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Development of a method to determine vapor pressure data of low volatile chemicals from a Knudsen effusion technique

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Development of a Method to Determine Vapor Pressure Data of Low Volatile Chemicals
from a Knudsen Effusion Technique

by

Andrew R. Harshman

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science in Chemical Engineering
Department of Chemical Engineering
College of Engineering
University of South Florida

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Dedication

I dedicate this thesis to my wife, Krissy, my life, my love, and my inspiration. You have given me the courage to do what I want to do and to be more than I thought I could. Thank you for helping me to realize my potential and for giving me the strength to pursue happiness.

I also dedicate this work to my parents, Jim and Judy. The support, education, and encouragement you have provided have formed who I am and have given me the strength to accomplish my goals. Thank you for being a guiding light, showing me the way to live a happy and successful life.

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- The members of the Sensors Research Laboratory and Dr. Wolan's research group at USF for their continued help and guidance toward the completion of this thesis.
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Andrew R. Harshman

ABSTRACT

Vapor pressure data are vital to understanding impacts that substances, specifically pesticides, may exert on the environment. They enter into atmospheric deposition models for such chemicals which determine the fate and transport of these species in the environment. At normal application temperatures (i.e. room temperature) the vapor pressures of many of these chemicals are too low to be determined by conventional means. An isothermal Knudsen effusion technique was designed and developed in our laboratory for such measurements. The effusion mass as a function of time is measured in our technique using a thickness shear mode (TSM) acoustic wave sensor, which allows for extremely high (few nanograms) sensitivity. This sensitivity allows for much more rapid determination of low vapor pressures (10^{-1} to 10^{-5} Pa) than is possible by other Knudsen effusion techniques. Basing the effusion mass measurement on the TSM sensor as in our apparatus eliminates the typically seen dependence on vibration in conventional microbalance-based effusion techniques. Full design details of our apparatus and specifically the Knudsen cell, based on original equations derived by Knudsen, and many corrections that have been noted in the literature for cell and effusion-hole dimensions, are presented. The accuracy of our method

was tested by a comparison of published vapor pressure data to vapor pressure data acquired in our laboratory with measurements on naphthalene and catechol.

Chapter 1

Introduction

1.1 Pesticides

Pesticides are very useful in the protection of foods that are threatened by insects during growth. Pesticide sales in the United States is a multi-billion dollar business, and companies work to develop new pesticides each year that are made to fit the needs of their consumers. The Environmental Protection Agency (EPA) reported in 2001 that \$11.1 billion was spent on pesticides in the United States alone, accounting for 35% of the World market [1]. The majority of the money is spent for agricultural purposes.

While the pesticide business is vast, the potential dangers that they pose to humans and other living things are substantial and must not be overlooked. Certain properties of every pesticide must be known and submitted to the EPA before it can be used legally in the United States due to the potential threats they pose to humans and the environment in general [2]. One of the properties of each pesticide that must be submitted in order to pass EPA certification is vapor pressure, the pressure (at a certain temperatures) at which the pesticide changes phase from a solid or liquid to a vapor. This property is vital to understanding the potential harmful impacts pesticides pose to the environment.

It has been estimated that of the pesticide applied, only 0.1% impacts the insects, leaving 99.9% lost to the environment [3]. This research focuses on low-vapor pressure pesticides. With a lower vapor pressure and subsequent relative volatility, the chemical

will tend not to vaporize and in turn will display properties of higher solubility in water and higher absorptivity onto the land. This creates a hazard for the environment and can negatively influence water and crops. By knowing the vapor pressure data, the EPA can regulate the amount of pollution created by controlling the use of these contaminants.

1.2 Knudsen Effusion Method

Vapor pressure determination may be accomplished by a variety of methods. The method chosen for this research was the Knudsen Effusion method [4] because of temperature control and time constraint advantages over other methods. The Knudsen Effusion method utilizes an isothermal cell (K-Cell) with a very small orifice (0.1-1.0mm.) out of which a chemical effuses (flows under pressure). The measured mass loss over time is proportional to the vapor pressure. The mass effusion rate is measured using a quartz crystal microbalance (QCM). A QCM is an extremely sensitive mass sensor able to sense mass changes in the nanogram (10^{-9} g.) level. This makes it extremely attractive for use in a small application like this. The QCM consists of a piezoelectric device on a thin quartz plate with two electrodes attached to the plate. Vibrations from mass collection change the frequency of the QCM. The frequency change is directly proportional to the mass accumulation rate. The sensitivity and subsequent accuracy of the QCM make it a very attractive option for the mass change measurement.

Chapter 2

Apparatus and Experimental Design

2.1 Components

The apparatus was constructed with the QCM and K-Cell serving as the basis of design. Goodman [4] constructed an apparatus utilizing both a Knudsen Effusion method and a QCM. As with Goodman's design, Conflat components comprise the base structure for the apparatus. The Conflat components are comprised of a stainless steel frame with flanges designed for a tight seal for all connections using copper or viton rubber gaskets and bolts and nuts for tension. The structure and seals are designed to withstand the low vacuum associated with the objectives of this research.

The apparatus includes a vacuum to reduce pressure, a QCM with temperature control, a K-Cell with temperature control, a pressure gauge to for chamber pressure estimation, and a thermocouple to determine an accurate temperature of the cell enclosed in a 5-way cross.

The K-Cell requires temperature control because of the strict isothermal conditions required for vapor pressure data collection and calculations. Temperature control is obtained using a water chamber fed through and welded to the bottom of a blind flange. Two stainless steel tubes are fed into the chamber and connected to a temperature controlled water bath. The base of the K-cell is machined directly on top of the chamber to provide good heat transfer. A notch is formed around the top of the base so an o-ring may be placed to provide a seal between the base and a lid. Another notch is

formed around the circumference of the base below the top to ensure compression between the other o-ring and the lid. Thin (0.0254 mm. or 0.1016 mm. thick) stainless steel plates were constructed to fit on top of the o-ring. Small (0.1 – 1.0 mm. diameter) orifices were laser drilled in the center of each plate. Pictures of these holes and their respective areas may be found in Appendix A. A stainless steel lid fits directly over the orifice plate and along the side of the base. A graphical representation of the K-Cell is shown in Figure 1.

The QCM holder is fed into the side of the 5-way cross so that it is parallel to the K-Cell, with the sensor directly above the orifice. The QCM is housed in a chamber through which refrigerated liquid passes, keeping the QCM at its desired temperature. It must be at a temperature significantly below what the K-Cell temperature is so that the molecules recrystallize after effusion. The QCM holder was purchased from and fabricated by Maxtek, Inc. The QCM electrode itself is connected to an oscillator, which transmits the frequency of the sensor at any given time to a counter, from which data is transmitted to a computer. The computer is equipped with a LabView program which is designed to display and store the frequency change of the crystal over time.

The experimental vapor pressures that are deemed accessible to this apparatus are in the range of 10^{-5} - 10^{-1} Pa. Pressures that are at least two orders of magnitude lower should be maintained outside the Knudsen cell. To achieve this a turbomolecular vacuum pump from Leybold (model BMH-70, which includes the roughing pump) is utilized. A flexible hose connects the vacuum to the side of the 5-way cross. A pressure gauge (Leybold model ITR 90) is utilized to monitor the chamber pressure.

A thermocouple is fed through the top of the apparatus. Connected to this are wires that transmit a temperature reading to a LED readout so that the temperature of the Knudsen cell may be read during runs. The thermocouple wires are attached via an adhesive to the side of the K-Cell. The thermocouple was calibrated using a NIST traceable mercury-in-glass thermometer.

Two Thermo (NESLAB RTE 17 AND 740) temperature controlled water baths are connected by Tygon rubber hose to the K-Cell water bath and the crystal holder, respectively. A mixture of commercial antifreeze and deionized water is used as the control liquid in each bath.

A graphical representation of the entire apparatus configuration is shown in Figure 2.

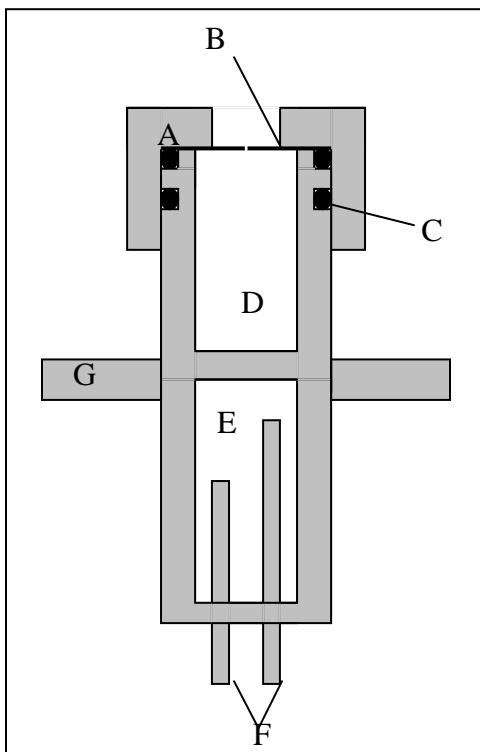


Figure 1. Knudsen Effusion Cell and Liquid Temperature Control Feedthrough. A. Cell lid; B. Orifice plate; C. Sealing O-rings; D. Cell chamber; E. Liquid temperature control chamber; F. Liquid feedthrough tubes; G. Conflat flange

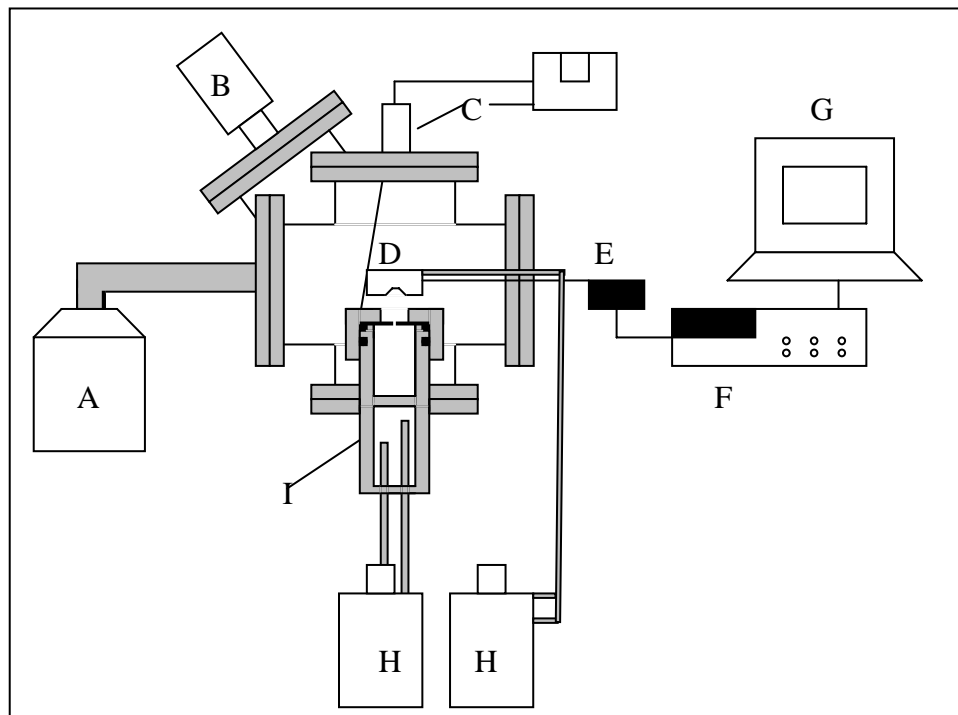


Figure 2. Overall Knudsen Effusion Apparatus. A. Turbomolecular vacuum pump; B. Pressure gauge; C. Thermocouple feedthrough and temperature readout; D. QCM in holder; E. Oscillator; F. Frequency counter; G. Computer; H. Liquid recirculating baths; I. K-cell/ liquid feedthrough

2.2 Experimental Procedure

A small amount of the chemical of which vapor pressure data is desired is placed in the base of the K-Cell. The o-rings, orifice plate, and lid are then placed on the base. The K-Cell/temperature control feedthrough is fed into the bottom of the apparatus and sealed. The thermocouple readout, oscillator, counter, and computer are all turned on. Assuming all connections are sealed properly and a properly functioning crystal is placed in the holder, the vacuum pump is initiated. The water bath controlling the temperature of the K-Cell is then initiated, followed by the water bath controlling the temperature of the crystal. Once the thermocouple readout and frequency shift are stable, the initial frequency is recorded and the LabView program is initiated and run for approximately 10 minutes. The temperature of the water bath controlling the K-Cell temperature is then

changed, and all subsequent procedure steps are repeated. This process is repeated for each desired temperature.

Chapter 3

Theory and Calculations

3.1 General Equation Derivations

The vapor pressure at each temperature was calculated from the measured frequency shift data by applying several corrections to the equation given below, which applies to substances under Knusden Effusion conditions [4]:

$$p = \frac{1}{A_o} \frac{dM_e}{dt} \left[\frac{2\pi RT}{M_w} \right]^{\frac{1}{2}} \quad (1.1)$$

Where p is the pressure (Pa), A_o is the cross-sectional area of the orifice (m^2), $\frac{dM_e}{dt}$ is the mass effusion rate (kg/s), R is the universal gas constant (J/(mol*K)), T is the temperature of the K-Cell (K), and M_w is molecular weight (kg/mol).

The mass effusion rate is obtained using the measured frequency shift $\frac{d(\Delta f)}{dt}$ (Hz/s) with the following equation, which additionally corrects for the distance between the orifice hole and the QCM [5]:

$$\frac{dM_e}{dt} = \frac{\pi r_q^2}{\cos \phi \cos \psi} \frac{1}{C_f} \frac{d(\Delta f)}{dt} \quad (2.1)$$

Where r_q is the radius of the active area of the QCM sensor (m), ϕ and ψ are angles between the QCM and the orifice hole as shown in Fig. 3, and C_f is a conversion factor found using the following equation:

$$C_f = \frac{2f_q^2}{\rho_q v_q} \quad (2.2)$$

Where f_q is the frequency of the crystal without any deposited material (Hz), ρ_q is the density of the quartz (kg/m^3), and v_q is the shear wave velocity of the crystal (m/s).

3.2 Corrections

To correct for the length of the orifice and the effect of the orifice on the equilibrium pressure of the K-Cell, the following equation is derived [6]:

$$p_s = p_o \left(1 + \frac{K_{\text{Clausing}} A_o}{A_s} \left(\frac{1}{\alpha} + \frac{1}{W} - 2 \right) \right) \quad (3.1)$$

Where p_s is the equilibrium vapor pressure in K-Cell (Pa), p_o is the pressure near the orifice (Pa), A_s is the cross sectional area of K-Cell (m^2), α is the vaporization coefficient (≈ 1 for loosely-packed solids), and the constants K_{Clausing} and W are found using the following equations:

$$K_{\text{Clausing}} = \frac{1}{1 + \frac{3L}{8r_o}} \quad (3.2)$$

and

$$W = \frac{r_c}{h_c} \quad (3.3)$$

Where L is the length of the orifice (m), r_o is the radius of the orifice (m), r_c is the radius of inside of the K-Cell (m), and h_c is the height of K-Cell (m).

When all of the equations and correction factors are combined, the following equation results and is used in the determination of vapor pressures for various temperatures.

$$p_s = \left(\frac{1}{K_{\text{Clausing}}} \left(\frac{1}{A_o \cos \phi \cos \psi C_f} \frac{d(\Delta f)}{dt} \left[\frac{2\pi RT}{M_w} \right]^{\frac{1}{2}} \right) \right) \left(1 + \frac{K_{\text{Clausing}} A_o}{A_s} \left(\frac{1}{\alpha} + \frac{1}{W} - 2 \right) \right) \quad (4.0)$$

Chapter 4

Results and Discussion

4.1 Naphthalene

Naphthalene was tested due to its known volatility and use in a similar Knudsen Effusion apparatus by Torres [7] to determine its enthalpy of sublimation at various temperatures. The experimental vapor pressure data evidenced by Figure 3 is erratic and does not reproduce accepted published results by Ambrose, et. al. [8]. Although the results by Torres [7] were reported as accurate in terms of enthalpy change, a simple calculation using the enthalpy of sublimation reported proved to be quite puzzling. Using the equations provided in the text of Torres [7], it was found that the effusion rate naphthalene at a temperature of 298 K was 8.96×10^{-24} kg/s resulting in a vapor pressure of 1.77×10^{-13} Pa. The vapor pressure reported by Ambrose, et. al. [8] at 298 K is around 11 Pa. This major discrepancy between the data retrieved through the Knudsen method (This work and Torres [7]) and the accepted data (Ambrose, et. al. [8]) suggests that the Knudsen method should not be used with chemicals as volatile as naphthalene.

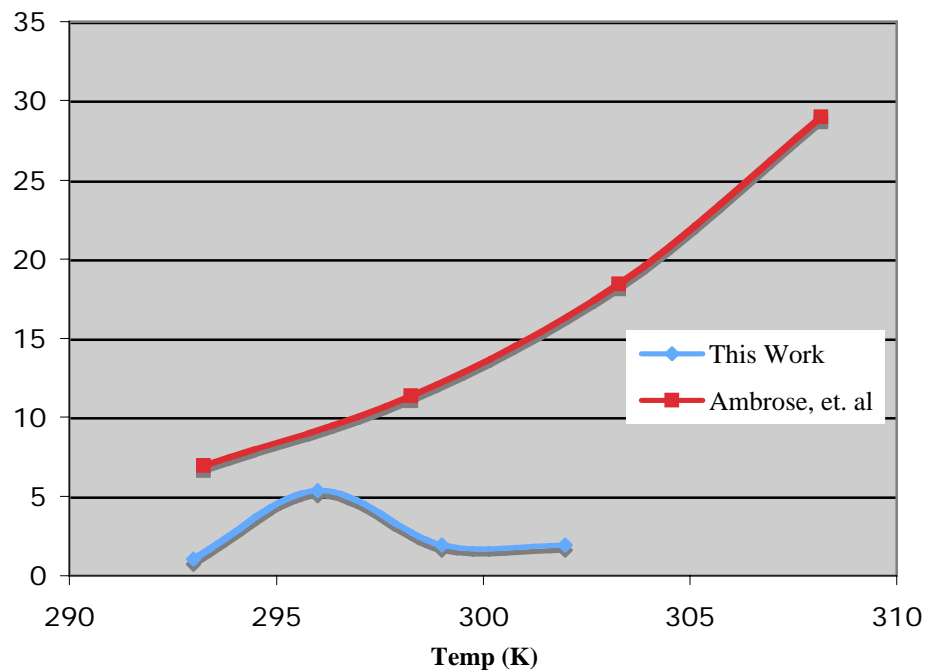


Figure 3. Naphthalene Vapor Pressure Data

4.2 Catechol

Following the testing and subsequent results of naphthalene, it was determined that chemicals with lower volatility at application temperatures (i.e. room temperature) should be tested. Vapor pressure data for chemicals commonly used in pesticides were collected by Chen [6] utilizing a Knudsen Effusion method and these chemicals were selected to be tested using the apparatus to validate the accuracy of the apparatus in collecting vapor pressure data. These chemicals and respective temperature ranges for vapor pressure measurement are anthracene (320-360 K), catechol (290-310 K), hydroquinone (320-340 K), caffeic acid (410-430 K), ferulic acid (360-390 K), gentisic acid (360-380 K), and myoinositol (440-460 K). Catechol was selected to be tested first

based on the temperature range being close to room temperature (25° C) for ease of testing. Individual frequency shift data for catechol (301-310 K) may be found in Figure 4. These data were compiled utilizing an orifice plate 0.0254 mm. thick and with a hole diameter of 0.275 mm. Figure 5 shows the calculated vapor pressure data as compared to Chen [6]. These experimental data, while resembling the trend of the published data, are not within acceptable agreement with it. One of the major contributors to this error may have been the sizeable distance between the orifice and the sensor (1.905 cm.). This distance was lessened to 1.003 cm. with the addition of Teflon washers between the orifice plate and the o-ring seal normally below the plate. The results of this test may be found in Figure 6. While this test slightly decreases the difference between published and experimental data, it does not change it enough to make the data acceptable.

The results of these two tests seemingly dictate that the apparatus does not produce accurate results. Reasons for this error may include the distance between the orifice and the sensor, possible leaks in the K-Cell, and vacuum chamber contamination. The distance between the orifice and the sensor is a factor in that all the mass that effused out of the cell did not collect on the sensor. This was evident by the observation of mass on the QCM holder following tests. The mass observed on the QCM holder also suggests possible K-Cell leaking. If the seal between the lid and the orifice plate was not sufficient, the mass may have escaped out in that gap. The result of all of the mass not collecting on the sensor shows that the vacuum chamber was contaminated for future runs. Therefore, when the apparatus is running, vapor already in the chamber collected on the sensor impeding the results.

Steps were taken to minimize the error, including the aforementioned distance reduction between the orifice and the sensor, using Kapton tape to seal the orifice plate directly to the K-Cell, and baking the chamber overnight to try and remove containments. Other tests followed, including changing the orifice size and direct coating of the QCM to measure mass loss. The procedure for direct coating of the QCM may be found in Appendix B. No alternatives provided accurate results for catechol. Other chemicals were not tested due to time constraints and the fact that they were less volatile than catechol and would have theoretically effused at even slower rates. The error is not thought to be attributed to the chemical that was tested, rather something internal with the apparatus or process.

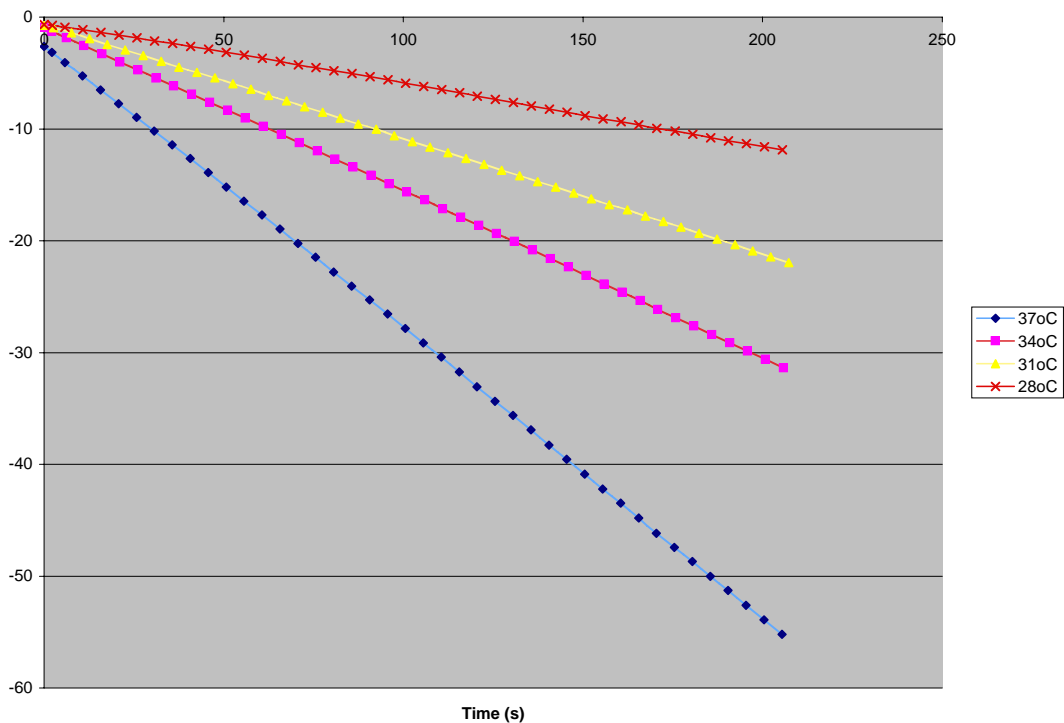


Figure 4. Catechol Frequency Shifts at Various Temperatures. 1.905 cm. distance from orifice to sensor; 0.275 mm. diameter orifice; 0.0254 mm. plate thickness

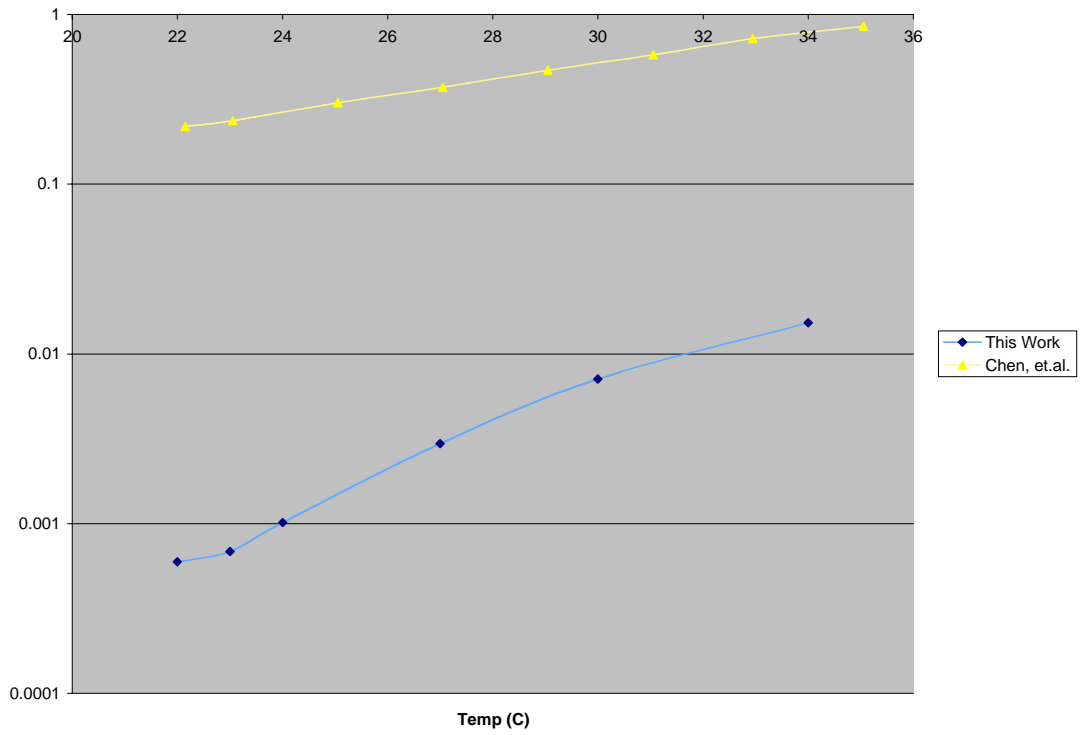


Figure 5. Catechol Vapor Pressure Data. 1.905 cm. distance from orifice to sensor; 0.275 mm. diameter orifice; 0.0254 mm. plate thickness

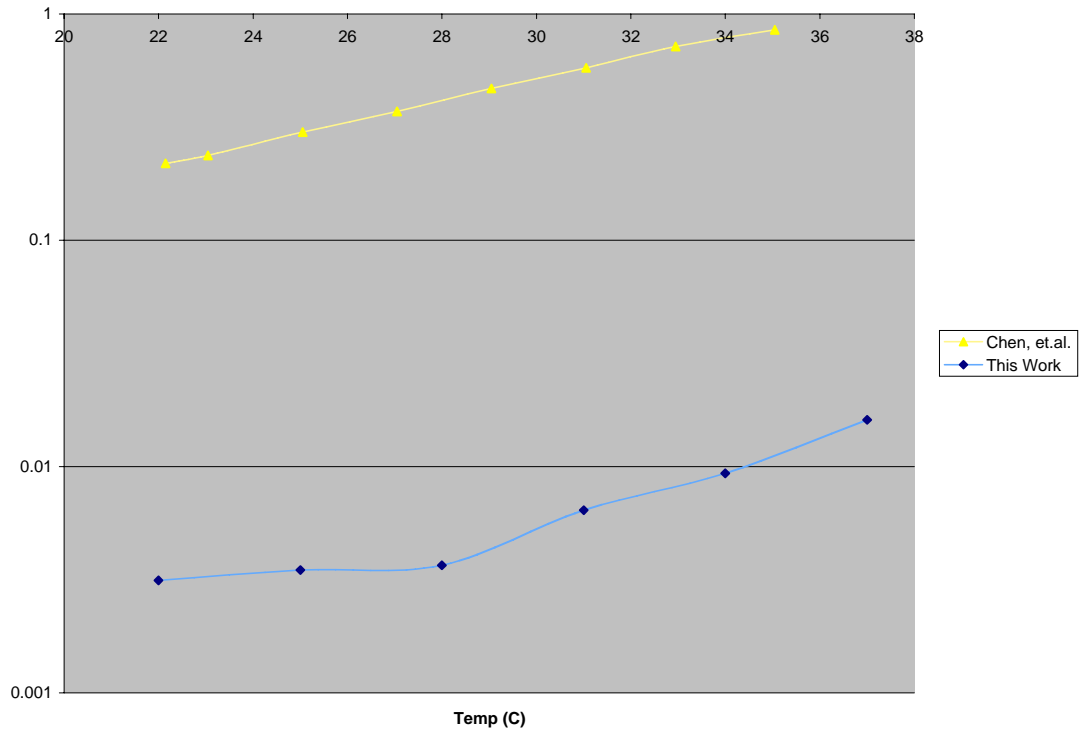


Figure 6. Catechol Vapor Pressure Data. 1.003 cm. distance from orifice to sensor; 0.275 mm. diameter orifice; 0.0254 mm. plate thickness

Chapter 5

Conclusions

It is concluded that the apparatus does not accurately measure vapor pressure data of low-volatile chemicals as it is currently configured. While the basis of the apparatus design stemmed from earlier research, accurate comparability with the vapor pressure data obtained from that research did not result for the chemicals naphthalene and catechol. Naphthalene is too volatile at possible operating temperatures to obtain accurate vapor pressure data. Distance between orifice and sensor, cell leaks, and vacuum chamber contamination may all have been factors in the error associated with obtaining accurate data for catechol. While there is a correction for the distance between the sensor and orifice included, it is only valid as a slight correction to reasonable data. With the degree of variance observed, this correction does not adjust the data within accurate limits. The respectably sizable distance was put in place to assure uniform coating of the sensor, but actually hindered the process. It was evident that most of the mass did not collect on the crystal by observations of solid mass on the perimeter of the crystal holder itself following operation. To eliminate possible error, direct coating of the sensor with the construction of a Knudsen Cell around it should be explored. This will ensure that all of the mass effusing out of the K-Cell is accounted for by the measurement of the mass loss of the crystal instead of mass gain. This option was briefly explored in this work by taping an orifice plate to the crystal holder after coating the sensor, but results are not included due to observation of the crystal holder following operation

finding that the tape did not remain sealed and thus resulted in not all of the chemical effusing through the orifice. A device needs to be designed and built to seal the new K-Cell mechanically.

The Knudsen Effusion Method has been utilized for almost a century, providing accurate vapor pressure and enthalpy data for low-volatile chemicals. While the Quartz Crystal Microbalance has many advantages, its use in conjunction with the Knudsen Effusion Method as shown in this research may need to be modified. In this apparatus, only a fraction of the effused mass was collected, and a mathematical correlation between that and the total mass could not be obtained. It is the finding of the work that to obtain truly accurate data, the total amount of mass escaping the Knudsen Cell must be accounted for.

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Appendices

Appendix A: Laser Drilled Holes in Orifice Plates

Pictures and measurements acquired using a Leica DMI 4000B Inverted Fluorescent Microscope with a Leica 340FX Cooled CCD Camera utilizing Media Cybernetix Image-Pro Plus Software.

PGX = Measured Area of Orifice

Thickness "A" = 0.1016 mm.

PG1 = .1952125 mm²

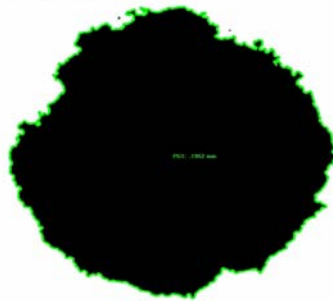


Figure 7. Orifice A.1

PG1 = .0074683 mm²
PG2 = .0002050 mm²

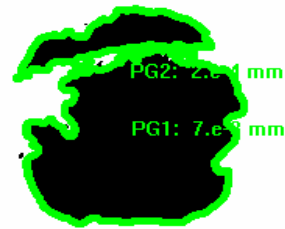


Figure 8. Orifice A.2

PG1 = .0521518 mm²

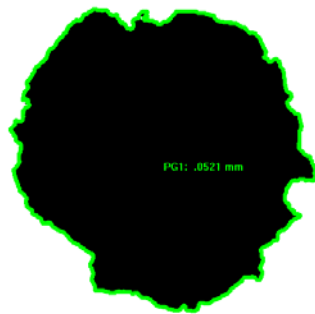


Figure 9. Orifice A.3

PG1 = .2018005 mm²
PG2 = .0001392 mm²

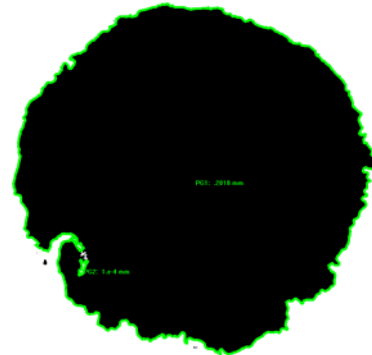


Figure 10. Orifice A.4

Appendix A: (Continued)

PG1 = .0548513 mm²

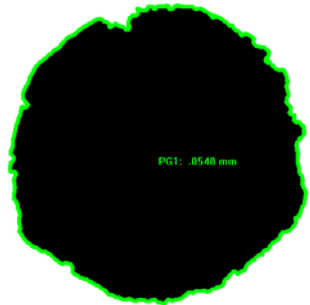


Figure 11. Orifice A.5

PG1 = .0072948 mm²

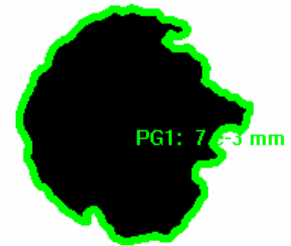


Figure 12. Orifice A.6

PG1 = .3787231 mm²

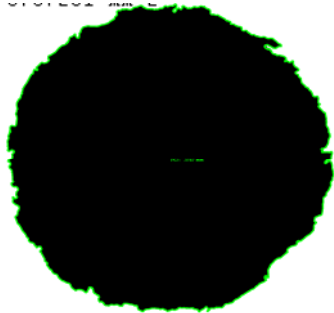


Figure 13. Orifice A.7

PG1 = .3822374 mm²

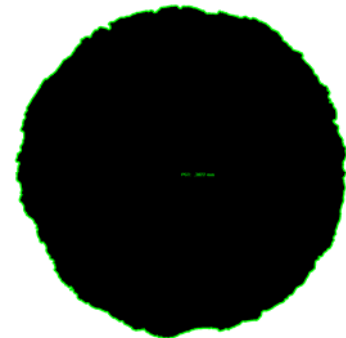


Figure 14. Orifice A.8

PG1 = .7212635 mm²
PG2 = .0022712 mm²

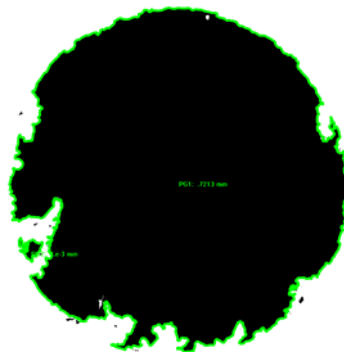


Figure 15. Orifice A.9

PG1 = .7535106 mm²

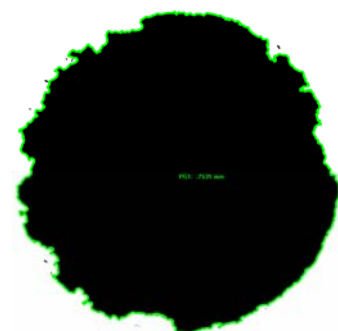


Figure 16. Orifice A.10

Appendix A: (Continued)

Thickness "B" = 0.0254 mm.

PG1 = .2394247 mm²

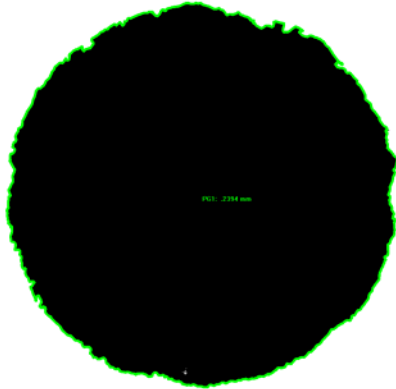


Figure 17. Orifice B.1

PG1 = .0821857 mm²

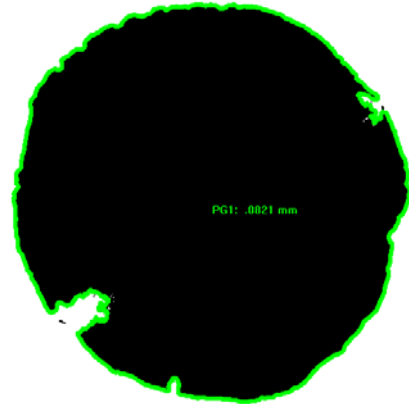


Figure 18. Orifice B.2

PG1 = .2453984 mm²

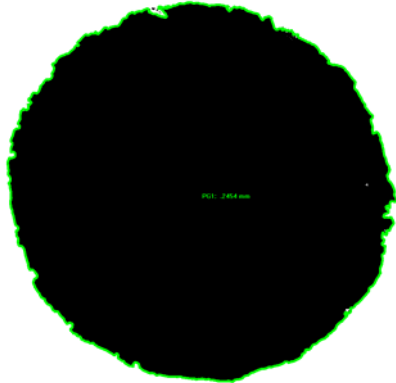


Figure 19. Orifice B.3

PG1 = .0845019 mm²

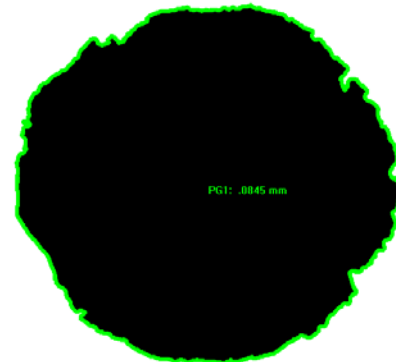


Figure 20. Orifice B.4

Appendix A: (Continued)

PG1 = .4397338 mm²

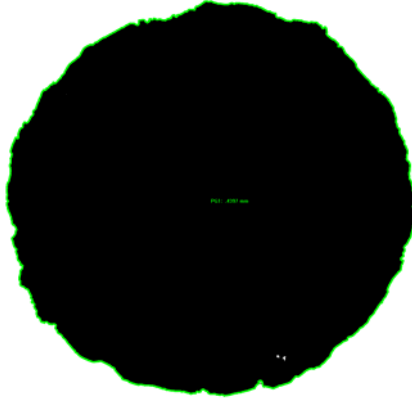


Figure 21. Orifice B.5

PG1 = .0172610 mm²

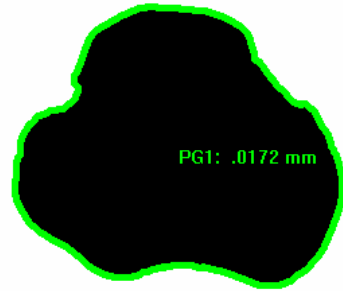


Figure 22. Orifice B.6

PG1 = .8017032 mm²

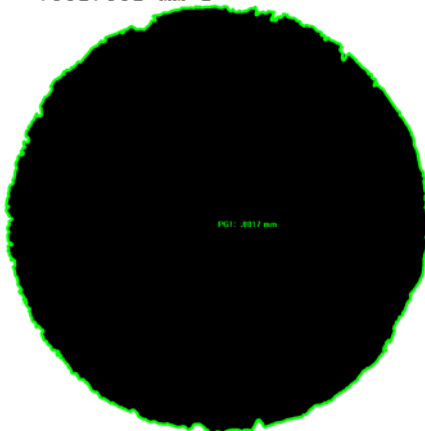


Figure 23. Orifice B.7

PG1 = .0206976 mm²

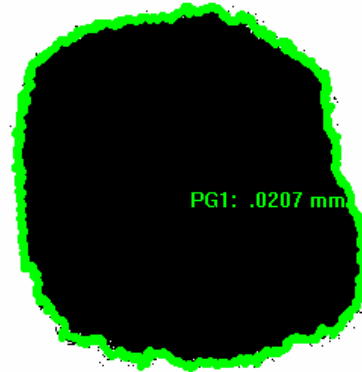


Figure 24. Orifice B.8

Appendix A: (Continued)

PG1 = .4225072 mm²

.4225072 mm²

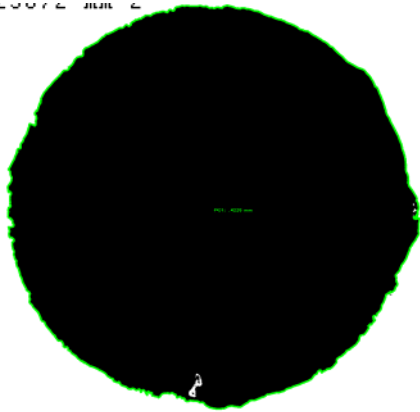


Figure 25. Orifice B.9

PG1 = .8128339 mm²

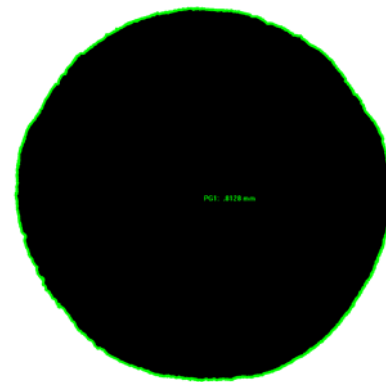


Figure 26. Orifice B.10

Appendix B: Direct Coating Procedure

1. Record initial frequency of crystal by placing it in the holder and connecting to frequency counter.
2. Dissolve chemical to be tested in appropriate solvent (Make sure to record concentration on vial).
3. Place a drop of the solution on a clean crystal and let stand for 30 min.
4. Place an orifice plate over the crystal holder and seal every possible outlet (Record size of hole).
5. Place the crystal in the holder and seal every possible outlet.
6. Record frequency of crystal and use this to calculate the approximate mass of chemical on crystal. If frequency is not stable, clean the crystal and lower the concentration of the tested chemical. Repeat from step 3.
7. Place crystal holder into apparatus and seal all arms of the chamber.
8. Turn on water bath to control temperature of QCM.
9. Start Labview program and set to 5 sec./read. Run under name "Pumpdown" and save in folder of name "Chemical_Date" (i.e. "Catechol_02092007").
10. Turn on forepump and then turbopump.
11. Watch frequency change on the monitor. When frequency shift stabilizes at a steady increase and the pressure reading stabilizes, begin recording data and save in the same folder as "Chemical_Temperature" (i.e. "Catechol_22oC"). Record for 5-10 min. and then stop recording.
12. Change the temperature of the water bath to the next desired setting. Record data as "Chemical_Temperature1-Temperature2" (i.e. "Catechol_22oC-25oC").
13. Repeat step 12. Allow for at least 5 min. after water bath temperature has stabilized for QCM to reach that temperature.
14. Repeat steps 13 and 14 for all subsequent desired temperatures.
15. Once tests are completed, turn off water bath, then turbopump, then forepump.
16. Once the vacuum has shut down, open valve to release pressure, remove crystal holder, and clean crystal.