FURFURAL

$C_5H_4O_2$ MW: 96.09 CAS: 98-01-1 RTECS: LT7000000

METHOD: 2529, Issue 2 **EVALUATION: FULL** **Issue 1: 15 August 1987**
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OSHA : 5 ppm (skin)
NIOSH: no recommended standard
ACGIH: 2 ppm (skin)
(1 ppm = 3.93 mg/m^3 @ NTP)

PROPERTIES: liquid; d 1.160 g/mL @ 20 °C;
BP 162 °C; MP - 36 °C; VP 0.26 kPa
(2 mm Hg; 2600 ppm) @ 20 °C;
explosive range 2.1 to 19.3% v/v in air

SYNONYMS: 2-furaldehyde; 2-furancarboxaldehyde

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

VOL-MIN: 1 L @ 5 ppm
-MAX: 12 L

SHIPMENT: routine

SAMPLE STABILITY: at least 2 weeks @ 25 °C

FIELD BLANKS: 2 to 10 field blanks per set
MEDIA BLANKS: 18 per set (for DE)

ACCURACY

RANGE STUDIED: 2.6 to 40 mg/m^3 [1]
(15-L samples)

BIAS: - 7.0%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.076 [1]

ACCURACY: ± 21.9%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: oxazolidine derivative of furfural

DESORPTION: 2 mL toluene; 30 min ultrasonic

INJECTION VOLUME: 1 µL; splitless

TEMPERATURE-INJECTION: 250 °C
-DETECTOR: 280 °C
-COLUMN: 1 min @ 70 °C; 20 °C/min; hold 2 min @ 290 °C

CARRIER GAS: He, 20 cm/sec

COLUMN: 10 m x 0.25-mm, 1 µm DB5

CALIBRATION: furfural standards spiked on sampler

RANGE: 16 to 640 µg per sample [1]

ESTIMATED LOD: 5 µg per sample [1]

PRECISION ($\bar{S}_r$): 0.057 [1]

APPLICABILITY: The working range is 0.3 to 5.5 ppm (1.3 to 22 mg/m^3) for a 12-L air sample. The method is suitable for the simultaneous determination of furfural and glutaraldehyde [1].

INTERFERENCES: None have been observed.

OTHER METHODS: Method S17 [2] is an alternate, less sensitive method for furfural which uses bubbler collection and derivatization with Girard T reagent.

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. Extract 4 h in Soxhlet with 50/50 (v/v) acetone/methylene chloride. Replace with fresh solvent and repeat. Vacuum dry overnight.
4. Furfural,* freshly distilled under N_2 to remove impurities. Store at 0 °C.
5. Calibration stock solution, 100 µg/µL. Add 1 g furfural to toluene and dilute to 10 mL. Prepare in duplicate.
6. Furfural oxazolidine (see APPENDIX) stock solution, 2.5 mg/mL. Add 25 mg to toluene and dilute to 10 mL.
7. Water, deionized, then distilled.
8. Hydrogen, prepurified.
9. Air, filtered.
10. Helium, purified.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 10 cm x 4-mm ID, flame-sealed, with plastic caps, containing a 120-mg front section and a 60-mg back-up section of the 2-(hydroxymethyl)piperidine-coated XAD-2 (see APPENDIX) with flame-sealed ends. Sorbent sections are 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 756 kPa. Tubes are commercially available (Supelco 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, integrator and column (page 2529-1).
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.
11. Beakers, 50-mL.
12. Magnetic stirrer.
13. Flasks, round-bottomed, 100-mL.
14. Soxhlet extraction apparatus.
15. Vacuum oven.
16. Distillation apparatus.

SPECIAL PRECAUTIONS: Furfural can irritate the mucous membranes and act on the central nervous system [3,4]. Work with this compound only 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 before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.05 L/min for a total sample size of 1 to 12 L.

   NOTE: Furfural reacts with 2-(hydroxymethyl)piperidine to form a derivative during sampling. Sampling rate is limited by the speed of this reaction; rates above 0.05 L/min may cause breakthrough owing to incomplete reaction.

SAMPLE PREPARATION:

4. Score each sampler with a file in back of the rear sorbent section.
5. Break sampler at score line. Remove and place rear glass wool plug and rear 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 vials in an ultrasonic bath for 30 min.

CALIBRATION AND QUALITY CONTROL:

9. Prepare oxazolidine standard solutions.
   a. Add known amounts of furfural oxazolidine stock solution (equivalent to the range of the samples) 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 at least six working standards covering the range of the samples.
   a. Weigh 120-mg portions of unused sorbent into vials.
   b. Add aliquots of calibration stock solution or dilutions thereof. Cap vials and allow them 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 (peak area vs. µg furfural).
      NOTE: Because the working standards are prepared on media blanks, no additional blank correction or desorption efficiency correction is necessary.
11. Analyze three quality control blind spikes to ensure that the calibration graph is in control.

MEASUREMENT:

12. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2529-1. 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 and apply the appropriate dilution factor in calculations.
13. Measure total peak area of the two analyte peaks.
    NOTE: On the DB-5 column, the oxazolidine derivative of furfural gives two peaks, since the diastereoisomers are resolved. t_r for the furfural derivative = 5.0 and 5.3 min; glutaraldehyde derivative = 9.4 and 9.7 min; and t_r for 2-(hydroxymethyl)piperidine = 2.6 min for these conditions.

CALCULATIONS:

14. Determine the mass, µg of furfural 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 furfural in the air volume sampled, V (L):

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

EVALUATION OF METHOD:

Atmospheres were generated by flash vaporization of an aqueous furfural solution into a stream of air flowing at a fixed rate [1]. Relative humidity during generation was 80% ±5%. The generator and sampling manifold system have been described previously [5]. Concentration of furfural vapor was independently verified by the 2,4-dinitrophenylhydrazine procedure of Lipari and Swarin [6]. The method was studied over the range of 2.6 to 40 mg/m^3 using 15-L samples. Desorption efficiencies on statically-spiked samples averaged 94% in the range 16 to 640 -µg per sample. Recovery of dynamically-generated samples was 93%, owing to breakthrough of furfural at the highest level studied (40 mg/m^3). Recovery was quantitative at lower levels.

REFERENCES:

[1] E. R. Kennedy, Y. T. Gagnon, J. R. Okenfuss and 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).
[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 4, S17, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[3] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as Stock #PB83-154609 from NTIS, Springfield, VA 22161.
[4] The Merck Index, 10th ed., Merck & Co., Rahway, NJ (1983).
[5] Kennedy, E. R. and R. H. Hill, Jr. "Determination of Formaldehyde in Air as an Oxazolidine Derivative by Capillary Gas Chromatography," Anal. Chem., 54, 1739-1741 (1982).
[6] Lipari, F. and S. J. Swarin. "Determination of Formaldehyde and other Aldehydes in Automobile Exhaust with an Improved 2,4-Dinitrophenylhydrazine Method", J. Chromatog., 247, 297-306, (1982).

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APPENDIX:

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 hr with occasional swirling. Remove the solvent by rotary evaporation at 37 °C and dry at 130 Pa (1 mm Hg) at ambient temperature for approximately 1 hr. 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 furfural.

SYNTHESIS OF FURFURAL OXAZOLIDINE [1]:
Place a solution of 0.58 g (0.5 mL; 6 mmol) freshly distilled furfural in 10 mL toluene in a 50-mL round-bottomed flask. Add 2.5 g magnesium sulfate to the flask to remove water which forms during the reaction. Add a solution of 0.61 g (5.3 mmol) purified 2-hydroxymethylpiperidine in 10 mL toluene dropwise with stirring over 1 hr. Stir the solution overnight, then filter to remove the magnesium sulfate. Remove the toluene from the solution at reduced pressure by rotary evaporation. The product is a yellow viscous oil.

DESORPTION EFFICIENCY:
The determination of desorption efficiency (DE) is not necessary when using the calibration procedure in step 10. If desired, the following procedure can be used to determine DE:
a. Prepare and analyze a set of 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 (mg) of oxazolidine found in each working standard (W), and in the average media blank (B).
c. Using the mass of furfural, mg, spiked onto the working standard (W_o) and the stoichiometric conversion factor between furfural and furfural oxazolidine (2.01), calculate the desorption efficiency:

$$DE = \frac{W - B}{W_o \cdot 2.01}.$$

d. Prepare a graph of DE vs. µg furfural recovered per sample [(W - B)/2.01].