3. A.S.T.M. Standards on Petroleum Products and Lubricants, p. 320, Comm. D-2, American Society for Testing Materials, Philadelphia, Pa., 1951.
4. Barber, A., Chinnick, C. C. T., and Lincoln, P. A., Analyst, *81*, 18 (1956).
5. Barr, T., Oliver, J., and Stubbings, W. V., J. Soc. Chem. Ind., *67*, 45 (1948).
6. Bergeron, J., Bull. Mens. ITERG, *4*, 118 (1950).
7. Berkowitz, D., and Bernstein, R., Ind., Eng. Chem., Anal. Ed., *16*, 239 (1944).
8. Brauns, F. E., Hlava, J. B., and Seiler, H., Anal. Chem., *26*, 607 (1954).
9. Brooks, F. R., Peters, E. D., and Lykken, L., Ind. Eng. Chem., Anal Ed., *18*, 544 (1946).
10. Brown, E. G., and Hayes, T. J., Analyst, *80*, 755 (1955).
11. Carkhuff, E. D., and Boyd, W. F., J. Am. Pharm. Assoc., *43*, 240 (1954).
12. Caswell, R. L., J. Assoc. Offic. Agr. Chemists, *38*, 304 (1955).
13. Caswell, R. L., *ibid.*, *34*, 675 (1951).
14. Chinnick, C. C. T., Lincoln, P. A., Anal. Abs., vol. I, No. 3035 (1954).
15. Coppini, D., and Cameroni, R., Boll. chim. farm., *92*, 363 (1953).
16. Coughlin, F. J., Soap and Sanit. Chemicals, *32*, No. 2, 51 (1956).
17. Critchfield, F. E., and Johnson, J. B., Anal. Chem., *26*, 1803. (1954).
18. Cucci, M. W., Soap and Sanit. Chemicals, *25*, No. 11, 133 (1949).
19. Degens, P. N., Evans, H. C., Kommer, J. D., Winsor, P. A., J. Appl. Chem., *3*, 54 (1953).
20. Davis, B. F., Wattman, K. E., and Speel, H. C., Soap and Sanit. Chemicals, *31*, No. 12, 73 (1955).
21. Delsemme, A. H., Mededel Vlaam Chem. Ver., *13*, 152 (1951).
22. Dubois, A. S., Soap and San. Chemicals, *24*, No. 11, 122 (1948).
23. Edwards, G. P., and Martin, E. G., Sewage and Ind. Wastes, *26*, 945 (1954).
24. Edwards, G. R., Ewers, W. E., and Mansfield, W. W., Analyst, *77*, 205 (1952).
25. Epton, S. R., Trans, Faraday Soc., *44*, 226 (1948).
26. Espector Y., J. C., Color AITEA (Argentina), *1*, No. 8, 39, 47 (1953).
27. Etienne, H., Ind. chim. Belge, *17*, 373 (1952).
28. Evans, H. C., J. Soc. Chem. Ind., *69*, Suppl. 2, S76 (1950).
29. Fessler, W. A., A.S.T.M. Papers on Eval. of Soaps and Detergents, Spec. Tech. Publ. *115*, 9 (1951).
30. Few, A. V., and Ottewill, R. H., J. Colloid Sci., *11*, 34 (1956).
31. Flotow, E., Pharm. Zentralhalle, *83*, 181 (1942).
32. Franks, F., Nature, *176*, 693 (1955).
33. Franks, F., Analyst, *81*, 390 (1956).
34. Gauthier, B., and Mazau, L., Ann. pharm. Franc, *9*, 678 (1951).
35. Gilby, J. A., and Hodgson, H. W., Mfg. Chemist, *21*, 371, 423 (1950).
36. Green, T., Harker, R. P., and Howitt, F. O., Analyst, *80*, 470 (1955).
37. Greif, N., and Kent, A., unpublished work.
38. Harper, W. J., Elliker, P. R., and Moseley, W. K., Soap and Sanit. Chemicals, *24*, (2) 159 (1948).
39. Haakh, H., Candie, D., and Mobus, W., Melliand Textilber, *32*, 699 (1951).
40. Harris, J. C., Ind. Eng. Chem., Anal. Ed., *15*, 254 (1943).
41. Harris, J. C., and Short, F. R., Food Tech., *6*, 275 (1952).
42. Hart, R., Ind. Eng. Chem., Anal. Ed., *11*, 33 (1939).
43. Hart, R., Ind. Eng. Chem., *9*, 850 (1917).
44. Hartley, G. S., and Runnicles, D. F., Proc. Roy. Soc. London, A-168, 420 (1938).
45. Hartley, G. S., Trans. Faraday Soc., *30*, 444 (1934).
46. Herbig, W., "Die Oele und Fette in der Textilindustrie," Wissenschaftlicher Verlag, Stuttgart, 1929, 2nd ed.
47. Hettche, H. O., Vom Wasser, *20*, 137 (1953).
48. Hoyt, L. F., and Walter, J. E., A.S.T.M. Bull., *192*, 56 (1953).
49. House, R., and Darragh, J. L., Anal. Chem., *26*, *1492 (1954)*.
50. Iwasenko, H., J. Assoc., Offic. Agr. Chemists, *36*, 1165 (1953).
51. Jones, J. H., J. Assoc. Offic. Agr. Chemists, *28*, 398 (1945).
52. Karabinos, J. V., Soap and Chem. Spec., *31*, (6) 50 (1955).
53. Karabinos, J. V., Hazdra, J. J., and Kapella, G. E., Soap and Chem. Spec., *31*, (No. 4) 49 (1955).
54. Karush, F., and Sonenberg, M., Anal. Chem., *22*, 175 (1950).
55. Kling, W., and Puschell, F., Melliand Textilber, *15*, 21 (1934).
56. Koch, J. M., Ind. Eng. Chem., Anal Ed., *16*, 25 (1944).
57. Kortland, C., and Dammers, H. F., J. Am. Oil Chemists' Soc., *32*, 58 (1955).
58. Kuentzel, L. E., Anal. Chem., *27*, 301 (1955).
59. Lambert, J. M., J. Colloid Sci., *2*, 479 (1947).
60. Lester, E., J. Inst. Sew. Purif., *393* (1950).
61. Lewis, G. R., and Herndon, L. K., Sewage and Ind. Waste, *24*, 1456 (1952).
62. Lewandowski, T., Soap and Sanit. Chemicals, *29*, No. 4, 49 (1953).
63. Lincoln, P. A., and Chinnick, C. C. T., Analyst, *81*, 100 (1956).
64. Linsenmeyer, K., Melliand Textilber, *21*, 468 (1940).
65. Longwell, J., and Maniece, W. D., Analyst, *80*, 167 (1955).
66. Loomeijer, F. J., Anal. Chim. Acta., *10*, 147 (1954).
67. MacAllister, R. V., and Lisk, R. J., Anal. Chem., *23*, 609 (1951).
68. Marron, T. U., and Schifferli, J., Ind. Eng. Chem., Anal. Ed., *18*, 49 (1946).
69. Miller, S. A., Bann, B., and Ponsford, A. P., J. Appl. Chem., *1*, 523 (1951).
70. Moore, W. A., and Kolbeson, R. A., Anal. Chem., *28*, 161 (1956).
71. Morgan, P. W., Ind. Eng. Chem., Anal. Ed., *18*, 500 (1946).
72. Mukerjee, P., Anal. Chem., *28*, 870 (1956).
73. News Page, Anal. Chem., *28*, No. 8, 17A (1956).
74. Nevison, J. A., J. Am. Oil Chemists' Soc., *29*, 576 (1952).
75. Neu, R., Fette u. Seifen, *52*, 349 (1950).
76. Oliver, J., and Preston, C., Nature, *164*, 242 (1949).
77. Pifer, C. W., and Wollish, E. G., Anal. Chem., *24*, 300 (1952).
78. Powell, R., and Taylor, C. G., Chem. and Ind., *726* (1954).
79. Preston, J. M., J. Soc. Dyers and Colourists, *61*, 165 (1945).
80. Reid, V. W., Alston, T., and Young, B. W., Analyst, *80*, 682 (1955).
81. Report on the Exam. of Det. Prep., Anal. Methods Comm., Soc. of Public Analysts and Other Anal. Chemists, Analyst, *76*, 279 (1951).
82. Sadtler, P., A.S.T.M. Bull., *190*, 51 (1953).
83. Salton, M. R. J., and Alexander, A. E., Research (London), *2*, 247 (1949).
84. Scales, F. M., and Kemp, W., Assoc. Bull. (Int. Assoc. Milk Dealers), *31*, 187 (1939).
85. Shaffer, C. B., and Critchfield, F. H., Anal. Chem., *19*, 32 (1947).
86. Shiraeff, D. A., Proc. Chem. Specialties Manuf. Assoc., June 1950, 117–22.
87. Shiraeff, D. A., Am. Dyestuff Reptr., *36*, 313 (1947); *37*, 411 (1948).
88. Spangler, W. G., Kent, A., and Casazza, W., unpublished report.
89. Steele, A. B., and Berger, L. D., Soap and Sanit. Chemicals, *32*, No. 2, 48 (1956).
90. Schonfeldt, N., Kolloid Z., *142*, 164 (1955).
91. Schönfeldt, N., J. Am. Oil Chemists' Soc., *32*, 77 (1955).
92. Shriner, R. L., and Fuson, R. C., Sys. Ident. of Organic Comps., ER3, John Wiley and Sons (1948), p. 50.
93. Snell, F. D., and Biffen, F. M., Comm. Methods of Analysis, McGraw-Hill, p. 373 (1954).
94. Stevenson, D. G., Analyst, *79*, 504 (1954).
95. Stupel, H., and Segesser, A., Fette u. Seifen, *53*, 260, 327 (1951).
96. Smith, T. D., and Glazer, J., Nature, *169*, 497 (1952).
97. T.G.A. Method No. 79, Toilet Goods Assoc. Inc., Rockefeller Center, New York, N. Y.
98. Thompson, W., and Fine, R., to be published.
99. Tschoegl, N. W., Revs. of Pure and Appl. Chem., *4*, 171 (1954).
100. van der Hoeve, J. A., Rec. trav. chim., *67*, 649 (1948); J. Soc. Dyers and Colourists, *70*, 145 (1954).
101. von K. Peter, Fette u. Seifen *56*, 997 (1954).
102. Weatherburn, A. S., J. Am. Oil Chemists' Soc., *28*, 233 (1951).
103. Weiss, F. T., O'Donnell, A. E., Shreve, R. J., and Peters, E. D., Anal. Chem., *27*, 198 (1955).
104. Wickbold, R., Fette u. Seifen, *54*, 394 (1952).
105. Widaly, Seifen-Ole-Fette-Wache, *78*, 143 (1952).
106. Wallin, G. R., Anal. Chem., *22*, 616 (1950).
107. Wijga, P. W. O., Chem. Weekblad., *45*, 477 (1949).
108. Wilson, J. B., J. Assoc. Offic. Agr. Chem., *29*, 311 (1946); *31*, 105 (1948).
109. Wurzschmitt, B., Chem. Ztg., *74*, 16 (1950).
110. Official Methods of Analysis, Assoc. of Offic. Agr. Chemists, 8th ed., p. 496, Assoc. of Offic. Agr. Chemists, Washington, D. C. (1955).

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Analytical Test Methods for the Inorganic Portion of the Detergent Products

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A 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 considerable variation as a result of batch operation, or variation in control of feeding rates if a continuous operation is involved, individual samples are indicative of the extent of process control. A specification sheet very probably shows individual components as controlled to within from a tenth to several thousandths of a percentage; this is an ideal or goal and seldom resembles the formula as it is broken down by analysis.

There are good reasons why a product varies from the formula. Among these are error or ignorance; control instrument variability or sensitivity; mixing variability; chemical reaction during mixing or drying; ineffectiveness of sampling; and sample uniformity once it has been taken. Probably all these plus others are operative by the time the analyst receives the sample for assay. The analyst will choose methods which are of sufficient reproducibility and accuracy for his requirements, but it should be evident that his results may give formula data considerably at variance with the formula used in manufacture.

Methods should be chosen which minimize the cost for analysis, provide control of raw materials, and indicate as nearly as reasonable how closely the formula conforms to the standard formula sheet. It may be argued that extreme precision is necessary, but, from the usage of the data reconstituted from the analysis, the chances are good that much analytical effort will have been needlessly expended. Another facet of the problem of accuracy with unknowns is filling in the missing portion of the analysis in the possible event that some constituent, present in small but functionally effective amounts, may have been overlooked. The type of analysis can probably be chosen which will most economically provide the required information.

Preliminary Examination

Several techniques are available for a necessary preliminary examination of a sample. They vary considerably from simple qualitative tests to semiquantitative, rather broad examinations.

Moisture and Volatile Matter. Moisture and volatile matter, by any one of several methods, should be one of the first assays made.

Alcohol Soluble-Insoluble. Combined with moisture or volatile content, the determination of alcohol-soluble to provide a rough assay of active content, and alcohol-insoluble will provide information which frequently proves adequate.

Water-Insoluble. This determination, either on the alcohol-insoluble portion, or preferably upon the sample, will indicate whether the water-insoluble constituent is a result of manufacture or designed addition and some information as to character of the composition.

Emission Spectrographic Examination. In many laboratories this is the first examination made as it can provide semiquantitative data for the guidance of subsequent chemical examination.

Ion Identification. These tests are commonly made and either replace or supplement spectrographic analysis.

X-Ray Diffraction. If the product is crystalline, x-ray diffraction data frequently will serve either for initial examination or may be adequate without further chemical analysis.

Integrated Analytical Schemes

An advantage of integrated methods is that an essentially complete analysis may be achieved in which sample preparation operations and interferences are minimized. Essentially identical methods are represented by American Oil Chemists' Society Official Methods Db 1-48 through Db 11-48 (3), American Society for Testing Materials Standard Method D 820-46 (9), and Canadian Government Methods (13). These methods provide analytical directions for moisture and other volatile matter; free alkali or free acid; anhydrous, salt-free soda soap; alcohol-soluble matter; matter insoluble in water; total alkalinity of matter insoluble in alcohol (alkaline salts); sodium silicate; fatty matter; chloride in alcohol-soluble matter; rosin (McNicoll method); synthetic detergent (by difference); and neutral inorganic salts. These methods may also be used individually where only single analyses are required.

A method designed for a different class of composition is A.S.T.M.'s method D 800-45, Chemical Analysis of Industrial Metal Cleaning Compositions (8). The methods can also be used separately in most cases: preparation of sample; total alkalinity; total fatty acids and rosin; Na_2O combined with fatty acids and rosin; anhydrous soap; rosin, qualitative and quantitative (McNicoll); total SiO_2; phosphates, qualitative and quantitative; combined sodium and potassium oxides; chlorides; sulfate; water, distillation method; carbon dioxide by evolution-adsorption method; loss at 105°C.; total matter insoluble in alcohol; free alkali; synthetic detergent or wetting agent; volatile hydrocarbons; loss on ignition.

Of lesser interest today are methods for the chemical analysis of sulfonated and sulfated oils. A.S.T.M. method D 500-55 (5) covers these determinations: water by distillation; moisture and volatile matter; organically combined sulfuric anhydride; total desulfated fatty matter; total active ingredients; unsaponifiable non-volatile matter; inorganic salts; total alkalinity; total ammonia; acidity as free fatty acids or acid number; water-immiscible organic solvents volatile with steam.

The inorganic builders considered as individual components are rather well covered by A.S.T.M. Method D 501-55 (6) relating to sampling and chemical analysis of alkaline detergents. These methods include caustic soda; soda ash; modified soda (sesquicarbonate type); sodium bicarbonate; sodium meta-, sesqui-, and ortho-silicates; trisodium phosphate; tetrasodium pyrophosphate; borax. Additionally the sampling and analysis of sodium triphosphate is covered by A.S.T.M. Method D 501-55T (7). The individual analyses under this scheme are: sampling; titratable Na_2O; total P_2O_5 (two methods); pH of 1% solution; turbidity; temperature rise; sulfate; ignition loss; matter insoluble in water; particle size; orthophosphate. The analysis for orthophosphate has been submitted as a tentative method; it is based on the spectrophotometric measurement of the reduced blue complex formed when the orthophosphate has been converted to phosphomolybdic acid. Of importance to the analysis of triphosphate are the efforts of two D-12 task groups which are separately investigating the assay by the tris(ethylenediamine) cobalt (III) chloride method (31), and a very promising paper chromatographic technique (20).

A colorimetric method is available also for the estimation of orthophosphate in the presence of crystalline, granular, or powdered triphosphate (16). The color depends upon the formation of phosphomolybdate in the presence of an aminonaphtholsulfonic acid reagent. The method can be performed either visually or photometrically, using a standard curve or Nessler standards.

Another scheme applicable to soap-synthetic detergent mixtures is that of Berkowitz and Bernstein (10). This procedure provides methods for sequential analysis of anhydrous, salt-free soda soap; alcohol-insoluble matter; alcohol-soluble matter; fatty matter; chlorides in alcohol-soluble matter; synthetic detergent by difference.

Federal Specification P-S-536b entitled Soap and Soap-Products (Including Synthetic Detergents); Methods of Sampling and Testing (17), includes essentially the same methods and schemes of analysis specified in the A.O.C.S. or A.S.T.M. methods.

In surveying these schemes for integrated analysis, it appears that those in present use should be critically examined with the objective of increasing accuracy and/or improving rapidity of analysis. All are relatively time-consuming.

Analysis of Individual Components

The methods to be discussed either are well-established through custom, recognition of adaptability, or accuracy. This does not mean that improved methods from the recent literature should not be investigated as possible substitutes for customary analyses. Furthermore, as advances in a field of manufacture occur, they impose a need for new methods or techniques. New products in a field provide their own problems in the way of analysis.

Phosphates. The present-day formulation will almost invariably contain a considerable proportion of a pyro- or polyphosphate builder. Dry compositions will contain the less expensive sodium salts, while the built liquids will utilize considerable amounts of potassium compounds. Polyphosphates, when subjected to high temperatures in the wet state or to alkalies, undergo at least partial reversion to the ortho state. Further, polyphosphates as produced frequently contain small amounts of other forms of phosphate which could complicate the analysis. From the analyst's viewpoint analysis for other than total P_2O_5 presents as yet a sticky problem.

The individual methods given under the integrated schemes of analysis are in most instances suitable for the determination of single components of compositions. However other methods may be either simpler or more quickly carried out where certain components may be ignored (provided they do not actually interfere).

A task group of the Joint A.O.C.S.-A.S.T.M. D-12 Subcommittee on Analysis of Soaps and Synthetic Detergents has presented for adoption a shortened differential titrimetric-potentiometric method for determination of total P_2O_5. This has the advantage of being applicable either to the integrated scheme or for determination without removal of the other constituents.

Another task group is concerned with the analysis of sodium triphosphate by the tris(ethylenediamine) cobalt (III) ion method (31).

Still another task group is working with a paper chromatographic technique which quantitatively analyzes for the phosphate components in polyphosphates or for phosphates in detergent compositions (20). This method was presented early this summer. While superficially it may seem involved, it can easily be learned by a laboratory technician without extensive analytical training.

Another procedure said to analyze mixtures of water-soluble phosphates rapidly and simply is based upon selective alkaline hydrolysis of triphosphate combined with a modified colorimetric procedure for determining orthophosphate (24). Other investigators (14) indicate that quantitative infrared analysis, utilizing the potassium bromide pressed disc technique, compares favorably with x-ray and chemical methods as to speed and accuracy. Dependent upon whether increased accuracy or lessened time for analysis can be achieved, either one or the other of these methods may supersede current ones. Too much cannot be said for the chromatographic method for the analysis of polyphosphate compositions as degradation products are determined simultaneously with the original phosphates added. It is predicted that this method will be adapted almost exclusively for analysis of phosphates in detergent compositions.

Silicates. Present in most built compositions by virtue of their functional and corrosion-inhibiting properties, the silicates provide another interesting problem. Silicates can be lowered in $Na_2O:SiO_2$ ratio during processing, and amounts of insoluble SiO_2 can result from acidification in manufacture (as in carbonation). Dehydration of a product can also produce water-insoluble SiO_2. The analyst's problem is to reconstitute the $Na_2O:SiO_2$ ratio from available analytical data.

The traditional method for silica estimation is separation and treatment with HF as a gravimetric procedure. While accurate, this method is both time-consuming and tedious.

A rapid colorimetric method for silica has been suggested (22), based on the color produced after development by silicomolybdic acid. Interference of phosphate can be eliminated by citric acid treatment. The method becomes semiquantitative by using visual comparison standards.

A rapid volumetric method (21) has recently been developed, based upon the conversion of soluble silica to Na_2SiF_6 by a differential titration method. Modifications of the method are indicated where carbonates, phosphates, and surface-active agents are present.

Sodium Carbonate and Bicarbonate. These are frequently present; the bicarbonate sometimes results from carbonation of available free alkali.

A recent improvement in the apparatus for the gravimetric determination has been published by Blank and Kelley (12). This method differentiates between bicarbonate and sodium carbonate.

Modifications of technique for the evolution method (28) make it possible to reduce foaming and bumping difficulties in the presence of non-hydrolyzable surface-active agents.

Sodium Sulfate. This builder may be present either by design or as a concomitant of manufacture. The more usual method of assay is the gravimetric barium sulfate procedure, but volumetric techniques seem to offer much in the way of increased speed and simplicity.

One titration method (26) is based upon dipotassium rhodizonate or tetrahydroquinone indicators by continuous observation during titration, using a filter photometer. House and Darragh (19) modified the dipotassium rhodizonate titration method for application to sulfonate products, either by removal of sulfonate (by acidification and ether extraction) or by addition of known amounts of sulfate to control the sulfonate-sulfate ratio to less than 80/20 where slightly less accurate but more rapid determinations are required. Another volumetric method (23) gives a colorimetric end-point based upon Eriochromeschwartz T indicator in the presence of standard disodium-dihydrogenethylenediamine tetra-acetate solution.

Sodium Chloride. This assay is not a difficult one, but sodium chloride is partially soluble in alcohol and must be accounted for in both the active ingredient extract and the alcohol-soluble portion. The potassium bichromate-silver nitrate method is normally specified for chloride determination. A potentiometric method, utilizing a silver electrode and titration with silver nitrate, is said to give excellent results. A means for removing chlorides from the alcohol-soluble matter in detergents (27) involves adsorbing the chloride on an anion-exchange resin, such as Dowex-2; it is eluted, and the chloride is then determined.

Borates. While borax is relatively infrequently encountered in detergent compositions, perborates are receiving considerable attention in detergent usage so that a method is desirable. Such a method is given in A.S.T.M. D 460 (4), which involves fusion, acidification, and titration in glycerol solution. A.O.C.S. method Da 17-52 (1) involves removal of interfering soap, phosphate, or silicate by strontium chloride or nitrate addition, removal of the strontium salts, and subsequent potentiometric titration of the purified liquor in the presence of mannitol.

Potassium. With the advent of liquid heavy-duty detergents, analysis for potassium salts has become a "must." Both A.O.C.S. (2) and A.S.T.M. methods are based upon precipitation as potassium chloroplatinate. Sodium oxide is determined by difference, that is, subtracting the Na_2O equivalent to potassium from the total alkali calculated as Na_2O.

Ethylenediamine Tetra-acetate (EDTA). Salts of the acid may be found in greater or lesser amounts in detergent compositions. A colorimetric analysis (15) has been developed, which involves sequestration of nickel by EDTA followed by acidification and determination of the nickel as dithio-oxalate. Interfering phosphates, copper, and presumably other builders would have to be removed.

Other Functional Additives. While of an organic nature, optical brighteners, organic corrosion inhibitors, tarnish inhibitors, and carboxymethyl cellulose can make up from a fraction to several per cent of the composition.

Optical Brighteners. These are almost universally present in detergent compositions meant for fabric cleansing and even in some designed for hard-surface cleansing. The amounts used vary but generally total less than 0.1% of the composition. While chemical methods for analysis in composition may fail to provide adquate data, photometric measurement of detergent solutions or preferably of fabrics subjected to the detergents may prove adequate. Additionally, spectrographic methods may prove of value in some cases. Present techniques leave much to be desired, particularly where identification of individual optical brightener components is the objective.

Corrosion Inhibitors. The most widely used inhibitor is an inorganic silicate, but organic corrosion inhibitors may eventually be developed. At that time analytical methods will be necessary for process control, if not for general analytical determination. It is suggested here that chromatographic techniques may prove valuable.

Tarnish Inhibitors. Compounds which prevent silverware tarnishing are in general use. Again these are present in relatively small percentages, and satisfactory control methods are desirable. Chromatographic or colorimetric tests may prove useful for identification.

Carboxymethyl Cellulose (CMC). These antiredeposition agents are in almost universal usage and represent from fractional to percentage amounts of the detergent formulation. CMC can vary in degree of substitution, which can make accurate estimation in an unknown a less than precise measurement. Additionally, preferential separation prior to analysis can be a difficult procedure.

Control analysis of the commercially concentrated product prior to addition to a detergent composition is not difficult, and several methods have been developed. Qualitative differentiation between cellulose ethers and cellulose ether glycolic acids has been achieved (25) by precipitation of cellulose glycolic acids by dimethylalkylbenzylammonium chloride; the cellulose ethers do not undergo this reaction. A gravimetric method (30) is based upon the isolation of the copper salt. The degree of substitution can be estimated from the copper content of the dried precipitate. The anthrone method (11) is rather accurate, and readings are made spectrophotometrically. Interfering substances are said to be other carbohydrates, or carbohydrate derivatives and certain polyoxyethylene derivatives of fatty acids and phenols. Another colorimetric technique (29) involves use of 2,7-dihydroxynaphthalene.

A method which is rather less than quantitative involves measurement of the antiredeposition properties of a detergent composition under carefully controlled arbitrary conditions.

Summary

Evaluation of available methods for preliminary examination of the inorganic portion of detergent compositions indicates that this phase of the analysis has a relatively satisfactory status. Utilization of various spectrographic devices can prove most helpful in both preliminary and in final analysis of detergent components.

Several integrated schemes of analysis are available. Most of them are as yet incomplete with respect to a good analysis of sodium tripolyphosphate, but recently described techniques hold considerable promise. These general schemes are under review with the objective of using in them more effective techniques for certain components.

Individual component analyses are under critical examination, particularly those for the phosphates. A recently introduced chromatographic technique promises improvement here. Improved techniques for the determination of silica merit examination for integrated schemes as well as for single component an-

alysis. Even sulfate analysis may be improved if published methods are indicative.

Analyses for optical brighteners, corrosion inhibitors, and carboxymethyl cellulose are needed and do not now exist in satisfactory form.

REFERENCES

1. Am. Oil Chemists' Soc., "Borax," Official and Tentative Methods Da 17-52 (1955).
2. Am. Oil Chemists' Soc., "Combined Sodium and Potassium Oxides," Official and Tentative Methods Da 27-48 (1948).
3. Am. Oil Chemists' Soc., "Soap Containing Synthetic Detergents," Official and Tentative Methods Db 1-48, Db 11-48 (1955).
4. A.S.T.M. Standard, "Sampling and Chemical Analysis of Soaps and Soap Products," D 460-54 (1954).
5. A.S.T.M. Standard, "Methods of Chemical Analysis of Sulfonated and Sulfated Oils," D 500-55 (1955).
6. A.S.T.M. Standard, "Methods and Sampling and Chemical Analysis of Alkaline Detergents," D 501-55 (1955).
7. A.S.T.M. Standard, "Methods for Sampling and Chemical Analysis of Sodium Triphosphate," Tentative D 501-55T (1955).
8. A.S.T.M. Standard, "Chemical Analysis of Industrial Metal Cleaning Compositions," D 800-45 (1955).
9. A.S.T.M. Standard, "Methods of Chemical Analysis of Soaps Containing Synthetic Detergents," D 820-46 (1955).
10. Berkowitz, D., and Bernstein, R., Ind. Eng. Chem., Anal. Ed., *16*, 239 (1944).
11. Black, H. C., Anal. Chem., *23*, 1792–1795 (1951).
12. Blank, E. W., and Kelley, R. M., J. Am. Oil Chemists' Soc., *33*, 75–78 (1956).
13. Canadian Government Specifications Board, "Methods of Testing and Analysis of Soaps and Detergents," Specification 2-GP-11, Nov. 4, 1954.
14. Corbridge, D. E. C., and Lowe, E. J., Anal. Chem., *27*, 1383–1387 (1955).
15. Darbey, A., Soap, vol. 29, No. 8, pp. 81, 83, 85, 87, 153 (1953).
16. Federal Specification, "Sodium Polyphosphates," Interim O-S-00635a (Navy Docks), Jan. 12, 1955.
17. Federal Specification, "Soap and Soap Products (Including Synthetic Detergents); Methods of Sampling and Testing," P-S-536b, Jan. 4, 1951.
18. Harris, J. C., and Bernstein, R., "Bibliographical Abstracts of Methods for Analysis of Synthetic Detergents," A.S.T.M. Special Technical Publication No. 150A.
19. House, R., and Darragh, J. L., Anal. Chem., *26*, 1492-1497 (1954).
20. Karl-Kroupa, E., Anal. Chem., *28*, 1091–1098 (1956).
21. Lawson, A. M., Jones, L. A., and Aepli, O. T., Anal. Chem., *27*, 1810–1811 (1955).
22. Miller, W. J., J. Am. Oil Chemists' Soc., *27*, 348–350 (1950).
23. Munger, J. R., Nippler, R. W., and Ingols, R. S., Anal. Chem., *22*, 1455–1456 (1950).
24. Netherton, L. E., Wreath, A. R., and Bernhart, D. N., Anal. Chem., *27*, 860–861 (1955).
25. Neu, R., Fette u. Seifen, *52*, 23 (1950): Chem. Abstracts, *44*, 7531 (1950).
26. Ogg, C. L., Willits, C. O., and Cooper, F. J., Anal. Chem., *20*, 83–85 (1948).
27. Pomeranz, J., Chemist Analyst, *43*, 89–90 (1954).
28. Schuck, N. M., and Koester, W. A., J. Am. Oil Chemists' Soc., *27*, 321–323 (1950).
29. Snell, F. D., and Snell, C. T., "Sodium Carboxymethyl Cellulose. Colorimetric Methods of Analysis," vol. III, p. 467, D. Van Nostrand Co. Inc., New York City, 1953.
30. Toilet Goods Asso. Inc., "Determination of Sodium Carboxymethyl Cellulose," TGA Method No. 42 (1950).
31. Weiser, H. J., Anal. Chem., *28*, 477–481 (1956).

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Surfactant Survey[1]

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SATISFACTORY PAPERS have appeared from time to time on the total production of surface-active agents or on their most important uses. Relatively little data are available however on the types and quantities of surfactants used in specific applications. The principal reason for this is the difficulty of obtaining even reasonably reliable estimates. For some uses, as in household cleaning products, knowledge of the formulations used combined with confidential but available data on the sales of the individual products permit a fairly accurate analysis to be made. In other applications the estimates, guesses, and conjectures of men experienced in the field can be analyzed to provide a fair estimate. In still other applications however, notably those concerned with industrial cleaning, it seems likely that no one anywhere has the answer. For such cases we have provided only guesses.

While this survey is as exhaustive as time would permit, the subject is so vast that it cannot be considered final. It is presented as a start on which others can build, and so our method of calculation is given for those applications where we consider our estimates doubtful.

There are other limitations to be noted. The first of these concerns confidential applications. Many companies have one or two applications tucked away that are unknown to some or all of their competitors. Even where such information is known to us, specific reference has been omitted from this paper though it may be concealed in the totals.

There is also the important question as to which materials should be included as surface-active agents. In general, we used the classification of the U. S. Tariff Commission (18) with two notable exceptions. We omitted both sulfonated oils and the salts of fatty acids since we do not include soaps in this survey. While both classes are undoubtedly surface-active agents and undoubtedly synthetic, it was felt that they require a separate study of their own.

We did include certain materials listed by the U. S. Tariff Commission under "Ore-Flotation Agents" as their function is surface-active. We recognize this to be somewhat inconsistent as there are many such products, notably fatty amines and fatty alcohols, which are also used for surface-active properties but not generally included in the common usage of the term "surface-active agents." We can only plead that time did not permit this more thorough treatment.

Another point to be noted is that the art of application of surface-active agents is still in its adolescence. Changes are constantly being made both in the type of surface-active agents used for given applications and the concentration used. Also it is believed that, in some household products, the type and proportion of surface-active agent in the formula may be varied, depending on the relative costs of the competitive raw materials. Nationally sold household products also seem to vary in composition in various areas of the country, depending on local conditions, such as water hardness, public demand for certain properties, and raw material supply in that area. A survey such as this therefore must be considered, at best, representative of a fleeting instant of time so that greater importance should be placed on the properties required for specific applications rather than the numerical values representing consumption. All figures shown are on an active-agent basis, that is, 100% of organic surfactant.

Principal Product Types

Our method of presenting some of the data requires that abbreviations be used to designate the surfactant types. These abbreviations are shown below.