GLYCOL ETHERS 2554

(1) $CH_3OCH_2CHOHCH_3$	MW: 90.1	CAS: 107-98-2	RTECS: UB7700000
(2) $CH_3OC_3H_6OC_3H_6OH$	148.2	34590-94-8	JM1575000
(3) $CH_3OCH_2CH(CH_3)COOCH_3$	132.16	108-65-6	AI8925000

METHOD: 2554 **EVALUATION: PARTIAL** **Issue 1: 15 March 2003**

OSHA : See Table I
NIOSH: See Table I
ACGIH: See Table I

PROPERTIES: See Table I

SYNONYMS: (1) propylene glycol monomethyl ether, 1-methoxy-2-propanol, 2-methoxy-1-methylethanol, propylene glycol methyl ether
(2) dipropylene glycol monomethyl ether
(3) propylene glycol monomethyl ether acetate, propylene glycol methyl ether acetate, 1-methoxy-2-propyl acetate

SAMPLING

SAMPLER: SOLID SORBENT TUBE (Anasorb® 747, 140 mg/70 mg)

FLOW RATE: 0.1 to 0.2 L/min

VOL-MIN: 3 L
-MAX: 25 L (at lower flow rates)

SHIPMENT: Keep cold, pack securely for shipping

SAMPLE STABILITY: 14 days @ 5°C for analytes 1 and 3; 7 days @ 5°C for analyte 2

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: Not determined.

BIAS: Not determined.

OVERALL PRECISION ($\hat{S}_{rT}$): Not determined.

ACCURACY: Not determined

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: See Table I

DESORPTION: 1 mL of methylene chloride/methanol (85:15) for 30 minutes in ultrasonic bath

INJECTION VOLUME: 1 µL

TEMPERATURE
-INJECTION: 195°C
-DETECTOR: 240°C
-COLUMN: 90°C (1 min) to 200°C (10°C/min)

CARRIER GAS: Helium, 2.8 mL/min

COLUMN: Capillary, fused silica, 30 m x 0.32-mm ID; 100% PEG-DA, Stabilwax or equivalent

CALIBRATION: Solutions of analytes in desorption solvent

RANGE: (1) 1.5 to 369 µg[3]
(2) 3.0 to 375 µg[3]
(3) 1.5 to 369 µg[3]

ESTIMATED LOD: (1) 0.5 µg[3]
(2) 1.0 µg[3]
(3) 0.5 µg[3]

PRECISION ($\bar{S}_r$): (1) 0.013[3]
(2) 0.031[3]
(3) 0.016[3]

APPLICABILITY: The working range for propylene glycol monomethyl ether was 0.041 to 10.0 ppm (0.154 to 36.9 mg/m^3), for dipropylene glycol monomethyl ether was 0.050 to 6.19 ppm (0.305 to 37.5 mg/m^3), and propylene glycol monomethyl ether acetate was 0.030 to 6.83 ppm (0.151 to 36.9 mg/m^3) for a 10 L sample . Other methods used for the collection of these analytes used a different solid sorbent and were evaluated at higher analyte concentrations [1,2]. Collection and DE recovery at levels greater than the working range listed should be equal or better than those achieved using charcoal sorbent tubes.

INTERFERENCES: No specific interferences were identified. However, any compound with a similar retention time as the analytes of interest may interfere.

OTHER METHODS: OSHA method 99 [1] and OSHA method 101 [2] can also be used for sampling glycol ethers at or above the REL and PEL. NIOSH Method S69, from the 2nd edition of the NIOSH Manual of Analytical Methods, was used previously for the collection and analysis of dipropylene glycol monomethyl ether and had acceptable recovery at a concentrations at or above the REL/PEL [4].

REAGENTS:

1. Propylene glycol monomethyl ether, reagent grade.*
2. Dipropylene glycol monomethyl ether, reagent grade.*
3. Propylene glycol monomethyl ether acetate, reagent grade.*
4. Methylene chloride, chromatographic grade.*
5. Methanol, chromatographic grade.*
6. Desorbing solution, 15% methanol in 85% methylene chloride (V/V).
7. Propylene glycol monomethyl ether calibration stock solution, 46.2 mg/mL. Dilute 0.5 mL analyte to 10 mL with desorbing solution.
8. Dipropylene glycol monomethyl ether calibration stock solution, 47.5 mg/mL. Dilute 0.5 mL analyte to 10 mL with desorbing solution.
9. Propylene glycol monomethyl ether acetate calibration stock solution, 48.5 mg/mL. Dilute 0.5 mL nitrobenzene to 10 mL with desorbing solution.
10. Air, compressed, purified, and filtered.
11. Helium, purified and filtered.
12. Hydrogen, filtered.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends, containing two sections of Anasorb® 747 (140mg/70 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section. A urethane foam plug follows the back section. Tubes are commercially available from SKC, Inc.
2. Personal sampling pump, 0.1 to 0.2 L/min, connected with flexible tubing.
3. Gas chromatograph, FID, integrator, and 30-m Stabilwax-DA or equivalent capillary column (page 2554-1).
4. Vials, autosampler, with PTFE-lined caps.
5. Syringes, 10-µL, 25-µL, and 1-mL.
6. Volumetric flasks, 10-mL.
7. Refrigerant packs for shipping.

SPECIAL PRECAUTIONS: Methylene chloride is a carcinogen [3]. Methanol is very flammable and toxic. Glycol ethers are irritants and hazardous compounds. Wear appropriate protective clothing and work with these compounds in a well-ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately prior to sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.1 and 0.2 L/min for a total sample size of 10 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment. Samples should be kept cold.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Place the glass wool preceding the front section into the vial containing the front section. Discard the remaining foam plugs.
6. Add 1.0 mL of the desorbing solution into each vial. Attach crimp caps to each vial.
7. Place the sample vials in an ultrasonic bath for 30 minutes.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards to cover the analytical range. If necessary, additional standards may be added to extend the calibration curve.
   a. Add known amounts of analytes to solvent solution in 10-mL volumetric flasks and dilute to the mark. Mix well.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area versus µg analyte).
9. Determine desorption efficiency (DE) at least once for each lot of Anasorb 747 used for sampling in the calibration ranges (step 8).
   a. Prepare three tubes at each of five levels plus three media blanks.
   b. Inject a known amount of calibration stock solution directly onto the front sorbent section of each Anasorb 747 tube with a microliter syringe.
   c. Allow the tubes to air equilibrate for several minutes, then cap the ends of each tube and allow to stand overnight.
   d. Desorb (steps 5-7) and analyze together with standards and blanks (steps 11 and 12).
   e. Prepare a graph of DE versus µg analyte recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2554-1. Inject a 1-µL sample aliquot manually using the solvent flush technique or with an autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with solvent, reanalyze and apply the appropriate dilution factor in the calculations.
12. Measure peak areas.

CALCULATIONS:

13. Determine the mass, µg (corrected for DE) of analyte found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of analyte in the air volume sampled, V(L):

$$C = \frac{(W_f + W_b - B_f - B_b)}{V}, mg/m^3$$

NOTE: µg/L = mg/m^3

EVALUATION OF METHOD:

In order to obtain improved analyte collection and recovery results, several procedures were incorporated in the method development. These included the use of a stainless steel inlet liner in the injection port to reduce the possibility of degradation of analytes, lower injection port and detector temperatures to prevent thermal decomposition of analytes, and the use of Anasorb 747 solid sorbent tubes to reduce the possibility of the hydrolysis of the analytes.

This method was developed in support of a field survey to identify and quantitate glycol ether vapors emitted from heat-cured solder mask paints. This method is applicable when levels below the REL/PEL are expected. The average desorption efficiency (DE) recovery for propylene glycol monomethyl ether was 100.6% (RSD = 1.6), for dipropylene glycol monomethyl ether, was 102.4% (RSD = 1.8), and for propylene glycol monomethyl

ether acetate was 102.0% (RSD = 1.7). The average 14-day storage stability recovery at approximately 75x the LOQ for propylene glycol monomethyl ether was 103.1% (RSD = 2.1), for dipropylene glycol monomethyl ether was 77.7% (RSD = 2.3), and propylene glycol monomethyl ether acetate was 95.4% (RSD = 3.7). Samples containing dipropylene glycol monomethyl ether should be analyzed soon after collection to minimize sample loss during storage.

REFERENCES:

[1] OSHA [1993]. Propylene Glycol Monomethyl Ethers/Acetate, Method 99. Organic Methods Evaluation Branch, OSHA Analytical Methods Manual. Salt Lake City, UT: U.S. Department of Labor, Occupational Safety and Health Administration, OSHA Salt Lake Technical Center.
[2] OSHA [1993]. Dipropylene Glycol Methyl Ether, Method 101. Organic Methods Evaluation Branch, OSHA Analytical Methods Manual. Salt Lake City, UT: U.S. Department of Labor, Occupational Safety and Health Administration, OSHA Salt Lake Technical Center.
[3] Pendergrass SM [1998]. Backup data report for glycol ethers. Unpublished report. NIOSH/DPSE.
[4] NIOSH [1977]. Documentation of the NIOSH Validation Tests, S69, U.S. Department of Health, Education, and Welfare; Publ. (NIOSH) 77-185 (1977).
[5] NIOSH Recommendations for Occupational Safety and Health, U.S. Department of Health and Human Services, (NIOSH) Publ. 92-100 (January 1992).

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TABLE 1. EXPOSURE LIMITS AND PHYSICAL PROPERTIES

Analyte	OSHA PEL (ppm)	NIOSH REL (ppm)	ACGIH TLV (ppm)	mg/m^3 = 1 ppm @ NTP	Physical Properties
Propylene glycol monomethyl ether	None	100	100	3.75	Liquid; d 0.9234 g/mL @20 °C, BP 120.1 °C, VP 1.6 kPa (12 mm Hg) @ 20°C
Dipropylene glycol monomethyl ether	100	100	100	6.16	Liquid; d 0.9500 g/mL @20 °C, BP 189.6 °C, VP 0.05 kPa (0.5 mm Hg) @ 20°C
Propylene glycol monomethyl ether acetate	None	None	None	5.40	Liquid; d 0.9700 g/mL @20 °C, BP 145.8 °C, VP 0.5 @ 20°C KPa