



MW: 108.14

CAS: 100-63-0

RTECS: MV8925000

METHOD: 3518, Issue 1

EVALUATION:

Issue 1: 15 August 1994

OSHA : 5 ppm (skin)
 NIOSH: C 0.14 ppm/120 min (skin)
 ACGIH: 5 ppm, STEL 10 ppm, suspect carcinogen
 (1 ppm = 4.42 mg/m³ @ NTP)

PROPERTIES: solid; MP 19.5 °C; d 1.098 g/mL @
 20 °C; VP 5 Pa (0.04 mm Hg; 50 ppm)
 @ 25 °C

SYNONYMS: hydrazinobenzene, hydrazine-benzene

SAMPLING		MEASUREMENT	
SAMPLER:	GLASS MIDGET BUBBLER (containing 15 mL 0.1 M hydrochloric acid)	TECHNIQUE:	VISIBLE ABSORPTION SPECTROPHOTOMETRY
FLOW RATE:	0.2 to 1 L/min	ANALYTE:	phenylhydrazine hydrochloride/ phosphomolybdic acid complex
VOL-MIN:	25 L @ 5 ppm	SAMPLE WORKUP:	transfer bubbler solution, two 5-mL rinses, and 10 mL phosphomolybdic acid to 50-mL volumetric flask
-MAX:	120 L	DILUTION:	3-mL aliquot diluted to 10 mL
SHIPMENT:	hand delivery or use of bubbler shipping cases	COLORIMETRY:	absorbance @ 730 nm
SAMPLE STABILITY:	at least 5 days at room temperature [1]	CALIBRATION:	phenylhydrazine hydrochloride in 0.1 M hydrochloric acid
BLANKS:	2 to 10 field blanks per set	RANGE:	0.5 to 4.4 mg per sample [1]
ACCURACY		ESTIMATED LOD:	0.2 mg per sample [2]
RANGE STUDIED:	10.4 to 44.8 mg/m ³ [1] (100-L samples)	PRECISION (\hat{S}_r):	0.023 [1]
BIAS:	4.8%		
OVERALL PRECISION ($\hat{S}_{r,T}$):	0.060 [1]		
ACCURACY:	± 16.6%		

APPLICABILITY: The working range is 1.1 to 11 ppm (5 to 45 mg/m³) for a 100-L air sample.

INTERFERENCES: Other hydrazines may interfere in the analysis; reducing agents such as ferrous salts may interfere also [2].

OTHER METHODS: This is Method S160 [2] in a revised format. Feinsilver et al. [3] provided the basis for this method. Murty et al. [4] used photometry and photometric titrations with cacotheline as a reagent to determine phenylhydrazine in the range of 0.1 to 2 mg. Hasan [5] determined phenylhydrazine spectrophotometrically over a range of 0.1 to 3.0 mg using copper (II) nitrate.

REAGENTS:

1. Phenylhydrazine hydrochloride*.
2. Hydrochloric acid, concentrated*.
3. Phosphomolybdic acid.
4. Distilled water.
5. Collection medium, 0.1 M HCl. Fill a 1-L volumetric flask with approximately 300 mL distilled water, add 8.6 mL concentrated HCl, mix and dilute to the mark.
6. Phosphomolybdic acid solution (PMA). Dissolve 15 g PMA in 500 mL distilled water, allow to stand one day, and filter before use through a fluted paper filter.
7. Phenylhydrazine hydrochloride stock solution. Weigh accurately 0.1 g phenylhydrazine hydrochloride into a 100-mL volumetric flask and fill to the mark with 0.1 M HCl.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: Glass, standard midget bubbler with a stem that has a fritted glass end. The fritted end should have a maximum pore diameter of approximately 170 to 220 μm .
2. Personal sampling pump, 0.2 to 1 L/min, with flexible connecting tubing. The sampling pump is protected from splashover or water condensation by a 5-cm (6-mm ID and 8-mm OD) glass tube loosely packed with glass wool and inserted between the exit arm of the bubbler and the pump.
3. Spectrophotometer, visible, 730 nm, with cuvettes, 1-cm.
4. Volumetric flasks, 1000-, 100-, 50-, and 10-mL.
5. Pipets, glass, 1-, 2-, 3-, 6-, 9-, and 10-mL, delivery, with pipet bulb.
6. Graduated cylinders, glass, 10- and 25-mL.

SPECIAL PRECAUTIONS: Concentrated hydrochloric acid is extremely corrosive; handle while wearing acid-resistant gloves, apron, and full face shield with goggles. Phenylhydrazine is viewed as a potential carcinogen [6,7] and should be handled in a hood. Exposure to phenylhydrazine has caused hemolytic anemia [6,7]. Phenylhydrazine is a highly reactive reducing agent, and contact with oxides of copper or iron and manganese, lead, copper, or their alloys can cause fires and explosions [7]. Phenylhydrazine will attack cork, some forms of plastics, coatings, and rubber [7].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Transfer 15 mL 0.1 M HCl into each bubbler. Connect the bubbler to trap and trap to pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.2 and 1 L/min for a total sample size of 25 to 120 L.
4. After sampling, tap bubbler stem gently against inside wall of bubbler bottle to recover as much sampling solution as possible. Wash stem with 5 mL distilled water and add wash to bubbler. Prior to shipping, seal bubblers with a hard, non-reactive stopper (preferably PTFE or glass).

SAMPLE PREPARATION:

5. Transfer liquid from bubbler to a 50-mL volumetric flask.
6. Rinse bubbler twice with 5 mL distilled water. Add rinses to volumetric flask.
7. Add 10 mL phosphomolybdic acid solution to volumetric flask and dilute to mark with distilled water.
8. Pipet a 3-mL aliquot into a 10-mL volumetric flask and dilute to mark with distilled water.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards.
 - a. Transfer 15 mL 0.1 M HCl to a 50-mL volumetric flask.
 - b. Pipet 1 to 10 mL of phenylhydrazine hydrochloride stock solution into the volumetric flask.
 - c. Continue preparation as with samples (steps 7 and 8).
 - d. Analyze together with samples and blanks (steps 11 and 12).
 - e. Prepare calibration graph (absorbance vs. mg phenylhydrazine hydrochloride per sample).
10. Analyze three quality control blind spikes and three analyst spikes to ensure that calibration graph is in control.

MEASUREMENT:

11. Set spectrophotometer according to manufacturer's recommendations and to conditions given on p. 3518-1. Fill 1-cm cuvette with sample from 10-mL volumetric flask.
12. Read sample absorbance at 730 nm against a reagent blank prepared in the same manner as the samples (steps 9.a, 7, and 8).

CALCULATIONS:

13. Calculate the mass, mg, of phenylhydrazine hydrochloride in each sample (W) and average field blank (B).
14. Calculate the concentration, C, of phenylhydrazine in the air volume sampled, V (L):

$$C = \frac{W - B}{V} \cdot \frac{108.1}{144.6} \cdot 10^3, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

This method was validated over the range 10.37 to 44.8 mg/m³ at 22 °C and 761 mm Hg using 100-L samples [1,2]. The average recovery was 95%, while the recovery from samples after five days storage was 100% [1]. Sample stability during storage was evaluated at a level of 4.4 mg phenylhydrazine per sample [1].

REFERENCES:

- [1] Documentation of the NIOSH Validation Tests, S160, U.S. Department of Health, Education, and Welfare; Publ. (NIOSH) 77-185 (1977).
- [2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 3, S160, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
- [3] Feinsilver, L. Perregrino, J.A., and Smith, C.J. Jr., "Estimation of Hydrazine and Three of Its Methyl Derivatives," *Am. Ind. Hyg. Assoc. J.*, 20, 26 (1959).
- [4] Murty, N.K., Rao, V.J., and Rao, N.V.S., "Detection and Determination of Phenylhydrazine," *Talanta*, 31 (6), 466 (1984).
- [5] Hasan, T., "Resin Bead Detection and Spectrophotometric Determination of Phenylhydrazine Using Inorganic Reagents," *Anal. Lett.*, 21 (4), 633 (1988).
- [6] NIOSH Criteria for a Recommended Standard: Occupational Exposure to Hydrazines, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-172 (1978).
- [7] NIOSH/OSHA Occupational Health Guidelines for Occupational Hazards, U.S. 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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