Vapor Pressure of Agrochemicals by the Knudsen Effusion Method Using a Quartz Crystal Microbalance

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Vapor pressure determination of agrochemicals is required for EPA and EC registration. The Knudsen effusion method is an approved regulatory method of performing vapor pressure measurements. The Knudsen effusion method is a dynamic technique based on the rate of escape of vapor molecules through an orifice into a vacuum. We have modified the Knudsen effusion apparatus, replacing a conventional microbalance with a quartz crystal microbalance (QCM). The QCM has a sensitivity of less than 1 ng; therefore, small mass rate losses can be observed, reducing experimental time. The use of the QCM allows rapid determination of vapor pressures as low as 10 μPa. The vapor pressure of several agrochemicals has been measured using this modified method, and the results agree with previously reported values. The results and methodology are discussed.

Introduction

The vapor pressures of pesticides, in addition to aqueous solubility and octanol/water partition coefficient data, are important physical and chemical properties needed for the estimation of their distribution in the environment. The vapor pressure is required to obtain registration with the EPA (U.S. Environmental Protection Agency) or the EC (European Community). The Knudsen effusion method is approved by the Organization for Economic Cooperation and Development as discussed in the OECD *Vapour Pressure Curve Guideline 104* and the EPA *Product Properties Test Guidelines OPPTS 830.7950 Vapor Pressure.*

Knudsen described the effusion method in several papers at the turn of the century. The Knudsen effusion method is a dynamic technique based on the rate of escape of vapor molecules through an orifice into a vacuum at a known temperature. The conventional Knudsen effusion method uses a balance to measure the rate of mass loss through the orifice. We have replaced the balance with a quartz crystal microbalance (QCM). In the Knudsen effusion/QCM method, molecules escaping from the orifice are trapped onto an externally cooled quartz crystal microbalance. In this case the mass loss through the orifice is the mass gain of the QCM.

The advantages of the QCM are increased sensitivity, reduced cost, and insensitivity to vibrational noise. However, for accurate operation of the quartz crystal microbalance, the deposited mass must be uniformly distributed on the crystal surface.

The intent of this work was to demonstrate the validity of the Knudsen effusion/QCM method. The validation was carried out by comparison of data generated using the Knudsen effusion/QCM method with compounds that had reported vapor pressure data at several temperatures that were believed to be reliable. Test compounds of different chemical composition, physical state, and vapor pressures in the range of 10^{-5} to 10^{-1} Pa were examined.

The test substance was sealed in the Knudsen cell containing an orifice of known area and was heated to the test temperature. The rate of mass loss is related to p, which is the vapor pressure of the condensed phase, by the Hertz−Knudsen equation

$$p/\mathrm{Pa} = 2285.5\left(\frac{m/\mathrm{g}}{t(\mathrm{s})(A/\mathrm{cm}^2)}\right)\sqrt{\frac{T/\mathrm{K}}{M}} \qquad (1)$$

where m is the mass loss, t the effusion time, A, the area of orifice, T the temperature, and M the molecular weight of the test substance.

The quartz crystal is configured with electrodes on both sides of a thin circular disk. Due to piezoelectric properties and crystalline orientation of the quartz, the application of voltage between these electrodes results in a shear deformation of the crystal. The crystal is electrically excited into resonance when the excitation frequency is such that the crystal thickness is an odd multiple of half the acoustic wavelength. Sauerbrey (1959) showed that a change in the resonant frequency was related to mass accumulated on the crystal. A quartz crystal with an AT cut is preferred because of its low temperature coefficient over a wide temperature range and its ability to respond linearly to a change in mass of uniform film thickness.

Experimental Section

Test Substances. The hexaconazole, atrazine, *cis*-permethrin, and lambda-cyhalothrin test substances were purified in our laboratory, and all were certified with purities greater than 99.4 mass %. Decachlorobiphenyl, 99.0 mass %, was obtained in acetone from Supelco (Bellefonte, PA). The acetone was evaporated in situ. The di-(2-ethylhexyl)phthalate, 99 mass %, was purchased from Lancaster Labs (Windham, NH) and used without any further purification.

Apparatus. A schematic diagram of the apparatus is given in Figure 1. The QCM was an XTM/2 Thin Film Monitor from Leybold Inficon (East Syracuse, NY). Data were collected with a personal computer attached to the QCM monitor. The Knudsen cell and the QCM were temperature controlled by recirculating baths. The QCM was maintained at a constant temperature between −2 °C and −8 °C.

The vacuum chamber shown in Figure 2 was made from a 2.75 in. Conflat Tee. The Knudsen cell was connected at the bottom of the straight end of the tee, and the QCM was installed at a right angle to the Knudsen cell with the quartz crystal facing downward. The top of the tee was connected to the high-vacuum system.

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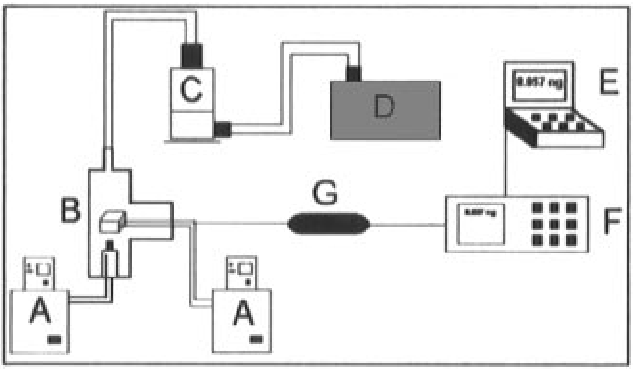

Figure 1. Knudsen effusion method apparatus: A, recirculating bath; B, vacuum chamber containing the Knudsen cell (see Figures 2 and 3) and QCM; C, turbomolecular pump; D, roughing pump; E, computer for data collection; F, QCM; G, oscillator.

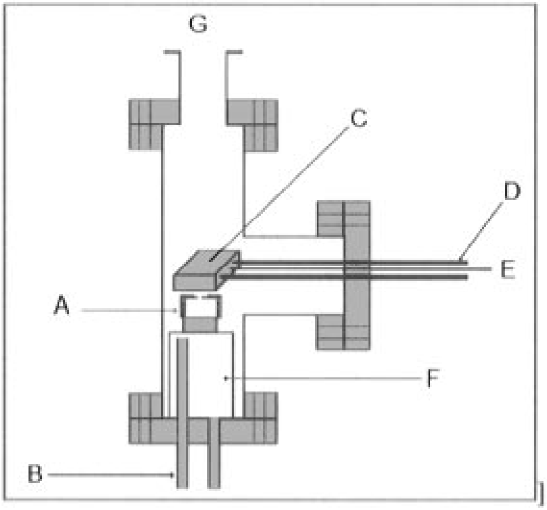

Figure 2. Vacuum chamber: A, Knudsen cell (see Figure 3); B, heating lines connected to recirculating pump; C, QCM; D, cooling lines for QCM; E, cable to oscillator; F, heating chamber; G, vacuum source.

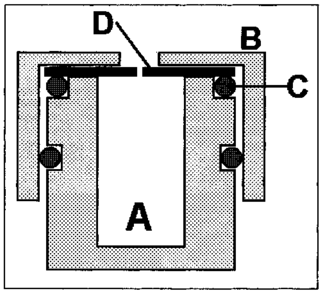

Figure 3. Top portion of the Knudsen cell: A, Knudsen cell chamber; B, cap for Knudsen cell; C, O-rings for sealing cap and orifice plate; D, orifice plate.

The Knudsen cell design is presented in Figure 3. The orifice plate was made from either 0.127 mm or 0.203 mm 302/304 stainless steel shim stock. Orifices were mechanically or laser drilled.

In the classical Knudsen vapor pressure experiment, the Knudsen effusion cell is an integral part of the balance. As molecules escape through the orifice into the vacuum, the mass of the Knudsen cell is reduced.

Our Knudsen effusion/QCM experiment is different, in that the molecules escaping from the Knudsen cell are trapped onto the QCM. The mass loss from the Knudsen cell is the mass gain of the QCM. To ensure that molecules are not vaporized from the quartz crystal, it is kept at least 40 °C lower in temperature than the Knudsen cell temperature. The distance from the top of the Knudsen cell to the top of the QCM holder was 3.4 mm.

Table 1. Vapor Pressure Data for Atrazine

t/°C	n^a	p/mPa (this work)^b	p/mPa (Grayson and Fosbraey, 1982)
40	2	0.67	0.75
50	3	2.2	2.9
60	3	9.5	10
70	3	30	35
80	5	98	110

[a] n = number of determinations. [b] 0.381 mm diameter orifice with 0.203 mm thickness.

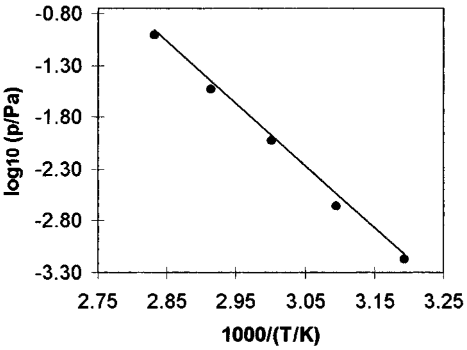

Figure 4. Plot of vapor pressure data for atrazine: ●, this work; —, Grayson and Fosbraey (1982).

Experimental Procedure

The Knudsen cell was filled with enough material to coat the bottom, to ensure good thermal conduction to the test substance. The Knudsen cell cap was installed on the Knudsen cell with an appropriate orifice plate.

The QCM was installed into the vacuum chamber. The QCM was equipped with cooling lines that were connected to a constant temperature recirculating bath. A second recirculating bath was connected to the Knudsen cell heating chamber and set to the test temperature. The vacuum system was initiated. At a given test temperature, the change in mass was measured over a period of 5 to 20 min at 15 to 60 s intervals. A least-squares regression fit of the mass data was performed yielding the slope in g s^{-1}, which was used to calculate the vapor pressure using eq 1. Mass and time data were collected in at least duplicate at a given temperature with the average vapor pressure being reported.

The measured vapor pressures were used to determine the constants A and B in the following integrated form of the Clausius–Clapeyron equation using a least-squares method.

$$\log_{10}(p/\mathrm{Pa}) = A - \frac{B}{T/\mathrm{K}} \tag{2}$$

Results

Atrazine, because of its moderate volatility, was near the upper limit of this method. The atrazine data were collected using an orifice plate with a 0.381 mm orifice diameter. The vapor pressure data are presented in Table 1. For comparison vapor pressure data reported by Grayson and Fosbraey (1982) are presented as a Clausius–Clapeyron plot with our data in Figure 4.

Decachlorobiphenyl was chosen because of its low volatility. Due to the sensitivity of the QCM, a small sample size can be used. The vapor pressure data for decachlorobiphenyl were collected using only 400 μg of sample.

Table 2. Vapor Pressure Data for Decachlorobiphenyl

t/°C	n^a	p/μPa (this work)^b	p/μPa (Burkhard et al., 1984)
65	3	26	29
70	2	51	46
75	3	81	74
80	3	110	120
85	3	180	180

^{a} n = number of determinations. ^{b} 0.381 mm diameter orifice with 0.203 mm thickness.

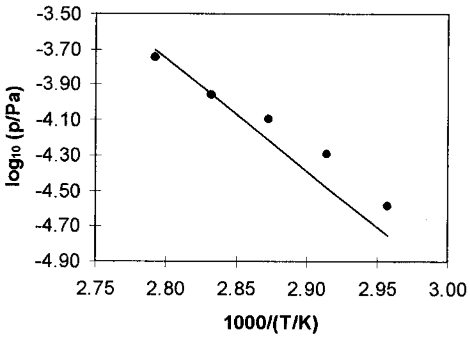

Figure 5. Plot of vapor pressure data for decachlorobiphenyl: ●, this work; —, Burkhard et al. (1984).

Table 3. Vapor Pressure Data for Lambda-Cyhalothrin

t/°C	n^a	p/μPa (this work)^a	p/μPa (Wollerton and Husband)
40	3	19	7.8
50	2	47	40
60	2	170	190
70	2	650	820
80	2	2000	3200

^{a} n = number of determinations. ^{b} 0.381 mm diameter orifice with 0.203 mm thickness.

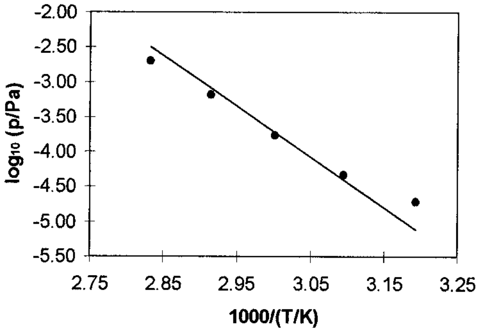

Figure 6. Plot of vapor pressure data for lambda-cyhalothrin: ■, this work; —, Wollerton and Husband.

The decachlorobiphenyl vapor pressure data were collected using an orifice plate with a 0.381 mm orifice diameter. The vapor pressure data are presented in Table 2. The Clausius–Clapeyron plot in Figure 5 of our data was prepared along with vapor pressure data reported by Burkhard et al. (1984).

The lambda-cyhalothrin (PP321) vapor pressure data were collected using an orifice plate with a 0.381 mm orifice diameter. The vapor pressure data are presented in Table 3. The study used for comparison was done by Wollerton and Husband. The Clausius–Clayperon plot of their vapor pressure data is given in Figure 6, along with our data.

Table 4. Vapor Pressure Data for *cis*-Permethrin

t/°C	n^a	p/μPa (this work)^a	p/μPa (Wollerton and Husband)
40	3	14	4.1
50	2	110	150
60	2	530	520
70	3	2300	1700
80	3	8900	5000

^{a} n = number of determinations. ^{b} 0.381 mm diameter orifice with 0.203 mm thickness.

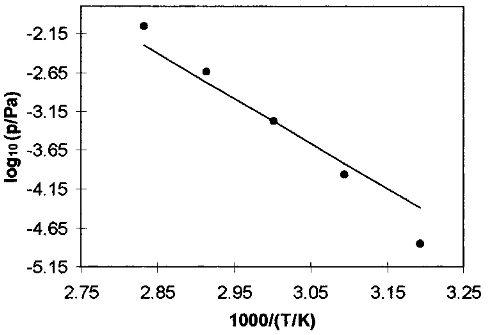

Figure 7. Plot of vapor pressure data for *cis*-permethrin: ●, this work; —, Wells and Wollerton, (1989).

The *cis*-permethrin vapor pressure data were collected using an orifice plate with a 0.381 mm orifice diameter. The vapor pressure data are presented in Table 4. The Clausius–Clapeyron plot of the vapor pressure data of Wells and Wollerton (1989) is given in Figure 7 along with our data.

The di(2-ethylhexyl)phthalate is an OECD reference material. Reproducibility of the method was determined using this compound. The vapor pressure was determined on three separate occasions using an orifice plate with either a 0.381 mm orifice diameter or a 0.229 mm diameter orifice. We also tested a variable height Knudsen cell. For this set of data a distance of 4 mm from the top of the Knudsen cell to the QCM was used. All the vapor pressure data are presented in Table 5. The Clausius–Clapeyron plot given in Figure 8 was prepared using the OECD *Vapour Pressure Curve Guideline 104* data and our vapor pressure data.

The hexaconazole (PP523) vapor pressure data was collected using three different orifices areas. Data were collected using the 0.381 mm diameter orifice for vapor pressure data from 45 °C to 55 °C. The 0.229 mm diameter orifice plate was used for vapor pressure data from 50 °C to 75 °C, and a 0.152 mm diameter orifice plate was used to obtain the vapor pressure data from 75 ° to 85 °C. The vapor pressure data are presented in Table 6. The Clausius–Clapeyron plot in Figure 9 of our vapor pressure data was prepared with reported vapor pressure data of Wollerton and Husband.

For each compound the logarithm of the average vapor pressure at each temperature was regressed by linear least squares as a function of the reciprocal temperature. Table 7 lists the regression coefficients A and B, the correlation coefficient, and the molecular weight of each test substance.

Discussion

The advantage of the Knudsen effusion/QCM method is that the QCM is unaffected by vibrational noise and has a sensitivity of 0.1 ng. The increased sensitivity of the QCM over a conventional microbalance results in reduced experimental time for each data set being between 5 and 20 min.

With the direct sample heating , our Knudsen cell design has greatly improved temperature control. One of the problems that has plagued the Knudsen effusion method has been the ambiguity in the temperature measurement

Table 5. Vapor Pressure Data for Di-(2-ethylhexyl)phthalate

	(this work)[b]		(this work)[b]		(this work)[c]		(this work)[c,d]		
t/°C	n[a]	p/mPa	n[a]	p/mPa	n[a]	p/mPa	n[a]	p/mPa	p/mPa[e]
40							3	0.15	0.12
50	2	0.44	2	0.31	2	0.21	3	0.49	0.48
55	2	0.98	2	0.65					0.93
60	2	2.0	2	1.3	2	0.97	3	1.5	1.8
65	2	3.8	2	2.3	2	4.1			3.3
70	2	6.3	2	4.2	2	6.8	2	4.6	5.9
75	2	9.2			2	9.2			11
80	2	12			2	10	4	16	19

[a] n = number of determinations. [b] 0.381 mm diameter orifice with 0.203 mm thickness. [c] 0.229 mm diameter orifice with 0.127 mm thickness. [d] Data using variable height Knudsen cell (see text). [e] OECD Vapour Pressure Curve Guideline 104.

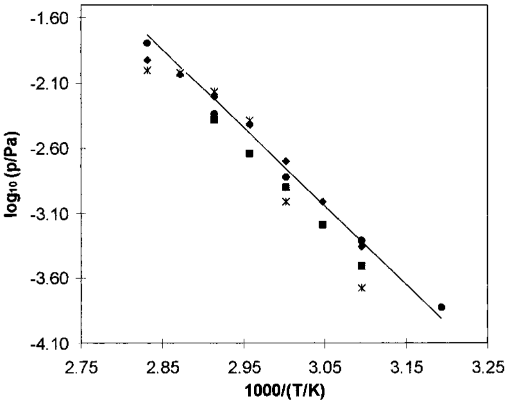

Figure 8. Plot of vapor pressure data for di(2-ethylhexylphthalate): ◆, this work using 0.0381 mm diameter orifice; ■, this work using 0.0381 mm diameter orifice repeat data; *, this work using 0.0229 mm diameter orifice repeat data; ●, this work using 0.0229 mm diameter orifice using variable height Knudsen cell set at 4 mm; —, OECD *Vapour Pressure Curve Guideline 104* data.

Table 6. Vapor Pressure Data for Hexaconazole

t/°C	orifice diameter (mm)	n	p/mPa (this work)	p/mPa (Wollerton and Husband)
45	0.381	2	0.16	0.73
50	0.381	3	0.75	1.4
50	0.229	2	3.0	1.4
55	0.381	2	1.3	2.7
55	0.229	3	1.7	2.7
60	0.229	2	3.6	5.2
65	0.229	3	8.0	9.5
70	0.229	3	15	17
75	0.229	3	28	31
75	0.152	3	50	31
80	0.152	4	87	54
85	0.152	4	140	93

[a] n = number of determinations.

and controlling the sample temperature. The reason is that the conventional Knudsen cell temperature cannot be easily measured since it is an integral part of the balance. In our design, the temperature of the Knudsen cell is directly controlled with a recirculating bath. The temperature of the recirculating bath and our Knudsen cell temperature were found to be within 0.1 °C over the temperature range of 40−90 °C.

The data presented in Table 5 and Figure 8 for di-(2-ethylhexyl)phthalate indicate that the vapor pressure data at 80 °C with 0.381 mm diameter orifice start to deviate from the reported data. This was because the rate of effusion was more than 400 ng/min, and the cooling capacity of the QCM had been exceeded. Therefore, for accurate results the mass rate of effusion should be between 2 and 350 ng/min.

We were unable to collect reliable vapor pressure data for lindane, even using our smallest orifice diameter of 0.0735 mm. Lindane, which exceeded our effusion rate upper limit, was also accompanied by uneven sample distribution on the quartz crystal. The other compounds studied had effusion rates and deposition characteristics that were acceptable.

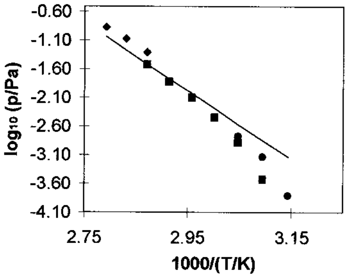

Figure 9. Plot of vapor pressure data for hexaconazole: ◆, this work using 0.0152 mm diameter orifice; ■, this work using 0.0229 mm diameter orifice; ●, this work using 0.0381 mm diameter orifice; —, Wollerton and Husband.

Table 7. Regression Parameters for $\log_{10}(p/\mathrm{Pa}) = A - B/(T/\mathrm{K})$

compound	molecular weight	A	B	r^2
atrazine	215.7	16.08	6040	0.999
decachlorobiphenyl	498.7	9.91	4886	0.993
lambda-cyhalothrin	449.9	13.47	5723	0.996
cis-permethrin	391.3	19.70	7677	0.999
di-(2-ethylhexyl)phthalate	390.6	14.90	5911	0.988
hexaconazole	314.2	22.60	8364	0.992

Lambda-cyhalothrin is a solid at room temperature and a liquid at 55 °C. Data were collected from 40 °C to 80 °C. It is interesting to note that no abrupt vapor pressure change was observed above the phase transition.

The hexaconazole vapor pressure for the different orifice areas used were consistent with the literature gas saturation data over its reported temperature range.

Quality Criteria. The quality criteria for repeatability and reproducibility of the Knudsen effusion method has been established by the OECD for vapor pressure studies. They estimated the repeatability of vapor pressure values to be 5−20%. The repeatability is the variation in the vapor pressure obtained when the same procedure is used several times while measuring the same sample at a given temperature. The repeatability for the vapor pressure measurements at each temperature, for the compounds studied, was within the specified guidelines.

The di-(2-ethylhexyl)phthalate was used to determine the methods reproducibility. Reproducibility is the average of the vapor pressure at a given temperature when measuring the same sample at different times using the same procedure. The estimated reproducibility by OECD for the Knudsen effusion method is up to 50%. The reproducibility of the OECD vapor pressure data and our data for di-(2-ethylhexyl)phthalate could be compared, since both were obtained using the Knudsen effusion method. The average reproducibility for di-(2-ethylhexyl)-phthalate was found to be 23.1%, which is within the OECD specified guidelines.

Conclusions

We have demonstrated the validity of the Knudsen effusion/QCM method. In comparison to reported vapor pressure data, there is good agreement with our data.

The method is quick and only requires several days of work to complete a vapor pressure curve. The computerized data collection reduces time in performing data analysis. The Knudsen cell design of the Knudsen effusion/QCM method allows for accurate temperature control of the test substance.

The Knudsen effusion/QCM method can be performed with extremely small amounts of material, on the order of milligrams and in some cases even less. The low cost of the QCM compared to a conventional microbalance makes this method attractive.

The repeatability and reproducibility of the method met the criteria established by the OECD.

Acknowledgment

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