CHLOROACETIC ACID 2008

$ClCH_2COOH$ MW: 94.50 CAS: 79-11-8 RTECS: AF8575000

METHOD: 2008, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : no PEL
NIOSH: no REL
ACGIH: no TLV
(1 ppm = 3.87 mg/m^3 @ NTP)

PROPERTIES: solid; MP 61 to 63 °C; BP 189 °C; VP 0.1 kPa (0.75 mm Hg) @ 20 °C; flash point 126 °C; lower explosive limit in air 8% v/v

SYNONYMS: chloroethanoic acid; monochloroacetic acid

SAMPLING

SAMPLER: SOLID SORBENT TUBE (silica gel, 100 mg/50 mg)

FLOW RATE: 0.05 to 0.2 L/min

VOL-MIN: 1 L @ 0.25 ppm
-MAX: 100 L

SHIPMENT: routine

SAMPLE STABILITY: at least 7 days @ 25 °C; 32 days refrigerated [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.35 to 29 mg/m^3 [1,2] (3-L samples)

BIAS: - 2.0%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.08 [1]

ACCURACY: ± 17.7%

MEASUREMENT

TECHNIQUE: ION CHROMATOGRAPHY, CONDUCTIVITY DETECTION

ANALYTE: chloroacetate ion

DESORPTION: 2 mL deionized water

INJECTION LOOP VOLUME: 500 µL

ELUENT: 1.5 mM $NaHCO_3$; 1.0 mL/min

COLUMNS: Ion Pac AS4A Separator, AG4A Guard, micromembrane suppressor (see OTHER METHODS)

CALIBRATION: standard solutions of chloroacetic acid in deionized water

RANGE: 1 to 80 µg per sample [1]

ESTIMATED LOD: 0.04 µg per sample [2]

PRECISION ($\hat{S}_r$): 0.016 [1]

APPLICABILITY: The working range is 0.09 to >85 ppm (0.3 to 30 mg/m^3) for a 3-L air sample.

INTERFERENCES: Chloroacetyl chloride is a positive interferent since it is hydrolyzed to monochloroacetic acid by the measurement procedure and is efficiently collected by silica gel [3]. Particulate salts of the acid are positive interfe rents. The chromatographic conditions given will separate acetate, chloride, dichloroacetate, fluoride, glycolate, and trichloroace tate ions from chloroacetate ion.

OTHER METHODS: This revises P&CAM 332 [2]. The columns used in P&CAM 332 are no longer available. The newer columns indicated here show improvements in the analytical range and sensitivity.

REAGENTS:

1. Water, filtered, deionized. Specific conductance ≤10 µS/cm.
2. Sodium bicarbonate ($NaHCO_3$), reagent grade.
3. Chloroacetic acid, ≥99%.*
4. Eluent: 1.5 m<u>M</u> $NaHCO_3$. Dissolve 0.504 g $NaHCO_3$ in 4 L filtered, deionized water.
5. Calibration stock solution, 1000 µg/mL. Dissolve 100 mg chloroacetic acid in 100 mL filtered, deionized water.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, with plastic caps, containing two sections of 20/40 mesh silica gel (front = 100 mg; back = 50 mg) contained and separated by three silanized glass wool plugs. Pressure drop across the tube at 0.2 L/min is ca. 0.6 kPa (2.6 in. H_2O). Tubes are commercially available (SKC, Inc. 226-47-01, or equivalent).
   NOTE: Chloroacetic acid is irreversibly adsorbed on urethane plugs. Use sorbent tubes with glass wool plugs.
2. Personal sampling pump, 0.05 to 0.2 L/min, with flexible connecting tubing.
3. Ion chromatograph (IC), anion separator and guard column, anion suppressor (page 2008-1), conductivity detector, integrator, and strip chart recorder.
4. Ultrasonic bath.
5. Vials, 20-mL, glass, with aluminum-lined plastic screw caps.
6. Syringes, 3-mL, polyethylene with luer tip.
7. Filter holder, luer tip, 13-mm, with PTFE filter, 5-µm pore size, or PTFE syringe filter.
8. Pipets, 10-µL to 2-mL.
9. Flasks, volumetric, 10- and 100-mL.

SPECIAL PRECAUTIONS: Chloroacetic acid is irritating to skin and mucous membranes [4]. Work with the concentrated material only in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break ends of sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.05 to 0.2 L/min for a total sample size of 1 to 100 L.
4. Cap the samplers. Pack securely for shipment.
   NOTE: Store samples in the dark. Refrigerate samples if stored longer than 7 days.

SAMPLE PREPARATION:

5. Allow refrigerated samples to equilibrate to room temperature.
6. Transfer front sorbent section with front glass wool plug to vial. Place back sorbent section and other two glass wool plugs in separate vial.
7. Add 2.0 mL deionized water to each vial. Cap immediately.
8. Agitate vials in ultrasonic bath for 30 min at room temperature.
9. Draw sample extract through 13-mm PTFE filter with 3-mL syringe.

CALIBRATION AND QUALITY CONTROL:

10. Calibrate daily with at least six working standards.
    a. Add known aliquots of calibration stock solution to deionized water in 10-mL volumetric flasks and dilute to the mark. Use serial dilutions as needed to obtain chloroacetic acid concentrations in the range 0.02 to 40 µg/mL.
    b. Analyze together with samples and blanks (steps 13 through 15).
    c. Prepare calibration graph [peak height (mm or µS) vs. µg chloroacetic acid per sample].
11. Determine desorption efficiency (DE) for each batch of silica gel used for sampling in the calibration range. Prepare at least three tubes at each of five levels.
    a. Place silica gel from unused front section in vial.
    b. Inject a known amount (2 to 20 µL) of calibration stock solution, or a serial dilution thereof, onto front sorbent section with a microliter syringe.
    c. Cap the vial. Allow to stand overnight.
    d. Desorb (steps 7 through 9) and analyze together with working standards (steps 13 through 15).
    e. Prepare graph of DE vs. µg chloroacetic acid recovered.
12. Analyze three quality control spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

13. Set ion chromatograph according to manufacturer's recommendations and to conditions given on page 2008-1.
14. Inject sample aliquot manually or use autosampler.
    a. Flush sample loop with 0.5 mL sample extract, then inject 0.5 mL sample.
    b. Rinse sample loop with 1 to 2 mL deionized water between determinations of separate samples.
    NOTE: All samples, eluents, and water flowing through the IC must be filtered to avoid plugging the system valves or columns.
15. Measure peak height.
    NOTE: If sample peak height exceeds linear calibration range, dilute with deionized water, reanalyze, and apply appropriate dilution factor.

CALCULATIONS:

16. Determine mass, µg (corrected for DE), of analyte 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.
17. Calculate concentration, C, of chloroacetic acid 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 developed and evaluated by Southern Research Institute [1] using dynamically-generated atmospheres of chloroacetic acid over the concentration range of 0.35 to 29 mg/m^3 at 25 to 27 °C and at relative humidity ≥80%. Average recovery based on 18 samples, six at each of three levels, was 98% representing a negligible bias. Precision at 0.35 mg/m^3 was inhomogeneous with those of higher levels; therefore, precisions were not pooled. Using this poorest precision ($S_r = 0.064$), the overall precision ($\hat{S}_{rT}$) was estimated to be ≤0.081.

The breakthrough volume of the 100-mg sorbent section was found to be >100 L at 0.2 L/min when sampling chloroacetic acid concentrations of 60 mg/m ^{3} at 42 °C and RH of 10 and 80% and 35 mg/m ^{3} at 27 °C and 10 and 90% RH. Samples stored at ambient temperature for 7 days had a mean recovery of 91% and a precision, S_r, of 0.047. Samples refrigerated after day 7, and stored for 32 days exhibited a mean recovery of 100% with a precision, S_r, of 0.085 based on samples analyzed on day 1.

REFERENCES:

[1] Dillon, H. K., D. W. Mason, and K. W. Boyd. Development of Air Sampling and Analytical Methods for Toxic Chlorinated Organic Compounds: Research Report for Monochloroacetic Acid, NIOSH Contract 210-78-0012, Southern Research Institute, Birmingham, AL (1980).

[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 6, P&CAM 322, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-125 (1980).

[3] McCullough, P. R. and J. W. Worley. "Sampling of Chloroacetyl Chloride in Air on Solid Support and Determination by Ion Chromatography," Anal. Chem., 51, 1120-1122 (1979).

[4] Merck Index, 11th ed., Merck & Co., Rahway, NJ (1989).

METHOD REVISED BY:

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