

ORGANOPHOSPHORUS PESTICIDES

5600

Analytes: Table 1 Formula: Table 1 MW: Table 1 CAS: Table 1 RTECS: Table 1

METHOD: 5600, Issue 2

EVALUATION: FULL

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OSHA: Table 2

PROPERTIES: Table 3

NIOSH: Table 2

SYNONYMS: Table 4

SAMPLING		MEASUREMENT	
SAMPLER:	FILTER + SOLID SORBENT TUBE (OVS-2 tube: 13-mm quartz filter; XAD-2, 270 mg/140 mg)	TECHNIQUE:	GC, flame photometric detection (FPD)
FLOW RATE:	0.2 to 1 L/min	ANALYTE:	Organophosphorus pesticides, Table 1
VOL-MIN:	12 L	EXTRACTION:	2 mL 90% toluene/10% acetone solution
-MAX:	480 L; 60 L (Malathion, Ronnel)	INJECTION VOLUME:	1 to 2 µL
SHIPMENT:	Routine	TEMPERATURE	
SAMPLE STABILITY:	at least 10 days @ 25 °C at least 29 days @ 0 °C	-INJECTION:	240 °C
BLANKS:	2 to 10 field blanks per set	-DETECTOR:	180 °C to 215 °C (follow manufacturer's recommendations)
ACCURACY [9]		CARRIER GAS:	Helium @ 15 psi (104 kPa)
RANGE STUDIED:	Table 5	COLUMN:	Fused silica capillary column; Table 6
BIAS:	Table 5	DETECTOR:	FPD (phosphorous mode)
OVERALL PRECISION ($\bar{S}_{r,T}$):	Table 5	CALIBRATION:	Standard solutions of organophosphorus compounds in toluene
ACCURACY:	Table 5	RANGE:	Table 8
		ESTIMATED LOD:	Table 9
		PRECISION (\bar{S}_r):	Table 5

APPLICABILITY: The working ranges are listed in Table 5. They cover a range of 1/10 to 2 times the OSHA PELs. This method also is applicable to STEL measurements using 12-L samples. This method may be applicable to the determination of other organophosphorous compounds after evaluation for desorption efficiency, sample capacity, sample stability, and precision and accuracy.

INTERFERENCES: Several organophosphates may co-elute with either target analyte or internal standard causing integration errors. These include other pesticides (see Table 7), and the following: tributyl phosphate (a plasticizer), tris-(2-butoxy ethyl) phosphate (a plasticizer used in some rubber stoppers), tricresyl phosphate (a petroleum oil additive, hydraulic fluid, plasticizer, flame-retardant, and solvent), and triphenyl phosphate (plasticizer and flame-retardant in plastics, laquers, and roofing paper).

OTHER METHODS: This method may be used to replace previous organophosphorous pesticide methods. See Table 11 for partial listing. The sampler recommended here is similar in concept to the device of Hill and Arnold [11], but offers greater convenience and lower flow resistance.

REAGENTS:

1. Organophosphorous analytes listed in Table 1; and triphenyl phosphate, analytical standard grade.*
2. Toluene, pesticide analytical grade.*
3. Acetone, ACS reagent grade or better.*
4. Desorbing solution. Add 50 mL acetone to a 500-mL volumetric flask. Dilute to volume with toluene. (Do not keep longer than 30 days at 0-4 °C).
NOTE: For optional internal standard, add 1 mL of a 5 mg/mL solution of triphenyl phosphate in toluene to 500 mL desorbing solution.
5. Organophosphorous stock solutions, 10 mg/mL. Prepare individual standard stock solutions of each pesticide of interest in 90/10 toluene/acetone (v/v). All pesticides in Table 1 were found to be soluble to at least 10 mg/mL.
6. Spiking solutions for calibration (step 9) and media fortification (steps 10, 11)
NOTE: Spiking solutions may contain more than one analyte.
 - a. Spiking solution SS-1: Dilute the volume of stock solution indicated in Table 12 to 10 mL with toluene or 90/10 toluene/acetone (v/v).
NOTE: Spiking solutions may contain more than one analyte.
 - b. Spiking solution SS-0.1: Dilute 1 mL of SS-1 solution with toluene to 10 mL.
7. Purified gases: Helium, Hydrogen, Dry air, Nitrogen, and Oxygen (if required by detector)

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: resin filled sampling tube; glass tube, 11-mm i.d. x 13-mm o.d. x 50-mm long, with the outlet end drawn to a 6-mm o.d. x 25-mm long tube. The enlarged part of the tube contains a 270-mg front section of 20/60 mesh XAD-2 sorbent held in place by a 9 to 10-mm o.d. quartz fiber filter and polytetrafluoroethylene (PTFE) retaining ring. The front section is separated from the back section of 140 mg XAD-2 sorbent with a short plug of polyurethane foam. The back section is held in place by a long plug of polyurethane foam. The tube is available commercially. See Figure 2.
NOTE: Some commercially available samplers contain glass fiber filters. These are specified in the OSHA methods (see Table 11). These tubes, however, did not perform as well for the more polar analytes (amides, phosphoramides, and sulfoxides; (see Table 10). Low or erratic recoveries for Malathion may be encountered with glass fiber filters.
2. Personal sampling pump, 0.2 to 1 L/min. with flexible connecting tubing, preferably silicon, polyethylene, or PTFE tubing.
3. Vials, 4-mL with PTFE-lined cap; 2-mL GC autosampler vials with PTFE-lined crimp caps.
4. Gas chromatograph, flame photometric detector with 525-nm bandpass filter for phosphorous mode, integrator, and column (Table 6).
5. Syringes, 5-mL and 100-, 50-, and 10-mL for making standard solutions and GC injections.
6. Volumetric flasks, 500-, 10-, and 2-mL.
7. Tweezers.
8. GC vial crimper.
9. Small ultrasonic cleaning bath.

SPECIAL PRECAUTIONS: Organophosphorous compounds are highly toxic. Special care must be taken to avoid inhalation or skin contact through the wearing of gloves and suitable clothing when handling pure material [13,14,15,16,17]. Toluene is flammable and toxic. Acetone is highly flammable. Prepare all samples in a well ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Connect the sampler to personal sampling pump with flexible tubing. The sampler should be placed vertically with the large end down, in the worker's breathing zone in such a manner that it does not impede work performance [12].
3. Sample at an accurately known flowrate between 0.2 and 1 L/min for a total sample size of 12 to 240 L.
4. Cap both ends of the sampler with plastic caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Remove cap from large end and remove PTFE retainer ring; transfer filter and front XAD-2 section to a 4-mL vial. Transfer the short polyurethane foam plug with back-up XAD-2 section to a second 4-mL vial.
6. Add 2-mL of desorbing solvent with internal standard to each vial using a 5-mL syringe or 2-mL pipette. Cap each vial.
7. Allow to stand 30 minutes, immerse vials approximately 1/2 inch in an ultrasonic bath for 30 minutes. Alternatively, place the vials in a shaker or tumbler for 1 hour.
8. Transfer 1 to 1.5 mL from each 4-mL vial to a clean 2-mL GC vial, cap and label.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards covering the analytical range of the method for individual analytes. See Table 12 for recommended preparation of spiking solutions.
 - a. Add known amounts of calibration spiking solution (SS-1 or SS-0.1 according to schedule in Table 12) to desorbing solution in 2-mL volumetric flasks and dilute to the mark.
NOTE: If an internal standard is included in the desorbing solution, then exactly 2 mL of desorbing solution in a volumetric flask must be concentrated slightly under a gentle stream of nitrogen in order to accommodate the specified volume of the spiking solutions. After adding the spiking solutions to the slightly concentrated desorbing solution, dilute to the 2-mL mark with toluene or 90/10 toluene/acetone.
 - b. Include a calibration blank of unspiked desorption solution.
 - c. Analyze together with field samples, field (trip) blanks, and laboratory control samples (step 12 and 13).
 - d. Prepare calibration graph (peak area vs. μg analyte), or if internal standard (IS) is used (peak area of analyte/peak area of IS vs. μg analyte).
10. Prepare Laboratory Control Samples (LCS) with each sample set, in duplicate.
 - a. Remove cap from large end of sampler tube, apply 30 μL of spiking solution SS-1 (refer to Table 13) to face of quartz fiber filter. Cap and allow to stand for a minimum of 1 hour. Preferably, these should be prepared as soon as samples arrive and should be stored with the field samples until analyzed.
 - b. Include an unspiked sampler as a media (method) blank.
 - c. Analyze along with field samples and blanks, and liquid calibration standards (steps 12 through 16).

11. When extending application of this method to other organophosphorous compounds, the following minimal desorption efficiency (DE) test may be performed as follows:
 - a. Determine the NIOSH REL or OSHA PEL, in mg/m³.
 - b. Prepare spiking solution SS-1 (refer to Table 12); or use the following formulae, which are specific for the calculation of the weight of analyte to add to 10 mL 90/10 toluene/acetone).
For REL > 1 mg/m³ (assuming 12-L collection vol.), let W = REL x 4 m³
For REL ≤ 1 mg/m³ (assuming 120-L collection vol.), let W = REL x 40 m³
Where W = weight (mg) of analyte to dissolve into 10 mL of desorbing solvent.
Let [SS-1] = W/10 mL where [SS-1] = concentration of spiking solution SS-1 in mg/mL.
 - c. Prepare spiking solution SS-0.1 by diluting 1 mL of SS-1 to 10 mL in a volumetric flask. Let [SS-0.1] = [SS-1] x 0.1 where [SS-0.1] = concentration of spiking solution SS-0.1.
 - d. Prepare three tubes at each of five levels plus three media blanks. Concentration at each level may be calculated using formulae in last entry of Table 12.
 - i. Remove plastic cap from large end of sampler, apply appropriate volume of spiking solution to face of quartz fiber filter following schedule in Table 13.
 - ii. Cap and allow sampler to stand overnight.
 - e. Prepare tubes for analysis (steps 5 through 8).
 - f. Analyze with liquid standards (steps 12 and 13).
 - g. Prepare a graph of desorption efficiency (DE) vs. µg of analyte.
 - h. Acceptable desorption criteria for 6 replicates is >75% average recovery with a standard deviation of < ±9%.

MEASUREMENT:

12. Set gas chromatograph according to manufacturer's recommendations and to conditions listed in Table 6 and on page 5600-1. Inject sample aliquot manually using solvent flush technique or with autosampler. See Table 7 for retention times of selected analytes.
NOTE: If peak area is greater than the linear range of the working standards, dilute with desorbing solution containing internal standard and reanalyze. Apply the appropriate dilution factor in calculations.
13. Measure peak area of analyte and of internal standard.

CALCULATIONS:

14. Determine the mass in 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.
NOTE: The filter is combined with 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):

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

CONFIRMATION:

16. Whenever an analyte is detected, and its identity is uncertain, confirmation may be achieved by analysis on a second column of different polarity. If primary analysis was performed using a non-polar or weakly polar column (DB-1 or DB-5), confirmation should be accomplished by reanalysis on a polar column (DB-1701 or DB-210). See Table 7 for approximate retention times for each column type. Fewer analytes co-elute on DB-210 than on DB-1701. Relative retention times are more convenient for the identification of unknown analytes. If triphenyl phosphate is not used as the retention time reference compound, then another related compound such as tributyl phosphate, Ronnel, or Parathion may be substituted.

EVALUATION OF METHOD:

This method was evaluated over the ranges specified in Table 5 at 25 °C using 240-L air samples. Sampler tubes were tested at 15% and 80% relative humidity and at 10 °C and 30 °C. In these tests, test atmospheres were not generated; instead, analytes were fortified on the face of the sampler filters. This was followed by pulling conditioned air at 1 L/min for 4 hours. No difference in sampler performance was noted at any of these temperature/humidity combinations. Evaluations of sampler precision and stability were conducted at 30 °C and 15% relative humidity. Overall sampling and measurement precisions, bias, accuracy, and average percent recovery after long-term storage are presented in Table 5. No breakthrough was detected after 12 hours of sampling at 1 L/min with a sampler fortified with the equivalent of 4x the NIOSH REL. Malathion and Ronnel were tested at 1/40 x REL, Sulprofos at 1/20 x REL (See Table 5, note 4). All criteria [9] were met.

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TABLE 1. Formula and registry numbers

Compound (alphabetically)	MW ⁽¹⁾ (Daltons)	Empirical Formula	CAS No. ^(2,3,4)	RTECS ⁽²⁾
Azinphos Methyl	317.32	C ₁₀ H ₁₂ N ₃ O ₃ PS ₂	86-50-0	TE1925000
Chlorpyrifos	350.58	C ₉ H ₁₁ Cl ₃ NO ₃ PS	2921-88-2	TF6300000
Diazinon	304.34	C ₁₂ H ₂₁ N ₂ O ₃ PS	33-41-5	TF3325000
Dicrotophos	237.19	C ₈ H ₁₆ NO ₅ P	141-66-2	TC3850000
Disulfoton	274.39	C ₈ H ₁₉ O ₂ PS	298-04-4	TD9275000
Ethion	384.46	C ₉ H ₂₂ O ₄ P ₂ S ₄	563-12-2	TE4550000
Ethoprop	242.33	C ₈ H ₁₉ O ₂ PS ₂	13194-48-4	TE4025000
Fenamiphos	303.36	C ₁₃ H ₂₂ NO ₃ PS	22224-92-6	TB3675000
Fonofos	246.32	C ₁₀ H ₁₅ OPS ₂	944-22-9	TA5950000
Malathion	330.35	C ₁₀ H ₁₉ O ₆ PS ₂	121-75-5	WM8400000
Methamidophos	141.12	C ₂ H ₈ O ₂ PS	10265-92-6	TB4970000
Methyl Parathion	263.20	C ₈ H ₁₀ NO ₅ PS	298-00-0	TG0175000
Mevinphos	224.15	C ₇ H ₁₃ O ₆ P	7786-34-7	GQ5250000
Monocrotophos	223.17	C ₇ H ₁₄ NO ₅ P	6923-22-4	TC437500
Parathion	291.26	C ₁₀ H ₁₄ NO ₅ PS	56-38-2	TF4550000
Phorate	260.36	C ₇ H ₁₇ O ₂ PS ₃	298-02-2	TD9450000
Ronnel	321.54	C ₈ H ₈ Cl ₃ O ₃ PS	299-84-3	TG0525000
Sulprofos	322.43	C ₁₂ H ₁₉ O ₂ PS ₃	35400-43-2	TE4165000
Terbufos	288.42	C ₉ H ₂₁ O ₂ PS ₃	13071-79-9	TD7740000

(1) Molecular weights are calculated from the empirical formula using 1979 IUPAC Atomic Weights of the Elements

(2) RTECS = NIOSH Registry of Toxic Effects of Chemical Substances [1]

(3) Merck Index [2]

(4) Farm Chemicals Handbook [3]

TABLE 2. Toxicity and maximum exposure limits

Compound (alphabetically)	LD ₅₀ , mg/kg ⁽¹⁾	OSHA PEL ⁽³⁾ (mg/m ³)	NIOSH REL ⁽⁴⁾ (mg/m ³)	NIOSH REL ⁽⁴⁾ (ppm)
Azinphos Methyl	11 f	0.2	0.2	0.015
Chlorpyrifos	145	0.2	0.2	0.014
Diazinon	250 m, 285 f	0.1	0.1	0.008
Dicrotophos	16 f, 21 m	0.25	0.25	0.026
Disulfoton	2.3 f, 6.8 m	0.1	0.1	0.009
Ethion	27 f, 65 m	0.4	0.4	0.025
Ethoprop	61.5 ⁽²⁾			
Fenamiphos	19.4	0.1	0.1	0.008
Fonofos	3-17 ⁽²⁾	0.1	0.1	0.010
Malathion	1000	15	10	0.740
Methamidophos	25 m, 27 f			
Methyl Parathion	14 m, 24 f	0.2	0.2	0.019
Mevinphos	3.7 f, 6.1 m	0.1 skin	0.1	0.01
Monocrotophos	17 m, 20 f	0.25	0.25	0.027
Parathion	3.6 f, 13m	0.1	0.05 skin	0.004
Phorate	1.1 f, 2.3 m	0.05	0.05 skin	0.005
Ronnel	1250 m, 2630 f	15	10	0.760
Sulprofos	227	1	1	0.076
Terbufos	1.6-1.7 m, 1.3-1.57 f			

(1) Rat-oral; from Merck Index, unless otherwise noted, f = female, m = male. [2]

(2) Farm Chemicals Handbook [3]

(3) OSHA Final Rule, 1989 (unenforceable, 1992); only Malathion and Parathion had previous PELs

(4) NIOSH Recommendations for Occupational Safety and Health [5]

TABLE 3. Physical properties ⁽¹⁾

Compound (Alphabetically)	Liquid Density (g/mL)	mp (°C)	bp (°C @ 1 atm)	Vapor Pressure (Pascal)	Vapor Pressure (mm Hg)	Solubility in Water ^(2,3) , % by weight (g/100mL @ 20 °C)
Azinphos Methyl	1.44	73-74	decomposes	0.024	8x10 ⁻⁹	0.003%
Chlorpyrifos	1.40	41-42	160 (decomposes)	0.0027	2x10 ⁻⁵	0.0002%
Diazinon	1.116-1.118	liquid	>120 (decomposes)	0.019	1.4x10 ⁻⁴	0.004%
Dicrotophos	1.216	liquid	400	0.013	0.0001	miscible
Disulfoton	1.144	oil	>180 °C flash pt.	0.0267	0.0002	0.003% (22.7 °C)
Ethion	1.220	-12 to -13	>150 (decomposes)	0.0002	1.5x10 ⁻⁶	0.0001%
Ethoprop	1.094	oil	86-91	0.047	3.5x10 ⁻⁴	0.075%
Fenaminphos	1.15	49	decomposes	0.00012	5x10 ⁻⁵	0.03%
Fonofos	1.16	30	130	0.03 (25 °C)	-	0.001%
Malathion	1.23	2.9	60 (decomposes) ⁽⁴⁾	0.005	4x10 ⁻⁵	0.02%
Methamidophos	1.31	44	-	0.002	3x10 ⁻⁴	-
Methyl Parathion	1.358	37-38	<120 (decomposes)	0.0002	7.5x10 ⁻⁶	0.006% (25 °C)
Mevinphos	1.25 ⁽⁵⁾	20.6 ⁽⁵⁾	300 ⁽⁵⁾ (decomposes)	0.4	3x10 ⁻³	miscible
Monocrotophos	1.3	53-54 ⁽⁶⁾	125	0.0003	7x10 ⁻⁶	miscible
Parathion	1.26	6	375	0.005	3.78x10 ⁻⁵	0.001%
Phorate	1.156	liquid	118-120	0.11	8.4x10 ⁻⁴	0.005%
Ronnel	1.49 ⁽⁷⁾	41	decomposes	0.1	8x10 ⁻⁴	0.004% (25 °C)
Sulprofos	1.20	liquid	210	<0.0001	<10 ⁻⁶	low
Terbufos	1.105	-29.2	88 °C flash pt.	0.0346	2.6x10 ⁻⁴	0.0005

(1) From Merck Index, unless otherwise noted [2].

(2) Farm Chemicals Handbook [3].

(3) NIOSH Pocket Guide [6].

(4) NIOSH 4th Edition Method 5012 (EPN, Malathion, Parathion) [8].

(5) NIOSH 4th Edition Method 2503 for Mevinphos [8].

(6) 54-55 °C for pure material, 25-30 °C for commercial mixture.

(7) NIOSH 2nd Edition Method for Ronnel, S299 [7]

TABLE 4. Synonyms

Compound ⁽¹⁾ (alphabetically)	Other name ⁽²⁾	CAS name ^(3,4)
Azinphos Methyl	Guthion*	O,O-dimethyl S-[(4-oxo-1,2,3-benzotriazin-3(4H)-yl)methyl] phosphorodithioate
Chlorpyrifos	Dursban*	O,O-diethyl 0-(3,5,6-trichloro-2-pyridinyl) ester
Diazinon	Spectracide*	O,O-diethyl 0-[6-methyl-2-(1-methylethyl)-4-pyrimidinyl] phosphorodithioate
Dicrotophos	Bidrin*	2-dimethyl-cis-2-dimethylcarbamoyl-1-methylvinyl phosphate
Disulfoton	Di-Syston*	O,O-diethyl S-[2-(ethylthio)ethyl] phosphorodithioate
Ethion		S,S'-methylene, O,O,O,'O'-tetraethyl ester, O,O,O'-O'-Tetra ethyl S,S'-methylene di-phosphorodithioate ⁽⁴⁾
Ethoprop	Prophos*	Phosphorodithioic acid, 0-ethyl S,S-dipropyl ester
Fenamiphos	Nemacur*,Phenamiphos ⁽¹⁾	Ethyl-3-methyl-4-(methylthio) phenyl (1-methylethyl) phosphoramidate
Fonofos	Dyfonate*	O-ethyl, S phenyl ethyl phosphorodithioate
Malathion	Cythion*	S-[1,2 bis(ethoxycarbonyl)ethyl] O,O-dimethyl-phosphorodithioate; Diethyl(dimethoxyphosphinothioylthio) succinate
Methamidophos	Monitor*	Phosphoramidothioic acid, O,S-dimethyl ester
Methyl Parathion	Parathion Methyl ⁽¹⁾	Phosphorothioic acid, O,O-dimethyl 0-[4-nitrophenyl] ester
Mevinphos	Phosdrin*	Methyl-3(dimethoxyphosphinyloxy)but-2-enoate 2-methoxy carbonyl-1-methylvinyl dimethyl phosphate
Moncrotophos	Azodrin* Monocron	Dimethyl [1-methyl-3-(methylamino)-3-oxo-1-propenyl] ester ⁽⁴⁾
Parathion	Ethyl Parathion ⁽¹⁾	O,O-diethyl 0-(4-nitrophenyl) phosphorodithioate
Phorate	Thimet*	Phosphorodithioic acid, O,O-diethyl S-[(ethylthio) methyl] phosphorodithioate
Ronnel	Fenclorphos ⁽¹⁾	O,O-dimethyl O-(2,4,5-trichlorophenyl) ester
Sulprofos	Bolstar*	O-ethyl 0-[4-(methylthio) phenyl] S-propyl phosphorodithioate ⁽⁴⁾
Terbufos	Counter*	O,O-diethyl S-[[[(1,1-dimethylethyl) thio] methyl] ester ⁽⁴⁾

(1) Common name as given in Farm Chemicals Handbook [3].

(2) *=Trade name (Trademark or Registered Name) as given in Farm Chemicals Handbook [3].

(3) Source, Merck Index [2].

(4) NIOSH RTECS [1] or alternate CAS name in Merck Index [2].

TABLE 5. Method Evaluation ⁽¹⁾

Compound (alphabetically)	Range Studied ⁽²⁾ (mg/m ³)	Range Studied ⁽²⁾ (mg/sample)	Accuracy	Bias Average	Overall Precision \hat{S}_{RT}	Measurement Precision \bar{S}_R	% Recovery at 30 days @ 25 °C (0 °C)
Azinphos Methyl	0.02-0.4	0.0048-0.096	±0.178	-0.038	0.070	0.030	97 (105)
Chlorpyrifos	0.02-0.4	0.0048-0.096	±0.163	-0.027	0.068	0.018	92 (90)
Diazinon	0.01-0.2	0.0024-0.048	±0.162	-0.032	0.065	0.020	94 (93)
Dicrotophos	0.025-0.5	0.006-0.120	±0.169	-0.037	0.66	0.025	89 (92)
Disulfoton	0.01-0.2	0.0024-0.048	±0.196	-0.064	0.066	0.024	87 (89)
Ethion	0.04-0.8	0.0096-0.192	±0.165	-0.29	0.068	0.18	96 (95)
Ethoprop ⁽³⁾	0.01-0.2	0.0024-0.048	±0.157	-0.025	0.066	0.024	97 (93)
Fenaminphos	0.01-0.2	0.0024-0.048	±0.155	-0.029	0.063	0.022	94 (96)
Fonofos	0.01-0.2	0.0024-0.048	±0.168	-0.036	0.66	0.023	95 (92)
Malathion ⁽⁴⁾	0.025-0.5	0.006-0.120	±0.172	-0.038	0.067	0.019	93 (93)
Methamidophos ⁽⁵⁾	0.02-0.4	0.0048-0.096	±0.156	-0.018	0.069	0.026	88 (95)
Methyl Parathion	0.02-0.4	0.0048-0.096	±0.160	-0.034	0.063	0.018	95 (95)
Mevinphos	0.01-0.2	0.0024-0.048	±0.176	-0.42	0.067	0.028	89 (91)
Moncrotophos	0.025-0.5	0.006-0.12	±0.185	-0.043	0.071	0.026	88 (92)
Parathion	0.005-0.1	0.0012-0.024	±0.163	-0.012	0.071	0.019	92 (92)
Phorate	0.005-0.1	0.0112-0.024	±0.202	-0.070	0.066	0.025	91 (91)
Ronnel ⁽⁴⁾	0.025-0.5	0.006-0.120	±0.172	-0.040	0.066	0.018	95 (94)
Sulprofos ⁽⁴⁾	0.01-0.2	0.0024-0.048	±0.181	-0.047	0.067	0.017	94 (94)
Terbufos ⁽³⁾	0.01-0.2	0.0024-0.048	±0.188	-0.054	0.067	0.022	92 (91)

(1) Back-up Data Report [9]

(2) The ranges studied were 1/10 to 2x the NIOSH REL (except as noted) using a flowrate of 1 L/min. over 4 hours sampling time.

(3) No NIOSH REL or OSHA PEL available; used 0.1 mg/m³.

(4) Malathion and Ronnel were studied at 1/400 to 1/20 the NIOSH REL, Sulprofos at 1/200 to 1/10 the NIOSH REL.

(5) No NIOSH REL or OSHA PEL available; used 0.2 mg/m³.

(6) Data in parentheses are for % recovery at 30 days at 0 °C

TABLE 6. Recommended gas chromatographic columns and conditions⁽¹⁾

	DB-1 ⁽²⁾	DB-5 ⁽²⁾	DB-1701 ⁽²⁾	DB-210 ⁽²⁾
Stationary Phase ⁽³⁾ Polarity	Non-	Weakly	Moderately	Moderately
Length (meters)	30	30	30	30
I.D. (millimeters)	0.32	0.32	0.32	0.32
Film thickness (mm) ⁽⁴⁾	0.25	1.0	1.0	0.25
Injection volume (μL) ⁽⁵⁾	1	1	1	1
Injection mode ⁽⁶⁾	SPL	DIR	DIR	SPL
Initial oven temp (°C)	100	125	125	100
Final oven temp (°C) ⁽⁶⁾	275	275	275	250
Recommended max oven temp (°C) ⁽⁷⁾	325	325	280	240/260
Oven temp program (°C/min)	3.0	4.0	4.0	3.0
He Carrier gas head pressure (psi)	15	15	15	15

(1) Actual conditions may vary depending on column and analytical objectives.

(2) Wide Bore Fused Silica Capillary Column

(3) DB-1, 100% methyl silicone; DB-5, 5% phenyl, methyl silicone; DB-1701, 14% cyanopropylphenyl, methyl silicone; DB-210, 50% trifluoropropyl, methyl silicone. DB-1 is non-polar, DB-5 is weakly polar, and DB-1701 and DB-210 are moderately strong polar phases. Equivalent phases are acceptable. Other phase types may also work well.

(4) Film thickness: Thinner films give faster separations at lower temperatures promoting analyte stability.

(5) Injection (Vol.): Use 2 mm i.d. injection port liners for 0.5 mL injection and 4 mm i.d. injection port liners for 1 to 2 mL injections with 0.32 mm i.d. capillary columns.

(6) Injection (mode): SPL = splitless mode, initial oven temp. 5 to 10 °C less than b.p. of desorption solvent; DIR = direct mode, initial oven temperature > b.p. of desorption solvent; OC = on-column, sample injected within the lumen of the column rather than within the injection port liner. In the splitless and direct injection modes, split-vent off time should be 60 seconds for 1 to 2 μL injections with 4 mm i.d. injection port liners, and 20 to 30 seconds for 0.5 μL injections with 2 mm i.d. injection port liners.

(7) J & W Scientific Catalog of High Resolution Chromatography Products, p. 21. [10]

TABLE 7. Approximate retention times (RT) of selected organophosphorous compounds on capillary columns^(1,2)

Compound (by RT on DB-1)	DB-1 RT (min)	DB-1 RRT ⁽³⁾	DB-1 Elution T, °C ⁽⁴⁾	DB-5 RT (min)	DB-1701 RT (min)	DB-210 RT (min)
TEPP	3.71	0.128	111	5.47	7.18 ^(B)	7.88
Triethylphosphorothioate	4.37	0.107	113	6.34	7.14 ^(B)	4.93
Methamidophos	5.12	0.125	115	7.64	13.61	12.03
Dichlorvos	5.81	0.142	117	8.24	10.67	10.54
Mevinphos	10.45	0.256	131	12.92	16.69	19.20
Ethoprop	17.15	0.420	151	19.09	21.52	20.10
Naled	17.61	0.431	153	(6)	23.17 ^(C)	21.46 ^(H)
Dicrotophos	18.00	0.440	154	19.94	25.84 ^(E)	31.43
Monocrotophos	18.27	0.447	155	20.12	28.11	31.60
Sulfotepp	19.06	0.466	157	(6)	23.09 ^(C)	21.11
Phorate	19.18	0.469	158	20.94	23.10 ^(C)	18.92
Dimethoate	19.44	0.476	158	21.84	(6)	29.33 ^(I)
Demeton-S	20.15	0.493	160	21.70	25.06 ^(D)	24.97
Dioxathion	21.30	0.521	164	23.04	26.33 ^(F)	23.46
Fonofos	22.04	0.539	166	23.57	25.87 ^(E)	22.20
Terbufos	22.22	0.544	168	23.80	25.02 ^(D)	21.52 ^(H)
Disulfoton	23.09	0.565	169	24.19	26.43 ^(F)	22.78
Diazinon	23.37	0.572	170	23.75	25.00 ^(D)	20.99
Methyl Parathion	25.37	0.621	176	26.48	31.37	33.21
Oxydemeton Methyl	26 ⁽⁵⁾	0.63 ⁽⁵⁾	179	(6)	(6)	(6)
Ronnel	26.86	0.657	181	27.39	29.30	26.27
Pirimiphos Methyl	28.13	0.688	184	27.90	29.72	26.77
Malathion	28.53	0.698	186	28.33	31.78 ^(G)	33.08 ^(J)
Fenthion	28.74	0.703	186	28.93	31.78 ^(G)	29.35 ^(I)
Parathion	28.98	0.709	187	29.10 ^(A)	33.28	35.60
Chlorpyrifos	29.11	0.712	187	29.10 ^(A)	30.79	27.72
Crufomate	29.64	0.725	189	29.54	34.00	35.34
Isofenphos	31.91	0.780	196	31.17	33.81	33.02 ^(J)
Tetrachlorvinphos	33.26	0.814	200	32.60	35.96	37.01
Fenamiphos	34.09	0.834	202	33.03	37.14	38.95
Merphos	35.19	0.861	206	(6)	30.57	23.89
Fensulfothion	36.61	0.896	210	35.78	42.41	46.98
Ethion	37.88	0.927	214	36.30	39.30	37.96
Sulprofos	38.49	0.942	216	36.96	39.54	37.11
Triphenyl Phosphate	40.88	1.000	223	39.06	(6)	(6)
EPN	42.64	1.043	228	41.06	47.83	47.13
Azinphos Methyl	44.16	1.080	232	43.67	(7)	49.24
Leptophos	45.12	1.104	235	43.91	47.38	41.68
Azinphos Ethyl	46.55	1.139	240	46.50	47.43	50.40
Coumaphos	49.31	1.206	248	50.10	67.86	60.88

(1) Actual retention times (RT) will vary with individual columns and chromatographic conditions. See Table 10 for chromatographic performance notes. Data from Backup Data Report [9].

(2) Capillary Column conditions given in Table 6. Sets of co-eluting or nearly co-eluting peaks are identified by letters: (A), (B), (C), (D), (E), (F), (G), (H), (I), and (J)

(3) Relative Retention Times, relative to Triphenyl Phosphate.

(4) Elution temperature (°C) for DB-1 column (see Table 6 for column conditions.)

(5) Broad, tailing peak.

(6) No data.

(7) Did not elute.

TABLE 8. Applicable working range

Compound	Atmospheric working range (mg/m ³) ⁽¹⁾	Atmospheric working range (ppm) ⁽²⁾	Sample working range (µg/sample) ⁽³⁾	Instrument working range (ng on column) ⁽⁴⁾
Azinphos Methyl	0.02-0.6	0.0015-0.046	2.4 to 72	1.2-36
Chlorpyrifos	0.02-0.6	0.0014-0.042	2.4 to 72	1.2-36
Diazinon	0.01-0.3	0.0008-0.024	1.2 to 36	0.6-18
Dicrctophos	0.025-0.75	0.0026-0.077	3.0 to 90	1.5-45
Disulfoton	0.01-0.3	0.0009-0.027	1.2 to 36	0.6-18
Ethion	0.04-1.2	0.0025-0.076	4.8 to 144	2.4-72
Ethoprop	0.01-0.3	0.0010-0.030	1.2 to 36	0.6-18
Fenamiphos	0.01-0.3	0.0008-0.024	1.2 to 36	0.6-18
Fonofos	0.01-0.3	0.0010-0.030	1.2 to 36	0.6-18
Malathion	1.0-30	0.074-2.2	12. to 360(5)	6.-180(5)
Methamidophos	0.02-0.6	0.0035-0.10	2.4 to 72	1.2-36
Methyl Parathion	0.02-0.6	0.0019-0.056	2.4 to 72	1.2-36
Mevinphos	0.01-0.3	0.0011-0.033	1.2 to 36	0.6-18
Monocrotophos	0.025-0.75	0.0027-0.082	3.0 to 90	1.5-45
Parathion	0.005-0.15	0.0004-0.013	0.6 to 18	0.3-9
Phorate	0.005-0.15	0.0005-0.014	0.6 to 18	0.3-9
Ronnel	1.0-30	0.076-2.3	12. to 360(5)	6.-180(5)
Sulprofos	0.1-3.0	0.0076-0.23	12. to 360	6.-180
Terbufos	0.01-0.3	0.0008-0.026	1.2 to 36	0.6-18

(1) To cover range of 1/10 to 3x NIOSH REL.

(2) Calculated for 25 °C and 760 mm Hg (NTP).

(3) Calculated for a collection volume of 120 L (2 hrs @ 1 L/min., 4 hrs @ 0.5 L/min., or 10 hrs @ 0.2 L/min.).

(4) Desorbing sample in 2.0 mL solvent and injecting 1 µL into gas chromatograph.

(5) Calculated for a collection volume of 12 L (12 min. @ 1 L/min., 24 min. @ 0.5 L/min., or 1 hour @ 0.2 L/min.).

TABLE 9. Limits of detection and margin of sensitivity

Compound	Instrument Estimated LOD (ng on column)	Sample estimated LOD ($\mu\text{g}/\text{sample}$) ⁽¹⁾	Atmospheric estimated LOD (mg/m^3) ⁽¹⁾	Margin of sensitivity (REL/LOD) ⁽²⁾
Azinphos Methyl	0.06	0.12	0.0012	167
Chlorpyrifos	0.02	0.04	0.0004	500
Diazinon	0.02	0.04	0.0004	250
Dicrotophos	0.1	0.2	0.002	125
Disulfoton	0.02	0.04	0.0004	250
Ethion	0.02	0.04	0.0004	1000
Ethoprop	0.02	0.04	0.0004	(3)
Fenamiphos	0.07	0.14	0.0014	71
Fonofos	0.02	0.04	0.0004	250
Malathion	0.05	0.1	0.001	10000
Methamidophos	0.3	0.6	0.005	(3)
Methyl Parathion	0.02	0.04	0.0004	500
Mevinphos	0.06	0.12	0.0012	83
Monocrotophos	0.2	0.4	0.004	63
Parathion	0.02	0.04	0.0004	125
Phorate	0.02	0.04	0.0004	125
Ronnel	0.02	0.04	0.0004	25000
Sulprofos	0.03	0.06	0.0005	2000
Terbufos	0.02	0.04	0.0004	(3)

(1) Calculated for a collection volume of 120 L (2 hrs @ 1 L/min., 4 hrs @ 0.5 L/min., or 10 hrs @ 0.2 L/min.).

(2) REL in mg/m^3 (Table 2) \div Atmospheric LOD (Table 9).

(3) No REL

TABLE 10. Notes on analytical characteristics of organophosphorous compounds^(1,2)

Compound (alphabetically)	A. Chemical and Physical	B. Desorption and Dissolution	C. Gas Chromatography
Azinphos Methyl (Guthion*)	-	-	3,5,6
Azinphos Ethyl (Guthion Ethyl)	-	-	5
Chlorpyrifos (Dursban*)	-	-	-
Coumaphos (Co-Ral*)	-	-	5
Crufomate (Ruelene*)	1	1,4	1
Demeton (Systox*)	2,6	5	3
Diazinon (Spectracide*)	-	-	-
Dichlorvos (DDVP, Vapona*)	7	-	4
Dicrotophos (Bidrin*)	-	-	-
Dimethoate (Cygon*)	1	1,4	1
Dioxathion (Delnav*)	-	-	-
Disulfoton (Di-Syston*)	2	-	2
EPN (Santox*)	-	-	5
Ethion	-	-	-
Ethoprop (Prophos*)	-	-	-
Fenamiphos (Nemacur*)	1	1,4	1
Fensulfothion (Dasanit*)	3	4	-
Fenthion (Baytex*)	-	5	-
Fonofos (Dyfonate*)	-	-	-
Isofenphos (Oftanol*)	1	1	1
Leptophos (Phosvel*)	-	5	5
Malathion (Cythion*)	-	1,3,4	-
Merphos (Folex*)	4	-	2
Methamidophos (Monitor*)	1	1,2,4	1,4
Methyl Parathion (Parathion Methyl)	-	5	-
Mevinphos (Phosdrin*)	6,7	1,5	3,4
Monocrotophos (Azodrin*)	1	-	1
Naled (Dibrom*)	5	-	2
Oxydemeton Methyl (Metasystox-R)	3	-	1,2
Parathion (Ethyl Parathion)	-	-	-
Phorate (Thimet*)	2,7	-	2
Pirimiphos Methyl (Actellic*)	-	-	4
Ronnel (Fenchlorphos)	-	-	-
Sulfotepp (TEDP)	-	-	-
Sulprofos (Bolstar*)	-	-	-
TEPP	7	5	4
Terbufos (Counter*)	2	-	2
Tetrachlorvinphos (Gardona*)	-	-	-
Tributyl Phosphate	-	-	7
Triphenyl Phosphate	-	-	7

* = Trade name, Registered name, or Trademark (Farm Chemicals Handbook [3]).

- (1) Observations made during selection and validation of selected analytes. [9]
- (2) Refer to notes on the following pages.

Table 10 continued. Notes on Analytical Characteristics**A. Chemical and Physical**

1. Amide or phosphoramidate, slightly acidic, very polar chemically.
 2. Alkyl thio-ether, easily oxidized to sulfone and sulfoxide.
 3. Sulfoxides, easily oxidized to sulfone. Also very polar chemically.
 4. Phosphite, easily air oxidized to phosphate (Merphos to DEF).
 5. Vicinal dibromide, easily debrominated (Naled to Dichlorvos).
 6. Two or more isomers commonly exist (e.g. Demeton-O and Demeton-S; cis- and trans-mevinphos).
 7. Relatively volatile, can be lost if media or vials are left uncapped for even a short period of time.
- General: Organophosphorous compounds are easily destroyed at mildly alkaline conditions (pH \geq 8). Losses can occur for trace levels of compounds on alkaline glass surfaces. Glassware should be neutralized after washing, if alkaline detergent is used.

B. Desorption and Dissolution

1. Solubility of concentrated solutions in toluene enhanced by the addition of 1% Methanol or 10% acetone. Solubility in hexane very unfavorable even for dilute solutions.
 2. Changing from 100% toluene to 90/10 toluene/acetone, desorption from glass fiber filters improved from 62% to 98%, desorption from quartz fiber filters improved from 30% to 101%.
 3. Changing from glass fiber filters to quartz fiber filters, desorption in toluene improved from 16% to 88% and desorption in 90/10 toluene/acetone improved from 70% to 99%.
 4. These compounds are more chemically polar than the other listed organophosphorous compounds; desorption from XAD-2 or from glass or quartz fiber filters in hexane was incomplete or non-existent. Desorption in toluene was adequate except as noted in 2 and 3 above. The use of toluene containing 10% acetone improved recoveries for all analytes to satisfactory levels.
 5. The desorption characteristics of these compounds were not evaluated.
- General:
1. The presence of acidic hydrogen or double bonded oxygen anywhere in the molecular structure greatly decreases solubility in non-polar solvents and increases the difficulty of desorption from polar surfaces and sorbents.
 2. While glass fiber filters and toluene desorbant were adequate for most compounds in preliminary tests, the method was given wider application for the more polar compounds by the use of quartz fiber filters and 90/10 toluene/acetone desorbant.
 3. Greater flame photometric detector response was observed for organophosphorous compounds when injections were made in toluene or 90/10 toluene/acetone. Solvents with lower boiling points (e.g. methylene chloride, chloroform, methyl-t-butyl ether, and ethyl acetate) possessed fair to good desorption power, but rendered less satisfactory gas chromatographic responses for the analytes. This effect may be due to better analyte mass-transfer from the injection port to the capillary column with higher boiling solvents using splitless or direct injection techniques.

C. Gas Chromatography

1. Poor chromatography may be encountered with dirty or undeactivated columns or injection ports. Clean quartz wool plugs stuffed in the injection port liner are better than silanized glass wool at reducing losses within the injection port.
2. Multiple, shifted, irregular, or severely tailing peaks may be observed in the chromatogram if degradation or oxidation of the analytes occur prior to injection, within the injection port, or during chromatographic separation on-column.
3. Multiple peaks may be observed due to presence of isomers.
4. Short elution time, compound may co-elute with solvent if oven temperature is too high.
5. Long elution time, compound may be lost if run time is too short, column or injection port is too cool, or split-vent-valve opens too soon when injected in splitless or direct injection mode.
6. Azinphos Methyl did not elute from DB-1701 even though Azinphos ethyl did elute.
7. Potential internal standards: Triphenyl phosphate is more favorable if multiple analytes are expected because it is less volatile and elutes in an area of the chromatogram having fewer competing analytes.

TABLE 11. Other methods of analysis for organophosphorous compounds in air

Document	Method Number	Organophosphorous Compound(s)
AEC&T ⁽¹⁾		Chlorpyrifos, Demeton-O, Demeton-S, Diazinon, Dimethoate, Malathion, Paraoxon, and Parathion
NMAM, 2 nd ed ⁽²⁾	v. 1 P&CAM 158 v. 5 P&CAM 295 v. 6 P&CAM 336 v. 3 S 208 v. 3 S 209 v. 3 S 210 v. 6 S 280 v. 3 S 285 v. 3 S 295 v. 6 S 296 v. 6 S 299 v. 3 S 370	Parathion Dichlorvos (DDVP) TEPP Tributyl phosphate Triorthocresyl phosphate Triphenyl phosphate Demeton EPN Parathion Mevinphos Ronnell Malathion
NMAM, 4th ed. ⁽³⁾	2503 2504 5012 5514	Mevinphos TEPP EPN, Malathion, and Parathion Demeton
OSHA A.M.M. ⁽⁴⁾	62	Chlorpyrifos, Diazinon, Parathion, DDVP, and Malathion
OSHA Partially Validated Methods ⁽⁵⁾	PV2087 PV2045 PV2134 PV2015 PV2027 PV2071 PV2099 PV2037 PV2105 PV2112	Azinphos methyl Monocrotophos Coumaphos Crufomate Fonofos Pirimiphos Methyl Dicrotophos Sulprofos Disulfoton Methyl Parathion

(1) Hill and Arnold in Arch. Environ. Contam. & Toxicol . [11]

(2) NIOSH Manual of Analytical Methods, 2nd ed., Volumes 1-7 [7]

(3) NIOSH Manual of Analytical Methods, 4th ed. [8]

(4) OSHA Analytical Methods Manual [12]

(5) OSHA Partially Validated Methods (refer to by name) [4]

TABLE 12. Spiking concentrations for organophosphorous compounds

Compound	Total µg spiked ⁽¹⁾ at 1/30 x REL	Total µg spiked ⁽¹⁾ at 1/10 x REL	Total µg spiked ⁽¹⁾ at 1/3 x REL	Total µg spiked ⁽¹⁾ at 1 x REL	Total µg spiked ⁽¹⁾ at 3 x REL	Volume (mL) of 10 mg/mL stock solution needed to prepare 10 mL of SS-1
Azinphos Methyl	0.8	2.4	8	24	72	0.8
Chlorpyrifos	0.8	2.4	8	24	72	0.8
Diazinon	0.4	1.2	4	12	36	0.4
Dicrotophos	1.0	3	10	30	90	1.0
Disulfoton	0.4	1.2	4	12	36	0.4
Ethion	1.6	4.8	16	48	144	1.6
Ethoprop	0.4	1.2	4	12	36	0.4
Fenamiphos	0.4	1.2	4	12	36	0.4
Fonofos	0.4	1.2	4	12	36	0.4
Malathion ⁽³⁾	4	12	40	120	360	4.0
Methamidophos	0.8	2.4	8	24	72	0.8
Methyl Parathion	0.8	2.4	8	24	72	0.8
Mevinphos	0.4	1.2	4	12	36	0.4
Monocrotophos	1.0	3	10	30	90	1.0
Parathion	0.2	0.6	2	6	18	0.2
Phorate	0.2	0.6	2	6	18	0.2
Ronnel ⁽³⁾	4	12	40	120	360	4.0
Sulprofos	4	12	40	120	360	4.0
Terbufos	0.4	1.2	4	12	36	0.4
General (for 120L) ^(2,3)	x/30	x/10	x/3	x	3x	4y

(1) Total µg per sample, for spiked media, or per 2 mL desorption solution for liquid calibration standards.

(2) Where x, µg/sample = REL, µg/L x 120 L/sample; and y, mg/mL = REL, mg/m³ x 4 m³/mL.

(3) For all REL > 1 mg/m³, use 1/10 x REL in the calculations (assumes that collection volume in these cases would be 12 L instead of 120 L).

TABLE 13. Spiking of media

Spiking Levels ⁽¹⁾ (fraction of REL)	Spiking Solution	Preferred Syringe Size	Spiking Volume ⁽²⁾
1/30x REL	SS-0.1	50 µL	10 µL
1/10x REL	SS-0.1	50 µL	30 µL
1/3x REL	SS-1	50 µL	10 µL
1x REL	SS-1	50 µL	30 µL
3x REL	SS-1	100 µL	90 µL

(1) For a collection volume of 120 L. Range corresponds to values within "Working Range" column, Table 8.

(2) For liquid calibration standard preparations, add specified volume to 2 mL desorption solution in 2-mL volumetric flask. For laboratory control samples spiked at the REL, apply volume specified in "Spiking Volume" column to front section of sampler; do in duplicate. For Desorption Efficiency determination, apply specified volume to front section of sampler; do each of five levels in triplicate.

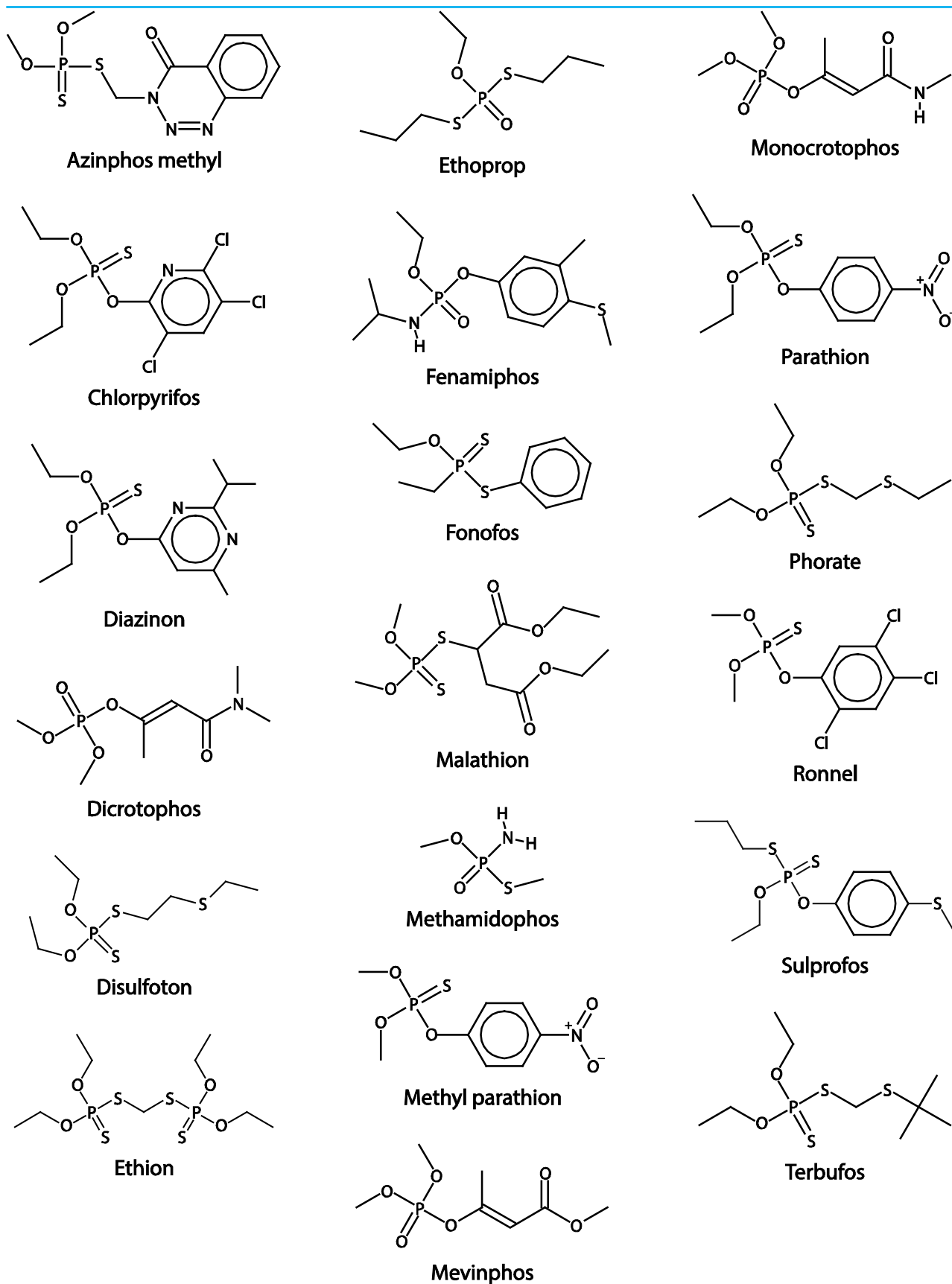


Figure 1. Structures of organophosphorus compounds

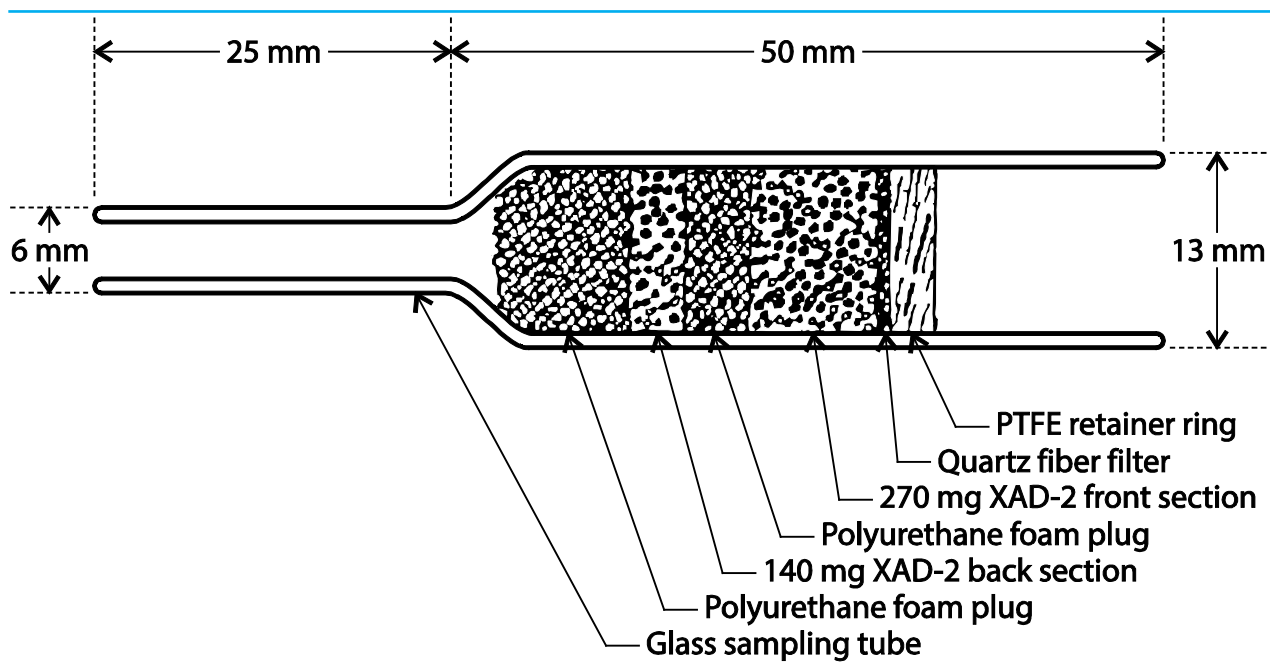


Figure 2. OVS-2 Sampler

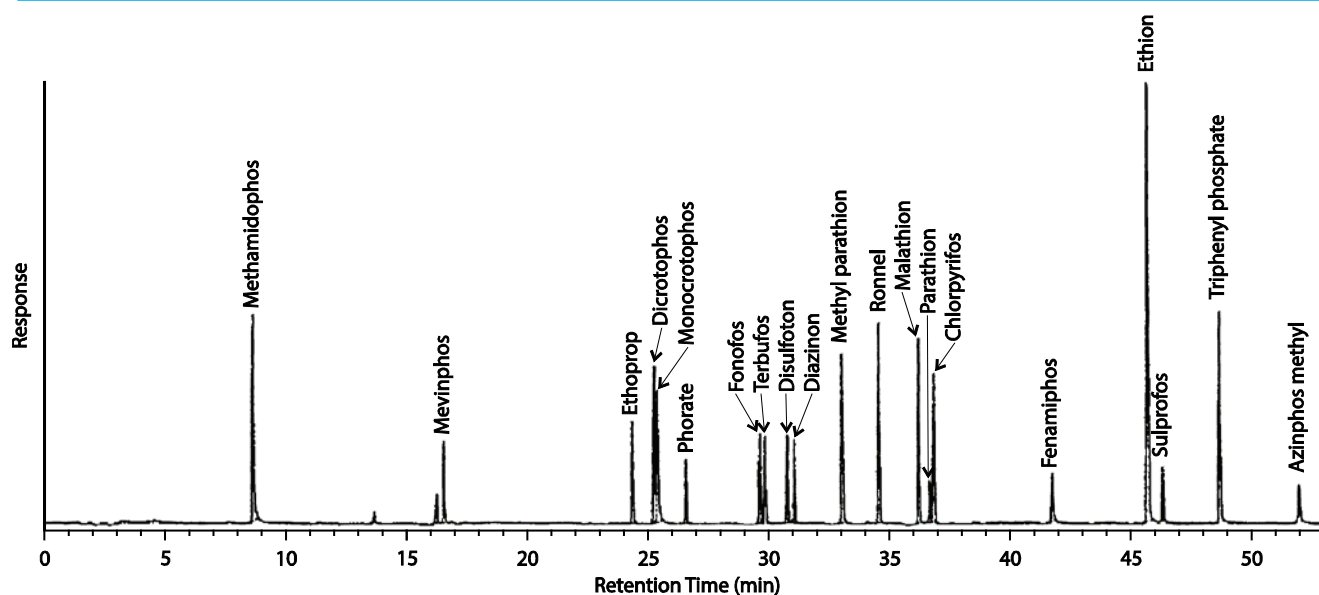


Figure 3. Typical chromatogram of organophosphorus compounds

Column: DB-1 fused silica capillary column, 30 meters x 0.32 mm I.D. x 0.25 μm film thickness

Temperature program: 80 to 275 $^{\circ}\text{C}$ at 3.0 $^{\circ}\text{C}$ per minute.

Concentration of analytes: 0.6 x NIOSH REL, except Sulprofos (0.06x REL), and Malathion and Ronnel (both at 0.006x)

1.8 $\mu\text{g}/\text{mL}$	Parathion and Phorate
3.6 $\mu\text{g}/\text{mL}$	All other compounds
7.2 $\mu\text{g}/\text{mL}$	Azinphos methyl, Chlorpyrifos, Methamidophos, and Methyl parathion
9.0 $\mu\text{g}/\text{mL}$	Dicrotophos and Monocrotophos
14 $\mu\text{g}/\text{mL}$	Triphenyl phosphate
14.4 $\mu\text{g}/\text{mL}$	Ethion