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

METHOD: 2539, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : Table 1
NIOSH: Table 1
ACGIH: Table 1

PROPERTIES: Table 1

COMPOUNDS: acetaldehyde; acrolein; butyraldehyde; crotonaldehyde; formaldehyde; furfural; heptanal; hexanal; isobutyraldehyde; isovaleraldehyde; propionaldehyde; valeraldehyde.
SYNONYMS: Table 1

SAMPLING

SAMPLER: SOLID SORBENT TUBE (10% 2-(hydroxymethyl)piperidine on XAD-2, 120 mg/60 mg)

FLOW RATE: 0.01 to 0.05 L/min

VOLUME: 5 L

SHIPMENT: @ 25 °C or lower

SAMPLE STABILITY: at least 1 week @ 25 °C

FIELD BLANKS: 2 to 10 field blanks per set

MEDIA BLANKS: 6 per set

ACCURACY

RANGE STUDIED: not studied

BIAS: not determined

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

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID & GC/MS

ANALYTE: oxazolidine prepared from aldehyde

DESORPTION: 1 mL toluene; 60 min ultrasonic

INJECTION VOLUME: 1 µL splitless; split vent time 30 sec

TEMPERATURE-INJECTION: 250 °C
-DETECTOR: 280 °C
-COLUMN: 1 min @ 70 °C; 6 °C/min to 100 °C for 2 min; 30 °C/min to 260 °C

CARRIER GAS: He, 0.5 mL/min; makeup flow, 29 mL/min

COLUMN: capillary, 15 m x 0.32-mm, 1.0-µm film 6% cyanopropyl-phenyl, DB-1301 or equivalent

CALIBRATION: standard solutions of aldehydes spiked on sorbent

RANGE AND PRECISION: not determined

ESTIMATED LOD: 2 µg aldehyde per sample

APPLICABILITY: This is a screening technique to determine the presence of aldehydes and should not be used for quantitation. Further confirmation of aldehyde identification should be performed by gas chromatography/mass spectrometry (See Table 2 for structural ion data). Methods for quantitation of some aldehydes listed in this method are available in the NIOSH Manual of Analytical Methods (See OTHER METHODS). All aldehydes tested have been detected by this method in bulk field samples.

INTERFERENCES: High-boiling naphtha mixtures, such as kerosene and mineral spirits may have components with retention times similiar to the oxazolidines and may be interferences in the gas chromatographic analysis. A second column (DB-5, DB-WAX) may be needed to separate some of the earlier C_3-C_4 aldehydes from excess HMP reagent.

OTHER METHODS: This method incorporates sampling technology used in NIOSH methods 2501 (acrolein), 2541 (formaldehyde), 2529 (furfural), 2531 (glutaraldehyde) [1], and 2526 (valeraldehyde), and OSHA methods 68 (acetaldehyde) and 52 (acrolein/formaldehyde) [2].

REAGENTS:

1. Toluene, chromatographic quality.
2. 2-(Hydroxymethyl)piperidine. Recrystallize several times from isooctane until there is one major peak (>95% of area) by GC analysis. Store in desiccator.
3. Amberlite XAD-2 (Rohm and Haas or equivalent).
4. Formaldehyde,* 37% (w/v) solution in water.
5. Formaldehyde stock solution, 1 µg/µL (see APPENDIX A).
6. Acetaldehyde*.
7. Acrolein*.
8. Propionaldehyde*.
9. Butyraldehyde*.
10. Isobutyraldehyde*.
11. Crotonaldehyde*.
12. Valeraldehyde*.
13. Isovaleraldehyde*.
14. Hexanal*.
15. Heptanal*.
16. Furfural*.
17. Sulfuric acid, 0.02 N.
18. Sodium hydroxide, 0.01 N.
19. Sodium sulfite, 1.13 M.
20. Water, deionized, then distilled.
21. Hydrogen, prepurified.
22. Air, filtered, compressed.
23. Helium, purified.

* See SPECIAL PRECAUTIONS.

SPECIAL PRECAUTIONS: Aldehydes can irritate the mucous membranes and act on the central nervous system [3]. Certain aldehydes are also suspect carcinogens. Work with these compounds only in a well-ventilated hood.

EQUIPMENT:

1. Sampler: glass tube, 10 cm long, 6-mm OD, 4-mm ID; flame-sealed ends and plastic caps, containing two sections of 40/60 mesh, 2-(hydroxymethyl)piperidine-coated XAD-2 (front = 120 mg; back = 60 mg: see APPENDIX A) retained and separated by small plugs of silanized glass wool. Pressure drop across the tube at 0.10 L/min airflow must be less than 760 kPa (5.7 mm Hg). Tubes are commercially available (Supelco, Inc. ORBO-23 or equivalent).
2. Personal sampling pump, 0.01 to 0.05 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector (FID), integrator and column (page 2539-1). GC/MS system for confirmation.
4. Ultrasonic bath.
5. Vials, glass, 1-mL, with PTFE-lined crimp caps.
6. Flasks, volumetric, 10-mL.
7. Pipets, volumetric, 1-mL with pipet bulb
8. Syringes, 10-µL (readable to 0.1-µL), 25-, and 50-µL.
9. File.
10. Beakers, 50-mL.
11. pH meter.
12. Magnetic stirrer.
13. Burets, 50-mL.
14. Flasks, round-bottomed, 100-mL.
15. Soxhlet extraction apparatus.
16. Vacuum oven.
17. Distillation apparatus.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. For general screening, sample at 0.01 to 0.05 L/min for a maximum sample volume of 5 L.
   NOTE: Aldehydes react with the 2-(hydroxymethyl)piperidine to form an oxazolidine derivative in the sorbent bed during sampling. Sampling rate is limited by the speed of this reaction. Owing to the lower reactivities of some aldehydes, sampling even at 0.02 L/min may cause breakthrough because of incomplete reaction.

SAMPLE PREPARATION:

4. Score each sampler with a file in front of the first sorbent section.
5. Break sampler at score line. Remove and place front glass wool plug and front sorbent section in a vial. Transfer back section with remaining glass wool plugs to a second vial.
6. Add 1.0 mL toluene to each vial. Crimp cap tightly onto each vial.

7. Agitate vials in an ultrasonic bath for 60 min.

CALIBRATION AND QUALITY CONTROL:

8. Prepare qualitative oxazolidine standard samples.
   a. Prepare aldehyde standard stock solutions.
      NOTE: Aldehydes can oxidize to other compounds on exposure to air. This will introduce bias into the method, so use of freshly-opened bottles of aldehydes is recommended.
      (1) Inject an aliquot of formaldehyde stock solution directly onto the sorbent.
      (2) Take special care with acetaldehyde because of its volatility. To prepare acetaldehyde standard solutions, weigh a 10-mL capped volumetric flask containing about 5 mL toluene. With a cooled pipette, transfer about 1 mL of acetaldehyde into the weighed flask, recap and reweigh. Dilute to the mark.
      (3) For the other aldehydes, add measured aliquots (ca. 12 µL) of each to toluene in 10-mL volumetric flasks and dilute to the mark. From the density of each aldehyde, determine the amount of each aldehyde present in each solution (ca. 1 µg/µL).
   b. Inject 10 µL of the standard aldehyde solutions separately onto blank tubes from the same lot as the field samples.
   c. Analyze (steps 4 through 7 and 10 through 12) along with blanks for qualitative identification of derivative peaks by retention times.
9. Determine limit of detection (LOD) for individual aldehydes by GC/FID with standards covering the range 0.5 to 10 µg per sample. Do this once, when first setting up the method to determine approximate sensitivities for the various aldehyde derivatives. Subsequently, analyze only low-level formaldehyde standard samples with each set of samples as an internal check that the analytical system is working.
   a. Weigh 120-mg portions of unused sorbent from media blanks into vials. Keep at least three 120-mg portions of this sorbent for determination of the background levels of each aldehyde.
   b. Add 0.5- to 10-µL aliquots of the individual aldehyde standard solutions to obtain standard samples in the range 0.5 to 10 µg per 120 mg portion of sorbent. Cap vials and allow to stand overnight at room temperature.
   c. Desorb the standard samples of aldehydes (steps 6 and 7) and analyze (steps 10 through 12) along with blanks.
   d. Determine lowest spike to be detected (peak area greater than three times the background or lowest standard observable) to estimate LOD for each aldehyde.
      NOTE: Because the working standards are prepared on media blanks, no additional blank correction or desorption efficiency correction is necessary.

MEASUREMENT:

10. Set gas chromatograph to manufacturer's recommendations and to conditions given on page 2539-1. Inject 1-µL sample aliquot.
    NOTE: If the amount of oxazolidine in the aliquot exceeds the capacity of the column, dilute the sample with toluene.
11. Compare retention times of unknown peaks in samples to the retention times for the oxazolidines as determined by the qualitative standard samples. (See Appendix B for sample chromatogram).
    a. Analyze samples with GC retention times matching any oxazolidine by GC/MS using the same GC columns and conditions if possible. Alternate columns such as a DB-WAX (formaldehyde, acetaldehyde, propanal) or DB-1 (remaining aldehydes) may also be used for GC/MS confirmation depending on which aldehyde is suspected.
    b. Determine the presence of oxazolidines by monitoring for specific ions known to be present in the derivative spectra. See Table 2 for characteristic ion table and Appendix C for

reference mass spectra. Retention times by GC/MS must also match authentic oxazolidine standards.

NOTE 1: This method may also sample aldehydes other than those listed. The presence of these other aldehydes can be confirmed by examination of the mass spectral data and observation of peaks at m/e 126 and at the molecular ion minus one mass unit. The molecular ion for a particular aldehyde is equal to the molecular weight of the original aldehyde plus 97. Fragmentation patterns are also important for the identification of the oxazolidines.

NOTE 2: The absence of some C_3-C_5 aldehydes, such as propionaldehyde, isobutyraldehyde and crotonaldehyde, does not necessarily mean that these compounds are not present in the air sampled. These compounds are not efficiently trapped by the sorbent, and will readily breakthrough the sampler sorbent beds.

NOTE 3: Higher molecular weight aldehydes, such as isovaleraldehyde, hexanal and heptanal, probably will be more efficiently collected on the sorbent owing to their lower vapor pressure. Thus, absence of these compounds in sample results may be indicative of the absence of these compounds in the environment sampled.

12. Report the presence of a particular aldehyde if:
    a. There is a detectable peak by GC-FID at the correct retention time for that aldehyde derivative.
    b. The correct mass spectrum for the derivative is obtained by GC/MS at the proper retention time.

REFERENCES:

[1] NIOSH Manual of Analytical Methods, 3rd ed., P.M. Eller, Ed., DHHS (NIOSH) Publication No. 84-100 (1984).

[2] Occupational Safety and Health Administration, "OSHA Analytical Method Manual," American Conference of Governmental Industrial Hygienists, Cincinnati, OH (1985).

[3] Kennedy, E. R., P. F. O'Connor, Y. T. Gagnon. Determination of Acrolein in Air as an Oxazolidine Derivative by Gas Chromatography. Anal. Chem., 56, 2120-2123 (1984).

[4] Kennedy, E. R., Y. T. Gagnon, J. R. Okenfuss, A. W. Teass. The Determination in Air of Selected Low-molecular Weight Aldehydes as Their Oxazolidines by Capillary Gas Chromatography. Appl. Ind. Hyg., 3, 274-279 (1988).

METHOD WRITTEN BY:

Ardith A. Grote and Eugene R. Kennedy, Ph.D., NIOSH/DPSE.

TABLE 1. GENERAL INFORMATION

Compound (Synonyms)	Formula	MW	d(g/mL) VP(mm Hg) @ 20 °C (@ 20 °C)	BP(°C)	Exposure Limits (ppm) OSHA	NIOSH	ACGIH
Formaldehyde (formic aldehyde; formalin; CAS #50-00-0 RTECS LP8925000	CH_2O	30.03	--	-19.5	3; C 5; P 10/30 min	C 0.1 Group I Pesticide	C 0.3 (-88°C) Suspected Carcinogen
Acetaldehyde (acetic aldehyde; ethyl aldehyde; CAS #75-07-0 RTECS AB1925000	C_2H_4O	44.05	0.788 (@ 16°C)	21	200	Carc.[a] 18	C 0.1 150 STEL
Propionaldehyde (propanal; CAS # 123-38-6) RTECS UE0350000	C_3H_6O	58.08	0.807	49	--	-- --	
Acrolein (2-propenal; allyl aldehyde; CAS #107-02-8) RTECS AS1050000	C_3H_4O	56.06	0.839	52.5	0.1	0.1 0.3 STEL	0.1 0.3 STEL
Butyraldehyde (butanal; CAS # 123-72-8) RTECS ES2275000	C_4H_8O	72.10	0.802	75	--	-- --	
Isobutyraldehyde (2-methylpropanal dimethylacetaldehyde; CAS #78-84-2) RTECS NQ4025000	C_4H_8O	72.10	0.794	64	--	-- --	
Crotonaldehyde (2-butenal; ß-methyl acrolein; CAS # 123-73-9) RTECS GP9625000	C_4H_6O	70.09	0 853	104	2	2 2	30
n-Valeraldehyde (pentanal; CAS # 110-62-3) RTECS YV3600000	$C_5H_{10}O$	86.13	0.810	102	no standard	50	50

Isovaleraldehyde (3-methylbutanal; isopentanal; CAS # 590-86-3) RTECS ES3450000	$C_5H_{10}O$	86.13	0.785	92	--	-- -- 50
Hexanal (caproaldehyde; CAS # 66-25-1) RTECS MN7175000	$C_6H_{12}O$	100.16	0.834	131	--	-- -- 10
Heptanal (enanthal; CAS #111-71-7) RTECS MI6900000	$C_7H_{14}O$	114.18	0.809 (@ 30°C)	153	--	-- -- 3
Furfural (2-furancarboxaldehyde; CAS # 98-01-1) RTECS LT7000000	$C_5H_4O_2$	96.08	1.16 (@ 25°C)	162	5 (skin)	-- 2 (skin)

[a] - Carcinogen

TABLE 2. MASS SPECTRAL DATA FOR ALDEHYDE DERIVATIVES OF 2-(HYDROXYMETHYL)PIPERIDINE (HMP)

	HMP DERIVATIVE		
Aldehyde	Formula	Base Peak m/z	Other Characteristic Ions m/z
Formaldehyde	$C_7H_{13}NO$	97	126, 127*
Acetaldehyde	$C_8H_{15}NO$	126	140, 141*
Propionaldehyde	$C_9H_{17}NO$	126	154, 155*
Acrolein	$C_9H_{15}NO$	126	152, 153*
Butyraldehyde	$C_{10}H_{19}NO$	126	168, 169*
Isobutyraldehyde	$C_{10}H_{19}NO$	126	168, 169*
Crotonaldehyde	$C_{10}H_{17}NO$	126	166, 167*
Valeraldehyde	$C_{11}H_{21}NO$	126	182, 183*
Isovaleraldehyde	$C_{11}H_{21}NO$	126	182, 183*
Hexanal	$C_{12}H_{23}NO$	126	196, 197*
Heptanal	$C_{13}H_{25}NO$	126	210, 211*
Furfural	$C_{11}H_{15}NO_2$	192	95, 163, 193*

* indicates molecular ion.

APPENDIX A:

SORBENT PREPARATION (optional if commercially prepared tubes are used):

Extract Amberlite XADS-2 for 4 h in Soxhlet with 50/50 (v/v) acetone/methylene chloride. Replace with fresh solvent and repeat. Vacuum dry overnight. Add 1 g purified 2-(hydroxymethyl)piperidine in 50 mL toluene for each 9 g extracted XAD-2 sorbent . Allow this mixture to stand 1 h with occasional swirling. Remove the solvent by rotary evaporation at 37 °C and dry at 1 30 kPa (1 mm Hg) at ambient temperature for ca. 1 h. To determine the amount of background for each batch, extract several 120-mg portions of the coated sorbent with toluene and analyze (steps 6 through 12). No blank peak is expected for any aldehyde s other than formaldehyde and possibly acetaldehyde.

SYNTHESIS OF ALDEHYDE OXAZOLIDINES:

Place a solution of purified 2-hydroxymethylpiperidine (0.57 g, 5 mmol) in 10 mL of toluene in a 50-mL round-bottomed flask. Use several 20 mL portions of toluene to rinse residual 1-(hydroxymethyl)piperidine from t he container used for weighing. Add anhydrous magnesium sulfate (2.5 g) to the round-bottomed flask to dry the aldehyde sol ution as it is added and to remove the water which forms during the reaction. Add a solution of 10 mole of aldehyde in 10 mL o f toluene to the 2-hydroxymethylpiperidine solution dropwise with stirring over 1 h. Stir the solution overnight, then fil ter to remove the magnesium sulfate. Remove the toluene and excess aldehyde from the solution at reduced pressure by rotary evaporatio n.

PREPARATION AND STANDARDIZATION OF FORMALDEHYDE STOCK SOLUTION (ca. 1 mg/mL):

Dilute 2.7 mL 37% aqueous formalin solution to 1 L with distilled, deionized water. This solution is stable for at least three months. Standardize by placing 5.0 mL of freshly prepared 1.13 M sodium sulfite solution in a 50-mL beaker and stir magnetically. Adjust pH to between 8.5 and 10 with base or acid. Record the pH. Add 10.0 mL stock formaldehyde solution. The pH should be greater than 11. Titrate the solution back to its original pH with 0.02 N sulfuric acid (1 mL acid ≅ 0.600 mg HCHO; about 17 mL acid needed). If the endpoint pH is overrun, back titrate to the endpoint with 0.01 N sodium hydroxide. Calculate the concentration, C_s (mg/mL), of the formaldehyde stock solution:

$$C_s = \frac{30.0 \times (N_a \cdot V_a - N_b \cdot V_b)}{V_s}.$$

where: 30.0 = 30.0 g/equivalent of formaldehyde
N_a = normality of sulfuric acid
V_a = volume of sulfuric acid (mL) used for titration
N_b = normality of NaOH
V_b = volume of NaOH (mL) used for back titration
V_s = volume of formaldehyde stock solution (10.0 mL).

APPENDIX B: Sample chromatogram of aldehyde oxazolidines on DB-1301 column using conditions listed on page 2539-1.

APPENDIX C: Reference mass spectra of oxazolidines of aldehydes individually spiked onto ORBO-23 tubes. GC/MS conditions : HP 5890 gas chromatograph interfaced (direct) to HP 5970 mass-selective detector (70eV); 30-m DB-1 column, 0.25-mm I.D., 1.0-µm film; 70 °C for 1 min, 15 °C/min to 300 °C; interface temperature, 280 °C; injector, 250 °C, 1 µL splitless injec tion; scan 20-400 amu.

APPENDIX C: (Continued)