n-BUTYLAMINE 2012

$CH_3(CH_2)_3NH_2$ MW: 73.16 CAS: 109-73-9 RTECS: EO2975000

METHOD: 2012, Issue 1 **EVALUATION: FULL** **Issue 1: 15 August 1994**

OSHA : 5 ppm (skin) ceiling
NIOSH: 5 ppm (skin) ceiling
ACGIH: 5 ppm (skin) ceiling
(1 ppm = 2.99 mg/m^3 @ NTP)

PROPERTIES: liquid, ammoniacal odor; MP -49 °C; BP 77.8 °C; d = 0.7327 g/mL @ 25 °C; VP 10.9 kPa (82 mm Hg) @ 20 °C; vapor density 2.5 (air = 1)

SYNONYMS: butylamine, 1-aminobutane, NBA

SAMPLING

SAMPLER: SOLID SORBENT TUBE (sulfuric acid-treated silica gel tube 150 mg/75 mg)

FLOW RATE: 0.01 to 1.0 L/min

VOL-MIN: 2 L
-MAX: 100 L

SHIPMENT: routine

SAMPLE STABILITY: at least 7 days @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 8.09 to 35.5 mg/m^3 [1] (15-L samples)

BIAS: - 5.1%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.092 [1]

ACCURACY: ± 23.1%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: n-butylamine

EXTRACTION: 1 mL 50% methanol; neutralize a 500µL aliquot with 1 N KOH

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTOR: 175 °C
-DETECTOR: 195 °C
-COLUMN: 90 °C

CARRIER GAS: N_2, 20 mL/min

COLUMN: 4% Carbowax 20M + 0.8% KOH on 60/80 mesh Carbopack B, 6 ft x 1/4"-O.D.

CALIBRATION: standard solutions of butylamine in aqueous methanol

RANGE: 0.03 to 1 mg per sample [1]

ESTIMATED LOD: 0.012 mg per sample [2]

PRECISION ($\hat{S}_r$): 0.0490 [1]

APPLICABILITY: The working range is 0.7 to 144 ppm (2 to 430 mg/m^3) for a 15-L air sample. Using a nitrogen-specific detector instead of a FID will greatly increase sensitivity. This alternate detector has been used for amines with a 30-m x 0.25- mm x 0.25-µm film DB-5 (5% methyl, phenyl-50% dimethyl-polysiloxane) fused-silica capillary column with a liner packed with KOH-co ated glass wool.

INTERFERENCES: Both concentrated sulfuric acid and silica gel are desiccants, so in sampling atmospheres above 60% relative humidity the sorbent tube may have lowered capacity.[1]

OTHER METHODS: This revises Method S138 [3]. Method 2010 for aliphatic amines may also be used for determination of n-butylamine.

REAGENTS:

1. n-Butylamine,* ACS reagent grade.
2. Potassium hydroxide,* (KOH) 1 N, ACS reagent grade.
3. Water, deionized.
4. n-Butyl alcohol, for internal standard.
5. Methanol, distilled in glass.
6. 50% methanol in water (v/v).
7. Calibration stock solution.

* See Special Precautions

EQUIPMENT:

1. Sampler: 150 mg/75 mg sulfuric acid coated (20/40 mesh) silica gel tube. See Appendix for instruction on preparation. (Tubes are commercially available, but have a designated shelf life).
2. Personal sampling pump, 0.01 to 1 L/min, with flexible polyethylene or PTFE tubing.
3. Hygrometer or other suitable device for measuring relative humidity.
4. Vials, glass, 2-mL with PTFE-lined caps.
5. Gas chromatograph with a flame ionization detector, recorder, integrator and column (page 2012-1).
6. Tweezers.
7. Syringes, 10- and 500-µL.
8. Volumetric flasks, 10-mL.
9. Pipets, 1- and 10-mL glass, delivery, with pipet bulb.

SPECIAL PRECAUTIONS: Butylamine vapor can cause irritation to the eyes, nose, and throat. Inhalation can cause headache and flushing of skin. Contact with the liquid may produce severe injury to eyes and skin [4]. Potassium hydroxide is a strong caustic, corrosive to tissue. Handle with gloves. Work in a hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the silica gel tube immediately prior to sampling. Attach outlet of tube to the sampling pump with flexible tubing.
3. Sample 2 to 100 L of air at an accurately known flow rate in the range 0.01 to 1.0 L/min.
4. The temperature, pressure, and relative humidity of the atmosphere being sampled should be recorded.
5. Cap and seal the sample tube for shipment and place in a suitable container in order to prevent damage during transit.
6. Collect a bulk sample (ca. 1 g) in a glass vial and ship it separately.

SAMPLE PREPARATION:

7. Place the front and back sorbent sections of the sampler tube in separate vials. Add the glass wool plug to the front sorbent section's vial.
8. Add 1 mL 50% methanol to the vial. Tightly cap the vial. Agitate the vial for 2 hours.
9. Neutralization of the sample solution. Allow the silica gel particles to settle. Transfer a 500 µL aliquot to a clean vial and add 500 µL of 1.0 N KOH.

   NOTE 1: If the internal standard is to be used, add the internal standard solution made up in 1.0 N KOH.

   NOTE 2: Analyze samples immediately to avoid loss of amine as free base.

CALIBRATION AND QUALITY CONTROL:

10. Prepare working standards (12 to 1000 µg/mL aqueous methanol) by adding appropriate aliquots of calibration stock solution to 50% methanol. Follow neutralization procedure in step 9.
11. Analyze working standards together with samples and blanks (steps 14 through 16). Prepare a calibration graph of area vs. µg of n-butylamine.
12. Determine recovery for each lot of silica gel used for sampling in the concentration range of interest. Prepare four silica gel tubes at each of five levels plus three media blanks.
    a. Remove and discard 75 mg back sorbent section of an unused sorbent tube.
    b. Spike aliquot of calibration solution onto front section sorbent section of silica gel tube with a microliter syringe.
    c. Cap and let stand overnight.
    d. Desorb following (steps 7 through 9) and analyze along with working standards and blanks (steps 14 through 16).
    e. Prepare graph of recovery vs. µg n-butylamine.
13. Analyze three quality control spikes and three analyst spikes to ensure that calibration graph and recovery graph are in control.

MEASUREMENT:

14. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2012-1.
15. Inject 5-µL sample aliquot.
    NOTE: If peak area is above the linear range of the working standards, dilute with 50% methanol, reanalyze, and apply the appropriate dilution factor in calculations.
16. Measure peak area.

CALCULATIONS:

17. Determine mass, µg (corrected for recovery), of n-butylamine 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 less.
18. Calculate concentration of n-butylamine in the air volume sampled, V (L):

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

EVALUATION OF METHOD:

This method was evaluated over the range 8.09 to 35.5 mg/m^3 at 24 °C and pressure of 769 mm Hg using 15-L samples [1,3]. Sampling and measurement precision, $\bar{S}_r$, was 0.049, with average recovery of 91.4%, representing a non-significant bias. Sample stability during storage was evaluated at 270 µg n-butylamine per sample. Samples showed 98.4% recovery after one day of storage at ambient conditions compared to 95.2% recovery for seven-day old samples.

REFERENCES:

[1] Backup Data Report for n-butylamine, prepared under NIOSH Contract 210-76-0123 (1978).
[2] NIOSH/DPSE Analytical Sequence #4975, Measurement Research Support Branch, NIOSH, Cincinnati, Ohio (unpublished, 1986).

[3] NIOSH Manual of Analytical Methods, 2nd. ed., V. 4, S138, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[4] 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.

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APPENDIX: PREPARATION OF SULFURIC ACID-TREATED SILICA GEL.

Place a known amount of 20/40 mesh silica gel in a drying oven set at 125 °C for one hour. Cool the silica gel to a constant weight (W). Add reagent grade concentrated sulfuric acid dropwise by means of a pipet to 1.25 (W) or 25% by weight of the acid. Return the treated silica gel to the drying oven for one hour with intermittent mixing. Store the treated silica gel in an airtight container.