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Analysis of Mixtures of Glycerol, Propylene Glycol, and Trimethylene Glycol*

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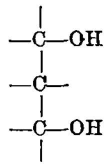
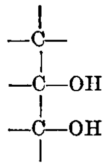
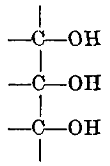
THE analysis of mixtures of glycerol, propylene glycol, and trimethylene glycol is difficult because of the close similarity between these compounds, the structures of which are indicated below:


Trimethylene Glycol


Propylene Glycol


Glycerol

These compounds may be found together in certain fractions from glycerin refining such as sweet water concentrate. Sweet water concentrate is an important source of trimethylene glycol. Neither the dichromate method (1), which oxidizes all organic compounds, nor the acetin method (2), in which acetic anhydride reacts with the hydroxyl group, nor a combination of these will give much information about the composition. However, there are now available other methods in which the reactions are more specific than those formerly used. These reactions were utilized in this study.

Glycerol can be determined by the periodic acid method (3) and this method in combination with the dichromate or acetin methods will give an approximation of the total trimethylene glycol and propylene glycol. A more exact evaluation can be obtained by taking advantage of the specific and selective action of periodic acid on polyhydric alcohols and using this in combination with an accurate method for the determination of total acetylatable material which is described herein.

Procedures making use of the special properties of periodic acid have been applied to mixtures of glycerol, ethylene glycol, and diethylene glycol (6), glycerol, ethylene glycol, and propylene glycol (7, 8).

Periodic acid oxidizes glycerol to formic acid and aldehydes, and propylene glycol only to aldehydes. It does not react with trimethylene glycol. The glycerol is thus determined by titration of the formic acid obtained from such an oxidation. Propylene glycol may then be calculated from the total periodic acid consumed in the reaction less that required to oxidize the glycerol.

$$CH_2OH{-}CHOH{-}CH_2OH + 2H_5IO_6 \rightarrow 2HCHO + HCOOH + 2HIO_3 + 5H_2O$$

$$CH_2OH{-}CHOH{-}CH_3 + H_5IO_6 \rightarrow HCHO + CH_3{-}CHO + HIO_3 + 3H_2O$$

Knowing the percentages of glycerol and propylene glycol, the trimethylene glycol can be calculated after determining the total acetylatable material. A series of analyses were performed on samples of known composition using these reactions with modifications of previous procedures for glycerol (3), monoglycerides (4), and glycerol by acetylation (5).

Experimental

C. P. grade glycerol (95.4% by sp. gr. and 95.5% by periodic acid method) and propylene glycol (Eastman Kodak Co., 1321 b.p. 85-86°/10 mm.) were obtained in a pure state. Some difficulty was encountered in obtaining pure trimethylene glycol. Analysis of a sample (Eastman Kodak Co., P. 264 b.p. 123-125°/30 mm.) showed the presence of 0.9% glycerol, 2.2% propylene glycol and 91.7% trimethylene glycol. We then tried to prepare pure trimethylene glycol by distilling a sweet water concentrate from a Podbielniak Column, collecting the fraction that distilled between 107° and 108°C. under a pressure of 13 mm. mercury. Analysis of the fraction indicated the presence of 0% glycerol, 1.2% propylene glycol, and 97.1% trimethylene glycol. These data indicated that either the trimethylene glycol is very difficult to purify or the methods of analysis under consideration were not entirely reliable when applied to this compound. To obtain more information on this point the Eastman Kodak Co. product was distilled from the Podbielniak Column and the portion distilling within a narrow range was collected in numerous fractions. The analyses of these fractions are given in Table I.

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TABLE I

Analyses of Fractions of Trimethylene Glycol Distilled from the Podbielniak Column

Fraction	Distillation Temp. °C.	Pressure, mm. of mercury	Refractive Index at 30°C.	Composition by Analysis		
				% Glycerol	% Propylene Glycol	% Trimethylene Glycol
2	108	11.7	1.4372	0	3.6	93.6
3	108.5	11.7	1.4370	....	2.4	96.1
4	107.5	12.3	1.4370	0	1.3	97.8
5	107.5	12.3	1.4369	....	0.9	98.7
6	108	12.3	1.4367	....	0.6	99.2
7	108	12.3	1.4368	0	0.4	99.8
8	113.5	17	1.4368	....	0.2	99.9
9	114	17	1.4368	0	0.14	100.4

These analyses show that fractions 7, 8, and 9 were practically free from propylene glycol and glycerol. A composite of these fractions was used in the tests reported in Table II.

The refractive index is frequently used to follow purification by distillation. Schierholtz and Staple (9) purified trimethylene glycol by distillation until the refractive index of successive fractions collected differed by less than 0.0038. The final product had a refractive index of 1.43940 at 21°C. and 1.43847 at 25°C. The calculated value of 1.4373 at 30°C. compares with 1.4372 for fraction 2 in Table I which analyzed 3.6% propylene glycol. The slight difference in refractive indices of fractions 3 to 9 shows that the refractive index does not indicate the presence of small amounts of impurities such as propylene glycol.

Analysis of propylene glycol, trimethylene glycol, and glycerin (84.5% glycerol) and mixtures of these are shown in Table II. The 84.5% glycerol was prepared by quantitative dilutions of previously analyzed 95% C. P. glycerin with distilled water. The diluted portion was checked by specific gravity and by determination of the moisture (Fischer method) (10).

TABLE II

Analyses of Pure Glycerin, Propylene Glycol, Trimethylene Glycol, and Mixtures of These

Sample	Composition of Sample					
	Glycerol, %		Propylene Glycol, %		Trimethylene Glycol, %	
	Found	Present	Found	Present	Found	Present
Glycerin	84.1	84.5	0	0	0	0
Propylene glycol	0	......	100.2	......	0	......
Trimethylene glycol	0	......	0.3	......	100.0	......
Mixtures:						
1. Glycerin + Propylene glycol	6.9	6.3	91.0	92.2	......	......
2. Glycerin+ Propylene glycol	25.8	25.9	68.7	69.3	......	......
3. All three compounds	27.6	26.8	29.0	30.7	36.5	36.5
	27.2	26.8	31.2	30.7	35.7	36.5
4. All three compounds	9.7	9.8	15.3	15.5	71.5	70.7
	10.0	9.8	15.0	15.5	71.4	70.7
5. All three compounds	0.8	0.7	2.0	1.9	94.4	94.5

These data indicate that glycerol, propylene glycol, and trimethylene glycol alone and in mixtures can be determined with a fair degree of accuracy, within about 0.8% for glycerol, within about 1.7% for propylene glycol, and within about 1.0% for trimethylene glycol.

The variations that occurred in individual determinations are shown in Table III:

TABLE III

Analyses of Mixtures of Glycerol, Propylene Glycol, and Trimethylene Glycol

Sample	Test	Composition of Sample					
		Glycerol, %		Propylene Glycol, %		Trimethylene Glycol, %	
		Found	Present	Found	Present	Found	Present
1	1	27.3	26.8	29.2	30.7	36.8	36.5
	2	27.8	26.8	28.8	30.7	36.2	36.5
	3	26.6	26.8	32.2	30.7	34.9	36.5
	4	27.6	26.8	30.3	30.7	36.5	36.5
2	1	9.6	9.8	15.2	15.5	71.3	70.7
	2	9.9	9.8	15.3	15.5	71.6	70.7
	3	9.9	9.8	14.9	15.5	71.6	70.7
	4	10.0	9.8	15.0	15.5	71.2	70.7
3	1	0.8	0.7	2.0	1.9	94.4	94.5
	2	0.8	0.7	2.0	1.9	94.3	94.5

The results are better than have been possible by other means. These methods of analysis are not limited to the compounds mentioned, but may be applied to mixtures of other compounds of similar structure and properties.

Analyses of sweet water concentrates are given in Table IV. The water content was determined by the Fischer volumetric method (10). The substance reported as propylene glycol was not confirmed by preparation of a derivative. However, it conformed in boiling point as well as by reaction with periodic acid and acetic anhydride. The portion unaccounted for by analysis is listed as "other compounds."

TABLE IV

Analyses of Sweet Water Concentrates

Sample	Glycerol	Propylene glycol	% Trimethylene glycol	"Other Compounds"	Water
1	19.5	10.2	51.3	9.1	9.9
2	25.2	10.4	39.7	14.9	9.8
3	19.1	4.8	50.7	15.5	9.9

Method

Reagents for Glycerol:

1. Periodic acid solution; dissolve 20 g. of H_5IO_6, reagent grade, in 1 liter of distilled H_2O. If the solution is not clear, filter through a sintered glass filter. Store the solution in a dark, amber, glass-stoppered bottle. The oxidizing power of this solution decreases slowly with time, therefore, a blank must be run each day that the solution is added.
2. Sodium hydroxide, 0.1250 *N*; standardized with potassium acid phthalate, using phenolphthalein indicator.
3. Phenolphthalein indicator solution; 1% in 95% alcohol.
4. Methyl red indicator solution; 0.1% in distilled water.
5. Sodium hydroxide, ca 0.05 *N*; keep in a dropping bottle for easy dispensing.
6. Sulfuric acid, ca 0.2 *N*; keep in a dropping bottle for easy dispensing.

Reagents for Propylene Glycol:

7. Sodium thiosulfate, 0.08 *N*; dissolve 19.9 g. of $Na_2S_2O_3 \cdot 5H_2O$, A.C.S. grade in 1 liter of boiled and cooled distilled H_2O. Store in a bottle that has been cleaned with dichromate cleaning solution and thoroughly rinsed with warm distilled H_2O. Maintain solution in a dark, cool place. Never return to the stock bottle any portion which has been withdrawn. Standardize with potassium dichromate.
8. Starch indicator solution.
9. Potassium iodide solution; dissolve 200 g. of KI, A.C.S. grade, in distilled H_2O and dilute to 1 liter.
10. Acetic acid, glacial, A.C.S. grade, 99.5%.

Reagents for Trimethylene Glycol:

11. Acetic anhydride-pyridine reagent; pour into a clean, dry glass-stoppered bottle 1 vol. of reagent grade acetic anhydride (assay minimum 95%) and 6 vols. of pyridine (Barrett's 2-A refined or Eastman Kodak Co. 214, b.p. 113.5 to 115.5°C.). Stopper the bottle and mix by gentle shaking. Solutions over two weeks old should be discarded. Prepare fresh solution when it becomes colored.
12. Alcoholic potassium hydroxide solution, 0.32 *N* to 0.35 *N* KOH in 95% (U.S.S.D. Formula No. 30 is satisfactory) ethyl alcohol, accurately standardized with potassium acid phthalate using phenolphthalein indicator.
13. Isobutyl alcohol, reagent quality.

Precautions:

Flasks and bottles in which periodic acid solutions are prepared, mixed, or diluted must be glass-stoppered. Rubber stoppers and cork stoppers must never be used where periodic acid can come in contact with them.

Procedure for Glycerol:

Weigh accurately ca 0.5 g. of sample, transfer to a clean 600-ml. beaker, and add ca 50 ml. of distilled H_2O. Add one drop of the methyl red indicator, acidify with ca 0.2 *N* H_2SO_4 and then neutralize with ca 0.05 *N* NaOH to the yellow color which corresponds to a pH of ca 6.2. If the color of this solution interferes with the detection of the color change of the indicator, use the pH-meter and adjust to pH 6.2. Add 50 ml. periodic acid solution from a volumetric pipet and shake gently to effect thorough mixing. Cover with a watch glass and allow to stand for 1 hour at room temperature. Dilute with distilled H_2O to 240 to 250 ml. and titrate with 0.1250 *N* NaOH using a glass electrode pH-meter to determine the end-point (pH 6.2). During the titration stir with an electric stirrer to assure a uniform solution. As the end-point is approached add the alkali in increments of 0.1 ml. to and past the end-point. Record the volume of the NaOH solution and the corresponding pH when within 0.1 to 0.2 ml. of the end-point and do likewise after passing the end-point. Reserve this solution for the determination of propylene glycol.

Conduct a blank determination in an identical manner using the same amount of reagents except that the blank is titrated to a pH of 5.4 instead of 6.2. Reserve for determination of the blank in the propylene glycol procedure.

Procedure for Propylene Glycol:

Transfer, quantitatively, into a 500-ml. glass-stoppered volumetric flask, the solution reserved from the determination of glycerol, make up to volume with distilled water and mix thoroughly. Pipet 50 ml. into a 300-ml. Erlenmeyer flask, add 10 ml. glacial acetic acid, mix and then add 10 ml. of KI solution and remix. Allow to stand 1 to 2 minutes. Titrate with 0.08 *N* sodium thiosulfate to the disappearance of the brown iodine color. Add I ml. of starch indicator and continue the titration to the disappearance of the blue iodo-starch color. Read the buret to hundredths of a ml. using a magnifier. Conduct a blank determination on the blank from the glycerol analysis in an identical manner using the same amounts of reagents.

The titration of the sample should be more than 80% of the blank. When the titration of the sample is less than 80% of the titration of the blank, repeat the determination using a smaller sample starting at the beginning with the glycerol analysis. When the difference between the titration of the blank and sample is small (less than 3 ml.) the accuracy may be improved by taking a larger sample.

Procedure for Trimethylene Glycol:

Weigh accurately ca 0.18 g. of sample into a 300-ml. glass-stoppered flask (See Note 1). Add 5 ml. of acetic anhydride-pyridine reagent with a volumetric pipet. Moisten the stopper with a little pyridine, place loosely in the flask and set the flask on a well-fitting hole on a steam bath. Loosen the stopper 2 or 3 times during the first 3 or 4 minutes the flask is on the steam bath to relieve the pressure. Then insert the stopper tightly and heat for 30 to 40 minutes. Remove the flask from the steam bath, cool at room temperature for 1 to 3 minutes and then add 5 ml. of distilled H_2O. Run the water down over the stopper and inside of the flask. Replace the stopper and heat on the steam bath for 1 to 2 minutes. Remove the flask from the steam bath, cool at room temperature for 10 to 15 minutes and add 25 ml. of isobutyl alcohol, washing down the stopper and sides of the flask. Add 0.5 ml. of phenolphthalein indicator solution and titrate with the alcoholic KOH solution. Conduct a blank determination simultaneously and in an identical manner except that the blank need not be heated on the steam bath.

When the titration of the sample is less than 65% of the titration of the blank, repeat the determination using a smaller sample. When the difference between the titration of the blank and sample is small (less than 3 ml.) the accuracy of the analysis can be improved by using a larger sample.

Calculation of Glycerol:

1. Calculations for volume of alkali required to titrate sample and blank to their respective end-points:

$$S_x = S_1 + (S_2 - S_1) \times \frac{pH_x - pH_1}{pH_2 - pH_1}$$

S_1 = volume of alkali before end-point and pH_1 equals pH at S_1.

S_2 = volume of alkali after end-point and pH_2 equals pH at S_2.

S_x = volume of alkali at end-point and pH_x equals pH at S_x.

The volume of alkali required to titrate the sample and blank is calculated in the same manner. In the former $pH_x = 6.2$ and in the latter $pH_x = 5.4$.

2. Calculation of glycerol:

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

S = ml. sodium hydroxide to titrate sample.
B = ml. sodium hydroxide to titrate blank.
N = normality of sodium hydroxide.
W = weight of sample, taken for glycerol determination.
G = % glycerol.

Calculation of Propylene Glycol:

Total material reacting with periodic acid calculated as

$$\text{\% glycerol} = \frac{(B - S) \times N \times 23.02}{W} = D.$$

B = ml. sodium thiosulfate to titrate blank.
S = ml. sodium thiosulfate to titrate sample.
N = normality of sodium thiosulfate.
W = weight of sample taken for glycerol determination.
P = % propylene glycol.
Propylene glycol, % = (D − G) × 1.6526 = P.

Calculation of Trimethylene Glycol:

Total acetylated material calculated as % glycerol=

$$\frac{(B-S)\times N\times 3.070}{W}=T.$$

B=ml. alcoholic potassium hydroxide.
S=ml. alcoholic potassium hydroxide to titrate sample.
N=normality of alcoholic potassium hydroxide.
W=weight of sample.
Trimethylene glycol, %=[(T−G)×1.239]−P.
T=total acetylatable calculated as % glycerol.

Note

1. The determinations of trimethylene glycol is limited to solutions containing less than 20% water. The acetylation procedure is not quantitative when the water is in excess of this amount.

Summary:

Procedures have been presented for the determination of glycerol, propylene glycol, and trimethylene glycol in the solutions containing all three and for analysis of sweet water concentrates. The methods are not limited to the products studied, but may be applied to mixtures of other hydroxy compounds which possess similar properties.

Acknowledgment

The authors wish to express their indebtedness to Dr. K. F. Mattil of the Swift & Co. Fat and Oil Research Division for the distillation and preparation of pure trimethylene glycol.

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Graphical Solution of Andre-Cook Relation for Computing Acetyl Values

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THE commonly used Andre-Cook (1) method for determining the acetyl value of a substance requires the use of a somewhat complex equation in its determination. However, this relation, given below, readily lends itself to a simple graphical solution.

$$A=\frac{S'-S}{1-.00075S}$$

Three nomograms (2, 3) are submitted which afford a straight-forward graphical solution to this relation. Figure 1 covers an extensive range of values from 0 to 500. This nomogram is useful for graphically visualizing the change produced in one variable by changes occurring in one or both of the other two variables; for roughly estimating values; and for spot-checking values numerically calculated. Due to its wide coverage of values, the accuracy with which the scales can be read is necessarily limited.

However, any portion of this "over-all" nomogram can be expanded to give any required degree of precision. Thus, Figure 2 is an expanded section of Figure 1 and covers a limited range of values applicable for the accurate calculation of the acetyl value of castor oil. Figure 3 is another expanded section and covers a range of values applicable for the accurate calculation of the acetyl values of such common fats as tallow, lard, cottonseed, soybean, and peanut oil.

Examples have been worked out on the three nomograms illustrating their use. Given saponification values of 180.0 and 308.0 before and after acetylation, the corresponding acetyl value works out to be 148.0 as indicated by the value at the intersection of the line connecting the two saponification values with the acetyl value scale (see Figures 1 and 2). Given saponification values of 200 and 217 before and after acetylation, the corresponding acetyl value works out to be 20 as indicated in Figure 3.

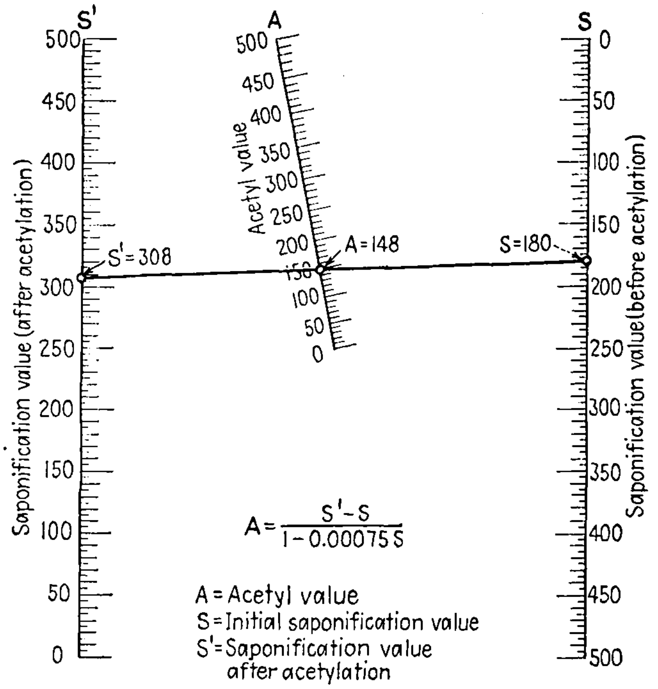

Fig. 1.