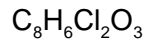


2,4-D

5001



MW: 221.04

CAS: 94-75-7

RTECS: AG6825000

METHOD: 5001, Issue 2

EVALUATION: FULL

Issue 1: 15 February 1984

Issue 2: 15 August 1994

OSHA : 10 mg/m³
 NIOSH: 10 mg/m³
 ACGIH: 10 mg/m³

PROPERTIES: solid; MP 138 °C; VP not significant

SYNONYMS: 2,4-D: (2,4-dichlorophenoxy)acetic acid; hedonal; Trinoxol

SAMPLING		MEASUREMENT	
SAMPLER:	FILTER (glass fiber, binderless)	TECHNIQUE:	HPLC, UV DETECTION
FLOW RATE:	1 to 3 L/min	ANALYTE:	2,4-D anion
VOL-MIN:	15 L @ 10 mg/m ³	DESORPTION:	15 mL CH ₃ OH; stand 30 min
-MAX:	200 L	INJECTION VOLUME:	50 µL
SHIPMENT:	routine	ELUENT:	0.001 M NaClO ₄ -0.001 M Na ₂ B ₄ O ₇
SAMPLE STABILITY:	at least 1 week @ 25 °C	FLOW RATE:	1.7 mL/min
BLANKS:	2 to 10 field blanks per set	DETECTOR:	UV @ 284 nm
ACCURACY		COLUMN:	stainless steel, 50 cm x 2-mm ID, packed with Zipax SAX (DuPont) ambient temperature; 6900 kPa (1000 psi)
RANGE STUDIED:	5 to 20 mg/m ³ [1,2] (100-L samples)	CALIBRATION:	solutions of analyte in methanol
BIAS:	- 1.26%	RANGE:	0.15 to 2 mg per filter
OVERALL PRECISION ($\hat{S}_{r,T}$):	0.051 (2,4-D) [1]	ESTIMATED LOD:	0.015 mg per filter [1]
ACCURACY:	± 10.21%	PRECISION (\hat{S}_r):	0.01 [1]

APPLICABILITY: This method determines 2,4-D, 2,4,5-T, and their salts, but not their esters. The working range is 1.5 to 20 mg/m³ of either compound for a 100-L air sample.

INTERFERENCES: High concentrations of esters of either compound do not interfere but require the use of a pre-column to prevent degradation of the HPLC column.

OTHER METHODS: This method combines and replaces Methods S279 [3] and S303 [3] which are the same except for eluent composition and UV detector wavelength.

REAGENTS:

1. 2,4-dichlorophenoxyacetic acid.*
2. 2,4,5-trichlorophenoxyacetic acid.*
3. Methanol, HPLC grade.
4. LC eluent:
 - a. 2,4-D: 0.001 N NaClO₄ and 0.001 N Na₂B₄O₇. Add 0.122 g NaClO₄ and 0.381 g Na₂B₄O₇·10H₂O to a 1-L volumetric flask. Bring to volume with distilled water. Mix, filter and de-gas the solution.
 - b. 2,4,5-T: 0.003 M NaClO₄ and 0.001 M Na₂B₄O₇·10H₂O. Add 0.366 g NaClO₄ and 0.381 g Na₂B₄O₇·10H₂O to a 1-L volumetric flask. Bring to volume with distilled water. Mix, filter and de-gas the solution.
5. Compressed, filtered air or nitrogen for drying syringes.
6. Ethanol, absolute.
7. Acetone.
8. Calibration stock solution, 400 µg/mL. Dissolve 0.400 g 2,4-D or 2,4,5-T in methanol and dilute to 1 L with methanol.
9. Recovery stock solution:
 - a. Dissolve 0.248 g 2,4-D in ethanol. Dilute to 10 mL with ethanol.
 - b. Dissolve 0.250 g 2,4,5-T, triethylamine salt, in acetone (or 0.250 g 2,4,5-T in methanol). Dilute to 10 mL with acetone.

NOTE: Use the same form (e.g., acid or salt) of 2,4,5-T as in the air sample. Recovery may vary with the chemical form.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: filter, glass fiber, binderless, in a 37-mm polystyrene two-piece cassette filter holder (Gelman type AE or equivalent).
2. Personal sampling pump, 1 to 3 L/min, with flexible connecting tubing.
3. High pressure liquid chromatograph, UV detector at 284 nm (2,4-D) and 289 nm (2,4,5-T), integrator and column (page 5001-1).
4. Filter, PTFE, 5-µm, 13-mm diameter in Swinny stainless (13-mm) filter holder.
5. Tweezers.
6. Syringes, 20-mL luer-lock.*
7. Vials, glass, 20-mL.*
8. Volumetric flasks, convenient sizes for preparing standard solutions.*

* Wash all glassware with detergent, thoroughly rinse with tap water and distilled water.

SAMPLING:

1. Calibrate each personal sampling pump with a representative filter in line.
2. Sample at an accurately known flow rate between 1 and 3 L/min for a total sample size of 15 to 200 L. Do not exceed a total dust loading of 2 mg on the filter.
3. Obtain information on the chemical form of the analyte (i.e., ester, salt or free acid) likely to be present in the air sample.

SPECIAL PRECAUTIONS: 2,4-D and 2,4,5-T are suspected animal carcinogens [4]. 2,3,7,8-Tetrachlorodibenzo-1,4-dioxin has been identified as an impurity in 2,4,5-T. Avoid any contact with these substances.

SAMPLE PREPARATION:

4. Remove the filter from the cassette with clean tweezers and place it in a 20-mL vial.
5. Add 15 mL methanol and mix by swirling. Allow to stand at least 30 min.
6. Filter the sample.
 - a. Pour the sample solution into a 20-mL syringe which is fitted with a 5- μ m PTFE filter.
 - b. Filter the sample into a clean vial.
 - c. Clean the PTFE filter by backflushing with methanol. Rinse the syringe and plunger with methanol. Dry with air or nitrogen.

CALIBRATION AND QUALITY CONTROL:

7. Calibrate daily with at least five working standards.
 - a. Dilute aliquots of calibration stock solution to 10 mL with methanol in volumetric flasks.
 - b. Analyze working standards (steps 9 and 10).
 - c. Prepare calibration graph (peak area vs. mg 2,4-D or mg 2,4,5-T).
8. Check recovery with at least four spiked media blanks at each of four levels.
 - a. Add aliquot of recovery stock solution to media blank.
 - b. Analyze using standards prepared from the recovery stock solution.
 - c. Calculate R (mg recovered/mg added).

MEASUREMENT:

9. Establish chromatographic conditions listed on page 5001-1 for either 2,4-D or 2,4,5-T.
10. Inject 50 μ L of sample in duplicate. Rinse and dry the syringe between samples.

NOTE 1: The analyte is the chlorinated phenoxyacetate, whether the air sample contained salts or free acid forms of 2,4-D and 2,4,5-T.

NOTE 2: Esters of 2,4-D and 2,4,5-T will not elute from the HPLC column and may, if present in large amounts, degrade the HPLC column. Protect the main column with a precolumn of Zipax SAX if esters are known to be present. The sample preparation conditions are sufficiently mild so as to preclude hydrolysis of the esters.

CALCULATIONS:

11. Read the mass of analyte, mg (corrected for recovery), in the sample (W) and average media blank (B) from the calibration curve.
12. Calculate the concentration, C (mg/m³), of 2,4-D or 2,4,5-T in air volume, V (L), taken:

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

EVALUATION OF METHOD:

Methods S279 (2,4-D) and S303 (2,4,5-T) were issued on February 17, 1978, and March 17, 1978, respectively [3], and validated using 100-L air samples [1,2,5]. Atmospheres were generated using 2,4-D dimethylamine salt for S279 and Weedar Amine BK (Amchem; equal parts of 2,4-D dimethylamine salt and 2,4,5-T triethylamine salt) for S303. Overall precision and recovery for 100-L samples were as shown, representing non-significant bias in each method:

Method	Overall Precision (\bar{S}_r)	Range Studied		Recovery @ 0.5 mg	7-Day Storage Stability, % of Day 1
		mg/m ³	mg per sample		
S279	0.051	5 to 20	0.5 to 2	0.97	99
S303	0.053	5 to 21	0.5 to 2	0.86 to 0.99	104

REFERENCES:

- [1] Backup Data Report S279 for 2,4-D prepared under NIOSH Contract No. 210-76-0123 (unpublished, 1976), available as "Ten NIOSH Analytical Methods, Set 6," Order No. PB 288-629 from NTIS, Springfield, VA 22161.
- [2] Backup Data Report S303 for 2,4,5-T prepared under NIOSH Contract No. 210-76-0123 (unpublished, 1976), available as "Ten NIOSH Analytical Methods, Set 6," Order No. PB 288-629 from NTIS, Springfield, VA 22161.
- [3] NIOSH Manual of Analytical Methods, 2nd ed., V. 5, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 (1979).
- [4] Criteria for a Recommended Standard...Occupational Exposure During Manufacture and Formulation of Pesticides, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-174 (1978). Welfare, Publ. (NIOSH) 79-141 (1979).
- [5] NIOSH Research Report-Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY:

Robert W. Kurimo, NIOSH/DPSE; originally validated under NIOSH Contract No. 210-76-0123.