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Journal of Chromatography A, 749 (1996) 123–129

JOURNAL OF
CHROMATOGRAPHY A

New method for estimating vapor pressure by the use of gas chromatography

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Received 18 October 1995; revised 23 April 1996; accepted 23 April 1996

Abstract

We have developed a new, simple, quick, precise and inexpensive method to estimate vapor pressure by the use of gas chromatography. This new method differs significantly from previous gas chromatography methods because it uses a temperature gradient rather than a series of isocratic experiments extrapolated back to room temperature using the Clausius–Clapeyron equation. In addition, it uses a typical methyl silicone capillary column rather than a short (1 m) non-polar capillary. To improve reproducibility of results between different instruments, a cocktail containing two standards with well-established vapor pressures is injected along with the sample compound(s). The vapor pressure at 25°C of the compound(s) in the liquid state is determined by simply finding the retention times of the compound(s) and those of the two standards. Corrections can be made for crystalline compounds. This method can be used for the measurement of the vapor pressures of organic compounds ranging from 10^2 to 10^{-7} Pa at 25°C (1 mmHg to 10^{-9} mmHg).

Keywords: Vapor pressure; Alkanes; Herbicides; Insecticides; Pesticides

1. Introduction

The vapor pressure of a substance is the pressure of the vapor phase of either a solid or a liquid under equilibrium conditions at a specified temperature. It can be used to estimate the rate at which it will volatilize from plant surfaces, soil and/or water. The vapor pressure is used to calculate the air–water partition coefficient (Henry's Law constant), which is used in turn to estimate the rate of volatilization from surface water to the atmosphere [1].

Vapor pressure measurements are generally carried out by the isoteniscope (i.e. ASTM D2879-75), dynamic, static, vapor pressure balance or the gas saturation (i.e. ASTM E1194-87) methods. The choice of method is dependent on the vapor pressure of the compound. The gas saturation method can

measure pressures as low as 10^{-7} Pa. The dynamic, static and isoteniscope methods can be used for impure substances, although the impurities will affect the results. The vapor pressure balance and the gas saturation method are only applicable to pure substances. The measured results are plotted in a log p versus $1/T$ graph and yield rectilinear curves for the temperature range. The estimated repeatability of the gas saturation method is 10–30% and the estimated reproducibility is up to 50% [2]. As such, it is not a particularly precise measurement and the values are somewhat method-dependent. Thus, the literature vapor pressure values can vary considerably. When attempting to correlate the estimated vapor pressures generated by the GC technique described in this report with those in the literature, it is difficult to decide what is the true vapor pressure

when there can be so many different reported values for a given compound.

For pesticides, most vapor pressures are reported at 25°C, some are reported at 20°C, and still others are reported at 0°C. We have chosen to estimate the vapor pressure at 25°C, although in principle this method could be adapted to other temperatures. The pressure at 25°C can be approximately 1.5–2 times that of the pressure at 20°C, depending on the nature of the compound. There are many units that are used to express vapor pressure, the two most common being Torr (mmHg) and Pascal (either kPa, Pa, mPa or nPa) (1 Torr=133.322 Pascal). There are a number of alternative methods for measuring the vapor pressure, including measuring droplet evaporation rates using Mie resonance spectroscopy [3–7], coupled gas saturation GC [8] and dynamically coupled gas saturation HPLC [9]. Previous methods of estimating the vapor pressure using gas chromatography are available. They typically use a short non-polar capillary column, i.e., 1 m long, run isothermally at a series of temperatures, with values extrapolated back to room temperature using the Clausius–Clapeyron equation [10–18].

2. Experimental

2.1. Apparatus

The gas chromatograph used was a Hewlett-Packard 5890 Series 2 using 20 ml/min helium as the carrier gas and FID detection. The column was run in an on-column mode. The column was a Megabore DB-1 capillary column with a 1.5- μ m bonded methyl silicone stationary phase and a maximum temperature of 332°C (15 m \times 0.53 mm I.D., Cat. No. 125-1012, J&W Scientific, Folsom, CA, USA). Among others, the DB-1 column is similar to an OV-1 or a SE-30 column. Retention times were determined on a Hewlett-Packard HP 3365 Chem-Station.

2.2. Reagents

The compounds were obtained from various commercial sources and used as received, except for terbufos (13071-79-9), flucythrinate (70124-77-5)

and pendimethalin (40487-42-1) which were obtained from the American Cyanamid Research Center (Princeton, NJ, USA) and the mixture of C₁₀ to C₄₀ *n*-alkanes which was obtained as “crude oil quantitative mix” (Cat. No. 4-8179 from Supelco, Bellefonte, PA, USA).

2.3. Chromatographic conditions

The temperature program was 50°C for 2 min followed by heating at 10°C/min to the maximum temperature (usually 250°C), then holding at the maximum temperature for 5 min. The maximum temperature was raised to 315°C for compounds of very low volatility (i.e. 10⁻⁶ to 10⁻⁷ Pa). It is very important to have all compounds of interest elute while the column is still in the heating mode. A cocktail of 1 g of di-*n*-butylphthalate (DBP), 1 g of bis-2-ethylhexyl phthalate (DEHP) and 200 g of ethyl acetate was prepared. Approximately 1 mg of the compound(s) and 1 ml of the cocktail were mixed and then 1 μ l was injected.

3. Results and discussion

The method reported here of estimating vapor pressure from gas chromatography differs from published methods in a number of ways: It uses the conditions typically found on a capillary gas chromatograph, namely, a normal 20 ml/min flow-rate of helium on a 15 m methyl silicone-bonded capillary column [not an abnormally high flow-rate (50–60 ml/min) on a 1–2 m column]. In addition, instead of a series of isothermal runs followed by extrapolation to 25°C using the Clausius–Clapeyron equation, a 10°C/min temperature gradient is employed.

Methyl silicone columns are often known as “boiling point columns”. They separate compounds based mainly on their boiling point, ideally with no observable acid–base, polar or π -interactions. The first task was to demonstrate that the DB-1 column was indeed functioning as a “boiling point column”. A mixture of linear alkanes [19] with known boiling points [20] was injected and the retention times measured. A plot of the literature boiling point versus the retention time showed excellent linearity,

with an $r^2=0.999913$. This demonstrated both good column characteristics and a good linear temperature gradient. A complicating factor for measuring the vapor pressure of solid compounds is that the vapor pressure measured by GC methods is actually the vapor pressure of the subcooled (or supercooled) liquid. The vapor pressure, P_S , will be lower than that of the subcooled liquid, P_L , by the factor of the fugacity ratio P_S/P_L . This ratio has previously been shown to be expressed by Eq. (1) [21]:

$$\text{Correction ratio} = \frac{P_S}{P_L} = \exp \left[\frac{S_f}{R} \left(1 - \frac{T_M}{T} \right) \right] \quad (1)$$

where T_M is the melting point (K), T is the temperature of interest (K), and S_f/R is the entropy of fusion divided by the ideal gas constant, which is equal to 6.79 in most cases. The value of 6.79 is an average empirical constant, but it may be in error for certain compounds. When needed, a more realistic value for the entropy of fusion can readily be determined by differential scanning calorimetry (DSC).

The next task was to show the relationship of vapor pressure to retention time. This required the measurement of retention times of a series of compounds of known vapor pressure (shown in Fig. 1). In the instances where the compound was a solid, the vapor pressure was converted to the vapor pressure of the subcooled liquid by Eq. (1).

It appeared that the relationship was diverging at vapor pressures less than 10^{-6} Pa, since both pyrethroids, flucythrinate and cypermethrin, were predicted to be more volatile than the literature values suggest. Two points should be made; the first point is that there is considerable error in making measurements at these low pressures and the second point is that the 95% confidence intervals are quite wide. Two of the cited cypermethrin values differ by 45%, yet are well within the 95% confidence interval [11]. Additionally, we found a literature value much closer to our predicted value of 2.8×10^{-6} Pa. The P_L° value for cypermethrin was determined to be 2.4×10^{-6} Pa at 25°C by Hinckley et al. [18] employing a much more complicated gas chromatographic method.

Since we have established that the log of the vapor pressure is proportional to the retention time, the retention time of compounds with unknown vapor

pressure can be determined. Two internal standards [di-*n*-butyl phthalate (DBP) and bis-2-ethylhexyl phthalate (DEHP)] with well-established vapor pressures were chosen to assure accuracy and repeatability. Since these compounds were both liquids, their vapor pressures did not need to be corrected as in the case of a solid. The literature vapor pressure values used for the standards were:

Di-*n*-butyl phthalate (DBP):

2.67 mPa (2.00×10^{-5} mmHg) at 25°C [11]

Bis-2-ethylhexyl phthalate (DEHP):

0.0190 mPa (1.43×10^{-7} mmHg) at 25°C [18]

Since it appeared that the plot of the \log_{10} of the vapor pressure versus the retention time was a straight line, the vapor phase of the unknown could be easily determined using the known vapor pressures of DBP and DEHP and the experimentally determined retention times of the unknown, DBP and DEHP. Let $(t_1, \log P_1^\circ)$ and $(t_2, \log P_2^\circ)$ be (x, y) points on the straight line $\log P^\circ = mt_R + b$, where $\log P^\circ$ is the log of the vapor pressure, t_R is the retention time, m is the slope, and b is the y intercept:

$$\log P^\circ = mt_R + b$$

By the definition of slope and intercept:

$$\log P^\circ = \left(\frac{\log P_1^\circ - \log P_2^\circ}{t_1 - t_2} \right) t_R + \left(\frac{t_1 \log P_2^\circ - t_2 \log P_1^\circ}{t_1 - t_2} \right)$$

Simplification gives:

$$\log P^\circ = \frac{(\log P_1^\circ - \log P_2^\circ)t_R + t_1 \log P_2^\circ - t_2 \log P_1^\circ}{t_1 - t_2}$$

When DBP and DEHP are chosen as the two vapor pressure standards, the vapor pressure of an unknown(s) is simply found by substitution of the appropriate retention times and vapor pressures:

$$\log P_{\text{Unknown}}^\circ = \frac{(\log P_{\text{DBP}}^\circ - \log P_{\text{DEHP}}^\circ)t_{\text{Unknown}} + t_{\text{DBP}} \log P_{\text{DEHP}}^\circ - t_{\text{DEHP}} \log P_{\text{DBP}}^\circ}{t_{\text{DBP}} - t_{\text{DEHP}}} \quad (2)$$

Eq. (2) will also correct for the vagaries in the flow and heating rates. If the carrier flow is slightly more or less than in the previous run, or if the oven is slower or faster in the rate of heating, or if another column with a slightly shorter or longer length was used, the same vapor pressure will be seen. This would come about because the plot of $\log P^\circ$ versus the t_R would still be a straight line. This is especially important in comparing results of this method from other instruments with greater confidence. While a single GC run is sufficient to estimate the vapor pressure of an unknown, additional runs will assure the precision of the measurement.

Based on this method, comparison of predicted vapor pressures with those found in the literature can now be made (Table 1). It can be seen that the $-\log P_{GC}^\circ$ compared favorably to the literature $-\log P_L^\circ$ values over nine orders of magnitude, giving an r^2 of 0.97 and a standard error of 0.35 $-\log P^\circ(\text{Pa})$ units. The precision of this method gave values of ≤ 0.01 $-\log P^\circ(\text{Pa})$ units. Hexachlorobenzene is an example where the correction factor is likely to be in error because the value of 6.79 (S_t/R) by Eq. (1) is probably in error. To get a better estimate of the

vapor pressure of crystalline solids with high melting points, one would need to measure the entropy of fusion by DSC. Fig. 2 gives a plot of the residuals from the $-\log P_{GC}^\circ$ minus the literature $\log P_L^\circ$ values.

An interesting example of this method was found when flucythrinate (Pay-off[®]) insecticide was injected in the gas chromatograph. Two separate peaks were observed [(*R,S*) and (*S,S*) esters]. One of the esters was found to be about 15% less volatile than the other (2.7×10^{-6} Pa versus 2.3×10^{-6} Pa), a difference that could not be detected with direct vapor pressure measurements unless pure compounds were available. Even then, uncertainties in those methods ($\pm 30\%$) would preclude the unambiguous determination of which ester was more volatile and by what factor.

4. Conclusion

A simple, quick, versatile and inexpensive method employing a gas chromatograph using less than 1 mg of sample has been developed for vapor pressure determinations and permitting the measurement of the vapor pressures of organic compounds ranging from 10^2 to 10^{-7} Pa at 25°C (1 mmHg to 10^{-9} mmHg). Those interested in vapor pressure values, and especially those involved in the measurement of vapor pressure, should consider using this method to give a rapid estimate of vapor pressure. Care should be taken when predicting the vapor pressure of solids with high melting points, since the 6.79 value from Eq. (1) is an *average* empirical constant related to the entropy of fusion and may be in error for certain compounds. This error, when present, will more seriously affect the apparent vapor pressure of high melting point compounds. In those cases, the entropy of fusion would have to be measured by DSC to obtain a more realistic value. This method is limited to those compounds that are stable to heat. For example, the carbamate pesticides will decompose to the parent phenols and isocyanates in the injector of the gas chromatograph.

Considering the wide variety of compounds represented in this paper, (alkanes, amides, esters, aromatic hydrocarbons, nitrobenzenamines, polychlori-

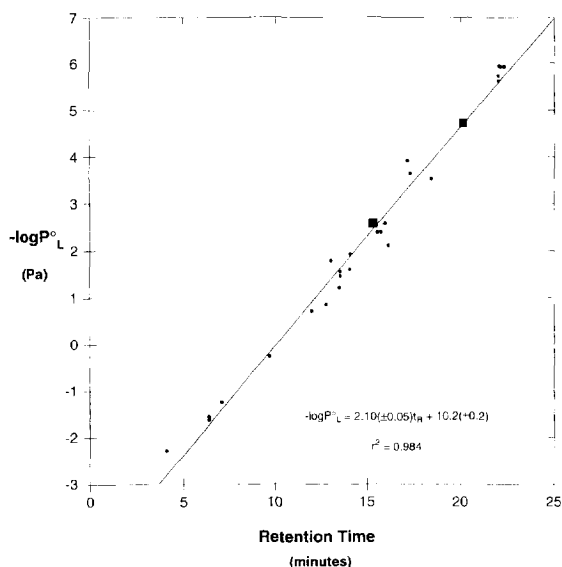


Fig. 1. Comparison of typical retention times with literature values of the vapor pressure in the liquid state at 25°C taken from Table 1. The P_S° values were converted to P_L° values by the use of Eq. (1). The 95% confidence intervals are shown as dotted lines. The solid squares are DBP and DEHP chosen to be the reference compounds in Eq. (2) that were used to generate the P_{GC}° values.

Table 1
Gas chromatograph-vapor pressure data

Compound	Typical t_R (min)	Melting point (°C)	Correction factor	$-\log P_{GC}, Pa^a$	$-\log P_L, Pa$ (Lit.)	$-\log P_S, Pa$ (Lit.)	$-\log P_L, Pa$ (Lit., conv.) ^b	Difference (found – Lit.)	Ref.
<i>n</i> -Decane	4.056	oil		-2.51	-2.26			-0.25	[23]
Naphthalene	6.374	80		-1.38	-1.62			0.24	[16]
Naphthalene	6.374	80	0.29	-1.38		-1.01	-1.56	0.18	[9]
<i>n</i> -Dodecane	7.084	oil		-1.15	-1.25			0.10	[23]
<i>n</i> -Tetradecane	9.689	oil		0.02	-0.26			0.29	[23]
<i>n</i> -Hexadecane	11.992	oil		1.06	0.71			0.35	[23]
Hexachlorobenzene	12.781	230	0.010	1.47		2.84	0.85	0.62	[27]
Trifluralin	13.021	49	0.58	1.44		2.02	1.78	-0.35	[24]
Anthracene	13.493	216	0.013	1.79		3.10	1.21	0.57	[9]
Fonofos	13.544	oil		1.76	1.55			0.20	[24]
Terbufos	13.548	oil		1.76	1.46			0.29	[24]
<i>n</i> -Octadecane	14.065	oil		1.99	1.59			0.40	[16]
Diazinon	14.070	oil		1.91	1.92			-0.01	[24]
Dibutyl phthalate	15.288	oil		2.57	2.57			0.00	[11]
Malathion	15.486	oil		2.62	2.54			0.08	[25]
Metolachlor	15.522	oil		2.64	2.38			0.27	[24]
Chlorpyrifos	15.719	42	0.68	2.66		2.57	2.40	0.26	[24]
Eicosane	15.949	37		2.84	2.58			0.26	[16]
Pendimethalin	16.107	54	0.52	2.91		2.40	2.11	0.80	[24]
Profenofos	17.130	oil		3.36	3.91			-0.55	[24]
Dieldrin	17.313	95	0.20	3.49		4.33	3.64	-0.15	[16]
<i>p,p'</i> -DDT	18.438	108	0.15	3.98		4.36	3.53	0.45	[26]
bis-2-Ethylhexyl phthalate	20.120	oil		4.72	4.72			0.00	[18]
Cypermethrin	22.013	80		5.56	5.62			-0.06	[18]
Cypermethrin	22.013	80	0.29	5.56		6.27	5.73	-0.16	[13] ^c
Cypermethrin	22.013	80	0.29	5.56		6.48	5.94	-0.37	[13] ^d
Flucythrinate #1	22.086	oil		5.57	5.92			-0.35	[24]
Flucythrinate #2	22.275	oil		5.66	5.92			-0.26	[24]

^a Average value based on at least three runs.

^b When the literature P_S° was used, it was converted to the P_L° by the equation correction factor.

^c ICI data.

^d Shell data.

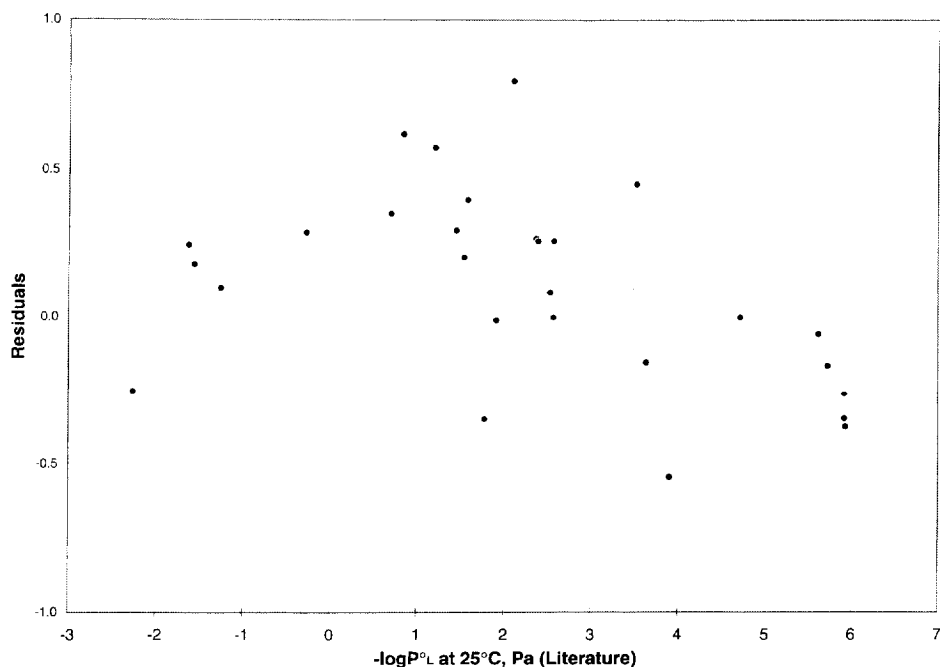


Fig. 2. Plot of vapor pressure found vs. literature residuals.

nated aromatic hydrocarbons, polychlorinated pyridyl phosphorothioates, alkyl phosphonodithioates and pyrethroids), the standard error of $0.35 \log P^\circ$ Pa units over nine orders of magnitude of pressure may not be so bad. There are a number of factors that can contribute to the differences seen in the predicted versus the literature values of the vapor pressure. There may be deviation from ideal behavior by some of the compounds on the non-polar column, some of the literature vapor pressure measurements are likely to be in error, and for solids the value of S_f/R may not be 6.79. For optimal accuracy, standards other than DBP and DEHP could be considered. They should be in the same chemical class as the compound(s) of interest. They should have well determined vapor pressures and they should well bracket the vapor pressure range of interest. In this way, if there is non-ideal behavior on the non-polar column, it should be somewhat constant throughout the same series of compounds. Likewise for solids, the correction for differences in the entropy of fusion

within a series of compounds should be somewhat constant as well. Thus, when this technique is applied to a new series of analogs, the vapor pressures can quickly be determined and the compounds ranked with good certainty and also with minimal effort and expense.

The measurements of physicochemical parameters, such as water solubility, $\log P_{ow}$ and vapor pressure are now an integral part of environmental exposure assessments since they provide considerable insight into how a chemical will be transported in the environment [23]. Researchers interested in vapor pressure for QSAR or field trials of new pesticides should consider using this method to rapidly estimate vapor pressure in order to avoid unfortunate and expensive surprises during the field trials. It is not recommended that this method supersede the traditional vapor pressure method for generating vapor pressure values for registration purposes. However, even in those cases, it can be used as a check for the validity of those vapor pressure values.

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