METHYL AND ETHYL METHACRYLATE 2537

(1) $H_2C=C(CH_3)COOCH_3$ MW: 100.12 CAS: 80-62-6 RTECS: OZ5075000
(2) $H_2C=C(CH_3)COOC_2H_5$ 114.15 97-63-2 OZ4550000

METHOD: 2537, Issue 3	EVALUATION: (1) FULL (2) PARTIAL	Issue 1: 15 August 1990 Issue 3: 15 March 2003

OSHA : (1) 100 ppm; (2) None
NIOSH: (1) 100 ppm; (2) None
ACGIH: (1) 100 ppm; (2) None

(1) 1 ppm = 4.10 mg/m³
(2) 1 ppm = 4.68 mg/m³

PROPERTIES: (1) liquid; d = 0.944 g/mL @ 20°C; BP = 100°C; VP = 4.7 kPa (35 mm Hg) @ 20°C; explosive range 1.7 to 8.2% v/v in air.
(2) liquid; d = 0.917 g/mL @ 20°C; BP = 119°C; flash point = 21.1°C; index of refraction = 1.4116 (25°C).

SYNONYMS: (1) Methyl ester of methacrylic acid, methyl-2-methyl-2-propenoate
(2) Ethyl ester of methacrylic acid; ethyl-2-methyl-2-propenoate

SAMPLING

SAMPLER: SOLID SORBENT TUBE (XAD-2, 400/200 mg)

FLOW RATE: 0.01 to 0.05 L/min

VOL-MIN: 1 L @ 100 ppm
-MAX: 8 L

SHIPMENT: In dry ice

SAMPLE STABILITY: 7 days @ 25°C; 31 days @ 5°C [1]

BLANKS: 2 - 10 samples per set

ACCURACY

RANGE STUDIED: (1) 193 to 725 mg/m³ (3-L samples) [3]
(2) Not studied

BIAS: (1) 2.55% [3]
(2) Not determined

OVERALL PRECISION ($\hat{S}_{rT}$): (1) 0.063 [3]
(2) Not determined

ACCURACY: (1) +/- 12.6% [3]
(2) Not determined

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: Methyl and ethyl methacrylate

DESORPTION: 2 mL CS_2 with sonication for 30 minutes

INJECTION VOLUME: 1 µL

TEMPERATURE
-INJECTION: 250°C
-DETECTOR: 300°C
-COLUMN: 50°C (3 min) to 150°C (8°C/min)

CARRIER GAS: Helium, 5.0 mL/min

COLUMN: Capillary, fused silica, 30-m x 0.53-mm ID, 3-µm film crossbonded® 35% diphenyl-65% dimethyl polysiloxane or equivalent

CALIBRATION: Solutions of analytes in CS_2

RANGE: (1) 0.9 to 8240 µg [1,2]
(2) 1.5 to 275 µg [1]

ESTIMATED LOD: (1) 0.4 µg/sample (Instrumental)[1]
(2) 0.5 µg/sample (Instrumental)[1]

PRECISION ($\bar{S}_r$): (1) 0.009 (2) 0.025 [1]

APPLICABILITY: The working range for methyl methacrylate is 0.07 to 670 ppm (0.30 to 2747 mg/m³) and for ethyl methacrylate is 0.11 to 19.7 ppm (0.50 to 91.7 mg/m³) for a 3-L air sample.

INTERFERENCES: None identified. Chromatographic conditions may be modified to resolve any interferences.

OTHER METHODS: This method updates NMAM 2537, Issue 2 (4th ed.) [4] which previously revised NIOSH method S43 [5]. Improvements include the evaluation and addition of ethyl methacrylate to the method, higher desorption efficiency (DE) recoveries at lower study levels for both analytes, lowered LOD values, the incorporation of capillary column chromatography for analyte resolution, and the completion of a 30 day storage stability study.

REAGENTS:

1. Methyl methacrylate, ACS reagent grade.*
2. Ethyl methacrylate, ACS reagent grade.*
3. Carbon disulfide, low benzene grade.*
4. Helium, prepurified.
5. Hydrogen, prepurified.
6. Air, filtered, compressed.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 8-mm OD, 6-mm ID, flame sealed ends with plastic caps, containing two sections (front = 400 mg, back = 200 mg) of XAD-2 resin (20/50 mesh), separated by silylated glass wool plugs (SKC # 226-30-06 or equivalent).
2. Personal sampling pump, 0.01 to 0.05 L/min, with flexible tubing attached.
3. Gas chromatograph, flame ionization detector, suitable integrator system, and Rtx®-35 or equivalent fused silica capillary column.
4. Syringes, 10-µL, 25-µL, 250-µL, and 1-mL.
5. Flasks, 10-mL volumetric type.
6. Vials, 5-mL, glass with PTFE-lined screw caps, and 2-mL autosampler vials.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and a dangerous fire and explosion hazard (flash point = -30°C) so work in a hood is mandatory. Methyl and ethyl methacrylate are strong irritants and lachrymators.

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 a known flow rate between 0.01 to 0.05 L/min for a sample size of 1 to 8 L.
4. Cap the samplers. Pack securely in dry ice for shipment.

SAMPLE PREPARATION:

5. Place the front (along with first glass wool plug) and back sorbent sections in separate 5-mL vials. Discard remaining plugs.
6. Add 2.0 mL of carbon disulfide to each vial and cap securely.
7. Place each vial in a sonication bath for 30 minutes.
8. After sonication, transfer aliquots from each sample to 2 mL autosampler vials and attach crimp caps.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards from below the LOD to 10 times the LOQ. If necessary additional standards may be added to extend the calibration curve.
   a. Add known amounts of calibration standards to carbon disulfide solvent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11and 12).
   c. Prepare calibration graph (peak area vs. µg analyte).
10. Determine the desorption efficiency (DE) at least once for each lot of XAD-2 used for sampling in the calibration range (step 9).
    a. Prepare three tubes at each of five levels plus three media blanks.
    b. Inject a known amount of calibration stock solution directly onto the front sorbent section of each XAD-2 tube.

c. Allow the tubes to air equilibrate for several minutes, then cap the ends of the tubes and allow to stand overnight.
d. Desorb (steps 5-8) and analyze together with standards and blanks (steps 11 and 12).
e. Prepare a graph of DE vs. µg analyte recovered.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2537-1. Inject a 1-µL sample aliquot manually using the solvent flush technique or with an autosampler.

    NOTE: If peak area is above the linear range of the working standards, dilute with the carbon disulfide solvent, reanalyze and apply the appropriate dilution factor corrections in the calculations.
12. Measure peak areas.

CALCULATIONS:

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

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

NOTE: µg/L=mg/m^3

EVALUATION OF METHOD:

Initial Method Development Effort (Issues 1 and 2)

Method S43 (methyl methacrylate) was issued on July 6, 1979, and validated over the range of 193 to 725 mg/m^3 [3]. Average DE recovery results achieved in two independent studies were 98.1% [3] and 96-100% [5] over the range of 560 to 2350 µg/sample. Overall precision (S_{rT}) was estimated to be 0.063. Breakthrough volume was 6.46 L at a generated air concentration of 786 mg/m^3 for methyl methacrylate under conditions of 90% relative humidity [3]. Subsequent storage stability results indicated that methyl methacrylate was stable for 32 days (97.3%) and ethyl methacrylate for 23 days (95-100%) @ 4°C [5].

Current Method Development Effort (Issue 3) [1]

The current method development effort was the result of requests to evaluate and improve problematic gas chromatography methods as part of the NMAM methods update project. Initial evaluations confirmed that XAD-2 (400/200 mg) sorbent tubes were still the most suitable media for the sampling and analysis of both methyl and ethyl methacrylate. The average DE recoveries, using substantially lower analyte concentration ranges than in previous studies (10x LOQ to 0.1x REL vs. 0.5x REL to 2.0x REL), were 100.4% for methyl methacrylate and 102.3% for ethyl methacrylate. The LOD values for both methyl and ethyl methacrylate were lowered by a factor of 20 to 0.4 and 0.5 µg/sample, respectively. A 31-day storage stability study was completed for both methyl methacrylate (96.2% @ 0.05x REL/PEL) and ethyl methacrylate (99.8% @ 0.05x REL/PEL) at 5°C.

REFERENCES:

[1] Pendergrass SM [1999]. Method Development Effort Backup Data Report for Methyl and Ethyl Methacrylate, NIOSH, DPSE, ARDB, ACS, (unpublished).
[2] Tanguay JF [1988]. Method Modification Effort for Methyl Methacrylate, NIOSH, DPSE, MRSB, (unpublished).
[3] NIOSH [1979]. Backup Data Report for Methyl Methacrylate (S43), prepared under NIOSH Contract 210-76-0123.
[4] NIOSH [1994]. Methyl Methacrylate: Method 2537, Issue 2. In: Eller PM, Cassinelli ME, eds. NIOSH Manual of Analytical Methods, 4th ed. Cincinnati, OH: U.S. Dept. of Health and Human Services, Public Health Service, Center for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113.
[5] NIOSH [1980]. Methyl Methacrylate, Method S43. In:Taylor DG, ed. NIOSH Manual of Analytical Methods, 2nd ed., Vol. 6. Cincinnati, OH: U.S. Dept. of Health and Human Services, Public Health Service, Center for Disease Control. DHHS (NIOSH) 80-125.

METHOD WRITTEN BY:

ISSUE 1 and 2:

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ISSUE 3:

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