# ORGANOPHOSPHORUS PESTICIDES 5600

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

**METHOD: 5600, Issue 1** **EVALUATION: FULL** **Issue 1: 15 August 1994**

| | |
|---|---|
| **OSHA :** | Table 2 |
| **NIOSH:** | Table 2 |
| **ACGIH:** | Table 2 |

**PROPERTIES:** Table 3

**SYNONYMS:** Table 4

## SAMPLING

| | |
|---|---|
| **SAMPLER:** | FILTER/SOLID SORBENT TUBE (OVS-2 tube: 13-mm quartz filter; XAD-2, 270 mg/140 mg) |
| **FLOW RATE:** | 0.2 to 1 L/min |
| **VOL-MIN:** | 12 L |
| **-MAX:** | 240 L; 60 L (Malathion, Ronnel) |
| **SHIPMENT:** | cap both ends of tube |
| **SAMPLE STABILITY:** | at least 10 days at 25 °C<br>at least 30 days at 0 °C |
| **BLANKS:** | 2 to 10 field blanks per set |

## ACCURACY

| | |
|---|---|
| **RANGE STUDIED:** | Table 5, Column A |
| **ACCURACY:** | Table 5, Column B |
| **BIAS:** | Table 5, Column C |
| **OVERALL PRECISION ($\hat{S}_{rT}$):** | Table 5, Column D |

**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 organophosphorus compounds after evaluation for desorption efficiency, sample capacity, sample stability, and precision and accuracy.

**OTHER METHODS:** This method may be used to replace previous organophosphorus pesticide methods. See Table 10 for partial listing. The OVS-2 tube is similar in concept to the device of Hill and Arnold [11], but offers greater convenience and lower flow resistance.

## MEASUREMENT

| | |
|---|---|
| **TECHNIQUE:** | GC, FLAME PHOTOMETRIC DETECTION (FPD) |
| **ANALYTE:** | organophosphorus pesticides, Table 1 |
| **EXTRACTION:** | 2-mL 90% toluene/10% acetone solution |
| **INJECTION VOLUME:** | 1-2 µL |
| **TEMPERATURE -INJECTION:** | 240 °C |
| **-DETECTOR:** | 180 °C to 215 °C (follow manufacturer's recommendation) |
| **-COLUMN:** | Table 6 |
| **CARRIER GAS:** | He at 15 psi (104 kPa) |
| **COLUMN:** | fused silica capillary column; Table 6 |
| **DETECTOR:** | FPD (phosphorus mode) |
| **CALIBRATION:** | standard solutions of organophosphorus compounds in toluene |
| **RANGE:** | Table 8, Column C |
| **ESTIMATED LOD:** | Table 8, Column F |
| **PRECISION ($\bar{S}_r$):** | Table 5, Column E |

**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 (plasticizer), tris-(2-butoxy ethyl) phosphate (plasticizer used in some rubber stoppers), tricresyl phosphate (petroleum oil additive, hydraulic fluid, plasticizer, flame-retardant, and solvent), and triphenyl phosphate (plasticizer and flame-retardant in plastics, lacquers, and roofing paper).

**REAGENTS:**

1. Organophosphorus analytes listed in Table 1. and (optional) 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.
   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. Organophosphorus 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 column F of Table 11 to 10 mL with toluene or 90/10 toluene/acetone.
   b. Spiking solution SS-2: Dilute 1 mL of SS-1 solution with toluene in a 10-mL volumetric flask.
7. Purified gases: Helium, hydrogen, nitrogen, dry air, and oxygen, (if required by detector).

* See Special Precautions

**SPECIAL PRECAUTIONS:** Organophosphorus 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 [13-17].

Toluene is flammable and toxic. Acetone is highly flammable. Prepare all samples in a well ventilated hood.

**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 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 or equivalent 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 or equivalent 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 as the OVS-2 sampler. See Figure 2.
   NOTE: Some OVS-2 tubes contain glass fiber filters, as specified in the OSHA methods (see Table 10). These tubes, however, did not perform as well for the more polar analytes (amides, phosphoramides, and sulfoxides; see Table 9). 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 phosphorus 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.

**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. [4, 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 along with back-up XAD-2 section to a second 4-mL vial.
6. Add 2 mL of desorbing solvent to each vial using a 5-mL syringe or 2-mL pipette. Cap each vial.
7. Allow to stand 30 minutes, immerse vials approximately 15 mm 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.
   a. Add known amounts of calibration spiking solution (SS-1 or SS-2 according to schedule in Table 11) 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 desorbing solution.
   c. Analyze together with field samples, field blanks, and laboratory control samples (steps 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 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 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 organophosphorus compounds, the following minimal desorption efficiency (DE) test may be performed as follows:
   a. Determine the NIOSH REL, OSHA PEL, or ACGIH TLV in mg/m$^3$.
   b. Prepare spiking solution SS-1 (refer to Table 11, or use the following formulae, which are specific for the calculation of the weight of analyte to add to 10 mL toluene/acetone 90:10).
      For REL > 1 mg/m$^3$ (assuming 12-L collection vol.), let W = REL x 4 m$^3$
      For REL $\leq$ 1 mg/m$^3$ (assuming 120-L collection vol.), let W = REL x 40 m$^3$
      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.
      Let [SS-2] = [SS-1] x 0.1 where [SS-2] = concentration of spiking solution SS-2.
   d. Prepare three tubes at each of five levels plus three media blanks. Concentration at each level may be calculated using formulae in entry 20, part II of Table 11.
      i. Remove plastic cap from large end of sampler, apply appropriate volume of spiking solution to face of quartz fiber filter following schedule in part I of Table 11.
      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 or 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 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):

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

## 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 Parathion is not used as the retention time reference compound, then another related compound such as tributyl phosphate, Ronnel, or triphenyl phosphate 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.

## REFERENCES:

[1] Sweet, D.V., Ed., Registry of Toxic Effects of Chemical Substances, DHHS (NIOSH) Publ. No. 87-114 (1987).
[2] Merck Index, 11th ed., S. Budavari, Ed., Merck and Co., Rahway, NJ (1989).
[3] Farm Chemicals Handbook, Meister Publishing Co., Willoughby, OH (1991).
[4] OSHA Stopgap Methods for individual organophosphorus pesticides (Refer to by compound name), Carcinogen and Pesticide Branch, OSHA Analytical Laboratory, Salt Lake City, UT.
[5] NIOSH Recommendations for Occupational Safety and Health, DHHS (NIOSH) Publ. No. 92-100 (1992).
[6] NIOSH Pocket Guide to Chemical Hazards, U.S. Dept. of Health and Human Services, (NIOSH) Publ. No. 90-117 (1990).
[7] NIOSH Manual of Analytical Methods, 2nd ed., v. 1, P & CAM 158; v. 3, S208, S209, S210, S285, S295, and S370; v. 5, P & CAM 295; v. 6, P & CAM 336, S280, S296, and S299, U.S. Dept. Health, Education, and Welfare, (NIOSH) Publ. 77-157-C (1977).
[8] NIOSH Manual of Analytical Methods, 3rd. ed., Methods 2503, 2504, 5012, and 5514, U.S. Dept. of Health and Human Services, (NIOSH) Publ. 84-100 (1984)
[9] Backup Data Report for Organophosphorus Pesticides, prepared under NIOSH Contract 200-88-2618 (unpublished, 1992).
[10] J & W Catalog of High Resolution Chromatography Products, 1991.
[11] Hill, Robert H., Jr., and James E. Arnold. A Personal Air Sampler for Pesticides, Arch. Environ. Contam. Toxicol., 8, 621-628 (1979).
[12] OSHA Method 62, OSHA Analytical Methods Manual, Carcinogen and Pesticide Branch, OSHA Analytical Laboratory, Salt Lake City, UT.
[13] Criteria for a Recommended Standard…Occupational Exposure to Malathion, U.S. Dept. Health, Education, and Welfare, (NIOSH) Publ. 76-205 (1976).
[14] Criteria for a Recommended Standard…Occupational Exposure to Parathion, U.S. Dept. Health, Education, and Welfare, (NIOSH) Publ. 76-190 (1976).
[15] Criteria for a Recommended Standard…Occupational Exposure to Methyl Parathion, U.S. Dept. Health, Education, and Welfare, (NIOSH) Publ. 77-106 (1976).
[16] Criteria for a Recommended Standard…Occupational Exposure During the Manufacture and Formulation of Pesticides, U.S. Dept. Health, Education, and Welfare, (NIOSH) Publ. 78-174 (1978).
[17] Occupational Exposure to Pesticides…Report to the Federal Working Group on Pest Management from the Task Group on Occupational Exposure to Pesticides; Federal Working Group on Pest Management, Washington, D.C., January 1974, U.S. Govt. Printing Office: 1975 0-551-026.
[18] 1993-1994 Threshold Limit Values for Chemical Substances and Physical Agents, American Conference of Governmental Industrial Hygienists, Cincinnati, OH (1993).

## METHOD WRITTEN BY:

John M. Reynolds and Don C. Wickman, DataChem Laboratories, Salt Lake City, UT.

**Table 1. Formula and Registry Numbers**

| Compound (alphabetically) | MW(1) (Daltons) | Empirical Formula | Structural Formula | CAS # (2,3,4) | RTECS(2) |
|---|---|---|---|---|---|
| 1. Azinphos methyl | 317.32 | $C_{10}H_{12}N_3O_3PS_2$ | $(CH_3O)_2P(=S)SCH_2(C_7H_4N_3O)$ | 86-50-0 | TE1925000 |
| 2. Chlorpyrifos | 350.58 | $C_9H_{11}Cl_3NO_3PS$ | $(C_2H_5O)_2P(=S)O(C_5HN)Cl_3$ | 2921-88-2 | TF6300000 |
| 3. Diazinon | 304.34 | $C_{12}H_{21}N_2O_3PS$ | $(C_2H_5O)_2P(=S)O(C_4HN_2)(CH_3)CH(CH_3)_2$ | 333-41-5 | TF3325000 |
| 4. Dicrotophos | 237.19 | $C_8H_{16}NO_5P$ | $(CH_3O)_2P(=O)OC(CH_3)=CHC(=O)N(CH_3)_2$ | 141-66-2 | TC3850000 |
| 5. Disulfoton | 274.39 | $C_8H_{19}O_2PS_3$ | $(C_2H_5O)_2P(=S)S(CH_2)_2SC_2H_5$ | 298-04-4 | TD9275000 |
| 6. Ethion | 384.46 | $C_9H_{22}O_4P_2S_4$ | $[(C_2H_5O)_2P(=S)S]_2CH_2$ | 563-12-2 | TE4550000 |
| 7. Ethoprop | 242.33 | $C_8H_{19}O_2PS_2$ | $(C_3H_7S)_2P(=O)OC_2H_5$ | 13194-48-4 | TE4025000 |
| 8. Fenamiphos | 303.36 | $C_{13}H_{22}NO_3PS$ | $(CH_3)_2CHNHP(=O)(O[C_2H_5])O(C_6H_3)(CH_3)SCH_3$ | 22224-92-6 | TB3675000 |
| 9. Fonofos | 246.32 | $C_{10}H_{15}OPS_2$ | $C_2H_5OP(C_2H_5)(=S)S(C_6H_5)$ | 944-22-9 | TA5950000 |
| 10. Malathion | 330.35 | $C_{10}H_{19}O_6PS_2$ | $(CH_3O)_2P(=S)SCH[C(=O)OC_2H_5]CH_2C(=O)OC_2H_5$ | 121-75-5 | WM8400000 |
| 11. Methamidophos | 141.12 | $C_2H_8NO_2PS$ | $CH_3OP(=O)(NH_2)SCH_3$ | 10265-92-6 | TB4970000 |
| 12. Methyl parathion | 263.20 | $C_8H_{10}NO_5PS$ | $(CH_3O)_2P(=S)O(C_6H_4)NO_2$ | 298-00-0 | TG0175000 |
| 13. Mevinphos (E) | 224.15 | $C_7H_{13}O_6P$ | $(CH_3O)_2P(=O)OC(CH_3)=CHC(=O)OCH_3$ | 298-01-1 (2) | GQ5250100 |
| Mevinphos (E & Z) | | | | 7786-34-7 (3,4) | GQ5250000 |
| 14. Monocrotophos (Z) | 223.17 | $C_7H_{14}NO_5P$ | $(CH_3O)_2P(=O)OC(CH_3)=CHC(=O)NHCH_3$ | 919-44-8 (2) | TC4981100 |
| Monocrotophos (E) | | | | 6923-22-4 (3,4) | TC4375000 |
| 15. Parathion | 291.26 | $C_{10}H_{14}NO_5PS$ | $(C_2H_5O)_2P(=S)O(C_6H_4)NO_2$ | 56-38-2 | TF4550000 |
| 16. Phorate | 260.36 | $C_7H_{17}O_2PS_3$ | $(C_2H_5O)_2P(=S)SCH_2SC_2H_5$ | 298-02-2 | TD9450000 |
| 17. Ronnel | 321.54 | $C_8H_8Cl_xO_3PS$ | $(CH_3O)_2P(=S)O(C_6H_2)Cl_3$ | 299-84-3 | TG0525000 |
| 18. Sulprofos | 322.43 | $C_{12}H_{19}O_2PS_3$ | $C_2H_5OP(S[C_3H_7])(=S)O(C_6H_4)SCH_3$ | 35400-43-2 | TE4165000 |
| 19. Terbufos | 288.42 | $C_9H_{21}O_2PS_3$ | $(C_2H_5O)_2P(=S)SCH_2SC(CH_3)_3$ | 13071-79-9 | TD7740000 |

(1) Molecular weights 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(4) mg/m$^3$ | NIOSH REL(5) mg/m$^3$ | NIOSH REL(5) (ppm) | ACGIH TLV mg/m$^3$ | STEL mg/m$^3$ |
|---|---|---|---|---|---|---|
| 1. Azinphos methyl | 11 f | 0.2 | 0.2 | (0.015) | 0.2 (skin) | |
| 2. Chlorpyrifos | 145 | 0.2 | 0.2 | (0.014) | 0.2 (skin) | 0.6(5) |
| 3. Diazinon | 250 m, 285 f | 0.1 | 0.1 | (0.008) | 0.1 (skin) | |
| 4. Dicrotophos | 16 f, 21 m | 0.25 | 0.25 | (0.026) | 0.25 (skin) | |
| 5. Disulfoton | 2.3 f, 6.8 m | 0.1 | 0.1 | (0.009) | 0.1(3) (skin) | |
| 6. Ethion | 27 f, 65 m | 0.4 | 0.4 | (0.025) | 0.4 (skin) | |
| 7. Ethoprop | 61.5(2) | | | | | |
| 8. Fenamiphos | 10 | 0.1 | 0.1 | (0.008) | 0.1 (skin) | |
| 9. Fonofos | 3 f, 13 m(3) | 0.1 | 0.1 | (0.010) | 0.1 (skin) | |
| 10. Malathion | 1000 f, 1375 m | 10 | 10 | (0.740) | 10 (skin) | |
| 11. Methamidophos | 25 m, 27 f | | | | | |
| 12. Methyl parathion | 14 m, 24 f | 0.2 | 0.2 | (0.019) | 0.2 (skin) | |
| 13. Mevinphos | 3.7 f, 6.1 m | 0.1 | 0.1 | (0.011) | 0.1 (skin) | 0.27(6) |
| 14. Monocrotophos | 17 m, 20 f | 0.25 | 0.25 | (0.027) | 0.25(3) (skin) | |
| 15. Parathion | 3.6 f, 13 m | 0.1 | 0.05 | (0.004) | 0.1 (skin) | |
| 16. Phorate | 1.1 f, 2.3 m | 0.05 | 0.05 | (0.005) | 0.05 (skin) | 0.2(5,6) |
| 17. Ronnel | 1250 m, 2630 f | 10 | 10 | (0.760) | 10 (skin) | |
| 18. Sulprofos | 227 | 1 | 1 | (0.076) | 1(3) (skin) | |
| 19. Terbufos | 1.6-4.5 m, 9.0 f | | | | | |

(1) Rat-oral; from Merck Index, unless otherwise noted, f = female, m = male [2].
(2) Farm Chemicals Handbook [3].
(3) RTECS [1].
(4) OSHA Final Rule, 1989 (unenforceable, 1992); only Malathion and Parathion had previous PELs.
(5) NIOSH Recommendations for Occupational Safety and Health [5].
(6) ACGIH [18].

**Table 3. Physical Properties(1)**

| Compound (alphabetically) | Liquid Density (g/mL) | MP (°C) | BP °C (mm Hg) | Vapor Pressure Pascal | Vapor Pressure mm Hg | @ °C | Solubility in Water (mg/L at 20 °C) |
|---|---|---|---|---|---|---|---|
| 1. Azinphos methyl | 1.44 | 73-74 | unstable >200 | 0.00018 | $1.35x10^{-6}$ | 20(3) | 30(8) |
| 2. Chlorpyrifos | none found | 41-42 | — | 0.0025 | $1.87x10^{-5}$ | 25 | — |
| 3. Diazinon | 1.116-1.118 | liquid | decomp. >120 | 0.019 | $1.4x10^{-4}$ | 20 | 40 |
| 4. Dicrotophos | 1.216 | liquid | 400 (760) | | none found | | miscible |
| 5. Disulfoton | 1.144 | oil | — | 0.024 | $1.8x10^{-4}$ | 20 | nearly insol. |
| | | | | 0.0074 | $5.4x10^{-5}$ | 20(3) | insol.(3) |
| 6. Ethion | 1.220 | -12 to -13 | — | 0.0002 | $1.5x10^{-6}$ | | slightly sol. |
| 7. Ethoprop | 1.094 | oil | — | 0.047 | $3.5x10^{-4}$ | 26 | 750 |
| 8. Fenamiphos | none found | 49 | — | 0.00012 | $9x10^{-7}$ | 20(3) | 329 |
| 9. Fonofos | 1.16 | liquid | — | | none found | | 13(7) |
| 10. Malathion | 1.23 | 2.9 | 156 (0.7)(6) | 0.005 | $4x10^{-5}$ | 30(6) | 145 |
| 11. Methamidophos | 1.31 | 54. | — | 0.04 | $3x10^{-4}$ | 30 | readily sol. |
| | | | | 0.0023 | $1.7x10^{-5}$ | 20(3) | — |
| 12. Methyl parathion | 1.358 | 37-38 | — | 0.0002 | $1.5x10^{-6}$ | 20(3) | 50 |
| 13. Mevinphos | 1.25 | 20.6(4) | 325 (760) (4) | 0.4 | $3x10^{-3}$ | 20(4) | miscible |
| | | | | 0.29 | $2.2x10^{-3}$ | 20(7) | — |
| 14. Monocrotophos | none found | 54-55(5) | — | 0.0009 | $7x10^{-6}$ | 20 | |

| | | | | | | |
|---|---|---|---|---|---|---|
| miscible | | | | | | |
| 15. Parathion | 1.26 | 6 | 375 (760) | 0.005 | $3.78x10^{-5}$ | |
| 20(6) | 20 | | | | | |
| | | | | 0.00089 | $6.7x10^{-6}$ | |
| 20(3) | 10(8) | | | | | |
| 16. Phorate | 1.156 | liquid | 118-120 (2.0) (3) | 0.11 | $8.4x10^{-4}$ | 20 |
| 50 | | | | | | |
| 17. Ronnel | sp. gr=1.48 (2) | 41 | — | 0.1 | $8.x10^{-4}$ | 25 |
| 40 @ 25 °C | | | | | | |
| 18. Sulprofos | 1.20 | liquid | 210 (0.1) (6) | <0.0001 | $<10^{-6}$ | |
| 20(3) | nearly insol. (3) | | | | | |
| 19. Terbufos | 1.105 | -29.2 | — | | none found | |
| 10-15 | | | | | | |

(1) From Merck Index, unless otherwise noted [2].
(2) NIOSH 2nd Edition Method for Ronnel, S299 [7].
(3) Farm Chemicals Handbook [3].
(4) NIOSH 3rd Edition Method 2503 for Mevinphos [8].
(5) 54-55 °C for pure material, 25-30 °C for commercial mixture.
(6) NIOSH 3rd Edition Method 5012 (EPN, Malathion, Parathion) [8].
(7) OSHA Stopgap Methods (See specific analyte Method) [4].
(8) NIOSH Pocket Guide [6].

**Table 4. Synonyms**

| **Compound**(1) (alphabetically) | **Other name**(2) | **CAS Name** |
|---|---|---|
| 1. Azinphos methyl | Guthion* | Phosphorodithioic acid, O,O-dimethyl S-[(4-oxo-1,2,3-benzotriazin-3(4H)-yl)methyl] ester (3) |
| 2. Chlorpyrifos | Dursban* | Phosphorothioic acid, O,O-diethyl O-(3,5,6-trichloro-2-pyridinyl) ester (3) |
| 3. Diazinon | Spectracide* | Phosphorothioic acid, O,O-diethyl O-[6-methyl-2-(1-methylethyl)-4-pyrimidinyl] ester (3) |
| 4. Dicrotophos | Bidrin* | Phosphoric acid, 3-(dimethylamino)-1-methyl-3-oxo-1-propenyl dimethyl ester (3)<br>Phosphoric acid, dimethyl ester, ester with cis-3-hydroxy-N,N-dimethylcrotonamide (4) |
| 5. Disulfoton | Di-Syston* | Phosphorodithio1x acid, O,O-diethyl S-[2-(ethylthio)ethyl] ester (3) |
| 6. Ethion | | Phosphorodithioic acid, S,S'-methylene O,O,O',O'-tetraethyl ester (3)<br>O,O,O',O'-Tetraethyl S,S'-methylenediphosphorodithioate (4) |
| 7. Ethoprop | Prophos* | Phosphorodithioic acid, O-ethyl S,S-dipropyl ester (3) |
| 8. Fenamiphos | Nemacur*,Phenamiphos (1) | (1-Methylethyl)phosphoramidic acid, ethyl 3-methyl-4-(methylthio)phenyl ester (3)<br>Phosphoramidic acid, isopropyl-, 4-(methylthio)-m-tolyl ethyl ester (4) |
| 9. Fonofos | Dyfonate* | Ethyl phosphonodithioic acid, O-ethyl S-phenyl ester(3)<br>Phosphonodithioic acid, ethyl-, O-ethyl S-phenyl ester(4) |
| 10. Malathion | Cythion* | [(Dimethoxyphosphinothioyl)thio]butanedioic acid diethyl ester (3)<br>Succinic acid, mercapto-, diethyl ester, S-ester with O,O-dimethylphosphorodithioate (4) |
| 11. Methamidophos | Monitor* | Phosphoramidothioic acid, O,S-dimethyl ester (3) |
| 12. Methyl parathion | Parathion Methyl (1) | Phosphorothioic acid, O,O-dimethyl O-(4-nitrophenyl) ester (3) |
| 13. Mevinphos | Phosdrin* | 3-[(Dimethyoxyphosphinyl)oxy]-2-butenoic acid, |

| | | | |
|---|---|---|---|
| | | | methyl ester (3)<br>Crotonic acid, 3-hydroxy-, methyl ester dimethyl phosphate (4) |
| 14. | Monocrotophos | Azodrin* | Phosphoric acid, dimethyl [1-methyl-3-(methylamino)-3-oxo-1-propenyl] ester (3)<br>Phosphoric acid, dimethyl ester, ester with (E)-3-hydroxy-N-methylcrotonamide (4) |
| 15. | Parathion | Ethyl Parathion (1) | Phosphorothioic acid, O,O-diethyl O-(4-nitrophenyl) ester (3) |
| 16. | Phorate | Thimet* | Phosphorodithioic acid, O,O-diethyl S-[(ethylthio)methyl] ester (3) |
| 17 | Ronnel | Fenchlorphos (1) | Phosphorothioic acid, O,O-dimethyl O-(2,4,5-trichlorophenyl) ester (3) |
| 18. | Sulprofos | Bolstar* | Phosphorodithioic acid, O-ethyl O-[4-(methylthio)phenyl] S-propyl ester (4) |
| 19. | Terbufos | Counter* | Phosphorodithioic acid, 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) Merck Index [2].
(4) RTECS [1] or alternate CAS name in Merck Index [2].

**Table 5. Method Evaluation**(1)

| **Compound** (alphabetically) | **A. Range Studied**(2) mg/m$^3$ | mg/sample | **B. Accuracy** | **C. Bias** Ave. | Range | **D. Precision** Overall $\hat{S}_{rT}$ | Measurement $\bar{S}_r$ | **E. % Recovery** at 30 days 25 °C (0 °C) |
|---|---|---|---|---|---|---|---|---|
| 1. Azinphos methyl | 0.02-0.4 | 0.0048-0.096 | ± 0.178 | -0.038 | (-0.120 - +0.028) | 0.070 | 0.030 | 97 (105) |
| 2. Chlorpyrifos | 0.02-0.4 | 0.0048-0.096 | ± 0.163 | -0.027 | (-0.054 - +0.017) | 0.068 | 0.018 | 92 (90) |
| 3. Diazinon | 0.01-0.2 | 0.0024-0.048 | ± 0.162 | -0.032 | (-0.057 - -0.005) | 0.065 | 0.020 | 94 (93) |
| 4. Dicrotophos | 0.025-0.5 | 0.006-0.120 | ± 0.169 | -0.037 | (-0.102 - -0.032) | 0.066 | 0.025 | 89 (92) |
| 5. Disulfoton | 0.01-0.2 | 0.0024-0.048 | ± 0.196 | -0.064 | (-0.081 - -0.032) | 0.066 | 0.024 | 87 (89) |
| 6. Ethion | 0.04-0.8 | 0.0096-0.192 | ± 0.165 | -0.029 | (-0.056 - -0.003) | 0.068 | 0.018 | 96 (95) |
| 7. Ethoprop (3) | 0.01-0.2 | 0.0024-0.048 | ± 0.157 | -0.025 | (-0.058 - +0.025) | 0.066 | 0.024 | 97 (93) |
| 8. Fenamiphos | 0.01-0.2 | 0.0024-0.048 | ± 0.155 | -0.029 | (-0.066 - +0.002) | 0.063 | 0.022 | 94 (96) |
| 9. Fonofos | 0.01-0.2 | 0.0024-0.048 | ± 0.168 | -0.036 | (-0.076 - +0.008) | 0.066 | 0.023 | 95 (92) |
| 10. Malathion (4) | 0.025-0.5 | 0.006-0.120 | ± 0.172 | -0.038 | (-0.064 - -0.014) | 0.067 | 0.019 | 93 (93) |
| 11. Methamidophos (5) | 0.02-0.4 | 0.0048-0.096 | ± 0.156 | -0.018 | (-0.046 - +0.011) | 0.069 | 0.026 | 88 (95) |
| 12. Methyl parathion | 0.02-0.4 | 0.0048-0.096 | ± 0.160 | -0.034 | (-0.082 - +0.016) | 0.063 | 0.018 | 95 (95) |
| 13. Mevinphos | 0.01-0.2 | 0.0024-0.048 | ± 0.176 | -0.042 | (-0.061 - -0.004) | 0.067 | 0.028 | 89 (91) |
| 14. Monocrotophos | 0.025-0.5 | 0.006-0.120 | ± 0.185 | -0.043 | (-0.047 - -0.020) | 0.071 | 0.026 | 88 (92) |
| 15. Parathion | 0.005-0.1 | 0.0012-0.024 | ± 0.163 | -0.021 | (-0.045 - +0.011) | 0.071 | 0.019 | 92 (92) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 16. Phorate | 0.005-0.1 | 0.0012-0.024 | ± 0.202 | -0.070 (-0.097 - -0.047) | 0.066 | 0.025 | 91 (91) |
| 17. Ronnel (4) | 0.025-0.5 | 0.006-0.120 | ± 0.172 | -0.040 (-0.076 - +0.021) | 0.066 | 0.018 | 95 (94) |
| 18. Sulprofos (4) | 0.01-0.2 | 0.0024-0.048 | ± 0.181 | -0.047 (-0.054 - -0.031) | 0.067 | 0.017 | 94 (94) |
| 19. Terbufos (3) | 0.01-0.2 | 0.0024-0.048 | ± 0.188 | -0.054 (-0.091 - -0.024) | 0.067 | 0.022 | 92 (91) |

(1) NIOSH Back-up Data Report [9]

(2) The ranges studied were 1/10 to 2x the NIOSH REL (except as noted) sampling at 1 L/min for 4 hours.

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

(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/m$^3$.

### Table 6. Recommended Gas Chromatographic Columns and Conditions (1)

| Parameter | Wide Bore Fused Silica Capillary Column | | | |
|---|---|---|---|---|
| Stationary Phase (2) | DB-1 | DB-5 | DB-1701 | DB-210 |
| Polarity | non-polar | weakly polar | mod. polar | mod. polar |
| Length (meters) | 30 | 30 | 30 | 30 |
| I.D. (millimeters) | 0.32 | 0.32 | 0.32 | 0.32 |
| Film thickness (mm) (3) | 0.25 | 1.0 | 1.0 | 0.25 |
| Injection (vol., mode) (4)(5) | 1 µL, SPL | 1 µL, DIR | 1 µL, DIR | 1 µL, SPL |
| Oven Temperatures | | | | |
| Initial (°C) | 100 | 125 | 125 | 100 |
| Final (°C) | 275 | 275 | 275 | 250 |
| Max. Recommended (°C) (5) | 325 | 325 | 280 | 240/260 |
| Program (°C/min.) | 3.0 | 4.0 | 4.0 | 3.0 |
| Carrier Gas (Helium) | | | | |
| Head pressure (p.s.i.) | 15 | 15 | 15 | 15 |

(1) Actual conditions may vary depending on column and analytical objectives. The conditions given above are those corresponding to the RT data in Table 7.

(2) DB-1, 100% methyl silicone; DB-5, 5% phenyl, 95% methyl silicone; DB-1701, 14% cyanopropylphenyl, 86% methyl silicone; DB-210, 50% trifluoropropyl, 50% methyl silicone. Other phase types may also work well.

(3) Thinner films give faster separations at lower temperatures promoting analyte stability.

(4) Use 2-mm i.d. injection port lines for 0.5-µL injection and 4-mm i.d. injection port liners for 1-to-2-µL injections with 0.32-mm i.d. capillary columns.

(5) SPL = splitless mode, initial oven temperature 5-10 °C < BP of desorption solvent;
DIR = direct mode, initial oven temperature 5-10 °C > BP of desorption solvent.
In both modes, split-vent off time should be 60 sec for 1-2 µL injections with 4-mm ID injection port liners, and 20-30 sec for 0.5-µL injections with 2-mm ID injection port liners. Use 2-mm ID injection port liners for 0.5-µL injection and 4-mm ID injection port liners for 1-2 µL injections with 0.32-mm ID capillary columns.

(6) J & W Scientific Catalog, p. 21. [10]

### **Table 7**. Approximate Retention Times of Selected Organophosphorous Compounds(1)

| Compound (by RT on DB-1) | Capillary Column(2) | | | | | |
|---|---|---|---|---|---|---|
| | DB-1 | | | DB-5 | DB-1701 | DB-210 |
| | RT min | RRT(3) | Elution T, °C(4) | RT, min | RT, min | RT, min |
| 1. TEPP | 3.71 | 0.128 | 111 | 5.47 | 7.18(B) | 7.88 |
| 2. Triethylphosphorothioate | 4.37 | 0.151 | 113 | 6.34 | 7.14(B) | 4.93 |
| 3. Methamidophos | 5.12 | 0.177 | 115 | 7.64 | 13.61 | 12.03 |
| 4. Dichlorvos | 5.81 | 0.200 | 117 | 8.24 | 10.67 | 10.54 |
| 5. Mevinphos | 10.45 | 0.360 | 131 | 12.92 | 16.69 | 19.20 |
| 6. Ethoprop | 17.15 | 0.592 | 151 | 19.09 | 21.52 | 20.10 |
| 7. Naled | 17.61 | 0.608 | 153 | no data | 23.17(C) | 21.46(H) |
| 8. Dicrotophos | 18.00 | 0.621 | 154 | 19.94 | 25.84(E) | 31.43 |
| 9. Monocrotophos | 18.27 | 0.630 | 155 | 20.12 | 28.11 | 31.60 |
| 10. Sulfotepp | 19.06 | 0.658 | 157 | no data | 23.09(C) | 21.11 |
| 11. Phorate | 19.18 | 0.662 | 158 | 20.94 | 23.10(C) | 18.92 |
| 12. Dimethoate | 19.44 | 0.671 | 158 | 21.84 | no data | 29.33(I) |
| 13. Demeton-S | 20.15 | 0.695 | 160 | 21.70 | 25.06(D) | 24.97 |
| 14. Dioxathion | 21.30 | 0.735 | 164 | 23.04 | 26.33(F) | 23.46 |
| 15. Fonofos | 22.04 | 0.760 | 166 | 23.57 | 25.87(E) | 22.20 |
| 16. Terbufos | 22.22 | 0.767 | 168 | 23.80 | 25.02(D) | 21.52(H) |
| 17. Disulfoton | 23.09 | 0.797 | 169 | 24.19 | 26.43(F) | 22.78 |
| 18. Diazinon | 23.37 | 0.806 | 170 | 23.75 | 25.00(D) | 20.99 |
| 19. Methyl parathion | 25.37 | 0.875 | 176 | 26.48 | 31.37 | 33.21 |
| 20. Oxydemeton methyl | 26.(5) | 0.90 | 179 | no data | no data | no data |
| 21. Ronnel | 26.86 | 0.927 | 181 | 27.39 | 29.30 | 26.27 |
| 22. Pirimiphos methyl | 28.13 | 0.971 | 184 | 27.90 | 29.72 | 26.77 |
| 23. Malathion | 28.53 | 0.984 | 186 | 28.33 | 31.78(G) | 33.08(J) |
| 24. Fenthion | 28.74 | 0.992 | 186 | 28.93 | 31.78(G) | 29.35(I) |
| 25. Parathion | 28.98 | 1.000 | 187 | 29.10(A) | 33.28 | 35.60 |
| 26. Chlorpyrifos | 29.11 | 1.004 | 187 | 29.10(A) | 30.79 | 27.72 |
| 27. Crufomate | 29.64 | 1.023 | 189 | 29.54 | 34.00 | 35.34 |
| 28. Isofenphos | 31.91 | 1.101 | 196 | 31.17 | 33.81 | 33.02(J) |
| 29. Tetrachlorvinphos | 33.26 | 1.148 | 200 | 32.60 | 35.96 | 37.01 |
| 30. Fenamiphos | 34.09 | 1.176 | 202 | 33.03 | 37.14 | 38.95 |
| 31. Merphos | 35.19 | 1.214 | 206 | no data | 30.57 | 23.89 |
| 32. Fensulfothion | 36.61 | 1.263 | 210 | 35.78 | 42.41 | 46.98 |
| 33. Ethion | 37.88 | 1.307 | 214 | 36.30 | 39.30 | 37.96 |
| 34. Sulprofos | 38.49 | 1.328 | 216 | 36.96 | 39.54 | 37.11 |
| 35. Triphenyl phosphate | 40.88 | 1.411 | 223 | 39.06 | no data | no data |
| 36. EPN | 42.64 | 1.471 | 228 | 41.06 | 47.83 | 47.13 |
| 37. Azinphos methyl | 44.16 | 1.524 | 232 | 43.67 | no elution | 49.24 |
| 38. Leptophos | 45.12 | 1.557 | 235 | 43.91 | 47.38 | 41.68 |
| 39. Azinphos ethyl | 46.55 | 1.606 | 240 | 46.50 | 47.43 | 50.40 |
| 40. Coumaphos | 49.31 | 1.702 | 248 | 50.10 | 67.86 | 60.88 |

(1) Actual retention times (RT) will vary with individual columns and chromatographic conditions. See Table 9 for chromatographic performance notes. Capillary Column conditions given in Table 6. Data from Backup Data Report [9].

(2) 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) Retention times relative to Parathion.

(4) Elution temperature (°C) for DB-1 column (see Table 6 for column conditions.) Elution temperatures are provided for convenience in selecting approximate GC oven temperatures for isothermal analyses of single or several closely eluting analytes.

(5) Broad, tailing peak.

**Table 8. Applicable Working Range and Estimated LOD**

| | A. | B. | C. | D. | E. | F. | G. | |
|---|---|---|---|---|---|---|---|---|
| | **Applicable Working Range** | | | | **Estimated LOD** | | | |
| **Compound** | **Atmospheric(1)** | | **Sample(4)** | **Instrument(6)** | **Instrument** | **Sample(4)** | **Atmospheric(4)** | **Margin of Sensitivity(2)** |
| (alphabetically) | mg/m$^3$ | ppm(3) | µg/sample | ng on column | ng on column | µg/sample | mg/m$^3$ | REL/LOD |
| 1. Azinphos methyl | 0.02-0.6 | 0.0015-0.046 | 2.4 to 72 | 1.2-36 | 0.06 | 0.12 | 0.0012 | 167 |
| 2. Chlorpyrifos | 0.02-0.6 | 0.0014-0.042 | 2.4 to 72 | 1.2-36 | 0.02 | 0.04 | 0.0004 | 500 |
| 3. Diazinon | 0.01-0.3 | 0.0008-0.024 | 1.2 to 36 | 0.6-18 | 0.02 | 0.04 | 0.0004 | 250 |
| 4. Dicrotophos | 0.025-0.75 | 0.0026-0.077 | 3.0 to 90 | 1.5-45 | 0.1 | 0.2 | 0.002 | 125 |
| 5. Disulfoton | 0.01-0.3 | 0.0009-0.027 | 1.2 to 36 | 0.6-18 | 0.02 | 0.04 | 0.0004 | 250 |
| 6. Ethion | 0.04-1.2 | 0.0025-0.076 | 4.8 to 144 | 2.4-72 | 0.02 | 0.04 | 0.0004 | 1000 |
| 7. Ethoprop | 0.01-0.3 | 0.0010-0.030 | 1.2 to 36 | 0.6-18 | 0.02 | 0.04 | 0.0004 | (7) |
| 8. Fenamiphos | 0.01-0.3 | 0.0008-0.024 | 1.2 to 36 | 0.6-18 | 0.07 | 0.14 | 0.0014 | 71 |
| 9. Fonofos | 0.01-0.3 | 0.0010-0.030 | 1.2 to 36 | 0.6-18 | 0.02 | 0.04 | 0.0004 | 250 |
| 10. Malathion | 1.0-30 | 0.074-2.2 | 12. to 360(5) | 6.-180(5) | 0.05 | 0.1 | 0.001 | 10,000 |
| 11. Methamidophos | 0.02-0.6 | 0.0035-0.10 | 2.4 to 72 | 1.2-36 | 0.3 | 0.6 | 0.005 | (7) |
| 12. Methyl parathion | 0.02-0.6 | 0.0019-0.056 | 2.4 to 72 | 1.2-36 | 0.02 | 0.04 | 0.0004 | 500 |
| 13. Mevinphos | 0.01-0.3 | 0.0011-0.033 | 1.2 to 36 | 0.6-18 | 0.06 | 0.12 | 0.0012 | 83 |
| 14. Monocrotophos | 0.025-0.75 | 0.0027-0.082 | 3.0 to 90 | 1.5-45 | 0.2 | 0.4 | 0.004 | 63 |
| 15. Parathion | 0.005-0.15 | 0.0004-0.013 | 0.6 to 18 | 0.3-9 | 0.02 | 0.04 | 0.0004 | 125 |
| 16. Phorate | 0.005-0.15 | 0.0005-0.014 | 0.6 to 18 | 0.3-9 | 0.02 | 0.04 | 0.0004 | 125 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 17. Ronnel | 1.0-30 | 0.076-2.3 | 12. to 360(5) | 6.-180(5) | 0.02 | 0.04 | 0.0004 | 25,000 |
| 18. Sulprofos | 0.1-3.0 | 0.0076-0.23 | 12. to 360 | 6.-180 | 0.03 | 0.06 | 0.0005 | 2000 |
| 19. Terbufos | 0.01-0.3 | 0.0008-0.026 | 1.2 to 36 | 0.6-18 | 0.02 | 0.04 | 0.0004 | (7) |

(1) To cover range of 1/10 to 3x NIOSH REL.
(2) REL in mg/$m^3$ (Table 2) ÷ Atmospheric LOD (Column G, Table 8).
(3) Calculated for 25 °C and 760 mm Hg (NTP).
(4) Calculated for a collection volume of 120 L (2 h @ 1 L/min, 4 h @ 0.5 L/min, or 10 h @ 0.2 L/min).
(5) Calculated for a collection volume of 12 L (12 min @ 1 L/min, 24 min @ 0.5 L/min, or 1 h @ 0.2 L/min).
(6) Desorbing sample in 2.0 mL solvent and injecting 1 µL into gas chromatograph.
(7) No REL

**Table 9. Notes on Analytical Characteristics of Organophosphorous Compounds(1)**

| | | **Analytical Characteristics** | | |
|---|---|---|---|---|
| | **Compound** (Alphabetically) | A Chemical and Physical | B Desorption and Solution | C Gas Chromatography |
| 1. | Azinphos methyl (Guthion*) | | | 3,5,6 |
| 2. | Azinphos ethyl (Guthion ethyl) | | | 5 |
| 3. | Chlorpyrifos (Dursban*) | | | |
| 4. | Coumaphos (Co-Ral*) | | | 5 |
| 5. | Crufomate (Ruelene*) | 1 | 1,4 | 1 |
| 6. | Demeton (Systox*) | 2,6 | 5 | 3 |
| 7. | Diazinon (Spectracide*) | | | |
| 8. | Dichlorvos (DDVP, Vapona*) | 7 | | 4 |
| 9. | Dicrotophos (Bidrin*) | | | |
| 10. | Dimethoate (Cygon*) | 1 | 1,4 | 1 |
| 11. | Dioxathion (Delnav*) | | | |
| 12. | Disulfoton (Di-Syston*) | 2 | | 2 |
| 13. | EPN (Santox*) | | | 5 |
| 14. | Ethion | | | |
| 15. | Ethoprop (Prophos*) | | | |
| 16. | Fenamiphos (Nemacur*) | 1 | 1,4 | 1 |
| 17. | Fensulfothion (Dasanit*) | 3 | 4 | |
| 18. | Fenthion (Baytex*) | | 5 | |
| 19. | Fonofos (Dyfonate*) | | | |
| 20. | Isofenphos (Oftanol*) | 1 | 1 | 1 |
| 21. | Leptophos (Phosvel*) | | 5 | 5 |
| 22. | Malathion (Cythion*) | | | |
| 23. | Merphos (Folex*) | 4 | 5 | 2 |
| 24. | Methamidophos (Monitor*) | 1 | 1,3,4 | 1,4 |
| 25. | Methyl parathion (Parathion methyl) | | | |
| 26. | Mevinphos (Phosdrin*) | 6,7 | | 3,4 |
| 27. | Monocrotophos (Azodrin*) | 1 | 1,2,4 | 1 |
| 28. | Naled (Dibrom*) | 5 | 5 | 2 |
| 29. | Oxydemeton methyl (Metasystox-R) | 3 | 1,5 | 1,2 |
| 30. | Parathion (Ethyl parathion) | | | |
| 31. | Phorate (Thimet*) | 2,7 | | 2 |
| 32. | Pirimiphos methyl (Actellic*) | | | 4 |
| 33. | Ronnel (Fenchlorphos) | | | |
| 34. | Sulfotepp (TEDP) | | | |
| 35. | Sulprofos (Bolstar*) | | | |
| 36. | TEPP | 7 | 5 | 4 |
| 37. | Terbufos (Counter*) | 2 | | 2 |
| 38. | Tetrachlorvinphos (Gardona*) | | | |
| 39. | Tributyl phosphate | | | 7 |
| 40. | Triphenyl phosphate | | | 7 |

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

(1) Observations made during selection and validation of selected analytes [9]; refer to notes on the following page.

**Table 9 (Continued) - Notes on ANALYTICAL CHARACTERISTICS**

A. CHEMICAL AND PHYSICAL

1. Amide or phosphoramide, some slightly acidic, very polar chemically.
2. Alkyl thioether, easily oxidized to sulfone and sulfoxide.
3. Sulfoxides, easily oxidized to sulfone. Also very polar chemically.
4. Phosphite, easily air oxidized to phosphate (Merphos → DEF).
5. Vicinal dibromide, easily debrominated (Naled → 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 $\geq 8$). Loses 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 SOLUTION

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:

a. 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.

b. 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.

c. Solvents with lower boiling points (e.g., methylene chloride, chloroform, methyl-t-butyl ether, and ethyl acetate) had good desorption power nearing equivalent to 90/10 toluene acetone, 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 10. Other Methods of Analysis for Organophosphorous Compounds in Air**

| Document | Method Number | Organophosphorous Compound(s) |
|---|---|---|
| Hill & Arnold (1) | | Chlorpyrifos, Demeton-O, Demeton-S, Diazinon, Dimethoate, Malathion, Paraoxon, and Parathion |
| NMAM, 2nd ed. (2) | v. 1 P&CAM 158 | Parathion |
| | v. 5 P&CAM 295 | Dichlorvos (DDVP) |
| | v. 6 P&CAM 336 | TEPP |
| | v. 3 S 208 | Tributyl phosphate |
| | v. 3 S 209 | Triorthocresyl phosphate |
| | v. 3 S 210 | Triphenyl phosphate |
| | v. 6 S 280 | Demeton |
| | v. 3 S 285 | EPN |
| | v. 3 S 295 | Parathion |
| | v. 6 S 296 | Mevinphos |
| | v. 6 S 299 | Ronnel |
| | v. 3 S 370 | Malathion |
| NMAM, 3rd ed. (3) | 2503 | Mevinphos |
| | 2504 | TEPP |
| | 5012 | EPN, Malathion, and Parathion |
| | 5514 | Demeton |
| OSHA (4) | 62 | Chlorpyrifos, Diazinon, Parathion, DDVP, and Malathion |
| OSHA Stopgap (5) | Each method is separate and unnumbered. Refer to by name. | Azinphos ethyl<br>Azinphos methyl<br>Coumaphos<br>Crufomate<br>Demeton<br>Dicrotophos<br>Dioxathion<br>Disulfoton<br>EPN<br>Ethion<br>Ethoprop<br>Fenamiphos<br>Fensulfothion<br>Fenthion<br>Fonofos<br>Isofenphos<br>Leptophos<br>Methamidophos<br>Methyl dematon<br>Methyl parathion<br>Mevinphos<br>Monocrotophos<br>Oxydemeton methyl<br>Phorate<br>Pirimiphos methyl<br>Sulprofos<br>TEDP (sulfotepp)<br>TEPP<br>Terbufos |

(1) Hill and Arnold [11]
(2) NMAM, 2nd ed. [7]
(3) NMAM, 3rd ed. [8]
(4) OSHA Analytical Methods Manual [12]
(5) OSHA Stopgap Methods [4]

**Table 11. Preparation of Spiked Media and Liquid Calibration Standards**

| | Spiked Concentration | | | | | Solutions |
|---|---|---|---|---|---|---|
| | **A.** | **B.** | **C.** | **D.** | **E.** | **F.** |
| Spiking Levels (Fraction of REL) (1) | 1/30x REL | 1/10x REL | 1/3x REL | 1x REL | 3x REL | |
| **I. Spiking of Media or Liquid** | | | | | | |
| 1. Spiking Solution to use: | SS-2 | SS-2 | SS-1 | SS-1 | SS-1 | Dilute this volume (mL) of 10 mg/mL stock solution to prepare 10 mL <u>of solution SS-1</u> |
| 2. Preferred Syringe Size: | 50 µL | 50 µL | 50 µL | 50 µL | 100 µL | |
| 3. Spiking Volume (2) to use: | 10 µL | 30 µL | 10 µL | 30 µL | 90 µL | |
| II. **Total µg spiked**(3) | | | | | | |
| 1. Azinphos methyl | 0.8 | 2.4 | 8 | 24 | 72 | 0.8 |
| 2. Chlorpyrifos | 0.8 | 2.4 | 8 | 24 | 72 | 0.8 |
| 3. Diazinon | 0.4 | 1.2 | 4 | 12 | 36 | 0.4 |
| 4. Dicrotophos | 1.0 | 3 | 10 | 30 | 90 | 1.0 |
| 5. Disulfoton | 0.4 | 1.2 | 4 | 12 | 36 | 0.4 |
| 6. Ethion | 1.6 | 4.8 | 16 | 48 | 144 | 1.6 |
| 7. Ethoprop | 0.4 | 1.2 | 4 | 12 | 36 | 0.4 |
| 8. Fenamiphos | 0.4 | 1.2 | 4 | 12 | 36 | 0.4 |
| 9. Fonofos | 0.4 | 1.2 | 4 | 12 | 36 | 0.4 |
| 10. Malathion (5) | 4 | 12 | 40 | 120 | 360 | 4.0 |
| 11. Methamidophos | 0.8 | 2.4 | 8 | 24 | 72 | 0.8 |
| 12. Methyl parathion | 0.8 | 2.4 | 8 | 24 | 72 | 0.8 |
| 13. Mevinphos | 0.4 | 1.2 | 4 | 12 | 36 | 0.4 |
| 14. Monocrotophos | 1.0 | 3 | 10 | 30 | 90 | 1.0 |
| 15. Parathion | 0.2 | 0.6 | 2 | 6 | 18 | 0.2 |
| 16. Phorate | 0.2 | 0.6 | 2 | 6 | 18 | 0.2 |
| 17. Ronnel (5) | 4 | 12 | 40 | 120 | 360 | 4.0 |
| 18. Sulprofos | 4 | 12 | 40 | 120 | 360 | 4.0 |
| 19. Terbufos | 0.4 | 1.2 | 4 | 12 | 36 | 0.4 |
| 20. General (for 120L) (4,5) | x/30 | x/10 | x/3 | x | 3x | 4y |

(1) For a collection volume of 120 L. Range corresponds to values within column C, 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 column D to front section of sampler; in duplicate. For Desorption Efficiency determination, apply specified volume to front section of sampler; do each of five levels in triplicate.

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

(4) Where x, µg/sample = REL, µg/L x 120 L/sample; and y, mg/mL = REL, mg/m$^3$ x 4 m$^3$/mL.

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

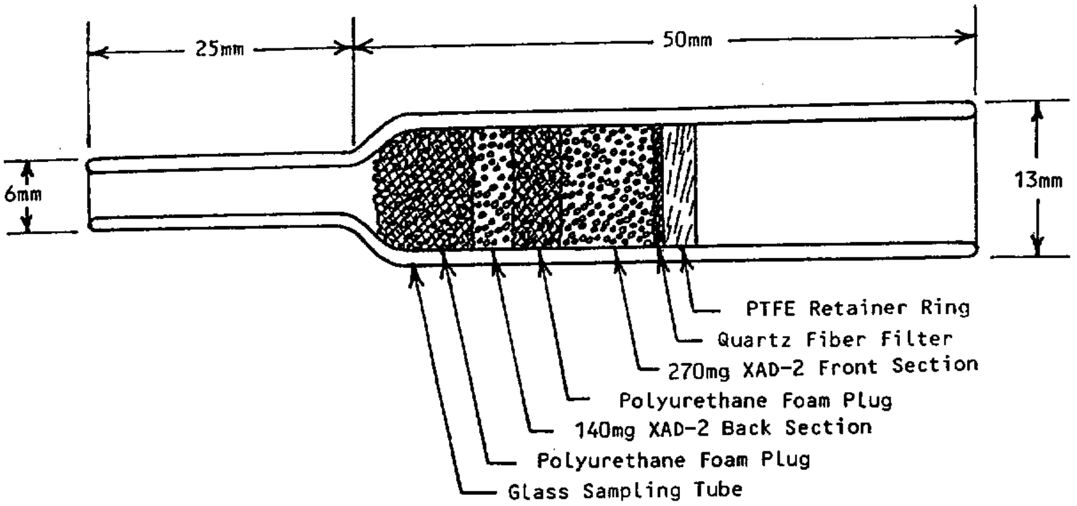

FIGURE 2.  OVS-2 SAMPLER