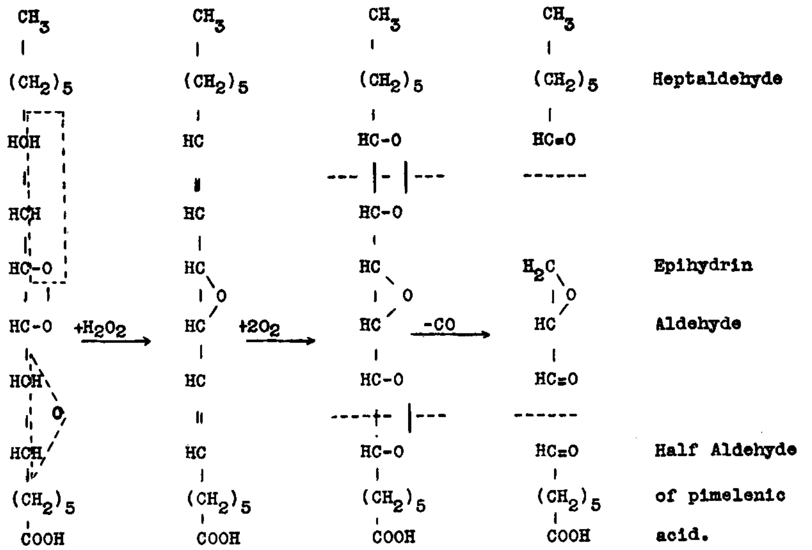

FIGURE VII

Oxidation of Oleic Acid According to Powick

cid lard at 100° C. and 3-5 mm. Hg pressure are inactive as catalysts of oxidation. These materials include the substances which are responsible for rancid odor and taste.

(2) That the peroxides are inactive as catalysts of oxidation.

Conclusion

The conclusion has been drawn that the active catalytic materials are of high molecular weight and not readily volatile at 200° C. and 3-5 mm. Hg pressure. This conclusion has been *tentatively* checked by the use of a synthetic product.

References

1. Scherer—Versuch einer populaeren Chemie (1795).
2. Ritsert—Untersuchungen ueber das Ranzig werden der Fette (1890).
3. Marx—Chem. Zeitg. 23, 704 (1899).
4. Kreis—Chem. Zeitg. 23, 802 (1899). Chem. Zeitg. 26, 897, 1014 (1902).
5. Kerr—J. I. E. C. 10, 471 (1918).
6. Powick—J. Agr. Res. 26, 323-63 (1923).
7. Holm & Greenbank—J. I. E. C. 16, 518 (1924).
8. Pritzker & Jungkunz—Zeits. Unters. Lebensm 57, 419-21 (1929).
9. A. S. Richardson, et al.—Soap 7, No. 6, 35-7 (1931).
10. Von Fellenberg-Mitteil, aus d. Geb. der Lebensm—unters. und Hygiene, Veroeffentl. von Sweitzer Gesundheitsamt 15, 198 (1924).
11. Grettie & Newton—J. I. E. C. Anal. Ed. 3, 171-3 (1931).
12. Greenbank & Holm—J. I. E. C. Anal. Ed. 2, 9-10 (1930).
13. Royce—Soap 7, No. 9, 24-7, 38 (1931).
14. Wheeler—Oil and Soap 9, 89-97 (1932).
15. Vibrans—Oil and Fat Ind. 8, 223-263 (1931).
16. King, Roschen & Irwin—Oil and Soap 10, 105-9 (1933).
17. Anonymous—Gaz. Chem. Italia 38, 307-27 (1908).

REPORT OF SULPHONATED OIL COMMITTEE

(*Continued from page* 230.)

that part of the condenser tube should reach within 0.25 inch of the surface of the liquid.

C. P. Long. It is very desirable that the F. A. C. hot-plate method, which is one of the official methods of the A. O. C. S., be standardized much better than it is now. We believe that the size of the sample, the dish used, and the hot plate itself, and its temperature should be specified. We have set a limit of 130° C. as the maximum temperature to which the oil should be heated.

It has been our sad experience that calcium chloride will give up moisture to dry samples long before its physical appearance will give any indication of its condition. For this reason the committee should place some limit on the use of desiccating agents to be used in the desiccator.

H. H. Mosher. We have compared the hot-plate and distillation methods with ten samples of different oils and obtained practically check results when the time factor and the temperature of the hot plate was accurately controlled. We have found, however, that there is a small progressive deterioration of oil by the hot-plate method with a gradual loss in weight, so that some care and intelligence must be exercised in determining the end point. We have usually estimated this at the point at which the loss of weight flattens out.

R. H. Pingree. In order to eliminate the difficulty and expense of replacing parts of the distillation apparatus, I would recommend that both ground joints be "Standard Taper and Interchangeable Joints" and would suggest for this purpose Standard Joint No. 25 (Bureau of Standards, Commercial Standard CS21-30).

W. H. Tiffany. After making a number of tests with rapid evaporation methods, it would appear that the results are unreliable and subject to variations due to the speed of the determination, superheating at walls of vessel, or other unknown factors. However, after running a number of analyses according to the specifications of the hot-plate method as modified by the committee, I find that the results check well and are in good agreement with those by the distillation method.

Ralph Wechsler. Concerning the distillation apparatus, I fully agree with Mr. Lauro that the lower end of the condenser tube should not dip into the liquid of the trap, but should extend only to about 0.25 inch above the surface, in order to prevent the liquid from shooting up into the tube.

Summary

The committee finds that both the A. A. T. C. C. distillation method and the modified hot-plate method are satisfactory for the determination of moisture in commercial sulfonated oils that are free from other volatile matter. The agreement among different analysts was about the same for both methods, with an average variation of about 0.3%, which may also be considered as the probable precision or reliability of each method. Hence, the committee recommends the A. A. T. C. C. distillation method as a standard method and the modified hot-plate method as an alternative method. In the proposed procedures, the A. A. T. C. C. moisture apparatus has been modified so that the end of the condenser tube is raised above the level of the liquid in the trap, and the specifications for the ground joints have been changed to correspond to Interchangeable Ground-Glass Joint 25 of Commercial Standard CS21-30. The F. A. C. hot-plate method has been modified to include a short thermometer (for the control of temperature and to serve as a stirring rod), heating in an air-oven before weighing, and the addition of oleic acid to keep the sample homogeneous and liquid.

Proposed Standard Method of Test for Water in Sulfonated (Sulfated) Oils

A. O. C. S. Distillation Method

1. *Scope.* This method of test determines water existing in a sample of sulfonated (sulfated) oil by distilling the sample with a volatile solvent. It applies only to sulfonated oils that do not contain the following: mineral acids, free sulfonic acids, or free sulfuric acid ester; or alcohol, glycerol, diethylene glycol, acetone, or other water-miscible volatile compounds.

Apparatus

2. *General.* The apparatus shall consist of a glass flask, heated by suitable means and provided with a reflux condenser, discharging into a trap and connected to the flask. The connections between the trap and condenser and flask shall be ground joints. The trap serves to collect and measure the condensed water and to return the solvent to the flask.

Before use, the condenser and the receiving tube shall be thoroughly cleaned with soap and warm water, rinsed well, then treated with hot cleaning solution (a mixture of 10 ml. of saturated potassium bichromate and 990 ml. of concentrated sulfuric acid), and finally thoroughly washed and dried.

3. *Flask.* The glass flask (Fig. 1A) shall be of the short-neck, round-bottom type, made of well-annealed glass, having an approximate capacity of 500 ml.

4. *Heat Source.* An oil bath (stearic acid, paraffin wax, etc.) or an electric

heater provided with a sliding rheostat shall be used as the source of heat.

5. *Condenser.* The condenser (Fig. 1A) shall be of the water-cooled, reflux, glass-tube type, having a condenser jacket not less than 400 mm. (15.75 inches) in length with an inner tube 9.5 to 12.7 mm. (0.375 to 0.5 inch) in outside diameter. The end of the condenser to be inserted in the trap shall be ground off at an angle of 30 deg. from the vertical axis of the condenser and the tip of the condenser tube when inserted in the trap shall extend about 7 mm. (0.25 inch) above the surface of the liquid in the trap after the distillation conditions have been established.

6. *Trap.* The trap shall be made of well-annealed glass constructed in accordance with Fig. 1B and shall be graduated as shown from 0 to 5 ml. in 0.1-ml. divisions. The error of any indicated capacity shall not be greater than 0.05 ml.

Reagents

7. *Solvent.* The solvent used shall be C. P. xylene.

8. *Oleic Acid.* The oleic acid used shall be the U.S.P. grade, and previous to use shall be heated for 5 to 10 minutes over a free flame at a temperature of 130° to 135° C.

Calibration

9. *Calibration.* To calibrate the apparatus, 1 gram of water shall be added to a mixture of 80 grams of xylene and 10 grams of oleic acid. The distillation shall be conducted as under Procedure below. When all the water is over, the apparatus shall be cooled, another gram of water added, and the distillation repeated. The calibration shall be continued up to the capacity of the receiving tube.

TABLE I.—MOISTURE BY THE A. A. T. C. C. DISTILLATION METHOD.

	Sample 1				Sample 1-A			
Analyst	I %	II %	Av. %	Deviation from Mean %	I %	II %	Av. %	Deviation from Mean %
Grimshaw	25.64	25.78	25.71	0.07	41.77	....	41.77	0.35
Hart	25.90	25.72	25.81	0.03	42.56	42.48	42.52	0.40
Irwin	26.00	25.80	25.90	0.12	41.9	42.1	42.00*	0.12
Lauro	25.57	25.61	25.59	0.19	42.55	42.59	42.57	0.45
Long	26.1	26.7	26.4*	0.62	41.5	41.3	41.4	0.72
Mosher	26.04	26.16	26.10*	0.32	42.17	42.27	42.22	0.10
Pingree	25.53	25.74	25.64*	0.14	42.26	42.34	42.31*	0.19
Sheely	25.8	25.2	25.5	0.28	42.1	42.1	42.1	0.02
Tiffany	25.80	26.00	25.92*	0.14	42.12	42.88	42.64*	0.52
Wechsler	25.26	25.28	25.27	0.51	41.65	41.67	41.66	0.46
Mean			25.78				42.12	
Greatest difference			1.13				1 24	
Average deviation			0.24				0.33	

*More than 2 determinations.

Procedure

10. *Procedure.* Enough of the sample to be tested shall be taken for analysis to yield about 4 ml. of water. The approximate quantity shall be introduced into a weighing bottle, from which the weighings into the flask shall be made, care being taken that after removal of the sample no drops of oil are left on the outside of the bottle. Eighty grams of xylene and oleic acid equal to about two and one-half times the weight of the bone-dry sample shall be added, glass beads introduced to prevent bumping, and the contents thoroughly mixed by swirling, proper care being taken to avoid any loss of material. The flask shall then be immediately connected with the distillation apparatus. The oleic acid is necessary to prevent foaming and jellying of the contents in the distillation flask. A loose cotton plug shall be inserted in the top of the condenser tube to prevent condensation of atmospheric moisture in the condenser tube.

Heat shall then be applied and so regulated that the condenser tube immediately below the water jacket shall be just barely hot. In this way a minimum of water condenses higher in the condenser, where it is difficult to volatilize.

The distillation shall be continued at the specified rate until practically no water is visible on any part of the apparatus except on the bottom of the trap. This operation usually requires less than an hour. The rate of distillation shall then be increased to remove all traces of

TABLE II.—MOISTURE BY THE MODIFIED HOT-PLATE METHOD.

Analyst	Sample 1 I %	 II %	 Av. %	 Deviation from Mean %	Sample 1-A I %	 II %	 Av. %	 Deviation from Mean %
Hart	25.77	25.92	25.85	0.12	42.41	42.29	42.35	0.06
Irwin	26.28	26.06	26.17	0.20	42.89	42.83	42.86	0.57
Lauro	25.80	26.00	25.90	0.07	42.50	42.60	42.55	0.26
Long	25.6	25.7	25.7	0.27	41.8	42.8	42.4*	0.11
Mosher	26.15	....	26.15	0.18	42.15	....	42.15	0.14
Pingree	25.14	25.48	25.31	0.66	41.73	41.92	41.83	0.46
Sheely	26.6	....	26.6	0.63	42.3	....	42.3	0.01
Tiffany	25.57	26.16	25.83*	0.14	42.10	42.70	42.32*	0.03
Wechsler	26.17	26.22	26.19*	0.22	41.86	41.85	41.86	0.43
Mean			25.97				42.29	
Greatest difference			1.29				1.03	
Average deviation			0.28				0.23	

*More than 2 determinations.

condensed water in the condenser tube, and the distillation continued until the water level in the trap remains unchanged after a 10-minute interval. Any droplets adhering to the sides of the receiver shall be dislodged with a thin copper wire twisted into a loop. The receiving tube shall now be immersed in warm water at about 40° C. for 15 minutes, or until the xylene layer becomes clear, when the exact reading and temperature shall be taken.

11. *Calculation of Results.* The volume of condensed water measured in the trap and converted into grams by means of Table A, divided by the weight of the sample used and multiplied by 100, shall be the percentage of water and shall be reported as "...... per cent water by weight, A. O. C. S. distillation method."

Accuracy

12. *Accuracy.* The accuracy to be expected with this method is that duplicate determinations of water should not differ from each other by more than 0.05 ml.

Density of Water

13. *Density of water.*

TABLE A.—RELATIVE DENSITY OF WATER

(Smithsonian Tables, compiled from various authors.)

Temperature °C.	Density
+44	1.00000
35	0.99406
36	0.99371
37	0.99336
38	0.99299
39	0.99262
40	0.99224
41	0.99186
42	0.99147
43	0.99107
44	0.99066
45	0.99025

Proposed Alternative Method of Test for Water and Other Compounds Volatile at About 100° C. in Sulfonated (Sulfated) Oils

A. O. C. S. Hot-Plate Method

1. *Scope.* This method of test determines water and other compounds volatile at about 100° C. existing in a sample of sulfonated (sulfated) oil by rapid evaporation. The method applies only to sulfonated oils that do not contain the following: mineral acids, free sulfonic acids, or free sulfuric acid esters; ammonia, acetic acid or similar volatile acids; sodium acetates or similar salts which may react with oleic acid at elevated temperatures liberating volatile acids; or glycerol, diethylene glycol, xylene, or other compounds of similar volatility.

Apparatus

2. *General.* The apparatus shall consist of a glass-stoppered weighing flask and a glass beaker, heated by suitable means and provided with a suitable thermometer.

3. *Weighing Flask.* Any suitable glass-stoppered weighing flask of 10 to 15 ml. capacity shall be used.

4. *Beaker.* The beaker shall be a Griffin low-form glass beaker with an approximate capacity of 150 ml. and a diameter of about 5 cm.

5. *Heat Source.* An electric hot plate, with or without asbestos paper or board cover, or an open flame under a suitable asbestos board and a wire gauze (to spread the heat) shall be the source of heat.

6. *Thermometer.* The thermometer shall be about 3 inches long, graduated from 90° to 150° C., and substantially constructed.

Reagents

7. *Oleic Acid.* The oleic acid used shall be the U.S.P. grade.

8. *Desiccating Agent.* Any suitable desiccating agent shall be used. *Note:* Recent investigations seem to indicate that calcium chloride is unreliable as a laboratory desiccating agent.

Procedure

9. *Procedure.* Approximately 5 grams of oleic acid shall be weighed into the beaker in which the thermometer is also placed. The oleic acid shall now be heated gradually, while stirring with the thermometer, until the temperature is 130° C. The beaker shall then be placed in an oven at 105° to 110° C. for 15 minutes, cooled in a desiccator, and weighed. The heating over the hot plate and in the oven shall be repeated until two contiguous weighings differ by less than 15 mg.

About 6 grams of the sample shall be introduced into the weighing flask, weighed exactly, the contents emptied into the beaker (containing the thermometer), and the flask weighed again. The mixture shall now be heated exactly as in the taring of the beaker, etc.

10. *Calculation of Results.* The loss in weight of the contents in the beaker divided by the weight of the sample and multiplied by 100 shall be the percentage of water and other volatile compounds at about 100° C. and shall be reported as ".... per cent water and other volatile compounds at about 100° C. by weight, A. O. C. S. hot-plate method."

Accuracy

11. *Accuracy.* The accuracy to be expected with this method is that duplicate determinations of water and other compounds volatile at about 100° C. should not differ from each other by more than 40 mg. or 0.4% on a 5-gram sample.

Acknowledgment

The committee is greatly indebted to Mr. Ralph Wechsler and to his firm, the National Oil Products Co., for furnishing the coöperative samples.

TABLE III.—SUMMARY OF MOISTURE RESULTS BY DISTILLATION AND MODIFIED HOT-PLATE METHODS.

	Sample 1 Distillation Method %	 Hot-Plate Method %	 Diff. %	Sample 1-A Distillation Method %	 Hot-Plate Method %	 Diff. %
Mean	25.78	25.97	0.19	42.12	42.29	0.17
Greatest difference	1.13	1.29	0.16	1.24	1.03	0.21
Average deviation	0.24	0.28	0.04	0.33	0.23	0.11

Literature Cited

1. Hart, R., et al., *Am. Dyestuff Reporter,* **21,** 667 (1932).
2. *Ibid.,* **22,** 695 (1933).
3. *Ibid.,* **23,** 290 (1934).
4. Schultz, G. W., et al., *J. Am. Leather Chem. Assoc.,* **14,** 266 (1919).
5. *Ibid.,* **15,** 283 (1920).
6. Alsop, W. K., and Schultz, G. W., *Ibid.,* **16,** 525 (1921).
7. Commercial Standard CS43-32, "Grading of Sulfonated (Sulfated) Oils, Saponifiable Type," Bur. Standards, Jan. 26, 1933.
8. Wizöff Report, *Chem. Umschau,* **38,** 34, 132 (1931).
9. Gillet, M., Jr., et al., *Intern. Soc. Leather Trades' Chem.,* **12,** 327, 389 (1928).
10. "Official and Tentative Methods," Am. Oil Chemists' Society, p. 27, August, 1933.
11. Am. Soc. Testing Materials, Standard D 95-30.
12. "Methods of Analysis," Assoc. Official Agr. Chem., p. 54 (1930).
13. Bidwell and Sterling, Ind. Eng. Chem., **17,** 147 (1925).
14. Hart, R., *Ibid.,* **10,** 598 (1918).
15. Davidsohn, J., *Chem. Ztg.,* **54,** 934 (1930).
16. Schlenker, E., *Seifensieder-Ztg.,* **58,** 58, 96 (1931).
17. Jamieson, Geo. S., *J. Assoc. Official Agr. Chem.,* **15,** 560 (1933).