

# "Acid" Pyrolysis-Capillary Chromatographic Analysis of Anionic and Nonionic Surfactants

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## Abstract

A tandem "acid" pyrolysis-capillary chromatographic method for analyzing surfactants has been developed, and its application to the more common anionic and nonionic surfactant types investigated. In this method a surfactant is mixed with an acid, such as  $P_2O_5$  or  $H_3PO_4$ , and dropped into a pyrolyzer attached to a capillary gas chromatograph. The resulting volatile pyrolyzate is carried into the chromatograph for analysis.

According to the chromatograms, the point of cleavage during "acid" pyrolysis is quite selective, usually at a C-S or C-O bond. For example, LAS and ABS give peaks corresponding to the alkylbenzene precursors; primary linear alkyl sulfates and sulfonates, peaks corresponding to olefins with the same number of carbon atoms as the alkyl group; and alcohol and alkylphenol ethoxylates and ethoxylate sulfates, peaks corresponding to olefins from the alkyl group and to acetaldehyde and a higher aldehyde from the polyethoxy group. Alkylphenol derivatives are probably cleaved to form an alkylphenoxy intermediate, which then dealkylates to give the olefins.

This method is quantitative for carbon number or carbon number and isomer distribution of hydrophobes in linear surfactants, semiquantitative for ethoxy content and for hydrophobes in branched chain surfactants, and qualitative for hydrotropes and certain foam additives. Surfactants, as well as mixtures of certain surfactant types, in built detergent formulations can be analyzed without isolation.

## Introduction

PREVIOUSLY AVAILABLE methods for determining surfactant molecular weight and structures are long and involved. For example, linear alkylbenzene sulfonates (LAS) and polypropylenebenzene sulfonates (ABS) were formerly analyzed by desulfonation to the alkylbenzene precursors by refluxing with phosphoric acid at 215°C by the method of Knight and House (1), in which the alkylbenzene formed is simultaneously recovered by steam distillation. The alkylbenzene is then isolated and analyzed by gas capillary chromatography or mass spectrometry. With  $C_{10}$ - $C_{13}$  LAS or dodecyl-type ABS, a 1.5-hr reflux is adequate for quantitative results; with  $C_{11}$ - $C_{14}$  LAS, 6 hr are necessary; and with  $C_{18}$ - $C_{20}$  LAS, it is virtually impossible to steam-distill the alkylbenzenes in a reasonable time.

Recent work by Liddicoet and Smithson (2) indicated that thermal pyrolysis might be applicable to the analysis of surfactants. Using  $\frac{1}{4}$ -in. packed columns and a thermal conductivity detector, they obtained different gas chromatographic patterns for pyrolyzates from different surfactants. However the high temperature (650°C) produces considerable cracking and therefore is not suitable for quantitative analysis.

The present method involves "acid" pyrolysis at 400°C (or 550°C), which appears to yield the same products as the method of Knight and House but does it almost instantaneously. The temperature is sufficiently high for rapid cleavage of C-S and C-O bonds but still low enough to minimize breaking of C-C bonds. The pyrolysis product is swept from the pyrolyzer directly into a gas capillary chromatograph for analysis. The over-all analysis time for  $C_{11}$ - $C_{14}$  LAS is about 0.5 hr as compared to 8-10 hr by the older method. The resulting "acid" pyrolysis chromatograms (PC) give quantitative information on hydrophobes for linear anionic and nonionic surfactants, semiquantitative information for branched surfactants, and other qualitative information for surfactants as well as certain detergent additives.

## Experimental

### Equipment

The pyrolyzer is similar to the ones previously described (2,3) except for cooling fins around the shaft, which keep the cap just warm to touch and slightly smaller internal diameters to reduce dead space (Fig. 1). The pyrolysis block is wired for 400 watts, insulated, and attached to the side of a Perkin-Elmer capillary chromatograph (Model 800). The helium line from one of the flow controllers is cut near the injection block. The section from the controller is connected to the top of the pyrolyzer, the other to the outlet of the pyrolyzer block. Helium flows through the top of the pyrolyzer, down into the pyrolyzer block, and over into the injection block. With this arrangement the pyrolyzer does not interfere with normal liquid sample injection.

A 200-ft, 0.02-in. I.D. stainless steel capillary column, coated with SF-96 silicone oil, was used as the sensing column and a similar 75-ft column as the reference. Helium pressure is normally 10 psig for sensing column and 8 psig for reference; injector

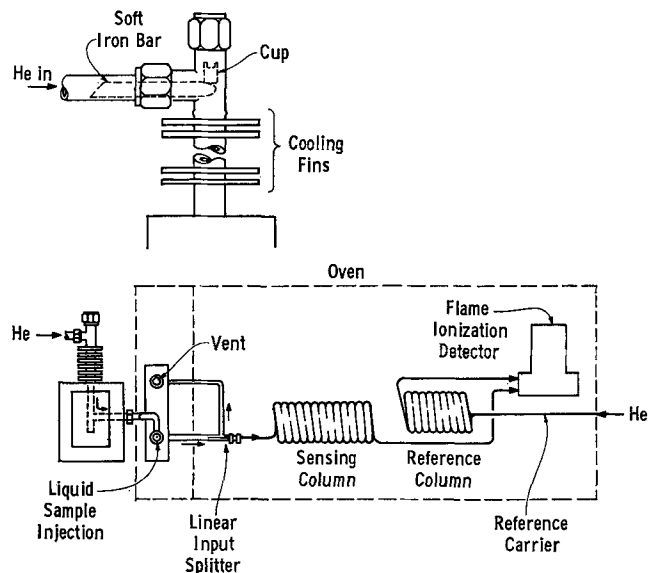


FIG. 1. Pyrolyzer-chromatograph unit.

<sup>1</sup> Winner, Bond Award Medal, Philadelphia, October 1966.

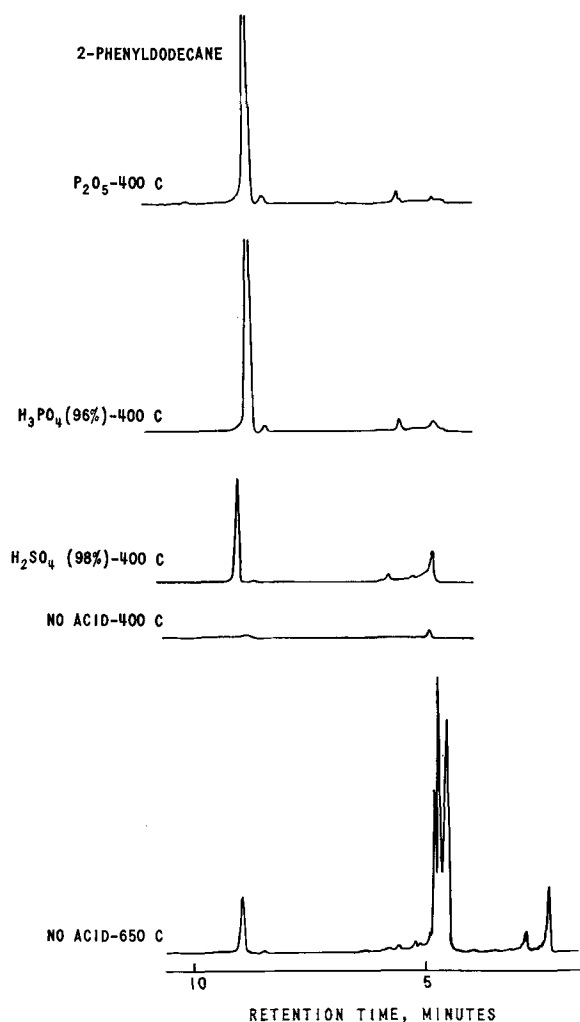


FIG. 2. Effect of variables on pyrolysis of 2-phenyldodecane sulfonate. 1.5 mg of sulfonate with about 10 mg  $P_2O_5$  or acid (when used). Chromatographic conditions, PE-800, 200 ft. 0.02-in. I.D. SF-96 capillary, column temperature 220C, attenuation  $\times 20$ .

temperature, 150C–250C; detector temperature, 125C–250C (injector and detector are at the low end of the temperature ranges when column is at 60C); column temperature, variable as indicated for different runs; splitter needle, No. 22 or 24 gauge. The detector output signal is fed to a Leeds and Northrup Speedomax G recorder with a Disc Integrator (Model 203).

#### Procedure

Into a stainless steel cup is weighed a 1–5 mg surfactant sample (5–15 mg if appreciable amount of inorganic builders is present); then 2–10 times by weight of phosphorus pentoxide ( $P_2O_5$ ), 96% phosphoric acid [215C bp (1)], or 115% polyphosphoric acid is added and mixed well with the end of a clean paper clip. If the mixture with  $P_2O_5$  is too viscous, such as with built detergents, 1–3  $\lambda$  of water is added to obtain better mixing.

Before the sample is inserted into the pyrolyzer, the soft iron bar is moved over the hole of the shaft with a magnet. Then the cap is removed, cup placed on top of the bar, and the cap replaced and finger-tightened. The cup is dropped into the pyrolysis chamber by moving the bar to the left with the magnet, and the recorder is started immediately.

After the run the cup is retrieved, cleaned in hot 5%  $H_3PO_4$ , rinsed, and then dried for subsequent use.

#### "Acid" Pyrolysis Chromatograms (PC)

The accuracy and versatility of this method are demonstrated by comparison of the "acid" PC of a surfactant with a chromatogram of its precursor or with an independent analysis for the more common anionic and nonionic types. The 200-ft, SF-96 capillary column resolves nearly all the isomers of detergent range linear alkylbenzenes. It appears adequate for pyrolysis products from other surfactants although additional information might be obtained with other columns. Packed columns would be satisfactory if the high resolution of capillary columns is not required.

Chromatographic conditions were selected for approximate optimum resolution and retention time for the particular pyrolysis products. Since the experimental data were accumulated over a long period of time and retention times do change with column age and operating conditions, standards were run periodically or whenever in doubt. The capillary chromatographic results are calculated from relative peak areas without corrections for molecule weight.

#### Discussion

##### "Acid" Pyrolysis of Linear Surfactants

This method is especially useful for quantitative analysis of linear surfactants because the fewer components in the pyrolyzate are more readily separated and identified by gas chromatography than the pyrolyzates from branched surfactants. In general, either  $P_2O_5$ ,  $H_3PO_4$  (96%), or polyphosphoric acid (115%) is suitable for "acid" pyrolysis although one may be superior for certain analyses as described later.

##### Linear Alkylbenzene Sulfonate (LAS)

Optimum "acid" pyrolysis temperature, as determined with sodium 2-phenyldodecane sulfonate, appears to be about 400C. With either  $P_2O_5$  or  $H_3PO_4$  the major peak in the PC corresponds to 2-phenyldodecane in retention time and comprises about 90% of the total area (Fig. 2). Conversion to 2-phenyldodecane is approximately 60% of theoretical and occurs almost instantaneously, as indicated by a retention time and peak width essentially identical with an authentic sample of 2-phenyldodecane.

Sulfuric acid not only yields considerably less 2-phenyldodecane (smaller peak for same sample size), but the 2-phenyldodecane peak area is only about 50% of the total. Without acid (at 400C) almost no degradation of the sulfonate occurs. (The combination of "pyrolysis without acid" and " $P_2O_5$  pyrolysis" for analysis of LAS and alkyl sulfate mixtures is discussed later.) Pyrolysis at 650C without acid (2) yields relatively little 2-phenyldodecane (8% of total area) but mostly lower molecular-weight pyrolysis products because of excessive cracking. Below 300C the pyrolysis rate appears slower with the broadening of peaks; and above 400C formation of lower molecular-weight products increases. (The minor peak before 2-phenyldodecane is probably 3-phenyldodecane originally present in the sample used for preparing the sulfonate.)

"Acid" pyrolysis of a  $C_{11}$ – $C_{14}$  LAS produces a chromatogram that is almost identical with that of the starting alkylbenzene (Fig. 3). Carbon number and isomer distributions calculated from these chromatograms in most cases are within the experimental error of about  $\pm 5\%$  normally achieved with gas

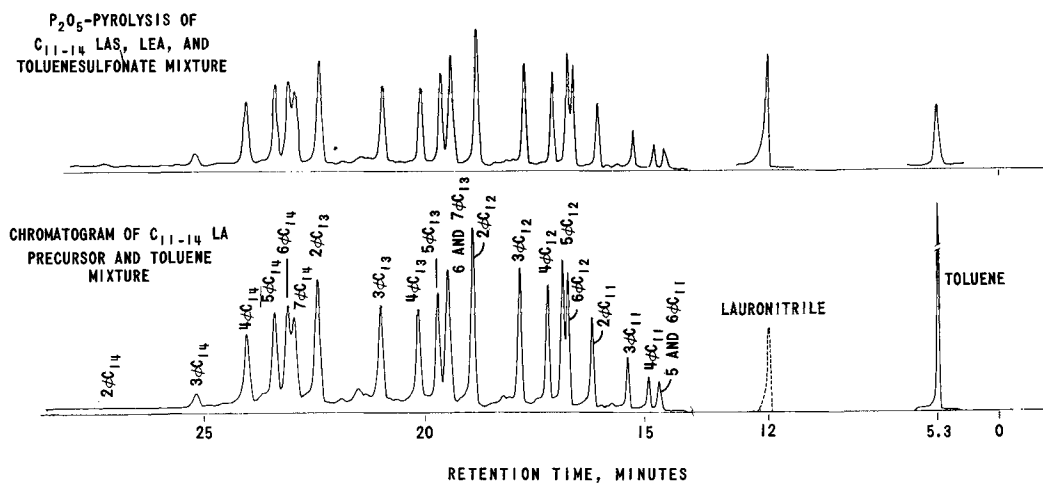


FIG. 3.  $P_2O_5$ -Pyrolysis of a mixture of sodium  $C_{11-14}$  LAS, lauric monoethanolamide (LEA), and sodium toluenesulfonate. Column temperature, programmed 120–220°C at 16°C per minute.

chromatographic methods. Deviations for minor constituents, the areas of which are too small to measure accurately, are higher, and 2-phenyl  $C_{14}$  always seems to be higher for the PC (Table I). Alkylbenzene average molecular weights are well within one unit.

Results are also quantitative for higher LAS's such as  $C_{18-20}$  LAS (Fig. 4 and Table II), when pyrolysis temperature is raised to 550°C to increase pyrolysis rate and accelerate vaporization of alkylbenzenes. With the higher pyrolysis temperature the amount of lower molecular-weight pyrolysis product increases because of cracking, as is evident by a sizable early peak. A shorter chromatographic column (75-ft) provides reasonably short retention time.

#### Primary Alkyl Sulfate and Sulfonate

"Acid" pyrolysis of primary alkyl sulfate or sulfonate produces a mixture of internal olefins and alpha olefins with the same number of carbons as the alkyl group. A PC for 1-nonyl sulfate is reproduced in Fig. 5.

Peak assignments for nonene-1, *trans*-nonene-4, *cis*-

nonene-4, and *trans*-nonene-2 are based on a comparison of retention times (RT) (24.1, 25.0, 25.4, and 26.8 min, respectively) with authentic samples. *cis*-Nonene-2 is assigned to the last peak (28.2 min) since, according to isomers of nonene-4 and octene-2 (RT's given later), the *cis* form has a longer RT than the *trans*. This assignment is further supported by a comparison of the RT's of octene and nonene isomers. It has been observed that the ratio of differences in RT of given isomers (for example, *trans*-2, *cis*-2, and 1-olefins) remains essentially constant from one carbon number to the next. Thus the ratios.

$$\frac{RT_{(trans\text{-}octene-2)} - RT_{(octene-1)}}{RT_{(cis\text{-}octene-2)} - RT_{(octene-1)}}$$

and

$$\frac{RT_{(trans\text{-}nonene-2)} - RT_{(nonene-1)}}{RT_{(last\ peak)} - RT_{(nonene-1)}}$$

should be about the same if the last peak is *cis*-nonene-2. RT's for octene-1, *trans*-octene-2, and *cis*-octene-2 are 12.1, 13.2, and 13.8 min, respectively, and the ratios are indeed very close, 1.1/1.7 or 0.65 for the octenes and 2.7/4.1 or 0.66 for the nonenes.

One would also expect the formation of *cis*- and *trans*-nonene-3 with *trans* having a shorter retention time than *cis* and appearing between *trans*-nonene-2 and *trans*-nonene-4. Therefore *trans*-nonene-3 is assigned to the third peak (also containing *cis*-nonene-4) and *cis*-nonene-3 to the shoulder following.

Higher alkyl sulfates also yield internal and *alpha* olefins. Because essentially no further degradation of the olefins occurs, this method quantitatively determines carbon number distribution in alkyl sulfates, such as tallow alcohol sulfates (TAS) (Table III).

1-Nonane sulfonate on  $P_2O_5$  pyrolysis gives the same nonene peaks as 1-nonyl sulfate. Primary  $C_{12}$ ,

TABLE I  
 $P_2O_5$  Pyrolysis of  $C_{11-14}$  LAS in Detergent Formulations

Alkylbenzene	$C_{11-14}$ Linear alkylate precursor	$P_2O_5$ Pyrolysis of $C_{11-14}$ LAS formulations					
		Light duty <sup>a</sup>	Heavy duty <sup>b</sup>				
Isomer distribution, wt %							
5- and 6-Phenyl	$C_{11}$	1.1	1.4	1.3	1.4	1.1	1.2
4-Phenyl	$C_{11}$	1.3	1.6	1.3	1.0	1.1	1.1
3-Phenyl	$C_{11}$	1.8	2.0	1.9	2.2	2.0	1.9
2-Phenyl	$C_{11}$	4.0	4.2	4.2	3.7	4.1	4.0
5- and 6-Phenyl	$C_{12}$	11.3	11.8	12.3	11.3	11.1	10.9
4-Phenyl	$C_{12}$	5.4	5.6	5.6	5.4	5.4	5.1
3-Phenyl	$C_{12}$	6.0	6.5	6.5	6.1	6.3	6.3
2-Phenyl	$C_{12}$	10.1	10.0	10.0	9.4	9.5	10.2
5-, 6-, and 7-Phenyl	$C_{13}$	14.0	13.6	14.4	14.2	13.6	13.7
4-Phenyl	$C_{13}$	5.0	5.5	5.6	5.4	5.5	5.3
3-Phenyl	$C_{13}$	5.5	5.9	6.2	6.0	6.4	6.2
2-Phenyl	$C_{13}$	9.6	8.7	8.6	7.8	9.1	9.5
5-, 6-, and 7-Phenyl	$C_{14}$	19.0	16.7	17.1	19.0	18.3	18.1
4-Phenyl	$C_{14}$	4.8	5.2	4.1	5.4	5.1	5.0
3-Phenyl	$C_{14}$	1.1	1.3	0.9	1.3	1.0	1.2
2-Phenyl	$C_{14}$	0.01	.....	.....	0.4	0.4	0.3
Side chain carbon number distribution, wt %							
	$C_{11}$	8.2	9.2	8.7	8.3	8.3	8.2
	$C_{12}$	32.8	33.9	34.4	32.2	32.3	32.5
	$C_{13}$	34.1	33.7	34.8	33.4	34.6	34.7
	$C_{14}$	24.9	23.2	22.1	26.1	24.8	24.6
Average molecular weight							
		256.6	256.0	255.9	256.9	256.7	256.6

<sup>a</sup> 18 parts  $C_{11-14}$  LAS, 2 parts lauric monoethanolamide, and 3 parts p-toluene sulfonate.

<sup>b</sup> 18%  $C_{11-14}$  LAS, 2% lauric monoethanolamide, 3% p-toluene sulfonate, 45% TPP, 8% N-silicate, 1% CMC, 15%  $Na_2SO_4$ , and 8% water.

TABLE II  
 $P_2O_5$  Pyrolysis of  $C_{18-20}$  LAS

Alkylbenzenes	$C_{18-20}$ Linear alkylate	$P_2O_5$ Pyrolysis of $C_{18-20}$ LAS
3,4,5,6,7,8,9- $\Phi C_{17}$	0.8	0.5
2- $\Phi C_{17}$		
3,4,5,6,7,8,9- $\Phi C_{18}$	23.6	23.4
2- $\Phi C_{18}$		
3,4,5,6,7,8,9,10- $\Phi C_{19}$	40.1	40.6
2- $\Phi C_{19}$		
3,4,5,6,7,8,9,10- $\Phi C_{20}$	28.6	29.4
2- $\Phi C_{20}$		
3,4,5,6,7,8,9,10,11- $\Phi C_{21}$	6.9	6.1

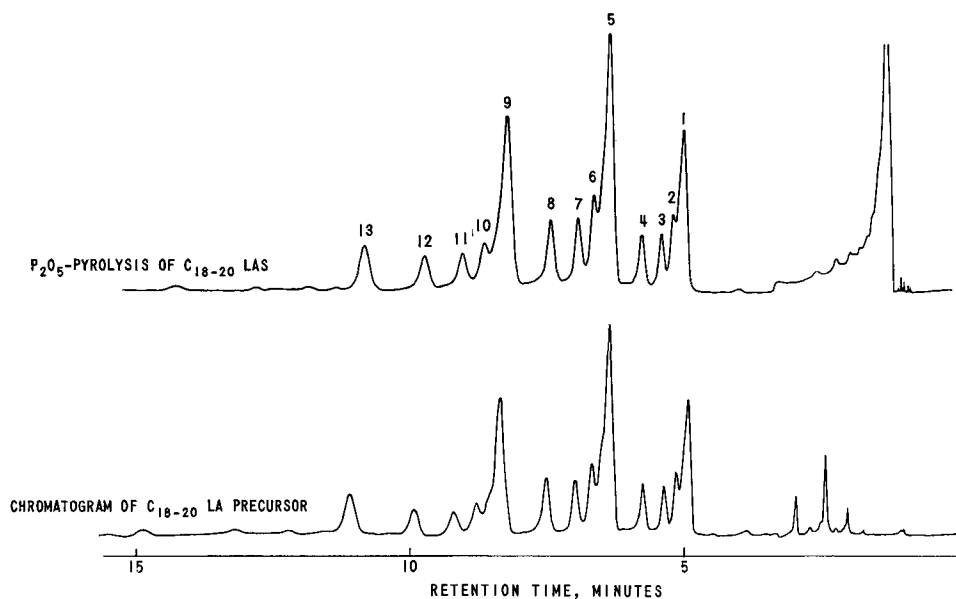


FIG. 4.  $P_2O_5$ -Pyrolysis of  $C_{18-20}$  LAS. Pyrolysis temperature 550C. Chromatographic conditions PE-800, 75-foot, 0.02-inch I.D. SF-96 capillary, column temperature 220C, Attenuation: x5 through Peak 13), x2 (after Peak 13).

Peak assignments:

- |  |   |   |   |
|--|---|---|---|
| 1. 6,7,8,9 $\phi$ $C_{18}$ , 2 $\phi$ $C_{17}$ | 5. 6,7,8,9,10 $\phi$ $C_{19}$ , 2 $\phi$ $C_{18}$ | 8. 3 $\phi$ $C_{19}$                              | 11. 4 $\phi$ $C_{20}$                                 |
| 2. 5 $\phi$ $C_{18}$                           | 6. 5 $\phi$ $C_{19}$                              | 9. 6,7,8,9,10 $\phi$ $C_{20}$ , 2 $\phi$ $C_{19}$ | 12. 3 $\phi$ $C_{20}$                                 |
| 3. 4 $\phi$ $C_{18}$                           | 7. 4 $\phi$ $C_{19}$                              | 10. 5 $\phi$ $C_{20}$                             | 13. 6,7,8,9,10,11 $\phi$ $C_{21}$ , 2 $\phi$ $C_{20}$ |
| 4. 3 $\phi$ $C_{18}$                           |   |   |   |

$C_{16}$ , and  $C_{18}$  sulfonates likewise yield the corresponding olefins with practically no further degradation.

#### Pyrolysis of Alkyl Sulfate and Sulfonate "Without Acid"

Alkyl sulfates and sulfonates are also pyrolyzed "without acid" at 400C to olefins corresponding to the alkyl group with formation of very little low molecular-weight pyrolysis products. 1-Nonyl sulfate "without acid" produces less, but still an appreciable amount, of internal olefins than "with acid" while 1-nonane sulfonate yields very little internal isomers "without acid." The formation of very little internal olefins suggests very little rearrangement on pyrolysis

of nonane sulfonates "without acid"; thus this method might be used to distinguish between primary and secondary sulfonates.

#### Analysis of Anionic Surfactants in Built Detergents Without Isolation

Anionic surfactants in detergents containing the usual builders, foam additives, and hydrotropes can be analyzed by "acid" pyrolysis without isolation. The isomer and carbon number distribution of  $C_{11}$ - $C_{14}$  LAS in a built or heavy-duty formulation, as determined by  $P_2O_5$  pyrolysis chromatography, agrees quite well with the values for the starting alkylate (Table I).

TABLE III  
Pyrolysis of TAS and  $C_{11}$ - $C_{14}$  LAS/TAS Formulation

Analysis	Based on alcohol <sup>a</sup> from TAS	$P_2O_5$ Pyrolysis of TAS	Pyrolysis (without acid) of LAS/TAS formulation <sup>b</sup>	$C_{11}$ - $C_{14}$ Linear alkylate	$P_2O_5$ Pyrolysis of LAS/TAS formulation <sup>b</sup>
TAS Alkyl chain carbon number distribution, wt %					
$C_{14}$	1.5	1.0	1.6		
$C_{15}$	0.8	0.6	0.7		
$C_{16}$	31.1	29.7	29.9		
$C_{17}$	3.4	3.9	3.6		
$C_{18}$	63.2	64.8	64.2		
TAS alkyl chain average molecular weight	242.6	243.3	224.9		
Alkylbenzene—Isomer distribution, wt %					
5- and 6-Phenyl				1.1	1.1
4-Phenyl				1.3	1.2
3-Phenyl				1.8	1.4
2-Phenyl				4.0	4.5
5- and 6-Phenyl				11.3	11.0
4-Phenyl				5.4	6.4
3-Phenyl				6.0	5.6
2-Phenyl				10.1	11.1
5-, 6-, and 7-Phenyl				14.0	13.1
4-Phenyl				5.0	5.3
3-Phenyl				5.5	5.2
2-Phenyl				9.6	8.7
5-, 6-, and 7-Phenyl				19.0	18.7
4-Phenyl				4.8	4.9
3-Phenyl				1.1	1.3
2-Phenyl				0.01	0.5
Alkylbenzene—					
Side chain carbon number distribution, wt %					
$C_{11}$				8.2	8.2
$C_{12}$				32.8	34.1
$C_{13}$				34.1	32.3
$C_{14}$				24.9	25.4
Alkylbenzene average molecular weight				256.6	256.5

<sup>a</sup> Alcohol from dilute acid hydrolysis of TAS was analyzed in Aerograph 202 with 10-foot,  $\frac{1}{4}$ -inch 20% Carbowax 20M on Chromosorb W (HMDS); column temperature, 200C; helium, 60 ml/minute. Correction factors for alcohols were:  $C_{14}$ , 0.90;  $C_{16}$ , 1.00;  $C_{18}$ , 1.16;  $C_{15}$  and  $C_{17}$  assumed to be 1.00.

<sup>b</sup> 10%  $C_{11-14}$  LAS, 5% TAS, 2% dodecanol-1, 45% TPP, 8% N-silicate, 1% CMC, 21%  $Na_2SO_4$ , and 8% water.

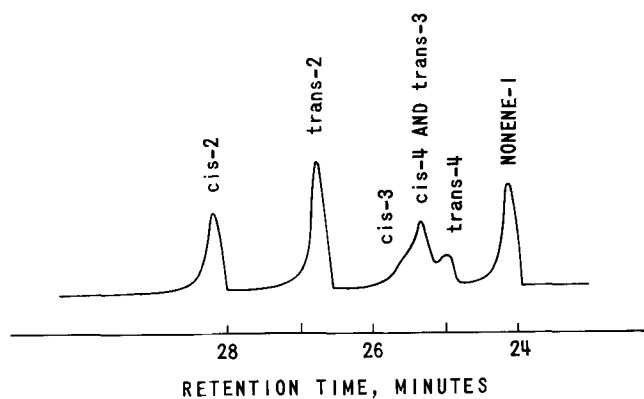


Fig. 5. Nonene isomers from  $P_2O_5$ -pyrolysis of 1-nonyl sulfate. Column temperature 60C.

Mixtures of certain surfactant types can also be analyzed without isolation. Fig. 6 shows the analyses of TAS and  $C_{11}$ - $C_{14}$  LAS in a built formulation by using two pyrolysis runs, one without and the other with  $P_2O_5$ . Without  $P_2O_5$  olefin peaks from TAS are obtained whereas, with  $P_2O_5$  peaks corresponding to  $C_{11}$ - $C_{14}$  alkylbenzenes and TAS olefins are obtained. LAS carbon number and isomer distribution can be calculated from the  $P_2O_5$ -PC with corrections for olefin peaks. (Alcohols, such as dodecanol in the LAS/TAS formulation, also yield olefins, but they can be differentiated from alkyl sulfates by a much smaller olefin peak without than with  $P_2O_5$ .) Agreement between analytical and expected values is excellent (Table III).

#### Nonionic Surfactants

The "acid" pyrolysis conditions for anionic surfactants are also suitable for alcohol and alkylphenol ethoxylates (Fig. 7) and ethoxylate (or ethoxy) sulfates. The PC usually consists of peaks corresponding to internal and alpha olefins with the same carbon number as the alcohol or alkyl group and two peaks occurring at about 4- and 5-min retention times.

From the relative areas of the olefin peaks (Fig. 8) the carbon number distribution for alkyl chains can be determined quantitatively as shown for an experimental ethoxylate from a  $C_{12}$ - $C_{15}$  oxo-type alcohol (Table IV). The agreement between results for a commercial ethoxylate and ethoxylate sulfate, supposedly from the same alcohol, indicates that this method is also applicable to ethoxylate sulfates (Table IV).

Primary and secondary linear alcohol ethoxylates

TABLE IV  
"Acid" Pyrolysis of Alkoxy Ethoxylates and Ethoxy Sulfate

Alkyl chain carbon number distribution	Weight percent			
	Experimental ethoxylate ( $C_{12}$ - $C_{15}$ Oxo alcohol + 8.9 EO)		Commercial samples (by $P_2O_5$ pyrolysis)	
	Based on alcohol analysis <sup>a</sup>	$P_2O_5$ Pyrolysis	$C_{12}$ - $C_{15}$ Oxo alcohol ethoxylate (9 EO)	$C_{12}$ - $C_{15}$ Oxo alcohol ethoxy (8 EO) sulfate
$C_{12}$	18.0	18.6	19.7	18.7
$C_{13}$	32.9	31.8	31.7	31.5
$C_{14}$	29.4	30.6	30.0	31.6
$C_{15}$	19.7	19.0	18.6	18.2
Alkyl chain average molecular weight	189.4	190.0	189.7	189.9

<sup>a</sup> Gas chromatographic analysis of alcohol on 6-foot,  $\frac{1}{4}$ -in. SE-30 column with temperature programmed from 160C at 1C per minute.

appear to give similar patterns of major peaks because of internal and  $\alpha$  olefins whereas oxo-type alcohol ethoxylates give measurable amounts of additional minor peaks with shorter retention time. These minor peaks, which are probably caused by branched olefins, might be used as a qualitative test for oxo-type alcohol derivatives.

The peak occurring at about 4 min has the same retention time as acetaldehyde and ethylene oxide, and the one at 5 min is the same as dioxane. However the evidence described below indicates that the first is acetaldehyde and the second probably a four-carbon aldehyde.

The early peaks for a secondary alcohol ethoxylate and a polyethylene glycol (1000 molecular weight) were trapped by using an Aerograph 202 chromatograph (thermal conductivity detector) with a 10 ft,  $\frac{1}{4}$ -in. column packed with 20% SF-96 on Chromosorb W (HMDS) and 35C column temperature. In both cases the first peak had the odor and retention time of acetaldehyde and gave a positive sodium nitroprusside-diethanolamine test (deep blue color) for acetaldehyde (4,5). Since the  $\frac{1}{4}$ -in. column did not give a sharp second peak, several peaks (considerably smaller and broader than the first) from the polyethylene glycol were trapped together. These produced an orange color, indicating aldehydes. From its retention time and the fact that aldehyde yields of about 90% have been reported for  $H_3PO_4$  pyrolysis of polyethylene glycol compounds (5), the second peak obtained in the capillary chromatogram is more likely a four-carbon aldehyde than dioxane.

The ratio of the areas of the two aldehyde peaks and the olefin peaks appears to be a semiquantitative

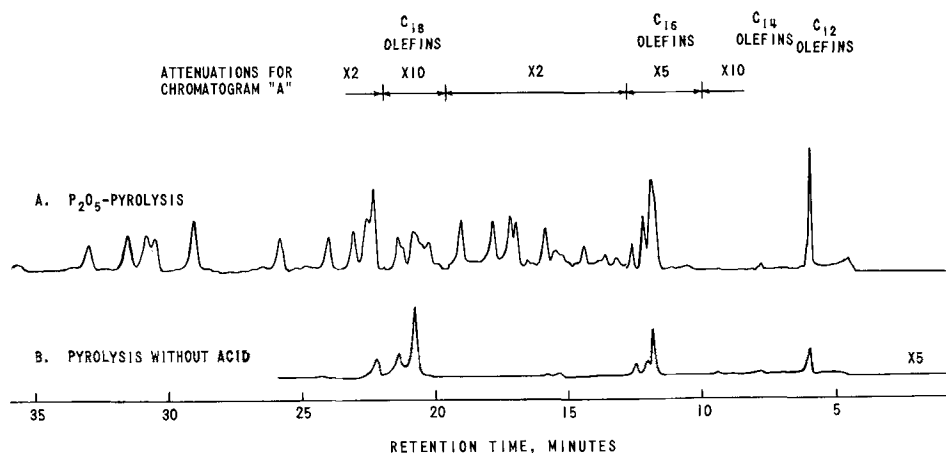


Fig. 6. Pyrolysis of built formulation containing  $C_{11}$ - $C_{14}$  LAS, TAS, and dodecanol. Column temperature 190C.

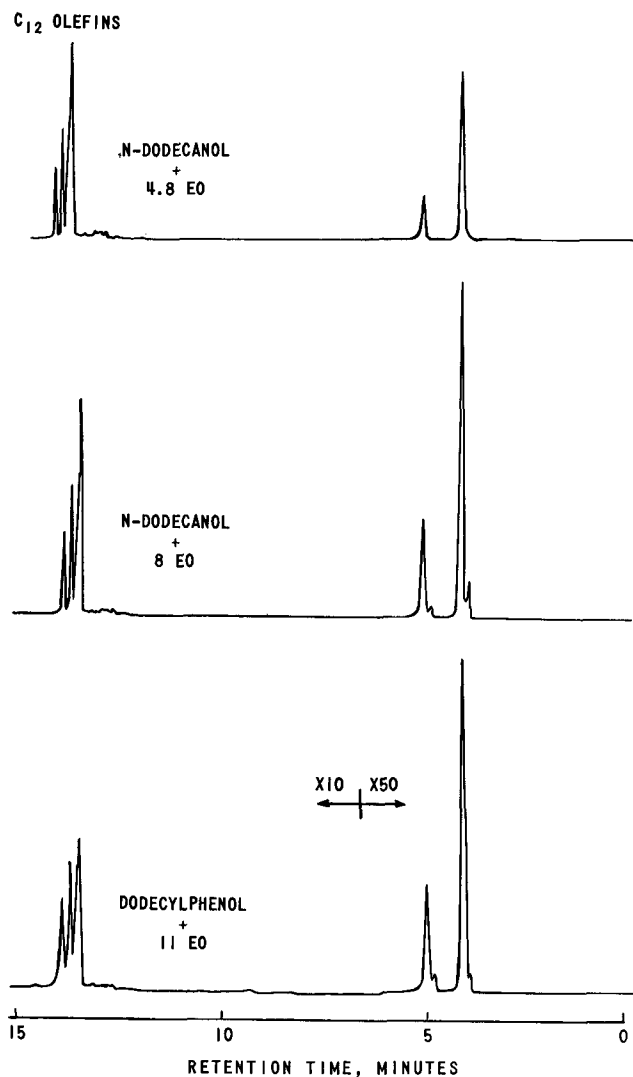


Fig. 7.  $H_3PO_4$  (96%) Pyrolysis of ethoxylates from n-dodecanol and dodecylphenol. Column temperature 100C.

estimate of ethoxy content for nonionics with similar hydrophobic groups when pyrolyzed under similar conditions. With about 10 parts by weight of 96%  $H_3PO_4$  to 1 part sample, the dodecanol ethoxylate with 4.8 EO gives an aldehyde/olefin ratio of 0.6 (Fig. 7), as compared with 1.1–1.5 for the 8 EO ethoxylate. However the ratio for the latter increases to a maximum of about 2.0 with 17 parts 96%  $H_3PO_4$  and decreases to 0.9 with 8 parts  $P_2O_5$ . Alkylphenol ethoxylates give very high ratios; the ratio for the  $C_{12}$  linear alkylphenol (LAP) with 11 EO is about 6.5 with 8 parts 96%  $H_3PO_4$ .  $H_3PO_4$  is preferred over  $P_2O_5$  for estimating ethoxy content because it reproduces better.

This procedure might be developed into a more quantitative method since Kudawara and Ishiwatari (6) were able to determine ratios of oxyethylene/oxypropylene groups in polyoxypropylene and polyoxyethylene condensates by  $H_3PO_4$  pyrolysis in sealed glass tubes, followed by gas chromatographic analysis of the acetaldehyde and propionaldehyde which were formed.

As with anionics, nonionics in built detergents can also be analyzed quantitatively for alkyl chain distribution without isolating the nonionics (Table V). Comparable results are obtained by direct  $P_2O_5$  pyrolysis of the built detergent and by isolation of the nonionic and then pyrolysis.

TABLE V  
Alkyl Chain Carbon Number Distribution for Nonionic in a Commercial Built Detergent

Alkyl chain carbon number distribution	Weight Percent	
	Direct $P_2O_5$ pyrolysis	$P_2O_5$ Pyrolysis of isolated nonionic
$C_{11}$	3.7	4.4
$C_{12}$	26.2	26.8
$C_{13}$	23.4	23.8
$C_{14}$	23.0	22.5
$C_{15}$	20.4	19.2
$C_{16}$	3.3	3.3
Alkyl chain average molecular weight	188.6	187.9

#### Accuracy and Reproducibility

The accuracy and reproducibility in determining carbon number or carbon number and isomer distribution of linear surfactants are about  $\pm 5\%$ , which is normal for gas chromatographic methods. Average molecular weights are well within one unit. Results can be improved by using isothermal instead of a programmed column temperature to reduce drift in base line. When peak areas are small, accuracy and reproducibility are poorer because of the difficulty in measuring areas accurately.

#### "Acid" Pyrolysis of Branched Chain Surfactants—Polypropylene ABS

Although "acid" pyrolysis does not give quantitative results for polypropylene ABS because resulting alkylbenzene peaks have not been identified, it can distinguish between dodecyl and tridecyl ABS (Fig. 9). The pyrolysis chromatograms are essentially identical, peak for peak, with dodecyl- and tridecylbenzene chromatograms. With tridecyl ABS, total area of peaks with retention times greater than 14 min is larger, indicating larger amounts of higher molecular-weight alkylbenzenes.

#### Branched Alkylphenol Ethoxylates and Ethoxylate Sulfates

The alkyl chains in branched alkylphenol ethoxylates and ethoxylate sulfates can be determined semi-quantitatively by "acid" pyrolysis (Fig. 10).  $P_2O_5$  PC's for a tripropylene (nonyl) phenol ethoxylate and an ethoxylate sulfate are similar to a tripropylene chromatogram, and the tetrapropylene (dodecyl) phenol ethoxylate is similar to a tetrapropylene chromatogram, with slight differences in the relative heights of certain peaks. The  $P_2O_5$  PC for t-octylphenol ethoxylate has Peaks 1–6 in common with diisobutylene; major peaks are 1 and 7 whereas in di-isobutylene they are 1 and 2. The t-octyl-, tripropylene, and tetrapropylene derivatives can be easily distinguished from each other and from linear surfactants by their retention times and peak patterns.

#### Limitations

Except for LAS and ABS, a  $P_2O_5$  PC reveals the distribution of the hydrophobe; additional analysis is necessary for identification of surfactant type. For example, alkyl sulfate and sulfonates, both of which produce olefins, might be distinguished by the stability of sulfonates in hot dilute acid. Alcohol and alkylphenol ethoxylates and ethoxylate sulfates can be differentiated from alkylsulfates and sulfonates by the peaks corresponding to acetaldehyde and a higher aldehyde. Alkoxy may be distinguished from alkylphenoxy compounds by infrared or ultraviolet analysis or nuclear magnetic resonance spectroscopy.

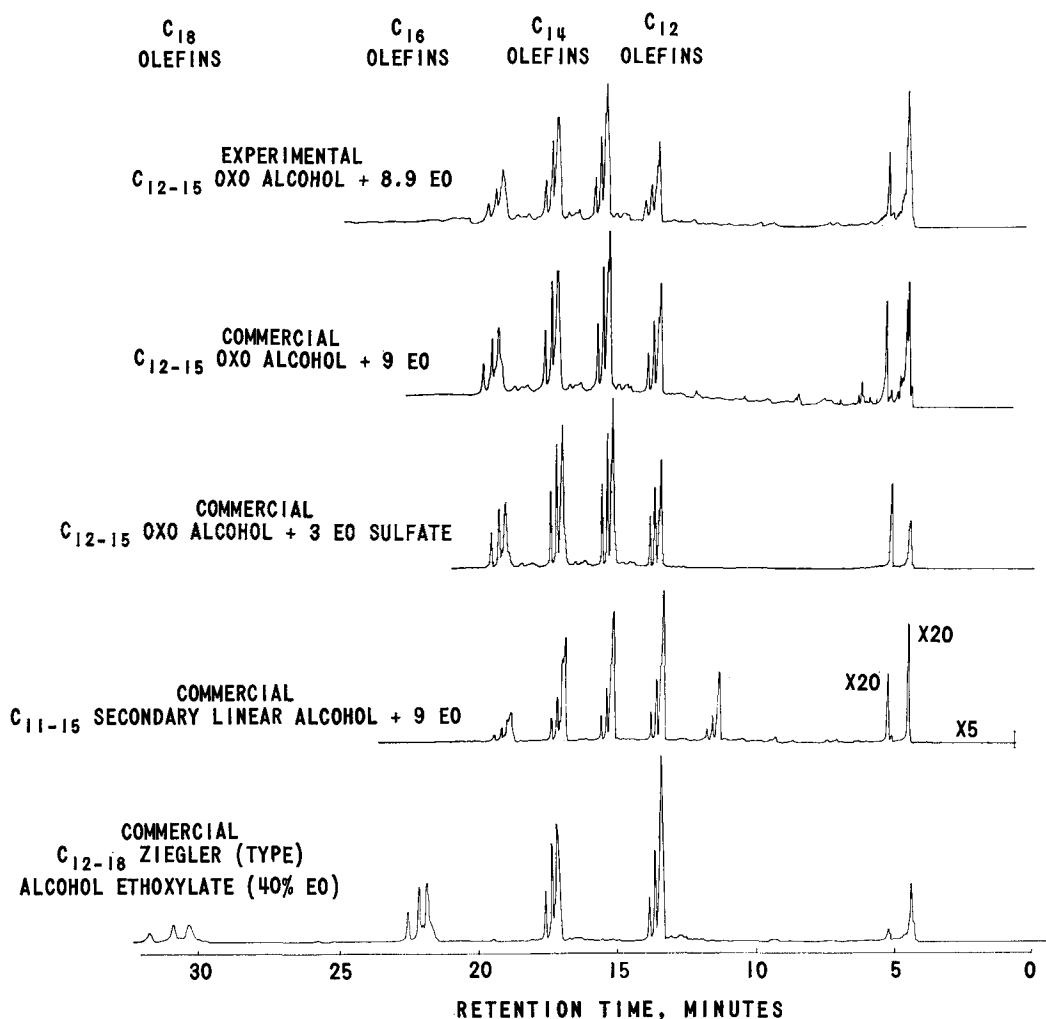


FIG. 8. P<sub>2</sub>O<sub>5</sub>-Pyrolysis of an experimental and several commercial alcohol-based ethoxylates and an ethoxy sulfate. Column is 100C for first 5 min, then temperature is programmed from 100-190C at 16C per minute.

For surfactant mixtures which contain more than one component that produces olefins, a prior separation before pyrolysis is necessary.

Mono- and dialkylphenoxy compounds cannot be distinguished by their P<sub>2</sub>O<sub>5</sub> PC's alone; additional information, such as equivalent weight, is necessary for confirmation.

**Miscellaneous Qualitative Analysis**

Under the conditions of P<sub>2</sub>O<sub>5</sub> pyrolysis, lauric monoethanolamide and lauric amide produce lauroni-

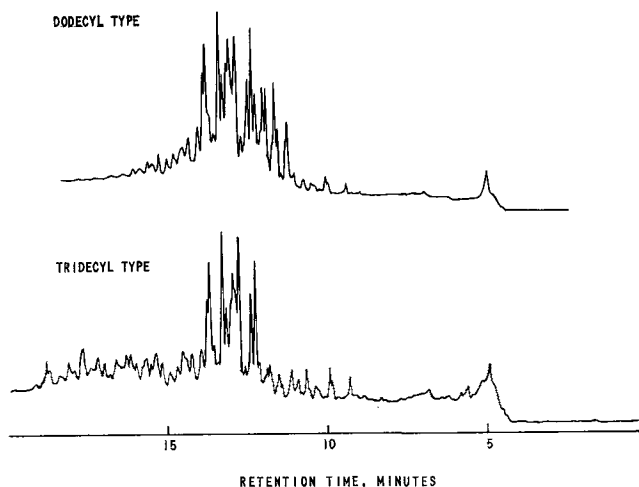


FIG. 9. P<sub>2</sub>O<sub>5</sub>-Pyrolysis of sodium polypropylene ABS. Column temperature, programmed 120-220C at 16C per minute.

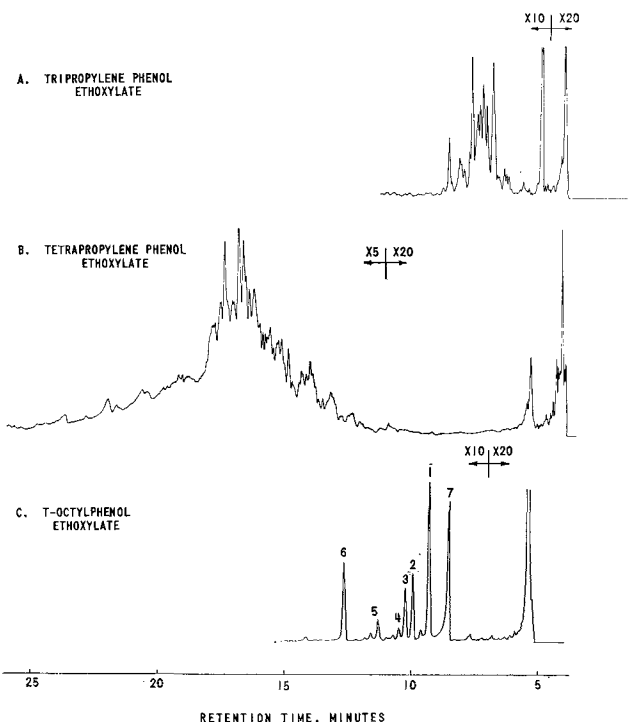


FIG. 10. P<sub>2</sub>O<sub>5</sub>-Pyrolysis of branched alkylphenol ethoxylates. Column temperatures: A and B-80C for 10 min, then programmed to 190C at 16C per min; C-50C.

trile (Fig. 2), which can be readily identified by retention time. However the peaks seems to diminish in size with the amount of water added before pyrolysis and is not observed with lauric diethanolamide. Nitrile peaks from higher fatty acid ethanolamides tend to be flat (under the chromatographic conditions used), have longer retention times, and may be obscured by alkylbenzenes.

A sharp peak at 5- to 6-min retention time with the column temperature programmed from 120–220C at 16C per minute (Fig. 2) is an indication of toluene or xylene sulfonate. A distinction between toluene and xylenes can be made by reducing column temperature to obtain larger differences in the retention times.

#### Other Possible Applications

Since 1 mg of surfactant is sufficient for an analysis even when 90% of the pyrolyzate is rejected by the

splitter, analysis of 0.1 mg should be possible without a splitter. Because of its ability to handle very small samples, this method should also be applicable to the analysis of surfactants in biodegradation, adsorption, and other studies involving very small quantities.

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