Determination of Ethylene and Propylene Glycols in Mixtures by Gas Chromatography

HERBERT G. NADEAU and DUDLEY M. OAKS

Central Analytical Services, Research, Olin Mathieson Chemical Corp., New Haven, Conn.

▶ A method employing gas-liquid chromatography techniques has been developed for the determination of ethylene and propylene glycols in mixtures. Water, or other glycols such as diethylene glycol, triethylene glycol, dipropylene glycol, and 1,2,6-hexanetriol, does not interfere. The method can be extended to the determination of these two glycols in solutions containing 90% water. In the range of 0 to 3% ethylene and propylene glycol, the method indicates a standard deviation of ±0.066% with a maximum sensitivity of 0.02%. Synthetic mixture analysis shows an accuracy of 94 to 100% based on the amount present. Calibration data for the analysis, as well as typical chromatograms, are presented. If commercially available chromatography equipment is used, with columns made up to 5% tetrahydroxyethylenediamine on Chromosorb W, the determination is rapid, accurate, and convenient compared to previous methods.

With the advent of commercial oxidation processes which convert olefinic compounds such as ethylene and propylene to monoethylene glycol (MEG) and monopropylene glycol (MPG), methods for the determination of mixtures of these glycols are necessary.

Conventional methods based on oxidation by either periodic acid (*9*) or dichromate (*10*) are nonselective for mixtures containing compounds with vicinal-type hydroxy groups. Ethylene glycol has been determined in diethylene glycol by a differential oxidation procedure using potassium chromate (*3*). Methods based on oxidation by periodic acid and detection of the formed aldehydes by instrumental techniques are given in the literature (*4, 8*), but usually do not determine ethylene glycol. Various methods for the determination of propylene glycol in ethylene glycol have appeared in the literature (*1, 2, 4–6, 8, 9*); however, ethylene glycol is again not determined. Recently, Ottenstein (*7*) has shown that close boiling glycols, including ethylene and propylene glycols, can be separated by the use of gas chromatographic techniques employing tetrahydroxyethylethylenediamine (THEED) on Chromosorb as the analytical column. However, separations were reported possible for only a short time, until the column became dehydrated. Ottenstein's work indicated that water was necessary on the inert support to act as a deactivator, and since it is difficult to maintain a consistent concentration of water, the work was not pursued.

Working along these lines in our laboratories, separations have been obtained of ethylene and propylene glycol in mixtures by themselves and in aqueous solution, using 5% THEED (Fisher Scientific Co.) on Chromosorb W (Johns-Manville). It was found that the functionality of water on the inert support is not as important as indicated by Ottenstein to obtain separations over a period of time. In our work, the inert support was used as received without regard to water content.

This paper presents a quantitative method based on a 5% THEED column; however, more recently it has been discovered that separations, response, and sensitivity are much improved by using concentrations of THEED close to 10% with an F & M programmed chromatograph.

Using a 2-meter column containing 5% THEED on Chromosorb W at 105° C. and a flow rate of helium of 300 ml. per minute, the observed retention time, without correction, for MPG is 14 minutes; MEG elutes from the column at 15 minutes. Table I shows observed retention times for a series of glycols and water on a THEED column. Figure 1 depicts a typical chromatogram of a synthetic MPG-MEG mixture where the MEG concentration is 1%. When either MPG or MEG concentrations fall below 0.1%, separations are still effective, as shown by Figure 2. The separation of an aqueous mixture of the two glycols is illustrated in Figure 3. Calibration curves were obtained by serial injection directly into the column via a 0.25-cc. syringe of 0.04-ml. aliquots of standard solutions containing varying amounts of the respective glycols. Peak areas were obtained by cutting out and weighing the area contained by the chromatogram curve and a line drawn tangential to the base line of the glycol in question. Table II shows the calibration data obtained. Inasmuch as the interest of this work was to determine small amounts of the respective glycols it is interesting that linearity is followed up to 17% concentration. Figure 4 shows a typical chromatogram of a mixture of MPG-MEG where the concentration of MPG is 0.9%.

Table I. Selectivity of THEED Column for Glycols and Water

Compound	Retention Time, Minutes
Water	1
MPG	14
MEG	15
DEG (diethylene glycol)	Does not elute
DPG (dipropylene glycol)	28
1,2,6-Hexanetriol	Does not elute

Table II. Calibration Data Obtained with Synthetic Standard Mixtures

Std.	Added, Wt. %	Area Found, Mg.
	MEG to MPG	MEG
1	0.129	1.54
2	0.217	3.41
3	0.265	4.75
4	0.388	7.59
5	0.524	12.04
6	0.801	14.55
7	1.179	24.66
8	1.557	34.74
9	2.270	54.36
10	17.530	476.30
11	0.03[a]	0.00063
12	0.06[a]	0.00244
13	0.08[a]	0.00480
	MPG to MEG	MPG
11	0.277	5.45
12	0.941	15.21
13	1.057	18.79
14	1.484	27.24
15	1.983	33.42
16	2.913	47.16
17	2.356	40.09
18	3.116	51.15
19	3.394	56.21
20	14.300	146.50

[a] Value obtained on F & M Model 202 chromatograph.

APPARATUS AND REAGENTS

Burrell Model K-2 Kromotog or F & M programmed temperature

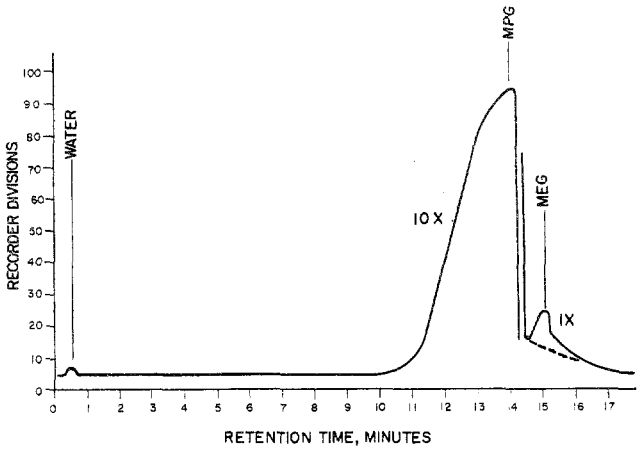

Figure 1. Typical chromatogram of MPG-MEG

MPG concentration 1 %

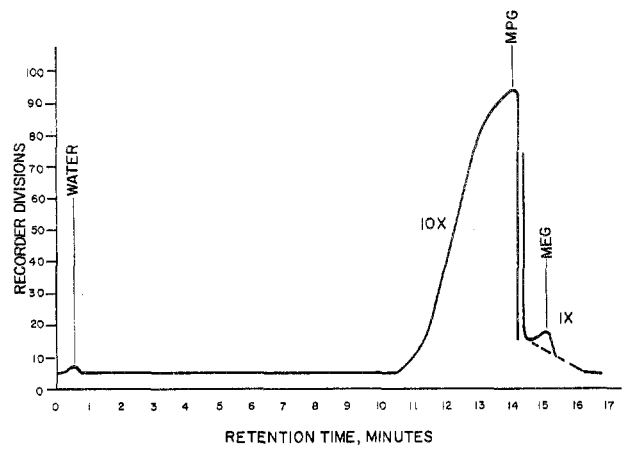

Figure 2. Typical chromatogram of MPG-MEG

MEG concentration 0.1%

chromatograph with thermistor-type detector.

Two-meter 1/4-inch outside diameter glass hairpin-type column packed with 5% THEED on Chromosorb W 30–60 mesh.

Monopropylene glycol was obtained from the Dow Chemical Co.; monoethylene, dipropylene, and diethylene glycols and 1,2,6-hexanetriol were obtained from Union Carbide Chemicals Co.

Samples of MPG and MEG screened to obtain standards with minimal concentrations of contaminants.

PROCEDURE

Preparation of Standard Solutions. A series of standard solutions containing MEG and MPG in concentrations of 0 to 3% of each was made on a weight-weight basis, employing a Mettler semimicrobalance. The standard solutions were made rapidly, so as to avoid contamination by water.

Preparation of Analytical Column. The column packing is prepared by mixing, in an electrically driven revolving mixer of our own design, 5 grams of THEED and 95 grams of Chromosorb W. The mixer is rotated at approximately 50 r.p.m. while a heat gun (hair dryer) is directed at the drum. A temperature of 50° to 60° C. allows homogeneous mixing of partitioning agent with support. Mixing is maintained for 5 hours.

The material is charged to a 2-meter column in a uniform manner by tapping the column at constant intervals while the partitioning material is being added. Glass-wool plugs are inserted about 1 inch from the top of each leg of the column, stoppers and thermocouples are inserted, and the column is attached to the instrument, where it is conditioned for 1 hour at 105° C. The detector cell temperature is 150° C. and the current 280 ma.

Operating Conditions.

Column temperature, ° C.	105
Detector cell temperature, ° C.	150
Detector cell current, ma.	280
Helium flow at exit, cc./mm.	300

With the recorder indicating a stable base line, the range selector switch is set at 1X, the base line is set at zero, and a 0.04-ml. sample of glycol mixture is introduced into the column with a sharp thrust of the syringe. After 1 minute, if water is present, a peak will be observed. The range selector switch is then switched to 10X; propylene glycol elutes from the column, giving a peak at 14 minutes. Shortly after propylene glycol peaks, the range selector switch is set at 1X. Ethylene glycol is observed to peak at 15 minutes. Dipropylene glycol, if present, is eluted from the column at 28.0 minutes.

The weight per cent composition of the glycol mixture is obtained by drawing lines tangential to the base line of the MPG and MEG peaks, cutting out the areas, and weighing them on a semimicro analytical balance. Using calibration curves of plotted weight per cent of standard *vs.* area in milligrams, the percentage composition is determined.

For measuring the high flow rate of helium, a soap bubble meter is connected to the exit stream of the column. The meter consists of a 25-ml. buret containing 1 ml. of a foaming detergent. The exit flow is connected to the tip of the buret. With the stopcock open, helium passing through causes large bubbles to form and move upward. The time for the bubble to traverse 20

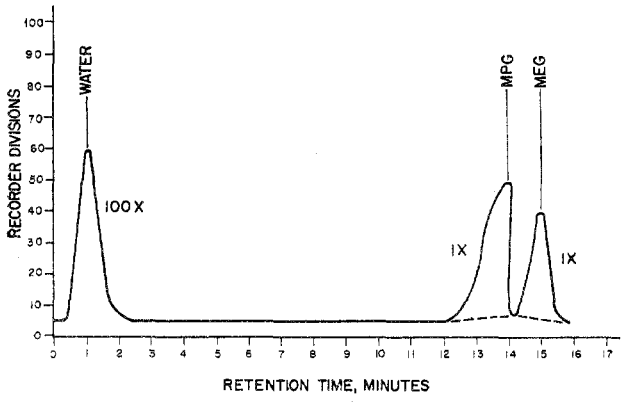

Figure 3. Typical chromatogram of aqueous mixture of MPG-MEG

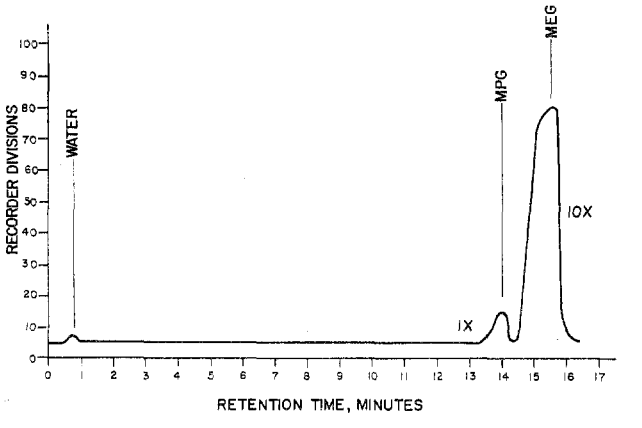

Figure 4. Typical chromatogram of MPG-MEG

MPG concentration < 1%

Table III. Analysis of Synthetic Mixtures

	Taken, Wt. %		Found, Wt. %		Recovery, %
	MEG	MPG	MEG	MPG	
A	99.08	0.92	[a]	0.90	97.8
B	99.62	0.38	[a]	0.36	94.7
C	97.32	2.68	[a]	2.60	97.0
D	0.68	99.32	0.64	[a]	94.1
E	1.31	98.69	1.32	[a]	100.8
F	2.99	97.01	2.93	[a]	98.0

[a] Not measured.

ml. is measured, and the flow rate is calculated.

DISCUSSION OF RESULTS

The typical chromatograms depicted in Figures 1 and 2 indicate the lack of complete separation of MEG from MPG obtained by the THEED analytical column. During the course of developing the method, many column materials were tried. The degree of separation effected was poor for columns containing Apiezon L, Igepal 880, and a polyester succinate, whereas polar materials, Carbowax 750 and Carbowax 20 M, gave a fair separation. From these data, it was concluded that the most polar material—THEED—was the most effective and that the separation was dependent to a large extent on the degree of hydrogen bonding between the respective glycols and partitioning material. The order of elution is MPG to MEG, whence it can be reasoned that the hydroxy groups in MPG are separated by one more carbon atom than that for MEG, giving rise to weaker hydrogen bonding, and vice versa for MEG. Presumably, any material more polar than THEED with respect to these glycols would give an even better separation.

The calibration data presented in Table II indicate an almost straight-line function between area and concentration. They further indicate that the lack of complete separation does not significantly interfere with quantitative analysis. In all cases, these data represent replicate values differing by less than 5% of the average.

A clue to the sensitivity of the method for MPG and MEG can be seen in the calibration data presented in Table II, where 0.129% MEG yields a response of 1.54 mg. and 0.277% MPG a response of 5.45 mg.

The minimum detectable amount of each glycol in the presence of the other, using the Burrell Kromotog K-2 under the conditions listed, is 0.08 weight %. However, it has recently been demonstrated that the F & M programmed temperature chromatograph, under identical conditions, will detect 0.02 weight %.

The data (Table III) give experimental proof of the quantitativeness of the method on synthetic samples within the ranges studied.

Since the temperature at which the analysis is conducted is at the recommended limit for THEED, decomposition of the column is not entirely unexpected. During the course of routine running, it has been found that after 36 hours of continuous use, some loss of sensitivity occurs. This affects only the results obtained in mixtures where the amount of either glycol is of the order of less than 0.1%. There appears to be no serious loss in accuracy for greater amounts.

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Identification of Oxygen Compounds in Gas-Liquid Chromatographic Fractions by Catalytic Deoxygenation

C. J. THOMPSON, H. J. COLEMAN, R. L. HOPKINS, C. C. WARD, and H. T. RALL

Petroleum Research Center, Bureau of Mines, U. S. Department of the Interior, Bartlesville, Okla.

▶ Positive identification of oxygen and sulfur derivatives of hydrocarbons by spectroscopic methods is limited by the number of reference spectra available. An earlier paper described a micromethod for vapor phase catalytic desulfurization of sulfur compounds to produce the analogous hydrocarbons, which then could be identified. This technique now has been applied for removing oxygen from oxygen-containing compounds. Data are presented to show that the deoxygenation of typical members of the oxygen-compound classes, such as alkyl and cyclic ethers, ketones, aldehydes, and, in part, alcohols, proceeds smoothly and yields the expected hydrocarbons. The method has been applied to fractions from gas-liquid chromatographic columns. Identification of the hydrocarbon compounds produced in the reaction identifies or contributes to the identification of the oxygen compound precursor.

IN AN EARLIER PAPER by Thompson *et al.* (*1*) the catalytic desulfurization of components in gas-liquid chromatographic fractions was described, and the usefulness of the method in sulfur-compound identification was discussed. That paper suggested the possible application of the method to the analogous deoxygenation and identification of oxygen compounds, and the present paper reports such application to a few representative individuals of various oxygen compound classes. By means