



Hexylene Glycol

Method no.: PV2101

Target concentration: 25 ppm (125 mg/m³) ACGIH Ceiling TLV

Procedure: Samples are collected by drawing a known volume of air through a charcoal tube. Samples are desorbed with a (95:5) solution of Methylene Chloride:Methanol, and analyzed by gas chromatography with a flame ionization detector (GC-FID).

Air volume and sampling rate recommended: 3 liters at 0.2 L/min

Status of method: Partially Validated. This method has been only partially evaluated and is presented for information and trial use.

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Mary E. Eide

SOLVENTS BRANCH
OSHA SALT LAKE TECHNICAL CENTER
SANDY UT 84070

1 General Discussion

1.1 Background

1.1.1 History of procedure

The OSHA Laboratory recently received samples requesting the analysis for Hexylene glycol collected on charcoal tubes. The desorption efficiency was highest using a (95:5) Methylene Chloride:Methanol solution. The other solvents tried and their recoveries at the TLV were Carbon disulfide (CS₂) at 66% and (99:1) Carbon Disulfide:Dimethyl formamide (CS₂:DMF) at 79.2%. The retention and storage studies remained above 95%.

1.1.2 Potential workplace exposure (Ref 5.1)

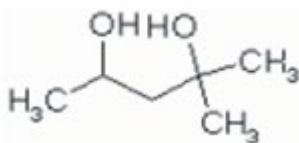
Hexylene glycol is used as a chemical intermediate, as a selective solvent in petroleum refining, as a component of hydraulic fluids, as a solvent for inks, in cosmetics, and as a cement additive.

1.1.3 Toxic Effects (This section is for information purposes and should not be taken as the basis for OSHA policy.)(Ref 5.1)

Oral administration of Hexylene glycol causes central nervous system depression. Skin irritation results from direct contact. In studies performed on humans, exposure to 50 ppm for 15 minutes caused slight eye irritation. At an exposure of 100 ppm for 5 minutes, there was slight nasal and respiratory discomfort, along with the eye irritation. At an exposure of 1000 ppm for 5 minutes, subjects had various degrees of eye irritation, throat irritation, and respiratory discomfort. The ACGIH recommends a ceiling level of 25 ppm to prevent eye irritation.

1.1.4 Physical properties (Ref 5.2):

CAS:	107-41-5
IMIS:	1389
Synonyms:	2-methyl-2,4-pentanediol; Pinakon
Molecular weight:	118.17
Density:	0.924
Boiling point:	198 °C
Flash point:	93 °C (200 °F)
Odor:	mild sweetish odor
Color:	clear liquid
Molecular formula:	C ₆ H ₁₄ O ₂
RTECS:	SA0810000
Structure:	



1.2 Limit defining parameters

1.2.1 The detection limit of the analytical procedure is 9.24 ng per injection. This is the smallest amount that could be detected under normal operating conditions, using a 1-μL injection volume.

1.2.2 An overall detection limit based on a 3 L air volume (15 minutes at 0.2 Lpm) and an overall desorption efficiency of 99.9% is 0.6 ppm. All ppm concentrations listed in this procedure are based on a 3 L air volume and a 1 mL desorption volume.

1.3 Advantages

1.3.1 The sampling procedure is convenient.

1.3.2 The analytical method is reproducible and sensitive.

1.3.3 Reanalysis of samples is possible

1.3.4 It may be possible to analyze other compounds at the same time.

1.3.5 Interferences may be avoided by proper selection of column and GC parameters.

1.4 Disadvantages

None known.

2 Sampling procedure

2.1 Apparatus

2.1.1 A calibrated personal sampling pump, the flow of which can be determined within $\pm 5\%$ at the recommended flow.

2.1.2 Charcoal tubes, coconut shell, containing a 100-mg adsorbing section with a 50-mg backup section separated by a 2 mm portion of urethane foam, with a silane-treated glass wool plug before the adsorbing section and a 3-mm plug of urethane foam at the back of the backup section. The ends are flame sealed and the glass tube containing the adsorbent is 7-cm long, with a 6-mm O.D. and 4 mm I.D., SKC tubes or equivalent.

2.2 Sampling technique

2.2.1 The ends of the charcoal tube are opened immediately before sampling.

2.2.2 Connect the charcoal tube to the sampling pump with flexible tubing.

2.2.3 Tubes should be placed in a vertical position to minimize channeling, with the smaller section closest to the pump.

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

2.2.5 Seal the charcoal tube with plastic caps immediately after sampling. Seal each sample lengthwise with Form OSHA-21 seal.

2.2.6 With each batch of samples, submit at least one blank tube from the same lot of charcoal used for samples. This tube should be subjected exactly the same handling as the samples (break ends, seal, & transport) except that no air is drawn through it.

2.2.7 Transport the samples (and corresponding paperwork) to the lab for analysis.

2.2.8 Bulks submitted for analysis must be shipped in a separate mailing container from the samples.

2.3 Desorption efficiency

Six tubes were liquid spiked at each loading of 0.1201 (8.283 ppm), 0.6006 (41.42 ppm), 1.201 (82.83 ppm), and 2.402 mg (165.7 ppm) Hexylene glycol. They were allowed to equilibrate overnight at room temperature. They were opened; each section was placed into a separate 2 mL vial, desorbed with 1 mL of the desorbing solution, desorbed for 30 minutes with occasional shaking, and analyzed by GC-FID. The overall average was 99.9% recovered (Table 2.3).

table 2.3
desorption efficiency

	2.402 mg 165.7 ppm	1.201 mg 82.83 ppm	0.6006 mg 41.42 ppm	0.1201 mg 8.283 ppm
tube #	% desorption			
1	99.5	104	99.7	101
2	98.7	98.0	99.2	99.0
3	99.8	99.2	99.8	98.4
4	101	lost	102	98.1
5	97.7	101	100	99.9
6	99.1	101	98.9	99.4
average	99.3	101	99.9	99.3

overall average = 99.9%
standard deviation = ±1.68

2.4 Retention efficiency

Six tubes were liquid spiked with 1.201 mg (82.83 ppm based on a 3-L air volume) Hexylene glycol, allowed to equilibrate overnight, and had 10 liters of humid air (91% RH) pulled through them. They were opened, desorbed, and analyzed by GC-FID. There was no Hexylene glycol found on the backup portions of the tubes (Table 2.4). The retention efficiency averaged 98.7%.

table 2.4
retention efficiency

tube #	% recovery 'A'	% recovery 'B'	total recovery
1	97.3	0.0	97.3
2	97.3	0.0	97.3
3	97.1	0.0	97.1
4	97.8	0.0	97.8
5	104	0.0	104
6	98.7	0.0	98.7
average			98.7

2.5 Storage

Nine charcoal tubes were spiked with 1.201 mg (82.83 ppm) Hexylene glycol and stored at room temperature until opened and analyzed. The total of all nine recoveries averaged 97.8% for the 15 days stored (Table 2.5).

table 2.5

days stored	% recovered
5	99.5
5	100
5	98.8
12	93.5
12	95.4
12	94.2
15	101
15	100
15	98.2
average	97.8

2.6 Precision

Precision was determined by injecting standard solutions six times. The standard solutions used were 0.1201 mg/mL (8.28 ppm), 0.6006 mg/mL (41.4 ppm), 1.201 mg/mL (82.8 ppm), and 2.402 mg/mL (166 ppm) Hexylene glycol in the desorbing solution, which correspond to approximately 0.3×, 1.6×, 3.3×, and 6.6× the TLV (Table 2.6).

table 2.6

injection number	2.402 mg/mL 166 ppm	1.201 mg/mL 82.8 ppm	0.6006 mg/mL 41.4 ppm	0.1201 mg/mL 8.28 ppm
1	6256149	3173206	1317202	309848
2	6284925	3185187	1327468	311433
3	6257428	3169345	1306625	303459
4	6368661	3146888	1336024	307956
5	6284569	3132323	1319897	305946
6	6284803	3115201	1306397	308072
average - standard deviation -	6289423	3153692	1318936	307786
CV -	±41169	±26841	±11641	±2820
pooled CV -	0.006546	0.008511	0.008826	0.009162

$$CV (\text{Coefficient of Variation}) = \frac{\text{standard deviation}}{\text{average}}$$

$$\text{Pooled CV} = \sqrt{\frac{A1(CV1)^2 + A2(CV2)^2 + A3(CV3)^2 + A4(CV4)^2}{A1 + A2 + A3 + A4}}$$

A(1), A(2), A(3), A(4) = # of injections at each level
 CV1, CV2, CV3, CV4 = Coefficients at each level

2.7 Air volume and sampling rate studied

2.7.1 The air volume studied is three liters.

2.7.2 The sampling rate studied is 0.2 liters per minute

2.8 Interferences

Suspected interferences should be listed on sample data sheets.

2.9 Safety precautions

2.9.1 Sampling equipment should be placed on an employee in a manner that does not interfere with work performance or safety.

2.9.2 Safety glasses should be worn at all times.

2.9.3 Follow all safety practices that apply to the workplace being sampled.

3 Analytical method

3.1 Apparatus

3.1.1 Gas chromatograph equipped with a flame ionization detector. GC must be capable of separating the analyte and an internal standard from any interference.

3.1.2 GC column - a 60-m DB-Wax capillary column was used.

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

3.1.4 Two milliliter vials with PTFE-lined caps.

3.1.5 A 10- μ L syringe or other convenient size for sample injection.

3.1.6 Pipettes for dispensing the desorbing solution. A Glenco 1-mL dispenser was used in this method.

3.1.7 Volumetric flasks - 5 mL and other convenient sizes for preparing standards.

3.2 Reagents

3.2.1 Purified GC grade nitrogen, hydrogen, oxygen, and air.

3.2.2 Methanol, Reagent grade.

3.2.3 Methylene chloride, Reagent grade.

3.2.4 Hexylene glycol, Reagent grade.

3.2.5 n-Hexanol, Reagent grade (Internal Standard).

3.2.6 The desorbing solvent was a 95:5 mixture of methylene chloride:methanol with 1 μ L/mL n-hexanol internal standard.

3.3 Sample preparation

3.3.1 Sample tubes are opened and the front and back section of each tube are placed in separate 2-mL vials.

3.3.2 Each section is desorbed with 1 mL of the desorbing solvent.

3.3.3 The vials are sealed immediately and allowed to desorb for 30 minutes with occasional shaking.

3.4 Standard preparation

3.4.1 Standards are prepared by diluting a known quantity of Hexylene glycol with the desorbing solvent. A 1 $\mu\text{L}/\text{mL}$ Hexylene glycol in the desorbing solvent corresponds to 63.73 ppm based on a 3-liter air volume, 1-mL desorption volume, and the 99.9% desorption efficiency.

3.4.2 At least two separate standards should be made.

3.4.3 A third standard at a different concentration should be made to check the linearity of the detector.

3.5 Analysis

3.5.1 Gas chromatograph conditions.

<u>Flow rates (mL/min)</u>		<u>Temperature ($^{\circ}\text{C}$)</u>	
Nitrogen (makeup):	24	Injector:	200 $^{\circ}\text{C}$
Hydrogen (carrier):	2	Detector:	220 $^{\circ}\text{C}$
Air (detector):	240	Column:	120 $^{\circ}\text{C}$ for 6 min 10 $^{\circ}\text{C}/\text{min}$ to 150 $^{\circ}\text{C}$
Hydrogen (detector):	30	Column:	60 meter DB-Wax capillary
Injection size:	1 μL		
Elution time:	12.41 min		

Chromatogram:

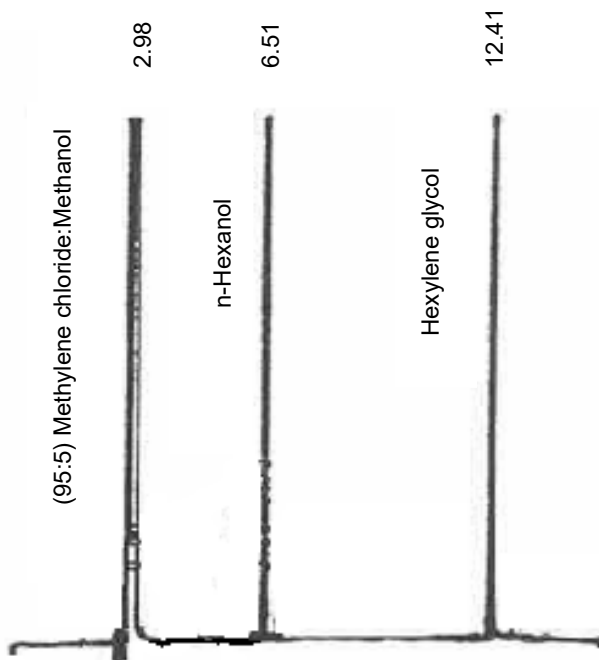


Figure 2.5.1 a standard of 1 $\mu\text{L}/\text{mL}$ (63.73 ppm) Hexylene glycol in the desorbing solvent.

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

3.6 Interferences (analytical)

3.6.1 Possible interferences should be listed on the sample data sheet. Any compound having the general retention time of the analyte or the internal standard used is interference. GC parameters should be adjusted if necessary so these compounds will pose no problems.

3.6.2 Retention time data on a single column is not considered proof of chemical identity. Samples over the target concentration should be confirmed by GC/Mass Spec or other suitable means.

3.7 Calculations

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

$$\text{mass of analyte, } \mu\text{g} = \frac{(\mu\text{g} / \text{mL})(\text{desorption volume, mL})}{(\text{desorption efficiency, decimal})}$$

$$\text{moles of analyte} = \frac{(\text{mass of analyte, } \mu\text{g})(1 \text{ g})}{(\text{molecular weight})(10^6 \mu\text{g})}$$

$$\text{volume of analyte (25 }^\circ\text{C \& 760 mmHg)} = (\text{moles analyte})(\text{molar volume (25 }^\circ\text{C \& 760 mmHg)})$$

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

* All units must cancel.

3.7.2 The above equations can be consolidated to form the following formula. To calculate the ppm of analyte in the sample based on a 3-liter air sample:

$$\text{ppm} = \frac{(\mu\text{g} / \text{mL})(\text{DV})(24.46)}{(3 \text{ L})(\text{DE})(\text{MW})}$$

$\mu\text{g/mL}$ = concentration of analyte in sample or standard
24.46 = Molar volume (liters/mole) at 25°C and 760 mmHg
MW = Molecular weight (118.17 g/mole)
DV = Desorption volume (mL)
3 L = 3 liter air sample
DE = Desorption efficiency

3.7.3 This calculation is done for each section of the sampling tube and the results added together.

3.8 Safety precautions

3.8.1 All handling of solvents should be done in a hood

3.8.2 Avoid skin contact with all solvents.

3.8.3 Wear safety glasses at all times.

4 Recommendations for further study

Vapor generated samples should be prepared to evaluate the collection efficiencies from an atmosphere.

5. References

- 5.1 "Documentation of the Threshold Limit Values and Biological Exposure Indices", Fifth Edition, American Conference of Governmental Industrial Hygienists Inc., Cincinnati, OH, 1986, p. 309.
- 5.2 Windholz, M., "The Merck Index", Tenth Edition, Merck & Co., Rahway, N.J., 1983, p. 681.