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

METHOD: 2522, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1989**
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OSHA : no PELs; N-nitrosodimethylamine is a carcinogen
NIOSH: no RELs; N-nitrosodimethylamine is suspect carcinogen
ACGIH: no TLVs; N-nitrosodimethylamine is suspect carcinogen

PROPERTIES: Table 1

SYNONYMS: Table 1.

SAMPLING

SAMPLER: SOLID SORBENT TUBE (Thermosorb/N™ air sampler)

FLOW RATE: 0.2 to 2 L/min

VOL-MIN: 15 L @ 10 µg/m^3
-MAX: 1000 L

SHIPMENT: routine

SAMPLE STABILITY: at least 6 weeks @ 20 °C [1,2]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: not studied

BIAS: not determined

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

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, TEA [1]

ANALYTE: nitrosamines (Table 1)

DESORPTION: 2 mL 3:1 (v/v) dichloromethane/methanol; stand 30 min

INJECTION VOLUME: 5 µL

COLUMN: stainless steel (10 in x $\frac{1}{8}$ in); 10% Carbowax 20M + 2% KOH on Chromosorb W-AW

TEMPERATURE-INJECTION: 200 °C
-DETECTOR: 550 °C to 600 °C
-COLUMN: 110 °C to 200 °C programmed @ 5°/min

GASES: N_2 carrier, 25 mL/min; oxygen, 5 mL/min; ozone, 0.2 mL/min

CALIBRATION: standard solutions of analytes in methanol/dichloromethane

RANGE: 0.15 to 0.5 µg per sample [2]

ESTIMATED LOD: 0.05 µg per sample [2]

PRECISION ($\hat{S}_r$): 0.014 @ 0.05 to 0.4 µg per sample [2]

APPLICABILITY: The working range is 0.003 to 10 mg/m^3 for a 50-L air sample. If high ambient concentrations of nitrosamines are expected, another Thermosorb/N tube should be used as a back-up in sampling.

INTERFERENCES: When the thermal energy analyzer (TEA) is operated in the nitrosamine mode, it is highly specific for N-nitroso compounds. Because of the TEA's selectivity and sensitivity, it is possible to chromatograph and quantitate N-nitroso compounds, even in the presence of other co-eluting compounds. Therefore, there is little or no interference from other compounds.

OTHER METHODS: This replaces NIOSH methods P&CAM 252 [3] and P&CAM 299 [4].

REAGENTS:

1. Dichloromethane, reagent grade.
2. Methanol, reagent grade.
3. Nitrogen, purified.
4. Oxygen, purified, 99.99%.
5. Standard solutions of N-nitrosodimethylamine, N-nitrosodiethylamine, N-nitrosodibutylamine, N-nitrosodipropylamine, N-nitrosomorpholine, N-nitrosopiperidine, N-nitrosopyrrolidine.
6. Eluent, 3:1 (v/v) dichloromethane/methanol.
7. Air, filtered, compressed.
8. Ozone, purified 99.99%.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: Commercially available tubes (Thermedics Detection, Inc., 220 Mill Rd., Chelmsford, MA 01824, 508/251-2000).
2. Personal sampling pump, 0.2 to 2 L/min, with flexible tubing.
3. Gas chromatograph equipped with thermal energy analyzer (TEA), integrator and column (page 2522-1).
4. Vials, glass, 2-mL, PTFE-lined crimp caps.
5. Pipets, various sizes for preparing standards.
6. Syringes, 1-, 5-, 10-, 25-, and 100-µL readable to 0.1 µL.
7. Volumetric flasks, 10-mL.
8. Gloves for safe handling of toxic chemicals.
9. Syringe, glass, 5.0-mL, with male Luer adapter.
10. Needle, industrial blunt, 20-gauge with female luer adapters.

S P E C I A L P R E C A U T I O N S :
N-nitrosodimethylamine is an OSHA-regulated carcinogen. Other nitrosamines are suspected carcinogens and are very toxic. Handle samples and standards in a well-ventilated hood or glove box.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Remove the Thermosorb/N tube from the foil pouch. Save the pouch.
3. Remove the red end caps from the inlet and outlet ports. Store red caps on the Thermosorb/N tube in the brackets under the "AIR IN" sign.
4. Label the Thermosorb/N tube with the peel-off "AIR SAMPLER" label provided on the foil pouch.
5. Attach the Thermosorb/N tube to the sampling pump with flexible tubing.
6. Sample at an accurately known flow rate between 0.2 and 2 L/min for a total sample size of 15 to 1000 L.
7. After sampling, detach the sampler from the pump.
8. Replace the red end caps on the inlet and outlet ports of the sampler.
9. Replace the Thermosorb/N tube in the foil pouch. Fold the pouch and seal it with the clip provided and pack securely for shipment.

SAMPLE PREPARATION:

10. Remove the sampler from the foil pouch.
11. Label analysis vial with the label from the Thermosorb/N air sampler.
12. Remove the red end-caps, store them in the bracket provided with the tube.
13. Attach a syringe needle to the male Luer fitting of the Thermosorb/N tube.
14. Attach a syringe barrel containing eluent to the female Luer fitting of the Thermosorb/N tube.
15. Elute by "backflushing" the Thermosorb/N tube with 2.0 mL of eluent. Collect the effluent in the labeled vial.
    NOTE: The optimum elution rate is 0.5 mL/min.

CALIBRATION AND QUALITY CONTROL:

16. Calibrate daily with at least six working standards over the range of 0.05 to 0.5 µg of analyte per sample (0.025 to 0.25 µg/mL).
    a. Add known amounts of the nitrosamines standard solution to eluent in 10-mL volumetric flasks and dilute to mark.
    b. Analyze together with samples and blanks (steps 19-22).
    c. Prepare calibration graph (peak area of analyte vs. µg analyte).
17. Determine desorption efficiency (DE) at least once for each batch of Thermosorb/N tubes used.
    a. Inject a known amount of nitrosamine standard solution directly onto the Thermosorb/N tube with a microliter syringe.
    b. Cap the tube. Allow to stand overnight.
    c. Desorb (steps 12 through 15) and analyze together with working standards (steps 19 through 22).
    d. Prepare a graph of DE vs. µg analyte recovered.
18. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

19. Set gas chromatograph and TEA to the conditions listed on page 2522-1.
20. Inject sample aliquot manually, using solvent flush technique or with an autosampler.
21. Approximate retention times of the seven nitrosamines at indicated column temperatures are:

COMPOUND	COLUMN TEMP. °C	RETENTION TIME (MIN)
N-nitrosodimethylamine	120	2.2
N-nitrosodiethylamine	125	3.1
N-nitrosodipropylamine	142	6.2
N-nitrosodibutylamine	145	7.4
N-nitrosomorpholine	178	13.2
N-nitrosopiperidine	169	12.0
N-nitrosopyrrolidine	166	11.2

22. Measure peak area.

CALCULATIONS:

23. Determine the mass, µg (corrected for DE) of analyte found in the sample (W) and blank (B).
24. Calculate concentration, C, analyte in the air volume sampled, V (L):

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

EVALUATION OF METHOD:

The method was evaluated over the range 0.05 to 0.5 µg of the seven nitrosamines per sample. Desorption efficiency was checked by spiking known amounts of the compounds on Thermosorb/N tubes and was found to be nearly 100% for all nitrosamines studied. The sampling device is small and interferences are minimal; large concentrations can be sampled (up to 1500 µg loading) with no breakthrough. Samples can be stored at room temperature for long periods of time (≥6 weeks). Some field samples were also used for evaluation of this method [2].

REFERENCES:

[1] Roundbehler, D. and Fajen J. N-Nitroso Compounds in the Factory Environment, NIOSH contract #210-77-0100 (1977).
[2] Foley, D. NIOSH/MRSB Method Development Efforts, Backup Data Report and Analysis for Nitrosamines, NIOSH, (Unpublished, 1983-1988).
[3] NIOSH Manual of Analytical Methods, 2nd ed., V. 1, P&CAM 252, U.S. Department of Health Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[4] Ibid., V.5, P&CAM 299, NIOSH Publ. 79-141 (1979).

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Table 1: General Information

Compounds (Synonyms)	Formula	MW	Properties
N-nitrosodimethylamine (N-Methyl-N-nitrosomethanamine; dimethylnitrosamine; DMN; DMNA; CAS #62-75-9) RTECS: IQ0525000	$(CH_3)_2N-N=O$	74.1	liquid; d 1.00 g/mL @ 20 °C; BP 151 °C; VP 0.36 kPa (2.7 mm Hg) @ 20 °C
N-nitrosodiethylamine (N-Ethyl-N-nitrosoethanamine; diethylnitrosamine; DEN; DENA; CAS #55-18-5) RTECS: IA3500000	$(C_2H_5)_2N-N=O$	102.1	liquid, d 0.94 g/mL @ 20 °C; BP 175 °C; VP 0.1 kPa (0.86 mm Hg) @ 20 °C
N-nitrosodipropylamine (N-Propyl-N-nitrosopropylamine DPN; DPNA; CAS #621-64-7) RTECS: JL9700000	$(C_3H_7)_2N-N=0$	130.2	liquid; d 0.916 g mL/@ 20 °C; BP 194.5 °C; VP 11 Pa (0.085 mm Hg) @ 20 °C
N-nitrosodibutylamine (N-Butyl-N-nitrosobutylamine; dibutylnitrosamine; CAS #924-16-3) RTECS: EJ4025000	$(C_4H_9)_2N-N=O$	158.3	liquid; d 9.901 g/mL @ 20 °C; BP 116 °C @ 14 mm Hg, VP 4 Pa (0.03 mm Hg) @ 20 °C
N-nitrosomorpholine (NMOR; 4-Nitrosomorpholine; MORNA; CAS #59-89-2) RTECS: QE7525000	$C_4H_8N_2O_2$	116.1	liquid/crystals; d unknown; BP 225 °C; MP 29 °C; VP unknown
N-nitrosopiperidine (N-NPIP; PIPNA; NPIP; CAS #100-75-4) RTECS: TN2100000	$(CH_2)_5N-N=0$	114.2	liquid; d 1.063 @ 19 °C; BP 217 °C @ 720 mm Hg; VP unknown
N-nitrosopyrrolidine (N-NPyr; NPYR, PYRNA; 1-Nitrosopynolodine; CAS #930-55-2) RTECS: UY1575000	$C_4H_8N-N=0$	100.1	liquid; d 1.09 g/mL @ 20 °C; BP 214 °C; VP 10 Pa (0.072 mm Hg) @ 20 °C