Report of Soap Section Committee

Definite Progress Achieved in Formulation of Standards for Acids Used in Glycerine Analysis.

By A. K. CHURCH, *Chairman*

AT THE fall meeting of the American Oil Chemists' Society, held in New York October 25-26, 1928, a Soap Section of the A. O. C. S. was organized. Later a committee was appointed. The personnel of the committee follows:

R. W. Bailey, Stillwell & Gladding, Inc., New York, N. Y.

A. K. Church, Lever Brothers Co., Cambridge, Mass.
Chairman, Soap Section, A. O. C. S.

C. J. Gundel, Fels & Co., Philadelphia, Pa.

L. F. Hoyt, Larkin Co. Inc., Buffalo, N. Y.

M. H. Ittner, Colgate & Co., Jersey City.

H. J. Morrison, Procter & Gamble, Ivorydale, Ohio

W. A. Peterson, Kirkman & Son, Brooklyn.
Secretary, Soap Section, A. O. C. S.

W. D. Richardson, Swift & Co., Chicago, Ill.

M. L. Sheely, Armour Soap Works, Chicago, Ill.

H. P. Trevithick, New York Produce Exchange, New York, N. Y.

R. B. Trusler, University of Pittsburgh, Pittsburgh, Pa.

The committee decided to undertake the establishment of an A. O. C. S. Standard Crude Glycerin sample and an A. O. C. S. Standard Soap sample. Mr. Morrison undertook to prepare the soap sample and Mr. Church the crude glycerin sample. Through the courtesy of the Procter & Gamble Co. the soap sample was donated and through the courtesy of Lever Brothers Co. the glycerin sample was donated.

Both of these samples have been prepared and distributed to the members of the committee. All soap chemists and glycerin chemists, whether members of the A. O. C. S. or not, are invited to do cooperative work in connection with these two samples. The following chemists are now cooperating with the committee on this work:

V. K. Cassady, The Palmolive Company, Milwaukee, Wis.

Curtis & Tompkins, Chemists, San Francisco, Cal.

H. C. Bennett, Los Angeles Soap Co., Los Angeles, Cal.

The committee cordially invites any other soap or glycerin chemist interested to participate in this work. Samples will be forwarded on request to our committee's Secretary, Mr. Peterson. It should be observed that results of individual industrial laboratories will not be published under the names of the laboratories but only under number designations. The idea back of this standardization work is to establish correct analyses for these standard samples and not to disclose differences between laboratories should there be differences.

The committee decided the standard crude glycerin sample was to be tested by the International Acetin Method, the method prescribed throughout the world in connection with sales of crude glycerin. The I. A. M. is explicit in its directions except in one respect and that is the precise method of standardizing the acid used. The Chairman suggested that each cooperating laboratory describe its method of standardizing the acid used in connection with the I. A. M. for crude glycerin. So much interest was displayed among the committee members in respect to methods of standardization of the acid that it seems likely that other chemists will also be interested in the discussion of the standardization methods actually used by representative laboratories and so comments of the committee members follow—but not in the order given above where the members of the committee are listed. It is agreed, we believe, that the use of one indicator does not give precisely the same results as the use of another indicator.

Laboratory No. 1

"We have always preferred to use N/2 hydrochloric acid for the acetin method. As a method of standardization, we use sodium carbonate that has been previously dried and have found this to be quite satisfactory. Weigh off about 2 grams of Baker's Special Sodium Carbonate C.P. into a platinum crucible and heat at a dull red heat till constant weight is obtained. Dissolve the dry sodium carbonate in 150 cc of distilled water, add 2 drops of methyl orange and titrate to a faint pink color. From this titration the factor is calculated. We have occasionally checked our N/2 HCl against silver chloride gravimetrically and obtained very close checks. The chance of error using silver chloride is less owing to the heavy weight of

AgCl handled as against the end point while using sodium carbonate."

Laboratory No. 2

"We standardize our normal sulphuric acid for glycerin determination using sodium carbonate with methyl orange as the indicator. Our method is as follows: We use the A. O. C. S. sodium carbonate or J. T. Baker's Special sodium carbonate. 10 to 15 grams of the carbonate are heated in a platinum dish over a low-flamed Argand burner to incipient redness, never hot enough for fusion, for about 2 hours to constant weight. The sodium carbonate is then put in a desiccator until it reaches room temperature. About 2.2 grams of the ignited and cooled sodium carbonate are then accurately weighed, transferred to a liter flask and dissolved in about 100 to 150 cc of cold distilled water. 3 drops of methyl orange indicator, 1 gram to the liter, are added. The tip of the burette containing the H_2SO_4 to be standardized is adjusted just outside the mouth of the neck of the flask and the mouth of the flask is covered as well as may be with a clean watch glass. This precaution is taken to prevent any loss from the rapid evolution of CO_2. When the titration is nearly completed, the watch glass and tip of the burette are rinsed with distilled water. The titration is then continued until the solution takes on, permanently, the first trace of pink. At the end of the titration the volume in flask is between 400-500 cc. A burette with Bureau of Standards certificate is used. Corrections are made for the burette reading and for the temperature. We make our standard temperature 20°C. Check results should be obtained having a spread of not more than 0.001 in normality. Finally about 4.4 g of Na_2CO_3, enough to require about 90 cc of N/1 acid, are titrated as a final checking. Various authors have been examined in respect to the standardization of acid. Scott standardizes H_2SO_4 by adding an excess of the acid to a sodium carbonate solution and titrating the excess with N/5 NaOH, using phenolphthalein as the indicator (p 494, 4th ed.). Griffin gives no standardization of H_2SO_4. His standardization of HCl is made by titrating sodium carbonate solution with methyl orange as an indicator (p 7, 1st ed.). Treadwell-Hall standardizes HCl by titration against sodium carbonate solution using methyl orange as an indicator. This authority states that H_2SO_4 may be standardized in the same manner (p 552, 5th English ed.). Sutton outlines a standardization of H_2SO_4 by titrating the acid against a sodium carbonate solution using methyl orange as the indicator (p 49, 11th ed.). The methyl orange end point is not so easy for different analysts to agree upon as is the end point with, for example, methyl red or phenolphthalein. We have done some work with methyl red and find it gives a sharper end point than does methyl orange. However, when methyl red is used as an indicator, the acid, we have found, is somewhat stronger, that is, contains a slightly greater weight of acid per cc, than when methyl orange is used. When phenolphthalein is used as an indicator, the strength of the acid, that is the number of grams of acid per cc, is somewhat different than when methyl orange is used, according to our tests. It is, therefore, rather important, although perhaps not vitally important, that all laboratories doing cooperative work using the International Acetin Method for glycerol, should standardize their master acid solutions using the same indicator."

Laboratory No. 3

This laboratory standardizes their sulfuric acid for glycerin determinations by the sodium carbonate method. Their proceeding is as follows: A 20 gram platinum crucible is half filled with J. T. Baker's C. P. Special Na_2CO_3, which is heated in the oven at 270-280°C. until it shows no loss in weight. This usually does not take longer than one hour. The crucible and contents are cooled in a desiccator. 2.0000 plus or minus .0003 grams of the dried Na_2CO_3 is weighed in a porcelain dish and brushed into a 250 cc Erlenmeyer flask. 50 cc of water is added and the carbonate dissolved without heating. Two (2) drops of methyl orange indicator are added and the solution titrated with the H_2SO_4, using a standardized burette. Calculation:

$$\frac{18.868 \times 2.00}{\text{cc. titration}} = \text{Normality}$$

The results of two titrations agreeing within 0.001 in normality are averaged, and the average used as the normality of the acid solution. This laboratory states: "We believe that this method is the one more generally recognized in all textbooks. We find it the preferred method in Mahin, Sutton, Treadwell-Hall, Fresenius, Griffin and Scott."

Laboratory No. 4

"Laboratory No. 8 puts forward a plea for the standardization of hydrochloric acid gravimetrically by means of silver chloride."

"We wish to register an objection to this method, first, on the old theoretical grounds that in standardizing by means of silver chloride, the standardization is of chlorine, not of acid hydrogen and, hence, is theoretically ques-

tionable and with impurities present practically imperfect. This laboratory standardizes N/1 sulfuric acid, for glycerin analysis, against sodium carbonate prepared from Merck's C.P. grade of sodium bicarbonate, by the well-known method standard in all textbooks. By this method, sodium bicarbonate is heated in a platinum vessel at a temperature of 270-300°C, with frequent stirring, to constant weight. About 2 grams of sodium carbonate thus prepared, accurately weighed, are dissolved without heat in recently boiled distilled water, two drops of methyl orange added and the solution titrated with the sulphuric acid, using a calibrated burette. The usual calculations and dilutions are made to adjust to normal."

Laboratory No. 5

"We use normal hydrochloric acid and standardize the same against sodium bicarbonate (Merck's C. P.). The sodium bicarbonate is heated in a platinum dish until there is no further loss in weight. The sodium carbonate is dissolved in water and titrated with the acid using methyl orange as an indicator. From this and other titrations it is adjusted and diluted to a normal solution."

Laboratory No. 6

"For the analyses of crude glycerines by the acetin method, we use N/2 hydrochloric acid standardized gravimetrically with silver chloride. As a check on this standardization, we titrate against sodium carbonate obtained from C. P. sodium bicarbonate which has previously been heated to 260-280°C for six hours, using methyl orange as an indicator. We have always used the acetin method for crude glycerines above a 60% glycerol concentration, and when all steps in the method have been carefully followed, we have been able to obtain quite satisfactory results."

Laboratory No. 7

"Our method of standardization of the N/2 sulphuric acid which we use as our main standard solution for all our work including the acetin determinations is with sodium carbonate as follows: A platinum dish is filled with C. P. sodium carbonate and heated to 270-280 and held there for 4-5 hours. It is cooled in a desiccator and one gram portions are used for the titrations, using methyl orange. Before the end point is reached the solution is boiled to expel CO_2, then cooled and the titration finished."

Laboratory No. 8

"In his letter of Feb. 12, 1929 on the Acetin Method for the determination of Glycerol, the Chairman of the Soap Section rightfully points out that the standardization of the acid used is of vital importance. Of course, the accuracy of burettes and other measuring instruments is also extremely important. There are a number of accepted ways of standardizing acids which do not always lead to the same results, as errors are apt to creep into some of these methods. To avoid inaccuracy from this source, I have always insisted that our analytical work be referred to hydrochloric acid standardized gravimetrically against silver chloride. Most of our atomic weights have been connected directly to silver chloride, and the determination of silver chloride can be done with accuracy and dispatch by any operator who is competent to standardize solutions. For the process in question, we would prefer to modify the method to the extent of using N/2 hydrochloric acid that had been standardized against silver chloride with closely agreeing duplicate determinations."

Laboratory No. 9

"This laboratory uses N/1 hydrochloric acid for the acetin method. As a method of standardization we have always preferred to use as a primary standard in acidimetry and alkalinity as recommended by the Bureau of Standards. Pure sublimed benzoic acid as supplied for a calorimetric standard is fused, for greater ease of handling. This acid in accurately weighed portions is used in neutral alcoholic solution, to standardize carbonate-free N/2 KOH and the N/1 HCl is titrated against the standardized KOH. The usual precautions of using calibrated burettes and temperature corrections are of course observed. In this method of standardization, phenolphthalein indicator is used throughout and it is also the indicator used in the Acetin Method.

NOTE: It may be of interest to this committee to know that I got in touch with the laboratories of four large chemical companies and found that of these four, one uses sodium carbonate and three use benzoic acid as their primary standard."

Laboratory No. 10

"The following is the method we use for standardizing our acid: Hydrochloric acid made up approximately N/4 is standardized against 0.5 gm. samples of Diack & Smith's Standard Sodium Carbonate using Methyl Orange for the indicator. The Sodium Carbonate has been previously dried at 140°C for one hour as per the seller's directions and is weighed from a weighing bottle into a dried clean flask and titrated immediately. The standard of purity of the carbonate used is always given on the label. The hydrochloric acid solution is made exactly N/4."

Laboratory No. 11

"Referring to the correspondence regarding hydrochloric acid we standardize gravimetrically as silver chloride. We also check by titration with sodium carbonate, using methyl orange as an indicator. We have used for this titration standardization the special sodium carbonate which has been prepared for the Society and which can be obtained from Mr. Helm, the Secretary. This material, I believe, analyzes 99.93% pure."

Method used in the Analytical Laboratory of Mellon Institute of Industrial Research—Method selected by Dr. W. W. Mills, Institute Analyst (*Quoted by permission of Dr. Trusler, Member of the Committee*)

"*Standardization of Sulphuric Acid*—The Analytical Laboratory of Mellon Institute standardizes acids against a specially prepared grade of sodium carbonate. It is prepared by precipitating sodium bicarbonate from a solution of pure sodium carbonate by saturating the solution with carbon dioxide gas. The sodium bicarbonate is filtered, washed two or three times with cold water, and dried in the air to constant weight at a temperature not above 270°C., producing pure sodium carbonate.

(NOTE: Foulk and Osborne, Department of Chemistry, Ohio State University, have studied the preparation and use of sodium bicarbonate as an ultimate standard. They have found that heating it in air above 270°C causes some decomposition. If heating and subsequent cooling is conducted in an atmosphere of carbon dioxide, the temperature may be above 270°. This investigation is to be published in the near future.)

The dried salt is dissolved in water and titrated, using methyl orange as indicator. When the first appearance of red shows, the solution is boiled to remove dissolved carbon dioxide. The solution is then cooled and the titration carried to the first color change. The usual precautions of using a calibrated burette and noting the temperature of the standard solution are observed."

Good progress is being made in the analysis of both the soap and glycerin samples and the committee hopes to be able to report accepted analyses of both samples at the fall meeting.

The Chairman and Secretary thank each member of the committee and also the cooperating laboratories not committee members for the splendid spirit of cooperation manifested in the work.

A. K. CHURCH
Chairman Soap Section Committee

Spanish production of olives and olive oil rose sharply in the 1928 season. As compared with 1927, the area planted to olives was 101.12 per cent, with a yield of 272.46 per cent in olives. The oil yield was 289.27 per cent of the 1927 crop. Production of olive oil in 1928 totaled 1,467,467,298 lbs. as compared with a 1927 crop of only 507,304,474 lbs.

Statement of the ownership, management, circulation, etc., required by the Act of Congress of August 24, 1912, of Oil & Fat Industries, published monthly at New York, N. Y. for April 1, 1929.

State of New York; County of New York.

Before me, a Notary Public in and for the State and county aforesaid, personally appeared Alan Porter Lee, who having been duly sworn according to law, deposes and says that he is the Editor of the Oil and Fat Industries and the following is, to the best of his knowledge and belief, a true statement of the ownership, management (and if a daily paper, the circulation), etc., of the aforesaid publication for the date shown in the above caption, required by the Act of August 24, 1912, embodied in section 411, Postal Laws and Regulations, printed on the reverse of this form, to wit:

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[Signed] Alan Porter Lee.

Sworn to and subscribed before me this 1st day of April, 1929.

Al. J. Ruggiero, Notary Public, Kings Co., No. 509 Reg. No. 1162; Cert. filed in N. Y. Co., No. 309 Reg. No. 1R242; Commission expires March 30th, 1931.

[SEAL.]