FORMALDEHYDE 2016

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

METHOD: 2016, Issue 2 **EVALUATION:** FULL **Issue 1:** 15 January 1998 **Issue 2:** 15 March 2003

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; BP -19.5 °C; specific gravity 1.067 (air = 1); explosive range 7 to 73% (v/v) in air

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

SAMPLING

SAMPLER: CARTRIDGE
(Cartridge containing silica gel coated with 2,4-dinitrophenylhydrazine)

FLOW RATE: 0.03 to 1.5 L/min

VOL-MIN: 1 L @ 0.25 mg/m^3
-MAX: 15 L @ 2.5 mg/m^3

SHIPMENT: Place caps onto cartridge. Ship on ice.

SAMPLE STABILITY: 34 days @ 5 °C [1]

BLANKS: 2 to 10 field blanks per set
6 to 10 media blanks per set

ACCURACY

RANGE STUDIED: 0.025 to 2.45 mg/m^3 (22-L samples) [2]

BIAS: +4.4%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.057 [1,2]

ACCURACY: ±19.0%

MEASUREMENT

TECHNIQUE: HPLC, UV DETECTION

ANALYTE: 2,4-dinitrophenylhydrazone of formaldehyde

EXTRACTION: Elution with 10 mL of carbonyl-free acetonitrile

INJECTION VOLUME: 20 µL

MOBILE PHASE: 45% acetonitrile/55% water (v/v), 1.3 mL/min

COLUMN: 3.9 x 150-mm, stainless steel, packed with 5-µm C-18, Symmetry™ or equivalent

DETECTOR: UV @ 360 nm

CALIBRATION: Samplers fortified with standard solutions of formaldehyde in water

RANGE: 0.23 to 37 µg per sample [1,2]

ESTIMATED LOD: 0.07 µg/sample [1]

PRECISION ($\bar{S}_r$): 0.032 @ 1.0 to 20.0 µg/sample [1]

APPLICABILITY: The working range is 0.015 to 2.5 mg/m^3 (0.012 to 2.0 ppm) for a 15-L sample. This method can be used for the determination of formaldehyde for both STEL and TWA exposures [1,2].

INTERFERENCES: Ozone has been observed to consume the 2,4-dinitrophenylhydrazine (2,4-DNPH) reagent and to degrade the formaldehyde derivative [3]. Ketones and other aldehydes can react with 2,4-DNPH; the derivatives produced, however, are separated chromatographically from the formaldehyde derivative.

OTHER METHODS: NIOSH methods 2541 [4] and 3500 [5] and OSHA method 52 [6] are other methods for determination of formaldehyde in air. NIOSH method 5700 employs 2,4-DNPH and HPLC for determination of formaldehyde on textile or wood dust [7]. A journal method employs the same procedure for formaldehyde in automobile exhaust [8].

REAGENTS:

1. Formaldehyde stock solution,* aqueous, standardized, 1 mg/mL (see APPENDIX A). Alternatively, standardized formaldehyde solution, aqueous, 4 mg/mL, is available commercially from Hach Co., Loveland, CO.
2. Acetonitrile,* distilled in glass, low carbonyl content.**
3. Water, deionized and distilled.
4. Sulfuric acid, 0.02 N (pH standardization procedure) or 0.1 N (colorimetric procedure).
5. Sodium hydroxide, 0.01 N.
6. Sodium sulfite (Na_2SO_3), 1.13 M (pH procedure) or 0.1 M (colorimetric procedure). Prepare fresh immediately before use.
7. Thymophthalein indicator solution, 0.04% (w/v) in 50:50 ethanol:water.

* See SPECIAL PRECAUTIONS.

** Carbonyl content of acetonitrile can be determined by passing 10 mL of the solvent through a cartridge of DNPH-coated silica gel and analyzing by HPLC. Formaldehyde content should be below the LOD.

EQUIPMENT:

1. Sampler: Plastic holder containing 0.35 g of 150-250 µm (60-100 mesh) silica gel coated with 1.0 mg of acidified 2,4-dinitrophenylhydrazine. Pressure drop across sampler should be less than 28 inches of water (7 kPa) at 1.5 L/min. Samplers are commercially available, [Supelco S10 LpDNPH cartridge, cat. No. 2-1014; Waters Corp. Sep-Pak XPoSure Aldehyde Sampler, part No.WATO47205; see APPENDIX B for SKC sampler].
2. Personal sampling pump, 0.03 to 1.5 L/min with flexible connecting tubing.
3. Vials, 4-mL, glass with PTFE-lined rubber septa caps.
4. Vials, 20-mL, glass.
   NOTE: Do not use vials with "polycone" liners (sources of high formaldehyde blanks)[5,9].
5. Liquid chromatograph with UV detector, recorder, integrator, and column (page 2016-1).
6. Syringes, 100-µL, 500-µL and 10-mL.
7. Volumetric flasks, 10-mL, 25-mL, and 1-L.
8. Burets, 50-mL.
9. pH meter.
10. Magnetic stirrer.
11. Beaker, 50-mL.
12. Flask, Erlenmeyer, 250-mL.
13. Ozone scrubber (Waters Corp.)(optional).
14. Aluminum foil or black electrical tape (optional).

SPECIAL PRECAUTIONS: Formaldehyde is a suspect carcinogen and a proven human sensitizer; it should be handled in a fume hood [10-12].
Acetonitrile is toxic and is a fire hazard (flash point = 12.8 °C).

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler (and ozone scrubber, if used) in line.
2. Open sampler packet and remove end caps.
3. Attach sampler to the sampling pump with flexible tubing. The Waters sampler is bi-directional and can be connected at either end.
   NOTE: The sampler does not have a backup section for determination of breakthrough. If high concentrations of aldehydes and ketones are anticipated, connect two samplers in series. The back pressure of the sampling train will be higher and a lower flow rate may be required.
4. Sample 1 to 15 L of air at 0.03 to 1.5 L/min.
   NOTE: To protect from intense light, such as bright sunlight, the sampler can be wrapped with aluminum foil or electrical tape.
5. Place end caps onto the sampler and seal sampler in an envelope. Protect samples from heat.
6. Ship samples on ice (0 °C).

SAMPLE PREPARATION:

NOTE: Check acetonitrile for formaldehyde content by elution and analysis of a blank cartridge; the formaldehyde level should be below the detection limit. Since background levels of formaldehyde on the samplers may change during storage, compare samples with sampler blanks from the same lot. Samples and blanks should be stored under the same conditions.

7. Elute the formaldehyde derivative from the cartridge samplers with 10-mL quantities of acetonitrile.
   a. Collect effluent from each sampler in a 10-mL volumetric flask.
   b. Add acetonitrile to the mark for each sampler.
      NOTE: The silica gel bed of the sampler will retain approximately 0.5 mL of the original 10 mL.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six media working standards over the range of interest.
   a. Prepare a series of aqueous formaldehyde solutions for the fortification of samplers. Suggested concentrations include 1, 4, and 20 µg/mL. See APPENDIX A for standardization of formaldehyde in water.
   b. Connect the outlet of a cartridge sampler to a personal sampling pump with flexible tubing. Turn on the pump and make sure there is a flow of air through the sampler.
   c. Load a 100-µL syringe with a selected volume of aqueous formaldehyde solution in the range of 30 to 90 µL. Suggested quantities of formaldehyde for spiking include 0.04, 0.10, 0.20, 0.30, 0.40, 0.80, 1.0 and 2.0 µg/sample.
   d. Place the tip of the syringe needle against the frit in the inlet of the sampler and eject the formaldehyde solution.
   e. Prepare the media working standard (steps 7.a and 7.b).
   f. Prepare additional working standards (steps 8.b. through 8.e.).
   g. Transfer 3-mL aliquots of working standards to 4-mL vials, and analyze (steps 10, 12 and 13).
   h. Prepare calibration graph, peak area or height vs. µg formaldehyde per sample.
9. Fortify and analyze three quality control spikes and three analyst spikes to ensure that calibration graph is in control.

MEASUREMENT:

10. Set liquid chromatograph according to manufacturer's recommendations and to conditions given on page 2016-1.
11. Transfer a 3-mL aliquot of the sample solution from step 7 to a 4-mL vial. Cap the vial.
12. Inject a 20-µL sample aliquot.
13. Measure peak area or peak height.
    NOTE 1: If sample peak is larger than the largest standard peak, dilute an aliquot of the remaining sample solution, reanalyze, and apply appropriate dilution factor in the calculations.
    NOTE 2: To ensure validity of the samples, identify those samples which contain more than 37 µg of formaldehyde. The capacity of the samplers before breakthrough may have been exceeded for these samples, and collection of smaller samples would be warranted.
    NOTE 3: The size of the 2,4-DNPH peak should be about 2.7 times the size of the formaldehyde-DNPH peak or larger. Otherwise, breakthrough from the sampler may have occurred.

CALCULATIONS:

14. Determine mass, µg, of formaldehyde, W, found in the sample and the average media blank, B, from the calibration graph.

15. Calculate concentration, C, of formaldehyde in the air volume sampled, V (L).

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

NOTE: µg/L ≡ mg/m^3

EVALUATION OF METHOD:

Issue 1

This method was originally evaluated with Waters Sep-Pak XPoSure Aldehyde samplers using data produced at NIOSH and at Waters Corporation [2]. Test atmospheres of formaldehyde were generated at Waters Corp. [2]. Overall measurement precision, $\hat{S}_{rT}$, was 0.057 based on NIOSH guidelines [13] including a 5% pump error factor and estimated bias of +4.4%. Sample storage stability was evaluated over the range of 0.5 to 55 µg formaldehyde/sample. Losses for Waters samplers were 4 to 8% when stored up to 14 days at 4 °C. An additional study with Waters samplers found that losses were 5% or less after 4 days of storage at ambient temperature. All calibration standards used at Waters Corporation were liquid standard solutions of formaldehyde-DNPH derivative in acetonitrile [2,14].

The capacity of DNPH-coated silica gel samplers was found to vary with relative humidity (RH) in addition to concentration of formaldehyde. At a formaldehyde concentration of 1.2 mg/m^3 and at 5% breakthrough, the Waters sampler had a capacity at <10% RH of 55 µg, and at >85% RH a capacity of 77 µg. At 2.4 mg/m^3 and <10% RH, the 5% breakthrough capacity of the Waters sampler was 59 µg of formaldehyde. At 2.6 mg/m^3 and >85% RH, the 5% breakthrough capacity was 106 µg. Thus, the smallest capacity at 5% breakthrough was 55 µg of formaldehyde; the upper limit of the range of the method is two thirds of 55 µg, or 37 µg. Capacity information for the Waters sampler is applicable to the Supelco sampler because (a) the Waters and Supelco samplers contain 0.9 and 1 mg of DNPH, respectively, and (b) each sampler contains 350 mg of silica gel.

Issue 2

In subsequent work on this method, additional formaldehyde samplers were evaluated, Supelco S10 LpDNPH cartridges and SKC, Inc. Aldehyde samplers (DNPH-coated silica gel tubes No.226-119) [1]. The sorbent beds of Supelco and Waters cartridges and front sections of SKC samplers were treated with acetonitrile. Formaldehyde was not detected on any blank sampler (LOD = 0.01 µg/mL). The SKC sampler for aldehydes may be used for formaldehyde with modifications of this method (See APPENDIX B). However, evaluation of the SKC sampler at NIOSH has been limited.

Supelco samplers were fortified with known quantities of free formaldehyde in water, and calibration was performed with media standards prepared from Supelco samplers fortified with known quantities of free formaldehyde in water; average recoveries ranged from 96.3% to 99.3% for five levels at 1.00 to 20 µg of formaldehyde per sampler (pooled S_r = 0.0316; n = 6 at each level).

In a storage study, six Supelco samplers were fortified with 4-µg quantities of free formaldehyde in water. Samplers were stored 34 days at 5 °C in the dark; the average recovery based on media standards was 99% (S_r = 0.014).

Eight media standards were prepared by fortification of Supelco samplers with solutions of free formaldehyde in water. The solutions were drawn through the DNPH-coated silica gel beds with an air pump. The resulting LOD and LOQ were 0.07 and 0.23 µg/sample, respectively, according to a least squares calibration graph.

Standard solutions of formaldehyde-DNPH at 0.10 and 1.0 µg/mL (formaldehyde equivalent concentrations) were stored in airtight vials at 5 °C in the dark and were analyzed periodically. The standard solutions were found to be stable (with no detectable loss) for at least 10 weeks and at least 12 weeks, respectively.

It is suggested that the reader see the Backup Data Report for a comparison of media standards with liquid standards for calibration [1]. Air sampling for a 24-hour period can be performed with a single Supelco sampler. Thus, background levels at <1 ppb can be determined.

REFERENCES:

[1] Tucker SP [2002]. Formaldehyde Backup Data Report for method 2016 Issue 2, National Institute for Occupational Safety and Health, DART, Cincinnati, OH. Unpublished report for evaluation of method mainly with Supelco S10 LpDNPH samplers.

[2] Iraneta PC, Collamati RA., Costello DN, Crowley RJ, Fernandes RL, Hopkins MR, Knowles CE, Martin DM [1995]. A Validation Study of a New Active Sampler for the Analysis of Formaldehyde in Workplace and Indoor Air, Waters Corp., Milford, MA. Unpublished report for evaluation of method with Waters Sep-Pak XPoSure Aldehyde samplers.

[3] Kleindienst TE, Corse EW, Blanchard FT [1998]. Evaluation of the Performance of DNPH-coated Silica Gel and C_{18} Cartridges in the Measurement of Formaldehyde in the Presence and Absence of Ozone. Environmental Science & Technology 32(1):124-130.

[4] NIOSH [1994]. Formaldehyde by GC: Method 2541. In: Eller PM, Cassinelli ME, eds. NIOSH Manual of Analytical Methods, 4th ed. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health. DHHS (NIOSH) Publication No. 94-113.

[5] NIOSH [1994]. Formaldehyde by VIS: Method 3500. In: Eller PM, Cassinelli ME, eds. NIOSH Manual of Analytical Methods, 4th ed. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Ocupational Saerty and Health. DHHS (NIOSH) Publication No. 94-113.

[6] OSHA [1985]. Formaldehyde: Method 52. In: OSHA Analytical Methods Manual, Salt Lake City, UT: U.S. Department of Labor, Occupational Safety and Health Administration, OSHA Analytical Laboratory.

[7] NIOSH [1994}. Formaldehyde on Dust (Textile or Wood): Method 5700. In: Eller PM, Cassinelli ME, eds. NIOSH Manual of Analytical Methods, 4th ed. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health. DHHS (NIOSH) Publication No. 94-113.

[8] Lipari F, Swarin S [1982]. Determination of Formaldehyde and Other Aldehydes in Automobile Exhaust with an Improved 2,4-Dinitrophenylhydrazine Method. J. Chromatogr. 247: 297-306.

[9] Dollberg DD, Smith DL, Tharr DG [1986]. Lab/Field Coordination. Appl. Ind. Hyg. 1:F44-F46.

[10] ACGIH [2001]. 2001 Threshold Limit Values® and Biological Exposure Indices. American Conference of Governmental Industrial Hygienists, Inc., Cincinnati, OH.

[11] ACGIH [1991]. Documentation of Threshold Limit Values and Biological Exposure Indices, Sixth ed. Formaldehyde, pp. 664-688. American Conference of Governmental Industrial Hygienists, Inc., Cincinnati, OH.

[12] Code of Federal Regulatons [1999]. Title 29, Part 1910.1048, 29 CFR Chapter XVII (7-1-99 Edition). Formaldehyde, pp. 354-378. Occupational Safety and Health Administration, Labor. U.S. Government Printing Office, Washington, D.C.

[13] Kennedy ER, Fischbach TJ, Song R, Eller PE, Shulman SA [1995]. Guidelines for Air Sampling and Analytical Method Development and Evaluation, Cincinnati, OH: National Institute for Occupational Safety and Health. DHHS (NIOSH) Publication No. 95-117.

[14] Waters Corp. [1994]. Waters Sep-Pak XPoSure Aldehyde Sampler Care and Use Manual, Waters Corp., Milford, MA, p. 31.

[15] Walker JF [1964]. Formaldehyde, Third Ed., Chapter 18, p. 486. American Chemical Society Monograph Series, Reinhold Publishing Corporation, New York.

METHOD REVISED BY:

Samuel P. Tucker, Ph.D., NIOSH/DART.
Method originally written by P Iraneta, Waters Corp., MJ Seymour and ER Kennedy, Ph.D., NIOSH/DART.

APPENDIX A - PREPARATION AND STANDARDIZATION OF FORMALDEHYDE STOCK SOLUTION (ca. 1 mg/mL)

Preparation. Dilute 2.7 mL 37% aqueous formalin solution to 1 L with distilled, deionized water. This solution is stable for at least three months when stored at room temperature.

Standardization by pH Titration.
Place 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 3.0 to 12.0 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:

$$Cs = \frac{30.0(N_a V_a - N_b V_b)}{Vs}, mg/mL$$

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 (mL)

Standardization by Colorimetric Titration.
Place 50 mL of freshly prepared 0.1 M sodium sulfite and 3 drops of 0.04% thymophthalein indicator (w/v) in 50:50 ethanol:water into a 250-mL Erlenmeyer flask. Titrate the contents of the flask to a colorless endpoint with 0.1 N sulfuric acid (usually 1 or 2 drops is sufficient). The indicator is blue at pH values above the endpoint and is colorless at pH values below the endpoint. Transfer 3.0 to 12.0 mL of the formaldehyde solution to the same flask and titrate the mixture with 0.1 N sulfuric acid to a colorless endpoint. Calculate the concentration, C (mg/mL), of formaldehyde in solution.

$$C = \frac{30.0(N_a V_a)}{V_s}, mg/mL$$

Where: 30.0 = g/equivalent of formaldehyde
N_a = normality of sulfuric acid (0.1 N)
V_a = volume of sulfuric acid used for titration (mL)
V_s = volume of formaldehyde stock solution (mL)

NOTE: Sulfuric acid (0.1 N) is substituted for 0.1 N hydrochloric acid, which is specified in OSHA Method 52, in order to prevent possible formation of bis(chloromethyl)ether, a potent carcinogen, by reaction of formaldehyde with hydrochloric acid [12].

This colorimetric titration was adapted from OSHA Method 52 [5], which was based on the procedure of Walker [15].

APPENDIX B - USE OF SKC SAMPLER FOR FORMALDEHYDE

The SKC, Inc. sampler for aldehydes (DNPH-coated silica gel tube, catalogue No. 226-119) may be used for sampling formaldehyde with modifications of this method. These modifications include the following:

(a) The maximum recommended air volume should be less than 15 L at an air concentration of 2.5 mg/m^3 (indicated on page 2016-1), because the upper limit of the method for the SKC sampler is probably less than 37 µg.

(b) The procedure for recovery of analyte from the sorbent would be modified, i.e., placement of the sorbent sections in vials, addition of solvent, and possible use of an ultrasonic bath.

(c) A volume of solvent much less than 10 mL can be used for recovery. However, the minimum volume should be tested for adequate recovery.

(d) Consequences of using a much smaller volume of solvent for recovery include a lower LOD and LOQ, the need for a different range of calibration standards, and the need for a different range of fortification levels (step 8).

(e) The maximum volume of solution for fortification of the front sorbent bed must be less than 90 µL and should be determined (step 8).