

NITROAROMATIC COMPOUNDS

2005

(1) Nitrobenzene: C ₆ H ₅ NO ₂	MW: (1) 123.11	CAS: (1) 98-95-3	RTECS: (1) DA6475000
(2) <i>o</i> -Nitrotoluene: CH ₃ C ₆ H ₄ NO ₂	(2) 137.14	(2) 88-72-2	(2) XT3150000
<i>m</i> -Nitrotoluene:		99-08-1	XT2975000
<i>p</i> -Nitrotoluene:		99-99-0	XT3325000
(3) 4-Chloronitrobenzene: C ₆ H ₄ ClNO ₂	(3) 157.56	(3) 100-00-5	(3) CZ1050000

METHOD: 2005, Issue 3

EVALUATION: Table 1

Issue 1: 15 August 1990

Issue 3: 15 January 1998

OSHA : Table 1

NIOSH: Table 1

ACGIH: Table 1

PROPERTIES: Table 1

SYNONYMS:

- (1) Nitrobenzol, oil of mirbane
- (2) *o*-Methylnitrobenzene, 2-Methylnitrobenzene, 2-Nitrotoluene
m-Methylnitrobenzene, 3-Methylnitrobenzene, 3-Nitrotoluene
p-Methylnitrobenzene, 4-Methylnitrobenzene, 4-Nitrotoluene
- (3) *p*-Chloronitrobenzene, 1-Chloro-4-nitrobenzene, 4-Nitrochlorobenzene, PCNB, PNCB

SAMPLING	MEASUREMENT												
<p>SAMPLER: SOLID SORBENT TUBE (Silica gel, 150 mg/75 mg)</p> <p>FLOW RATE: (1) and (3): 0.01 to 1 L/min; (2) 0.01 to 0.02 L/min</p> <table border="0" style="width: 100%;"> <tr> <td style="width: 33%;"></td> <td style="width: 33%; text-align: center;">(1)</td> <td style="width: 33%; text-align: center;">(2)</td> <td style="width: 33%; text-align: center;">(3)</td> </tr> <tr> <td>VOL-MIN:</td> <td style="text-align: center;">10 L</td> <td style="text-align: center;">1 L</td> <td style="text-align: center;">1 L</td> </tr> <tr> <td>-MAX:</td> <td style="text-align: center;">150 L</td> <td style="text-align: center;">30 L</td> <td style="text-align: center;">150 L</td> </tr> </table> <p>SHIPMENT: Routine</p> <p>SAMPLE STABILITY: 30 days @ 5°C</p> <p>BLANKS: 2 to 10 field blanks per set</p>		(1)	(2)	(3)	VOL-MIN:	10 L	1 L	1 L	-MAX:	150 L	30 L	150 L	<p>TECHNIQUE: GAS CHROMATOGRAPHY, FID</p> <p>ANALYTE: nitrobenzene, nitrotoluene isomers, 4-chloronitrobenzene</p> <p>DESORPTION: 1 mL methanol in ultrasonic bath for 30 minutes</p> <p>INJECTION VOLUME: 1 µL</p> <p>TEMPERATURE -INJECTION: 250°C -DETECTOR: 300°C -COLUMN: 80 °C, 1 min; 8 °C/min to 180 °C</p> <p>CARRIER GAS: He, 2.5 to 3.0 mL/min</p> <p>COLUMN: capillary, 30 m x 0.53-mm ID; µm film crossbonded 5% diphenyl 95% dimethylpolysiloxane, Rtx®-5 Amine or equivalent</p>
	(1)	(2)	(3)										
VOL-MIN:	10 L	1 L	1 L										
-MAX:	150 L	30 L	150 L										
ACCURACY													
<p>RANGE STUDIED: Table 1</p> <p>BIAS: Table 1</p> <p>OVERALL PRECISION (Ŝ_{r,T}): Table 1</p> <p>ACCURACY: Table 1</p>	<p>CALIBRATION: analytes in methanol</p> <p>RANGE: Table 1</p> <p>ESTIMATED LOD: Table 1</p> <p>PRECISION (Ŝ_r): Table 1</p>												

APPLICABILITY: The working ranges for a 30-L air samples are 0.396 to 1.92 ppm (1.98 to 9.60 mg/m³) for nitrobenzene; 0.346 to 1.73 ppm (1.97 to 9.86 mg/m³) for *o*-nitrotoluene; 0.344 to 1.72 ppm (1.96 to 9.81 mg/m³) for *m*-nitrotoluene; 0.303 to 1.52 ppm (1.73 to 8.67 mg/m³) for *p*-nitrotoluene; and 0.308 to 1.54 ppm (1.98 to 9.92 mg/m³) for 4-chloronitrobenzene [1,2].

INTERFERENCES: Any compounds with retention times similar to the analytes of interest will interfere. During sampling, high humidity may greatly decrease breakthrough volume.

OTHER METHODS: This method is an update of NMAM 2005, Nitrobenzenes, issued 15 August 1994, which combined and replaced methods S217, S218, and S223 [2,3].

REAGENTS:

1. Methanol, HPLC chromatographic grade.
2. Nitrobenzene*, reagent grade.
3. *o*-,*m*-,*p*-nitrotoluene isomers,* reagent grade.
4. 4-chloronitrobenzene*, reagent grade.
5. Calibration stock solution, 500 µg/mL. Prepare each analyte in methanol.
6. Helium, purified and filtered.
7. Hydrogen, purified and filtered.
8. Air, purified and filtered.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6-mm OD, 4-mm ID, flame-sealed ends with plastic caps, containing two sections (front=150 mg; back=75 mg) of 20/40 mesh silica gel separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section.
2. Personal sampling pump, 0.01 to 1 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 2005-1).
4. Autosampler vials, glass, 2-mL, with PTFE-lined crimp caps.
5. Volumetric flasks, 10-mL.
6. Pipets, 5-mL and 3-mL, with pipet bulb.
7. Syringes, 10-µL, 100-µL, and 1-mL.
8. Ultrasonic bath.

SPECIAL PRECAUTIONS: These analytes are severe poisons and irritants. Prevent contact with eyes, skin, or clothing by wearing eye protection, chemically resistant gloves, and a lab coat. Avoid inhalation. Nitrobenzene and *m*-nitrotoluene are absorbed through contact with skin and can cause methemoglobinemia [5,6]. 4-Chloronitrobenzene is a carcinogen. Methanol is highly flammable.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.2 L/min for nitrotoluene isomers. Use a flow rate of 1 L/min or less for nitrobenzene and 4-chloronitrobenzene. Note the maximum and minimum sample volumes on page 2005-1.
4. Cap both ends of the sampler. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front (include the glass wool plug) and back sorbent sections of each sample tube in separate vials. Discard the foam plugs.
6. Add 1.0 mL of methanol to each vial. Attach crimp cap securely to each vial.
7. Allow to desorb 30 min in an ultrasonic bath.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards to cover the analytical range of the method. If necessary, additional standards may be added to extend the calibration curve.
 - a. Add known amounts of calibration stock to methanol in 10-mL volumetric flasks and dilute to the mark.
 - b. Analyze together with samples and blanks (steps 11 and 12).
 - c. Prepare calibration graph (peak area vs µg analyte).
9. Determine desorption efficiency (DE) at least once for each lot of silica gel used for sampling in the calibration ranges (step 8).

- a. Prepare three tubes at each of five levels plus three media blanks.
 - b. Inject a known amount of calibration stock solution directly onto the front sorbent section of each silica gel tube with a microliter syringe.
 - c. Allow the tubes to air equilibrate for several minutes, then cap the ends of each tube and allow to stand overnight.
 - d. Desorb (steps 5 through 7) and analyze together with standards and blanks (steps 11 and 12).
 - e. Prepare a graph of DE vs μg analyte recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2005-1. Inject a 1- μL sample aliquot manually using the solvent flush technique or with an autosampler.
NOTE: If peak area is above the linear range of the working standards, dilute with methanol, reanalyze and apply the appropriate dilution factor in the calculations.
12. Measure peak areas.

CALCULATIONS:

13. Determine the mass, μg (corrected for DE) of analyte found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C , of analyte in the air volume sampled, $V(L)$:

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

NOTE: $\mu\text{g/mL} \equiv \text{mg/m}^3$

EVALUATION OF METHOD:

The update of this method included the use of capillary column chromatography that lowered the LOD/LOQ values, a lower 5-level desorption efficiency study, and a 30-day storage stability study for each analyte [1]. The method evaluation data for these compounds are listed in Table 2. Methods S217, Nitrobenzene, and S218, 4-nitrochlorobenzene, were initially issued on November 21, 1975 [4]. Method S228, nitrotoluene was issued on December 19, 1975 [4]. The analytes *m*-nitrotoluene and *p*-nitrotoluene were added on May 15, 1984 [3]. In the original method development work, sample tube capacity, or breakthrough, was determined as 5% of the generated atmosphere concentration as measured in the effluent of the sample tubes. Capacity was measured at >2.8 mg/sample for nitrobenzene; >2.5 mg/sample for nitrotoluene isomers; and >2.2 mg/sample for 4-chlorobenzene [2.]

REFERENCES:

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- [2] NIOSH [1977]. Documentation of the NIOSH Validation Tests, S217, S218, and S223, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185.
- [3] NIOSH [1994]. *m*-Nitrotoluene and *p*-Nitrotoluene: Method 2005. In: Eller PM, Cassinelli ME, eds. NIOSH Manual of Analytical Methods, 4th ed. Cincinnati, OH: U.S. Department of Health and Human

Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113.

- [4] NIOSH [1978]. Nitrobenzene: Method S217; *p*-Chloronitrobenzene: Method S218; and Nitrotoluene: Method S223. In: Taylor DG, ed. NIOSH Manual of Analytical Methods, 2nd ed., Cincinnati, OH: U.S. Department of Health, Education, and Welfare, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, Publ. (NIOSH) 77-157-C.
- [5] NIOSH [1977]. Occupational diseases, a guide to their recognition, revised ed., 235-238, 280-281, U.S. Department of Health, Education, and Welfare, DHEW (NIOSH) Publication No. 77-157-C.
- [6] NIOSH [1981]. NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, Nitrobenzene, Nitrochlorobenzene and Nitrotoluene, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123.

METHOD WRITTEN BY: Stephanie M. Pendergrass, NIOSH/DPSE

TABLE 1. GENERAL INFORMATION

<u>Chemical</u>	<u>TWA</u> OSHA NIOSH ACGIH	<u>Physical Properties</u>	<u>Method Evaluation</u>
Nitrobenzene	1 ppm (5.0 mg/m ³) (skin) 1 ppm (5.0 mg/m ³) (skin) 1 ppm (5.0 mg/m ³) (skin)	Colorless oily liquid, almond odor; d=1.196 g/mL @ 20°C; MP 6°C; BP 210- 211°C; VP=37 Pa (0.30 mm Hg) @ 20C	Full
<i>o</i> -Nitrotoluene	5 ppm (28.5 mg/m ³) (skin) 2 ppm (11.7 mg/m ³) 2 ppm (11.7 mg/m ³)	yellowish liquid; d=1.163 g/mL @ 20C; MP -4°C; BP 222°C; VP=20 Pa (0.15 mm Hg) @ 20°C	Full
<i>m</i> -Nitrotoluene	5 ppm (28.5 mg/m ³) 2 ppm (11.7 mg/m ³) 2 ppm (11.7 mg/m ³)	liquid; d=1.157 g/mL @ 20°C; MP 16°C; BP 232°C; VP=20 Pa (0.15 mm Hg) @ 20°C	Partial
<i>p</i> -Nitrotoluene	5 ppm (28.5 mg/m ³) 2 ppm (11.7 mg/m ³) 2 ppm (11.7 mg/m ³)	yellow crystals; d=1.163 g/mL @ 20C; MP 52°C; BP 238°C; VP=17 Pa (0.12 mm Hg) @ 20°C	Partial
4-Chloronitro- benzene	0.16 ppm (1.03 mg/m ³) Ca* 0.1 ppm (0.644 mg/m ³)	yellow crystals; d=1.298 g/mL @ 20C; MP 83°C; BP 242°C; VP=28 Pa (0.2 mm Hg) @ 30°C	Partial

* - Cancer suspect agent

TABLE 2. METHOD SUMMARY

Chemical	Range Studied^a (mg/m ³)	\hat{S}_{rT}	Bias	Accuracy (±%)	Analytical Range (µg/sample)	LOD (µg/sample)	\bar{S}_r	Desorption Efficiency (%)	30-Day Storage (% Rec)
Nitrobenzene	1.98 to 9.60	0.0590	0.0186	12.3	2 to 598	0.6	0.012	98.7	100.2
<i>o</i> -Nitrotoluene	1.97 to 9.86	0.0142	-0.120	21.1	3 to 582	0.8	0.028	98.2	101.2
<i>m</i> -Nitrotoluene	not studied	nd ^b	nd	nd	3 to 579	1.0	0.042	97.5	99.4
<i>p</i> -Nitrotoluene	not studied	nd	nd	nd	9 to 511	2.6	0.061	96.9	99.4
4-Chloro-nitrobenzene	1.98 to 9.92	0.1034	0.0869	27.3 ^c	8 to 595	2.5	0.063	100.3	97.6

^a 30-L air sample^b Not determined^c Exceeds the NIOSH accuracy criterion of ± 25% at the 95% confidence level