Method no.:	PV2051
Matrix:	Air
Target concentration:	25 mg/m^3 (8.0 ppm)
Procedure:	Samples are collected by drawing a known volume of air through OSHA versatile sampler (OVS-7) tubes, containing a glass fiber filter (GFF) and two sections of XAD-7 adsorbent. Samples are desorbed with methanol and analyzed by gas chromatography (GC) using a flame ionization detector (FID).
Recommended air volume and sampling rate:	60 L at 1.0 L/min
Reliable quantitation limit:	0.011 ppm (0.035 mg/m^3)
Status of method:	Partially Evaluated Method. This method has been subjected to established evaluation procedures, and is presented for information and trial use.

Date: December 1998

Chemist: Wayne Potter

Organic Service Branch I
OSHA Salt Lake Technical Center
Salt Lake City, UT 84115-1802

1. General Discussion

1.1 Background

1.1.1 History

Airborne propylene glycol has been determined by collection on a glass fiber filter in a Swinnex cassette followed by a midget impinger of isopropanol connected in series and analyzed by gas chromatograph with a flame ionization detector. (Ref. 5.1). Impingers are difficult for workers to wear and present a possibility of exposure to the solvent used. NIOSH method 5523 (Ref. 5.2) uses the XAD-7 OVS tube which combines a glass fiber filter and XAD-7 resin into one sampler and is also analyzed by gas chromatography with a flame ionization detector. One of the advantages of this method is not having to connect the glass fiber filter and impinger in series. Another advantage is not having to sample with an impinger and the associated solvent.

The purpose of this study was to evaluate the collection and analysis of propylene glycol with the OVS-7 tubes at the same level as the ACGIH Ceiling level for ethylene glycol.

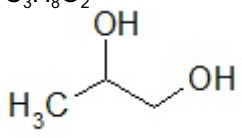
1.1.2 Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy.) (Ref. 5.3)

Taken internally, propylene glycol is harmless, probably because its oxidation yields pyruvic and acetic acids.

1.1.3 Workplace exposure (Ref. 5.4)

Propylene glycol is used in organic synthesis, especially polypropylene glycol, polyester resins, cellophane and antifreeze solutions. It is a solvent for fats, oils, waxes, resins, flavoring extracts, perfumes, colors, softdrink syrups, and antioxidants. Propylene glycol is also used as a coolant in refrigeration systems. It is used as an emulsifier, food additive, anticaking agent, solvent, wetting agent, humectant, preservative (retards molds and fungi), and in cleansing creams, suntan lotions, pharmaceuticals, plasticizers, hydraulic fluids, brake fluids, bactericide, textile conditioners and deicing fluids for airport runways.

1.1.4 Physical properties and other descriptive information (Ref. 5.4 unless otherwise indicated).

Synonyms:	1,2-Propanediol, 1,2-dihydroxypropane, methylene glycol, methyl glycol
CAS number:	57-55-6
IMIS:	P108
RTECS:	TY2000000 (Ref. 5.5)
Molecular weight:	76.10
Boiling point:	187.3°C
Melting point:	-60°C
Flash point:	210 °F (OC)
Vapor pressure:	0.05 mm @ 20°C
Density:	1.0381 @ 20°C / 20°C
Properties:	Colorless, viscous, stable, hygroscopic liquid, practically odorless and tasteless.
Solubility:	Miscible with water, alcohol and many organic solvents.
Molecular formula:	$C_3H_8O_2$
Structural formula:	

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

1.2 Limit defining parameters

1.2.1 Detection limit of the overall procedure (DLOP)

The detection limit of the overall procedure is 2.48 µg per sample (0.016 ppm or 0.041 mg/m³). 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.

The DLOP is defined as the concentration of analyte that gives a response (Y_{DLOP}) that is significantly different (three standard deviations (SD_{BR})) from the background response (Y_{BR}).

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

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 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 the DLOP:

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

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_{DLOP} on the regression curve

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

A = analytical sensitivity (slope)

therefore

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

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

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

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 analyte, such that the lowest sampler loading was 0.63 µg/sample. This is the amount, when spiked on a sampler, that would produce a peak approximately 10 times the background response for the sample blank. These spiked samplers, and the 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 532.52 and 111.31 were obtained for A and SEE respectively. DLOP was calculated to be 0.63 µg/sample (0.003 ppm or 0.010 mg/m^3).

Table 1.2.1
Detection Limit of the Overall Procedure

mass per sample (µg)	area counts (µV-s)
0	0
1.50	912
3.00	1727
4.49	2660
5.99	3177
7.49	4009
8.99	4887
10.48	5823
11.98	6316
13.48	7222
14.98	8137

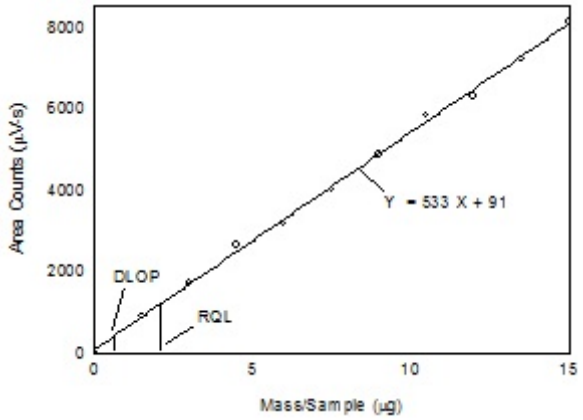


Figure 1.2.1. Plot of data to determine the DLOP/RQL.

1.2.2 Reliable quantitation limit (RQL)

The reliable quantitation limit is 2.09 µg per sample (0.011 ppm or 0.035 mg/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.

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 1.2.1), providing at least 75% of the analyte is recovered. The RQL is defined as the concentration of analyte that gives a response (Y_{RQL}) such that

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

therefore

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

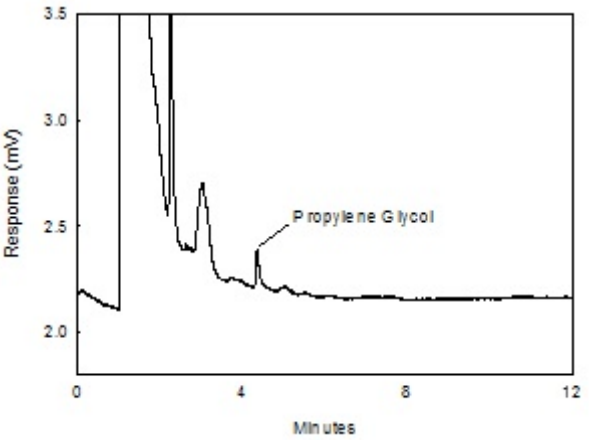


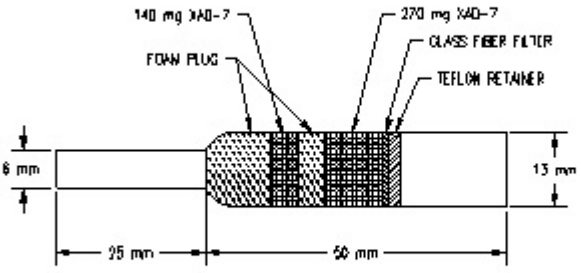
Figure 1.2.3. Chromatogram of the RQL.

2. Sampling Procedure

2.1 Apparatus

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

2.1.2 Samples are collected on OVS-7 tubes, which are specially made 11-mm i.d. × 13-mm o.d. × 5.0 cm long glass tubes that taper to 6-mm o.d. x 2.5 cm. Each tube is packed with a 140-mg back section and a 270-mg front section of XAD-7 and a 13-mm diameter glass fiber filter. The back



section is retained by two foam plugs and the sampling section is between one foam plug and the glass fiber filter. The glass fiber filter is held next to the sampling section by a polytetrafluoroethylene (PTFE) retainer. These tubes are commercially available from SKC Inc. and Forest Biomedical.

2.2 Technique

2.2.1 Immediately before sampling, remove the caps. All tubes should be from the same lot.

2.2.2 Attach small end of the sampling tube to the pump with flexible tubing. Position the tube so that sampled air passes through the front section of the tube first.

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

2.2.4 Attach the sampler vertically with the open end pointing downward, in the worker's breathing zone, and positioned so it does not impede work performance or safety.

2.2.5 After sampling for the appropriate time, remove the sample and seal the tube with plastic end caps. Wrap each sample end-to-end with a Form OSHA-21 seal.

2.2.6 Submit at least one blank sample with each set of samples. Handle the blank sampler in the same manner as the other samples except draw no air through it.

2.2.7 Record sample volumes (in liters of air) for each sample, along with any potential interferences.

2.2.8 Ship any bulk samples in separate containers from the air samples.

2.2.9 Submit the samples to the laboratory for analysis as soon as possible after sampling. If delay is unavoidable, store the samples in a refrigerator.

2.3 Desorption efficiency

The desorption efficiencies of propylene glycol were determined by liquid-spiking the 13-mm glass fiber filters and also an amount of XAD-7 adsorbent equal to the adsorbing section (270mg) of an OVS-7 tube with the analyte at 0.1 to 2 times the target concentration. The loadings on the glass fiber filters and the tubes were 149.8, 748.9, 1497.8, and 2995.6µg of propylene glycol. These samples were stored overnight at ambient temperature and then desorbed and analyzed by GC-FID. The average desorption efficiency over the studied range was 99.7%.

Table 2.3.1
Desorption Efficiency of Propylene Glycol
From GFF

Tube #	% Recovered			
	0.1 × 149.8µg	0.5 × 748.9ug	1.0 × 1497.8µg	2.0 × 2995.6µg
1	100.8	98.7	99.5	100.8
2	101.9	97.0	100.3	101.0
3	101.4	97.9	100.8	100.3
4	100.8	98.0	99.5	100.6
5	100.6	99.1	100.4	100.2
6	100.0	98.8	98.2	100.4
average	100.9	98.3	99.8	100.6
overall average	99.9			
standard deviation	±1.01			

Table 2.3.2
Desorption Efficiency of Propylene Glycol
From XAD-7

Tube #	% Recovered			
	0.1 × 145.8µg	0.5 × 729.1ug	1.0 × 1458.2µg	2.0 × 2916.4µg
1	94.0	99.2	101.2	98.8
2	95.5	99.1	101.7	101.9
3	95.7	99.7	101.0	101.1
4	100.0	99.1	101.5	100.7
5	93.7	99.6	101.1	101.9
6	97.1	99.3	101.4	101.1
average	96.0	99.3	101.3	100.9
overall average	99.4			
standard deviation	±2.09			

2.4 Retention efficiency

The sampling tubes were spiked with 2995.6 µg (199.7 mg/m^3 based on a 15L air sample) propylene glycol, allowed to equilibrate overnight at room temperature, and then had 60L humid air (80% RH at 25°C) drawn through them at 1.0 Lpm. The sampling tubes were opened and the GFF, the front section and the back section were each put in separate vials. The samples were desorbed and analyzed by GC-FID. The retention efficiency averaged 100.5%.

Table 2.4
Retention Efficiency of Propylene Glycol

Tube #	% Recovered			
	GFF	Front Section	Back Section	Total
1	46.9	52.2	1.0	100.2
2	33.3	66.7	1.6	101.6
3	21.0	78.1	1.8	100.9
4	20.2	78.0	1.9	100.1
5	19.7	78.7	1.9	100.3
6	32.7	65.3	1.8	99.8
		average		100.5

2.5 Sample storage

The glass fiber filter of twenty-four sampling tubes were each spiked with 1497.8 µg (99.9 mg/m³ based on a 15L air sample) of propylene glycol. They were sealed and stored at room temperature. The next day 60L of humid air (80% RH at 25°C) was drawn through each tube at 1.0 L/min. Half of the tubes were stored in a drawer at ambient temperature and the other half were stored in a refrigerator at 0°C. After 10 days of storage six samples from the tubes stored under refrigeration and six samples from ambient storage were analyzed. The remaining samples were analyzed after 17 days of storage.

Table 2.5
Storage Test for Propylene Glycol

Ambient Storage		Refrigerator Storage	
Time (days)	% Recovered	Time (days)	% Recovered
10	99.4	10	98.3
10	98.3	10	97.1
10	99.3	10	98.1
10	96.9	10	97.3
10	99.0	10	96.5
10	98.0	10	96.4
17	95.4	17	97.6
17	95.7	17	94.5
17	97.0	17	97.1
17	97.7	17	97.0
17	95.5	17	96.0
17	96.9	17	97.9
average	97.4	average	97.0

2.6 Recommended air volume and sampling rate.

Based on the data collected in this evaluation, 60L air samples should be collected at a sampling rate of 1.0 L/min (15L for ceiling samples).

2.7 Interferences (sampling)

2.7.1 It is not known if any compounds will severely interfere with the collection of propylene glycol on OVS-7 sampling tubes. In general, the presence of other contaminant vapors in the air will reduce the capacity of the sampling tube to collect propylene glycol.

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 worker in such a manner that it will not interfere with work performance or safety.

2.8.2 Follow all safety practices that apply to the work area being sampled.

2.8.3 Wear eye protection at all times while in the work areas.

3. Analytical Procedure

3.1 Apparatus

3.1.1 The instrument used in this study was a gas chromatograph equipped with a flame ionization detector, specifically a Hewlett Packard model 5890.

3.1.2 A GC column capable of separating the analyte from any interferences. The column used in this study was a 30 meter Rtx-35 fused silica capillary column with a 3.0 µm film thickness and 0.53 mm ID.

3.1.3 An electronic integrator or some suitable method of measuring peak areas.

3.1.4 Four milliliter vials with Teflon™-lined caps.

3.1.5 A 10 µL syringe or other convenient size for sample injection.

3.1.6 Pipets for dispensing the desorbing solution. A 2 mL dispenser was used in this study.

3.1.7 Volumetric flasks - 10 mL and other convenient sizes for preparing standards.

3.2 Reagents

3.2.1 GC grade nitrogen, hydrogen and air.

3.2.2 Propylene glycol, Reagent grade.

3.2.3 Methanol, Reagent grade.

3.3 Standard preparation

3.3.1 At least two separate stock standards are prepared by diluting a known quantity of propylene glycol with the desorbing solution of methanol. The concentration of these stock standards was 149.78 mg/mL.

3.3.2 Dilutions of these stock standards were prepared to bracket the samples. The range of the standards used in this study was from 74.9 to 1497.8 µg/mL.

3.4 Sample preparation

3.4.1 Sample tubes are opened and the front section (GFF and 270 mg adsorbent), and back section of each tube are placed in separate 4 mL vials.

3.4.2 Each section is desorbed with 2 mL of methanol.

3.4.3 The vials are sealed immediately and allowed to extract/desorb for one hour on a mechanical rotator or shake the vials vigorously by hand several times during the extraction/desorption time.

3.4.4 Transfer some of the solution from each of the 4 mL vials to smaller glass vials suitable for an autosampler if necessary.

3.5 Analysis

3.5.1 Gas chromatograph conditions.

Injection size:	1 µL
<u>Flow rates (mL/min)</u>	
Nitrogen (make-up):	30
Hydrogen (carrier):	2
Hydrogen (detector):	40
Air:	420
<u>Temperatures (°C)</u>	
Injector:	200

Detector: 275
Column: 40 isothermal
Chromatogram:

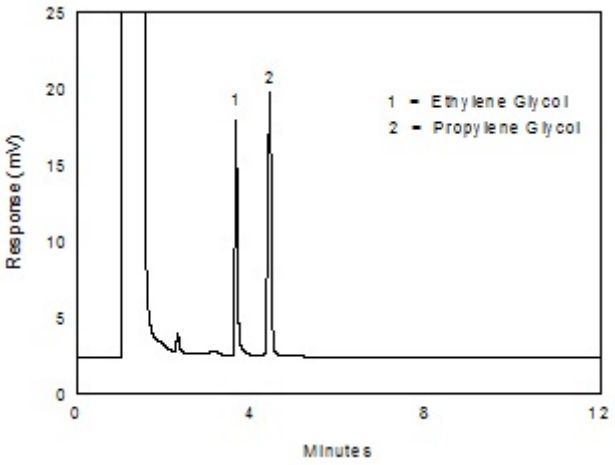


Figure 3.5.1 Chromatogram at the target concentration.

3.5.2 Peak areas are measured by an integrator or other suitable means.

3.6 Interferences (analytical)

3.6.1 Any compound that produces a response and has a similar retention time as the analyte is a potential interference. If any potential interferences were reported, they should be considered before samples are desorbed. Generally, chromatographic conditions can be altered to separate an interference from the analyte.

3.6.2 When necessary, the identity or purity of an analyte peak may be confirmed by a GC-mass spectrometer or by another analytical procedure.

3.7 Calculations

3.7.1 The calibration curve was made from at least four standards at different concentrations bracketing the samples.

3.7.2 The values for the samples are obtained from the calibration curve.

3.7.3 To calculate the concentration of analyte in the air sample the following formulas are used:

$$\text{mass of analyte in sample} = \frac{(\text{mg/mL})(\text{desorption volume})}{\text{desorption efficiency}}$$

$$\text{number of moles of analyte} = \frac{\text{mass of analyte in sample}}{\text{molecular weigth}}$$

Volume the analyte will occupy at 25 °C and 760 mmHg is number of moles of analyte times the molar volume at 25 °C and 760 mmHg.

$$\text{ppm} = \frac{(\text{volume analyte occupies})(10^6)}{\text{air volume}}$$

3.7.4 The above equations can be consolidated to the following formula.

$$\text{ppm} = \frac{(\text{mg/mL})(\text{DV})(24.46)(10^6)(\text{g})(\text{mg})}{(10\ \text{L})(\text{DE})(\text{MW})(1000\ \text{mg})(1000\ \text{mg})}$$

µg/mL = concentration of analyte in sample or standard

24.46 = molar volume (liters/mole) at 25 °C and 760 mmHg
MW = molecular weight (g/mole)
DV = desorption volume
10 L = 10 liter air sample
DE = desorption efficiency
* All units must cancel.

3.7.5 This calculation is done for each section of the sampling tube and the results added together after a blank correction is performed, if necessary.

3.8 Safety precautions

3.8.1 Avoid skin contact and inhalation of all chemicals.

3.8.2 Wear safety glasses, gloves and a lab coat at all times while in the laboratory areas.

4. Recommendations for Further Study

Collection studies should be performed.

5. References

5.1 Besser, B., OSHA Salt Lake Technical Center, Organic Division In-house file for Propylene Glycol, Study of Propylene Glycol, May 1983, OSHA SLTC, Salt Lake City, UT.

5.2 National Institute for Occupational Safety and Health: Method No. 5523, in *NIOSH Manual fo Analytical Methods*. 4th ed., Vol.1, Cincinnati,OH: National Institute for Occupational Safety and Health, 1996.

5.3 *The Merck Index,* 12th ed.; Budavari, S., Ed.; Merck & Co., Whitehouse Station, NJ,1996, p 1349.

5.4 *Hawley's Condensed Chemical Dictionary,* 12th ed.; Revised by Lewis, R. J.; Van Nostrand Reinhold: New York, 1993; pp 970-971.

5.5 Sweet, D., "Registry of Toxic Effects of Chemical Substances", 1985-86 Edition, U.S. Department of Health and Human Services, Public Health Service, Center for Disease Control, NIOSH, 1987, Vol. 4, Index Number TY2000000, p.3768.