DIAZOMETHANE 2515

$CH_2=N^+N^-$ MW: 42.04 CAS: 334-88-3 RTECS: PA7000000

METHOD: 2515, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1985**
Issue 2: 15 August 1994

OSHA : 0.2 ppm
NIOSH: 0.2 ppm
ACGIH: 0.2 ppm; suspect carcinogen
(1 ppm = 1.719 mg/m^3 @ NTP)

PROPERTIES: yellow gas; MP -145 °C; BP -23 °C; pure material explodes above 150 °C; impure material explodes at lower temp.

SYNONYMS: azimethylene; diazirine

SAMPLING

SAMPLER: SOLID SORBENT TUBE (octanoic acid-coated XAD-2 resin, 100 mg/50 mg)

FLOW RATE: 0.2 L/min

VOL-MIN: 6 L
-MAX: 30 L

SHIPMENT: routine

SAMPLE STABILITY: not determined

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.17 to 0.80 mg/m^3 [1] (10-L samples)

BIAS: -30% at 0.17 mg/m^3 [1]; -10% at 0.36 to 0.75 mg/m^3 [1]

OVERALL PRECISION ($\hat{S}_{rT}$): 0.084 [1]

ACCURACY: 22.5% at 0.36 to 0.75 mg/m^3

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: methyl octanoate

DESORPTION: 1 mL carbon disulfide; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 225 °C
-DETECTOR: 250 °C
-COLUMN: 95 °C

CARRIER GAS: N_2, 30 mL/min

COLUMN: stainless steel, 3 m x 3-mm OD, 5% SP-1000 on 100/120 mesh Chromosorb WHP preceded by a 15 cm x 3-mm OD stainless steel precolumn packed with 10% Carbowax 20M and 1.2% NaOH on 80/100 mesh Gas Chrom Q

CALIBRATION: methyl octanoate in carbon disulfide with internal standard

RANGE: 2 to 8 µg diazomethane (8 to 32 µg methyl octanoate) per sample

ESTIMATED LOD: not determined

PRECISION ($\hat{S}_r$): 0.024 [1]

APPLICABILITY: The working range is 0.1 to 0.6 ppm (0.2 to 1 mg/m^3) diazomethane for a 10-L air sample.

INTERFERENCES: None reported.

OTHER METHODS: This revises S137 [2].

REAGENTS:

1. Eluent: Carbon disulfide,* chromatographic quality, with internal standard, tridecane (ca. 20 µg/mL).
2. Methyl octanoate, reagent grade.
3. Octanoic acid-coated resin. Pack 20/50 mesh XAD-2 resin (Rohm & Haas Co.) into a column (length to diameter ratio ca. 10:1). Wash with three bed volumes of methanol and two bed volumes of pentane. Check the washings by GC for interfering peaks. Dry at room temperature. Weigh out ca. 10 g washed and dried XAD-2 into a round-bottomed flask. Add 25 mL acetone to form a slurry. Add octanoic acid equivalent to 1% of the sorbent weight. Evaporate the solvent in a rotary evaporator. Dry the coated resin at room temperature.
4. Hydrogen, prepurified.
5. Nitrogen, purified.
6. Air, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID,with plastic caps; two sections of 20/50 mesh 1% octanoic acid-coated XAD-2 resin preceded, separated and followed by silylated glass wool plugs (front = 100 mg; back = 50 mg). Tubes are commercially available (SKC, Inc. 226-23 or equivalent).
2. Personal sampling pump, 0.2 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 2515-1).
4. Vials, glass, 2-mL, PTFE-lined caps.
5. Syringe, 10-µL, readable to 0.1 µL.
6. Pipet, 1.0-mL, with pipet bulb.
7. Volumetric flasks, 10-mL.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and a serious fire and explosion hazard (flash point = -30 °C); all work with it must be done in a hood away from ignition sources.

Diazomethane is an explosive, insidious poison and a strong irritant which may cause delayed hypersensitivity and cancer [3]. Concentrated solutions may explode violently, especially if impurities are present. Rough surfaces, such as ground glass, may also cause explosions [4].

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 of 0.2 ±0.03 L/min for a total sample size of 6 to 30 L.
4. Cap the samplers. Pack securely for shipment.

SAMPLE PREPARATION:

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

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 1 to 32 µg methyl octanoate per sample.
   a. Add known amounts of methyl octanoate to eluent in 10-mL volumetric flasks and dilute to the mark.

b. Analyze with samples and blanks (steps 11 and 12).
c. Prepare calibration graph (ratio of peak area of methyl octanoate to that of the internal standard vs. µg methyl octanoate).

9. Determine desorption efficiency (DE) at least once for each lot of coated XAD-2 resin used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of methyl octanoate 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 with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. µg methyl octanoate recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure 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 2515-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, µg (corrected for DE) of methyl octanoate 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. Convert µg methyl octanoate to µg diazomethane by multiplying the corrected µg per sample by the conversion factor 0.2657 (molecular weight ratio, 42.04/158.24), and calculate apparent concentration, C_a (mg/m^3), of diazomethane in the air volume sampled, V (L):

$$C_a = \frac{(W_f + W_b - B_f - B_b) \cdot 0.2657}{V}, \text{ mg/m}^3.$$

15. Calculate the recovery (R) from the equation:

$$R = 0.971 - \frac{0.0327}{C_a}.$$

NOTE: This recovery was experimentally determined over the apparent concentration range 0.12 to 0.7 mg/m^3 and may not be valid outside that range [1].

16. Calculate corrected concentration, C (mg/m^3):

$$C = \frac{C_a}{R}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S137 was issued on June 6, 1975 [2]. The precision and bias were determined by analyzing generated atmospheres of diazomethane containing 0.17, 0.36 and 0.8 mg/m ^{3} at 26 °C and 765 mm Hg using 10-L samples [1]. The recovery (concentration found in air divided by concentration determined by an independent method involving collection in solutions of benzoic acid in xylene) was found to decrease with concentration according to the equation in step 15. Recoveries were 0.68 to 0.93 for six pairs of data in the apparent concentration range 0.12 to 7 mg/m ^{3}. Sample stability was not determined. The method does not meet the 10% bias criterion for a valid NIOSH method.

Breakthrough of the front section of the coated XAD-2 tube was not observed after sampling 53 L of dry test atmosphere containing 0.83 mg/m ^{3} for 240 min at 0.22 L/min. Desorption efficiencies for samples spiked with methyl octanoate were 1.01 to 1.05. The collection efficiency and reaction of diazomethane with the octanoic acid-coated resin may be strongly dependent on sample flow rates; therefore, all samples must be collected at a flow rate of 0.2 L/min only.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S137, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977), available as GPO Stock #017-033-00231-2 from Superintendent of Documents, Washington, DC 20402.
[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 3, S137, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
[3] 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 #017-033-00337-8 from Superintendent of Documents, Washington, DC 20402.
[4] Merck Index, 10th ed., Merck & Co., Inc., NJ (1983).

METHOD REVISED BY:

Julie R. Okenfuss, NIOSH/DPSE; S137 originally evaluated under NIOSH Contract CDC-99-74-45.