DIPROPYLENE GLYCOL METHYL ETHER

Method number:	101
Matrix:	Air
Target concentration:	100 ppm (606 mg/m^3)
OSHA PEL:	100 ppm (606 mg/m^3)
ACGIH TLV:	100 ppm (606 mg/m^3) TWA, 150 ppm (909 mg/m^3) STEL
Procedure:	Samples are collected by drawing air through standard size (6-mm o.d., 100/50-mg sections) coconut shell charcoal tubes. Samples are desorbed with 95/5 (v/v) methylene chloride/methanol and analyzed by gas chromatography using a flame ionization detector.
Recommended air volume and sampling rate:	10 L at 0.1 L/min
Reliable quantitation limit:	84 ppb (510 μg/m^3)
Standard error of estimate at the target concentration:	5.0%
Status of method:	Evaluated method. This method has been subjected to the established evaluation procedures of the Organic Methods Evaluation Branch.

Date: September 1993

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1. General Discussion

1.1 Background

1.1.1 History

Dipropylene glycol methyl ether (DPGME) is one of the most commonly used propylene glycol ethers in industry and is discussed in a recently published NEG/NIOSH document. (Ref. 5.1) DPGME is a collective term describing a mixture of structural isomers. In the past, OSHA has determined airborne concentrations based on a method validated by NIOSH (Ref. 5.2). The method specifies collection of the vapors on activated charcoal, desorption of the charcoal with carbon disulfide, and analysis by GC using flame ionization detection.

An examination of the Backup Data Report for the NIOSH method (Ref. 5.3) revealed that the desorption efficiency was not constant, the desorption efficiency of the individual isomers of DPGME was not investigated, and the desorption efficiency from wet charcoal was not addressed.

The reported desorption efficiency ranged from 60.4% at 2.954 mg to 89.1% at 12.01 mg of DPGME. In cases where the desorption efficiency is not constant, calculations to determine analyte concentrations are complicated through the use of a desorption efficiency curve. Also, a desorption efficiency less than 75% does not meet one of the evaluation requirements used by the Organic Methods Evaluation Branch of the OSHA Salt Lake Technical Center (SLTC).

For analytes such as DPGME, which are comprised as mixtures of related compounds, quantitation is accomplished by summing the peak areas of each component and treating the summed areas as one analyte. This is an accepted and convenient practice when using a flame ionization detector because the responses for all of the isomers of DPGME are identical. But if the desorption efficiencies are not the same for each isomer, they must be quantitated separately with individual desorption efficiency corrections, and then the resulting amounts are summed to determine the total amount of DPGME. This procedure is necessary for any method using charcoal collection and carbon disulfide desorption because the relative proportion of isomers in DPGME can vary by lot and manufacturer.

Because charcoal will always collect some water from sampled air, the desorption of DPGME from wet charcoal is an important consideration as evidenced by evaluations done at SLTC for other chemically similar analytes. (Refs. 5.4-5.5) For those analytes, the recovery from wet charcoal is significantly lower unless a drying agent such as magnesium sulfate is used in the desorption step.

The present evaluation was accomplished using a desorption solvent consisting of 95/5 (v/v) methylene chloride/methanol, which is used for other chemically similar compounds evaluated at SLTC. (Refs. 5.4-5.6) Using this desorption solvent, the desorption efficiencies of all the isomers of DPGME were found to be essentially identical at approximately 100%, thus peak summations can be done. The desorption efficiencies are constant with concentration and are not affected by the presence of water, so a drying agent is not needed for the desorption step.

The use of 99/1 (v/v) carbon disulfide/*N,N*-dimethylformamide (CS_2/DMF) was investigated as an alternative desorption solvent because it is used for the analysis

of many solvent vapors collected on charcoal and analyzed at SLTC. The desorption efficiencies from dry charcoal ranged from 76-93% for the isomers at a loading of 6.0 mg of DPGME. When tests were repeated with charcoal that previously had 10 L of 80% relative humidity air drawn through it, the desorption efficiencies ranged from 52-86%. Reanalysis of these samples after addition of 125 mg of magnesium sulfate brought the efficiencies nearly up to that from dry charcoal. Thus this solvent system would be acceptable if each of the isomers was quantitated separately with its appropriate desorption efficiency correction, but it is clearly not the desorption solvent of choice.

1.1.2 Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy.)

In the review presented in the previously mentioned NEG/NIOSH document, it was concluded that DPGME seems to lack reproductive toxicity, unlike some other chemically similar compounds. (Ref. 5.1)

At very high air concentrations, DPGME causes narcosis in animals. It is expected that severe exposure would produce similar effects in humans, but high concentrations are disagreeable and not tolerated. Also, concentrations over 200 ppm (40% saturated atmosphere) are difficult to attain, which suggests these high concentrations would not likely be found in workplace air. DPGME at 300 ppm caused eye and nasal irritation to humans. There was no evidence of skin irritation from prolonged or repeated contact with the pure liquid. High vapor concentrations or direct contact of the eyes with the liquid causes transient irritation. (Ref. 5.7) The OSHA PEL-TWA is 100 ppm. (Ref. 5.8) ACGIH has established a TLV-TWA of 100 ppm and a TLV-STEL of 150 ppm for DPGME. (Ref. 5.9)

1.1.3 Workplace exposure

DPGME is used as a solvent for paints, lacquers, resins, dyes, oil/greases, cleaners and cellulose and as a heat-transfer agent. It is frequently used as a substitute for the more toxic DEGME (diethylene glycol methyl ether). (Ref. 5.10).

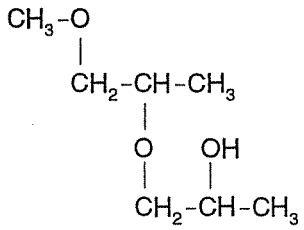
1.1.4 Physical properties (Ref. 5.1 unless otherwise noted)

CAS number:	34590-94-8 (unspecified isomer)
molecular weight:	148.2
melting point:	−80°C
boiling point:	189.6°C
flash point:	85°C (185°F)
vapor pressure:	0.05 kPa at 25°C
vapor density:	5.14 (air=1)
saturation concentration:	510 ppm at 25°C
liquid density:	0.948 (25°C/4°C)
description:	clear, colorless liquid
odor:	sweet, ether-like
solubility: (Ref. 5.11)	completely miscible with water, VM&P naphtha, acetone, ethanol, benzene, carbon tetrachloride, ether, methanol, monochlorobenzene, and petroleum ether
synonyms:	dipropylene glycol monomethyl ether; DPGME
trade names: (Ref. 5.10)	Arcosolv DPM; Dowanol 50B; Dowanol DPM; Glycol Ether DPM; Propasol Solvent DM; Ucar Solvent 2LM

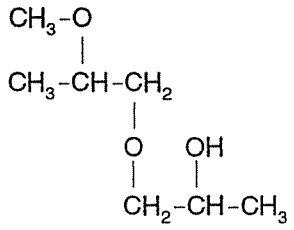
molecular formula: $C_7H_{16}O_3$

structural formula: (Note: DPGME is a mixture of structural isomers. Also, each isomer has two asymmetrical carbon atoms, thus configurational isomers can exist. The numbers in parentheses are approximate percentages by weight of each isomer found in the DPGME used in this evaluation. The abbreviations in the brackets are used in chromatograms in this method.)

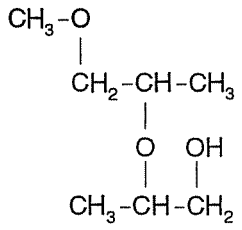
1-(2-methoxy-1-methylethoxy)-2-propanol: (69.3%)
[1-(2-M-1-ME)-2-P], CAS number: 20324-32-7



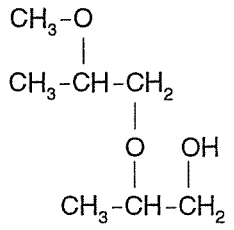
1-(2-methoxy-2-methylethoxy)-2-propanol: (27.8%)
[1-(2-M-2-ME)-2-P], CAS number: 13429-07-7



2-(2-methoxy-1-methylethoxy)-1-propanol: (1.4%)
[2-(2-M-1-ME)-1-P], CAS number: 55956-21-3



2-(2-methoxy-2-methylethoxy)-1-propanol: (1.1%)
[2-(2-M-2-ME)-1-P], CAS number: 13588-28-8



The analyte air concentrations throughout this method are based on the recommended sampling and analytical parameters. Air concentrations listed in ppm and ppb are referenced to 25°C and 101.3 kPa (760 mmHg).

1.2 Limit defining parameters

1.2.1 Detection limit of the analytical procedure

The detection limit of the analytical procedure is 0.13 ng. This is the amount of analyte that will give a response that is significantly different from the background response of a reagent blank. (Sections 4.1 and 4.2)

1.2.2 Detection limit of the overall procedure

The detection limit of the overall procedure is 1.5 μg per sample (25 ppb or 150 $\mu g/m^3$). This is the amount of analyte spiked on the sampler that will give a response that is significantly different from the background response of a sampler blank. (Sections 4.1 and 4.3)

1.2.3 Reliable quantitation limit

The reliable quantitation limit is 5.1 μg per sample (84 ppb or 510 $\mu g/m^3$). This is the amount of analyte spiked on a sampler that will give a signal that is considered the lower limit for precise quantitative measurements. (Section 4.4)

1.2.4 Precision (analytical procedure)

The precision of the analytical procedure, measured as the pooled relative standard deviation over a concentration range equivalent to 0.5 to 2 times the target concentration, is 0.14%. (Section 4.5)

1.2.5 Precision (overall procedure)

The precision of the overall procedure at the 95% confidence level for the ambient temperature 15-day storage test (at the target concentration) is ±9.8%. (Section 4.6) This includes an additional 5% for sampling error.

1.2.6 Recovery

The recovery of DPGME from samples used in a 15-day storage test remained above 99% when the samples were stored at ambient temperatures. (Section 4.7)

1.2.7 Reproducibility

Six samples collected from controlled test atmospheres, with a draft copy of this procedure, were submitted to an SLTC service branch for analysis. The samples were analyzed after 27 days of storage. No individual sample result deviated from its theoretical value by more than the precision reported in Section 1.2.5. (Section 4.8)

2. Sampling Procedure

2.1 Apparatus

2.1.1 Samples are collected using a personal sampling pump calibrated, with a sampling device attached, to within ±5% at the recommended flow rate.

2.1.2 Samples are collected with 7-cm × 4-mm i.d. × 6-mm o.d. glass sampling tubes packed with two sections of coconut shell charcoal. The front section contains 100 mg and the back section contains 50 mg of charcoal. The sections are held in place with glass wool plugs and are separated by a urethane foam plug. For this evaluation, commercially prepared sampling tubes were purchased from SKC, Inc. (Fullerton, CA, Catalog No. 226-01, Lot 120).

2.2 Reagents

None required

2.3 Technique

2.3.1 Immediately before sampling, break off the ends of the charcoal tube. All tubes should be from the same lot.

2.3.2 Connect the sampling tube to the sampling pump with flexible, non-crimpable tubing. It is desirable to utilize a sampling tube holder that shields the employee from the sharp, jagged end of the sampling tube. Position the tube so that sampled air first passes through the 100-mg section.

2.3.3 Air being sampled should not pass through any hose or tubing before entering the sampling tube.

2.3.4 To avoid channeling, place the sampling tube vertically in the employee's breathing zone. Position the sampler so it does not impede work performance or safety.

2.3.5 After sampling for the appropriate time, immediately remove the sampling tube and seal it with plastic caps. Wrap each sample lengthwise with a Form OSHA-21 seal.

2.3.6 Submit at least one blank sampling tube with each sample set. Blanks should be handled in the same manner as samples, except no air is drawn through them.

2.3.7 Record sample volumes (in liters of air) for each sample.

2.3.8 List any compounds that could be considered potential interferences, especially solvents, that are being used in the sampling area.

2.3.9 Ship any bulk sample(s) in a container separate from the air samples.

2.4 Sampler capacity

Sampler capacity is determined by measuring how much air can be sampled before breakthrough of analyte through the sampler occurs, i.e., the sampler capacity is exceeded. Breakthrough is considered to occur when the effluent from the sampler contains a concentration of analyte that is 5% of the upstream concentration (5% breakthrough). Testing for breakthrough was performed by using a total hydrocarbon analyzer to monitor the effluent from sampling tubes containing only the 100-mg section of charcoal while sampling at 0.1 L/min from an atmosphere containing 202 ppm of DPGME. The atmosphere was at approximately 80% relative humidity and 20-25°C. The average 5% breakthrough volume from three determinations was 31.5 L (RSD=6.7%). (Section 4.9)

2.5 Desorption efficiency

2.5.1 The average desorption efficiency for DPGME from Lot 120 charcoal over the range of 0.5 to 2 times the target concentration is 99.4%. (Section 4.10.1)

2.5.2 The desorption efficiency at 0.05, 0.1, and 0.2 times the target concentration was found to be 97.0%, 98.0%, and 98.2% respectively. (Section 4.10.1)

2.5.3 Desorbed samples remain stable for at least 24 h. (Section 4.10.2)

2.6 Recommended air volume and sampling rate

2.6.1 For long-term samples collect 10 L of air at 0.1 L/min (100-min samples). The recommended air volume is significantly lower than the breakthrough volume, but 10 L was chosen to provide a reasonable safety margin in the event other solvent vapors are present in the sampled air. Also, 10 L is commonly recommended for solvent vapors collected on charcoal tubes.

2.6.2 For short-term samples collect 1.5 L at 0.1 L/min (15-min samples).

2.6.3 When short-term samples are collected, the air concentration equivalent to the reliable quantitation limit becomes larger. For example, the reliable quantitation limit is 560 ppb (3390 $\mu g/m^3$) when 1.5 L is collected.

2.7 Interferences (sampling)

2.7.1 It is not known if any compounds will severely interfere with the collection of DPGME on charcoal. In general, the presence of other contaminant vapors in the air will reduce the capacity of charcoal to collect DPGME.

2.7.2 Suspected interferences should be reported to the laboratory with submitted samples.

2.8 Safety precautions (sampling)

2.8.1 Attach the sampling equipment to the employee so that it will not interfere with work performance or safety.

2.8.2 Wear eye protection when breaking the ends of the charcoal tubes.

2.8.3 Follow all safety procedures that apply to the work area being sampled.

3. Analytical Procedure

3.1 Apparatus

3.1.1 A GC equipped with a flame ionization detector. For this evaluation, a Hewlett-Packard 5890A Gas Chromatograph equipped with a 7673A Automatic Sampler was used.

3.1.2 A GC column capable of separating the analyte of interest from the desorption solvent, internal standard and any interferences. A 30-m × 0.32-mm i.d. fused silica Stabilwax-DA® column with a 1-μm df (Restek Corp., Bellefonte, PA) was used in this evaluation.

3.1.3 An electronic integrator or some other suitable means of measuring peak areas. A Waters 860 Networking Computer System was used in this evaluation.

3.1.4 Two-milliliter vials with Teflon®-lined caps.

3.1.5 A dispenser capable of delivering 1.0 mL of desorption solvent to prepare standards and samples. If a dispenser is not available, a 1.0-mL volumetric pipet may be used.

3.2 Reagents

3.2.1 Dipropylene glycol methyl ether, reagent grade. Aldrich Chemical Lot 08413CY was used in this evaluation.

3.2.2 Methylene chloride, chromatographic grade. Burdick and Jackson Lot BB551 was used in this evaluation.

3.2.3 Methanol, chromatographic grade. Fisher Lot 913607 was used in this evaluation.

3.2.4 A suitable internal standard, reagent grade. Aldrich Chemical Lot 11329LW 3-octanol was used in this evaluation.

3.2.5 The desorption solvent consists of 95/5 (v/v) methylene chloride/methanol containing an internal standard at a concentration of 1 μL/mL.

3.2.6 GC grade nitrogen, air, and hydrogen.

3.3 Standard preparation

3.3.1 Prepare standards by injecting microliter amounts of DPGME into vials containing 1.0 mL of desorption solvent delivered from the same dispenser used to desorb samples. For example, inject 6.00 μL of DPGME into a vial containing 1.0 mL of desorption solvent. This standard contains 5688 μg of DPGME per sample.

3.3.2 Bracket sample concentrations with working standard concentrations. If samples fall outside of the concentration range of prepared standards, prepare and analyze additional standards to ascertain the linearity of response.

3.4 Sample preparation

3.4.1 Transfer each section of charcoal of the samples to separate vials. Discard the glass tubes, urethane foam plugs and glass wool plugs.

3.4.2 Add 1.0 mL of desorption solvent to each vial using the same dispenser as used for preparation of standards.

3.4.3 Immediately cap the vials and shake them several times over the next 15 min.

3.5 Analysis

3.5.1 GC conditions

zone temperatures:	column-	110°C for 11 min, then 10°C/min to 150°C, hold for 2 min
	injector-	200°C
	detector-	240°C
gas flows:	hydrogen (carrier)-	3.0 mL/min (60 kPa head pressure)
	nitrogen (makeup)-	37 mL/min
	hydrogen (flame)-	33 mL/min
	air-	390 mL/min
signal range:	0	
injection volume:	1.0 μL (with a 15:1 split)	

column:	30-m × 0.32-mm i.d. fused silica, Stabilwax-DA®, 1-μm df	
retention times:	3-octanol	6.1 min (internal standard)
	DPGME isomers	9.3 min (33.9% by wt), 9.7 min (35.4%), 11.7 min (27.8%), 12.6 min (1.4%), 13.3 min (0.6%), 13.5 min (0.6%)

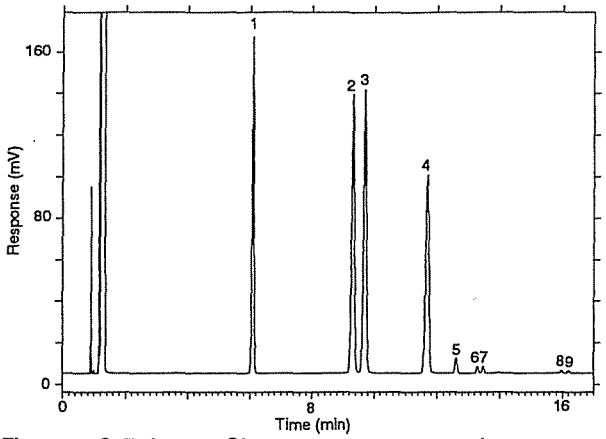


Figure 3.5.1. Chromatogram at the target concentration. Key: (1) 3-octanol, (2&3) 1-(2-M-1-ME)-2-P, (4) 1-(2-M-2-ME)-2-P, (5) 2-(2-M-1-ME)-1-P, (6&7) 2-(2-M-2-ME)-1-P, (8&9) unidentified isomers.

3.5.2 Peak areas are measured by an integrator or other suitable means. The areas of the isomers of DPGME are summed together and treated as one analyte.

3.5.3 An internal standard (ISTD) calibration method is used. A calibration curve is prepared by plotting micrograms of DPGME per sample versus ISTD-corrected area counts of the summed DPGME isomer peaks of the standards. Sample concentrations must be bracketed by standards.

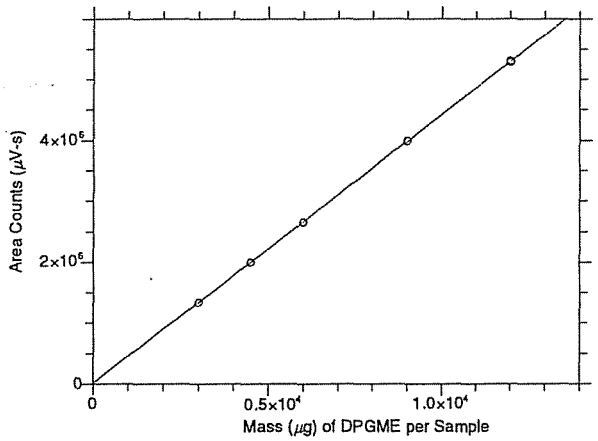


Figure 3.5.3. Calibration curve constructed from the data in Table 4.5. The equation of the line is Y = 440X + 15400.

3.6 Interferences (analytical)

3.6.1 Any compound that produces a response on a flame ionization detector and has the same general retention time of any of the DPGME isomers or the internal standard is a potential interference. Possible interferences should be reported to the laboratory with submitted samples by the industrial hygienist. These interferences should be considered before samples are desorbed.

3.6.2 GC parameters (i.e. column and column temperature) may be changed to possibly circumvent interferences.

3.6.3 When necessary, the identity or purity of an analyte peak may be confirmed with additional analytical data. (Section 4.11)

3.7 Calculations

The DPGME concentration for samples is obtained from the appropriate calibration curve in terms of micrograms of analyte per sample, uncorrected for desorption efficiency. The air concentration is calculated using the following formulae. The back (50-mg) section is analyzed primarily to determine if there was any breakthrough from the front (100-mg) section during sampling. If a significant amount of analyte is found on the back section (e.g., greater than 25% of the amount found on the front section), this fact should be reported with sample results. If any analyte is found on the back section, it is added to the amount found on the front section. This total amount is then corrected by subtracting the total amount (if any) found on the blank.

mg/m^3 = (micrograms of DPGME per sample)/((liters of air sampled)(desorption efficiency))

where the desorption efficiency = 0.994

ppm = $(mg/m^3)(24.46)$/(molecular weight of analyte) = $(mg/m^3)(0.1650)$

where 24.46 is the molar volume at 25°C and 101.3 kPa (760 mmHg)
and the molecular weight of DPGME = 148.2

3.8 Safety precautions (analytical)

3.8.1 Adhere to the rules set down in your Chemical Hygiene Plan.

3.8.2 Avoid skin contact and inhalation of all chemicals.

3.8.3 Wear safety glasses and a lab coat at all times while in the lab area.

4. Backup Data

4.1 Determination of detection limits

Detection limits (DL), in general, are defined as the amount (or concentration) of analyte that gives a response (Y_{DL}) that is significantly different (three standard deviations (SD_{BR})) from the background response (Y_{BR}).

$$Y_{DL} - Y_{BR} = 3(SD_{BR})$$

The direct measurement of Y_{BR} and SD_{BR} in chromatographic methods is typically inconvenient and difficult because Y_{BR} is usually extremely low. Estimates of these parameters can be made with data obtained from the analysis of a series of analytical standards or samples whose responses are in the vicinity of the background response. The regression curve obtained for a plot of instrument response versus concentration of analyte will usually be linear. Assuming SD_{BR} and the precision of data about the curve are similar, the standard

error of estimate (SEE) for the regression curve can be substituted for SD_{BR} in the above equation. The following calculations derive a formula for DL:

$$SEE = \sqrt{\frac{\sum (Y_{obs} - Y_{est})^2}{n - k}}$$

Y_{obs} = observed response
Y_{est} = estimated response from regression curve
n = total no. of data points
k = 2 for a linear regression curve

At point Y_{DL} on the regression curve

$$Y_{DL} = A(DL) + Y_{BR}$$

A = analytical sensitivity (slope)

therefore

$$DL = \frac{(Y_{DL} - Y_{BR})}{A}$$

Substituting $3(SEE) + Y_{BR}$ for Y_{DL} gives

$$DL = \frac{3(SEE)}{A}$$

4.2 Detection limit of the analytical procedure (DLAP)

The DLAP is measured as the mass of analyte actually introduced into the chromatographic column. Ten analytical standards were prepared in equal descending increments with the highest standard containing 12.0 μg/mL. This is the concentration that would produce a peak approximately 10 times the baseline noise of a reagent blank. These standards, plus a solvent blank, were analyzed with the recommended analytical parameters (1-μL injection with a 10:1 split), and the data obtained were used to determine the required parameters (A and SEE) for the calculation of the DLAP. Values of 2267.4 and 101.4 were obtained for A and SEE respectively. The DLAP was calculated to be 0.13 ng.

Table 4.2
Detection Limit of the Analytical Procedure

concentration (μg/mL)	mass on column (ng)	area counts (μV-s)
0.00	0.00	0
1.20	0.12	162
2.40	0.24	302
3.60	0.36	553
4.80	0.48	857
6.00	0.60	1227
7.20	0.72	1443
8.40	0.84	1617
9.61	0.96	2049
10.8	1.08	2267
12.0	1.20	2711

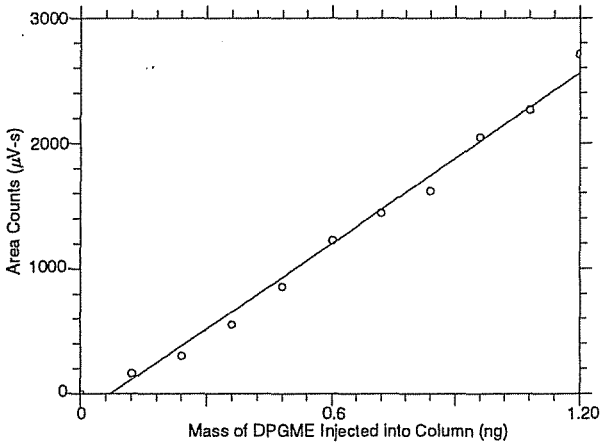


Figure 4.2. Plot of the data from Table 4.2 to determine the DLAP of 0.13 ng. The equation of the line is Y = 2267X − 162.

4.3 Detection limit of the overall procedure (DLOP)

The DLOP is measured as mass per sample and expressed as equivalent air concentrations, based on the recommended sampling parameters. Ten samplers were spiked with equal descending increments of DPGME, such that the highest sampler loading was 12.0 μg/sample. This is the amount, when spiked on a sampler, that would produce a peak approximately 10 times the baseline noise for a sample blank. These spiked samplers, plus a sample blank, were analyzed with the recommended analytical parameters, and the data obtained used to calculate the required parameters (A and SEE) for the calculation of the DLOP. Values of 203.9 and 104.3 were obtained for A and SEE respectively. The DLOP was calculated to be 1.5 μg/sample (25 ppb, 150 μg/m^3).

Table 4.3
Detection Limit of the Overall Procedure

mass (μg) per sample	area counts (μV-s)
0.00	0
1.20	214
2.40	352
3.60	494
4.80	768
6.00	995
7.20	1248
8.40	1660
9.61	1785
10.8	2236
12.0	2349

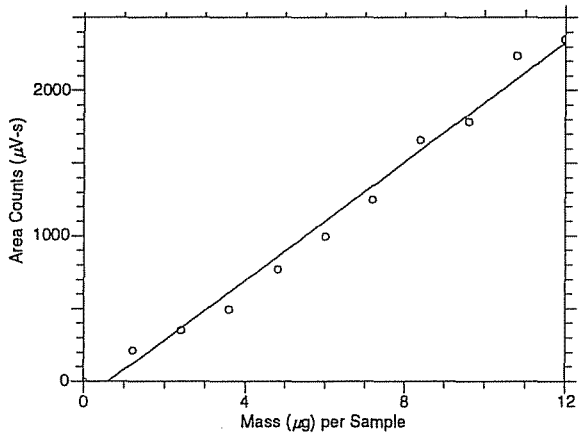


Figure 4.3. Plot of data from Table 4.3 to determine the DLOP of 1.5 μg/sample (25 ppb, 150 μg/m^3). The equation of the line is Y = 203.9X − 124.

4.4 Reliable quantitation limit (RQL)

The RQL is considered the lower limit for precise quantitative measurements. It is determined from the regression line data obtained for the calculation of the DLOP (Section 4.3). The RQL is defined as the amount of analyte that gives a response (Y_{RQL}) such that

$$Y_{RQL} - Y_{BR} = 10(SD_{BR})$$

therefore

$$RQL = \frac{10(SEE)}{A}$$

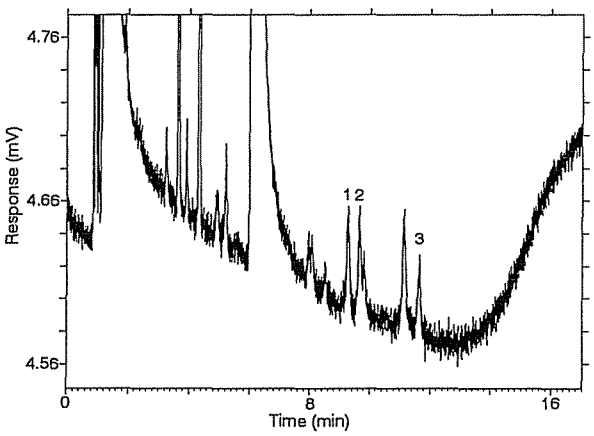


Figure 4.4. Chromatogram of the RQL. Key: (1&2) 1-(2-M-1-ME)-2-P, (3) 1-(2-M-2-ME)-2-P.

The RQL was calculated to be 5.1 μg/sample (84 ppb, 510 μg/m^3). Recovery at this concentration is 92.1%.

4.5 Precision (analytical method)

The precision of the analytical procedure is defined as the pooled relative standard deviation (RSD_p). Relative standard deviations were determined from six replicate injections of DPGME standards at 0.5, 0.75, 1, 1.5, and 2 times the target concentration. After assuring that the RSDs satisfy the Cochran test for homogeneity at the 95% confidence level, the RSD_p was calculated to be 0.14%.

Table 4.5
Instrument Response to DPGME

× target concn (μg/sample)	0.5× 3002	0.75× 4502	1.0× 6003	1.5× 9005	2.0× 12006
area counts (μV-s)	1336700	1995500	2659300	3994400	5285100
	1339300	1996700	2653900	3993700	5298000
	1337200	1998900	2647700	3993200	5293400
	1336500	1998200	2644500	3991600	5309400
	1338000	2001300	2654800	3987700	5300800
	1340000	1999600	2649300	3986500	5296700
$\bar{X}$	1337950	1998370	2651580	3991180	5297230
SD	1432.1	2070.4	5398.7	3316.3	8044.1
RSD (%)	0.107	0.104	0.204	0.083	0.152

The Cochran test for homogeneity:

$$g = \frac{\text{largest RSD}^2}{RSD_{0.5x}^2 + RSD_{0.75x}^2 + RSD_{1x}^2 + RSD_{1.5x}^2 + RSD_{2x}^2} = 0.4433$$

Because the *g* statistic does not exceed the critical value of 0.5065, the RSDs can be considered equal and they can be pooled (RSD_p) to give an estimated RSD for the concentration range studied.

$$RSD_p = \sqrt{\frac{5(RSD_{0.5x}^2+RSD_{0.75x}^2+RSD_{1x}^2+RSD_{1.5x}^2+RSD_{2x}^2)}{5+5+5+5+5}} = 0.14\%$$

4.6 Precision (overall procedure)

The precision of the overall procedure is determined from the storage data in Section 4.7. The determination of the standard error of estimate (SEE_R) for a regression line plotted through the graphed storage data allows the inclusion of storage time as one of the factors affecting overall precision. The SEE_R is similar to the standard deviation, except it is a measure of dispersion of data about a regression line instead of about a mean. It is determined with the following equation:

$$SEE_R = \sqrt{\frac{\sum (Y_{obs} - Y_{est})^2}{n - k}}$$

n = total no. of data points
k = 2 for linear regression
k = 3 for quadratic regression
Y_{obs} = observed % recovery at a given time
Y_{est} = estimated % recovery from the regression line at the same given time

An additional 5% for pump error (SP) is added to the SEE_R by the addition of variances to obtain the total standard error of estimate.

$$SEE = \sqrt{(SEE_R)^2 + (SP)^2}$$

The precision at the 95% confidence level is obtained by multiplying the standard error of estimate (with pump error included) by 1.96 (the z-statistic from the standard normal distribution at the 95% confidence level). The 95% confidence intervals are drawn about their respective regression lines in the storage graphs, as shown in Figures 4.7.1 and 4.7.2. The precision of the overall procedure of ±9.8% was obtained from Figure 4.7.2.

4.7 Storage test

Storage samples were generated by sampling from test atmospheres containing DPGME at the target concentration. Six samples were analyzed immediately after generation, fifteen were stored in a refrigerator at 0°C, and fifteen were stored in a closed drawer at ambient temperatures of 20-25°C. At 2-4 day intervals, three samples were selected from each of the two storage sets and analyzed.

Table 4.7
Storage Test for DPGME

time (days)	refrigerated storage recovery (%)			ambient storage recovery (%)		
0	100.4	100.3	100.2	100.4	100.3	100.2
0	100.2	100.3	100.0	100.2	100.3	100.0
4	98.6	99.6	100.0	99.3	99.9	99.5
6	98.9	99.9	100.1	99.0	100.0	100.3
8	99.0	99.2	99.7	99.0	100.0	99.7
11	100.2	100.0	100.4	98.0	99.4	99.4
15	100.3	100.3	100.6	98.1	99.5	99.5

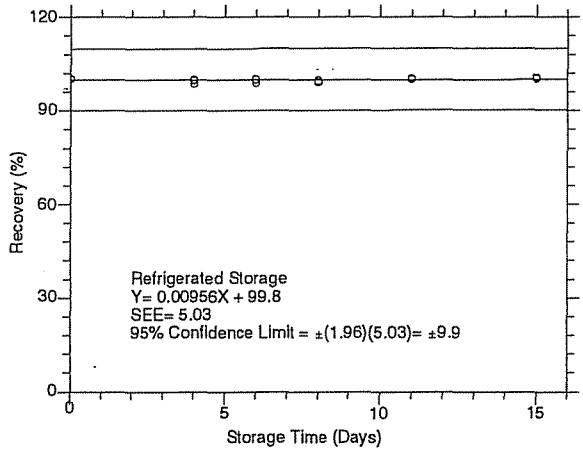


Figure 4.7.1. Refrigerated storage test for DPGME.

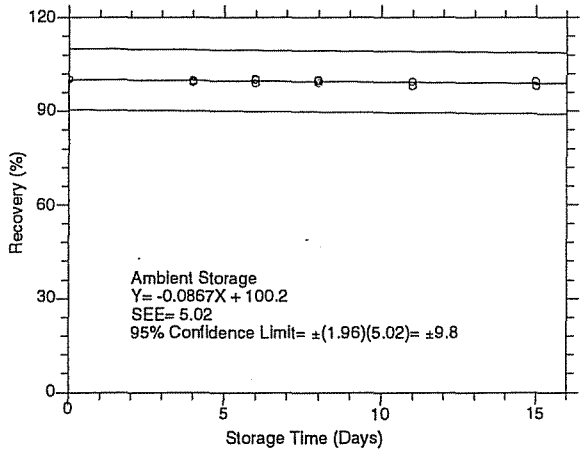


Figure 4.7.2. Ambient storage test for DPGME.

4.8 Reproducibility

Six samples were prepared by collecting them from a controlled test atmosphere similar to that which was used in the collection of the storage samples. The samples were submitted to an SLTC service branch for analysis. Samples 1-4 were stored for 27 days at 0°C and sample 5 and 6 were stored for 27 days at 20-25°C before they were analyzed. No sample result deviated greater than the precisions of the overall procedure determined in Section 4.7,

which are ±9.9% and ±9.8% for samples stored under refrigerated and ambient temperatures respectively.

Table 4.8
Reproducibility Data for DPGME

sample	ppm reported	ppm expected	percent	deviation
1	93.2	92.4	100.9	+0.9
2	83.2	86.1	96.6	−3.4
3	85.8	87.0	98.6	−1.4
4	85.8	87.0	98.6	−1.4
5	90.7	94.2	96.3	−3.7
6	91.8	92.0	99.8	−0.2

4.9 Sampler capacity

Sampler capacity was determined by using a total hydrocarbon analyzer to monitor the effluent from sampling tubes containing only the 100-mg section of charcoal while sampling at 0.1 L/min from an atmosphere containing 202 ppm of DPGME. The atmosphere was at approximately 80% relative humidity and 20-25°C. The average 5% breakthrough volume from three determinations was 31.5 L (RSD=6.7%). A graphical representation of one of the tests is shown in Figure 4.9.

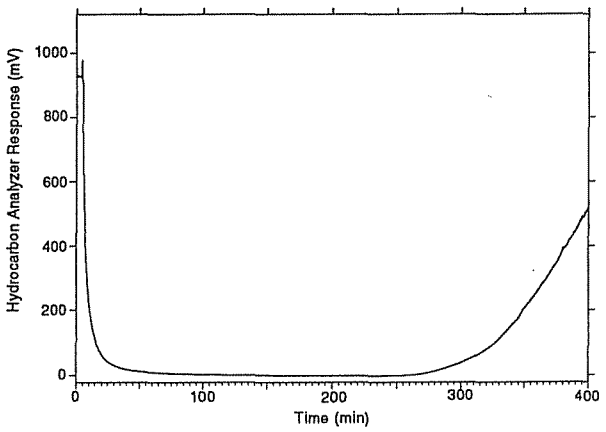


Figure 4.9. Example of one determination of the 5% breakthrough volume. The tube was put in line at 4.0 min and the 5% breakthrough occurred at 306 min to give a breakthrough volume of 30.2 L.

4.10 Desorption efficiency and stability of desorbed samples

4.10.1 Desorption efficiency

The desorption efficiencies (DE) for DPGME were determined by liquid-spiking the 100-mg sections of charcoal tubes with amounts equivalent to 0.05 to 2 times the target concentration. These samples were stored overnight at ambient temperature and then desorbed and analyzed. The average desorption efficiency over the working range of 0.5 to 2 times the target concentration is 99.4%.

Table 4.10.1
Desorption Efficiency for DPGME

× target concn mass spiked (μg)	0.05× 300.2	0.1× 600.3	0.2× 1201	0.5× 3002	1.0× 6003	2.0× 12010
DE (%)	97.0	97.7	97.9	98.8	99.6	99.8
	97.3	98.7	98.4	98.6	99.6	99.8
	97.3	98.1	97.3	99.1	99.6	99.8
	96.8	98.0	98.6	98.7	99.4	99.9
	97.6	97.7	97.8	99.1	99.5	99.8
	96.0	97.7	99.2	98.8	99.5	99.8
$\overline{X}$	97.0	98.0	98.2	98.8	99.5	99.8

4.10.2 Stability of desorbed samples

The stability of desorbed samples was investigated by reanalyzing the target concentration samples 24 h after initial analysis. After the original analysis was performed three vials were recapped with new septa while the remaining three retained their punctured septa. The samples were reanalyzed with fresh standards. The average percent change was +0.3% for samples that were resealed with new septa, and +0.2% for those that retained their punctured septa.

Table 4.10.2
Stability of Desorbed Samples

punctured septa replaced			punctured septa retained		
initial DE (%)	DE after one day (%)	difference	initial DE (%)	DE after one day (%)	difference
99.6	100.0	+0.4	99.4	99.8	+0.4
99.6	100.0	+0.4	99.5	99.6	+0.1
99.6	99.8	+0.2	99.5	99.7	+0.2
	(averages)			(averages)	
99.6	99.9	+0.3	99.5	99.7	+0.2

4.11 Qualitative analysis

The isomers of DPGME can easily be separated and identified by GC/MS. Mass spectra for six of the isomers, which were separated using similar conditions given in Section 3.5, were obtained from a Perkin-Elmer Ion Trap Detector interfaced to a Hewlett-Packard Series II GC.

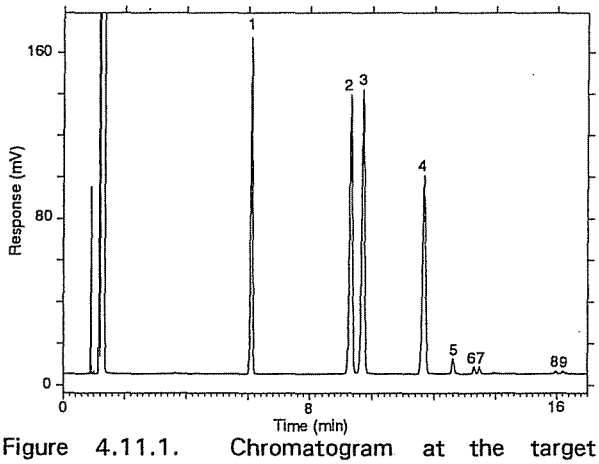


Figure 4.11.1. Chromatogram at the target concentration. Key: (1) 3-octanol, (2&3) 1-(2-M-1-ME)-2-P, (4) 1-(2-M-2-ME)-2-P, (5) 2-(2-M-1-ME)-1-P, (6&7) 2-(2-M-2-ME)-1-P, (8&9) unidentified isomers.

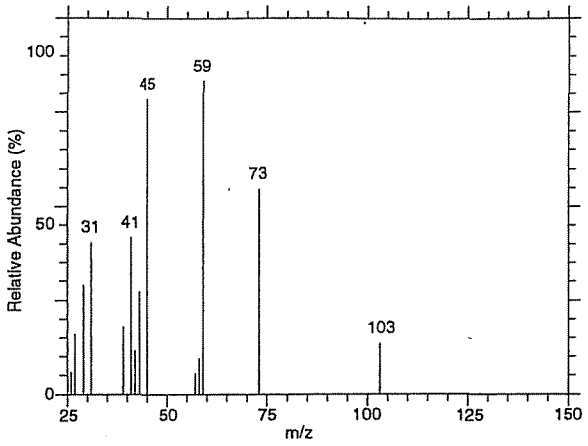


Figure 4.11.2. Mass spectrum of Peak 2 identified as 1-(2-methoxy-1-methylethoxy)-2-propanol.

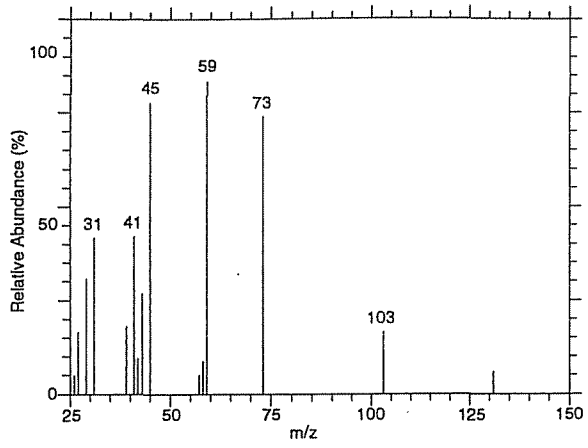


Figure 4.11.3. Mass spectrum of Peak 3 identified as 1-(2-methoxy-1-methylethoxy)-2-propanol.

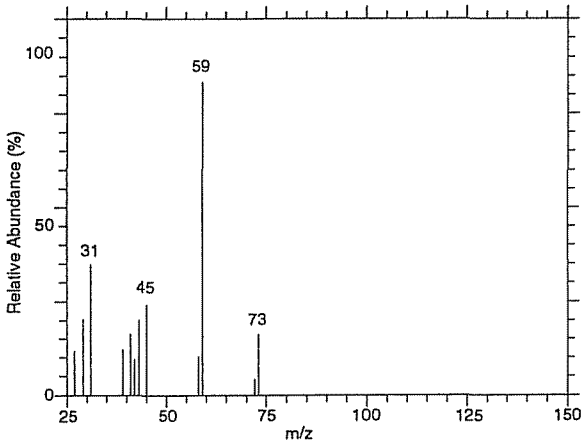


Figure 4.11.4. Mass spectrum of Peak 4 identified as 1-(2-methoxy-2-methylethoxy)-2-propanol.

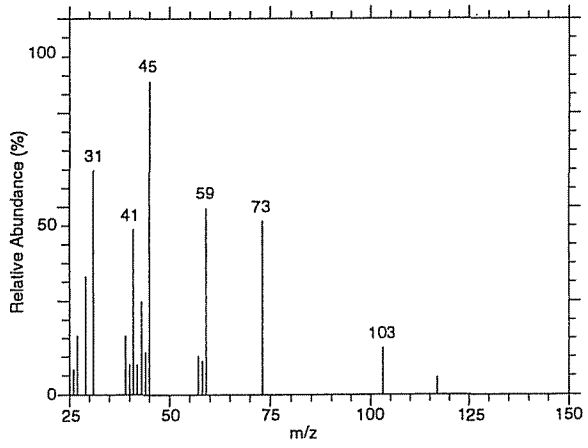


Figure 4.11.5. Mass spectrum of Peak 5 identified as 2-(2-methoxy-1-methylethoxy)-1-propanol.

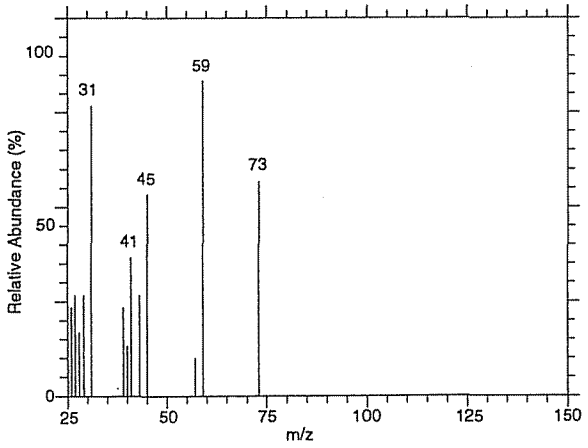


Figure 4.11.6. Mass spectrum of Peak 6 identified as 2-(2-methoxy-2-methylethoxy)-1-propanol.

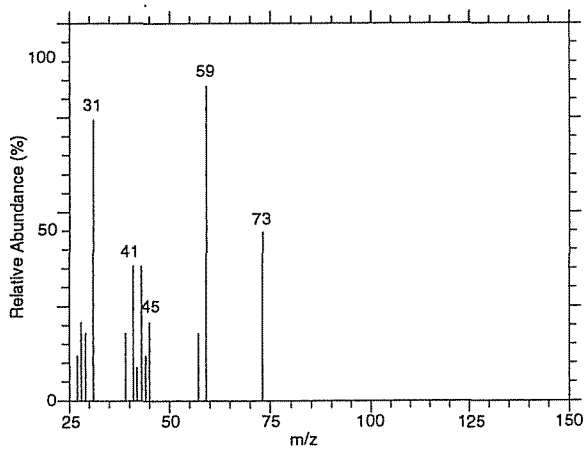


Figure 4.11.7. Mass spectrum of Peak 7 identified as 2-(2-methoxy-2-methylethoxy)-1-propanol.

5. References

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