

**p-NITROANILINE****5033**

MW: 138.14

CAS: 100-01-6

RTECS: BY7000000

METHOD: 5033, Issue 1

EVALUATION: FULL

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OSHA : 6 mg/m<sup>3</sup> (skin)  
 NIOSH: 3 mg/m<sup>3</sup> (skin)  
 ACGIH: 3 mg/m<sup>3</sup> (skin)

PROPERTIES: yellow crystals; MP 146 °C; BP 332 °C;  
 VP 0.02 Pa (1.5 x 10<sup>-4</sup> mm Hg) @ 20 °C

SYNONYMS: 4-nitrobenzenamine, *p*-aminonitrobenzene, *p*-nitrophenylamine

SAMPLING		MEASUREMENT	
<b>SAMPLER:</b>	FILTER (0.8 µm mixed cellulose ester membrane)	<b>TECHNIQUE:</b>	HPLC, UV DETECTION
<b>FLOW RATE:</b>	1 to 3 L/min	<b>ANALYTE:</b>	<i>p</i> -nitroaniline
<b>VOL-MIN:</b>	16 L @ 6 mg/m <sup>3</sup>	<b>EXTRACTION:</b>	5 mL isopropanol
<b>-MAX:</b>	350 L	<b>MOBILE PHASE:</b>	40% isopropanol/60% hexane isocratic, 1 mL/min
<b>SHIPMENT:</b>	routine	<b>COLUMN:</b>	silica (Partisil 10, 25-cm x 4.6-mm x 6.4-mm stainless steel)
<b>SAMPLE STABILITY:</b>	at least 7 days @ 25 °C	<b>DETECTOR:</b>	UV @ 375 nm
<b>BLANKS:</b>	2 to 10 field blanks per set	<b>CALIBRATION:</b>	solutions of <i>p</i> -nitroaniline in isopropanol
<b>ACCURACY</b>		<b>RANGE:</b>	100 to 2000 µg per sample [1]
<b>RANGE STUDIED:</b>	3.9 to 12.9 mg/m <sup>3</sup> (90-L samples) [1]	<b>ESTIMATED LOD:</b>	20 µg per sample [1]
<b>BIAS:</b>	-1.7%	<b>PRECISION (<math>\hat{S}_r</math>):</b>	0.020 [1]
<b>OVERALL PRECISION (<math>\hat{S}_{rT}</math>):</b>	0.054 for range studied [1]		
<b>ACCURACY:</b>	±11.0%		

**APPLICABILITY:** The working range is 1.1 to 22 mg/m<sup>3</sup> for a 90-L air sample. This method is applicable to *p*-nitroaniline aerosol but not for environments where vapor may be present.

**INTERFERENCES:** None identified.

**OTHER METHODS:** This revises Method S7 [2].

**REAGENTS:**

1. p-Nitroaniline, 99%.\*
2. Isopropanol, distilled in glass.\*
3. Hexane, distilled in glass.\*
4. Calibration stock solution, 10 mg/mL: dissolve 0.100 g p-nitroaniline in 10 mL 2-propanol.

\* See SPECIAL PRECAUTIONS.

**EQUIPMENT:**

1. Sampler: mixed cellulose ester membrane filter (37-mm) and cellulose backup pad (37-mm) in a 2-piece filter holder held together by shrinkable band.
2. Personal sampling pump, calibrated, capable of operating 8 h at 1 to 3 L/min, with flexible connecting tubing.
3. HPLC with UV detector (375 nm), silica column (Partisil 10 or equivalent), injector, and electronic integrator.
4. Microliter syringes, various sizes.
5. Volumetric flasks, various sizes.
6. Squat form ointment jars with Teflon gaskets and screw caps.
7. Pipet, 5-mL, with pipet bulb.
8. Tweezers.

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**SPECIAL PRECAUTIONS:** p-Nitroaniline is a toxic agent that may be absorbed through the skin [3]. It is an explosion risk. Hexane and isopropanol are flammable liquids.

**SAMPLING:**

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Remove the front and rear plugs immediately before sampling and attach sampler to personal sampling pump with flexible tubing. Sample at a known flowrate between 1 and 3 L/min and collect a total sample of 16 to 350 liters of air.
3. Cap the filters, record sample identity and all relevant sample data (duration, ambient temperature and pressure).
4. Prepare blank sample filters by handling in the same manner (open, seal, and transport) as samples except that no air is sampled through the blanks.
5. Ship in suitable container with blanks.

**SAMPLE PREPARATION:**

6. Open the filter holder and using tweezers, transfer each mixed cellulose ester filter to an ointment jar.
7. Add 5 mL isopropanol, cap, and swirl the jar to ensure that the filter is thoroughly wetted.

**CALIBRATION AND QUALITY CONTROL:**

8. Calibrate daily with at least six working standards.
  - a. Dilute aliquots of p-nitroaniline stock solution with isopropanol in volumetric flasks to encompass the range of interest.
  - b. Prepare calibration graph (peak area vs.  $\mu\text{g}$  p-nitroaniline per sample).
9. Determine the recovery (R) of the filters at least once for each lot of filters used in the range of interest.
  - a. Using a microliter syringe, spike 6 filters at each of 3 concentration levels with p-nitroaniline in isopropanol. Allow the filters to dry overnight for solvent evaporation.
  - b. Analyze the spiked filters. Prepare graph of  $\mu\text{g}$  recovered vs.  $\mu\text{g}$  spiked.

10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and recovery graph are in control.

#### MEASUREMENT:

11. Set HPLC according to manufacturer's recommendations and to conditions on page 5033-1.
12. Separation is achieved on a silica column using a mobile phase of 40% isopropanol/60% hexane at 1 mL/min. Inject 20- $\mu$ L sample aliquot.  
NOTE: If peak area is above the linear range of the working standards, dilute with isopropanol and apply the appropriate dilution factor in calculations.
13. Measure peak areas.

#### CALCULATIONS:

14. Determine the mass of p-nitroaniline,  $\mu$ g (corrected for recovery), for the sample (W) and average media blank (B).
15. Calculate the concentration of p-nitroaniline, C ( $\text{mg}/\text{m}^3$ ), in the air volume sampled, V (L):

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

#### EVALUATION OF METHOD:

The method is not applicable to environments where p-nitroaniline vapor is present. However, experiments indicate that less than  $0.04 \text{ mg}/\text{m}^3$  of p-nitroaniline would exist as a vapor at  $40^\circ\text{C}$  [1]. Extraction efficiencies of spiked filters containing 0.278, 0.556, or 1.112 mg of p-nitroaniline were 96.6%, 94.7%, and 94.6%, respectively [1]. Samples generated to measure the filter's collection efficiency at 1.5 L/min for concentration of 3.9, 6.75, and  $12.88 \text{ mg}/\text{m}^3$  showed recoveries of 95.9%, 98.8%, and 100.9% respectively [1]. The average recovery for 7-day-old samples was 98.6% [1].

#### REFERENCES:

- [1] Back-up Data Report for p-Nitroaniline, S7, prepared under NIOSH Contract No. 210-76-0123, (1977).
- [2] NIOSH Manual of Analytical Methods, 2nd ed., V 3, S7, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B (1977).
- [3] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as stock #PB 83-154609 from NTIS, Springfield, VA 22161.

#### METHOD REVISED BY:

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