



# Vapour Pressure Measurement of Pesticides using the Knudsen effusion cell method with the VPA instrument

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*The vapour pressure solid materials can be useful in predicting thermodynamic stability. The Vapour pressure analyser (VPA) allows for reliable determination of solid vapour pressures and enthalpies of vaporisation. This note describes this technique and uses two pesticides (bifenthrin and quinclorac) as examples. VPA results are compared to literature values.*

## Introduction

The vapour pressure of materials is important in a number of environmental and toxicology arenas. In addition, vapour pressure of solid compounds is a property that reflects both thermodynamic stability and shelf life of a wide range of products, in particular those from the pharmaceutical industry. The ability to accurately quantify the vapour pressure of solid compounds can therefore be of great use in the safe use, thermodynamic stability and handling of such compounds.

## Theory

In this work the vapour pressure of two pesticides, bifenthrin and quinclorac, were measured using a vacuum DVS Knudsen method [1,2,3,4]. The vapour pressure and the enthalpy of vaporization (heat of vaporization) were calculated from the experimental data using the classic Knudsen Equation (Equation 1) and Clausius-Clapeyron Equation (Equation 2) below.

$$P = \sqrt{\frac{2\pi RT}{M}} \frac{dm}{dt} \quad (1)$$

$$\log P = \frac{b}{T} + a \quad (2)$$

$$b = \frac{-\Delta H}{R} \quad (3)$$

where P, R, T, M and A are the vapour pressure, universal gas constant (8.314 m<sup>3</sup> .Pa.K<sup>-1</sup>.mol<sup>-1</sup>), temperature in Kelvin, molecular weight and the area of the aperture of the Knudsen cell respectively. The gradient of the linear part of mass vs time data is used to calculate dm/dt, as shown in Figure 1. The ΔH is the enthalpy of vaporization or heat of vaporization, a and b are constants.

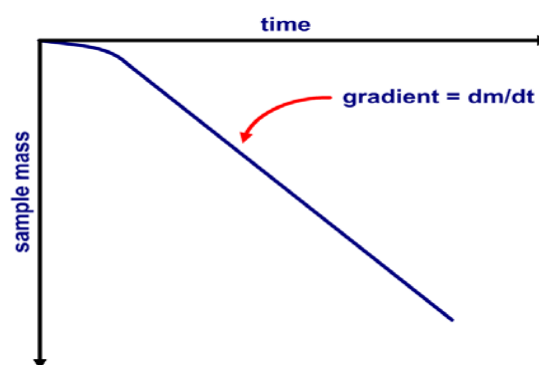


Figure 1. A schematic form of Knudsen mass vs time data



## Method

About 0.5mg sample was placed in a Knudsen effusion cell with an aperture size of 191.8 $\mu$ m. The experiment was conducted in a VPA system at a range of constant temperatures. The pressure of the sample cell was pumped down to and maintained at approximately  $10^{-3}$  Torr by a rotary pump throughout the measurements. A lower ultimate vacuum in the range of  $10^{-5}$ ~ $10^{-6}$  Torr is achievable by a turbo pump used in conjunction with the rotary pump. The linear part of the raw experimental data of the measurements is shown in Figure 2.

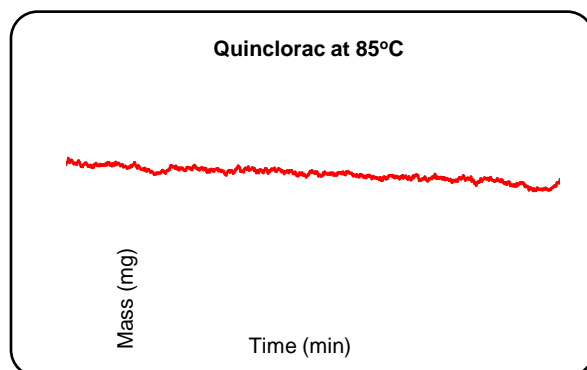
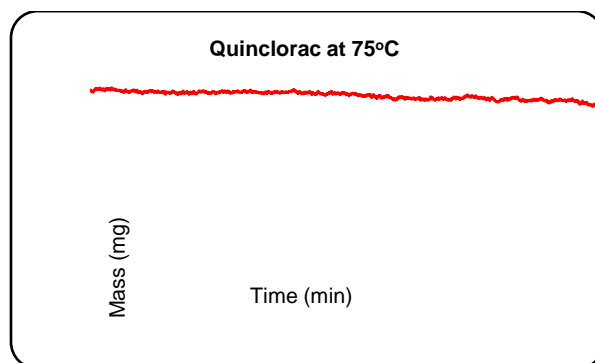
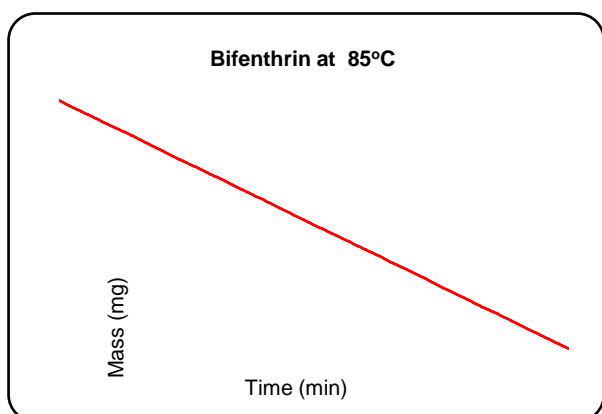
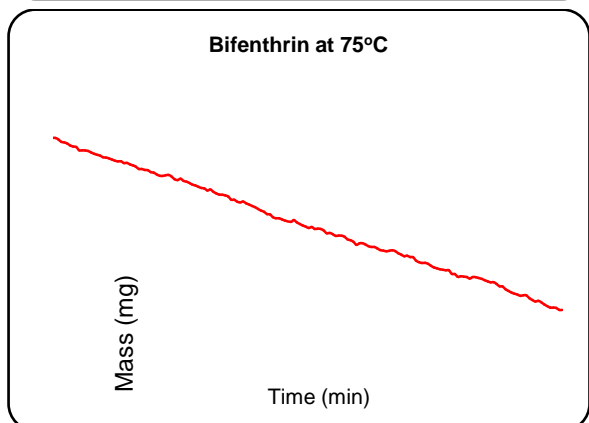
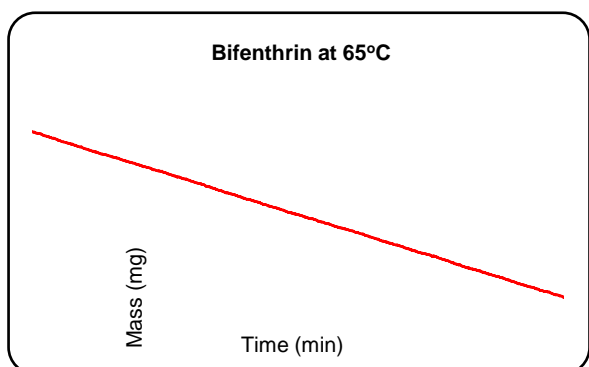


Figure 2. Raw data of the Knudsen vapour measurement at various temperatures

The vapour pressure of bifenthrin (molecular weight: 422.9 g/mol<sup>-1</sup>) was calculated by DVS Knudsen software included in our VPA, whereas that of quinclorac (molecular weight: 242.1 g/mol<sup>-1</sup>) was calculated from the gradient of the linear part of the graphs. The calculation results are summarised in the Tables 1 and 2 for bifenthrin and quinclorac respectively.

Table 1. Summary of the calculation of vapour pressure of bifenthrin

Temp (°C)	Temp (K)	Vapour pressure (Pa)	Log P	1/T (K <sup>-1</sup> )
65	338	$2.149 \times 10^{-2}$	-1.668	$2.959 \times 10^{-3}$
75	348	$9.796 \times 10^{-2}$	-1.009	$2.874 \times 10^{-3}$
85	358	$2.221 \times 10^{-1}$	-0.653	$2.793 \times 10^{-3}$

Table 2. Summary of the calculation of vapour pressure of quinclorac

Temp (°C)	Temp (K)	Vapour pressure (Pa)	Log P	1/T (Kelvin <sup>-1</sup> )
75	348	$7.9 \times 10^{-4}$	-3.102	$2.874 \times 10^{-3}$
85	358	$1.6 \times 10^{-3}$	-2.796	$2.793 \times 10^{-3}$

In order to calculate enthalpy of vaporization (heat of vaporization), the relationship between the vapour pressure and the temperature needs to be plotted. The logarithm of the vapour pressure against the reciprocal of the temperature in Kelvin is expected to be linear. The data was then fitted with a straight line (see the graphs shown in Figure 3 and 4 below).

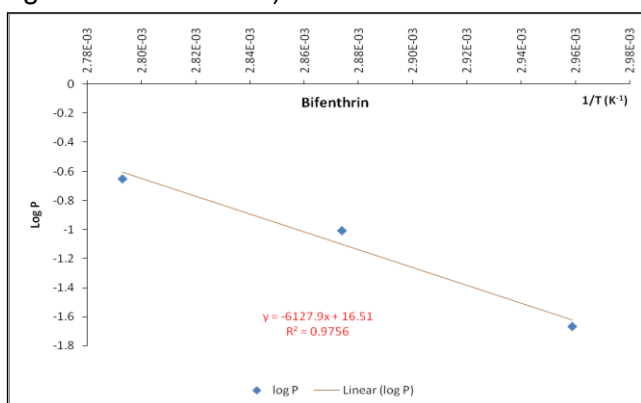


Figure 3. Vapour pressure-temperature relationship for bifenthrin

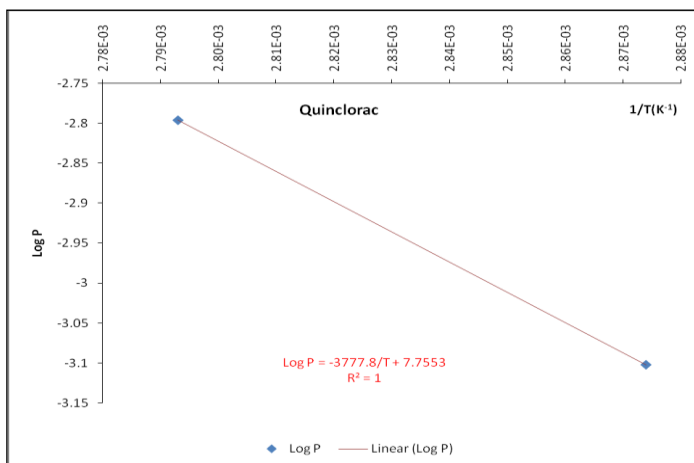


Figure 4. Vapour pressure-temperature relationship for quinclorac

The above fitted straight lines can be expressed mathematically by the following Equations 4 and 5 for bifenthrin and quinclorac respectively:

$$\log P = \frac{-6127.9}{T} + 16.5 \quad \text{for bifenthrin} \quad (4)$$

$$\log P = \frac{-3777.8}{T} + 7.7553 \quad \text{for quinclorac} \quad (5)$$

In comparison with Equations 2 and 3, one can see that the constant b for bifenthrin and quinclorac is -6127.9 and -3777.8 respectively. So the enthalpy of vaporization for the two chemicals will be:

$$\Delta H = -bR = -(-6127.9) \times 8.314 = 50947.36 \text{ (J.mol}^{-1}\text{)} \quad \text{for bifenthrin}$$

$$\Delta H = -bR = -(-3777.8) \times 8.314 = 31408.63 \text{ (J.mol}^{-1}\text{)} \quad \text{for quinclorac}$$

### Verification of measurement data

In order to verify the experimental data and calculation, vapour pressures calculated from Equations 4 and 5 will be compared with the published results. The vapour pressure of bifenthrin at 25 °C can be calculated as follows:

$$\log P = \frac{-6127.9}{(25 + 273)} + 16.5 = -4.063$$

$$P = 8.65 \times 10^{-5} \text{ Pa} = 6.49 \times 10^{-7} \text{ mmHg}$$

Similarly, for quinclorac at 20 °C:

$$\log P = \frac{-3777.8}{(20 + 273)} + 7.7553 = -5.138$$

$$P = 7.27 \times 10^{-6} \text{ Pa} = 5.42 \times 10^{-8} \text{ mmHg}$$

According to the safety data sheet and the published documents, the vapour pressure of bifenthrin at 25°C and that of quinclorac at 20°C is  $1.81 \times 10^{-7}$  mmHg and  $7.50 \times 10^{-8}$  mmHg respectively [5,6], which are in good agreement with above calculation.



## Conclusion

The vapour pressures of the two pesticides, bifenthrin and quinclorac were measured in the VPA system using the Knudsen method. The vapour pressure calculated from the measurement data for bifenthrin and quinclorac at 25 °C and 20 °C is  $6.49 \times 10^{-7}$  mmHg and  $5.42 \times 10^{-8}$  mmHg, respectively, which are in the same order of magnitude of the published data of  $1.81 \times 10^{-7}$  mmHg for bifenthrin and  $7.50 \times 10^{-8}$  mmHg for quinclorac

## References

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