$C_{10}H_7OC(=O)NHCH_3$ MW: 201.22 CAS: 63-25-2 RTECS: FC5950000

METHOD: 5006, Issue 2 **EVALUATION: FULL** **Issue 1: 15 May 1985**
Issue 2: 15 August 1994

OSHA : 5 mg/m^3
NIOSH: 5 mg/m^3; Group II Pesticide
ACGIH: 5 mg/m^3

PROPERTIES: solid; crystal; d 1.230 g/mL @ 20 °C; BP decomposes; MP 142 °C; VP <0.005 Pa (<4 x 10-5 mm Hg; <0.4 mg/m^3) @ 20 °C

SYNONYMS: Sevin; 1-naphthalenol N-methylcarbamate; 1-Naphthyl-N-methylcarbamate

SAMPLING

SAMPLER: FILTER (glass fiber)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 20 L @ 5 mg/m^3
-MAX: 400 L

SHIPMENT: ship filters in 25-mL scintillation vials

SAMPLE STABILITY: at least 7 days @ 25 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 2 to 13 mg/m^3 [1] (90-L samples)

BIAS: - 0.73%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.057 [1]

ACCURACY: ± 11.3%

MEASUREMENT

TECHNIQUE: VISIBLE ABSORPTION SPECTROPHOTOMETRY

ANALYTE: p-nitrobenzenediazonium tetrafluoroborate complex

SAMPLE WORKUP: 20 mL 0.1 M methanolic potassium hydroxide; to 2-mL aliquot, add 17 mL glacial acetic acid; add 1 mL p-nitrobenzenediazonium tetrafluorobate

WAVELENGTH: 475 nm

CALIBRATION: Carbaryl in methylene chloride

RANGE: 0.1 to 1.0 mg per sample [2]

ESTIMATED LOD: 0.03 mg per sample [3,4]

PRECISION ($\hat{S}_r$): 0.015 [1]

APPLICABILITY: The working range is 0.5 to 20 mg/m^3 for a 200-L air sample.

INTERFERENCES: Phenols such as 1-naphthol will give a positive interference [2]. Interferences from other aromatic carbamates and phenoxyacetic acid pesticides may occur but have not been documented.

OTHER METHODS: This revises Method S273 [2].

REAGENTS:

1. Carbaryl, reagent grade.*
2. Methanol, absolute.*
3. Methylene chloride, distilled in glass.*
4. 0.1 M KOH in absolute methanol. Dissolve 0.1 mole (5.612 g) in 10 mL methanol in a 1-L volumetric flask; dilute to mark with methanol.
5. Glacial acetic acid.*
6. p-Nitrobenzenediazoniumtetrafluoroborate. Dissolve 25 mg in 5 mL methanol. Add 20 mL glacial acetic acid. Prepare just before use. Keep in an ice bath (4 °C) during use. Discard if the solution becomes deep yellow.
7. Calibration stock solution, 2 mg/mL.* Dissolve an accurately weighed 20-mg portion of Carbaryl in methylene chloride to make 10 mL solution.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: 37-mm filter cassette with 37-mm Type A/E glass fiber filter (Gelman Sciences, or equivalent).
   NOTE: The filter must be free of organic binders.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. Spectrophotometer capable of measuring at 475 nm with matched glass cuvettes (1-cm path length).
4. Vials, scintillation, 25-mL, with PTFE-lined screw caps.
5. Tweezers.
6. Syringe, Luer-Lok glass, 10-mL, with 13-mm stainless steel filter holder and PTFE filters.
7. Shaker, mechanical wrist-action.
8. Flasks, volumetric, 10-mL and 1 L.
9. Pipets, 1-, 2-, 17- and 20-mL with pipet bulb.
10. Syringes or micropipets, 10-, 25- and 50-µL.
11. Timer, 5- and 20-min.
12. Ice bath.

SPECIAL PRECAUTIONS: Carbaryl is a cholinesterase inhibitor; use precautions to prevent skin contamination [5,6]. Methylene chloride is toxic; use only in a hood. Methylene chloride is a suspect human carcinogen. Methanol is flammable and toxic (flash point = 11 °C); use only in a hood. Glacial acetic acid is corrosive; handle only with gloves and facial splash protection.

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 sample size of 20 to 400 L.
3. Within 1 h after sampling, remove the filter carefully to prevent sample loss and place it in a vial. Handle filter only with tweezers.

SAMPLE PREPARATION:

NOTE: Process the samples, blanks, recovery spikes, and working standards in small groups (e.g., two to four) to maintain consistent timing for all analyses. Include a reagent blank in each small group for use in the reference cell of the spectrophotometer.

4. Add 20 mL methanolic 0.1 M KOH to the vial containing the filter.
5. Place the vial on a shaker for 5 min.
6. Transfer 2 mL sample solution to another vial. Start reagent blank at this step.
   NOTE: For filter samples containing >1 g Carbaryl, dilute the sample solution with methanolic 0.1 M KOH prior to this step.
7. Add 17.0 mL glacial acetic acid to the 2 mL of sample solution and cover vial with a PTFE-lined screw cap. Mix by swirling.
8. Add 1 mL p-nitrobenzenediazonium tetrafluoroborate solution. Mix by swirling. Start a 20-min timer for each vial at this point.
9. Use a syringe fitted with a PTFE in-line filter to transfer the solution from the sample vial to the cuvette. Proceed directly to step 15 after exactly 20 min from step 8.

NOTE 1: The color degrades steadily with time. All samples, blanks, recovery spikes, and working standards must have exactly the same time for color development.

NOTE 2: The PTFE in-line filter removes glass fibers from the samples. (Standards do not have to be filtered.)

CALIBRATION AND QUALITY CONTROL:

10. Calibrate with at least six working standards over the range 0.05 to 1.0 mg Carbaryl per sample.
    a. Add known amounts of calibration stock solution to methanolic 0.1 M KOH in vials to make 20 mL of solution.
    b. After 5 min, transfer 2.0 mL of each solution into a clean vial.
    c. Prepare as in steps 7 through 9.
    d. Analyze together with samples and blanks (steps 13 through 15).
    e. Prepare calibration graph (absorbance vs. mg Carbaryl).
11. Check recovery with at least three spiked media blanks per sample set.
    a. Add aliquot of calibration stock solution with a microliter syringe directly to a representative filter. Air dry.
    b. Prepare and analyze together with working standards (steps 4 through 9 and 13 through 15).
    c. Calculate recovery [(mg recovered - mg blank)/mg added].
12. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph is in control.

MEASUREMENT:

13. Set spectrophotometer at 475 nm.
14. Adjust baseline to zero with distilled water in both cells.
15. Read the absorbance of the sample against the absorbance of the reagent blank.
    NOTE 1: Prepare a fresh reagent blank with each small group of samples. The absorbance of reagent blanks increases with time [5].
    NOTE 2: If absorbance of the sample is >1.0, dilute the filter extract (step 4) with methanolic 0.1 M KOH, reanalyze, and apply the appropriate dilution factor in calculations.

CALCULATIONS:

16. Determine the mass, mg of Carbaryl found on the filter, W, and average media blank, B, from the calibration graph.
17. Calculate the concentration, C (mg/m ^{3}), of Carbaryl in the air volume sampled, V (L):

$$C = \frac{(W - B) \cdot 10^3}{V}, mg/m^3.$$

EVALUATION OF METHOD:

Method S273 [2] was issued on February 27, 1976, and validated over the range of 1.96 to 13.4 mg/m ^{3} at 24 °C and 763 mm Hg [1]. Overall precision, $\hat{S}_{rT}$, was 0.057 with an average recovery of 102%, representing a non-significant bias. The concentration of Carbaryl was independently verified by a Thermo Systems particle mass monitor. Generated atmospheres were produced by nebulization of a toluene solution of a commercial formulation of Sevin containing 15% Carbaryl by weight. No Carbaryl was detected in bubblers (containing 0.1 M KOH in methanol) placed behind the glass fiber filters when 90-L air samples were taken of an atmosphere containing 15 mg/m ^{3} Carbaryl. Thus, it was concluded that Carbaryl vapor was not a significant factor.

REFERENCES:

[1] Documentation of NIOSH Validation Tests, S273, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).
[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 3, S273, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[3] User check, UBTL, Inc., NIOSH Sequence #4213-V (unpublished, August 16, 1984).
[4] User check, Kettering Laboratory, University of Cincinnati (NIOSH, unpublished, November 5, 1984).
[5] NIOSH Criteria for a Recommended Standard...Occupational Exposure to Carbaryl, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-107 (1976).
[6] NIOSH Criteria for a Recommended Standard...Occupational Exposure During the Manufacture and Formulation of Pesticides, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-174 (July, 1978).

METHOD REVISED BY:

P. Fey O'Connor, NIOSH/DPSE; S273 originally validated under NIOSH Contract 99-74-45.