TABLE III

Biodegradability of Sodium p-(N-thia-*n*-dodecyl)benzenesulfonate

| Sodium p-(N-thia-*n*-dodecyl)-benzenesulfonate | Number of days for 100% biodegradation | |
|---|---|---|
| | Method | |
| N | A[a] | B[b] |
| 0 [c] | 8 | 7 |
| 1 | 5 | 5 |
| 2 | 9 | 7 |
| 3 | 15 | 14 |
| 4 | 14 | 14 |
| 5 | >15 | >14 |
| 6 | >15 | >14 |
| 7 | >15 | >14 |
| 8 | >15 | >14 |
| 9 | >15 | >14 |
| 10 | >15 | >14 |
| 11 | >15 | >14 |

[a] Shake fiask mehod. Allred, R. C., E. A. Setzkorn and R. L. Huddleston, JAOCS *41*, 13 (1964).
[b] River die-away method, Setzkorn, E. A., R. L. Huddleston and R. C. Allred, *Ibid*, *41*, 826 (1964).
[c] LAS.

The results of the preliminary biodegradability tests are shown in Table III.

Since the introduction of a single heteroatom in the alkyl side-chain of the LAS molecule has bestowed increased biodegradability on the molecule in one case, possibilities would appear to exist for the synthesis of new and improved biodegradable detergents.

The biological and technical behavior of the isomeric sodium p-(thia-*n*-dodecyl)benzenesulfonates are being further investigated, and the results will be reported in detail in another paper.

ACKNOWLEDGMENTS

F. H. Bissett assisted in determining the NMR spectra; J. Sousa and J. Weinstein, the infrared spectra; C. DiPietro, the elemental analyses; A. M. Kaplan and M. Rogers, the biodegradability tests.

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# Analysis of Surfactants Using Pyrolysis-Gas Chromatography[1]

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## Abstract

A pyrolysis-gas chromatographic method has been devised for the rapid analysis of surfactants and surfactant mixtures. The method involves pyrolysis of the surfactant in a unit directly attached to a gas chromatograph. The resulting pyrolysis products give characteristic gas chromatographic patterns which are useful for analysis of the original surfactant.

This method is useful for the qualitative identification of surfactants either alone, in synthetic mixtures, or in commercial products. In many cases, the technique can also be used for semiquantitative estimation of (1) relative amounts of the individual components in mixtures and (2) structural distribution of the surfactants. The method is amenable to both solid and liquid and both light-duty and heavy-duty detergent formulations.

## Introduction

THE RAPID, INEXPENSIVE analysis of surfactants is of considerable interest to the detergent industry. Such analytical techniques as ultraviolet and infrared spectrometry and nuclear magnetic resonance are of particular value in the case of individual surfactants, but these techniques can give only limited information about surfactant mixtures found in many commercial detergent products.

Pyrolysis-gas chromatography (P-GC) as an analytical tool for surfactants is not reported in the literature, although the technique has been developing rapidly as a simple and useful tool for identification of nonvolatile organic compounds (1–4), polymers (5–7), and volatile compounds (8,9). The present paper discusses the application of P-GC to surfactants. For surfactants, it is a relatively simple method which can give a surprising amount of information, both qualitative and semiquantitative. The experimental technique involves pyrolysis of the surfactant in the absence of air at 650C in a unit which is directly attached to the inlet port of a gas chromatograph. The pyrolysis products are immediately swept into the gas chromatograph by the carrier gas, helium. Under these conditions, most common surfactant materials decompose into characteristic products from which the original surfactants can be identified by interpretation of the resulting gas chromatogram.

The data are useful for qualitative identification of surfactants in mixtures and in commercial detergent products. In many cases, semiquantitative estimation of the various components in the surfactant mixtures is also possible. In addition, pertinent surfactant structural information, such as the molecular weight distribution of the hydrophobic portion of the molecule, can often be estimated.

Usefulness of this analytical method is shown by data on several individual surfactants and some synthetic surfactant mixtures and commercial detergent products.

## Experimental

### Apparatus

The pyrolysis unit is a modification of one previously described (10) and is shown in Figure 1. Also required are an external magnet of sufficient strength to move the soft iron bar, a cylindrical stainless steel pyrolysis cup (¼ in. O.D. by ½ in. height), and a cup remover as shown in Figure 1. The tapered end of the cup remover is just small enough so that its machined end can be forced into the top of the pyrolysis cup. On the cup remover's

[1] Presented at the AOCS meeting, Houston, 1965.
[2] Company name formerly "California Research Corporation."

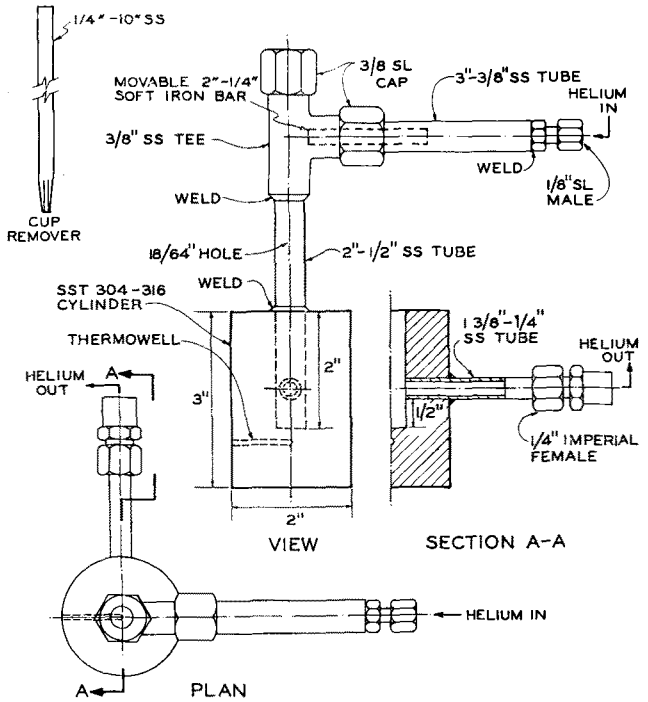


FIG. 1. Pyrolysis units.

withdrawal from the pyrolysis chamber, the cup is held by the remover as it is withdrawn from the unit.

The pyrolysis unit is attached to the inlet port of an Aerograph gas chromatograph, Model 202 (Wilkens Instrument and Research, Inc.), equipped with dual 15 ft by ¼ in. O.D. aluminum columns packed with 20% SF-96 on 60–80 mesh Chromosorb W; helium rate, 60 ml/minute; injector temperature, 215C; column temperature, programmed from 50–250C at 4C/minute.

#### Procedure

The pyrolysis block is heated to a constant 650C by means of externally wrapped electrical heating wire. The temperature is controlled by a voltage regulator. Then, 7–15 mg of detergent sample is weighed into a stainless steel pyrolysis cup. Using the external magnet, the soft iron bar is moved to the left in the pyrolysis unit so that the cup is blocked from falling directly into the pyrolysis chamber. The sample cup is inserted by first removing the cap from the unit, dropping the cup into the vertical tube, and then replacing the cap. After 2 min the soft iron bar is moved to the right so that the cup falls directly into the pyrolysis chamber. The temperature programming is started immediately upon elution of the first large peak (approximately 2 min). After completion of the P-GC run, the pyrolysis cup is removed by first removing the cap and then inserting the cup remover down through the vertical tube and into the top of the pyrolysis cup. After use, the cup is cleaned only by scraping out the residue with a spatula cut to fit exactly into the cup. The cup is *not* rinsed with a solvent, such as water, alcohol, or acetone.

#### Gas Chromatographic Data

For convenience of calculation and in order to overcome possible discrepancies caused by variations in the gas chromatographic temperature programming, relative retention time (RRT) values of chromatogram peaks are calculated based on a time of 100 for 1-decene and a time of zero for the start of temperature programming. If necessary, in order to determine the exact peak position for 1-decene, the unknown sample is mixed with 1-decene and pyrolyzed again. Peaks with RRT less than 10 and greater than 240 are ignored. Peaks less than 10 RRT are not very reproducible, while those at times greater than 240 RRT are normally not significant. Figure 2 gives average RRT values for various pyrolysis products which were identified by retention times, using standards.

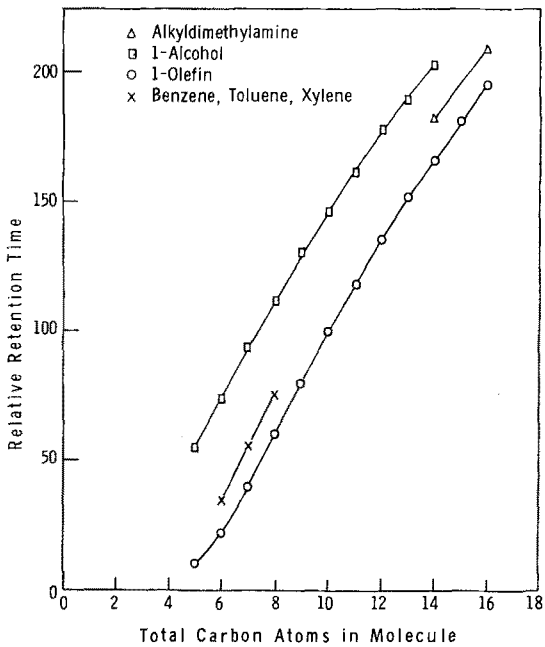


FIG. 2. Relative retention times of pyrolysis products.

Relative areas (RA) of chromatogram peaks are calculated based on an area of 100 for the peak with the greatest area lying between 10 and 240 RRT, inclusive.

The P-GC results are conveniently reported in the form of histograms, examples of which are given in Figure 3.

## Discussion

#### Pyrolysis of Surfactants

The suitability of this P-GC technique for analysis was first investigated by pyrolyzing individual surfactants (Fig. 3). For the purposes of this study, individual surfactants are defined as either commercial surfactants or laboratory prepared surfactants containing only one surfactant type.

*Alkylbenzenesulfonates.* Pyrolysis-gas chromatographic breakdown patterns of three detergent range alkylbenzenesulfonates [two linear alkylate sulfonates (LAS), 340 and 358 molecular weight, and a propylene polymer-derived alkylbenzenesulfonate (PPABS) of the tridecyl type] are shown in Figure 3. For use as "fingerprints" in qualitative analysis it is, of course, not necessary to identify the various peaks in histograms. However, many of the pyrolysis products from these and other surfactants have been identified by using pure compounds as standards, and their RRT values are given in Figure 2.

Readily identifiable pyrolysis products of linear alkylate sulfonates are: (1) straight chain 1-olefins from $C_5$-$C_{10}$ (the $C_2$-$C_4$ homologs are also formed,

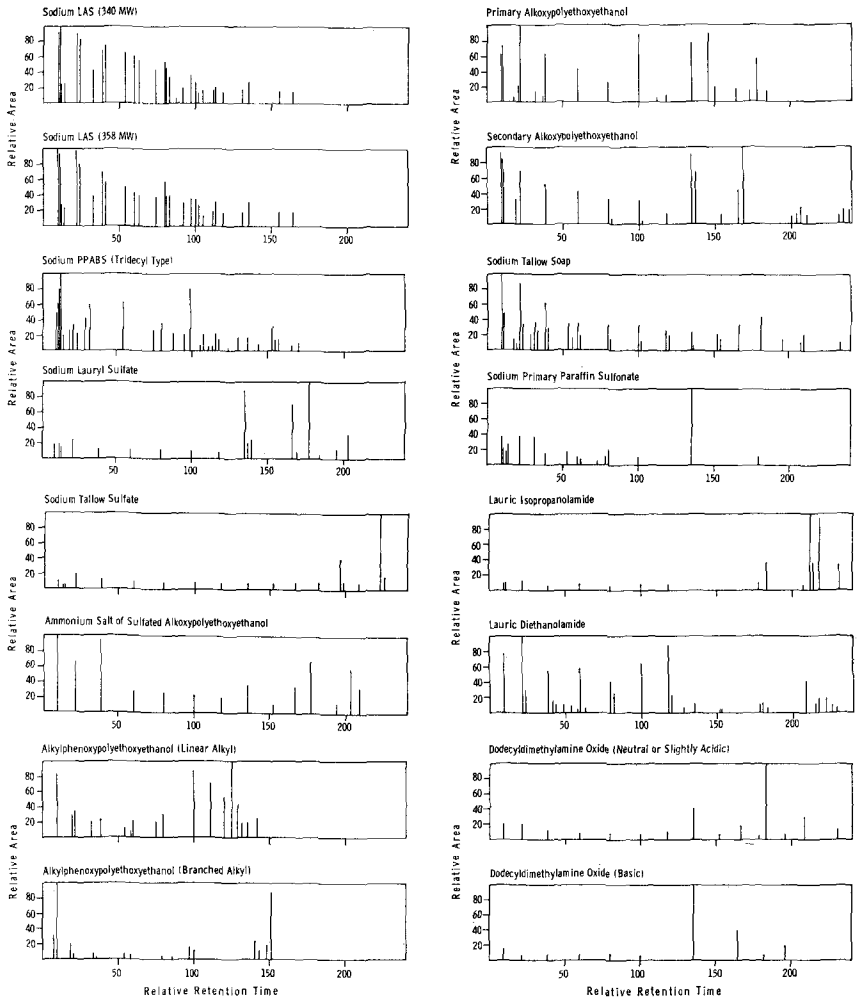


FIG. 3. Relative retention time.

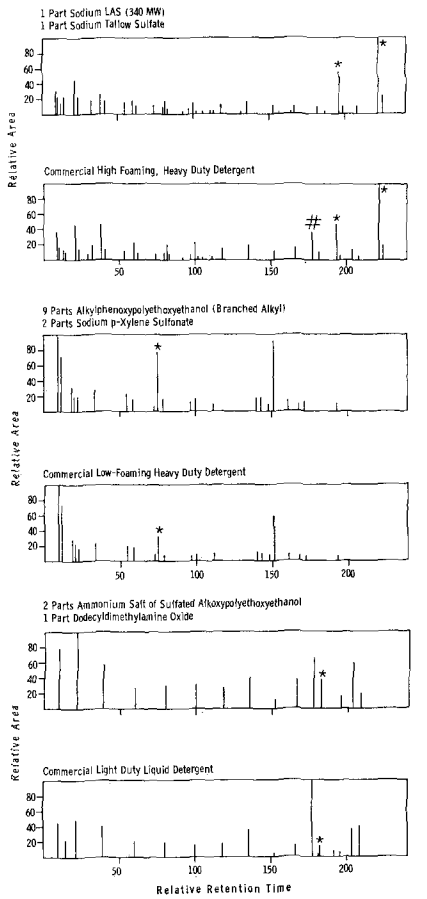


FIG. 4. Relative retention time.

but their RRT values are below 10); (2) straight chain paraffins in the same molecular weight range (these peaks come immediately after those of the straight chain 1-olefins); and (3) benzene (34 RRT), toluene (54 RRT), and xylene (74 RRT). (The experimental gas chromatographic conditions do not distinguish among the isomeric xylenes.) The remaining peaks in the histogram are not identified.

The two LAS samples give quite similar histograms. Analysis of P-GC results for several runs of both LAS samples shows that the most reproducible difference between the 340 molecular weight material and the 358 molecular weight material appears to be in the RA values for the $C_7$ 1-olefin (39 RRT) and the $C_7$ straight chain paraffin (41RRT). For the 340 molecular weight LAS, the olefin peak is smaller than the paraffin peak; but for the 358 molecular weight LAS, just the opposite is found. This may be a general way of distinguishing between higher and lower molecular weight LAS products, as pyrolysis of a pair of higher and lower sulfonates derived from linear alkylates from a different manufacturer showed the same relationships between the $C_7$ olefin and paraffin peaks.

The PPABS pyrolysis differs significantly from those for LAS in that it does not show the regular spacing of straight chain olefin and paraffin peaks as found for LAS. The only peaks identified in this histogram are those for benzene, toluene and xylene. The pyrolysis products from a dodecyl-type PPABS are essentially indistinguishable from those for the tridecyl-type.

The foregoing pyrolysis data are for pure (deoiled and desalted) alkylbenzenesulfonates. However, the presence of either the small amounts of unsulfonated oil usually found in detergent sulfonates or of large amounts of sodium sulfate does not significantly affect the pyrolysis histograms. Water in the amounts commonly found in commercial surfactants also appears to have no significant effect on the course of pyrolysis, although its presence can interfere somewhat in the interpretation of the gas chromatograms. On the other hand, condensed phosphates such as tripolyphosphate can significantly affect the breakdown pattern and, therefore, should be avoided.

Pyrolysis of the ammonium salts rather than the sodium salts of the alkylbenzenesulfonates results in the formation of detectable amounts of undecomposed alkylbenzene. However, this material has a range of RRT values greater than 240 and thus does not interfere with P-GC interpretations.

*Alcohol Sulfates and Ethoxy Sulfate.* Commercial lauryl sulfate pyrolyzes to give small amounts of 1-olefins from $C_5$-$C_{11}$ and much more significant amounts of the $C_{12}$ and $C_{14}$ 1-olefins (RRT values of 135 and 166, respectively). The two other large peaks at 177 RRT and 203 RRT are due to dodecanol-1 and tetradecanol-1. The large amounts of $C_{14}$ alcohol and $C_{14}$ olefin show that the lauryl sulfate is actually a blend of dodecanol and tetradecanol sulfates. In

TABLE I

Reproducibility of Relative Retention Times of Straight Chain Olefins

| Olefin carbon number | Mean relative retention time | Standard deviation |
|---|---|---|
| 5 | 10 | 0.9 |
| 6 | 22 | 1.7 |
| 7 | 39 | 1.5 |
| 8 | 60 | 1.2 |
| 9 | 80 | 0.8 |
| 10 | 100 | 0 |
| 11 | 118 | 1.1 |
| 12 | 135 | 1.3 |
| 13 | 152 | 2.2 |
| 14 | 166 | 1.7 |
| 15 | 181 | 1.5 |
| 16 | 195 | 1.9 |

estimating the ratio of $C_{12}/C_{14}$ alcohols present in the original alcohol sulfate, the $C_{12}/C_{14}$ 1-olefin RA ratio is more reliable than the $C_{12}/C_{14}$ primary alcohol RA ratio.

Sodium tallow alcohol sulfate appears to pyrolyze in a very similar manner to lauryl sulfate. Small amounts of 1-olefin from $C_5$-$C_{15}$ are observed, but the significant peaks are the two due to $C_{16}$ and $C_{18}$ 1-olefins (195 RRT and 224 RRT, respectively). Again, the ratio of $C_{16}$ to $C_{18}$ olefin gives a very good estimation of the ratio of $C_{16}/C_{18}$ in the original tallow sulfate. By analogy with the lauryl alcohol sulfate results, hexadecanol-1 and octadecanol-1 might be expected in the tallow sulfate pyrolyzate. However, the RRT values for these compounds would be greater than 240; and they are, therefore, not observed.

The ammonium salt of a sulfated alkoxypolyethoxyethanol pyrolyzes in a somewhat different manner. (This surfactant is derived from lauryl alcohol and has an average of about three ethoxy groups per molecule.) Significant peaks for the $C_{12}$ and $C_{14}$ straight chain primary alcohols are present; however, even stronger peaks are shown for the $C_5$, $C_6$, and $C_7$ 1-olefins. The large RA values of the lower olefin peaks are distinguishing characteristics of lauryl ethoxy sulfate as opposed to lauryl sulfate.

For both alcohol sulfates and alcohol ethoxyl sulfates, sodium and ammonium salts give essentially the same pyrolysis histograms.

*Alkylphenoxypolyethoxyethanols.* P-GC is a very simple and straightforward means of distinguishing between an alkylphenoxypolyethoxyethanol (APPEE) with a linear alkyl group and one with a propylene polymer-derived branched chain alkyl group. A commercial sample of linear chain APPEE (average alkyl chain of $C_9$ and average of 9 ethoxy units) pyrolyzes to give: (1) 1-olefins from $C_5$-$C_9$; (2) small amounts of benzene, toluene, and xylene; and (3) several considerably stronger peaks lying at 100 RRT and greater which are not identified.

On the other hand, a commercial branched chain APPEE (an average alkyl chain of $C_9$ and an average of 9 ethoxy units) gives a large peak near 10 RRT but only very minor amounts of other peaks up through 100 RRT. This histogram also shows a very strong peak at about 152 RRT preceded by three smaller peaks. This group of four peaks near 150 RRT appears to be very characteristic of branched-chain APPEE nonionics. Other APPEE nonionics with different alkyl and ethoxy chain lengths show this same characteristic peak grouping.

Pyrolysis of the sulfates of either branched or linear APPEE gives histograms similar but not identical to that of the parent nonionic. Sodium and ammonium salts of the sulfated nonionics give essentially identical breakdowns.

*Alkoxypolyethoxyethanols.* Figure 3 also shows the pyrolysis patterns for two types of alkoxypolyethoxyethanols (APEE). The upper histogram is from a commercial sample of a primary APEE having a blend of $C_{10}$ and $C_{12}$ straight alkyl chains and containing about 60% ethylene oxide. The ethoxy chain is attached to the primary position of the alkyl group. Significant peaks are observed for $C_{10}$ and $C_{12}$ 1-olefins and for decanol-1 and dodecanol-1. Lower 1-olefins are also present, their RA values peaking at $C_6$ and falling off to $C_9$. As might be expected, this primary APEE nonionic gives a histogram very similar to that of a sulfated primary APEE discussed earlier.

A laboratory sample of a secondary APEE pyrolyzes in a somewhat different manner. This APEE is composed of a $C_{12}$ straight alkyl chain and an average of 7 ethoxy units per molecule. The ethoxy chain is attached to a secondary carbon atom in the alkyl chain. The histogram shows: (1) a mixture of $C_{12}$ olefins, apparently both alpha and internal (135 RRT to 138 RRT) and (2) 2- and 3-dodecanol along with other internal straight chain dodecanols (165 RRT to 170 RRT). Lower straight chain olefins are also observed with the RA values peaking at $C_5$ and falling off to $C_{11}$. Small unidentified peaks are located at 200 RRT and above.

*Soap and Primary Paraffin Sulfonate.* The pyrolysis breakdown pattern for a commercial sodium tallow soap shows 1-olefin peaks from $C_5$–$C_{17}$. In general, the RA values decrease in the same order, although a moderate peak in the RA distribution appears at pentadecene-1. The other products are not identified.

Primary paraffin sulfonate (a laboratory sample containing essentially only a $C_{12}$ straight chain alkyl group) gives a fairly simple histogram with a very large peak for $C_{12}$ 1-olefin and minor amounts of other products with lower RRT values, some of which are 1-olefins. Contrary to the case of primary alcohol sulfates, no straight chain primary alcohols are formed from primary paraffin sulfonate.

*Alkanolamides.* Lauric isopropanolamide (a commercial foam additive) pyrolyzes to give relatively small amounts of low RRT compounds, mostly 1-olefins in the $C_5$–$C_{11}$ range, compared with the larger amounts of higher RRT compounds (RRT's greater than 140). (Preliminary data indicate that some of these compounds above 140 RRT are nitriles and amides, but identification is not complete.)

A commercial sample of lauric diethanolamide, on the other hand, gives larger amounts of the lower RRT compounds than of the higher RRT compounds. Several other mono- and dialkanolamides show this same difference in relative areas for lower and higher RRT compounds. Thus, this characteristic may be useful in distinguishing between mono- and dialkanolamides.

*Alkyldimethylamine Oxides.* Alkyldimethylamine oxides on pyrolysis may yield different products, depending on the pyrolysis conditions. A commercial sample of dodecyldimethylamine oxide when pyrolyzed under basic conditions (in the presence of a small amount of sodium hydroxide or other strong base) gives large amounts of $C_{12}$ and $C_{14}$ 1-olefins and very minor amounts of lower 1-olefins. These results show that the dodecyldimethylamine oxide actually contains a mixture of both $C_{12}$ and $C_{14}$ straight chain alkyl groups.

If dodecyldimethylamine oxide is pyrolyzed under neutral or slightly acidic conditions, the most significant peaks are those due to dodecyl- and tetra-

decyldimethylamines (182 and 208 RRT, respectively). Moderate amounts of $C_{12}$ and $C_{14}$ 1-olefins and very small amounts of lower 1-olefins are also observed. Thus, the neutral or slightly acidic pyrolysis conditions are much preferred for amine oxide analysis because of the formation of the characteristic alkyldimethylamines.

#### Reproducibility

In the development of analytical techniques, experimental data must show adequate reproducibility. In this regard, some reproducibility data for RRT values are given in Table I for straight chain 1-olefins from $C_5$–$C_{16}$. The data are from 24 different pyrolyses of several of the surfactants shown in Figures 3 through 10. Reproducibility data for RA values are given in Table II. These results are from 7 different pyrolysis runs on identical sodium LAS sulfonate (340 molecular weight) and are representative of the usual RA reproducibility, although in a few cases RA values have differed by as much as 25%. These results indicate that the RRT reproducibility is excellent while the RA reproducibility is considered adequate for satisfactory analysis.

TABLE II
Reproducibility of Relative Areas of Major Peaks for Sodium LAS (340 MW)

| Relative retention time | Mean relative areas | Standard deviation |
|---|---|---|
| 10 | 93 | 13 |
| 11 | 100 | 4 |
| 22 | 90 | 12 |
| 24 | 84 | 12 |
| 34 | 43 | 13 |
| 39 | 71 | 7 |
| 41 | 75 | 6 |
| 54 | 66 | 14 |
| 60 | 62 | 6 |
| 63 | 57 | 5 |
| 74 | 43 | 6 |
| 80 | 54 | 15 |
| 81 | 46 | 9 |
| 83 | 33 | 4 |
| 97 | 36 | 10 |
| 100 | 28 | 3 |

#### Pyrolysis of Synthetic Mixtures and Commercial Products

In general, the pyrolysates derived from the several surfactants are the same whether pyrolyzed in mixtures of surfactants or by separate pyrolyses of the individual surfactants. Pyrolysis-gas chromatographic analyses of synthetic surfactant mixtures and commercial detergent products are shown in Figure 4. The data show quite clearly that adequate qualitative identification of individual surfactants in mixtures can be made by this pyrolysis technique. Also, in some cases helpful quantitative estimations of the individual components are possible.

The synthetic mixtures were prepared by simple physical mixing of the components, either commercial surfactants or laboratory preparations. In the case of commercial detergent products, the pyrolyses were carried out on the alcohol-soluble portions of heavy-duty built formulations because, as previously discussed, the condensed phosphates can materially affect the breakdown patterns. The total solids portions of light-duty liquid formulations were used; however, moderate amounts of water or low molecular weight alcohols do not adversely affect the results.

*LAS/Tallow Sulfate Blend.* A blend of 1 part sodium LAS, 340 molecular weight, and 1 part sodium tallow alcohol sulfate pyrolyzes to give the first histogram of Figure 4. The peaks at 100 RRT and lower are mostly due to the LAS, although the 1-olefin RA values are augmented by contributions due to pyrolysis of the tallow sulfate. The most significant tallow sulfate peaks are the two marked with asterisks. The RA ratio of $C_{16}$ 1-olefin (195 RRT) to $C_{18}$ 1-olefin (208 RRT) indicates an approximate 35/65 ratio of $C_{16}/C_{18}$ alkyl groups in the tallow sulfate.

*Commercial High Foaming, Heavy-Duty Detergent.* Pyrolysis of the alcohol-soluble portion of a commercial high foaming, heavy-duty detergent shows clearly the presence of approximately equal amounts of LAS and a tallow-type alcohol sulfate. The $C_{16}/C_{18}$ 1-olefin ratio (these peaks are marked with asterisks) is quite close to that of the synthetic mixture above. The strong peak at 177 RRT (marked with a crosshatch) is not present in the synthetic mixture and is indicative of dodecanol-1. Dodecanol-1 must be present in the formulation as the alcohol itself not as the alcohol sulfate. The $C_{12}$ alcohol sulfate, if present, would give about equal amounts of $C_{12}$ 1-olefin and dodecanol-1. This is not found in the present histogram. Therefore, the $C_{12}$ entity must be present as the alcohol. A more complete analysis of the alcohol-soluble portion of this commercial sample using conventional analytical procedures confirms the presence of dodecanol-1.

*APPEE/Xylene Sulfonate Blend.* Pyrolysis of a blend of 9 parts branched chain APPEE and 2 parts sodium p-xylene sulfonate is also shown in Figure 4. Nearly all of the peaks are characteristic of the branched chain APPEE. As noted earlier, the grouping of a strong peak near 150 RRT preceded by three much weaker peaks is very characteristic of this type nonionic. The strong peak marked with an asterisk is due to p-xylene. (The three xylene isomers are not resolved by our gas chromatographic technique.)

*Commericial Low Foaming, Heavy-Duty Detergent.* The P-GC of the alcohol-soluble portion of a commerical low foaming, heavy-duty detergent indicates that this commercial detergent contains a branched chain APPEE nonionic and xylene sulfonate. The ratio of the xylene peak (marked with an asterisk) to the large peak near 150 RRT is somewhat less for the commercial detergent than for the synthetic mixture; therefore, it probably contains slightly less than a 2/9 ration of xylene sulfonate to APPEE.

*Sulfated APEE/Amine Oxide Blend.* Two parts of the ammonium salt of a sulfated primary APEE blended with 1 part of dodecyldimethylamine oxide give a breakdown pattern in which most of the peaks are due to the sulfated nonionic. Readily apparent are those for the $C_{12}$ and $C_{14}$ 1-olefins (135 RRT and 156 RRT, respectively) and the $C_{12}$ and $C_{14}$ straight chain 1-alcohols (177 RRT and 203 RRT, respectively). The asterisk-labeled peak at 182 is due to dodecyldimethylamine derived from the amine oxide. Also, the peak at 208 RRT may be partly due to the corresponding $C_{14}$ alkyldimethylamine.

*Commercial Light-Duty Detergent.* The bottom histogram of Figure 4 shows the pyrolysis data for the total solids portion of a commercial light-duty liquid detergent. The presence of a sulfated APEE is indicated by the $C_{12}$ and $C_{14}$ 1-olefins and the $C_{12}$ and $C_{14}$ straight chain 1-alcohols. The peak marked with an asterisk is due to dodecyldimethylamine derived from the amine oxide. The ratios of the 177 peak to the 182 peak in the two histograms indicate that the commercial detergent contains amine oxide and sulfated nonionic in a ratio of about 1/6. Independent analysis using the quaternary titration method of Lew (11) shows the actual ratio is about 1/5.

## Conclusions

The present pyrolysis-gas chromatographic method does not furnish a single analytical scheme for all conceivable surfactant mixtures. As formulations become more complicated and the number of components increases, interpretation of the experimental data becomes more difficult. However, when used in conjunction with other analytical procedures, such as ultraviolet, infrared, nuclear magnetic resonance, mass spectrometry, phosphoric acid decomposition (12), ion exchange, and quaternary titration (11), this technique can be of significant value in the analysis of surfactants.

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Experimental assistance by G. E. McKim; helpful suggestions by R. House and other members of the Surfactant Section and by R. S. Porter of the Analytical Section, Chevron Research Company. Interest in and funds for this work provided by the Oronite Division of the Chevron Chemical Company.

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# Gas-Liquid Chromatography of the Positional Isomers of Methyl Nonynoate[1]

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## Abstract

A mixture of all the positional isomers of methyl nonynoate is poorly resolved by gas-liquid chromatography on packed polar (diethylene glycol succinate) and packed nonpolar (Apiezon L) columns. Better resolution is obtained on capillary columns, with the polar liquid phase giving baseline separations between all the isomers except 9:T4 and 9:T5. The nonynoic esters are eluted later than methyl nonanoate on either liquid phase. The isomers with the triple bond near the center of the molecule come off first, and the elution time increases as the triple bond moves toward either end of the chain. Methyl 8-nonynoate, the only isomer with a terminal triple bond, does not follow this pattern.

## Introduction

ONLY ISOLATED EXAMPLES appear in the literature on the gas-liquid chromatographic (GLC) separation of mixtures of acetylenic esters; what has appeared has been confined to a few naturally occurring or easily prepared compounds. Zeman (1) determined the elution times for saturated, monoenoic, and monoynoic esters and found that on polyethylene glycol adipate the elution order was 18:0[3] (methyl stearate), 18:Δ9 (methyl oleate) and 18:T9 (methyl stearolate), while on Apiezon L it was 18:Δ9, 18:T9, and 18:0. Analogous results were obtained on both liquid phases with 22:0 (methyl behenate), 22:Δ13 (methyl erucate) and 22:T13 (methyl behenolate). The equivalent chain lengths for 18:T9 and 18:T6 (methyl tarirate) were found by Miwa et al. (2) to be identical on packed columns of either Apiezon L or of diethylene glycol pentaerythritol adipate, and thus the esters were not separable. Lefort et al. (3) found the equivalent chain lengths for 18:T6 and 18:T9 to be identical on diethylene glycol succinate (DEGS) and also on Apiezon M. They found an elution order identical to that of Zeman for 18:0, 18:Δ9, and 18:T9 on the polar and nonpolar phases. Achaya et al. (4) made an extensive study of the separation of fatty acetylenic, ethylenic, and saturated compounds by thin-layer chromatography. They were unable to separate positional isomers, either acetylenic or ethylenic, as esters, acids, or alcohols by any of the systems tried. For example, they could not separate 18:T9 from 18:T6.

To our knowledge, no separation of a series of isomeric acetylenic esters has been reported. This paper describes the behavior of the isomeric methyl nonynoates on both packed and capillary columns of DEGS and Apiezon L.

## Experimental

3-Nonynoic acid was prepared by a method similar to that of Knight and Diamond (5) for the preparation of 3-octynoic acid. The other nonynoic acids were prepared by the method of Wotiz and Hudak (6) with minor modifications. Nonanoic acid, used as the reference for calculation of relative retention times, was prepared by hydrogenation of 9:T7. Methyl esters were prepared with diazomethane (7).

The esters were assayed by analytical GLC and found to be about 99% pure, except for 9:T3, which contained a small amount of an unknown contaminant. To establish the identities of the peaks in the mixture, each individual acetylenic ester was chromatographed with methyl nonanoate (9:0).

Four columns were used in this study: a) 6 ft × ¼ in. 15% DEGS on 60–80 mesh Gas-Chrom RZ (Applied Science Laboratories, State College, Pa.), b) 3 ft × ¼ in. 10% Apiezon L on 60–80 mesh Gas-Chrom RZ, c) 85 ft × 0.01 in. I.D. DEGS capillary, and d) 100 ft Apiezon L capillary. The capillary

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[3] Abbreviations used in the text and graphs are interpreted as follows: The number before the colon specifies the chain length, zero after the colon indicates a saturated compound, Δ (delta) indicates an ethylenic ester, and T (tau) an acetylenic ester. Numbers following Δ or T specify the position of the unsaturation.