

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

METHOD: 5600, Issue 1

EVALUATION: FULL

Issue 1: 15 August 1993

OSHA : Table 2  
 NIOSH: Table 2  
 ACGIH: Table 2

PROPERTIES: Table 3

SYNONYMS: Table 4

SAMPLING	MEASUREMENT
<p><b>SAMPLER:</b> FILTER/SOLID SORBENT TUBE (OVS-2 Tube: 13-mm quartz filter; XAD-2, 270 mg/140 mg)</p> <p><b>FLOW RATE:</b> 0.2 to 1 L/min</p> <p><b>VOL-MIN:</b> 12 L  <b>-MAX:</b> 480 L; 60 L, Malathion, Ronnel</p> <p><b>SHIPMENT:</b> Cap both ends of tube.</p> <p><b>SAMPLE STABILITY:</b> At least 30 days of 0 °C                      At least 10 days of 25 °C</p> <p><b>BLANKS:</b> 2 to 10 field blanks per set</p>	<p><b>TECHNIQUE:</b> GC, flame photometric detection (FPD)</p> <p><b>ANALYTE:</b> Organophosphorus pesticides, Table 1</p> <p><b>EXTRACTION:</b> 2-mL 90% toluene/10% acetone solution</p> <p><b>INJECTION VOLUME:</b> 1-2 µL</p> <p><b>TEMPERATURE</b>  <b>-INJECTION:</b> 240 °C  <b>-DETECTOR:</b> 180 °C to 215 °C (follow manufacturer's recommendation)  <b>-COLUMN:</b> Table 6</p> <p><b>CARRIER GAS:</b> Helium at 15 p.s.i. (104 kPa)</p> <p><b>COLUMN:</b> Fused silica capillary column; Table 6</p> <p><b>DETECTOR:</b> FPD (phosphorus mode)</p> <p><b>CALIBRATION:</b> Standard solutions of organophosphorus compounds in toluene</p> <p><b>RANGE:</b> Table 8, Column C</p> <p><b>ESTIMATED LOD:</b> Table 8, Column F</p> <p><b>PRECISION (<math>\bar{S}</math>):</b> Table 5, Column E</p>
ACCURACY	
<p><b>RANGE STUDIED:</b> Table 5, Column A</p> <p><b>ACCURACY:</b> Table 5, Column B</p> <p><b>BIAS:</b> Table 5, Column C</p> <p><b>OVERALL PRECISION (<math>\hat{S}_{rt}</math>):</b> Table 5, Column D</p>	

**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.

**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-but oxy 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 (platicizer and flame-retardant in plastics, laquers, and roofing paper).

**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.

**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. Prepare desorbing solution containing internal standard (Do not keep longer than 30 days at 0-4 °C).
  - a. Prepare triphenyl phosphate stock solution at 5 mg/mL by dissolving approximately 50 mg in 10 mL of toluene.
  - b. Add 50 mL of acetone and 1 mL of triphenyl phosphate stock solution to a 500-mL volumetric flask; dilute to volume with toluene.
5. Prepare spiking and calibration solutions for each organophosphorous analyte or combinations thereof.
  - a. Prepare spiking solution #SS-1 to be used in the preparation of both calibration standards (step 9) and for media fortification (steps 10 and 11). The recommended concentration in mg per mL are given in column F in part I of Table 11. Make these standards up in toluene. If any organophosphorous compound is incompletely soluble in toluene (refer to Note B1 in Table 9), then use toluene containing 10% acetone or 1% methanol.
  - b. Dilute 1 mL of #SS-1 to 10 mL to prepare spiking solution #SS-0.1.

NOTE: More than one analyte may be combined into the spiking solutions.
7. Purified gases.
  - a. Helium
  - b. Hydrogen
  - c. Dry air
  - d. Oxygen ( if required by detector model)
  - e. Nitrogen

\* See Special Precautions

**EQUIPMENT:**

1. Sampler: 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 or equivalent held in place by a 9-10-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. These are 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 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. [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 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 1-1.5 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 11, part I for recommended preparation of spiking solutions.
  - a. Prepare liquid calibration standards.
    - i. Add 2 mL of desorption solution to a 2-mL volumetric flask and using a gentle stream of nitrogen gas at room temperature, blow-down the volume by about 50 to 100 mL.
    - ii. Spike the concentrated desorption solution with the appropriate amount of spiking solution #SS-1 or #SS-0.1 according to the schedule in part II of Table 11.
    - iii. Bring to volume with toluene.

NOTE: If no internal standard is to be used, then simply spike 1 mL of toluene containing 10% acetone within a 2-mL volumetric flask according to the schedule in Part II of Table 11, and bring to volume with toluene containing 10% 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 through 16).
  - d. Prepare calibration graph according to either i. or ii.
    - i. without internal standard: peak area vs. mg analyte.
    - ii. with internal standard (IS): (peak area analyte / peak area IS) vs. mg analyte.
10. Prepare Laboratory Control Samples (LCS) with each sample set, in duplicate.
  - a. Remove cap from large end of sampler tube, apply 30 mL of spiking solution #SS-1 (refer to Table 11, part I) 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, OSHA PEL, or ACGIH TLV in  $\text{mg}/\text{m}^3$ .
  - b. Prepare spiking solution #SS-1 (refer to Table 11, part I; 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  $\text{REL} > 1 \text{ mg}/\text{m}^3$  (assuming 12-L collection vol.), let  $W = \text{REL} \times 4 \text{ m}^3$   
For  $\text{REL} \leq 1 \text{ mg}/\text{m}^3$  (assuming 120-L collection vol.), let  $W = \text{REL} \times 40 \text{ m}^3$   
where  $W =$  weight (mg) of analyte to dissolve into 10 mL of desorbing solvent.  
Let  $[\text{SS-1}] = W/10 \text{ mL}$  where  $[\text{SS-1}] =$  concentration of spiking solution #SS-1 in  $\text{mg}/\text{mL}$ .
  - c. Prepare spiking solution #SS-0.1 by diluting 1 mL of SS-1 to 10 mL in a volumetric flask. Let  $[\text{SS-0.1}] = [\text{SS-1}] \times 0.1$  where  $[\text{SS-0.1}] =$  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 entry 20, part III 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 II of Table 11.
    - ii. Cap and allow sampler to stand overnight.
  - e. Prepare tubes for analysis (Steps 5-8).
  - f. Analyze with liquid standards (Step 9).
  - g. Prepare a graph of desorption efficiency (DE) vs. mg of analyte.
  - h. Acceptable desorption criteria for 6 replicates is  $>75\%$  average recovery with a standard deviation of  $<\pm 9\%$ .

#### 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. Calculate desorption efficiency (DE) for each analyte from step 10 or 11 above:  $\text{DE} = \text{mg detected per sampler} \div \text{mg applied}$ .
15. Determine the mass in mg (corrected for DE) of respective analyte found in the sample front ( $W_f$ ) and back ( $W_s$ ) sorbent sections, and in the media blank front ( $B_f$ ) and back ( $B_b$ ) sorbent sections. Make determination by correlating either analyte peak areas (when IS is not used) or normalized peak areas (area analyte  $\div$  IS area when IS is used) to mg analyte.  
e.g. for constant injection volumes:

$$W_f = \frac{\mu\text{g analyte in front section calculated by standard curve}}{\text{DE}}$$

NOTE: The filters are combined with the front sections. If  $W_s > W_f/10$ , report breakthrough and possible sample loss.

16. Calculate concentration, C of analyte in the air volume sampled, V (L):

#### CONFIRMATION:

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

17. 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.

#### REFERENCES:

- [1] Sweet, D.V., Ed. Registry of Toxic Effects of Chemical Substances, DHHS (NIOSH) Publ. No. 87-114 (1987).
- [2] Merck Index, Eleventh edition, S. Budavari, ed., Merck and Company, Rahway, NJ, 1989.
- [3] Farm Chemicals Handbook, Meister Publishing Co., Willoughby, OH, 1991.
- [4] OSHA Stopgap Methods for individual organophosphorous 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. Health, Education, and Welfare, (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. Health, Education, and Welfare, (NIOSH) Publ. 84-100 (1984)
- [9] Kennedy, E.R., M. T. Abell, J. Reynolds, and D. Wickman. A Sampling and Analytical Method for the Simultaneous Determination of Multiple Organophosphorus Pesticides in Air. Submitted to Am. Ind. Hyg. Assoc. J. (1993).
- [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.

**METHOD WRITTEN BY:** John Reynolds and Donald Wickman, DataChem, Salt Lake City.

**Table 1. Formula and Registry Numbers**

<b>Compound</b> (alphabetically)	<b>MW<sup>(1)</sup></b> (Daltons)	<b>Empirical Formula</b>	<b>Structural Formula &amp; RTECS<sup>(2)</sup></b>
1. Azinphos Methyl	317.32	C <sub>10</sub> H <sub>12</sub> N <sub>3</sub> O <sub>3</sub> PS <sub>2</sub>	(CH <sub>3</sub> O) <sub>2</sub> P(=S)SCH <sub>2</sub> (C <sub>7</sub> H <sub>4</sub> N <sub>3</sub> O) <sub>86-50-0</sub> TE1925000
2. Chlorpyrifos	350.58	C <sub>9</sub> H <sub>11</sub> Cl <sub>3</sub> NO <sub>3</sub> PS	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(=S)O(C <sub>5</sub> HN)Cl <sub>3</sub> <sub>2921-88-2</sub> TF6300000
3. Diazinon TF3325000	304.34	C <sub>12</sub> H <sub>21</sub> N <sub>2</sub> O <sub>3</sub> PS	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(=S)O(C <sub>4</sub> HN <sub>2</sub> )(CH <sub>3</sub> )CH(CH <sub>3</sub> ) <sub>333-41-5</sub>
4. Dicrotophos TC3850000	237.19	C <sub>8</sub> H <sub>16</sub> NO <sub>5</sub> P	(CH <sub>3</sub> O) <sub>2</sub> P(=O)OC(CH <sub>3</sub> )=CHC(=O)N(CH <sub>3</sub> ) <sub>2</sub> <sub>141-66-2</sub>
5. Disulfoton	274.39	C <sub>8</sub> H <sub>19</sub> O <sub>2</sub> PS <sub>3</sub>	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(=S)S(CH <sub>2</sub> ) <sub>2</sub> SC <sub>2</sub> H <sub>5</sub> <sub>298-04-4</sub> TD9275000
6. Ethion	384.46	C <sub>9</sub> H <sub>22</sub> O <sub>4</sub> P <sub>2</sub> S <sub>4</sub>	[(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(=S)] <sub>2</sub> CH <sub>2</sub> <sub>563-12-2</sub> TE4550000
7. Ethoprop	242.33	C <sub>8</sub> H <sub>19</sub> O <sub>2</sub> PS <sub>2</sub>	(C <sub>3</sub> H <sub>7</sub> S) <sub>2</sub> P(=O)OC <sub>2</sub> H <sub>5</sub> <sub>13194-48-4</sub> TE4025000
8. Fenamiphos 22224-92-6 TB3675000	303.36	C <sub>13</sub> H <sub>22</sub> NO <sub>3</sub> PS	(CH <sub>3</sub> ) <sub>2</sub> CHNHP(=O)(O[C <sub>2</sub> H <sub>5</sub> ])O(C <sub>6</sub> H <sub>3</sub> )(CH <sub>3</sub> )SCH <sub>3</sub>
9. Fonofos	246.32	C <sub>10</sub> H <sub>15</sub> OPS <sub>2</sub>	C <sub>2</sub> H <sub>5</sub> OP(C <sub>2</sub> H <sub>5</sub> )(=S)S(C <sub>6</sub> H <sub>5</sub> ) <sub>944-22-9</sub> TA5950000
10. Malathion 121-75-5 WM8400000	330.35	C <sub>10</sub> H <sub>19</sub> O <sub>6</sub> PS <sub>2</sub>	(CH <sub>3</sub> O) <sub>2</sub> P(=S)SCH[C(=O)OC <sub>2</sub> H <sub>5</sub> ]CH <sub>2</sub> C(=O)OC <sub>2</sub> H <sub>5</sub>
11. Methamidophos	141.12	C <sub>2</sub> H <sub>8</sub> O <sub>2</sub> PS	CH <sub>3</sub> OP(=O)(NH <sub>2</sub> )SCH <sub>3</sub> <sub>10265-92-6</sub> TB4970000
12. Methyl Parathion	263.20	C <sub>8</sub> H <sub>10</sub> NO <sub>5</sub> PS	(CH <sub>3</sub> O) <sub>2</sub> P(=S)O(C <sub>6</sub> H <sub>4</sub> )NO <sub>2</sub> <sub>298-00-0</sub> TG0175000
13. Mevinphos GQ5250000	224.15	C <sub>7</sub> H <sub>13</sub> O <sub>6</sub> P	(CH <sub>3</sub> O) <sub>2</sub> P(=O)OC(CH <sub>3</sub> )=CHC(=O)OCH <sub>3</sub> <sub>298-01-1</sub> <sup>(2)</sup>
14. Monocrotophos TC4375000	223.17	C <sub>7</sub> H <sub>14</sub> NO <sub>5</sub> P	<sub>7786-34-7</sub> <sup>(3,4)</sup> (CH <sub>3</sub> O) <sub>2</sub> P(=O)OC(CH <sub>3</sub> )=CHC(=O)NHCH <sub>3</sub> <sub>919-44-8</sub> <sup>(2)</sup>
15. Parathion	291.26	C <sub>10</sub> H <sub>14</sub> NO <sub>5</sub> PS	<sub>6923-22-4</sub> <sup>(3,4)</sup> (C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(=S)O(C <sub>6</sub> H <sub>4</sub> )NO <sub>2</sub> <sub>56-38-2</sub> TF4550000
16. Phorate	260.36	C <sub>7</sub> H <sub>17</sub> O <sub>2</sub> PS <sub>3</sub>	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(=S)SCH <sub>2</sub> SC <sub>2</sub> H <sub>5</sub> <sub>298-02-2</sub> TD9450000
17. Ronnel	321.54	C <sub>8</sub> H <sub>8</sub> Cl <sub>3</sub> O <sub>3</sub> PS	(CH <sub>3</sub> O) <sub>2</sub> P(=S)O(C <sub>6</sub> H <sub>2</sub> )Cl <sub>3</sub> <sub>299-84-3</sub> TG0525000
18. Sulprofos TE4165000	322.43	C <sub>12</sub> H <sub>19</sub> O <sub>2</sub> PS <sub>3</sub>	C <sub>2</sub> H <sub>5</sub> OP(S[C <sub>3</sub> H <sub>7</sub> ])(=S)O(C <sub>6</sub> H <sub>4</sub> )SCH <sub>3</sub> <sub>35400-43-2</sub>
19. Terbufos	288.42	C <sub>9</sub> H <sub>21</sub> O <sub>2</sub> PS <sub>3</sub>	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(=S)SCH <sub>2</sub> SC(CH <sub>3</sub> ) <sub>3</sub> <sub>13071-79-9</sub> 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 Special (alphabetically) Notation <sup>(5,6)</sup>	LD <sub>50</sub> , mg/Kg <sup>(1)</sup>	Time Weighted Averages <sup>(4, 5, 6)</sup>		
		OSHA PEL <sup>(4)</sup> mg/m <sup>3</sup>	NIOSH REL mg/m <sup>3</sup> (ppm)	ACGIH TSVEL mg/m <sup>3</sup> (ppm)
1. Azinphos Methyl	11 f	0.2	0.2 (0.015)	0.2SKIN
2. Chlorpyrifos (0.083) <sup>(6)</sup>	145 SKIN	0.2	0.2 (0.014)	0.2 0.6
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)	0.25SKIN
5. Disulfoton	2.3 f, 6.8 m	0.1	0.1 (0.009)	SKIN
6. Ethion	27 f, 65 m	0.4	0.4 (0.025)	0.4SKIN
7. Ethoprop	61.5 <sup>(2)</sup>	—	—	—
8. Fenamiphos	10	0.1	0.1 (0.008)	0.1SKIN
9. Fonofos	3 f, 13 m <sup>(3)</sup>	0.1	0.1 (0.010)	0.1SKIN
10. Malathion	1000 f, 1375 m	10	10 (0.740)	10—
11. Methamidophos	25 m, 27 f	—	—	—
12. Methyl Parathion	14 m, 24 f	0.2	0.2 (0.019)	0.2SKIN
13. Mevinphos (0.033) <sup>(7,8)</sup>	3.7 f, 6.1 m SKIN	0.1	0.1 (0.011)	0.0.3
14. Monocrotophos	17 m, 20 f	0.25	0.25 (0.027)	—
15. Parathion	3.6 f, 13 m	0.1	0.05 (0.004)	0.1 SKIN
16. Phorate (0.019) <sup>(7,8)</sup>	1.1 f, 2.3 m SKIN	0.05	0.05 (0.005)	0.050.2
17. Ronnel	1250 m, 2630 f	10	10 (0.760)	10—
18. Sulprofos	227	1	1 (0.076)	—
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) NIOSH Registry of Toxic Effects of Chemical Substances. [1]

(4) OSHA Final Rule, 1989 (unenforceable, 1992).

(7) NIOSH

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

(8) OSHA



**Table 3. Physical Properties<sup>(1)</sup>**

<b>Compound Solubility in Water</b> (alphabetically) (mg/L at 20 °C)	<b>Liquid Density</b> (g/mL)	<b>m.p.</b> (°C)	<b>b.p.</b> (°C at 1 atm)	<b>Vapor Pressure</b> (Pascal)	<b>Vapor Pressure</b> [mm. Hg; mg/m <sup>3</sup> ] @C)	
1. Azinphos Methyl 20 <sup>(3)</sup>	1.44	73-74 30 ppm <sup>(8)</sup>	unstable >200	0.00018	[1.35x10 <sup>-6</sup> ;	@
2. Chlorpyrifos 25	none found	41-42 —	—	0.0025	[1.87x10 <sup>-5</sup> ;	@
3. Diazinon 20	1.116-1.118	liquid 40 ppm	decomp. >120	0.019	[1.4x10 <sup>-4</sup> ; 2.4]	@
4. Dicrotophos miscible	1.216	liquid	400		none found	
5. Disulfoton 20	1.144	oil nearly insol.	—	0.024	[1.8x10 <sup>-4</sup> ;	@
20 <sup>(3)</sup>		insol. <sup>(3)</sup>		0.0074	[5.4x10 <sup>-5</sup> ;	@
6. Ethion slightly sol.	1.220	-12 to -13	—	0.0002	[1.5x10 <sup>-6</sup> ;	@
7. Ethoprop 26	1.094	oil 750 ppm	—	0.047	[3.5x10 <sup>-4</sup> ;	@
8. Fenamiphos 20 <sup>(3)</sup>	none found	49 329 ppm	—	0.00012	[9x10 <sup>-7</sup> ;	@
9. Fonofos ppm <sup>(7)</sup>	1.16	liquid	—		none found	13
10. Malathion 30	1.23 145 ppm	2.9	156 <sup>(6)</sup>	0.005	[4x10 <sup>-5</sup> ; 0.7 <sup>(6)</sup> ]	@
11. Methamidophos 30	1.31 readily sol.	54.	—	0.04	[3x10 <sup>-4</sup> ;	@
20 <sup>(3)</sup>	—			0.0023	[1.7x10 <sup>-5</sup> ;	@
12. Methyl Parathion 20 <sup>(3)</sup>	1.358 50 ppm	37-38	—	0.0002	[1.5x10 <sup>-6</sup> ;	@
13. Mevinphos 20 <sup>(4)</sup>	1.25 miscible	20.6 <sup>(4)</sup>	325 <sup>(4)</sup>	0.4	[3x10 <sup>-3</sup> ; 4 ppm]	@
20 <sup>(7)</sup>	—			0.29	[2.2x10 <sup>-3</sup> ;	@
14. Monocrotophos 20	none found miscible	54-55 <sup>(5)</sup>	—	0.0009	[7x10 <sup>-6</sup> ;	@
15. Parathion 20	1.26 20 ppm	6	375	0.005	[3.78x10 <sup>-5</sup> ; 6 <sup>(6)</sup> ]	@
				0.00089	[6.7x10 <sup>-6</sup> ;	@

20 <sup>(3)</sup>	10 ppm <sup>(8)</sup>					
16. Phorate	1.156	liquid	118-120 <sup>(3)</sup>	0.11	[8.4x10 <sup>-4</sup> ;]	@
20	50 ppm					
17. Ronnel	sp. gr=1.48 <sup>(2)</sup>	41	—	0.1	[8.x10 <sup>-4</sup> ;]	@
25	40 ppm @ 25 °C					
18. Sulprofos	1.20	liquid	210 <sup>(3)</sup>	<0.0001	[<10 <sup>-6</sup> ;]	@
20 <sup>(3)</sup>	nearly insol. <sup>(3)</sup>					
19. Terbufos	1.105	-29.2	—		none found	
10-15 ppm						

(1) From Merck Index, unless otherwise noted [2].  
°C for commercial mixture.

(2) NIOSH 2nd Edition Method for Ronnel, S299 [7].  
(EPN, Malathion, Parathion) [8].

(3) Farm Chemicals Handbook [3].  
specific analyte Method.) [4]

(4) NIOSH 3rd Edition Method 2503 for Mevinphos [8].

(5) 54-55 °C for pure material, 25-30

(6) NIOSH 3rd Edition Method 5012

(7) OSHA Stopgap Methods. (See

(8) NIOSH Pocket Guide [6].

**Table 4. Synonyms**

<b>Compound<sup>(1)</sup></b> (alphabetically)	<b>Other name<sup>(2)</sup></b>	<b>CAS Name<sup>(3)</sup></b>
1. Azinphos Methyl S-[(4-oxo-1,2,3-benzotriazin-3(4H)-yl)methyl] ester	Guthion*	Phosphorodithioic acid, 0,0-dimethyl
2. Chlorpyrifos 0-(3,5,6-trichloro-2-pyridinyl) ester	Dursban*	Phosphorothioic acid, 0,0-diethyl
3. Diazinon 0-[6-methyl-2-(1-methylethyl)-4-pyrimidinyl] ester	Spectracide*	Phosphorothioic acid, 0,0-diethyl
4. Dicrotophos 3-(dimethylamino)-1-methyl-3-oxo-1-propenyl dimethyl ester, cis-3-hydroxy-N,N-dimethyl crotonamide <sup>(4)</sup>	Bidrin*	Phosphoric acid, Phosphoric acid, dimethyl ester, ester with
5. Disulfoton S-[2-(ethylthio)ethyl] ester	Di-Syston*	Phosphorodithioic acid, 0,0-diethyl
6. Ethion 0,0,0,0'-tetraethyl ester		Phosphorodithioic acid, S,S'-methylene 0,0,0'-0'-Tetra ethyl S,S'-methylene
7. Ethoprop 3-methyl-4-(methylthio) phenyl ester	Prophos*	Phosphorodithioic acid, 0-ethyl S,S-dipropyl ester
8. Fenamiphos 4-(methylthio)-m-tolyl ethyl ester <sup>(4)</sup>	Nemacur*, Phenamiphos <sup>(1)</sup>	(1-Methylethyl) phosphoramidic acid, ethyl Phosphoramidic acid, isopropyl-,
9. Fonofos ester	Dyfonate*	Ethyl phosphonodithioic acid, O-ethyl, S-phenyl Phosphonodithioic acid, ethyl-, 0-ethyl, S-phenyl
10. Malathion diethyl ester	Cythion*	[(Dimethoxyphosphinothioyl)thio] butanedioic acid Succinic acid, mercapto-, diethyl ester S-ester with
11. Methamidophos 12. Methyl Parathion ester	Monitor* Parathion Methyl <sup>(1)</sup>	Phosphoramidothioic acid, 0,S-dimethyl ester Phosphorothioic acid, 0,0-dimethyl 0-[4-nitrophenyl]
13. Mevinphos methyl ester	Phosdrin*	3-[(Dimethoxyphosphinyl)oxy]-2-butenic acid Crotonic acid, 3-hydroxy-, methyl ester dimethyl
14. Monocrotophos [1-methyl-3-(methylamino)-3-oxo-1-propenyl] ester	Azodrin*	Phosphoric acid, dimethyl

(E)-3-hydroxy-N-methylcrotonamide <sup>(4)</sup>		Phosphoric acid, dimethyl ester ester with
15. Parathion ester	Ethyl Parathion <sup>(1)</sup>	Phosphorothioic acid, 0,0-diethyl 0-(4-nitrophenyl)
16. Phorate methyl] ester	Thimet*	Phosphorodithioic acid, 0,0-diethyl S-[(ethylthio)
17 Ronnel 0-(2,4,5-trichlorophenyl) ester	Fenclorphos <sup>(1)</sup>	Phosphorothioic acid, 0,0-dimethyl
18. Sulprofos phenyl] S-propyl ester <sup>(4)</sup>	Bolstar*	Phosphorodithioic acid, 0-ethyl 0-[4-(methylthio)
19. Terbufos S-[[[(1,1-dimethylethyl) thio] methyl] ester <sup>(4)</sup>	Counter*	Phosphorodithioic acid, 0,0-diethyl

- (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<sup>(1)</sup>**

Compound (alphabetically) days	A.		B. Accuracy	CDEG.	
	Range Studied <sup>(2)</sup>			Bias	Precision
	mg/m <sup>3</sup>	mg/sample		Ave.	Range, %
25 °C (0 °C)					
1. Azinphos Methyl 0.070	0.02-0.4 0.030	0.0048-0.096 97 (105)	± 0.178	-0.038	(-0.120 - +0.028)
2. Chlorpyrifos 0.068	0.02-0.4 0.018	0.0048-0.096 92 (90)	± 0.163	-0.027	(-0.054 - +0.017)
3. Diazinon 0.065	0.01-0.2 0.020	0.0024-0.048 94 (93)	± 0.162	-0.032	(-0.057 - -0.005)
4. Dicrotophos 0.066	0.025-0.5 0.025	0.006-0.120 89 (92)	± 0.169	-0.037	(-0.102 - -0.032)
5. Disulfoton 0.066	0.01-0.2 0.024	0.0024-0.048 87 (89)	± 0.196	-0.064	(-0.081 - -0.032)
6. Ethion 0.068	0.04-0.8 0.018	0.0096-0.192 96 (95)	± 0.165	-0.029	(-0.056 - -0.003)
7. Ethoprop <sup>(3)</sup> 0.066	0.01-0.2 0.024	0.0024-0.048 97 (93)	± 0.157	-0.025	(-0.058 - +0.025)
8. Fenamiphos 0.063	0.01-0.2 0.022	0.0024-0.048 94 (96)	± 0.155	-0.029	(-0.066 - +0.002)
9. Fonofos 0.066	0.01-0.2 0.023	0.024-0.048 95 (92)	± 0.168	-0.036	(-0.076 - +0.008)
10. Malathion <sup>(4)</sup> 0.067	0.025-0.5 0.019	0.006-0.120 93 (93)	± 0.172	-0.038	(-0.064 - -0.014)
11. Methamidophos <sup>(5)</sup> 0.069	0.02-0.4 0.026	0.0048-0.096 88 (95)	± 0.156	-0.018	(-0.046 - +0.011)
12. Methyl Parathion 0.063	0.02-0.4 0.018	0.0048-0.096 95 (95)	± 0.160	-0.034	(-0.082 - +0.016)
13. Mevinphos 0.067	0.01-0.2 0.028	0.0024-0.048 89 (91)	± 0.176	-0.042	(-0.061 - -0.004)
14. Monocrotophos 0.071	0.025-0.5 0.026	0.006-0.120 88 (92)	± 0.185	-0.043	(-0.047 - -0.020)
15. Parathion 0.071	0.005-0.1 0.019	0.0012-0.024 92 (92)	± 0.163	-0.021	(-0.045 - +0.011)
16. Phorate 0.066	0.005-0.1 0.025	0.0012-0.024 91 (91)	± 0.202	-0.070	(-0.047 - -0.097)
17. Ronnel <sup>(4)</sup> 0.066	0.025-0.5 0.018	0.006-0.120 95 (94)	± 0.172	-0.040	(-0.076 - +0.021)
18. Sulprofos <sup>(4)</sup>	0.01-0.2	0.0024-0.048	± 0.181	-0.047	(-0.054 - -0.031)

0.067	0.017	94 (94)		
19. Terbufos <sup>(3)</sup>	0.01-0.2	0.0024-0.048	± 0.188	-0.054 (-0.091 - -0.024)
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/m<sup>3</sup>.
- (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<sup>3</sup>.

**Table 6. Recommended Gas Chromatographic Columns and Conditions<sup>(4)</sup>**

Parameter	Conditions for Retention Times, Table 7. Wide Bore Fused Silica Capillary Column			
	DB-1	DB-5	DB-1701	DB-210
Stationary Phase <sup>(2)</sup>	DB-1	DB-5	DB-1701	DB-210
Length (meters)	30	30	30	30
I.D. (millimeters)	0.32	0.32	0.32	0.32
Film thickness (mm) <sup>(3)</sup>	0.25	1.0	1.0	0.25
Injection (vol., mode) <sup>(4)(5)</sup>	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) <sup>(6)</sup>	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.
- (2) 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.
- (3) Film thickness: Thinner films give faster separations at lower temperatures promoting analyte stability.
- (4) Injection (mode): SPL = splitless mode, initial oven temp. 5-10 °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 1-2 mL injections with 4 mm i.d. injection port liners, and 20-30 seconds for 0.5 mL injections with 2 mm i.d. injection port liners.
- (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 1-2 mL injections with 0.32 mm i.d. capillary columns.
- (6) J & W Scientific Catalog of High Resolution Chromatography Products, p. 21. [10]

**Table 7. Approximate Retention Times of Selected Organophosphorous Compounds<sup>(1)</sup>**

Compound (by RT on DB-1)	Capillary Column <sup>(2)</sup>					
	DB-1			DB-5	DB-1701	DB-210
	RT (min.)	RRT <sup>(3)</sup>	Elution Temp. <sup>(4)</sup>	RRT (min.)	RT (min.)	RT (min.)
1. TEPP	3.71	0.091	111	5.47	7.18 <sup>(B)</sup>	7.88
2. Triethylphosphorothioate	4.37	0.107	113	6.34	7.14 <sup>(B)</sup>	4.93
3. Methamidophos	5.12	0.125	115	7.64	13.61	12.03
4. Dichlorvos	5.81	0.142	117	8.24	10.67	10.54
5. Mevinphos	10.45	0.256	131	12.92	16.69	19.20
6. Ethoprop	17.15	0.420	151	19.09	21.52	20.10
7. Naled	17.61	0.431	153	(6)	23.17 <sup>(C)</sup>	21.46 <sup>(H)</sup>
8. Dicrotophos	18.00	0.440	154	19.94	25.84 <sup>(E)</sup>	31.43
9. Monocrotophos	18.27	0.447	155	20.12	28.11	31.60
10. Sulfotepp	19.06	0.466	157	(6)	23.09 <sup>(C)</sup>	21.11
11. Phorate	19.18	0.469	158	20.94	23.10 <sup>(C)</sup>	18.92
12. Dimethoate	19.44	0.476	158	21.84	(6)	29.33 <sup>(I)</sup>
13. Demeton-S	20.15	0.493	160	21.70	25.06 <sup>(D)</sup>	24.97
14. Dioxathion	21.30	0.521	164	23.04	26.33 <sup>(F)</sup>	23.46
15. Fonofos	22.04	0.539	166	23.57	25.87 <sup>(E)</sup>	22.20
16. Terbufos	22.22	0.544	168	23.80	25.02 <sup>(D)</sup>	21.52 <sup>(H)</sup>
17. Disulfoton	23.09	0.565	169	24.19	26.43 <sup>(F)</sup>	22.78
18. Diazinon	23.37	0.572	170	23.75	25.00 <sup>(D)</sup>	20.99
19. Methyl Parathion	25.37	0.621	176	26.48	31.37	33.21
20. Oxydemeton Methyl	26. <sup>(5)</sup>	0.63 <sup>(5)</sup>	179	(6)	(6)	(6)
21. Ronnel	26.86	0.657	181	27.39	29.30	26.27
22. Pirimiphos Methyl	28.13	0.688	184	27.90	29.72	26.77
23. Malathion	28.53	0.698	186	28.33	31.78 <sup>(G)</sup>	33.08 <sup>(J)</sup>
24. Fenthion	28.74	0.703	186	28.93	31.78 <sup>(G)</sup>	29.35 <sup>(I)</sup>
25. Parathion	28.98	0.709	187	29.10 <sup>(A)</sup>	33.28	35.60
26. Chlorpyrifos	29.11	0.712	187	29.10 <sup>(A)</sup>	30.79	27.72
27. Cruformate	29.64	0.725	189	29.54	34.00	35.34
28. Isofenphos	31.91	0.780	196	31.17	33.81	33.02 <sup>(J)</sup>
29. Tetrachlorvinphos	33.26	0.814	200	32.60	35.96	37.01
30. Fenamiphos	34.09	0.834	202	33.03	37.14	38.95
31. Merphos	35.19	0.861	206	(6)	30.57	23.89
32. Fensulfothion	36.61	0.896	210	35.78	42.41	46.98
33. Ethion	37.88	0.927	214	36.30	39.30	37.96
34. Sulprofos	38.49	0.942	216	36.96	39.54	37.11
35. Triphenyl Phosphate	40.88	1.000	223	39.06	(6)	(6)
36. EPN	42.64	1.043	228	41.06	47.83	47.13
37. Azinphos Methyl	44.16	1.080	232	43.67	(7)	49.24
38. Leptophos	45.12	1.104	235	43.91	47.38	41.68
39. Azinphos Ethyl	46.55	1.139	240	46.50	47.43	50.40
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 9 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 and Estimated LOD**

Compound Sensitivity <sup>(2)</sup> (alphabetically) REL/LOD	Applicable Working Range <sup>(1)</sup>		Sample <sup>(4)</sup> µg/sample	Margin of	
	Atmospheric			Instrument <sup>(6)</sup>	Instrument <sup>(6)</sup>
	mg/m <sup>3</sup> A.	ppm <sup>(3)</sup> B.		ng/mL D.	ng/mL E.G.H.
1. Azinphos Methyl 0.2	0.02-0.6 0.002	0.0015-0.046 100	2.4 to 72	1.2-36	0.06
2. Chlorpyrifos 0.04	0.02-0.6 0.0004	0.0014-0.042 500	2.4 to 72	1.2-36	0.02
3. Diazinon 0.04	0.01-0.3 0.0004	0.0008-0.024 250	1.2 to 36	0.6-18	0.02
4. Dicrotophos 0.2	0.025-0.75 0.002	0.0026-0.077 125	3.0 to 90	1.5-45	0.1
5. Disulfoton 0.04	0.01-0.3 0.0004	0.0009-0.027 125	1.2 to 36	0.6-18	0.02
6. Ethion 0.04	0.04-1.2 0.0004	0.0025-0.076 1000	4.8 to 144	2.4-72	0.02
7. Ethoprop 0.04	0.01-0.3 0.0004	0.0010-0.030 125	1.2 to 36	0.6-18	0.02
8. Fenamiphos 0.2	0.01-0.3 0.002	0.0008-0.024 50	1.2 to 36	0.6-18	0.07
9. Fonofos 0.04	0.01-0.3 0.0004	0.0010-0.030 125	1.2 to 36	0.6-18	0.02
10. Malathion 0.1 0.001	1.0-30 10,000	0.074-2.2	12. to 360 <sup>(5)</sup>	6.-180	0.05
11. Methamidophos 0.6 0.005	0.02-0.6 40	0.0035-0.10	2.4 to 72	1.2-36	0.3
12. Methyl Parathion 0.04	0.02-0.6 0.0004	0.0019-0.056 500	2.4 to 72	1.2-36	0.02
13. Mevinphos 0.2 0.002	0.01-0.3 50	0.0011-0.033	1.2 to 36	0.6-18	0.06
14. Monocrotophos 0.4 0.004	0.025-0.75 63	0.0027-0.082	3.0 to 90	1.5-45	0.2
15. Parathion 0.04	0.005-0.15 0.0004	0.0004-0.013 125	0.6 to 18	0.3-9	0.02
16. Phorate 0.04	0.005-0.015 0.0004	0.0005-0.014 125	0.6 to 18	0.3-9	0.02
17. Ronnel 0.04	1.0-30 0.0004	0.076-2.3 25,000	12. to 360 <sup>(5)</sup>	6.-180	0.02
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	250			

- (1) To cover range of 1/10 to 3x NIOSH REL.
- (2)  $\text{REL in mg/m}^3 \text{ (Table 2)} \div \text{Atmospheric LOD (Column G, Table 8)}$ .
- (3) Calculated for 25 °C and 760 mm Hg (NTP).
- (4) Calculated for a collection volume of 120 L (2 hrs @ 1 L/min., 4 hrs @ 0.5 L/min., or 10 hrs @ 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 hour @ 0.2 L/min.).
- (6) Desorbing sample in 2.0 mL solvent and injecting 1 mL into gas chromatograph.

**Table 9. Notes on Analytical Characteristics of Organophosphorous Compounds<sup>(1)</sup>**

Compound (Alphabetically)	Analytical Characteristics <sup>(2)</sup>		
	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]

(2) Refer to notes on the following pages.

## Notes on ANALYTICAL CHARACTERISTICS, Table 9

### 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  $\neq$  DEF).
  5. Vicinal dibromide, easily debrominated (Naled  $\neq$  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 CHROMATOGRAPHIC

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)		
AEC & T <sup>(1)</sup>		Chlorpyrifos, Demeton-O, Demeton-S, Diazinon, Dimethoate, Malathion, Paraoxon, and Parathion		
NMAM, 2nd ed. <sup>(2)</sup>	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. <sup>(3)</sup>	2503	Mevinphos		
	2504	TEPP		
	5012	EPN, Malathion, and Parathion		
	5514	Demeton		
OSHA A.M.M. <sup>(4)</sup>	62	Chlorpyrifos, Diazinon, Parathion, DDVP, and Malathion		
OSHA Stopgap Methods <sup>(5)</sup>	Each method is separate and unnumbered. Refer to by name.	Azinphos ethyl	Ethoprop	Mevinphos
		Azinphos methyl	Fenamiphos	Monocrotophos
		Coumaphos	Fensulfothion	Oxydemeton methyl
		Crufomate	Fenthion	Phorate
		Demeton	Fonofos	Pirimiphos Methyl
		Dicrotophos	Isofenphos	Sulprofos
		Dioxathion	Leptophos	TEDP (sulfotepp)
		Disulfoton	Methamidophos	TEPP
		EPN	Methyl Dematon	Terbufos
		Ethion	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, 3rd ed. [8]

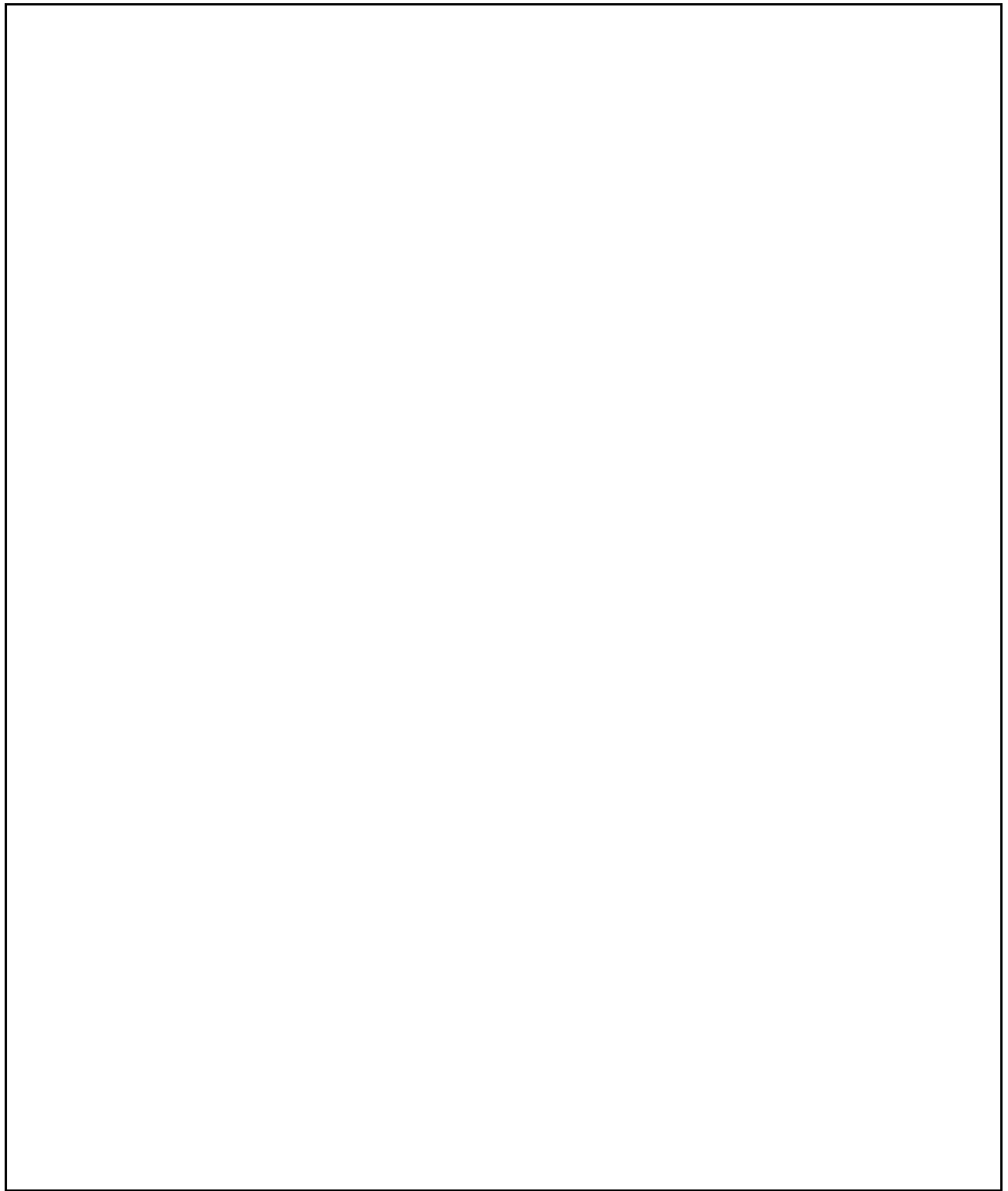
(4) OSHA Analytical Methods Manual [12]

(5) OSHA Stopgap Methods (unpublished interim methods, refer to by name) [4]

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

Spiking Levels (Fraction of REL) <sup>(1)</sup>	Liquid Calibration Standards, Laboratory Control Samples, Desorption Efficiency Samples					I. Preparation of Spiking Solutions	
	1/30x	1/10x	1/3x	1x	3x	mg analyte to add per mL of toluene/acetone (9:1)	
	A.	B.	C.	D.	E.		
<b>II. Spiking of Media or Liquid</b>							
1. Spiking Solution to use:	SS-0.1	SS-0.1	SS-1	SS-1	SS-1		
2. Preferred Syringe Size:	50 µL	50 µL	50 µL	50 µL	100 µL	SS-1	SS-0.1
3. Spiking Volume <sup>(2)</sup> to use:	10 µL	30 µL	10 µL	30 µL	90 µL	F.	G.
<b>III. Total mg spiked<sup>(3)</sup></b>							
1. Azinphos Methyl	0.8	2.4	8	24	72	0.8	0.08
2. Chlorpyrifos	0.8	2.4	8	24	72	0.8	0.08
3. Diazinon	0.4	1.2	4	12	36	0.4	0.04
4. Dicrotophos	1.0	3	10	30	90	1.0	0.1
5. Disulfoton	0.4	1.2	4	12	36	0.4	0.04
6. Ethion	1.6	4.8	16	48	144	1.6	0.16
7. Ethoprop	0.4	1.2	4	12	36	0.4	0.04
8. Fenamiphos	0.4	1.2	4	12	36	0.4	0.04
9. Fonofos	0.4	1.2	4	12	36	0.4	0.04
10. Malathion <sup>(5)</sup>	4	12	40	120	360	4.0	0.4
11. Methamidophos	0.8	2.4	8	24	72	0.8	0.08
12. Methyl Parathion	0.8	2.4	8	24	72	0.8	0.08
13. Mevinphos	0.4	1.2	4	12	36	0.4	0.04
14. Monocrotophos	1.0	3	10	30	90	1.0	0.1
15. Parathion	0.2	0.6	2	6	18	0.2	0.02
16. Phorate	0.2	0.6	2	6	18	0.2	0.02
17. Ronnel <sup>(5)</sup>	4	12	40	120	360	4.0	0.4
18. Sulprofos	4	12	40	120	360	4.0	0.4
19. Terbufos	0.4	1.2	4	12	36	0.4	0.04
20. General (for 120L) <sup>(4,5)</sup>	x/30	x/10	x/3	x	3x	4y	4y/10

- (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; do in duplicate. For Desorption Efficiency determination, apply specified volume to front section of sampler; do each of five levels in triplicate.
- (3) Total mg per sample, for spiked media, or per 2 mL desorption solution for liquid calibration standards.
- (4) Where x, mg/sample = REL, mg/L x 120 L/sample; and y, mg/mL = REL, mg/m<sup>3</sup> x 4 m<sup>3</sup>/mL.
- (5) For all REL > 1 mg/m<sup>3</sup>, use 1/10 x REL in the calculations (assumes that collection volume in these cases would be 12 L instead of 120 L).



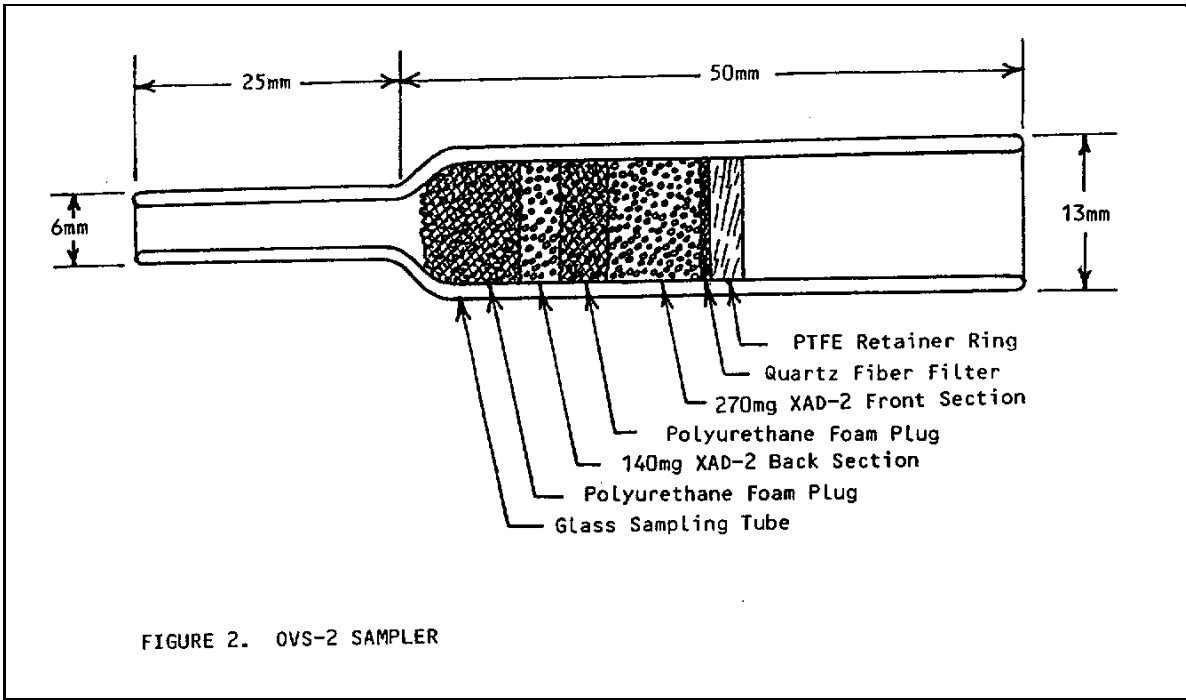


FIGURE 2. OVS-2 SAMPLER



