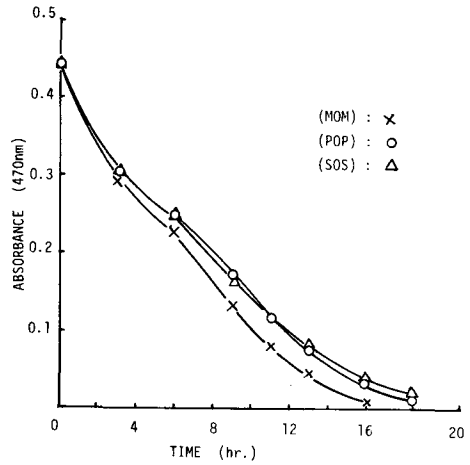

FIG. 10. Oxidation rates of triglyceride in the early stages of oxidation as measured by β-carotene decoloration.

the influences ascribed to the difference in carbon chain lengths are essentially the same.

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Hydrogen Bromide Titration for Soaps in Fat Products

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ABSTRACT

Since none of the existing methods for determining soaps in fat products have been found to be entirely satisfactory, a method has been devised for the determination of alkali metal soaps by direct titration with Durbetaki reagent (hydrogen bromide dissolved in glacial acetic acid). When the titration was conducted at room temperature in acetic acid-benzene solution with crystal violet as indicator, soaps of potassium, sodium and lithium could be determined accurately in anhydrous oils, monoglycerides, and sucrose esters. The presence of alcohols, glycerol and sucrose did not interfere in the direct titration. However, oxidized oils, epoxides, and cyclopropenoid acids, which are known to consume hydrogen bromide, did interfere. Products containing the interfering substances could be analyzed by a modified procedure in which the alkali metal cations were extracted from a mixture of amyl acetate and *n*-butanol (1:3) into an aqueous solution of acetic acid, and titrated as the acetates.

INTRODUCTION

A number of methods have been proposed for the quantitative determination of soaps in fats and oils, the main emphasis being on soaps in refined oils. The oldest methods depend on ashing the sample (1-3). Others depend on the titration of the free fatty acids liberated when soapy oils are acidulated (4). A method enabling the spectrophotometric determination of calcium complexes of soaps has also been developed (5).

[1]Retired.

There are two official AOCS methods (6) for the determination of soap in oil: one measures the conductivity of soapy water obtained on washing the oil sample, the other is a titrimetric method that determines the alkalinity of the sample by an aqueous hydrochloric acid titration of the sample dissolved in acetone containing 2% water. The quantitative determination of soaps in fat products is difficult and so far no one method has been found universally acceptable.

In our experimental work with such fat derivatives as sucrose esters, we required a relatively simple method capable of measuring a wide range of soap concentrations. Haeberer and Maerker (7) demonstrated that the Durbetaki (8) reagent can be used to determine the purity of soaps.

The principle on which our method of titrating for soaps relies is based on a study of Kolthoff and Willman (9), who noted that electrolytes which are neutral in water may not be neutral when dissolved in glacial acetic acid. Differences in acidic and basic properties become quite pronounced. The alkali metal acetates, for example, are strongly basic in glacial acetic acid solution, and can be readily titrated. This basicity increases in the order Li < Na < K (9).

MATERIALS AND METHODS

Apparatus and Technique

The apparatus and technique employed in titrating for soap content are similar to those reported earlier (10). The

TABLE I

Determination of Sodium, Potassium and Lithium Soaps in Purified Safflower Oil by HBr Titration

Sample	% Soap Present	Found
Sodium palmitate	35.66	33.87
Sodium palmitate	15.98	15.85
Sodium palmitate	4.00	4.01
Sodium palmitate	2.08	2.03
Sodium palmitate	0.52	0.51
Sodium palmitate	0.23	0.21
Potassium palmitate	35.09	35.00
Potassium palmitate	18.08	17.90
Potassium palmitate	9.03	8.89
Potassium palmitate	3.80	3.74
Potassium palmitate	1.85	1.83
Potassium palmitate	0.96	0.97
Potassium palmitate	0.49	0.49
Potassium palmitate	0.25	0.25
Lithium palmitate	31.63	31.68
Lithium palmitate	15.85	15.86
Lithium palmitate	7.93	7.89
Lithium palmitate	3.98	3.99
Lithium palmitate	1.00	1.01
Lithium palmitate	0.50	0.51
Lithium palmitate	0.23	0.23

hydrogen bromide/acetic acid solution used as titrant was stored in an automatic buret equipped with a Teflon plug, a drying tube, and a Luer tip. A small-diameter Teflon tube or needle was used to transfer the titrant from the buret tip, through a neoprene stopper, and into the bottom of the titration flask. The sample, which was dissolved in 15 mL glacial acetic acid and 5 mL benzene, and mixed using a Teflon-coated magnetic stirring bar, was titrated at room temperature. Crystal violet was used as an indicator. The titrant was standardized daily against sodium carbonate.

Soaps. Soaps are difficult to prepare and keep in pure form; they usually were prepared in situ. A standardized solution of the appropriate hydroxide in alcohol was added to a slight excess of free fatty acid, or the alcohol solution was added to the ester and the mixture was heated to form the soap and drive off the alcohol.

Oils. A highly purified safflower oil was used as a substrate for the titrations of soap in oil.

Monoglycerides. Monoglycerides were prepared in the laboratory from a commercially hydrogenated cottonseed oil which had an iodine value of 70. Standard procedures were employed to prepare a soap-free and glycerol-free product containing ca. 50% monoglycerides, 40% diglycerides and 10% triglycerides.

Sucrose esters. Sucrose monoesters were prepared by the method described by Osipow et al. (11), using dimethylformamide as solvent. To purify the sucrose monoesters, the crude esters dissolved in *n*-butanol were washed first with a 1:1 mole mixture of mono- and disodium citrate solutions containing 10% NaCl, then four times with 10% NaCl solution only. The emulsions broke readily. When the washed solution was partially stripped under nitrogen and filtered, a clear solution was obtained. Further stripping caused white solids to precipitate out of solution. The solids were removed by filtration and found to consist mostly of NaCl. Removing the rest of the butanol did not produce more solids. Hexane added to the stripped esters gave a clear solution. When the hexane was evaporated the sucrose monoesters still were clear, indicating that salts are not soluble in an anhydrous solution of sucrose monoesters in butanol. The esters could not be purified to give a zero HBr titration; they contained an impurity equivalent to 0.19% potassium oleate. Thin layer chromatography detected a ninhydrin positive spot, indicating that this impurity might be a nitrogen-containing compound.

Experimental Procedure

In the first series of experiments, carefully measured volumes of standardized sodium hydroxide solution were added to portions of purified palmitic acid in 50-mL Erlenmeyer flasks. In each case, the proportion was such that 98% of the palmitic acid was neutralized. Alcohol was added to promote the reaction, then the alcohol and water were driven off by heating. Purified safflower oil was added and the dry sodium palmitate and oil were heated and mixed. In each case, the total weight of oil and soap was ca. 2 g. To this mixture was added 15 mL of glacial acetic acid and 5 mL benzene. The solution was titrated with standardized 0.1N hydrogen bromide in glacial acetic acid to an end point that was indicated when the color of the indicator changed from violet to blue-green. The end point was sharp. Identical series of experiments were performed using sodium and lithium hydroxides.

Preparation of soaps in monoglycerides was accomplished by adding standardized sodium hydroxide or potassium hydroxide solutions, diluted with alcohol, then heating the mixtures to drive off the alcohol and water. For the low concentrations, 100 g samples were titrated, for the higher concentrations 2 g and 20 g samples were titrated. Soaps in sucrose monoesters were prepared in the same manner as above, 5 g and 20 g samples of the esters were titrated.

A modified procedure was developed for products containing titratable nonsoap impurities such as oxidized oils, epoxides, cyclopropenes and water. A carefully weighed sample of the product was dissolved in a mixture of amyl acetate (3 parts) and *n*-butanol (9 parts). The resulting solu-

TABLE II

Sodium and Potassium Soaps in Monoglycerides and Sucrose Esters[a], Determined by HBr Titration

Sample	Soap, % in monoglycerides Present	Found	Soap, % in sucrose esters Percent	Found
Sodium palmitate	14.80	14.6 8	15.03	14.87
Sodium palmitate	5.05	5.01	5.05	5.01
Sodium palmitate	0.28	0.28	1.03	1.01
Potassium palmitate	9.68	9.81	15.05	14.98
Potassium palmitate	4.83	4.83	13.50	13.52
Potassium palmitate	0.30	0.30	5.02	5.01
Potassium palmitate			1.01	1.00

[a]Corrected for HBr titration of an impurity present in sucrose esters equivalent to 0.19% potassium palmitate.

TABLE III

Soaps Determined by Extraction Procedure followed by HBr Titration

Sample	% Soaps Present	% Soaps Found
Potassium palmitate in safflower oil	3.01	2.97
Potassium palmitate in safflower oil	0.30	0.29
Potassium palmitate in oxidized safflower oil[a]	3.01	2.99
Potassium palmitate in oxidized safflower oil[a]	0.31	0.30
Potassium palmitate in cottonseed oil[b]	3.01	2.96
Potassium palmitate in cottonseed oil[b]	0.03	0.03
Potassium palmitate in sucrose esters	4.61	4.56
Potassium palmitate in sucrose esters	0.30	0.34

[a]Oxidized by allowing it to sit exposed to sunlight on a window sill in a beaker covered with filter paper until a peroxide value of 35.19 was reached.
[b]Cottonseed oil contained 0.67% cyclopropenoids, calculated as trimalvalin.

tion was then washed 3 times with 15% acetic acid (2 parts) and twice with acetic acid (1 part). The washings were combined, the solution was evaporated to dryness and the acetates titrated in acetic acid in the usual manner.

RESULTS AND DISCUSSIONS

The results obtained by titrating soaps in oils are listed in Table I. The percentages of soap found are in good agreement with the exception that at the highest level of sodium palmitate the agreement is less than desirable; however, 35% of anhydrous sodium palmitate in safflower oil is an unusual mixture, which does not dissolve well at room temperature. At the lowest levels the agreement is almost perfect.

Table II shows results obtained titrating soaps in monoglycerides and sucrose esters. The amount of soaps found in monoglycerides is in excellent agreement with soaps present, even though HBr in acetic acid reacts slowly with monoglycerides and with diglycerides at elevated temperatures. The results obtained titrating soaps in sucrose esters are in good agreement after correcting for the titratable impurity.

Table III shows results obtained with our modified procedure: partitioning samples between organic solvent and acetic acid. This technique converts the alkali metal portions of the soaps to acetates, which are removed and titrated. The amyl acetate and *n*-butanol solution used in this procedure reduce viscosity and practically eliminate the formation of emulsions when surface-active samples containing such products as sucrose esters and monoglycerides are being analyzed. The modified technique can also be used to an advantage for oils containing small amounts of soaps.

It is essential for the regular procedure, as well as for the modified procedure, that all glassware used should be thoroughly rinsed and dried; water will change the end point of the titration significantly when present in amounts of 1-2%.

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