

Review

Determination of vapor pressures using gas chromatography

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Abstract

The determination of vapor pressures, p^0 , of compounds with low vapor pressures (10^{-8} Pa $<$ p^0 $<$ 10^3 Pa) is becoming increasingly important as a result of the need to measure p^0 for environmentally sensitive compounds such as organophosphorus pesticides, biphenyls, dioxins and alkylbenzenes. Under strict conditions, the components of gas–liquid chromatography (GLC) (a volatile solute, an involatile solvent and a mobile carrier gas) are in equilibrium and as a result it is possible to use the technique to measure equilibrium properties such as vapor pressure. The technique is rapid, reliable and reproducible. These advantages have tempted many workers to measure physicochemical properties, including vapor pressures, under conditions for which the basic theories do not hold. In this review, the GLC techniques used to measure vapor pressures from GLC data together with the basic theory, limitations of the techniques and some recent measurements are discussed.

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Contents

1. Introduction	107
2. GLC retention volume techniques	108
3. Theory	108
4. Limitations and errors	110
4.1. Gas imperfections	110
4.2. Sample size	110
4.3. Adsorption	110
4.4. Activity coefficients	110
5. Results and discussion	110
6. Other GLC methods	112
7. Conclusions	113
Acknowledgements	113
References	113

1. Introduction

The measurement of vapor pressures, p^0 , of organic compounds used industrially and in particular environmentally

significant organic chemicals, is becoming increasingly important as a result of forceful environmental lobbies in most countries today [1–4]. For volatile substances ($p^0 > 1$ kPa), well tried and direct methods (e.g. manometric methods) are available [5–7]. Unfortunately, most organic compounds which are considered as potential pollutants, have very low vapor pressures. Typical classes of compounds of this type are given in Table 1. The measurement of these low vapor

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Table 1

Typical classes of compounds considered to be potential environmental pollutants, together with their vapor pressure range p^0 , at 25 °C

Chemical class	p^0 (Pa)
Polychlorinated biphenyls (PCBs)	10^{-8} to 10^{-1}
Polycyclic aromatic hydrocarbons (PAHs)	10^{-7} to 20
Polychlorinated dibenzo- <i>p</i> -dioxans	10^{-10} to 10^{-6}
Polychlorinated dibenzofurans (PCDFs)	10^{-10} to 10^{-6}
Organochlorine and organophosphorus pesticides	10^{-5} to 10^{-2}
<i>p,p'</i> -DDT	1.2×10^{-4}
Dieldrin (CAS 60-57-1)	3.6×10^{-4}

pressures are however very much more difficult and more unreliable than the measurement of p^0 of more volatile substances. No one method is able to measure p^0 over the whole spectrum of pressures [8]. A list of direct and indirect techniques used today to measure vapor pressures, and the limiting range of each technique, is given in Table 2. The available methods have recently been reviewed by Site [18].

The importance of vapor pressure measurements in modeling the fate of organic chemicals in the environment has been demonstrated by many workers [19–21]. Vapor pressures, p^0 , together with water solubilities, S , Henry's law constants H , distribution coefficients and partition coefficients are some of the necessary parameters needed to predict the distribution of organic chemicals in the environmental compartments of air, water, sediments, soil, aerosols, animal and plant biota [19]. Vapor pressure and water solubility are the two fundamental properties as the others can be derived from them, and both can be combined [18,22–25] to calculate the Henry's law constant:

$$H = \frac{p^0}{S}. \quad (1)$$

A number of gas–liquid chromatography (GLC) techniques have been used to measure vapor pressures. These include an adsorption process followed by GLC analysis, headspace sampling followed by GLC analysis, GLC solvent evaporation and retention volume methods. It is the latter set of methods that have become very popular and is the focus of this review. The other methods will be discussed briefly, at the end of this review, in Section 6.

Table 2

Methods for the determination of vapor pressures, p^0 and their ranges

Method	Reference	Range of p^0 (Pa)
Gas saturation	[6]	10^{-8} to 10^4
Effusion	[10]	10^{-5} to 10^{-1}
Manometry	[5–11]	1 – 10^5
GL solute retention	[12–14]	10^{-8} to 10^{-1}
GLC solvent evaporation	[15]	10^{-5} to 10^2
Relative volatilization	[16,17]	10^{-5} to 10^{-1}

2. GLC retention volume techniques

The use of GLC retention volume methods, to determine a range of physicochemical properties (including vapor pressures) has been developed over the past 60 years. The techniques offer great advantages of speed, small sample size, purity, stability and reproducibility. As GLC involves an equilibrium between a volatile solute, an involatile solvent and a mobile and inert carrier gas, it is not surprising that simple relationships exist between chromatographic properties such as retention volume or retention time and physical properties such as solute vapor pressure, boiling points, enthalpy of vaporization, molar mass, activity coefficients and even solute molecular geometry [26,27]. One of the notable successes in the latter area was due to Matukama [28] who reported discrepancies between API listed boiling points [29] and those he had obtained from GLC retention data. This work was later extended by Walravan and Ladon [30] who found further errors in the API tables and on the basis of their GLC work the geometric configuration of some hydrocarbons were corrected [31].

Unfortunately, not all GLC derived physicochemical properties have been so successfully related. The strength of these techniques lies in the proper understanding of the theory behind the GLC measurements.

3. Theory

The thermodynamics of GLC was developed in 1950s and 1960s by a number of workers including Martin and Synge [32], Martin and James [33], Everett [34] and Cruickshank et al. [35]. A very basic equation relating the net solute retention volume V_N at temperature T , to the activity coefficient at infinite dilution, γ_{13}^∞ , of the solute (subscript 1) in a solvent (subscript 3), is given by [36]:

$$V_N = \frac{RTw_3}{\gamma_{13}^\infty p_1^0 M_3} = J_3^2 (t'_R - t'_G) u_0, \quad (2)$$

where w_3 is the mass of solvent on the GLC column and M_3 its molar mass, p_1^0 is the solute vapor pressure at temperature T , t'_R and t'_G are the retention times of the solute and unretained air sample, respectively, u_0 is the flow rate of the carrier gas (usually Ar, He or N₂) measured at the exit of the GLC column and J_3^2 (the pressure drop across the column) can be inferred from:

$$J_n^m = \frac{n (p_i/p_o)^m - 1}{m (p_i/p_o)^n - 1}, \quad (3)$$

where p_i and p_o refer to the column inlet and outlet pressure, respectively.

A more exact equation which takes into account the solute–carrier gas imperfections, was developed by Everett and Stoddart [37] and Cruickshank and co-workers [38–40]:

$$\ln V_N = \ln V_N^0 - \frac{(\beta_{11} - V_1^0) p_1^0}{RT} + \frac{2(\beta_{12} - V_1^0) p_o J_3^4}{RT}, \quad (4)$$

where $V_N = J_3^2(t'_R - t'_G)u_0$,

$$V_N^0 = \frac{RTw_3}{\gamma_{13}^\infty p_1^0 M_3}, \quad (5)$$

β_{11} and V_1^0 refer to the solute variable coefficient and molar volume at temperature T , β_{12} refers to the mixed variable coefficient for the solute and carrier gas (subscript 2) and J_3^4 is given by Eq. (3).

Eqs. (2) and (4) are based on the assumption that the only physical processes allowed during the chromatographic experiment are dissolving of the solute in the involatile liquid solvent and the subsequent evaporation of the solute from the solvent as the carrier gas sweeps the solute along the column. It is also assumed that no surface adsorption takes place. Eq. (4) was developed with the aim of determining accurate activity coefficients at infinite dilution and is used extensively [41]. It can, of course, also be used to determine solute vapor pressures, p_1^0 , assuming that the activity coefficient, γ_{13}^∞ is known. It is however Eq. (2), which is used by many workers to determine p_1^0 . It is usually expressed as:

$$V_g^T = \frac{RT}{\gamma_{13}^\infty p_1^0 M_3}, \quad (6)$$

where V_g^T is the retention volume of species 1, per gram of solvent at temperature T [42], or as:

$$V_g = \frac{273.15R}{\gamma_{13}^\infty p_1^0 M_3}, \quad (7)$$

where V_g is known as the specific retention volume at 273.15 K [43,44]. This can be related to the net retention volume, V_N , by:

$$V_g = \frac{273.15V_N}{Tw_3}. \quad (8)$$

From Eq. (8) or (2), it can be shown that for two solutes (a standard reference, s, and an unknown solute x) passing down the same GLC column at the same temperature:

$$\frac{t_x}{t_s} = \frac{\gamma_s^\infty p_s^0}{\gamma_x^\infty p_x^0}, \quad (9)$$

where t_i refers to the net retention time: $t_i = t'_R - t'_G$ as in Eq. (2).

Eq. (9) was established by Herrington in log form in 1957 [12]:

$$\log\left(\frac{t_x}{t_s}\right) = \log\left(\frac{p_s^0}{p_x^0}\right) + \log\left(\frac{\gamma_s^\infty}{\gamma_x^\infty}\right). \quad (10)$$

The ratio in the last term of Eq. (10) is usually not known and many workers have assumed that if the solvent is a non-polar substance, this term approximates to unity and:

$$\frac{t_x}{t_s} = \frac{p_s^0}{p_x^0}. \quad (11)$$

Thus, from a knowledge of retention times for solutes s and x, together with the vapor pressure of s, it is possible to determine p_x^0 .

Very often GLC measurements are made at temperatures very different to the one required for vapor pressure determination. Hamilton [45] solved the problem by incorporating the Clausius–Clapeyron relationship involving enthalpies of vaporization $\Delta_{\text{vap}}H_i^\circ$ into Eq. (11) and arriving at:

$$\ln\left(\frac{t_x}{t_s}\right) = \left(1 - \frac{\Delta_{\text{vap}}H_x^\circ}{\Delta_{\text{vap}}H_s^\circ}\right) \ln p_s^0 - C \quad (12)$$

and

$$\ln(p_x^0)_{298} = \left[\left(\frac{\Delta_{\text{vap}}H_x^\circ}{\Delta_{\text{vap}}H_s^\circ}\right) \ln p_s^0\right]_{298} + C. \quad (13)$$

Thus, from a plot of $\ln(t_x/t_s)$ versus $\ln p_s^0$ at different temperatures, it is possible to obtain a value for $(\Delta_{\text{vap}}H_x^\circ/\Delta_{\text{vap}}H_s^\circ)$ and a value for C , both of which can be incorporated into Eq. (13) to determine p_x^0 at a defined temperature, which could be 298 K.

The Kovats' index, I , [46] has been related to physicochemical properties including mixed variable coefficients [47] and vapor pressures. The main justification for relating I to p_1^0 is given below. Other considerations are that I is less dependent on changes in experimental conditions than other GLC properties; I is only weakly temperature dependent and that a large number of I values are available in the literature. The relationship between I and p_i^0 is usually done through equations of the type:

$$\log p_s^0 = a \times I_s + b. \quad (14)$$

Once I_s and p_s^0 values for a number of chemically-related compounds have been measured, a and b can be found through linear regression and the vapor pressures of other members of the family, p_x^0 , can be obtained from a knowledge of I_x . The relationship does appear to correlate some families of compounds. It can be derived from the definition of I [46]:

$$I_x = 100 \times \frac{\log[V_g(x)/V_g(P_n)]}{\log[V_g(P_n+1)/V_g(P_n)]} + 100n, \quad (15)$$

where $V_g(x)$ is the specific retention volume of substance x, P_n refers to a paraffin of the series C_nH_{2n+2} . The quantity $V_g(P_n)$ is chosen such that $V_g(P_n) < V_g(x) < V_g(P_{n+1})$. Usually the retention volumes are replaced by retention times or even distances on a chart recorder.

Because $V_g(i)$ is proportional to $(\gamma_i^\infty p_i^0)$, Eq. (15) can be rewritten as:

$$I_x = 100 \times \left\{ n + \frac{\log[(\gamma_x^\infty p_x^0)/(\gamma_n^\infty p_n^0)]}{\log[(\gamma_{n+1}^\infty p_{n+1}^0)/(\gamma_n^\infty p_n^0)]} \right\} \quad (16)$$

or

$$\log p_x^0 = 0.01I_x - n + \log\left(\frac{p_n \gamma_n^\infty}{\gamma_x^\infty}\right) + \log\left(\frac{\gamma_{n+1}^\infty p_{n+1}^0}{\gamma_n^\infty p_n^0}\right). \quad (17)$$

If it can be assumed that $\gamma_{n+1}^\infty = \gamma_n^\infty = \gamma_x^\infty$, then

$$\log p_x^0 = 0.01I_x - n + \log(p_{n+1}^0). \quad (18)$$

The method is based on the standard reference samples being *n*-alkanes and that the retention time for the unknown compound is chosen so that it lies between the retention times of the *n*-alkanes C_nH_{2n+1} and $C_{n+1}H_{2n+3}$.

A complicating factor in measuring vapor pressures by GLC, is that the GLC experiments are often done at temperatures which are higher than the melting point of the compound under investigation, which in turn is higher than the temperature (usually 25 °C) at which the vapor pressure is required. As a result, for these compounds the vapor pressure, as measured by GLC (p_{GC}^0), is actually the vapor pressure of the sub-cooled (or super cooled) liquid [48]. The magnitude of the vapor pressure of the solid p_{solid}^0 is lower than p_{GC}^0 and Mackay et al. [25] have shown that:

$$\frac{p_{solid}^0}{p_{GC}^0} = \exp\left[\frac{\Delta_f S^0}{R(1 - T_M/T)}\right], \quad (19)$$

where $\Delta_f S^0$ is the entropy of fusion, T_M is the melting point and T is the temperature of interest. Very often $\Delta_f S^0/R$ is assumed to be 6.79.

4. Limitations and errors

4.1. Gas imperfections

The solute and carrier gas imperfection term in Eq. (4) is:

$$A = -\frac{(\beta_{11} - V_1^0)p_1^0}{RT} + 2\frac{(\beta_{12} - V_1^0)p_1 J_3^4}{RT}. \quad (20)$$

And ignoring it can lead to significant errors in the determination of activity coefficients at infinite dilution and other physicochemical properties, which includes vapor pressures. From Eq. (4) it can be shown that:

$$\ln\left[\frac{p_{x(\text{uncorrected})}^0}{p_{x(\text{corrected})}^0}\right] = A. \quad (21)$$

As an example, consider a compound with a vapor pressure of 10^5 Pa, a variable coefficient of $-2000 \text{ cm}^3 \text{ mol}^{-1}$, $V_1^0 = 100 \text{ cm}^3 \text{ mol}^{-1}$ and a β_{12} value of $200 \text{ cm}^3 \text{ mol}^{-1}$ at 300 K.

Substituting these values into Eq. (21) shows that the uncorrected p_x^0 value is in error by 10%. However, for compounds with low vapor pressures ($p_i^0 < 1 \text{ kPa}$), the error in p_i^0 is small and will rarely be greater than 1%.

4.2. Sample size

The derivation of Eqs. (2) and (4) is based on the assumption that the amount of solute traveling along the GLC column is small and in solution approximates to infinite dilution. This can be achieved with solute injections between 0.1 and 1 μl onto a column loaded with solvent amounts between 10^{-3} and 10^{-2} moles, respectively.

4.3. Adsorption

The constraint in the derivation of Eqs. (2) and (4) of NO adsorption of the solute on the solid support is very important. This limits the technique to non-polar solutes [41]. For weakly polar substances, it is usually sufficient to use a high solvent to solid support mass ratio of greater than 0.20. This ensures good coverage of the solid support (usually celite or a silanized diatomaceous earth) but does depend on how well the solvent wets the support. Adsorption effects can be detected by measuring the change of the retention volume per mole of solvent with GLC columns of different solvent to solid support ratios. The property $(V_N M_3)/w_3$ should be independent of column loading (expressed as mass solid support/moles solvent). If not a plot of $(V_N M_3)/w_3$ against the mass of solid support (e.g. celite) per mole of solvent should be made and extrapolated to zero, i.e. infinite coverage [41], in that case Eq. (2) becomes:

$$\left(\frac{V_N M_3}{w_3}\right)_{\text{infinite coverage}} = \frac{RT}{\gamma_{13}^\infty p_1^0}. \quad (22)$$

This equation or an equivalent one related to Eq. (4), can then be used to determine γ_{13}^∞ or p_1^0 . Unfortunately, no measurements of this nature have ever been made to correct vapor pressure measurements from GLC analysis.

4.4. Activity coefficients

Perhaps the largest error incurred in the methods used to determine vapor pressures from Eq. (11) or (14) is the assumption that $\gamma_x^\infty/\gamma_s^\infty$ can be equated to unity. If, however, the standard substance, *s*, is chosen with care, the errors will be small. To give some idea of the possible errors, it is useful to look at the values of activity coefficients at infinite dilution, of some related compounds for which accurate data is known. In Table 3, γ_{13}^∞ for some alkane solutes in solvents squalane, tetracosane and octadecane are given, together with the activity coefficients at infinite dilution for weakly polar chloro-compounds in solvents squalane, dinonylphthalate and ketones or esters or nitriles in squalane or in octadecane. In the table, one substance from each family of related compounds has been chosen as the standard reference substance and the ratio of $\gamma_x^\infty/\gamma_s^\infty$ is calculated for each solute. The results show that on these grounds alone, errors in the determination of vapor pressure can be as high as two-fold. Extrapolation to higher homologues will obviously result in even greater errors.

5. Results and discussion

Kwantes and Rijnders [53] were the first to relate $\ln V_g$ to $\ln p^0$ and showed that a good relationship was possible, provided that the lowest members of a homologous series are avoided, as they usually did not conform.

Table 3

Literature values of activity coefficients at infinite dilution, γ_{xy}^∞ , for temperature T , for a number of related solutes (x) in a non-polar solvent (y)

Solute (x)	Solvent (y)	T (K)	γ_{xy}^∞	$\gamma_{xy}^\infty/\gamma_{sy}^\infty$	Reference			
Hexane	Tetracosane	353.15	0.792	0.90	[49]			
Heptane			0.815	0.93				
Octane			0.849	0.97				
Nonane (s)			0.877	1.00				
Hexane	Octadecane	308.15	0.740	0.91	[50]			
Heptane			0.771	0.95				
Octane (s)			0.813	1.00				
1,1-Dichloroethane	Squalane	313.15	0.820	1.59	[51]			
1,2-Dichloroethane			1.143	2.22				
1,1,1-Trichloroethane			0.586	1.14				
<i>cis</i> -1,2-Dichloroethylene			0.740	1.43				
<i>trans</i> -1,2-Dichloroethylene			0.516	1.00				
Trichloromethane			0.627	1.22				
Dichloromethane			0.830	1.61				
Tetrachloromethane (s)			0.516	1.00				
1,1-Dichloroethane			Dinonylphthalate	313.15		0.453	1.68	[51]
1,2-Dichloroethane						0.460	1.71	
1,1,1-Trichloroethane	0.490	1.82						
<i>cis</i> -1,2-Dichloroethylene	0.301	1.12						
<i>trans</i> -1,2-Dichloroethylene	0.456	1.70						
Trichloromethane	0.332	1.23						
Dichloromethane (s)	0.269	1.00						
Tetrachloromethane	0.581	2.16						
Ethyl acetate	Squalane	353.15			1.27	1.08	[52]	
Isopropyl acetate					1.20	1.03		
<i>n</i> -Propyl acetate (s)			1.17	1.00				
Acetonitrile	Squalane	353.15	6.4	1.45	[52]			
Propionitrile (s)			4.4	1.00				
Acetone	Squalane	353.15	1.93	1.50	[52]			
Methyl ethyl ketone			1.50	1.16				
Cyclopentanone			1.64	1.27				
Methyl isopropyl ketone (s)			1.29	1.00				
Ethyl acetate	Octadecane	353.15	1.86	1.11	[52]			
Isopropyl acetate			1.74	1.04				
<i>n</i> -Propyl acetate (s)			1.68	1.00				
Acetonitrile	Octadecane	353.15	9.7	1.50	[52]			
Propionitrile (s)			6.5	1.00				
Acetone	Octadecane	353.15	2.96	1.57	[52]			
Methyl ethyl ketone			2.20	1.16				
Cyclopentanone			2.46	1.30				
Methyl isopropyl ketone (s)			1.89	1.00				

Within each family, a reference solute, s, has been chosen and the ratio $\gamma_{xy}^\infty/\gamma_{sy}^\infty$ has been calculated.

Hamilton [45] was the first to consider the temperature effect and this has led to many workers using his method [13,14,54–62] which is based on Eqs. (11)–(13). Hamilton determined the vapor pressures of herbicide esters [45] using dibutylphthalate as a standard solute with a non-polar solvent SE30 column. The results were extrapolated to 25 °C and the reported differences with other methods ranged from a factor of 2 to 4. The differences were attributed to the implicit assumption of a constant enthalpy of vaporization but the lack of activity coefficient data should not be overlooked.

One of the earliest workers to take the activity coefficients into account were Castello and D'Amato [63,64]. The activity coefficients were calculated and correlated with the molecular structure involving the position of the carbon atoms and the methyl groups.

Koutek and co-workers have investigated a number of families of pheromone-like compounds which includes alkyl acetates [65,66], alcohols [67] and aldehydes [68]. They have compared their results with vapor pressure measurements by ebulliometric methods and have used *n*-alkanes

as reference standards. Their vapor pressure measurements are within 10% of the ebulliometric results. More recently Koutek et al. [69] embarked on a comparison of four GLC methods used to measure vapor pressures. The methods are as follows:

- (a) Hamilton's method based on Eqs. (11)–(13) [45];
- (b) the method incorporating Kovats' indices, based on Eqs. (14) and (16) [70];
- (c) a method similar to (b) above, but incorporating an estimate of the activity coefficient ratios [71–73]; and
- (d) a method similar to (c) above, but incorporating a temperature dependence term for the Kovats' index I [74].

In this exercise, Koutek, chose five homologous series of the type $H-(CH_2)_n-Y$, where Y denotes Cl, Br, CHO, $OCOCH_3$ and $COOCH_3$ with n varying from 6 to 14. The results were interesting in that the percentage error incurred by any one of these models was less than 18%. "These conclusions", states Koutek, "should be applicable to other non-polar and/or moderately polar series of homologues." The vapor pressures of the substances measured ranged from 0.02 to 1300 Pa.

Bidleman and co-workers [13,54,56,58] also used the Hamilton method. Their work included the determination of the vapor pressures of many organochloro- and organophosphate pesticides and polycyclic aromatic hydrocarbons (PAHs). They re-iterated that the limitations to the method were due to the lack of activity coefficient data and stated that possible errors were of the order of 5–10-fold. They suggested that caution must be exercised when the GLC method is applied to polar substances. The vapor pressures measured were in the range of 10^{-7} to 10^{-2} Pa.

Recent measurements by Lei et al. [75], using the Hamilton method included the determination of 35 unsubstituted and alkylated PAHs using pyrene and 1,2-benzanthracene as standard reference samples. More recently they have determined the vapor pressures of 17 polychlorinated naphthalenes [76], 9 chlorinated catechols, syringols and syringaldehydes, [77], 23 polybrominated diphenyl compounds [78] and 35 PAHs [75]. A variety of reference standards were used including pyrene and 1,2-benzanthracene for the PAHs and chlorinated phenols for the chlorinated catechols, etc. In most cases, a DB-1 capillary column was used. They estimated that in some cases, errors as high as three-fold were possible. Lei et al. came to similar conclusions to Falconer and Bidleman [79]. The work involved vapor pressures in the range of 10^{-6} to 50 Pa.

Hinckley et al. [58] used the Hamilton method to determine vapor pressures of non-polar and semi-polar compounds. They compared some of their results to literature values and came to the conclusion that vapor pressures of these compounds were determined within a factor of two-fold of the literature values, well within the precision of other techniques. The vapor pressures measured, ranged from 10^{-5} to 70 Pa.

Donovan [80], using the basic ideas of Hamilton, developed a temperature gradient method, involving a simultaneous injection of a cocktail of standards and unknown solutes. This method proved to be much quicker than the usual method involving a series of isocratic experiments, extrapolated back to 25 °C using the Clausius–Clapeyron equation. The method was based on Donovan's experimental evidence that the retention time of solutes undergoing the temperature gradient regime, was related to the log of the vapor pressure. The vapor pressure at 25 °C in the liquid state for a compound was determined by finding its retention time and those of at least two standards. Corrections were made for crystalline compounds. The method is quick and easy but is more of an empirical method than the other methods discussed above. The method also suffers from the problems related to the relative non-ideality of the standards and unknown solutes and works best when the compounds of unknown vapor pressure are chemically related to the standard compounds. Donovan estimated that the method was capable of predicting the vapor pressure of compounds in the range of 10^2 to 10^{-7} Pa, better than an order of magnitude.

The first reported use of Kovats' retention indices to determine vapor pressures, was given by Dimov et al. [81]. Ballschmiter and co-workers [82–84] have, more recently used this technique to great advantage. They have measured the vapor pressures of halogenated methylphenylethers and have highlighted the importance of the method for vapor pressure measurements used in determining the fate of organic pollutants in the atmosphere. The range of vapor pressures was 10^{-2} to 10^2 Pa.

Attempts to upgrade the Kovats' index method by improving the assumption that $\gamma_n^\infty = \gamma_x^\infty$ (see Eq. (17)) was recently made by Govers and co-workers [71,72]. They related the activity coefficient ratio to the McReynolds number and also included a temperature dependent term for the Kovats' index. They determined the vapor pressure of chlorophenols and tetrachlorobenzyltoluenes in the range of 10^{-2} to 10^4 Pa.

The application of the averaged numerical value of the constant, $\Delta_f S^0/R$, as being 6.79, must be used with caution. The differences between the average numerical value and the correct values may be as high as a factor of 2 [58,68].

6. Other GLC methods

There have been a number of other GLC methods which have been used to determine vapor pressures. Friedrich and Stammach [85] used a method which involved absorbing a fixed amount of vapor of a substance (of unknown vapor pressure) in equilibrium with its liquid phase, onto a GLC column. This column was then inserted into a GLC apparatus and the substance eluted together with a reference sample. From the peak areas, the amount of material was determined and hence the vapor pressure was calculated.

There have been many head space techniques used to determine vapor pressure [86–89]. One of the first was by Mackle and Mayrick [86]. The substance of unknown vapor pressure was allowed to equilibrate (liquid/vapor) at temperature T . The vapor filled a loop of glass (fitted with taps) which was linked to a GLC apparatus. Once equilibrium had been established, the vapor in the loop was flushed into the GLC apparatus and the peak area was measured. This was repeated at a number of temperatures and a plot of $\ln(\text{peak area})$ versus $1/T$ was made and $\Delta_{\text{vap}}H^\circ$ was determined, assuming the Clausius–Clapeyron equation. From the knowledge of the boiling point of the substance under investigation together with $\Delta_{\text{vap}}H^\circ$ and the Clausius–Clapeyron equation, the unknown vapor pressure can be evaluated.

A simple method, but fraught with problems of reproducibility, was recently reported by Kildahl and Berka [90]. They used a gas syringe to obtain a constant 2 cm^3 volume of vapor from an equilibrium mixture at temperature T . This volume was diluted with a large volume of air (to make up 10 cm^3) to ensure that condensation did not take place. The sample was injected into a GLC apparatus and the peak area measured. The experiment was repeated at a number of temperatures and $\Delta_{\text{vap}}H^\circ$ and p^0 were determined as reported above [86].

A novel method which involved a controlled and monitored evaporation of a GLC solvent has been reported by the author [91,92]. In this work, it is the vapor of the solvent, that is determined. This technique is linked to the determination of the activity coefficients at infinite dilution of the solutes in the evaporating solvent. The technique appears to be capable of measuring vapor pressures of liquids in the range of 10–500 Pa within 20%.

7. Conclusions

The GLC retention volume techniques used for determining vapor pressures in the range 10^{-8} Pa to 1 kPa, have been found to be extremely useful and reasonably precise. The strength of these methods lies in their rapidity, reliability and reproducibility. Their main weakness lies in the possibility of adsorption effects if polar solutes are used and in not knowing the values of the activity coefficients concerned. With a good choice of reference substance and making sure that adsorption does not take place, errors in GLC determined vapor pressures could be as low as 10%. At worst these errors have been estimated to be as high as 5- and 10-fold. For vapor pressures of the order 1×10^{-8} Pa, this magnitude of error is sometimes comparable or even better than other techniques.

The GLC vapor pressure determination methods have been shown to be particularly useful for low vapor pressure determinations ($<10^{-2}$ Pa) and is ideal for the rapid analysis of the fate of many new compounds entering the market and hence our environment.

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