be unsatisfactory for use in corn or cottonseed oils because of the off-flavors imparted by them to the oils or because of their insolubility. Some of these substances, for example, 6-palmitoyl-l-ascorbic acid and lecithin, did not impart off-flavors to the oils directly but these developed during storage. Various combinations of these substances failed to give enough protection to the oils to permit lowering of the concentration to avoid the off-flavors. Catalase, gallic acid, and corn germ oil were the most promising substances of those tested. Some of the antioxidants did stabilize the oils for short periods after the container had been opened and stored in the dark.

Neither deaeration nor deodorization affected the stability of the oils when they were aged in the presence of light in sealed containers. Poor quality oils deteriorated rapidly, even when stored in the absence of light at low temperatures.

The most important factors governing the potential keeping quality of an oil were its original quality and exposure to light. A satisfactory storage life can be obtained if fresh corn or cottonseed oil is packed under conditions which prevent the inclusion of air, stored at room temperature or lower, and protected from light either by its total exclusion or by the use of amber-glass bottles.

REFERENCES

1. Green, T. G., and Hilditch, T. P., J. Soc. Chem. Ind., London, *56*, 23 (1937).
2. Sumner, J. B., and Dounce, A. L., J. Biol. Chem. *127*, 439 (1939).
3. Euler, H. von, and Josephson, K., Ann. *452*, 158 (1927).
4. Esselen, W. B., Jr., and Barnby, H. A., Modern Packaging, Sept., 1939, 42 (1939).
5. McConnell, J. E. W., and Esselen, W. B., Jr., Oil and Soap. In press.
6. Greenbank, G. R., and Holm, G. E., Ind. Eng. Chem. *33*, 1058 (1941).
7. Ford, K. L., Canning Age *14*, 307 (1933).
8. Purcell, C. S., Glass Packer *13*, 367 (1934).
9. Hammer, B. W., and Cordes, W. A., Iowa Agr. Expt. Sta. Res. Bull. *64*, 99 (1920).
10. Gudheim, A. R., Oil and Soap *20*, 197 (1943).
11. Mattil, K. F., Filer, L. J., Jr., and Longenecker, H. E., Oil and Soap *21*, 160 (1944).
12. Smith, F. H., Brady, D. E., and Comstock, R. E., Ind. Eng. Chem. *37*, 1206 (1945).
13. Nagy, J. J., Vibrans, F. C., and Kraybill, H. R., Oil and Soap *21*, 349 (1944).
14. Higgins, J. W., and Black, H. C., Oil and Soap *21*, 277 (1944).
15. Tarr, H. L. A., J. Can. Dietetic Assoc. *6*, 71 (1944).
16. Tracy, D. N., Hoskisson, W. A., and Trimble, J. M., J. Dairy Sci. *27*, 311 (1944).
17. Coulter, S. T., Can. Dairy and Ice Cream J. *23*, No. 10, 28 (1944).
18. Vibrans, F. C., Oil and Soap *12*, 14 (1935).
19. Bickford, W. G., Oil and Soap *18*, 95 (1941).
20. Sundberg, T., and Hultberg, S. O., Iva 1942, 243 (1942). Oil and Soap *21*, 280 (1944).
21. Riemenschneider, R. W., Herb, S. F., Hammaker, E. M., and Luddy, F. E., Oil and Soap *21*, 307 (1944).
22. Bailey, A. E., and Feuge, R. O., Oil and Soap *21*, 286 (1944).

Determination of Silica in Soaps and Soap Flakes. Perchloric Acid Method

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ABSTRACT

SOAP and soap flakes are decomposed by nitric-perchloric acid, with the aid of a catalyst. Silica is then dehydrated, filtered off, and determined in the usual manner.

An acid digestion method for the determination of silica in soap and soap powders has not been reported to our knowledge. Since perchloric acid is constantly used for the dehydration of silica in inorganic analysis and the nitric-perchloric acids technique has been applied to organic compounds (2), as in the determination of sulfates, it then follows that silica in soap may be conveniently determined by the same technique.

The A.S.T.M. method (1) is accurate, if applied to water soluble silicates but is rather long and time-consuming. In this procedure the soap is charred, the soluble matter leached, the residue ignited, the two portions combined, and silica twice dehydrated in hydrochloric acid. Finally, a fluoride volatilization is necessary. An alternative method is the use of the "insoluble in alcohol" (1) precipitate which contains nearly all the silica and inorganic salts and some organic matter. The low results obtained in this procedure are caused by the solubility of silicates in alcohol and by the incomplete solution of silicate in the water solution. The procedure is also rather long.

Almost all types of organic matter can be safely oxidized by a mixture of nitric and perchloric acids (3). In soap, the organic matter consists of the fatty acids, glycerol, proteins, and small amounts of miscellaneous materials. All these can be destroyed by nitric and perchloric acids. The alkali is converted to the perchlorate salt, and the silica is dehydrated in hot perchloric acid.

In a previous study on the oxidation of coke (2), it was found necessary to use a catalyst—a mixture of potassium permanganate and potassium dichromate. The catalyst serves a two-fold purpose, i.e., it hastens the complete oxidation of the organic material and indicates the completion of the reaction by the formation of the red chromic acid color.

Experimental

The size of sample chosen was two grams. Experimental samples were digested with 15-, 20-, and 25-ml. portions of nitric acid (sp. g. 1.4) mixed with 15- and 20-ml. portions of perchloric acid (70%). Liquid bromine was added to some samples. Fifty to 60 mg. of catalyst were also used.

Another group of samples was treated in a similar manner except that fuming nitric acid (sp. g. 1.5) was substituted for concentrated nitric acid. A comparison was also made of the speed of reaction when the soap was digested with fuming nitric acid alone, and with a mixture of the nitric and perchloric acids.

Reagents

Nitric Acid (sp. g. 1.4).
Catalyst. Separately dry $K_2Cr_2O_7$ and $KMnO_4$. Powder. Mix equal weights.
Fuming Nitric Acid (sp. g. 1.5).
Perchloric Acid 70-72%.
Hydrochloric Acid (sp. g. 1.2).
Hydrochloric Acid, wash liquid. 1 part acid (sp. g. 1.2) to 2 parts water.
Hydrofluoric Acid, 48%.

TABLE I.

Determination of Silica in Soaps and Soap Powders

Sample	Sample Weight	Catalyst Weight	HNO_3	$HClO_4$	SiO_2	Na_2SiO_3[8]	A.S.T.M.[9] Na_2SiO_3
	gm.	*mg.*	*ml.*	*ml.*	*gm.*	%	%
1	1	0[3]	15[1,4]	12	0.0053	1.08	......
2	2	60[3]	45[1]	25	0.0120	1.22	......
3	2	50	25[2]	15	0.0076	0.78	......
4	2	30	15[2,4]	10	0.0088	0.89	......
	2	30	15[2,4]	10	0.0086	0.87	......
5	2	30	20[2,4]	15	0.0083	0.84	......
	2	30	20[2,4]	15	0.0085	0.86	......
6	2	50	25[2]	15	0.0064	0.65	......
	2	50	25[2]	15	0.0064	0.65	......
7[5]	1	0	25[2]	20	0.0090	1.83	......
	1	0	25[2]	20	0.0089	1.81	......
8	2	50	25[2]	20	0.0013[6]	0.13	......
	2	50	25[2]	20	0.0016[7]	0.16	......
9	2	50	25[2]	20	0.0740	7.52	......
10	2	50	25[2]	20	0.0723	7.35	......
11	2	50	25[2]	20	0.0690	7.01	......
12	2	50	25[2]	20	0.0680	6.92	......
13	2	50	25[2]	20	0.00055	0.06	0.07
14	2	50	25[2]	20	0.0012	0.10	0.12
15	2	50	25[2]	20	0.0032	0.33	0.26
16	2	50	25[2]	20	0.0031	0.32	0.31
17	2	50	25[2]	20	0.0035	0.36	0.37
18	2	50	25[2]	20	0.0052	0.53	0.52
19	2	50	25[2]	20	0.0828	8.45	8.28
20	2	50	25[2]	20	0.1368	13.98	13.93

[1] Sp. g., 1.4.
[2] Fuming acid, sp. g., 1.5.
[3] Bromine added.
[4] Small addition of nitric acid required.
[5] Residue from soap solution.
[6] Heated 20 minutes at 105°C., then 30 minutes at 250°C.
[7] Digested first with nitric acid. Perchloric acid added later.
[8] Factor used: 204% × gm. SiO_2 ÷ weight of sample.
[9] A.S.T.M. D 460-41.

Results

Samples digested with nitric acid (sp. g. 1.4), perchloric acid, bromine, and catalyst were not satisfactory. Charring frequently occurred and in several instances the samples flamed. Samples digested with fuming nitric acid (sp. g. 1.5) and perchloric acid were satisfactory. If the digestion is carried on too rapidly, i.e., if the nitric acid is evaporated too rapidly, a slight charring in the perchloric acid solvent may occur. This will not introduce error for the perchloric acid oxidizes the organic matter, but the addition of several drops of nitric acid (sp. g. 1.4) at this point is beneficial. Otherwise, the digestion is carried out with the aid of heat only. Shaking of the reaction beaker is unnecessary. No advantage in time was noted if the samples were digested first with fuming nitric acid alone and perchloric acid added later.

In Table I are tabulated the results of silica determinations in soaps and soap powders, using the procedure herein proposed. A.S.T.M. method figures are included.

Proposed Procedure

Weigh 2 gm. of soap. Transfer to a 400-ml. beaker and add about 50 mg. of catalyst. Slowly add 25 ml. of *fuming* nitric acid (sp. g. 1.5) and cover. After the reaction subsides, add 20 ml. of perchloric acid (70%). Place on a cold hotplate. Adjust the heat on the plate so as to maintain a temperature of about 100°. After about 20 minutes raise the heat to 200-250° and maintain for another period of 20 minutes. The nitric acid should now have volatilized, and the solution should be green (tervalent chromium). Increase the heat until the green color turns red (chromic acid) then remove the beaker from the heat and cool.

Add about 100 ml. of water and several drops of hydrogen peroxide (3%) and mix well. Add 10 ml. of hydrochloric acid (sp. g. 1.2). Heat to boiling. Remove from the heat and filter through a No. 40, 11 cm. Whatman paper. Wash with hot (1:2) hydrochloric acid, four times, then four times more with hot water. Dry and char the paper in a crucible on the hotplate, then ignite the crucible. Cool. Weigh as SiO_2. There should be no residue if the silica is volatilized by hydrofluoric acid in platinum.

Use the proper factor and calculate to the desired sodium silicate composition. The silica filtrate contains negligible amounts of silica. The filtrate may be used for the determination of sulfur (2).

General Precautions Involving the Use of Perchloric Acid

There are particular hazards in the use of nitric-perchloric acid mixtures. Hot concentrated perchloric acid *alone* will react *explosively* with many organic compounds, therefore, perchloric acid must be used in conjunction with nitric acid. Furthermore, in the digestion of soaps and soap powders *fuming* nitric acid must be used. Concentrated nitric acid is not satisfactory.

Discussion

The proposed procedure is especially useful for the rapid routine determination of silica in soap. There is a minimum of handling of the reaction beaker. Temperature, rate, and time of heating are the important factors. The rather long heating time (about 40 minutes) is necessitated by the resistance of aliphatic carbon chains to oxidation. Fuming nitric acid is required since it is more effective than concentrated (sp. g. 1.4) nitric acid.

The various dyes, perfumes, and proteins usually present should offer no difficulties. As much as 2% of glycerine was found in some soap powders which were oxidized without difficulty. The size of sample is limited by the sodium content of the soap since the presence of larger amounts of sodium increases the solubility of silica, requiring a double dehydration. Thus, if the sample is limited to about two grams, only one dehydration will be needed, and very little silica will be retained by the perchloric acid.

Certain soap powders contain abrasives which are not dissolved by nitric and perchloric acids. These abrasives must be treated with hydrofluoric acid for identification as to silica content.

Summary

A new technique for the rapid determination of silica in soaps and certain powders is proposed. It is analogous to methods used in inorganic analysis. The results are similar to those obtained by the well-known hydrochloric acid dehydration method.

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Addenda

Perchloric acid should not be used in wooden hoods.

REFERENCES

1. A.S.T.M. D 460-41, Section 42.
2. Silverman, Louis, Ind. Eng. Chem., Anal. Ed., *13*, 524 (1941).
3. Smith, G. Frederick. "Mixed Perchloric, Sulfuric and Phosphoric Acids and Their Applications in Analysis." G. F. Smith Chem. Co., Columbus, Ohio, 1942, Second edition, Page 10.