

GLYCOL AND CAROM SOLVENT DISTRIBUTION IN MIXTURES BY GC

UOP Method 523-96

SCOPE

This method is for determining glycol distribution in mixtures of mono-, di-, tri- and tetraethylene glycols and for component distribution in CAROM[®] process solvent. Glycol impurities can also be determined. The method is quantitative down to 0.05 mass-% for any component.

OUTLINE OF METHOD

The sample is diluted with methanol and injected into a gas chromatograph that is equipped with a flame ionization detector and a fused silica capillary column internally coated with cross-linked Carbowax 20M. The mass-% composition is obtained by the normalization of peak areas after relative response factors are applied to correct for detector mass response differences.

APPARATUS

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Balance, readability 0.1-mg

Chromatographic column, 60 m of 0.32-mm ID fused silica capillary, internally coated to a film thickness of 0.5- μ m with cross-linked Carbowax 20M, Supelco, Cat. No. 2-4085

Gas chromatograph, temperature programmable, built for capillary column chromatography, utilizing a split injection system having a glass injection port insert, and equipped with a flame ionization detector that will give a minimum peak height response of 10 times the background noise for 0.05 mass-% triethylene glycol when operated at the recommended conditions, Hewlett Packard, Model 6890

Gas purifier, hydrogen, used to remove oxygen from the carrier gas, UOP Mat/Sen, Cat. No. P-200-1

Leak detector, gas, Alltech Associates, Cat. No. 21-250

IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. MATERIAL SAFETY DATA SHEETS (MSDS) OR EXPERIMENTAL MATERIAL SAFETY DATA SHEETS (EMSDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).

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UOP Methods are available through ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken PA 19428-2959, United States. The Methods may be obtained through the ASTM website, www.astm.org, or by contacting Customer Service at service@astm.org, 610.832.9555 FAX, or 610.832.9585 PHONE.

Integrator, electronic, for obtaining peak areas. This device must integrate areas at a sufficiently fast rate so that the narrow peaks typically resulting from use of a capillary column can be accurately measured.

Pipet, Pasteur, disposable, 146-mm, Fisher Scientific, Cat. No. 13-678-20A

Pipet bulb, 1-mL, Fisher Scientific, Cat. No. 13-678-9A

Recorder (optional), used to supplement integrator plot

Regulator, air, two-stage, high purity, Matheson Gas Products, Model 3122-590

Regulator, hydrogen, two-stage, high purity, Matheson Gas Products, Model 3122-350

Regulator, nitrogen, two-stage, high purity, Matheson Gas Products, Model 3122-580

Sample injector. Any syringe or injector capable of introducing a 1.0- μ L volume of sample, such as a Hamilton 701-NWG syringe, Alltech Associates, Cat. No. 80307

Vial, sample, 4-dram, screw thread, with 24-mm black phenolic closure, Kimble[®], Fisher Scientific, Cat. Nos. 03-339-10H and 02-883-5G, respectively

Vortex mixer, Fisher Scientific, Cat. No. 12-810R

REAGENTS AND MATERIALS

All reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, when such specifications are available, unless otherwise specified.

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Air, zero-gas, total hydrocarbons less than 2 ppm as methane

CAROM concentrate, UOP

Diethylene glycol (2-hydroxyethylether), 99%, Aldrich Chemical, Cat. No. H2, 645-6

Dipropylene glycol, mixture of isomers, Aldrich Chemical, Cat. No. D21,555-4

Ethylene glycol, 99%, Aldrich Chemical, Cat. No. 10,246-6

Hydrogen, zero-gas, 99.95% minimum purity, total hydrocarbons less than 0.5 ppm as methane

Methanol, 99.9% purity, Fisher Scientific, Cat. No. A457-4

Nitrogen, zero-gas, 99.99% minimum purity, total hydrocarbons less than 0.5 ppm as methane

Propylene glycol (1,2-propanediol), 99%, Aldrich Chemical, Cat. No. 13, 436-8

Tetraethylene glycol, 99% minimum purity, Aldrich Chemical, Cat. No. 11,017-5

Triethylene glycol, 99% Aldrich Chemical, Cat. No. T5,945-5

PROCEDURE

Chromatographic Technique

1. Install the gas purifier in the supply line between the carrier gas source and the carrier gas inlet on the gas chromatograph.
 - Column life is significantly reduced if the gas purifier is not used.
2. Install the fused silica capillary column in the gas chromatograph.
 - CAUTION: Hydrogen carrier gas leakage into the confined volume of the column oven can cause a violent explosion. It is, therefore, mandatory to check for leaks each time a connection is made and periodically thereafter.
3. Establish the recommended operating conditions as given in Table 1.
 - Other conditions may be used if they provide the required sensitivity and chromatographic separations equivalent to those shown in the Typical Chromatogram.
4. Program the column oven to 250°C and maintain this temperature until a stable baseline has been obtained at the required sensitivity.
5. Cool the column oven to a stabilized 40°C.
6. Mix the sample with a vortex mixer.
7. Dilute the sample (or calibration blend) with methanol in a small vial by volume: 1 part sample, 2 parts methanol.
 - Methanol, the solvent peak, is not quantitated during the analysis.
8. Cap the vial and mix the diluted sample with a vortex mixer.
9. Inject 1.0 μL of the diluted sample into the gas chromatograph and immediately start the recorder, temperature programming sequence and integrator.
 - Methanol is used to clean the syringe between samples.
10. Identify the components of interest by comparing the chromatogram obtained to the Typical Chromatogram (see Figure) and determine the areas of the components.

Table 1

Recommended Operating Conditions

Carrier gas	hydrogen
Column head pressure	50 kPa gauge (7 psig)
Equivalent flow	1.5 mL/min
Equivalent linear velocity	25 cm/min
Split flow	100 mL/min
Injection port temperature	280°C
Column temperature program	
Initial temperature	40°C
Initial time	10 min
Programming rate A	8°C/min
Intermediate temperature	160°C
Intermediate time	0 min
Programming rate B	15°C/min
Final temperature	250°C
Final time	30 min
Detector	
Temperature	280°C
Hydrogen flow rate*	30 mL/min
Air flow rate*	350 mL/min
Makeup nitrogen flow rate*	30 mL/min
Sample size	1.0 µL

* Consult the manufacturer's instrument manual for suggested flow rates.

Calibration

Relative response factors are required to relate the peak areas for sample components to mass-%, since all components do not respond equally in a flame ionization detector.

1. Prepare a calibration blend as described in ASTM Method D 4307 to contain tetraethylene glycol and other components of interest at expected levels (minimum level of approximately 2 mass-%).
 - Calibration should be performed when the instrument is set up and whenever operating conditions or the column are changed.
2. Run the calibration blend three times as described in Steps 7 through 9 under *Chromatographic Technique*.
3. Identify the peaks and average the individual peak areas from the triplicate runs.
4. Use the average peak areas to calculate the relative response factor for each component to three decimal places, using tetraethylene glycol as a reference, and Eq. 1.
 - A relative response factor of 1.000 is used for any unknown components.

$$F = \frac{A B}{C D} \quad (1)$$

where:

- A** = concentration of a component in the blend, mass-%
- B** = average peak area of tetraethylene glycol
- C** = concentration of tetraethylene glycol in the blend, mass-%
- D** = average peak area for component
- F** = relative response factor for component

CALCULATIONS

Calculate the concentration of each component to the nearest 0.01 mass-% below one mass-%, and to three significant figures at or above one mass-%, using Eq. 2.

$$\text{Component, mass-\%} = 100 \frac{G F}{N} \quad (2)$$

where:

- F** = relative response factor for component, Eq. 1
- G** = peak area of individual component in the sample
- N** = sum of the products **GF** of all components in the sample
- 100** = factor to convert to mass-%

PRECISION

Repeatability

Based on two tests performed by each of two analysts on each of two different days (8 tests), the within-laboratory estimated standard deviations (esd) were calculated for components at specific concentrations and are listed in Table 2. Two tests performed in one laboratory by different analysts on different days should not differ by more than the allowable differences in Table 2 at the concentrations listed (95% probability). The data in Table 2 were obtained using an autoinjector.

Table 2**Repeatability**

Component	Concentration mass-%	Within-Lab esd, mass-%	Allowable Difference, mass-%
CAROM Concentrate	19.2	0.20	0.6
Tetraethylene Glycol	78.6	0.19	0.6

Reproducibility

There is insufficient data to calculate the reproducibility of the test at this time.

TIME FOR ANALYSIS

The elapsed time for one analysis (or calibration) is 1.7 hours. The labor requirement is 0.3 hour.

REFERENCE

ASTM Method D 4307, www.astm.org

SUGGESTED SUPPLIERS

Aldrich Chemical Co., Inc., P.O. Box 355, Milwaukee, WI 53201 (414-273-3850)
 Alltech Associates, Inc., 2051 Waukegan Rd., Deerfield, IL 60015 (708-948-8600)
 Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219 (412-562-8300)
 Hewlett Packard Co., 2850 Centerville Rd., Wilmington, DE 19808-1610 (302-633-8001)
 Matheson Gas Products, Inc., P.O. Box 96, Joliet, IL 60434 (815-727-4848)
 Supelco Inc., Supelco Park, Bellefonte, PA 16823 (814-359-3441)
 UOP Mat/Sen, 4509 Golden Foothill Parkway, El Dorado Hills, CA 95762 (916-939-8800)
 UOP, 25 E. Algonquin Rd., Des Plaines, IL 60017-5017 (847-391-2529)

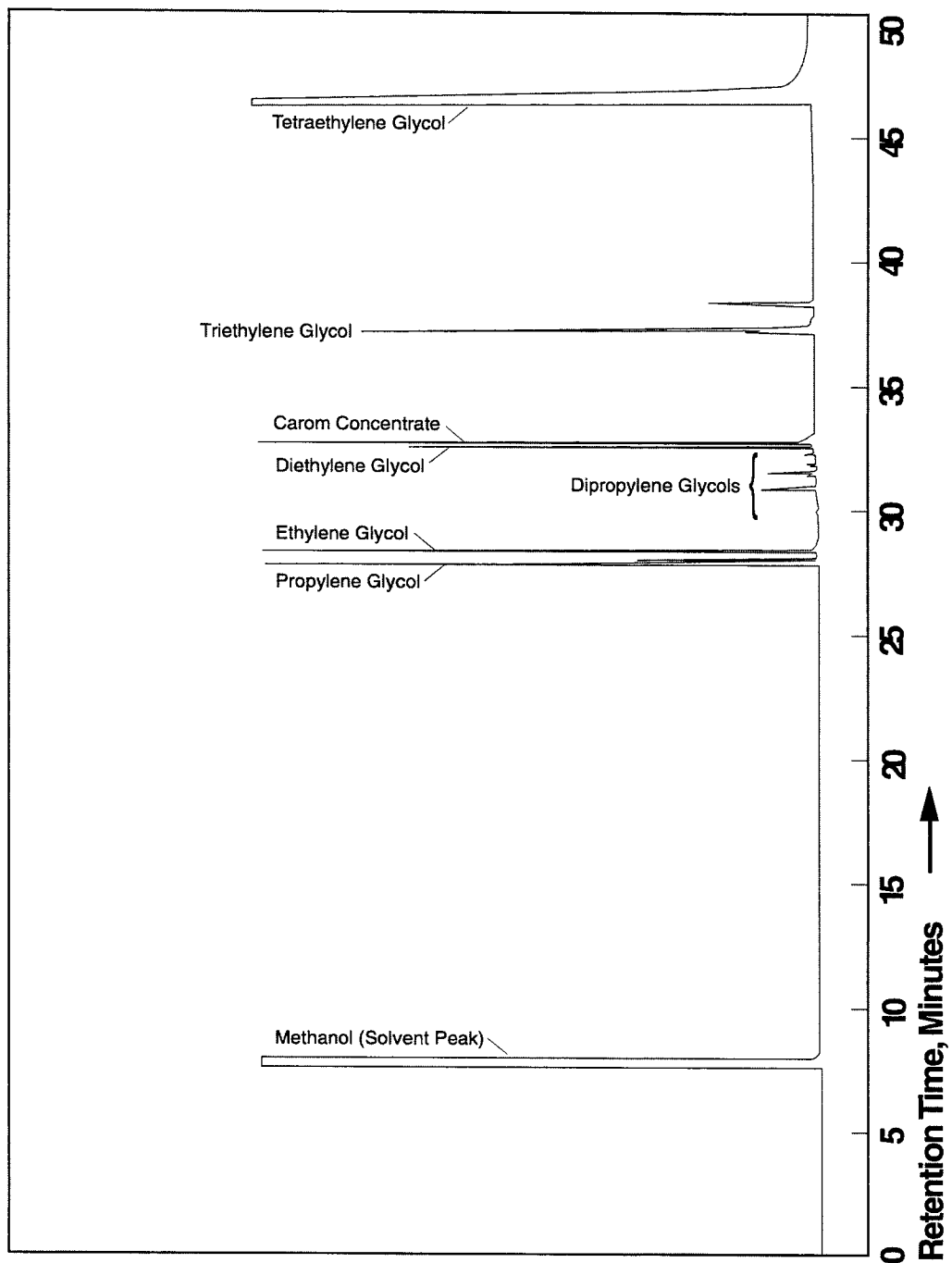


Figure
Typical Chromatogram Carom Solvent Sample