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EVALUATION OF A GAS CHROMATOGRAPHIC METHOD FOR CALCULATING VAPOR PRESSURES WITH ORGANOPHOSPHORUS PESTICIDES

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SUMMARY

The vapor pressures of 20 organophosphorus pesticides varying widely in structure, polarity and volatility were calculated using a method based upon gas chromatographic (GC) retention data. For seven of the pesticides, vapor pressures were determined experimentally by a standard gas saturation method for comparison with the GC-calculated values. Several experimental variables, including the number of GC temperatures and spread between them, nature of the liquid phase in either packed or capillary columns, and nature of the reference compound, were studied for their influence on the GC method's error. The GC calculation, using a short SE-30 capillary column, single reference compound (methyl parathion), and melting point correction for those test compounds which are solids at room temperature, provided vapor pressures agreeing with an average factor of approximately 4 with experimental vapor pressures. The agreement improved when the comparison was with test compounds which are liquids at room temperature and when the polarity of the GC reference compound approximated that of the test compounds.

INTRODUCTION

Among the physico-chemical properties which determine the transport, persistence, and fate of chemicals in the environment, vapor pressure is one of the most important. Vapor pressure governs the distribution between solid phases (residues on soil and crop surfaces) and the atmosphere and, along with water solubility, the distribution between aqueous solutions and the atmosphere¹. However, while vapor pressure is required for most environmental fate predictive models, the literature may provide no tabulation for a specific chemical of interest, a single value whose accuracy is unknown, or several values which disagree by an order of magnitude or more. This is particularly true of chemicals of low vapor pressures ($< ca. 10^{-2}$ mmHg), which include many pesticides and other classes of environmental contaminants. In part, the poor literature data base is due to the difficulty in directly measuring vapor pressures by isoteniscope², Knudsen effusion^{3,4} or gas saturation techniques⁵. The latter can provide accurate experimental values for vapor pressures of low volatility chemicals providing they are relatively stable and detectable at the low concentrations

encountered in the saturated gas⁶. However, compilations of vapor pressures for many compounds under the same gas saturation experimental conditions are not yet available.

The potential use of gas chromatographic (GC) retention data for calculating vapor pressures of unknowns based upon the retention of a reference compound whose vapor pressure is known has been recognized by several authors⁷⁻⁹. This approach offers advantages over the gas saturation technique in terms of speed, solute sample size, purity, and stability requirements; additionally, the wide availability of GC instruments is a distinct advantage for laboratories lacking the time or budget to meet the requirements of the more rigorous gas saturation technique. Jensen and Schall⁷ applied the GC retention approach to calculate ambient vapor pressures of phenoxy acid ester herbicides. Hamilton⁸ improved the applicability by introducing a latent heat ratio term for unknown and reference compound. Westcott and Bidleman⁹ applied the technique to a few organochlorine compounds (polychlorinated biphenyl isomers and chlorinated pesticides). All of these authors stayed within closely related chemical classes and employed a single "universal" reference (dibutyl phthalate).

We have attempted to extend this technique to a more heterogeneous class of chemicals (organophosphorus insecticides of varying polarities), investigating some variables (column type and temperature; nature of reference compound) in the process. Gas saturation values of vapor pressure of seven organophosphorus pesticides were determined experimentally for comparison with GC-calculated vapor pressure. GC-calculated vapor pressures of thirteen additional pesticides whose gas saturation values were not determined in this study were compared with literature values of vapor pressure, to confirm the applicability of the GC method and further assess the method's error.

EXPERIMENTAL

Chemicals and chromatographic phases

Analytical standards were obtained from the EPA (Research Triangle Park, NC, U.S.A.) and used without further purification. Purity of the chemicals was as follows: dichlorvos (100%), phorate (98%), diazinon (99.4%), dimethoate (98.8%), methyl parathion (99.9%), parathion (99%) and malathion (98.5%). Chemicals for gas saturation were provided by the EPA Pesticide Reference Standards Lab. (Beltsville, MD, U.S.A.) and were used as received. Purity of the chemicals was as follows: dichlorvos (98%), phorate (98.6%), diazinon (87.2%), dimethoate (98.8%), methyl parathion (99.9%), parathion (99%) and malathion (99.5%). Chemical standards for gas chromatographic retention time were phosphamidon (Chevron Chemical, Richmond, CA, U.S.A.), monocrotophos (Shell Chemical, Houston, TX, U.S.A.), fenitron (Mobay Chemical, Kansas City, MO, U.S.A.), disulfoton (Mobay), chlorpyrifos (Dow Chemical, Midland, MI, U.S.A.), ronnel (Dow), carbophenothion (Stauffer Chemical, Westport, CT, U.S.A.), demeton-O (mobay), tetrachlorvinphos (Shell), thionazin (American Cyanamid, Princeton, NJ, U.S.A.), trichlorfon (Mobay), mevinphos (Shell), and azinphos-methyl (Mobay) with purities above 95%.

Stationary phases for packed columns were squalane (Eastman Organic Chemicals, Rochester, NY, U.S.A.), Apiezon L (Varian Aerograph, Walnut Creek, CA,

U.S.A.) and SE-30 (Varian Aerograph). They were coated on Chromosorb G AW-DMCS (80/100 mesh, Johns-Manville, Denver, CO, U.S.A.) at 10% loading. A Pyrex glass column 15 cm \times 2 mm I.D. was silanized with 10% DMCS (Pierce, Rockford, IL, U.S.A.) in hexane. Separate fused-silica capillary columns contained SE-30 (J & W Scientific, Rancho Cordova, CA, U.S.A.), SE-54 (J & W Scientific), and RSL-10 (Alltech Assoc., Deerfield, IL, U.S.A.).

XAD-4 (Rohm & Haas, Philadelphia, PA, U.S.A.) was washed with 0.5 *N* hydrochloric acid, 0.5 *N* sodium hydroxide, and distilled water using three times the volume of the resin, Soxhlet extracted in turn with methanol, ethyl acetate, and diethyl ether for one day per solvent, and dried with air purified through a charcoal and/or cleaned XAD-4 column. All solvents used were "Baker Resi-Analysed" grade.

Gas saturation vapor pressure

An apparatus was constructed for six simultaneous determinations of vapor pressure using the gas saturation technique of Spencer and Cliath⁵. The apparatus, a modification of that of Ferreira and Seiber¹⁰, consisted of six identical assemblies of two glass tubes each (ball joint $\text{S } 28/45 \times 14$ cm). Each lower section contained sand (washed and ignited, Mallinckrodt, Paris, KY, U.S.A.) coated with the organophosphorus pesticide of interest. Methyl parathion, parathion, diazinon and dimethoate were coated with the same technique and amount of solvent and chemical as used by Spencer *et al.*¹¹, except that removal of solvent was done with a rotary evaporator and ethyl acetate was used as the solvent for dimethoate. Neat dichlorvos, phorate and malathion were added dropwise to the sand, which was coated with the chemicals by mixing for 2 h in a rotating flask. Each upper section contained two 3-g portions of cleaned XAD-4 resin separated by a glass wool plug. All six tubes were immersed in a constant-temperature water bath (Forma Scientific, Marietta, OH, U.S.A., heating-cooling mode, $\pm 0.1^\circ\text{C}$), the temperature of which was measured with a mercury thermometer (range -1°C to 100°C , 0.1°C division, Ertco 9047), and were supplied with nitrogen carrier gas, the flow-rate of which was measured with a soap-bubble tube and timer at least four times during each run. The average flow-rate of the carrier gas was used in the calculation of vapor pressure. When the runs were completed, the XAD-4 resin was transferred to a 50-ml Erlenmeyer flask and extracted with 20 ml of ethyl acetate by shaking for 1 h. The extraction was repeated twice with 10-ml portions of ethyl acetate. The extracts were filtered through a small plug of glass wool, contained in a funnel, into a volumetric flask when volatile chemicals (dichlorvos, phorate and dimethoate) were analyzed or to a round bottom flask for vacuum evaporation when less volatile compounds were analyzed.

Analysis of the prepared samples was carried out by gas chromatography using a Varian Model 2100 gas chromatograph equipped with an alkali flame ionization detector and Pyrex columns 1.83 m \times 0.64 cm O.D. packed with 5% OV-210 on 80-100 mesh Supelcoport, 7.5% DC-200 on 60/80-mesh Chromosorb G, or 1.5% SP 2250 and 1.15% SP 2401 on 100/200-mesh Supelcoport. The other operating parameters were the following: nitrogen flow, 30 ml/min; hydrogen flow, 40 ml/min; air flow, 230 ml/min; inlet, column, and detector temperatures of 240, 190-235, and 240°C , respectively. Hydrogen and nitrogen flow-rates were adjusted when necessary to achieve maximum sensitivity. Vapor pressure was calculated by the ideal gas law:

$$P^\circ = dRT/m$$

where P° is the vapor pressure in atm, d is the GC-determined saturation vapor density (g/l), M is the molecular weight (g), T is the absolute temperature ($^\circ\text{K}$), and R is the gas constant (0.082 l atm/ $^\circ\text{K}$ mol).

Recoveries of test compounds from XAD-4 were determined by the procedure of Thomas and Seiber¹². A known amount (Table II, the same level as trapped in the gas saturation experiment) of test compound was added to a glass U-tube immersed in a constant-temperature oil bath (60–70 $^\circ\text{C}$). An amount of 3 g XAD-4 was loaded into one end of the U-tube with glass wool plugs holding the resin in place. Clean air was allowed to flow through the apparatus at 7 l/min, for 1–2 h. At the end of this period, the XAD-4 resin was extracted and the U-tube was rinsed with ethyl acetate. The ethyl acetate solutions were adjusted in volume and analyzed by GC as described above. Total recoveries were calculated as the amount in resin plus amount remaining in the U-tube, the sum of which was divided by the amount spiked, and trapping efficiencies of the resin were calculated as the amount in resin divided by the difference between the amount spiked to the U-tube and the amount remaining in the U-tube. With some exceptions, since recovery and trapping efficiency were over 90%, no correction was made to the gas saturation result in consideration of the fact that the quantitation procedure had about a 10% deviation.

Gas chromatographic vapor pressure determination

A Varian Model 1700 gas chromatograph was used for measuring retention times of the chemicals of interest. The dual column instrument was equipped with a capillary column with glass splitter and a packed column. Oven temperatures were monitored by averaging the temperatures recorded by thermocouples (Chromel-Constantan, Omega type E, size 003), eight and three of which were placed close to the capillary and packed columns, respectively, with a supporting wire. The temperature in the oven was maintained at $\pm 1\%$ variation. Gas flows for the packed columns were *ca.* 23 ml/min, 18 ml/min and 22 ml/min for nitrogen, hydrogen and air, respectively. Hydrogen and air flow were maintained at the same rates for the capillary column, but nitrogen flow was varied from 10.3 to 3 ml/min so that the methyl parathion peak would elute in less than 5 min. Split ratio for the capillary column was approximately 1:100. Concentration of each chemical for GC was approximately 1 mg/ml and 1 μl was injected routinely.

Retention time of a chemical was defined as the time elapsed after injection for a capillary column and distance from the solvent front for a packed column. Adjusted retention time for a capillary column was calculated by subtracting the retention time of methane from the retention time of the chemical. Adjusted retention time for a packed column was considered the same as the retention time, since gas hold-up time was negligible.

Vapor pressure of an unknown chemical was calculated by Hamilton's method⁸ using several reference compounds. The calculation starts with retention time (t_{R}') for the unknown and reference compound at several GC temperatures. Using the equation

$$\ln \frac{t_{\text{R}}'(\text{unknown})}{t_{\text{R}}'(\text{reference})} = \left[1 - \frac{L(\text{unknown})}{L(\text{reference})} \right] \ln P_{(\text{reference})} - C \quad (1)$$

where L is the latent heat of vaporization and C is a constant, values of $1 - \frac{L(\text{unknown})}{L(\text{reference})}$ and C are obtained graphically. Then, using the relationship

$$\ln P_{(\text{unknown})} = \left[\frac{L(\text{unknown})}{L(\text{reference})} \right] \ln P_{(\text{reference})} + C \quad (2)$$

the vapor pressure P for the unknown can be calculated at any temperature for which a value of P for the reference is available. For the compounds with melting points higher than the calculation temperature and lower than the lowest GC temperature, a melting point correction was applied using the equation¹³:

$$\ln \frac{P_s}{P_L} = 6.79 \left(1 - \frac{T_m}{T} \right) \quad (3)$$

where P_s and P_L are vapor pressures for the solid and liquid and T_m and T are the absolute melting point and the temperature at which the vapor pressure is to be calculated.

Several reference compounds were used and their vapor pressure-temperature relationships are listed in each Table. Routine calculations were carried out with the aid of a Burroughs computer using a program written in BASIC. This program required the following input to obtain vapor pressure of compounds of interest (unknown) at 10 to 50°C with 5°C intervals: temperature-vapor pressure relationship of reference compound, number of temperature sets used in GC, absolute temperatures, and adjusted retention time of unknown and reference compounds.

Beroza p-value

The Beroza p -value of dibutyl phthalate with the hexane-acetonitrile solvent system was measured by following the GC quantitation method of Beroza *et al.*¹⁴. Those of diazinon and methyl parathion were also measured to confirm the reproducibility of the method.

RESULTS AND DISCUSSION

Gas saturation vapor pressure

The vapor pressures of seven organophosphorus pesticides were measured with the standard gas saturation technique at various temperatures (Table I). The vapor pressure of methyl parathion was measured at six different temperatures and showed very good overall agreement with the data of Spencer *et al.*¹¹, with a trend toward better agreement at higher temperatures than was obtained near room temperature. These results indicate that, within experimental error, our system successfully reproduced the results of Spencer *et al.*¹¹ and did so with nearly the same precision. Vapor pressures of parathion and diazinon were measured at three temperatures with the intention of using them as reference compounds for the GC method, where the vapor pressure-temperature relationship of the reference compounds is needed. The data for parathion confirmed the reproducibility of the gas saturation system.

TABLE I

VAPOR PRESSURES OF ORGANOPHOSPHORUS PESTICIDES AT VARIOUS TEMPERATURES DETERMINED BY THE GAS SATURATION METHOD

Temperature ($^{\circ}\text{C}$)	No. of determinations	Vapor pressure (torr) \pm S.D. (% R.S.D.)
Methyl parathion		
25.4	6	1.54 ± 0.11 (7.0) $\cdot 10^{-5}$
30.1	5	3.67 ± 0.29 (7.9) $\cdot 10^{-5}$
34.3	5	6.59 ± 0.53 (8.0) $\cdot 10^{-5}$
38.5	6	11.23 ± 0.89 (7.9) $\cdot 10^{-5}$
41.7	6	15.13 ± 1.16 (7.7) $\cdot 10^{-5}$
45.1	6	20.85 ± 2.49 (11.9) $\cdot 10^{-5}$
Parathion		
25.3	3	0.98 ± 0.01 (0.7) $\cdot 10^{-5}$
34.9	3	3.07 ± 0.16 (5.3) $\cdot 10^{-5}$
45.0	3	9.01 ± 0.15 (1.7) $\cdot 10^{-5}$
Diazinon		
25.3	3	8.47 ± 1.29 (15.3) $\cdot 10^{-5}$
34.9	3	22.41 ± 3.32 (14.8) $\cdot 10^{-5}$
45.0	3	57.73 ± 8.21 (14.2) $\cdot 10^{-5}$
Phorate		
25.0	3	5.54 ± 0.43 (7.7) $\cdot 10^{-4}$ (8.24)*
Malathion		
25.0	3	7.95 ± 1.28 (16.1) $\cdot 10^{-6}$ (12.06)*
Dimethoate		
25.0	3	5.06 ± 0.40 (7.8) $\cdot 10^{-6}$
Dichlorvos		
25.0	3	5.27 ± 0.92 (17.5) $\cdot 10^{-2}$

* Recovery correction data in parentheses. See text for details.

In order to validate the use of XAD-4 resin to trap vaporized chemicals in the gas saturation apparatus, recovery tests were run (Table II). The recoveries of methyl parathion, parathion, diazinon and dichlorvos were quantitative at all spiking levels, which were approximately the same level as the amount trapped in the gas saturation run. Phorate and malathion were not recovered as well. The presumed instability or incomplete extraction of malathion and phorate illustrates a potential drawback to the gas saturation technique for vapor pressure determination, especially when vapor generation is done at elevated temperatures. It also raises questions regarding the integrity of vapor pressure values in the literature when they are not, as in most cases, accompanied by details of the method of determination. This, along with a discrepancy in temperatures used in various sources, complicated a comparison of our experimental vapor pressures with those in the literature (Table III). For the relatively

TABLE II

MASS RECOVERY AND TRAPPING EFFICIENCY OF ORGANOPHOSPHORUS PESTICIDES FOR XAD-4 RESIN AND U-TUBE

<i>Compound</i>	<i>Spiked amount (μg)</i>	<i>Total recovery* (%)</i>	<i>Trapping efficiency* (%)</i>
Methyl parathion	1.0	98.8 \pm 5.4	98.2 \pm 12.2
	5.0	103.1 \pm 4.7	103.2 \pm 5.1
	10.0	97.2 \pm 5.6	97.4 \pm 6.1
Average		99.7 \pm 3.1	99.6 \pm 3.1
Parathion	1.13	100.9 \pm 8.3	100.7 \pm 14.4
	5.64	101.6 \pm 2.4	101.8 \pm 2.6
	22.56	95.6 \pm 10.2	91.1 \pm 20.0
Average		99.4 \pm 3.3	97.9 \pm 5.9
Diazinon	5.07	93.0 \pm 1.1	90.5 \pm 1.6
	20.28	97.1 \pm 12.3	96.9 \pm 12.7
	101.40	96.8 \pm 6.1	96.6 \pm 6.2
Average		95.6 \pm 2.3	94.7 \pm 3.6
Phorate	53.38	67.2 \pm 4.4	67.2 \pm 4.4
Malathion	12.38	78.0 \pm 8.0	65.9 \pm 9.04
Dimethoate	2.00	82.2 \pm 5.4	78.6 \pm 6.0
Dichlorvos	250.20	94.5 \pm 1.3	93.3 \pm 3.0

* Average and one standard deviation of three determinations.

TABLE III

COMPARISON OF VAPOR PRESSURES ($\text{torr} \cdot 10^5$) MEASURED BY GAS SATURATION TECHNIQUE (THIS WORK) WITH LITERATURE VALUES

<i>Compound</i>	<i>This work</i>		<i>Literature</i>		
	<i>25°C</i>	<i>20°C</i>	<i>Spencer et al.¹¹ (gas saturation) 20°C</i>	<i>Handbook¹⁵ 20°C</i>	<i>Others 20°C</i>
Dichlorvos	5270	3009**		1200	1060 ^{16,*}
Phorate	55.4	31.7**		84	
Diazinon	8.2	4.8***		8.4	7.3 ¹⁷ , 14 ^{16,*}
Dimethoate	0.51	0.29**		0.85	0.32 ¹⁸ , 12,000 ^{16,*}
Methyl parathion	1.5	0.63***	0.82	0.97	
Parathion	0.98	0.52***	0.47	0.57	1.9 ^{16,*}
Malathion	0.79	0.45**		0.125	0.55 ¹⁸

* Some data are extrapolated using the Clausius-Clapeyron equation.

** Extrapolation with the equation $\log P = A - 4241.13/T$, where 4241.13 came from the average of constants for diazinon, methyl parathion and parathion; and constant A could be calculated by inputting vapor pressure and temperature at 25°C.

*** Extrapolated by the Clausius-Clapeyron equation with vapor pressures at several temperatures.

stable compounds diazinon, methyl parathion and parathion, our experimental values agreed closely (factor of 2 or less) with literature values from several sources. For phorate, malathion and dichlorvos, a somewhat larger disparity existed between our experimental and literature values. The largest disparity (factors of 1.2, 3.3 and 46,000 when compared with three different literature citations) was for dimethoate.

GC vapor pressure

Several operational parameters of the gas chromatograph which might affect retention data, and thus vapor pressures calculated from the retention data, were checked in detail. One was the accuracy of column oven temperature measurement. To obtain an accurate measurement, eight calibrated thermocouples were inserted at various points in the oven in close proximity to the 1-m capillary column. The maximum temperature difference in the oven was found to be about 1%, and thus the temperature values from these thermocouples were averaged for all runs. Also, because the ends of the column were inserted into the injector and detector which were kept at temperatures higher than that of the oven, a solute would experience an average column temperature higher than that recorded in the oven only. To correct this, two 25-cm pieces of deactivated and uncoated fused-silica capillary tubing were substituted for the coated column in the injector port and detector compartment, and joined to the 1-m coated column in the oven. There was no significant difference in relative retention or calculated vapor pressures for four organophosphorus pesticides when this substitution was made, indicating that some overheating of the capillary column ends could be tolerated without significantly influencing retention results. However, injector and detector temperature for packed columns were maintained at the same temperature as the column oven to avoid heat transfer from both ends. Column length as a variable was checked by interchanging SE-30 fused-silica capillary column lengths of 1 and 27 m; no significant difference in calculated vapor pressure was observed.

A variable investigated in detail was the number and ranges of temperature over which retention data should be obtained by GC to give adequate vapor pressure results. A series of tests were run using ethyl parathion as the unknown compound and methyl parathion as the GC reference compound with the 1-m SE-30 fused-silica capillary column. Table IV shows the variation in GC-calculated vapor pressure when 3, 4, 5 or 8 temperatures were used, with a 5°C difference among selected

TABLE IV

DEPENDENCE OF GC-CALCULATED VAPOR PRESSURE (25°C) OF PARATHION ON NUMBER OF TEMPERATURES USED FOR GC RETENTION MEASUREMENTS

Methyl parathion was used as reference. GC temperature: 100–170°C with 1-m SE-30 fused-silica capillary column.

<i>No. of temperatures</i>	<i>Data set (n)</i>	<i>Vapor pressure torr · 10⁵ ± S.D. (% R.S.D.)</i>
3	13	1.078 ± 0.225 (20.7)
4	12	1.062 ± 0.166 (15.6)
5	11	1.042 ± 0.125 (12.0)
8	8	1.015 ± 0.087 (8.6)

TABLE V

DEPENDENCE OF GC-CALCULATED VAPOR PRESSURE (25°C) OF PARATHION ON TEMPERATURE DIFFERENCE OF GC MEASUREMENT IN A 3-TEMPERATURE SET

Methyl parathion was used as reference. GC temperature: 100–170°C with 1-m SE-30 fused-silica capillary column.

Temperature difference (°C)	Data set (n)	Vapor pressure torr · 10 ⁵ ± S.D. (% R.S.D.)
5	13	1.078 ± 0.225 (20.9%)
10	11	1.038 ± 0.116 (11.2%)
15	9	1.024 ± 0.107 (10.4%)
20	7	1.009 ± 0.033 (3.3%)
25	5	1.014 ± 0.019 (1.9%)
30	3	1.04 ± 0.026 (2.5%)

temperatures, to obtain relative retention and temperature relationship for extrapolation. Variability was least with the 8-temperature set, but the average vapor pressure for the entire temperature range is not markedly influenced by this choice. Table V shows a similar trend in which the temperature sets (3 temperatures in each set) had a 5, 10, 20, 25, or 30°C difference between selected temperatures. Variability was notably affected by choice of temperature difference, being greatest when only 5°C separated temperatures employed and least when the difference was 25°C or more. The conclusion from these tests was that at least 5 temperatures with 5°C separation, or at least 15°C difference with a 3-temperature set should be employed in making GC retention measurements for vapor pressure in order to achieve less than 10%

TABLE VI

DEPENDENCE OF GC-CALCULATED VAPOR PRESSURES (torr · 10⁵) (25°C) ON GC REFERENCE COMPOUND

1-m SE-30 fused-silica capillary column was used with a 3-temperature set (100, 135, and 170°C).

Compound	Gas saturation vapor pressure	Reference compound*.**			
		Dibutyl phthalate	Diazinon	Methyl parathion	Parathion
Dichlorvos	5270	740	740	260	210
Phorate	55.4	30.1	35.7	12.4	10.3
Diazinon	8.2	6.41	Ref	2.85	2.38
Dimethoate	0.51	25.7	30.8	10.7	8.90
Methyl parathion	1.5	6.59	8.26	Ref	2.39
Parathion	0.98	2.52	3.29	1.14	Ref
Malathion	0.79	1.85	2.48	0.86	0.72

* Equations for vapor pressure–temperature relationships of references were:

Dibutyl phthalate $\log P = 7.065 - 1666/T - 547700/T^2$

Diazinon $\log P = 9.3871 - 4014.67/T$

Methyl parathion $\log P = 9.0935 - 4063.65/T$

Parathion $\log P = 10.5654 - 4645.07/T$.

** Average relative standard deviation with triplicate measurement of the chemicals was 4.8% without dichlorvos (54%).

TABLE VII
GC-CALCULATED VAPOR PRESSURES ($\text{torr} \cdot 10^5$) (25°C) USING DIFFERENT GC COLUMNS. COMPARISON WITH GAS SATURATION VALUES*

Compound	Gas saturation vapor pressure	Packed column**		Capillary column***				
		Squalane		Apiezon L	SE-30	RSL-110	SE-30	SE-54
		A	B					
Dichlorvos	5270	510 (-10.3) [§]	750 (-7.0)	890 (-5.9)	290 (-18.2)	1050 (-5.0)	260 (-20.3)	870 (-6.1)
Phorate	55.4	47.3 (-1.2)	20.0 (-2.8)	11.3 (-4.9)	21.3 (-2.6)	13.2 (-4.2)	12.4 (-4.5)	14.8 (-3.7)
Diazinon	8.2	10.3 (+1.3)	3.70 (-2.2)	3.32 (-2.5)	2.67 (-3.1)	3.91 (-2.1)	2.85 (-2.9)	3.40 (-2.4)
Dimethoate	0.51	2.78 (+5.5)	8.66 (+16.0)	-	-	-	10.7 (+21.0)	-
Methyl parathion	1.5	Ref	Ref	Ref	Ref	Ref	Ref	Ref
Parathion	0.98	1.77 (+1.8)	0.83 (-1.2)	0.96 (-1.0)	1.09 (+1.1)	0.99 (+1.0)	1.14 (+1.2)	1.03 (+1.1)
Malathion	0.79	1.36 (+1.7)	1.47 (+1.9)	1.60 (+2.0)	0.84 (+1.1)	1.43 (+1.8)	0.86 (+1.1)	0.81 (+1.0)
\bar{x} all values		(3.6)	(5.2)	(3.3)	(5.2)	(2.8)	(8.5)	(2.9)
\bar{x} excluding dichlorvos and dimethoate		(1.5)	(2.0)	(2.6)	(2.0)	(2.3)	(2.4)	(2.1)

* Methyl parathion was the reference in all cases.

** 140-135-130°C temperature set, except for squalane B for which the temperature set was 120-115-110°C after conditioning for 11 h at 125°C.

*** Factors of error (in parentheses) are defined as the ratio of GC vapor pressure and gas saturation vapor pressure with the larger value as the numerator. A negative sign indicates that GC vapor pressure is lower than the gas saturation vapor pressure.

§ 170-135-100°C temperature set.

relative standard deviation (R.S.D.) in the results. No difference was observed in calculated vapor pressures owing to the choice of a high *versus* a low temperature set.

Another experimental variable dealt with the nature of the reference compound. Table VI lists vapor pressures calculated by GC for seven organophosphorus compounds using four different reference chemicals. The results indicate that use of either methyl parathion or parathion as a reference gives equivalent results and either diazinon or dibutyl phthalate as a reference gives equivalent results as well. However, the agreement with gas saturation values differed between the two groups of chemicals. The parathion group (methyl parathion and parathion) predicted well the vapor pressures for methyl parathion, parathion and malathion, but the diazinon group (diazinon and dibutyl phthalate) predicted those of phorate and diazinon better. Neither group satisfactorily predicted vapor pressures of dichlorvos and dimethoate.

We also investigated the GC liquid phase as a variable. Apolane 87, used by Westcott and Bidleman⁹, was not commercially available in precoated fused-silica capillary columns apparently because of its poor heat stability. RSL-110, a new phase reported to be of very low polarity, was checked against SE-30, as was SE-54, a more polar phase than SE-30. Two other non-polar phases (squalane and Apiezon L) were compared with SE-30 in packed columns. The results are in Table VII.

Squalane (packed column) and RSL-110 (capillary column) gave calculated vapor pressures in slightly better agreement with gas saturation vapor pressures when compared with the appropriate SE-30 counterpart. However, the differences between the liquid phases were so minor as to be insignificant. The squalane packed column was very susceptible to bleeding at temperatures required to elute the less volatile organophosphates and was considered unacceptable for general use for this reason. Limited experience with and availability of RSL-110 appeared to outweigh any minor advantages of this phase over the more widely used SE-30 (or its bonded phase equivalent, DB-1) in capillary columns. There was no significant difference between vapor pressure results on packed *versus* capillary columns; either column type, with SE-30 as liquid phase, could thus be used for vapor pressure calculation. Further

TABLE VIII

THEORETICAL PLATES* OF GC COLUMNS AT 135°C BASED UPON METHYL PARATHION AS SOLUTE

Column type	Liquid phase	Theoretical plates
Packed**	10% Squalane (10-27-83)	99.4
	10% Squalane (2-28-84)	160.1
	10% Apiezon L	173.7
	10% SE-30	216.4
Capillary	RSL-110 (1 m)	967.4
	SE-30 (1 m)	2317
	SE-54 (1 m)	2458

* Calculated as $5.54 \left(\frac{t_R}{w_{0.5}} \right)^2$ (ref. 19).

** On Chromosorb G AW DMCS (80-100 mesh) in a 15 cm × 2 mm I.D. glass column.

TABLE IX

REPRODUCIBILITY (% R.S.D.) OF GC-CALCULATED VAPOR PRESSURES (25°C) FROM REPLICATION ON SAME DAY AND DIFFERENT DAYS*

Replication	Column	Compound				
		Dichlorvos	Phorate	Diazinon	Parathion	Malathion
Same day	SE-30 (capillary)	—	—	6.8	7.9	6.9
	Apiezon L (packed)	43.5	4.3	8.7	3.4	15.2
Different days	SE-30 (capillary)	54	4.6	6.7	6.3	3.6
	Squalane (packed)	70.2	16.4	10.2	14.8	11.2
Different days following column change	SE-30 (capillary)	—	—	10.7	11.6	11.2
	Squalane (packed)	79.1	52.6	73.8	15.8	27.1

* Methyl parathion was the reference compound in all cases.

method development in this study was done with a 1-m SE-30 capillary column because it offered superior efficiency when compared with packed columns (Table VIII), bypassed potential solute interactions with the solid support, and allowed the elution of the less stable and less volatile solutes at low column temperatures.

In order to assess reproducibility of the GC method for calculating vapor pressures, several determinations were made successively on the same days and different days, or on different days after an intervening column change (Table IX). The largest variation was for dichlorvos, apparently due to the very short retention time of this solute at column temperatures required to elute the reference compound (methyl parathion) in a convenient time period. The excessively short retention time of dichlorvos was difficult to measure accurately, even with a stopwatch. These tests also showed a further shortcoming of squalane, whose retention characteristics changed continuously during operation with this column, again due to liquid phase bleeding. With these difficulties in mind, the reproducibility measured as relative standard deviations was generally less than 10% for the solutes phorate, diazinon, parathion and malathion on SE-30 capillary or Apiezon L packed columns; this is an average value which should be aimed for in further application of the technique. To overcome the difficulty mentioned above with dichlorvos and other early eluting solutes, it may be necessary to use a reference compound with similar retention characteristics so that both solute and reference can be moved well past the solvent front by lowering the column temperature.

Returning to the assessment of accuracy [agreement between GC-calculated and experimental gas saturation vapor pressures (Tables VI and VII) we investigated the possibility that accuracy would be a function of the polarity of the solute and reference compound, and that this factor could be predicted from polarity considerations. Table X lists three physical properties (water solubility, octanol-water partition coefficient and Beroza partition *p*-value) for each of seven organophosphates. Generally, the two most polar solutes (dichlorvos and dimethoate) had the largest disagreement between GC-calculated and gas saturation vapor pressures when meth-

TABLE X
PHYSICAL PROPERTIES OF ORGANOPHOSPHORUS TEST COMPOUNDS (25°C)

Compound	MW	Water solubility ²⁰ (ppm)	Octanol-water partition coeff. ²¹	Beroza <i>p</i> -value hexane-acetonitrile	
				Literature ^{14,22}	Measured
Dichlorvos	221	10,000	195	< 0.01	
Dimethoate	229	25,000	—	< 0.01	
Phorate	260	50	823	0.26	
Diazinon	304	40	1052	0.28	0.3
Methyl parathion	263	57	2076	0.022	0.03
Parathion	291	24	6455	0.044	
Malathion	330	145	230	0.042	
Dibutyl phthalate	278	400			0.21

yl parathion (which is considerably less polar than either of these solutes) was the reference. This suggests that a more polar reference compound would improve the accuracy of the GC method with solutes such as dichlorvos and dimethoate. While the water solubility and octanol-water partition coefficients of phorate and diazinon did not differ markedly from those of methyl parathion, parathion, and malathion, there was a clear distinction between the two groups in their hexane-acetonitrile *p*-values. This polarity parameter, developed for non-aqueous partition systems, might better describe the polarity of various solutes in the phase distribution occurring in GC columns, also a non-aqueous system. This indicates that less polar organophosphates such as phorate and diazinon might produce more accurate GC-calculated vapor pressures when a reference of similar hexane-acetonitrile *p*-value is available. From Tables VI and X, it is clear that dibutyl phthalate was a suitable reference compound for phorate and diazinon. Furthermore, the Beroza *p*-value approach may be used to explain why previous workers⁹ successfully used dibutyl phthalate as a reference for organochlorine compounds. *p*-Values for *p,p'*-DDT (0.38) and many other organochlorine compounds are in the same range as that of dibutyl phthalate (0.21).

The GC approach was extended to include additional organophosphorus compounds whose vapor pressures are also available in the literature^{15,16}. These compounds were chosen because of their availability in relatively pure form. Literature and GC-calculated vapor pressures are listed in Table XI for fourteen organophosphorus compounds (8–21); included for comparison are literature, gas saturation, and GC-derived vapor pressures for the seven organophosphates (1–7) described in prior sections of this report. Note that a GC temperature set not used in the previous tables was employed (Table XI) and vapor pressures in Table XI are for 20°C.

The correlation between experimental values [considering gas saturation (compound 1–7) and literature sources (compound 8–21) as experimental] and GC-calculated values (Fig. 1 and Table XII) when all 20 compounds were included was fairly low ($r = 0.811$ and average of all factors of error $|\bar{x}| = 10.4$). When a melting point correction was applied to the seven compounds which are solids at room temperature, the correlation was improved to 0.863 with an average factor of error of

TABLE XI

COMPARISON OF GC-CALCULATED VAPOR PRESSURES (torr · 10⁵) (20°C) WITH EXPERIMENTAL VALUESGas saturation values determined in this study (Table III) were used for compounds 1-7; literature values^{15,23} of unknown method of measurement were used for compounds 8-21.

Compound		Experimental value	GC-calculated value*			
No.	Name		No m.p. correction		With m.p. correction	
1	Dichlorvos	3009	560	(-5.4)**		
2	Phorate	31.7	8.2	(+3.9)		
3	Diazinon	4.8	1.83	(-2.6)		
4	Dimethoate	0.29	6.4	(+22.1)	3.1	(+12.2)
5	Methyl parathion	0.63	Ref			
6	Parathion	0.52	0.61	(+1.2)		
7	Malathion	0.45	0.50	(+1.1)		
8	Mevinphos	220	56.8***	(-3.9)		
9	Thionazin	75	15.1	(-5.0)		
10	Ronnel	40	1.29	(-31)	0.79	(-50.6)
11	Demeton-O (thiono)	26	5.3	(-4.9)		
12	Demeton-O (thiolo)	24.8	12.5	(-2.0)		
13	Disulfoton	18	3.04	(-5.9)		
14	Monocrotophos	7	3.82	(-1.8)	1.72	(-4.1)
15	Fenthion	3	6.31	(+2.1)		
16	Phosphamidon	2.5	2.24 [§]	(-1.1)		
			1.38 [§]	(+1.8)		
17	Chlorpyrifos	1.09	0.66	(-1.7)	0.39	(-2.8)
18	Trichlorfon	0.78	48	(+61.5)	14	(+17.9)
19	Carbophenothion	0.031	0.058	(+1.9)		
20	Azinphos-methyl	0.022	0.0083	(-2.7)	0.0023	(-9.6)
21	Tetrachlorvinphos	0.0042	0.193	(+46)	0.032	(+7.6)

* Methyl parathion was reference compound in all cases with equation $\log P = 9.0935 - 4063.65/T$ for vapor pressure calculation. A 1-m SE-30 fused silica capillary column was used with 180-165-150-135°C temperature set.

** Factor of error compared to experimental. Negative sign means GC value is less than experimental value.

*** Two isomers did not separate under the GC conditions.

§ Two isomers. Lower value was not included in the calculation of average factors of error.

7.3. It should be noted that these seven solids, when correlated separately, gave $r = 0.532$ for a plot of log vapor pressure (experimental value) versus log vapor pressure (GC-calculated value) before melting point correction, and $r = 0.634$ after melting point correction. It appears that solute phase at room temperature is one feature which influences the quality of GC-calculated vapor pressure data, providing a lower error with liquids than with solids even after the calculated vapor pressures of solids are corrected for phase change from liquid to solid with the existing technique. This was shown further with the improved correlation ($r = 0.972$) and the average factor of error ($|\bar{x}| = 3.2$) by considering liquids only in the calculation.

It was recognized that the literature values for some of the pesticides tested could be in error. Also, some compounds may break down upon GC producing a peak (from which vapor pressure was calculated) which is not due to the parent

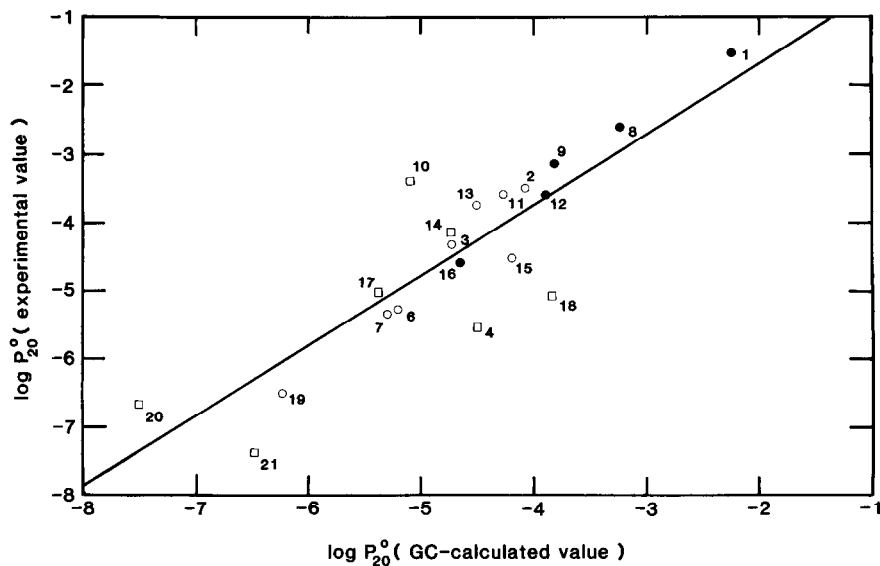


Fig. 1. Comparison of GC-calculated vapor pressures of organophosphate pesticides with experimental values from gas saturation (compounds 1-7) or literature sources (compounds 8-21). Reference compound for GC method was methyl parathion. Number for each compound is the same as in Table XI. Symbols and correlation were for solids (\square , $r = 0.634$), all pesticides (\bullet , \circ and \square , $r = 0.863$, the straight line is fitted to this correlation), liquids (\bullet and \circ , $r = 0.972$), non-polar liquids (\circ , $r = 0.938$) and polar liquids (\bullet , $r = 0.988$).

compound. Considering these two factors, three compounds were removed from the correlation. These were trichlorfon, which is known to break down upon GC producing chloral and dimethyl phosphite²⁴; and ronnel and tetrachlorvinphos, whose literature vapor pressures vary by a factor of 10^5 even though their structures are somewhat similar, indicating that the literature values for one or both are in serious error. When these outliers (suspect compounds) were removed, the correlation for

TABLE XII

CORRELATION OF GC-CALCULATED VAPOR PRESSURES AND EXPERIMENTAL VALUES

	Number of compounds	Absolute mean factor of error		Correlation coefficient	
		No m.p. corr.	With m.p. corr.	No m.p. corr.	With m.p. corr.
All pesticides	20	10.4	7.3	0.811	0.863
Excluding three outliers*	17	4.1	4.1	0.922	0.922
Liquids polar**	5	3.5		0.988	
nonpolar**	8	3.0		0.938	
total	13	3.2		0.972	
Solids	7	23.8	14.9	0.532	0.634

* Ronnel, trichlorfon and tetrachlorvinphos.

** Polar, water solubility higher than 1000 ppm; nonpolar, water solubility lower than 100 ppm.

the seventeen remaining compounds improved to 0.922, and the average factor of error was reduced to 4.1 with or without melting point correction.

We also examined polarity for influence on correlation but found that, unlike the preliminary indication obtained for compounds 1–7, there was no significant effect on correlation when polar liquid compounds (water solubility greater than 1000 ppm, $r = 0.988$) and non-polar liquid compounds (water solubility less than 1000 ppm, $r = 0.938$) were correlated separately in the larger data set.

CONCLUSIONS

Vapor pressures measured by gas saturation were in reasonably good agreement with literature values, except for two compounds (malathion and phorate) which gave less than quantitative recoveries in the gas saturation experiment. The quality of vapor pressures calculated from GC retention data was influenced by the number of temperatures chosen and the spread between these temperatures, producing acceptable precision ($\pm 10\%$ R.S.D.) when at least five temperatures with at least a 5°C difference between them, or three temperatures with at least a 15°C difference were used. While several column types and low polarity liquid phases can be used for the calculation, a short fused-silica capillary column coated with SE-30 (or its bonded phase equivalent, DB-1) appears to be a good choice because of the absence of solid support–solute interactions, chromatographic efficiency, and ability to provide conveniently short retention times at relatively low column temperatures. The choice of GC reference appeared to influence the accuracy of calculated vapor pressures for the six compounds examined in depth in this study; for compounds of lower polarity (as signalled by Beroza partition p -values) dibutyl phthalate represents a convenient reference, while for more polar organophosphates methyl parathion was a suitable reference.

When 20 organophosphates were examined, it was clear that simple conclusions on the correlation between experimental and GC-calculated vapor pressures could not be reached without some judgement of the input data. By removing three outliers (trichlorfon, ronnel and tetrachlorvinphos) from the correlation because of suspicions about their literature values and chromatographic stability, the correlation improved from 0.863 to 0.922 with melting point correction for solids. Compounds which are solids at room temperature gave a poor correlation, although using a melting point correction for liquid–solid phase change improved this somewhat. The correlation after removing all solids from the calculation was improved to 0.971 with an average factor of error of 3.2. This correlation was obtained using a single reference compound, methyl parathion, as the GC reference even though our study showed that choosing separate reference compounds which approximate the polarity of individual solutes could potentially improve the correlation further.

The conclusion reached from the experimental results is that GC calculation can provide estimates of vapor pressure with an average factor of approximately 4 of the experimental values for organophosphates. This figure is somewhat higher than the errors estimated by other authors working with esters of phenoxy acid herbicides⁷ (factor of error of 1.31 with three closely related compounds) and organochlorine compounds⁹ (factor of error of 1.51 with five related compounds) as test compounds. This is expected because our test series was more heterogeneous in terms

of structure, polarity, and volatility than the series employed in the published work. For many purposes, however, ± 4 can be an acceptable latitude for vapor pressure data for compounds of low volatility. Taking into account its other advantages (speed, precision, sample size and purity requirements), the GC method can be considered a viable means for calculating vapor pressures for low volatility chemicals. Further study with the GC method should be focused on improving its applicability to solids, perhaps by modifying the melting point correction technique, and extending it to other classes of chemicals whose vapor pressures have been accurately determined by the gas saturation technique.

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