FORMALDEHYDE by GC 2541

$H_2C=0$ MW: 30.03 CAS: 50-00-0 RTECS: LP8925000

METHOD: 2541, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1989**
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OSHA : 0.75 ppm; 2 ppm STEL
NIOSH: 0.016 ppm; C 0.1 ppm; carcinogen
ACGIH: C 0.3 ppm; suspected human carcinogen
(1 ppm = 1.23 mg/m^3 @ NTP)

PROPERTIES: gas; vapor density 1.067 (air = 1); BP 19.5 °C; explosive range 7 to 73% v/v in air

SYNONYMS: methanal; formalin (aqueous 30 to 60% w/v HCHO); methylene oxide

SAMPLING

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

FLOW RATE: 0.01 to 0.10 L/min

VOL-MIN: 1 @ 3 ppm
-MAX: 36 L

SHIPMENT: routine

SAMPLE STABILITY: 3 weeks @ 25 °C [1]

FIELD BLANKS: 2 to 10 field blanks per set

MEDIA BLANKS: 10 per sample 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: oxazolidine derivative of formaldehyde

DESORPTION: 1 mL toluene; 60 min ultrasonic

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

TEMPERATURE-INJECTOR: 250 °C
-DETECTOR: 300 °C
-COLUMN: 70 °C for 1 min; 15 °C/min; hold @ 240 °C for 10 min

CARRIER GAS: He, 1 to 2 mL/min: makeup flow 29 mL/min

COLUMN: capillary, 30 m x 0.32-mm ID, 0.5-µm film, DB-Wax or equivalent

CALIBRATION: formalin solution spiked on sorbent

RANGE: 3 to 200 µg per sample [2,3]

ESTIMATED LOD: 1 µg per sample [2]

PRECISION ($\hat{S}_r$): 0.0052 @ 38 to 194 µg per sample [2]

APPLICABILITY: The working range is 0.24 to 16 ppm (0.3 to 20 mg/m^3) for a 10-L air sample. The method is suitable for the simultaneous determinations of acrolein and formaldehyde.

INTERFERENCES: None have been observed. Acid mists may inactivate the sorbent leading to inefficient collection of formaldehyde. A 15 m x 0.32-mm ID DB-1301 fused silica capillary column can also be used. This column will also separate the acetaldehyde and acrolein oxazolidines. A nitrogen-specific detector (NPD) can be used for improved sensitivity.

OTHER METHODS: OSHA Method 52 is similar but uses slightly larger sampling tubes [2]. This method has improved sample stability and ease of personal sampling compared to NIOSH Methods 2502 (which has been withdrawn), 3500 and 3501. However, Method 3500 (chromotropic acid) is the most sensitive.

REAGENTS:

1. Toluene, chromatographic quality.
2. 2-(Hydroxymethyl)piperidine (2-HMP). Recrystallize several times from isooctane until there is one major peak (>95% of area) by GC analysis. Store in desiccator.
3. Formalin solution, 37%*.
4. Formaldehyde* stock solution, 1 mg/mL (see Appendix A).
5. Sulfuric acid, 0.02 N.
6. Sodium hydroxide, 0.01 N.
7. Sodium sulfite (Na_2SO_3), 1.13 M. Prepare fresh immediately before use.
8. Water, deionized, distilled
9. Hydrogen, prepurified.
10. Air, filtered.
11. Helium, purified
12. Magnesium sulfate.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: glass tube, 10 cm long, 6-mm OD, 4-mm ID, with flame-sealed ends and plastic caps, containing two sections of 2-(hydroxymethyl) piperidine-coated XAD-2 (see APPENDIX B) (front = 120 mg; back = 60 mg) 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 ORBO-23; SKC 226-118; or equivalent).
2. Personal sampling pump, 0.01 to 0.10 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator and column (page 2541-1).
4. Ultrasonic water bath.
5. Vials, glass, 2-mL, with PTFE-lined crimp caps.
6. Flasks, volumetric, 10-, 25-, and 50-mL.
7. Pipets, volumetric, 1-, 2-, and 10-mL with pipet bulb.
8. Syringes, 10-mL (readable to 0.1 mL), 25-, and 50-mL.
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.

SPECIAL PRECAUTIONS: Formaldehyde is viewed as a potential occupational carcinogen [4,5].

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 0.10 L/min for a total sample size of 1 to 36 L.
   NOTE: Formaldehyde reacts with 2-(hydroxymethyl)piperidine on the sorbent bed during sampling. Sampling rate is limited by the speed of this reaction. Sampling above 0.10 L/min may cause appreciable breakthrough owing to incomplete reaction, possibly invalidating the sample. Further discussion of this reaction is included in Ref. [6].
4. Cap the samplers and pack securely for shipment.

SAMPLE PREPARATION:

5. Score each sampler with a file in front of the first sorbent section.
6. Break sampler at score line. Remove and place front glass wool plug and front sorbent section

in a vial.

7. Transfer back section with remaining glass wool plugs to a second vial.
8. Add 1.0 mL toluene to each vial. Crimp cap tightly onto each vial.
   NOTE: An appropriate internal standard, such as 1 µL/mL dimethylformamide, may be added at this point [3].
9. Agitate vials in an ultrasonic water bath for 60 min.

CALIBRATION AND QUALITY CONTROL:

10. Calibrate daily with at least six working standards, in duplicate, covering the range of interest.
    a. Weigh ten 120-mg portions of the coated sorbent into 4-mL vials with septum caps. If the bulk coated sorbent is not available, remove the front section from ten unused samplers (media blanks).
    b. Inject aliquots of formaldehyde stock solution into the vials at six different levels and allow to sit overnight at room temperature. Use serial dilutions of the calibration stock solutions to spike the absorbent in the range of interest.
    c. Desorb (steps 7 through 9) and analyze (steps 12 and 13) with samples and blanks.
    d. Prepare calibration graph (peak area or peak height) vs. µg of formaldehyde.
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 2541-1. 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, reanalyze, and apply the appropriate correction factor in calculations.
13. Measure peak area or peak height. For formaldehyde derivative t_r = 6.4 min and for 2-(hydroxymethyl)piperidine t_r = 9.4 min under these conditions.
    NOTE: If necessary, verify the identity of the formaldehyde oxazolidine by comparison of retention time with an authentic sample (see APPENDIX C).

CALCULATIONS:

14. Determine the mass, µg (corrected for DE) of oxazolidine derivative found in the sample front (W_f) and back (W_b) sorbent sections from the calibration graph.
    NOTE: if $W_b > W_f/10$, report breakthrough and possible sample loss.
15. Calculate concentration, C (mg/m ^{3}), of formaldehyde in the air volume sampled, V (L):

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

NOTE: Because the working standards are prepared on media blanks, no additional blank correction is necessary. Report field blanks as samples.

EVALUATION OF METHOD:

This method is similar to OSHA Method 52 [2]; however, the OSHA samplers contained 20% more coated sorbent than the samplers used in this method. In a study by OSHA, 5% breakthrough occurred after 396 min at a flow rate of 0.1 L/min and a test atmosphere concentration of 5.3 mg/m ^{3}. The relative

humidity in the study was 49% at 24 °C. A storage study was done by NIOSH/MRSB [1] by spiking samplers at two concentrations, 10.0 and 61.0 µg/sample [1]. Three spikes at each concentration were stored at different temperatures for seven days. The storage conditions were as follows:

Sample set no.	Storage temp.	Storage time
1	20 °C	7 days
2 (a)	20 ° and 40 ° C	1 day
(b)	20 ° C	6 days
3	4 ° C (refrigeration)	7 days

The recovery of formaldehyde was essentially 100% for all of the storage temperatures.

REFERENCES:

[1] Williams, K. J. Methods Development Efforts, NIOSH/MRSB, (NIOSH, Unpublished, 1989).
[2] "OSHA Analytical Methods Manual, method #52", U. S. Department of Labor, Occupational Safety and Health Administration, OSHA Analytical Laboratory, Salt Lake City, UT, March, 1985.
[3] User Check, DataChem Inc., NIOSH Seq. #6701-J (unpublished, June 1, 1989).
[4] NIOSH testimony on the OSHA Proposed Rules on Air Contaminants, Docket #H-020, August 1, 1988.
[5] NIOSH/OSHA Occupational Health Guidelines for Occupational Hazards, U. S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.
[6] Kennedy, E.R., Ashley, K. Appl. Spectrosc., 46, 266-272 (1992).

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APPENDIX A: 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 formaldehyde stock solution. The pH should now 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:

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

where 30.0 = 30.0 g/equivalent of formaldehyde
N_a = normality of sulfuric acid (0.02 N)
V_a = volume of sulfuric acid (mL) used for titration
N_b = normality of NaOH (0.01 N)
V_b = volume of NaOH (mL) used for back-titration
V_s = volume of formaldehyde stock solution (10.0 mL)

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

Extract 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 130 kPa (1 mm Hg) at ambient temperature for ca. 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 12 and 13). No blank peak is expected for any aldehydes other than formaldehyde and possibly acetaldehyde.

APPENDIX C: SYNTHESIS OF FORMALDEHYDE OXAZOLIDINE

Place a solution of purified 2-(hydroxymethyl)piperidine (0.57 g, 5 mmol) in 10 mL of toluene in a 50-mL round-bottomed flask. Use several 2-mL portions of toluene to rinse residual 2-(hydroxymethyl) piperidine from the container used for weighing. Add magnesium sulfate (2.5 g) to the round-bottomed flask to dry the aldehyde solution as it is added and to remove the water which forms during the reaction. Add a solution of 1 mL 37% aqueous formaldehyde in 10 mL toluene to the 2-(hydroxymethyl)piperidine solution dropwise with stirring over 1 h. Stir the solution overnight, then filter to remove the magnesium sulfate. Remove the toluene from the solution at reduced pressure by rotary evaporation.