



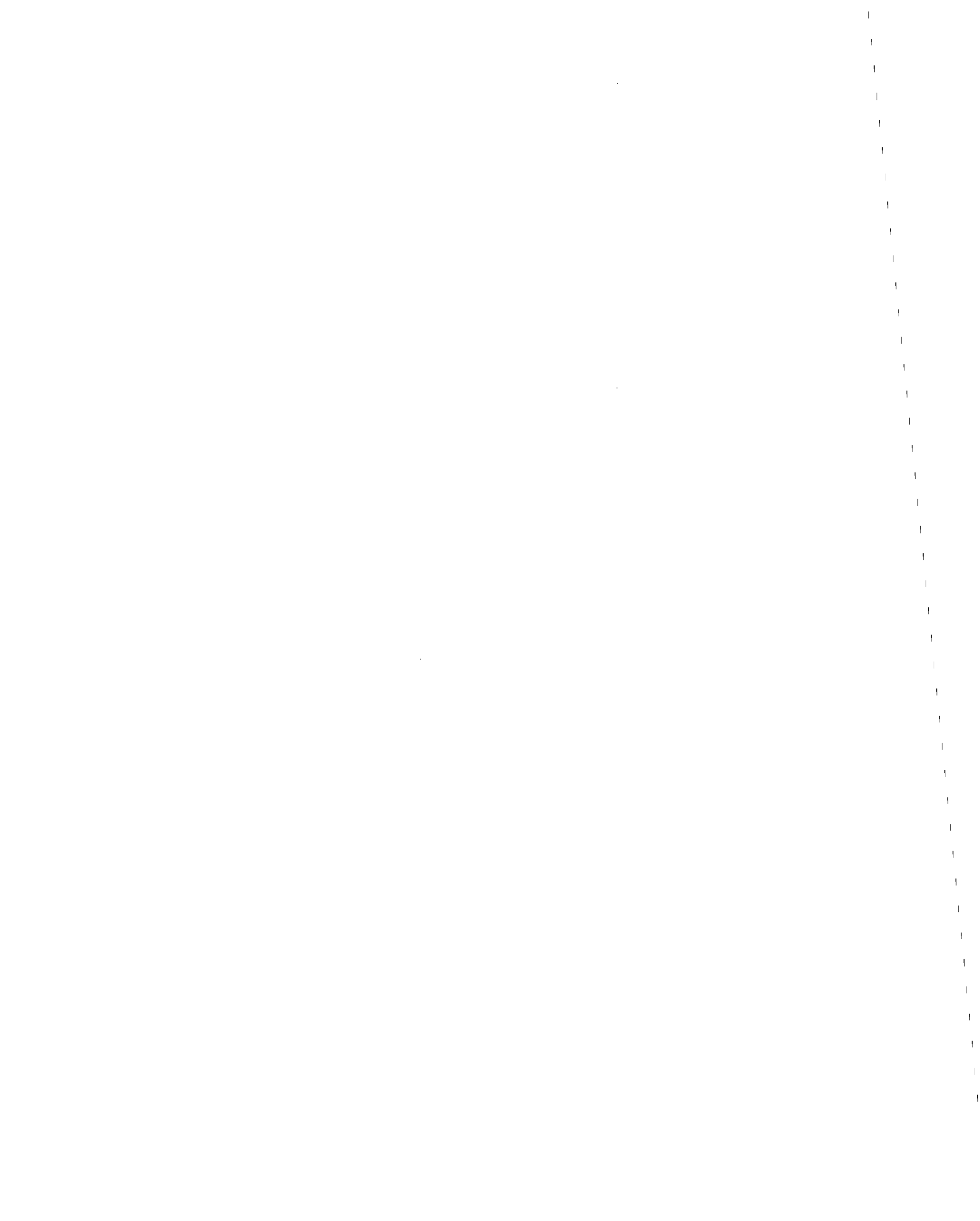
PB95-171104

Final Report for Project No. 5 K01 OH00087-03:
Adsorption of Vapor Mixtures onto Activated Carbon

Division of Environmental Health Engineering, Room 6010
Department of Environmental Health Sciences
The Johns Hopkins University School of Hygiene and Public Health
615 North Wolfe Street
Baltimore, Maryland 21205

by: Patrick N. Breysse, Ph.D.,
Principal Investigator/Program Director
and Coreen Robbins, Ph.D.

September 1994



REPORT DOCUMENTATION PAGE		1. REPORT NO.	2.		
4. Title and Subtitle Adsorption of Vapor Mixtures onto Activated Carbon			FB95-171104 5. Report Date 1994/10/00		
7. Author(s) Breysse, P. N., and C. Robbins			8. Performing Organization Rept. No.		
9. Performing Organization Name and Address Department of Environmental Health Sciences, School of Hygiene and Public Health, Johns Hopkins University, Baltimore, Maryland			10. Project/Task/Work Unit No.		
			11. Contract (C) or Grant(G) No. (C) (G) K01-OH-00087		
12. Sponsoring Organization Name and Address			13. Type of Report & Period Covered		
			14.		
15. Supplementary Notes					
16. Abstract (Limit: 200 words) A method was developed for the study of the adsorption of one vapor in a mixture onto activated-carbon for use in the estimation of organic vapor respirator service life. It was possible to study the absorption of one vapor in the presence of a second vapor using methods developed with a dual flame ionization detector/photoionization detector without any interference from the second vapor. The Wheeler and Dubinin models were used to study the potential effect of the polarity of a vapor on the adsorption of a polar or a nonpolar vapor. The polarity of the accompanying vapor did not systematically affect the Wheeler model 1% breakthrough. The polarity of the vapor did not systematically affect the Test vapor Wheeler model adsorption capacity. The Wheeler model adsorption rate constants for Test vapors were not significantly different when compared according to Probe vapor polarity. The polarity of the probe vapor appeared to subtly affect the affinity of p-xylene (1330207) as determined by the Dubinin model. In the presence of polar and lower boiling point compounds, p-xylene appeared to have greater affinity for carbon than when in the presence of nonpolar higher boiling point compounds. The authors suggest that it may be possible to estimate the service life of a respirator for a vapor in a mixture using the carbon capacity for the vapor, and the mole fraction of the vapor in the mixture. Errors of 30% or more can be expected for vapors in the ranges of polarity, boiling point, and concentration tested.					
17. Document Analysis a. Descriptors					
b. Identifiers/Open-Ended Terms NIOSH-Publication, NIOSH-Grant, Grant-Number-K01-OH-00087, End-Date-05-27-1994, Respirators, Respiratory-protective-equipment, Organic-vapors, Adsorbents, Chemical-properties					
c. COSATI Field/Group					
18. Availability Statement			19. Security Class (This Report)		21. No. of Pages
					97
			22. Security Class (This Page)		22. Price

Table of Contents

List of Abbreviations	iii
List of Figures	iv
List of Tables.	v
Significant Findings.	vii
Usefulness of Findings.	ix
Abstract.	x
Final Report.	1
1. Introduction.	1
2. Background.	2
2.1 Models of Equilibrium Adsorption.	2
2.2 Kinetic Adsorption Models	3
2.3 Models of Kinetic Adsorption of Vapor Mixtures.	6
2.4 Other Studies of the Kinetic Adsorption of Binary Organic Vapor Mixtures	7
2.5 Summary	8
3. Specific Aims	9
4. Procedures and Methodology.	12
4.1 Vapor Selection	12
4.2 Kinetic Experiments	16
4.3 The Gas Chromatographic System.	19
4.4 Equilibrium Adsorption Experiments.	20
5. Results and Discussion.	26
5.1 Method Development.	26
5.2 Kinetic Adsorption Experiments.	26
5.2.1 The Order of Vapor Breakthrough	26
5.2.2 Time to 1% Test Vapor Breakthrough.	33
5.2.3 Kinetic Adsorption Capacity	39
5.2.4 Kinetic Rate Constant	44
5.2.5 Summary of Kinetic Results.	48
5.3 Equilibrium Adsorption Experiments.	49
5.3.1 Dubinin Transformation of Isotherms	49
5.3.2 Equilibrium Adsorption of <i>p</i> -xylene.	55
5.3.3 Equilibrium Adsorption of pyrrole	56
5.3.4 Equilibrium Adsorption Summary.	57
6. Conclusions	59

Acknowledgements	61
References	62
Appendix A: Calibration of GC Detectors.	66
Appendix B: Reproducibility of Carbon Transfer to GC Column.	73
Appendix C: Measurements and Calculations for Use in the Chromatographic Method of Isotherm Determination.	76
List of Present and Possible Future Publications.	83

List of Abbreviations, Symbols, and Greek Letters

Abbreviations

ANOVA	analysis of variance
°C	degrees Celsius
cm	centimeters
D	Debye
eV	electron volts
FID	flame ionization detector
GC	gas chromatograph
GSV	gas sampling valve
HP	Hewlett-Packard
ID	inside diameter
IP	ionization potential
J	Joules
L	liters
Lpm	liters per minute
μL	microliter
m ²	square meters
m ³	cubic meters
min	minutes
mm	millimeter
mL	milliliter
mol	moles
MSHA	Mine Safety and Health Administration
NIOSH	National Institute for Occupational Safety and Health
PEL	permissible exposure limit

PID	photoionization detector
ppm	parts per million —
RH	relative humidity
s	seconds
UV	ultraviolet
U.S.A.	United States of America

Symbols

C_o	bed inlet concentration (g/mL)
C_r	bed exit concentration (g/mL)
C_o/C_r	breakthrough concentration (g/mL)
D	detector sensitivity
E	adsorbate-adsorbent interaction potential
k	Dubinin adsorbent structural constant (mol/cal) ²
k_v	kinetic adsorption capacity
l	length from GC injection to a point on the chromatogram
l_o	length from GC injection to the appearance of a non-adsorbing gas
n	moles
M	adsorbate molecular weight (g/mol)
m	moles of solute injected
n_i	height of a point i on the chromatogram
P	adsorbate equilibrium pressure
P	vapor pressure of a substance at temperature T (torr or N/m ²)
P_o	saturation vapor pressure of a substance at temperature T (torr or N/m ²)
Q	flow rate through adsorbent bed (mL/min or mL/s)

Q_c	GC carrier gas flow rate (mL/min or mL/s)
q	adsorbate concentration (g/mL)
R	gas constant (1.9872 cal/mol $^{\circ}$ K, 8.24281 J/mol $^{\circ}$ K, or 8.31 N $\cdot$ m/mol $^{\circ}$ K)
S_t	total area of reference chromatogram (cm ^{2})
S_i	total adsorbent surface area (cm ^{2})
T	temperature
$^{\circ}T$	absolute temperature $^{\circ}$ K (Kelvin)
t	time to breakthrough (min or s)
t_b	time to breakthrough of C_i/C_o (min or s)
u	chart speed (cm/min)
V	volume (mL)
W_b	mass of carbon bed (g)
W_e	kinetic adsorption capacity
W_o	maximum adsorption volume (mL/g)
W_v	volume of adsorbed substance (mL/g)

Greek Letters

β	Dubinin affinity coefficient
ϵ	Polanyi adsorption potential
μ	micro
ρ_B	bulk density of carbon bed packing (g/mL)

List of Figures

2.1.1	Example of a Dubinin characteristic curve for <i>p</i> -xylene.	4
2.2.1	Breakthrough of <i>p</i> -xylene alone, plotted according to the Wheeler equation	5
4.1.1	Molecular structure of <i>Test</i> and <i>Probe</i> vapors.	15
4.1.2	Spectral output of an 8.4 eV photoionization detector lamp	17
4.2.1.1	Schematic of vapor-generation, adsorption, and detection system for kinetic experiments.	18
4.4.1	Diagram of the areas of the chromatogram needed to calculate the adsorption isotherm	25
5.1.1	PID chromatogram of the breakthrough of pyrrole and toluene showing detection of pyrrole only	27
5.1.2	FID chromatogram of the breakthrough of pyrrole and toluene showing detection of both vapors.	28
5.1.3	Chromatograms from injections of <i>p</i> -xylene with <i>o</i> -dichlorobenzene, showing the detection of only <i>p</i> -xylene with the PID (A), and detection of both vapors with the FID (B)	29
5.2.1.1	Complete breakthrough of a mixture of <i>p</i> -xylene and <i>p</i> -fluorotoluene.	31
5.2.2.1	One percent t_b versus total vapor concentration on a log-log scale for <i>p</i> -xylene alone, and in the presence of <i>Probe</i> vapors.	37
5.2.2.2	One percent t_b versus total vapor concentration on a log-log scale for pyrrole alone, and in the presence of <i>Probe</i> vapors.	38
5.3.1.1	Dubinin characteristic curves for <i>p</i> -xylene alone, and with <i>Probe</i> vapors.	53
5.3.1.2	Dubinin characteristic curves for pyrrole alone, and with <i>Probe</i> vapors.	54

List of Tables

4.1.1	Pairing of the non-polar <i>Test</i> vapor (<i>p</i> -xylene) with polar and non-polar <i>Probe</i> vapors.	.13
4.1.2	Pairing of the polar <i>Test</i> vapor (pyrrole) with polar and non-polar <i>Probe</i> vapors.	.13
4.1.3	Selected physicochemical properties of chemicals used as <i>Test</i> and <i>Probe</i> vapors	.14
5.2.1.1	Percent breakthrough (C_i/C_o) of <i>Probe</i> vapors when <i>Test</i> vapor C_i/C_o is at 1%.	.32
5.2.2.1	Observed ($n=6$) and predicted 1% breakthrough time (t_b) for <i>p</i> -xylene alone, and with <i>Probe</i> vapors at varying concentrations.	.34
5.2.2.2	Observed ($n=6$) and predicted 1% breakthrough time (t_b) for pyrrole alone, and with <i>Probe</i> vapors at varying concentrations.	.35
5.2.3.1	Observed ($n=6$) and predicted kinetic adsorption capacity (W_e) for <i>p</i> -xylene alone, and with <i>Probe</i> vapors at varying concentrations.	.40
5.2.3.2	Observed ($n=6$) and predicted kinetic adsorption capacity (W_e) for pyrrole alone, and with <i>Probe</i> vapors at varying concentrations.	.41
5.2.4.1	The average k_v ($n=6$) for <i>p</i> -xylene alone, and in equimolar binary mixtures.	.45
5.2.4.2	The average k_v ($n=6$) for pyrrole alone, and in equimolar binary mixtures.	.46
5.3.1.1	Dubinin equilibrium adsorption volume (W_o) and affinity (k/β^2) for <i>p</i> -xylene alone, and in approximately equimolar mixtures with <i>Probe</i> vapors.	.51
5.3.1.2	Dubinin equilibrium adsorption volume (W_o) and affinity (k/β^2) for pyrrole alone, and in approximately equimolar mixtures with <i>Probe</i> vapors	.52

Significant Findings

The purpose of this study was to develop a method to study the adsorption of one vapor in a mixture, and to extend the current knowledge of models used to estimate respirator service-life for eventual use with vapor mixtures. Significant findings based in this research include:

1. Using methods developed with a dual FID/PID detector, it was possible to study the adsorption of one vapor in the presence of a second vapor without interference from the second vapor.
2. The Wheeler model 1% breakthrough (t_b) was not systematically affected by the polarity of the accompanying vapor. The 1% t_b for Test vapors (either p-xylene or pyrrole) appeared to be dependent on the total concentration of the vapor system, and for practical purposes, was not affected by the polarity or boiling point of the accompanying Probe vapor (either toluene, p-fluorotoluene, o-dichlorobenzene or p-dichlorobenzene).
3. Since the 1% t_b and thus, the respirator service-life depend mainly on total vapor concentration; the presence of other vapors must be taken into account when estimating the respirator service-life for a vapor in a mixture.
4. The Test vapor Wheeler model adsorption capacity (W_e) was not systematically affected by the polarity of the accompanying vapor. The Test vapor W_e varied in proportion to its mole fraction in the mixture. Estimates of the W_e ($\pm 20\%$) for a vapor in a mix were obtained from single-vapor data. An effect of the relative boiling points of the vapors is suggested for the W_e , and tests with vapors of more widely ranging boiling point are warranted.
5. The Wheeler model adsorption rate constants (k_v) for Test vapors were not significantly different when compared according to Probe vapor polarity. The k_v was significantly different for p-xylene when compared according to Probe vapor boiling point. However, the k_v 's for Test vapors alone were generally lower than for Test vapors in equimolar binary mixtures.
6. The affinity of p-xylene, as measured by the Dubinin model, appears to be subtly affected by the polarity of the Probe vapor. Para-xylene appears to have greater affinity for carbon when in the presence of polar, and lower boiling point compounds than when with non-polar, higher boiling point compounds. However, the changes in affinity are small and are not practically important. Additional research is

needed to determine if this effect is observed for other vapors. The affinity of pyrrole in binary mixtures is not different when compared according to Probe vapor polarity.

7. The Dubinin capacities (W_0 's) for Test vapors alone are not significantly different from their W_0 in mixtures. The W_0 for pyrrole is about half that of *p*-xylene. The reasons for this are unclear, however a possible explanation is that hydrogen bonding may affect the isotherms of pyrrole, making the calculation of isotherms using the chromatographic method difficult.

This research suggests that it may be possible to estimate the service-life of a respirator for a vapor in a mixture using the carbon capacity for the vapor, and the mole fraction of the vapor in the mixture. However, errors of 30% or more can be expected for vapors in the ranges of polarity, boiling point, and concentration tested. Further investigation of more diverse mixtures is required before this approach can be more broadly generalized

Usefulness of Findings

1. Method Development: The dual FID/PID detector system, with an 8.4 eV PID ion source, is a useful tool for studying the adsorption of one vapor in the presence of other vapors. It can be used to study a particular vapor in a mixture: (1) for kinetic studies to follow the breakthrough of the vapor, or (2) to obtain the equilibrium isotherm (by using the chromatographic method). However, the limited temperature range (to 220°C) suggests that other methods need to be developed to efficiently study the adsorption of higher boiling-point compounds. Using the PID detector in combination with the chromatographic method of isotherm determination, it is possible to obtain Dubinin characteristic curves for a single vapor in a mixture.
2. Practical Application: Since the 1% t_b was not systematically affected by the polarity of the accompanying vapor, reasonably good estimates of the 1% t_b ($\pm 30\%$) can be obtained for vapors in mixtures (in the range of polarity and boiling point tested) by using the Wheeler model and single-vapor data. Thus, activated carbon respirator service-life can be estimated by using: (1) the Wheeler model carbon capacity for the vapor, and (2) the mole fraction of the vapor in the mixture. However, errors of 30% or more can be expected.
3. Importance to Worker Health: Since the breakthrough time, and thus the respirator service-life is mainly dependent on total vapor concentration, the presence of other vapors must be taken into account when estimating the respirator service-life for a vapor in a mixture. For example, a typical respirator with activated carbon cartridges (100 g carbon total) has an estimated service-life (using the Wheeler model) of 116 ± 29 minutes in an environment containing 1000 ppm p-xylene (assuming a respiration rate of $0.5 \text{ m}^3/\text{h}$). If the environment also contains 1000 ppm toluene, the service-life is reduced to 47 ± 12 minutes. In this case, calculating the service-life of the respirator for p-xylene without considering the presence of toluene results in a significant over-estimation of service-life and the potential for over-exposure to the respirator wearer.

Abstract

Carbon respirator cartridges are recommended for use by the National Institute for Occupational Safety and Health (NIOSH) for many organic substances. It has been estimated that over seven million organic vapor respirator cartridges are used annually in the United States.

Historically, respirator service-life testing, research, and model development, has been limited to single-vapor systems. Since real-world conditions of respirator use often involve mixtures of vapors, models used to predict the service-life of organic vapor respirators in the workplace must address mixed vapors. Proposed single-vapor models are limited because they do not include provisions for vapor mixtures, and a better understanding of the physicochemistry of adsorption of organic vapor mixtures on activated carbon is required to expand single-vapor models to mixtures.

The purpose of this research is to develop a method to study the adsorption of one vapor in a mixture, and to extend the current knowledge of models used to estimate respirator service-life for eventual use with vapor mixtures. A method utilizing a photoionization detector was developed to selectively study one vapor in a mixture, and the potential effect of the polarity of a second vapor on the adsorption of a polar and a non-polar vapor was studied as measured by the Wheeler and Dubinin models. The Wheeler and Dubinin models were selected because they have been often used successfully to model respirator service-life for single vapors.

Experimental systems were designed and constructed to generate, control, and monitor the concentration of binary organic vapors. Experiments were planned to allow the study of adsorption of a single organic vapor in the presence of another vapor, without interference from the second vapor, to determine whether the adsorption of a vapor in a binary mixture is affected by the polarity of the accompanying vapor.

The 1% breakthrough time ($1\% t_b$) kinetic adsorption capacity (W_p) and rate constant (k_v) of the Wheeler model were determined (for vapor challenges on carbon beds) for both *p*-xylene and pyrrole (referred to as *Test* vapors) alone, and in equimolar binary mixtures with polar and non-polar vapors (referred to as *Probe* vapors). The *Probe* vapors were toluene, *p*-fluorotoluene, *o*-dichlorobenzene, and *p*-dichlorobenzene.

The characteristic curves of the Dubinin model were obtained from isotherms for *Test* vapors alone, and in equimolar binary mixtures, injected onto carbon columns. The slope of the Dubinin curve represents the vapor-carbon affinity; and these slopes were compared to determine whether the *Test* vapor's affinity is influenced by the presence of a second vapor, and if the changes depend on the polarity of the *Probe* vapor.

The polarity of the accompanying vapor did not systematically effect the $1\% t_b$ of the *Test* vapors. The $1\% t_b$ for

a vapor in a binary mixture can be estimated reasonably well from single-vapor data ($\pm 30\%$). Since the 1% t_b , and thus, respirator service-life, is mainly dependent on total vapor concentration, the presence of other vapors must be taken into account when estimating respirator service-life for a vapor in a mixture. For example, the 1% breakthrough time for *p*-xylene at a concentration of 0.15 $\mu\text{mol/mL}$ is 35 minutes for *p*-xylene alone, and 24 minutes for *p*-xylene at a similar concentration in an equimolar mix with toluene (0.14 $\mu\text{mol/mL}$ *p*-xylene with 0.14 $\mu\text{mol/mL}$ toluene).

The W_v was not systematically affected by the polarity of the second vapor. The W_v for Test vapors in equimolar mixtures ranged from 0.18 to 0.29 g/g for *p*-xylene, and 0.14 to 0.18 g/g for pyrrole. The W_v for a vapor in a binary mixture could be estimated reasonably well ($\pm 20\%$) from the single-vapor W_v , and the mole fraction of the vapor in the mixture. For example, the W_v for *p*-xylene alone is 0.41 g/g, and is 0.18 g/g when in a equimolar mixture with *o*-dichlorobenzene.

The k_v for Test vapors in equimolar mixtures ranged from 47.7 to 78.2 s^{-1} for *p*-xylene, and 67.7 to 79.8 s^{-1} for pyrrole. The Test vapor k_v was not affected by the polarity of the accompanying vapor; however, the k_v for *p*-xylene in mixtures was significantly different ($p < .001$) when compared according to the boiling point of the accompanying vapor. For *p*-xylene, the k_v was higher in the presence of higher boiling point vapors, and lower in the presence of lower boiling point vapors (e.g., 78.2 s^{-1} with *o*-dichlorobenzene, and 47.7 s^{-1} with toluene). These differences are not practically important in estimating 1% t_b and respirator service-life. Significant differences were not found for the k_v of pyrrole.

Comparison of the slopes of the Dubinin characteristic curves suggest that the affinity of *p*-xylene is influenced by the polarity of the accompanying Probe vapor. Para-xylene appears to have slightly enhanced affinity for carbon when in the presence of polar, and lower boiling point compounds than when with non-polar, higher boiling point compounds. However, the changes in affinity are small and are of limited practical importance. The affinity of pyrrole in binary mixtures is not different when compared according to Probe vapor polarity or boiling point.

These results indicate that the polarity and boiling point of the vapors in the range tested appears to be practically unimportant in predicting service-life; however, an effect due to the relative boiling points of the accompanying vapor is suggested, and tests with vapors of more widely ranging boiling point are warranted.

The 1% breakthrough time, and thus the respirator service-life is mainly dependent on total vapor concentration; therefore, the presence of other vapors must be taken into account when estimating the respirator service-life for a vapor in a mixture. For example, a typical respirator with activated carbon cartridges (100 g carbon total) has an estimated service life (using the Wheeler model) of 116 ± 29 minutes in an environment

containing 1000 ppm *p*-xylene (assuming a respiration rate of 0.5 m³/h). If the environment also contains 1000 ppm toluene, the service life is reduced to 47±12 minutes. In this case, calculating the service-life of the respirator for *p*-xylene without considering the presence of toluene results in a significant over-estimation of service-life and the potential for over-exposure to the respirator wearer.

This research indicates that it may be possible to estimate the service-life of a respirator (1% t_b, ±30%) for a vapor in a binary mixture using the carbon capacity for the vapor, and the mole fraction of the vapor in the mixture. However, before this approach can be more broadly generalized, further investigation of more diverse mixtures is required.

Additional research is needed before the Dubinin and Wheeler models can be reliably extended for use with mixtures containing vapors with more diverse vapor concentration, molecular weight, boiling point, and polarity, than those used in this study. Future research should be expanded to include adsorption studies of mixtures to determine the contribution of vapor boiling point and molecular weight to changes in capacity and breakthrough time and the investigation of mixtures of more widely variable polarity and more extreme differences in vapor concentration.

Final Report: Adsorption of Vapor Mixtures onto Activated Carbon

1. Introduction

Carbon respirator cartridges are recommended for use by the National Institute for Occupational Safety and Health (NIOSH) for many organic substances. It has been estimated that over seven million organic vapor respirator cartridges are used annually in the United States.¹ Approval of respirators by NIOSH and MSHA (Mine Safety Health Administration) requires that they provide protection for at least 50 minutes against 1000 ppm (parts per million) of carbon tetrachloride when tested at 50±5 percent RH (relative humidity), at 25°C, and a continuous flow rate of 64 Lpm (liters per minute), and at a flow rate of 32 Lpm when the cartridges are preconditioned (for six hours at 25 Lpm, 85 or 25 percent RH).²

Because of the difficulty of accurately predicting their service-life during field use, respirator cartridges are typically changed daily, or more often if the wearer detects odor or irritation indicating breakthrough. The use of respirator cartridges is therefore limited to vapors with warning properties (odor, taste, and eye and/or respiratory tract irritation) that can be detected below the Permissible Exposure Limit (PEL).^{2,3} Even with this restriction, reliance on warning properties to determine the need for respirator cartridge change is of limited safety because individuals differ in sensitivity, because workers can be desensitized to an odor and no longer notice it, and because the worker's environment frequently contains a variety of compounds which may mask and/or alter each others warning properties.^{2,3} Thus, respirators may be changed less often than required for adequate protection, resulting in potentially hazardous exposures, or changed more frequently than necessary, resulting in inconvenience for the worker and increased financial burden on the employer.

These factors highlight the need for accurate models of activated carbon adsorption behavior that are capable of predicting bed service-life under the actual conditions of respirator use.² Since real-world conditions of respirator use often involve mixtures of vapors, models used to predict the service-life of organic vapor respirators in the workplace must address mixed vapors. Proposed single-vapor models are limited because they do not include provisions for vapor mixtures, and a better understanding of the physicochemistry of organic vapor mixtures on activated carbon is required to expand single-vapor models to mixtures.^{4,5}

2. Background

2.1 Models of Equilibrium Adsorption

Over the years, many models have been developed to describe equilibrium adsorption.^{6,7} Dubinin and co-workers developed a modified form of the Polanyi potential theory that allows calculation of adsorption isotherms at additional temperatures from a single isotherm.⁴ This model was developed specifically for microporous adsorbents.⁴

Polanyi defined the adsorption potential as the isothermal work of compression necessary to condense the vapor from equilibrium pressure in the gas phase to the saturated vapor pressure of the liquid adsorbate at the adsorbent surface.⁸ According to Polanyi, the adsorption potential is defined as:⁸

$$\epsilon = RT^\circ \log \left(\frac{P_o}{P} \right) \quad 2.1.1$$

where:

ϵ = Polanyi adsorption potential (J/mol);
 R = gas constant (8.2429 J/mol $^\circ$ K);
 T° = absolute temperature.

The adsorption potential is greatest at the adsorbent surface; and at equal distances from this surface, equipotential planes (ϵ_i) exist which contain a specific volume of adsorbate (W_v) between the planes and the adsorbent surface. At some distance from the adsorbent surface, ϵ will equal zero, and the volume enclosed by the carbon surface and the planes will be equal to the maximum adsorption volume, W_o . The linear form of the Dubinin equation can be written as:

$$\log(W_v) = \log(W_o) - \frac{k_s \epsilon^2}{\beta^2} \quad 2.1.2$$

where:

W_v = adsorption volume (mL/g);
 W_o = maximum adsorption space (mL/g);
 k_s = structural constant of the adsorbent (mol/cal)²;
 β = dimensionless affinity coefficient;

and ϵ as previously defined.

Experimentally determined values of W_v are plotted against ϵ^2 , resulting in a curve that characterizes an adsorbate-adsorbent system.^{5,8} An example of a characteristic curve is

shown in Figure 2.1.1.

The constants W_o and k , which are related to the pore structure of the adsorbent, are obtained from the characteristic curve of a reference compound (usually carbon tetrachloride). The affinity coefficient (β) compares the strength of the adsorbate-adsorbent interaction for the test vapor to a reference adsorbate, and is best predicted by utilizing the ratio of the electronic polarizations of the adsorbates.⁹ Having calculated β , and using W_o and k from the characteristic curve of the reference adsorbate, characteristic curves of untested adsorbates can be predicted. Using W_o and k , isotherms at different temperatures can also be predicted.

The predictive utility of the Dubinin equation has been verified for a range of single-vapor challenge concentrations on microporous surfaces by a number of investigators.^{4,6,10-12} Earlier investigators used reference vapors with dipole moments similar to those of the test vapors; however, recent evidence suggests that this is not required for test vapor polarities in the range of 0 to 2.50 Debye (D).¹³

2.2 Kinetic Adsorption Models

Several models have been proposed to describe the process of kinetic adsorption.^{4,14-18} The Wheeler theoretical model was developed to predict adsorbent bed behavior in dynamic systems.¹⁶ It is based on a continuity mass balance relationship of the vapor entering an adsorbent bed, and the vapor adsorbed before bed penetration occurs, according to the following equation.¹⁹

$$t_b = \frac{W_e}{C_o Q} \left[W_B - \frac{\rho_B \ln \left(\frac{C_o}{C_x} \right)}{k_v} \right] \quad 2.2.2$$

where:

- W_e = kinetic saturation capacity (g/g);
- W_B = mass of the carbon bed (g);
- ρ_B = bulk density of the packing (g/mL);
- Q = flow rate (mL/s);
- k_v = pseudo first-order rate constant (s⁻¹).

This equation is valid when available adsorption sites greatly exceed the number of adsorbate molecules, thus it is a 'pseudo' first-order kinetic model.²⁰ The pseudo first-order rate constant is valid at low relative breakthrough concentrations ($C_x/C_o < 0.04$). A graph of $\ln(C_x/C_o)$ versus the breakthrough time allows the calculation of k_v and W_e . An example of such a graph is shown in Figure 2.2.1. This kinetic model has been validated by Jonas and others for a number of vapors.^{4,19,21,22}

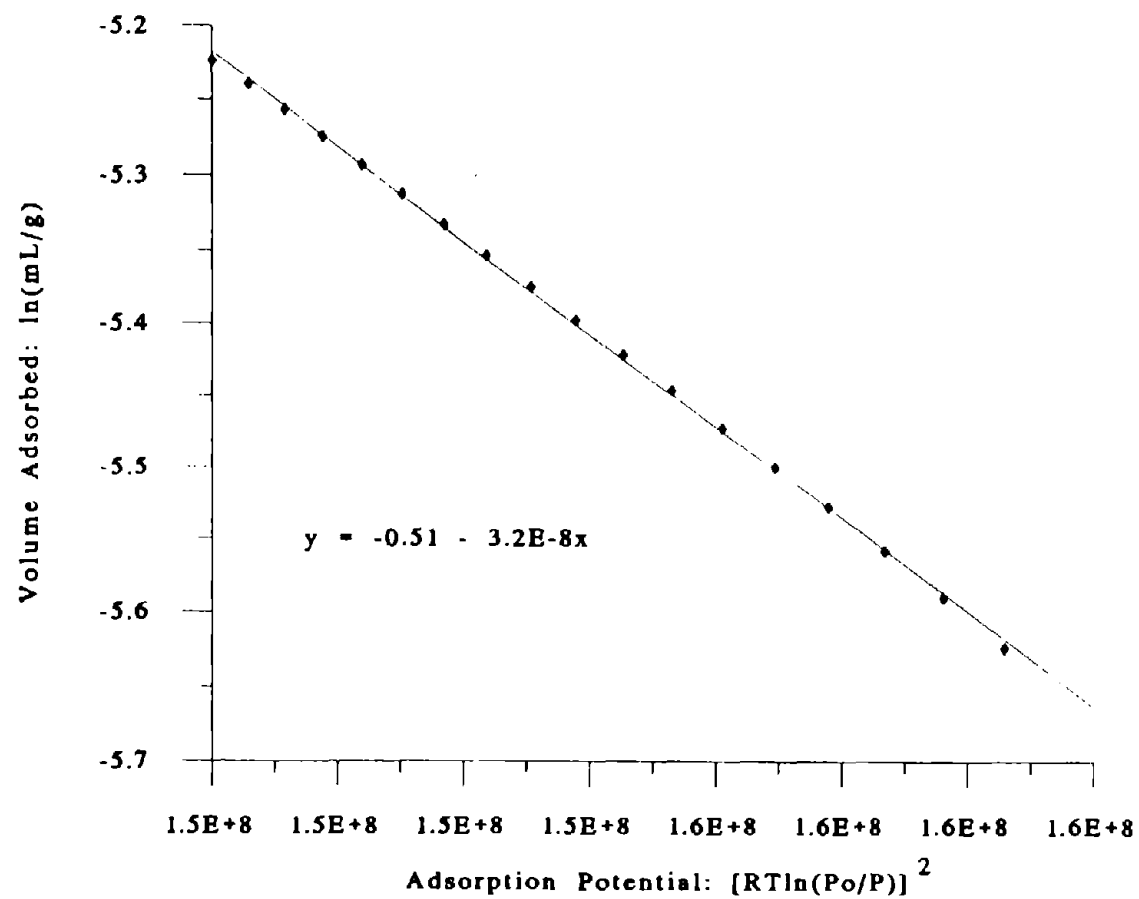


Figure 2.1.1. Example of a Dubinin characteristic curve for *p*-xylene (intercept = W_0 ; slope = k/β^2).

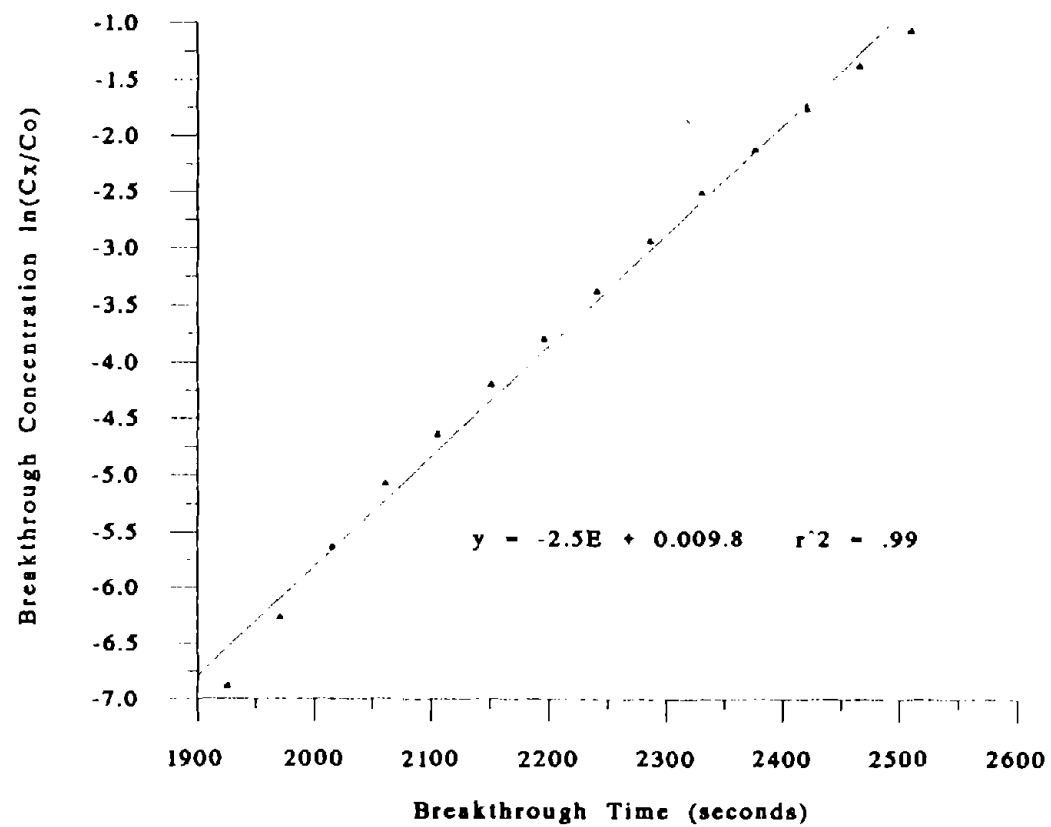


Figure 2.2.1. Breakthrough of *p*-xylene *alone*, plotted according to the Wheeler equation.

Jonas also combined the Wheeler model and Dubinin isotherm equation to predict breakthrough times for untested vapors.²³ The parameters of the Dubinin and Wheeler models were determined once from a reference vapor. The Dubinin model W_0 (mL/g) from the reference vapor is converted to the Wheeler model W_e (g/g) using the density (liquid) of the untested vapor. The k_v was predicted from:

$$(k_v M^{1/2})_i = (k_v M^{1/2})_{ref} \quad 2.2.2$$

where:

k_{vi} = untested vapor rate constant;
 M_i = untested vapor molecular weight;
 k_{vref} = reference vapor rate constant;
 M_{ref} = reference vapor molecular weight.

The new values of k_v and W_e are then used in the Wheeler model to predict breakthrough time for the untested vapor.^{24,25} Using dimethyl methylphosphonate as the reference vapor, Jonas found good agreement between experimental and predicted W_e 's and k_v 's for dichloromethane, benzene, carbon tetrachloride, chloroform, and isomethylphosphonate.²⁴ Sansone et al., found agreement within $\pm 15\%$ between experimental and predicted values of W_e and k_v for 31 carcinogenic organic vapors (using carbon tetrachloride as the reference vapor).²⁶ These results suggest that a combination of the Dubinin and Wheeler models could be used to estimate the breakthrough times of untested vapors with a minimum of experimental data.

2.3 Models of Kinetic Adsorption of Vapor Mixtures

Investigations of adsorption and respirator service-life have focused primarily on single vapor systems, and there are few published reports of mixed vapor studies.^{2,4,27} Yoon^{28,29} and Jonas³⁰ have attempted to modify single-vapor models to predict kinetic adsorption parameters for multiple vapors.

The Wheeler-Jonas Model: Jonas extended the use of the combination of the Dubinin and Wheeler models for vapor mixtures. Kinetic adsorption parameters were predicted for vapors in mixtures using single-vapor equilibrium data (Dubinin model) and incorporating the mole fractions of each component in the calculations.³⁰ Using this approach, Jonas studied the adsorption of binary mixtures of chloroform, benzene, and carbon tetrachloride. The agreement between experimental and predicted values was reasonable, with variations of $\pm 20\%$ for W_e , and $\pm 30\%$ for k_v .³⁰ In addition, he found that the adsorption space occupied by each component was proportional to its mole fraction in the mixture.³⁰ The prediction of adsorption parameters based on this study is limited to cases of similar vapor

concentrations, where the vapors have similar physicochemical properties and no interaction occurs between vapor molecules.³⁰

2.4 Other Studies of the Kinetic Adsorption of Binary Organic Vapor Mixtures

Studies of binary organic vapor mixtures describing the kinetic adsorption parameters of one vapor in the presence of another vapor containing a different dipole moment are limited. Since studies based on kinetic models are fewer, the following studies are discussed although they are not based on a kinetic model. They are relevant because they involve adsorption of mixtures of higher molecular weight organic vapors on activated carbon.

Swearengen and Weaver challenged respirator cartridges with binary mixtures of polar and non-polar organic vapor's at concentrations of 1000 and 2000 ppm, at humidities of 50 and 85 percent.³¹ They found single and binary vapor t_b 's (at equal total vapor concentrations) different for some vapors. With mixtures containing low boiling-point vapors, the lower-molecular weight component t_b decreased while the higher-molecular weight component t_b increased, relative to each vapor's singular t_b . With higher-molecular weight mixtures, the breakthrough time was reduced for both vapors in the mixture. The effect, if any, of vapor polarity on breakthrough time was not discernable from the experiments conducted.

A study of activated charcoal sampling tubes showed that the adsorption capacity is reduced for each vapor in binary mixtures of styrene with acetone or dichloromethane.³² Styrene appears to be adsorbed in preference to acetone and dichloromethane; acetone or dichloromethane breaks through first, their concentration eventually exceeds their C_0 concentration, returning to the C_0 only after styrene breakthrough is under way. These results are qualitatively similar to those reported by Yoon, et al. for acetone with styrene.^{28,29}

In studies of binary mixtures of carbon tetrachloride with pyridine, and carbon tetrachloride with hexane on respirator carbon, the carbon capacity for each component was approximately equal to the product of the capacity of the individual vapor and the their mole fraction in the mixture.³³ However, only minor decreases of capacity were observed for pyridine in the presence of increasing concentrations of carbon tetrachloride. The authors suggest that this may be the result of the polar nature of the pyridine molecule causing multi-layer adsorption due to hydrogen-bonding and adsorption of molecules normal (instead of parallel) to the carbon surface, resulting in self-association.

A study of mixed-vapor adsorption in activated charcoal sampling tubes suggested that polar compounds (isopropanol, ethanol, acetone) are displaced by non-polar vapors (xylenes, toluene).³⁴ Displaced polar compounds were collected on silica in tubes placed behind the charcoal sampling tubes.

2.5 Summary

Although a number of investigators have studied the adsorption of single vapors onto activated carbon, few have examined these parameters for mixed vapor systems, and fewer still have employed models to interpret their data or to develop an understanding of the underlying physicochemical processes. Studies in which mixed organic vapor adsorption has been predicted with the Dubinin and Wheeler models have been restricted to mixtures of components of similar polarity. Studies including binary vapor components of different polarity have provided limited information regarding the mechanisms underlying the observed differences in adsorption. Some studies suggest that the polarity of a mixture component may affect the adsorption of the other component.^{28,29,32-34} Investigation of the adsorption of binary organic vapor mixtures of variable polarity are needed to determine whether the adsorption parameters for a vapor component are affected by the polarity of the component vapors.

3. Specific Aims

This application proposed to evaluate the effect of adsorbate polarity on equilibrium and kinetics of organic vapor adsorption on activated carbon and silica gel. Experiments were designed to test the hypothesis that mixtures composed of differing polarities and functional groups will have different adsorption kinetics and equilibria than single vapors or mixtures with differing polarities and functional groups. The following specific aims were listed in the original proposal:

1. Evaluate adsorption equilibria of single vapors and binary mixtures of organic vapors onto activated carbon and silica gel at different relative humidities. Equilibrium data will be analyzed using the Dubinin isotherm and model for adsorption onto microporous adsorbents. Apparent heats of adsorption will also be determined.
2. Evaluate adsorption kinetics for single vapors and binary mixtures of organic vapors onto activated carbon and silica gel at different relative humidities. Kinetic data will be analyzed using parameters of the Wheeler Equation.
3. Suggest modifications of existing adsorption models to account for adsorbate mixtures of varying polarities and functional groups.

Due to equipment constraints, difficulties and time delays associated with developing the two detector system, and initial determinations made on preliminary data, it was not possible or desirable to complete all the specific aims as originally listed above.

Experiments involving silica gel were not completed after preliminary data indicated that the breakthrough times were much less than for carbon under the same conditions. Because of the large amount of time required to develop the two-detector methodology, experiments were carried with dry air only. Delays resulted from several problems which occurred during the development of this system; some were related to degradation of internal components of the PID (by solvents, or temperatures above 200°C) causing non-linear behavior and erratic baseline data, and some were the result of injection-port design flaws. Although we worked closely with Hewlett-Packard (HP) GC technicians (using other monies, we had purchased a service-contract for the entire GC system) the problems took a large amount of time to resolve because they were problems that the HP technicians were unfamiliar with. This is because: (1) it was a relatively new detector system, and (2) we were using it in a manner that was completely different from the way other labs were using it.

Once operating, the system performed well; however, we estimate that nearly a year was needed to get the two-detector

system to work properly. Fortunately we were able to afford a service contract for the GC system, otherwise it would have been difficult to complete this work.

Silica gel experiments: Breakthrough experiments with silica gel were not pursued after initial experiments with p-xylene and o-dichlorobenzene indicated that breakthrough times were extremely short compared to those for carbon. For example, at low p-xylene concentrations ($0.08 \mu\text{moles/mL}$) the breakthrough time on a 1 g carbon bed is approximately 142 minutes, and on a 1 g silica bed is less than 20 minutes. In addition, breakthrough on the silica occurs too quickly to obtain enough points to plot a reasonable breakthrough curve (5 to 6 points are needed in the interval $0.25\% < C_i/C_o < 4.0\%$) for use with the Wheeler model (vapor injections had to be spaced at 35 to 45 second intervals to prevent column/detector saturation). These problems also preclude the development of breakthrough curves at vapor higher concentrations. From these results, it was also concluded that the retention time for silica gel-packed GC columns would be too short to provide the peak-spreading needed to determine adsorption isotherms using the chromatographic method.

Degradation of internal PID components: Historically, calibration curves for use with breakthrough experiments were developed from injections of serial dilutions of each vapor, using CS_2 as the solvent; or from vapor-calibration studies (the vapor is collected on carbon, and with known mass collected and known volume, the concentration is determined). Since the latter method is time-consuming and is not feasible at extremely low vapor concentrations (points below $C_i/C_o < 0.25\%$ in this study), we attempted to use the liquid-injection technique. Several trials revealed that these two curves (vapor and liquid injection) are not superimposable. Later, it was discovered that this is due to a "solvent effect," according to HP technicians, whereby the presence of the solvent changes (usually increasing) the area of the chromatogram for a given mass compared to the same mass injected as a vapor. Thus it was necessary to use the liquid-calibration method to establish the linear range of the detector, and the vapor-calibration method to determine vapor concentrations during experiments.

After several liquid-calibration curves were obtained, the GC chromatograms began to exhibit severe and erratic peak tailing. After more than four months of fruitless troubleshooting, we were informed by the detector manufacturer (O.I. Analytical) that integral detector parts are degraded by the presence of solvents like CS_2 . After the parts are degraded, injected components (liquid or vapor) adsorb and desorb on them. Since these detectors were relatively new, and only a few were used with solvent injections, this problem was not well-known. The entire detector system was replaced, and the remaining serial-dilution calibration curves (only one was needed per substance to establish the linearity of the detectors) were completed with the fewest possible injections.

Another delay occurred during the beginning of the equilibrium experiments, when it was found that peak areas (on a standard packed column) were not reproducible (with CV's varying from 1% to 20%) due to erratic peak tailing. After several more months of trouble-shooting, it was discovered that the problem was due to a PID o-ring which degraded at temperatures $>200^{\circ}\text{C}$ (up to this point all experiments had been conducted with the detectors at 200°C). The detector as sold, was purported to be good to 300°C , and the HP technicians were unaware of the o-ring problem. Its source was discovered only because we happened to re-order detector o-rings. The replacement o-ring was supposed to be usable up to temperatures of 300°C ; however, it too began to degrade at temperatures over 220°C . Thus, the higher-temperature ($>200^{\circ}\text{C}$ oven temperatures) injections needed to develop adsorption isosteres were not possible.

Injection-port design flaws: Replacing the defective o-ring and lowering the detector temperature greatly improved the consistency of the chromatograms; however, throughout a day of injections on the standard column, a few chromatograms still exhibited extreme variation ($\pm 100\%$, apparently random) in area from most other injections. Reliable peaks for use with the chromatographic technique could not be obtained under these conditions.

After again investigating many possible causes of this problem (syringes, flow-controllers, gas-tank regulators, gas-purifying compounds, ferrules, o-rings, septa, the PID and its electronic controller, and the column were replaced; all systems were leak-tested, and an oxygen-trap was added to the N_2 line) it was finally determined that the injection port design was flawed. The N_2 flowed into the lower portion of the old port, below the point of sample injection, which apparently caused sample flow irregularities. The irregularities sometimes caused peak tailing, which in turn caused errors in chromatogram area. These irregularities were problematic because of the small volumes that were injected ($0.05 - 0.1 \mu\text{L}$) for equilibrium experiments. The problem was solved after the port was replaced with a different one which had N_2 flowing in above the injection point.

4. Procedures and Methodology

4.1 Vapor Selection

The effect of component polarity differences on adsorption of binary vapor mixtures was investigated using a gas chromatograph (GC) equipped with both a flame ionization detector (FID) and a photoionization detector (PID). Binary mixtures were selected that included only one component to which the PID responds; the adsorption of this one component (referred to as the Test vapor) was studied in the presence of a second vapor (referred to as the Probe vapor) by analyzing the PID output.

To detect an effect of polarity on adsorption of a vapor in a binary mixture, it was necessary to match Test and Probe vapor physicochemical properties, such as molecular weight and boiling point while varying the dipole moment. (In a polar molecule the centers of positive and negative charge do not coincide, resulting in a dipole moment, the magnitude of which is a measure of the polarity of the molecule.)³⁵ However, the polarity of a molecule is influenced by factors such as molecular structure and functional group; and the polarity of a molecule will affect properties such as boiling point. Because of these selection requirements, it was not possible to simply pair a polar and non-polar vapor, and then study the effects of one on the other. The effect of polarity was elucidated by pairing each Test vapor with four Probe vapors, which had similar physicochemical properties except for polarity; and then comparing the adsorption of the Test vapor as the Probe vapor was varied. To distinguish changes in Test vapor adsorption due to Probe vapor polarity, from those due to differences between the boiling points of Test and Probe vapors, pairs of polar and non-polar Probe vapors were selected which have boiling points above and below that of the Test vapors. Within pairs of Probe vapors, the molecular weight and boiling point are similar.

Para-xylene and pyrrole were selected as Test vapors, and o-dichlorobenzene, p-dichlorobenzene, p-fluorotoluene and toluene were selected as Probe vapors. The chemical pairings used are shown in Tables 4.1.1 and 4.1.2, and the relevant physicochemical properties of the substances are shown in Table 4.1.3. Structural formulas of the chemicals are shown in Figure 4.1.1.³⁶ Tables 4.1.1 and 4.1.2 show how p-xylene and pyrrole were each paired with o- and p-dichlorobenzene, p-fluorotoluene, and toluene. Because p-xylene and pyrrole have ionization potentials at or below 8.4 eV, they are selectively detected in each binary vapor pair by using a PID lamp with an ionization potential of 8.4 eV.

In the photoionization process, a molecule absorbs energy from a photon which causes an electronic transition from the discrete, low energy level of the molecule to the higher energy continuum of the ion. Photon energies of about 5-20 eV are capable of producing this transition, requiring photon excitation

Table 4.1.1. Pairing of the non-polar *Test* vapor (*p*-xylene) with polar and non-polar *Probe* vapors (BP = boiling point).

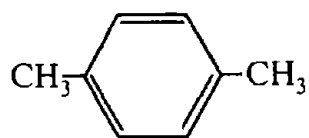
	BP < <i>p</i> -xylene	BP > <i>p</i> -xylene	
non-polar <i>Test</i> vapor: <i>p</i> -xylene	toluene	<i>p</i> -dichlorobenzene	non-polar <i>Probe</i> vapor
	<i>p</i> -fluorotoluene	<i>o</i> -dichlorobenzene	polar <i>Probe</i> vapor

Table 4.1.2. Pairing of the polar *Test* vapor (pyrrole) with polar and non-polar *Probe* vapors (BP = boiling point).

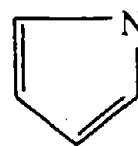
	BP < pyrrole	BP > pyrrole	
polar <i>Test</i> vapor: pyrrole	toluene	<i>p</i> -dichlorobenzene	non-polar <i>Probe</i> vapor
	<i>p</i> -fluorotoluene	<i>o</i> -dichlorobenzene	polar <i>Probe</i> vapor

Table 4.1.3. Selected physicochemical properties of chemicals used as *Test* and *Probe* vapors.

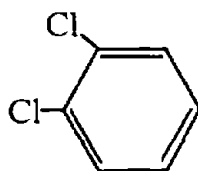
Chemical	Molecular Weight g/mol	Boiling Point °C	Dipole Moment Debye	Vapor Pressure at 24.4 °C torr	Ionization Potential eV
Test Vapors:					
p-xylene	106.2	13	0.0	8.5	8.4
pyrrole	67.1	130	1.9	8.0	7.7
Probe Vapors:					
o-dichlorobenzene	147.0	180	2.5	1.1	9.1
p-dichlorobenzene	147.0	174	0.0	1.7	8.9
p-fluorotoluene	110.1	117	2.0	17.0	8.8
toluene	92.2	111	0.4	27.6	8.8



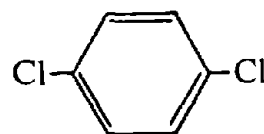
Para-xylene



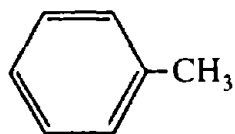
Pyrrole



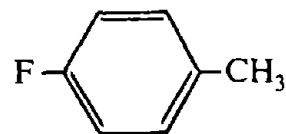
Ortho-dichlorobenzene



Para-dichlorobenzene



Toluene



Para-fluorotoluene

Figure 4.1.1. Molecular structure of *Test* and *Probe* chemicals.

in the far ultraviolet (UV).³⁷ The UV source is the "lamp" which contains an inert gas at low pressure. The lamp emits monochromatic light of a specific energy, which depends on the gases inside the lamp and the window material of the lamp. In this study, an 8.4 eV lamp was used. The photon energy level was achieved by using Xenon gas with a sapphire window. The spectral output of the lamp is shown in Figure 4.1.2.^a The peak at 146.96 nanometers corresponds to a photon energy of 8.4 eV.

Pairing of vapors as described allowed the study of each Test vapor in the presence of Probe vapors without analytical interference from the Probe vapors. The polarity of the Probe vapors is indicated on the right-hand side of Tables 4.1.1 and 4.1.2, and the relative boiling point difference is indicated at the top of each table. The Test vapors are bracketed in this way to distinguish effects due to polarity differences from those due to boiling point difference between the Test and Probe vapor.

Trials were conducted for each Test-Probe vapor pair, and for each Test vapor alone (at approximately the same concentrations used in the binary experiments).

4.2 Kinetic Experiments

Kinetic experiments entailed challenging a carbon bed with one or more vapors until the vapor started to appear in the air stream post-carbon bed. A vapor generation apparatus was constructed to conduct carbon bed challenges. The vapor concentrations were monitored with a gas chromatograph equipped with a gas sampling valve.

The Vapor Generation System: The vapor generation system was constructed of 0.4 cm (ID) stainless steel tubing, and 0.6 cm (ID) borosilicate glass, ball-and-socket tubing. The system was joined together by gas-tight Swagelok® fittings. A schematic of the vapor-generation system is shown in Figure 4.2.1. Details of the construction and function of this system have been described previously;^{38,39} however, the current system was built with some modification. An additional compressed air-supply line was added for the second vapor. The air was filtered and dried by passing it through mole sieve (Analabs® HGC-149B, 5A pellets) and a desiccant, anhydrous CaSO₄ (Drierite®, 10-20 mesh). The flow rate for each compressed air line was controlled with a fine metering valve, and monitored with a capillary flow meter. Two diaphragm vacuum pumps were used to supply negative pressure. Both pumps pulled air through the carbon bed, but one pump also provided air flow through the GC gas sampling valve (GSV). The individual and combined flow rates of the pumps were monitored before and after each experimental trial with a soap bubble meter.

^aPID 8.4 eV lamp spectral output courtesy of Robert Gauthier, Scientific Services, Inc., Rocky Hill, NJ.

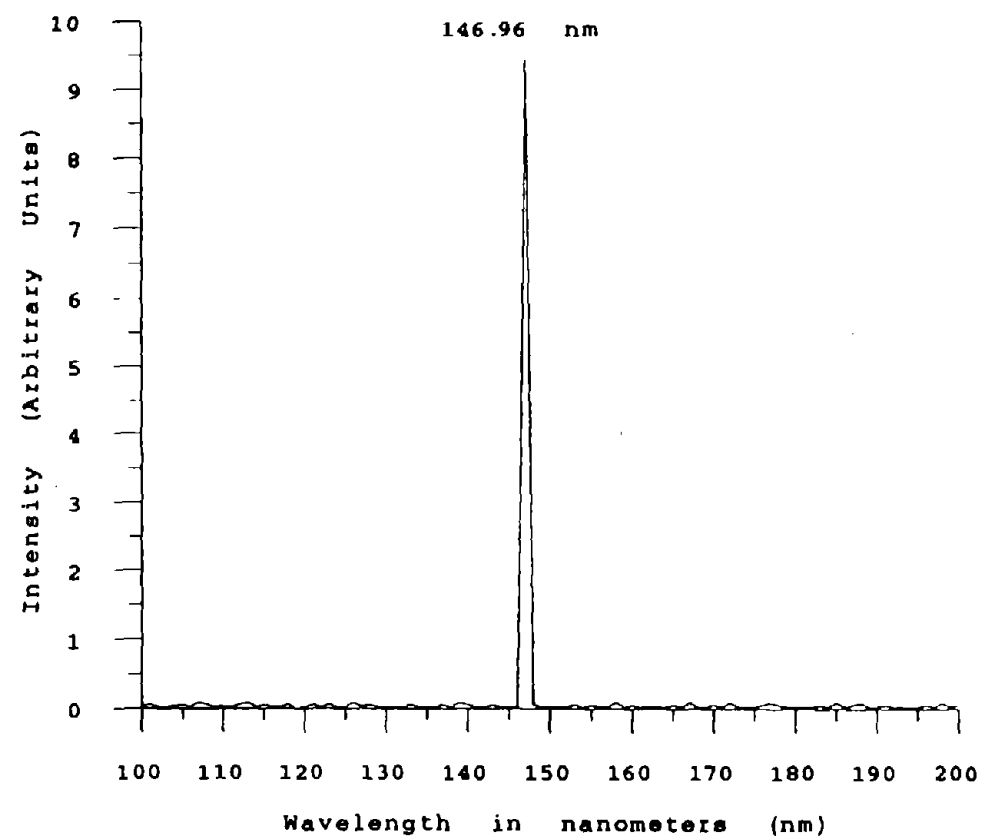


Figure 4.1.2. Spectral output of an 8.4 eV photoionization detector lamp.

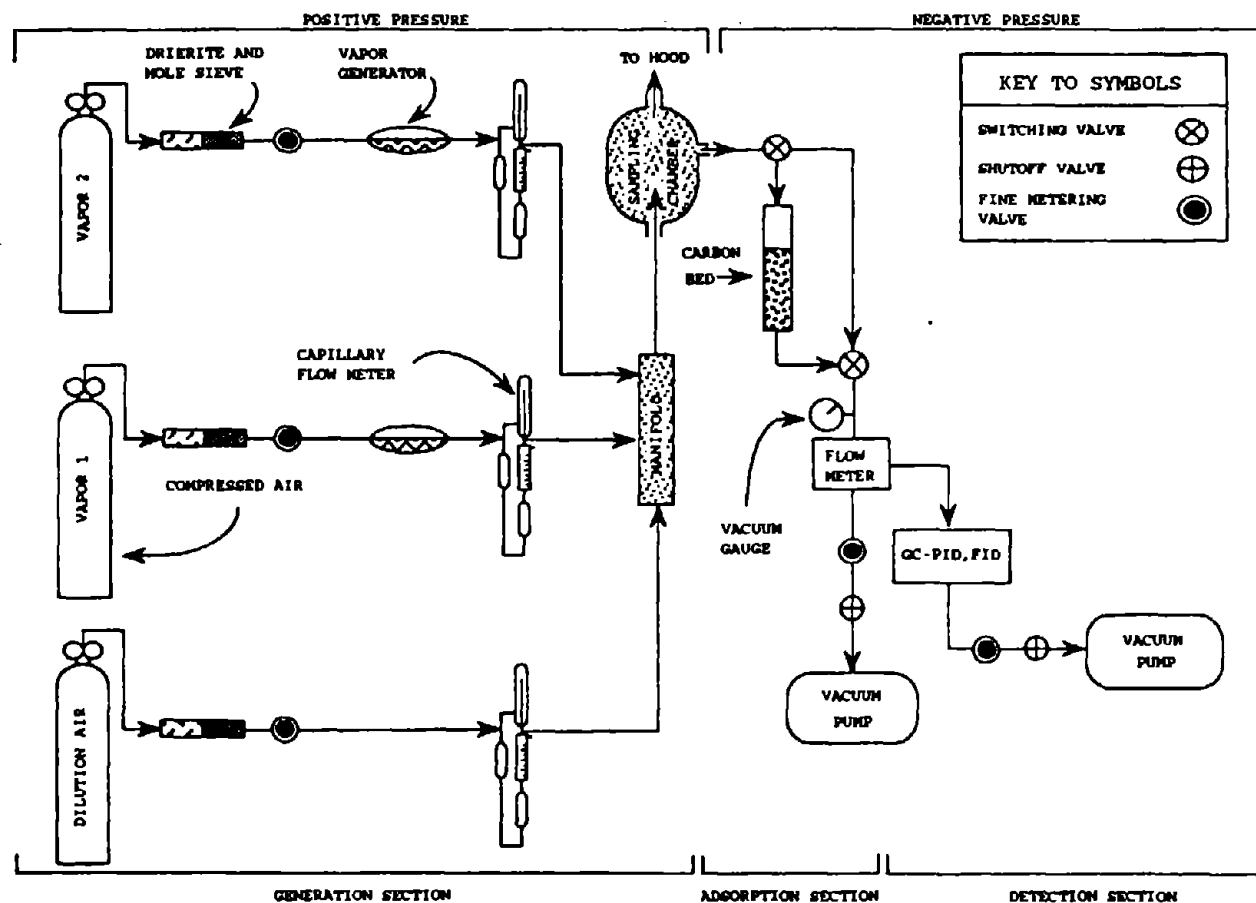


Figure 4.2.1.1. Schematic of vapor-generation, adsorption, and detection system for kinetic experiments.

The Carbon Bed: Activated carbon was obtained from organic vapor respirator cartridges (AO Safety[™], Chemical Cartridge R51A, 11720C). After removal from the cartridge, carbon was sieved with No. 12 (1.7 mm) and No. 20 (0.65 mm) mesh pans, and dried in an oven for a minimum of 24 hours at temperatures from 110°C to 120°C. The carbon was stored until use in an air-tight jar containing desiccant.

The carbon bed consisted of a 14.5 cm long, 0.6 cm (ID) glass tube, fitted with a coarse glass frit, filled with 1 ± 0.005 g of activated carbon. Carbon was gravity-packed; this method has been described and verified by others³⁸.

Carbon Bed Challenges: After generating vapors of the appropriate concentration, the carbon bed was packed, weighed, and placed securely in the vapor generation apparatus. The valves were switched to send the vapor flow through the carbon bed. Challenges were conducted at flow rates of 335-350 mL/minute, and concentrations of 1000-14,000 parts per million (ppm). Trials were conducted for equimolar mixtures of Test and Probe vapors; and for each Test vapor with three higher concentrations of toluene and p-fluorotoluene. Initial conditions of flow rate, temperature, and time were recorded. When breakthrough began, samples were acquired with the GSV at 45 second intervals. Breakthrough was monitored until C_i was approximately 30% of C_o . Flow rate and temperature were recorded again after the trial was complete.

The breakthrough concentrations (C_i/C_o) from 0.25% to 2.5% were regressed with the corresponding breakthrough times, according to equation 2.2.1, and the regression values were used with the Wheeler equation to calculate W_e and k_v . This process was repeated six times for each vapor pair, and for each Test vapor alone. The average W_e and k_v were calculated from the 6 trials.

Data calculations, conversions and regressions were carried out using Excel[®] V.4 spreadsheets.

4.3 The Gas Chromatograph System

A Hewlett-Packard (HP) 5890 gas chromatograph, equipped with a gas sampling valve (0.5 ml sample loop) was used to monitor vapor concentration. A non-polar methylsilicone gum capillary column was used (HP-1, cross-linked, 30 m long, 0.50 mm ID, 0.88 mm film thickness).

The GC was equipped with both an FID and a PID. The FID responds generally to hydrocarbons, while the PID was equipped with an ionization source (lamp) that responded only to vapors with ionization potentials (IP's) less than or equal to the lamp IP. An 8.4 eV lamp was used throughout this study. The responses of the detectors were recorded as chromatograms for which area is proportional to the concentration of vapor injected. Calibration of detector response is described in Appendix A.

The HP 3365 Chemstation® software program was used to control the GC, to acquire data from the GC detectors, and to calculate the total area of each chromatogram. Chemstation® was used to program the GC to inject samples with the GSV at 45 second intervals.

4.4 Equilibrium Adsorption Experiments

Equilibrium adsorption experiments involved generating chromatograms by injecting approximately equimolar mixtures of *Test* and *Probe* compounds into the GC equipped with a column containing activated carbon. From these chromatograms, isotherms were obtained using the chromatographic technique of isotherm determination. The isotherm points were converted to variables of the Dubinin equation to construct characteristics curves. The slope (k/β^2) and intercept (W_0) of the characteristic curve were compared for *Test* vapors in mixtures containing components of varying polarity and boiling point. The result is a comparison of the effect of *Probe* vapor polarity and boiling point on the vapor-carbon affinity for the *Test* vapors.

Chemical Mixtures and Injection Volumes: *Test* and *Probe* chemicals were combined in volumes needed to acquire 50:50 molar mixtures. The chemicals were measured with a volumetric pipette to the nearest 0.10 mL to obtain required volumes of each chemical.

The technique for obtaining equimolar mixtures containing *p*-dichlorobenzene differed since it is a solid at room temperature. The mass of *p*-dichlorobenzene required to make an equimolar mixture with slightly less than 2 mL of *Test* vapor was calculated. This mass of *p*-dichlorobenzene was weighed and deposited into a 2 mL volumetric flask, and the calculated volume of *Test* chemical was added to the flask. This procedure was repeated, after adjusting the amounts of the chemicals added, until the combined volume of the two chemicals was equal to 2 mL. Molar ratios of 1.7:1 were used with mixtures of pyrrole and *p*-dichlorobenzene in order to dissolve the *p*-dichlorobenzene. The mixture had to be maintained in a 38°C water bath to prevent re-crystallization of *p*-dichlorobenzene, thus the volume of the mix was assessed at 38°C. The syringe used to inject this mixture was warmed to approximately 38°C to prevent re-crystallization of *p*-dichlorobenzene. Chemicals were otherwise used as received (Aldrich 99% HPLC grade).

Sample volumes of 0.05 µL for single *Test* chemicals, and 0.1 µL for binary *Test-Probe* experiments were injected onto the carbon columns. Small injection volumes were used because the chromatographic technique of isotherm determination requires that the surface area coverage of the adsorbate is on the order of 1%. The amount injected results in carbon surface area coverage of less than 2%, assuming a carbon surface area of 1420 m². Each injection was repeated three times.

Reference chromatograms required for the chromatographic method of isotherm determination (see section 4.3.4) were obtained by injecting Test vapors alone, and each mixture onto a non-adsorbing column (Supelco 10% SP-1000, 80/100 Supelcoport, 610 cm length) at oven temperatures of 100°C. The average of three chromatograms was used in determining the reference peak area.

Carbon Column Preparation: The activated carbon was obtained from new organic vapor respirator cartridges, ground in a ceramic mortar and pestle (to U.S.A. Standard Testing Sieve mesh sizes 60 to 65), dried at temperatures of 110 to 120°C, and stored in a desiccator.

The carbon was pre-weighed in 0.01 g portions for each column. This amount of carbon was used because impractically long retention times resulted (>2 hours) when using larger amounts. The carbon was packed under vacuum into a pre-weighed, 14.5 cm long, 0.32 cm O.D. stainless steel column which contained a fiber glass plug in one end. The column was weighed again to assure successful transfer of the carbon. This technique of portioning very small carbon beds was accurate within 5 percent (see Appendix B). The carbon was then packed according a method described elsewhere.^{13,39,40} The carbon columns were conditioned in a separate oven overnight (>12 hours) with dried and filtered nitrogen (desiccant: Drierite®; filter: Analabs® HGC-149B, 5A pellets; adsorbent: activated carbon) flowing at a minimum of 30 mL/min, through the columns which were heated to 220°-250°C.

Chromatogram Generation: A conditioned carbon column was removed from the conditioning oven and installed in the HP 5890, where the column fittings were leak-tested. The GC oven was heated (210°C for *p*-xylene, 100°C for pyrrole and reference chromatograms) and the system allowed to equilibrate for at least 15 minutes. Samples were injected using a 0.50 µl syringe, and the resulting chromatograms were collected using Hewlett-Packard Chemstation® software. Columns were re-used after conditioning in the auxiliary oven for a period >8 hours at temperatures of 250°C-275°C.

Chromatograms from the PID, which responds only to the Test vapor, were analyzed with the chromatographic technique to obtain isotherms for the Test vapors alone and in binary mixtures.

The Chromatographic Method of Isotherm Determination: The classical method of isotherm determination involves exposing a carbon bed contained in a vessel to a known vapor pressure, and then recording the weight gained or lost by the carbon as successively higher or lower concentrations of the vapor are introduced into the vessel. This technique is suitable for single vapors; however, its usefulness for vapor mixtures is limited. Using the chromatographic technique in conjunction with the two-detector system, it was possible to obtain the isotherm for the Test vapor in each mixture.

The detailed theoretical relationships between adsorption isotherms and the chromatographic peak shape have been worked out

by a number of authors.⁴¹ The theories generally define an "ideal chromatographic process" using the same assumptions used to derive plate theory.⁴¹ A mass-balance equation is used to describe the transport of gas-phase adsorbate through a differential column volume, and this leads to a relationship between the amount adsorbed per unit mass adsorbent, and various experimental parameters.⁴¹

The chromatographic technique of isotherm determination has been used successfully for single-vapor studies, and was used here to evaluate the chromatograms from the PID.^{13,39,42,43} The technique, described by Habgood⁴⁴ and further developed by Dollimore,⁴³ translates the chromatographic peak shape to an isotherm.

The chromatogram is a record of the elution of an adsorbate from an adsorbent column as a function of time. Points along the trailing edge of the chromatogram correspond to specific concentrations and vapor pressures of the adsorbate as it is eluted. These points constitute an adsorption isotherm. Isotherm points are obtained using the following formula:⁴³

$$f(C_i) = \frac{Q_c D}{uM} \int_0^{n_i} (1-l_0) dn \quad 4.4.1$$

where:

- C_i = concentration of adsorbate in the gas phase ($\mu\text{mol/mL}$);
- Q_c = carrier gas flow rate (mL/min);
- D = sensitivity of the detector ($\mu\text{mol/cm}^4$);
- n_i = deviation of the chart pen from baseline (cm);
- u = chart speed (cm/min);
- M = mass of the adsorbent;
- l = distance from the injection point to a point of the chromatogram (cm);
- l_0 = distance from injection to appearance of a non-adsorbing gas (cm).

The detector sensitivity is evaluated by:

$$D = \frac{um}{Q_c S_1} \quad 4.4.2$$

where:

- m = moles injected;
- S_1 = total chromatogram area corresponding to m , determined on a non-adsorbing column.

The distance from injection to the appearance of a non-adsorbing gas approaches zero for well-packed beds with small dead volume, so that l_0 is dropped. After replacing D , equation

4.4.1 is rewritten:

$$a = f(C_i) = \frac{m}{S_i M} \int_0^{n_i} t dn \quad 4.4.3$$

where:

a = total adsorbed volume.

t = l/u , time to n_i after injection (u is a constant).

The complete integral is equal to the total adsorbed volume, a (mL/g). The amount adsorbed is equal to the area of the chromatographic peak (assuming that the mass injected is proportional to the chromatographic area).

Points on the isotherm are obtained by evaluating the area of the chromatogram (using equation 4.4.3) from top to bottom. Historically, the peak was evaluated from bottom to top; however, the technique was improved by integrating the peak from the top down, because this eliminates errors in the area calculation that are associated with the slow return to baseline.⁴³

The maximum value of the integral occurs at n_0 , and corresponds to the total adsorbed volume, a (see Figure 4.4.1). The point with n_i deviation from baseline is found at t from injection, so that at $n_i=1$, the integral is represented by the stippled area. Multiplying the value of the integral (the stippled strip) by the constants gives the amount adsorbed (a_i) at that point. Finally, a_i is subtracted from the total a , to give one point on the isotherm.⁴³ Further isotherm points are obtained by calculating additional a_i , summing the successive a_i , and then subtracting the summed a_i from the total a .

It is assumed that the area of the chromatogram is proportional to the mass of the sample injected. However, an accurate relationship of mass to area is difficult to establish from activated carbon column chromatograms.⁴³ Large errors in area calculation can occur because of difficulty in determining when the trailing peak edge returns to baseline. For this reason, the correct area for the mass injected (S_i) is determined from a chromatogram from a relatively non-adsorbing column, where the return to baseline can be more accurately determined.⁴³

The experimental peak area is also corrected for diffusion by assuming that the areas x , are equal (diffusion at the front of the peak is equal to diffusion at the rear) and subtracting x from the trailing edge of the peak.^{43,45}

The adsorbate pressure corresponding to each a_i is calculated assuming ideal gas behavior from the following:

$$P_i V = nRT \quad 4.4.4$$

$$P_i = qRT \quad \left(q = \frac{n}{V} \right) \quad 4.4.5$$

$$P_i = n_i D R T \quad (q = n_i D) \quad 4.4.6$$

$$P_i = \frac{n_i u m R T}{Q_c S_1} \quad \left(D = \frac{u m}{Q_c S_1} \right) \quad 4.4.7$$

where:

P_i = adsorbate pressure (N/m²) at n_i ;
 V = volume (cm³);
 n = moles;
 q = adsorbate concentration (μmol/cm³);
 R = gas constant (8.31 N·m/mol·K);

and other variables as previously described.

Details of the calculation of areas for the chromatogram integration, and calculations of adsorbate pressures are contained in Appendix C.

The amount adsorbed (a_i) and vapor pressure (P_i) of the isotherm were transformed to adsorption space (W_o) and adsorption potential (ϵ) of the Dubinin equation (equation 2.1.2). From the regression of these points, the adsorption space (W_o) and the vapor affinity coefficient (k/β^2) of the Dubinin equation were calculated. This was carried out for the chromatograms of *Test* vapors alone, and for *Test* vapors in the presence of each *Probe* vapor. The average W_o and k/β^2 were calculated from 3 trials for each vapor pair, and for the *Test* vapor alone. The calculations and regressions were done using Excel® spreadsheets (see Appendix D).

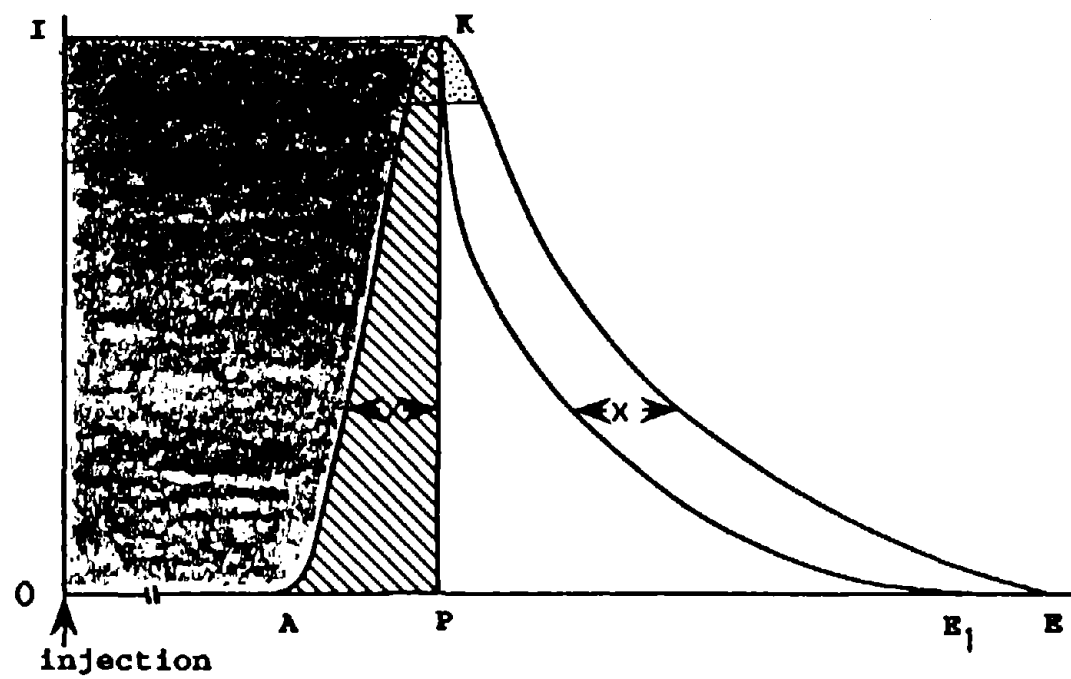


Figure 4.4.1. Diagram of the areas of the chromatogram needed to calculate the adsorption isotherm.

5. Results and Discussion

5.1 Method Development

As predicted by photoionization theory, the PID detector responded only to vapors with IP's less than or equal to the energy of the 8.4 eV lamp.^{37,46}

Kinetic Adsorption Studies: The responses of both detectors for a binary mixture of pyrrole and toluene vapors (injected with the GSV) are shown in Figures 5.1.1 and 5.1.2, for the PID and FID, respectively. The PID responds only to the pyrrole, as shown in Figure 5.1.1, allowing study of pyrrole (the Test vapor) in the presence of toluene (the Probe vapor) without interference from the Probe vapor. Both Test and Probe vapor were detected by the FID as shown in Figure 5.1.2, and as expected, the resulting overlap of the two chromatograms in kinetic adsorption experiments generally precluded accurate analysis of the 1% t_b of the Probe vapor. Although Test and Probe peaks did not always overlap, due to constraints of the GC software, it was not possible to always simultaneously track the breakthrough of Test and Probe vapors in the breakthrough region of $0.25\% < C_i/C_o < 4.0\%$. Experiments were designed to follow the breakthrough of the Test vapor for $0.25\% < C_i/C_o < 4\%$ for use in the Wheeler model. Several trials were followed until the Test vapor reached 100% C_i/C_o , but because the breakthrough region of $0.25\% < C_i/C_o < 4\%$ was of interest, trials were normally stopped when the Test vapor C_i/C_o was approximately 30%.

Equilibrium Adsorption Experiments: The PID produced chromatograms of the Test vapor without interference from the Probe vapor, whereas the FID produced chromatograms with overlapping Test and Probe vapor peaks for injections on carbon columns as shown in Figure 5.1.3. This confirms the utility of the PID with an 8.4 eV lamp as a selective detector to evaluate the chromatogram of one vapor in a binary mixture. Using this technique, it is possible to selectively study one vapor in higher-order mixtures if all the other vapors have ionization potentials above that of the PID lamp.

5.2 Kinetic Adsorption Experiments

These experiments were conducted to determine whether the Wheeler model one percent breakthrough time (1% t_b) carbon capacity (W_c) and kinetic rate constant (k_v) for Test vapors were affected by the presence of an accompanying Probe vapor; and if these parameters change with differences in the polarity of the Probe vapor.

5.2.1 The Order of Vapor Breakthrough

As expected, in most cases the breakthrough of the Probe vapor could not be determined accurately because of the overlap

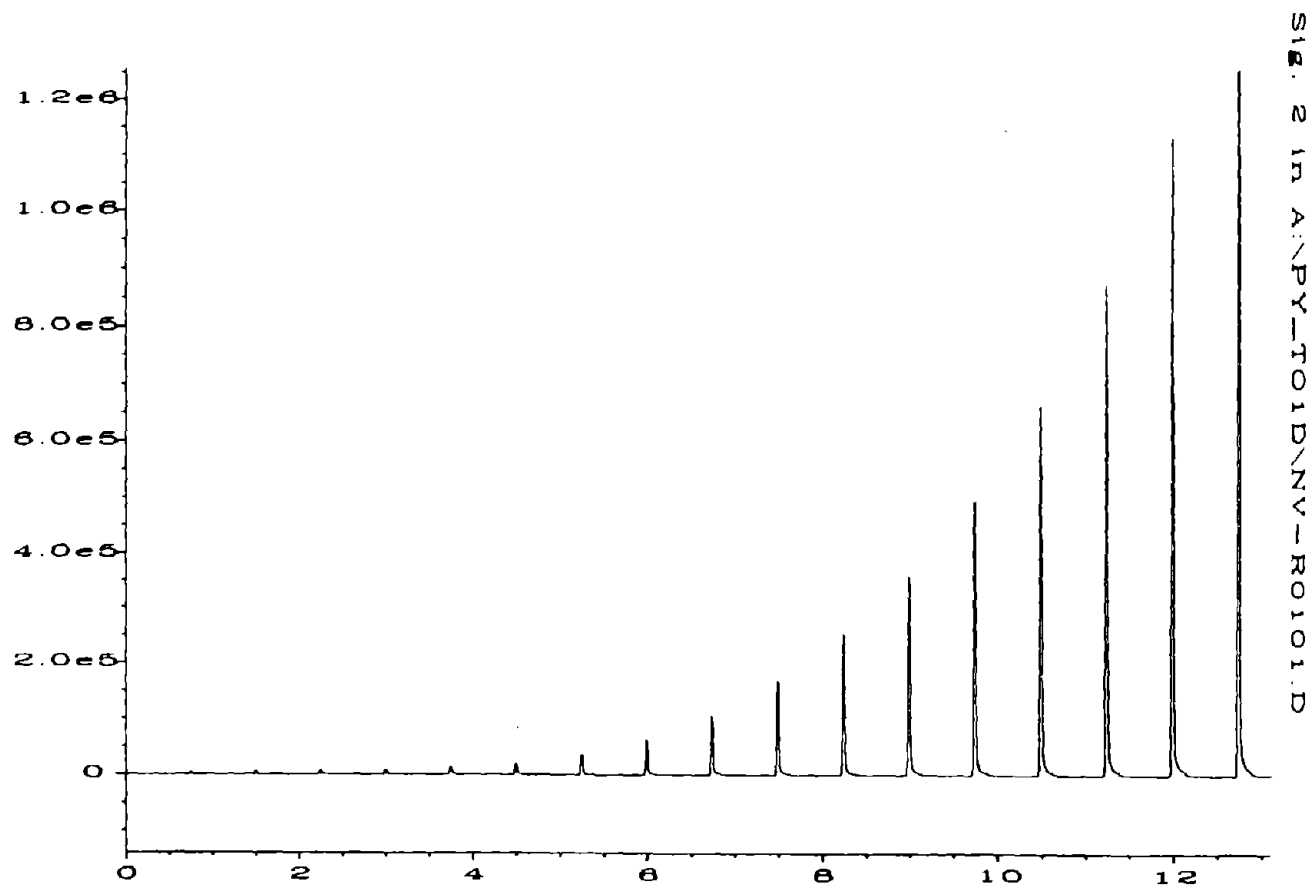


Figure 5.1.1. PID chromatogram of the breakthrough of pyrrole and toluene showing detection of pyrrole only.

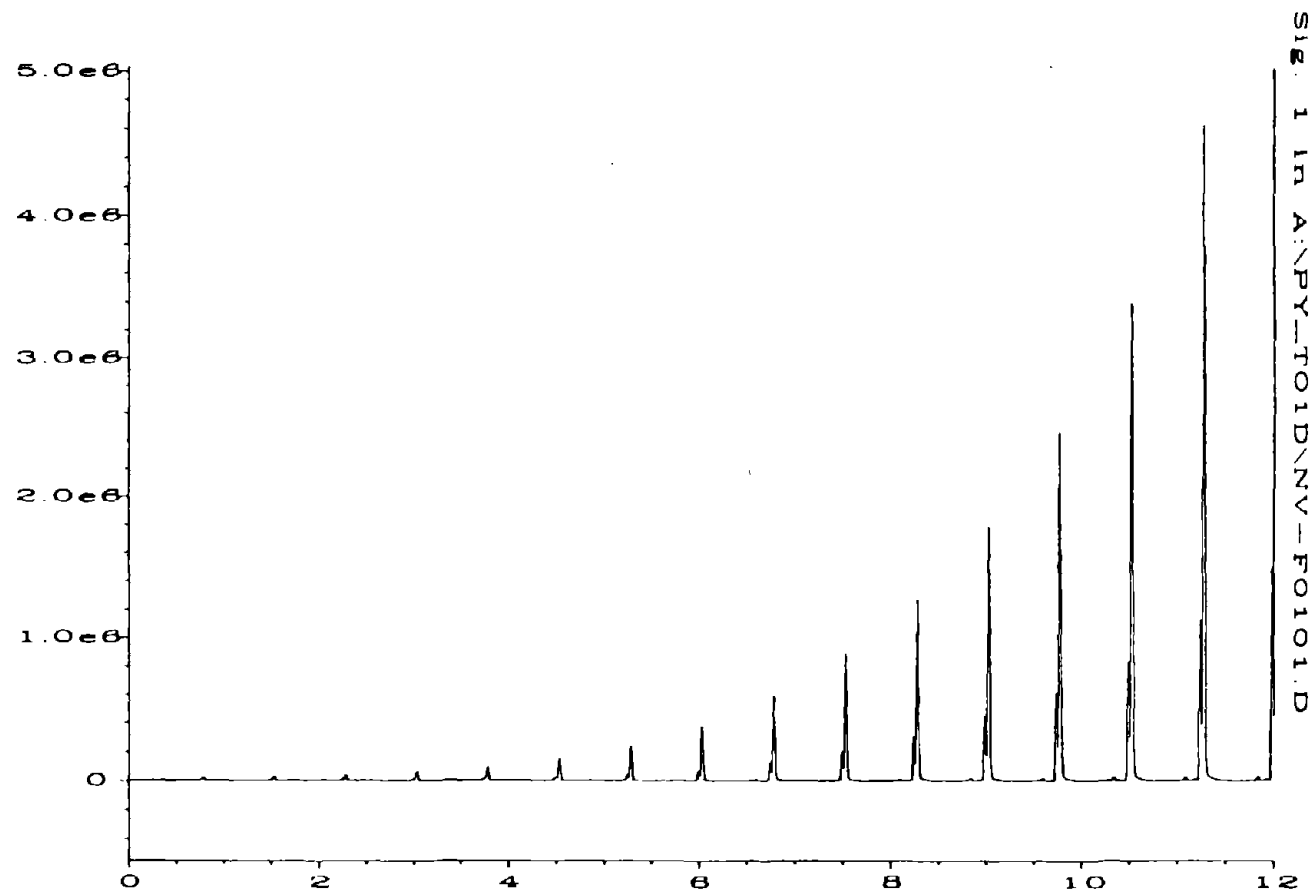


Figure 5.1.2. FID chromatogram of the breakthrough of pyrrole and toluene showing detection of both vapors.

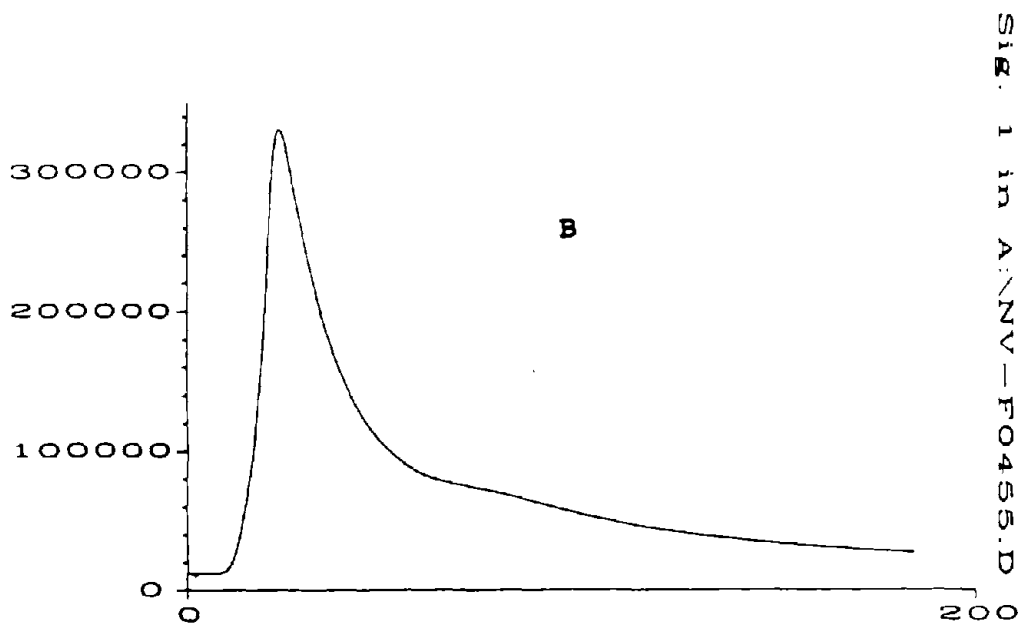
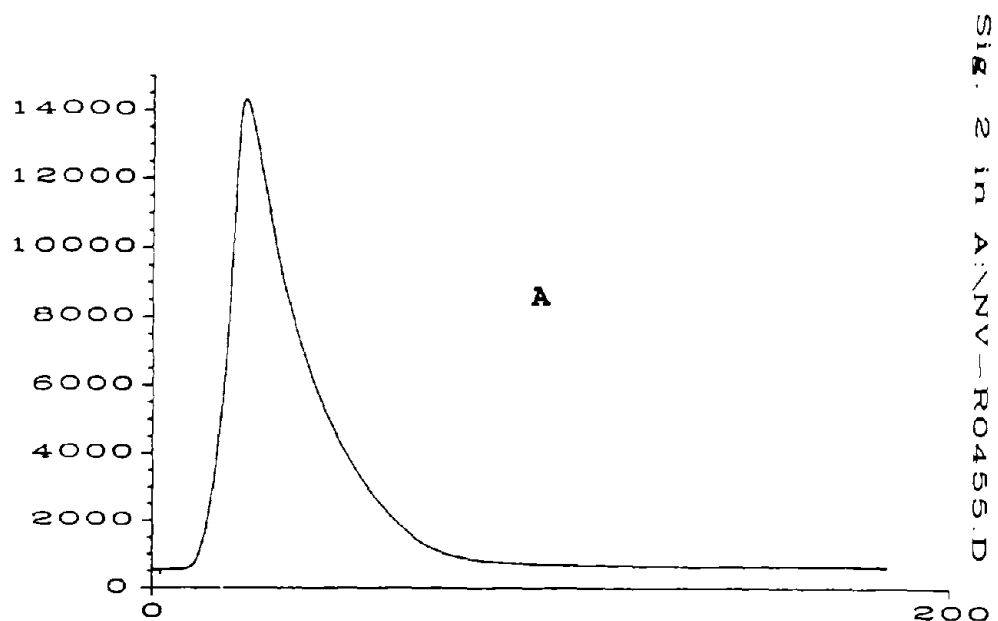


Figure 5.1.3. Chromatograms from injections of *p*-xylene with *o*-dichlorobenzene, showing the detection of only *p*-xylene with the PID (A), and detection of both vapors with the FID (B).

of the chromatographic peaks from the FID signal and sampling limitations of the GC software; however, the C_i/C_o for Probe vapors was estimated at the point when the Test vapor reached 1% C_i/C_o . The vapor with the lowest boiling point and highest vapor pressure broke through first, except for the mixture of pyrrole with *p*-fluorotoluene. The percent breakthrough (% C_i/C_o) of Probe vapor when the Test vapor concentration was equal to 1% is shown in Table 5.2.1.1.

The graph of the complete breakthrough of *p*-xylene in the presence on *p*-fluorotoluene is shown in Figure 5.2.1.1. The breakthrough of *p*-fluorotoluene is shown also. This graph shows the concentration of the first vapor to break through, *p*-fluorotoluene, exceeding its C_o , while C_i/C_o of the higher boiling point vapor, *p*-xylene, continued to increase. This also occurred with binary mixtures of *p*-xylene with *o*-dichlorobenzene, and toluene; and with mixtures of pyrrole with toluene. Whether this occurred with mixtures of *p*-xylene with *p*-dichlorobenzene, and with mixtures of pyrrole with *p*-fluorotoluene or *o*- or *p*-dichlorobenzene is uncertain because these breakthrough trials were followed only until the Test vapor had reached about 30% C_i/C_o .

Toluene and *p*-fluorotoluene broke through before *p*-xylene. When *p*-xylene reached 1% C_i/C_o , toluene was at 22% C_i/C_o ; and *p*-fluorotoluene was at 8% C_i/C_o (see Table 5.2.1.1). *Ortho*- and *p*-dichlorobenzene broke through more than 50 minutes after *p*-xylene, and were not detected when *p*-xylene reached 1% C_i/C_o .

Toluene broke through slightly ahead of pyrrole, reaching C_i/C_o of about 2% when pyrrole reached 1% C_i/C_o . *Para*-fluorotoluene appeared to break through at about the same time as pyrrole; *p*-fluorotoluene appeared to be slightly less than 1% when pyrrole was at 1% C_i/C_o . Since the *p*-fluorotoluene data were obtained from the FID signal which contained partially overlapping pyrrole and *p*-fluorotoluene peaks, whether *p*-fluorotoluene breaks through slightly before or after pyrrole is uncertain. *Ortho*- and *p*-dichlorobenzene broke through more than 50 minutes after pyrrole, and were not detected when pyrrole reached 1% C_i/C_o .

Yoon reported similar results for binary mixtures, with the lower boiling point vapor breaking through first, for mixtures of *m*-xylene with acetone, and styrene with acetone.^{28,29} For both mixtures, acetone broke through first, exceeded its C_o , then returned to C_o as the second vapor approached its maximum breakthrough concentration. Yoon has suggested that this phenomenon is due to "displacement" of acetone by *m*-xylene or styrene.^{28,32}

If the time between Test and Probe vapor breakthrough is governed only by boiling point and vapor pressure differences, toluene and *p*-fluorotoluene would be expected to break through well ahead of pyrrole, as they do with *p*-xylene, which has a boiling point (138°C) similar to pyrrole (130°C). However, toluene and *p*-fluorotoluene break through at nearly the same time

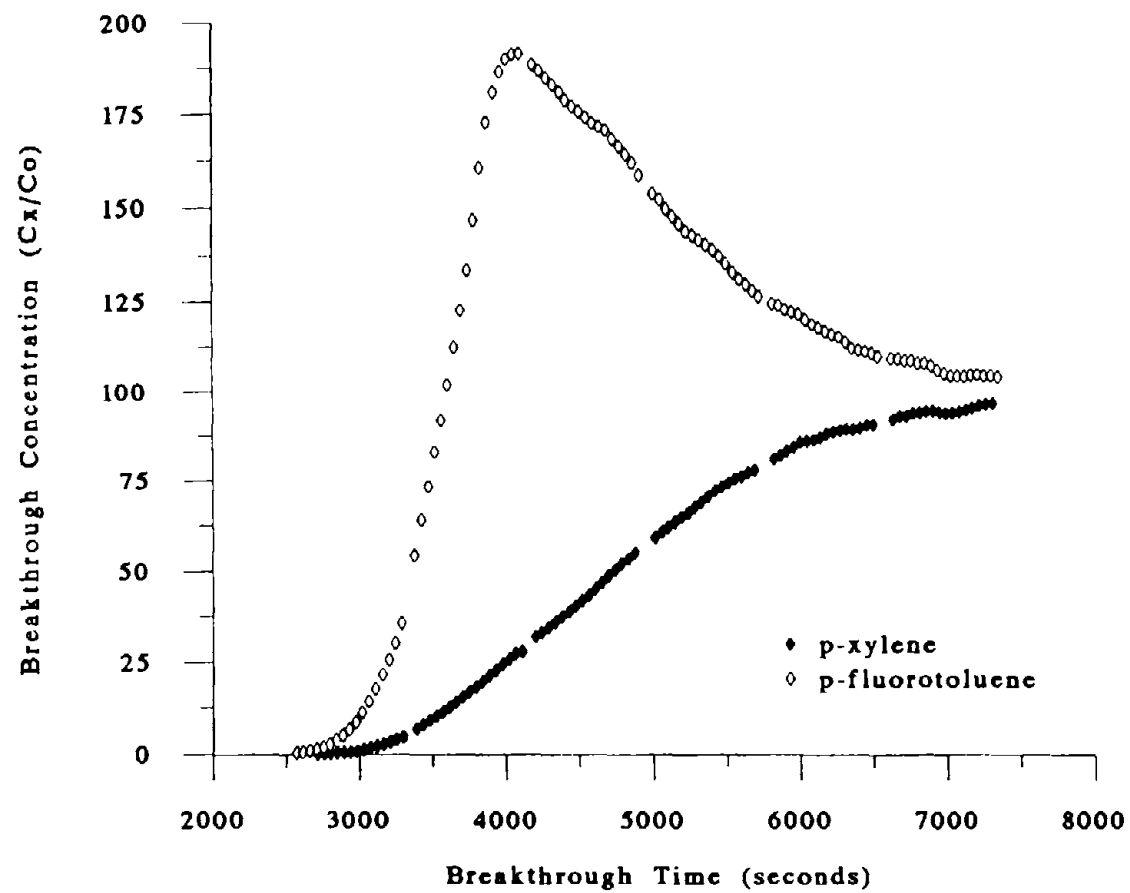


Figure 5.2.1.1. Complete breakthrough of a mixture of p-xylene and p-fluorotoluene.

Table 5.2.1.1. Percent breakthrough (C_x/C_o) of Probe vapors when Test vapor C_x/C_o is at 1% (followed by selected physical-chemical properties of the vapors).

Mixture of pyrrole with:	Probe Vapor % Breakthrough with <i>p</i> -xylene ^a	Probe Vapor % Breakthrough with Pyrrole ^a	Molecular Weight	Boiling Point°C	Vapor Pressure @24°C (torr)
<i>p</i> -dichlorobenzene	ND ^b	ND	147	174	1.7
<i>o</i> -dichlorobenzene	ND	ND	147	180	1.1
toluene	22%	2%	92	111	27.6
<i>p</i> -fluorotoluene	8%	<1%	110	117	17.0
<i>p</i> -xylene	-	-	106	138	8.5
pyrrole	-	-	67	130	8.0

^a *p*-xylene and pyrrole $C_x/C_o = 1\%$

^b ND = none detected; $C_x/C_o \ll 1\%$

as pyrrole. The proximity of pyrrole to either toluene or *p*-fluorotoluene breakthrough suggests that factors other than boiling point and vapor pressure may affect the breakthrough times of the components.

When studying breakthrough times of equimolar binary mixtures of butyl acetate, ethyl benzene, isopropyl alcohol, methyl ethyl ketone, and hexane, Swearengen³¹ found that boiling point and vapor pressure alone could not be used to reliably predict which vapor of a pair would break through first. However, the lower molecular weight vapor of a pair always broke through first when vapors were grouped into relative classes of higher boiling point and lower vapor pressure, versus lower boiling point and higher vapor pressure. In the case of pyrrole, its relatively low molecular weight (67.1 g/mol) could reduce its breakthrough time relative to toluene and *p*-fluorotoluene.

The polarity of pyrrole could also decrease its 1% t_b in the presence of toluene and fluorotoluene compared to non-polar *p*-xylene in these binary systems. Goller found that the polar vapors, acetone, isopropanol, and ethanol were displaced in charcoal sampling tubes by the non-polar vapors toluene and xylenes.³⁴ Among the polar vapors, the lighter ethanol was displaced by acetone and isopropanol.³⁴

Summary of Order of Breakthrough: For all vapor mixtures except for pyrrole with *p*-fluorotoluene, the vapor with the lower boiling point, lower molecular weight broke through first. Whether *p*-fluorotoluene breaks through slightly before or after pyrrole is uncertain. Although the relative time of breakthrough of one vapor to another appears to be dependent on the boiling point of the vapors, the proximity of pyrrole and *p*-fluorotoluene breakthrough compared to that of *p*-xylene and *p*-fluorotoluene, suggests that it also may be influenced by vapor molecular weight and polarity.^{31,34}

5.2.2 Time to 1% Test Vapor Breakthrough

The average ($n=6$) 1% breakthrough time for the Test vapors alone and in mixtures are shown in Tables 5.2.2.1 and 5.2.2.2, for *p*-xylene and pyrrole, respectively. For comparison, the trials shown together are those for which the molar concentration of the Test vapor alone is approximately equal to the molar concentration of Test vapor in each binary mixture. The 1% t_b for Test vapors paired with increasing concentrations of toluene and *p*-fluorotoluene are shown together. (Trials with increasing concentrations of dichlorobenzene isomers are not available since it is impossible to increase their concentrations further due to their low vapor pressure.) The next column contains the 1% t_b 's predicted for Test vapors in mixtures. The predicted 1% t_b 's were calculated in a manner similar to that used by Jonas.³⁰ The k_i and W_i of the Test vapor alone were used to calculate the predicted 1% t_b after multiplying the W_i by the mole fraction of the Test vapor in the mixture. The final column shows the mean

Table 5.2.2.1. Observed (n=6) and predicted 1% breakthrough time (t_b) for *p*-xylene alone, and with Probe vapors at varying concentrations (1% t_b predicted with the Wheeler model using *p*-xylene alone data).

Challenge Vapors and Concentrations, $\mu\text{mol/mL}$		<i>p</i> -xylene Mole Fraction	Experimental <i>p</i> -xylene 1% t_b , minutes (S.E.) ^a	Predicted <i>p</i> -xylene 1% t_b , minutes	Average Percent Deviation
toluene	<i>p</i>-xylene				
.00	.15	1.00	64 (0.8)		
.14	.14	0.50	45 (1.2)	35	-22%
.26	.14	0.35	32 (0.8)	24	-25%
.39	.14	0.26	24 (0.8)	19	-21%
<i>p</i>-fluoro.^b	<i>p</i>-xylene				
.00	.09	1.00	106 (0.8)		
.10	.11	0.51	50 (0.4)	48	- 4%
.24	.09	0.28	33 (0.4)	30	- 9%
.44	.11	0.20	24 (0.4)	18	- 8%
<i>p</i>-dichlo.^c	<i>p</i>-xylene				
.00	.05	1.00	200 (2.0)		
.04	.04	0.53	129 (1.6)	123	- 5%
<i>o</i>-dichlo.^d	<i>p</i>-xylene				
.00	.05	1.00	200 (2.0)		
.05	.04	0.48	98 (0.8)	107	+ 9%

^a Standard error

^b *p*-fluorotoluene, ^c *p*-dichlorobenzene, ^d *o*-dichlorobenzene

Table 5.2.2.2. Observed (n=6) and predicted 1% breakthrough time (t_b) for pyrrole alone, and with Probe vapors at varying concentrations (1% t_b predicted with the Wheeler model using pyrrole alone data).

Challenge Vapors and Concentrations, $\mu\text{mol/mL}$		pyrrole Mole Fraction	Experimental pyrrole 1% t_b , minutes (S.E.) ^a	Predicted pyrrole 1% t_b , minutes	Average Percent Deviation
toluene	pyrrole				
.00	.15	1.00	80 (2.0)		
.15	.15	0.49	47 (0.4)	40	-15%
.30	.14	0.32	31 (0.4)	27	-13%
.43	.14	0.24	22 (0.8)	*21	- 5%
p-fluoro.^b	pyrrole				
.00	.12	1.00	107 (2.4)		
.12	.12	0.48	57 (0.4)	52	- 9%
.22	.11	0.33	36 (0.4)	39	+ 8%
.33	.11	0.26	26 (0.4)	29	+12%
p-dichlo.^c	pyrrole				
.00	.04	1.00	303 (9.8)		
.04	.04	0.48	129 (2.9)	157	+21%
o-dichlo.^d	pyrrole				
.00	.04	1.00	303 (9.8)		
.04	.04	0.48	140 (2.4)	153	+ 9%

^a Standard error

^b p-fluorotoluene, ^c p-dichlorobenzene, ^d o-dichlorobenzene

*Predicted value within experimental 95% confidence interval

percent deviation of the experimental and predicted 1% t_b 's.

The 1% t_b appears to decrease in proportion to increasing overall vapor concentration for both Test vapors without regard to the nature of the Probe vapor present. This is illustrated in Figure 5.2.2.1 for *p*-xylene and Figure 5.2.2.2 for pyrrole, where the 1% t_b is plotted with the total vapor concentration on a log-log scale. These data suggest that the 1% t_b for Test vapors is a function of the total concentration of the vapor mixture and is independent of the polarity and boiling point of the accompanying Probe vapor.

The experimental and predicted 1% t_b 's agreed within -25% to +21%. The agreement between experimental and predicted 1% t_b 's is acceptable, and is similar to the variation reported by Jonas (-12.4% to +17.8) for sequential binary mixtures of benzene and carbon tetrachloride.⁴⁷ In that study, the vapors were introduced sequentially, with a second vapor added after first partially saturating the carbon with the first vapor. The t_b of the second vapor was predicted with the Wheeler model using single-vapor data with the assumption that W_c was constant at 0.49 g/g.⁴⁷

The predicted 1% t_b for *p*-xylene in the presence of either toluene or *p*-fluorotoluene was consistently underestimated (*p*-xylene takes longer to break through than predicted). In practical terms the differences between the experimental and predicted 1% t_b 's are small, although all predicted 1% t_b 's are outside the experimental 1% t_b 95% confidence interval (average $t_b \pm 1.96$ [standard error]).

The predicted 1% t_b for pyrrole in the presence of toluene is consistently underestimated, and in the presence of *p*- and *o*-dichlorobenzene is overestimated. In practical terms the differences between the experimental and predicted 1% t_b 's are again small; however, all but one of the predicted 1% t_b 's are outside of the experimental 1% t_b 95% confidence interval (95% CI).

The predicted 1% t_b for either *p*-xylene or pyrrole in the presence of toluene was consistently underestimated. This may be the result of these Test vapors "displacing" toluene and delaying their own breakthrough.^{28,32} Some of the results reported here and by others suggests that higher boiling point vapors displace the lower boiling point vapors at high breakthrough concentrations.^{28,32} The *p*-xylene data support this since the 1% t_b for *p*-xylene with the lower boiling point compounds is consistently underestimated, and is overestimated with the higher boiling point *o*-dichlorobenzene. With pyrrole mixtures, however, the direction of the deviation of experimental and predicted 1% t_b 's are not all consistent with the displacement theory. For example, if the higher boiling point vapor always displaced the lower boiling point vapor, the predicted 1% t_b of pyrrole with *p*-fluorotoluene would always be too low. However, this occurs only when the concentrations of *p*-fluorotoluene exceeds that of pyrrole. This suggests that other factors, such as vapor polarity or molecular weight may contribute to or mitigate the

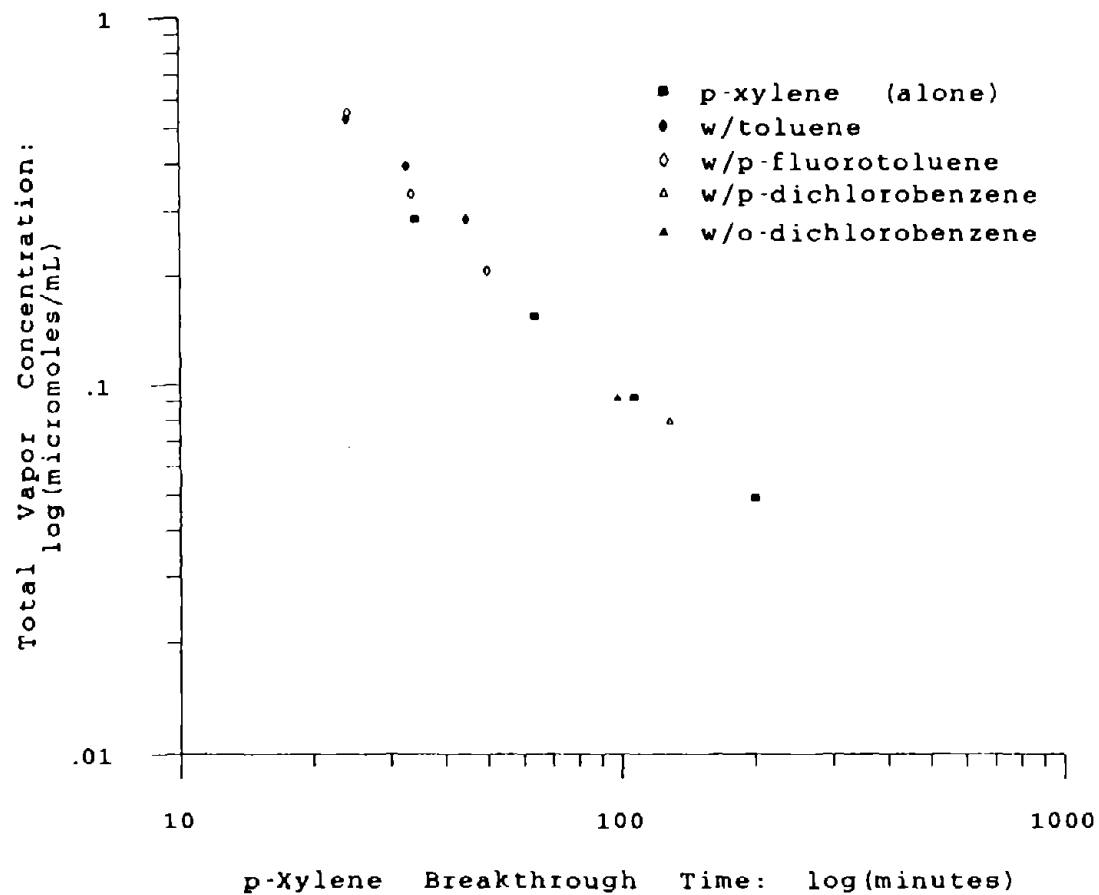


Figure 5.2.2.1. One percent t_b versus total vapor concentration on a log-log scale for p-xylene alone, and in the presence of Probe vapors.

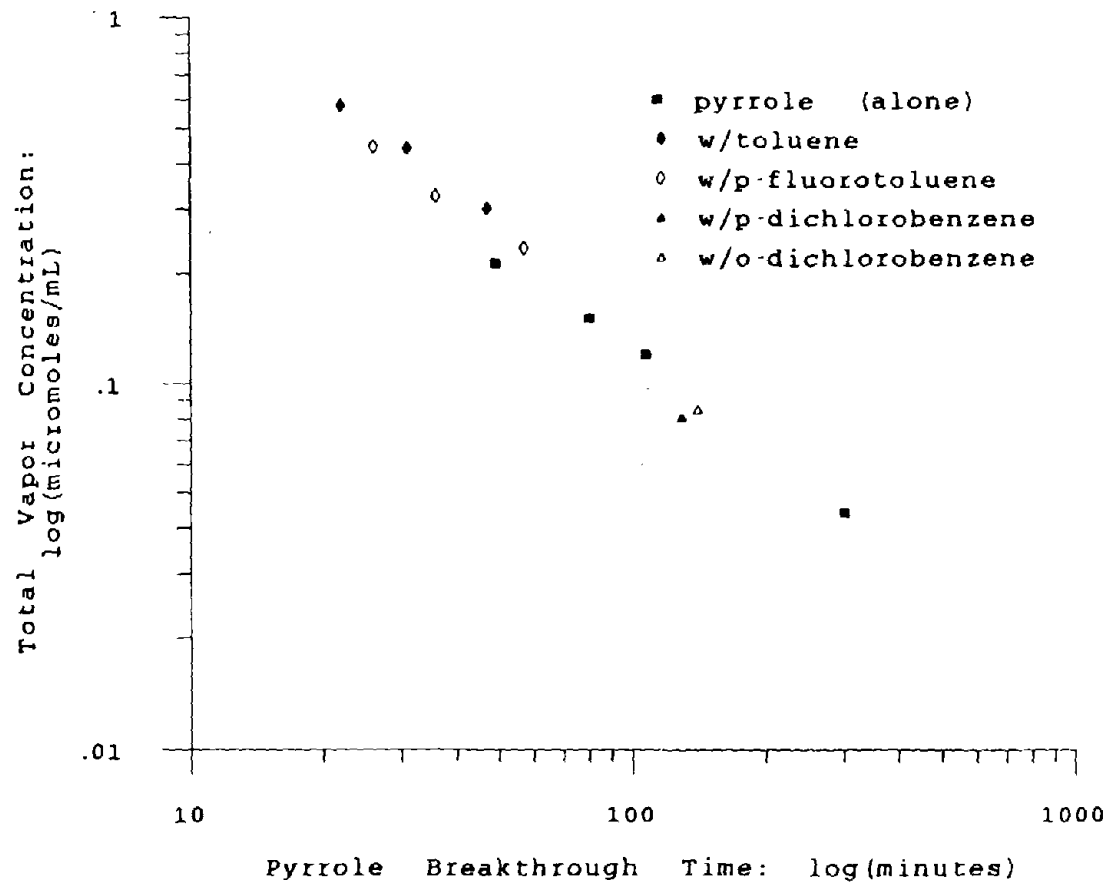


Figure 5.2.2.2. One percent t_b versus total vapor concentration on a log-log scale for pyrrole alone, and in the presence of Probe vapors.

displacement of one vapor by another. However, in the case of the vapors studied, the effect of these factors does not prohibit relatively accurate prediction of the 1% t_b ($\pm 25\%$) for a vapor in a mixture from its single-vapor data.

Summary of 1% Breakthrough Time: In the ranges tested, it appears that the polarity of the accompanying Probe vapor does not systematically affect the 1% t_b of either the polar or non-polar Test vapor.

The predicted 1% t_b of *p*-xylene or pyrrole in the presence of toluene is consistently underestimated. This may be the result of "displacement" of the lower boiling point vapor, toluene, by the Test vapor. Although there is evidence that "displacement" of one vapor by another occurs at high breakthrough concentrations^{28,32} ($C_i/C_o > 10\%$) the results of this study suggest that it is not practically important at lower breakthrough concentrations ($C_i/C_o = 1\%$) for the vapors tested. Further information is needed to determine if displacement is important at 1% breakthrough for vapor pairs with more divergent structures, boiling points, vapor pressures, or molecular weights than the vapors studied; or for vapors mixtures of more extreme concentration differences (molar ratios $> 3:1$).

These results suggest that the 1% t_b for a vapor in a binary mixture can be predicted with reasonable certainty ($\pm 25\%$) from the k_i and W_i from single vapor experiments if the mole fraction of the vapor in the mixture is known. Although the predicted 1% t_b 's were often outside of the experimental 1% t_b 95% CI; the differences in practical terms are small.

5.2.3 Kinetic Adsorption Capacity (W_i)

The average W_i 's ($n=6$) are shown in Tables 5.2.3.1 and 5.2.3.2, for *p*-xylene and pyrrole, respectively. The W_i for the Test vapor alone is compared to its W_i in the presence of each Probe vapor. The data are arranged as they were for 1% t_b , with the trials grouped together according to the molar concentration of Test vapor. The molar ratios of Test to Probe vapor are shown, followed by the experimental and predicted W_i 's. The final column shows the average percent deviation of the experimental and predicted W_i 's.

Para-xylene Capacity: The W_i for *p*-xylene alone ranged from 0.41 to 0.42 g/g at concentrations ranging from 0.04 to 0.15 $\mu\text{mol/mL}$. Although the W_i did not change significantly as the concentration for *p*-xylene alone varied, the W_i was in general reduced directly in proportion to the decreasing *p*-xylene mole fraction in binary mixtures.

The experimental W_i differed from the predicted W_i by -1% to -28% for equimolar mixtures, and -18% to -35% percent for mixtures containing $> 50\%$ Probe vapor. This variation is similar to that reported by Jonas for mixtures of benzene, carbon tetrachloride, and chloroform; where expected W_i 's for individual components in binary mixtures were calculated

Table 5.2.3.1. Observed (n=6) and predicted kinetic adsorption capacity (W_e) for *p*-xylene alone, and with Probe vapors at varying concentrations (predicted W_e calculated from *p*-xylene alone data).

Challenge Vapors and Concentrations, $\mu\text{mol/mL}$		<i>p</i> -xylene Mole Fraction	Experimental <i>p</i> -xylene W_e , g/g (S.E) ^a	Predicted <i>p</i> -xylene W_e , g/g	Average Percent Deviation
toluene	<i>p</i> -xylene				
.00	.15	1.00	.42 (.002)		
.14	.14	0.50	.29 (.023)	.21	-28%
.26	.14	0.35	.22 (.009)	.15	-33%
.39	.14	0.26	.17 (.016)	.11	-35%
<i>p</i> -fluoro. ^b	<i>p</i> -xylene				
.00	.09	1.00	.42 (.003)		
.10	.11	0.51	.23 (.008)	*.21	- 9%
.24	.09	0.27	.14 (.003)	.11	-18%
.44	.11	0.20	.12 (.005)	.08	-30%
<i>p</i> -dichlo. ^c	<i>p</i> -xylene				
.00	.05	1.00	.41 (.004)		
.04	.04	0.50	.23 (.004)	.21	-11%
<i>o</i> -dichlo. ^d	<i>p</i> -xylene				
.00	.05	1.00	.41 (.004)		
.05	.04	0.44	.18 (.009)	*.18	0%

^a Standard error

^b *p*-fluorotoluene, ^c *p*-dichlorobenzene, ^d *o*-dichlorobenzene

* Predicted value within experimental 95% confidence interval

Table 5.2.3.2. Observed (n=6) and predicted kinetic adsorption capacity (W_e) for pyrrole alone, and with Probe vapors at varying concentrations (predicted W_e calculated from pyrrole alone data).

Challenge Vapors and Concentrations, $\mu\text{mol/mL}$		pyrrole Mole Fraction	Experimental pyrrole W_e , g/g (S.E.) ^a	Predicted pyrrole W_e , g/g	Average Percent Deviation
toluene	pyrrole				
.00	.15	1.00	.33 (.006)		
.15	.15	0.50	.18 (.002)	.17	- 2%
.30	.14	0.32	.12 (.002)	*.11	-13%
.43	.14	0.25	.08 (.003)	*.08	0%
p-fluoro. ^b	pyrrole				
.00	.12	1.00	.35 (.010)		
.12	.12	0.50	.18 (.004)	*.18	0%
.22	.11	0.33	.11 (.001)	*.12	+ 6%
.33	.11	0.25	.08 (.001)	.09	+ 9%
p-dichlo. ^c	pyrrole				
.00	.04	1.00	.37 (.007)		
.04	.04	0.50	.14 (.005)	.19	+32%
o-dichlo. ^d	pyrrole				
.00	.04	1.00	.37 (.007)		
.04	.04	0.50	.16 (.002)	.19	+16%

^a Standard error

^b p-fluorotoluene, ^c p-dichlorobenzene, ^d o-dichlorobenzene

* Predicted value within experimental 95% confidence interval

using the W_e for each vapor alone, and its mole fraction in each binary vapor trial.³⁰ The differences reported between observed and expected W_e 's in that study ranged from -10% to +20%.

The W_e for p-xylene in mixtures was consistently higher than the W_e predicted from its mole fraction. The largest deviations occurred with mixtures of toluene, with increasing deviation (-9% to -30%) with rising concentrations of toluene (0.10 to 0.44 $\mu\text{mol/mL}$). The increasing deviation with rising Probe vapor concentration also occurs with p-fluorotoluene, although it is not as pronounced. The increase in W_e for p-xylene in the presence of toluene or p-fluorotoluene is consistent with the longer than expected t_b for p-xylene with these vapors.

In all but two challenges the predicted W_e was outside of the experimental W_e 95% CI. However, the differences between the experimental and predicted W_e are relatively small and of limited practical consequence. The differences are in the range of variability of the adsorption space (mL/g) of carbon used in organic vapor respirator cartridges, which vary by as much as 30%.⁴⁰

The decrease in W_e for a vapor as its mole fraction in a mixture is reduced conforms with results reported by Jonas for different binary vapor mixtures of carbon tetrachloride, chloroform, and benzene.³⁰ Cohen et.al., also reported that the W_e was decreased in proportion to vapor concentration for mixtures of carbon tetrachloride and hexane.³³ In both of these studies better agreement was found between experimental and predicted W_e 's when vapors of similar boiling point and vapor pressure were combined. Cohen et al., reported pronounced variation from expected W_e for mixtures of pyridine and carbon tetrachloride. The W_e was reduced only slightly for pyridine alone, compared to pyridine in an equimolar mixture with carbon tetrachloride (from 0.59 g/g to 0.48 g/g). It appears that the higher boiling point pyridine (115.5°C) displaces carbon tetrachloride (boiling point=76°C). However, the author suggested that the displacement was the result of the polar nature of pyridine.³³

Displacement of a lower boiling point vapor by a higher boiling point vapor is suggested by the larger than expected W_e for p-xylene in the presence of toluene or p-fluorotoluene. The apparent effect is more pronounced with toluene, possibly because it has the lowest molecular weight and boiling point of the Probe vapors, and both of these factors may cause it to be displaced more readily.^{28,29,32,34}

In summary, the reduction of W_e with decreasing p-xylene mole fraction is not systematically influenced by the polarity difference between p-xylene and the Probe vapor; since in all but one mixture (p-xylene with o-dichlorobenzene) the W_e is underestimated. There appears to be no consistent variation from the expected W_e due to Probe boiling point; however, the displacement of lower boiling point vapors by higher boiling point vapors is suggested by the uniform underestimation of W_e 's

for *p*-xylene with either toluene or *p*-fluorotoluene.

Pyrrole Capacity: Capacity data for pyrrole alone and in the presence of Probe vapors is presented in Table 5.2.3.2. The capacity for pyrrole alone ranged from 0.33 to 0.37 g/g for concentrations from 0.04 to 0.15 $\mu\text{mol/mL}$. When pyrrole was paired with a second vapor, the reduction in W_t was approximately proportional to the decreasing pyrrole mole fraction; with the largest deviation from expected occurring for pyrrole with *p*-dichlorobenzene trials. The W_t of pyrrole in this mixture was 32% less than predicted from the mole fraction of pyrrole.

As with *p*-xylene, the decrease in W_t for pyrrole as its mole fraction in a mixture is reduced conforms with results reported by others.^{30,33} The agreement between pyrrole's predicted and experimental W_t was better than for *p*-xylene, with half of pyrrole's predicted W_t 's occurring within the experimental 95% CI.

The experimental and predicted W_t 's were in better agreement for pyrrole with either toluene or *p*-fluorotoluene (-13% to +9% deviation) than for pyrrole paired with *o*- or *p*-dichlorobenzene (+16 to +32% deviation). The predicted W_t 's for pyrrole with either toluene or *p*-fluorotoluene were very similar to experimental values (often within the experimental W_t 95% CI) but the predicted values for pyrrole with *p*- or *o*-dichlorobenzene were too high. The lower than expected W_t for pyrrole with *p*- or *o*-dichlorobenzene suggests that these two Probe vapors may displace pyrrole. The decreased W_t agrees with the shorter than expected $1\% t_b$ for pyrrole with these vapors.

As with *p*-xylene, the reduction of W_t for pyrrole is primarily related to its decreasing mole fraction in a mixture, and does not appear to be systematically affected by the polarity of the Probe vapor. The deviations of experimental and predicted W_t 's are similar to those reported by others for binary mixtures;³⁰ and are within the range of variability of the adsorption space (mL/g) for activated carbon.⁴⁰

Summary of Carbon Capacity: These results suggest that the W_t is not consistently affected by the polarity of the Test or Probe vapor (for vapors of 0 to 2.5 Debye). The W_t for the Test vapor alone is relatively invariant as its concentration changes; and the Test vapor W_t is reduced approximately in proportion to its decreasing mole fraction in binary mixtures. The decrease in W_t for a vapor as its mole fraction in a mixture is reduced conforms with results reported by others for binary vapor mixtures.^{30,33}

The W_t is consistently higher than predicted from Test vapor mole fractions for *p*-xylene with toluene or *p*-fluorotoluene, with increasing deviation as the Probe vapor concentration rises. Underestimation of the *p*-xylene W_t with these vapors may be due to displacement of toluene and *p*-fluorotoluene by *p*-xylene. Displacement by the higher boiling point vapor is also suggested by the overestimated (from predicted) W_t for pyrrole with *p*- or *o*-dichlorobenzene.

Although this and other studies have suggested that displacement of one vapor by another may modify the W_e ,^{28,32,33} this change does not practically affect the estimation of W_e for a vapor in a binary mixture from single-vapor data (using the Wheeler model). The differences between experimental and predicted W_e 's are similar to those reported elsewhere for binary vapors.³⁰ In addition, the differences between predicted and experimental W_e 's are of limited practical importance since they are within the range of variability of the adsorption space (mL/g) of respirator carbon (2 to 30%).⁴⁰

These data suggest that it is possible to predict with reasonable certainty (within 32%) the W_e for a vapor in an equimolar binary mixture (without regard to the polarity of the accompanying vapor) from single vapor data. The uncertainty is within the range of that for the adsorption space for activated carbon.⁴⁰ Although many industrial solvents have boiling points and polarities in the range of the vapors tested, additional tests with vapors having greater polarity and boiling point differences need to be conducted before these results can be generalized to more widely varying vapor mixtures.

5.2.4 Kinetic Rate Constant

The average k_v 's ($n=6$) for *p*-xylene or pyrrole alone and in the presence of each Probe vapor are shown in Tables 5.2.4.1 and 5.2.4.2. The vapor concentrations are shown for each trial. Trials of Test vapor alone were conducted at concentrations ($\mu\text{mol/mL}$) equal to Test vapor concentrations in binary trials. Results from trials of Test vapor alone are displayed with binary trials matched according to Test vapor concentration.

T-tests were conducted to compare the k_v of Test vapors alone to Test vapors with Probe vapors. ANOVA was carried out to compare the k_v of Test vapors, when in the presence of Probe vapors, according to Probe vapor polarity and boiling point.

Para-xylene Rate Constant (k_v): The k_v for *p*-xylene alone compared to the k_v of *p*-xylene in the presence of each Probe vapor is shown in Table 5.2.4.1. Single and binary trials with the same *p*-xylene concentrations are shown together.

The k_v for *p*-xylene alone ranged from 62.4 to 69.3 s^{-1} , for concentrations of 0.05 - 0.15 $\mu\text{mol/mL}$, and are not significantly different from one another. The magnitude and range of k_v are similar to previously reported k_v 's for carbon tetrachloride on comparable carbon (mean=75.6 s^{-1} , CV=9.4%).³⁰ Jonas also found the k_v of carbon tetrachloride to be unaffected by its concentration³⁰

The k_v for *p*-xylene in mixtures ranged from 47.7 to 78.2 s^{-1} . The k_v 's for *p*-xylene in mixtures appear to be different when compared according to Probe boiling point; with lower k_v 's when *p*-xylene is with lower boiling point Probe vapors (toluene and *p*-fluorotoluene). Upon inspection, there appears to be little difference between the k_v 's for *p*-xylene in mixtures when compared according to Probe vapor polarity.

Table 5.2.4.1. Comparison of the average k_v ($n=6$) for *p*-xylene alone, to the k_v of *p*-xylene in equimolar binary mixtures.

Challenge Vapors and Concentrations, $\mu\text{mol/mL}$		Average <i>p</i> -xylene k_v , s^{-1} (S.E.) ^a
toluene	<i>p</i> -xylene	
.00	.15	69.3 (3.3)
.14	.14	47.7 (2.0)
<i>p</i> -fluoro. ^b	<i>p</i> -xylene	
.00	.09	68.0 (2.4)
.10	.10	51.9 (2.1)
<i>p</i> -dichlo. ^c	<i>p</i> -xylene	
.00	.05	62.4 (4.0)
.04	.04	78.1 (4.9)
<i>o</i> -dichlo. ^d	<i>p</i> -xylene	
.00	.05	62.4 (4.0)
.05	.04	78.2 (4.9)

^a Standard error

^b *p*-fluorotoluene

^c *p*-dichlorobenzene

^d *o*-dichlorobenzene

Table 5.2.4.2. Comparison of the average k_v ($n=6$) for pyrrole alone, to the k_v of pyrrole in equimolar binary mixtures.

Challenge Vapors and Concentrations, $\mu\text{mol/mL}$		Average pyrrole k_v , s^{-1} (S.E.) ^a
toluene	pyrrole	
.00	.15	67.6 (3.1)
.15	.15	79.8 (4.1)
p-fluoro. ^b	pyrrole	
.00	.12	65.0 (3.0)
.12	.12	68.3 (4.3)
p-dichlo. ^c	pyrrole	
.00	.04	60.6 (2.9)
.04	.04	67.7 (4.4)
o-dichlo. ^d	pyrrole	
.00	.04	60.6 (2.9)
.04	.04	73.1 (4.4)

^a Standard error

^b p-fluorotoluene

^c p-dichlorobenzene

^d o-dichlorobenzene

To evaluate whether the k_v for *p*-xylene was systematically changed by the presence of a second vapor, *t*-tests were used to compare the k_v for *p*-xylene alone, to the k_v for *p*-xylene in mixtures. The results indicate that the k_v is significantly different for *p*-xylene alone compared to *p*-xylene in the presence of each Probe vapor. The k_v of *p*-xylene decreases when *p*-xylene is in the presence of toluene or *p*-fluorotoluene, and increases when *p*-xylene is accompanied by either *p*- or *o*-dichlorobenzene (see Table 5.2.4.1).

Analysis of variance (ANOVA) comparing the k_v 's of *p*-xylene in binary mixtures with vapors of different polarity and boiling point was conducted to determine whether the k_v of *p*-xylene depends on the relative polarity of the accompanying Probe vapor. The two-by-two experimental design underlying the analysis is shown in Table 4.1.1. The results indicate that the k_v for *p*-xylene is not significantly different when compared on the basis of polarity of the Probe vapor ($p=0.64$); but that significant differences occur when k_v 's are compared according to Probe boiling point ($p<0.001$). There was no interaction between polarity and boiling point ($p=0.66$).

The ANOVA and *t*-tests suggest that the k_v of *p*-xylene changes when it is in the presence of another vapor. The decrease or increase in *p*-xylene's k_v with respectively lower or higher boiling point Probe vapors suggests that the change in *p*-xylene k_v depends on the relative difference between the boiling point of *p*-xylene and the accompanying Probe vapor. However, because molecular weight often varies along with boiling point, i.e., higher molecular weight compounds have higher boiling points, lower molecular weight compounds have lower boiling points, a study that examines the effect of boiling point while controlling for molecular weight is needed to address this question.

In Jonas' study of binary mixtures of benzene, chloroform, and carbon tetrachloride, the data indicate that the k_v of vapors alone were different from the k_v of vapors in mixtures.³⁰ The k_v 's were increased in the presence of a second vapor by 9% to 73%, except for chloroform with benzene, where the k_v is reduced by 2%. Whether the differences were statistically significant was not reported. In that study, Jonas did not evaluate the effect of polarity, boiling point, vapor pressure or molecular weight of the components on the k_v , and there is no discernable pattern to the change in k_v due to these factors.

Pyrrole Rate Constant: Table 5.2.4.2 contains the k_v for pyrrole alone, and with each Probe vapor. Single and binary trials with the same pyrrole concentration are shown together. The k_v for pyrrole alone ranged from 60.6 to 67.6 s⁻¹ for concentrations of 0.05 - 0.15 $\mu\text{mol/mL}$. The 95% confidence intervals overlap for these k_v 's and the range of k_v 's is similar to those for *p*-xylene alone.

The k_v for pyrrole in mixtures was similar to that of pyrrole alone, ranging from 67.7 to 79.8 s⁻¹. The k_v for pyrrole

in the presence of toluene or o-dichlorobenzene are similar (79.8 and 73.1 s⁻¹) as were the k_v 's for pyrrole with p-fluorotoluene or p-dichlorobenzene (68.3 and 67.7 s⁻¹).

To determine whether the k_v for pyrrole was changed by the presence of a second vapor, t-tests were used to compare the k_v for pyrrole alone, to the k_v for pyrrole in mixtures. The k_v for pyrrole alone compared to pyrrole with toluene is significantly different ($p=0.03$). The k_v for pyrrole alone compared to pyrrole with o-dichlorobenzene is also significantly different ($p=0.02$). The k_v 's for pyrrole alone compared to pyrrole with either p-fluorotoluene or p-dichlorobenzene were not significantly different.

Analysis of variance comparing the k_v 's of pyrrole in binary mixtures with vapors of different polarity and boiling point was conducted to determine whether the k_v of pyrrole depends on the relative polarity of the accompanying Probe vapor. The two-by-two experimental design underlying this analysis is shown in Table 4.1.2. The result of this analysis indicates that the k_v for pyrrole is not significantly changed by the polarity or relative boiling point difference of the Probe vapors used. However, the interaction term for polarity and boiling point was significant at $p=0.05$. Statistical interaction is present because pyrrole's k_v is increased to a lesser extent when the Probe vapors are p-fluorotoluene and p-dichlorobenzene, than when the Probe vapors are toluene and o-dichlorobenzene (the k_v for pyrrole is always increased in the presence of a second vapor compared to the k_v of pyrrole alone). These results are similar to those reported by Jonas, where the k_v is higher for a vapor in a mixture than when alone, with no obvious pattern of change in k_v due to component polarity, molecular weight, boiling point, or vapor pressure.³⁰

Rate Constant Summary: The data for p-xylene and pyrrole in the presence of selected Probe vapors suggest that the Wheeler kinetic model rate constant is not affected by the polarity of the Test or accompanying Probe vapor. For p-xylene, significant changes in k_v from one vapor mixture to another appear to be related to the boiling point of the Probe vapors. Jonas has reported changes in k_v 's for vapors alone compared to their k_v 's in mixtures; however, patterns in the change in k_v , or whether the changes were significant were not reported.³⁰ The k_v is generally the most variable of the parameters of the Wheeler equation,⁴⁸ and much more research is needed to better understand what factors contribute to its variability in binary vapor mixtures.

5.2.5 Summary of Kinetic Results

The relative order of vapor breakthrough appears to depend primarily on boiling point, with lower boiling point vapors breaking through first. Vapor molecular weight and polarity may also affect the relative breakthrough order, with lighter, polar

molecules breaking through more quickly.

The 1% t_b for Test vapors was dependent on the total concentration of the vapor system, and for practical purposes, was not affected by the polarity or boiling point of the accompanying Probe vapor. Reasonably good estimates of the 1% t_b for a vapor in a mixture were obtained with the Wheeler model using single-vapor data (using W_e adjusted for the Test vapor mole fraction in each mixture).

The Test vapor W_e varied in proportion to its mole fraction in the mixture, and did not appear to be systematically affected by the polarity of the accompanying Probe vapor. Estimates of W_e for Test vapors in mixtures (obtained by multiplying single-vapor W_e 's by Test vapor mole fractions) agreed reasonably well with experimental values.

The k_v 's for Test vapors were not significantly different when compared according to Probe vapor polarity. The p-xylene k_v 's were significantly different ($p < 0.001$) when compared across Probe boiling point. There was significant interaction ($p = 0.05$) for polarity - boiling point for pyrrole in the presence of Probe vapors. Although there was no consistent pattern of increasing or decreasing k_v according to Probe vapor polarity or boiling point, the k_v 's for Test vapors alone were generally lower than for Test vapors in equimolar binary mixtures.

While the polarity and boiling point of the vapors in the range tested appears to be practically unimportant in predicting service-life, an effect of the relative boiling points of the vapors is suggested, and tests with vapors of more widely ranging boiling point are warranted.

These data suggest that the presence of other vapors must be taken into account when estimating the service life of a respirator for a vapor in a mixture. The breakthrough time, and thus the respirator service life is mainly dependent on total vapor concentration. Although a respirator may be worn to protect against a particular noxious vapor, the presence of other vapors (noxious or otherwise) must be considered when estimating the service-life of a respirator cartridge.

This research suggests that it may be possible to estimate the service-life of a respirator for a vapor in a mixture using the carbon capacity for the vapor, and the mole fraction of the vapor in the mixture. However, before this approach can be broadly generalized, further investigation of more diverse mixtures is required.

5.3 Equilibrium Adsorption Experiments

5.3.1 Dubinin Transformation of Isotherms

Isotherms were obtained by evaluating each Test vapor chromatogram (from the PID signal) using the chromatographic method of isotherm determination (hereafter referred to as the *chromatographic method*).⁴³ Chromatograms were obtained from 0.05

μL injections of Test chemicals alone, and 0.10 μL injections of approximately equimolar mixtures of Test and Probe chemicals (the pyrrole and *p*-dichlorobenzene mixture was not equimolar as described previously, Methods 4.4). Each adsorption isotherm was converted to a characteristic curve using the Dubinin equation (equation 2.1.2). For each point on the isotherm, the amount adsorbed (a) was converted to volume adsorbed (W_0) and the adsorbate pressure was converted to the adsorption potential squared (ϵ^2). The intercept (W_0) and slope ($-k/\beta^2$) were calculated from the regression of these points, and the average ($n=3$) W_0 and $-k/\beta^2$ were determined for each mixture. These data are shown in Tables 5.3.1.1 and 5.3.1.2 for *p*-xylene and pyrrole, respectively. Plots of the average regression lines are shown in Figure 5.3.1.1 for *p*-xylene and Figure 5.3.1.2 for pyrrole.

For the purpose of comparing Test vapor k/β^2 in the presence of different Probe vapors, the k/β^2 represents the affinity coefficient in the form $1/\beta^2$, assuming that the carbon structural constant k is unchanged between trials. This is a reasonable assumption since the carbon used for all trials was from the same lot number, and the k has been shown to be similar for carbon from the same supplier (2% to 7% difference between lots).⁴⁰ Therefore, changes in the Dubinin slope should be comparable to changes in vapor-carbon affinity.

T-tests were employed to compare the affinity (k/β^2) of Test vapors alone to Test vapors in binary mixtures. To assess the potential effect of Probe vapor polarity on Test vapor k/β^2 , ANOVA was used to compare the k/β^2 for Test vapors when with Probe vapors according to Probe vapor polarity and boiling point.

The W_0 is also a characteristic of the carbon,³⁰ and is slightly more variable than k ($\pm 30\%$ within a single lot).⁴⁰ To verify that the W_0 was similar for single and binary vapor injections, t-tests were used to compare the W_0 of Test vapor alone to the W_0 of Test vapors with Probe vapors.

In general, comparison of the results of this study with the published literature is limited because adsorption studies of vapor mixtures are infrequent, and mixture data on activated carbon adsorption is extremely scarce.⁴⁶ Less information is available for adsorption equilibrium studies of organic vapors on carbon using the Dubinin model.

Table 5.3.1.1. Dubinin equilibrium adsorption volume (W_0) and affinity (k/β^2) for p-xylene alone, and in approximately equimolar mixtures with Probe vapors.

Vapor Mixture p-xylene with:	W_0 (mL/g)		k/β^2 [(J/mol) $^{-1}$]*	
	Trials	Average	Trials	Average
nothing	0.57		-3.14	
	0.33		-2.66	
	0.41	0.43	-2.87	-2.89
toluene	0.38		-2.85	
	0.25		-2.46	
	0.34	0.32	-2.77	-2.69
p-fluorotoluene	0.17		-2.18	
	0.21		-2.42	
	0.23	0.20	-2.54	-2.38
p-dichlorobenzene	0.54		-3.38	
	0.49		-3.15	
	0.40	0.48	-2.95	-3.16
o-dichlorobenzene	0.34		-2.85	
	0.47		-3.12	
	0.38	0.40	-3.01	-3.25

* $\times 10^8$

Table 5.3.1.2. Dubinin equilibrium adsorption volume (W_0) and affinity (k/β^2) for pyrrole alone, and in approximately equimolar mixtures with *Probe* vapors.

Vapor Mixture pyrrole with:	W_0 (mL/g)		k/β^2 [(J/mol) ⁻²] *	
	Trials	Average	Trials	Average
nothing	0.12		-5.45	
	0.11		-4.96	
	0.13	0.12	-5.59	-5.33
toluene	0.15		-6.20	
	0.14		-5.92	
	0.15	0.15	-6.03	-6.05
<i>p</i> -fluorotoluene	0.13		-5.81	
	0.13		-5.77	
	0.14	0.13	-5.79	-5.79
<i>p</i> -dichlorobenzene	0.12		-5.44	
	0.13		-5.66	
	0.15	0.13	-6.00	-6.25
<i>o</i> -dichlorobenzene	0.16		-6.05	
	0.16		-6.05	
	0.14	0.15	-5.70	-5.93

* $\times 10^8$

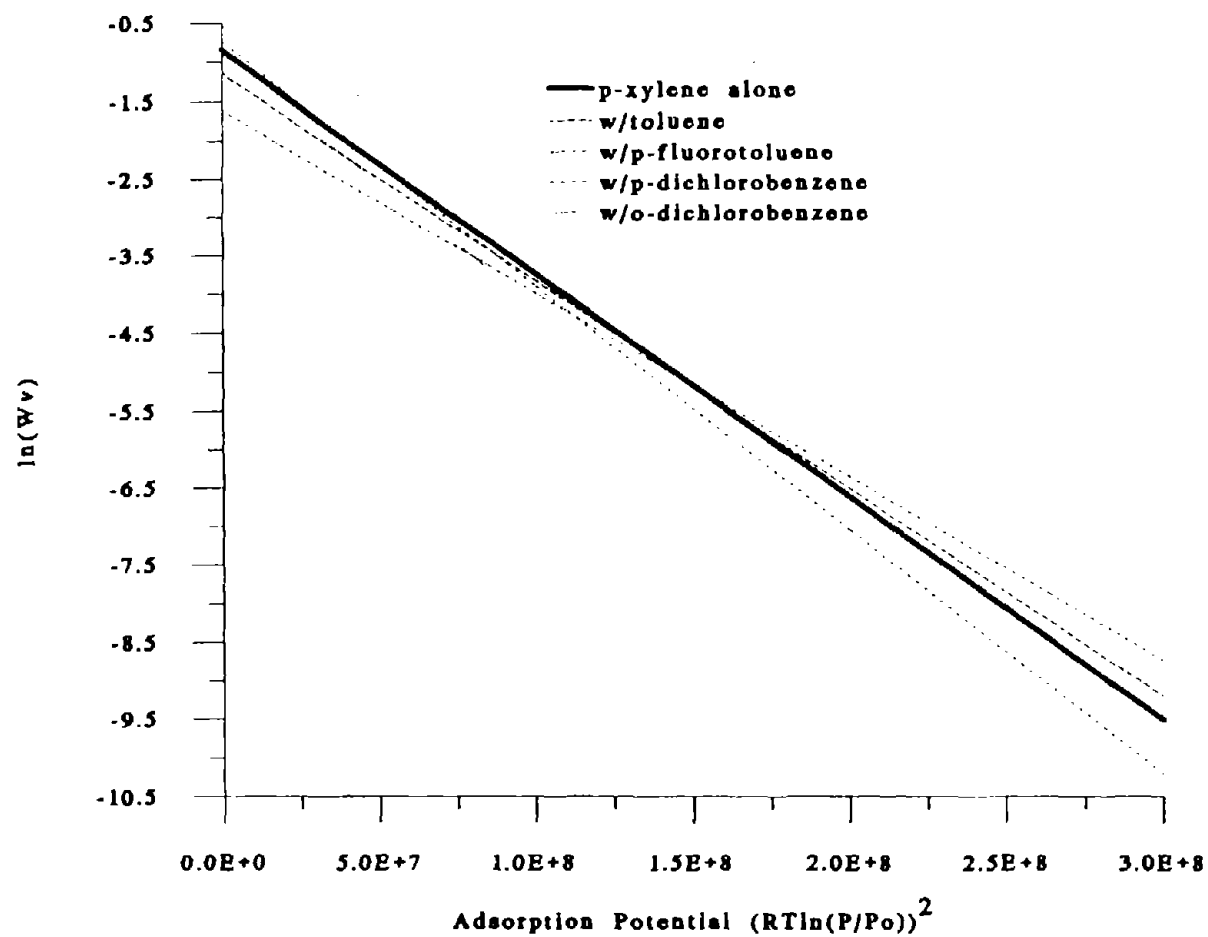


Figure 5.3.1.1. Dubinin characteristic curves for p-xylene alone, and with *Probe* vapors.

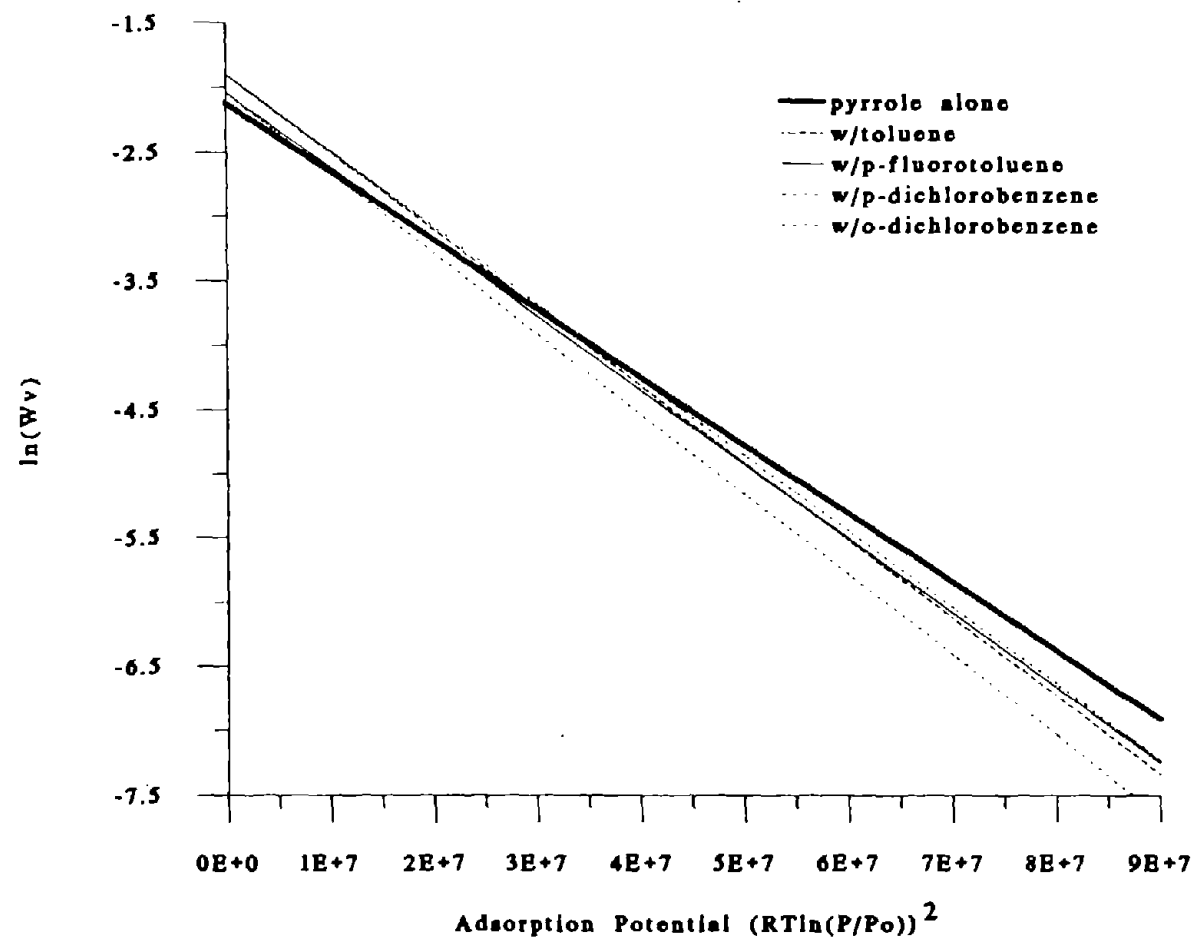


Figure 5.3.1.2. Dubinin characteristic curves for pyrrole alone, and with Probe vapors.

5.3.2 Equilibrium Adsorption of p-xylene

The W_0 for p-xylene alone and accompanied by Probe vapors is shown in Table 5.3.1.1. The W_0 for each trial and the average W_0 for each vapor system are indicated. The average W_0 for p-xylene ranged from 0.20 mL/g for p-xylene with p-fluorotoluene, to 0.43 mL/g for p-xylene with p-dichlorobenzene.

T-tests were used to compare the W_0 of p-xylene alone to the W_0 of p-xylene in mixtures. The difference between p-xylene alone and p-xylene with p-fluorotoluene appeared to be significant ($p=0.03$). However, the difference is not significant when the acceptable p-value is adjusted from $p \leq 0.05$ to $p \leq 0.0125$ to account for multiple statistical tests using the same data.⁴⁹ In addition, these differences may be unimportant in practice since the variability of the W_0 for different carbons is $\pm 30\%$.³⁹ The apparent 50% decrease in the average W_0 for p-xylene in the presence of p-fluorotoluene may be of practical importance; however, verification of these results by others is needed.

Affinity (k/β^2) of Para-xylene: The k/β^2 for each trial and the average k/β^2 for each vapor system are shown in Table 5.3.1.1. The average k/β^2 for p-xylene ranged from -3.16×10^{-8} for p-xylene with p-dichlorobenzene, to -2.38×10^{-8} for p-xylene with p-fluorotoluene.

To determine whether the affinity of p-xylene was affected by the presence a second vapor, the k/β^2 of p-xylene alone was compared to the k/β^2 of p-xylene in mixtures. The k/β^2 of p-xylene alone compared to the k/β^2 of p-xylene in mixtures is not significantly different using the t-test. The difference between p-xylene alone and p-xylene with p-fluorotoluene appears to be significant ($p=0.02$) but is not when the p-value accepted as significant is adjusted to $p \leq 0.0125$ to account for multiple statistical tests.⁴⁹ The average k/β^2 for p-xylene alone is between that of p-xylene with p- or o-dichlorobenzene, and p-xylene with toluene or p-fluorotoluene.

Analysis of variance comparing the k/β^2 of p-xylene in binary mixtures containing vapors of different polarity and boiling point was conducted to determine whether the affinity (as represented by k/β^2) of p-xylene depends on the relative polarity of the accompanying Probe vapor. The model is significant ($p=0.002$) and accounts for the majority of the variability of the data ($r^2=0.83$). The k/β^2 is significantly different when compared according to Probe vapor polarity ($p < 0.001$). The effect of Probe boiling point was also significant ($p=0.02$) but the interaction term was not ($p=0.42$).

These results suggest that p-xylene with p- or o-dichlorobenzene has on average, less affinity (steeper slope, see Figure 5.3.1.1) for carbon than p-xylene in the presence of toluene or p-fluorotoluene. Thus, it appears that the affinity of p-xylene is decreased in the presence of non-polar and higher boiling point vapors, compared to its affinity in the presence of polar and lower boiling point vapors.

The result of the ANOVA suggests that the presence of the second vapor that is either polar, or has a boiling point lower than *p*-xylene may slightly enhance the affinity of *p*-xylene for carbon, while the non-polar and higher boiling point vapors slightly diminish it. These small differences in affinity are not detected when *p*-xylene alone is compared to *p*-xylene in mixtures, but are detected when the affinity of *p*-xylene in mixtures is compared according to Probe boiling point and polarity. The differences are small and may be of limited practical importance with respect to predicting respirator service-life.

The reasons for the apparent enhanced or diminished affinity for *p*-xylene in the presence of other vapors is unknown. The decrease in affinity for *p*-xylene in the presence of higher boiling point and higher molecular weight vapors agrees with results reported by Lewis.⁵⁰ In that study, the higher-molecular weight gas in a binary mixture (for combinations of hydrocarbon gases from methane to butane) was preferentially adsorbed. However, the magnitude of the differences and their significance was not reported. In Reucroft's study of binary vapor adsorption, different k/β^2 are indicated for the Dubinin plot of CNCl alone compared to CNCl with HCN.⁵¹ Whether these differences were statistically significant was not reported. It is difficult to compare these studies to the current one, since both were done at high surface area coverage, and this study was done at low surface area coverage.

In summary, *p*-xylene appears to have greater affinity for carbon when in the presence of polar and lower boiling point compounds compared to *p*-xylene with non-polar, higher boiling point compounds. However, the magnitude of the affinity does not change significantly for *p*-xylene alone compared to *p*-xylene in mixtures. The changes in affinity are small and may not be practically important.

5.3.3 Equilibrium Adsorption of Pyrrole

The W_0 for pyrrole alone and accompanied by Probe vapors is shown in Table 5.3.1.2. The W_0 for pyrrole ranged from 0.12 mL/g for pyrrole alone to 0.15 mL/g for pyrrole with *o*-dichlorobenzene or toluene. Upon inspection, the average W_0 's do not appear to be different.

T-tests were used to compare the W_0 of pyrrole alone to the W_0 of pyrrole in mixtures. The difference between pyrrole alone and pyrrole with toluene appears to be significant ($p=0.03$) however, the difference is not significant when the p -value is adjusted from $p \leq 0.05$ to $p \leq 0.0125$ to account for multiple statistical tests on the same data set.⁴⁹

The W_0 is a function of the carbon adsorption space and its determination should be independent of the vapor used.^{24,25} It is therefore unclear why the W_0 for pyrrole is less than half that of *p*-xylene. Data from capacity measurements using kinetic

methods at (24°C, P/P_0 from 0.07 to 0.11) indicate that the capacity of pyrrole is approximately 0.40 mL/g. This value is similar to the average W_0 for p-xylene (0.43 mL/g) obtained with the chromatographic method. This suggests that the apparent decrease in the W_0 for pyrrole occurs when using the chromatographic method. This may be the result (indirectly) of hydrogen-bonding with pyrrole's two free nitrogen electrons. If significant hydrogen bonding occurs, the adsorption and desorption isotherms may not be superimposable; and since the trailing edge of the chromatogram (used in determining the isotherm from the chromatographic method) is the result of both adsorption and desorption processes, hysteresis may affect the trailing edge making the interpretation of results using the chromatographic method problematic. However, it is still reasonable to compare the relative changes in the Dubinin slope for pyrrole, since the isotherms were all determined using the same technique.

Affinity (k/β^2) of Pyrrole: The k/β^2 for pyrrole alone and accompanied by Probe vapors are shown in Table 5.3.1.2. The average k/β^2 ranged from -6.05×10^{-8} for pyrrole with toluene, to -5.33×10^{-8} for pyrrole alone. The affinity of pyrrole for carbon is approximately half that of p-xylene.

To determine whether the affinity of pyrrole was affected by the presence a second vapor, the k/β^2 of pyrrole alone was compared to the k/β^2 of pyrrole in mixtures. The k/β^2 of pyrrole alone compared to the k/β^2 of pyrrole in mixtures is not significantly different using the t-test. The difference between pyrrole alone and pyrrole with o-dichlorobenzene, and between pyrrole alone and pyrrole with toluene appear to be significant (both $p=0.02$) however, these differences are not significant using the adjusted p-value of $p \leq 0.0125$.⁴⁹

Analysis of variance comparing the k/β^2 of pyrrole in binary mixtures containing vapors of different polarity and boiling point was conducted to determine whether the affinity (as represented by k/β^2) of pyrrole depends on the relative polarity of the accompanying Probe vapor. The model is not significant ($p=0.25$) and accounts for less than half of the variability of the data ($r^2=0.39$). The k/β^2 is not significantly different when compared according to Probe vapor polarity ($p=0.89$) or Probe boiling point ($p=0.50$). The interaction term is not significant ($p=0.07$).

Results of the ANOVA and t-tests suggest that the affinity of pyrrole is unchanged when comparing pyrrole in one mixture to another, or pyrrole alone to pyrrole in mixtures. For pyrrole, obtaining the adsorption isotherm using the chromatographic method may be problematic.

5.3.4 Equilibrium Adsorption Summary

The PID with an 8.4 eV lamp was used successfully to selectively study the adsorption of one vapor in the presence of

another. It will be possible to extend the use of the PID to higher-order mixtures.

The W_0 for *p*-xylene alone is not significantly different from the W_0 for *p*-xylene in mixtures. The affinity of *p*-xylene in mixtures is significantly different when compared according to Probe vapor polarity and boiling point. The affinity of *p*-xylene is decreased slightly by the presence of non-polar or higher boiling point Probe vapors; and increased slightly by the presence of polar or lower boiling point Probe vapors. The k/β^2 does not appear to be different for *p*-xylene alone compared to *p*-xylene in mixtures.

The W_0 for pyrrole alone is not significantly different from the W_0 for pyrrole in mixtures. The W_0 for pyrrole is about half that of *p*-xylene. The reasons for this are unclear, however a possible explanation is that hydrogen bonding may affect the isotherms of pyrrole, making the calculation of isotherms using the *chromatographic method* difficult. Complete adsorption-desorption isotherms are needed to determine if hysteresis is occurring.

The k/β^2 was not significantly different for pyrrole in mixtures according to Probe vapor polarity or boiling point. Also, the k/β^2 was not different for pyrrole alone compared to pyrrole in mixtures.

In practical terms, the changes in k/β^2 for the Test vapors compared between and among single and binary mixtures are small. Since the capacity and affinity of the Test vapors alone are not significantly different from those in mixtures, it should be possible to estimate the capacity and affinity for a vapor in a mixture from single vapor data. However, data from the *p*-xylene trials and from previous work^{33,51} suggest that comparing a vapor's affinity from one mixture to another is complicated. Further study is warranted to determine what factors influence the affinity of a vapor in a mixture.

6. Conclusions

The purpose of this research was to develop a method to study the adsorption of a vapor in a mixture and to extend the current knowledge of models used to estimate respirator service-life for eventual use with vapor mixtures. A method was developed utilizing a photoionization detector, which allowed the study of one vapor in the presence of a second vapor, without interference from the second vapor. The potential effect of the polarity of a second vapor on the adsorption of a polar and a non-polar vapor, as measured by the Wheeler and Dubinin models, was studied to determine whether the adsorption of a vapor is affected by the polarity of the accompanying vapor. To this end, the 1% breakthrough time, kinetic adsorption capacity and rate constant of the Wheeler model were determined for equimolar binary vapor challenges (of polar and non-polar vapors) on carbon beds; and the characteristic curves of the Dubinin model were obtained from isotherms for vapors in equimolar binary mixtures injected onto carbon columns. On the basis of these studies, the following conclusions were reached:

1. The method of using the PID equipped with an 8.4 eV lamp is effective for studying kinetic (breakthrough) and equilibrium (isotherms) adsorption of one vapor in the presence of a second vapor. This method can be extended to other vapors and higher order mixtures; however, the range of vapor boiling points that can be investigated is limited (in the case of our PID) by the maximum-use temperature (220°C) of the detector.
2. The Wheeler model 1% t_b was not systematically affected by the polarity of the accompanying vapor. The 1% t_b for Test vapors appeared to be dependent on the total concentration of the vapor system, and for practical purposes, was not affected by the polarity or boiling point of the accompanying Probe vapor. Reasonably good estimates of the 1% t_b ($\pm 30\%$) for a vapor in a mixture were obtained with the Wheeler model using single-vapor data.
3. Since the 1% t_b and thus, the respirator service-life depend mainly on total vapor concentration; the presence of other vapors must be taken into account when estimating the respirator service-life for a vapor in a mixture.
4. The Test vapor W_t was not systematically affected by the polarity of the accompanying vapor. The Test vapor W_t varied in proportion to its mole fraction in the mixture. Estimates of the W_t ($\pm 20\%$) for a vapor in a mix were obtained from single-vapor data. Although the polarity and boiling point of the vapors in the range tested appears to be practically unimportant in predicting respirator service-life using the Wheeler model, an effect of the relative boiling points of the vapors is suggested

for the W_0 , and tests with vapors of more widely ranging boiling point are warranted.

5. The k_v 's for Test vapors were not significantly different when compared according to Probe vapor polarity. The k_v was significantly different for p-xylene when compared according to Probe vapor boiling point. However, the k_v 's for Test vapors alone were generally lower than for Test vapors in equimolar binary mixtures.

6. The affinity of p-xylene, as measured by the Dubinin model, appears to be affected by the polarity of the Probe vapor. Para-xylene appears to have greater affinity for carbon when in the presence of polar, and lower boiling point compounds than when with non-polar, higher boiling point compounds. However, the changes in affinity are small and are not practically important. Additional research is needed to determine if this effect is observed for other vapors. The affinity of pyrrole in binary mixtures is not different when compared according to Probe vapor polarity.

7. The Dubinin capacities (W_0 's) for Test vapors alone are not significantly different from their W_0 in mixtures. The W_0 for pyrrole is about half that of p-xylene. The reasons for this are unclear, however a possible explanation is that hydrogen bonding may affect the isotherms of pyrrole, making the calculation of isotherms using the chromatographic method difficult.

This research suggests that it may be possible to estimate the service-life of a respirator for a vapor in a mixture using the carbon capacity for the vapor, and the mole fraction of the vapor in the mixture. However, errors of 30% or more can be expected for vapors in the ranges of polarity, boiling point, and concentration tested. Further investigation of more diverse mixtures is required before this approach can be more broadly generalized.

Acknowledgments

We would like to thank Ernest Moyer, of NIOSH, for his helpful suggestions at the beginning of this project.

References

1. U.S. Government (1982): United States Office of Technology Assessment, Committee on Control Technologies in the Workplace, Washington, D.C.
2. Moyer, ES; Linn, H (1986): Organic vapor cartridge testing: selection and use. *J. Int. Soc. Respir. Prot.* 4(2), 1-19.
3. Reist, PC; Rex, F (1977): Odor detection and respirator cartridge replacement. *Am. Ind. Hyg. Assoc. J.* 38(10), 563-566.
4. Smoot, DM; Smith, DL (1977): Development of Improved Respirator Cartridge and Canister Test Methods. U.S. DHEW (NIOSH), Pub. No. 77-209.
5. Breysse, PN (1985): Prediction of Activated Carbon Bed Service-life Using the Dubinin-Wheeler Model. Ph.D. Thesis, Johns Hopkins University School of Hygiene and Public Health.
6. Oscik, J (1982): *Adsorption*. John Wiley and Sons, NY.
7. Ruthven, DM (1984): *Principles of Adsorption and Adsorption Processes*. John Wiley & Sons, NY.
8. Dubinin, MM (1960): The potential theory of adsorption of gases and vapors for adsorbents with energetically nonuniform surfaces. *Chemistry Reviews* 60, 235-241.
9. Reucroft, PJ; Simpson, WH; Jonas, LA (1971): Sorption properties of activated carbon. *J. Phys. Chem.* 75(23), 3526-3531.
10. Jonas, LA (1971): *Prediction of equilibrium gas adsorption by activated carbon*. Edgewood Arsenal Technical Report, Edgewood Arsenal, Maryland.
11. Finger, G; Bulow, M (1979): The applicability of the Dubinin-Astakhov equation in the sorption systems n-heptane/saran carbon and benzene/saran carbon. *Carbon* 17, 81-91.
12. Jaroniec, M; Jaroniec, JA (1977): On the characterization of microporous adsorbents. *Carbon* 15, 107-111.
13. Breysse, PN; Cappabianca, AM; Hall, TA; Risby, T (1987): Effect of polarity on the adsorption of dichlorobenzene isomers. *Carbon* 25(6), 803-808.
14. Bohart, GS; Adams, EQ (1920): Behavior of charcoal toward chlorine. *J. Am. Chem. Soc.* 42, 523-544.

15. Klotz, IM (1946): The adsorption wave. *Chem. Rev.* 39, 241-268.
16. Wheeler, A; Robell, AJ (1969): Performance of fixed-bed catalytic reactors with poison in feed. *J. Catal.* 13(3), 299-305.
17. Yoon, YH; Nelson, JH (1984): Application of gas adsorption kinetics - II. A theoretical model for respirator cartridge service life and its practical applications. *Am. Ind. Hyg. Assoc. J.* 45(8), 517-524.
18. Ackley, MW (1985): Residence time model for respirator sorbent beds. *Am. Ind. Hyg. Assoc. J.* 46(11), 679-689.
19. Jonas, LA; Tewari, YB; Sansone, EB (1979): Prediction of adsorption rate constants of activated carbon for various vapors. *Carbon* 17(4), 345-349.
20. Jonas, LA; Svirbely, W (1972): The kinetics of adsorption of carbon tetrachloride and chloroform from air mixtures by activated carbon. *J. Catal.* 24, 446-459.
21. Jonas, LA; Rehrmann, JA (1972): The kinetics of adsorption of organo-phosphorus vapors from air mixtures by activated carbons. *Carbon* 10, 657-663.
22. Moyer, ES (1987): Organic vapor (OV) respirator cartridge testing - potential Jonas model applicability. *Am. Ind. Hyg. Assoc. J.* 48(9), 791-797.
23. Costa, E; Sotelo, JL; Calleja, G; Marron, C (1981): Adsorption of binary and ternary hydrocarbon gas mixtures on activated carbon: experimental determination and theoretical prediction of the ternary equilibrium data. *Amer. Inst. Chem. Eng. J.* 27(1), 5-12.
24. Jonas, LA; Rehrmann, JA (1973): Predictive equations in gas adsorption kinetics. *Carbon* 11(1), 59-64.
25. Sansone, EB; Tewari, YB; Jonas, LA (1979): Prediction of removal of vapors from air by adsorption on activated carbon. *Environ. Sci. Technol.* 13, 1511-1513.
26. Sansone, EB; Jonas, LA (1981): Prediction of activated carbon performance for carcinogenic vapors. *Am. Ind. Hyg. Assoc. J.* 42(9), 688-691.
27. Moyer, ES (1983): Review of influential factors affecting the performance of organic vapor air-purifying respirator cartridges. *Am. Ind. Hyg. Assoc. J.* 44(1), 46-51.

28. Yoon,YH; Nelson,JH; Lara,J; Kamel,C; Fregeau,D (1992): A theoretical model for respirator cartridge service life for binary systems: application to acetone/styrene mixtures. *Am. Ind. Hyg. Assoc. J.* 53(8), 493-502.
29. Yoon,YH; Nelson,JH; Lara,J; Kamel,C; Fregeau,D (1991): A theoretical interpretation of the service life of respirator cartridges for the binary acetone/meta-xylene system. *Am. Ind. Hyg. Assoc. J.* 52(2), 65-74.
30. Jonas,LA; Sansone,EB; Farris,TS (1983): Prediction of activated carbon performance for binary vapor mixtures. *Am. Ind. Hyg. Assoc. J.* 44(10), 716-719.
31. Swearengen,PM; Weaver,SC (1988): Respirator cartridge study using organic-vapor mixtures. *Am. Ind. Hyg. Assoc. J.* 49(2), 70-74.
32. Guenier,JP; Muller,J (1984): Sampling of gaseous pollutants on activated charcoal with 900 mg tubes. *Ann. Occup. Hyg.* 28(1), 61-75.
33. Cohen,HJ; Briggs,DE; Garrison,RP (1991): Development of a field method for evaluating the service lives of organic vapor cartridges - Part III: results of laboratory testing using binary organic vapor mixtures. *Am. Ind. Hyg. Assoc. J.* 52(1), 34-43.
34. Goller,JW (1985): Displacement of polar by non-polar organic vapors in sampling systems. *Am. Ind. Hyg. Assoc. J.* 46(3), 170-173.
35. Gillispie,Rj; Humphreys,DA; Baird,NC; Robinson,EA (1986): *Chemistry*, 1st ed. Allyn and Bacon, Inc., Boston.
36. Weast,RC (Ed.) (1977): *Handbook of Chemistry and Physics*, 58th ed. CRC Press, Cleveland, OH.
37. Driscoll,JN; Duffy,M (1987): Photoionization detector: A versatile tool for environmental analysis. *Chromat.* 2(4), 21-27.
38. Hall,TA (1992): *Effects of Adsorbed Water Vapor on the Wheeler Kinetic Rate Constant and Kinetic Adsorption Capacity for Activated Carbon Adsorbents*. Ph.D. Thesis, The Johns Hopkins University.
39. Trout,DB (1985): *Determination of Organic Vapor Respirator Cartridge Variability in Terms of Degree of Activation of the Carbon and Cartridge Packing Density*. M.H.S. Thesis, Johns Hopkins University School of Hygiene and Public Health.

40. Trout,D; Breysse,PN; Hall,T; Corn,M; Risby,T (1986): Determination of organic vapor respirator cartridge variability in terms of degree of activation of the carbon and cartridge packing density. *Am. Ind. Hyg. Assoc. J.* 47(8), 491-496.
41. Neumann,MG (1976): The calculation of adsorption isotherms from chromatographic peak shapes. *Journal of Chemical Education* 53(11), 708-710.
41. Jaroniec,M; Lu,X; Madey,R; Choma,J (1990): Comparative studies of the overall adsorption isotherm associated with Dubinin-Astakhov equation. *Carbon* 28(1), 243-245.
42. Dollimore,D; Heal,HT; Martin,DR (1970): An improvement in the elution technique for measurement of adsorption isotherms by gas chromatography. *J. Chrom.* 50, 209-218.
43. Habgood,HW (1967): Chromatography and the solid-gas interface. Chap. 20. In: *The Solid-Gas Interface*, Vol. 2. (Ed: Flood,AE) Marcel Dekker, Inc., New York, 611-647.
44. Bechtold,E (1962): In: *Gas Chromatography*. 1st ed. (Ed: Van Swaay,M) Butterworths, London.
45. John,PT (1984): A method to determine the total and partial adsorptions from a binary mixture when component gases have similar adsorbabilities. *Carbon* 22(6), 559-562.
46. Jonas,LA; Sansone,EB (1986): Prediction of activated carbon performance for sequential adsorbates. *Am. Ind. Hyg. Assoc. J.* 47(8), 509-511.
47. Wood,GO; Stampfer,JF (1993): Adsorption rate coefficients for gases and vapors on activated carbons. *Carbon* 31(1), 195-200.
48. Schulman,RS (1993): *Statistics in Plain English with Computer Applications*, 1st ed. Van Nostrand Reinhold, NY.
49. Lewis,WK; Gilliland,ER; Chertow,B; Cadogan,WP (1950): Adsorption equilibria, hydrocarbon gas mixtures. *Ind. Eng. Chem.* 42(7), 1319-1326.
50. Reucroft,PJ; Rao,PB; Freeman,GB (1983): Binary vapor adsorption by activated carbon. *Carbon* 21(3), 171-176.

Appendices

Appendix A

Calibration of GC Detectors

The GC detector responses were calibrated for each chemical using both serial dilution injections, and vapor injections (from vapors generated under the same conditions for carbon bed challenges). Although the chromatographic area for a given mass injected should theoretically be equal for these techniques, the calibration curves did not coincide. As a result, serial dilution injections were used to establish the linearity of the detector response over a wide range of concentrations and a vapor-injection based calibration method was used to generate calibration curves for determining vapor concentrations for kinetic experiments.

Serial dilutions were prepared by pipetting 1 mL of a chemical into a 10 mL volumetric flask and filling the flask with solvent (carbon disulfide) to the 10 mL mark. Subsequent dilutions were made by pipetting 1 mL of the new solution into another 10 mL volumetric flask and filling it to the mark with CS₂.

Beginning at the lowest concentration, three on-column injections of 1.0 μ l were made for each dilution. Calibration points were generated from the average area of the 3 injections.

Calibration curves were made by fitting a line to the logarithms of the mass injected (μ g) and the average detector response (area). These curves for p-xylene and o-dichlorobenzene calibration, of the PID and FID, are shown in Figures A.1 and A.2, respectively.

The calibration of detectors with vapors was also carried out for each chemical. Each vapor was generated and diverted around the carbon bed while being sampled with the gas sampling valve (GSV). The vapor concentration was adjusted by changing the flow rates through the vapor-generation system until the desired detector response range was obtained, after which sampling continued until three consecutive peaks of consistent area (within 5 percent of the mean) were obtained during a six minute interval.

The vapor stream was then diverted through a pre-weighed carbon bed placed in the system. After a period of time, the air exiting the bed was sampled to ascertain that bed breakthrough had not occurred, and the carbon bed was removed and weighed. The vapor stream was sampled again to verify that the concentration was constant. The concentration of the vapor was calculated using the mass of vapor adsorbed, the time of bed exposure, and bed flow-rate.

This process was repeated three times for each concentration tested. If the repetitions differed by more than 5 percent, the point was repeated. A mid-range point was checked each week during data collection, and if the value differed by more than 5 percent from the original, the calibration was repeated. A data collection sheet from a typical calibration trial is shown in Figure A.3.

The calibration data were used to generate regression lines of the log of the vapor concentration ($\mu\text{g/mL}$) on the logarithm of the detector response (area). Typical calibration data for *p*-xylene are shown in Table A.1. A graph of these data and the resulting regression lines and equations are shown in Figure A.4. Regression equations produced in this manner were used to estimate vapor concentrations during carbon bed challenge experiments.

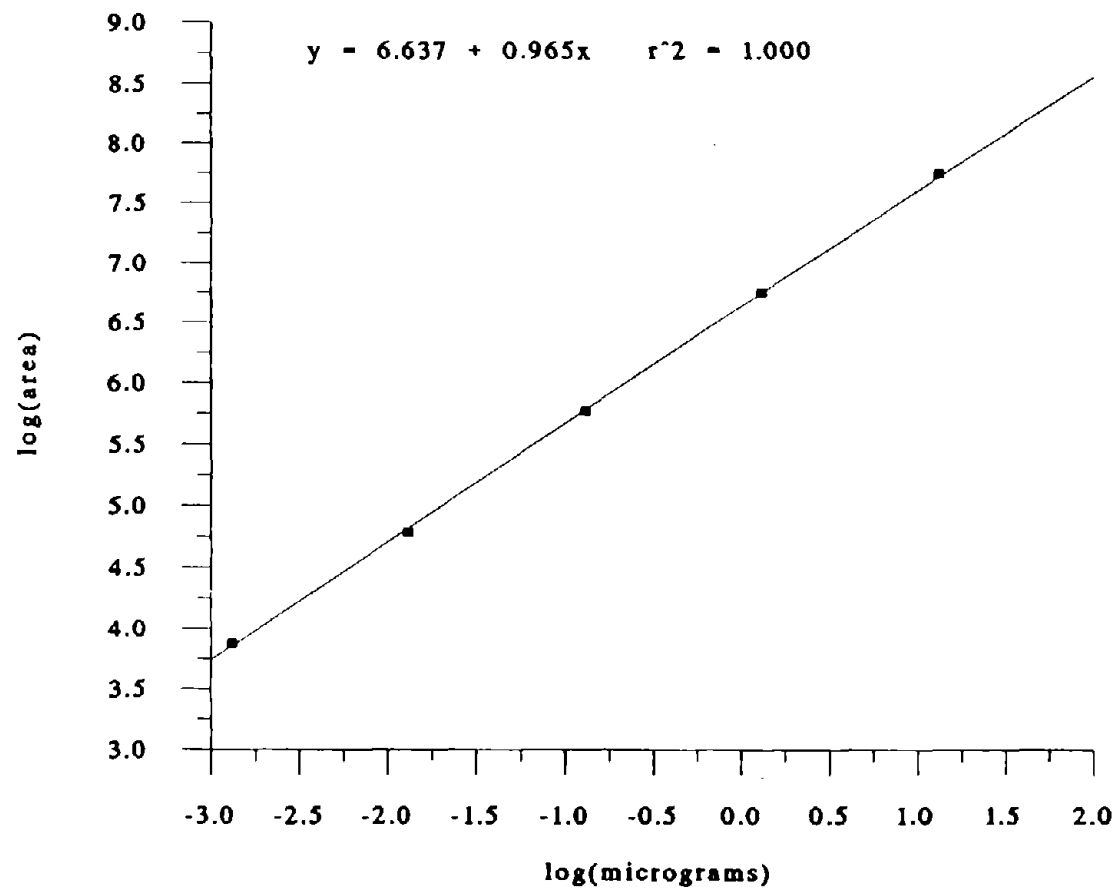


Figure A.1. Serial-dilution method PID calibration for p-xylene, plotted as the logarithm of mass injected, $\log(\mu\text{g/mL})$ versus the logarithm of the PID response, $\log(\text{area})$.

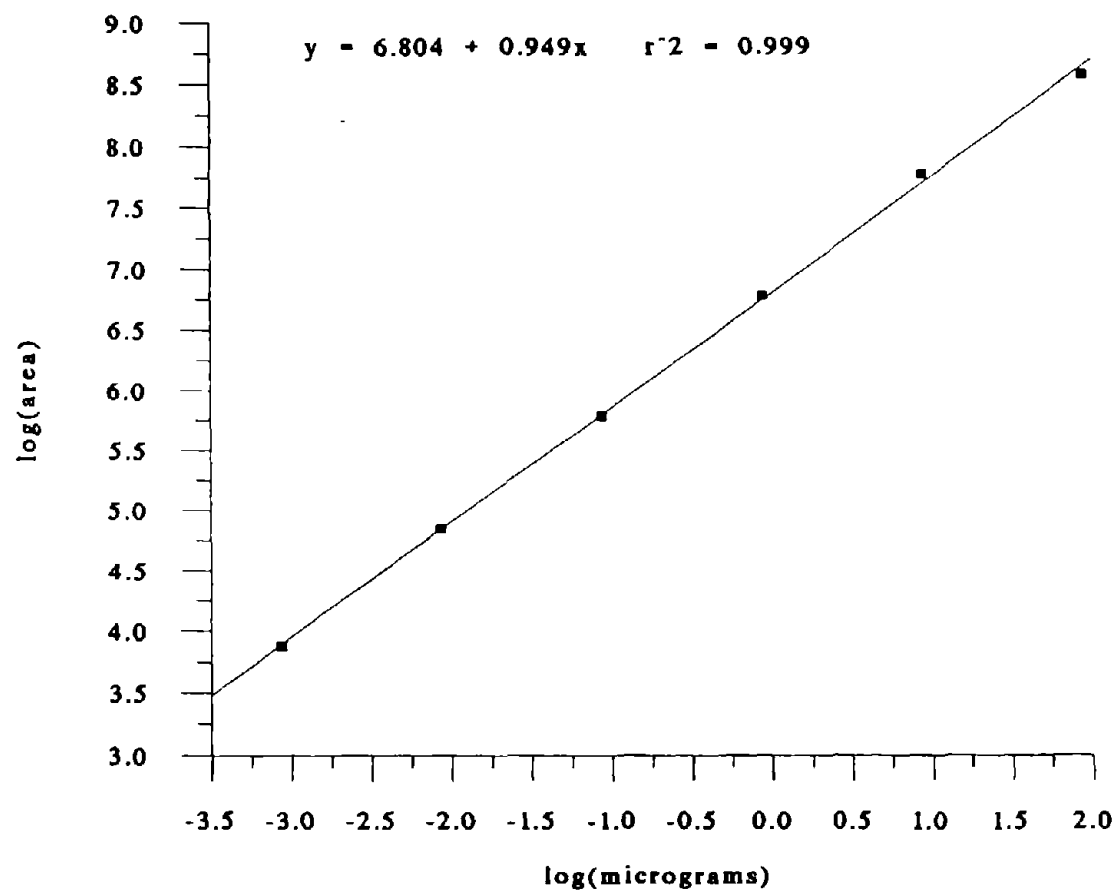


Figure A.2. Serial-dilution method FID calibration for o-dichlorobenzene, plotted as the logarithm of mass injected, $\log(\mu\text{g/mL})$ versus the logarithm of the FID response $\log(\text{area})$.

CALIBRATION

Date of experiment	1-26-92			Notes
Vapor	p-xylene			
Molecular wt.	106.17			
Run No.	85			
Flow meter (cm) air:	5.0	Q = ~900. ml/min		
Flow meter (cm) vapor:	1.0	Q = ~250. ml/min		
	a	b	c	d
START - Tube weight (g)	—	—	12.7158	—
- Tube + Carbon (g)	13.40288	12.71157	13.25005	12.63225
- Time	13.3	:	:	10:28:05
- Temp. (C)	24.2	24.1	24.3	24.3
- Flow rate (ml/min)	303.	303.	303.	303.
- Carbon weight (g)	—	—	—	—
	a	b	c	d
END - Flow rate (ml/min)	303.	303.	303.	303.0
- Temp. (C)	24.3	24.3	24.4	24.3
- Time (clock)	—	—	—	—
- Stopwatch	1:01:02	1:00:32	1:00:00	1:05:00
- RUN TIME (min)	61.0	60.5	60.0	65.0
- Tube + Carbon (g)	13.53268	12.83166	13.31181	12.76802
- Tube (empty) (g)	—	—	—	—
- Carbon wt. (g)	—	—	—	—
	a	b	c	d
Meta data				
total volume (ml)	184183.	183315	18180.	18786.
ml/mole				
mass (g)	0.12980	0.12529	0.12176	0.13577
Concentration (ug/ml)	3.03×10^{-6}	6.82×10^{-6}	6.70×10^{-6}	6.89×10^{-6}
ppm	—	—	—	—

Figure A.3. Sample data-collection sheet for the vapor method of calibration.

Table A.1. Vapor-method calibration data for *p*-xylene.

Run No.	Time min.	Flow rate mL/min	Concentration g/mL	Response (area)	
				PID	FID
1A	45	311	1.53×10^{-5}	3519109	41707900
1B	45	311	1.50×10^{-5}	3222269	44135067
1C	45	311	1.54×10^{-5}	3276506	44647500
		Average =	1.53×10^{-5}	2792285	31060822
2A	153	321	8.63×10^{-7}	255909	2657915
2B	124	321	1.01×10^{-6}	272544	2709987
2C	120	321	1.06×10^{-6}	279830	2738930
		Average =	9.78×10^{-7}	269428	2702277
3A	120	303	2.33×10^{-6}	617474	6217792
3B	120	303	2.26×10^{-6}	616732	6184214
3C	62	303	2.21×10^{-6}	625942	6288087
		Average =	2.27×10^{-6}	620049	6230031
4A	61	303	7.02×10^{-6}	1968111	17078667
4B	61	303	6.83×10^{-6}	1966684	18122400
4C	60	303	6.70×10^{-6}	1975897	18156133
		Average =	6.85×10^{-6}	1970231	17785733

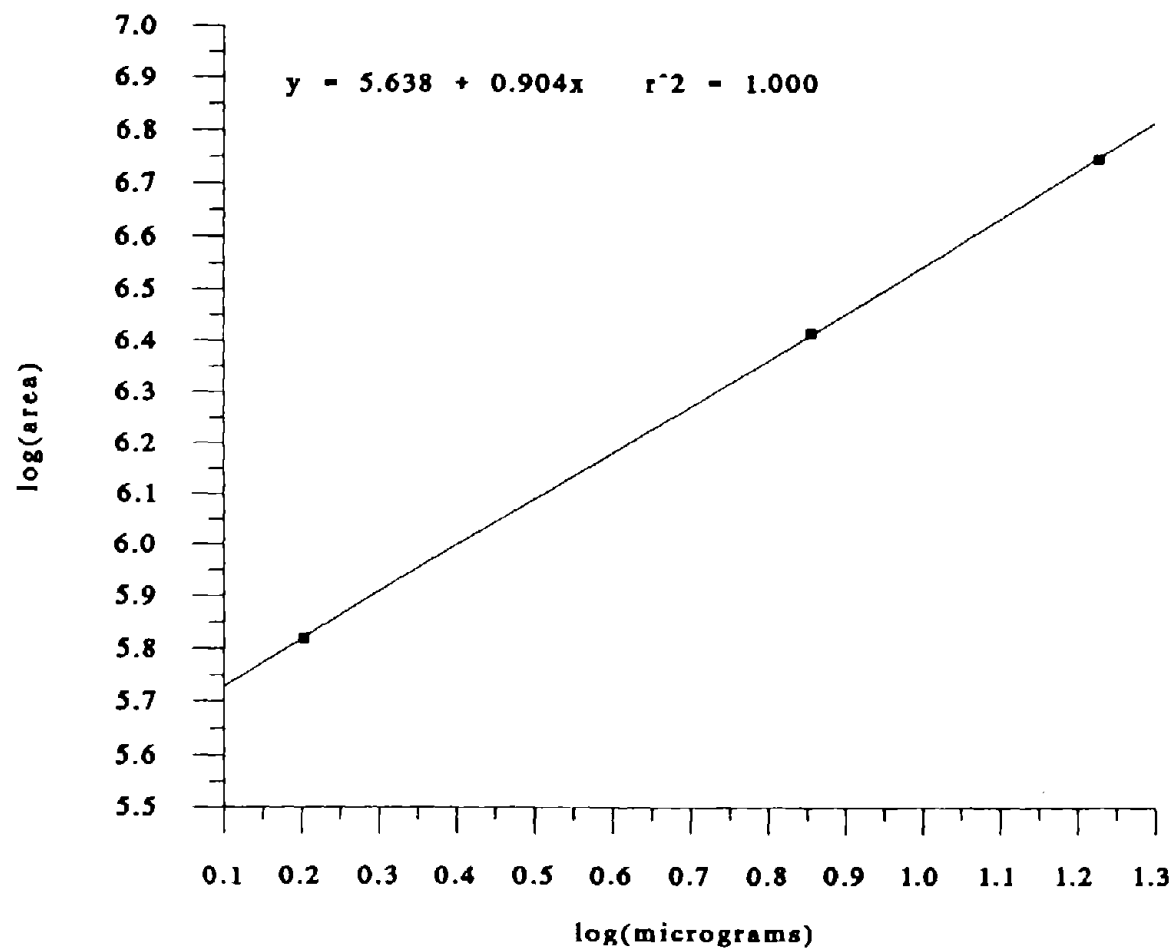


Figure A.4. Vapor-method PID calibration regression for p-xylene, plotted as the logarithm of mass injected, $\log(\mu\text{g/mL})$ versus the logarithm of the PID response, $\log(\text{area})$.

Appendix B

Reproducibility of Carbon Transfer to GC Column

Carbon was pre-weighed to create carbon columns of a consistent mass of 0.01 g. The carbon was then transferred and packed into stainless steel columns. A schematic of the steel column is shown in Figure B.1. To ascertain that transfer was complete, each column was packed and weighed using the following procedure:

- Step 1: Add carbon to a pre-weighed container, positioned on the balance pan, until 0.01 g of carbon is obtained.
- Step 2: Weigh a stainless steel column containing a fiber glass plug in one end.
- Step 3: Add the pre-weighed carbon to the column as vacuum is applied to the plugged end.
- Step 4: Weigh the column with carbon.
- Step 5: Subtract the empty-column weight from the column-with-carbon weight to determine the mass of carbon transferred.

The net weight of carbon transferred was compared to that found in Step 1, and the results of 10 separate trials are shown in Table B.1. The proportion of carbon transferred, greater than 95 percent, was acceptable.

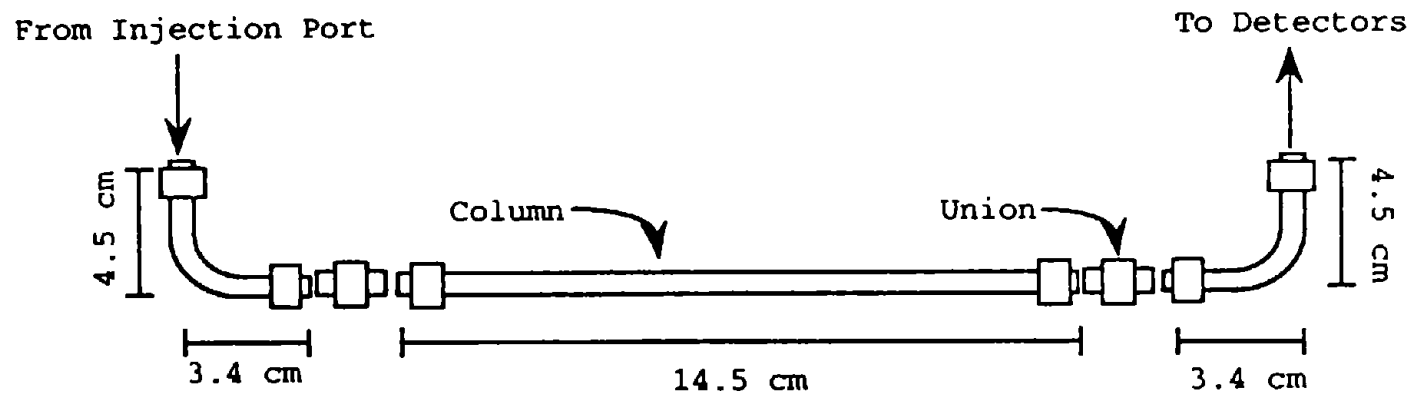


Figure B.1. Schematic of the stainless steel column used in equilibrium experiments.

Table B.1 Ten repetitions of carbon transfer to the GC column.

Column Number	Column Weight g	Carbon Mass g	Column + Carbon g	Carbon Transfer %
5	19.10712	0.01022	19.11744	99
14	19.05560	0.01075	19.06647	99
17	19.61573	0.01013	19.62648	95
6	19.09783	0.01026	19.10855	96
11	18.93277	0.00931	18.94183	97

Appendix C

Measurements and Calculations for Use in the Chromatographic Method of Isotherm Determination

Chromatographic peaks were divided into areas as shown in Figure C.1. These areas were required to evaluate chromatographic peaks to obtain adsorption isotherms using:

$$a = f(C_i) = \frac{m}{S_1 M} \int_0^{n_i} t dn \quad \text{C.1}$$

- a = adsorbed volume (mL/g);
- C_i = concentration of adsorbate in the gas phase ($\mu\text{mol/mL}$);
- n_i = deviation of the chart pen from baseline (cm);
- M = mass of the adsorbent (g);
- m = moles injected;
- S_1 = total chromatogram area corresponding to m , determined on a non-adsorbing column.
- t = time to n_i after injection.

The amount adsorbed (a_i) is equal to the value, at each n_i , of the integral multiplied by the constants. The area of the integral is equal to the total chromatogram area (corrected for diffusion) less the area of successive horizontal slice, $n_i \text{CKI}$. An example of a slice is shown as the stippled area in Figure C.1.

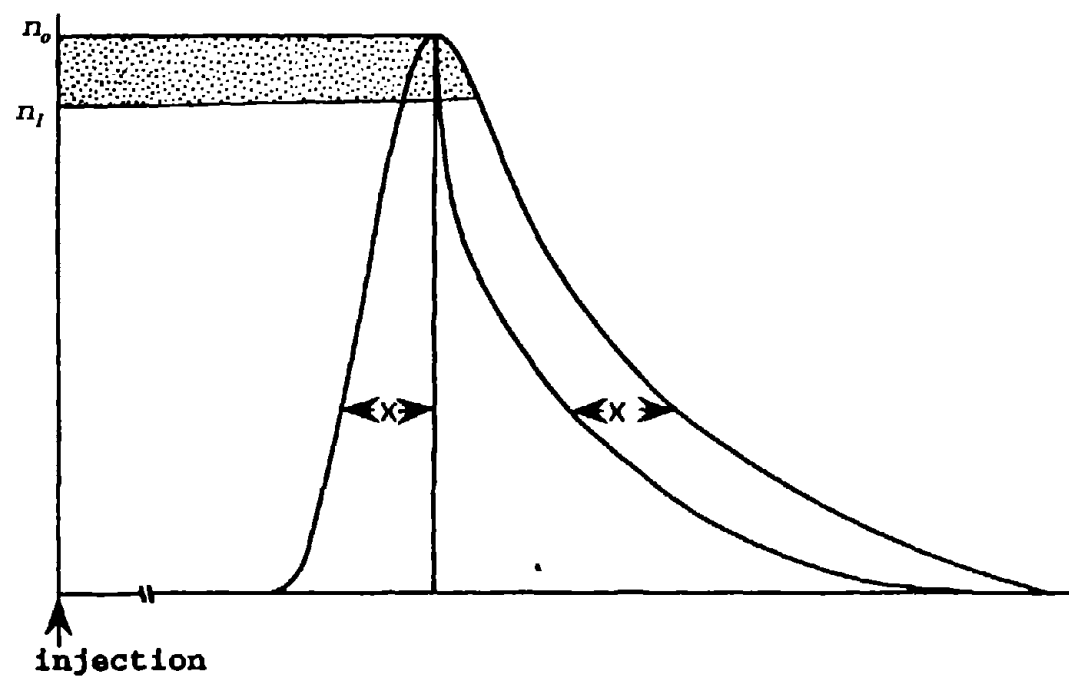


Figure C.1. Examples of the areas needed to calculate the amount adsorbed (a) from a chromatogram.

Thus, the amount adsorbed is calculated from:

$$a_i = \frac{m}{S_1 M} [(AKIO + S_1 - PKA) - n_i CKI] \quad C.2$$

The areas are illustrated in Figure C.1. AKIO is the shaded area, PKA the striped area, and $n_i CKI$ the stippled horizontal area.

Maximum adsorption is given by the area EKIO. Since baseline uncertainty results in error at E, S_1 is used to replace the area EKA. In Figure C.1, the area E_1KA represents S_1 , which is the needed area EKA, plus E_1KE . Equal diffusion at the front and rear of the peak is assumed, so that the x 's shown in Figure C.2 are assumed equal. This means that the areas of E_1KE and PKA are equivalent. Thus, subtracting PKA from S_1 gives the required area EKA. PKA was easily obtained by dividing the peak into horizontal strips and using points along the curve AK (see Figure C.3).

AKIO is simply the rectangle PKIO, less the area of PKA. AKIO added to EKA results in the required total area EKIO. Points on the isotherm are then found by subtracting successive trapezia $n_i CKI$. The area determination for $n_i CKI$ is illustrated in Figure C.4.

The areas of slices of the various parts of the chromatogram were approximated by calculating the area of the rectangle that included the entire slice, and then subtracting the extraneous triangle associated with it. This is illustrated in Figure C.3. All areas are in units of cm^2 .

The peak height, slice height, and the distances from 0 to A_i and from 0 to C_i were needed to calculate the areas of slices, and other required areas. The slice height was held constant at 0.25 cm. A grid divided into millimeters vertically and 0.25 cm horizontally was placed over each chromatogram to facilitate accurate measurements. The number of cm in 100 minutes was measured to obtain u , the chart speed (cm/min) used in calculating the pressure, P for each a_i .

The measured distances and other variables were entered into an Excel® spreadsheet to calculate a and P . The transformation of a and P to the Dubinin model parameters W_v and ϵ^2 , and the regression of W_v and ϵ^2 are also accomplished in this same spreadsheet. A sample of the spreadsheet is shown in Figure C.5.

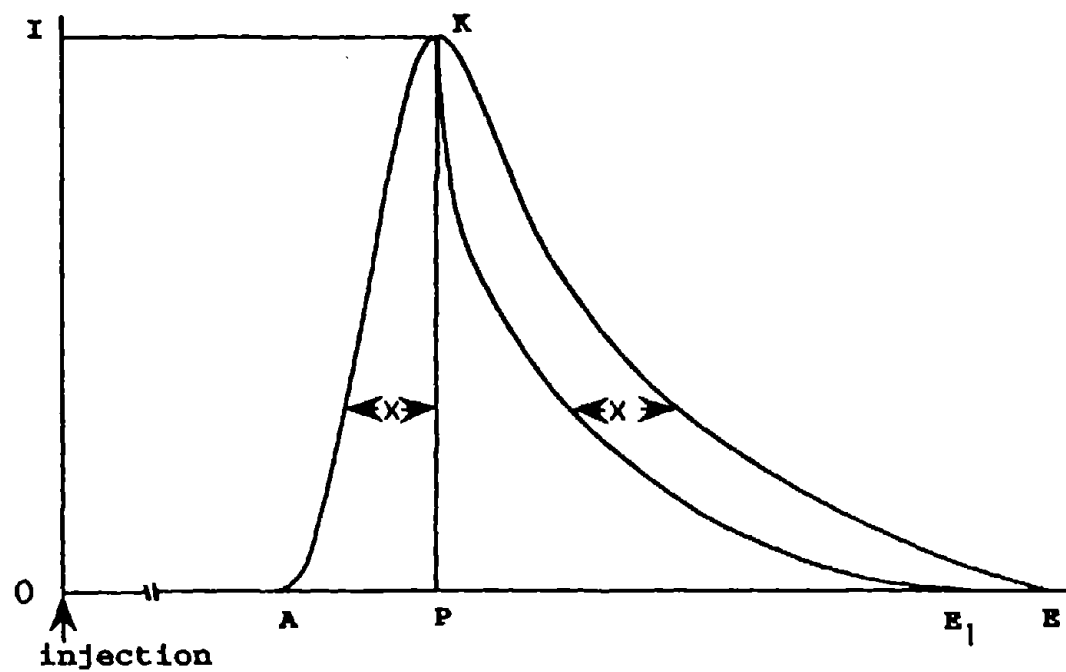


Figure C.2. Chromatogram showing equivalent areas due to diffusion at the front and rear of the peak.

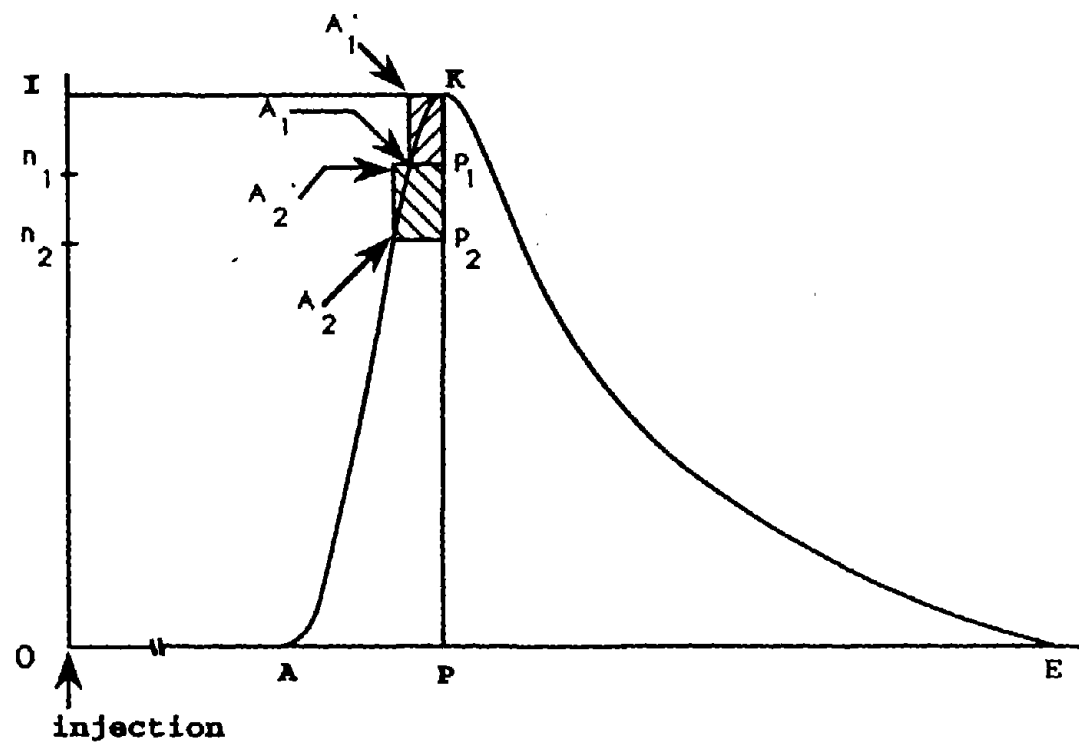


Figure C.3. Example of the measurements and areas used to calculate the area of PKA.

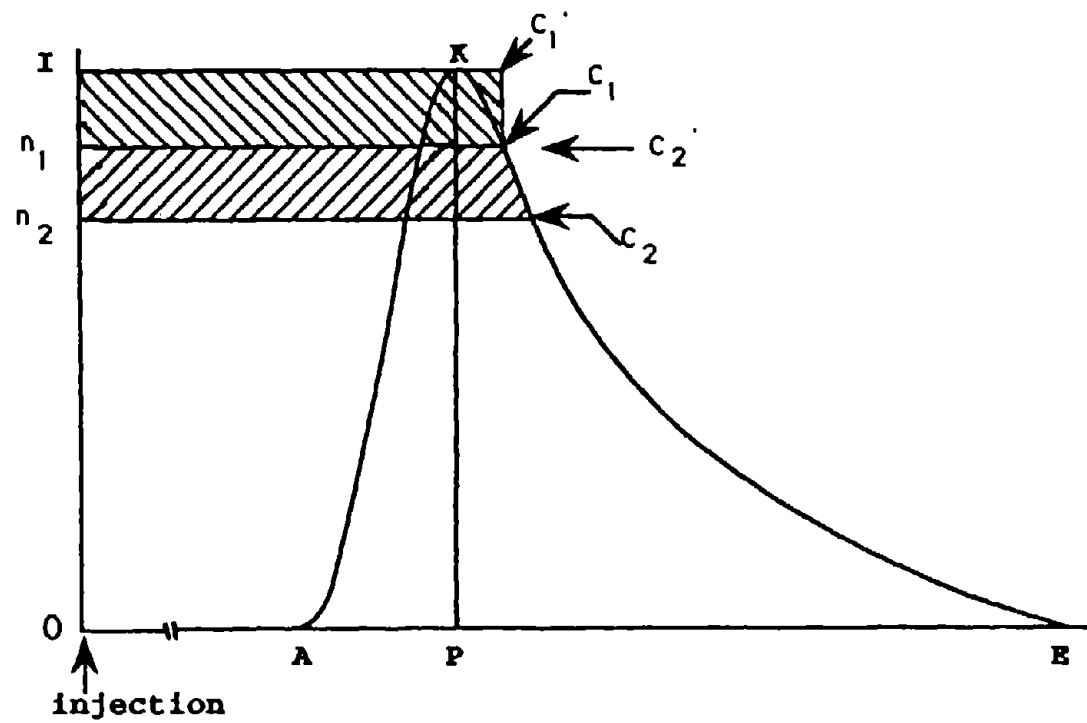


Figure C.4. Example of the measurements and areas used to calculate the area of slices n_iCKI .

Figure C.5. Sample spreadsheet used for the calculation of chromatograms areas, amounts adsorbed, and adsorbate pressures.

List of Present and Possible Future Publications

1. C.A. Robbins and P.N. Breysse: A two-detector gas chromatograph system for studying the adsorption of binary organic vapor mixtures on organic vapor respirator carbon. *Presented at the AIHCE, Poster Session 4, Boston, MA, June 1992.*
2. C.A. Robbins and P.N. Breysse: The effect of component polarity difference on the parameters of the Wheeler kinetic model for the adsorption of binary organic vapor mixtures on respirator carbon. *Presented at the AIHCE, Student Poster Session, Anaheim, CA, May 1994.*
3. C.A. Robbins: The effect of component polarity on the adsorption of binary organic vapor mixtures onto respirator carbon. Ph.D. Thesis, The Johns Hopkins University, 1994.
4. C.A. Robbins and P.N. Breysse: The effect of component polarity on the parameters of the Wheeler kinetic model for binary organic vapor mixtures. *In Preparation, September 1994.*
5. C.A. Robbins and P.N. Breysse: The effect of component polarity on the parameters of the Dubinin model for binary organic vapor mixtures. *In Preparation, September 1994.*
6. C.A. Robbins and P.N. Breysse: Critical Review: Activated-carbon respirator cartridge breakthrough models for organic vapor mixtures. *Planned Paper, October 1994.*

