



FORMALDEHYDE ON DUST (TEXTILE OR WOOD)

5700

H₂C=O

MW: 30.03

CAS: 50-00-0

RTECS: LP8925000

METHOD: 5700, Issue 2

EVALUATION: FULL

Issue 1: 15 August 1994

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OSHA: 0.75 ppm; 2 ppm STEL
NIOSH: 0.016 ppm; C 0.1 ppm (15 min); carcinogen

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

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

SAMPLING		MEASUREMENT	
SAMPLER:	Institute of Occupational Medicine (IOM) inhalable dust sampler or equivalent containing a 25-mm PVC filter, 5 µm pore size	TECHNIQUE:	HPLC, UV DETECTION
FLOW RATE:	2.0 L/min	ANALYTE:	2,4-dinitrophenylhydrazone derivative of formaldehyde
VOL-MIN:	240 L @ 0.002 mg/m ³	EXTRACTION:	10 mL distilled water @ 37 °C, 4 h; 1 mL to 3 mL 2,4-dinitrophenyl - hydrazine/acetonitrile (1.3 mg/mL DNPH/ACN)
-MAX:	1050 L	INJECTION VOLUME:	15 µL
SHIPMENT:	Place cassette with filter in 30-mL screw-cap low density polyethylene (LDPE) bottle; keep upright. Ship cold.	MOBILE PHASE:	30% acetonitrile/66% methanol/water (1:1v/v), 1 mL/min
SAMPLE STABILITY:	21 days (matrix dependent) (cold storage advised)	COLUMN:	C18, 5-µm particle size, 10-cm x 8-mm ID (with a C18 guard column)
BLANKS:	2 to 10 field blanks per set	DETECTOR:	UV @ 365 nm
ACCURACY		CALIBRATION:	standard solutions of formaldehyde in 1.3 mg/mL DNPH/ACN
RANGE STUDIED:	0.007 to 0.16 mg/m ³ [1] (1050-L samples)	RANGE:	0.4 to 4000 µg/sample [1]
BIAS:	-4%	ESTIMATED LOD:	0.8 µg/sample [1]
OVERALL PRECISION (\hat{S}_{RT}):	0.093 [1]	PRECISION (\bar{S}_r):	0.078 @ 7 to 174 µg per sample [1].
ACCURACY:	± 22%		

APPLICABILITY: The working range is 0.0004 to 3.8 mg/m³ for a 1050-L air sample. This method has been used for the determination of formaldehyde in both textile dusts and wood dusts [1]. Caution should be exercised in the way that data collected with this method are interpreted. These results should be reported separately from vapor-phase formaldehyde exposure data until sufficient data has been collected to allow appropriate epidemiological interpretation of formaldehyde-containing particulate exposures.

INTERFERENCES: None identified

OTHER METHODS: In the absence of phenol or other substances known to interfere with the chromotropic acid analysis of formaldehyde, the analysis procedure described in NIOSH method 3500 [2] can also be used with this extraction technique (See Appendix). The analysis procedure used in this method has also been used for the determination of formaldehyde in automobile exhaust [3]. An alternate analysis [4] may be used in conjunction with this method to determine the amount of "released" formaldehyde from the collected particulate material. NIOSH method 5700 determines both "released" formaldehyde and formaldehyde equivalents (e.g., small oligomeric pieces of formaldehyde-containing resin) present in the hydrolysis solutions. The use of these two analytical approaches may differentiate between the two forms of formaldehyde present in the sample by the difference in results.

REAGENTS:

1. 2,4-dinitrophenylhydrazine (2,4-DNP) (1.3 g) in 1 L acetonitrile; 1.3 mg/mL solution.
2. Formaldehyde stock solution, 1 mg/mL (see Appendix).
3. Methanol, distilled in glass.
4. Acetonitrile, distilled in glass.
5. Water, deionized and distilled.
6. Perchloric acid solution, 1 N. *

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: 25-mm PVC filter (5.0- μ m pore size) in a 25-mm Institute of Occupational Medicine Inhalable (IOM) dust sampler. The sampler should meet the American Conference of Governmental Industrial Hygienists (ACGIH) definition for collection of the inhalable fraction of particulate mass [5].
2. Personal sampling pump, 2.0 L/min, with flexible polyethylene or polytetrafluoroethylene (PTFE) tubing.
3. Bottles, screw-cap, low-density polyethylene (LDPE), 30-mL.
Note: Do NOT use bottles with 'polycone' liners (source of high formaldehyde blank).
4. Liquid chromatograph with a UV detector, recorder, integrator and column (page 5700-1).
5. Tweezers.
6. Syringes, 10-, 25-, 50-, and 100- μ L.
7. Volumetric flasks, 10-, 100-mL and 1 L.
8. Pipets, 0.1-, 0.5-, 1.0-, and 3-mL glass, delivery, with pipet bulb.
9. Graduated cylinders, glass, 25-mL.
10. Cotton gloves.
11. Equipment for standardizing formaldehyde stock solution, Burets, 50-mL.
12. pH meter.
13. Magnetic stirrer.
14. Beaker, 50-mL.
15. Vials, 5-mL.
16. Filters, 0.45 μ m.
17. Scintillation vials, 20-mL.

SPECIAL PRECAUTIONS: Perchloric acid is a strong oxidizing agent, toxic by ingestion and inhalation and is a strong irritant. Use only in a well-ventilated fume hood. Formaldehyde is a suspect carcinogen [1,6] and should be handled in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. If gravimetric measurements are needed, handle the IOM cassettes only while wearing cotton gloves. Follow NIOSH method 0500 [7] for pre- and post-collection weighing procedure. Place the cassette containing a 25-mm PVC 5- μ m pore filter in the filter holder.
3. Attach outlet of filter holder to the sampling pump.
4. Sample 240 to 1050 L of air at 2.0 L/min flow rate.
5. Transfer cassette from filter holder carefully to a 30-mL LDPE screw-cap bottle while wearing cotton gloves and seal the bottle. Ship in a suitable container in order to prevent damage during transit and keep bottles upright.

6. Collect a bulk sample (ca. 1 g) of the dust/fiber in a glass vial and ship separately.

SAMPLE PREPARATION:

7. If gravimetric weighing is done, post-weigh the entire cassette (see NIOSH method 0500 [7]) then return the cassette to the screw-cap bottle.
8. Transfer 8-mL distilled water to the LDPE screw-cap bottle containing the cassette. Use tweezers (two) to disassemble cassette which is immersed in water, remove all cassette pieces (shake off excess water) leaving the filter and dust in the bottle. Transfer the resulting solution to a 20-mL scintillation vial and rinse the screw-cap bottle with an additional 2 mL of distilled water. Replace the cap on the vial and then place the vial in a 37 °C water bath for four hours. Remove from the bath and allow to cool 1/2 hour. Filter through a 0.45 µm pore size filter into another bottle.

CALIBRATION AND QUALITY CONTROL:

9. Prepare a calibration stock solution by dilution of 1-mL of 1 mg/mL formaldehyde stock solution to 100 mL with distilled water.
10. Pipet aliquots of calibration stock solution (e.g., 40, 200, 750, 2000, 5000, and 10000 µL) into 10-mL volumetric flasks to prepare working standards. Higher level standards, if needed, can be prepared by using different dilutions of the formaldehyde stock solution.
11. Add distilled water to bring the volume of each working standard to 10 mL.
12. Analyze working standards together with samples and blanks (steps 14 through 17).
13. Prepare calibration graph of area vs. amount (µg) of formaldehyde per sample (10-mL total volume).

MEASUREMENT:

14. Transfer a 1-mL aliquot of the solution from step 8 (or step 11) to a 5-mL vial containing 3-mL of an 2,4-dinitrophenylhydrazine/acetonitrile solution (1.3 mg/mL). Add one drop 1 N perchloric acid (to catalyze the reaction to form the corresponding hydrazone), cap the vial and shake it gently for several seconds.
15. Set liquid chromatograph to conditions given on page 5700-1.
16. Inject 15-µL sample aliquot.
17. Measure peak area.

NOTE 1: If peak area is greater than the highest standard, take a smaller aliquot of the remaining unreacted sample solution, dilute to 1 mL with distilled water and analyze (steps 14 through 17) and apply appropriate dilution factor in the calculations.

NOTE 2: For optimum results, all samples containing over 400 µg/mL should be diluted and reanalyzed, since the maximum amount of formaldehyde that can react with 3.9 mg of 2,4-dinitrophenylhydrazine is 590 µg.

CALCULATIONS:

18. Determine mass, µg, of formaldehyde (W) found in the sample and the average media blank (B) from the calibration graph. Use the appropriate aliquot factor (e. g., 1 mL aliquot/original volume from step 14) and the total sample volume (10-mL) unless corrected for in calibration plot (step 13).
NOTE: Include dilution factor for any sample which exceeded the highest calibration standard.
19. Calculate concentration, C, of formaldehyde from dust in the air volume, V (L).

$$C = \frac{W - B}{V}, mg/m^3$$

EVALUATION OF METHOD:

This method was evaluated over the range of 7 to 174 $\mu\text{g}/\text{sample}$ at 24 °C and pressure of 761 mm Hg [1] using the chromotropic analysis procedure. Overall measurement precision, \hat{S}_{rT} , was 0.093 including a 5% pump error factor. Similar precision was observed with the 2,4-dinitrophenylhydrazine analysis procedure. Sample stability during storage was evaluated at 7 μg formaldehyde/2 mg of wood dust treated with a urea/formaldehyde resin. Samples showed 101% recovery after 21 days of storage at ambient conditions compared to one-day old samples. However, studies with a different matrix (urea- formaldehyde treated wood fibers) indicated that samples may be unstable when stored at room temperature.

Comparison of results from 2,4-DNP analyses with those from acetylacetone analyses [4] indicated that there was a significant difference between the two methods. The acetylacetone analyses used much milder conditions and appears to be reacting only with released formaldehyde, whereas the 2,4-DNP analysis required the addition of perchloric acid and may be breaking up oligomeric pieces of the partially hydrolyzed resin in the sample. By analyzing samples with the two methods, a further characterization of the sample matrix and potential exposure may be obtained. In matrices where materials that can form complexes with formaldehyde are present, such as sulfites, the acetylacetone analysis may be biased low, since it is unable to break up these complexes [8].

Two comparisons of the IOM samplers with closed-face cassette samplers were conducted in field situations [1]. The IOM samplers, on average, collected more dust/fibers measured gravimetrically than the closed-face cassette samplers in both studies. Formaldehyde levels in the dust/fibers on a $\mu\text{g}/\text{mg}$ basis measured with the extraction procedure used in this method were comparable for both the IOM and closed-face cassette samplers. On the average, the IOM sampler tended to collect more dust than the closed-face cassette sampler.

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APPENDIX: 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 formaldehyde; 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:

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

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)

Alternate Analysis Procedure for the Determination of Formaldehyde Liberated from Dust/Fiber Samples

NOTE: This analysis procedure should only be used where interferences to the chromotropic acid analysis are not present. These interferences include phenol, oxidizable organic material, other aldehydes and alcohols.

For formaldehyde determination by the chromotropic acid method, a 4-mL aliquot of the solution resulting from the desorption and incubation of the filter (step 8.) was analyzed by the procedure described in NIOSH Method 3500 [2]. The amount of chromotropic acid added to the sample could react with a maximum of 42 μg of formaldehyde per sample aliquot. (Whenever the amount of formaldehyde approached 30 μg per aliquot, the sample was diluted and reanalyzed.) The absorbance of samples at 580 nm was then compared to a calibration curve constructed from results obtained from analysis of calibration standards containing known amounts of formaldehyde. The amount of formaldehyde present in each sample was determined based on the calibration curve.

Calibration standards were prepared by dilution of a standard solution of formalin in distilled water (1 mg/mL) and analyzed in the same manner as the samples. The calibration range usually covered 1 to 25 μg of formaldehyde/4-mL aliquot. A limit of detection of 0.44 μg formaldehyde/filter sampler was determined in laboratory evaluation of this analysis procedure.

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