lauryl alcohol in the aqueous solution but a proportional amount of the myristyl alcohol was partitioned into the aqueous phase. Thus the extract contained proportional amounts of the lauryl and myristyl alcohols and could be analyzed directly by VPC. Since the accuracy of this analysis is dependent upon partitioning proportional amts of unknown and standard into the aqueous phase, the choice of a proper standard is important. The standard should have a similar structure to the unknown to insure similar partition coefficients.

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Determination of Ricinoleic Acid by Differentiating Titrations

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Abstract

A technique based on a method of differentiating titrations was developed for the resolution of mixtures of ricinoleic, sulfuric and ethylsulfuric acids. The total and partial acid values were determined by potentiometric titration with a glass-calomel electrode using aqueous sodium hydroxide as titrant. For the determination of the total acid value the mixture was diluted with ten times its volume of ethanol and completely neutralized with the titrant. For the partial acid value the solvent used was methyl ethyl ketone; sulfuric and ethylsulfuric acids were completely neutralized.

When rapid determinations are needed, thymol blue and bromophenol blue can be used as indicators.

THE TECHNIQUE of differential titrations has been used to follow the course of the esterification of ricinoleic acid with ethanol, catalyzed by sulfuric acid (1). For the purpose of kinetic studies, the total acidity of mixtures of ricinoleic, sulfuric, and ethylsulfuric acids, and the content of ricinoleic acid were determined, which permitted the calculation of the concn of each acid in the mixture.

The resolution of mixtures of strong and weak acids has been investigated by Fritz and Lisicki (6), Fritz and Marple (7), Cundiff and Markunas (3), Deal and Wyld (4), Bruss and Wyld (2), and Reynolds, Little and Pattengiel (9). Bruss and Wyld analyzed a mixture of perchloric, hydrochloric, salicilic, and acetic acids with phenol which was resolved quantitatively in methyl isobutyl ketone by titrating with tetrabutyl ammonium hydroxide using a glass-calomel electrode.

A search of the literature prior to our experimental work did not reveal a simple solvent-titrant system that could be used for mixtures of ricinoleic, sulfuric, and ethylsulfuric acids.

Experimental

The techniques which were adapted consist of potentiometric titrations which were performed manually using a Leeds and Northrup potentiometer, model 7664, with a glass-calomel electrode. The titration procedure consisted of dissolving the sample in 100 ml of an appropriate solvent, and adding the titrant from a 25 ml burette graduated in 0.1 ml intervals. No inert atmosphere was required. The titrant selected was 0.810*N* aqueous sodium hydroxide because its behavior with the components of the samples titrated was known and because of its stability. Ethanol, ether, chloroform, methyl isobutyl ketone and methyl ethyl ketone were tested for interferences in the titrations and investigated as solvents.

The validity of the analytical method was established by comparison of analyses of mixtures of the three acids (ricinoleic, sulfuric and ethylsulfuric) with parallel anaylses of samples of the pure components.

Titrations of sulfuric and of mixtures of sulfuric and ethylsulfuric acids in methyl ethyl ketone were performed. The results were verified by parallel titrations in water. These results agreed with those reported by Evans and Albertson (5) who investigated the esterification of sulfuric acid by the method of titrations and verified the method by isolation of the ethylsulfuric acid formed as potassium hydrogen sulfate.

Titrations of ricinoleic acid in methyl ethyl ketone were conducted on two samples containing 0.2284 and 0.3386 equivalents of the acid diluted in ethanol.

The analyses of mixtures of sulfuric and ricinoleic acids were verified by the titration in both ethanol and methyl ethyl ketone on a soulution of 0.0149*N* ricinoleic acid and 0.902*N* sulfuric acid. This solution was prepared by dissolving ricinoleic acid in ethanol and slowly adding sulfuric acid, under continuous stirring at 20F to reduce to a minimum the esterification.

Mixtures of sulfuric, ethylsulfuric and ricinoleic acids, withdrawn from a reactor, where the esterifica-

TABLE I

Material Balance

	Sample Composition		Acid Value in NaOH
	Before quenching	After quenching	
Ricinoleic acid	$n_{Ao}—y$	$n_{Ao}—u$	$n_{Ao}—u$
H_2SO_4	$n_{CSo}—v—y+u$	$n_{CSo}—v$	$2(n_{CSo}—v)$
$C_2H_5HSO_4$	v	v	v
C_2H_5OH	$n_{Bo}—v—y+u$	$n_{Bo}—v—y+u$	
H_2O	v+y	v+y	
Ethyl ricinoleate	u	u	
Intermediate	y—u	zero	

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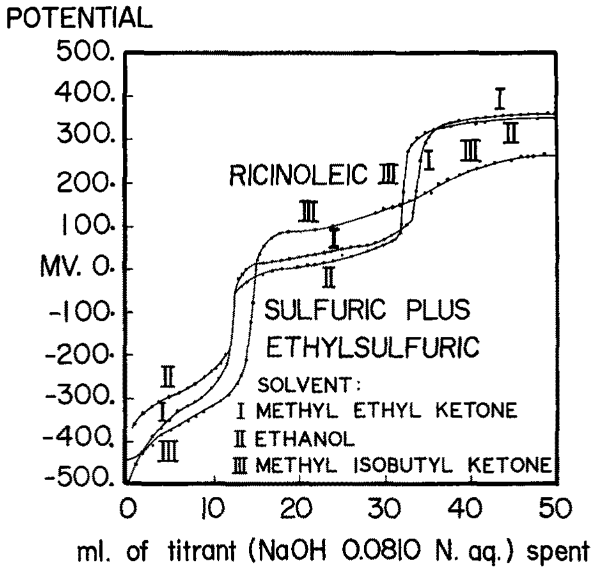

Fig. 1. Resolutions of ricinoleic and sulfuric acids.

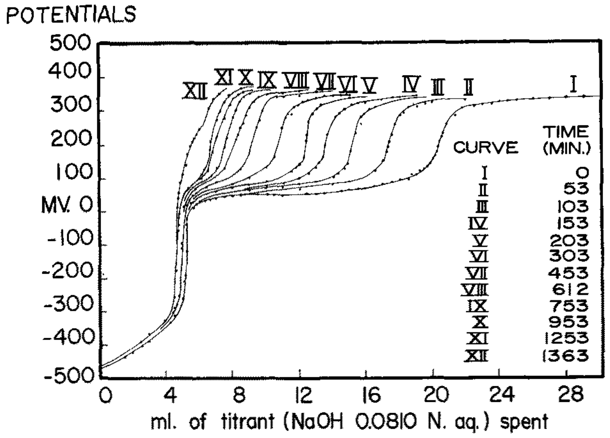

Fig. 2. Titrations of mixtures of ricinoleic, sulfuric, and ethylsulfuric acids at various concentrations of ricinoleic acid.

tion of ricinoleic was carried on, were titrated independently in ethanol and in methyl ethyl ketone. The entire range of concns of ricinoleic acid was investigated.

Interpretation of the Analyses

In the esterification of ricinoleic acid, the composition of the samples is related to the conversions, by the material balance shown in Column 1 of Table I. When the samples are quenched to stop the reaction the composition changes to that shown in Column 2 because the intermediate splits into the original constituents (1). The following equations relate the conversions to the total acid value (TAV) and the partial acid value (PAV), and the esterification can be followed by measuring these quantities:

$$TAV = 2n_{CS_o}+n_{A_o}\text{-}u\text{-}v \qquad [1]$$

$$PAV = 2n_{CS_o}\text{-}v \qquad [2]$$

n_{A_o}, n_{CS_o}, n_{B_o}, initial number of moles of ricinoleic acid, sulfuric acid and ethanol, respectively; u, v, w, and y, moles of ethyl ricinoleate, ethylsulfuric acid, alkali, and ricinoleic acid converted, respectively, at any time, t.

Results and Discussion

The ability of a solvent to resolve a mixture of acids depends upon the leveling effect that the solvent has on the acids. Mixtures of weak and moderately strong acids are resolved in a solvent which is weakly acidic as well as weakly basic with respect to the acids titrated. A hydrocarbon satisfies this requirement, although its low conductivity results in poor operation of the potentiometer (2).

Figure 1, Curve I, represents the potentiometric titration of sulfuric and ethylsulfuric acids in methyl ethyl ketone, and shows evidence of the resolution of ricinoleic from sulfuric and ethyl-sulfuric acids. In our work the resolution of these two acids from each other was not required. The resolution in ethanol was also satisfactory (Curve II); however, methyl ethyl ketone is a better solvent for a wider range of concns. The difference in the results exhibited by Curves I and II is due to the presence of 1% wt. CH_3COOH in the ketone. Once the appropriate correction was made, the results were equal. Methyl isobutyl ketone (Curve III) shows no end point at the end of the neutralization of ricinoleic acid. In ether and chloroform no resolution was attained.

TABLE II

Accuracy of the Analytical Method

	H_2SO_4+$C_2H_5.HSO_4$ acids		Ricinoleic acid	
	S_I	R.P.	S_I	R.P.
Methyl ethyl ketone..........	55.5	99.51	46.7	99.705
Ethanol..............................	55.5	99.51	66.5	99.42
Methyl isobutyl ketone	53.0	99.18	—	—

S_I = Sharpness index; R.P. = Relative precision.

The results of the titrations were in agreement with the known compositions of the solutions tested. In most of the cases, toward the end of the titrations, the system separated into two phases. Proper stirring provided a uniform disperse medium where the transfer of titrant was relatively easy.

The resolution of ricinoleic in the presence of sulfuric and ethylsulfuric acids over the entire range of concns is shown in Figure 2. It must be noted that titration potentials remained constant for both, ricinoleic and the mixture of sulfuric and ethylsulfuric acids. The potential span in methyl ethyl ketone was large enough to offer a substantial difference in the midpoint potentials of the acids titrated; these are: –380 mv for the mixture of sulfuric and ethylsulfuric acids and +45 mv for ricinoleic acid.

Accuracy of the Method

The accuracy of the method is expressed in terms of the sharpness indices and the relative precisions which were evaluated by the method recommended by Kolthoff (8) and are reported in Table II. The relative precisions were calculated from the limits of observation of the potentiometer which were ± 3.mv.

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