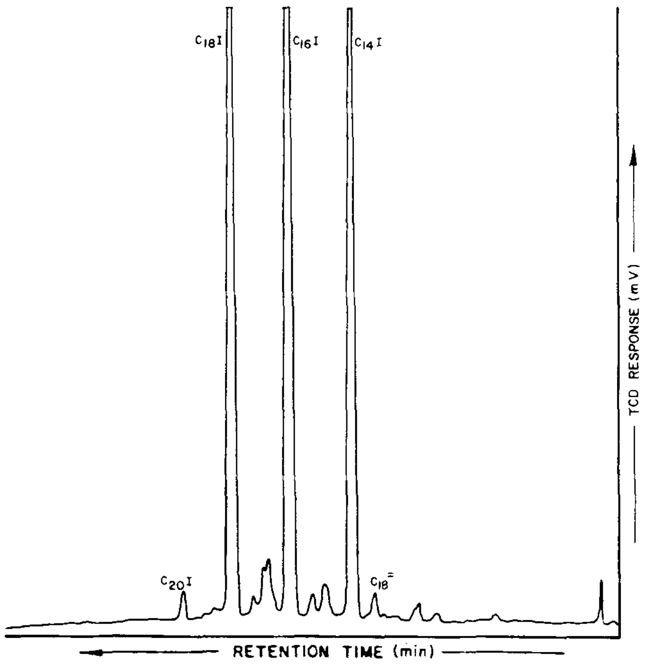

FIG. 11. RI-AHNI of No. 160 sample alkyl iodides from a 16-18 AS and a 14-18 AES.

octadecene ($C_{18}^{=}$) shown in Figure 11 often occurs when C_{18}OH-sulfate is present but has never been a significant problem. The dehydrohalogenation is usually eliminated by cleaning the GC injection liner.

The FNI fraction may be complicated by excessive free oils from the anionic or by other additives such as amides or polyethylene glycol ether. Through the information gained by the GC analysis of the fraction, the EO determination and the GC of the RI fraction, these interferences can at least be recognized when encountered and often resolved without further analytical effort.

The three sets of distribution values for the AES and the variation in replicates are disturbing to the analytical chemist, but the differences are not surprising. The AES determinations are so indirect that experimental errors are compounded to a larger degree than with the other, more direct measurements. Method A has the poorest sensitivity; Method B is the most technically correct procedure but has the greatest compounded error problems; and Method C frequently can not be applied. In actual practice the three sets of data can be merged along with a knowledge of available alcohol blends to clearly identify the alcohol source. The resulting distribution may be subjective but is more valuable than no information or objective, erroneous data.

The molecular weights and EO content calculated directly from the data by this procedure can vary significantly from the values for the blending material but do not always represent error. The AS in the AES is added to the AS blending material in this procedure and effects rather large changes in the average molecular weights of each component and the calculated EO content of the AES. Lesser variations in the AS/AES ratios and distributions of each are caused by the dual source of AS. Likewise, unsulfated organic materials in the anionic will affect the calculated values of the free nonionic.

Comments on Procedure

The gas chromatography conditions used in this study are somewhat arbitrary. Almost any high temperature, nonpolar column (SE-30, W98, OV-101) should work and perhaps work better. Glass injection liners would be preferable. The TCD choice is deliverate for several reasons: the TCD avoids silicon dioxide deposition problems which

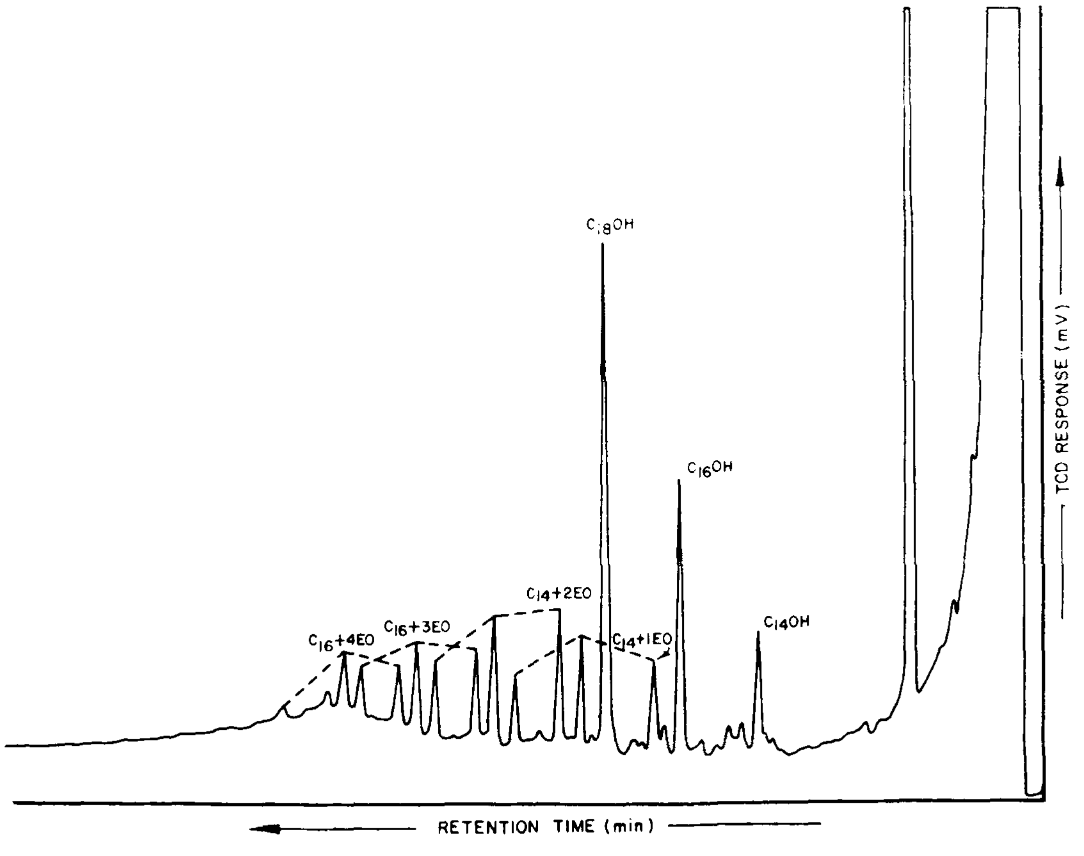

FIG. 12. FNI of No. 160 sample TMSE from the free oils of a 16-18 AS and a 14-18 AES.

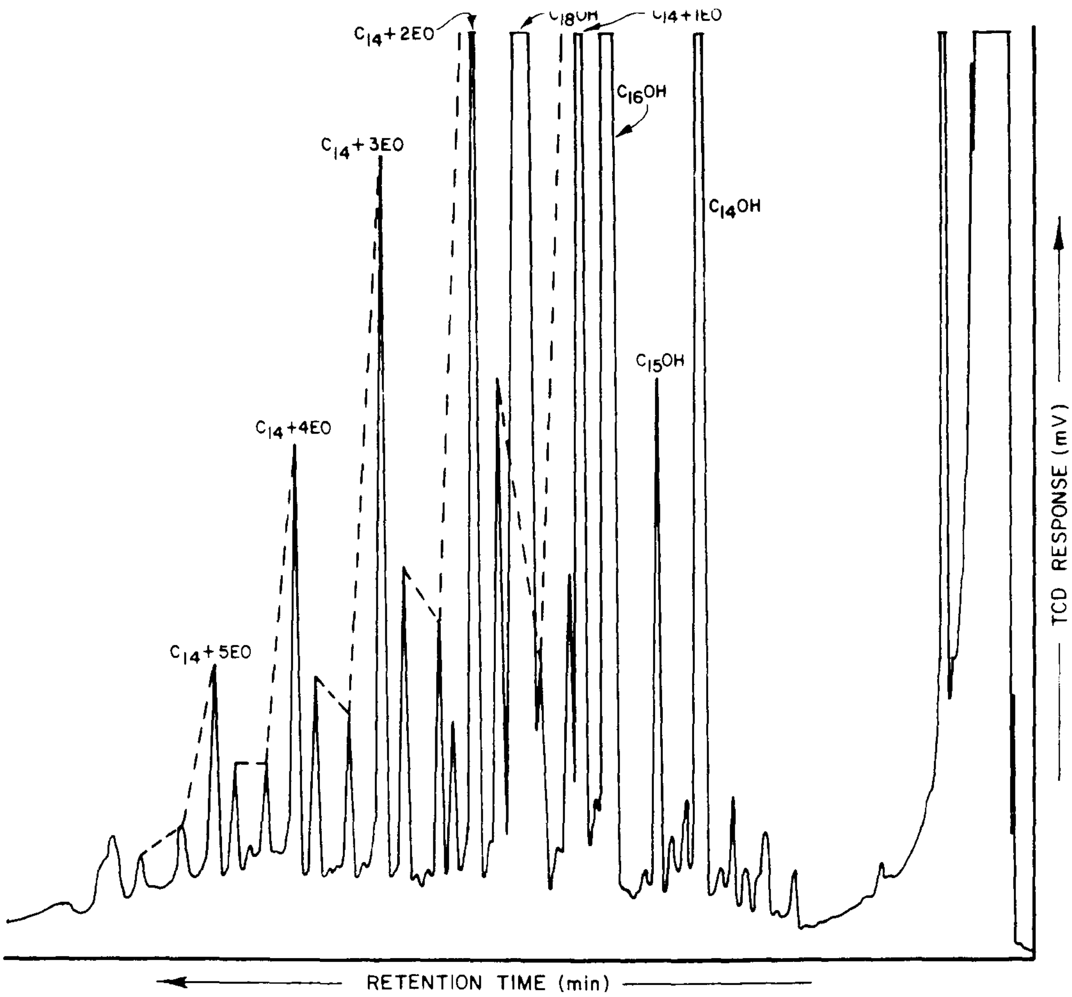

FIG. 13. AHNI of No. 157 sample TMSE from a 16-18 AS, a 14-16 AES, and a 14-15 AES.

are encountered with use of Tri-Sil with flame ionization detection; and the thermal responses on a weight percent basis of all the compounds in question very closely equal unity for each derivative, negating any calibration problems requiring known standards of each compound.

The reagent Tri-Sil, as available from Pierce Chemical Company, Rockford, IL, has shown no purity problems. Similar products by other manufacturers have not been evaluated. Tri-Sil is used because the trimethylsilyl ethers of ethoxylated alcohols elute more quantitatively and with better peak shapes than the corresponding free-hydroxyl compounds. The reaction is essentially immediate and quantitative. A major problem can be that the reagent is being used in a marginally low concentration to avoid excessive dilution and can possible be depleted with certain samples. The TMSE solutions are stable in standard, polyethylene-capped vials but will hydrolyze rather rapidly if exposed to air (10 min may recreate free-hydroxyl compounds). Special septa-protected vials may be of aid, but they are not necessary if samples are handled with care.

REFERENCES

1. Hoyt, J.L., A.J. Sooter, and E.L. Sones, JAOCS 56:701 (1979).

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