Table 1 MW: Table 1 CAS: Table 2 RTECS: Table 2

**METHOD: 2002, Issue 2** **EVALUATION: FULL (1-3); PARTIAL (4,5)** **Issue 1: 15 May 1985**
**Issue 2: 15 August 1994**

**OSHA :** Table 2
**NIOSH:** Table 2
**ACGIH:** Table 2

**PROPERTIES:** Table 1

**SYNONYMS:** (1) aniline: benzenamine; aminobenzene; phenylamine
(2) o-toluidine: 2-aminotoluene
(3) 2,4-xylidine: 2,4-dimethylaniline; dimethylaminobenzene
(4) N,N-dimethyl-p-toluidine: p-dimethylaminotoluene
(5) N,N-dimethylaniline: N,N-dimethylbenzeneamine

## SAMPLING

**SAMPLER:** SOLID SORBENT TUBE (silica gel, 150 mg/75 mg)

**FLOW RATE:** Table 2

**VOL-MIN:** Table 2
**-MAX:** Table 2

**SHIPMENT:** routine

**SAMPLE STABILITY:** (1), (2), and (3) stable for ≥ 7 days [1]; stability data not available for (4) and (5)

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

## ACCURACY

**RANGE STUDIED:** see EVALUATION OF METHOD

**BIAS:** see EVALUATION OF METHOD

**OVERALL PRECISION ($\hat{S}_{rT}$):** see EVALUATION OF METHOD

**ACCURACY:** see EVALUATION OF METHOD

## MEASUREMENT

**TECHNIQUE:** GAS CHROMATOGRAPHY, FID

**ANALYTE:** amines listed above

**DESORPTION:** 1 mL 95% ethanol; 1 h in ultrasonic bath

**INJECTION VOLUME:** 5 µL

**CARRIER GAS:** $N_2$ or He, 25 mL/min

**COLUMN:** stainless steel, 0.6 m x 3-mm OD, packed with 80/100 mesh Chromosorb 103

**CALIBRATION:** standard solutions of analytes in 95% ethanol

**RANGE:** 0.1 to 3 mg per sample

**ESTIMATED LOD:** 0.01 mg per sample [2]; not determined for (3)

**PRECISION ($\hat{S}_r$):** see EVALUATION OF METHOD

**APPLICABILITY:** See Table 2 for working ranges. A modification of this method has been used for aniline and o-toluidine at a vulcanized rubber manufacturing plant [2]. Applicability of this method for simultaneous determination of the analytes has not been investigated. A nitrogen-specific GC detector instead of an FID will greatly increase sensitivity.

**INTERFERENCES:** None known. Silica gel has reduced capacity for organic compounds at high humidity.

**OTHER METHODS:** This combines Methods S162 (xylidine) [3], S164 (dimethylaniline) [3], S168 ( o-toluidine) [3], S310 (aniline) [3], P&CAM 280 (N,N-dimethyl-p-toluidine) [4], and P&CAM 168 (aromatic amines) [5,6].

**REAGENTS:**

1. Ethanol, 95%, non-denatured, chromatographic quality.
2. n-Hexane.
3. Benzene.*
4. Analytes, reagent grade.*
5. Aniline calibration stock solution, 102.2 mg/mL.* Dissolve 1 mL aniline in 2 mL benzene; dilute to 10 mL with hexane.
   NOTE: Benzene possibly could be replaced with toluene, alcohol, or acetone to minimize the analyst's exposure to suspect carcinogens. Effects of this substitution are not known and should be tested.
6. o-Toluidine calibration stock solution, 100.6 mg/mL.* Dilute 1 mL o-toluidine to 10 mL with n-hexane.
7. 2,4-Xylidine calibration stock solution, 97.8 mg/mL.* Dilute 1 mL 2,4-xylidine to 10 mL with n-hexane.
8. N,N-Dimethyl- p-toluidine calibration stock solution, 93.5 mg/mL.* Dilute 1 mL N,N-dimethyl- p-toluidine to 10 mL with n-hexane.
9. N,N-Dimethylaniline calibration stock solution, 95.6 mg/mL.* Dilute 1 mL N,N-dimethylaniline to 10 mL with hexane.
10. Hydrogen, prepurified.
11. Helium, purified.
12. Nitrogen, purified.
13. Air, filtered, compressed.

* See SPECIAL PRECAUTIONS.

**EQUIPMENT:**

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID; with plastic caps; containing two sections of 20/40 mesh silica gel separated by a 2-mm portion of urethane foam (front = 150 mg; back = 75 mg). For N,N-dimethyl- p-toluidine, a front section of 100 mg and back section of 50 mg may be used. 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, 0.02 to 1 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 2002-1).
4. Vials, glass, 2-mL, PTFE-lined crimp caps.
5. Syringes, 10-, 25-, 50- and 100-µL.
6. Pipets, 1- and 2-mL.
7. Ultrasonic bath.
8. File.
9. Tweezers.
10. Flasks, volumetric, 10-mL.

**SPECIAL PRECAUTIONS:** n-Hexane and ethanol are flammable. Aniline, o-toluidine, 2,4-xylidine, and benzene are suspect carcinogens [7,8]. Absorption through skin is a potential hazard. All work with these chemicals should be performed in a hood. Use proper protective clothing including gloves. Analytes (1), (2), (3), and (5) are severe poisons.

**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 for a total sample size according to Table 3.
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. Add the glass wool plug to the front sorbent section vial. Discard the foam plugs.
6. Add 1.0 mL 95% ethanol to each vial. Attach crimp cap to each vial.
7. Agitate 1 h in an ultrasonic bath.

**CALIBRATION AND QUALITY CONTROL:**

8. Calibrate daily with at least six working standards over the range 0.01 to 3 mg analyte per sample.
   a. Add known amounts of calibration stock solution, or a dilution thereof, in n-hexane to 95% ethanol in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (peak area or height vs. mg analyte).
9. Determine desorption efficiency (DE) at least once for each lot of silica gel used for sampling in the calibration range. 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 (1 to 20 µL) of calibration stock solution, or a dilution thereof, in hexane 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 analyte 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 2002-1. Inject sample aliquot manually using solvent flush technique or with autosampler. Use the following conditions as a guide (these were used in development of the methods [1]):

| | TEMPERATURES, °C | | |
|---|---|---|---|
| COMPOUND | Injection | Column | Detector |
| Aniline | 230 | 165 | 245 |
| o-Toluidine | 240 | 180 | 265 |
| 2,4-Xylidine | 230 | 170 | 235 |
| N,N-Dimethyl- p-toluidine | 250 | 180 | 250 |
| N,N-Dimethylaniline | 150 | 100 for 4 min, then 8°C/min to 225 | 250 |

NOTE: If peak response is above the linear range of the working standards, dilute with 95% ethanol, reanalyze, and apply the appropriate dilution factor in calculations.

12. Measure peak area or height.

**CALCULATIONS:**

13. Determine the mass, mg (corrected for DE) of analyte 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 analyte 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:**

Precisions, biases and recoveries listed below were determined by analyzing generated atmospheres containing one-half, one and two times the OSHA standard [1]. Generated concentrations were independently verified. Breakthrough of the front section of the silica gel tube was not observed after sampling a dry test atmosphere. The first three analytes were stable on silica gel for at least one week. Method S164 using collection on activated charcoal was also developed for N,N-dimethylaniline [3].

| Substance | Breakthrough volume in dry air at concentration (L) | Sampling at concentration ($mg/m^3$) | Range $mg/m^3$ (volume) | Bias (%) | Overall Precision ($\hat{S}_{rT}$) | Accuracy (%) | Measurement Range (mg) | Measurement Precision ($\hat{S}_r$) | Desorption efficiency |
|---|---|---|---|---|---|---|---|---|---|
| Aniline | >44.4 | 38 | 9.5-38.2 (20 L) | -4.9 | 0.060 | ±15.1 | 0.20-0.82 | 0.013 | 0.980-1.00 |
| o-Toluidine | >221.3 | 47 | 11.7-46.9 (50 L) | -1.5 | 0.060 | ±12.0 | 0.55-2.2 | 0.032 | 0.970-0.983 |
| 2,4-Xylidine | >44.4 | 50 | 12.5-50.0 (20 L) | -1.2 | 0.057 | ±11.2 | 0.25-1.01 | 0.021 | 0.959-1.015 |
| N,N-Dimethyl-p-toluidine | * | * | 9.4-30.0 (100 L) | * | * | * | 0.47 | 0.035 | 0.88 |
| N,N-Dimethyl-aniline | * | * | * | -7.9 | 0.090 | ±16.0 | 0.05-3.0 | * | 0.997 (1.9-mg samples) |

*Not determined

**REFERENCES:**

[1] Documentation of the NIOSH Validation Tests, S162, S164, S168, S310, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977), available as GPO Stock #017-033-00231-2 from Superintendent of Documents, Washington, DC 20402.

[2] UBTL, Inc., Sequence #2300-S, Aniline (May 15, 1980), and Sequence #2551-M, o-Toluidine (August 28, 1980) (NIOSH, unpublished).

[3] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 3, S162, S164, S168, S310, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).

[4] Ibid., Vol. 4, P&CAM 280, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).

[5] Ibid., Vol. 1, P&CAM 168, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).

[6] Campbell, E. E., G. O. Wood and R. G. Anderson. Los Alamos Scientific Laboratory Progress Reports LA-5104-PR, LA-5164-PR, LA-5308-PR, LA-5389-PR, LA-5484-PR and LA-5634-PR, Los Alamos, NM (November, 1972; January, 1973; June, 1973; August, 1973; December, 1973; and June, 1974).

[7] Registry of Toxic Effects of Chemical Substances, 1979 eds., Vols. 1 and 2, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-111 (1980).

[8] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, Aniline and o-Toluidine, 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 WRITTEN BY:**

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**TABLE 1. PHYSICAL PROPERTIES AND PERSONAL EXPOSURE LIMITS**

| Substance Formula | MW | BP (°C) | MP (°C) | d, g/mL @ 20 °C | VP @ 20 °C kPa (mm Hg) | Conversion factor (ppm to mg/m$^3$ @ NTP) |
|---|---|---|---|---|---|---|
| Aniline; $C_6H_7N$ | 93.13 | 184 | -6 | 1.022 | 0.089 (0.3) | 3.81 |
| o-Toluidine; $C_7H_9N$ | 107.16 | 200 | -15 | 1.006 | 0.043 (0.32) | 4.38 |
| 2,4-Xylidine; $C_8H_{11}N$ | 121.18 | 214 | -14 | 0.9723 | <0.1 (<1) | 4.95 |
| N,N-Dimethyl- p-toluidine; $C_9H_{13}N$ | 135.21 | 211 | NA | 0.935 | NA | 5.53 |
| N,N-Dimethylaniline; $C_8H_{11}N$ | 121.18 | 192 | 2 | 0.956 | <0.1 (0.5) | 4.95 |

NA = not available.

**TABLE 2. GENERAL INFORMATION.**

| Substance | CAS | RTECS | Exposure Limits (ppm) OSHA | NIOSH | ACGIH |
|---|---|---|---|---|---|
| Aniline | 62-53-3 | BW6650000 | 5 (skin) | lowest feasible (carcinogen) | 2 (skin) |
| o-Toluidine | 95-53-4 | XU2975000 | 5 (skin) | lowest feasible (carcinogen; skin) | 2 (skin) (carcinogen) |
| 2,4-Xylidine | 1300-73-8 | ZE8575000 | 5 (skin) | 2 (skin) | 0.5 (skin) |
| N,N-Dimethyl- p-toluidine | 99-97-8 | XU5803000 | ----- | ----- | ----- |
| N,N-Dimethylaniline | 121-69-7 | BX4275000 | 5 (skin) | 5 TWA; 10 STEL (skin) | 5 TWA; 10 STEL (skin) |

**TABLE 3. SAMPLING FLOW RATES AND VOLUMES.**

| Substance | SAMPLING Flow Rate (L/min) | Volume (L) MIN | MAX | Working Range ($mg/m^3$) |
|---|---|---|---|---|
| Aniline | 0.02 - 0.2 | 5 | 30 | 5 - 60 (20-L samples) |
| o-Toluidine | 0.02 - 1.0 | 10 | 150 | 5 - 60 (55-L samples) |
| 2,4-Xylidine | 0.02 - 0.2 | 3 | 20 | 3 - 75 (20-L samples) |
| N,N-Dimethyl- p-toluidine | 0.02 - 1.0 | * | * | 9 - 30 (100-L samples) |
| N,N-Dimethylaniline | 0.02 - 1.0 | 3 | 30 | 1.3 - 79 (38-L samples) |

*Not determined.