Analytical Methodology for Emulsifiers Used in Fatty Foods: a Review[1]

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ABSTRACT

The current status of analytical methodology for emulsifiers used in fatty foods is reviewed. Faster and more precise methodology for both quality control purposes and for quantitative removal from foods is desirable. A key problem is the quantitative removal from foods to the exclusion of interfering substances. This aspect is complicated by (a) the presence of other food ingredients such as proteins and carbohydrates, (b) innate heterogeneity of most of the emulsifiers, and (c) wide variability in composition of most of the emulsifiers. The broad applicability of chromatography is discussed, with the prediction made that high pressure liquid chromatography will be the technique of the future. Analytical details are not included, as these are available in the cited publications.

INTRODUCTION

Emulsifiers are the most important class of food additives, insofar as amount produced and consumed is concerned. 1970 production was estimated at 188 million pounds. In dollar volume, emulsifiers rank third behind flavorings and stabilizers-thickeners in the various classes of food additives. Emulsifiers may be present in some basic ingredient of a food product, or they may be added by the finished product manufacturer to achieve the desired properties. With the trend toward already processed or convenience foods, emulsifiers are assuming an increasingly important role in food processing and the quality of the finished food products.

This is a review paper. Its intent is to provide insight into the current state of the analytical technology and to point out the needs for additional method development effort as they now exist.

The development of analytical methods for emulsifiers used in fatty foods is difficult for three main reasons: (a) The fatty food emulsifiers have many chemical similarities which make it difficult to separate and distinguish the materials when present in mixtures. These similarities are not surprising when one considers the basic need for fatty acid esters of polyols in order to obtain the required surface chemistry. (b) None of the emulsifiers is a single compound and most are quite heterogeneous mixtures. (c) The very nature of emulsifiers makes them difficult to remove from constituent proteins and carbohydrates present in finished foods. A subordinate editorial problem in dealing with this subject is the definition of the fatty food emulsifiers. No system of classifying emulsifiers is all-inclusive. Usually emulsifiers are classified based upon the function or performance in the product. This frequently means that only a fine line may distinguish a stabilizer from an emulsifier, particularly since some additives may exhibit both properties. For the purpose of this paper, the emulsifiers used in fatty foods in this country are those listed in Table I.

It will be of interest to touch, in an introductory manner, on the growth of chemical complexity of fatty food emulsifiers. Monoglycerides are the first fatty emulsifier to be added to foods. They were introduced in 1933 as a component of shortening for cake baking. They remain the dominant emulsifier, both from the standpoints of total use (75% of the current total tonnage being monoglycerides) and breadth of use, reflecting not only performance but also the fact that monoglycerides occur naturally in foods. There was little additional activity on emulsifiers until the late 1940's, and the major research and development effort and product introduction took place in the 1950's. Monoglycerides are compounds of glycerol and fatty acids. In the search for edible materials of comparable surfactant properties, it was natural to turn toward other polyols and other acids. Most of the resulting products are dealt with in this report.

NEED FOR IMPROVED METHODS

There are essentially two analytical methodology needs. First, there is a distinct need for faster and even more precise methods. The existing methods have been adequate for quality control of emulsifiers as manufactured, but are not completely suitable for monitoring the output of the food industry's present continuous processes. Second, as will be seen, there is a need for improved methodology for the analyses of mixtures of emulsifiers, particularly in finished products. In finished goods the analyst seeks to determine the levels of chemically similar heterogeneous materials of variable composition, where these levels are often as low as 0.1%. Methods for the separation, identification and quantitation of food emulsifiers need further improvement and refinement.

Both industry and regulatory agencies have need for

TABLE I

Emulsifiers Used in Fatty Foods

GRAS status	Via petition (permitted as additives)
Lecithin	Sorbitan polyoxyethylene fatty acid esters (polysorbates)
Mono- and diglycerides (monoglycerides)	Lactic acid esters of mono- and diglycerides
Diacetyl tartaric acid esters of mono- and diglycerides (TEMS)	Propylene glycol fatty acid esters
	Polyglycerol fatty acid esters
	Sorbitan fatty acid esters
	Lactylic esters of fatty acids and their salts (Ca, Na)
	Ethoxylated monoglycerides
	Hydroxylated lecithin
	Succinylated monoglycerides
	Acetylated monoglycerides
	Succistearin (SPGHS)

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[1] Presented at the AOCS Meeting, October 1971, Atlantic City, Symposium on Food Additives in Fat and Oil Bearing Foods.

TABLE II

Methods for Analysis of Mixtures of Fatty Food Emulsifiers

Technique	Applicable emulsifiers
Sample hydrolyzed, physical and solvent separations plus various qualitative tests (74)	Polyoxyethylene types
Two paper chromatographic solvent systems plus qualitative tests (75)	Polyoxyalkylene types
Column, thin layer, and gas liquid chromatographies (32, 76, 77)	Lactylated monoglycerides Monoglycerides Polyglycerol esters Propylene glycol esters Sorbitan esters
Thin layer chromatography of methanol solubles from extracted fat, R_f and color response to selected sprays[a]	Citric acid esters Lactic acid esters Lecithin Monoglycerides Polyglycerol esters Polysorbates Propylene glycol esters

[a] Unpublished.

methods to determine emulsifiers in foods. Industry, in addition to quality control of finished product, is interested in methodology to make sure that only those additives approved for a particular foodstuff are present and that the ingredient statement is authentic. These needs are likely to increase as food formulations become even more complex.

EMULSIFIERS BEING REVIEWED

Table I lists the main emulsifers used in fatty foods in this country. The first portion of the table covers the generally recognized as safe (GRAS) materials. Lecithin is a widely occurring natural substance commonly added to fatty foods, but at a low level. Tartaric acid esters of mono- and diglycerides, otherwise known as TEMS, are widely used in Europe, but to a smaller extent in this country.

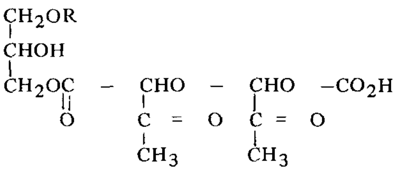
The balance of Table I lists the 11 most important emulsifiers having food additive status, materials whose permitted use in foods has been established via a petition to the FDA. The listing is in estimated priority order of present commercial use in this country.

Two additional materials are the citric acid esters of mono- and diglycerides and the sugar fatty acid esters. Both have received considerable product application attention in the past few years in the U.S. and abroad.

CHEMICAL NATURE OF APPROVED EMULSIFIERS

A review of the chemical nature of the materials will indicate the inherent analytical problems in this area and the analytical difficulties. The general similarity between the various materials should be noted—most are based on glycerol. Sometimes other polyols, such as propylene glycol, polyglycerol and sorbitol are substituted for glycerol, and low molecular weight acids, such as acetic, succinic and fumaric, are substituted for a portion of the fatty acids. Also, complexity increases when either mixtures of polyols or mixtures of acids are used. This is particularly true when bifunctional, both alcoholic and acidic, reactants such as lactic, citric and tartaric acids, are involved. Moreover the reaction conditions frequently bring about random interesterification of the ester groups already present. A few examples will illustrate the preceding points.

The semistructural formula of TEMS or tartaric acid esters of monoglycerides is shown in Figure 1. TEMS are made by the acid-catalyzed reaction of diacetyl tartaric acid with monoglycerides. The structure represented is a dominant species; however the secondary alcohol can also be esterified. Usually the fatty acyl radical is on the glycerol molecule and the acetyl groups are on the tartaric acid, but rearrangement does occur in manufacture.



$$\mathrm{CH_2OR{-}CHOH{-}CH_2OC(=O){-}CHO(C(=O)CH_3){-}CHO(C(=O)CH_3){-}CO_2H}$$

FIG. 1. TEMS, where R = fatty acyl radicals (R′CO).

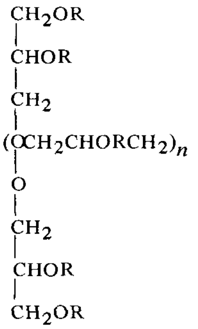


FIG. 2. Partial polyglycerol esters where R = H or fatty acyl radical, but both present.

The partial polyglycerol esters are tremendously complex mixtures. Figure 2 presents the generic formula. In manufacture, the polyglycerol is first made by heating glycerol in the presence of an alkaline or acidic catalyst, which by itself results in a very heterogeneous product. As an example, decaglycerol, a material with an alleged average of ten and an actual average of five glycerol moieties, in fact contains compounds having from 2 to ca. 30 glycerol moieties. Linear species predominate, but some cyclic structures may occur. The polyglycerol is then esterified with fatty acids.

With the sorbitan esters, heterogenous mixtures are again encountered. A main contributing factor is that, under the conditions of reaction, usually heating sorbitol with fatty acids alone or with an acidic or alkaline catalyst, anhydro sorbitols or sorbitans are produced; in fact, there is little if any esterified sorbitol present in the final product. The anhydro sorbitols can be monocyclic such as the 1,4 as pictured in Figure 3, or dycyclic such as the isosorbide shown in Figure 3. Mono- and diesters are required in order to have emulsifier properties. Again the primary alcohol group is favored in the esterification. The esters may also be produced by transesterification using fatty acid esters.

The polysorbates or sorbitan polyoxyethylene esters are made by adding ethylene oxide to the sorbitan esters using an alkaline catalyst. A generic formula is shown in Figure 4. It should be noted that in this reaction the fatty acyl radical becomes mobile and will migrate from its initial position on the polyol to esterify the OH group at the end of the polyoxyethylene chains. Both the degree of esterification and number of polyoxyethylene residues ascribed to the commercial products are estimates of the dominant species. With several sites open for condensation, variations can be considerable.

ANALYTICAL CONSIDERATIONS

The various analytical considerations that are important are: (a) internal quality control, (b) removal and determination of a single emulsifier from a food, and (c) removal and determination of mixtures of emulsifiers in foods.

The accepted methodology for quality control in the manufacture of emulsifiers is summarized in Outline I. For only two emulsifiers, lecithin and monoglycerides, have technical societies such as ours adopted control methods. MacDonald has published a review on this general subject of quality control (1). Outline I also summarizes the methodology on all the emulsifiers reported on in this review.

OUTLINE I.

METHODS OF ANALYSIS

A. Methods for Lecithin

Acetone-insoluble (2) Method Ja 4-46 Rev. May, 1957; (3) Method 58-35
P_2O_5 content of $CHCl_3$ ab. alcohol insoluble (4) Method 13.049
Acetone-insoluble, AV, % water (5) p. 376
Column followed by paper chromatography (6)
Paper chromatography (7,8)
Thin layer chromatography (9,10)

B. Methods for Monoglycerides

Oxidation of 1-monoglycerides (2) Method Cd 11-57 Rev. 1971; (3) Method 58-45
Oxidation of 1-monoglycerides and column chromatography (4) Method 28.114-134
Oxidation of 1-monoglycerides. Total monoglycerides by column chromatography, HV, PV, SV (5) p. 452, 753, 754
Column chromatography, both adsorption (11) and partition[a]
Thin layer chromatography (12-16)
Gas liquid chromatography of trimethyl silyl ethers (17-20) and allyl esters (21)
Spectrophotometry of hydroxamic acid derivatives (22) and 2,4 dinitrophenylhydrozones (23)
Dielectric constant (24)

C. Methods for TEMS

Tartaric and acetic acids, SV, AV, TFA, glycerol (5) p. 4
Column chromatography[a]
Thin layer chromatography[a]
Paper chromatography (25,26)

D. Methods for Acetylated Monoglycerides

Reichert-Meissel Value (acetic acid content), free glycerol, SV, IV (5) p. 15
Reichert-Meissel Value (27) p. 121. 1018

E. Methods for Partial Polyglycerol Esters

SV, AV, HV, IV, sodium salts of fatty acids (5) p. 11
Removal from fat by column chromatography, split and analyze fatty acids by gas chromatography (27) 121.1099
HV, SV, AV, molecular weight[a]
Solvent fractionation followed by thin layer and gas liquid chromatographies[a]
Paper chromatography on polyols (28)
Column chromatography[a]
Thin layer chromatography on polyols (29-31)
Gas liquid chromatography on trimethyl silyl ether derivatives of polyols (30)
Gas liquid chromatography on acetates and trimethyl silyl ether derivatives of polyols[a]

F. Methods for Propylene Glycol Esters

HV, SV, IV, monoester calculated from free glycol, HV, and AV of separated fatty acids (5) p. 567
None listed–propylene glycol and TFA are suggested (27)
Column chromatography[a]
Column chromatography followed by gas liquid chromatography[a]
Gas liquid chromatography as is and as trimethyl silyl ethers (32)[a]

G. Methods for Sorbitan Partial Esters

Polyols, SV, HV, AV (5) p. 655
Remove from product by ethyl ether extraction, concentrate by column chromatography, analyze for polyols (27) 121.1029, 121.272
Paper chromatography on polyols (33,34)
Column chromatography[a]
Column and thin layer chromatographies followed by gas liquid chromatography of trimethyl silyl ethers of polyols (35)
Thin layer chromatography (36)
Gas liquid chromatography on polyols (34-37)
IR spectrophotometry (38)

H. Methods for Polysorbates

Oxyethylene content, HV, SV, TFA (5) p. 525, 526, 529
Hydrolyzed sample analyzed gravimetrically for oxyethylene content and fatty acids by gas liquid chromatography (27) 121.1099, 121.1030, 121.236
Colorimetry (39)
Paper chromatography (40)
Column chromatography (41)
Paper chromatography of hydroxamic acids (42)
Column chromatography followed by thin layer chromatography (43)
Thin layer chromatography[a] (44-47)
Gas liquid chromatography (48)
Atomic adsorption on residual molybdenum after precipitation by phosphomolybdic acid complex (49)
IR spectrophotometry (38)
Potentiometric titration (50)
Titration with aqueous sodium tetraphenylborate (50)

I. Methods for Glycol in Polysorbates

Colorimetry (51)
Gravimetry (52-54)
Paper chromatography (55)
Thin layer chromatography (56-58)
Paper (59,60), thin layer (59,61) and column (59) chromatographies of 3,5 dinitro benzoate esters
Gas liquid chromatography of trimethyl silyl ethers (62,63)
Colorimetry on 2,4 dinitrophenyl hydrazones (64)
Potentiometric titration (50)

J. Methods for Lactylic Lactates

On free acids–total lactic, SV, AV, % water, and acylated mono- and polylactics by gas liquid chromatography (5) p. 365
On calcium salt–calcium, total lactic ester value, AV (5) second supplement p. 2
On free acids–column chromatography and colorimetric measurement of water-insoluble lactic (27) 121.1048
On calcium salt–see free acids (27) 121.1047
On sodium salt–none listed (27) 121.1211

K. Methods for Lactic Acid Esters

1-Monoglycerides, total lactic acid, AV, free glycerol, water (5) p. 362
Silica gel column chromatography (27) 121.1004
Total and water-insoluble lactic acid (65)
Column chromatography followed by gas liquid chromatography of trimethyl silyl ethers (66)

L. Methods for Ethoxylated Monoglycerides

Oxyethylene content, SV, HV, TFA (5) third supple-

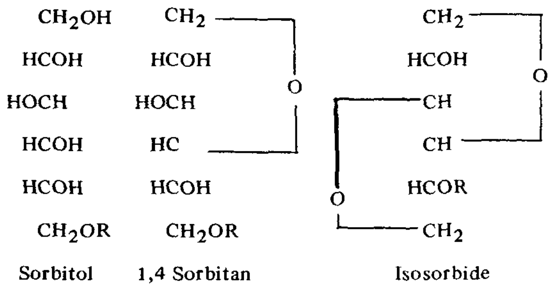


FIG. 3. Sorbitan esters, where R = fatty acyl radicals (R'CO).

ment p. 10
In bread, gravimetric measurement of phosphomolybdic acid complex after concentration and hydrolysis (27) 121.1221
Gas liquid chromatography of polyols[b]

M. Methods for Succinylated Monoglycerides

Only succinic acid method listed (5) p. 669 (addition of free and bound succinic planned)
Separation of bound succinic and its determination by gas liquid chromatography (27) 121.1195

N. Methods for Succistearin

Column chromatography[a]

O. Methods for Hydroxylated Lecithin

Acetone-insoluble, benzene-insoluble, PV, IV, AV, % water (5) fourth supplement p. 4

P. Methods for Citric Acid Esters

Only citric acid method listed (5) p. 187
Paper chromatography[a]
Column chromatography[a]

Q. Methods for Sugar Esters

Paper chromatography (67)
Column chromatography[a] (68)
Column chromatography followed by paper chromatography (69-71)
Thin layer chromatography[a] (72)
HV, SV, IV[a]

[a] Unpublished, Procter & Gamble Co.

[b] Private communication, Ashland Chemical Co. Presented at the AOCS-ISF World Congress, Chicago, October 1970.

Petitions for approval of a food additive must include methodology for the determination of that substance in the food at the levels involved. The *Food Additives Analytical Manual* is the published source for this information dealing primarily with the determination of single emulsifiers in foods. A recent, fairly complete review article by Murphy and Hibbert is another notable source (73).

The key steps required for reliable methodology for the determination of emulsifiers in foods are: (a) separation from food product, (b) classification or identification of component emulsifiers, (c) separation of the individual emulsifiers, and (d) quantitative determination. Separation of the emulsifiers from the food is the most important and most difficult of the four steps. This is true because emulsifiers are frequently complex chemicals, the addition level may be as low as 0.1%, the emulsifiers may complex with food components such as proteins and starches, and, for quantitative determination, all of the emulsifier has to be removed with a minimum of interfering substances. The methodology for this first step is not well established. Detection of the various emulsifiers is now within reasonable analytical capability via thin layer chromatography, and determination of the emulsifiers, once separated, can be achieved. Absolute quantitation in a food is possible, however, only if one has available a sample of the additive or has knowledge of its composition.

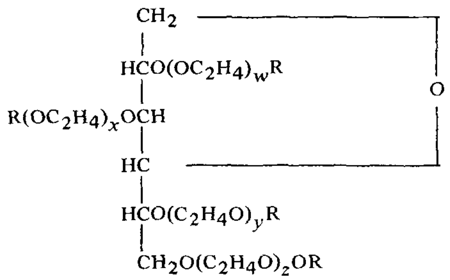


FIG. 4. Sorbitan polyoxyethylene esters (Polysorbates), where R = either H or fatty acyl radicals, but both present, e.g., $w+x+y+z = 20$.

Considerably less effort has been expended on the determination of mixtures of emulsifiers in foods. Table II lists a summary of the pertinent literature articles dealing with multicomponent systems. These will be discussed briefly later.

APPLICATION OF VARIOUS ANALYTICAL TECHNIQUES TO EMULSIFIER METHODOLOGY

The traditional wet chemical methods, such as gravimetry and colorimetry, are valuable for production control of the emulsifiers. As the tables on methods indicate, they are also used to determine levels of components in mixtures after separation. In many instances, wet chemical methods are used to determine a distinct moiety of the emulsifier or emulsifiers, e.g., the polyoxyethylene contents of polysorbates or ethoxylated monoglycerides, or the particular acids that distinguish the acidic emulsifiers such as lactic and acetic. In other instances methods such as SV, HV and AV are used to calculate the compositions of the emulsifiers.

Instrumental methods have not been very useful in the analyses for food emulsifiers. Spectrophotometric methods have been developed, and the literature contains isolated reports such as the use of dielectric constant to measure monoglyceride level. But this general approach lacks applicability despite its speed and simplicity. The explanation is that emulsifiers are mixtures, and instrumentation such as IR analysis normally requires single entities or comparatively pure materials for characterization.

The utility of chromatography is presented in more detail in Table III. This approach deserves separate treatment, since it has received by far the greatest attention and is of the greatest value. One compelling reason is that certain types of chromatography afford means of separating, of resolving some of the heterogeneity of the emulsifier systems that have to be dealt with. No effort has been made to distinguish between adsorption and partition chromatographies. Both have been used, with partition generally giving the superior results. Gel permeation chromatography is not listed, as it has received relatively little study. Paper, thin layer and column chromatographies have all been used because of their simplicity and comparatively low costs. Both paper and column chromatography are very time consuming. Column chromatography yields more precise analytical results. Thin layer chromatography is outstanding in its ability to characterize mixtures. Both column and thin layer are effectively used to clean up extracts obtained from a foodstuff.

There are considerably more methods in the literature based on thin layer than column chromatography. This should not be surprising considering its advantages in time

TABLE III

Value of Chromatographic Techniques in Analysis of Fatty Food Emulsifiers

Characteristic	Paper	Thin layer chromatography	Column	Gas liquid chromatography	HPLC
Speed	Slow	Fairly fast	Fairly slow	Fast	Fast
Sample size	Small	Small	Large	Quite small	Small
Specificity (identification)	Poor	Fair	Poor	Good	?
Ability to characterize	Poor	Good	Fair	Poor	?
Quantitative capability	Poor	Poor	Fair	Good	?
General applicability	Poor	Good	Good	Limited	?

and sample size, the availability of many characterizing sprays, and the ease of evaluating small and large differences in developing media; and precisions of ±5% are attainable with thin layer by the use of optical scanning and densitometry. For an excellent review of the recent advances in thin layer chromatography consult Volume II of Boekenoogen (78).

To summarize the present and projected status of paper, thin layer and column chromatographies, paper is no longer used, while thin layer and column continue to receive attention for purifying, separating and characterizing mixtures. These are key needs in dealing with the mixtures now being encountered.

Gas liquid chromatography can be applied only to volatile materials or materials that will yield volatile derivatives. It will continue to be a valuable quantitative tool for emulsifiers themselves, or for distinguishing moieties therein. For example, it can be used to measure the monoesters of glycerol and propylene glycol, where it is faster and as precise as the conventional wet chemical methods. Outstanding examples of the use of gas liquid chromatography for moiety analysis are the glycols from the polysorbates or polyglycerol esters and the acids from the acidic emulsifiers such as the TEMS. In addition, gas liquid chromatography is used to determine the fatty acid content and source of the fat stock used in preparing the emulsifiers. The current utility of this technique will continue and probably expand.

A 1971 report (48) dealing with reaction gas chromatography deserves special mention. In this work, the polysorbates after removal from the food and minimum cleanup are injected directly onto a reactive column filled with soda-lime beads. The polysorbates are saponified and the polyols determined directly, saving considerable time.

Several years ago it was predicated on theoretical grounds that high pressure liquid chromatography (HPLC) would be developed to have a speed approaching gas liquid chromatography while retaining the advantages of column chromatography in requiring no volatility and not destroying the sample. Although no published reports of HPLC exist dealing with food emulsifiers, the demonstrated value on other materials strongly suggests an excellent potential for the separation, characterization and analysis of these materials. It is very likely the technique of tomorrow.

METHODS ADOPTED BY TECHNICAL SOCIETIES

Outline I includes the methods adopted by the various technical societies concerned with fatty foods. The societies are the American Oil Chemists' Society (AOCS) (2), the American Association of Cereal Chemists (AACC) (3), the Institute of Food Technologists (IFT) and the Association of Official Analytical Chemists (AOAC) (4). The comparative sparsity of adopted methods is quite apparent.

Official methods of the three industry-based societies are identical with the IFT using the AOAC methodology.

The industry procedure for lecithin is based on the yield of acetone insoluble. The AOAC lecithin procedure is based on the P_2O_5 determination in the $CHCl_3$/absolute alcohol insolubles.

The procedures for 1-monoglycerides, as mentioned in Outline IB, involve oxidation of the adjacent hydroxyl groups by periodic acid. In additional AOAC procedures, the analysis of monoglyceride concentrates and glycerides in shortenings both use column chromatography with silica gel as the adsorbent. AOAC procedure 28.120-28.123 (4) is identical to the AOCS and AOAC procedures. Procedure 28.124-28.128 (4) also uses periodic acid as the oxidizing agent and, in performance, differs from 28.120-28.123 in yielding significantly greater accuracy at the lower levels of monoglycerides as found in shortenings. It is worth noting that both the AOCS and AOAC are moving toward a single official method, periodic acid oxidation, with two procedures: one, 28.124-28.128, for materials whose monoglyceride content is below 15%, and the other, 28.120-28.123, for 15% levels and above. This is consistent with the desirability of various societies having uniform methods.

METHODOLOGY FOR INDIVIDUAL EMULSIFIERS

The analytical approaches reported in the literature for the commonly used emulsifiers are summarized in Outline I. Included are methods for citric acid fatty acid esters and sugar fatty acid esters. Inspection of methods yields a reasonable idea of the amount of effort and the number and types of methods that have resulted. In the interest of brevity, details are not presented.

For review papers on individual emulsifiers the reader may want to consult Boekenoogen's Vol. I (79) for information on monoglycerides and related materials, and the *Fifth International Symposium on Chromatography and Electrophoresis* (38) for information on sorbitan esters and polysorbates, and lecithin. Periodic surveillance of the *Food Chemical Codex and Food Additives Analytical Manual* is encouraged.

The references listed in the cited tables will include methodology for the determination in foods as well as on the isolated or manufactured emulsifier. Which of the various approaches listed is preferred can best be answered by each individual or laboratory that has need for a method, since only that laboratory can know its own requirements. It is the writer's experience that for monoglycerides, gas liquid chromatography appears the preferred technique (20). This technique can be used for the simultaneous determination of monoesters of both glycerol and propylene glycol, and these esters are frequently used together in commerce. There are no published tests for specific polyglycerol esters; however solvent fractionation followed by chromatography of the fatty acid and polyol moieties will characterize the composition. For polysorbates, it would seem that reaction gas chromatography

TABLE IV

Extractions of Emulsifiers from Fatty Foods

Food product	Emulsifier	Solvent[a]
Baked goods	Ethoxylated monoglycerides	Chloroform-methanol[b]
	Polysorbates	Chloroform (43)
	Sugar esters	Chloroform (67)
Bread	Ethoxylated monoglycerides	Chloroform-methanol[b]
	Monoglycerides	Petroleum ether (80)
	Polysorbates	*n*-Propanol-water (54)
	Succinated monoglycerides	*n*-Propanol-water (27) 121.1195
Cake	Polysorbates	*n*-Propanol-water (54)
	Sorbitan esters	Ethanol (34)
	Succinated monoglycerides	*n*-Propanol-water (27) 121.1195
Cake mix	Lactic acid esters	Petroleum ether[a]
	Monoglyceride	Petroleum ether[a]
	Polysorbates	Chloroform-ethanol (54) Chloroform (43)
	Propylene glycol esters	Petroleum ether[a]
	Sorbitan esters	Ethanol (34)
Candy	Sorbitan esters	Benzene (36)
Cocoa	Lecithin	Chloroform-absolute ethanol (4) method 13.049
Doughnuts	Polysorbates	*n*-Propanol-water (54)
Fat	Polyglycerol esters	Chloroform[a]
	Polysorbates	Chloroform (43) No solvent required (54)
	Succinylated monoglycerides	*n*-Propanol-water (27) 121.1195
Frosting mixes	Polysorbates	Chloroform, methylene chloride[a]
Flour	TEMS	Methanol (25) Methylene chloride (26)
Frozen desserts-ice cream	Monoglycerides	Ethyl ether (81)
Ice cream mixes	Sorbitan esters	Ethanol (82)
Margarine	Citric acid esters	Methanol (26)
	Polyglycerol esters	Methanol[a]
	Sugar esters	Methanol (67)
Pastry	Lactylic acid esters	Methanol (83)
	Polysorbates	Ethyl acetate (38)
	Sorbitan esters	Ethyl acetate (38)
Potato flakes	Polysorbates	*n*-Propanol-water (54)
Salad dressing	Polysorbates	No solvent required (54)
Topping	Sorbitan esters	Diethyl ether (27) 121.1029

[a] Use of dilute acid such as hydrochloric in conjunction with solvent can be of value with the more polar emulsifiers (Unpublished, Procter & Gamble).

[b] Private communication, Ashland Chemical Co. Presented at the AOCS-ISF World Congress, Chicago, October 1970.

merits additional study, particularly to save analysis time. And finally, Sahasrabudhe and coworkers (32,76,77; Table II) merit special mention, in view of his success on a number of materials using a combination of column, thin layer and gas liquid chromatographies.

REMOVAL OF EMULSIFIERS FROM FOODS

The key basic need for accurate and precise measurement of emulsifiers in foods, particularly when present in mixtures, is their complete removal to the exclusion of interfering substances. Much of the effort has dealt with single emulsifiers. The key to successful removal is the solvent system used, although the equipment and conditions can also be factors. Table IV summarizes the food products, emulsifiers, and solvent systems that have received attention. The effort is extensive. The objective is to separate the emulsifier from the carbohydrate and protein in the food, without also removing lipids, glycoprotein, etc. from the food. Precise quantitation requires knowledge of the composition of the emulsifier added, particularly with such heterogeneous materials as the acidic emulsifiers, polysorbates, and polyglycerol esters.

METHODOLOGY ON MIXTURES OF EMULSIFIERS

In addition to developing more certain means for quantitative removal of emulsifiers from foods, investigators should devote further effort to methodology involving mixtures of emulsifiers. There are published reports on binary mixtures such as the sorbitan-polysorbate combination (84) and glycerol and propylene glycol esters (private communications from General Mills and Swift & Co.). There is also a report on a mixture of lactic acid esters, polyglycerol esters, and monoglycerides (76). Table II summarizes what has been done toward the analyses of mixtures containing several components. The first two references deal with efforts directed toward nonionics used in detergent manufacture. Both approaches are applicable to food emulsifiers, but neither yields quantitative results. Sahasrabudhe's work at the Canadian Food and Drug Directorate represents a real effort to separate the emulsifiers into various classes of lipids and then determine the individual materials by gas liquid chromatography. The last

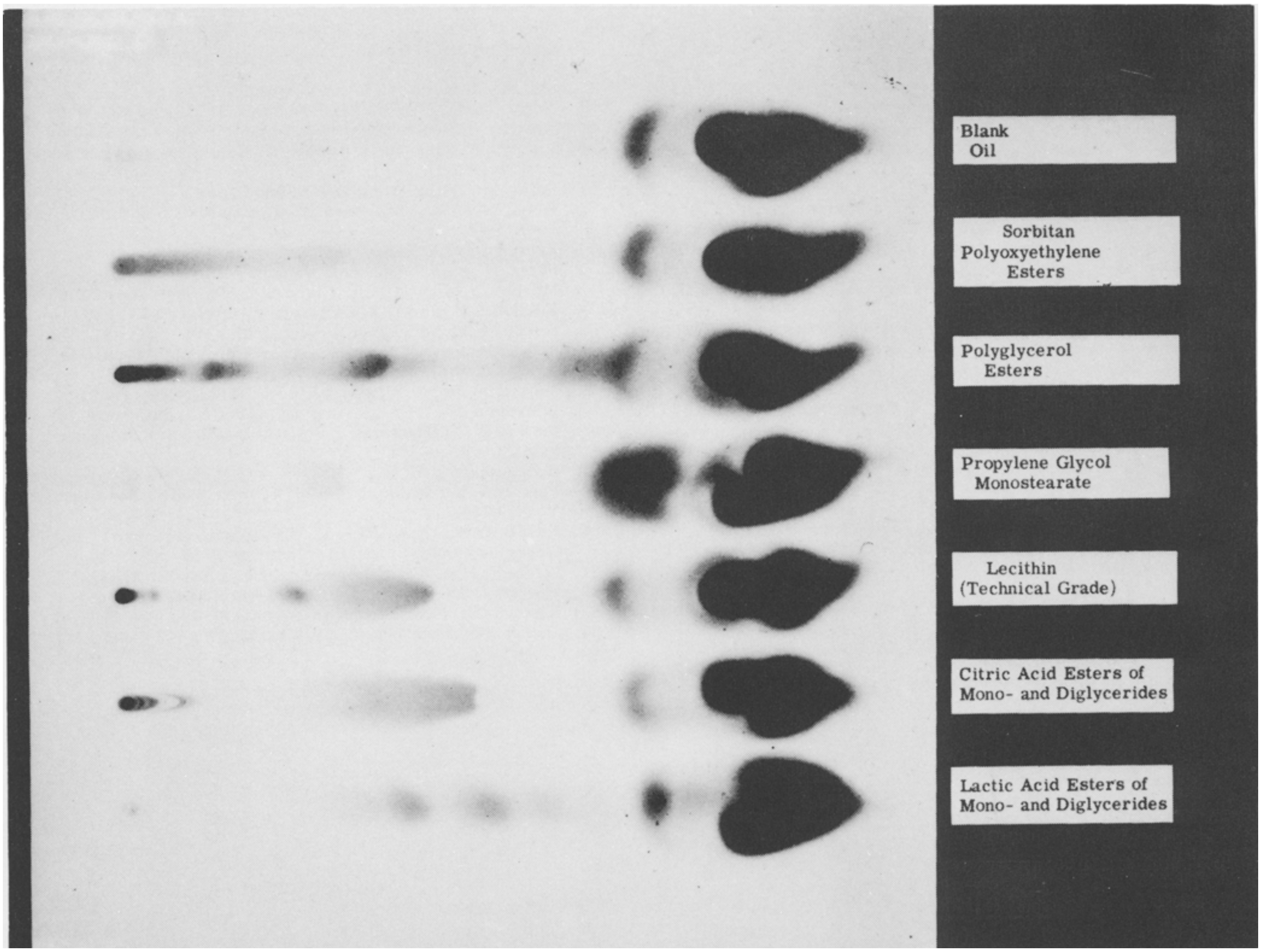


FIG. 5. Differences between emulsifiers after sulfuric acid charring of plate.

listing refers to unpublished effort in our laboratories directed toward a semiquantitative method of broad applicability. As an illustration, Figure 5 shows the differences between the emulsifiers after sulfuric acid charring of the plate. The adsorbent is Silica Gel G and the developing solvent 5% methanol in chloroform. A precollaborative study run in 1970 indicated the approach was too unreliable for use. Modification of the method is now underway, using different solvent systems for removal of the emulsifiers and concentration of the emulsifiers by preparatory thin layer chromatography.

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