MALEIC ANHYDRIDE

$C_4H_2O_3$ MW: 98.06 CAS: 108-31-6 RTECS: ON3675000

METHOD: 3512, Issue 1 **EVALUATION: FULL** **Issue 1: 15 August 1994**

OSHA : 0.25 ppm TWA
NIOSH: 0.25 ppm TWA
ACGIH: 0.25 ppm TWA
(1 ppm = 4.01 mg/m^3 @ NTP)

PROPERTIES: solid; MP 53 °C; d 1.43 @ 22 °C; VP <0.16 mm Hg @ 20 °C; vapor density (air = 1) 3.38

SYNONYMS: 2,5-furandione; cis-butenedioic anhydride; toxilic anhydride

SAMPLING

SAMPLER: BUBBLER
(15 mL distilled water)

FLOW RATE: 0.2 to 1.5 L/min

VOL-MIN: 40 L @ 1.0 mg/m^3
-MAX: 500 L

SHIPMENT: plug inlet and outlet with Teflon plugs to prevent spillage during shipment.

SAMPLE STABILITY: less than 7 days @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.50 to 2.14 mg/m^3 [1] (340-L samples)

BIAS: - 6.7%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.063 [1]

ACCURACY: ± 19.0%

MEASUREMENT

TECHNIQUE: HPLC, UV DETECTION

ANALYTE: maleic anhydride

INJECTION VOLUME: 50 µL

MOBILE PHASE: 0.5% dicyclohexylamine/0.5% formic acid/25% methanol/74% water, 1.7 mL/min

COLUMN: µ-Bondapak C_{18}, 10-µm particle size, 30 cm x 3.9-mm ID or equivalent

DETECTOR: UV @ 254 nm

CALIBRATION: standard solutions of maleic anhydride in acetone and distilled water

RANGE: 36 to 1080 µg per sample [1]

ESTIMATED LOD: 15 µg per sample [2]

PRECISION ($\bar{S}_r$): 0.035 @ 181 to 723 µg per sample [1]

APPLICABILITY: The working range is 0.025 to 0.75 ppm (0.1 to 3 mg/m^3) for a 360-L air sample. This method does not distinguish between maleic anhydride and maleic acid, and has limited sample stability [1].

INTERFERENCES: Since maleic anhydride is converted to maleic acid, maleic acid can be considered an interference and will result in a positive bias.

OTHER METHODS: This revises Method P&CAM 302 [2]. Geyer and Saunders reported a modified mobile phase for the determination of maleic anhydride, but used the same sampling technique [3]. A method for the trace analysis of maleic a nhydride in workplace air was published by Kallio [4].

REAGENTS:

1. Maleic Anhydride *, ACS reagent grade.
2. Dicyclohexylamine, ACS reagent grade.
3. Formic acid, ACS reagent grade.
4. Methanol, distilled in glass.
5. Acetone, distilled in glass.
6. Water, deionized and distilled.
7. Calibration stock solution, 1 mg/mL. Dissolve 10 mg maleic anhydride in 10 mL acetone.
8. Mobile Phase: Dilute 10 mL of dicyclohexylamine and 10 mL of formic acid to 100 mL with distilled water. Dilute 10 mL of this solution, plus 250 mL methanol, to 1 L with distilled water.

* See Special Precautions

EQUIPMENT:

1. Sampler: A 25-mL bubbler with 15 mL distilled water.
2. Personal sampling pump, 0.2 to 1.5 mL/min, with flexible polyethylene or Teflon tubing.
3. Teflon plugs and/or tubing.
4. Liquid chromatograph with a UV detector, recorder, integrator and column (page 3512-1).
5. Syringes, 50-1000-µL.
6. Volumetric flasks, 10-, 100-, and 1000-mL.
7. Pipets, 10- and 15-mL glass, delivery, with pipet bulb.
8. Graduated cylinders, glass, 25-mL.

SPECIAL PRECAUTIONS: Maleic anhydride is a powerful irritant. Avoid contact with skin, eyes, and respiratory tract [5].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Transfer 15 mL distilled water to a bubbler.
3. Connect outlet arm of bubbler to a second empty bubbler and then to the sampling pump.
4. Sample 40 to 500 L of air at an accurately known rate between 0.2 and 1.5 L/min.
5. Seal bubbler for shipment in a suitable container in order to prevent damage during transit. Seal the inlet and outlet of the bubbler stem by connecting a piece of Teflon tubing between them or by inserting Teflon plugs in the inlet and outlet.
6. Collect a bulk sample (ca. 1 g) in a glass vial and ship it separately.

SAMPLE PREPARATION:

7. Transfer the liquid from the bubbler, quantitatively, to a graduated cylinder.
8. Bring volume to 15 mL with distilled water.

CALIBRATION AND QUALITY CONTROL:

9. Prepare working standards (20 to 800 µg/10 mL) by adding appropriate aliquots of calibration stock solution to distilled water.
10. Analyze working standards together with samples and blanks (steps 11 through 13). Prepare a calibration graph of area vs. µg of maleic anhydride per 15 mL of sample.

MEASUREMENT:

11. Set liquid chromatograph to conditions given on page 3512-1.
12. Inject 50-µL sample aliquot.
13. Measure peak area.

CALCULATIONS:

14. Read mass, µg, of maleic anhydride (W) found in the sample from the calibration graph.
15. Calculate concentration of maleic anhydride in the actual air volume, V (L), at the sampling site:

$$C = \frac{W}{V}, \ \mu g/m^3.$$

EVALUATION OF METHOD:

This method was validated over the range 0.50 to 2.14 mg/m ^{3} at 20 °C and pressure of 757 mm Hg using 360-L samples [1,2]. Overall sampling and measurement precision, $\hat{S}_{rT}$, was 0.063, with a bias of - 6.7%. Recovery of maleic anhydride was 104% in the range of 181 to 723 µg maleic acid per sample. Sample stability during storage was evaluated at 367 µg per sample. Samples showed an average loss of 13% after seven days of storage at ambient conditions compared to one-day old samples. Refrigeration of samples may retard loss but this has not been experimentally determined.

REFERENCES:

[1] Backup Data Report for Maleic anhydride, prepared under NIOSH Contract 210-76-0123 (1977).
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 5, P&CAM 302, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[3] Geyer, R. and Saunders, G. A. Determination of Maleic Anhydride in Workplace Air by Reverse Phase HPLC, J. Chromatogr., 368 (2), 456-458 (1986).
[4] Kallio, H. Determination of Trace Concentrations of Maleic Anhydride in Workplace Air, Khig. Zdraveopaz, 32 (3), 86-94 (1989).
[5] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, 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.

METHOD REVISED BY:

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