FORMALDEHYDE by VIS   3500
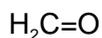
$H_2C=O$ MW: 30.03   CAS: 50-00-0   RTECS: LP8925000

METHOD: 3500, Issue 2	**EVALUATION: FULL**	**Issue 1: 15 May 1989** **Issue 2: 15 August 1994**

OSHA : 0.75 ppm; 2ppm 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; vapor density 1.067 (air = 1.00); explosive range 7 to 73 % v/v in air

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

SAMPLING		MEASUREMENT	
SAMPLER:	FILTER + IMPINGERS (1-µm PTFE membrane and 2 impingers, each with 20 mL 1% sodium bisulfite solution)	**TECHNIQUE:**	VISIBLE ABSORPTION SPECTROMETRY
FLOW RATE:	0.2 to 1 L/min	**ANALYTE:**	formaldehyde
VOL-MIN: **-MAX:**	1 L @ 3 ppm 100 L	**SAMPLE WORKUP:**	note liquid volume; remove 4-mL aliquot
SHIPMENT:	transfer samples to low-density polyethylene bottles before shipping	**COLOR DEVELOPMENT:**	chromotropic acid + sulfuric acid; absorbance @ 580 nm
SAMPLE STABILITY:	30 day @ 25 °C [1]	**CALIBRATION:**	standard solutions of formaldehyde in distilled water
BLANKS:	2 to 10 field blanks per set	**RANGE:**	2 to 40 µg per sample [1,2]
		ESTIMATED LOD:	0.5 µg per sample [2,3]
		PRECISION ($\hat{S}_r$):	0.03 @ 1 to 20 µg per sample [3]

ACCURACY

RANGE STUDIED:	1.25 to 7.5 mg/m^3 [2] (80-L samples)
BIAS:	none identified
OVERALL PRECISION ($\hat{S}_{rT}$):	0.09 [2]
ACCURACY:	± 18%

APPLICABILITY: The working range is 0.02 to 4 ppm (0.025 to 4.6 mg/m^3) for an 80-L air sample. This is the most sensitive formaldehyde method in the NIOSH Manual of Analytical Methods and is able to measure ceiling levels as low as 0.1 ppm (1 5-L sample). It is best suited for the determination of formaldehyde in area samples.

INTERFERENCES: Oxidizable organic materials may give a positive interference [2]. Phenol to formaldehyde ratios as low as 0.3 produce a - 15% bias [4]. A method for the removal of the phenol interference has been reported by Hakes et. al. [5] . Ethanol and higher M.W. alcohols, olefins, aromatic hydrocarbons [6] and cyclohexanone also produce small negative interferences [7]. Little interference is seen from other aldehydes [7].

OTHER METHODS: This method was originally adapted from the Intersociety Committee [8] and designated P&CAM 125 [4]. For personal samples or where interferences to this method are present, use Method 2541. Ref [9] is a recent review of formaldehyde methods.

REAGENTS:

1. Chromotropic acid, 1%. Dilute 0.10 g 4,5-dihydroxy-2,7-naphthalene disulfonic acid disodium salt to 10 mL with distilled water. Filter. Store in brown bottle. Prepare fresh weekly.
2. Sulfuric acid (H_2SO_4), 96%.*
3. Formaldehyde stock solution, 1 mg/mL (See APPENDIX).
4. Formalin solution, 37%.*
5. Distilled, deionized water.
6. Sulfuric acid, 0.02 $\underline{N}$, aqueous.
7. Sodium hydroxide, 0.01 $\underline{N}$, aqueous.
8. Sodium sulfite, 1.13 $\underline{M}$, aqueous. Prepare fresh immediately before use.
9. Sodium bisulfite ($NaHSO_3$), 1%. Dissolve 1 g in distilled water. Dilute to 100 mL. Prepare fresh weekly.
10. Magnesium sulfate.

   *   See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: 37-mm filter cassette with 37-mm polytetrafluoroethylene (PTFE) membrane filter, 1- to 3-µm pore size supported by stainless steel screen or O-ring followed by two midget impingers; inert, flexible tubing for cassette-to-impinger connection.
2. Personal sampling pump, 0.2 to 1 L/min, with flexible connecting tubing.
3. Bottles, screw-cap low-density polyethylene (Nalgene CPE or equivalent), 50-mL.
   NOTE: Do not use bottles with "polycone" liners   (see step 4)
4. Spectrophotometer, visible, 580 nm, with cuvettes, 1-cm.
5. Volumetric pipettes, 0.1-, 0.5-, 1-, 4-, 5-, 6- and 10-mL; 1-, 2- and 5-m, graduated in 0.1-mL units, with pipet bulb.
6. Volumetric flasks, 10- and 100-mL, and 1-L.
7. Burets, 50-mL.
8. pH meter.
9. Flasks, glass-stoppered, 25-mL.
10. Graduated cylinder, 25-mL.
11. Waterbath at 95 °C.
12. Magnetic stirrer.
13. Beaker, 50-mL.

SPECIAL PRECAUTIONS: Sulfuric acid is extremely corrosive; handle while wearing acid-resistant gloves, apron and full face shield with goggles. Formaldehyde is viewed as a potential carcinogen [9,10] and should be handled in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Fill the two impingers for each sample with 20 mL, 1% sodium bisulfite solution. Make cassette-to-impinger and impinger-to-sampling pump connections with flexible, inert tubing. Insert a second filter/cassette assembly in line between the sampler and sampling pump to trap any liquid which might splash over from the impingers during sampling.
   NOTE: The PTFE filter is necessary when sampling is to be conducted in a dusty environment, which could contribute either a positive or negative interferences to the method [1]. The use of dual impingers in series is recommended to ensure efficient collection of formaldehyde.
3. Sample at an accurately known flow rate between 0.2 and 1 L/min for a total sample size of 1 to 100 L.
4. Transfer the contents of the impingers to separate low-density polyethylene bottles for shipping.
   Note: Sample contamination may occur if glass scintillation vials with "polycone" plastic lined caps are used [11].

SAMPLE PREPARATION:

5. Transfer each impinger solution to a clean, dry 25-mL graduated cylinder. Record volume of solution from front impinger, V_f (mL) and backup impinger, V_b (mL).

6.   Pipette 4-mL aliquots from each sample solution into 25-mL glass-stoppered flasks.
     NOTE: Adjust aliquot size to contain between 2 and 20 µg formaldehyde for optimum
            absorbance. The calibration graph between becomes non-linear above an absorbance
            of ca. 1.0. A.U.
7.   Add 0.1 mL 1% chromotropic acid to the flask and mix.
     NOTE: This amount of chromotropic acid can react with ca. 40 µg of formaldehyde. Due to this
            fact, the range of the calibration curve should not exceed 36 µg (90% of theoretical).
8.   Add 6 mL conc. H_2SO_4 slowly to the flask. Replace the stopper gently. Gently swirl the solution
     to mix.
     CAUTION: Mixing of the sample solution with concentrated sulfuric acid is highly exothermic.
9.   Heat the solution to 95 °C for 15 min. Allow the solution to cool at room temperature for 2 to 3
     hours.
     NOTE: Use caution due to the corrosive nature of hot sulfuric acid and the possible pressure
            buildup within the flask.

CALIBRATION AND QUALITY CONTROL:

10. Calibrate daily with at least six working standards.
     a. Prepare a calibration stock solution by dilution of 1 mL of 1 mg/mL formaldehyde stock
         solution to 100 mL 1% sodium bisulfite solution.
     b. Pipet, e.g., 0.1, 0.3, 0.5, 0.7, 1.0, and 2.0 mL calibration stock solution into 25-mL glass-
         stoppered flasks.
     c. Add 1% sodium bisulfite solution to bring the volume of each working standard to 4 mL.
         Also prepare a reagent blank.
     d. Analyze together with samples and blanks (steps 5 through 9, and steps 11 and 12).
     e. Prepare calibration graph (absorbance vs. µg formaldehyde/mL).

MEASUREMENT:

11. Set spectrophotometer according to manufacturer's recommendations and to conditions given on
     p. 3500-1. Fill 1-cm cuvette with sample.
12. Read sample absorbance at 580 nm.
     NOTE: If absorbance is greater than the highest standard, take a smaller aliquot of the
            remaining unreacted sample solution, dilute to 4 mL with 1% sodium bisulfite solution,
            and analyze. (Steps 11 and 12). For optimum results, all samples containing over
            20 µg formaldehyde should be diluted and reanalyzed.

CALCULATIONS:

13. Calculate the mass, µg, of formaldehyde in each front impinger (M_f), back impinger (M_b) and
     average reagent blank (M_B). Use the appropriate aliquot factor (e.g., 4 mL aliquot from step 6)
     and the total sample volume noted in step 5.
     NOTE: Discard the sample if the mass found in the backup impinger exceeds 1/3 the mass
            found in the front impinger. Collection efficiency is ca. 95% for each impinger [15], but
            may be reduced due to chipped or mismatched impinger parts, or by carryover from the
            front impinger.
14. Calculate the concentration, C, of formaldehyde in the air volume sampled, V (L):

$$C = \frac{M_f + M_b - 2M_B}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

The method was checked for reproducibility by having three different analysts in three different laboratories analyze standard samples containing between 1 and 20 µg formaldehyde. The results agreed within ± 5% [8]. This method was independently compared with the 2,4,-dinitrophenylhydrazine-coated silica gel method of Beasley et al. [12] over the range of 0.8 to 2.2 ppm formaldehyde and was found to give approximately 25% lower concentrations.

In another study comparing this method and the method of Beasley, et al., all three methods were found to be statistically equivalent for loadings from 8.2 to 22.4 µg per sample [13]. The method of Septon and Ku [14] was compared with this method. The slope of the correlation line was 1.09. The concentration range of the comparison was not given.

In a study comparing the pararosaniline method [4] and NIOSH P&CAM 125 over the range of 0.021 to 0.5 ppm, the NIOSH method gave better collection efficiency and accuracy [15]. Precision for both methods was equivalent.

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APPENDIX:

PREPARATION AND STANDARDIZATION OF FORMALDEHYDE STOCK SOLUTION (ca. 6.6 mg/mL)

Dilute 2.7 mL 37% 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 $\underline{M}$ 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 solution. The pH should now be about 11. Titrate the solution back to its original pH with 0.02 $\underline{N}$ 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 $\underline{N}$ sulfuric 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 $\underline{N}$)
V_a = volume of sulfuric acid (mL) used for titration
N_b = normality of NaOH (0.01 $\underline{N}$)
V_b = volume of NaOH (mL) for back-titration
V_s = volume of formaldehyde stock solution (10.0 mL).