

METHYL ACRYLATE

2552

C₄H₆O₂

MW: 86.1

CAS: 96-33-3

RTECS: AT2800000

METHOD: 2552, Issue 1

EVALUATION: PARTIAL

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OSHA: 10 ppm
NIOSH: 10 ppm
ACGIH: 2 ppm (skin notation)
 (1 ppm = 3.52 mg/m³)

PROPERTIES: flammable liquid; den = 0.9574 g/mL @ 20°C; BP = 80.5°C; VP = 65 mm Hg @ 20°C; Flash Point = -3°C; FP = -76.7°C; Vapor Density = 2.95.

SYNONYMS: Methoxycarbonylethylene, Methyl ester of acrylic acid, Methyl propenoate, 2-propenoic acid methyl ester.

SAMPLING		MEASUREMENT	
SAMPLER:	SOLID SORBENT TUBE (Anasorb CMS, 150/75 mg)	TECHNIQUE:	GAS CHROMATOGRAPHY, FID
FLOW RATE:	0.01 to 0.2 L/min	ANALYTE:	methyl acrylate
VOL-MIN:	1 L @ 10 ppm	DESORPTION:	1 mL of carbon disulfide with agitation.
-MAX:	5 L	INJECTION VOLUME:	1 µL
SHIPMENT:	Keep cold; pack securely for shipment.	TEMPERATURE	
SAMPLE STABILITY:	30 days @ 5°C	-INJECTION:	250 °C
BLANKS:	2 - 10 field blanks per set	-DETECTOR:	300 °C
		-COLUMN:	35 °C (hold 3 min) to 150 °C (8°C/min)
		CARRIER GAS:	He (2.6 mL/min)
		COLUMN:	Capillary, fused silica, 30-m x 0.53-mm ID; 3µm film crossbonded@ 35% diphenyl-65% dimethyl polysiloxane or equivalent
		CALIBRATION:	Solutions of methyl acrylate in CS ₂
		RANGE:	1.9 to 172.3 µg per sample [1]
		ESTIMATED LOD:	0.5 ug per sample [1]
		PRECISION (S_r):	0.007 [1]
ACCURACY			
RANGE STUDIED:	Not studied.		
BIAS:	Not determined.		
OVERALL PRECISION (S_{r,t}):	Not determined.		
ACCURACY:	Not determined.		

APPLICABILITY: The working range is 0.11 to 9.79 ppm (0.39 to 34.5 mg/m³) for a 5 L air sample [1]. Method is applicable to any sampling environment where methyl acrylate is present in the vapor state.

INTERFERENCES: Any compound eluting during the analysis and having a similar retention time.

OTHER METHODS: This method updates NMAM 1459 [2] which is Method S38 from the 2nd edition of the NIOSH Manual of Analytical Methods [3]. Improvements include but are not limited to the following: smaller volume of desorption solvent required, desorption efficiency (DE) results were improved by using a different solid sorbent tube, and a lower LOD/LOQ was established [1]. A storage stability study was completed and was found acceptable with a 105.3% recovery after 4 weeks at 5°C [1].

REAGENTS:

1. Methyl acrylate, reagent grade (99.9+).*
2. Carbon disulfide, chromatographic grade*.
3. Helium, purified.
4. Hydrogen, purified.
5. Air, prefiltered and purified.
6. Calibration stock: Dilute 3 μL of Methyl acrylate in 10 mL solvent. Prepare remaining standards by serial dilution.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: glass tube, 7 cm long x 6-mm ID, containing two sections of Anasorb CMS separated by a 3-mm section of polyurethane foam. Silanized glass wool plugs hold each section in place. Tubes are commercially available (SKC # 226-121 or equivalent).
2. Personal sampling pump, 0.01 to 0.2 L/min, with flexible tubing.
3. Gas chromatograph, flame ionization detector (FID), integrator, and Rtx-35 fused silica capillary column.
4. Autosampler vials, glass, 12-mm crimp caps.
5. Syringes, 10- μL to 1-mL.
6. Volumetric flasks, 10-mL.
7. Pipets, various sizes.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and flammable and should be handled in a well ventilated fume hood. Methyl acrylate reacts violently with strong oxidants resulting in an explosion and fire hazard. Methyl acrylate polymerizes easily under the effects of heat, light, and peroxides.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sample tube in line.
2. Break open the ends of the sample tube immediately prior to sampling. Attach sample tube to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for a total sample size of 1 to 5 L.
4. Cap both ends of the sample tubes with plastic caps and pack cold for shipment.

SAMPLE PREPARATION:

5. Place the initial glass wool plug and front sorbent section of the sample tube into autosampler vial. Place the back sorbent section of the sample tube in separate autosampler vial. Discard the polyurethane foam separator and the remaining glass wool plug.
6. Add 1.0 mL of carbon disulfide to each vial and cap securely.
7. Let each vial stand for 30 minutes with occasional agitation.
8. Analyze each sample by GC.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working calibration 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 stock solution to carbon disulfide solvent 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. μg methyl acrylate).
10. Determine the desorption efficiency (DE) at least once for each lot of Anasorb CMS 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 Anasorb CMS 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 methyl acrylate recovered.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2552-1. 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 carbon disulfide solvent, reanalyze and apply the appropriate dilution factor in the calculations.

12. Measure peak areas.

CALCULATIONS:

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

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

NOTE: $\mu\text{g}/\text{L} = \text{mg}/\text{m}^3$

EVALUATION OF METHOD:

This method development was a result of requests to update and improve problematic gas chromatography methods. After determining that Anasorb CMS sorbent tubes resulted in improved DE recoveries when compared to the results previously obtained using coconut shell charcoal tubes [1], the desorption efficiency was determined for methyl acrylate at 5 levels ranging from 19.2 μg to 172.3 μg . The average DE for methyl acrylate was determined to be 92.3% using Anasorb CMS sorbent tubes [1] while the previously determined DE for methyl acrylate using charcoal tubes was 81% [4]. The LOD was determined to be 0.5 μg per sample. The precision, as determined from the pooled relative standard deviation (S_r), was determined to be 0.007. Methyl acrylate storage stability @ 0.5xREL was acceptable after 30 days (105.3%) [1].

REFERENCES:

- [1] Pendergrass SM [1999]. Backup Data Report for Methyl Acrylate Method Development, NIOSH/MRSB, Cincinnati, OH., (unpublished, January).
- [2] NIOSH [1984]. Methyl Acrylate: Method 1459 (supplement issued 8/15/94). In: Eller PM, ed. NIOSH Manual of Analytical Methods. 3rd rev. ed. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 84-100.
- [3] NIOSH [1978]. Method S38 In: Taylor DG, ed. NIOSH Manual of Analytical Methods, 2nd ed., Vol. 2. U.S. Department of Health, Education, and Welfare, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health. DHEW(NIOSH)Publ. No.77-157-B.
- [4] NIOSH [1977]. Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

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