TETRANITROMETHANE

$C(NO_2)_4$ MW: 196.0 CAS: 509-14-8 RTECS: PB4025000

METHOD: 3513, Issue 1 **EVALUATION: FULL** **Issue 1: 15 August 1994**

OSHA : 1 ppm
NIOSH: 1 ppm
ACGIH: 1 ppm
(1 ppm = 8.02 mg/m^3)

PROPERTIES: colorless liquid, pungent odor; BP = 125.7 °C; MP = 12.5 °C; sp. gravity = 1.650 (13 °C)

SYNONYMS: TNM; Tetan

SAMPLING

SAMPLER: IMPINGER (ethyl acetate, 15 mL)

FLOW RATE: 0.5 to 1.0 L/min

VOL-MIN: 20 L @ 1 ppm
-MAX: 250 L

SHIPMENT: refrigeration recommended

SAMPLE STABILITY: 14 days refrigerated

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 2.70 to 11.5 mg/m^3 [1] (250-L sample)

BIAS: 0%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.076 [1]

ACCURACY: ± 21.7%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, NPD

ANALYTE: tetranitromethane

DILUTION: ethyl acetate

INJECTION VOLUME: 1 µL

TEMPERATURE-INJECTOR: 160 °C
-DETECTOR: 200 °C
-COLUMN: 40 °C

COLUMN: 30 m, 0.32-mm ID, 1-µm film thickness DB-1 capillary column [2]

CALIBRATION: solutions of tetranitromethane in ethyl acetate

RANGE: 17 to 660 µg per sample

ESTIMATED LOD: 5 µg per sample [2]

PRECISION ($\bar{S}_r$): 0.011 [2]

APPLICABILITY: The working range is 0.02 to 2.5 ppm (0.2 to 20 mg/m^3) for a 100-L air sample. A flame ionization detector can be used but has less sensitivity. A Stabilwax-DB capillary column can be used as an alternate to a DB-1 capillary co lumn [2].

INTERFERENCES: Any nitrogen or phosphorus compound with a similar retention time as tetranitromethane.

OTHER METHODS: This method revises and modifies S224 [1].

REAGENTS:

1. Tetranitromethane.
2. Ethyl acetate, nanograde.
3. Helium, purified.
4. Nitrogen, purified.
5. Hydrogen, purified.
6. Compressed air, filtered.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: midget impinger containing 15 mL ethyl acetate.
2. Personal sampling pump, 0.5 to 1.0 L/min, with flexible connecting tubing and splash over protection.
3. Gas chromatograph, NPD, integrator and column (page 3513-1).
4. Vials, 20-mL, with PTFE screw caps.
5. Syringes, 10-µL, and other convenient sizes.
6. Volumetric flasks, 25-mL, 10-mL.

SPECIAL PRECAUTIONS: Tetranitromethane is highly toxic and extremely explosive [3]. Use fume hood and protective equipment.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler inline.
2. Pipette 15 mL of ethyl acetate into each impinger. Attach midget impinger to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate of 0.5 to 1.0 L/minute for a total sample size of 20 to 250 L.
   NOTE: Routinely check and fill impingers to insure that the level of ethyl acetate remains at a volume of 10 to 15 mL.
4. Transfer the sample solution to 20-mL vial. Rinse impinger stem and body with 1 to 2 mL ethyl acetate, and add to the 20-mL vial.
5. Pack securely for shipment.

SAMPLE PREPARATION:

6. Transfer samples into 25-mL volumetric flasks and dilute to volume with ethyl acetate.
7. Transfer 1 mL aliquot to autosampler vials and immediately cap vials.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range 17 to 660 µg tetranitromethane per sample.
   a. Add known amounts of tetranitromethane to ethyl acetate in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 10 and 11).
   c. Prepare calibration graph (peak area vs. µg tetranitromethane).
9. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph is in control.

MEASUREMENT:

10. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 3513-1. Inject 1-µL sample aliquot manually using solvent flush technique or with autosampler.
    NOTE: If peak area is above the linear range of the working standards, dilute with ethyl acetate,

reanalyze and apply the appropriate dilution factor in calculations.

11. Measure peak area.

CALCULATIONS:

12. Determine the mass, µg, of tetranitromethane found in the impinger sample (W) and average media blank (B).
13. Calculate concentration, C (mg/m ^{3}), of tetranitromethane in the air volume sampled, V (L):

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

EVALUATION OF METHOD:

This method was validated over the range of 2.70 to 11.5 mg/m ^{3} at 19 °C and 763 mm Hg using a 250-L sample [1]. Collection efficiency was 0.895 ± 0.01 at 11.5 mg/m ^{3}; this was used as a correction factor in the validation experiments. The overall precision ($\hat{S}_{rT}$) was 0.076 and the bias was not significant [1]. In a later study, the LOD was determined to be 5 µg per sample and the analytical precision was 0.011 [2]. Tetranitromethane was stable for 14 days in 15-mL ethyl acetate solution. However, it is recommended that the samples be stored under refrigeration.

REFERENCES:

[1] NIOSH Manual of Analytical Methods, 2 ed., Vol. 3, S224, DHEW (NIOSH) Publication No. 77-157-C (1977).

[2] Pendergrass, S.M. Method Development for Tetranitromethane, MRSB, DPSE, NIOSH (unpublished, 1991).

[3] Hawley's Condensed Chemical Dictionary, 11th ed., N.I. Sax and R.J. Lewis, Eds. Van Nostrand Reinhold Co., New York (1987).

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