1,1-DIMETHYLHYDRAZINE

\[(\text{CH}_3)\text{NNH}_2\]  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/m\(^3\) @ 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.

SAMPLING

SAMPLER: BUBBLER (0.1 M hydrochloric acid)
FLOW RATE: 0.2 to 1.0 L/min
VOL-MIN: 2 L @ 0.5 ppm
-MAX: 100 L
SHIPMENT: remove bubbler stem and rinse with 0.1 M hydrochloric acid; seal bubbles with non-reactive stopper
SAMPLE STABILITY: at least 5 days @ 25 °C
BLANKS: 2 to 10 field blanks per set

TECHNIQUE: VISIBLE SPECTROPHOTOMETRY

ANALYTE: complex of phosphomolybdic acid and 1,1-dimethyl hydrazine

PROCEDURE: add phosphomolybdic acid; heat sample solution at 95 °C for 60 min; cool solution under tap water; transfer sample to 1-cm cell; read absorbance at 730 nm

CALIBRATION: standard solutions of 1,1-dimethylhydrazine in 0.1 M hydrochloric acid

RANGE: 2 to 250 µg per sample [1]
ESTIMATED LOD: 1 µg per sample [2]

PRECISION (S\(_p\)): 0.072 [1]

ACCURACY

RANGE STUDIED: 0.506 to 2.22 mg/m\(^3\) [1] (91-L samples)
BIAS: - 1.9%
OVERALL PRECISION (\(\bar{S}_{\text{PR}}\)): 0.062 [1]
ACCURACY: ± 14.0%

APPLICABILITY: The working range is 0.008 to 1 ppm (0.02 to 2.5 mg/m\(^3\)) 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.

* See SPECIAL PRECAUTIONS.

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.
10. Graduated cylinders, glass, 10-mL, 25-mL.
11. Water bath at 95 °C.
12. Stopwatch.
13. Thermometer, ca. 0-120 °C.

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 µg 1,1-dimethyl hydrazine 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):

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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, $S_{\bar{x}}$, 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:


METHOD REVISED BY:

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