CHLORINATED AND ORGANONITROGEN HERBICIDES (AIR SAMPLING) 5602

ANALYTES: Figure 1 Formula: Table 1 MW: Table 1 CAS: Table 1 RTECS: Table 1

METHOD: 5602, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 January 1998**

OSHA: Table 1
NIOSH: Table 1
ACGIH: Table 1

PROPERTIES: Table 1

NAMES:	Alachlor	Atrazine	2,4-D acid	2,4-D, 2-ethylhexyl ester
	Cyanazine	Metolachlor	Simazine	2,4-D, 2-butoxyethyl ester

SAMPLING

SAMPLER: FILTER/SOLID SORBENT TUBE (OVS tube: 11-mm quartz filter; XAD-2)

FLOW RATE: 0.2 to 1 L/min

VOL-MIN: 12 L
-MAX: 480 L

SHIPMENT: routine

SAMPLE STABILITY: at least 30 days @ 5 °C
at least 10 days @ 25 °C [1]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: Table 3

ACCURACY: Table 3

BIAS: Table 3

OVERALL PRECISION ($\hat{S}_{rT}$): Table 3

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY/ ELECTRON CAPTURE DETECTOR (GC/ECD)

ANALYTE: Table 1

EXTRACTION: 2 mL 10% methanol/90% methyl t-butyl ether (with diazomethane), shaker ≥ 1 h

INJECTION VOLUME: 2 µL

TEMPERATURE-INJECTION: 270 °C
-DETECTOR: 300 °C
-COLUMN: 90 °C, 1 min; 35 °C/min to 160 °C; 3 °C/min to 230 °C; hold 9 min.

CARRIER GAS: He at 1 mL/min

COLUMN: capillary, fused silica, 30 m X 0.25-mm ID, 0.25-µm film, 50% phenyl, 50% methyl silicone, DB-17 or equivalent. See Table 2.

CALIBRATION: standard solutions of herbicides in methanol/ methyl t-butyl ether (10:90)

RANGE: Table 3

ESTIMATED LOD: Table 3

PRECISION ($\tilde{S}_r$): Table 3

APPLICABILITY: The working ranges, listed in Table 3, cover ranges from the LOQ to approximately 30 X LOQ. This method may be applicable to the determination of many other thermally stable organonitrogen, aryl and alkyl acidic, and phenolic pesticides after evaluation. Determination of cyanazine is semiquantitative using this method.

INTERFERENCES: Because of the great sensitivity of the ECD, there are many potential interferences. Those observed are plasticizers (e.g., dibutyl phthalate), methylated fatty acids (negative response), phenols, antioxidants, and other additives (e.g., BHT) , any volatile or semivolatile halogenated or nitrated organic, organophosphorous compounds, and other pesticides. Agricultural spray additives, such as solvents, emulsifiers, wetting agents, breakdown products, and fertilizers (e.g., fatty acids and urea), can present serious interferences. Second-column confirmation is very desirable (See Table 3). The background levels of different lots of OVS tubes vary widely and may interfere at the lower levels.

OTHER METHODS: This method replaces previously related pesticide methods. Alternate methods for the determination of 2,4-D in air are S279 [2] and 5001 [3]. The OVS tube is similar in concept to the device of Hill and Arnold [4], but offers greater convenience and lower flow resistance. Other methods allowing simultaneous determination of organonitrogen and acid compounds and their esters are unknown.

REAGENTS:

1. Analytes listed in Table 1.
2. Methanol, pesticide analytical grade.
3. Methyl t-butyl ether, pesticide analytical grade.
4. Extraction solvent. Add 10 mL of methanol to a 100-mL volumetric flask. Dilute to volume with methyl t-butyl ether.
5. Diazald® (N-methyl-N-nitroso-*p*-toluenesulfonamide.)*
6. Silicic Acid, 100-mesh.
7. Diazomethane* derivatizing reagent. (See APPENDIX)
8. Herbicide stock solutions. Prepare individual standard stock solutions of each herbicide of interest in extraction solvent.
   NOTE: All herbicides in Table 1 were found to be soluble to at least 1 mg/mL, except simazine, which is soluble to 0.5 mg/mL.
9. Calibration stock solution. Dilute the appropriate volume of herbicide stock solution to a known volume with extraction solvent.
   NOTE: Spiking solutions may contain more than one analyte.
10. Purified gases: helium, 5% methane in argon, or nitrogen.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tube, 11-mm ID x 13-mm OD x 50 mm long, with the outlet end drawn to a 6-mm OD x 25 mm long tube (Figure 2). The enlarged part of the tube contains a 270-mg front section of 20/60 mesh XAD-2 sorbent held in place by a 11-mm quartz fiber filter and polytetrafluoroethylene (PTFE) retaining ring at inlet and a small plug of polyurethane foam at the back end. The back section consists of 140-mg XAD-2 sorbent held in place by a long plug of polyurethane foam. Tubes commercially available (SKC, Inc. Cat. No. 226-58).
2. Personal sampling pump, 0.2 to 1 L/min with flexible connecting tubing.
3. Gas chromatograph, electron capture detector, integrator, and column (Table 2).
4. Vials, glass, 4-, 2-, and 0.1-mL limited-volume vials with PTFE-lined caps.
5. Syringes, 1- and 5-mL; 10-, 50-, and 100-µL as needed.
6. Volumetric flasks, 2-, 5-, 10-, 25-, 50-, and 100-mL for working standard preparation and solutions.
7. Forceps.
8. PTFE syringe filters, 0.45-µm pore size (Gelman Sciences or equivalent).
9. Syringe, luer lock, 1-, 2.5-, or 5-mL, for sample filtering.
10. Platform shaker

SPECIAL PRECAUTIONS: Diazomethane has been cited as a carcinogen. It is extremely toxic and highly irritating. Diazomethane may explode under some conditions. Do not heat above 90 °C. Avoid rough surfaces: fire-polish glass tubing, or use Teflon®. Do not expose solutions to strong light. Keep dilute solutions at 0 °C. Prepare in a hood [5]. Avoid skin contact with *Diazald*® and herbicides. Avoid skin contact and open flame with solvents. Wear appropriate protective clothing and work with these compounds in a well ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Connect the sampler to the personal sampling pump with flexible tubing. The sampler should be placed vertically with the large end down.
3. Sample at a known flow rate between 0.2 and 1 L/min for a total sample size of 12 to 480 L.
4. Cap both ends of the sampler with plastic caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Remove cap from large end of sampler and remove PTFE retainer ring; carefully transfer filter and front XAD-2 resin section to a 4-mL vial. Transfer the short polyurethane foam plug along with the back-up XAD-2 resin bed to a second 4-mL vial. Discard back-up plug.
6. Add 2 mL of diazomethane derivatizing reagent to each vial using a 5-mL syringe or 2-mL pipette; cap each vial. Mix by rotating at 5 to 10 RPM on a platform shaker for a minimum of one hour.
7. Add approximately 10 mg of silicic acid to the solution, mix, and allow to stand for one hour.

8. Filter an aliquot through a 0.45-µm PTFE filter into a 2-mL GC vial or limited volume GC vial.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards covering the analytical range of the method for individual analytes. Three standards (in duplicate) should cover the range from LOD to LOQ.
   a. Add known amounts of calibration stock solution to the diazomethane derivatizing reagent in a volumetric flask and let stand for 1 hour. Include a calibration blank of unspiked diazomethane derivatizing reagent solution.
   b. Add 10 mg silicic acid to each standard vial, and let stand for an additional hour.
   c. Filter through a 0.45-µm syringe filter into a GC vial.
   d. Analyze together with field samples and blanks (steps 12 and 13).
   e. Prepare calibration graph (peak area or height vs. µg analyte).
10. Determine desorption efficiency (DE) at least once for each lot of OVS tubes used for sampling. Independently prepared quality control herbicide solutions in extraction solvent must be prepared at concentrations within the analytical range. Prepare three samplers at each of six levels plus three media blanks.
    a. Remove and discard back sorbent sections of samplers and media blanks.
    b. Remove cap from large end of sampler tube. Pull up PTFE retainer ring to prevent trapping of spiking solution under ring. Apply a known amount of calibration stock solution to face of quartz fiber filter. Pull air through for one hour at 0.2 to 1 L/min.
    c. Desorb the samples (steps 5 through 8) and analyze together with working standards and blanks (steps 12 and 13).
    d. Prepare a graph of DE vs. µg analyte recovered.
11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration and DE graphs are in control.

MEASUREMENT:

12. Set gas chromatograph according to manufacturer's recommendations and to conditions listed in Table 2.. Inject 2-µL aliquot manually using solvent flush technique or with autosampler. See Table 4 for retention times of selected analytes.
    NOTE: If peak height is greater than the range of the working standards, dilute with extraction solvent and reanalyze. Apply the appropriate dilution factor in calculations.
13. Measure peak height or area of analyte.

CALCULATIONS:

14. Determine the mass, µg (corrected for DE), of respective analyte found in the sample front (W_f) and back (W_b) sorbent sections, and in the media blank front (B_f) and back (B_b) sorbent sections from the calibration graph.
    NOTE: The filter is combined with the front section. If $W_b > W_f/10$, report breakthrough and possible sample loss.
15. Calculate concentration, C, of analyte in the air volume sampled, V (L):

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

NOTE: µg/mL ≡ mg/m^3

CONFIRMATION:

Whenever the identity of an analyte is uncertain, confirmation may be achieved by analysis on a column of

different polarity. If primary analysis was performed using a nonpolar or weakly polar column (*e.g.*, DB-1 or DB-5) confirmation should be accomplished by reanalysis on a polar column (*e.g.*, DB-17 or DB-1701). See Table 4 for approximate retention times for each column type. For positive identification of high-level analytes (1 to 10 µg/mL or greater), GC/MS may be used. Figure 4 shows a typical chromatogram using a DB-17 column. Figure 5 shows a typical chromatogram using a DB-5 column. Table 5 gives notes on the analytical characteristics of the chlorinated organonitrogen and acid herbicides.

EVALUATION OF METHOD:

The method was evaluated over the ranges listed in Table 3. These ranges represent 3 x LOQ to 30 x LOQ for each of the compounds. Table 3 also lists the measurement precision ($\bar{S}_r$), overall sampling and measurement precision ($\hat{S}_{rT}$), bias, and accuracy for the compounds evaluated using this method. The analytical conditions used in the evaluation are in Table 4 with the DB-5ms column. The front filter of each sample tube was fortified with an aliquot of a solution containing the 8 herbicides. Air was then drawn through the tubes at 1 L/min for 8 h (480 L total volume) at 30 °C. One set of samplers was tested at 15% relative humidity (RH) and the other set was tested at 80% RH. All samples were stored at 4 °C. Humidity did not affect the analyte recoveries from the samplers. A long-term storage study also was done. Samples were loaded at the 10 x LOQ level and 480 L of 80% RH air was pulled through the samples. Average recovery for individual pesticides on Day 1 was 110 to 120% with cyanazine having a high recovery of 150% and 2,4-D acid having a recovery of 91%. Day 30 storage samples had a range of recoveries from 70 to 82% based on Day 1, with 2,4-D acid and simazine having recoveries of 104% and 88%, respectively. Day 50 samples had average recoveries of 80% of Day 1, with 2,4-D acid having 101 % recovery, and cyanazine having a 69% recovery.

REFERENCES:

[1] NIOSH [1995]. Back-up data report for chlorinated organonitrogen and carboxylic acid herbicides. Prepared under NIOSH Contract 200-88-2618 (unpublished).
[2] NIOSH [1977]. 2,4-D: Method S279. In: Taylor DG, ed. NIOSH Manual of Analytical Methods (NMAM), 2nd ed., v. 5. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 77-157C.
[3] NIOSH [1984]. 2,4-D and 2,4,5-T: Method 5001. In: Eller PM, ed. NIOSH Manual of Analytical Methods (NMAM), 3rd ed. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 84-100
[4] Hill RH Jr, Arnold JE [1979]. A personal air sampler for pesticides. Arch Environ Contam Toxicol *8*:621-628.
[5] Black TH [1983]. The preparation and reactions of diazomethane. Aldrichimica Acta 16(1).

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APPENDIX - DIAZOMETHANE DERIVATIZING REAGENT

The diazomethane generator (see Figure 3) consists of two 40-mL test tubes, each fitted with a two-hole rubber stopper. In one hole of the first test tube, a glass tube is placed which extends to within one centimeter of the bottom. The other end of the glass tube is connected to a supply of nitrogen. A short piece of Teflon® tubing is placed in the second hole and is directed to the bottom of the second tube through the second stopper. A third piece of Teflon® tubing leads from the second tube into the receiving flask. The first test tube contains a small quantity of diethyl ether. Nitrogen bubbled through the ether is led to the second tube containing 3 mL of a 37% KOH-in-water solution and 4 mL "*Diazald*® Reagent," which is prepared by dissolving 10 g of *Diazald*® in 100 mL of 1:1 Ethyl ether: Carbitol. Diethyl ether vapor in the first tube prevents loss of diethyl ether from the second tube by evaporation. Diethyl ether stabilizes diazomethane through adduct formation. The resulting diazomethane gas is swept by a flow of nitrogen gas into a flask of chilled (0 °C) methyl t-butyl ether/methanol extraction solvent (maximum volume, 500 mL).

NOTE: KOH solution (37% w/v) will become weaker over time owing to adsorption of atmospheric carbon dioxide. Under such circumstances, diazomethane generation will be considerably slower.

TABLE 1. SYNONYMS, FORMULA, MOLECULAR WEIGHT, PROPERTIES

Name / Synonym	Empirical Formula	Molecular Weight	Physical Properties	Solubility in Water (mg/L)	LD50 mg/kg	TWA (mg/m3)
Alachlor 2-Chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl) acetamide CAS #15972-60-8 RTECS AE1225000	$C_{14}H_{20}ClNO_2$	269.77	Colorless crystals; d 1.133 g/mL@ 25°C; MP 39.5-41.5°C; VP 0.0029 Pa (2.2 x 10^{-5} mm Hg) @ 25°C	140 @23°C	1200	
Atrazine 6-Chloro-N^2-ethyl-N-isopropyl-1,3,5-triazine-2,4-diamine CAS # 1912-24-9 RTECS XY5600000	$C_8H_{14}ClN_5$	215.68	Colorless crystals; MP 173-175°C; VP 4 x 10^{-5} Pa (3.0 x 10^{-7} mm Hg) @ 20°C	70 @ 25°C	1780	NIOSH 5 ACGIH 5
Cyanazine 2[[4-chloro-6-(ethylamino)-1,3,5-triazin-2-yl]amino]-2-methylpropionitrile CAS #21725-46-2 RTECS UG1490000	$C_9H_{13}ClN_6$	240.69	White crystalline solid; MP 167.5-169°C; VP 2.1 x 10^{-7} Pa (1.6 x 10^{-9} mm Hg) @ 20°C	171 @ 25°C	182	
2,4-D acid 2,4-Dichlorophenoxyacetic acid CAS #94-75-7 RTECS AG6825000	$C_8H_6Cl_2O_3$	221.04	White powder; MP 140.5°C; <10^{-5} Pa (<7.5 x 10^{-8} mm Hg) @ 25°C	almost insoluble	375	NIOSH 10 ACGIH 10 OSHA 10
2,4-D, ME 2,4-Dichorophenoxyacetic acid, methyl ester CAS #1928-38-7	$C_9H_8Cl_2O_3$	235.07				
2,4-D, BE 2,4-Dichlorophenoxyacetic, 2-butoxyethyl ester CAS #1929-73-3 RTECS AG7700000	$C_{14}H_{18}Cl_2O_4$	321.20			150	
2,4-D, EH 2,4-2,4-Dichlorophenoxyacetic acid, 2-ethylhexylester CAS #1928-43-4	$C_{16}H_{22}Cl_2O_3$	333.25			300 - 1000	
Metolachlor 2-Chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)acetamide CAS #51218-45-2 RTECS AN3430000	$C_{15}H_{22}Cl_2NO_2$	283.80	Odorless tan liquid; 0.0017 Pa (1.3 x 10^{-5} mm Hg) @ 20°C	530 @ 20°C	2780	
Simazine 6-Chloro-N,N'-diethyl-1,3,5-trazine-2,4-diamine CAS #122-34-9 RTECS XY5250000	$C_7H_{12}ClN_5$	201.66	Crystals; MP 225 -227°C; 8.1 x 10^{-7} Pa (6.1 x 10^{-7} mm Hg) @ 20°C	3.5 @ 20°C	5000	

TABLE 2. USEFUL GAS CHROMATOGRAPHIC COLUMNS AND CONDITIONS [1]

Parameter	Conditions							
Column Parameters:								
Stationary phase[2]	DB-1	DB-5	DB-5ms	DB-17[3]	DB-1701[4]	DB-210[4]	DB-225[4]	DB-WAX
Length (meters)	30	30	30	30	30	30	30	30
I.D. (millimeters)	0.25	0.32	0.32	0.25	0.53	0.32	0.32	0.32
Film thickness (µm)	0.25	0.50	1.00	0.25	1.00	0.25	0.25	0.50
Oven Temperatures:								
Initial temperature (°C)	120	50	90	90	90	140	140	160
Initial temperature hold time (min.)	0	1	1	1	0.5	0	0	0
First temperature ramp (°C/min.)	5	10	35	35	15	3	5	5
First intermediate temperature (°C)			160	160	180			
Second temperature ramp (°C/min.)			5	5	2			
Second intermediate temperature (°C)			200	200	210			
Third temperature ramp (°C/min.)			3	3	10			
Final temperature (°C)	250	290	230	230	235	215	220	250
Final temperature hold time (min.)	4	5	9	9	10	5	15	20
Mobile Phase and Injection conditions:								
Carrier Gas	Helium	Helium	Helium	Helium	Helium	Helium	Helium	Helium
Head pressure (p.s.i.)	10	10	12	12	3.5	10	10	10
Injection volume (µL)	2-4	2-4	2-4	2-4	2	2-4	2-4	2-4
Injection mode	splitless	splitless	splitless	splitless	splitless	splitless	splitless	splitless

(1) Actual column and conditions may vary depending on analyte, interferences, and analytical objectives. The conditions given above correspond to Table 4.

(2) Other types of fused silica capillary columns may also work well.

(3) Column and conditions used for method evaluation. Good column for separation of atrazine and simazine.

(4) Useful columns for separating cyanazine from other listed analytes.

TABLE 3. METHOD EVALUATION

Compound	Range Studied (µg/sample)	Accuracy	Bias	Precision-Measurement $\bar{S}_r$	Precision-Method $\hat{S}_{rT}$	Limit of Detection (µg/sample)
Alachlor	0.5 - 5	±0.139	0.025	0.041	0.0644	0.05
Atrazine	2.5 - 25	±0.154	0.032	0.0487	0.0698	0.2
Cyanazine	0.75 - 7.5	±0.320	0.16	0.0662	0.0830	0.08
2,4-D acid	0.3 - 3	±0.151	0.029	0.0484	0.0696	0.03
2,4-D, BE	0.4 - 4	±0.215	0.057	0.0739	0.0892	0.04
2,4,-D, EH	0.3 - 3	±0.173	0.056	0.0447	0.0671	0.03
Metolachlor	0.5 - 5	±0.135	0.030	0.033	0.0601	0.05
Simazine	2.0 - 20	±0.130	0.0007	0.0438	0.0665	0.2

TABLE 4. APPROXIMATE RETENTION TIMES OF SELECTED CHLORINATED ORGANONITROGEN AND CARBOXYLIC ACID COMPOUNDS[1]

	Compound (by retention time on DB5)	Retention Times in Minutes (Capillary Column by Approximate Increase in Polarity)							
	Capillary Column:	DB-1	DB-5	DB-5ms	DB-17	DB-1701	DB-210	DB-225	DB-WAX
1	**CDAA**		14.37						
2	**2,4-D, ME[2]**			10.13	10.25	12.25			
3	**Dicamba, ME[2]**		16.72						
	2,4-D, iPE[3]		19.20						
5	**Simazine**	12.90	19.42	12.02	12.91	16.52	7.59	16.90	18.62
6	**Atrazine**	12.96	19.50	12.18	12.59	16.34	7.79	15.93	17.17
7	**Propazine**		19.61						
8	**2,4-DB, ME[2]**				14.03				
9	**Metribuzin**	13.89	21.10		17.51		9.72	22.01	23.08
10	**Dimethenamid**		21.13						
11	**Acetochlor**		21.18		14.66				
12	**Alachlor**	14.37	21.44	15.24	15.19	19.78	12.95	17.45	14.95
13	**Cyanazine**	14.97	22.23	17.17	19.99	27.07	19.67	30.00	36.00
14	**Metolachlor**	15.11	22.26	16.96	16.67	22.17	14.85	19.43	15.96
15	**Pendimethalin**		22.98		18.67				
16	**2,4-D, BE[4]**	17.01	23.73	21.46	20.60	26.25	16.79	25.86	20.50
17	**2,4-D, EH[5]**	17.70	24.38	22.73	20.12	26.71	17.17	23.49	18.55

(1) Actual retention times will vary with individual columns and chromatographic conditions. Column conditions are give in Table 2. Data is from Backup Data Report [1].

(2) ME = Methyl ester. Methyl ester formed by reaction of the free acid form with diazomethane.

(3) iPE = Isopropyl ester.

(4) BE = 2-Butoxyethyl ester.

(5) EH = 2-Ethylhexyl ester.

TABLE 5. NOTES ON ANALYTICAL CHARACTERISTICS OF CHLORINATED ORGANONITROGEN AND ACID HERBICIDES

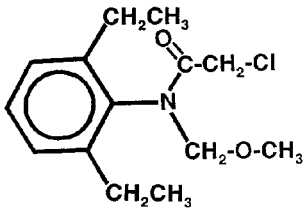
	Compound (alphabetically)	A. CHEMICAL AND PHYSICAL	B. SAMPLE PREPARATION	C. GAS CHROMATOGRAPHIC
1	Alachlor		3	1
2	Atrazine		3	2,3
3	Cyanazine	2	1,3,4	2,4
4	2,4-D, acid		2(methyl ester)	
5	2.4-D, BE	1	1,2,4	5
6	2,4-D, EH	1	2	
7	Metoloachlor		3	1
8	Simazine		3	2,3

A. CHEMICAL AND PHYSICAL
   1. Esters may hydrolyze to the free acid. Free acid may also be present in formulations.
   2. Cyanazine contains a cyano group that appears to adversely affect analytical behavior.

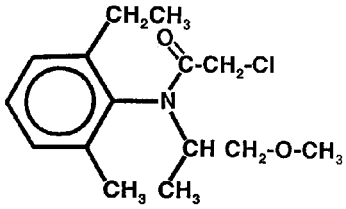
B. SAMPLE PREPARATION
   1. Lower recoveries from glass fiber filters compared to quartz fiber filters.
   2. The esters are not affected by the diazomethane reagent provided the solutions are quenched within one hour with silicic acid. Recoveries for all esters diminish otherwise. This makes possible the speciation of 2,4-D esters and of the free acid in one analysis.
   3. Analytes were not affected by the diazomethane reagent.
   4. Generally high recoveries (120 to 150% or more) from XAD-2 resin compared to liquid standards for reasons unknown. Recoveries appear to be more realistic (80 to 90%) if the filter and the XAD-2 are desorbed and analyzed separately and the analytical results combined.

C. GAS CHROMATOGRAPHIC
   1. Very good peak shape.
   2. Analyte has tendency to tailing on most column phases. Columns and injection ports must be clean and in good condition.
   3. The s-triazines, simazine, atrazine, and propazine, elute very close in that order on the non-polar columns DB1and DB-5. The order is reversed on most polar columns.
   4. Cyanazine is very polar and tends to tail and to elute very late on very polar columns. It has very unpredictable behavior and peak areas either diminish or increase noticeably in subsequent injections. This behavior appears to be associated with the cyano group.
   5. 2,4-D BE behaves similarly to cyanazine, chromatographically (see C.4.), though to a much lesser extent.

ACETANILIDES:

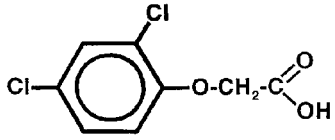


1. ALACHLOR

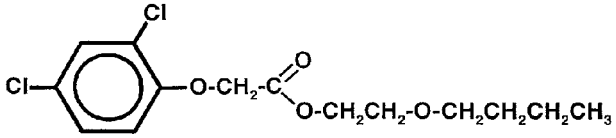


2. METOLACHLOR

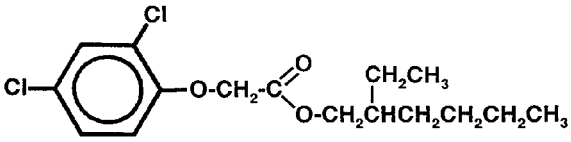
PHENOXYALKANOIC ACID AND ESTERS:



3. 2,4-D, ACID

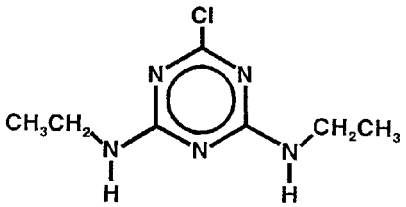


4. 2,4-D, 2-BUTOXYETHYL ESTER

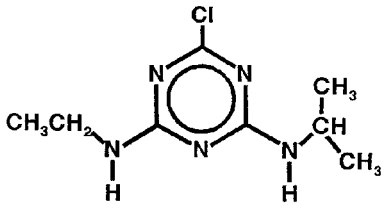


5. 2,4-D, 2-ETHYLHEXYL ESTER

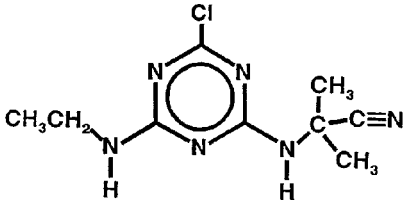
s-TRIAZINES:



6. SIMAZINE



7. ATRAZINE



8. CYANAZINE

STRUCTURES OF CHLORINATED ORGANONITROGEN and ACID HERBICIDES

Figure 1.

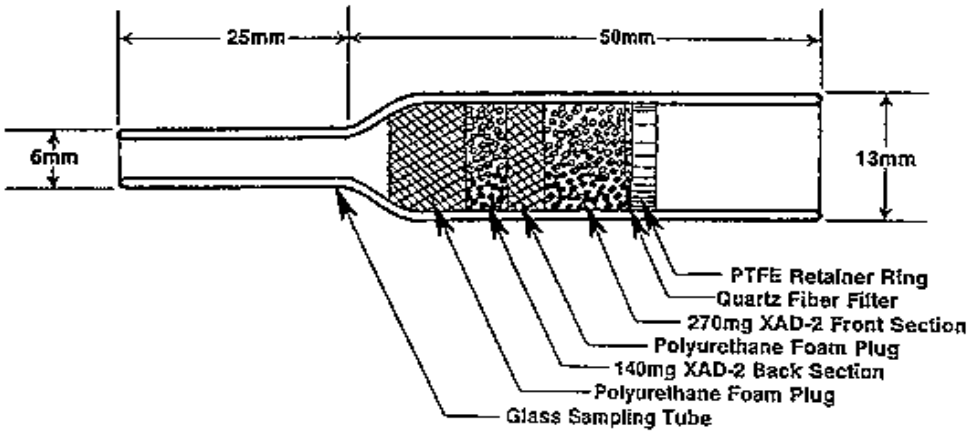


Figure 2. Diagram of OVS Sampler

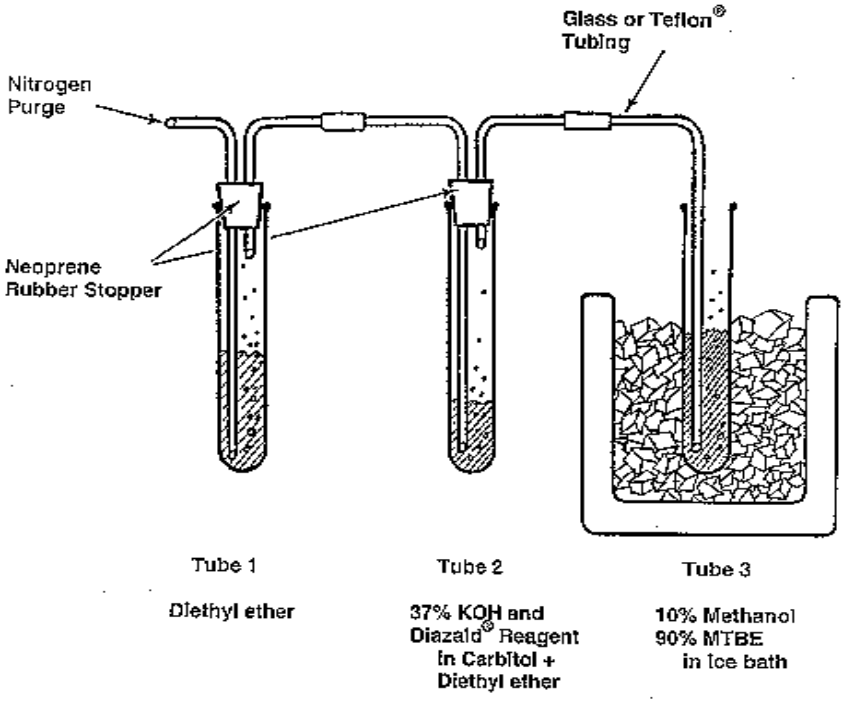


Figure 3. Diazomethane Generator

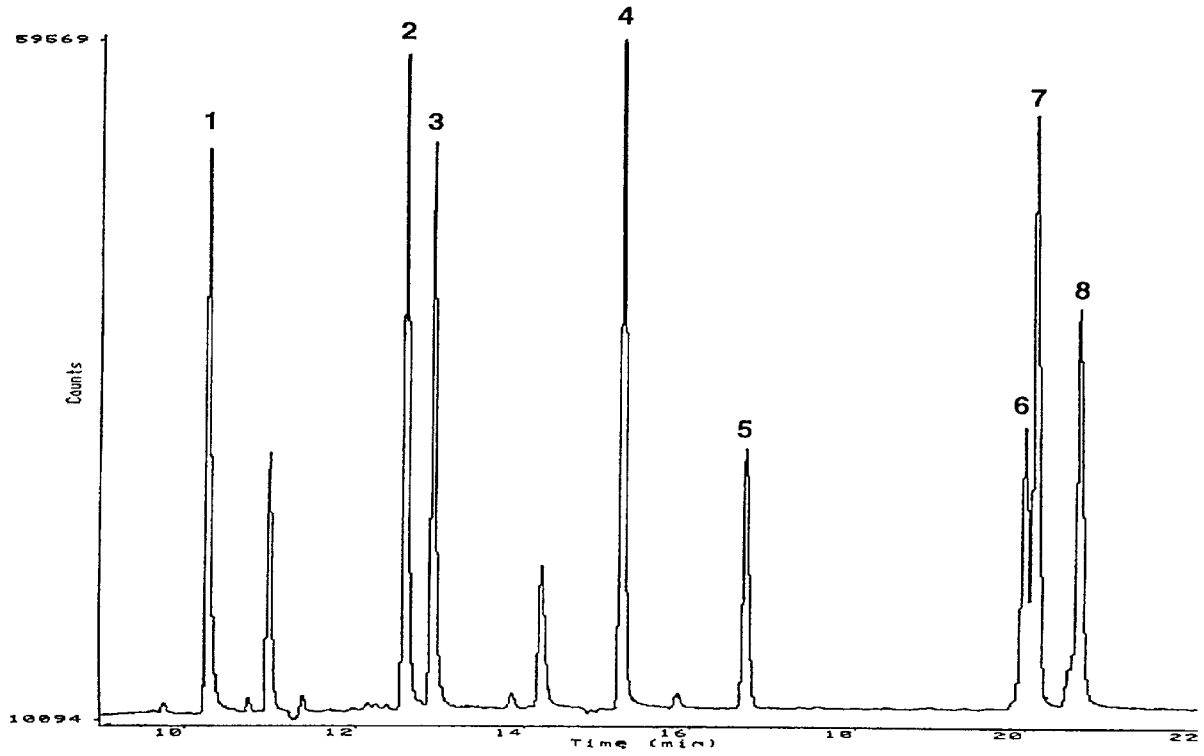


FIGURE 4. TYPICAL CHROMATOGRAM OF CHLORINATED HERBICIDE STANDARDS ON DB-17 COLUMN

COLUMN: DB-17 Fused Silica Capillary Column, 30 meters X 0.25 mm I.D. X 0.25 µm thick film.
TEMPERATURE PROGRAM: 90 °C (1 min. Hold), to 160 °C at 35 °C/min, then to 200 °C at 5 °C/min, then to 230 °C at 3 °C/min, hold for 9 minutes.
INJECTION VOLUME AND MODE: 2- µL, splitless.

ANALYTES:

1. 2,4-D, Methyl ester	0.15 µg/mL
2. Atrazine	4.50 µg/mL
3. Simazine	4.50 µg/mL
4. Alachlor	0.22 µg/mL
5. Metolachlor	0.25 µg/mL
6. Cyanazine	0.25 µg/mL
7. 2,4-D, 2-Ethylhexyl ester	0.22 µg/mL
8. 2,4-D, Butoxyethyl ester	0.22 µg/mL

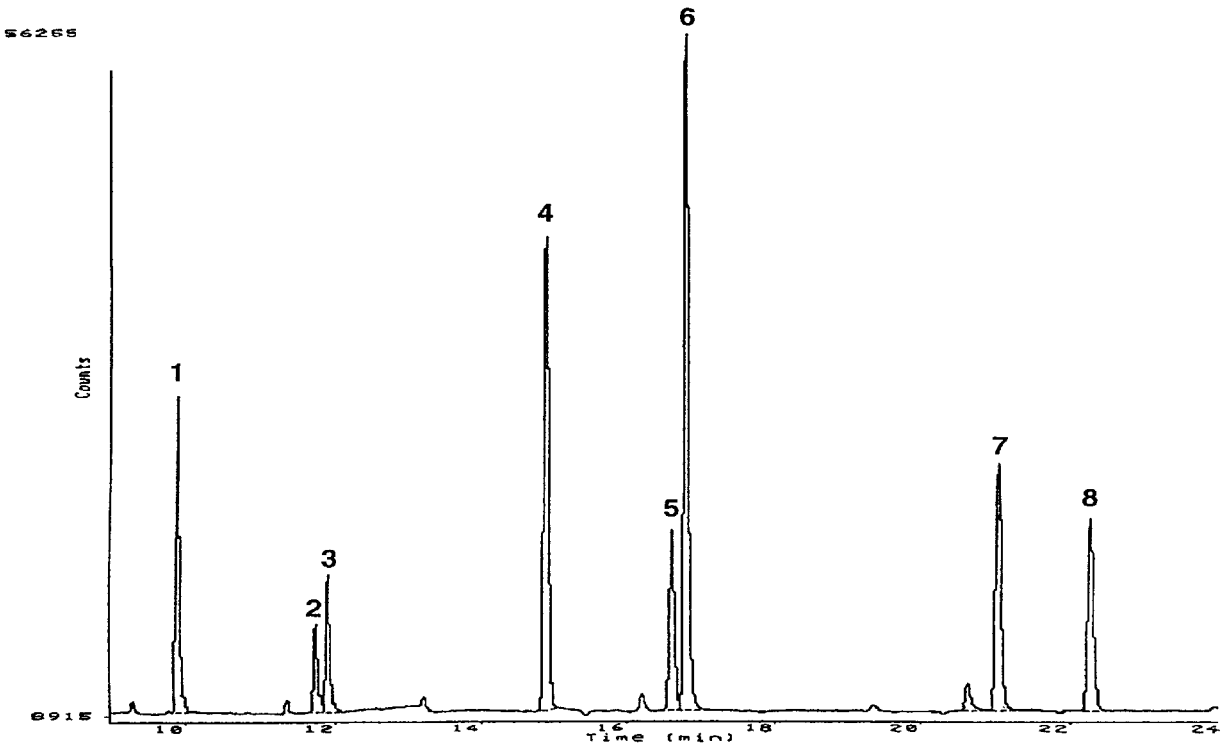


FIGURE 5. TYPICAL CHROMATOGRAM OF CHLORINATED HERBICIDE STANDARDS ON DB-5 COLUMN

COLUMN: DB-5ms Fused Silica Capillary Column, 30 meters X 0.32 mm I.D. X 1.0 µm thick film.
TEMPERATURE PROGRAM: 90 °C (1 min. Hold), to 160 °C at 35 °C/min, then to 200 °C at 5 °C/min, then to 230 °C at 3 °C/min, hold for 9 minutes.
INJECTION VOLUME AND MODE: 2-µL, splitless.

ANALYTES:

1.	2,4-D, Methyl Ester	0.3 µg/mL
2.	Simazine	2.0 µg/mL
3.	Atrazine	2.5 µg/mL
4.	Alachlor	0.5 µg/mL
5.	Metolachlor	0.5 µg/mL
6.	Cyanazine	0.8 µg/mL
7.	2,4-D, Butoxyethyl ester	0.4 µg/mL
8.	2,4-D, 2-Ethylhexyl ester	0.3 µg/mL