

## Low Vapor Pressure Determination by the Radiotracer Transpiration Method

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A new gas saturation method was developed for determining the vapor pressure of low volatility compounds, such as pesticides. A carbon-14-labeled pesticide or low volatility compound is coated on a sand bed, and the vapors are collected on charcoal adsorbent tubes at various temperatures below the melting point of the compound. The charcoal tubes are combusted and then counted by liquid scintillation spectrometry. Additional charcoal tubes are extracted and analyzed by high-performance liquid chromatography to quantitate the  $^{14}\text{C}$  vapor composition in the air stream. The utilization of charcoal tubes to collect  $^{14}\text{C}$  vapors, along with high-performance LC eluent collection and counting, greatly improves the sensitivity and limit of detection over that of conventional methods. Another advantage of this method is that the determinations are done at or near the normal temperatures that the pesticide would experience in the field. The vapor pressure of *p, p'*-DDT was determined by using this method, and the results are compared with those of four other experimenters. The obtained value of  $4.3 \times 10^{-7}$  torr at 25 °C agrees with the three best prior results.

Techniques for accurately determining vapor pressures have had difficulties with the very low vapor pressures of many pesticides (Thomson, 1959). The Knudsen effusion technique, as classically performed by Balson (1947), gave good results for slightly volatile substances but had a detection limit of  $5 \times 10^{-6}$  torr. The method suffered from the limitation that the exact composition of the vapor could not be determined. More volatile minor impurities could drastically affect the result. The differential thermal analyzer technique (Hamaker and Kerlinger, 1969; Eggers et al., 1969; Blaine and Levy, 1974) could measure vapor pressures to  $10^{-7}$  torr. This method suffers from the drawback that the material under study is heated above its melting point and the vapor pressure is extrapolated below the melting point. Since the solid-vapor equilibrium phase diagram changes slope at the melting point, this extrapolation means that the obtained vapor pressure will be too high by a factor of  $\Delta H_{\text{sublimation}} - \Delta H_{\text{vaporization}}$ . Additionally, this method suffers from the same limitation of the effusion method in that the detector cannot distinguish impurities in the vapor stream. Once again, more volatile minor components drastically bias the result.

The gas saturation (transpiration)/concentration method, which includes trapping and concentration of the vapors and analysis, overcomes these two major drawbacks. In this method, the material in question is coated on a sand bed, and an air stream is passed through the bed at various temperatures below the melting point of the material. The vapor equilibrated in the air stream is trapped and concentrated for subsequent analysis by the most appropriate means, usually by GLC. The actual analysis of the vapor quantitates and separates out the interference of volatile impurities. Dickinson (1956), in his vapor pressure determination of *p, p'*-DDT, used UV absorbance as a measure of vapor purity and showed the work of Kuhn and Massini (1949) to be in error since they made no determination of vapor composition. It should be noted that Gueckel and Rittig's (1974) gravimetric collection method suffered from the same reliance on chemically pure pesticide for accurate results. Although many researchers have utilized the transpiration method with GLC analysis of the vapor (Smith, 1970; Parochetti et al., 1971, 1973, 1976; Swann and Behrens, 1972), Spencer and Cliath (1969, 1970, 1972, 1973) have seemingly done the most work to

establish the technique as routine.

The Spencer and Cliath method relies on the ability of the chemist to analyze the trapped vapor by GLC. Many pesticides, however, cannot be analyzed by GLC because of volatility or thermal degradation problems. It would appear that analysis of a carbon-14-labeled vapor would greatly increase the sensitivity of such a determination, especially if the trapped vapor could be counted in toto.

Que Hee and Sutherland (1974) used  $^{14}\text{C}$ -labeled pesticide only to obtain a material balance to check their trapping efficiency for GLC analysis. Several researchers utilized radiotracers in volatilization, i.e., kinetic rate, studies rather than vapor pressure, i.e., equilibrium, studies to both simplify their measurement and increase their sensitivity (Burt, 1974; Walker, 1972; Deming, 1963; Phillips, 1971). Carson, Stranks, and Wilmshurst (1958) employed mercury-203 labeling and the effusion technique to determine the vapor pressure of mercury diphenyl. In all these cases, the radiotracer measurement was not strictly specific for the component being examined.

The only reported use of a radiotracer method with subsequent vapor component analysis seems to be that of Kearney and Kontson (1976). These experimenters used carbon-14 techniques to measure both the volatilization and metabolic  $\text{CO}_2$  evolution from soils. A polyurethane plug trapped volatile  $^{14}\text{C}$  pesticides but allowed  $^{14}\text{CO}_2$  to be passed and trapped by an alkali solution. The plug was extracted and the concentrated extract was examined by TLC as well as by liquid scintillation counting.

In the classical gas saturation method, the collection of vapor in solvent traps with subsequent chromatographic analysis has two inherent difficulties. First, the collection of a large statistically valid multitemperature set of data points is very time consuming. Second, the sensitivity of the technique is limited by conventional detection limits.

This paper reports a modification of the gas saturation (transpiration) method in which the sand bed is coated with carbon-14-labeled pesticide and the subsequent  $^{14}\text{C}$  vapor is trapped on charcoal collection tubes. The determinations are made at or near the normal temperatures that the pesticide would experience in the field. The tubes are combusted on an oxidizer and the collected  $^{14}\text{CO}_2$  is counted by liquid scintillation spectrometry. A small number of representative tubes are also eluted and the eluents chromatographically analyzed and counted to determine vapor composition. The chromatographic detection of  $^{14}\text{C}$  components is potentially more sensitive than for the unlabeled technique since eluant collection

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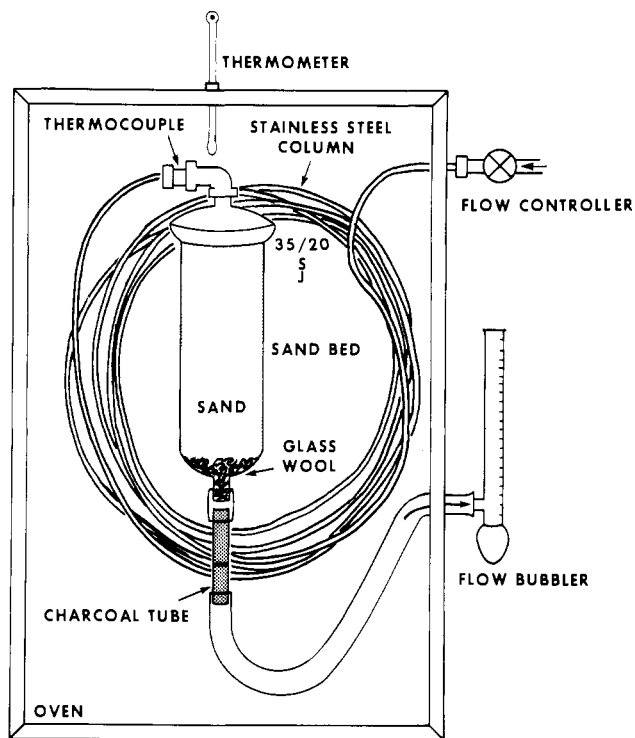


Figure 1. Vapor pressure apparatus.

and counting can be performed with the reverse isotope dilution technique.

As a consequence of the historical difficulty in determining vapor pressures of pesticides, little data are available on the vapor pressures of more than a handful of common pesticides. There is, therefore, little available, let alone reliable, vapor pressure data to be used for comparative testing of new techniques for determining vapor pressures of pesticides. Several investigators have determined the vapor pressure of *p,p'*-DDT (Balson, 1947; Dickinson, 1956; Kuhn and Massini, 1949; Spencer and Cliath, 1972), and therefore this pesticide was selected for evaluating our technique.

#### EXPERIMENTAL SECTION

The sand bed, charcoal tube, and equilibration coil were enclosed in a thermostatically controlled oven. For these determinations, the oven temperature was set at various temperatures between 20 and 78 °C.

Uniformly ring labeled [ $^{14}\text{C}$ ] *p,p'*-DDT (1.003 g) was dissolved in acetone and was coated on 99 g of Ottawa sand (20–30 mesh). The coated sand was tightly packed in a 15 × 3 cm glass tube as shown in Figure 1. Air from a compressed gas cylinder was passed through the sand bed, usually at a flow rate of 50 mL/min. One series of experiments used a flow rate of 10 mL/min to check that this flow rate allows equilibration. The flow rate was measured with a soap bubbler at the exit of the charcoal tube. A rotameter before the bubbler was used to monitor the consistency of flow. The bubbler was at a great enough distance that the temperature was never more than a few degrees above ambient, as determined by thermometer measurement at the inlet of the bubbler. The flow rate was corrected for the temperature differential between the bed and the bubbler. We assumed that the pressure was atmospheric. By checking flow rate with and without the sand bed in the system, we could detect only a negligible pressure drop across the sand bed. Flow exposure times for combustion tubes were generally 2–3 h. Exposure times for tubes destined for extraction were 8 h.

The charcoal collection tubes used for collecting samples of vapor were obtained from SKS, Inc. (Catalogue No. 226-01), and contained 100- and 50-mg sections of activated charcoal. The second 50-mg section of charcoal is used to detect breakthrough.

Combustions of the charcoal tube sections were performed in a Packard Model 306 Biological Oxidizer, and resultant counting samples were counted by liquid scintillation spectrometry on various Series 3000 Packard Tri-Carb liquid spectrometers.

Extraction of DDT from charcoal tubes was performed with 5 mL of methanol, acetonitrile, or methylene chloride. After agitation on a sonic bath for 5 min, the supernatant was transferred to a 4-mL conical vial and the solvent was evaporated to less than 1 mL with a nitrogen stream. The remaining solution was transferred via pipet to a 1-mL conical vial and rinsed with additional solvent, and the solvent was evaporated in a nitrogen stream. To the residue in the vial was added 250  $\mu\text{L}$  of methanol, and this solution was analyzed by high-performance LC. Methylene chloride was found to be the most satisfactory extraction solvent.

High-performance LC analyses were performed on a Du Pont Zorbax C-8 6- $\mu\text{m}$  spherical particle column (25 cm × 4.6 mm) plus a LiChrosorb C-18 10- $\mu\text{m}$  (5 cm × 4 mm) guard column, in series, with a mobile phase of methanol/water/acetic acid (75:25:0.2 v/v) at a flow rate of 2 mL/min. The DDT and associated impurities were detected by a Schoeffel UV detector at 254 nm. Cuts of the eluant were counted by liquid scintillation spectrometry. A standard of *p,p'*-DDT and associated impurities was coinjected to visually aid in the collection of cuts since the extracted DDT and impurity quantities were below the level of detector sensitivity.

To ensure that there were no volatiles present to impart incorrectly high values to the early runs, the sand bed was flushed for several days before taking readings and several of the higher temperatures were run first, to speed any stripping of the volatiles. Readings at various temperatures were repeated later in time to ensure that the vapor composition was not changing with time. Although it would not normally be the case, the whole measurement was gradually done over a period of 4 months, with a total throughput of several hundred liters. Vapor component extraction analyses were done periodically during this time also, indicating that the vapor composition studied was constant over the time of the experiment.

#### RESULTS AND DISCUSSION

A total of 53 tubes were combusted for six different temperatures between 20 and 78 °C. Combustion of the charcoal adsorbent with subsequent liquid scintillation counting gave the total carbon-14-labeled species in the adsorbed vapor. However, even though the *p,p'*- $^{14}\text{C}$ DDT was >96% radiopure, only a small portion of the vapor over the sand bed was actually *p,p'*- $^{14}\text{C}$ DDT. High-performance LC vapor composition analyses were used to correct the total combustion counting results.

Replicate high-performance LC vapor component analyses of tubes at two selected temperatures, 36 and 78 °C, showed that most of the vapor was actually *o,p'*-DDT and *o,p'*-DDE. Both sets gave the same result within our experimental error of  $\pm 2\%$ . This indicates that at least within this temperature range, heats of sublimation of the components were constant. For a representative high-performance LC chromatogram and computer histogram of the collected cuts see Figure 2.

The extraction efficiency varied from 11 to 93% between methanol and MDC, but the extraction efficiency was not

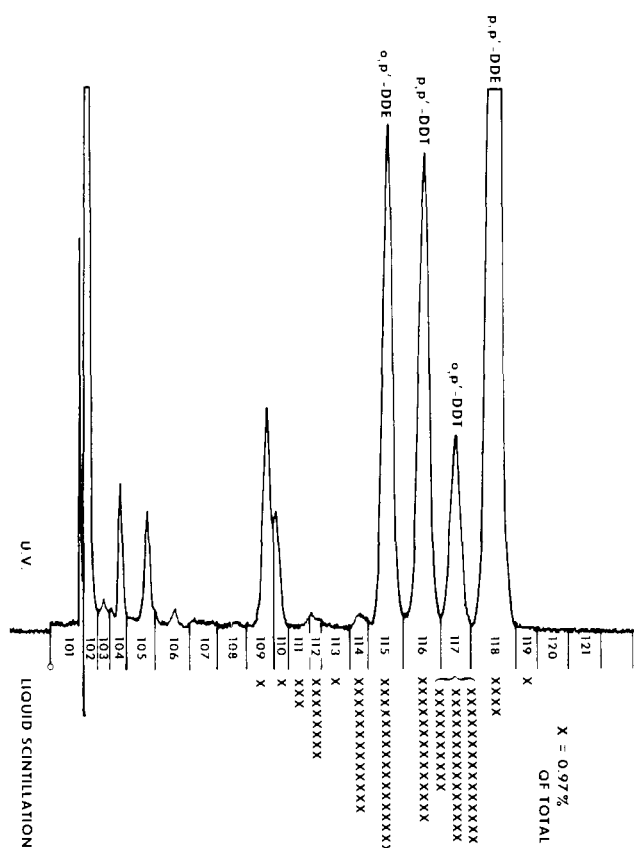


Figure 2. High-performance LC vapor analysis.

Table I. Vapor Pressure of *p,p'*-DDT at Different Temperatures

temp, °C	vapor pressure, torr	95% confidence limits
20	$2.2 \times 10^{-7}$	$1.7 \times 10^{-7}$ to $2.8 \times 10^{-7}$
25	$4.3 \times 10^{-7}$	$3.5 \times 10^{-7}$ to $5.1 \times 10^{-7}$
30	$9.3 \times 10^{-7}$	$7.9 \times 10^{-7}$ to $1.1 \times 10^{-6}$
40	$4.0 \times 10^{-6}$	$3.6 \times 10^{-6}$ to $4.5 \times 10^{-6}$
50	$1.5 \times 10^{-5}$	$1.4 \times 10^{-5}$ to $1.6 \times 10^{-5}$
60	$4.8 \times 10^{-5}$	$4.3 \times 10^{-5}$ to $5.5 \times 10^{-5}$
70	$1.5 \times 10^{-4}$	$1.3 \times 10^{-4}$ to $1.7 \times 10^{-4}$
80	$4.5 \times 10^{-4}$	$3.7 \times 10^{-4}$ to $5.6 \times 10^{-4}$

a crucial parameter in this case since the *p,p'*-DDT content of the extract was still 14% in both cases. It is possible, however, that this would not be the case for other systems.

A graph of  $\log P$  vs.  $1/T$  was plotted (see Figure 3) by a least-squares fit to the data. The final calculated vapor pressure results at incremental temperatures from 20 to 80 °C are tabulated in Table I. Also included are the 95% confidence limits as determined by a SAS (statistical analysis system) General Linear Model computer program (Barr et al., 1976).

Figure 4 plots the *p,p'*-DDT vapor pressure determination of this paper and four other researchers (Balson, 1947; Dickinson, 1956; Kuhn and Massini, 1949; Spencer and Cliath, 1972).

The results of Spencer and Cliath clearly demonstrate that the composition of the vapor must be determined to accurately quantitate the total pressure. They determined that the vapor pressure of *o,p'*-DDT, a major contaminant in technical DDT, is 7.5 times that of *p,p'*-DDT. The vapor pressure of *p,p'*-DDE, a minor contaminant in technical DDT, is 8.9 times that of *p,p'*-DDT. Therefore, although *o,p'*-DDT and *p,p'*-DDE would presumably be present at low levels in pure *p,p'*-DDT, their vapor pressures are almost ten times that of *p,p'*-DDT and would be

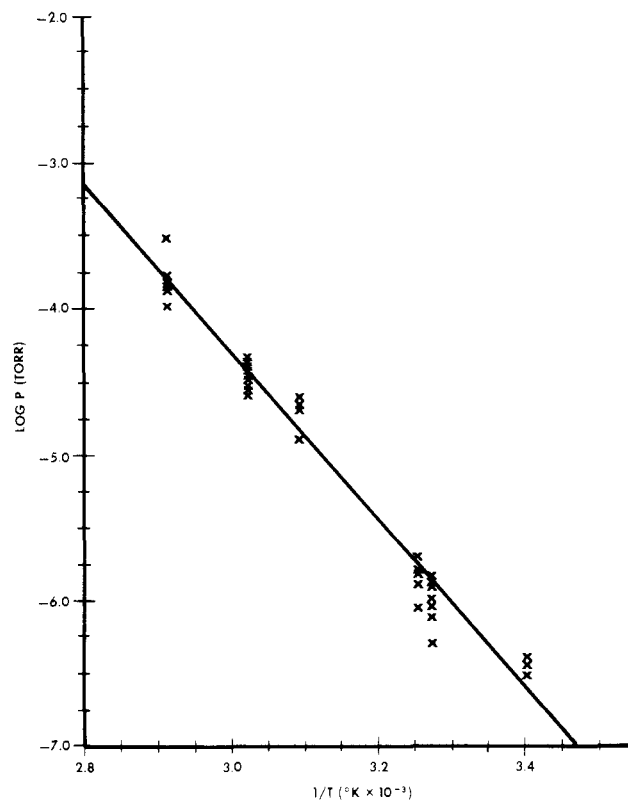


Figure 3. *p,p'*-DDT vapor pressure.

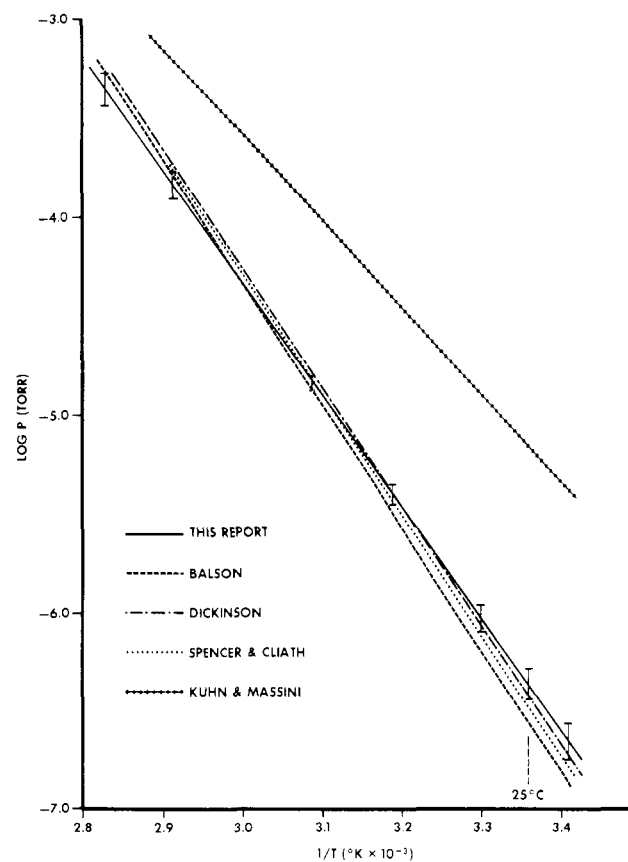


Figure 4. *p,p'*-DDT vapor pressure studies,  $\log P$  vs.  $1/T$ .

present in the vapor at a level greatly disproportionate to the chemical purity.

Dickinson, whose results agree with Spencer and Cliath's, determined vapor composition spectrophotometrically. Kuhn and Massini, whose results do not agree,

did no compositional determination. They began with what they felt was very pure *p,p'*-DDT and performed a eutectic melting point of the condensed DDT vapor. On the basis of Spencer and Cliath's vapor pressure values for *p,p'*-DDT and *p,p'*-DDE, it seems evident that Kuhn and Massini were measuring the vapor pressure of a composite mixture.

In this light it seems quite remarkable that Balson, who never determined the impurity level of his *p,p'*-DDT, should agree so well with those who were able to make this necessary correction. His sample must fortunately have been extremely pure.

My *p,p'*-<sup>14</sup>C]DDT was 96% radiopure, containing only 2.1% *o,p'*-DDT and 0.2% *p,p'*-DDE, but high-performance LC analyses showed that *p,p'*-DDT was only about 14% of the vapor collected. Before correcting for the compositional makeup of the vapor, the gross combustion results agreed fairly well with Kuhn and Massini's results. After correcting for the impurity composition, however, my results fell more in line with the others.

We would have preferred using a purer sample of [<sup>14</sup>C]DDT, but this sample was apparently available at the state of the art purity. Although it was claimed to be greater than 98% by our supplier, our high-performance LC analysis method, where we assayed in a similar fashion to our extract studies, indicated lower purity. We obtained samples of [<sup>14</sup>C]DDT from other nuclear suppliers and found radiopurities of 50% and 92%. Obviously the conventional TLC/autoradiograph analysis method is unsatisfactory in this case.

We also would have liked to have studied another tagged compound for calibration purposes, but DDT was really the only candidate which was (1) readily available for purchase and (2) sufficiently studied and reported in the literature.

The slope of  $\log P$  vs  $1/T$  for this work is a little lower than the others, but the curve crosses the others at about 40 °C and the results are comparable in the range of environmental temperatures.

Although this slope difference may suggest incomplete equilibration of the vapor from the sand, this seems unlikely to be the case since runs performed at 78 °C with a 10 mL/min flow rate are the same as for a 50 mL/min flow rate. Although Spencer and Cliath used a very low flow rate of 3.5 mL/min, Dickinson's flow rates were in the range of 20–150 mL/min. Since we observed no flow rate dependency in the range of 10–100 mL/min in this work and other similar studies, equilibration is likely not the problem.

This difference in slope may just be a reflection of the error in the vapor composition analysis. If the percent composition of DDT in the vapor were indeed lower at 36 °C, then the slope would be increased.

A useful physical constant to be calculated from the vapor pressure data is the heat of sublimation. Over a short range the heat of sublimation can be calculated by using

$$\Delta H \text{ (cal/mol)} = -(\text{slope})(2.303)(1.987)$$

A summary of the  $\Delta H$  sublimation for *p,p'*-DDT is given in Table II. Included in the table is the slope used for calculation.

When the wide disparity of published data on pesticide vapor pressures, where discrepancies of orders of magnitude are found, is considered, the gas saturation (transpiration) method seems to have the potential of close agreement if vapor compositional analysis is performed.

The radiotracer technique reported here is a time saver since it cuts down on the number of chromatographic

Table II. Heat of Sublimation for *p,p'*-DDT

experimenter	slope	$\Delta H_{\text{sub}}$ , cal/mol
Kuhn and Massini	-4400	20 000
Dickinson	-6000	27 500
Balson	-6200	28 200
Spencer and Cliath	-6200	28 300
this work	-5700	26 200

analyses and gives greater assurance of quantitative vapor collection.

We performed 3 to 4 combustion collections a day and we were able to collect vapor at room temperature. Dickinson's work was done in the range of 50–90 °C, Kuhn and Massini's in the range of 40–90 °C, Balson's in the range of 66–100 °C. Spencer appears to have gone down to 30 °C, but his paper suggests that it took 10 days to collect enough vapor for analysis. Therefore, we should have a lower detection limit and greater confidence in determinations performed at environmental temperatures.

The great advantage here is that we have added sensitivity for nonvolatile compounds which melt at fairly low temperatures, such as within the range of temperatures used to measure DDT.

Additionally, if higher specific activity labeled compounds were used, the limit of detection can be greatly increased over that of conventional methods. Although we did not try it, one could decrease the specific activity loss by diluting with less untagged material and coat the bed with a smaller amount of material. Alternatively, one could obtain higher specific activity material from the supplier.

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