DIMETHYLACETAMIDE 2004

$CH_3CON(CH_3)_2$ MW: 87.12 CAS: 127-19-5 RTECS: AB7700000

METHOD: 2004, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : 10 ppm (skin)
NIOSH: 10 ppm (skin)
ACGIH: 10 ppm (skin)
(1 ppm = 3.56 mg/m^3 @ NTP)

PROPERTIES: liquid; BP 164.5 - 166 °C; MP -20 °C; d 0.937 g/mL @ 25 ° C; VP 1.5 mm Hg @ 20 °C; flash point 70 °C, explosive range 1.8 to 11.5%

SYNONYMS: N,N-dimethylacetamide; acetyldimethylamine; DMAC

SAMPLING

SAMPLER: SOLID SORBENT TUBE (silica gel, 150 mg/75 mg)

FLOW RATE: 0.01 to 1 L/min

VOL-MIN: 15 L @ 30 mg/m^3
-MAX: 80 L

SHIPMENT: routine

SAMPLE STABILITY: at least 5 days @ 25 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 18 to 105 mg/m^3 [1]; (45-L samples)

BIAS: - 0.8%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.067 [1]

ACCURACY: ± 11.7%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: dimethylacetamide

DESORPTION: 1 mL methanol; 1 h in ultrasonic bath

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 240 °C
-DETECTOR: 320 °C
-COLUMN: 140 °C

CARRIER GAS: N_2, 50 mL/min

COLUMNS: 1.5 m x 6-mm OD glass; 10% UCON 50-HB-5100, 2% KOH on 100/120 mesh Chromosorb WHP

CALIBRATION: analyte in methanol

RANGE: 0.5 to 4 mg per sample [1,2]

ESTIMATED LOD: 0.05 mg per sample [2]

PRECISION ($\bar{S}_r$): 0.032 [1]

APPLICABILITY: The working range is 10 to 80 mg/m^3 of dimethylacetamide or dimethyformamdide for a 50-L air sample. The lower limit is determined by the desorption efficiency which must be determined over the range used. Silica gel has a hi gh affinity for water; high relative humidity may adversely affect the efficiency of analyte adsorption.

INTERFERENCES: None identified. Separation conditions (column, temperature, etc.) may be changed to circumvent problems. Alternate columns include: 60/80 mesh Chromosorb P coated with 20% UCON LB 550X and 2% KOH; 100/120 mesh Chromosorb WHP with 10% Carbowax 20M and 2% KOH; 100/120 mesh Chromosorb WHP with 10% SP-2250; and 30-m x 0.32-mm capillary column coated with 0.5 µm DB Wax..

OTHER METHODS: This combines and replace Methods S254 and S255 [2].

DIMETHYLFORMAMIDE 2004
(See Method 2004, DIMETHYLACETAMIDE, for procedure)

$O=CHN(CH_3)$ MW: 73.10 CAS: 68-12-2 RTECS: LQ2100000

METHOD: 2004, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : 10 ppm (skin)
NIOSH: 10 ppm (skin)
ACGIH: 10 ppm (skin)
1 ppm = 2.99 mg/m^3 @ NTP

PROPERTIES: liquid; d 0.95 g/mL @ 25 °C; BP 153 °C; MP -61 °C; VP 2.7 mm Hg @ 20 °C; explosive range in air (v/v) 2.2 to 15.2%

SYNONYMS: N-formyldimethylamine; DMF; N,N-dimethylformamide

SAMPLING

SAMPLER: SOLID SORBENT TUBE (silica gel, 150 mg/75 mg)

FLOW RATE: 0.01 to 1 L/min

VOL-MIN: 15 L @ 30 mg/m^3
-MAX: 80 L

SHIPMENT: routine

SAMPLE STABILITY: at least 5 days @ 25 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 11 to 61 mg/m^3 [1]; (45-L samples)

BIAS: - 1.1%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.056 [1]

ACCURACY: ± 11.7%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: dimethylformamide

DESORPTION: 1 mL methanol; 1 h in ultrasonic bath

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTION: 240 °C
-DETECTOR: 320 °C
-COLUMN: 140 °C

CARRIER GAS: N_2, 50 mL/min

COLUMNS: 1.5 m x 6-mm OD glass; 10% UCON 50-HB-5100, 2% KOH on 100/120 mesh Chromosorb WHP

CALIBRATION: analyte in methanol

RANGE: 0.5 to 4 mg per sample [1,2]

ESTIMATED LOD: 0.05 mg per sample [2]

PRECISION ($\bar{S}_r$): 0.037 [1]

APPLICABILITY: The working range is 3.3 to 27 ppm (10 to 80 mg/m^3) for a 50-L air sample. The lower limit is determined by the desorption efficiency which must be determined over the range used. Silica gel has a high affinity for water; high r elative humidity may adversely affect the efficiency of analyte adsorption.

INTERFERENCES: None identified. Separation conditions (column, temperature, etc.) may be changed to circumvent problems. Alternate columns include: 60/80 mesh Chromosorb P coated with 20% UCON LB 550X and 2% KOH; 100/120 mesh Chromosorb WHP with 10% Carbowax 20M and 2% KOH; 100/120 mesh Chromosorb WHP with 10% SP-2250; and 30-m x 0.32-mm capillary coated with 0.5 µm DB Wax.

OTHER METHODS: This combines and replace Methods S254 and S255 [2].

REAGENTS:

1. Methanol, reagent grade.*
2. Analyte: dimethylacetamide, reagent grade, or dimethylformamide, reagent grade.*
3. Acetone, reagent grade.*
4. Desorption efficiency (DE) stock solution, 0.05 mg/mL. Prepare solutions of dimethylacetamide or dimethylformamide fresh daily in acetone.
5. Hydrogen, prepurified.
6. Air, filtered, compressed.
7. Nitrogen, purified.

* 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 = 150 mg; back = 75 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. The pressure drop across the tube must be less than 3.4 kPa (2.5 cm Hg) at an airflow of 1 L/min. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 1 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator, and column (page 2004-1).
4. Vials, 2-mL, PTFE-lined crimp cap, or automatic sampler vials.
5. Microliter syringes, 10-µL and other convenient size for making standards.
6. Pipets, 1.0 mL.
7. Volumetric flasks, 10-mL.
8. Ultrasonic bath.

SPECIAL PRECAUTIONS: Acetone and methanol are flammable and a dangerous fire and explosion risk. They are moderately toxic by ingestion and inhalation.

Dimethylacetamide and dimethylformamide are strong irritants to skin and tissue and moderate fire risks.

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 0.01 to 1 L/min for a total sample size of 15 to 80 L.
4. Cap the samplers. 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 methanol to each vial. Attach crimp cap to each vial.
7. Agitate for 60 min in an ultrasonic bath.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the ranges 0.05 to 4 mg dimethylacetamide or dimethylformamide per sample.
   a. Add known amounts of analyte (neat or diluted with methanol) to methanol 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 analyte).

9. Determine desorption efficiency (DE) at least once for each lot of silica gel 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 (1 to 20 µL) of pure analyte or DE 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 analyte 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 2004-1. 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 methanol, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine mass, mg (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.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of analyte 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 S254 for dimethylacetamide was evaluated over the range of 18 to 105 mg/m^3 at an atmospheric temperature and pressure of 24 °C and 760 mm Hg using a 45-L sample [1]. Breakthrough occurred when sampling a test atmosphere containing 105.6 mg/m^3 of dimethylacetamide at 0.876 L/min for 240 min. The front section of the silica gel tube was found to hold 22.2 mg dimethylacetamide under these conditions. The collection efficiency test conducted at a concentration of 105.6 mg/m^3 was determined to be 1.00. Desorption efficiency at 0.943, 1.886, and 3.77 mg per silica gel tube was 88.8, 93.8, and 94.9%, respectively. A storage study for five days at 1.866 mg per silica gel tube gave a recovery of 93.6%. Overall sampling and measurement precision, $\hat{S}_{rT}$, was 0.067.

Method S255 for dimethylformamide was evaluated over the range of 11 to 61 mg/m^3 at an atmospheric temperature and pressure of 23 °C and 761 mm Hg using a 45-L sample [1]. Breakthrough occurred when a test atmosphere containing 119.5 mg/m^3 of dimethylformamide was sampled at 0.859 L/min for 146 min. The front section of the silica gel tube was found to hold 15 mg of dimethylformamide under these conditions. The collection efficiency test conducted at a concentration of 61.1 mg/m^3 was determined to be 1.00. Desorption efficiency at 0.759, 1.518, and 3.04 mg per silica gel tube was 88.7,

90.4, and 92.2%, respectively. A storage study for five days at 1.5 mg dimethylformamide per silica gel tube gave a recovery of 91.7%. Overall sampling and measurement precision, $\hat{S}_{rT}$, was 0.056.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S254 (Dimethylacetamide) and S255 (Dimethylformamide), 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, S254 and S255, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).

METHOD REVISED BY:

C. Neumeister, NIOSH/DPSE; S254 and S255 originally validated under NIOSH Contract CDC-99-74-45.