VALERALDEHYDE 2536

$CH_3(CH_2)_3CH=O$ MW: 86.13 CAS: 110-62-3 RTECS: YV3600000

METHOD: 2536, Issue 4 **EVALUATION:** FULL **Issue 1:** 15 May 1989
Issue 4: 3 March 2016

OSHA: none
NIOSH: 50 ppm

PROPERTIES: liquid; d 0.810 g/mL @ 20 °C; BP 103 °C; VP 6.7 kPa (50 mm Hg) @ 25 °C; vapor density (air = 1) 3.0; flash point = 12.2 °C

SYNONYMS: pentanal; amyl aldehyde.

SAMPLING

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

FLOW RATE: 0.01 - 0.04 L/min

VOL-MIN: 0.5 L @ 50 ppm
-MAX: 10 L

SHIPMENT: routine

SAMPLE STABILITY: at least 4 weeds @ 25 °C [1]

FIELD BLANKS: 2 to 10 field blanks per set

MEDIA BLANKS: 18 per set

ACCURACY

RANGE STUDIED: 9 to 374 mg/m^3 [1] (12-L samples)

BIAS: 0.12%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.073 [1]

ACCURACY: ± 14.4%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: valeraldehyde oxazolidine (9-butyl-1-aza-8-oxabicyclo[4.3.0]nonane)

DESORPTION: 2 mL toluene, 60 min ultrasonic

INJECTION VOLUME: 1 µL splitless

TEMPERATURE
INJECTION: 250 °C
- DETCTOR: 280 °C
-COLUMN: 0.5 min @ 70°C; 50 °C/min to 120°C, hold 4 min; 20°C/min to 170°C, hold 7 min

CARRIER GAS: He, 27 cm/sec linear velocity
makeup flow 29 mL/min

COLUMN: capillary, 15 m x 0.32-mm, 5% phenyl, 95% methyl polysiloxane, 1-µm film (US Pharmacopeia (USP) G-27)

CALIBRATION: standard solutions of valeraldehyde on sorbent

RANGE: 4 to 3900 µg/sample [1]

ESTIMATED LOD: 2 µg/sample [1]

PRECISION ($\bar{S}_r$): 0.066 @ 2 to 508 µg per sample [1]

APPLICABILITY: The working range is 0.11 to 110 ppm (0.4 to 390 mg/m^3) for a 10-L air sample. The method is also suitable for determination of furfural and glutaraldehyde in a mixture [2].

INTERFERENCES: None have been observed; an alternate capillary column, 15 m x 0.32-mm cyanopropylphenyl dimethylpolysiloxane 1-µm film (USP G43) can be used.

OTHER METHODS: The method of Lipari and Swarin [3] uses 2,4-dinitrophenylhydrazine for the collection of valeraldehyde.

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. XAD-2. Extract 4 h in Soxhlet with 50/50 (v/v) acetone/methylene chloride. Replace with fresh solvent and repeat. Vacuum dry overnight. (Optional if commercial tubes are used.)
4. Valeraldehyde, * 99% purity.
5. Valeraldehyde stock solution, 40 µg/µL (see APPENDIX). Add 400 mg valeraldehyde to toluene and dilute to 10 mL.
6. Valeraldehyde oxazolidine stock solution, 10 mg/mL (see APPENDIX A). Add 0.10 g 9-butyl-1-aza-8-oxabicyclo-[4.3.0] nonane to toluene and dilute to 10 mL.
7. Hydrogen, prepurified.
8. Air, filtered, compressed.
9. Helium, purified.
10. Magnesium sulfate, anhydrous.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: resin-filled sampling tube; glass tube, 10 cm long, 6-mm OD, 4-mm ID, flame-sealed ends with plastic caps, containing two sections of 2-(hydroxymethyl) piperidine-coated XAD-2 (front = 120 mg, back = 60 mg) (see APPENDIX B). Sorbent sections are retained and separated by small plugs of silanized glass wool. Pressure drop across the tube at 0.1 L/min must be less than 760 Pa (5.7 mm Hg). Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.04 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator and column (page 2536-1).
4. Ultrasonic bath.
5. Vials, glass, 4-mL, with septum and plastic screw caps.
6. Flasks, volumetric, 10-, 25-, and 50-mL.
7. Pipets, volumetric, 1-, 2-, and 10-mL with pipet bulb.
8. Pipets, disposable, 2-mL.
9. Syringes, 10-µL (readable to 0.1 µL), 25-, and 50-µL.
10. File or tube scorer.
11. Beakers, 50-mL.
12. Magnetic stirrer.
13. Flasks, round-bottomed, 100-mL.
14. Soxhlet extraction apparatus.
15. Vacuum oxen.
16. Distillation apparatus.

SPECIAL PRECAUTIONS: Valeraldehyde can irritate the mucous membranes [4]. It is flammable, a dangerous fire risk. Toluene is extremely flammable. All work should be performed in a well-ventilated fume hood.

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. Sample at an accurately known flow rate between 0.01 and 0.04 L/min for a total sample size of 0.5 to 10 L.
   NOTE: Sampling rate is limited by the speed of the following reaction. Rates above 0.04 L/min may cause appreciable breakthrough owing to incomplete reaction, possibly invalidating the sample.

$CH_3(CH_2)_3CH=0$ valeraldehyde	+	$C_5H_9NHCH_2OH$ 2-(hydroxymethyl)- piperidine	→ toluene/ ultrasonic energy	$C_5H_9NHC_2H_2O(CH_2)_3CH_3$ valeraldehyde oxazolidine	+	H_20

SAMPLE PREPARATION:

4. Score each sampler with a file or tube scorer in back of the back sorbent section.
5. Break sampler at score line. Remove and place back glass wool plug and back sorbent section in a vial.
6. Transfer front section with remaining glass wool plugs to a second vial.
7. Add 2.0 mL toluene to each vial. Screw cap tightly onto each vial.
8. Agitate in an ultrasonic bath for 60 min.

CALIBRATION AND QUALITY CONTROL:

9. Identification of analytical peaks.
   a. Add known amounts of valeraldehyde oxazolidine stock solution to toluene in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze (steps 12 and 13) with samples and blanks for qualitative identification of derivative peaks.
10. Calibrate daily with a least six working standards prepared in triplicate covering the range 2 to 3900 µg valeraldehyde per sample.
    a. Weigh 120-mg portions of unused sorbent from media blanks into vials.
    b. Add aliquots (1 to 10 µL) of valeraldehyde stock solution, or dilutions thereof, to the sorbent. Cap vials and allow to stand overnight at room temperature.
    c. Desorb (steps 7 and 8) and analyze (steps 12 and 13) with samples and blanks.
    d. Prepare calibration graph (combined peak area vs. µg valeraldehyde).
    NOTE: Because the standard samples are prepared on media blanks, no additional blank correction or desorption efficiency correction is necessary. Check desorption efficiency in the range of interest and at least once over the entire range of the method with each lot of sorbent used. (see APPENDIX C).
11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph is in control.

MEASUREMENT:

12. Set gas chromatograph to manufacturer's recommendations and to conditions given on page 2536-1. Inject 1-µL sample aliquot.
    NOTE: If the amount of valeraldehyde oxazolidine in the aliquot exceeds the capacity of the column, dilute with toluene, reanalyze and apply the appropriate dilution factor in calculations. The upper limit for the column on (page 2536-1) is equivalent to ca. 260 µg valeraldehyde per sample.
13. Measure total peak area of the two analyte peaks.
    NOTE: Valeraldehyde oxazolidine gives two peaks, since the diastereoisomers are resolved with retention times 5.4 and 6.3 min. Retention time for 2-(hydroxymethyl) piperidine is 2.2 min for these conditions.

CALCULATIONS:

14. Determine the mass, µg, of valeraldehyde found in the sample front (W_f) and back (W_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
15. Calculate concentration, C, of valeraldehyde in the air volume sampled, V (L):

$$C = \frac{W_f + W_b}{V}, mg/m^3$$

EVALUATION OF METHOD:

Atmospheres were generated by injection of valeraldehyde with a syringe pump into a heated block injector and flash vaporizer into a stream of air at 80% ± 5% RH flowing at a fixed rate. The generator and sampling manifold system have been described previously [5]. Concentration of valeraldehyde vapor was independently verified by the 2,4-dinitrophenylhydrazine procedure of Lipari and Swarin [3] or by monitoring with an AID Model 590 organic vapor monitor. Breakthrough studies of valeraldehyde at 100 ppm, conducted at 75 and 50 mL/min flow rates, gave 5% breakthrough at 170 min and 280 min, respectively.

The method was evaluated over the range of 9 to 374 mg/m^3 using 12-L samples. Desorption efficiencies from statically-spiked samples average 102.5% (89.2-126.6%) for the range 2 to 508 µg/sample. No bias with dynamically-generated samples was observed with the method when samples were collected at 40 mL/min and below. When samples were collected at ca. 60 mL/min, a negative bias of approximately 20-30% was observed. Samples were found to be stable for at least 4 weeks when stored at room temperature.

REFERENCES:

[1] Kennedy ER, Gagnon YT, Okenfuss JR, Teass AW [1988]. The determination in air of selected low-molecular weight aldehydes as their oxazolidines by capillary gas chromatography. Appl Ind Hyg *3*(10): 274-279.

[2] NIOSH [1984]. Glutaraldhyde: Method 2531. In: Eller PM, Cassinelli ME, eds. NIOSH manual of analytical methods. 3rd. ed. Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 84-100.

[3] Lipari F, Swarin SJ [1982]. Determination of formaldehyde and other aldehydes in automobile exhaust with an improved 2,4-dinitrophenylhydrazine method. J Chromatog *247*:297-306.

[4] Budavari S, ed. [1989]. The Merck Index. 11th ed. Rahway, NJ: Merck & Co., Inc.

[5] Kennedy ER Hill RH, Jr. [1982]. Determination of formaldehyde in air as an oxazolidine derivative by capillary gas chromatography. Anal Chem *54*:1739-1741.

METHOD REVISED BY:

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APPENDIX A: Synthesis of 9-Butyl-1-Aza-8-Oxabicyclo[4.3.0]nonane:

Place a solution of purified 2-(hydroxymethyl)piperidine (1.15 g; 10 mmol) in 20 mL of toluene in a 100- mL round-bottomed flask. Use several 2-mL portions of toluene to rinse residual 2- (hydroxymethyl)piperidine from the container used for weighing. Add anhydrous magnesium sulfate (2.0 g) to the flask to dry the valeraldehyde solution as it is added and to remove the water which forms during the reaction. Add a solution of 0.947 g valeraldehyde (11 mmole) in 20 mL of toluene to the 2- (hydroxymethyl)piperidine solution dropwise with stirring over 1 h. (NOTE: Excess aldehyde was added to ensure complete conversion of 2-(hydroxymethyl)piperidine to oxazolidine.) Stir the solution overnight, then filter to remove the magnesium sulfate. Remove the toluene from the solution at reduced pressure (1 mm Hg) by rotary evaporation. The product is a pale yellow viscous oil, ca. 90 to 95% pure by gas chromatography. Store the oxazolidine at 0 °C to prevent decomposition.

Mass spectral data for 9-butyl-1-aza-8-oxabicyclo[4.3.0]nonane: m/e with relative intensities in parenthesis, 182 (7.0%), 152 (4.6%), 126 (100%), 110 (11.3%), 98 (37%). IR data (Vapor phase @ 280 °C) for this compound in cm-1 with relative intensity in parenthesis are: 2945 (s), 2874 (m), 2781 (m), 1455 (w), 1383 (w), 1339 (w), 1265 (w), 1203 (w), 1133 (m), 1075 (w), 1028 (m).

APPENDIX B: Sorbent Preparation (optional if commercially-prepared tubes are used):

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. Dry at 130 Pa (1 mm Hg) at ambient temperature for approximately 1 h. To determine the amount of background for each batch, desorb several 120-mg portions of the coated sorbent with toluene and analyze (steps 7 through 13). No blank peak is expected for valeraldehyde.

APPENDIX C: Desorption Efficiency:

The determination of desorption efficiency (DE) is not necessary when using the calibration procedure in step 10, although the DE should be determined once for each lot of sorbent used, using the following procedure:

a. Prepare and analyze a set of valeraldehyde oxazolidine standard solutions (step 9.a) and a set of working standards (step 10), including media blanks.
b. Treating the working standards as unknowns, read the mass (µg) of valeraldehyde oxazolidine found in each working standard (W), and in the average media blank (B).
c. Using the mass of valeraldehyde, µg, spiked onto the working standard (W_o) and the stoichiometric conversion factor of 2.13 between valeraldehyde and valeraldehyde oxazolidine, calculate the desorption efficiency:

$$DE = \frac{W - B}{W_o \cdot 2.13}$$

d. Prepare a graph of DE vs. µg valeraldehyde recovered per sample, (W - B)/2.13.