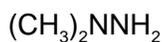


1,1-DIMETHYLHYDRAZINE

3515



MW: 60.10

CAS: 57-14-7

RTECS: MV2450000

METHOD: 3515, Issue 1

EVALUATION: PARTIAL

Issue 1: 15 August 1994

OSHA : C 0.5 ppm (skin)
NIOSH: C 0.06 ppm/120 min; carcinogen
ACGIH: C 0.5 ppm (skin); suspected human carcinogen
 (1 ppm = 2.46 mg/m³ @ NTP)

PROPERTIES: liquid; MP - 58 °C; BP 63 °C; d 0.80 @ 20 °C; VP 157 mm Hg @ 25 °C; vapor density (air = 1) 2.07; flash point - 15 °C (closed cup); flammable range 2 to 95% v/v in air

SYNONYMS: dimazine; unsym-dimethylhydrazine; N,N-dimethylhydrazine.

APPLICABILITY: The working range is 0.008 to 1 ppm (0.02 to 2.5 mg/m³) for a 100-L air sample. This method is also applicable to ceiling measurements.

INTERFERENCES: Other hydrazines, as well as, stannous ion, ferrous ion, zinc, sulfur dioxide, and hydrogen sulfide, may give a positive interference. Negative interferences in the method may occur by oxidation of the 1,1-dimethylhydrazine by halogens, oxygen (especially in the presence of copper (I) ion) and hydrogen dioxide.

OTHER METHODS: This revises Method S143 [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 phenylhydrazine. Sample stability problems have been noted with P&CAM 248 [4].

REAGENTS:

1. 1,1-Dimethylhydrazine,* 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 through a fluted paper filter.
5. Water, deionized and distilled.
6. Calibration stock solution, 1 mg/mL. Weigh 500 mg of 1,1-dimethylhydrazine in a 100-mL volumetric flask and fill to the mark with 0.1 M hydrochloric acid.

EQUIPMENT:

1. Sampler: 25-mL bubbler with 10 mL 0.1 M hydrochloric acid.
2. Personal sampling pump, 0.2 to 1.0 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. 1-cm spectrophotometer cells.
7. Test tube, large.
8. Volumetric flasks, 50-mL, 100-mL, 500-mL, 1000-mL.
9. Pipets, 10-, 15-, 25, and 50- μ L; 10- and 15-mL glass, delivery, with pipet bulb.
10. Graduated cylinders, glass, 10-mL, 25-mL.
11. Water bath at 95 °C.
12. Stopwatch.
13. Thermometer, ca. 0-120 °C.

* See SPECIAL PRECAUTIONS.

SPECIAL PRECAUTIONS: 1,1-Dimethylhydrazine may be fatal if inhaled, swallowed or absorbed through the skin [5]. Contact may cause burns to skin and eyes. Vapor may be irritating to the eyes, skin, and mucous membranes. Handle with caution and use appropriate protective equipment.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Transfer 10 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 of 0.2 to 1.0 L/min for total sample size of 2 to 100 L.
5. Remove bubbler stem and rinse with 2 mL of 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 volumetric flask.
7. Add 10 mL of phosphomolybdic acid solution and bring volume to 50 mL with 0.1 M hydrochloric acid.
8. Transfer an aliquot of this solution to a large test tube and heat to 95 °C for 60 min. Place test tube under running tap water to cool before measurement.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards to cover the range of 1 to 250 μ g 1,1-dimethylhydrazine per sample.

- a. Add appropriate aliquots (10, 20, 30, 40 and 50 μL) of calibration stock solution to 10 mL of 0.1 M hydrochloric acid in 50-mL volumetric flasks. Prepare a reagent blank using only 10 mL of 0.1 M hydrochloric acid.
- b. Treat with (steps 7 and 8) phosphomolybdic acid solution.
- c. Analyze working standards together with samples and reagent blanks (steps 10 through 12) on a spectrophotometer at 730 nm, using a 1-cm cell. Correct standards for reagent blank absorbance.
- d. Prepare a calibration graph of absorbance vs. amount (μg) of 1,1-dimethylhydrazine per 50 mL of sample.

MEASUREMENT:

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

CALCULATIONS:

13. Determine mass, μg , of analyte found in sample (W) and average reagent blank (B).
14. Calculate concentration (C) of 1,1-dimethylhydrazine in the air volume sampled V (L):

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

EVALUATION OF METHOD:

This method was evaluated over the range 0.5 to 2.3 mg/m^3 using 91-L samples [1]. Sampling and measurement precision, \hat{S}_{rT} was 0.062 for samples collected at the OSHA standard. Bias could not be determined owing to instability of the 1,1-dimethylhydrazine in the generator. Collection efficiency of the bubblers was determined to be 99.1% at 2.2 mg/m^3 . Sample stability during storage was evaluated at 100 μg 1,1-dimethylhydrazine per sample. Samples showed 101.3% recovery after five days of storage at ambient conditions.

REFERENCES:

- [1] Backup Data Report for 1,1-Dimethylhydrazine, prepared under NIOSH Contract 210-76-0123 (1977).
- [2] NIOSH Manual of Analytical Methods, 2nd e.d., V. 3, S143, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
- [3] NIOSH Manual of Analytical Methods, 2nd e.d., V. 4, 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/OSHA Occupational Health 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.

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