alcohol, and oleic acid as 31.6, 28.3, and 31.5 dynes per cm, respectively, it can be shown that:

$$(K_2 - 90.5)^2 = 6.45 - (\gamma - 30.8)^2$$

where, γ = soil surface tension in dynes per cm.

C. *Correlation of Detergency of Nonyl Phenol Polyethenoxyethers Using Oleic Acil Soil*

In section A of this report, analyses of the detergent-solubilization equations for the three analogs of the nonyl phenol polyethenoxyethers using triolein soil indicated that the K_1 of the equations varied linearily with the HLB values of the analogs and that the K_2-log interfacial tension function (at the CC-1 point) was linear.

TABLE II
Nonyl Phenol Polyethenoxyether Detergency-Solubilization Data at 180F—Oleic Acid Soil

Adduct	Ethylene oxide mole ratio	Molarity	Detergency, % soil removal	Micellar solubilization. mg orange OT per 100 ml
NPEGE	20	.00152, CC-1	90.0	4.2 at .00145M
		.00291, CC-2	96.5	8.18
		.00249	96.5	7.0
NP50E	50	.00455, CC-1	89.7	5.07
		.00910, CC-2	99.4	10.08
		.00517	93.5	......
NP100E	100	.00351, CC-1	90.1	7.4
		.00702, CC-2	97.7	14.5
		.00400	97.7	......

It was now considered essential to determine the correlation, if any, existing for analogs of the same surfactant when using oleic acid as the soil. Table II contains the detergency-solubilization data at 180F, using oleic acid soil, for the 20, 50, and 100 ethylene oxide mole ratio adducts of nonyl phenol. The 30 and 40 mole ratio analogs were not included in this analysis because their detergency isotherms deviated in part from the normal characteristics of our CC-1 system. While both possessed CC-1 and CC-2 points, the CMC of the former coincided with its CC-1, and the CMC of the latter was larger than its CC-2 concentration. From the data of Table II, the following equations were computed, the terms having the same significance as heretofore:

Adduct	Ethylene oxide ratio	Equation
NPEGE	20	$D = 1.31\ S + 85.75$
NP5OE	50	$D = 1.66\ S + 82.62$
NP100E	100	$D = 0.60\ S + 89.06$

Remembering that the equations are in the form of $D = K_1\,S + K_2$, and utilizing the following additional information:

Adduct	K_1	K_2	HLB	Interfacial tension at CC-1, ergs per cm²
NPEGE	1.31	85.75	16.00	3.0
NP50E	1.66	82.62	18.18	3.4
NP100E	0.60	89.06	19.05	3.2

It can be shown that K_1 varies parabolically with HLB; viz.,

$$K_1 = 2.24 - \frac{(\mathrm{HLB} - 17.3)^2}{1.85}$$

A relationship also exists between K_2 and the interfacial tension, as follows:

$$(K_2 - 86.25)^2 = 264.06 - (\mathrm{IT} - 19.25)^2$$

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Graphic Aid for Interpreting Gas Chromatograms[1]

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Abstract

A simple semilogarithm plot of elution volumes can be constructed as an aid to identify components that are members of the same homologous series. This technique is especially useful in organoleptic and flavor studies for identifying small peaks in any gas chromatogram. The method is applicable to chromatograms containing 20 or more peaks, which do not have to be completely resolved. Any member of the homologous series within 4 or 5 carbons of the unknown can be used as a standard for identification. The tentative plots also help in examining chromatograms obtained with hydrogen flame or with β ray-type detector equipment where samples are too small for collection and identification by chemical and physical tests.

THE LINEAR RELATIONSHIP of the carbon number to the logarithm of the retention volume has been widely used for identification and expression of results in the terms of one component (2,5,6).

The log-log plot (2–4) allows a fairly accurate identification of unknown constituents when more than one suitable standard is available. Many extracts of natural products present a whole series of unknowns in a single sample, such as the volatiles from autoxidation of fats and the flavor essence of natural fruits. In many cases standards for the identification of these materials are not available. Because many of these substances are homologs, they follow the linear plot of carbon number vs. the logarithm of the retention volume. The problem of identifying the unknowns is helped tremendously if they can be grouped together as a homologous series. The usual preliminary separations involving alkali washing, preferential solubility, or removal of insoluble derivatives all tend to concentrate certain of the homologs. The graphic technique aids in the identification of a large number of unknown components where many of them belong to one or more homologous series.

Retention volumes or retention times are plotted in the usual fashion on a semilogarithm paper. At each retention time lines are drawn across the full width of the paper, i.e., parallel to the carbon number base. If colored lines are drawn to contrast with the lines

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[1] Presented at fall meeting, American Oil Chemists' Society, 1961.

[2] This is a laboratory of the Northern Utilization Research and Development Division, Agricultural Research Service, U.S.D.A.

on the graph paper, the plots will be easier to use. If the first number of the arithmetic base line is X, then at unit intervals the carbon numbers will be X + 1, X + 2, etc. (Figure 1). The shortest member of any homologous series present in the chromatogram of an unknown has the lowest retention time. If it is assumed that the first line represents the lowest number of such a series, a pin is placed on this line at the locus of X and a ruler laid against the pin. By moving the ruler across the face of the graph with the pin acting as the pivot point other members of the same homologous series will be found where the ruler intersects the points where the retention lines cross the vertical carbon number lines. A line is drawn connecting these intersections and, for convenience, this line is called the identity line.

For one homologous series of compounds any number of identity lines with decreasing slopes can be drawn connecting the individual members of a series. Only that line having the greatest slope and connecting all the points is used. Lines of lesser slope are equivalent since the lower slope results from increasing the unit value on the X axis. If the second, third, or any retention line is not intersected by the first drawn identity line, the process is repeated to establish the second homologous series. For convenience in plotting, the value selected for X is different in each homologous series. By such a process of elimination one or more points may not fall on any of the identification lines. Any two of these may be part of a homologous series, but for classification either the unknowns must be run on a different type of column or knowns of the same homologous series added to the sample and the chromatograms repeated and similar plottings made of the retention volumes.

Figures 1 and 2 show tentative identification plots constructed from isothermal chromatograms of known materials. The range of the homologous series covered in a single chromatogram is about 5 or 6 carbon units for lower boiling materials. However, for higher boiling members, like normal fatty acid esters, the range will extend to about 11 carbon atoms. The slope of each identity line in Figure 1 is different and depends upon the retention characteristics of a particular column. For a given set of conditions this slope is helpful in establishing the unknown belonging to any particular homologous series. In Figure 2 the slopes are identical for the two homologous series of hydrocarbons. The nonlinearity shown for the first two members of the normal alkanes results from insufficient retention time in the 4-ft columns used for these separations. In highly polar materials such as alcohols, the first members of the series always show nonlinear retentions because of the preponderant effect of the polar group.

Volatile compounds obtained by high-vacuum stripping of melted vacuum stopcock grease (C) illustrate the technique on unknown materials. Figure 3 shows the gas chromatogram of volatiles obtained from a U.S. brand product that were trapped under liquid nitrogen. Because this product had been partially used, it had been exposed to the vapors of a chemical laboratory. Thirteen peaks are shown for the highly volatile materials that were chromatogrammed in a 4-ft glass column at 0°C. The tentative identification plot shown in Figure 4 indicates that there are at least 5 homologous series represented by these volatiles. Since there are only two unknown materials on the identity line, to the far right, these may or may not be members of the same homologous series. However the slope of the line and the spacing between the two points on this line agree with the other identity lines and indicate the possibility that

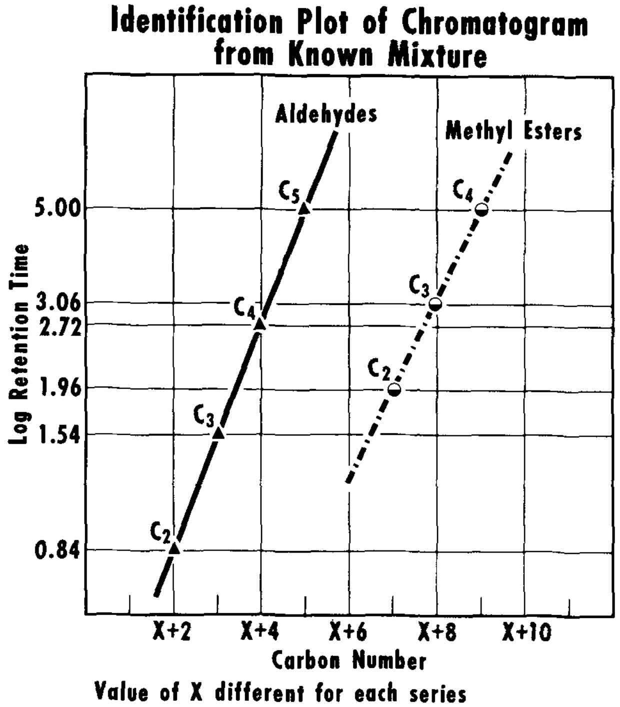

FIG. 1. Identification plot of chromatogram obtained from a known mixture of methyl esters (C_1 to C_8) and normal aliphatic aldehydes (C_2 to C_5).

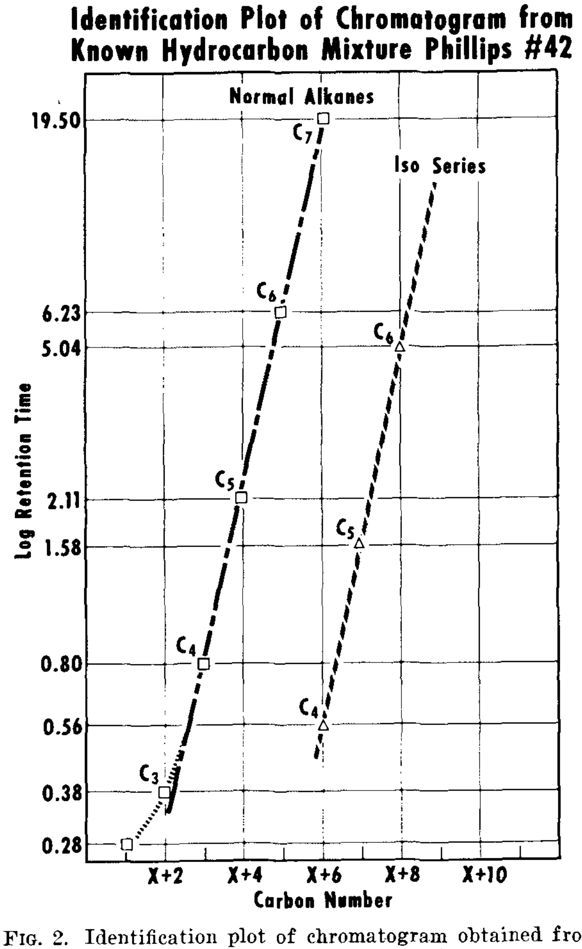

FIG. 2. Identification plot of chromatogram obtained from a known hydrocarbon mixture (Phillips No. 42).

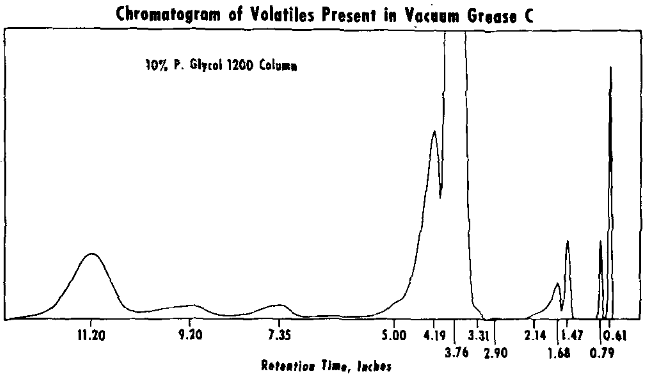

FIG. 3. Chromatogram of volatiles obtained from melted vacuum grease "C" by high-vacuum stripping.

these are members of the same homologous series. A repeat chromatogram run of the same material on a column of different polarity would establish these conclusions. One line representing a very small peak at the log retention ratio of 0.85 does not fall on any identity line. By similar retention values this peak has been identified as acetone.

Individual members of each homologous series have been identified from retention volumes of one or more known members of the series. The use of log retention ratio is advantageous in recording the retention times since it corrects the small differences that occur in flow rates, temperature, and time of injection for repeat runs. Normal pentane has been used as the standard in Figures 4 and 5.

Figure 5 shows the tentative identification plot of the volatiles obtained by stripping a fresh and a previously unopened sample of a British-made stopcock grease (A). Four identity lines include all the peaks except two, which are identified by retention volumes as an acetone and pentene-2. The slope of the last identity line is not parallel to the other three lines, and the spacing of the points is much closer than on the rest of the plot. Although the lowest retention volume of this line corresponds to methyl formate, the other two points do not correspond to methyl acetate and propionate; consequently these three substances are not members of a methyl ester homologous series. Fractionation on other types of columns and the plotting of retention volumes on a trilinear diagram by the method of Brown (1) would resolve the identity of these materials.

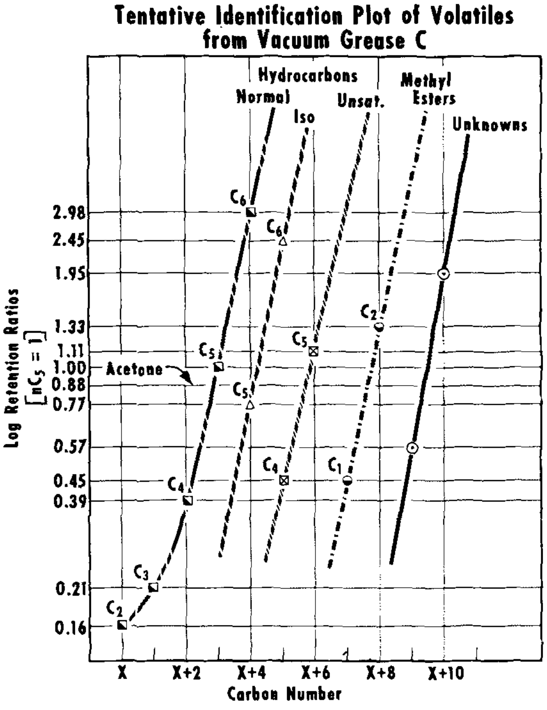

FIG. 4. Tentative identification plot of volatiles present in vacuum grease "C".

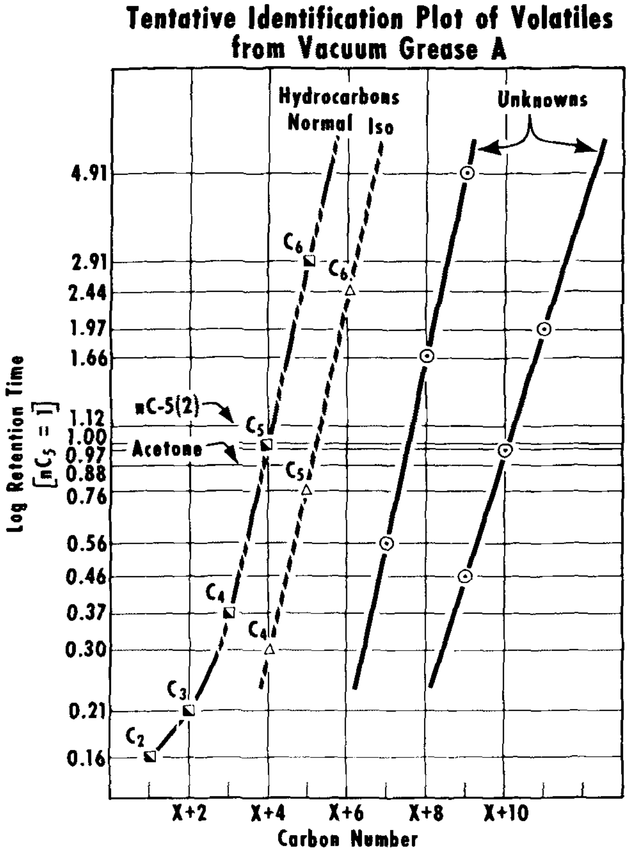

FIG. 5. Tentative identification plot of volatiles present in vacuum grease "A".

Discussion

Many lines, each of lesser slope, can be drawn connecting the same series of points on any of the plots. Lines that fan from a single point indicate that the units along the X axis have been doubled, tripled, etc. The uniform absence of every other member of a series does offer a special problem in identification. To identify the value of X, one or preferably two standards of each homologous series should be run with the unknown. The standards can be any member of the homologous series within 4 or 5 carbons of the unknown, which in many cases is an added advantage. Because the value assigned to X can be any positive or negative integer, the identity line need not be taken at the zero origin, but it can be started anywhere on the graph, and a line of identical slope will be obtained but displaced by a given number of units. If the identity lines are conveniently spaced, the value assigned for X will most likely be different for each of the homologous series lines drawn on the graph. The retention volume must be known for at least one member of the series to determine the value of X.

In many plots of unknowns one point may fit two homologous series lines; this point could represent one or two different materials (Figure 1). If it is only a single component, the question of which one can be resolved by running the sample on a column having different retention characteristics. The same type of a semilogarithm plot is constructed for the second chromatogram, and it can be deduced to which homologous series the unknown belongs. If the point is resolved and appears on both lines, it can be assumed that the peak contains at least two components. For samples having only a few unknown components, it is possible to add knowns from two or three different homologous series and in this manner to construct identification plots.

Another advantage of the technique is the identification of very small sample peaks. The procedure has proved highly useful on chromatograms obtained with equipment using a β-ray detector where sufficient amounts of a sample cannot be obtained by condensing and trapping the effluent of the gas chromatogram for chemical or infrared analysis. Obviously the technique works best where high resolutions of components are obtained and where the equipment is sufficiently stable to give good, reproducible, retention volumes. Still another advantage is that the method works well on partially resolved peaks. After experience with the method had been acquired, coupled with a knowledge of the limitations of gas chromatography, chromatograms containing 20 or more components were resolved.

The method may also have application in liquid chromatography where good resolution and a linear relationship can be obtained between elution volumes and some chemical or physical property such as the molecular weight, degree of polymerization, or other noncolligative property.

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Continuous High Temperature Preparation of Alkylolamides

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Abstract

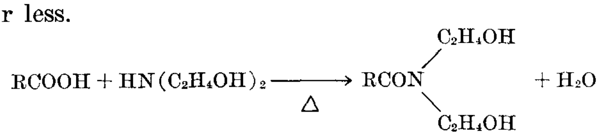
Lauric diethanolamide was prepared from methyl laurate and diethanolamine in the presence of an alkaline catalyst by a continuous high temperature process. The conventional batch process requires cycle times of 2–6 hr which can lead to undesirable by-products.

With a reaction time of about 10 sec, product purity of 91–94% was obtained at 149C for an absolute pressure range of 10–760 mm Hg. When reaction temperature was lowered to 110C, product purity became poorer as the absolute pressure was increased from 30 mm Hg to 760 mm Hg.

Two studies for optimum catalyst content of either KOH or sodium methylate showed that maximum product purity of about 97% was obtained at 0.20% catalyst by weight.

Alkylolamides are a widely used class of nonionic surface active agents, particularly fatty diethanolamides which are popular as foam builders for the alkyl aryl sulfonates. They are found in products ranging from laundry detergents to high-quality shampoos. The composition of alkylolamides can vary considerably, however, depending on the reactants employed.

One of the earliest commercial alkylolamides was the Kritchevsky detergent (1). For a typical product, one mole of coconut fatty acid was mixed with two moles of diethanolamine in a still. The mixture was heated to about 150–170C, and water was slowly distilled off until the free fatty acid content was 5% or less.

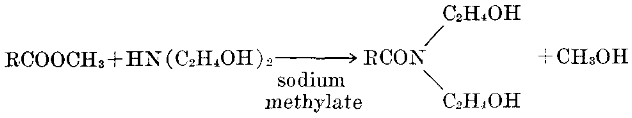


$$RCOOH + HN(C_2H_4OH)_2 \xrightarrow[\Delta]{} RCON(C_2H_4OH)_2 + H_2O$$

The final product was a clear, yellowish-brown, viscous liquid which was readily soluble in water, and had a pH of about 9.

The reaction product contained only 60–70% of pure coco-fatty acid diethanolamide, plus free amine, amine soap, fatty acid, fatty amide, esteramide, piperazine, and other compounds in lesser amounts.

In 1949 E. M. Meade was granted patents on the amidation of esters (2,3). His process reacted an ester with an amine containing a replaceable hydrogen attached to a nitrogen atom, in the presence of catalyst such as an alkali metal alcoholoxide. For example, a fatty methyl ester would be reacted with an alkyl amine at 100C for 3 hr in the presence of sodium methylate. In commercial practice, product purity as high as 92% is available.



$$RCOOCH_3 + HN(C_2H_4OH)_2 \xrightarrow[\text{sodium methylate}]{} RCON(C_2H_4OH)_2 + CH_3OH$$

Comparison of alkylolamides made by these two methods shows the difference in composition (4).

	Kritchevsky patent	Meade patent
Diethanolamine, %	29.0	7.0
Fatty acid, %	4.0	0.5
Ester amide, %	3.5	2.5
Fatty alkylolamide (by diff.), %	63.5	90.0

The purer alkylolamides have been called "extra" or "super" in comparison with the product made from fatty acids. The more active form is superior in its ability to stabilize foam and increase product viscosity (5).

The following work was conducted with methyl laurate at temperatures of 110–150C in a short-time, continuous reactor. The objective of this program was to save reaction time without sacrificing purity or quality.

Experimental

Experimental work was carried out in a thin-film evaporator. Figure 1 shows the detailed construction of this equipment, whereby spinning vanes spread