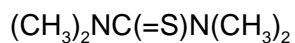


TETRAMETHYL THIOUREA

3505



MW: 132.23

CAS: 2782-91-4

RTECS: YU2750000

METHOD: 3505, Issue 2

EVALUATION: PARTIAL

Issue 1: 15 May 1985

Issue 2: 15 August 1994

OSHA : no standard
 NIOSH: no recommended exposure limit
 ACGIH: no standard

PROPERTIES: solid; MP 78 °C; BP 245 °C

SYNONYMS: 1,1,3,3-tetramethyl-2-thiourea; TMTU

APPLICABILITY: The working range is 0.15 to 10 mg/m³ for a 100-L air sample. Tetramethyl thiourea is used in the manufacture of adhesives and polychloroprene rubber. The method was also applied to ethylene thiourea [1].

INTERFERENCES: Compounds containing a thione (C=S) group will complex with the pentacyanoamineferrate reagent and may interfere with the analyte absorbance band at 590 nm. Other compounds that absorb at 590 nm may interfere.

OTHER METHODS: This method was originally designated P&CAM 282 [1], which it replaces.

REAGENTS:

1. Bromine, Br₂, ACS reagent grade.*
2. Disodium pentacyanonitrosyl ferrate dihydrate (sodium nitroferricyanide; sodium nitroprusside), Na₂Fe(CN)₅NO·2H₂O, ACS reagent grade.
3. Hydroxylamine hydrochloride, NH₂OH·HCl, ACS reagent grade.
4. Sodium bicarbonate, NaHCO₃.
5. Water, distilled or deionized.
6. Complexing reagent (see APPENDIX).
7. Dilute complexing reagent. Mix one volume complexing reagent with two volumes water. Prepare fresh daily.
8. Tetramethyl thiourea (TMTU), reagent grade.*
9. TMTU stock solution, 1000 µg/mL.* Dilute 0.250 g TMTU to 250 mL with distilled water.
10. Calibration stock solution, 20 µg/mL. Dilute 5 mL TMTU stock solution to 250 mL with distilled water.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass midget impinger with 15 mL water.
2. Personal sampling pump, 0.2 to 1 L/min, with flexible connecting tubing and splashover protection (empty impinger or glass wool in tube between sampler and pump).
3. Spectrophotometer to operate at 590 nm with matched glass cuvettes, 5-cm optical path length.
4. Analytical balance, 0.1 mg.
5. Mortar and pestle.
6. Test tubes, 20-mL, calibrated at 15.0 mL.
7. Vials, glass, 20-mL, with PTFE-lined screw caps.
8. Beaker, 50-mL.
9. Pipets, adjustable (0.1- to 5-mL), with disposable tips.
10. Volumetric flasks, 25- and 250-mL.
11. Tweezers.
12. Microspatula.
13. Rubber suction bulb.
14. Weighing paper.
15. Filter funnel, stand and filter paper.

SPECIAL PRECAUTIONS: Bromine is very corrosive and causes severe burns; vapors are extremely irritating and toxic. Wear gloves and handle only in a hood.

Tetramethyl thiourea is an animal teratogen and carcinogen [3]. Avoid inhalation, ingestion or skin contact. Keep TMTU in a bottle labelled "animal carcinogen" and place the bottle in a resealable thick-walled plastic bag in locked storage.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 0.2 and 1 L/min for a total sample size of 50 to 250 L. Transfer the sample solution to a 20-mL vial for shipment.
3. Collect a high-volume air sample or rafter dust sample. Ship in a glass vial in a separate container.

SAMPLE PREPARATION:

4. Transfer contents of the vial to a test tube. Add water to the 15-mL mark.

CALIBRATION AND QUALITY CONTROL:

5. Calibrate daily with at least six working standards over the range 3 to 150 µg TMTU per sample.
 - a. Pipet 0- to 10-mL aliquots of calibration stock solution into clean vials. Bring the total volume to 15 mL with distilled water.

- b. Analyze together with the samples and blanks (steps 6 through 8).
- c. Prepare calibration graph (absorbance vs. μg TMTU).

MEASUREMENT:

6. Complexation.

NOTE: Perform this step at the same time for both working standards and samples. Color degradation occurs at the rate of ca. 2% in 3 h.

- a. Pipet 1.5 mL dilute complexing reagent into each test tube or vial.
- b. Allow to stand for at least 30 min with occasional shaking to ensure full color development.

NOTE: The color of the complex varies with increasing concentration from yellow to light green to turquoise. Very high concentrations have Prussian blue color; dilute these with distilled water before analysis and use the appropriate dilution factor in calculations.

7. Transfer the solution to a clean 5-cm cuvette. Remove droplets from cuvette windows with lens paper.
8. Measure absorbance at 590 nm vs. reference cell containing 15 mL distilled water and 1.5 mL dilute complexing reagent.

NOTE 1: Sensitivity is ca. 0.006 absorbance unit/ μg .

NOTE 2: Scan the absorbance of the bulk sample (several mg of bulk sample dissolved in 15 mL water and treated as in steps 6 through 8) in the range 350 to 700 nm. Compare to spectrum of TMTU to detect possible interferences.

CALCULATIONS:

9. Determine the mass of TMTU (μg) for the sample (M) and average media blank (B).
10. Calculate the concentration of TMTU, C, in the air volume sampled, V (L):

$$C = \frac{(M - B)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

The method was tested with 35 standards in the range 15 to 150 μg per sample with an average \bar{S}_r of 2% [1,2]. All calibration graphs indicated a minimum linear correlation coefficient of 0.9999 [2]. TMTU spiked on VM-1 (PVC) filter samples could not be recovered with water or methanol in waterbath temperatures up to 60 °C because it reacted with the filter material [2]. The method was also used on 42 field samples collected in midjet impingers in a survey [2]. The amounts of TMTU found ranged from 9 to 302 μg per sample.

REFERENCES:

- [1] NIOSH Manual of Analytical Methods, 2nd. ed., V. 4, P&CAM 282, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
- [2] Palassis, J. Sampling and Analytical Determination of Airborne Tetramethyl and Ethylene Thiourea, *Am. Ind. Hyg. Assoc. J.*, **41**, 91-97 (1980).
- [3] Registry of Toxic Effects of Chemical Substances, V. 3, U.S. Department of Health and Human Services, Publ. (NIOSH) 83-107 (1983).

METHOD WRITTEN BY:

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APPENDIX:

PREPARATION OF COMPLEXING REAGENT

1. Weigh 0.500 g $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO}\cdot 2\text{H}_2\text{O}$ in a 50-mL beaker. Dissolve in 10 mL distilled water.
2. Grind together 0.500 g $\text{NH}_2\text{OH}\cdot\text{HCl}$ and 1.00 g NaHCO_3 in a mortar.
3. In a hood, add the ground mixture to the solution from step 1 above. When bubbling ceases, add 0.10 mL bromine. When reaction stops, add ca. 10 mL distilled water. Filter. Rinse beaker with 4 mL distilled water and filter. Transfer filtrate to a 25-mL volumetric flask and dilute with distilled water to the mark. Refrigerate.