(1) $C_7H_3Br_2NO$ MW: (1) 276.93 CAS: (1) 1689-84-5 RTECS: (1) DI3150000
(2) $C_{15}H_{17}Br_2NO_2$ (2) 403.13 (2) 1689-99-2 (2) DI3325000

METHOD: 5010, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 May 1989**
Issue 2: 15 August 1994

OSHA : no PEL
NIOSH: no REL
ACGIH: no TLV

PROPERTIES: (1) liquid; BP 194 to 195 °C;
(2) solid; MP 45 to 47 °C

SYNONYMS: (1): 2,6-dibromo-4-cyanophenol; 3,5-dibromo-4-hydroxybenzonitrile;
(2): 2,6-dibromo-4-cyanophenyl octanoate.

SAMPLING

SAMPLER: FILTER
(2-µm PTFE membrane)

FLOW RATE: 1 to 3 L/min

VOL-MIN: 2 L @ 0.1 mg/m^3
-MAX: 400 L

SHIPMENT: refrigerated; protect from light

SAMPLE STABILITY: at least 25 days @ 4 °C in the dark [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: not studied

BIAS: none identified

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

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: HPLC, UV DETECTION

ANALYTE: Bromoxynil; Bromoxynil octanoate

EXTRACTION: 3 mL acetonitrile; 60 min

MOBILE PHASE: acetonitrile/water gradient; 1 mL/min

COLUMN: µ-Bondapack C_{18}, 25 cm x 4.6 mm-ID reverse phase or equivalent

DETECTOR: UV detector @ 254 nm

CALIBRATION: solutions of analytes in acetonitrile

RANGE: 2 to 30 µg per sample [1]

ESTIMATED LOD: (1) 0.6 and (2) 0.3 µg per sample [1]

PRECISION ($\hat{S}_r$): (1) 0.011 @ 18 µg per sample [1]
(2) 0.042 @ 35 µg per sample [1]

APPLICABILITY: The working range is 0.02 to 0.3 mg/m^3 for a 100-L air sample. This method permits the simultaneous determination of both analytes.

INTERFERENCES: None known. Both analytes photodecompose.

OTHER METHODS: A gas chromatographic method has been described [2].

REAGENTS:

1. Bromoxynil.
2. Bromoxynil octanoate.
3. Acetonitrile, HPLC grade.
4. Water, distilled, deionized.
5. Calibration stock solution, 1 mg/mL. Dissolve 0.100 g each of Bromoxynil and Bromoxynil octanoate in acetonitrile; dilute to 100 mL in a volumetric flask. Prepare daily, in duplicate.

EQUIPMENT:

1. Sampler: PTFE-coated glass fiber (Pallflex T60A20) or 2-µm PTFE membrane (GHIA), 37-mm diameter. (Filters commercially available).
   NOTE: Use opaque or light-protected cassette filter holder.
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. Jars, ointment, 60-mL, squat form, with PTFE-lined screw caps.
4. Volumetric flasks, 10- and 100-mL
5. Pipet, 3-mL.
6. Vials (for autosampler).
7. Liquid chromatograph with gradient capability, UV detector (254 nm) and column, (see page 5010-1).
8. Syringes, 5-mL.
9. Syringe filters, PTFE; or Swinnex adaptor with luer fitting containing 0.5-µm PTFE filter, 13-mm.

SPECIAL PRECAUTIONS: None.

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 total sample size of 20 to 400 L. Do not exceed 2 mg total dust loading on filter.
3. After sampling, cap the filter holders, ship at 4 °C and protect from light.

SAMPLE PREPARATION:

4. Transfer the filter to a jar. Add 3.0 mL acetonitrile and desorb with occasional swirling for at least 1 h.
5. Filter an aliquot through a PTFE syringe filter or a 0.5-µm PTFE filter using a syringe with a Swinnex adaptor to remove particulate. Transfer the aliquot to a sample vial and seal.

CALIBRATION AND QUALITY CONTROL:

6. Calibrate daily with at least six working standards over the range 0.6 to 30 µg of both analytes per sample.
   a. Add known amounts of calibration stock solution to acetonitrile 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).
      NOTE: Before processing any samples, demonstrate, through the analysis of a solvent blank, that all glassware and reagents are interference-free. Each time a new set of samples is analyzed or there is a change in reagents, process a solvent blank as a safeguard against chronic laboratory contamination.

MEASUREMENT:

7. Set the liquid chromatograph to the conditions on page 5010-1 using the following mobile phase gradient: 50% CH_3CN/50% H_2O for 10 min; 10 min gradient to 100% CH_3N; hold 10 min; 2 min gradient to 50% CH_3CN/50% H_2O; hold 15 min.
8. Inject 100 µL sample extract with a high-pressure syringe or a sampling loop. Record the volume injected to the nearest 0.5 µL. Under these conditions, the retention times are 3.6 min for Bromoxynil and 33 min for Bromoxynil octanoate.
9. Measure peak area.
   NOTE: If the peak area exceeds the linear range of the system, dilute with acetonitrile and reanalyze. If the peak area measurement is hindered by the presence of interferences, other chromatographic conditions may be required.

CALCULATIONS:

10. Read the mass of analytes (including appropriate aliquot factors) in the sample extract, W (µg), and average media blank, B (µg), from the calibration graph.
11. Determine the concentrations, C (mg/m^3), of each analyte in the air volume sampled, V (L):

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

EVALUATION OF METHOD:

This method was developed with laboratory samples during the period June to September, 1983 [1]. PTFE-coated glass fiber filters were spiked with 50 µg Bromoxynil and 90 µg Bromoxynil octanoate, after which 90 L of clean air at 80% RH was drawn through the filters. Recoveries averaged 93% for Bromoxynil and 100% for Bromoxynil octanoate with relative standard deviations, $\bar{S}_r$, of 0.046 and 0.020, respectively. Storage at ambient conditions for 14 days gave recoveries of 70 to 80% for both compounds, while storage under refrigeration for 25 days or at ambient conditions for two days followed by refrigeration for 23 days gave recoveries in the range 95 to 98%.

REFERENCES:

[1] Arthur D. Little, Inc., Backup Data Report prepared under NIOSH Contract 200-82-2528 (unpublished, October 7, 1983).
[2] Thrun, K., J. Harris, and V. Grady. "Sampling and Analysis Procedures for Pesticide Manufacturing Wastes," Report, EPA Contract No. 68-02-3111 (1982).

METHOD WRITTEN BY:

K. T. Menzies, K. J. Beltis, A. C. Roche, Arthur D. Little, Inc.; and B. R. Belinky, NIOSH/DPSE.