ETHYLENE THIOUREA 5011

$C_3H_6N_2S$ MW: 102.17 CAS: 96-45-7 RTECS: NI9625000

METHOD: 5011, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 February 1984**
Issue 2: 15 August 1994

OSHA : suspect carcinogen
NIOSH: lowest feasible; carcinogen
ACGIH: no TLV

PROPERTIES: solid; MP 203 to 204 °C

SYNONYMS: 2-imidazolidinethione, ETU; 4,5-dihydroimidazole-2(3H)-thione.

SAMPLING

SAMPLER: FILTER
(5-µm PVC or mixed cellulose ester membrane)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 200 L @ 0.05 mg/m^3
-MAX: 800 L

SHIPMENT: routine

SAMPLE STABILITY: unknown

BLANKS: 2 to 10 field blanks per set

BULK SAMPLE: required; high-volume air or settled dust

ACCURACY

RANGE STUDIED: 0.03 to 1.5 mg/m^3 (100-L sample)

BIAS: not significant [3]

OVERALL PRECISION ($\hat{S}_{rT}$): not determined

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: VISIBLE ABSORPTION SPECTROPHOTOMETRY

ANALYTE: ETU-pentacyanoamineferrate coordination complex

EXTRACTION: distilled water, stand 45 min @ 60 °C

COMPLEXATION: pentacyanoamineferrate reagent

WAVELENGTH: 590 nm

CALIBRATION: solutions of ETU in water

RANGE: 10 to 150 µg per sample

ESTIMATED LOD: 0.75 µg per sample

PRECISION ($\hat{S}_r$): 0.03

APPLICABILITY: The working range is 0.05 to 0.75 mg/m^3 for a 200-L air sample. Ethylene thiourea is used in the manufacture of fungicides, rubber vulcanization and in dyes, pharmaceuticals, synthetic resins and electroplating baths [1]. The met hod was also applied to tetramethyl thiourea [1].

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

OTHER METHODS: This method was originally designated P&CAM 281 [2], which it replaces.

REAGENTS:

1. Bromine, Br_2, ACS reagent.*
2. Disodium pentacyanonitrosyl ferrate dihydrate (sodium nitroferricyanide; sodium nitroprusside), $Na_2Fe(CN)_5NO \cdot 2H_2O$, ACS reagent.
3. Hydroxylamine hydrochloride, $NH_2OH \cdot HCl$, ACS reagent.
4. Sodium bicarbonate, $NaHCO_3$, ACS reagent.
5. Hexane, spectrophotometric quality.
6. Methanol, spectrophotometric quality.
7. Water, distilled or deionized.
8. Complexing reagent (see APPENDIX).
9. Dilute complexing reagent. Mix 1 volume complexing reagent with 2 volumes water. Prepare fresh daily.
10. Ethylene thiourea (ETU) (see APPENDIX).
11. Calibration stock solution, 1000 µg/mL. Dilute 0.250 g recrystallized ETU to 250 mL with distilled water.

* See Special Precautions

EQUIPMENT:

1. Sampler: PVC filters, 5-µm pore size, 37-mm diameter or mixed cellulose ester filters, 0.8-µm pore size, 37-mm diameter; plastic filter holders (cassettes).
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. Spectrophotometer to operate at 590 nm.
4. Matched glass cuvettes, 5-cm optical path length.
5. Analytical balance capable of weighing to the nearest 0.1 mg.
6. Mortar and pestle.
7. Waterbath thermostatically controlled to 60 ± 1 °C.
8. Glass vials, 20-mL capacity, with PTFE-lined screw caps.
9. Beakers, assortment of 50- to 250-mL.
10. Adjustable pipettes (5- to 50-µL, 50- to 250-µL, 0.5- to 5-mL) with disposable tips.
11. Volumetric pipettes, assortment of 1- to 25-mL, with pipet bulb.
12. Volumetric flasks, 25-, 100-, 200- and 250-mL capacity.
13. Miscellaneous: tweezers, microspatula, rubber suction bulb, wood applicator stick weighing paper, filter paper and filter funnel with stand.

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

Ethylene thiourea is an animal teratogen and carcinogen [3,4]. Extra care must be taken to avoid inhalation, ingestion or skin contact. Keep ETU 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 1 and 3 L/min for a total sample size of 200 to 800 L. Do not exceed 2 mg dust loading on the filter.
3. Collect a high-volume air sample or rafter dust sample. Ship in a glass vial in a separate container from the filters.

SAMPLE PREPARATION:

4. Remove the top portion of the filter holder. Hold the bottom portion containing the filter and filter support over a piece of weighing paper. Remove the plug from the bottom of the filter holder and insert the applicator stick through the hole. Gently raise the filter and grasp the edge with tweezers. Very carefully transfer the filter to a 20-mL glass vial and push it gently to the bottom. Add to the vial any material remaining in the filter holder or collected on the weighing paper.

5. Pipet 7.0 mL distilled water into the vial to completely immerse the filter. Cap the vial.
6. Place vials in a 60 °C waterbath (thermostatically controlled) for 45 min. The waterbath level must be above the water level in the vial. Shake each vial every 5 min.
   NOTE: Do not use an ultrasonic bath, because it breaks up the filters.
7. Lift the filter with tweezers above the water level in the vial. Wash the filter two times with 4-mL aliquots of water using a 5-mL adjustable pipette. Collect the rinsings in the vial. Discard the filter.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standrds over the range of 0 to 150 µg/mL.
   a. Prepare a 15 µg/mL ETU standard solution by pipetting 3.0 mL of the 1000 µg/mL calibration stock solution into a 200-mL volumetric flask and diluting to the mark with distilled water.
   b. Prepare working standards by pipetting 0- to 10-mL aliquots of the 15 µg/mL standard solution into clean vials. Bring the total volume to 15 mL with distilled water. Follow steps 10 and 11 to analyze the working standards.
   c. Prepare a calibration graph (absorbance vs. µg per sample).
9. Determine recovery at least once for each lot of filters used.
   a. Place eight filters on a plastic test tube rack. Using an adjustable pipette, add to the center of each filter 0, 7.5, 15, 30, 45, 60, 90, 120, and 150 µL of 1000-µg/mL calibration stock solution. Let filters air dry overnight at room temperature. Extract (steps 4 through 7) and analyze (steps 10 and 11).
   b. Convert the absorbance of each sample to µg from the calibration graph. Calculate recovery, R (µg found/µg taken).

MEASUREMENT:

10. Complexation.
    NOTE: Perform this step at the same time for both standards and samples to reduce errors due to color degradation.
    a. Pipet a 1.5-mL aliquot of dilute complexing reagent into each vial.
    b. Allow the vials to stand for at least 30 min before analysis to insure full color development. Shake the vials every 10 min.
       NOTE: The color of the complexed samples varies with increasing concentration from yellow to light green to turquoise. Very high concentrations have Prussian blue color; dilute these with distilled water and use the appropriate dilution factor in the calculations.
11. Measurement.
    a. Transfer the solution to a clean 5-cm cuvette. Wipe cuvette with a lens paper to remove any droplets on the cuvette windows.
    b. Place the cell in the sample compartment and measure absorbance at 590 nm vs. a reference sample (15 mL distilled water and 1.5 mL dilute complexing reagent) in a 5-cm cuvette. Record the absorbance for each sample.
       NOTE: Scan the absorbance of the bulk sample (dissolve several mg of bulk sample in 15 mL water and treat as in steps 10 and 11) in the range 350 to 700 nm to detect possible interferences.

CALCULATIONS:

12. Determine the mass of ETU, µg (corrected for recovery), for the sample (W) and average media blank (B).

13. Calculate the concentration of ETU, C (mg/m ^{3}), in the air volume sampled, V (L):

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

EVALUATION OF METHOD:

The method was tested with 21 PVC (VM-1)/ETU spiked samples in the range 15 to 150 µg per sample with an average recovery of 98.0 ± 3.2% [1]. It was also tested with 20 mixed cellulose ester filters spiked with ETU in the range of 15 to 150 µg per sample, giving an average recovery of 99.2% ± 3.6% [1]. All calibration graphs indicated a minimum linear correlation coefficient of 0.9999 [1]. The method was also used on 50 field samples on VM-1 filters in two surveys [1]. The amounts of ETU found ranged from 5 to 56 µg per sample. Storage stability was not determined, nor was overall method bias determined.

REFERENCES:

[1] Palassis, J. Sampling and Analytical Determination of Airborne Tetramethyl and Ethylene Thiourea, Am. Ind. Hyg. Assoc. J., 41, 91-97 (1980).
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 4, P&CAM 281, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[3] Special Occupational Hazard Review...Ethylene Thiourea, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-109 (1978).
[4] NIOSH Current Intelligence Bulletin No. 22: Ethylene Thiourea, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-144 (1978).

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APPENDIX:

1. PREPARATION OF COMPLEXING REAGENT
   a. Weigh 0.500 g $Na_2Fe(CN)_5NO \cdot 2H_2O$ in a 50-mL beaker. Dissolve in 10 mL distilled water.
   b. Grind together 0.500 g $NH_2OH \cdot HCl$ and 1.00 g $NaHCO_3$ in a mortar.
   c. In a hood, add the ground mixture to the solution from (a.). 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. Stable at least two weeks at 4 °C [3].

2. PURIFICATION OF ETU
   a. In a 250-mL Erlenmeyer flask, weigh 3 to 5 g ETU. Dissolve in 100 mL 1:1 methanol:water. Heat to boiling in a hood. Cool 5 min at room temperature. Add 5 mL hexane. Shake 30 sec. Cover with watchglass. Let stand 1 h at room temperature. Filter the ETU crystals, and wash with 100 mL 1:1 methanol:water. Let the crystals air dry in a hood.