	Water Added <i>Ml</i> .	Approximate Water Content of Sample	Choline Dihydrogen Citrate Found, %		
Solution			Indicator End Point	Potentiometric End Point	
$     \begin{array}{c}       1 \\       2 \\       3 \\       4 \\       5 \\       6     \end{array} $	$\begin{array}{c} 0.0\\ 0.1\\ 0.2\\ 0.4\\ 0.8\\ 1.6\\ \end{array}$	$\begin{array}{c} 0 \\ 10 \\ 15 \\ 26 \\ 41 \\ 58 \end{array}$	99.86 99.86 99.86	$\begin{array}{c} 99.95 \\ 100.08 \\ 100.06 \\ 99.81 \\ 99.95 \\ 100.03 \\ \end{array}$	
7	2.0	63	99.83	99.81	

Table II. Determination of Choline Dihydrogen Citrate in Presence of Water

ble to correct for presence of the trimethylammonium salt after determining its content by a recently developed method (1).

Small amounts of water have no detectable effect upon the determination of choline carboxylic acid salts, but large amounts of water give high results. The magnitude of this effect is indicated by the values in Table I.

Determination of Choline Salts in Presence of Water. By a slight modification of the described procedure it is possible to assay accurately samples of choline salts containing as much as 90<sup>c</sup>/<sub>0</sub> water. This modification, designated Method III, consists of adding sufficient acetic anhydride to the sample in acetic acid to react with the water introduced with the sample, very gently boiling the mixture for 5 minutes, cooling to room temperature, and titrating with the 0.1 N perchloric acid solution, using either the indicator or potentiometric procedure to obtain the end point.

When Method III was applied to a number of 25-ml, aliquots of the sample solution to which known amounts of water were added, the values shown in Table II were obtained.

An approximately 50% aqueous solution of choline bicarbonate analyzed by an aqueous acidimetric procedure gave values of 49.49, 49.49, 49.46, 49.43, 49.40, and 49.44; average 49.45%. When this sample was analyzed by Method III, employing an indicator end point, the results obtained were: 49.38, 49.38, 49.44, 49.45, 49.42, and 49.43; average 49.42%. These values not only indicate the high precision and accuracy of Method III but also substantiate the fact that the described nonaqueous titrimetric procedure is as precise and accurate as aqueous acidimetric and alkalimetric methods.

Application. A sample of choline hydrogen tartrate which had a moisture content of 1.00% (by the Karl Fischer method) and free tartaric acid content of 1.95% was assaved by Method I.

An average value of 96.91% was obtained. A production sample of choline gluconate, manufactured to contain very close to 62.5% choline gluconate, assayed by Method III (indicator end point) gave replicate values of 62.15, 62.14, 62.09, 62.12, 62.04, 62.00, 62.09, 62.11, and 62.07; average 62.09%. This sample had free gluconic acid and moisture con-tents of 5.1 and 32.9%, respectively.

These two examples illustrate the applicability of the described methods to the analysis of production samples of choline carboxylic acid salts and demonstrate that the proposed procedures seem to have no error in excess of  $\pm 0.2\%$ .

## DISCUSSION

When aqueous solutions of choline dihydrogen citrate or choline hydrogen tartrate are analyzed by Method III, slightly lower results are obtained by the indicator than by the potentiometric end-point procedure. This is due to the slight obscuring of the indicator end point by darkening (browning) of the solution during the refluxing period. The discoloration does not interfere with the assay, and after a few trials the end point can be duplicated without difficulty. The discoloration does not occur with choline gluconate or bicarbonate,

The amount of acetic anhydride added in Method III is not critical. Excess acetic anhydride does not interfere with the determination and equally good results can be obtained if only enough anhydride is added to react with 80 to 90% of the water introduced with the sample.

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# Fatty Amine Products of High Molecular Weight

Quantitative Titration in Acetic Acid

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QUEOUS titrimetry appears adequate for the fatty primary amines of high molecular weight. However, it has been found of little or no value when applied to the acetates of the fatty primary amines, which are commercial products useful in ore beneficiation, and certain secondary and tertiary amines of high molecular weight. This paper concerns the adaptability of titrimetry in glacial acetic acid to diverse fatty amine products of high molecular weight.

Conant and Hall (3) in their study of "superacid solutions" found that many organic compounds behave as strong bases in glacial acetic acid whereas they show no basic property in water. In view of the acid-base relationships which exist in glacial acetic acid (1, 3-5, 7, 8, 11), it appeared probable that these fatty

amine products could be quantitatively titrated in glacial acetic acid with perchloric acid. Accordingly, different compounds such as the fatty primary amine acetates, fatty secondary amines, mixed tertiary amines, fatty aminonitriles-for example, N-alkyl- $\beta$ -aminopropionitriles—and fatty materials containing both primary and secondary amino groups-for example, N-alkyl- $\gamma$ aminopropylamines-were tested. In the present study, it was found that glacial acetic acid was an excellent solvent for all the fatty amine products tested and perchloric acid was a highly satisfactory titrant.

**REAGENTS AND SOLUTIONS** Perchloric acid, 70 to 72%, ACS grade Acetic anhydride, ACS grade

Because conventional aqueous titrimetry methods are not applicable for a number of fatty amine products of high molecular weight, such as fatty amine acetates, fatty secondary and tertiary amines, and fatty aminonitriles, it was desirable to develop a method for titrimetric determination of diverse fatty amine products. The use of perchloric acid as titrant in glacial acetic acid as solvent gives excellent re-

Acetic acid, glacial, ACS grade Perchloric acid solution, 0.1 N

The standard acid solution, 0.1 iv The standard acid solution is prepared by adding 14.2 grams of the perchloric acid reagent to 500 ml. of glacial acetic acid; ace-tic anhydride (23.3 grams) is added with stirring and the solution is then made up to 1000 ml. by dilution to the mark with more gla-cial acetic acid. The solution is standardized against anhydrous sodium carbonate (AR grade material is heated to 350° C. for 2 hours) to the crystal violet end point. Acid potassium phthalate NBS has been recommended as the primary standard (10

Crystal violet indicator, 1 gram of crystal violet dissolved in 100 ml. of glacial acetic acid.

Table I. I	Representative	Fatty.	Amine	Products
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	Amine Number		
Fatty Amine Product	Theory	Found	
Octadecylamine Hexadecylamine Oleyl amine <sup>a</sup> Dioctadecylamine N-Methyldioctadecylamine Octadecylamine acetate <sup>b</sup> N-Dodecyl-3-aminopropionitrile N-Octadecyl-7-aminopropylamine	$\begin{array}{c} 208.2\\ 232.4\\ 209.8\\ 107.5\\ 104.7\\ 170.3\\ 235.3\\ 343.6\\ 6\\ 343.6\end{array}$	$\begin{array}{c} 208.0\\ 233.7\\ 209.0\\ 107.8\\ 105.0\\ 170.3\\ 235.6\\ 342.0\\ 342.0\\ \end{array}$	
N-Dodecylaminoacetomtrife $N$ -Dodecyl- $\beta$ -aminoethylamine	491.3	486.3	
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<sup>a</sup> Iodine value, theory 95.5, found 96.1.
 <sup>b</sup> Prepared from 99% octadecylamine by addition of requisite quantity of glacial acetic acid.

## ANALYTICAL PROCEDURES

The fatty amine product (0.5 to 1.0 gram) is weighed accurately into a 200-ml. Erlenmeyer flask and dissolved in 50 ml. of glacial acetic acid by gentle warming. One drop of the crystal violet indicator is added and the warm solution is titrated with 0.1 Nperchloric acid in acetic acid to a green color (solutions are main-tained at a slightly elevated temperature (30° to 45° C.) in order to avoid the precipitation of the perchloric salts].

## CALCULATION

Amine No. = 
$$\frac{\text{ml. of } 0.1 \text{ } N \text{ acid } \times N \times 56.11}{\text{sample weight}}$$

The amine number may be defined as the number of milligrams of potassium hydroxide which is equivalent to 1 gram of the amine product.

## EXPERIMENTAL

The primary and secondary fatty amines were prepared by the catalytic hydrogenation of the corresponding nitriles. The Nmethyldialkyl amines were prepared from the secondary fatty amines by the formaldehyde-formic acid procedure (2). The reaction between acrylonitrile and the fatty amines yielded the N-alkyl- $\beta$ -aminopropionitriles which were converted to the Nalkyl- $\gamma$ -aminopropylamines ( $\theta$ ). The N-alkylaminoacetonitriles were prepared by the reaction of the fatty amines with sodium cyanide, formaldehyde, and sodium bisulfite (9). Reduction of the substituted acetonitriles with lithium aluminum hydride gave the N-alkyl- $\beta$ -aminoethylamines. All the above products were highly purified by distillation and crystallization procedures. The results of the analyses of a number of representative fatty amine products are summarized in Table I.

sults with a wide variety of fatty amine products including the primary, secondary, and tertiary fatty amines and their acetates, as well as fatty amino nitriles and compounds containing both primary and secondary amino groups. The method makes possible the rapid and accurate determination of a large number of fatty amino compounds which cannot be titrated by the conventional aqueous method.

## DISCUSSION

Whereas aqueous titrimetry is satisfactory for the fatty primary amines, it gives erratic results with some fatty secondary amines because of solubility factors and is of little or no value when applied to the N-methyldialkyl amines, fatty tertiary amines, fatty amine acetates, and N-alkylaminoacetonitriles. In Table I, the octadecylamine acetate is given as the representative example of an acetate of a fatty amine product. However, the acetates (either mono- or di-) of the other products were also prepared and tested. The colorimetric titration with perchloric acid in acetic acid was highly satisfactory for all the acetate materials.

The data presented in Table I clearly demonstrate the versatility and accuracy of the nonaqueous method and its applicability to diverse fatty amine products.

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