β-CHLOROPRENE 1002

CH_2=CClCH=CH_2 MW: 88.54 CAS: 126-99-8 RTECS: EI9625000

METHOD: 1002, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : 25 ppm (skin)
NIOSH: C 1 ppm/15 min; carcinogen
ACGIH: 10 ppm (skin)
(1 ppm = 3.62 mg/m^3 @ NTP)

PROPERTIES: liquid; d = 0.958 g/mL @ 20 °C; BP 59.4 °C; MP -130 °C; VP 25 kPa (188 mm Hg; 25% v/v) @ 20 °C; explosive range 4 to 20% v/v in air

SYNONYMS: chloroprene; 2-chloro-1,3-butadiene; chlorobutadiene

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.1 L/min

VOL-MIN: 1.5 L @ 25 ppm
-MAX: 8 L

SHIPMENT: routine

SAMPLE STABILITY: at least 8 days @ 25 °C [1,2]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 44 to 174 mg/m^3 [2] (3-L samples)

BIAS: - 1.1%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.071 [2]

ACCURACY: ± 13.9%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: chloroprene

DESORPTION: 1 mL CS_2; stand 30 min

INJECTION VOLUME: 1 to 2 µL, splitless

TEMPERATURE-INJECTION: 250 °C
-DETECTOR: 280 °C
-COLUMN: 35 °C, 2 min; 15 °C/min to 300 °C, hold 5 min

CARRIER GAS: N_2 or He, 1-3 mL/min

MAKEUP GAS: nitrogen, 30 ml/min

COLUMN: DB-1 fused capillary, 30 m x 0.25-mm ID, 1.0-µm film [3]

CALIBRATION: solutions of distilled chloroprene in CS_2; hexane reference standard

RANGE: 0.1 to 0.6 mg per sample [2]

ESTIMATED LOD: 0.03 mg per sample [2,3]

PRECISION ($\hat{S}_r$): 0.021 [2]

APPLICABILITY: The working range is 10 to 60 ppm (40 to 200 mg/m^3) for a 3-L air sample. The method is sensitive enough to determine concentrations as low as 12 ppm in 15-min samples taken at 0.2 L/min. NIOSH has sampled for chloroprene at two polychloroprene processing plants.

INTERFERENCES: None known.

OTHER METHODS: This is Method S112 with improved GC column in a new format [4]. A similar method appears in the chloroprene criteria document [1].

REAGENTS:

1. Carbon disulfide, chromatographic quality.*
2. Chloroprene*, freshly distilled from xylene solution at reduced pressure; BP = 31 °C at 354 mm Hg (47 kPa).
3. n-Pentane, reagent grade.
4. n-Hexane, reagent grade.
5. Calibration stock solution, 47.9 mg/mL. Deliver 0.500 mL (0.479 g at 20 °C) freshly distilled chloroprene from a delivery pipet under the surface of pentane in a partially filled 10-mL volumetric flask. Dilute to the mark with pentane. Stable one day at -15 °C.
6. Nitrogen, purified.
7. Hydrogen, prepurified.
8. Air, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. 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, 0.01 to 0.1 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 1002-1).
4. Micro-distillation apparatus for vacuum distillation of chloroprene.
5. Vials, 2-mL, glass with PTFE-lined septa and crimp seals.
6. Syringe, 10-µL, readable to 0.1 µL.
7. Volumetric flasks, 10-mL.
8. Pipets, 1-mL, graduated in 0.1 mL, with pipet bulb.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and flammable. Work with it only in a hood.

Chloroprene incompatibilities by contact with oxidizers (e.g., peroxides) may cause polymerization with evolution of heat and rupture of containers. Chloroprene attacks some plastics, rubber, and coatings. It will autoxidize very rapidly, even at 0 °C, producing an unstable peroxide (mixed 1,2- and 1,4-addition copolymer with oxygen) which catalyzes exothermic polymerization. Therefore, immediately after distilling, store at -15 °C.

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 0.01 and 0.1 L/min for a total sample size of 1.5 to 8 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL CS_2 to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation. Decant the liquid into a clean vial.

   NOTE 1: Desorbed samples are unstable in the presence of charcoal, losing significant amounts over several hours.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 0.03 to 0.5 mg chloroprene per sample.
   a. Add known amounts of calibration stock solution below the surface of CS_2 in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. mg chloroprene).
9. Determine desorption efficiency (DE) at least once for each batch of charcoal 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 back sorbent section of a media blank sampler.
   b. Inject a known amount of calibration stock solution 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 and 12).
   e. Prepare a graph of DE vs. mg chloroprene recovered.
10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1002-1. Inject sample aliquot either with autosampler or manually using solvent flush technique.
    NOTE: If peak area is above the linear range of the working standards, dilute with CS_2, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of chloroprene 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.
14. Calculate concentration, C, of chloroprene in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S112 was issued on October 29, 1976, and validated over the range 44 to 175 mg/m^3 with eighteen 3-L samples from dynamically-generated test atmospheres, as well as a set of six samples at one times the OSHA standard concentration stored at room temperature for eight days to establish stability [2,5]. Eighteen more samples were spiked (six each at one-half, one and two times the OSHA standard, 0.14 to 0.54 mg) directly. The pooled precision ($\bar{S}_r$) for these three sets of analytical samples was 0.021. The average recovery for all three concentrations was 98.8%, representing a non-significant bias. The value for the taken concentration was obtained by monitoring during generation with a gas chromatograph with a 2-mL sampling loop. Bag standards were used to calibrate the gas chromatograph. The stored samples results were within 1% of samples analyzed after one day, indicating adequate storage stability for eight days. Six parallel breakthrough tubes were run at a time. The generated atmosphere was pulled through the charcoal tubes (critical orifices to control flow).

Several breakthrough studies were done. With 94% relative humidity, breakthrough occurred at 30 min when sampling 0.194 L/min of 195 mg/m ^{3} (5.8 L). With 91% relative humidity, no breakthrough occurred after 240 min when sampling 0.045 L/min of 197 mg/m ^{3} (10.8 L).

REFERENCES:

[1] Criteria for a Recommended Standard-Occupational Exposure to Chloroprene, Appendices I and III, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-210 (1977).
[2] NIOSH Backup Data Report, S112, prepared under NIOSH Contract 210-76-0123, available as "Ten NIOSH Analytical Methods, Set 1," Order No. PB 271-712 from NTIS, Springfield, VA 22161.
[3] Grote, A. Sequence 7239 and 7316 Reports, DPSE/MRSB internal reports (unpublished) (1991).
[4] NIOSH Manual of Analytical Methods, 2nd ed., V. 2, S112, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[5] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY:

Y. T. Gagnon, NIOSH/DPSE; S112 originally validated in NIOSH Contract 210-76-0123.