$C_5H_5N$ MW: 79.10 CAS: 110-86-1 RTECS: UR8400000

**METHOD: 1613, Issue 2** **EVALUATION: FULL** **Issue 1: 15 August 1987**
**Issue 2: 15 August 1994**

**OSHA :** 5 ppm
**NIOSH:** 5 ppm; Group III Pesticide
**ACGIH:** 5 ppm
(1 ppm = 3.23 mg/m$^3$ @ NTP)

**PROPERTIES:** liquid; d 0.982 g/mL @ 20 °C;
BP 115 °C; MP -42 °C; VP 2.4 kPa
(18 mm Hg; 2.4% v/v) @ 20 °C;
explosive limits 1.8 to 12.4% v/v in air

**SYNONYMS:** azine; azabenzene

## SAMPLING

**SAMPLER:** SOLID SORBENT TUBE
(coconut shell charcoal, 100 mg/50 mg)

**FLOW RATE:** 0.01 to 1.0 L/min

**VOL-MIN:** 18 L
**-MAX:** 150 L

**SHIPMENT:** routine

**SAMPLE STABILITY:** not determined

**FIELD BLANKS:** 2 to 10 field blanks per set

## ACCURACY

**RANGE STUDIED:** 7.6 to 30 mg/m$^3$ [1]
(100-L samples)

**BIAS:** 9.2%

**OVERALL PRECISION ($\hat{S}_{rT}$):** 0.059 [1]

**ACCURACY:** ± 19.8%

## MEASUREMENT

**TECHNIQUE:** GAS CHROMATOGRAPHY, FID

**ANALYTE:** pyridine

**DESORPTION:** 1 mL methylene chloride; stand 30 min

**INJECTION VOLUME:** 5 µL

**TEMPERATURE-INJECTION:** 260 °C
**-DETECTOR:** 285 °C
**-COLUMN:** 140 °C

**CARRIER GAS:** $N_2$, 30 mL/min

**COLUMN:** 3 m x 3-mm OD stainless steel packed with 5% Carbowax 20M on 80/100 mesh acid-washed DMCS Chromosorb W

**CALIBRATION:** standard solutions of pyridine in methylene chloride

**RANGE:** 0.3 to 4.5 mg per sample

**ESTIMATED LOD:** 0.02 mg per sample [2]

**PRECISION ($\bar{S}_r$):** 0.014 @ 0.8 to 3.1 mg per sample [1]

**APPLICABILITY:** The working range is 1 to 14 ppm (3 to 45 mg/m$^3$) for a 100-L air sample.

**INTERFERENCES:** None detected. The chromatographic column or separation may be changed to circumvent interference problems (e.g., 30 m x 0.32-mm capillary column with 1 µm DB-5 at 50 °C [2]).

**OTHER METHODS:** This revises Method S161 [3].

**REAGENTS:**

1. Methylene chloride ($CH_2Cl_2$), chromatographic quality.
2. Pyridine, reagent grade.*
3. Hexane, chromatographic quality.
4. DE stock solution, 300 mg/mL. Weigh 3 g pyridine (ca. 3.1 mL) into a 10-mL volumetric flask. Dilute to volume with hexane. Prepare in duplicate.
5. Nitrogen, purified.
6. Hydrogen, prepurified.
7. Air, filtered, compressed.

*See SPECIAL PRECAUTIONS.

**EQUIPMENT:**

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends, with plastic caps, containing two sections of activated (600 °C) coconut shell charcoal (front = 100 mg; back = 50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 1 L/min, with flexible connecting tubing.
3. Gas chromatograph, flame ionization detector, integrator and column (page 1613-1).
4. Vials, 2-mL, PTFE-lined crimp caps.
5. Syringes, 10-µL, readable to 0.1 µL.
6. Volumetric flasks, 10-mL.
7. Pipet, TD, 1-mL.
8. Balance, analytical.

**SPECIAL PRECAUTIONS:** Pyridine can cause liver and kidney damage, and CNS depression if it is inhaled or contacts the eyes or skin [4,5]. Methylene chloride is a suspect carcinogen [6].

**SAMPLING:**

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 1 L/min for a total sample size of 18 to 150 L.
4. Cap the samplers. Pack securely for shipment.

**SAMPLE PREPARATION:**

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Pipet 1.0 mL $CH_2Cl_2$ into each vial. Cap each vial.
   NOTE: A suitable internal standard, such as toluene, may be added at this step [2].
7. Allow to stand 30 min with occasional agitation.

**CALIBRATION AND QUALITY CONTROL:**

8. Calibrate daily with at least six working standards.
   a. Add known amounts of pyridine to $CH_2Cl_2$ in 10-mL volumetric flasks and dilute to the mark. Use serial dilutions as needed to obtain pyridine concentrations in the range 0.02 to 4.5 mg/mL.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area vs. mg pyridine).

9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount (2 to 20 µL) of DE stock solution, or a serial dilution thereof, directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. mg pyridine recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

**MEASUREMENT:**

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1613-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with $CH_2Cl_2$, reanalyze, and apply the appropriate dilution factor in calculations.
12. Measure peak area.

**CALCULATIONS:**

13. Determine the mass, mg (corrected for DE) of pyridine found in the sample front ($W_f$) and back ($W_b$) sorbent sections, and in the average media blank front ($B_f$) and back ($B_b$) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of pyridine in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3.$$

**EVALUATION OF METHOD:**

Method S161 was issued on August 1, 1975 [3], and validated with atmospheres generated by calibrated syringe pump and confirmed using a total hydrocarbon analyzer [2]. Average recovery was 109% ±3.6% (18 samples) in the range 7.6 to 30.4 mg/m$^3$ for 100-L samples. Breakthrough (effluent concentration = 5% of test concentration) was not observed after sampling for 240 min at 0.93 L/min from an atmosphere containing 30.4 mg/m$^3$ pyridine in dry air. Carbon disulfide and methanol were tested and rejected as possible desorbing solvents. Carbon disulfide gave an average DE of 0.734; methanol, 0.201. Desorption efficiency using methylene chloride for 18 spiked samples in the range 0.8 to 3.1 mg pyridine per sample averaged 0.81 with $S_r = 0.013$.

**REFERENCES:**

[1] Documentation of the NIOSH Validation Tests, S161, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977), available as Stock No. PB 274-248 from NTIS, Springfield, VA 22161.
[2] UBTL, Inc. Report, NIOSH Sequences 4949-K (unpublished, May 24, 1985) and 3030-K (unpublished, July 20, 1981).
[3] NIOSH Manual of Analytical Methods, 2nd. ed., V. 3, S161, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).

[4] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as Stock #PB83-154609 from NTIS, Springfield, VA 22161.
[5] Merck Index, 10th ed., Merck & Co., Rahway, NJ (1983).
[6] NIOSH Current Intelligence Bulletin 46, U.S. Department of Health and Human Services, Publ. (NIOSH) 86-114 (1986).

**METHOD REVISED BY:**

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