Determination of Fatty Alcohols in Fatty Alcohol Sulfates

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Abstract

A simplified procedure for the quantitative determination of very small amts of fatty alcohols in fatty alcohol sulfates has been developed. In the present work this procedure was applied to the determination of lauryl alcohol in lauryl alcohol sulfate.

Introduction

THE ACTIVE ingredients in fatty alcohol sulfate solutions can be readily determined by such established methods as cationic titration (1) or hydrolysis (2). However, there has been no such simple technique for the direct analysis of small amts of impurities, such as free alcohols, which also might be present in these mixtures.

Solvent extraction followed by gravimetric determination (2) of the organic impurities is lengthy because multiple extraction of the solution is needed to insure complete removal of the impurities. Likewise, the concn of these impurities in the aqueous solution is too low to allow direct analysis by vapor phase chromatography (VPC).

A simplified procedure for quantitatively determining small amts of fatty alcohols in aqueous solutions of the alcohol sulfate has been developed. This method involves a single extraction with a solvent containing an internal standard followed by VPC analysis of the extract. Specifically, the method has been applied to the determination of lauryl alcohol in a lauryl sulfate solution.

Experimental

Extraction Technique With Internal Standard

Standard solutions were made by dissolving a known amt of lauryl alcohol in 100 ml of a solution of 15% lauryl sulfate in water. A 20 ml aliquot of the standard solution was extracted with 20 ml of a solution composed of 3.403 g myristyl alcohol (*n*-tetradecanol) in 2.00 liters of heptane. The resulting emulsion was broken by addition of small amts of isopropyl alcohol, and the heptane phase was separated and concd to ca. 1 to 2 ml on a rotary evaporator. This conc was analyzed directly by VPC.

Extraction Technique Without Internal Standard

Lauryl alcohol was weighed into 100 ml of 15% lauryl sulfate solution. The solution was extracted with exactly 100 ml of heptane. Myristyl alcohol was added as an internal VPC standard *after* the extraction, and the conc was analyzed by VPC.

TABLE I

Analyses for Lauryl Alcohol with Internal Standard

Run No.	g. Lauryl Alcohol Present	Found	% Error
1 [b]	0.140	0.139	0.7
2 [a]	0.245	0.265	8.0
3 [b]	0.252	0.245	2.8
4 [a]	0.355	0.340	3.0
5 [b]	0.382	0.350	8.4
6 [b]	0.509	0.466	8.5
7 [a]	0.515	0.490	6.0
8 [a]	0.590	0.550	7.0
9 [b]	0.624	0.588	5.8

[a] One determination.
[b] Average of two determinations.

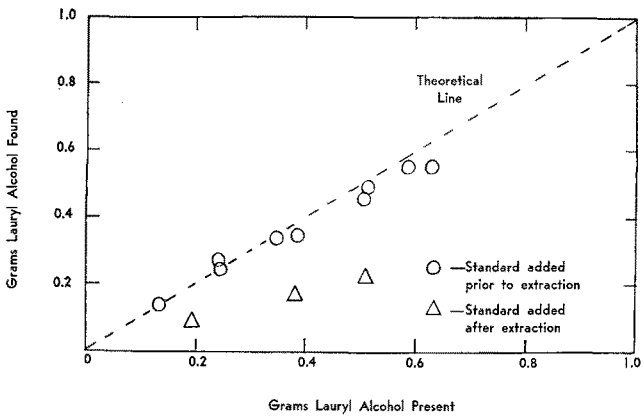

FIG. 1. Data correlation.

Vapor Phase Chromatography Analysis

The VPC analysis was performed on a Perkin-Elmer Vapor Fractometer with a 15 in. column of Carbowax 20M on Diatoport (20%) operated at 163C at 6 psig of helium. The peak areas were calculated by multiplying the peak height by the width at the half-height. A calibration factor (F) (0.861) was determined experimentally from known mixtures of lauryl alcohol and myristyl alcohol. The following expression was used to calculate the amount of lauryl alcohol in each sample:

$$\text{Wt } C_{12} = \frac{A_{12}}{A_{14}} \times \text{Wt } C_{14} \times F$$

where $\text{Wt } C_{12}$ = weight lauryl alcohol
A_{12} = area lauryl alcohol
$\text{Wt } C_{14}$ = weight myristyl alcohol
A_{14} = area myristyl alcohol
F = calibration factor

Results and Discussion

A quantity of lauryl alcohol was weighed into a lauryl sulfate solution and the mixture was extracted with heptane to which had been added myristyl alcohol as an internal standard. The extract was concd and then analyzed by VPC. The results were in good agreement with the actual values as summarized in Table I and Figure 1. On the other hand, when the internal standard was added after extraction, only about 50% of the lauryl alcohol present could be accounted for (Table II).

These data demonstrate that a single extraction with heptane removes less than 50% of the lauryl alcohol present in the sulfate solution. Thus, an analysis dependent on complete removal of the lauryl alcohol would need several extractions to be accurate. Conversely, when myristyl alcohol was added to the heptane prior to extraction a single extraction was sufficient. The single extraction still left part of the

TABLE II

Analyses for Lauryl Alcohol without Internal Standard

Run No.	Present	Found	% Extracted
1	0.1978	0.0942	47.6
2	0.3848	0.1710	44.5
3	0.5022	0.2191	43.7

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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