prepared. This combination was thoroughly ground and mixed to ensure homogeneity. Content of the mixture follows:

	Grams		Grams		Grams
NaCl	2.5000	Na_2SO_3	2.5000	$C_6H_5SO_2Na$	40.0000
Na_2SO_4	2.5000	$C_6H_5SO_3Na$	2.5000		

An analysis of the mixture containing 80.00% sodium benzene sulfinate gave the results shown in Table II.

ACKNOWLEDGMENT

The author is duly grateful to J. Werner for guidance, and to P. Nawiasky and R. H. Zappert for cooperation and constructive criticism.

Thanks are extended to H. M. Schramm for the sulfur determination, and L. T. Hallett for the carbon and hydrogen determinations.

LITERATURE CITED

(1) Krishna, S., and Das, Bhagwan, *Quart. J. Indian Chem. Soc.*, **4**, 367–74 (1927).
(2) Krishna, S., and Singh, Harnam, *J. Am. Chem. Soc.*, **50**, 792–8 (1928).
(3) Thomas, J., *J. Chem. Soc.*, **95**, 342–5 (1909).

Determination of 1,2-Propylene Glycol in Ethylene Glycol

R. C. REINKE AND E. N. LUCE, The Dow Chemical Company, Midland, Mich.

A procedure for the determination of 1,2-propylene glycol in the presence of ethylene glycol consists of a periodate oxidation of 1,2-propylene glycol to acetaldehyde and formaldehyde and of ethylene glycol to formaldehyde, and the separation of the two aldehydes by a blowing-out process, forming the acetaldehyde sulfite addition compound which is titrated with iodine. By this method it is possible to determine 98% of the 1,2-propylene glycol present over a range of 0 to 90% 1,2-propylene glycol in ethylene glycol. A method for determining total glycols by periodate is also given.

A METHOD was desired for the determination of 1,2-propylene glycol in ethylene glycol, in varying amounts and in various types of samples. Fractionation procedures were impractical, since they required too much time and did not easily permit analytical separation because of the small difference in boiling points. Furthermore, this type of method would not be satisfactory when dilute aqueous solutions were encountered.

A search of the literature revealed much work on this problem, but none suitable to the authors' needs.

Hoepe and Treadwell (*4*) developed a method for the quantitative determination of glycerol, ethylene glycol, and 1,2-propylene glycol involving periodate oxidation of the alcohols and depending on accurate determination by the potassium cyanide method of formaldehyde in the presence of acetaldehyde. The authors found this procedure unsuitable, owing to interference of the acetaldehyde. In a method for determining small amounts of lactic acid in blood and urine, developed by Clausen (*1*), the lactic acid was oxidized to acetaldehyde which was removed by an aeration process from the other oxidized materials. Nicolet and Shinn (*6*) determined methyl pentose in the presence of pentoses by a periodate oxidation and separation of aldehydes by aeration. As the basis for the present work Shupe's (*7*) micro application of the Nicolet and Shinn procedure to glycols in cosmetic ingredients was used. Changes in design of equipment and procedure were made to ensure theoretical results in the type samples encountered.

OUTLINE

The oxidation of glycerol by the periodate method of Malaprade (*5*), Fleury and Fatôme (*3*) and adaptation to glycols by Denice (*2*) may be expressed as follows:

$$C_2H_4(OH)_2 + HIO_4 \longrightarrow 2CH_2O + HIO_3 + H_2O$$

$$CH_3CHOHCH_2OH + HIO_4 \longrightarrow CH_2O + CH_3CHO + HIO_3 + H_2O$$

The ethylene glycol yields two molecules of formaldehyde, while the 1,2-propylene glycol reacts to give one molecule each of formaldehyde and acetaldehyde. The aldehydes are separated by blowing them through a saturated solution of sodium bicarbonate containing a definite quantity of glycine. This treatment removes the formaldehyde, and the acetaldehyde is then determined by the sodium bisulfite procedure:

$$HCHO + NH_2CH_2COOH \longrightarrow CH_2NCH_2COOH + H_2O$$

$$CH_3CHO + NaHSO_3 \longrightarrow CH_3C(OH)(H)—SO_3Na$$

$$2NaHSO_3 + 2I_2 + 2H_2O \longrightarrow 4HI + H_2SO_4 + Na_2SO_4$$

The sulfite solution containing the absorbed acetaldehyde is treated with iodine to remove excess sulfite and then made alkaline with saturated sodium bicarbonate which destroys the addition compound. The sulfite thus liberated is titrated with a standard iodine solution with a buffer added just before the end point.

REAGENTS

PERIODIC ACID, 0.1 *M*. Weigh 10.7 grams of sodium metaperiodate into a 500-ml. volumetric flask, and add 200 ml. of water followed by 100 ml. of 1 *N* sulfuric acid. Dilute the solution to volume with distilled water and shake the flask until solution is complete.

IODINE, standard 0.1 *N*.

IODINE, standard 0.02 *N*. Dissolve 30 grams of potassium iodide in 100 ml. of water in a 500-ml. volumetric flask and measure in accurately from a buret 100 ml. of standard 0.1 *N* iodine. Make to volume with distilled water.

IODINE, approximately 0.1 *N*.

SODIUM BISULFITE, 5%. Dissolve 5 grams of sodium bisulfite in 100 ml. of water.

BUFFER (Borax–sodium carbonate mixture). Dissolve 4 grams of borax ($Na_2B_4O_7.10H_2O$) and 5 grams of anhydrous sodium carbonate in 100 ml. of water.

GLYCINE (aminoacetic acid). Dissolve 5 grams of U.S.P. glycine in saturated sodium bicarbonate solution and dilute to 250-ml. volume with saturated sodium bicarbonate solution.

STARCH. Dissolve 0.5 gram of soluble starch in 10 ml. of cold water and add to 90 ml. of boiling water. Boil 5 minutes and cool.

SODIUM BICARBONATE, U.S.P. powder.

SODIUM BICARBONATE, saturated aqueous solution.

SODIUM ARSENITE, standard 0.1 *N*.

POTASSIUM IODIDE, approximately 10%.

APPARATUS

Special equipment used in determining 1,2-propylene glycol consisted of:

CARBON DIOXIDE OR NITROGEN, one cylinder.

FLOWMETER, calibrated for 1.5 liters of carbon dioxide per minute.

REACTION AND ABSORPTION TUBES. The equipment consists of a series of 4 test tubes connected in a manner satisfactory for passing gas through the solutions. The first tube (200 × 29 mm.) is fitted with a 3-hole rubber stopper carrying a small separatory funnel through which the sample aliquot and periodate solutions are added. This funnel also serves as an inlet tube for carbon dioxide. A large-bore glass tube, also inserted in the stopper of the first tube, is divided above the stopper by a piece of rubber tubing. It serves as a reservoir and inlet for the sodium

bicarbonate powder. A pinchclamp on the rubber tubing prevents loss of gas when the sodium bicarbonate is added. The other 3 tubes in the series are 150 × 25 mm.

PROCEDURE

TOTAL GLYCOLS. Pipet an aliquot of not more than 30 ml., containing not less than 15 mg. nor more than 90 mg. of glycols calculated as ethylene glycol, into a 125-ml. Erlenmeyer flask. Pipet in 15.00 ml. of 0.1 *M* periodic acid, mix well, and allow to stand 15 minutes. Add 30 ml. of saturated sodium bicarbonate solution, after which the solution should be approximately neutral. Measure in accurately 50.00 ml. of 0.1 *N* sodium arsenite and finally add 1 ml. of 10% potassium iodide and an excess of solid sodium bicarbonate. Titrate with 0.1 *N* iodine. With a little practice the yellow end point can readily be detected, and the use of this end point without the addition of starch is preferred. The presence of solid sodium bicarbonate improves the quality of the end point by ensuring a saturated solution.

Run a blank determination by placing 15.00 ml. of 0.1 *M* periodic acid in a 125-ml. Erlenmeyer flask, add 30 ml. of saturated sodium bicarbonate solution, 50.00 ml. of 0.1 *N* sodium arsenite, and 1 ml. of 10% potassium iodide, and allow the solution to stand 15 minutes. Add solid sodium bicarbonate in excess and titrate with 0.1 *N* iodine to the yellow end point.

The milliliters of 0.1 *N* iodine used for the determination minus the milliliter used for the blank gives the milliliter of 0.1 *N* iodine equivalent to the periodic acid used to oxidize the ethylene glycol and 1,2-propylene glycol.

$$\frac{\text{Net ml. of 0.1 } N \text{ iodine} \times 0.003102 \times 100}{\text{sample weight}} = \%$$ by weight of ethylene glycol + 1,2-propylene glycol, as ethylene glycol

The above result (total glycol as ethylene glycol), minus per cent of 1,2-propylene glycol from the following determination times 31/38, equals per cent by weight of ethylene glycol.

Glycerol, if present, must be determined and accounted for, since it is also oxidized by periodate in accordance with the following equation:

$$CH_2OHCHOHCH_2OH + 2KIO_4 \longrightarrow 2CH_2O + HCOOH + 2KIO_3 + H_2O$$

In this case the formic acid may be titrated.

1,2-PROPYLENE GLYCOL. Accurately weigh a sample of the proper size and dilute to a suitable volume, so that a 10- to 20-ml. aliquot will contain not more than 50 mg. of total glycols and not more than 10 mg. as 1,2-propylene glycol. Pipet an aliquot to the largest test tube of the series described above and stopper it after adding water, if necessary, to make a final volume of 25 ml. Pipet into the second test tube sufficient glycine solution to leave a 10% excess of glycine over the amount required to remove the formaldehyde. Too large an excess will remove some acetaldehyde and cause low results. If the ethylene glycol content is unknown, make a trial determination first and calculate the amount of glycine from the result. Add to the second tube saturated sodium bicarbonate solution sufficient to make the final volume 10 ml. In the third and fourth tubes place 1 ml. of 5% sodium bisulfite and 15 ml. of distilled water.

Place 15 ml. of 0.1 *M* periodic acid in the separatory funnel and connect the carbon dioxide line. Open the stopcock and allow the acid to run into the reaction tube. Mix the solution gently for 15 minutes by passing in a small amount of carbon dioxide. Meanwhile place 4 grams of solid sodium bicarbonate in the large-bore glass tube. After the 15-minute mixing, remove the pinchclamp and tap in the sodium bicarbonate. Replace the clamp and pass in carbon dioxide at the rate of 1.5 liters per minute for 1 hour.

Transfer the contents of tubes 3 and 4 to a 250-ml. Erlenmeyer flask with the aid of a wash bottle. Add 5 ml. of starch indicator and run in the approximately 0.1 *N* iodine from a buret until a blue color persists, shaking the flask continually. Avoid the addition of a large excess at any one time. Discharge the blue color with a drop of 5% sodium bisulfite. After 5 minutes add 0.02 *N* iodine dropwise to the blue starch-iodine end point. Now add 10 ml. of saturated sodium bicarbonate solution and again titrate with 0.02 *N* iodine to the blue color. Before taking the final end point add 10 ml. of the borax-carbonate buffer solution. Record the total volume of 0.02 *N* iodine solution used after the excess sodium bisulfite was removed by the first addition of 0.02 *N* iodine, and calculate the per cent by weight of 1,2-propylene glycol as follows:

Table I. Analytical Data

Sample Weight	Ethylene Glycol Present	1,2-Propylene Glycol Present	1,2-Propylene Glycol Found by Acetaldehyde	Error
Mg.	%	%	%	%
43.98	95.44	4.56	4.59	+0.7
45.98	91.29	8.71	8.61	−1.2
47.98	87.50	12.50	12.50	±0.0
49.98	84.00	16.00	16.22	+1.4
25.85	61.10	38.90	38.16	−1.9
16.90	41.13	58.87	58.24	−1.1
12.61	20.65	79.35	78.22	−1.4
11.06	9.50	90.50	89.56	−2.1

$$\frac{\text{Ml. of 0.02}N \text{ iodine} \times 0.00076 \times \text{aliquot factor} \times 100}{\text{sample weight}} = \%$$ by weight of 1,2-propylene glycol

DISCUSSION

Various methods were tried to secure better results on the acetaldehyde determination. No noticeable difference was observed when the periodate oxidation was carried out at 0° and 100° C. (In order to keep the contents of the reaction tube at 100° C. without concentration, a condenser was used on the reaction tube.) Following the procedure of Nicolet and Shinn, alanine was used instead of glycine and 0.1 *N* arsenite solution was used to take care of excess periodate, without improving the method.

Best results were obtained by adding the periodate solution to the reaction tube through a separatory funnel and maintaining a closed system by adding the solid sodium bicarbonate through the large-bore glass tube.

That glycine, if present in too high a concentration, will remove some acetaldehyde was demonstrated by placing a glass ampoule containing a known amount of acetaldehyde in the reaction tube and going through the complete procedure. The recovery was 86%. Experimental results showed that formaldehyde was completely removed by the glycine; a 10% excess of glycine over that required to react with the formaldehyde formed proved to be satisfactory. In the lower percentage range of 1,2-propylene glycol very good recovery is obtained. However, in the higher ranges the results tended to run slightly low, since the glycine reacted with a very small amount of acetaldehyde.

The analytical data are given in Table I. The 1,2-propylene glycol used in this work was a regular Dow product and analyzed 100.8% by the periodate method. The ethylene glycol was Eastman Kodak Co.'s No. 133, analyzing 100.1% by the same procedure. Values given in Table I have not been corrected for the fact that the pure materials analyzed more than 100%.

Interfering substances are molecules containing adjacent hydroxyl groups or an amino group adjacent to a hydroxyl group.

An attempt was made to oxidize the formaldehyde to formic acid with hydrogen peroxide: the formic acid could then be determined by reduction of mercuric chloride to the insoluble mercurous chloride. Very high results were obtained, since hydrogen peroxide itself reduces mercuric chloride. However, when silver oxide was tried instead of hydrogen peroxide, the recovery was about 75%.

LITERATURE CITED

(1) Clausen, S. W., *J. Biol. Chem.*, **52**, 263 (1922).
(2) Denice, E. C., Dow Chemical Co., Midland, Mich., private communication.
(3) Fleury, P., and Fatôme, M., *J. pharm. chim.*, **21**, 247–66 (1935).
(4) Hoepe, G., and Treadwell, W. D., *Helv. Chim. Acta*, **25**, 353–61 (1942).
(5) Malaprade, *Compt. rend.*, **186**, 382–4 (1928).
(6) Nicolet, B. H., and Shinn, L. A., *J. Am. Chem. Soc.*, **63**, 1456 (1941).
(7) Shupe, I. S., *J. Assoc. Official Agr. Chem.*, **26**, 249–56 (1943).

PRESENTED before the Meeting-in-Miniature, Midland Section, AMERICAN CHEMICAL SOCIETY, September 15, 1945.