temperatures controlled by the heat of the incoming soap. The product is continuously scraped from the walls of the chamber and fed to a plodder for extrusion in bar form.

In summary, spray drying of soaps and detergents in bead form has been discussed at some length, concluding with a variety of spray systems designed principally for nonpuffed products and suitable for industrial use. The Mazzoni vacuum spray-dryer for toilet soap is mentioned.

Recent Advances in the Analysis of Soaps and Synthetic Detergents

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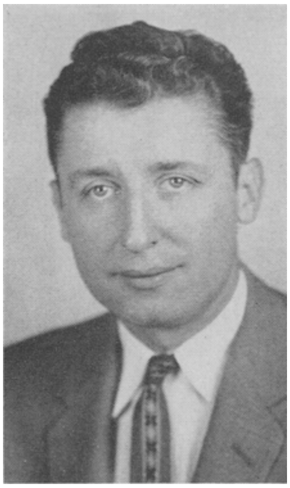
The methods of analysis for soaps and synthetic detergents in this paper are divided according to the various existing types of these materials. The methods to be discussed will include qualitative and quantitative approaches and will also include methods of separation. Whenever possible, the quantitative methods will range from the assay of the relatively pure soap or syndet to methods for determining trace quantities.


Sidney Siggia

The methods described in this paper include some not generally used for the determination of surfactants. These apply to classes of chemical compounds of which the surfactants are members. For example, existing methods for the analysis of carboxylate salts automatically can be applied to soaps; methods for tertiary and quaternary amine salts can be applied to many cationics; methods for hydroxy compounds and polyglycol ethers and esters can be applied to many nonionics.

General Methods

Those described in this section are not specific for any surfactant type and are generally applied to unknown samples for characterizing the soap or detergent present, or they are methods which are generally applicable to all types of surfactants.

Wurtzschmitt (58) describes a scheme of analysis for characterizing surface-active agents, which uses elemental and functional group analyses for generally classifying the materials and employs the preparation and isolation of derivatives for further clarification of structure and composition. It is possible to estimate the amounts of certain agents by isolation and then by determination.

Gilby and Hodgson (14, 15) also describe a scheme for characterizing surfactants. This scheme is based mainly on the Lassaigne test for certain elements. Briefly the scheme is as follows.

a) The presence of carbon, hydrogen, and oxygen alone generally signifies a soap or a nonionic.
b) Sulfur generally indicates a sulfate or sulfonate.
c) Sulfur and nitrogen indicates fatty acid esters of sulfoacetamides.
d) Nitrogen indicates cationics.

Yet another series of characterization tests is given (3), which can be summarized as follows.

a) Methylene blue associates with sulfated and sulfonated surfactants, making them soluble in chloroform. If a blue color develops in the chloroform layer after addition of methylene blue, then these types of anionics are likely to be present.
b) A reagent composed of ammonium thiocyanate and cobalt nitrate should give a colored solution that remains colored in the presence of a nonionic.
c) Quaternary ammonium salts cause bromphenol blue to go into a chloroform layer.

The latter includes methods for detecting various ingredients in surfactant formulations and also includes some quantitative approaches that might be used for determining the active ingredients.

Kortland and Dammers (19) describe a rather intricate system of qualitative and quantitative methods for analyzing anionics, cationics, and nonionics. Balthazar (7, 8) also describes a scheme for the same general purpose.

The most conclusive and most rapid method available today for identifying a surfactant is infrared absorption. The American Society for Testing Materials (31) has published infrared absorption curves for many types of known surfactants. Therefore the first step to be taken in an identification is to obtain an infrared absorption curve on an unknown and to compare this with the curves for the known surfactants. If a matching curve is found, then the identification is complete with no further work required. If no matching curve is found, then the problem of identification becomes more complex though infrared absorption can help in these cases as well. Infrared will differentiate the aromatic from the aliphatic type of compounds. Also it will identify the functional groups on the molecules as a great aid in an identification. Applications of infrared absorption to the quantitative analysis of organic compounds are discussed by Siggia and Stolten (48).

Ultraviolet absorption does not have the range of applicability as infrared absorption. However the ultraviolet approach has the advantage of being less bothered by interferences. Most compounds absorb in the infrared region of the spectrum whereas a much lower percentage absorb in the ultraviolet region. Hence infrared analysis may require some resolution of components in a mixture before the analysis is applied; analysis *via* ultraviolet requires resolution of components less often. Another strong point for ultraviolet absorption is the determination of trace quantities. Materials which do absorb in the ultraviolet region usually do so very strongly so that concentrations of 0.001% are often readily determined. Compounds containing aromatic groups absorb strongly in this region and are readily detected qualitatively or determined quantitatively. The use of the ultraviolet absorption approach in the analysis of organic materials is described by Siggia and Stolten (48).

Anionics

The above described general methods of course apply in some degree to the analysis of anionics. However there also are some methods which apply solely to anionics.

Methods Involving Reactions of Sulfonates with Amine Salts. Kling and Puschel (18) used precipitations with benzidine hydrochloride to determine sulfonates. The final determination is gravimetric in nature. Alkyl groups of C_{10} or lower are not readily determinable however, because of the solubility of the resulting amine salts.

Shiraeff (35) used a gravimetric approach involving benzidine precipitation for sulfonates and employed special washing techniques to minimize solubility problems.

Marron and Schifferli (20) also developed a method for determining alkyl and alkylaryl sulfonates involving the addition of p-toluidine hydrochloride or benzidine hydrochloride. The resulting amine sulfonate salt is extracted with carbon tetrachloride and is titrated with sodium hydroxide. This extraction approach circumvents the solubility difficulties encountered in the gravimetric approach.

Stüpel and von Segesser (52) used the p-toluidine hydrochloride in much the same manner as Marron and Schifferli.

Methods Involving Reactions with Dyes for Determining Sulfates and Some Sulfonates. Epton (11) and Barr *et al.* (9) both used very much the same approach involving methylene blue. This is relatively insoluble in chloroform; alkyl sulfates with alkyl groups of C_8 or longer are soluble in chloroform. The sulfate reacts with the methylene blue, forming a salt and thus solubilizing it in chloroform. The blue color thus transfers to the chloroform layer. To this system is added a solution of a quaternary, cetyl pyridinium bromide which displaces the methylene blue from its salt and thus forces it back into the aqueous layer. The amount of quaternary required to equalize the color intensity of each layer is calculated in terms of sulfated detergent. Some relatively water-insoluble sulfonates can also be determined with this method.

Barr *et al.* (9) used bromphenol blue as well as methylene blue and noted certain advantages to both indicator systems.

Antara Chemicals (4) distributes a procedure similar to the Epton-Barr methylene blue method that uses Hyamine[1] (para diisobutylphenoxyethoxyethyl dimethyl benzyl ammonium chloride monohydrate) as the quaternary instead of the cetyl pyridinium bromide. The Hyamine[1] is used since it is more readily available and is easier to use: it yields somewhat better end-points. Included in the Antara procedure is a method for standardizing the solutions of quaternaries. The latter makes possible the preparation of standard solutions of quaternaries without necessitating purification of these salts and is described under Cationics. The Antara method has been applied to alkyl sulfates, alkyl amide sulfonates, alkyl ester sulfonates, and sulfosuccinates.

Fairing and Short (12) used methylene blue in a colorimetric approach to determine traces of alkyl benzene sulfonates in water and sewage.

Moore and Kolbeson (22) used methyl green to determine traces of sulfated and sulfonated detergents in water and sewage. The colored salt is extracted into benzene and measured colorimetrically.

Miscellaneous Methods. Ram (29) determined sulfonates in compositions containing alkali sulfates. An ash determination yields the total of anionic plus alkali sulfate. A separate sample of dried powder is extracted with saturated brine, which removes the alkali sulfate. This is then measured, and the sulfonate is determined by the difference.

The American Oil Chemists' Society (1) describes a method for determining sulfated and sulfonated organics by extracting the active component with ether. The ether extract is then evaporated in a tared crucible, and the residue is then ashed. The ash is calculated as the anionic.

For solely sulfated organics the American Oil Chemists' Society has a separate method (2), involving hydrolysis of the compound to liberate acid which is titrated with sodium hydroxide.

Nevison (25) identified sulfated alcohols by hydrolysis back to the alcohol and identification of the alcohol. He also discusses the use of infrared in the analysis of sulfated alcohols and olefins, particularly in differentiating straight-chain compounds from branched-chain compounds. The use of mass spectrometry is described for analyzing alkyl aryl sulfonates.

Neu (24) describes a method for anionics, using ion exchange resins. The cation is replaced with hydrogen, and the resulting acidity is titrated. Takama and Nishida (53) describe a similar approach. These ion exchange methods lack specificity since any material with an exchangeable cation will interfere.

Anionics (and soaps) suppress maxima on polarographic waves. This has been used as the basis for a method of analysis of these materials (50).

Sallee *et al.* (32) determined traces of alkyl benzene sulfonates in water by adsorption on charcoal. The concentrated material was eventually analyzed by infrared absorption.

Soaps

Soaps are included at this point because they are essentially anionic detergents. However, since the trade differentiates between soaps and anionics and since the analytical methods are different, the discussion on soaps has been made a separate section.

The classical approach to the determination of soap has been acidification and extraction of the fatty acid with petroleum ether. This is followed by titration of the acid. One of the more modern versions of this approach is that of Berkowitz and Bernstein (10). Their scheme follows and can be used to analyze mixtures of soaps and synthetic detergents.

a) Soap and fatty matter are determined by acidification and extraction of the fatty acid, which is then determined by titration.

b) The alcohol-insoluble matter is determined by successive

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[1] Trademark of Rohm and Haas Company.

extractions of the sample with alcohol and by filtering the residue.

c) The alcohol-soluble matter is determined by combining the extracts from b), evaporating the solvent, and weighing the residue.

d) The fatty matter is measured by taking the residue from c) and dissolving in a 1:1 water-alcohol mixture and extracting with petroleum ether. The extract is washed, dried, and weighed.

$$a - d = \text{soap content of sample.}$$

e) Chlorides in the alcohol-soluble matter are determined by taking the remaining alcohol-water solution from d) and running a Volhard analysis.

f) The synthetic detergent is determined by difference

$$\%\ \text{synthetic detergent} = c - (a + e).$$

The A.S.T.M. Committee D-12 (6) and D-820-46 (5) discuss methods for determining soaps alone or in mixtures with synthetic detergents. These methods are essentially adopted from the method of Berkowitz and Bernstein.

Jenkins (16) developed an ion exchange method for determining soaps, whereby the salt is converted to the free acid and is titrated.

As mentioned at the beginning of this paper, soaps and surfactants are chemical materials with characteristic groupings and hence can be determined by the general methods used to determine these groups even though these methods are not considered in the surfactant literature. In this regard soaps are salts of carboxy acids and hence can be determined as such. Carboxylate salts can be titrated directly as bases (37, 45). The presence of other basic materials can be dealt with in several ways. A potentiometric titration of a sample containing more than one base will often yield a separate inflection point in the titration curve for each base (47). The content of each base can then be computed.

Nonaqueous titrations can be used. It is well to mention that nonaqueous titrations yield more accurate and precise titrations for soaps than do titrations in aqueous media; in fact, the accuracy and precision are of the order of strong base-strong acid titrations. The analysis of samples containing mixtures of bases, of which one is a soap, can often be handled by the manipulation of solvents (46). If the potentiometric titration does not yield a separate break for the soap in one solvent, then other solvents can be tried. In addition, solvents can be generally found in which only the soap is soluble and the other bases, generally inorganic, do not dissolve. The soap then can be titrated directly in the extract. The glycol-hydrocarbon solvent (37) is an excellent medium for soap titrations. The soap is soluble, and the end-points are quite sharp. Also the composition of the solvent can be varied so that several glycols and/or hydrocarbon solvents can be used in wide ratios to each other. Since this is so, a composition to extract only the soap from other basic materials can often be found and the soap can be titrated directly in the extract.

The direct titration of the soap, of course, provides a very rapid analysis that can be very selective under the proper conditions. Another method for carboxylate salts exists, which utilizes combustion of the sample converting the carboxylate to sodium carbonate and volumetric determination of the carbonate (43). Free strong bases should be pre-determined and the proper corrections applied.

For qualitative identification of soaps, infrared provides a fast, conclusive test for the carboxylate grouping. This general approach was discussed under General Methods. Infrared however cannot readily distinguish between the different soaps which contain only a saturated fatty chain on the carboxylate group. This results from the fact that the functional groups and general structure of these soaps are essentially the same. However if the fatty chain is unsaturated, such as occurs in oleates, these soaps are readily differentiated from saturated soaps.

For differentiating the saturated soaps X-ray diffraction is recommended (49). The diffraction patterns of these materials are more characteristic than the infrared curves. The difficulty with X-ray diffraction however is that the soap has to be in a crystalline form to yield a pattern; and some soaps, especially mixtures of soaps, resist crystallization. It is well to note that though most soaps have a waxy appearance, they are often crystalline; their crystals are merely soft and difficult to define by eye and touch.

Nonionics (41)

In the formulation and use of nonionic surface-active agents there are three general types of analyses of value: a) characterization methods to determine the composition and structure of the nonionic; b) quantitative methods to determine the nonionic component in such mixtures as a finished formulated product. The nonionic content in these cases is fairly high, generally 5% or greater; c) quantitative methods to determine small amounts of nonionic in complex mixtures such as occur in the application of surfactants.

Characterization. The objectives of a characterization of a nonionic fall into three categories: identity of the nonionic as a whole, identity of the hydrophobic portion only, and ratio of hydrophilic portion to hydrophobic portion.

In terms of characterizing the different classes of nonionics Steele and Berger (51) observed that a combination of density and cloud-point of a nonionic could serve to indicate the type of nonionic under study. A plot of density *versus* cloud-point for nonionics showed that each class of nonionic fell in a different zone on the graph. The classes of nonionics plotted were tall oil esters, polyoxyalkylated phenols, thioethers, and alcohol ethers.

Infrared analysis, as discussed under General Methods, is of much value in the characterization of nonionics, particularly in identifying the hydrophobic group. It will not only differentiate aromatic from aliphatic hydrophobes but will also indicate amine, phenol, alcohol, mercaptan, carboxy, or amide hydrophobes. This approach will detect polyglycol chains and thus indicate this variety of nonionic.

The hydroprobic group can also be identified by reacting the nonionic surfactant with hydrobromic (57) or hydrochloric (19) acid. The acid will cleave the polyglycol chain to the dihalo ethane (or dihalo propane as the case may be) and yield the corresponding alkyl halide from an alcohol hydhophobe, aryl halide from a phenolic hydrophobe, carboxylic acid from the carboxylic and amide hydrophobes. The hydrobromic acid reaction is preferable to the hydrochloric acid treatment because of the speed and completeness of the reaction. The amine hydrophobes do not give clear-cut reactions, and the mercaptan hydrophobes are reacted beyond the desirable limits; possibly they are oxidized to the corresponding disulfide or beyond that to the corresponding sulfonic acid.

It is well to state that the method of choice for identification of the derivatives prepared *via* the hydrohalogen acid treatment is infrared comparison against the derivatives from known hydrophobes. The more classical techniques such as melting or boiling point, elementary analysis, or refractive index can also be used to characterize the derivative of the hydrophobe, but these yield less conclusive identifications and generally require the derivative to be rather pure. Since the hydrophobes used in nonionics generally are a range of similar compounds, it is almost impossible to obtain a pure derivative. Infrared does not require a rigidly pure derivative; also if the derivative is not one of the suspected compounds, infrared will yield clues as to what type of compound it could be (48). It is well to indicate that relatively inexpensive infrared instruments are now available which are adequate for the purposes discussed in this paper.

Rosen (30) devised a test, using sulfuric acid and formaldehyde, which gives a characteristic red color when used with nonionics containing a phenyl nucleus. Also Kortland and Dammers (19) devised a scheme of separating and identifying nonionics in mixtures with other surfactants.

Another characterization aspect involved in the analysis of nonionics is the ratio of the hydrophilic portion of the nonionic molecule to the hydrophobic portion. It is this ratio that generally governs the behavior of the nonionic (21). If the hydrophobe is known, then infrared absorption will yield the length of the polyethylene or polypropylene glycol chains. Compounds with known polyglycol chains on known hydrophobes are required for this analysis, but once the calibration is established for each hydrophobe, the analysis of unknowns generally requires only a few minutes.

Cloud-point is another method for determining the hydrophile-hydrophobe ratio. The cloud-point of a nonionic is the solubility limit under specified solution conditions. The solubility limit, of course, is directly related to the hydrophile-hydrophobe ratio. One general method for cloud-point determination is the solution of a given amount of a nonionic in a given volume of water containing a stated concentration of an inorganic salt. The temperature of the solution is varied until the solution becomes turbid. This temperature is then listed as the cloud-point. To obtain the hydrophile to hydrophobe ratio, a calibration curve is established for cloud-point *versus* the ratio; this is done by using known nonionics of varying ratios. There is no one specific method for determining the cloud-points of all nonionics. The solubility characteristics of the nonionics vary so widely that many different solution conditions have to be used to cover all the nonionics presently being manufactured. A cloud-point method was devised by Weeks, Lewis, and Ginn (56) which utilizes solution of the nonionic in a dimethylformamide-benzene system and titration of the solution with water to the first turbidity. The ratio of hydrophile to hydrophobe controls the water needed to cause the turbidity. Fatty alcohol and alkyl phenol condensates with ethylene oxide were studied, using this method. Cloud-point determinations using organic solvents were studied by Tanaka (54).

The hydrophobe-hydrophile ratio can also be determined using density (51) or refractive index (21) measurements. These approaches require calibration curves of density or refractive index *versus* the hydrophile-hydrophobe ratio for the nonionics involved.

Elementary or functional group analyses can also be used to determine the hydrophile-hydrophobe ratio. If the identity of the hydrophobe group is known and it contains nitrogen or sulfur, then quantitative analysis for these elements can yield the hydrophile-hydrophobe ratio. Also analysis for the terminal hydroxyl group (26, 36) will yield the ratio of hydrophile to hydrophobe if the identity of the hydrophobe is known. Along the same lines analyses for amino groups can be used in cases of amine-alkylene oxide condensation products (38).

The above methods for determining the hydrophobe to hydrophile ratio can only be used if the identity of the hydrophobe is known. Methods also exist for the determination of the hydrophile portion of nonionics independent of the hydrophobe portion. These methods then can be used to determine the ratios in compounds of unknown hydrophobic groups. Morgan (23) describes a method for determining polyglycol ethers and esters by using hydriodic acid. The ether linkages are split, yielding ethyl iodide and ethylene from the polyglycol chain. These fragments are collected and measured.

$$-(CH_2CH_2O)_x- + 2x\,HI \longrightarrow xI\,CH_2CH_2I + xH_2O$$

$$I\,CH_2CH_2I \xrightarrow{\text{decomp.}} CH_2 = CH_2 + I_2$$

$$\xrightarrow{HI} CH_3CH_2I + I_2$$

Siggia *et al.* (44) has simplified this method so that only the iodine liberated by the hydriodic acid reaction need be titrated with thiosulfate. The latter paper has also extended the approach to polyoxypropylene chains as well as the polyoxyethylene chains. The hydriodic acid approach cannot be used for polyglycol chains stemming from nitrogen or sulfur atoms. Also sulfated polyglycol chains cannot be analyzed by this method.

Quantitative Determination of Nonionics in Mixtures Containing More Than 5% Nonionic. The most common examples of the mixtures with which this section will deal are the formulated nonionic materials. Analysis of these mixtures can sometimes be applied to this mixture as is, or separation techniques can be applied to remove the nonionic from interfering components in the sample.

Analysis of Mixtures Without Separation of Components

It is always ideal to analyze samples as received whenever possible since separations are usually quite time-consuming. It is possible in many instances quantitatively to measure a nonionic in mixtures without any separation. Ultraviolet absorption techniques, for instance, are applicable for determining nonionics containing phenyl groups (48). Many formulated products do not contain components which absorb in the ultraviolet region of the spectrum other than the phenyl containing component.

Infrared absorption cannot generally be applied to mixtures as discussed in this section since most of the components of formulated nonionics absorb radiation in this region of the spectrum.

Elementary analysis for nitrogen and sulfur can be applied to determine nonionics in these mixtures in instances where the nonionic alone contains these elements. Enough such instances occur to make this approach worth mentioning.

The hydriodic acid reaction mentioned above (23, 44) for determining the polyglycol chain can also be used to determine the nonionic in these formulations since the method has a fairly high degree of specificity. Sulfate ion is the most common interference. Also the hydroxyl analysis (26, 36) for determining the terminal hydroxy group can sometimes be applied.

Shaffer and Critchfield (34) determined nonionics in mixtures by precipitation with either phosphomolybdic acid or silicotungstic acid. The phosphomolybdic acid precipitate is determined colorimetrically; the silicotungstic precipitate is determined gravimetrically. This method has a fairly high degree of specificity. Oliver and Preston (27) also used the phosphomolybdic acid method of determination.

Schonfeldt (33) utilized potassium ferrocyanide to precipitate the nonionic. The precipitate is filtered off, and the residual ferrocyanide in the filtrate is then titrated with zinc sulfate, using potassium ferricyanide-diphenylamine indicator.

Of course, when a mixture is too complex for analysis of the material as received, separation methods can sometimes be applied to resolve the mixture to a sufficient degree to permit analysis. The two most commonly applied separation techniques used in the analysis of mixtures containing nonionics are extraction and ion exchange.

Separation Techniques

a) *Extraction.* In some instances the nonionic in a solid formulation can be extracted by using a suitable organic solvent (19). The nonionic is determined by either weighing the solid before and after extraction or by taking an aliquot of the solution after extraction, evaporating the solvent, and weighing the residue. Obviously this method can only be applied to samples where the nonionic is the only component soluble in the solvent. Fortunately most of the other components in solid-formulated materials are inorganic salts and polar organic materials and, as such, are generally insoluble in organic solvents, especially the less polar solvents.

In cases where some other components are extracted along with the nonionic, the extraction approach obviously cannot be used as described above. However, even though the nonionic has not been isolated, the extraction often does separate the nonionic from a component which interferes in one or more of the chemical or instrumental analyses discussed above. Thus the extract can then be analyzed by these methods with no interference whereas the original sample could not.

b) *Ion Exchange.* Most of the components in a nonionic formulation are ionic in nature. Thus ion exchange provides an ideal method for separating the nonionic component from the ionizable components. Weeks, Ginn, and Baker (55) describe the ion exchange separation technique for isolating nonionic surfactants from mixtures containing ionic surfactants. The amount of nonionic in these mixtures was determined by taking the deionized solution of the sample and evaporating it to dryness; the residue was the nonionic. Most builders and modifiers used in formulations are ionic in nature and thus can also be separated by this technique quite readily.

As in the case of extraction, ion exchange cannot always achieve complete isolation of the nonionic. However the separation of nonionic is often effective enough so that some of the chemical or instrumental analytical methods discussed above for determining the nonionic might be applied, using the deionized sample which was not possible with the original sample.

Determination of Nonionic Components in Mixtures Containing Less Than 5% Nonionic. This section encompasses analysis of those formulations which contain a small percentage of nonionic. Also the application of nonionics to actual use operations often necessitates the determination of small amounts of the nonionic in the applied system. These mixtures are generally quite complex, not only because of the components present in the nonionic formulation but also because of all the components present in the operation to which the surfactant is applied. These systems thus require analytical methods with high degrees of specificity for determining the nonionic components. The concentration of nonionic in these systems is often very low, as low as a few parts per million in many cases; this condition demands a method with a high degree of sensitivity.

The gravimetric phosphomolybdic acid and silicotungstic acid methods (27, 34) and the volumetric ferrocyanide method (33) discussed above can be applied for the determination of nonionics in the range of concentration with which this section deals. These methods have the specificity but, in general, cannot be applied for determining nonionics in concentrations of less than 0.1%. The colorimetric approach (34), using phosphomolybdic acid, can be applied to systems containing somewhat smaller amounts of nonionics though systems containing less than 0.02% cannot generally be handled except in some fairly well defined systems.

The best method yet found for traces of nonionics (0–1%) is that of Kho and Stolten (17). This method utilizes potassium iodomercurate, which forms a turbidity with low concentrations of nonionics. Comparison of the turbidity against standards (visually, colorimetrically, or nephelometrically) yields the content of nonionic. The method will detect 1–10 parts per million in many though not all instances; a limit of 10 parts per million however is attainable in almost all cases. The following types of nonionics have been determined by using this method: phenolic-ethylene oxide adducts, alcohol-ethylene oxide adducts, carboxylic acid-ethylene oxide adducts, amide-ethylene oxide adducts, amine-ethylene oxide adducts, mercaptan-ethylene oxide adducts, polyethylene glycols, and polypropylene glycols. The method has a high degree of specificity and is being used to determine traces of nonionics in complex mixtures. The only known interferences are alkaloids, some quaternary ammonium compounds, and some proteinaceous materials.

Cationics

Cationic detergents are generally amines or quaternary ammonium salts. In the case of quaternaries they can be determined by the reverse methylene blue method. As described above, the methylene blue method for anionics involves titration with a standard solution of a quaternary salt. For the determination of the quaternary a standard solution of an anionic detergent is used. The quaternary may be titrated with the anionic though some technicians prefer to use a known aliquot of standard anionic solution with a solution of the unknown quaternary. Those who prefer titration with the quaternary claim better end-points though this may be merely a question of habit.

In the section dealing with methylene blue a procedure was referred to (4) which contains a method for determining quaternary halides. This method (28, 40) consists of adding mercuric acetate, which complexes the halide ion forming the quaternary ammonium acetate. The latter compound can be titrated as a base in the solvent system used. The method has a relatively high accuracy, and precision has been successfully applied by the author to the determination of quaternary cationics.

Flanagan *et al.* (13) determined quaternaries by the formation and measurement of a turbidity formed on reaction with a condensed aryl sodium sulfonate (Tamol N). The turbidity is compared against knowns.

Another type of cationic is the amine type. This variety of cationic is best determined by the procedures used for amines in general. Siggia (38) describes a number of methods for determining a variety of amines. The preferred method is the direct titration of the amine as a base or titration of the amine salt as an acid. This can be done in aqueous media, but it is preferable to use the nonaqueous media described by Siggia and Stolten (46) because of the greater accuracy and precision attainable. Mixtures of free amine and amine salts can be determined by titrating one sample with standard acid to obtain the free amine and then by titrating a second sample with standard base to obtain the amine salt.

Some alkylated or ethoxylated amines consist of mixtures of primary, secondary, and tertiary amine mixtures. Such mixtures can be analyzed for their individual amine components by using a scheme of volumetric analysis described by Siggia (39, 42).

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Economics of Syndets and Soap[1]

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This is open to several treatments, one of which is the comparison of the "plant" costs of syndets and soaps. Before data on these costs are discussed, I believe that it might be of interest to review a tabulation of estimated sales of syndets and soaps for the years 1947–1957 inclusive. These data have been compiled with the assistance of the staff of the association of American Soap and Glycerine Producers Inc. ("Soap Association"). They represent an attempt to estimate the United States totals and do not bear a constant relationship to the published data released by the Soap Association. This variation arises from the fact that data released are compiled from reports received from the membership. Membership is not all-inclusive and moreover fluctuates. The sharp change in the ratio of syndet to soap tonnage in the past decade should be noted. Syndets now outsell soaps about 2.5 to 1!

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[1] Dinner lecture.