

# Oil Chemists' Soap Section Reports

## *Complete Summary of Results of Cooperative Work on Analysis of Glycerine and Standardization of Reagent Acid*

By W. A. PETERSON, *Secretary*

**T**HE committee is glad to be able to announce that the work on the standardization of the A. O. C. S. crude glycerine sample is complete and an accepted analysis can be reported at this time. Results in close agreement have been received from 16 laboratories. These values have been averaged according to a method agreed upon by the committee, with the final accepted averages shown in the following tabulation as "average C." This final average is considered as representing the most accurate results obtainable by the International Acetin Method for crude glycerine on the sample under examination and is to be the accepted analysis for the A. O. C. S. Standard Crude Glycerine sample. The results of the individual labora-

tories and the derivation of the final average is given in the following tabulation.

Considering the fact that the analysis of a crude glycerine by the International Acetin Method is rather difficult, the agreement shown by 16 different laboratories is exceptionally good. The I. A. M. does not prescribe definitely the method to be used in standardizing the acid. In the opinion of the committee this should be more specifically defined. With this in view, the committee submits two methods; one for the standardization of normal sulphuric acid and an alternate one for hydrochloric acid for consideration by the proper committee of the A. O. C. S., to the end that if it be considered advisable these methods might be inserted in the "A. O. C. S. Standard Methods." The method follows:

### *A. O. C. S. Standard Sample Crude Glycerine*

Lab.	% Total Acetylizabile	% Acetin Residue	% True Glycerol	% Total Residue at 160°C	% Ash	% Organic Residue
(1)	83.73	.53	83.20	10.20	8.54	1.66
(2)	83.69	.53	83.34	10.52	8.61	1.91
(3)	83.56	.54	83.02	10.75	8.79	1.96
(4)	83.77	.54	83.23	10.45	8.52	1.93
(5)	83.85	.42	83.43	10.14	8.69	1.45
(6)	83.70	.46	83.24	10.10	8.85	1.23
(7)	83.45	.20	83.25	10.19	8.82	1.37
(8)	83.93	.52	83.41	10.61	9.11	1.50
(9)	83.72	.25	83.47	10.00	9.02	.98
(10)	83.71	.44	83.27	10.61	8.56	2.05
(11)	83.89	.76	83.13	10.00	8.93	1.07
(12)	83.90	.44	83.46	10.27	8.61	1.66
(13)	84.03	.57	83.46	10.32	8.79	1.53
(14)	83.87	.68	83.19	10.27	8.73	1.54
(15)	83.90	.73	83.17	10.78	8.87	1.91
(16)	83.29	.23	83.06	10.37	8.80	1.57
Ave. (a)	83.75	.48	83.27	10.35	8.77	1.58
From Above Averages						
	Excl. Items more than .25 from Ave. (a)	Excl. Items more than .25 from Ave. (a)		Excl. Items more than .50 from Ave. (a)	Excl. Items more than .25 from Ave. (a)	
	Items 7, 13 & 16 out	Items 7 & 11 out		No items out	Item 8 out	
Ave. (b)	83.79	.48	83.31	10.35	8.74	1.61
	Excl. Items more than .20 from Ave. (b)	Excl. Items more than .15 from Ave. (b)		Excl. Items more than .25 from Ave. (b)	Excl. Items more than .15 from Ave. (b)	
	Items 3, 7, 13 & 16 out	Items 7, 9, 11, 14, 15 & 16 out		Items 3, 8, 9, 10, 11 & 15 out	Items 1, 4, 8, 9, 10 & 11 out	
Ave. (c)	83.81	.48	83.33	10.28	8.76	1.52

*Standardization of Normal Sulphuric  
Acid Against Sodium Carbonate*

*The Na<sub>2</sub>CO<sub>3</sub>*

The Na<sub>2</sub>CO<sub>3</sub> may best be prepared by precipitating NaHCO<sub>3</sub> from a cold solution of pure Na<sub>2</sub>CO<sub>3</sub> by saturating the solution with CO<sub>2</sub> gas. The NaHCO<sub>3</sub> filtered, washed two or three times with cold distilled water, and heated in the air (in an oven or other air bath) to constant weight at a temperature not above 270°C. This produces Na<sub>2</sub>CO<sub>3</sub> of definite purity. Sodium carbonate, or bicarbonate known to be of a satisfactory quality and specially prepared for standardization use by reputable manufacturers, laboratories, chemical societies or government bureaus, may be employed. The A. O. C. S. has a suitable Na<sub>2</sub>CO<sub>3</sub>.

*The Acid*

Use C. P. sulphuric acid 1.835=1.84 sp. gr. For each liter of solution use 30 cc of the C. P. acid making up to 1 liter with distilled water. This approximate solution will have a normality of around 1.03=1.04 and is to be adjusted to exact normality later.

*The Burette*

The burette must have a Bureau of Standards certificate. A 50 cc burette is preferred.

*The Indicator*

Methyl orange of indicator quality must be used as the indicator; 1 gram of methyl orange to a liter of distilled water.

*The Technic*

Put 10-15 g. of the special Na<sub>2</sub>CO<sub>3</sub>, (or NaHCO<sub>3</sub>) in a platinum dish or crucible and heat to constant weight at a temperature of 260-270°C but not to exceed 270°C. This usually does not take over an hour. Then cool dish and contents in a desiccator. Weigh accurately 2 to 2.2 g. of the constant weight Na<sub>2</sub>CO<sub>3</sub> in an aluminum weighing pan or small porcelain dish and brush into a suitable flask (250-500 cc Erlenmeyer, or a liter Florence flask). Add 50 to 150 cc of distilled water, the quantity depending on size of flask used, and dissolve the carbonate without heating. Add 2 drops of methyl orange indicator, 3 drops if 150 cc, and titrate with the H<sub>2</sub>SO<sub>4</sub> solution using a burette with B. of S. Certificate.

*Calculation:*

$$\frac{\text{Wt. of Na}_2\text{CO}_3}{\text{cc titration} \times .053} = \text{Normality}$$

The normality should be over one for easy adjustment—suppose it comes 1.0400 normality. Dilution to approach exact normality: To calculate the amount of water to add to

approach normality, multiply the volume by the normality and subtract the volume, thus: Suppose about 10 liters of solution are to be made up and the exact volume to be diluted is 9900 cc with 1.0400 normality; (9900 x 1.0400) —9900=396 cc of H<sub>2</sub>O indicated to give a normality of 1. Add, however, only about 90%, say, of the 396 cc. Less than the exact amount is added to prevent obtaining a solution below normal, which is harder to adjust. Once again determine the normality of the diluted solution and again dilute as before. For the third time obtain the normality of the solution and dilute with the amount of water indicated to make exactly normal. The solution should now be very close to precisely normal. Consider the solution standardized when duplicate titrations agree within 0.001 in normality, using the average as the normality of the acid solution. If this last normality is not precisely 1, the solution may, if desired, be finally adjusted to the exact normality of 1 if it is not desired to use a factor.

In connection with the titration: At the first appearance of red, place a small funnel in the mouth of the flask and boil for 10 minutes to remove the dissolved CO<sub>2</sub>. The solution is then cooled and the titration carried to the first color change.

If the temperature at which the titration is made is other than the standard temperature of 20°C, a temperature correction must be made. The temperature correction table is given below. The corrections are for each 100 cc used.

Corrections for Temperature per 100 cc			
°C	cc	°C	cc
15	+0.13	23	—0.09
16	+0.11	24	—0.12
17	+0.08	25	—0.15
18	+0.06	26	—0.18
19	+0.03	27	—0.21
20	0.00	28	—0.25
21	—0.03	29	—0.28
22	—0.06	30	—0.31

(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°C. This investigation is to be published in the near future.)

*Private communication to Dr. W. W. Mills, Mellon Institute Analyst.*

*Preparing Acid Solution*

THE method of preparing a master solution of hydrochloric acid is to weigh out a definite amount of constant boiling solution of hydrochloric acid and dilute this to a certain volume. The following table gives the composition of a constant boiling solution prepared at various barometric pressures:

Barometric Pressure	Per Cent HCl	Grams Constant Boiling Distillate Containing 1 mol. HCl
770	20.218	180.390
760	20.242	180.170
750	20.266	179.960
740	20.290	179.745
730	20.314	179.530

Since the composition of the distillate is a straight line function of the pressure within the usual range, extrapolation may be employed for pressures between the points given.

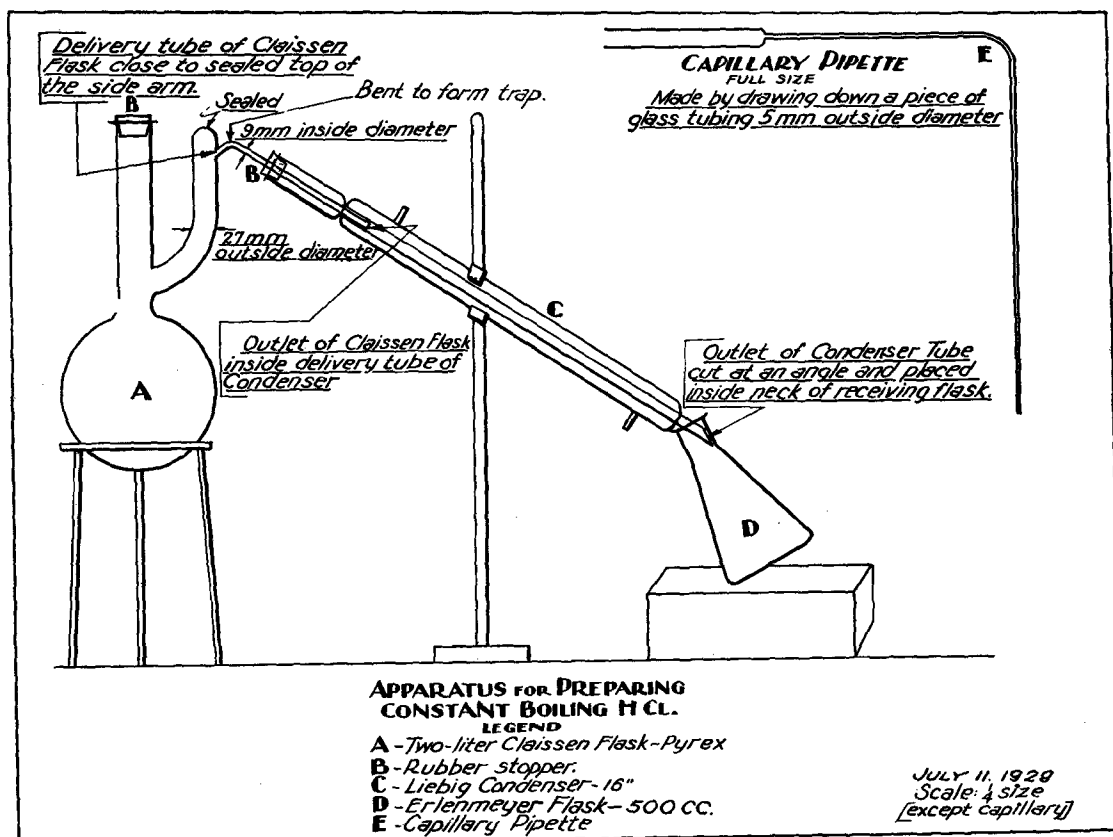
(Hulett and Bonner, *J. Amer. Chem. Soc.*, 31,309)

The following apparatus has been found desirable for the preparation of the constant boiling acid. (Description of apparatus and technique furnished by Dr. E. P. Clark, of the Bureau of Chemistry and Soils of the U. S. Dept. of Agriculture, in a private communication dated May 29, 1929). The accompanying sketch illustrates the set-up.

The distillation flask (A) is a two liter pyrex Claissen flask with the side tube sealed at the top. A small piece of crumpled platinum foil is placed in the flask to cause steady boiling. 750 cc of reagent quality concentrated hydrochloric acid are diluted with 750 cc of distilled water. This is placed in the flask and the solution is distilled at a slow

rate, using a Leibig condenser (C); when  $\frac{3}{4}$  has been distilled off, change the receiver (D)—a 500 cc Erlenmeyer flask—and collect as much of the remainder as is desirable. The last fraction is the constant boiling solution and, if the barometric pressure is noted, the exact weight of HCl in this distillate may be calculated from the table given above. By weighing out the requisite amount of the constant boiling acid and diluting with distilled water to one liter, or any other volume, a solution of the desired normality may be prepared. In weighing the liquid it is desirable to tare the flask, add approximately the desired quantity, and finally get the exact weight by adding or subtracting the necessary amount by means of a capillary pipette (E) bent at right angles as shown in the sketch. The pipette may be made from a small piece of glass tubing about 5 mm outside diameter. Experience has shown that if attention is given the following points in connection with the set-up of the apparatus, excellent results will be obtained.

(1) Use a two-liter pyrex Claissen distillation flask with the side-arm sealed to avoid the use of a rubber stopper.



(2) Have the delivery tube of the Claissen flask close to sealed top of the side-arm. Bend the delivery tube to form a trap, thereby preventing any droplets from being carried over mechanically.

(3) Use a 16-inch Liebig condenser and have the outlet of the delivery tube of the Claissen flask long enough to go inside the delivery tube of the condenser. This arrangement keeps the acid out of contact with the rubber stopper.

(4) Cut the outlet tube of the condenser at an angle and adjust the mouth of the receiving flask. This is done as an extra precaution against possible evaporation or contamination.

(5) Use equal volumes of reagent quality concentrated hydrochloric acid and distilled water, discarding the first three-quarters of the distillate and collecting as much of the last quarter portion as may be desired.

(6) The exact weighing of the distillate is greatly facilitated by employing the special capillary pipette recommended.

The committee suggests that HCl prepared by the above method be checked against sodium carbonate so that no matter which acid is used, there will be a uniform standardization method. It is understood that B. of S. weights are to be used in these standardizations. There will be available about one hundred bottles of the A. O. C. S. Standard Crude Glycerine Sample which the committee will turn over to the A. O. C. S. for sale at a nominal price.

The work on the soap sample is making good progress and the committee hopes that an accepted analysis can be reported at the next meeting. The personnel of the Soap Section Committee and the co-operating laboratories working on the soap and glycerine samples follows. It should be noted that all the laboratories did not work on the glycerine sample.

Ralph W. Bailey, Stillwell & Gladding, Inc., New York City.

A. K. Church, Chief Chemist, Lever Bros. Co., Cambridge.

Chas. J. Gundel, Works Chemist, Fels & Co., Philadelphia.

L. F. Hoyt, Manager, Research Dept., Larkin Co., Inc., Buffalo.

Martin H. Ittner, Chief Chemist, Colgate-P. O. -Peet Co., Jersey City

H. J. Morrison, the Procter & Gamble Co., Ivorydale.

Wm. A. Peterson, Chief Chemist, Kirkman & Son, Brooklyn.

W. D. Richardson, Chief Chemist, Swift & Co., Chicago.

M. L. Sheely, Chief Chemist, Armour Soap Works, Chicago.

H. P. Trevithick, Chief Chemist, N. Y. Prod. Exchange, New York City.

R. B. Trusler, Industrial Fellow, Mellon Institute, Pittsburgh.

H. C. Bennett, Chief Chemist, Los Angeles Soap Co., Los Angeles.

V. K. Cassady, Chief Chemist, The Palmolive Co., Milwaukee.

Curtis & Tompkins, San Francisco.

R. C. Dickson, Chief Chemist, Colgate-P. O. -Peet Co., Berkeley.

M. M. Durkee, The A. E. Staley Mfg. Co., Decatur.

F. E. Joyce, Haskins Bros. & Co., Omaha.

A. J. Harvey, Technical Director, Lever Bros., Ltd., Toronto.

John Ornfelt, LaFrance Mfg. Co., Philadelphia.

Foster D. Snell, Brooklyn.

W. J. Reese, Chief Chemist, Colgate-P. O. -Peet Co., Kansas City.

The chairman and secretary wish to express to each member of the committee and each cooperating laboratory their appreciation of the splendid way in which this first piece of work undertaken by the Soap Section was carried out.

### Olive Oil Situation in Spain

THE American Consul at Barcelona reports there has been no cause, during the third quarter of 1929, to change the earlier optimistic estimates of the season's olive and olive oil crop. The trees were benefited by recent rains and the fruit is said to be in good condition. There are still large stocks of olive oil on hand remaining from previous harvests, due to the unprecedented output of 1927. The result is a confused condition of the market, characterized by falling prices.

According to American Trade Commissioner Ehrhardt, shipments of soya beans from Mukden, Manchuria to the south were amounting to between twenty-five and thirty thousand tons daily during November. The shipments taxed the facilities of both the Chinese Eastern and South Manchurian railways.