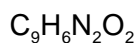


TOLUENE-2,4-DIISOCYANATE

2535



MW: 174.16

CAS: 584-84-9

RTECS: CZ6300000

METHOD: 2535, Issue 2

EVALUATION: FULL

Issue 1: 15 August 1987

Issue 2: 15 August 1994

OSHA : C 0.02 ppm
NIOSH: lowest feasible; carcinogen
ACGIH: 0.005 ppm; STEL 0.02 ppm
 (1 ppm = 7.12 mg/m³ @ NTP)

PROPERTIES: liquid; MP 19.5-21.5 °C; BP 251 °C;
 density 1.2244 g/mL @ 20 °C; VP ca.
 1.3 Pa (0.01 mm Hg; 0.96 mg/m³)
 @ 20 °C

SYNONYMS: 2,4-TDI; 2,4-bis(carbonylamino)toluene; 2,4-tolylene diisocyanate

APPLICABILITY: The working range is 0.004 to 0.35 ppm (0.03 to 2.5 mg/m³) for a 10-L air sample. This method is applicable to isocyanate vapors (2,4-TDI vapor, 2,6-TDI vapor, and hexamethylene diisocyanate (HDI) vapor) [2,3], but not aerosols because of inefficient collection of aerosols and incomplete reaction of aerosol isocyanates with reagent.

INTERFERENCES: The reagent is slightly unstable in the dark at 25 °C. Tailing during HPLC, a result of reagent deterioration, may raise detection limits.

OTHER METHODS: This revises P&CAM 326 [4]. Sangö used similar HPLC conditions [5]. Melcher reviewed methods for isocyanates [6]. Method 5521 (Isocyanates, Monomers), using collection in an impinger, is an alternative method.

REAGENTS:

1. 2,4-TDI* (see APPENDIX A).
2. N-[(4-nitrophenyl)methyl]-propylamine hydrochloride.
3. 2,4-TDIU (see APPENDIX B).
4. Methanol, chromatographic quality.
5. Calibration stock solution, 10 mg/mL. Dissolve 50 mg 2,4-TDIU in methanol to make 5 mL solution.
6. Water, distilled.
7. NaOH, 1 M.
8. Toluene, reagent grade.
9. Dichloromethane, reagent grade.
10. Hexane, reagent grade.*
11. Nitrogen, purified, compressed.
12. Mobile phase. Mix 0.8 mL triethylamine and 1.6 mL H₃PO₄ with 1 L 55:45 CH₃CN:H₂O (v/v).*
13. Dibutylamine, 99% pure.
14. Tetrahydrofuran, reagent grade.*
15. Bromocresol purple indicator solution.
16. HCl, 0.05 M, standardized.
17. 2,4-TDI stock solution, 100 mg/mL. Dissolve 500 mg 2,4-TDI in dichloromethane to make 5 mL solution.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 4 cm x 6-mm ID, containing two sections of tightly compressed, reagent-coated glass wool (see Appendix C) (front = 7 mm; back = 5 mm), wrapped entirely with black tape; open ends with plastic caps. NOTE: Protect sampler from light. Store sampler in the dark at -21 °C up to 4 weeks, or at 25 °C up to 7 days. Pressure drop across the tube must be <3.4 kPa at 1 L/min air flow. Tubes available commercially by special order (SKC, Inc.).
2. Separatory funnels, 125-mL.
3. Beakers, 50- and 125-mL.
4. Aluminum foil.
5. Glass wool, silanized.
6. Glass rod, 15 cm x 4 mm.
7. Tweezers.
8. Rubber tubing, opaque 1.5 cm x ca. 8-mm ID.
9. Personal sampling pump, 0.2 to 1 L/min, with flexible connecting tubing.
10. High pressure liquid chromatograph, 254-nm UV detector, integrator, and column (page 2535-1).
11. Vials, glass, 2-mL, caps lined with PTFE.
12. Pipets, 2-, 15-, and 25-mL.
13. Ultrasonic bath.
14. Syringes, 100- μ L, readable to 1 μ L.
15. Syringes, 10- μ L, readable to 0.1 μ L.
16. Volumetric flasks, 5-mL.
17. Buret, 50-mL.
18. U-tube, glass, 25 cm x 15-mm ID, glass stopcocks.
19. Sorbent tube, glass, 7 cm x 6 mm, coconut shell charcoal, ca. 150 mg.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Remove plastic caps from sampler. Attach sampler to personal sampling pump with flexible tubing.
3. Sample 2 to 170 L of air at 0.2 to 1 L/min.
4. Seal ends of sampler with plastic caps. Pack securely for shipment.

SPECIAL PRECAUTIONS: 2,4-TDI can irritate the eyes and skin, and can cause bronchial asthma and allergic eczema. Flash points of hexane, tetrahydrofuran and triethylamine are -26 °C, -17 °C, and -6 °C, respectively.

SAMPLE PREPARATION:

5. Transfer front and back sections of reagent-coated glass wool to separate vials. Add 2 mL methanol. Seal vials.
6. Place vials into ultrasonic bath for 3 min.

CALIBRATION AND QUALITY CONTROL:

7. Calibrate daily with at least six working standards over the range 0.3 to 80 µg 2,4-TDIU per sample (equivalent to 0.1 to 25 µg 2,4-TDI per sample).
 - a. Prepare a series of standard solutions of 2,4-TDIU in methanol over the range of 0.15 to 40 µg/mL.
 - b. Analyze together with samples and blanks (steps 9 and 10).
 - c. Prepare calibration graph (peak area vs. µg 2,4-TDIU).
8. Determine recoveries from samplers in the range 0.3 to 25 µg 2,4-TDI per sample. Prepare three samples at each of three levels plus three media blanks.

NOTE: Recoveries should be quantitative. If recoveries are not quantitative, determine the reason for error.

 - a. Prepare a series of standard solutions of 2,4-TDI in dichloromethane in the range 0.06 to 5 mg/mL.
 - b. Connect a U-tube to the inlet of a sampler with a short piece of tubing.

NOTE: The length of tubing should be minimal to prevent losses of TDI by adsorption or reaction on the inside wall of the tubing.
 - c. Connect charcoal sorbent tube to inlet of U-tube (charcoal can adsorb contaminants of air which would react with 2,4-TDI).
 - d. Draw ambient air through the charcoal tube, U-tube, and sampler with a sampling pump at 1 L/min.
 - e. Place 5 µL of a standard solution of 2,4-TDI into the U-tube.
 - f. Allow operation of the pump to continue for 20 min.
 - g. Desorb (steps 5 and 6) and analyze with working standards (steps 9 and 10).

MEASUREMENT:

9. Establish chromatographic conditions indicated on page 2535-1.
10. Inject sample aliquot manually or with autosampler. Measure peak area.

CALCULATIONS:

11. Determine the mass (µg) of 2,4-TDIU found on the sample front (W_f) and back (W_b) sections and in the average media blank front (B_f) and back (B_b) sections.

NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
12. Calculate concentration, C, of 2,4-TDI in the air volume sampled, V (L):

$$C = \frac{0.310 (W_f + W_b - B_f - B_b)}{V}, \text{ mg/m}^3,$$

where 0.310 = MW of 2,4-TDI/MW of 2,4-TDIU.

EVALUATION OF METHOD:

A variation of this method which involved normal-phase HPLC (Method P&CAM 326) was tested with fortified samplers and atmospheres generated with a diffusion cell [1,4]. Average recoveries of 2,4-TDIU from front sections of reagent-coated glass wool were 0.97 to 0.99 after applications of 1.0-, 2.1-, 9.9-, and 20.0- μg quantities of 2,4-TDI from a U-tube; \bar{S}_r was 0.067 (21 samples, pooled). \bar{S}_r was 0.033 (29 samples, pooled) for 67-L samples at 0.039 to 0.53 mg/m^3 . The independent method used for evaluation was that of Meddle and Wood [7]. Average concentrations ranged from 0.054 to 0.46 mg/m^3 by the independent method [1]. Conclusive evidence for bias in the reagent-coated glass wool method was not found. Breakthrough volume was 71 L (0.53 mg/m^3 , 1 L/min); breakthrough volume was 279 L (0.14 mg/m^3 , 1 L/min). 2,4-TDIU was stable on coated glass wool at room temperature in the dark for 14 days. The reagent, N-[(4-nitrophenyl)methyl]propylamine, is unstable [1].

Evaluation of samplers with 2,4-TDI aerosols was not performed. However, samplers were inefficient collectors when aerosol particles were present in an atmosphere of 4,4'-methylenediphenylisocyanate (MDI). The collection efficiency of each sampler for MDI was about 90% (flow rate, 1 L/min; total concentration of MDI in vapor and aerosol forms, about 0.52 mg/m^3 ; mass median diameter of MDI particles, about 0.6 μm ; geometric standard deviation, about 2.2) [1].

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METHOD WRITTEN BY:

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APPENDIX A: Determination of Purity of 2,4-TDI

Dissolve 480 μL (365 mg, 0.00282 mole) dibutylamine in 10 mL tetrahydrofuran. Add 100 μL (122 mg, 0.000701 mole) 2,4-TDI. Stir the mixture and allow to stand 6 min. Add a few drops of bromocresol purple indicator solution. Prepare two additional samples in this manner. Titrate excess dibutylamine with 0.05 M HCl. Calculate percent purity, P, of 2,4-TDI for each sample:

$$P = \frac{B - (V \cdot M)}{2W} \cdot 100.$$

- where: B = Molar quantity of dibutylamine before reaction (0.00282)
 V = Volume of 0.05 M HCl (L)
 M = Concentration of HCl (0.05 M)
 2 = Number of moles of dibutylamine required to react with 1 mole of 2,4-TDI
 W = Molar quantity of 2,4-TDI added to tetrahydrofuran solution (0.000701)

APPENDIX B: Preparation of 2,4-TDIU [8]

Dissolve 1.03 g (0.00446 mole) N-[(4-nitrophenyl)methyl]-propylamine hydrochloride in 25 mL water in a 125-mL separatory funnel. Add 15 mL 1 M NaOH and shake the mixture. Extract the N-[(4-nitrophenyl)methyl]propylamine with 50 mL toluene, and separate the phases. Add a solution of 262 μ L (321 mg, 0.00184 mole) 2,4-TDI in 30 mL toluene to the solution of N-[(4-nitrophenyl)methyl]propylamine. Collect the precipitate by filtration. Purify the product by dissolving it in a small volume of dichloromethane and precipitating it with hexane. Dry the product in vacuo (MP = 136 to 139 °C).

APPENDIX C: Preparation of Reagent-Coated Glass Wool

Dissolve 300 mg (0.00130 mole) N-[(4-nitrophenyl)methyl]propylamine hydrochloride in 25 mL water in a 125-mL separatory funnel. Add 15 mL 1 M NaOH and shake the mixture. Extract the N-[(4-nitrophenyl)-methyl]propylamine with 50 mL hexane. Transfer 40 mL of the hexane solution to a 50-mL beaker which is wrapped with aluminum foil and contains 1.82 g silanized glass wool. Under dim light, evaporate hexane from the beaker with the aid of a stream of nitrogen. Knead the glass wool with a glass rod to produce a uniform coating. Continue to evaporate hexane until the glass wool appears dry. Protect the coated glass wool from bright light. The quantity of coated glass wool is sufficient for the preparation of the front and back sections for twenty samplers.