

CHLOROACETALDEHYDE

2015

CH₂CICHO

MW: 78.50

CAS: 107-20-0

RTECS: AB2450000

METHOD: 2015, Issue 1

EVALUATION: FULL

Issue 1: 15 August 1994

OSHA : C 1 ppm
NIOSH: C 1 ppm
ACGIH: C 1 ppm
 (1 ppm = 3.21 mg/m³ @ NTP)

PROPERTIES: liquid; d 1.236 g/mL @ 20 °C; sp. gr. (40% aq. soln.) 1.19; BP 85 °C; MP -16.3 °C; VP 13.3 kPa (100 mm Hg)

SYNONYMS: 2-chloroacetaldehyde; 2-chloroethanal

SAMPLING		MEASUREMENT	
SAMPLER:	SOLID SORBENT TUBE (silica gel, 520 mg/260 mg)	TECHNIQUE:	GAS CHROMATOGRAPHY, ⁶³ Ni ECD
FLOW RATE:	0.05 to 0.2 L/min (0.2 L/min for 15-min ceiling sample)	ANALYTE:	chloroacetaldehyde
VOL-MIN:	0.3 L @ 1 ppm	DESORPTION:	25 mL 50% aqueous methanol, 30 min
-MAX:	16 L	INJECTION VOLUME:	2 µL with 3 µL water as flush
SHIPMENT:	routine; submit separate bulk sample	TEMPERATURE-INJECTION:	250 °C
SAMPLE STABILITY:	at least 7 days @ 25 °C	-DETECTOR:	300 °C
FIELD BLANKS:	2 to 10 field blanks per set	-COLUMN:	150 °C
ACCURACY		CARRIER GAS:	5% argon in methane, 50 mL/min
RANGE STUDIED:	1.8 to 6.4 mg/m ³ (3-L samples)	COLUMN:	glass, 1.8 m x 6 mm OD, packed with 60/80 mesh Chromosorb 101
BIAS:	-0.4%	CALIBRATION:	standard solutions of chloroacetaldehyde in 50% aqueous methanol
OVERALL PRECISION (\hat{S}_{rT}):	0.060 [1]	RANGE:	1 to 19 µg per sample [1]
ACCURACY:	±12.2%	ESTIMATED LOD:	0.1 µg per sample [1]
		PRECISION (\hat{S}_p):	0.036 [1]

APPLICABILITY: The working range is 0.1 to 2 ppm (0.33 to 6.3 mg/m³) for a 3-L air sample. The method is not able to distinguish between chloroacetaldehyde and the monomer or dimer hydrate forms of chloroacetaldehyde.

INTERFERENCES: None identified.

OTHER METHODS: This is method S11 [2] in a revised format. Chloroacetaldehyde in air has also been determined by differential pulse polarography [3].

REAGENTS:

1. Chloroacetaldehyde*, ~50% (w/w) solution in water.
2. Water, deionized, distilled.
3. 50% Aqueous methanol.
4. 5% Hydrazine sulfate solution. Dissolve 12.5 g hydrazine sulfate in 250 mL deionized distilled water.
5. Ferric ammonium sulfate solution, saturated, in 1 M HNO₃.
6. Ammonium thiocyanate, 0.100 N. Accurately weigh 7.6139 ammonium thiocyanate and dilute to 1 L with deionized distilled water.
7. Silver nitrate solution, 0.100 N. Accurately weigh 16.987g silver nitrate and dilute to 1 L with deionized distilled water.
8. Nitric acid solution. Add 25 mL conc. nitric acid to 25 mL water. Boil until colorless to remove nitrous acid.
9. Nitrobenzene.
10. 5% Argon/methane.
11. Calibration stock solution. Dilute 1 mL 50 % chloroacetaldehyde solution to 250 mL with deionized distilled water. See APPENDIX for standardization method.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass, 8 cm long, 6-mm ID, containing two sections of 20/40 mesh silica gel (front = 520 mg; back = 260 mg), separated by 2 mm of urethane foam. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.05 to 0.2 L/min with flexible connecting tubing.
3. Gas chromatograph, ⁶³Ni electron-capture detector, integrator and column (page 2015-1).
4. Volumetric flasks, 25-mL, 1-L and other convenient sizes for preparing standards.
5. Erlenmeyer flasks, 50-mL, 250-mL.
6. Buret, 10-mL.
7. Pipets, glass, 25-mL and other convenient sizes for making dilutions.
8. Syringes, 10-, 50-, and 100- μ L.

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 0.05 and 0.2 L/min for a total sample size of 3 to 16 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SPECIAL PRECAUTIONS: Chloroacetaldehyde is corrosive to the skin and an eye irritant in low vapor concentrations. In storage, chloroacetaldehyde forms a water-insoluble polymer [4].

SAMPLE PREPARATION:

5. Transfer the glass wool plug and front section of silica gel to a 50-mL Erlenmeyer flask. Transfer the backup sorbent section to another flask.
6. Pipet 25 mL 50% aqueous methanol into each flask.
7. Shake each flask occasionally over a 30-min period. Analyze samples within 1 day.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 0.1 to 19 μ g chloroacetaldehyde per sample.
 - a. Add known amounts of calibration stock solution to 25-mL volumetric flasks and dilute to the marks with 50% aqueous methanol. Use serial dilution as necessary to prepare lower

- concentrations.
- b. Analyze together with samples and blanks (steps 11 through 13).
 - c. Prepare calibration graph of μg chloroacetaldehyde/25 mL vs. peak area.
9. Determine desorption efficiency (DE) at least once for each batch of silica gel used for sampling in the calibration range (step 8). Prepare three tubes at each of five concentrations plus three media blanks.
 - a. Remove and discard the back sorbent section of a media blank sampler.
 - b. Inject a known amount of standard ($\leq 100 \mu\text{L}$) directly onto front sorbent section with a microliter syringe.
 - c. Cap the tube. Allow to stand overnight.
 - d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 through 13).
 - e. Prepare a graph of DE vs. μg chloroacetaldehyde recovered.
 10. Analyze three quality control blind spikes and five analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacture's recommendations and to conditions given on page 2015-1.
 12. Inject 2- μL sample aliquot along with 3 μL of water as solvent flush.
 13. Measure peak area.
- NOTE: If peak area is above the linear range of the working standards, dilute an aliquot of the desorbed liquid, reanalyze, and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

14. Determine the mass, μg (corrected for DE), of chloroacetaldehyde found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
15. Calculate concentration, C, of chloroacetaldehyde in the air volume sampled, V (L):

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

EVALUATION OF METHOD:

This method was evaluated over the range 1.8 to 6.4 mg/m^3 at 20 °C and 761 mm Hg using 3-L samples [1]. The concentration of chloroacetaldehyde in the test atmospheres was independently monitored using bubblers containing 15 mL deionized distilled water. Breakthrough from front sorbent sections occurred after sampling for 92 min at 0.2 L/min in an atmosphere containing 5.16 mg/m^3 . The relative humidity was 80%. Samples collected at 1X the OSHA standard and stored at room temperature for 1 week lost 8.3% and 5.3% when the relative humidity was 20% and 80%, respectively. No correction for desorption efficiency was needed for loadings at 0.5-, 1-, and 2X the OSHA standard.

Recoveries of samples collected at 80% RH had a positive bias of 3.4%, and samples collected at 20% RH had a negative bias of -4.2%. The overall mean bias was -0.4%.

REFERENCES:

- [1] Backup Data Report No. S11 for Chloroacetaldehyde, prepared under NIOSH Contract No. 210-76-0123.
- [2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 5, S11, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).
- [3] Williams, R.G., Determination of Chloroacetaldehyde in Air by Differential Pulse Polarography, Anal. Chem. **54**(12), 2121-2 (1982).
- [4] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as GPO Stock #17-033-00337-8 from Superintendent of Documents, Washington, D.C. 20402.

METHOD REVISED BY:

James E. Arnold, NIOSH/DPSE; S11 originally developed under NIOSH Contract 210-76-0123.

APPENDIX: STANDARDIZATION OF CALIBRATION STOCK SOLUTION.

Pipet 10-mL aliquots of the stock solution into two separate 250-mL Erlenmeyer flasks. Add 10 mL 2.5% hydrazine sulfate to one of the flasks and allow to stand 10 minutes with occasional swirling. The other flask serves as a blank and determines any free halide ion already present.

Add 10 mL 0.100 N silver nitrate solution, 5 mL nitric acid solution, and 2 mL ferric ammonium sulfate solution to each flask. Swirl and add 2 mL nitrobenzene. The nitrobenzene forms an oily coating on the particles of precipitated silver chloride and prevents their undesired reaction with the thiocyanate ion.

Titrate contents of each flask with 0.1 N ammonium thiocyanate to a faint orange-brown color that is permanent on shaking. The endpoint color is due to the formation of the $\text{Fe}(\text{SCN})_6^{-3}$ ion.

Compute the volumes, V_S , of standard silver solution in excess of that used by the chloride in each flask.

$$V_S = V_T \times \frac{N_T}{N_S}, \text{ mL}$$

where: V_T = volume, mL, of standard thiocyanate solution titrated
 N_T = normality of NH_4SCN solution
 N_S = normality of AgNO_3 solution

Compute the net volume, V_N , of silver solution required for the precipitation of the chloride liberated from chloroacetaldehyde.

$$V_N = V_S (\text{blank}) - V_S (\text{stock}), \text{ mL}$$

Calculate the concentration, C , of chloroacetaldehyde in calibration stock solution.

$$C = V_N \times N_S \times 7.85, \text{ mg/mL}$$