H_2NNH_2 MW: 32.05 CAS: 302-01-2 RTECS: MU7175000

METHOD: 3503, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : 1 ppm (skin)
NIOSH: C 0.03 ppm/120 min(suspect carcinogen)
ACGIH: 0.1 ppm (skin; suspect carcinogen)
(1 ppm = 1.31 mg/m^3 @ NTP)

PROPERTIES: liquid; d 1.004 g/mL @ 25 °C;
BP 113.5 °C; MP 2 °C; VP 1.92 kPa
(14.4 mm Hg; 18,900 ppm) @ 25 °C)

SYNONYMS: diamide; diamine

SAMPLING

SAMPLER: BUBBLER
(15 mL 0.1 M HCl)

FLOW RATE: 0.2 to 1.0 L/min

VOL-MIN: 7 L @ 1 ppm
-MAX: 100 L

SHIPMENT: routine

SAMPLE STABILITY: ≥ 6 days @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.59 to 3.4 mg/m^3 [1]
(91-L samples)

BIAS: - 0.3%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.094 [1]

ACCURACY: ± 17.1%

MEASUREMENT

TECHNIQUE: SPECTROPHOTOMETRY, VISIBLE ABSORPTION

ANALYTE: quinoid derivative of p-dimethylaminobenzaldazine [2]

COMPLEXATION: p-dimethylaminobenzaldehyde; stand 30 min; acetic acid

FINAL VOLUME: 625 mL

WAVELENGTH: 480 nm

CALIBRATION: hydrazine in methanol

RANGE: 9 to 400 µg per sample

ESTIMATED LOD: 0.9 µg per sample

PRECISION ($\hat{S}_r$): 0.031 [1]

APPLICABILITY: The working ranges are 0.07 to 3 ppm (0.09 to 4 mg/m ^{3}) for 100-L air samples and 0.45 to 21 ppm (0.6 to 27 mg/m^3) for 15-L air samples. This method is applicable to hydrazine vapor. It has not been tested with aerosol forms. The free base cannot be distinguished from salts, such as hydrazine monohydrochloride and hydrazine sulfate, which are aeros ols.

INTERFERENCES: Methylhydrazine is an interference. Other hydrazines may interfere.

OTHER METHODS: This method is a modification of and replaces Method S237 [2]. Method P&CAM 248 is a gas chromatographic method which can be used for quantitation of hydrazine or substituted hydrazines [3]. Methods S143, S149 and S160 utilize a non-specific colorimetric method for substituted hydrazines [4].

REAGENTS:

1. Hydrochloric acid, 0.1 M. Dilute 8.6 mL conc. HCl to 1 L with distilled water.
2. Methanol, reagent grade.*
3. Calibration stock solution, 1.0 mg/mL. Dissolve 0.10 mL hydrazine* in methanol to make 100 mL solution.
4. Solution of p-dimethylaminobenzaldehyde in methanol, 0.168 M. Dissolve 12.5 g p-dimethylaminobenzaldehyde in methanol to make 500 mL solution.
5. Glacial acetic acid.*
6. Sodium hydroxide solution, 1.8 M. Dissolve 7.2 g NaOH in distilled water to make 100 mL solution.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: midget bubbler, glass, with 15 mL 0.1 M HCl.
2. Glass tube, 5 cm x 6-mm ID, packed loosely with glass wool.
3. Personal sampling pump, 0.2 to 1 L/min, with flexible connecting tubing.
4. Vials, 20-mL, with PTFE-lined screw caps.
5. Spectrophotometer set at 480 nm, with matched cuvettes, glass, 1-cm path length.
6. Volumetric flasks, 25-, 50-, 100- and 500-mL and 1 L.
7. Pipets, 1-, 2-, 10- and 15-mL, with pipet bulb.
8. Syringe, 10-µL, readable to 0.1 µL.
9. Syringe, 50-µL, readable to 1 µL.
10. pH paper.

SPECIAL PRECAUTIONS: Hydrazine is carcinogenic, toxic, and flammable, and can be absorbed through the skin [5].

Acetic acid and methanol are flammable. Wear gloves, handle compounds in a well-ventilated fume cabinet, avoid inhalation of vapors, and protect compounds from sparks and flames.

SAMPLING:

1. Connect the outlet of the sampler and the inlet of the pump to a tube packed with glass wool to protect the pump from splashover.
2. Calibrate the personal sampling pump with sampler in line.
3. Sample at 0.2 to 1.0 L/min for a sample size of 7 to 100 L.
4. Transfer the solution from the bubbler to a glass vial, rinsing both the bubbler stem and body with 1-mL portions of 0.1 M HCl. Cap the vial securely for shipment.

SAMPLE PREPARATION:

5. Transfer bubbler solution to a 50-mL volumetric flask.
6. Rinse vial with 1 mL 0.1 M HCl, and add rinse to the flask.
7. Add 1.8 M NaOH (ca. 1 mL) to make the solution neutral or slightly alkaline to pH paper.
8. Immediately add 10 mL 0.168 M p-dimethylaminobenzaldehyde solution. Agitate the mixture and allow to stand 30 min.
9. Bring volume of solution to 50 mL with glacial acetic acid.
10. Dilute 2 mL of the solution to 25 mL with glacial acetic acid.
11. Prepare field blanks and media blanks according to steps 4 through 10.

CALIBRATION AND QUALITY CONTROL:

12. Calibrate daily with a blank and six working standards over the range 1 to 400 µg hydrazine per sample.
    a. Add aliquots of calibration stock solution to 15 mL 0.1 M HCl in 50-mL volumetric flasks and dilute to the mark. Designate one flask as a blank and do not add hydrazine to that flask.

b. Process the working standards according to steps 7 through 10.
c. Determine absorbance for each solution (steps 13 and 14).
d. Prepare calibration graph (absorbance vs. µg hydrazine).

MEASUREMENT:

13. Set up the spectrophotometer according to manufacturer's instructions. Place blank solution (from step 12.a) into reference cuvette.
14. Determine absorbance of solution at 480 nm.

CALCULATIONS:

15. Determine the quantities of hydrazine in the sample, W (µg), and average media blank, B (µg), from the calibration graph.
16. Calculate the concentration, C (mg/m ^{3}), of hydrazine in the air volume sampled, V (L):

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

EVALUATION OF METHOD:

This method is based on Method S237 using 15 mL of 0.1 M HCl for sampling instead of 10 mL. Method S237 was validated with controlled atmospheres of hydrazine [1]. Overall precision ($\hat{S}_{rT}$) was 0.094 (18 samples, pooled) for 91-L samples at 0.59 to 3.4 mg/m ^{3}. Concentrations of hydrazine in controlled atmospheres were not verified by an independent method. Average collection efficiency at 0.9 L/min for six bubblers was 0.997 at 3.4 mg/m ^{3}. Average recoveries from HCl solution were 1.03, 0.98 and 1.01 at the 60.7-, 121- and 243-µg levels of hydrazine, respectively. The $\bar{S}_r$ for analysis = 0.031 (18 samples, pooled). Samples at the 121-µg level were stable during storage in 0.1 M HCl for six days at room temperature.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S237, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 3, S237, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[3] Ibid. V. 1, P&CAM 248, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[4] Ibid. S143, S149, S160.
[5] Criteria for a Recommended Standard...Occupational Exposure to Hydrazine, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-172 (1978).
[6] Dambrauskas, T., and H. H. Cornish. Am. Ind. Hyg. Assoc. J., 23, 151-156 (1962).

METHOD REVISED BY:

Samuel P. Tucker, Ph.D., NIOSH/DPSE; S237 developed under NIOSH Contract CDC-99-74-45.