FORMULA: Table 1 MW: Table 1 CAS: Table 1 RTECS: Table 1

METHOD: 5523, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 May 1996**

OSHA : No PEL
NIOSH: No REL
ACGIH: C 50 ppm (ethylene glycol)
(1 ppm = 2.54 mg/m^3 @ NTP)

PROPERTIES: See Table 1

NAMES & SYNONYMS: (1) ethylene glycol: 1,2-ethanediol; (2) propylene glycol: 1,2-propanediol
(3) 1,3-butylene glycol: 1,3-butanediol (4) diethylene glycol: 2-hydroxyethyl ether, 2,2'-oxydiethanol

SAMPLING

SAMPLER: XAD-7 OVS tube (glass fiber filter, 13-mm; XAD-7, 200mg/100mg)

FLOW RATE: 0.5 to 2 L/min

VOL-MIN: 5 L
-MAX: 60 L

SHIPMENT: pack cold for shipment

SAMPLE STABILITY: 28 days @ 5 °C [1]
ethylene glycol 14 days @ 5 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: see EVALUATION OF METHOD

BIAS: see EVALUATION OF METHOD

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

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTES: compounds above

DESORPTION: 2 mL methanol; ultrasonicate 30 min

INJECTION VOLUME: 1 µL

TEMPERATURE-INJECTION: 250 °C
-DETECTOR: 300 °C
-COLUMN: 40 °C, 8 °C/min to 230 °C

CARRIER GAS: He_2 @ 2.4 to 2.6 mL/min

COLUMN: Rtx-35 fused silica capillary, 30 m, 0.53-mm ID, 3-µm film

CALIBRATION: solutions of glycols in methanol

RANGE: 15 to 800 µg/sample

ESTIMATED LOD: see Table 2

PRECISION ($\bar{S}_r$): 0.04 to 0.09 [1]

APPLICABILITY: Under the GC parameters given in the method, the glycols listed above are baseline separated and can be identified based on retention time and quantified. Hexylene glycol can be determined by this method; however, no sampling or analytical evaluation has been conducted.

INTERFERENCES: No specific interferences were identified. The method yields baseline separation for all analytes.

OTHER METHODS: This method replaces NMAM 5500 [2], which was found deficient in the collection of ethylene glycol in aerosol form. Also ethylene glycol was not separated from propylene glycol by the chromatography.

REAGENTS:

1. Ethylene glycol, reagent grade.*
2. Propylene glycol, reagent grade.*
3. 1,3-Butylene glycol, reagent grade.*
4. Diethylene glycol, reagent grade.*
5. Triethylene glycol, reagent grade.*
6. Tetraethylene glycol, reagent grade.*
7. Methanol, chromatographic grade.*
8. Calibration stock solution, 10 mg/mL: Weigh aliquots of each glycol and dissolve in methanol.
9. Helium, purified.
10. Hydrogen, prepurified.
11. Air, filtered.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: XAD-7 OVS tube, 13-mm OD, containing two sections of XAD-7 (200 mg front/100 mg back section) separated by polyurethane foam plug. A glass fiber filter plug precedes the front section and a polyurethane foam plug follows the back section. Tubes are commercially available (SKC, Inc., #226-57).
2. Personal sampling pump, 0.5 to 2 mL/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator, and column (page 5523-1).
4. Ultrasonic bath.
5. Vials, autosampler, with PTFE-lined caps.
6. Vials, 4 mL, with screw caps.
7. Syringes, 10-µL and other sizes as needed, readable to 0.1 µL.
8. Flasks, volumetric, various sizes.
9. Pipets, various sizes.

SPECIAL PRECAUTIONS: Inhalation of glycol mists causes respiratory irritation, shortness of breath, and coughing. Methanol is flammable and a dangerous fire risk. Work with these compounds in a well-ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Remove front and rear caps from the tube immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.5 and 2 L/min for a total sample size of 5 to 60 L.
4. Cap the samplers and pack securely in dry ice for shipment.

SAMPLE PREPARATION:

5. Place front sorbent section and glass fiber filter in a 4-mL screw cap vial. Place backup sorbent section in a separate vial. Discard foam plugs.
6. Add 2 mL of methanol to each vial and cap.
7. Place vials in an ultrasonic bath for 30 min to aid desorption.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range of interest. Three standards (in duplicate) should cover the range from LOD to LOQ.
   a. Add known amounts of calibration stock solution to methanol in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area or height vs. µg glycol).
9. Determine desorption efficiency (DE) at least once for each lot of OVS tubes used for sampling in the calibration range (step 8).
   a. Prepare three samplers at each of six levels plus three media blanks.
   b. Inject a known amount of calibration stock solution directly onto the filter of OVS tubes. Draw air

through the sampler at 1 L/min for 60 min.
c. Cap the ends of the tubes and allow to stand overnight.
d. Desorb (steps 5 through 7) and analyze together with standards and blanks (steps 11 and 12).
e. Prepare a graph of DE vs. µg analyte recovered.

10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graphs are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 5523-1. Inject 1-µL sample aliquot manually using solvent flush technique or with autosampler.
NOTE: If peak area is above the linear range of the working standards, dilute with methanol, reanalyze and apply the appropriate dilution factor in the calculations.
12. Measure peak areas.

CALCULATIONS:

13. Determine the mass, µg (corrected for DE), of each glycol 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 each analyte in the air volume sampled, V (L):

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

EVALUATION OF METHOD:

The method was evaluated for six glycols (ethylene, propylene, 1,3-butylene, diethylene, triethylene, and tetraethylene). Desorption efficiency (DE) was determined by spiking known amounts of each glycol in methanol solution onto the glass fiber filter plug of the XAD-7 OVS tubes, drawing air through the spiked tubes at 1 L/min for 60 min, and analyzing. Recovery data along with LODs and LOQs for each analyte are listed in Table 2. When stored at 5°C, ethylene glycol samples on XAD-7 OVS tubes were stable for 14 days, and the other glycols were stable up to 28 days. Glycol aerosols were generated at three concentration levels (6 samples per concentration) from a ROSCO™ Model 1500 Fog Machine. Precision [as calculated from the pooled relative standard deviation ($\bar{S}_r$)] and mean bias for the glycols are as follows:

Analyte	Range Studied (µg/sample)	Precision ($\bar{S}_r$)	Bias
Ethylene glycol	33 to 218	0.043	-15%
Propylene glycol	26 to 187	0.062	-3.2%
1,3-butylene glycol	34 to 178	0.054	-0.5%
Diethylene glycol	68 to 219	0.047	-0.2%
Triethylene glycol	33 to 201	0.075	-4.0%
Tetraethylene glycol (2 levels)	32 to 197	0.035	+20%

The low recovery for ethylene glycol possibly may be attributed to increased volitility when sampled at 1 L/min [1]. Although hexylene glycol is separated by the chromatographic conditions given in the method, no evaluation of sampling or analytical parameters was done for this compound.

REFERENCES:

[1] Pendergrass, S.M. [1994]. Development of a sampling and analytical methodology for the

determination of glycols in air: Application to theatrical smokes. Unpublished paper presented at Pittsburgh Conference, Chicago, IL, March 1994.

[2] NIOSH [1984]. Ethylene glycol: Method 5500. In: Eller PM, Ed. NIOSH manual of analytical methods, 3rd ed. Cincinnati, OH: U.S. Department of Health and Human Services, HHS (NIOSH) Publication No. 84-100.

METHOD WRITTEN BY:

Stephanie M. Pendergrass, MRSB, DPSE

TABLE 1. GLYCOLS GENERAL INFORMATION

Analyte	Formula	MW	CAS #	RTECS #	Properties
Ethylene glycol	$C_2H_6O_2$	62.07	107-21-1	KW2975000	liquid; BP 197.2 °C; FP -13 °C; d 1.113 g/mL @ 20 °C; n_D 1.4310; vp 0.007 kPa (0.05 mm Hg) @ 20°C; explosive limits 3.2 to 15.3% v/v in air
Propylene glycol	$C_3H_8O_2$	76.10	57-55-6	TY2000000	liquid; BP 188 °C; FP -60 °C ; d 1.038 g/mL @ 20 °C; n_D 1.4320; vp 0.009 kPa (0.07 mm Hg) @ 20°C; explosive limits 2.6 to 12.5% v/v in air
1,3-Butylene glycol	$C_4H_{10}O_2$	90.12	107-88-0	EK0440000	liquid; BP 207.5 °C; d 1.0059 g/mL @ 20 °C; n_D 1.4400; vp 0.06 mm Hg @ 20 °C
Diethylene glycol	$C_4H_{10}O_3$	106.12	111-46-6	ID5950000	liquid; BP 245 °C; FP -6.5 °C; d 1.118 g/mL @ 20 °C; n_D 1.4460 @ 25 °C; vp <0.01 mm Hg @ 20°C; explosive limits 3 to 7% v/v in air
Triethylene glycol	$C_6H_{14}O_4$	150.17	112-27-6	YE4550000	liquid; BP 285 °C; FP -5 °C; d 1.125 g/mL @ 20 °C; n_D 1.4550; vp <0.001 mm Hg @ 20 °C; explosive limits 0.9 to 9.2% v/v in air
Tetraethylene glycol	$C_8H_{18}O_5$	194.23	112-60-7	XC2100000	liquid; BP 327.3 °C; FP -4 °C; d 1.125 g/mL @ 20 °C; n_D 1.4577; vp >0.001 mm Hg @ 20 °C

TABLE 2. GLYCOL RECOVERY DATA

Analyte	LOD (µg/sample)	LOQ (µg/sample)	Desorption Efficiency Spikes[a]		$\bar{S}_r$[b]
			100 µg (% Recovery)	200 µg (% Recovery)	
Ethylene glycol	7	22	93.4	101	0.059
Propylene glycol	6	13	83.4	92.5	0.064
1,3-Butylene glycol	6	12	98.8	102	0.072
Diethylene glycol	16	48	94.6	114	0.041
Triethylene glycol	14	42	85.3	98.7	0.043
Tetraethylene glycol	14	42	111	141	0.092

[a] n = 6 for each spiking level
[b] Pooled Relative Standard Deviation