The Analysis of Soaps

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IN considering the analysis of soaps, one naturally wonders first why analysis is necessary at all. The average customer is not interested in the analysis, in fact has little or no idea of soap composition, so the question naturally arises why not control quality by physical performance tests. The facts are that the validity, reliability, and sensitivity of tests for sudsing and detergency are so low that the tests are unsuited for control, thus making chemical analysis necessary. It is also necessary to check the composition when soap is made to a certain chemical specification. Rubber Reserve soap is an example of such a soap.

R. C. Stillman

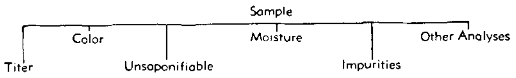
Let us review the repertoire of the analytical chemist in the soap field; no attempt will be made to detail any of the analytical steps involved in the determination of any of the constituents of soap, glycerine, or their raw materials. Such details are abundantly available in many places, the foremost of which is the Official and Tentative Methods of the American Oil Chemists' Society. Many textbooks, for example, "Soaps and Detergents" by Thomasen and McCutcheon or "Oils, Fats, and Soap" by Benjamin Levitt have chapters on analysis, setting forth the details of weights, procedures, and calculations. Methods were well worked out as long as 50 years ago, many have changed but little although new techniques and procedures have been incorporated. All of these are available without search to those of you interested in the precise details of any determination.

The Analytical Picture

All analyses start with the sampling of the product to be analyzed. This side of the picture cannot be over-emphasized. Too frequently complaints of poor analyses are received in the laboratory only to be traced, after hours of analytical time have been spent, to a poor sample, representing a short-cut in the designated sampling procedure. Sampling instructions are part of the Official Methods of the American Oil Chemists' Society and the rules of the National Cottonseed Products and National Soybean Processors Associations. Where rules for buying and selling are laid down, sampling is not forgotten. In factory control operations frequently the methods of analysis and the sampling instructions are in different hands. A wise course of action demands that those specifying the analyses to be used at least see and agree to the sampling conditions outlined. Many errors are thereby avoided. A sample worth analyzing needs to be obtained as carefully as possible, keeping in mind the precision required in the results obtained. Normally a system which cannot be sampled with certainty needs no analysis. In general, when product limits are not met, look at sampling techniques and laboratory techniques at the same time. The question arises shall there be a reanalysis or a resample; the consideration of one requires the consideration of the other.

And now to the actual analyses themselves: In the following diagrams we have shown the schematic analysis of soap and related materials. In the first diagram is given the "Incoming Fat Analyses"; in the second, "Chemical Analysis on Soap"; in the third, "Glycerine Manufacturing Analyses"; and in the fourth, "Finished Product Analyses." The general principles involved are set forth, but no details are given.

INCOMING FAT ANALYSES



Titer is partly a hangover from bar soap days. It enables the firmness of the bar to be controlled. However low titer means high iodine value and therefore has value in predicting the stability of the soap toward rancidity. Color is obvious. Light fats make white soap. Unsap. cannot be made into soap and acts as a load in detergency. Some companies base premiums and discounts used in fat purchasing on unsap. content. Moisture and impurities are diluents and are troublesome. Other determinations such as iodine value, sap. value, etc., are run to enable fats to be blended to the desired characteristics.

Test Methods

Titer. The fat is saponified with glycerol potash, split with acid, and the dried fatty acids obtained. The titer is the maximum temperature reached when the fatty acids are cooled and allowed to crystallize under controlled conditions.

Color. Two systems are in wide use, Lovibond Colors and FAC Colors. The first method is widely used in fat processing, and color values are obtained by matching the melted fat with yellow and red glasses in a suitable viewing colorimeter. The FAC Color numbers are obtained by comparing the melted fat against numbered tubes containing colored solutions. Neither method is satisfactory but are rough measures of the oil color.

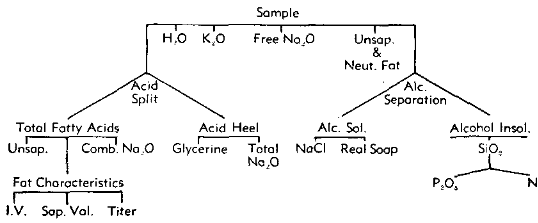
Unsaponifiable. The sample is saponified with alcoholic KOH, diluted with water, and the unsaponifiable material extracted with petroleum ether from a 50% alcohol solution. The extracted material is dried and weighed.

Moisture. Normally the hot plate method is used. A weighed portion of the fat is placed in a moisture dish, heated to 130°C. with swirling over a hot plate, and the loss in weight determined.

Impurities. A weighed sample is dissolved in hot kerosene and the insoluble material separated on a weighed Gooch crucible. The insoluble matter washed with petroleum ether is dried and weighed.

Other Analyses. Iodine value, saponification value, free fatty acid, etc., may be desired and are frequently run.

CHEMICAL ANALYSIS ON SOAP



Moisture in different forms of soap has different effects. It is necessary to control it at the level desired in the product being made. Potash, when used, needs to be controlled for softness. Free Na_2O—a ridiculous term—means uncombined NaOH; obviously to be kept low. Unsap. and neutral fat—the neutral fat is glycerine lost and is undesirable for other reasons. Glycerine is a money loss. NaCl is a useful measure of the carefulness of the kettle boil. Real soap is the active ingredient and in most cases must be known. The builders, carbonate, phosphate, and silicate, have their functions and need to be controlled at the desirable level for each.

Moisture. Oven, toluene, or Fischer.

Potash. Potassium is determined by precipitation as the chloroplatinate or as the periodate or by use of the flame photometer.

Free Na_2O. Sample is dissolved in alcohol and titrated to phenolphthalein with standard acid.

Unsaponifiable. The saponified sample is dissolved in 50-50 alcohol-water and extracted with petroleum ether. The extract corrected for fatty acid is freed of solvent and weighed.

Neutral Fat. Normally determined by extraction with petroleum ether without prior saponification. Will in general need to be corrected for unsaponifiable material.

Total Fatty Acid. The saponified sample is acidulated and the total fatty acid extracted with ether and weighed.

Combined Na_2O. The weighed total fatty acids are titrated in alcohol with standard alkali.

Iodine Value. Normally the Wijs method is used. The fatty acids are treated with an iodine-chlorine mixture in glacial acetic acid and the unabsorbed iodine titrated with thiosulfate. Iodine value equals the percent iodine absorbed.

Saponification Value. The fatty acids are saponified with standard alcoholic KOH and the excess KOH determined by titration with standard acid. Saponification value equals the milligrams of KOH required to saponify completely one gram of sample.

Titer. The fatty acids are split out, carefully dried, and placed in a titer tube. The melted acids are cooled to incipient crystallization, and as they crystallize, the maximum temperature reached is measured by a thermometer and recorded as the titer.

Glycerine. The sample is split with acid, and glycerine is determined in the acid seat by oxidation with potassium dichromate or by oxidation with periodate.

Total Na_2O. The sample is split with standard acid and the acid seat back titrated with standard alkali.

Alcohol Soluble, Insoluble. Separation of builders from active detergent is accomplished by the use of alcohol. NaCl will be found wholly or partially in the alcohol soluble.

NaCl. Normally determined by titration with silver nitrate, using potassium chromate as an indicator.

Real Soap. Can be determined as alcohol soluble minus sodium chloride or by determining the total fatty acids, titrating the TFA to obtain combined Na_2O and calculating the soap. The soda soap modification is necessary for coconut and other low molecular weight soaps.

Total Builders. Alcohol insoluble plus NaCl.

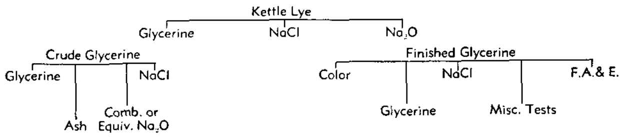
SiO_2. Dehydration of the alcohol insoluble with HCl followed by removal of SiO_2, ashing, and weighing.

P_2O_5. The filtrate from the SiO_2 determination is boiled with HNO_3, phosphate precipitated with ammonium molybdate. The precipitate is washed and titrated with NaOH.

Na_2SO_4. Sulfate is precipitated as $BaSO_4$, filtered off, ignited, and weighed.

Na_2CO_3. Normally carbonate is obtained by evolution. The sample is acidified and the liberated CO_2, freed from water, is absorbed on ascarite and weighed, or absorbed in caustic and excess caustic titrated.

GLYCERINE MANUFACTURING ANALYSES



On crude glycerine the determinations are of impurities. The combined or equivalent Na_2O is somewhat misleading for, if the organic acids are calculated as caproic, the organic acids are 4 times the Na_2O. On finished glycerine the tests are those needed to meet the U.S.P. requirements or those of various dynamite manufacturers.

Glycerine. Glycerine is usually determined by oxidation with potassium dichromate, but the periodate method is specific for glycerine and therefore preferred in many instances. In the periodate test one molecule of formic acid is developed for each glycerine molecule oxidized and is titrated with standard alkali. All oxidizable material shows as glycreine by the dichromate method. Finished glycerine (C.P. or equivalent) is frequently analyzed for purity by determining the specific gravity using a picnometer. Very precise tables for converting gravity to % glycerine are available.

NaCl. Normally determined by direct titration with $AgNO_3$.

Na_2O. Directly determined by titration with standard acid.

Ash. The sample is ashed under controlled conditions and the residue weighed. In some instances the ash is converted to sulfates before weighing.

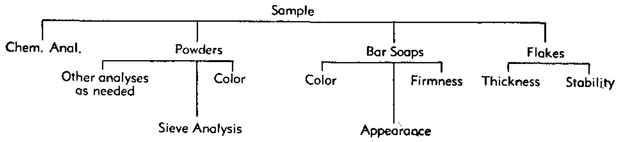
Combined Na_2O. Normally the sample is ashed and the alkalinity of the ash determined. Corrections are made for free and carbonate alkalinity.

Color. The color of finished glycerine is obtained by comparison against standards in long Nessler type tubes. The U.S.P. standard is a dilute ferric chloride solution.

F. A. & E. The fatty acid and ester content of a sample is expressed in terms of the ml. of alkali consumed in an aqueous saponification at steam bath temperatures.

Other Tests. Many other tests are applied to finished glycerine. These tests which include sugar, aldehydes, heavy metals, odor, chlorides, etc., are varied to meet the needs and specifications of the consumer.

FINISHED PRODUCT ANALYSES



The finished product tests are mostly of a physical nature to assure ourselves that the products look, feel, and behave properly.

Chemical Analyses. See previous diagram.

Sieve. Shaking machine with desired screens.

Color. Gradings are made visually or using a reflectometer.

Firmness. Firmness tester or other mechanical device.

Appearance. Visual grading, applies to flakes and powders as well.

Thickness. Thickness tester, such as standard thickness gauge.

Stability. Peroxide No. is sometimes used. Iodine is liberated and titrated with $Na_2S_2O_3$. Also used on soaps including bars and powders.

The Laboratory Set-Up Picture

There are many important items to be considered in a general discussion of the control laboratory and the work carried out therein. None are as important as the laboratory staff and the analysts themselves. Each individual from top to bottom must be trustworthy and earnest in his endeavors. One false link in the chain of dependability can ruin an otherwise well-oiled machine. The higher up the weak link, the less sure the entire structure and an uninterested, careless worker as a foreman results in a situation wherein the factory is worse off than with no controls at all. One must not forget that the laboratory is a part of production itself, a control and service part, measuring and controlling the flow of raw materials and products from the moment they enter the plant until the final product is packed and ready to be delivered to the consumer who has every right to believe that the product as received meets the implied warranty of the brand name carried on the package. A false result anywhere along the line hits both the factory management and the consumer below the belt. For reliability of results, integrity of the analysts, call it what you will, there is no substitute.

Second to reliability of the workers comes adequate training of the analysts. Not only must the training be thorough, but it must be sure. Too frequently an analyst is trained for a short time by his predecessor and shortly left to shift for himself. Perhaps the man leaving the job has relied upon his notes and his memory to teach the new analyst not only his job but his own errors and sloppy procedures. Seldom is it advisable to allow a man to learn from the man whose job he is taking. Especially is it true when the teacher is leaving the organization. A training job must be planned. A new man coming into the laboratory given faulty information is as handicapped as when given a faulty burette or an incorrect calculation which he is incompetent to correct himself. Correct equipment, correct knowledge of the methods, and correct manipulative instructions are the proper tools with which to begin his job. Failure to provide these tools may start him on a road where many hours of corrective instruction will be needed while the analyst himself suffers needlessly in his contribution to the laboratory and in dollars in his pay check.

The educational level of any laboratory is important, but the degree of formal education previously obtained by the analyst plays an insignificant role along-side the integrity of the analyst and the training actually given on the job. It goes without saying that the higher the level of formal training, the less training required on the job, the easier the task of supervision, and the less the number of errors that will occur. In general, high school graduates make good analysts. One or two years of college work makes better analysts.

The laboratory itself is important, even though not as important as the people in it. The location should be such that the flow of samples from the plant is easy and requires as little interference from plant personnel as possible. The flow of samples through the laboratory should be planned, orderly, and logical. Samples for moisture, color, etc., should be handled quickly and with care against overheating, exposure to light, etc. The laboratory itself should be well lighted and well planned to avoid job interference. Equipment should be adequate and kept clean and in good repair. The production of a disorderly laboratory is confusion, poor results, poor records, misplaced samples, mixed-up samples, miscalculations, and poor control. Good planning provides 135 to 140 square feet of working space for each man working on a given shift, provides adequate protection for safety at all times, and makes each job a self-contained unit with chemicals, equipment, and samples readily available.

What about equipment? A burette or a pipette is as important to an analyst as a rule to a carpenter. The analyst cannot do good work with a faulty burette nor a carpenter with non-linear rule. A poorly standardized caustic solution gives results only as good as the standardization itself. Hence a standards job is a must, and the standards man as good as can be picked from those available. In many companies the standardization of equipment such as burettes, pipettes, thermometers, hydrometers, etc., is handled in a central location and all laboratories' requisition equipment already tested. Such a procedure is to be recommended. To each laboratory still falls the job of making sure that the equipment remains in standards, and a careful check program falls upon the standards analyst. In a like manner restandardization of solutions, instruments, etc., must follow a well worked-out plan. The kind and nature of the equipment used is dictated by the determination to be made. The equipment should be reliable and adequate.

How can a laboratory foreman know that the results his laboratory obtained are correct? There are two good ways, both of which are widely employed: the analysis of standard samples and participation in a cooperative check program. The American Oil Chemists' Society furnishes certain standard samples and conducts a checking program under the auspices of the Smalley Committee. The scope of samples handled by the committee is extremely limited. Most companies have in addition their own standard samples and their own cooperative checking programs. Some standard samples are analyzed carefully by experts and extremely exact values assigned to the desired constituents. The Bureau of Standards will furnish many such standards. Other samples need no 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