ment with hydrogen, the oil is said to be still suitable for use as a salad oil. The essential feature of the method patented by Gudheim (7) is the use of a very low hydrogenation temperature, i.e. a temperature below about 110°C. Paterson (10) subjects the oil first to treatment under conventional hydrogenation conditions and thereafter hydrogenates with a catalyst of the copper chromite type, under high pressure. The principal object in his process is a high degree of decolorization of the oil, but improved flavor stability is also claimed.

The suggested role of isolinoleic acid in flavor reversion naturally focuses attention on the possibility of hydrogenating in such a manner as to avoid the presence of this isomer. It is well known that the amount of "iso-oleic" acids appearing in a hydrogenated oil is greatly influenced by the conditions of hydrogenation. The available data (3, 8) do not indicate that it will be possible to eliminate isolinoleic acid in a plastic product hydrogenated under conventional conditions with a nickel catalyst. However, it appears possible to choose conditions that will maintain this acid at a minimum.

Apparently, linolenic acid adds hydrogen with approximately equal readiness at the 12:13 and 15:16 double bonds, regardless of hydrogenation conditions (3). The formation of isolinoleic acid, therefore, seems unavoidable. Once formed, this acid is much more difficult to eliminate by hydrogenation than is normal linoleic acid, apparently because double bonds in the 9:10 and 15:16 positions are too widely separated to exert a mutual activating influence. The degree to which elimination of diethenoid acids is feasible is determined to a large extent by the relative affinities for hydrogen of these acids and the monoethenoid acids (oleic acid) occurring together in the form of glycerides in the raw oil. Whereas under selective conditions normal linoleic acid hydrogenates 20 to 30 times as readily as oleic acid, the 9:10, 15:16 isomer hydrogenates only about three times as readily (3).

Because of the isolated positions of its double bonds, isolinoleic acid behaves similarly to oleic acid and differently from normal linoleic and linolenic acids with respect to selectivity in hydrogenation (3). In the earlier stages of hydrogenation, therefore, isolinoleic acid may be kept relatively low by application of the same conditions that lead to the minimum production of total oleic acids in cottonseed or other oleic-linoleic acid oils (low temperature, high pressure, high agitation, low concentration of catalyst). However, in the latter stages, such conditions may well produce a higher isolinoleic acid content than "selective" hydrogenation conditions, since linolenic acid, the precursor of isolinoleic acid is more quickly eliminated under selective conditions.

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A Direct Volumetric Method for the Analysis of Soap[*]

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THERE has been no accurate method of directly titrating soap with acid. One obstacle to such titration in aqueous solution is the liberation of fatty acids and acid soaps in a finely divided state, preventing accurate observation of the color change of the indicator. In alcohol the soaps are often not sufficiently soluble and the indicators which must be used do not give a sharp end-point.

It is now found (1) that a mixture of a glycol with a higher alcohol or with a chlorinated hydrocarbon forms a very powerful solvent for any soap, and the solution thus formed admits of a direct titration of the soap by a strong acid dissolved in the same mixed solvent, the end-point being determined by an indicator with a sharp color change. The method is general, being applicable not only to soaps but to practically all weak monobasic acids, as will be discussed elsewhere.

Method and Results

The solvent medium chosen is a mixture containing an equal volume of ethylene or propylene glycol and isopropyl alcohol, the latter being chosen for its easy availability, lower volatility, freedom from toxicity and low viscosity, but any other higher straight-chain alcohol or any chlorinated hydrocarbon may equally well serve the purpose. One gram of the soap is dissolved in 10 to 20 ml. of the solvent mixture. The dissolving is best carried out by first adding the glycol and allowing a few minutes if necessary, by standing in a warm place, for the swelling of the soap. The alcohol is then added and on shaking, the soap dissolves to a clear solution. If the soap contains a large proportion of stearate, chloroform may be used with great advantage in place of isopropyl alcohol as

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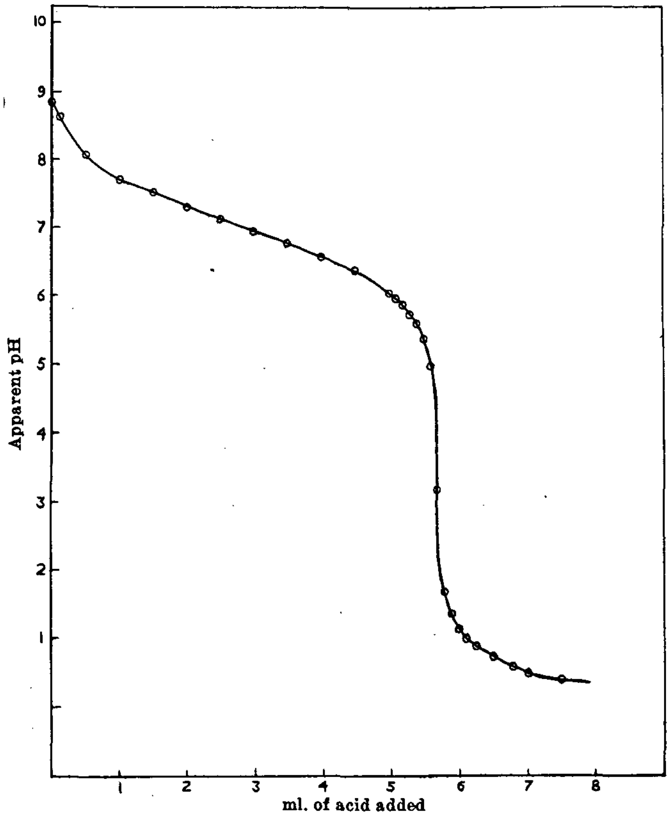

Fig. 1. Potentiometric titration of sodium oleate by N/6 perchloric acid in G-H mixtures.

it forms a much stronger solvent mixture. In extreme cases shaking for a few minutes in a mechanical shaker will effect complete solution. Among the usual substances present in soap only the free alkali dissolves in the solvent medium but none of the fillers like silicate, carbonate, or phosphate dissolve to an appreciable extent.

The soap solution is now titrated with hydrochloric or perchloric acid in the same solvent medium by a double indicator method, first using phenolphthalein or cresol red to determine the free base and then using methyl orange or methyl red (three drops of 0.05% alcoholic indicator solution per 10 ml.). The color of the indicator is slightly different from those in the aqueous medium; it is canary yellow in alkaline and bright pink in acid solution. The sharp change to a bright pink color is taken as the end-point.

The following are the results of two typical titrations by this method using pure sodium oleate: (1) taken 1.1790 gms.; found 1.1759 gms., using 0.3752 (N) perchloric acid with methyl red as indicator; error 0.28%; (2) taken 0.9265 gms.; found 0.9249 gms., using 0.188 (N) perchloric acid; error 0.18%.

That the method gives a real end-point is corroborated by a study of the potentiometric behavior of the system. The result is graphically represented in Fig. 1, which was obtained by titrating 0.3 gm. of sodium oleate with N/6 perchloric acid in 20 cc. of propylene glycol-isopropyl alcohol (1:1) mixture, using a Beckman pH meter with glass electrode. Though the pH values have no established absolute significance owing to the uncertainties involved in the use of a non-aqueous medium, it is very clear from the sharp inflection in pH that a true end-point is obtainable by the method.

In order to study the double indicator method potentiometrically Fig. 2 has been obtained by titrating a known weight of pure sodium oleate in the presence of a definite amount of excess alkali, the proper indicators being added during the titration to find out how far these indicators respond to the true end-points. The two inflections in the curve corresponding to the two end-points are clearly shown in the diagram and thus provide a sound basis for our method of analysis. It was observed that phenolphthalein was decolorized exactly in the interval where $\Delta pH/\Delta V$ was at a maximum at the first inflection, and methyl red similarly responded to the true acid end-point. The results are: (1) taken 0.7841 gms. of sodium oleate and 0.3664 milli-equivalents of sodium hydroxide; found potentiometrically 0.7864 gms. and 0.3644 milli-equivalents, and by indicator method 0.7875 gms. and 0.3698 milli-equivalents, respectively; (2) taken 0.9271 gms. sodium oleate and 0.3664 milli-equivalents alkali; found by double indicator method 0.9247 gms. and 0.3698 milli-equivalents, respectively.

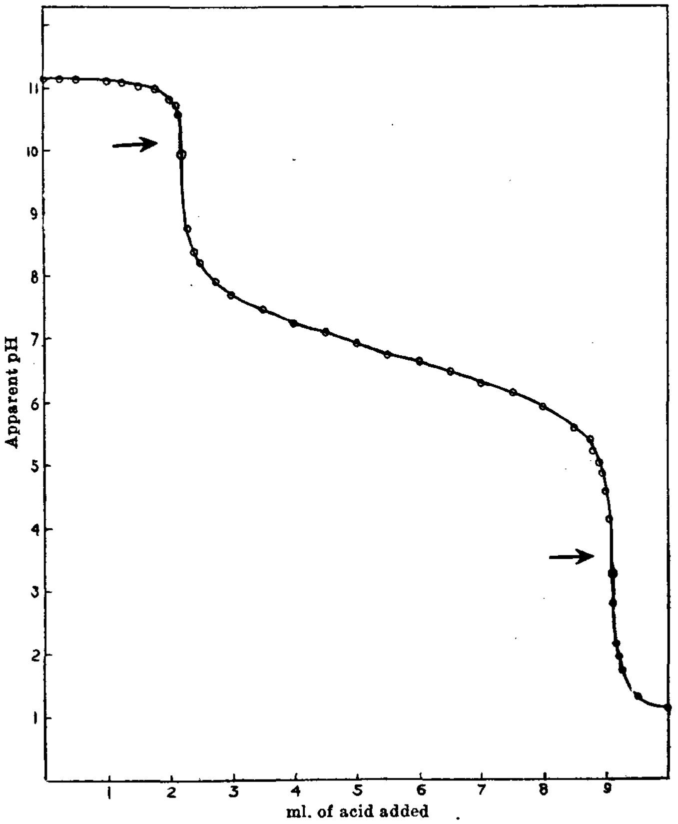

Fig. 2. Potentiometric titration of 0.7861 gm. sodium oleate in presence of 0.3664 milliequivalents of excess alkali by 0.3652 (N) perchloric acid using glass electrode (arrows indicate the two equivalence points and the phenolphthalein and methyl red was found to change their colors respectively).

In analyzing commercial soaps not only the equivalents of base but also the weight of fatty acid is customarily determined. We can do this in a very easy way as follows: After finishing the titration with acid, 5 ml. of chloroform, if it does not already contain chloroform, and a little excess acid are added to the solution. It is then diluted with 100 to 200 ml. of water when the chloroform separates as an immiscible layer which contains all the free fatty acid and any unsaponified fat present in the soap. The chloroform sometimes tends to spread or emulsify, in which case a little amyl alcohol with chloroform has been found satisfactory. The whole is filtered through a moist filter paper which retains all of the chloroform. At the end of the filtration the chloroform is transferred from the filter paper by puncturing the apex and finally washing the cone of the filter paper with a little alcohol. The free fatty acid can be checked by titration of this chloroform-alcohol solution with alcoholic potash and the total fatty matter by actual weighing after evaporation of the chloroform on a water-bath. It might be noted that by using chloroform, as described above, the tedious process of repeatedly extracting with ether can be avoided even if this direct titration method is not applied. This is easier and quicker and dispenses altogether with the use of a separatory funnel.

In order to investigate how far the usual substances present in commercial soap may introduce complications due to their solubility in the solvent medium, we have determined the solubility of these salts in the mixed solvent. These are given in Table I.

TABLE I.

The Solubility at 25° of Salts in a Mixed Solvent Containing Equal Volumes of Propylene Glycol and Isopropyl Alcohol.

	NaCl	Na_2CO_3	$Na_2B_4O_7$, $10H_2O$	Na_3PO_4, $12H_2O$	Na silicate
g. anhydrous salt per 100 g. solvent............	0.898	0.143	9.05	traces	traces

It is seen that with the exception of borates and possibly to some extent carbonates, none of the salts is soluble enough or basic enough to affect the results appreciably. The soap may be separated from borates and carbonates by extracting it with hot alcohol. However, the method is primarily applicable to the analysis of pure soaps for which purpose it was developed, and extension of it to commercial soaps could be done only after finding a suitable method to separate the soap from the extraneous matter. Appreciable amounts of water affect the accuracy of the titration but by using 1 gm. of soap per 10 to 15 ml. of solvent no special drying is necessary since the presence of water to the extent of as much as 30% of the weight of soap will not noticeably affect the result. Commercial samples of the solvents have been used throughout without any purification or dehydration as they generally contain less than 1% water.

In a comparative study of the present method with the standard method (2), the results obtained by analysis of a sample of commercial toilet soap are compiled below in Table II. The proposed method is simpler and quicker and gives equally accurate results.

TABLE II.

Comparison of the Analysis of Toilet Soap by Scott's Method and by the Present Method of Direct Titration.

	Wt. of soap used (gms.)	Per cent free alkali	Per cent Na_2O	Per cent fatty acid	Per cent soap
Standard method..........	5.0821	0.00	10.76	83.12	90.86
Direct titration..............	1.1910	0.00	10.80	82.23	90.90

Summary

Glycol, or preferably its mixture with a solvent for hydrocarbons, such as isopropyl alcohol or chloroform, possesses high solvent power for soaps, which may be directly titrated with strong acids, either potentiometrically or with the use of methyl red or methyl orange. The ionization of the organic acid is suppressed so that salts of weak acids can be directly titrated by this method. The colors of the indicators are brighter and the end-point sharper than those in alcohol or water.

Acknowledgment

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Abstracts

Oils and Fats

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M. M. PISKUR and SARAH HICKS

VISCOSITIES AND DENSITIES OF SOLVENT-VEGETABLE OIL MIXTURES. F. C. Magne and E. L. Skau. *Ind. Eng. Chem. 37,* 1097-1101 (1945). A pycnometer and a viscometer suitable for use with volatile mixtures and for low-temperature determinations are described. Density and viscosity measurements are made from incipient crystallization to a temperature near the boiling point of the solvent for the complete binary systems cottonseed oil-Skellysolve B (commercial hexane), cottonseed oil-acetone, cottonseed oil-2-butanone, peanut oil-Skellysolve B, and soybean oil-Skellysolve B. From these data it is possible to construct soybean oil-Skellysolve B. From these data it is possible to construct for any of these systems the density-composition and viscosity-composition curves for any temperature as well as the density-temperature and viscosity-temperature curves for any composition. The various systems are compared and their idealities discussed. The density-composition curves for the binary systems of Skellysolve B with the 3 oils practically coincide. The viscosity-composition curves for these systems almost coincide up to about 60% by weight of oil and then diverge to the values of 100% oil. The same is true of the binary systems of cottonseed oil with the 3 solvents, except that the curves start to converge again at about 90% to meet at the 100% oil value. The applicability of these data to other random samples of these vegetable oils is discussed.

THE SYNTHESIS AND CONFIGURATION OF D-14-METHYLPALMITIC ACID AND ITS IDENTITY WITH THE NATURAL ACID FROM WOOL FAT. S. F. Velick and J. English, Jr. *J. Biol. Chem. 160,* 473-80 (1945). *d*-14-Methylpalmitic acid has been synthesized, starting from the *d*-2-methylbutanol-1 of fusel oil. The synthetic acid is identical with the natural acid isolated from wool.