assigned values and are used only as controls representing the desired level of the product being produced. The product being analyzed either meets the standard or falls below it.

For a multiple plant set-up, a really successful cooperative testing program requires a lot of work, not only in analytical time but in planning and administration as well. The value of such a program is hard to establish. Careful preparation of samples, up to 5% of each laboratory's analytical time, followed by careful compilation of the data received represents a considerable investment in dollars. Is it worth the effort? Yes! For not only does each laboratory know wherein it is weak, but it knows its relative overall rating, and everyone concerned knows the limits of error involved in the analysis carried out. Standard deviations for each determination can be calculated. Trouble spots can be investigated, and the need for new and better methods is highlighted. For single plant set-up, internal checking with duplicate or triplicate samples must be relied upon.

Job Organization

Job organization in the control laboratory is as important as job organization anywhere else. Grouping of various samples and maximum utilization of analytical skills is one of the administrative jobs of the laboratory foreman. In some laboratories the job grouping is based on sample types, for instance, one finds a soap job, a glycerine job, a fat job, and a finished products job. In larger laboratories the breakdown may be into the titer job, the color job, the iodine value job, etc. In general, good organization requires some analysts sufficiently trained to be able to fill in on any of the jobs in the laboratory.

Conclusion

In conclusion, let us say that, while the basic methods for soap analysis were pretty well worked out 50 years ago, laboratory techniques and equipment have changed greatly. Many new analyses have been added due mainly to the use of new builders, antioxidants, and additives of all kinds. Instrumental analyses, such as pH and photometric colors, coupled with a change-over to rapid analytical methods utilizing polarographs, spectrophotometers, flame photometers, and electronic devices of all kinds have changed the laboratory equipment picture and the man-power requirements. The analysts must be trained to handle the tools and maintain the equipment. A continuing search for newer and better methods and tools continues.

Analysis of Syndets

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ANALYSIS of synthetic detergents, and of cleaning compositions built around them, involves such a great variety of chemical compounds and mixtures of compounds that their complete identification may severely tax the ingenuity and patience of the analytical chemist. The what, when, why, and how of detergent analyses bring into play the principal tools of chemical and physical science and may include analytical exercises on detergent raw materials, retail packaged products, or wastes. While a synthetic detergent is defined by the ASTM as "a detergent produced by chemical synthesis and comprising an organic composition other than soap," it is felt that a discussion of syndet analyses should be broadened to include all detergent compositions in which they are used. In today's popular household detergents, besides the syndet, we find an assortment of both organic and inorganic ingredients which are principal components and contribute substantially to the detergent properties.

Despite the great number of syndets and detergent formulas which have been built around them, we find analytical techniques have been keeping reasonable pace with the art of synthesis and formulation. Separation of components, elemental analyses, and chemical characterization of functional groups are the basic techniques most generally relied upon. However increased use of spectrometry is being made to hasten both qualitative and quantitative aspects of analyses. The desirability for shorter methods, more accurate results, and greater simplicity of procedures gives rise to continuing research effort in this as in other fields of analytical chemistry.

The problems involved in the analysis of detergents can best be reviewed by first considering a representative lot of the more frequently encountered chemical types, the raw materials used in their preparation, distinguishing product characteristics, and analytical methods used for their accounting. Next, consideration will be given to an assortment of package formulas and their analysis, and finally brief mention will be made of analytical problems related to syndet residues and wastes.

Syndets

Syndets are hydrophobic-hydrophyllic type of molecules whose dual functionality gives them the valuable property of breaking through phase boundaries between cleaning solution and soils to be suspended and removed from the surface being cleaned. Practical performance limitations (solubility and detergency) restrict the molecular and structural balance in these compounds. Economic considerations further limit the number which find widespread usage. The better known syndets include:

a) Salts of alkyl sulfuric acid esters
    Ex.: $C_{12}H_{25}OSO_3Na$,
    Sodium salt of sulfated lauryl alcohol

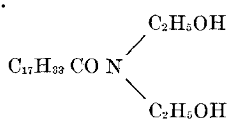
b) Salts of alkyl aryl sulfonates
    Ex. $C_{12}H_{25}C_6H_4SO_3Na$,
    Sodium dodecyl benzene sulfonate

c) Fatty acid derivatives from which carboxylic acids may be separated by hydrolysis:

1. Salts of sulfated fatty acid glycerides
    Ex.: $C_{11}H_{23}COOCH_2CH(OH)CHOSO_3Na$
    Sodium salt of sulfated glycerine monolaurate
2. Salts of oleic acid condensation products with taurine.
    Ex.: $C_{17}H_{33}CONHC_2H_4SO_3Na$
    Oleylamide ethyl sulfonate

3. Condensation products of fatty acids and di-alkanol amines.

Ex.:



$$C_{17}H_{33}\,CO\,N(C_2H_5OH)_2$$

d) Polyalkeneoxy ethers, esters, and thioethers
Ex.: $C_8H_{17}\,C_6H_4\,(OC_2H_4)_n\,OH$, $n = 8$ to 10
octylphenyl ether of polyethylene glycol

To the analyst it is important to know that the given formulas represent compound types present in the respective syndets. In actuality, each product usually is composed of an extensive mixture of such homologous and isomeric compounds, depending upon the composition of the raw materials and processing treatment used in their synthesis.

Sulfated Alcohols and Olefins

The salts of sulfated coconut oil alcohols, commonly described as sulfated lauryl alcohols—a principal constituent, are the best known example of sulfated alcohol type syndets. These alcohols, prepared by hydrogenation of coconut oil fatty acids and further refined by distillation, may be of mixed molecular weight, as shown by analysis of a typical commercial product: 2.6% decanol, 60.4% docecanol, 23.0% tetradecanol, 11.0% hexadecanol, and 3.0% octadecanol.

While less frequently encountered in this country, other syndets of this same sulfuric acid ester type may be prepared from a) olefins obtained from paraffins by cracking or chlorination and dehydrochlorination reactions; b) alcohols resulting from either paraffin oxidation or reduction of aldehyde condensation products; and c) normal alcohols with branched chain alkyl groups produced by the OXO type process.

These aliphatic alcohols form half esters of sulfuric acid upon treatment with sulfating agents, such as fuming sulfuric acid or chlorosulfonic acid, the latter being a preferred reagent to obtain good quality products in good yield at low reaction temperatures.

$$ROH + Cl\,SO_3H \xrightarrow{0\text{-}30^\circ C.} RO - SO_3H + H\,Cl \nearrow$$

$$ROH + H_2\,SO_4 \xleftarrow[H_2O]{100\text{-}110^\circ C} \diagup$$

The alkyl sulfuric acid esters formed readily undergo hydrolysis in acid media as illustrated in the above equation. This hydrolysis step is the key used in the analysis of the sulfuric acid ester type syndets (American Oil Chemists' Society Official Method F2a-44).

Alkyl sulfates derived from the different sources mentioned above have different behavior characteristics upon acid hydrolysis, which may serve as qualitative evidence of their origin. Those sulfates derived from saturated normal alcohols undergo hydrolysis to regenerate the normal alcohols. The branched skeleton OXO alcohols are distinguishable from the straight chain alcohols by a difference of physical properties and by infra-red absorption spectra. In the other alkyl sulfates the sulfate radical is attached to a secondary carbon, and upon hydrolysis small amounts of olefin (about 5%) may result in the secondary alcohols produced. These products may be further characterized by the typical reactions of secondary alcohols, such as oxidation to ketones which may be identified by carbonyl number.

If the secondary alcohol has been prepared by an oxidation process, it will very probably contain glycols or keto alcohols of the same molecular weight or boiling range of the alcohols. Such products have been analyzed by silica gel adsorption and elution techniques. Two typical results on such alcohols show the following composition range:

Alcohol	68 wt. %	—	83 wt. %
Glycol	8 wt. %	—	17 wt. %
Keto-alcohol	9 wt. %	—	nil wt. %
Ketone	15 wt. %	—	nil wt. %

Boiling range—150-203°C @ 1mm Hg.
Molecular wt. range—270-314

The successive steps in the adsorption-elution sequence used in analyzing such mixtures are:

a) Fractionate by distillation at reduced pressure.
b) Adsorb on silica gel.
c) Elute (desorb) components successively, using:
  a. warm isohexane to remove paraffins as major constituent
  b. cool benzene to remove ketones as major constituent
  c. warm benzene to remove alcohols as major constituent
  d. warm methanol to remove poly functional molecules as major constituent.
d) Remove solvent from desorbed fractions and analyze for carbonyl and hydroxyl groups, using adaptations of published procedures of Bryant and Smith (4, 12).

Alkyl Aryl Sulfonates

A great variety of alkyl aromatic hydrocarbons have been used in the preparation of sulfonates. Of these the monoalkyl benzenes of 16 to 22 carbons have won the most widespread usage because of their combination of chemical stability, low cost, and outstanding performance. A variety of analyses is used to elucidate relationships between sulfonation stock composition and end-product performance. A typical commercial monoalkyl benzene sulfonation stock has these inspections:

Detergent Alkylate Specifications

Gravity (API)	29.5 - 31.5
Bromine No	0.2 Max.
Sulfur	0.05 Max.

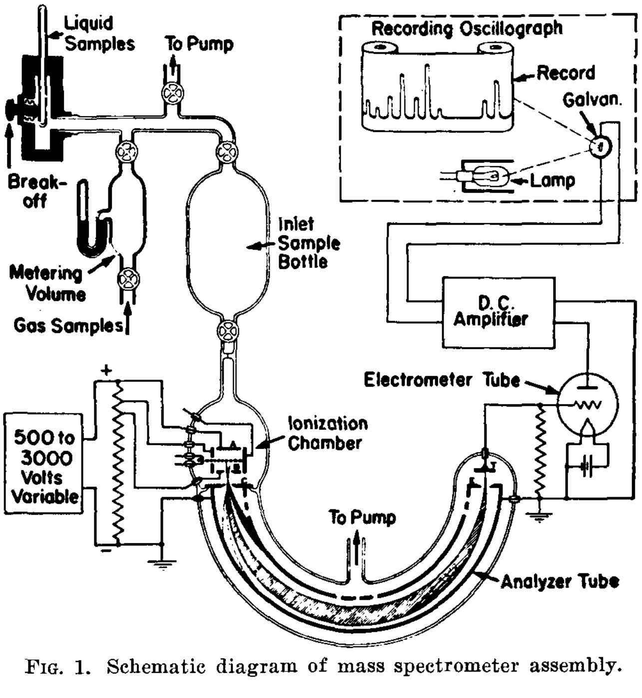


FIG. 1. Schematic diagram of mass spectrometer assembly.

I.B.P. °F. (ASTM)	490	Min.
5%	520	Min.
95%	600	Max.
Color (Saybolt)	+21	Min.
Flash, C.O.C.	220	Min.
Sulfonation Yield	98%	Min.

The analyst's best picture of composition and structure of such an alkyl benzene stock may be obtained by mass and infra-red spectrometry.

The mass spectrometer was brought into industrial usage for light hydrocarbon analyses as the last World War was getting under way. Since that time its use has been growing rapidly as new techniques have permitted application to analysis of increasingly complex and higher molecular weight hydrocarbons (3). A diagram of the principles involved in mass spectrometry is shown in Figure 1.

Samples are introduced to the mass spectrometer in vapor form via a metering device into a sample chamber held under reduced pressure. From this chamber the vapor molecules pass through a small orifice, termed a "molecular leak," into an ionization chamber held under very low pressure, about 10^{-5} mm. Hg. Here the molecules are bombarded with electrons emitted from a tungsten filament. Under this electron bombardment the molecules rupture according to characteristic patterns into charged particles. The positively charged particles then traverse a magnetic field which causes them to be deflected from a mean course in proportion to their mass before they collide with a target plate. These collisions cause current to flow in the target plate circuit, which is amplified and measured by a galvanometer. An ion-accelerating voltage is automatically varied so as to focus different successive mass particles on the target plate, and their relative abundance is then recorded on a photographic sheet. Interpretation of these records reveal molecular weight and structural configurations of the hydrocarbons. Complete structural information is currently limited to hydrocarbons below those found most frequently in synthetic detergent syntheses.

Typical m.s. analyses on detergent alkylates show a molecular weight distribution of alkyl groups as follows: 0-2% C_{10}, 12-28% C_{11}, 40-55% C_{12}, 15-20% C_{13}, and 3.5-4.5% others.

Continuing with the typical monoalkyl benzene, which is predominantly dodecyl benzene, the sulfonation reaction used in its conversion to a syndet is itself an important procedure.

$$C_{12}H_{25}C_6H_5 + H_2SO_4 \xrightarrow{0\text{-}68^\circ C.} C_{12}H_{25}C_6H_4SO_3H + H_2O$$

$$C_{12}H_{25}C_6H_4SO_3H + NaOH \longrightarrow C_{12}H_{25}C_6H_4SO_3Na + H_2O$$

The sulfonation is carried out by adding, over a period of 20 to 25 minutes, 24 ml. (60 vol. %) 20% fuming acid to a weighed 60 ml. portion of detergent alkylate with good agitation, and temperature controlled at 38°C. (100°F.). Stirring is continued to a total sulfonation time of one hour. In commercial sulfonation procedures less acid is used with longer reaction times to achieve maximum efficiency. Greater quantities of acid assure complete sulfonation in a short time, which is very desirable to the analyst. The sulfonation mixture is neutralized over dilute caustic and chipped ice and diluted with methanol to hold the entire neutralized sulfonate mixture in solution as it is cooled to room temperature.

The alcohol-water sulfonate solution containing about 15 wt. % solids may then be separated into a) unsulfonated oil, b) alkyl aryl sulfonate, and c) sodium sulfate by methods used in ASTM Procedure D-820-46. An aliquot of the alcohol-water solution is extracted with petroleum ether, and the ether washes are evaporated to yield residual unsulfonated oil. For good accuracy this oil residue is ashed and corrected for sulfonate content.

Another aliquot is evaporated to dryness, the dry product is dissolved in hot 95% ethanol to complete disintegration, and then the alcohol-soluble portion is filtered from the insoluble sodium sulfate, which is determined as dried residue. The alcohol soluble, upon drying, is weighed and ashed, using either sulfuric acid or peroxide to yield a sodium sulfate ash.

$$2\ Na\ SO_3C_6H_4\ C_{12}H_{25} + Air \xrightarrow[\Delta H]{H_2SO_4} Na_2\ SO_4 + CO_2 + H_2O$$

A typical sulfonation product processed and assayed as described would be found to contain:

Oil—0.6 wt. % (1.5 wt. % oil charged)
Alkylaryl sulfonate—50.6 wt. % (98.3 wt. % theoretical)
Sodium sulfate—48.8 wt. %

To answer the need of the plant product control analysts for simpler and quicker tests, a para-toluidine hydrochloride (P.T.H.) volumetric method for determining the sulfonates (8) has been developed and widely accepted. This test can be run on an aliquot of the alcohol-water-sulfonation solution resulting from the above alkane evaluation procedure. However it is limited to use on sulfonates of known molecular weight; hence gravimetric data as described above are necessary for use of the P.T.H. method. In this method the reaction of para-toluidine hydrochloride is used as shown by equation (8):

$$R\text{-}C_6H_4 - SO_3Na + CH_3C_6H_4\text{-}NH_2\text{-}HCl \longrightarrow R\text{-}C_6H_4\text{-}SO_3H\text{-}NH_2\text{-}C_6H_4\text{-}CH_3 + NaCl$$

The P.T.H.-sulfonate addition product is extracted in carbon tetrachloride or tetrachloroethane, and then this extract is titrated with dilute alkali to quantitatively determine sulfonate.

Another test of the same principle, using benzidine hydrochloride, has been used successfully with sulfonates of the Igepon variety, isothionic acid salts, or tourine condensation products with oleic acid (11).

Fatty Acid Derivatives

The number of syndet-type materials which have been prepared from fatty acids run into the hundreds, most of them resulting from the early work of German scientists in this field. Of these a great number fall into a class which are capable of hydrolysis to free fatty acid. Three of these which have achieved renown will serve to illustrate further the diversity of products with which the syndet analyst must cope:

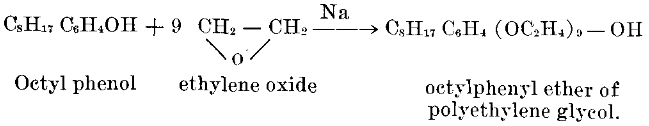
a) Salts of sulfated coconut oil fatty acid monoglycerides.
b) Oleylamide ethyl sulfonate (oleic acid, tourine condensation product)
c) Oleic acid, alkanol amine condensation products.

Analysis of these products would first involve separation of free acid or fatty matter contaminants by petroleum ether washing an alcohol-water solution of the syndet. Refluxing with dilute mineral acid would free the respective fatty acids, which would extract with petroleum ether and be identified by acid number, bromine number, and melting or boiling points. The aqueous solutions following hydrolysis would contain in the above three cases a) glycerine and sulfuric acid, b) amine ethyl sulfonic acid, and c) alkanol amines or condensation products of the alkanol amines, which would permit their separation and identification. Greater detail for these steps of the analysis is suggested in a more comprehensive syndet anaylsis scheme described later.

The syndets we have discussed thus far have been salts of strong bases, the most usual base being sodium hydroxide. The sodium salts of the anionic syndets are of relatively low solubility in water and may usually be further reduced in solubility by the addition of inorganic salts. Where concentrated liquid detergents are desired, such as in dishwashing, shampoo, and bubble bath agents, salts of organic bases such as ammonia, alkyl, and alkanol amines, have been successfully used. These products are capable of titration with alkali followed by distillation and identification of the volatile bases.

Non-ionics

The most important remaining group of syndets are the poly alkene-oxy ethers, thioethers, and esters which are usually prepared by reaction of an appropriate stem hydrocarbon (alcohol, mercaptan, or carboxylic acid, all of which contain an active hydrogen in a functional group) with an olefin oxide, such as ethylene oxide. A good exemplary reaction is that shown in equation 5, where the stem hydrocarbon is octyl phenol and about nine etheneoxy groups are required to give the molecule the proper hydrophobe-hydrophyll balance for good performance characteristics.


$$C_8H_{17}\,C_6H_4OH + 9\ \underset{\diagdown O \diagup}{CH_2 - CH_2} \xrightarrow{Na} C_8H_{17}\,C_6H_4\,(OC_2H_4)_9 - OH$$

Other stem hydrocarbons which have been used to produce good quality syndets include aliphatic alcohols, (10 to 18 carbons), aliphatic mercaptans (dodecyl mercaptan), and carboxylic acids. Of these the reaction products of the aliphatic alcohols and phenols are difficult of analysis by chemical reactivity. Here infra-red spectroscopy can be very helpful in characterizing detergent components. Polyetheneoxy derivatives of the carboxylic acids are capable of hydrolysis and identification by the usual tests on the separated acids. Thiols derived from branched olefins, such as triisobutylene, have been condensed with ethylene oxide to form non-ionic syndets of good quality but, when subjected to acid hydrolysis, they quantitatively split back to the original branched chain olefin. Other olefin oxides may add variance to non-ionic structures, but the only one which is known to have practical use is propylene oxide. For optimum preparations it is understood to be used in conjunction with ethylene oxide. The optimum number of alkeneoxy groups in each product is of course dependent upon the oxide and stem hydrocarbon structures. Usually an average of eight to 15 alkeneoxy groups are found per molecule. In the usual initial stages of syndet analysis small fractions of a non-ionic prepared from a broad molecular weight range mixture of stem hydrocarbons will usually be found in the petroleum ether soluble fraction. Subsequent inspection usually reveals this fraction to contain the higher molecular weight components of the parent compound, containing a deficiency of alkeneoxy groups for good alcohol and water solubility.

The non-ionics have a number of characteristics which are at once helpful in their qualitative detection: they are fluid in concentrated form (a very few are soft pastes or waxy solids having relatively low melting points); and they have inverse solubility characteristics, i.e., their solubility in water decreases with increasing temperature.

The analyst must note in discussing the non-ionic detergents that their terminal hydroxyl groups may be determined and serve as a convenient characterization reaction from which molecular weights may be deduced. Further the alkeneoxy condensation products containing these hydroxyl groups may be sulfated to form an analogous line of anionic detergents. Such products are usually made to contain fewer alkeneoxy groups than their non-ionic cousins.

Package Detergents

With this necessarily limited consideration of the most commonly encountered syndets and with due apologies for the dozens of other variant products not as yet discussed, let us consider the package products with which the detergent analysts have to cope. The syndets discussed above may appear on the market in retail packages, either alone or in carefully formulated mixtures designed for specific cleaning applications. The one certainty upon which the analyst can count in viewing the diverse products of the highly competitive and intense advertising detergent industry is that no formula introduced can be expected to remain unchanged for any great length of time. A representative list of applications for which specific formulas are designed include: laundering of cotton, laundering of wool, silk, and synthetics; dishwashing; car-washing; abrasive and non-abrasive household cleaners, and the toilet products, bars, shampoos, and bubble baths.

Only a few formulas are required to illustrate the variety of ingredients in addition to the syndets which may be introduced to serve these applications.

Liquid detergents are usually water or water-alcohol solutions of syndets which may vary widely in solids (non-volatile ingredient) concentration with but little difference in appearance or viscosity.

a)	Non-ionic Syndet	20-100 wt. %
	Water	80-0%
b)	Anionic Syndet	10-25 wt. %
	Non-ionic Syndet	10-25
	Alcohol	0-10
	Water	80-40
c)	Anionic Syndet	15 to 70 wt. %
	Alcohol	0-20 wt.
	Water	85-20

The dry products, usually spray-dried into dust-free and readily soluble beads, may be designed for light duty or mild detergent jobs: wool, silk, and synthetic fabric laundering, dishwashing, and car-washing, or for heavy duty detergent jobs: cotton laundering and washing greasy surfaces.

d)	Syndet	35 –40	wt. %
	Neutral salts	65 –60	wt. %
e)	Syndet	20 –35	wt. %
	Sodium tripoly phosphate	5 –10	wt. %
	Fluorescent dye	0 – 0.5	wt. %
	Neutral salts	75 –55	wt. %

f) Syndet	20 –40 wt. %
Sodium tripoly phosphate	25 –50 wt. %
Carboxymethyl cellulose	1 – 4 wt. %
Sodium silicate	0 –10 wt. %
Sodium sulfate	49 – 2 wt. %
Fluorescent dye	0.02–0.1 wt. %

Other dry products include the abrasive cleansers and bar soaps (6).

g) Syndet	5–20 wt. %
Polyphosphate	0–25 wt. %
Neutral salts	25– 0 wt. %
Talc or silica	95–40 wt. %

h) Syndet	52 wt. %
Lecithin	18 wt. %
Corn starch	15 wt. %
Talc	15 wt. %

Many potential variations of these formulas include combinations of fatty acid soaps with different syndets and synergistic combinations of different syndets. Fortunately for the analyst, practical considerations tend to limit the number of different materials which are used in combination in any one formula.

In addition to these principal components which are amenable to analysis by established procedures, one variety or another of modifying agent is usually present in most formulas. These materials and the extent of their occurrence may be: 1 to 5% heavy alcohols as odorant and foam extenders in sulfation products, 0 to 5% fatty acid amides or organic base salts (detergency builders), and traces of perfume oils or odor masking agents, stabilizers (antioxidants), dyes or color agents, and antibiotic agents in antiseptic cleaners.

The presence of these components may be evidenced qualitatively by appearance and odor or in performance tests (storage stability, bactericidal performance, etc.).

General Test Methods

An established approach to analysis of packaged detergents is found in ASTM D 820-46 procedure entitled "Method of Analysis for Soaps Containing Synthetic Detergents."

This method serves reasonably well to separate away water insolubles (abrasives); water soluble but alcohol insolubles (inorganic salts exclusive of sodium chloride); fatty matter, oils, and fatty acid soaps; and syndets (alcohol-water soluble, petroleum ether insoluble). However it requires a great deal of supplementation to portray accurately the compositions of today's packaged products.

Of the components in the exemplary formulas shown above the alcohol-soluble portion would contain the syndets, carboxymethyl-cellulose, most of the lecithin, and sodium chloride. The presence of lecithin, starch, substituted celluloses, and like bodying materials may be indicated by the physical form and behavior characteristics of the product in question and thus suitable steps would be invoked for their identification. As in all analytical work, whether using quantitative reactions and separations or dealing with spectroscopic or other physical properties, a large amount of background information on individual components and mixtures of products is essential to accurate analyses.

Elemental analyses have been successfully applied to the analysis of syndets. While requiring extreme attention to detail and very efficient organization of procedures to achieve results in reasonable time, such methods are capable of giving absolute results. An elemental scheme of analysis is described in the German literature by Wurzschmitt (13). His subdivision of syndets into classes according to functional groups and elemental analyses is shown in Table I. While his subdivisions do not cover all syndets which are described in the literature (10), all are possible of analysis by this method. Great reliance is placed in the accuracy of micro methods for C,H,N,O, and sulfur, using adaptations of the methods of Pregl, Zimmerman, and Schutze. A simplified outline illustrates the steps involved in distinguishing the different classes of syndets.

TABLE I
Syndet Classification According to Functional Groups and Elemental Analyses

Elements	Constituents
(I) C,H,O	Ethylene oxide addition products of fatty acids, fatty alcohols, alkyl phenols, naphthols
(II) C,H,O,N	Ethylene oxide addition products of fatty acid amides
(III) C,H,O,N	Condensation products of fatty acids with ethanolamine (amide or ester)
(IV) C,H,O,H,Na	........with aminocarboxylic acid (protein decomp'n product)
(V) C,H,O,S,Na	........with sulfonic acid or aliphatic alcohol
(VI) C,H,O,S,N,Na	........with sulfonic acid of aliphatic amines
(VII) C,H,O,N	........with urea or guanidine derivatives
(VIII) C,H,O,N	........with diamines or their salts (acid soaps)
(IX) C,H,O.N,Cl	Quaternary ammonium bases
(X) C,H,O,S,Na	Salts of sulfonic acid of aliphatic or aliphatic-aromatic hydrocarbons
(XI) C,H,S,O,Na	Salts of sulfonated carboxylic acids
(XII) C,H,O,S,Na	Fatty alcohol sulfates
(XIII)—1, C,H,O,S,Na	Sulfates of I,
(XIII)—2, C,H,O,N,S,Na	Sulfates of II, and
(XIII)—3, C,H,O,N,S,Na	Sulfates of III

Plan of Wurzschmitt for Elemental Analysis of Syndets

Unknown
↓
Purify
↓
Elemental Analysis

a) C,H and O are found, Class I
  1. Esters are saponified and acids determined.
  2. Alcohols are disclosed by hydroxyl number.
  3. Ethers are disclosed by oxygen balance difference.
  4. Aliphatic ethers are converted to acids by oxidation cracking with nitric acid.
  5. Molecular weights and complexity from elemental balance sheet.

b) All sulfur containing compounds free of nitrogen, Classes V, X, XI, XII, XIII.
  1. Reflux with dilute inorganic acid, separate organic portion split out and subject to analysis as in *a)*.
  2. H_2SO_4 splits from Classes XII and XIII.
  3. Isothionic acid splits from V.
  4. Unsaponifiable Classes X and XI are identified by S: Na: O ratios, supplemented by alkali fusion and ashing tests.

c) All nitrogen containing compounds, Classes II, III, IV, VI, VII, VIII, and IX.
  1. High oxygen content indicates Class II, confirm by saponification, titres, and C,H,O,N balances.
  2. High nitrogen indicates Class VII, the organic matter separated upon acidification consists of fatty acids.
  3. N:Cl ratio of 1:1 indicates Class IX. Fused alkali splits tertiary amine; Zeisal's method splits alkyl amines which may be determined by HI reduction.

4. Compounds of Class IV can be present only as ammonia or amine salts which split out fatty acids upon digestion with dilute acid.
5. Nitrogen bases may be separated in general by distillation over alkali.

   Primary amine is identified by Van Slyke's method, treating with nitrite in acid media and volumetrically determining N_2.

   Primary and secondary amines are determined by acetylation.

   Aromatic amines may be identified by diazotizing and coupling.

   Aromatic NH groups undergo nitrosation.
6. Nitrogen groups can further be identified by perchloric acid titration in anhydrous acetic acid, using crystal violet, naphthol-benzoin and cresol red as indicators (9), these latter two groups of tests serving to identify Classes III, VI, and VIII.

A colorimetric method for the determination of carboxymethyl-cellulose in household detergents has been described in which color developed by an anthrone-cellulosic complex is utilized (2).

Spectral analyses are being used to an ever increasing extent to identify unknown products and may be used to particular advantage in the analysis of detergents. Ultra-violet and/or infra-red spectra show different functional groups and combinations thereof to have characteristic light absorption patterns which may be used to advantage in obtaining both qualitative and quantitative information. Crystalline components show characteristic x-ray diffraction patterns that greatly simplify their analysis. Metal cations may be qualitatively determined by emission spectra resulting from combustion of a sample in a standard electric arc.

The popular heavy duty household detergent formulas in widespread use today serve as good examples of how spectrometry may be used in detergent analysis. A typical formula representative of (f) above was analyzed by ultra-violet and x-ray spectroscopy, supplemented by a chemical method for CMC, to determine the weight composition as follows:

	Made (%)	Found (%)	Method
Alkyl aryl sulfonate (360 mol. wt.)	28	29.5	u.v.
Carboxy methyl cellulose	3	2.5	Chem.
Optical bleach	0.04	0.03	u.v.
Sodium tripoly phosphate	40	39	x-ray
Sodium silicate	10	9.5	x-ray
Sodium sulfate	19.0	19.5	by diff.

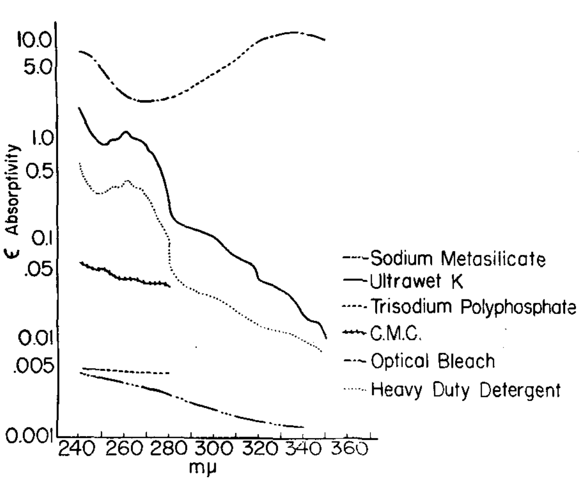
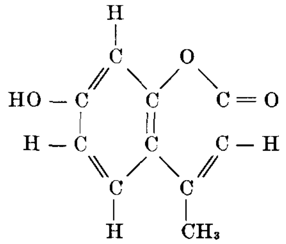


FIG. 2. Ultraviolet absorption patterns for a heavy duty detergent and components.

The ultra-violet (u.v.) absorption spectra for the individual components in the formula which absorb significantly are shown in Figure 2 along with the absorption spectra of the formula itself. The high relative absorptivity at 335 mμ of the optical bleaches, which are compounds of the general type of beta-methyl umbelliferone,



make it detectable in the u.v. spectra even when used in very low concentration. Likewise an alkylaryl sulfonate (Ultrawet K) has strong absorption in the vicinity of 260 mμ. Corrections must be made for absorptivity of other components at these respective wavelengths. In like manner x-ray diffraction spectra may accurately show sodium tripoly phosphate and sodium silicate.

It is important to note that x-ray spectrometry is capable of distinguishing the different phosphates, a fact which is very necessary in present day detergent formulation. Sodium tripoly phosphate ($Na_5P_3O_{10}$) and sodium tetra pyrophosphate ($Na_4P_2O_7$) have been of greatest interest in the formulation of detergents, and their determination as Na_2O and P_2O_5 equivalents by older methods is inadequate. The different forms of sodium tripolyphosphate, phase I and phase II anhydrides and hexahydrate, may be distinguished by x-ray methods (7).

Syndet Residues

A discussion of synthetic detergent analyses cannot be closed without mention of analytical problems which arise in connection with the use of products or materials which have been washed with the syndets and other problems relating to the disposition of detergent wastes.

Tests have been devised to detect trace quantities of syndet residues on washed products, for example, fruits and vegetables washed in canning factories. A colorimetric test for sulfonates, for example, based on their reaction with methylene blue to form colored salts, is applicable down to concentrations of 0.1 ppm of sulfonate (1, 5).

In solving other residue problems or tracing syndets in waste disposal, use may be made of products containing tagged atoms, radioactive C, S, or Na, etc. Such techniques are new, and little work in this field has as yet been published (14).

In summary, it may be stated that much good analytical work has gone into the development of syndets. Qualitative physical characteristics, reactions typical of functional groups, elemental analyses, and spectrometry techniques provide the means for the analytical technologist to keep pace with new product developments.

The work of many colleagues on the staff of the Research and Development Department of the Atlantic Refining Company has been of assistance in the preparation of this paper. The cooperation of these people is gratefully acknowledged.

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Detergency Evaluation

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IN setting out to evaluate detergents certain decisions will perhaps already have been reached, probably on the basis of the field of application involved. If it is one of flat surfaces, as in metal cleaning, dish washing, or floor maintenance, then some one type of experimental equipment will have been decided upon. If it is a problem in the dry cleaning of garments, a different approach will be required. In the textile line the decision may depend upon the stage in processing of the fiber or fabric chosen, and certainly will depend upon what fiber is involved. If laundering of garments is the problem, this may arbitrarily be divided into commercial and home laundering phases.

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Decisions will necessarily be made concerning the following factors: Surface (fiber or hard surface), soil encountered and standard soil for laboratory evaluation, test machine, test method, evaluation of test pieces, and evaluation of data.

Hard Surface Cleaning

Probably the greatest volume of work on hard surfaces has been reported for metal cleaning. This work has not yet been standardized, but ASTM Committee D-12 has suggested a procedure which can be very helpful (1). A thorough survey of this general field is available (2).

The early work on cleaning painted surfaces resulted in a Bureau of Ships Specification 51S46 (3) and Federal Specification P-C-431 (4). Recent work using the apparatus described (Figure 1) has indicated its considerable utility (5).

Work on asphalt tile cleaning is represented by the work done by Trusler in furthering committee work for the Chemical Specialties Manufacturers' Association (6).

Glass washing has been the subject of considerable investigation, the most recent being that of Mann and Ruchhoft (7, 8). Here an especially designed machine was used in the evaluation of detergents.

All of the foregoing methods possess the same general characteristics of requiring a selection of those elements listed above, not the least of which is the standard soil chosen for investigation.

These fields have perhaps received less investigational effort, and perhaps represent a smaller tonnage outlet for detergents than the textile field, and reference should be made to the individual papers given in the bibliography.

Textile Operations

Much effort has been given to the evaluation of detergents for textile purposes. The American Association of Textile Chemists and Colorists has been foremost in promoting investigation of this field. Under its auspices the Detergent Comparator has been developed for the evaluation of detergents used for wool, in knitted tubular form (9), in a manner similar to mill scouring conditions. Leonard and coworkers (10, 11) have developed a laboratory method for continuous scouring of grease (raw) wool which has also been the subject of investigation by a special committee of AATCC. This latter method closely approximates the results obtained in a mill for the scouring of raw wool. Reference should be made to the original papers and to the 1951 AATCC Technical Manual and Yearbook for a discussion of the soils and methods used.

Many papers have been published on dry cleaning detergency. The most pertinent are those written by Fulton (12) of the National Institute of Cleaning and Dyeing. Standardization work on evaluation has been attempted by ASTM Committee D-12, but no satisfactory laboratory evaluation method has as yet been developed.

Garment Cleaning

Probably the greatest single market for detergents is for the wet cleaning of wearing apparel, so entitled to distinguish it from textile mill operations and dry cleaning.

Aside from garments which must be dry cleaned, there are two arbitrary classes of garments which can be wet-cleaned. Those are represented by wool and wool-like fabrics and cotton (or cellulosic) fabrics. Different detergents and washing methods are indicated for these two classifications while a further breakdown may be made as to whether the garments are to be washed in the home, by hand or machine, or in commercial power laundries.

Power Laundries. Experimental work in power laundering may be carried out initially in pony wheels (as low as 25-pound dry-weight loads) but should be verified in commercial size wheels. Frequently the small-wheel work is dispensed with entirely, and investigation carried out on large scale wheels.

The American Institute of Laundering has for years been the leader in the standardization of equip-