

Wetting as a Function of pH and Chain Length. Wetting action is another area in which ampholytics, as such, probably cannot compete directly with less expensive products. However, in conjunction with other properties for a specific application, wetting becomes a definite plus feature. In general, wetting action of an ampholytic follows the typical pattern of being quite specific as regards chain length with the optimum for the N-fatty β -aminopropionates occurring at a chain length of about C₁₂, at which chain length is exhibited an almost instantaneous wetting time. The pH functionality of wetting action follows the general trend of that of the majority of the other performance characteristics, going through a minimum in the isoelectric range.

Surface and Interfacial Tension Data. The N-fatty β -aminopropionates exhibit a very high degree of surface and interfacial tension lowering. When the fatty group is essentially 12 carbons in length, interfacial tensions are well below 2 dynes per cm. at concentrations of 0.1% active. Likewise, at 0.1% active concentration, this product (sodium N-dodecyl

β -aminopropionate) will exhibit a surface tension of about 25 dynes per cm. As with wetting, these values are more or less independent of pH except in the isoelectric range.

Compatibility with Other Surfactants. In the complex realm of multi-component formulations, ampholytic surfactants have very interesting possibilities. In general, ampholytics are compatible over wide ranges of detergent ratios and with anionic, non-ionic, and cationic surfactants. Cationic surfactant compatibility is probably the most interesting. Virtually all anionic surfactants will almost quantitatively precipitate or inactivate cationic detergents, especially quaternary ammonium compounds. However, even in ratios as high as 16 parts of sodium N-alkyl β -aminopropionate and 1 part quaternary, the germicidal effectiveness of the quaternary is virtually unaffected. Hence it is possible to formulate a quaternary with an ampholytic in its anionic form and enjoy the advantages of both cationic and anionic behavior.

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Analytical Test Methods for Organic Detergents

W. G. SPANGLER, Analytical Division, Research and Development Department, Colgate-Palmolive Company, Jersey City, New Jersey

THE AMERICAN SOCIETY FOR TESTING MATERIALS has defined a detergent as a composition that cleans. A synthetic detergent, it is further stated, is produced by chemical synthesis and comprises an organic composition other than soap. This paper will attempt to summarize some of the current analytical methods employed to isolate, identify, and measure the most important detergents being manufactured today.

Versatility is a word that might be used to keynote the problem of analyzing these organic substances. Surface-active agents (detergents, in particular) are versatile performers. Versatility (plus complexity) is evidenced by the organic chemist in the way he tailors the "detergent molecule" to fit a given set of requirements. Dexterity is also displayed by the formulator in creating balance within a product so that it adequately performs its task. Finally the adept analyst employs a diversity of tools and methods to enable him to keep abreast of the changing scene.

In order to control production of syndets, rapid analytical procedures are necessary each step of the way. These methods must have a reasonable degree of accuracy in order to yield material balance and supply accounting figures. The analyst must also concern himself with the composition of competitive products and the nature of his own organic synthesis. There is no one analytical scheme, nor is there one method for a given classification of surfactants, that will work with all the compositions the chemist will encounter. The detergents known as anionics and nonionics comprise the bulk of the market, and the methods reported for the analyses of these are of the most importance to the analytical chemist.

Classification

The molecules of surface-active agents are characterized by a water-loving portion (hydrophilic) and a water-hating portion (hydrophobic). In dilute aqueous solutions they lower the surface tension of water considerably, and phase boundaries are easily broken. The properties (wetting, foaming, detergency, etc.) can be varied by changing the shape and size of the hydrocarbon group or by modifying the nature

of the solubilizing group or a combination of both. The surface-active agents are most commonly classified on the basis of the charge on the colloidal particles dispersed in water. The anionic has an active portion which carries a negative electrical charge, whereas the effective portion of the cationic has a positive charge. The nonionics are electrically neutral in solution and may be classified with the ester and ether compounds. Sometimes the molecule contains both anionic and cationic groups, and these are said to be amphoteric or ampholytic. They are usually anionic in alkaline medium and cationic in acid medium. Typical examples of each class are given herewith:

Anionics

- | | |
|--------------------------|---------------------------|
| a. Alkyl aryl sulfonates | R aryl SO ₂ Na |
| b. Alkyl sulfates | ROSO ₂ Na |

Nonionics

- | | |
|--|---|
| a. Alkyl phenol ethylene oxide derivatives | R phenol (C ₂ H ₄ O) _n |
|--|---|

Cationics

- | | |
|----------------------------------|---|
| a. Quaternary ammonium compounds | $\begin{array}{c} (R)_3 \\ \diagdown \\ N \\ \diagup \\ (R)_1 \end{array} Cl$ |
|----------------------------------|---|

Ampholytic

- | | |
|-------------------------------|--|
| a. Salts of alkyl amino acids | R NH CH ₂ CH ₂ COON _a |
|-------------------------------|--|

Sampling

Although the literature contains many references in regard to the analysis of syndets, very little has been written about sampling. Discrepancies in results are probably as frequently caused by inadequate sampling practices as by poor analytical procedures. There are few official sampling methods for detergent products. Spray-dried built detergents are mixtures of varying particle size and usually require adequate blending and riffing, followed by rapid grinding, if small samples are to be representative. Liquid detergent mixtures containing volatile constituents must be sampled carefully if the volatile constituents are to be determined quantitatively and subsequent samples used for analysis are to give results that can be

correlated with the original sample. Maintaining slurries at a slightly elevated temperature in sealed containers has been found effective in preventing crystallization of the inorganic constituents. Acid mixes must be analyzed without delay so that further chemical action will not give rise to misleading results. As a final reminder, careful consideration must be given to the type of container used for delivery of the sample.

General Analysis of Syndets

The detergent product as found on the grocer's shelf is usually a mixture of several organic surfactants and inorganic builders. In addition, it may include "organic additives" and traces of unsulfonated or unsulfated materials. Several general analytical schemes have been published that are applicable to these products, which represent roughly about 80% of the detergent market.

A.S.T.M. Method D 820-46 (2) is a general method for analysis of soaps admixed with synthetic detergents. The total surfactant (soap plus synthetic detergent) is determined by weighing the alcohol-soluble material. The writer has found this to be a good control procedure when a mixture of detergent material is present. The procedure (slightly modified) consists of leaching a 1-g. sample several times with warm isopropanol, combining the filtrates, and bringing to volume in a 100-ml. volumetric flask. A 10-ml. aliquot is evaporated and heated at 105°C. in a platinum or aluminum dish. This method requires little time, possesses good accuracy and precision, and is independent of an equivalent weight. If desired, another aliquot can be corrected for chlorides, and a third aliquot can be extracted or passed through either an adsorbing medium (alumina) or an ion exchange column to measure individual components or unreacted material.

The Report on the Examination of Detergent Preparations by the Analytical Methods Committee Society of Public Analysts and Other Analytical Chemists (81) gives qualitative and quantitative methods for examination of detergent preparations. Nevison (74) discusses the analysis of packaged detergents and covers the elemental analysis scheme of Wurzschnitt (109). Kortland and Dammers (57) present a scheme which is based on the resistance to acids of the various types of surface-active agents. It can be made quantitative by weighing the extraction residues obtained and determining their physical and chemical constants.

Gilby and Hodgson (35) isolate builders and other additives by azeotropic distillation and alcohol extraction. They also extend the scheme of Linsmeyer (64) and obtain more information regarding the active ingredient based on conventional systematic organic analysis.

Many general schemes occur in the literature that are applicable only to a particular class of surfactants, are only qualitative in nature, or do not include mixtures. In 1940 Linsmeyer (64) set up a qualitative scheme that divided the surface-active agents into eight groups on the basis of solubility of their calcium salts and according to their acid resistance. Bergeron (6) discusses the analysis of anion-active detergents and separates them on the basis of three successive acid treatments of increasing intensity. Van der Hoeve (100) analyzed textile auxiliary prod-

ucts by detecting any organically combined nitrogen present and determining the ionic nature of the compound and the hydrocarbon group by specific tests.

Hart (42) pioneered in the determination of active ingredient and fatty matter in surface-active agents. He extracted the active principle over salt solution and ashed the residue. Koch (56) used Attapulugus clay in separating the sulfonated and non-sulfonated fractions of petroleum sulfonates. This method was not satisfactory if appreciable amounts of water and inorganic salts were present and if the elution of the sulfonates with methanol were not complete. Brooks *et al.* (9) tried to overcome some of the difficulties of the A.S.T.M. D 855 method, as first written in 1944, for the analysis of oil-soluble, sodium petroleum sulfonates. They separated the organic portion by extracting an acidified aqueous suspension with chloroform. A portion of the extract was titrated potentiometrically for strong and weak acids, and the mineral oil was isolated from another portion by adsorbing the carboxylates and sulfonates on Attapulugus clay. Weiss *et al.* (103) have modified the A.S.T.M. D 855-46T method (3) (revised in 1952) so that it is applicable to sodium alkyl aryl sulfonate detergents containing organic and inorganic builders. With minor changes it can also be applied to sodium alkyl sulfate detergents.

Separation of Mixtures

In order to apply the majority of the general analytical schemes referred to previously, it is necessary to make a preliminary separation. Ethyl alcohol has been mentioned most frequently as the agent employed to separate organic from inorganic matter. Isopropanol is a good substitute. Kortland and Dammers (57) state that wash and foam promoters (higher alcohols, fatty acid amides, and fatty alkylol amides) can best be separated from surface-active agents by restricting the alcohol extracts to a maximum of 10% solids in 10-20% aqueous isopropanol and extracting 5 to 10 times with 1:1 ether pentane. Weiss *et al.* (103) separated an aqueous alcoholic solution of sodium alkyl aryl sulfonate and a nonionic by passing it through a mixed ion exchange bed. The sulfonate could be desorbed from the anion exchange resin by use of a 2% solution of sodium hydroxide in a 1:1 isopropyl alcohol-water mixture. Miller *et al.* (69) extract the active principle from a dilute aqueous solution with n-butyl alcohol in the presence of sodium carbonate. Green, Parker, and Howitt (36) developed a technique that used an ion exchange resin or adsorbents containing an ion exchange resin whereby the separation of an oil in water emulsion could be accomplished. The analysis of an emulsion stabilized by a cationic detergent was achieved by adsorption on a column of anion exchange resin. An emulsion stabilized by a nonionic detergent was passed through an intimate mixture of an anion and cation exchange resin. By using various solvents, the pure components could be isolated and estimated separately. A mixture of an anionic and lanolin was separated by using a cationic resin mixed with powdered animal charcoal. Harris and Short (41) developed two methods for the extraction of sodium dodecylbenzene sulfonate from food products. In one method the compound was extracted with alcohol, and in the other 7N NaOH was used.

Barber *et al.* (4), in describing the analysis of

mixtures of surface-active quaternary ammonium compounds and polyethylene oxide type of nonionic surface-active agents, state that the quaternaries can be removed quantitatively from solution by a cation exchange resin, leaving the nonionic in solution. The subcommittee on analytical methods of the Association of American Soap and Glycerine Producers (16, 73) have concentrated the alkyl benzene sulfonate in surface waters by adsorption on activated carbon. This is eluted with a benzene-methanol solution, purified, and finally complexed with 1-methylheptylamine and extracted with chloroform. House and Darragh (49) separated low molecular weight sulfonates from higher-weight detergent types of sulfonates by extracting between ethyl ether and 3 to 4N HCl solution. The low molecular weight sulfonates (*e.g.*, toluene sulfonate) are found quantitatively in the aqueous phase and the detergent type sulfonates in the ether phase. Franks (32) made a qualitative separation of alkyl sulfates by ascending and circular chromatography. Franks (33) also developed a paper chromatographic method for separating mixtures of surface-active agents and commercial detergents. He states that most analytical schemes for analysis of commercial detergents are laborious and dependent on a large number of tests. They also require that the active ingredient be separated by extraction. In his proposed method all inorganic substances are washed off the paper by the water in the solvent, and the non-surface-active organic substances are held at the origin by the stationary solvent. Only the surface-active substances would be distributed on the paper in accordance with their hydrocarbon chain lengths. It is evident from these references that selective adsorption, selective solvent action, and ion exchange methods play an important role in separating the active ingredient that is to be measured or identified.

Instrumental Methods

The increased use of instrumental methods has been evident in characterizing surface-active agents, usually after some method of separation. The qualitative and quantitative nature of these substances can often be ascertained by a combination of infrared and ultraviolet absorption. Mechanization of sorting and filing operations, together with automatic recording, places absorption photometry in a unique position for quick analysis and in supplementing the usual wet methods of analytical chemistry.

Reid, Alston, and Young (80) developed a simple qualitative scheme for the characterization of surface-active agents by first examining the ultraviolet spectra and then applying some of the tests suggested in the scheme of van der Hoeve (100). The dry, active ingredient was solubilized, and a spectrum was run with a Beckman DU Spectrophotometer in the range of 210 to 350 $m\mu$. Tests were then made to show the ionic character of the product and the presence or absence of nitrogen. Four main classifications were thus obtained. Numerous spectra are shown.

Delsemme (21) describes the technique for infrared analysis of functional groups in surface-active agents. Sadtler (82) states that infrared absorption methods definitely identify the type of compound and very frequently give a clue to the exact identification of the compound. A representative list of

the various types of spectra are shown which enables one to identify the characteristic grouping of organic agents as a means of identification and predicting their probable function or activity. Kuentzel (58) found it necessary to calibrate for the quantitative analysis of mixtures of sodium toluene sulfonate and alkyl benzene sulfonate by infrared method. A common solvent that was relatively transparent in the analytical region of the spectrum could not be found, and it was decided to use calcium carbonate as an internal standard and calibrate with mineral oil suspensions. Grief and Kent (37) have analyzed the same mixture by ultraviolet methods. The alkyl benzene sulfonate is separated from the hydrotropic agent according to House and Darragh (49), and then the absorption of the toluene sulfonate is measured at 220 $m\mu$ and 240 $m\mu$. A set of simultaneous equations has been devised which gives the para to ortho ratio, and from this ratio a graphical factor is obtained which allows direct determination of both ortho and para toluene sulfonate at one time.

Thompson and Fine (38) report an ultraviolet procedure for determining dodecylbenzene sulfonate in built detergents and slurries. One gram of sample is dissolved in water and diluted to 500 ml. A 5-ml. aliquot is then taken and again diluted to 250 ml. with water. In using a 1-cm. cell in the Beckman DU spectrophotometer, the optical density is measured at 224 $m\mu$ and 270 $m\mu$ with water as a blank. The absorption of 224 $m\mu$ minus the absorption at 270 $m\mu$, multiplied by the factor 69.45, and divided by the weight of sample gives the percentage of dodecyl benzene sulfonate present.

Anionics

The most important members of this group are the alkyl sulfates and the alkyl benzene sulfonates. Most of the anionics are strong electrolytes and cannot be titrated directly. As previously stated, many rapid methods are based on ultraviolet and infrared absorption. Most of the remaining methods depend on the interaction of high molecular weight cations and anions to form complexes. These compounds may be weighed, extracted by partition methods, measured colorimetrically or turbidimetrically, etc. In some instances amine complexes are formed and are weighed or titrated. Direct titration of liberated acids or precipitation of barium salts are also sometimes employed.

Acid Titrations. The sodium cation is often replaced by hydrogen ion as a result of adding mineral acid or using ion exchange resins. The liberated acids can be titrated with standard alkali after elution or extraction with the proper solvent. Neu (75), in analyzing washing and cleaning agents, uses the cation exchange resin Wolfatit K and titrates the acid solutions to obtain acid numbers and equivalent weights. Etienne (27) mixes 3 to 15 g. of sulfonate or sulfate with 25 ml. of 3N HCl, extracts with ethyl ether, and evaporates to a small volume with a stream of air. The material is titrated with N NaOH to the methyl orange end-point, adding water toward the end of the titration. The acidity due to the HCl is then determined by adding potassium chromate and titrating with 0.10 N silver nitrate. Espector (26) releases the sulfonic acid by adding sulfuric acid. The sample is then heated until foam ceases and is poured into a graduate cylinder. The volume of sulfonic acid is determined, and the percentage of detergent is calcu-

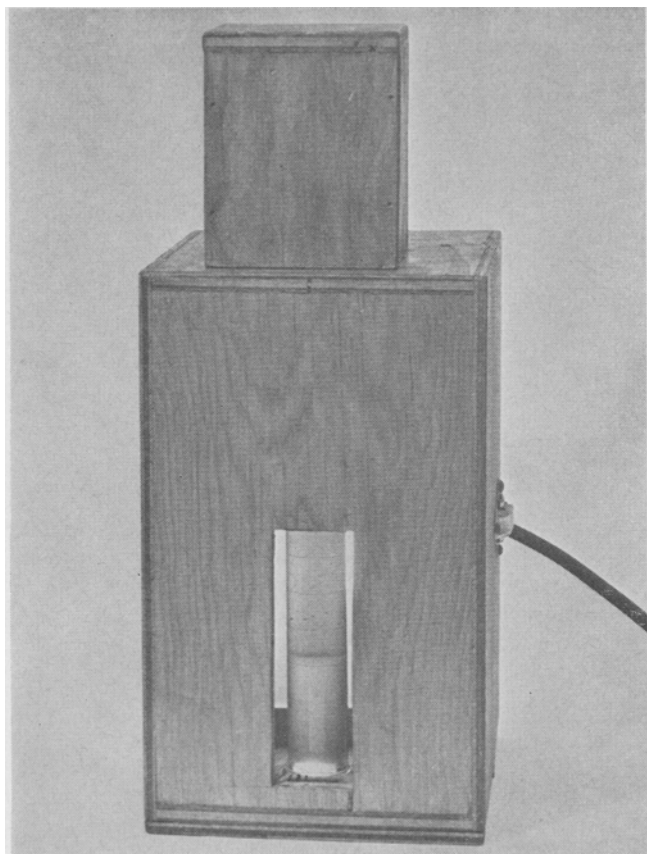


FIG. 1.

lated. Sometimes the sulfuric acid esters are decomposed by boiling with mineral acids, and the acidity is determined by titration. Hart (43) analyzed sulfated oils by acid hydrolysis and titration with standard alkali. The total alkalinity of the sample was also determined. A.S.T.M. method D-500-55 (2) adopted this procedure with some modifications. Since sulfonates do not hydrolyze readily, it is common practice to determine alcohol sulfates in the presence of sulfonates by this method. Snell and Biffen (93) determine alkyl sulfates in a similar manner.

Spangler, Kent, Casazza (88) have modified the method of Critchfield and Johnson (17) so that sulfonic acids can be titrated in the presence of sulfuric acid. The acid mixture is dissolved in 1:1 ethylene glycol isopropanol solution and titrated potentiometrically with $N/2$ morpholine in acetonitrile. The first equivalent point represents all of the sulfonic acid and half of the sulfuric acid. The second equivalent point represents the total acidity.

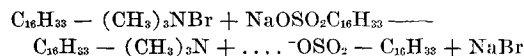
Amine Complexes. Kling and Puschel (55) used benzidine hydrochloride to precipitate alkyl sulfates. The precipitate is dissolved in alcohol to separate it from inorganic sulfate and is titrated with standard alkali, employing bromocresol as indicator. Shiraeff (87) showed that it is quite general for high molecular weight sulfonic acids to react with this aromatic diamine. The salt is easily isolated by filtration and is stable enough to permit drying at moderate temperatures. The Colgate-Palmolive laboratory has used this method frequently for determining the molecular weight of alkanes or unknown sulfonates. The precipitate is washed free of unsulfonated material with isopentane and dissolved in alcohol. A

known weight of the dried precipitate is then titrated with a pH meter and standard alkali to a pH of 8.5.

Marron and Schifferli (68) objected to the usual methods for determining the active ingredients of commercial products on the grounds that the methods were generally lengthy and were calculated for the most part by difference (7, 42). They reacted alkyl aryl sulfonates and alkyl sulfonates with *p*-toluidine hydrochloride and extracted the complex with CCl_4 . The extract was then titrated with standard alkali. The method was further investigated by Stupel and Segesser (95). They applied the method to the determination of alkyl aryl sulfonates, alkyl sulfonates, secondary alkyl sulfates, and fatty acid condensation products, such as amides and amines. Gauthier and Mazau (34) and Wickbold (104) did work similar to that of Shiraeff in that they weighed the insoluble *p*-toluidine salt and used it for an equivalent weight determination. Widaly (105) applied the method of Stupel and Segesser for factory-control purposes. Harris (40) reported at the time that few of the published methods were entirely satisfactory because they included impurities or were inoperative with dilute solutions. He modified the qualitative test of Scales and Kemp (84), which is based on the blue color formed with *o*-toluidine and sodium hypochlorite, in such a manner that alkyl benzene sulfonate could be determined quantitatively.

Barium Precipitate. Herbig (46) determined organically combined sulfuric anhydride in sulfated oils by hydrolyzing with hydrochloric acid, extracting the fat with ether, and determining the sulfate in the water layer as the barium salt. Brauns *et al.* (8) separated barium from sulfonic acid by use of a cation exchange column. The filtrate is oxidized with nitric and perchloric acid, and the sulfuric acid is precipitated with barium chloride.

Action with Cationic Dyes or Surface-Active Agents. Tschögl (99) refers to the reaction between any substance having a hydrophobic and a hydrophilic portion with any similar one of the opposite charge as an antagonist reaction and classifies methods involving this type of reaction under the heading of dyestuff antagonist and soap antagonist. He describes the reaction between a cationic material cetyl trimethyl ammonium bromide and a typical anionic one, such as cetane sulfonate, as follows:



and explains that in the new compound the hydrophobic/hydrophilic balance is heavily in favor of the hydrophobic part, thereby making it insoluble in water but soluble in organic solvents.

The investigations of Mukerjee (72) have shown that the interaction between ionic dyes and surfactants of the opposite charge is a simple metathetical one between the large surfactant ion and the large dye ion of the opposite charge, producing compounds which usually have only slight solubility in water. These compounds are stoichiometrically simple 1:1 salts, in which electroneutrality is maintained by the dye ions only (except when acid or basic salts are formed by divalent dyes).

The reaction between anionic surface-active agents and cationic surface-active agents or dyes is the basis for most of the determinations of surfactants in sewage, water-supply treatment, and built detergents.

Hartley (45) observed that the purplish blue color of bromophenol blue in alkaline solution is displaced toward a clear blue in presence of cation-active compounds. In 1938 he collaborated with Runnicles (44) in publishing a method utilizing this dye as an indicator. The color change was used as the end-point for titration of cetyl pyridinium chloride with cetyl sulfate. Wijga (107) sought to improve the reproducibility of Hartley's method by using bromophenol blue in a solution buffered at pH 4.9. Salton and Alexander (83) used pinacyanol bromide in place of bromophenol blue and found the color change superior to Hartley's.

Jones (51) reacted the cationic dye methylene blue with anionic surfactants to form compounds extractable in chloroform. The extract is examined colorimetrically. Edwards *et al.* (24) determined sodium cetyl sulfate at low levels by modifying the Jones procedure. The methylene blue cetyl sulfate complex was filtered through ground quartz, extruding the column and redissolving the complex in ethyl alcohol for color determination. Evans (28) eliminated some of the interferences encountered when analyzing sewage by the method of Jones. The results were more accurate as a result of corrections made from values obtained at two different pH levels. Lester (60) suggested that the influence of nitrates and urine-interfering compounds could be eliminated by application of corrections and that thiocyanate ion could be removed by previous precipitation with silver sulfate. Degens *et al.* (19) determined the total anionic active material (sulfate and sulfonate) in sewage by extraction of the stoichiometric methylene blue detergent complex by means of CHCl_3 and estimating the color photometrically. This was repeated after acid hydrolysis to determine the amount of sulfonate present. Conditions of extraction must be adjusted so that interfering compounds, such as nitrates and thiocyanates present, are not simultaneously extracted as methylene blue derivatives. The method of Longwell and Maniece (65) differed from that of Degens in respect to the extraction, which was carried out in alkaline solution; and the extracts were subsequently washed with an acid solution of methylene blue. This method is not subject to interferences from inorganic ions, which give positive readings in the Degens method. It also gives improved recovery. Sodium dioctylsulfosuccinate was chosen as a standard. The use of methyl green by Moore and Kolbeson (70) was designed to eliminate or minimize interferences encountered in analyzing sewage for anionic detergents by the methylene blue method. Interferences were greatly reduced. The procedure is not affected by high concentrations of sulfate, chloride, sulfite, and phosphate. Recoveries of alkyl sulfate added to river water as well as sewage were more consistent and accurate by this procedure. By way of comment Coughlin (16) states that methods for analysis of low concentrations of alkyl benzene sulfonates in water and sewage treatment are inadequate. The methylene blue procedure was generally used in the past, and only recently are its weaknesses coming to be recognized. It is far from satisfactory because urine, tea, coffee, distilled-water extracts of straw, leaves, etc, all of which contain natural surfactants, assay as alkyl benzene sulfonate by this method when, in fact, it is not present.

Wallin (106) published a method similar to Jones

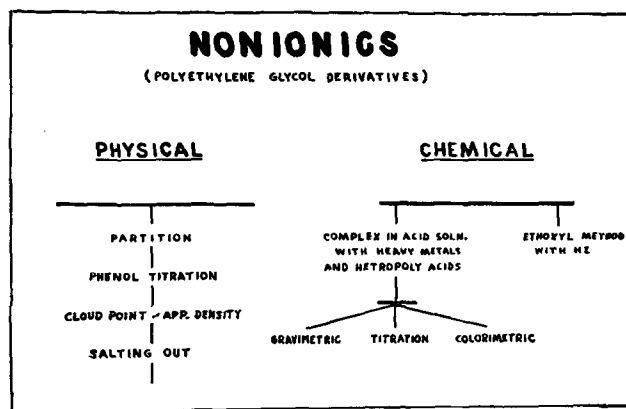


Fig. 2.

but used basic fuchsin because of its insolubility in chloroform. Karush and Sonnenberg (54) used rosaniline or pararosaniline hydrochloride and extracted with 1:1 chloroform and ethyl acetate. Loomeijer (66) states that many types of anionic detergents can be determined colorimetrically by their action on a protein-bromocresol purple complex. The amount of free dye liberated from the complex is proportional within certain limits to the amount of detergent added. The accuracy is not as satisfactory as that of the rosaniline method. Lewandowski (62) developed a possible field test by adding an anionic detergent solution to a cationic detergent-bromophenol blue mixture in aqueous solution (acid pH) and observing the color produced. The color reactions were dependent on molar rather than weight concentration relationships. Von K. Peter (101) determined anion-active, colloidal electrolytes in acid solution with thymolblue. They gave a definite red-violet color. Powell and Taylor (78) were able to complex ferrous chelates with long chain alkyl sulfates and sulfonates and extract them with chloroform. This poses the possibility of determining these surfactants by titrating with metallo-organic cations and measuring the absorbence of the chloroform extract.

Barr, Oliver, and Stubbings (5) aimed to control surface-active agents in textile processing. They objected to Hartley's method because the indicator transition was ill-defined. The preferential reaction of the anion-active with the cation-active enabled the direct titration procedure of Hartley and Runnicles (44) to be combined with the extraction procedure of Jones. Hoyt and Walter (48) adapted the method to the determination of active sulfonate in mixtures of soap and Naccenal R B 85. The titration is carried out in dilute solution with bromophenol blue as a transition indicator in a two-phase system of water and chloroform. With cationic detergent the indicator forms a dark-blue-colored complex, which is soluble in chloroform. Hence as soon as a trace of excess cationic detergent is available, its presence is revealed as the indicator (initially in the aqueous phase) begins to migrate into the chloroform layer. Edwards and Martin (23) modified the two-phase titration method of Barr for determination of anionics in sewage. Interference by soap and protein has been eliminated by adjustment of pH to 7.0-7.5 during the reaction. The use of EDTA avoids errors because of Ca and Mg. This method is not affected by sodium chloride or sulfate in concentrations up to

1,000 p.p.m., nor do thiocyanates, nitrates, nitrites, or urine interfere.

Harper, Ellicker, and Mosely (38) employed eosin as an indicator. The mixture of tetrachloroethane, dye, and buffer is titrated with the anionic until the color disappears. Fessler (29) decided the end-point was best determined when the intensity of color in both layers was identical. Wijga (107) estimated sulfates, sulfonates, and carboxylates by titrating in both acid and alkaline media with Pontamine Fast Red 8 BNL.

Epton (25) observed the change of intensity on methylene blue in the chloroform layer as related to the addition of the titrating agent hexadecylpyridinium bromide. At first the blue is concentrated in the chloroform layer but slowly is transferred to the water layer. When the two layers possess the same color, the equivalent point is reached. Weatherburn (102) pointed out certain discrepancies in Epton's method and modified it by adding a blank. This is necessary because a small concentration of anionic must be present to give equal color in the two layers, hence the true equivalent point has not actually been reached when the two phases are equal in intensity. Lewis and Herndon (61) recommended the use of Pontamine fast red or Brilliant blue in using the two-phase dye transfer titration method. Smith and Glazer (96) adapted Epton's method for the determination of small amounts of sodium oleate in dilute, aqueous solution. A pH of 10 was maintained by excess alkali, and the oleate solution was added from a burette. Since the methylene blue becomes pink soon after its addition, it is not added immediately.

Method 79 of the Toilet Goods Association (97) uses Epton's method for the determination of sodium alkyl sulfate. A sample containing approximately 0.32 g. of SO_3 is dissolved and transferred to a liter flask with 6% butanol. Ten ml. of this solution are added to methylene blue and chloroform and are titrated with cetyl trimethyl ammonium bromide. House and Darragh (49) made the following four changes in the Epton method: used a 100-ml. stoppered graduate; viewed the sample by a combination of reflected and transmitted light; instead of employing cetyl pyridinium bromide as a titrant, used a long-chained quaternary ammonium compound—ATM-50; and used sulfonic acids for standardization in place of potassium dichromate.

The Colgate-Palmolive laboratory has further modified the method of House and Darragh. A standard viewing-box has been constructed so that the end-point is always determined under the same lighting conditions. Standardization is based on a purified, alcohol-soluble portion of the product being tested or by the ultraviolet absorption method of Thompson and Fine (98). The sample is also partially solubilized with chloroform and brought to volume in this solvent. Helene Iwasenko (50) modified Epton's method by titrating with standard quaternary ammonium chloride solution, using dichlorofluorescein as an indicator. This produces a pink color with the cationic.

Preston (79) experienced difficulty in using the method of Hartley and Runnicles (44) and of Kling and Puschel (55). This led him to develop a new method based on the change in surface tension during titration of anionic-active substances with cationic-active substances or *vice versa*. In order to follow the change in surface tension conveniently and continu-

ously during titration, he modified the standard bubble pressure method. At the equivalent point there was a marked fall in bubble pressure. This fall varied with the concentration and the different complexes. Alexander and Tomlinson (1) measured interfacial tension as cationic-active material was added in increments by the drop volume method. The interfacial tension rises before the equivalent point and falls beyond it.

Lambert (59) felt that the methods available at that time were neither rapid nor convenient for determining small amounts of different types of surface-active agents. Using available equipment, he titrated an anionic surface-active agent and determined the end-point by measuring the maximum turbidity with a colorimeter.

Hettche (47) claims that pollution in water supplies can be continuously measured by changes in surface activity. A ring tensiometer incorporated into an automatic sampling and recording device can measure surface activity every three minutes. The apparatus detected 0.007 p.p.m. of a household detergent.

Nonionics

Nonionics are next to anionics in commercial importance. At present they account for approximately 18% of the detergent market. Because they are compatible with both anionics and cationics, they are found in liquid detergent formulations, controlled sudsing mixtures, detergent-sanitizer combinations, etc. Most of the nonionics produced have the polyoxyethylene chain as the hydrophilic portion. The hydrophobic portion usually consists of alkyl phenols, fatty and tall oil acids, and fatty amides. A glance at these "molecular compositions" is sufficient evidence to show why nonionics, in general, are mixtures. Being nonionic also means being more stable and less reactive than ionics. Thus we are confronted with two hurdles when attempting to analyze or characterize them, first, to find reagents that will react with them, and, secondly, to try and measure, in many cases, a combination of homologues and polymers.

These difficulties are reflected in the nature of the published methods. They are, for the most part, slow, not specific, and not too accurate. This places a hardship on both the supplier and the consumer.

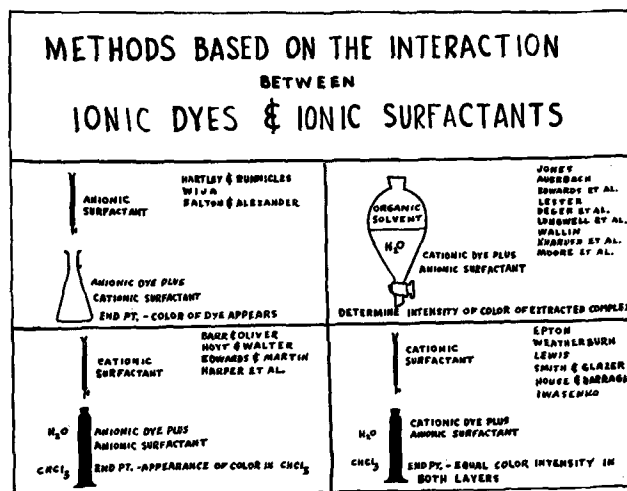


FIG. 3.

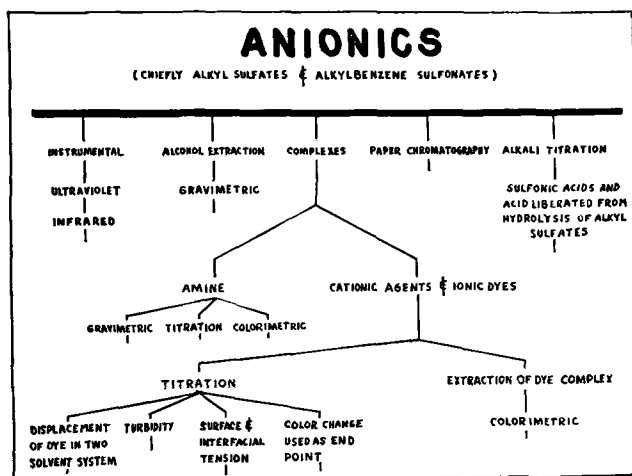


FIG. 4.

For a rough classification of methods the divisions physical and chemical might be named. The chemical can be further subdivided into gravimetric, colorimetric, and titration procedures. In practically all cases it is necessary to base the results of analysis of the product of a particular supplier and many times on a particular batch of the material. Being mixtures, standardization cannot be based on a specific chemical compound. Frequently partition methods are used for determining nonionics in the presence of anionics. Experimental data are derived from a given mixture partitioned between two solvents like methanol and pentane. These data are then applied to the finished product, treated in the same manner.

Physical Methods. Karabinos (52) noted that water solutions of polyoxyethylene nonionics titrated with aqueous phenol produced a definite opalescent end-point. The longer the ethenoxy chain, the more phenol was needed to reach the end-point. This method is useful in the analysis of the chain length where the hydrophobic group is known. Karabinos, Hazdra, and Kapella (53) also describe another method for determining the number of ethenoxy units. A molecular weight is first determined by the method of Rast (92) (m.p. depression of camphor because of the nonionic), and from the weight is subtracted the empirical value of 245, which represents an average weight for the most common hydrophobic radicals. The difference is divided by 44, the molecular weights of ethylene oxide.

Davis, Wattman, and Speel (20) expanded on the phenol titration to determine the percentage of nonionic in solution, provided the type is known. A plot of the milliliters of phenol solution *versus* concentration of nonionic results in a straight line for a great many different types. In general, this method has been found applicable to nonionics whose hydrophobic group consists of C_5 and longer alkyl phenols, fatty alcohols, and alkyl amines, and whose hydrophilic group is composed of ethylene oxide units. It has not proven successful for fatty acid esters or completely successful for polyethylene glycols.

Steele and Berger (89) have characterized nonionics by relating cloud point (the temperature at which the nonionic separates from dilute, aqueous solution as a second liquid phase) with the apparent density. A plot of cloud point in degrees centigrade

versus apparent density shows that values for a particular nonionic fall into a characteristic band which serves to differentiate the nonionic.

Shiraeff (86) separated Igepal from aqueous solutions by salting out with a 25% solution of ammonium sulfate and measuring the volume in a Babcock bottle.

Chemical Methods. A review of the literature shows that most chemical methods are dependent on the formation of insoluble complexes by reacting the ethylene adducts with heteropoly inorganic acids. These complexes can be quantitatively measured, and a direct relationship can be established with the particular surfactant being measured.

Shaeffer and Critchfield (85) precipitate high molecular weight polyethylene glycols (Carbowaxes) in the presence of barium chloride and hydrochloric acid with silicotungstic acid and weigh the precipitate. They also modified the procedure, using phosphomolybdic acid as the precipitating agent. This precipitate was then digested in concentrated sulfuric acid and neutralized; the molybdenum was determined colorimetrically, using phenylhydrazine sulfate.

Oliver and Preston (76) also precipitate with phosphomolybdic acid and barium chloride and then dry the precipitate at 105°C. and weigh. Haakh, Candie, and Mobus (39) tested for polyglycol ethers in woolen clothes by forming a red brown precipitate with a prepared tannin from resorcinol and glucose. These ethers could be extracted quantitatively from aqueous solution with hot n-butanol. Stevenson (94) describes two procedures for determination of Lissapol N, based on precipitation with phosphomolybdic acid. In one case the precipitate is dissolved in warm sulfuric acid, and after 40 minutes the red color is measured at 520 $m\mu$; in the other instance, the dissolved precipitate is reacted with ammonium thiocyanate and stannous chloride, and the concentration of the amber solution is determined after 20 min. at 470 $m\mu$.

Brown and Hayes (10) formed a blue complex (polyethylene glycol-mono-oleate cobalt thiocyanate), by reacting polyethylene glycol mono-oleate with ammonium cobalt thiocyanate, and extracted with chloroform. The absorption was determined at either 318.5 $m\mu$ or 620 $m\mu$. Not all polyethylene glycols and their derivatives reacted. Coppini and Camerini (15) analyzed Carbowax 1,500 and 4,000 by precipitating with a 10% solution of potassium ferrocyanide. The excess reagent is combined with ferric chloride, and the intensity of the blue color is determined. The same principle was applied by MacAllister and Lisk (67), who formed a complex between polyoxyethylene stearate and the amylose fraction of potato starch; the excess reagent was combined with iodine, and the complex was determined colorimetrically.

By dissolving an azo dye in an aqueous solution of the adduct, Schonfeldt (90) was able to titrate ethylene oxide adducts with silicotungstic acid. The solution is over-layered with an organic solvent, and the precipitate rises along with the dye to the liquid interphase. The end-point is reached when the aqueous layer is decolorized. In another method (91) the adducts in hydrochloric acid solution are precipitated with a known quantity of ferrocyanic acid, and the excess reagent is titrated with standard zinc sulfate. The consumption of ferrocyanic acid is then determined by difference. For nonionics having 15 or more

oxide units in the hydrophilic polymer, the precision of the method deteriorates.

Another method based on ethoxyl determination for quantitative analysis of ethers and esters of ethylene glycol has been used by Morgan (71). By using a modified alkoxy apparatus, hot constant boiling hydriodic acid is used to decompose ethylene oxide residue into ethylene iodide and ethylene, which are collected and determined in standard silver nitrate and bromine, respectively. The polyoxyethylene content is calculated from the sum of the equivalents of ethylene, and ethyl iodide is recovered.

Cationics

The hydrophobic group of cationic surface-active agents form cations in aqueous solution. They are essentially used as algicides, in sanitizer-detergents, textile-fiber processing, etc. They are technically important but have not gained the poundage status of the other two classes. No attempt will be made to review this field in any detail, but some mention will be made of methods of analysis being used to measure quaternary ammonium salts. Excellent reviews on cationics can be found in references 18, 22, and 35.

Most of the quaternary ammonium bromides and chlorides can be controlled by determination of nitrogen or total halides. The latter can be done by modifying one of the standard procedures. The electro-metric titration and absorption indicator methods have been found to be most convenient (13).

Non-aqueous titration has been used by Pifer and Wollish (77) to determine cetyl pyridinium chloride and similar quaternary ammonium compounds by adding mercuric acetate to a solution of the sample in glacial acetic acid and titrating potentiometrically with perchloric acid in dioxane.

Caswell (12) mentions several quaternary ammonium compounds that may be determined by ultraviolet spectrophotometry. The absorbance of the solution is determined from 290 $m\mu$ to 245 $m\mu$ with water or water and alcohol as a blank.

Several methods precipitate the quaternary ammonium compounds by using complex ions to form a salt which is insoluble. Examples of insoluble salts are ferricyanides (108), dichromates (31), reineckates (108), and phosphotungstates (63). The ferricyanide and reineckate methods are given in detail in reference 110. For identification purposes a table of optical properties of reineckates is included.

Lincoln and Chinnick (63) propose a method which does not require that the molecular weight of the quaternary ammonium compound be known. They precipitate with phosphotungstic acid and weigh the dried precipitate. The precipitate is then ashed and reweighed. From these two results it is possible to calculate the amount of quaternary ammonium compounds in an unknown sample and also the ionic weight of the quaternary salt.

As in the case of anionics, many methods for determining high molecular weight cationics are based on reactions with dyes or surface-active agents of the opposite charge. An official bromphenol blue method is published in the official methods of the A.O.A.C. (110). Carkhuff and Boyd (11) describe a method for assaying a wide variety of pharmaceutical preparations for quaternary ammonium compounds by titrating with sodium dodecyl sulfate with dimethyl-

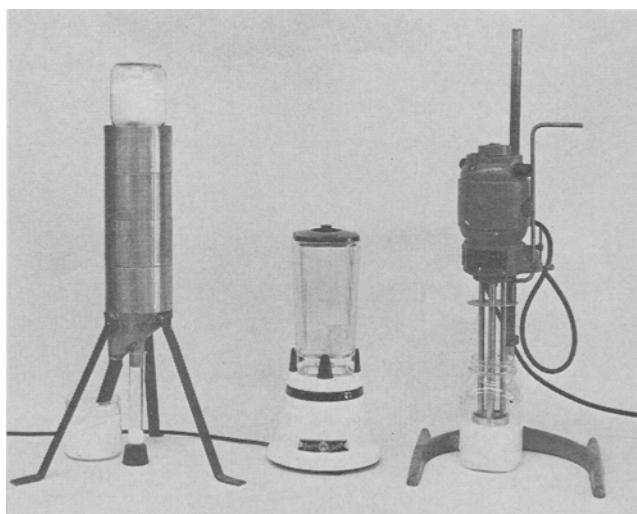


FIG. 5.

aminoazobenzene as an indicator, in the presence of sulfuric acid and chloroform.

Chinnick and Lincoln (14) developed a field test in which 3 ml. of ethylene dichloride, 5 ml. of indicator solution (bromphenol blue, NaCl, Na_2CO_3), and 2 ml. of 0.001 N octyl sulfosuccinate are placed in a 25-ml. cylinder. The volume of quaternary ammonium compound necessary to turn the organic layer blue is a measure of its concentration.

Barber, Chinnick, and Lincoln (4) have eliminated the interference of nonionic in the bromphenol blue method for determining quaternary ammonium compounds by using a matching end-point technique. Few and Ottewill (30) developed a method for determining quaternary ammonium compounds in aqueous solution at low concentrations by forming a complex between the detergent and an anionic dye. The complex is extracted in chloroform, and the color is measured spectrophotometrically.

Conclusion

To date the conditions regarding the analysis of organic detergents and mixtures containing them can be summarized as follows:

1. Methods for complete analysis and identification of the many surface-active agents available are very limited.
2. Absorption spectrophotometry (ultraviolet and infrared) shows great promise as a means of identifying and characterizing these surface-active agents after some preliminary separation.
3. Chromatographic procedures will probably become an ideal way to bring about separations and might well compete against present titration methods for quantitative results.
4. Reference compounds for standardization are badly needed.

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Analytical Test Methods for the Inorganic Portion of the Detergent Products

J. C. HARRIS, Monsanto Chemical Company, Dayton, Ohio

FORTHCOMING PUBLICATION (18) will indicate that the development of methods of analysis for synthetic detergents has received considerable research effort. Much of the effort however has been pointed toward the identification and determination of various organic actives, and comparatively less toward the analysis of the inorganic (and organic) builder or filler components in such compositions. It is true that a multitude of methods have been developed for the individual chemicals involved, but less

effort has been expended toward their separation and determination as combinations. This paper will be devoted to the builder portion of the problem, to indicate the course of such analyses, and to suggest the application of newer techniques where they seem applicable.

Most, if not all, detergent analyses are made on commercial compositions for the purpose of either manufacturing control or for composition identification. Since commercial preparations are subject to