CH_3NHNH_2 MW: 46.07 CAS: 60-34-4 RTECS: MV5600000

METHOD: 3510, Issue 1 **EVALUATION: FULL** **Issue 1: 15 August 1994**

OSHA : C 0.2 ppm (skin)
NIOSH: C 0.04 ppm/120 min; carcinogen
ACGIH: C 0.2 ppm (skin; Suspect Carcinogen)
(1 ppm = 1.88 mg/m^3 @ NTP)

PROPERTIES: liquid; MP -52.4 °C; BP 87.5 °C; d 0.874 g/mL @ 25 °C; VP 6.6 kPa (49.6 mm Hg) @ 25 °C; vapor density (air = 1) 1.59; flammability limits in air 2.5 to 97% v/v

SYNONYMS: hydrazomethane; 1-methylhydrazine; methylhydrazine

SAMPLING

SAMPLER: BUBBLER
(0.1 M hydrochloric acid)

FLOW RATE: 0.5 to 1.5 L/min

VOL-MIN: 3 L @ 0.2 ppm
-MAX: 20 L

SHIPMENT: remove bubbler stem and rinse with 0.1 M hydrochloric acid; seal bubblers with non-reactive stopper

SAMPLE STABILITY: at least five days @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.17 to 0.78 mg/m^3 [1] (20-L samples)

BIAS: - 3.4%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.106 [1]

ACCURACY: ± 21.6%

MEASUREMENT

TECHNIQUE: VISIBLE SPECTROPHOTOMETRY

ANALYTE: monomethylhydrazine phosphomolybdic acid complex

DILUTION: 7.5 mL of phosphomolybdic acid solution and 0.1 M hydrochloric acid to 25 mL

WAVELENGTH: 730 nm; 5-cm cell

CALIBRATION: standard solutions of monomethylhydrazine sulfate in 0.1 M hydrochloric acid

RANGE: 1 to 100 µg per sample [1]

ESTIMATED LOD: 0.7 µg per sample [2]

PRECISION ($\hat{S}_r$): 0.029 @ 3.9 to 16.0 µg per sample [1]

APPLICABILITY: The working range is 0.027 to 2.7 ppm (0.05 to 5 mg/m ^{3}) for a 20-L air sample. This method is applicable to STEL and ceiling measurements.

INTERFERENCES: Other hydrazines, as well as stannous ion, ferrous ion, zinc, sulfur dioxide and hydrogen sulfide, may give a positive interference. Negative interference in the method may occur by oxidation of the monomethylhydrazine by haloge ns, oxygen(especially in the presence of copper (I) ions) and hydrogen dioxide.

OTHER METHODS: This revises Method S149 [2]. Method P&CAM 248 [3] describes an acid-coated silica gel sorbent tube/gas chromatographic method for the determination of hydrazine, monomethylhydrazine, 1,1-dimethylhydrazine and phenylhydrazin e, but sample stability problems have been noted with it [4].

REAGENTS:

1. Methylhydrazine sulfate *, ACS reagent grade.
2. Hydrochloric acid, ACS reagent grade.
3. Collection medium, 0.1 M hydrochloric acid. To 300 mL of distilled water in a 1000-mL volumetric flask, add 8.6 mL of concentrated hydrochloric acid with caution. Mix and bring to volume with distilled water.
4. Phosphomolybdic acid solution. Dissolve 15 g of phosphomolybdic acid in 500 mL distilled water, allow to stand one day, and filter before use through a fluted paper filter.
5. Water, deionized and distilled.
6. Calibration stock solution, 1 mg/mL. Weigh 100 mg of methylhydrazine sulfate in a 100-mL volumetric flask and fill to the mark with 0.1 M hydrochloric acid.

* See Special Precautions

EQUIPMENT:

1. Sampler: 25-mL bubbler with 15 mL 0.1 M hydrochloric acid.
2. Personal sampling pump, 1.5 L/min, with flexible polyethylene or PTFE tubing.
3. Glass or non-reactive stopper for bubbler.
4. Glass tube, 5 cm long by 6-mm I.D., loosely packed with glass wool.
5. Spectrophotometer, set at 730 nm.
6. Spectrophotometer cells, 5-cm.
7. Test tube, large.
8. Volumetric flasks, 25-mL, 100-mL, 500-mL, 1000-mL.
9. Pipets, 10-, 15-, 25-, and 50-µL; 10- and 15-mL glass, delivery, with pipet bulb.
10. Graduated cylinders, glass, 10-mL, 25-mL.
11. Water bath at 87 °C.
12. Stopwatch.
13. Thermometer, ca. 0-120 °C.

SPECIAL PRECAUTIONS: Monomethylhydrazine may be fatal if inhaled, swallowed or absorbed through skin contact [5,6]. Contact may cause burns to skin and eyes. Vapor may cause irritation to eyes, nose, throat, and skin. Handle with caution and use appropriate protective equipment.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Transfer 15 mL 0.1 M hydrochloric acid to a bubbler.
3. Connect outlet arm of bubbler to the glass-wool-packed tube (to prevent splashover into the pump) and then to the sampling pump with the flexible tubing.
4. Sample at an accurately known rate between 0.5 and 1.5 L/min for a total air sample of 3 to 20 L.
5. Remove bubbler stem and rinse with 0.1 M hydrochloric acid into bubbler body. Seal bubbler with an inert stopper for shipment in a suitable container in order to prevent damage during transit.

SAMPLE PREPARATION:

6. Transfer the liquid from the bubbler, quantitatively, to a 25-mL volumetric flask.
7. Add 7.5 mL of phosphomolybdic acid solution and bring volume to 25 mL with 0.1 M hydrochloric acid.
8. Transfer an aliquot of this solution to a large test tube and heat to 87 °C for 50 min. Place test tube under running tap water to cool before measurement.

CALIBRATION AND QUALITY CONTROL:

9. Prepare working standards over the range of 10 to 100 µg/25 mL.
   a. Add aliquots (10, 25, 50 and 100 µL) of calibration stock solution to 15 mL of 0.1 M hydrochloric acid in 25-mL volumetric flasks. Prepare a reagent blank using only 15 mL of

0.1 M hydrochloric acid.

b. Add 7.5 mL of phosphomolybdic acid solution to all standards and blank and bring the volume up to 25 mL with 0.1 M hydrochloric acid.
c. Transfer aliquots of these solutions to large test tubes and heat to 87 °C for 50 min.
d. Place test tubes under running tap water to cool before measurement.
e. Analyze working standards together with samples and reagent blanks (steps 10 through 12) on a spectrophotometer at 730 nm, using a 5-cm cell. Correct standards for reagent blank absorbance.
f. Prepare a calibration graph of absorbance vs. amount (µg) of monomethylhydrazine per sample.

MEASUREMENT:

10. Set spectrophotometer according to manufacturer's recommendations and to conditions on p. 3510-1 to monitor 730 nm.
11. Fill 5-cm sample cell with sample or standard.
12. Measure absorbance.

CALCULATIONS:

13. Determine mass, µg, of monomethylhydrazine found in the sample (W) and blank (B) from the calibration graph.
15. Calculate concentration of monomethylhydrazine in the actual air volume, V (L):

$$C = \frac{W - B}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

This method was evaluated over the range 0.17 to 0.78 mg/m ^{3} using 20-L samples [1,2]. Overall sampling and measurement precision, $\hat{S}_{rT}$, was 0.106. Collection efficiency of the bubblers was determined to be 96.5% at 1.7 mg/m ^{3} for a 20-L sample. Sample stability during storage was evaluated at 8 µg monomethylhydrazine per sample. Samples showed 104.4% recovery after five days of storage at ambient conditions compared to one-day old samples.

REFERENCES:

[1] Backup Data Report for Monomethylhydrazine, prepared under NIOSH Contract 210-76-0123 (1977).
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 4, S149, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[3] NIOSH Manual of Analytical Methods, 2nd. ed., V. 4, P&CAM 248, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[4] L.R. Cook, R.E. Glenn and G.E. Podolak, Am. Ind. Hyg. Assoc. J., 40, 69-74 (1979).
[5] NIOSH Criteria for a Recommended Standard....Occupational Exposure to Hydrazines, DHEW (NIOSH) Publ. No. 78-122 (1978).
[6] NIOSH/OSHA Occupational Guidelines for Chemical Hazards, U.S. Department of Health and Human Services Publ. (NIOSH) 81-123 (1981), available as GPO Stock #17-033-00337-8 from Superintendent of Documents, Washington, D.C. 20402.

METHOD REVISED BY:

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