Report of the Glycerin Analysis Committee, September 1950

DURING the past year the Glycerin Analysis Committee has been investigating a new method for the determination of glycerol. This procedure employs sodium periodate in place of periodic acid, is more reproducible, and overcomes the following disadvantage of the periodic acid method, namely, small size of sample and small titration for the sample. Results on 1949 and 1950 collaborative samples are attached.

The 1949 results clearly show the superiority of the sodium periodate method over the periodic acid method. The data on C. P. glycerin indicate that the results were 0.2 to 0.3% low, but a modification has brought the results more in line. The committee recommends withdrawal of the present Tentative Method Ea 6-49, and advancement of the sodium periodate method to tentative status.

H. C. BENNETT
E. L. BOLEY
W. C. CLARK
L. B. PARSONS
J. B. SEGUR
ARNOLD TROY
J. T. R. ANDREWS
W. D. POHLE, chairman

GLYCEROL SODIUM PERIODATE OXIDATION METHOD

Definition: This method determines glycerol and other polyalcohols containing three or more adjacent hydroxyl groups. The glycerol reacts with the sodium periodate in an acid soln., forming aldehydes and formic acid. The latter is a measure of the glycerol in the sample.

Scope: Applicable to any glycerin soln., but especially useful in analyses of samples containing oxidizable organic impurities and certain hydroxylated compounds which interfere with the dichromate and acetin procedures. Trimethylene glycol and other polyalcohols in which the hydroxyl groups are not adjacent do not react at room temperature. This method is not applicable when the sample contains, in addition to glycerol, polyhydroxyl compounds with three or more adjacent hydroxyl groups.

A. APPARATUS:

1. Buret, 50-ml., calibrated to meet U. S. Bureau of Standards Specifications. Delivery time must not be less than 90 seconds for 50 ml.
2. Meniscus magnifier which will permit reading the buret to 0.01 ml.
3. Pipet, 50-ml., drainage time standardized so that same quantity will be delivered to sample and blanks.
4. Variable speed stirrer, electrical or mechanical, with glass stirrer.
5. Electrometric pH meter assembly with glass electrode.
6. Beakers, 600-ml.
7. Volumetric flask, 250-ml.

B. REAGENTS:

1. Sodium periodate soln.:
   a) Dissolve 60 g. of sodium meta periodate ($NaIO_4$) reagent grade in distilled water containing 120 ml. of 0.1 *N* sulfuric acid, total volume 1 liter. Do not heat to dissolve sodium periodate. If the soln. is not clear, filter thru sintered glass filter. Store in a dark, glass-stoppered bottle (see Note 2). The acidity of this reagent may change slowly with time so a blank must be run each day that analyses are made. Sodium meta periodate ($NaIO_4$) reagent grade supplied by G. Frederick Smith or equivalent is satisfactory. If sodium meta periodate does not dissolve, it is not reagent quality and a new supply must be obtained.
   b) Test for Quality: Pipet 10 ml. of sodium periodate solution into 250-ml. volumetric flask, dilute to mark and mix thoroughly. To 0.5 to 0.6 g. of C. P. glycerin in 50 ml. of distilled water add 50 ml. of diluted sodium periodate soln. with a pipet. Prepare a blank using only 50 ml. of distilled water. Allow to stand 30 minutes, add 5 ml. of hydrochloric acid, 10 ml. of a 15% potassium iodide soln., and rotate to mix. Allow to stand 5 minutes and then add 100 ml. of distilled water. Titrate with 0.1 *N* sodium thiosulfate soln., shaking continuously until yellow color has almost disappeared. Add 1 to 2 ml. of starch indicator soln. and continue titration, adding the thiosulfate soln. slowly until blue color has just disappeared. The sodium periodate is satisfactory when the titration of soln. containing glycerol divided by titration of the blank is between 0.750 and 0.765.
2. Sodium hydroxide soln., ca 0.1000 *N* but accurately standardized with potassium acid phthalate using phenolphthalein indicator.
3. Sodium hydroxide soln., ca 0.05 *N*.
4. Sulfuric acid soln., 0.2 *N*.
5. Potassium acid phthalate, acidimetric standard quality and dry.
   Note: A standard sample of potassium acid phthalate with a certificate of analysis may be obtained from the National Bureau of Standards at Washington, D. C. This sample is strongly recommended as a primary standard for this method. Use as directed in certificate of analysis accompanying the sample.
6. Phenolphthalein indicator soln., 1% in 95% alcohol.
7. Brom-thymol blue indicator soln., 0.1% in distilled water prepared as follows: Dissolve 0.1 g. of dry indicator in 16 ml. of 0.01 *N* NaOH by grinding indicator with the alkali in a mortar. Transfer to a 100-ml. volumetric flask, dilute to volume with distilled water, and mix thoroughly.

Analyses of Collaborative Samples, 1950, Glycerol, %

Analyst	C. P. Glycerin by—					Soap Lye Crude by—		Saponification Crude by—		Half Crude by—	Spent Lye by—
	Sp. gr., Ea 7-46	100%—Moisture,% by Fischer Method, Ea 8-46	Sodium Periodate Method		Periodic Acid Method, Ea 6-46	Acetin Method, Ea 4-46	Sodium Periodate	Acetin Method, Ea 4-46	Sodium Periodate	Sodium Periodate	Sodium Periodate
			1950	Modified[1]							
1	94.96	95.1	95.0	95.2	95.1	80.0	81.1	89.0	90.0	31.1	5.45
2	94.96	95.3	94.5	94.6		80.2	80.7	89.0	90.0	30.9	5.42
3	94.96	95.3	94.5	94.7		79.0	80.1	87.2	89.2	30.7	5.42
4	94.90	95.0	94.6	94.8		80.5	80.7	89.2	89.6	31.0	5.45
5	94.89		95.0	95.2		79.1	80.4	88.4	89.5	30.8	5.44
6	94.89		94.8	95.0		79.6	80.7	89.6	89.5	31.0	5.38
7	94.90	94.9	95.5	95.7		80.9	81.2	89.7	90.4	31.4	5.50
8	94.92	95.2	94.4	94.6		80.1	80.8	89.0	89.8	31.1	5.48
Average	94.9	95.1	94.8 94.7[2]	95.0 94.9[2]		79.9	80.7	88.9	89.8	31.0	5.44
Range	.07	0.4	1.1 0.5[3]	1.1 0.6[3]		1.9	1.1	2.5	1.2	0.7	0.12

[1] Per cent glycerol, based on titration of blank to pH 6.5. [2] One result omitted when calculating average. [3] One result omitted when calculating this range.

Analyses of Collaborative Samples, 1949, Glycerol, %

Laboratory	C. P. Glycerin by—				Crude Glycerin by—				Salt and Glycerin Solution, by—			Trimethylene Glycol Concentration by—		
	Sp. Gr., Ea 7-46	Periodic Acid, Ea 6-46	Sodium Periodate		Acetin, Ea 4-38	Periodic Acid, Ea 6-46	Sodium Periodate		Periodic Acid, Ea 6-46	Sodium Periodate		Periodic Acid, Ea 6-46	Sodium Periodate	
			pH Meter	Indicator			pH Meter	Indicator		pH Meter	Indicator		pH Meter	Indicator
1	95.1	95.7	94.8	94.7	80.4	81.4	80.5	80.4	2.32	2.24	2.24	41.5	41.1	41.0
2	95.0	95.1	94.8	94.7	80.1	81.1	80.3	80.0	2.26	2.24	2.23	41.2	40.9	40.7
3	95.2	95.3	94.6		80.9	80.8	80.9		2.29	2.25		41.5	41.0	
4	94.9	96.1	95.6	95.5	79.7	80.1	80.4	80.0	2.35	2.22	2.21	41.4	40.7	40.7
5	95.0	94.9	94.7		80.3	80.3	80.1		2.25	2.24		41.2	40.8	
6	95.1	96.0	94.8		81.0	81.6	80.5		2.28	2.24		42.0	41.1	
Average	95.1	95.5	94.9 94.7*		80.4	80.9	80.5		2.29	2.24		41.5	40.9	
Range	0.3	1.2	1.0 0.2*		1.3	1.5	0.8		0.10	0.03		0.8	0.4	

* One test omitted.

8. Ethylene glycol soln.; mix 1 volume of ethylene glycol and 1 volume of distilled water.
9. Sodium thiosulfate soln., 0.1 *N*, accurately standardized.
10. Hydrochloric acid, sp. gr. 1.19, A.C.S. grade.
11. Starch indicator soln., make a homogeneous paste of 10 g. of soluble starch in cold distilled water. Add to this 1 liter of boiling distilled water, stir rapidly and cool. Salicylic acid (1.25 g. per liter) may be added to preserve the indicator. If long storage is required, the soln., must be kept in a refrigerator at 4° to 10°C. (40° to 50°F.). Fresh indicator must be prepared when the endpoint of the titration fails to be sharp from blue to colorless.
12. Potassium iodide, A.C.S. grade. Prepare 15% soln., by weight of solid KI in distilled water.

C. PREPARATION OF SAMPLE:

1. Samples containing separated salt, sediment, or suspended matter must be warmed and thoroughly mixed to insure uniform distribution. Some sediment tends to cling to the bottom of the container, and the viscosity of glycerin retards rapid dispersion. Any mixing procedure which will secure positive distribution is satisfactory. Careful preparation of sample is necessary to obtain an accurate analysis.

D. PROCEDURE:

1. Make all weighings accurately and rapidly. This is conveniently done from a weighing pipet into the 600-ml. beaker when the sample contains more than 20% glycerol. When the sample contains less than 20% glycerol, it may be weighed onto a tared dish and then wash the sample into the 600-ml. beaker with distilled water. When sample is less than 50 ml., dilute to 50 ml. with distilled water.

   For accurate results, weigh approximately the amount specified in Table I. Smaller samples, half the specified amount, give slightly higher and less precise results. When 18 g. of salt is weighed for analysis, dissolve in 100 ml. of distilled water; and when salt contains 1% or less glycerol, weigh 25 g. and dissolve in 150 ml. of distilled water. When glycerol content is not known, make a single preliminary test using the amount specified for 100% glycerol. From the results of this test select the proper sample size.
2. Add 5 to 7 drops of brom-thymol blue indicator to the sample in the 600-ml. beaker and acidify with 0.2 *N* H_2SO_4 to a definite green or greenish yellow color. Neutralize with 0.05 *N* NaOH, to indicator endpoint, a definite blue free of green color. Add a drop at a time when approaching the endpoint, sharp green to blue transition. When color of soln. (see Note 1) interferes with the detection of the color change of the indicator, use the pH meter and adjust to pH 8.1 ± 0.1.
3. At this point prepare a blank containing 50 ml. of distilled water but no glycerol and carry through simultaneously with the sample in an identical manner.
4. Add 50 ml. of sodium periodate soln. with a pipet, swirl gently to insure thorough mixing, cover with a watch glass, and allow to stand for 30 min. at room temperature.
5. At the end of this period add 10 ml. of 50% ethylene glycol-water soln. and allow to stand 20 minutes.
6. Dilute to approximately 300 ml. and titrate, using pH meter to determine the endpoint pH 6.5 ± 0.1 for the blank and 8.1 ± 0.1 for the sample. When approaching the endpoint, add alkali, a drop or part of a drop at a time. Read buret to 0.01 ml. and record reading.

TABLE I

Weight of Sample to be Taken for Analysis Based Upon the Glycerol Content

Glycerol in Product to be Analyzed	Grams of Sample to be Weighed—
100 or less	0.45
90 or less	0.50
80 or less	0.55
70 or less	0.65
60 or less	0.75
50 or less	0.90
40 or less	1.10
30 or less	1.50
20 or less	2.20
10 or less	4.50
5 or less	9.00
2.5 or less	18.00
1.0 or less	40.00
0.5 or less	80.00

E. CALCULATIONS:

$$\text{Glycerol, \%} = \frac{(S - B) \times N \times 9.209}{W}$$

S = ml. of NaOH soln. to titrate sample.

B = ml. of NaOH soln. to titrate blank. B must not be less than 5.0 ml.

N = normality of NaOH.

W = weight of sample in grams.

F. NOTES:

1. If the sample contains an appreciable amount of buffering material the pH must be adjusted with pH meter to the endpoint to which the sample will be titrated. In some instances buffering action may be sufficiently great to prevent good reproducibility of results.
2. Cork must not be used to stopper any flasks used in this determination or in any other way allowed to come in contact with any of the materials used in or for the analysis.
3. The presence of a sufficient excess of sodium periodate in a given test can be checked as follows: Test the sample using three-fourths the sample size used in the original test. This can be done when running duplicate tests by weighing one approximately three-fourths of the other. If analysis of the smaller sample agrees with that of the larger sample, there is sufficient excess sodium periodate in both cases. If the analysis of the smaller shows higher glycerol content, differing more than experimental error, there was not sufficient excess of sodium periodate for oxidation of larger sample. Another test must be run using a smaller sample. When glycerol content is unknown, weigh the amount specified for 100% glycerol and from the results of this test select the proper size sample.