ISOPHORONE 2556

$C_9H_{14}O$ MW: 138.21 CAS: 78-59-1 RTECS: GW7700000

METHOD: 2556, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 March 2003**

OSHA : 25 ppm
NIOSH: 4 ppm; Group III Pesticide
ACGIH: C 5 ppm (animal carcinogen)

PROPERTIES: liquid; d 0.923 g/mL @ 25 °C; BP 213 °C; VP 26 kPa (0.2 mm Hg 260 ppm) @ 20 °C

SYNONYMS: 3,5,5-trimethyl-2-cyclohexen-1-one

SAMPLING

SAMPLER: SOLID SORBENT TUBE (XAD-4, 80 mg/40 mg)

FLOW RATE: 0.01 to 1 L/min

VOL-MIN: 2 L @ 25 ppm
-MAX: 25 L

SHIPMENT: Ship cold.

SAMPLE STABILITY: At least 14 days @ 5 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: Not Determined.

ACCURACY: Not Determined.

BIAS: Not Determined.

OVERALL PRECISION (S_{rT}): Not Determined.

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: Isophorone

EXTRACTION: 1 mL diethyl ether; stand 30 min and rotate 1.5 hours

INJECTION VOLUME: 1 µL

TEMPERATURE
-INJECTOR: 240 °C
-DETECTOR: 300 °C
-COLUMN: 50 °C (0.5 min) to 225°C (10 °C/min)

CARRIER GAS: He, 3.0 mL/min

COLUMN: Capillary, fused silica 30-m x 0.32-mm ID; 1 µm film crossbond carbowax- PEG for acidic compounds

CALIBRATION: isophorone in diethyl ether

RANGE: 6 to 831 µg per sample [1]

ESTIMATED LOD: 1.0 µg per sample [1]

PRECISION ($\bar{S}_r$): 0.01 [1]

APPLICABILITY: The working range for this method is 0.042 to 5.88 ppm (0.24 to 33.2 mg/m^3) for a 25-L air sample. High humidity may greatly decrease breakthrough volume.

INTERFERENCES: None identified.

OTHER METHODS: This method was developed for air sampling at lower concentrations of isophorone. NMAM Method 2508, for isophorone, is based on the 2nd edition method S367 [2,3]. This older method uses a petroleum-based charcoal sorbent tube and packed-column gas chromatography.

REAGENTS:

1. Diethyl Ether, chromatographic grade.*
2. Isophorone.*
3. Helium, prepurified and filtered.
4. Hydrogen, prepurified and filtered.
5. 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 20/40 mesh XAD-4 (80 mg front/40 mg back) 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 must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 1 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator, base-deactivated inlet liner, and column Stabilwax-DA or equivalent (see page 2556-1).
4. Vials, 2-mL, PTFE-lined caps.
5. Syringes, 250-, 25-, 10-µL, readable to 0.1 µL.
6. Volumetric flasks, 10-mL.
7. Pipets, 3- and 5-mL, with pipet bulb.
8. Cold packs for shipping.
9. Mechanical rotary mixer.

SPECIAL PRECAUTIONS: Diethyl ether is highly volatile and an acute fire and explosion hazard. Work with it only in a hood. Isophorone is a lachrymator [2]. Work with it should be done in a hood and caution should be taken while it is being used.

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 1.0 L/min for a total sample size of 2 to 25 L.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front (and glass wool plug) and back sorbent sections of the sampler tube in separate vials. Discard the foam plugs.
6. Add 1.0 mL diethyl ether to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation and place on a rotary mixer for 1.5 hours.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 6 to 831µg isophorone per sample.
   a. Add known amounts of isophorone to a 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. µg isophorone).

9. Determine desorption efficiency (DE) at least once for each batch of XAD-4 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 isophorone 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. µg isophorone 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 2556-1. 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 diethyl ether, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, µg (corrected for DE) of isophorone 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 isophorone in the air volume sampled, V (L):

$$C = \frac{(Wf + Wb - Bf = Bb)}{V}, mg/m^3$$

EVALUATION OF METHOD:

NIOSH method NMAM 2508 for isophorone reported an average DE recovery of 86% over the high concentration range of 849 to 3400 µg [1]. While the results are considered acceptable, at the lower levels encountered in current analyses, the recoveries would most likely fall below those considered acceptable. Therefore, a method development effort was initiated to improve the recovery and analysis of isophorone at these lower levels.

In 1987, Levin and Carleborg reported that isophorone was quantitatively recovered from XAD polymer using diethyl ether as the desorption solvent at the 750 µg level [4]. Initial results using this approach were plagued by varying recoveries and poor peak resolution which was solved by using a Stabilwax-DA fused silica capillary column and a base-deactivated inlet liner in the gc injection port. The base-deactivated inlet liner should be replaced after 35-40 injections. Additionally, the samples were placed on a rotary mixer for 1.5 hours after the addition of the diethyl ether. These changes resulted in an average recovery of 94.1% over the range of 55 to 831µg and the LOD being lowered to 1 µg/sample. Isophorone samples, when spiked at levels 0.15 times the REL, were stable (89% recovery) for 30 days when stored at 5°C.

REFERENCES:

[1] Pendergrass SM, Moody E [2000] Backup Data Report for Isophorone: Method 2556. NIOSH, DART, CEMB (unpublished).
[2] NIOSH [1994]. NMAM Method 2508: Isophorone. In: Eller PM, Cassinelli ME, eds. NIOSH Manual of Analytical Methods, 4th edition. Cincinnati, OH: U.S. Deptartment of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health. DHHS(NIOSH) Publication No. 94-113.
[3] NIOSH [1977]. NIOSH Manual of Analytical Methods, 2nd. ed., V. 3, S367, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C.
[4] Levin JO, Carleborg L [1987]. Evaluation of Solid Sorbents for Sampling Ketones in Work-Room Air, Ann. Occup. Hyg., Vol. 21(1):31-38.

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