

TABLE II

Standard Deviation of Cyclic Monomers from Linseed Oil and Linolenic Acid as Determined by GLC

Number of tests on different days	Linseed oil		Linolenic acid	
	Saturated	Unsaturated	Saturated	Unsaturated
1.....	52.5	52.6	90.4	88.5
2.....	53.0	53.6	89.9	89.3
3.....	52.7	51.9	89.7	88.9
Standard deviation..	0.25	0.85	0.36	0.40

ple. The true separation point was determined by elution time. Unsaturated samples of the same series could then be determined for cyclic content. Data given in Table II agree very well; however, this agreement was frequently inconsistent.

This method of determining cyclic content on un-

saturates was considered generally inferior to the method using saturated esters because a breakoff point between unsaturated cyclic and unsaturated straight-chain esters could not be located directly.

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Analysis of Soaps with Hydrogen Bromide in Glacial Acetic Acid

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Abstract

Alkali metal carboxylic acid salts of long-chain fatty acids and of α -sulfo fatty acids are determined by titration with hydrogen bromide in glacial acetic acid medium. Crystal violet is used as indicator.

Introduction

THE ANALYSIS of soaps of epoxidized fatty acids by the Durbetaki (1) method led to the discovery that the titrant, a solution of hydrobromic acid in acetic acid, reacted not only with the oxirane function, but with the carboxylic acid salt as well. A survey of the literature disclosed no study of the quantitative determination of soaps by this method, although the reaction of soaps with hydrogen bromide was known (2). An investigation to discover whether the Durbetaki method was applicable to the quantitative determination of soap therefore seemed desirable, especially if the procedure could be carried out in the presence of salts of strong acids.

As early as 1927, Hall and Conant (3,4) experimented with the titration of bases in glacial acetic acid. These authors used either potentiometric methods or visual indicators to obtain sharp endpoints in this medium.

Of the various indicators used in non-aqueous titrations, crystal violet is fairly popular. There have been reports of some difficulties with this indicator due to the several color changes it undergoes (5) when various types of compounds are titrated. However, potentiometric titration may be used to select the crystal violet color change which coincides with the equivalence point of the particular type of compound titrated. The accuracy and precision of the results is directly related to the length of experience of the analyst (6). For the determination of soaps, Palit (7) employed a double indicator method using phenolphthalein or cresol red in combination with

methyl orange or methyl red. The analysis was carried out in a solvent mixture of a glycol with either a higher alcohol or chlorinated hydrocarbon. Pure sodium oleate and commercially available soaps, dissolved in a mixture of either ethylene or propylene glycol and isopropyl alcohol, were titrated with either hydrochloric acid or perchloric acid in the same medium. Potentiometric titrations were employed to substantiate the results.

Markunas and Riddick (8) determined carboxylic acid salts and other weak bases with potentiometric and visual indicator titrations using glacial acetic acid as solvent and perchloric acid in acetic acid as the titrant. The authors did not, however, analyze any long chain fatty acid salts.

Fritz and Fulda (9) titrated tertiary amines and lithium nitrate potentiometrically in glacial acetic acid, using perchloric acid as titrant. Acetic anhydride was added to remove traces of water. Again, soaps were not analyzed.

Pellerin (10) stated that salts of acetates, propionates, citrates, tartrates, benzoates, salicylates, etc. can be titrated with perchloric acid in acetic acid.

Reagents and Apparatus

Acetic acid, glacial, analytical reagent grade.

Hydrogen bromide in acetic acid, 0.1N, anhydrous.

Crystal violet indicator solution. Prepare a saturated solution (approximately 1%) of crystal violet (Eastman) in glacial acetic acid.

Sodium carbonate, primary standard grade, dried for 3 hr at 240C, or potassium acid phthalate, primary standard grade, dried to constant weight at 125C.

Automatic buret, 50 ml, reservoir type, equipped with drying tubes to protect content from atmospheric moisture.

Procedure

Weigh accurately a sample of 0.4-0.6 g into a 250 ml Erlenmeyer flask fitted with a rubber stopper. Add 50 ml glacial acetic acid and dissolve the sample, with

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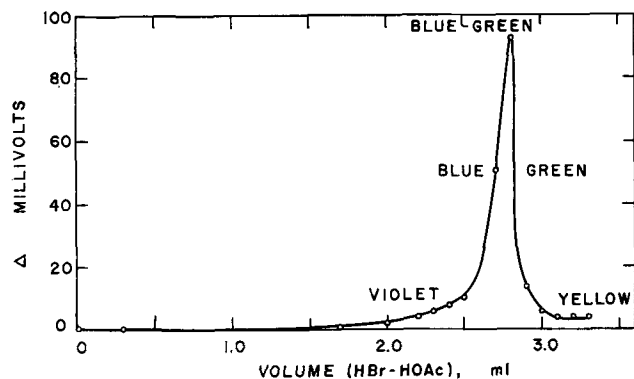


FIG. 1. Potentiometric titration of potassium palmitate with HBr-acetic acid in the presence of crystal violet indicator.

heating if necessary. Cool the sample solution to room temperature, add crystal violet indicator solution, and titrate with hydrogen bromide solution to a blue-green endpoint. Carry out a blank titration on the reagents.

Calculation:

- Percent soap = $(A - B) \times N \times E \times 0.1/W$ where
- A = ml of hydrogen bromide solution required for sample
- B = ml of hydrogen bromide solution required for blank
- N = normality of hydrogen bromide solution
- E = equivalent weight of soap
- W = sample weight

The procedure may also be carried out on a semi-micro scale by dissolving approximately 0.1 g sample in 25 ml glacial acetic acid and titrating with 0.02N hydrogen bromide in glacial acetic acid as above. Alternatively, 0.1 g samples may be analyzed, at some sacrifice in accuracy, by titrating with 0.1N hydrogen bromide from a 5 ml burette. The latter procedure was used in the comparison of the potentiometric and the visual endpoints, shown in Figure 1.

The hydrogen bromide solution is standardized daily against sodium carbonate or potassium acid phthalate.

Oxirane compounds and materials which are known to interfere in the HBr oxirane determination, e.g. α, β -unsaturated carbonyl compounds, are expected to interfere in this determination also.

Results and Discussion

Table I lists the soap samples used in this investigation, together with comparative results obtained by the HBr titration method and by alkali metal determination. Two types of soaps were studied: alkali metal salts of straight chain fatty acids and alkali metal soaps of α -sulfo fatty acids. The latter type was poorly soluble in acetic acid at room temperature but gave reproducible results. On the other hand, alkaline earth salts of α -sulfo fatty acids gave erratic results and could not be determined by this method.

The results shown in Table I indicate good agree-

TABLE I
Analysis of Soaps by HBr Titration and by Alkali Metal Determination

Soap	Percent concentration of soap	
	HBr titration	Alkali metal determination
Potassium stearate.....	100	99.4
Sodium stearate.....	97.5	97.5
Sodium palmitate.....	97.6	98.3
Potassium palmitate.....	99.8	100
Potassium myristate.....	99.0	97.5
Disodium α -sulfo stearate.....	99.0	95.5
Dipotassium α -sulfo palmitate.....	98.9	98.1

TABLE II
HBr Titration of Stearic Acid-Sodium Stearate Mixtures

Weight percent sodium stearate in mixture	Weight percent sodium stearate determined
9.6	9.7
23.7	24.1
46.7	46.9
73.7	74.0

ment between the two methods of analysis. The HBr titration results listed for the salts of α -sulfo fatty acids were calculated under the assumption that only the carboxylic acid salt is determined while the sulfonic acid salt remains unaffected by this method. That this assumption of selectivity is justified was shown by subjecting ammonium α -sulfo stearic acid, calcium α -sulfo stearic acid, and magnesium α -sulfo stearic acid to the analysis. None of these compounds were titrated by the HBr.

The HBr titration method was tested at various soap concentration levels by analyzing several known mixtures of stearic acid and sodium stearate. The data, shown in Table II, demonstrate the applicability of the method to the full range of concentrations.

A precision check of the hydrogen bromide method was made on all samples as shown in Table III, using the visual endpoint. The reproducibility would appear to be satisfactory for most applications.

TABLE III
Reproducibility of Soap Determinations

Experiment	Soap						
	Potassium stearate	Sodium stearate	Sodium palmitate	Potassium palmitate	Potassium myristate	Disodium α -sulfo stearate	Dipotassium α -sulfo stearate
1	100%	97.4%	98.0%	99.9%	99.2%	99.0%	98.8%
2	100	97.6	97.5	99.8	99.3	99.0	98.9
3	100	97.2	97.4	99.7	99.1	99.0	98.9
4	100	98.0	97.5	99.7	98.9	99.1	99.1
5	99.9	97.1	97.6	99.8	98.7	99.1	98.9
6	99.9	97.6	97.5	99.7	98.9	99.0	99.0

Standard deviation = 0.18.

Agreement of the visual endpoint with the potentiometrically determined equivalence point is shown in Figure 1. With some operator experience, the visual endpoint was found to be quite reproducible. While traces of moisture and small variations in temperature do not affect the crystal violet endpoint significantly, excessive introduction of moisture or variations in temperature should be avoided.

Trial experiments were also carried out to determine whether the HBr method is applicable to sodium salts of α -phosphono fatty acids and α -phosphono fatty esters. The results indicate that all three sodium ions of the trisodium salts of α -phosphono fatty acids and both sodium ions of the disodium salts of α -phosphono fatty esters are determined quantitatively by this method.

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