COMPETITIVE DESORPTION OF CARBON TETRACHLORIDE + WATER

FROM MESOPOROUS SILICA PARTICLES

By

MATTHEW B. MOWER

A thesis submitted in partial fulfillment of
the requirements for the degree of

MASTER OF SCIENCE IN CHEMICAL ENGINEERING

WASHINGTON STATE UNIVERSITY
Department of Chemical Engineering

AUGUST 2005

To the Faculty of Washington State University:

      The members of the Committee appointed to examine the dissertation/thesis of MATTHEW B. MOWER find it satisfactory and recommend that it be accepted.

_____
Chair

_____

_____

ACKNOWLEDGMENTS

I would first like to thank my mother and father for instilling in me at a young age the importance of setting and achieving lofty goals. Because of their teachings and guidance I attribute a large majority of the success I have had thus far or ever will have to them. Their support has been unwavering throughout my life and I can only hope to have made them a bit proud to be my parents.

Thank you to my wife, Cat, and our children, Sophie and Benjamin, who have stood by me through all the trials and tribulations that have culminated in this work. I am glad that they like a good adventure as much as I do. It is only because of their great sacrifices that I am the person who I am today. They deserve as much of the credit for this as I do, and perhaps more.

I would like to acknowledge the previous work done by Oscar Marin-Flores. His help in understand the instrumentation in good times and bad has been most helpful. He is also a good friend. Thank you to Brent Peyton for funding me on this project and allowing me to do research in an area that suited me.

Finally, a very special thank you to Dr. Reid Miller. It has been my privilege to have him as my advisor. He is one of the most accomplished professors that I am aware of. He has been supportive of me in all research and personal aspects of my life these past two years. He has been an excellent mentor and a man for whom I have the highest admiration.

COMPETITIVE DESORPTION OF CARBON TETRACHLORIDE + WATER

FROM MESOPOROUS SILICA PARTICLES

Abstract

by Matthew B. Mower, MS
Washington State University
August 2005

Chair: Reid C. Miller

Equilibrium and desorption rate studies have been conducted for carbon tetrachloride + water on prepared mesoporous silica particles with mean pore sizes of 27 Å and 47 Å. Partial carbon tetrachloride isotherms were obtained for the purpose of determining the equilibrium amount of carbon tetrachloride required to completely fill the pores. The total volume of carbon tetrachloride adsorbed by the 27 Å particles agreed with previous work done on these particles.

A novel measurement technique was developed to measure the very high carbon tetrachloride desorption rates (> 0.1 g/g sample/h) encountered at the start of a sweep experiment, by use of gas chromatography. By performing a carbon tetrachloride sweep using 27 Å particles, current measurement techniques were found to yield data in close agreement with prior work.

Empty holder sweeps were done to determine release rates of carbon tetrachloride from the gas phase of the microbalance cell under standard operating conditions. The amount of carbon tetrachloride from integration of these rate curves agreed with ideal gas law calculations based on the estimated cell volume. The empty holder sweep results

were used to correct desorption rates of carbon tetrachloride for sweep experiments with particles present.

Water and carbon tetrachloride + water mixtures were loaded onto both types of particles, and amounts of each component determined for both the gas phase and the adsorbed phase. It was found that a much smaller volume of pure water was adsorbed by both particles than for pure carbon tetrachloride. However, the volumes of mixtures loaded were higher than pure water for the 47 Å particles and were both lower and higher than pure water for the 27 Å particles. Sweeps were performed on both particles loaded with pure water and carbon tetrachloride + water mixtures, to determine total and individual component desorption rates. It appeared that pore size had a small effect on the overall desorption rates, with slightly higher rates for the larger pore particles. However, the more water initially loaded on the particles, the larger the total amount of mass remaining on the particles at the end of a sweep. It appeared that the residual mass for the mixture sweeps was mostly water.

In spite of the improved accuracy with which the early parts of the sweeps were defined, it was not possible to quantify the amounts of each component in the residual masses by integration of the individual rate curves. An analytical technique still needs to be developed to measure the amount of carbon tetrachloride remaining on the particles at the end of a sweep experiment.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Dedication

Pour tous mes ancêtres qui m'ont précédé. Car, c'est à cause de vos sacrifices suprêmes

que je suis ou je suis. Qu'ils ne soient pas en vain.

Chapter 1

Introduction

1.1 Volatile Organics in the Environment

Since the beginning of the 20th century, volatile organic compounds (VOCs) have become increasingly important. They have been used in fuels, paints, aerosols, cosmetics, disinfectants, refrigerants, pesticides and solvents. While VOCs have many chemically ideal properties, they have an adverse effect on human health and on the environment. Unfortunately, these effects were not brought to light until after millions of gallons worldwide had been released into the environment, mainly by directly pumping spent solvents into the soil. Due to the increased potential for human health risk, the remediation of these contaminated sites has become of increasing importance; however, many factors that govern the remediation of these sites remain unclear.

Studies of VOCs are challenging due to their volatility. Volatile compounds are difficult to recover in a soil environment, making it very difficult to close mass balance calculations during these studies (*Wang et al. 1996*). In short, it is difficult to explain where the VOCs go, when they will move, and how long it takes. In an effort to further elucidate several of the factors that influence remediation of VOC contaminated soils, many scientists and engineers have turned to studying individual VOCs. One of the VOCs of recent concern is carbon tetrachloride

Carbon tetrachloride is a major contaminant of many hazardous waste sites in the world today. Until recently, carbon tetrachloride was used primarily in the production of chlorofluorocarbons and other chlorinated hydrocarbons. It has also been used in

plutonium production, chemical processing, waste management and research and development. With the signing of the Montreal Protocol on Substances that Deplete the Ozone Layer, carbon tetrachloride production has gradually decreased from its high, which amounted to 960,000 tonnes in 1987 (*de Fouw 1999*).

In earlier times and in many places around the world, disposal of carbon tetrachloride and other hazardous wastes has consisted of pumping wastes either into underground storage tanks that subsequently leaked or directly into the soil. For most VOCs it has been the later. It has been reported that at the United States Department of Energy site in Hanford, WA, from July, 1955, through June, 1962, approximately 233,840 L of carbon tetrachloride was discharged into the ground (*Rockhold 2003*). The carbon tetrachloride has since migrated deep into the vadose or unsaturated zone, and into the aquifer lying underneath the Hanford site.

The vadose zone is of great importance, as it essentially controls the interrelationships between precipitation, infiltration, surface runoff, evapotranspirtation, groundwater recharge and capillary flow. It also serves as the soils' natural filtration system; filtering and attenuating potential contaminants that could potentially arrive in the groundwater.

In order to clean up VOC spills, several different remediation methods have been developed, such as soil vapor extraction, air sparging, anaerobic bioremediation, and chemical oxidation. The most common of these are soil vapor extraction and air sparging, both of which involve desorption of VOCs from the liquid phase into the gas phase and the subsequent removal of the gas from the soil.

Soil vapor extraction has become one of the most common and effective methods to remediate volatile organic compounds (VOCs) affected soils (*O'Melia & Parson, 1996*). This is done by applying a vacuum on wells drilled into the contaminated soil. This causes a negative pressure gradient which results in movement of vapors to the wells. The recovered gas is then passed over granular activated carbon which adsorbs the VOC. The VOC is then extracted from the granular activated carbon and disposed of.

Soil vapor extraction works very well in non-saturated, highly permeable soils. However, this method is less effective as the amount of water in the soil increases. The moisture in the soil reduces the effectiveness of soil vapor extraction in two ways: 1) it prevents the movement of gasses within the soil matrix, and 2) it restricts the flow of air within the soil pores (*EPA 1994*).

Air sparging consists of pumping contaminant free air into the saturated zone of the soil. This initiates a driving force for the adsorbed VOC towards the vapor phase. The air is then vented to the unsaturated zone and eventually the atmosphere.

Like soil vapor extraction, air sparging is also negatively effected by the presence of water in the soil; however the effect is different. Air sparging is highly dependent on the vapor/dissolved phase partitioning coefficient (*EPA 1994*). This coefficient is dependent on the water content and the water partitioning coefficient of the VOC.

While some of the factors that determine the effectiveness of these and other remediation techniques are known, many are poorly understood and fail to predict the release, transport and fate of contaminants in soils (*Farrell & Reinhard 1994*, *Wang et al. 1996*, *Pignatello & Xing 1996*). Models that are currently in place lack the quality data on the individual variables that determine contaminant transport for them to be effective

(*Harter & Hopmans 2004*). In order to accurately model the fate of contaminants in soils, it is necessary to understand the roles of the individual properties of the soil and the contaminant and their interactions. This increased understanding would lead to improved remediation techniques, a better implementation of current techniques and a savings in both time and money in remediation projects.

It has been recently noted that a notable portion of the VOC being extracted from the soil will either remain permanently in the soil or exhibit very slow release rates into the soil matrix. This portion has been termed the migration resistant fraction (*Riley et al. 2001*). Since substantial data are lacking in this area, the role of this migration resistant fraction is not fully understood, and its fate and transport are not clearly predicted in the current numerical models.

Marin-Flores (2004) suggests that the reasons for these inaccuracies are due to the models' inability to account for contaminant-soil interactions that occur in near-molecular size intraparticle pore spaces. He also suggests that it is necessary to determine the significance of each potential factor that can affect carbon tetrachloride release in order to successfully model its transport and fate in the subsurface environment. *Harter & Hopmans (2004)* report that current models do not accurately model flow in the vadose zone, because the dynamics of the vadose zone have not been subjected to regular monitoring at regional scales and is, therefore, not a part of the regulatory or planning guidelines that most models consider.

The objective of the current work is to determine the effect that water has on the desorption rates of carbon tetrachloride in soils of various pore sizes. This will be done by desorbing water, carbon tetrachloride, and carbon tetrachloride + water mixtures from

porous silica particles with well defined pore size distributions. The resulting data will begin to provide an understanding of how the interactions between water and carbon tetrachloride affects desorption rates and, hopefully, how they affect the amount of carbon tetrachloride sequestered on the particles as a migration resistant fraction.

1.2   Background

1.2.1   Fluid transport in the soil environment

The movement of contaminants within the deep unsaturated or vadose zone is of particular importance due to its close proximity to groundwater. There are several different modes of fluid transport within the vadose zone. A diagram of different fluid movements within the vadose zone is shown in Figure 1.
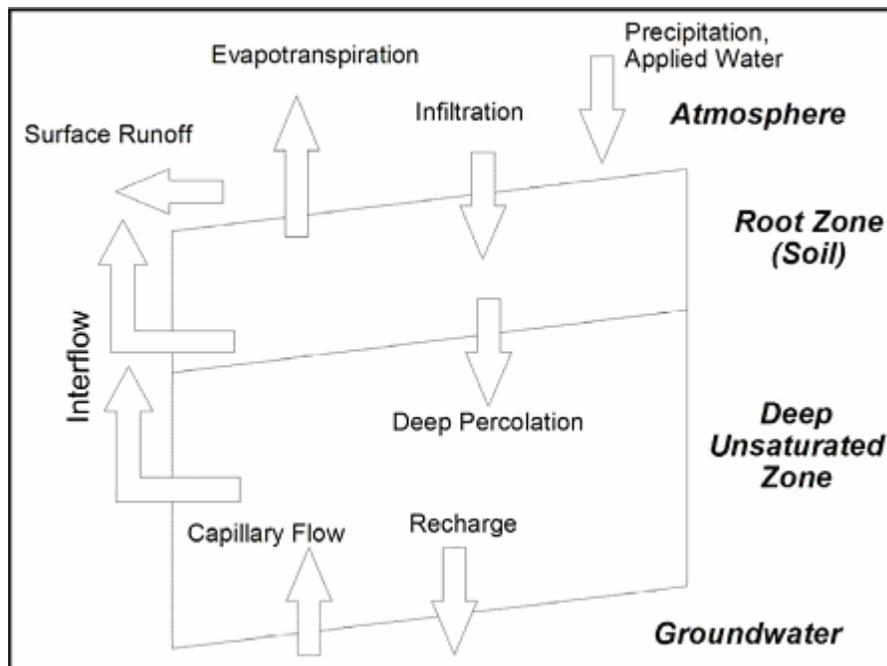
Figure 1. Diagram of modes of fluid transport in soils (Taken from *EPA 1994*)

In the case of volatile organic compounds (VOCs), the movements of contaminants within the vadose zone are affected by four primary factors; 1) soil moisture content (*Armstrong et al. 1994, Werth & Reinhard 1997, Thibaud et al. 1993*) 2) naturally occurring organic matter (*Chiou & Shoup 1985, Ong & Lion 1991, Farrell & Reinhard 1994*) 3) soil mineralogy/surface chemistry (*Burgos et al. 2002, Kawi & Te 1998*), and 4) intraparticle pore size distribution (*Pignatello & Xing 1996*). While these factors are known to affect contaminant movement within the vadose zone, to what extent these individual factors affect contaminant movement is poorly understood.

The vadose zone serves as the intermediate between soil and groundwater. With the increasing push to keep drinking water sources safe from toxins, study of the vadose zone has seen an increase in recent years. One of the characteristic features of the vadose zone is the high amount of soil moisture present. In order to better understand the role that the vadose zone plays in contaminant transport, it is first important to elucidate the effect that water has on contaminant transport in porous media.

Though there are contradictory views as to which mechanisms dominate the sorption of VOCs on soils in the presence of water, there are six that have been recognized: 1) adsorption onto the mineral surface from the gas phase by competition with water molecules for adsorption sites, 2) adsorption onto the mineral surface through the adsorbed water phase, 3) dissolution into organic matter from the gas phase, 4) dissolution into organic matter through the adsorbed water phase, 5) adsorption onto the surface of an adsorbed water film, 6) dissolution into the adsorbed water film (*Thibaud et al. 1993)* or 7) as a free liquid, filling pore space not filled by water (assuming the soil is not saturated).

Ong and Lion (1991) found that, under oven-dried conditions, specific surface area best described the sorption of trichloroethylene vapors onto porous media, but that with the introduction of moisture, factors other than surface area controlled sorption. At low relative humidity (68%), the authors attributed this to a competition with water onto the mineral surfaces and partitioning into organic matter. However, at higher relative humidity, they found that sorption was due to dissolution of trichloroethylene in the surface bound water.

Pennell et al. (1992) studied the competitive adsorption of p-xylene and water on soil materials by considering adsorption at the gas-liquid interface, dissolution into adsorbed water, partitioning into soil organic matter and adsorption on mineral surfaces. Adsorption at the gas-liquid interface was found to be a significant contribution, while portioning onto soil organic matter and dissolution into water were negligible.

Peng and Dural (1998) studied the adsorption of three chlorinated solvents on three different types of soil. They placed aqueous solutions of the chlorinated solvent in jars containing the soils and allowed them to come to equilibrium. The supernate was then removed and analyzed to determine the amount of uptake of each component into the soil. They concluded that the polarity of the compound, rather than its aqueous solubility, dominated the competitive adsorption in soils.

Riley et al. (2001) found that porous silica particles exposed to aqueous phenanthrene solutions showed a very slow increase in the amount of phenanthrene on the particles, and that equilibrium was not reached until the particles had been exposed to the solution for more than 350 h. However, when phenanthrene was exposed to particles which had been previously hydrated and subsequently dried under evacuation at room

temperature, the particles adsorbed phenanthrene more readily (i.e. the time that it took for the system to come to equailbrium was much smaller; less than 24 h). This was attributed to the differential hydration states of the particle surfaces. After initial preparation, the particles were hydrophobic, however, rehydration tended to make these particles hydrophilic, which persisted after evacuation at room temperature.

Several authors have measured the effect of water on contaminant sorption on soils and found that the presence of water greatly decreased the amount of various organics adsorbed to soils and clay minerals (*Chiou & Shoup 1985, Johnston et al. 1992*). Adsorption is not only dominated by the mineral content, suggested *Poe et al. (1988),* but, also, adsorption of organic compounds is mostly limited to the dry pore surface.

While nearly all of the current literature is focused on the adsorption of VOCs on porous material, there are several authors who have performed desorption experiments. *O'Neill et al (1993)* extracted phenol and aniline from silty clay using deionized water, hydrogen peroxide and sodium hydroxide. They report a difficulty in determining how much adsorbate placed in the testing system was actually adsorbed by the pores of the soil and how much existed as free liquid outside the pores. They were able to recover 71% of the amount of phenol applied to the system but were unable to determine whether this phenol came solely from phenol adsorbed to soil surfaces or from free liquid outside of the pores or a combination of the two. *Thibaud et al. (1993)* looked at adsorption and desorption of chlorobenzene and toluene on a standard EPA soil at different relative humidities. They used both a dry gas stream and a water-saturated gas stream as the desorption fluid. They found that the water-saturated gas stream achieved 100% removal efficiency while the dry gas stream achieved only 90% efficiency. The increased

efficiency was attributed to the adsorptive displacement of the organic compound by water. While the results in these studies were favorable, the mechanisms of how desorption occurs, and knowledge of how much of the contaminant is left of the particles is poorly understood.

One reason for the poor understanding is due to the heterogeneity of the porous material being studied. The heterogeneity arises from samples with varying pore size distributions, organic material content and mineralogy. The lack of a homogeneous material has resulted in studies which preclude the elucidation of the mechanisms governing contaminant uptake and release (*Farrell & Reinhard 1994*). It has been noted by several researchers that structural heterogeneity may play a key role in understanding contaminant sorption in porous solids (*Goyne et al. 2004, Farrell et al. 1999, Werth & Reinhard 1997, Pignatello & Xing 1996, Farrell & Reinhard 1994*).

In 1992, researchers at Mobil reported a new catalytic material with regular arrays of uniformly-sized channels that were created from the calcination of aluminosilicate gels formed in the presence of surfactants (*Kresge et al. 1992, Beck et al. 1992*). By using the technique known as liquid crystal templating, narrow pore size distributions were obtained leading to an inert material with high structural homogeneity.

Recently, several different mesoporous silica materials have been developed. Descriptions and references can be found in prior theses (*Hudson 2003, Marin-Flores 2004*). These materials are ideal for studying individual desorption mechanisms. Several recent studies by members of this lab group have tried to elucidate the desorption mechanisms of carbon tetrachloride.

Hudson (2003) studied carbon tetrachloride desorption from several different porous silicas, both locally prepared and obtained commercially, with pore sizes ranging between 20 Å and 60 Å. Pore size distributions were determined using both nitrogen and carbon tetrachloride isotherms. It was found that the desorption rate of carbon tetrachloride started out higher for particles with larger pore sizes, but the rate curves for all the particles were similar at lower values of mass adsorbed. This was attributed to adsorption forces within the pores limiting the mass transfer of carbon tetrachloride from the particles.

The measurements made by *Hudson (2003)* were obtained using a novel microbalance system. This system allowed the measurement of gas adsorption by direct mass measurements instead of relying on pressure, volume and temperature measurements. The result is increased accuracy in the measurement of the mass of gas adsorbed onto the media being studied.

Hudson (2003) also performed an extensive literature search on VOC adsorption and desorption studies. For an in depth study of the theory and the equations governing adsorption, as well as a short history of the development of these equations, the reader is referred to that thesis.

Marin-Flores (2004) built on Hudson's results by studying carbon tetrachloride desorption rates from ordered porous silicas, all prepared in our lab. Three particles with pore sizes of 27, 47, and 55 Å were prepared using the method of (*Zhao et al. 1998)*. Both nitrogen and carbon tetrachloride isotherms where used to characterized the particles. Pure carbon tetrachloride desorption sweeps were performed on all three particles, with approximately 2-3 mg of mass per gram of sample remaining on the

particles. Once the particles had been swept, they were placed in an accelerated solvent extraction system to determine if the mass remaining on the particles was all carbon tetrachloride, however this proved unsuccessful. Approximately 8.5% − 22% of the carbon tetrachloride that was measured to be on the particles at the end of a sweep was able to be extracted using the solvent extraction system. Whether the remaining mass on the particles that was not extracted was carbon tetrachloride was unknown. The mass balance on carbon tetrachloride was not closed. A two-step modeling procedure was developed that effectively fit desorption rates. It was concluded that pore volume and pore surface area seem to have a significant effect on the release of carbon tetrachloride.

May (2003) performed equilibrium measurements with carbon tetrachloride and water + carbon tetrachloride mixtures on six different porous silicas; one commercially available (Davisil), four prepared by a group at the Pacific Northwest National Laboratory and one prepared at Washington State University (Tween 40, same as T-27 in this work). In each case, the volume adsorbed for water + carbon tetrachloride was approximately 106% of the volume adsorbed of pure carbon tetrachloride.

May (2003) proved that the microbalance system could be used to accurately determine the release rates of two different compounds on a porous media. He briefly looked at the competitive desorption of carbon tetrachloride and water from the Tween 40 particles studied by Hudson. In this study, the water mass percentage initially on the particles was 88 %. It was found that significant amounts of carbon tetrachloride and water remained on the particles after sweeping them with dry helium for more then 150 hours. The water remaining after the sweep was about 20 mg/g sample

However, May observed high concentrations of carbon tetrachloride during the first hour of the sweep. These concentrations were not corrected for carbon tetrachloride that was initially present in the gas phase in the microbalance system, thus, the calculated amounts of carbon tetrachloride on the particles are questionable. Additionally, the sampling of carbon tetrachloride was done using plastic syringes and injecting them in the gas chromatograph at a latter time. This allows carbon tetrachloride to be adsorbed into the plastic in the syringe, increasing the uncertainty of the gas chromatograph concentrations. Since the total amount of carbon tetrachloride in the system was small, the water results should closely reflect the microbalance results, and may be more accurate.

To accurately determine the desorption characteristics of carbon tetrachloride within the vadose zone, it is necessary to understand the role that water plays. While some previous attempts have been made, many things are still unclear, due to the adsorbed mass being calculated by gas-phase measurements instead of direct mass measurements, the use of soils instead of highly order porous media and a lack of accurate off-gas sampling. It is the goal of the present study to measure the competitive desorption of water and carbon tetrachloride using the mesoporous silicas studied by Marin-Flores as a model soil.

1.2.2   *Porous Media Characterization*

In order to determine the mechanisms of desorption, it is necessary to understand the physical properties of the media. Gas adsorption and desorption are the primary methods to determine pore size, surface area, and pore volume. The relationship of the

amount of gas adsorbed onto a particle at a given gas-phase pressure results in an isotherm which, when analyzed, will provide the physical characteristics of the porous media.

All isotherms are obtained using the same procedure. A porous solid is placed in an isothermal, closed system. The sample is then exposed to gaseous vapor at a low pressure. Some of the gas will adsorb on solid surfaces and/or condense in the pores as the system comes to equilibrium. Once equilibrium is reached, the amount of gas adsorbed and the pressure inside the cell are recorded. The pressure of the gas is then raised slightly, the system is allowed to come to equilibrium, and the amount of gas adsorbed and the pressure inside the cell are again recorded. This is repeated until the pressure inside the cell reaches the saturation pressure of the gas. The condensed gas is then desorbed from the cell by reducing the pressure gradually and allowing the system to come to equilibrium. The same values are recorded and both values for adsorption and desorption are plotted on the same amount adsorbed vs. relative pressure graph. The relative pressure is the ratio of gas-phase pressure to saturation pressure for the adsorbate at the temperature at which the isotherm is being measured.

Six different types of isotherms have been recognized by the International Union of Pure and Applied Chemistry (IUPAC). These are illustrated in Figure 2 with the desorption branch of the isotherms shown as the upper branch in those isotherms that have two branches. In isotherms II, III, and VI no hysteresis is observed between the desorption and adsorption branches.
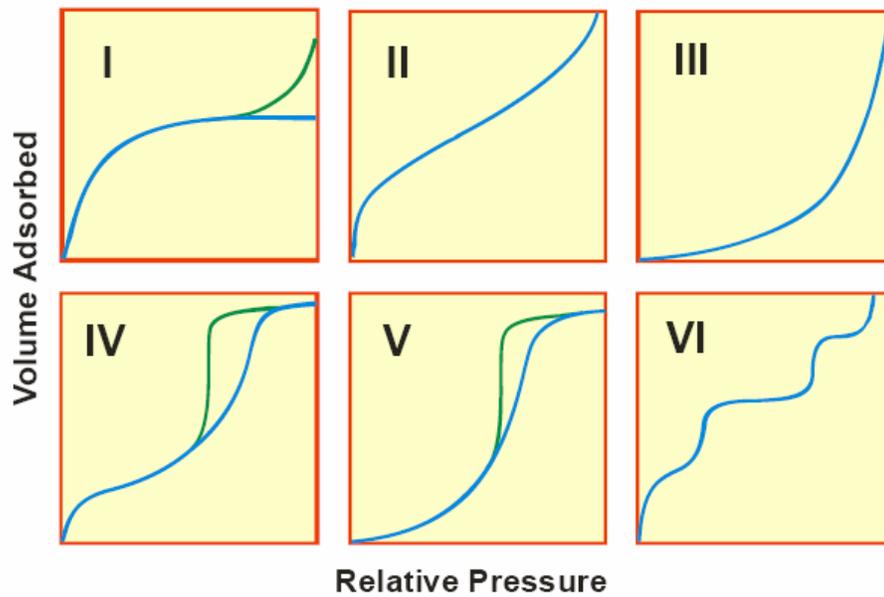
Figure 2. Six IUPAC isotherms (Taken from *Marin-Flores (2004)*)

Type IV isotherms are normally associated with mesoporous (pores measuring 2 – 50 nm in diameter) material. These types of isotherms are recognized by their characteristic sharp decline of volume adsorbed at very low relative pressures, and also by their hysteresis loop which can vary in shape. Within the hysteresis region, the mass adsorbed for the desorption of branch of the isotherm is greater than the mass adsorbed for the adsorption branch for the same relative pressure. A major reason for the hysteresis is thought to be due to differences in the shape of the liquid-gas interface during capillary condensation and vaporization.
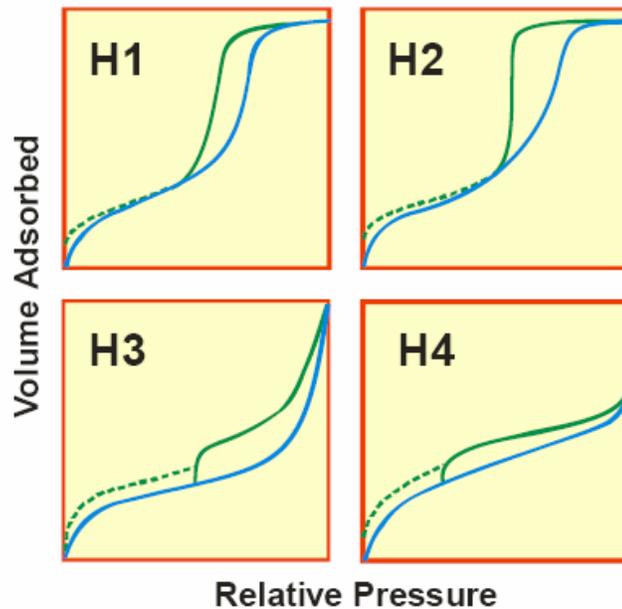
Figure 3. IUPAC classification of hysteresis loops. Dashed line represents the variability of the loop based on operating temperature. (Taken from *Marin-Flores (2004)*)

IUPAC has also classified four different types of hysteresis loops as shown in Figure 3. *Rouquerol et al. (1999)* has correlated these hysteresis loop classifications to physical descriptions of the pores themselves. According to *Rouquerol et al.*, H1 hysteresis loops are found in solids having nearly uniform pore diameters. H2 hysteresis loops indicate the existence of a complex, interconnected network of pores with varying shapes and sizes. H3 hysteresis loops are found in solids with non-rigid, slit-shaped pores in the mesopore range, whereas H4 hysteresis loops are found in slit-shaped pores in the micropore range (less then a 2 nm diameter).

Nitrogen gas has long been the main adsorbent for performing isotherms to describe the physical characteristics of a porous material; however, recent studies have found that nitrogen may not be the most appropriate gas to use. Many researchers

(*Hakuman & Naono 2001, Carrott et al. 2001, Ravikovitch et al. 1997, Branton et al. 1997*) have found that by performing an isotherm using an organic molecule as the adsorptive gas, physical characteristics such as pore size distribution and surface area differ from isotherms using nitrogen as the adsorptive gas.

Although there are several published opinions on why this phenomenon is observed, no firm conclusions have been made. Recent theories include inaccurate assumptions made in the Kelvin equation (*Barrett et al. 1951*), the influence of the adsorption forces on the curvature of the meniscus (*Galarneau et al. 1999, Lukens et al. 1999*), and a significant change of density of nitrogen in small pores (*Carrott et al. 2001*). However, despite the lack of firm conclusions, several researchers have provided models in which nitrogen and organic vapor isotherms provide similar pore size distributions and pore volumes.

Hakuman and Naono (2001) proposed a method for carbon tetrachloride isotherm analysis which modifies the Kelvin equation to account for the thickness of the adsorbed layer. This modified equation calculates the adsorbed layer thickness using two different equations for high (>0.6) and low (<0.6) relative pressures. In using their method, the carbon tetrachloride pore size distributions obtained were the same as those obtained using nitrogen.

Miyata et al. (2003) take this analysis one step further. They used nitrogen data obtained by *Naono et al. (1997)* and obtained a revised Kelvin equation that takes into account the effect of the interfacial curvature on the interfacial tension of the condensation phase–gas phase interface as well as the thickness of the condensation

layer. They conclude that by accounting for this curvature, their method is more accurate then that proposed by Naono et al.

Some work has also been done investigating the nature of prepared silica particles, using water as the adsorptive gas. *Oh et al. (2003)* did water isotherms on five different prepared silica particles. Though the particles had different pore sizes, the shapes of the water isotherms were very similar. Oh et al. found that the adsorption of water is very dependent on temperature and pore size.

Inagaki & Fukushima (1998) examined water desorption on one prepared silica solid. They observed a decrease in hydrophobicity after the particles was exposed to water vapor due to irreversibly adsorbed water on the particles. This was determined by comparing infrared spectroscopy and benzene adsorption isotherms before and after contact with water vapor.

Results have been conclusive that water is a poor molecule to use to determine pore size distributions, since it can alter pore sizes due to swelling. Water isotherms should be used only to determine how much water can be adsorbed by a particular porous solid (*Carrott et al. 1998, Koyano et al. 1997*).

Chapter 2

Materials and Methods

2.1 Fabrication and Preparation of Porous Media

Three different porous particles were used during this study; all were fabricated in our lab by Diana Washington using a modified version of the method proposed by *Zhao et al. (1998)*. This method consists of forming a silica gel matrix around nonionic alkyl poly (oxyethylene) surfactant molecules. This silica gel is then calcined, which removes the surfactant molecules, forming a material with an array of highly uniform pores. The surfactant molecules used to develop these particles were Tween 40 and Pluronic P123. In the case of the Pluronic P123 surfactant, two particles were made with that surfactant at two different temperatures. This produced porous material with two different pore sizes. In keeping with terminology suggested by *Marin-Flores (2004),* these particles are called T-27, P-47, and P-55. The letter in this terminology represents the surfactant used in fabrication, T for Tween 40 and P for Pluronic 123, while the number represents the average pore size in angstroms. Further information detailing the fabrication of these particles will soon be published in a doctorial thesis by Diana Washington.

Prior to their being used in any experiment, the calcined particles were heated in an oven for 12 h at 150 °C to remove water and any other volatile contaminants that may be present. The particles were then loaded into a four tray, cylindrical sample holder fabricated by a previous group member. Dimensional details can be found elsewhere (*Hudson 2003*). A schematic of this holder is shown in Figure 4. The holder and the particles were placed back in the oven at 150 °C for another 12 h. The holder with the

sample was then transferred to the microbalance system where they were heated to 90 °C under vacuum for a minimum of 12 h. The system was then cooled to 25 °C in preparation for the experiments to be run.
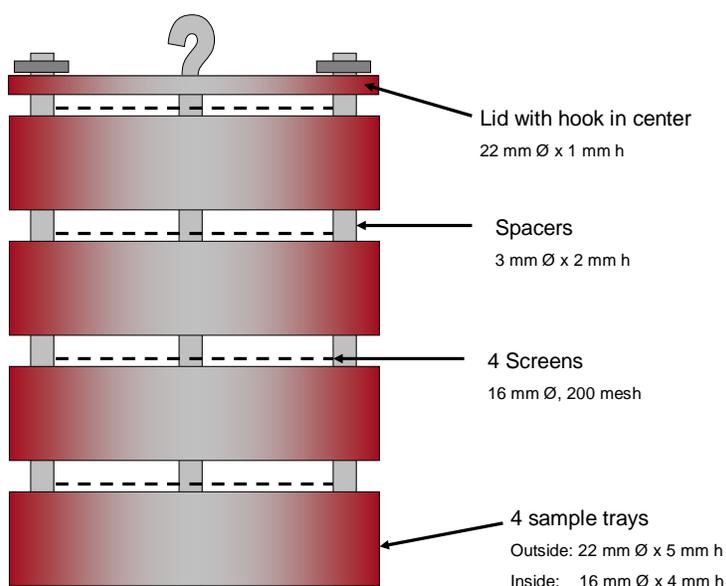
Figure 4. Schematic of microbalance sample holder

Precautions were taken during the transfer of the holder to the microbalance from the oven to decrease the amount of water adsorbed from the air by the particles. When taken out of the oven, the particles were placed in a desiccator until the holder was cool enough to handle. Additionally, during the installation of the holder in the microbalance, helium was passed over the particles from the microbalance gas inlet to ensure a dry environment immediately around the holder. The helium was continually passed over the particles until the holder was sealed into its containment cell and the evacuation at 90 °C begun.

2.2 Microbalance Measuring System

The adsorption and desorption of carbon tetrachloride and water were measured using a magnetically coupled microbalance sorption measurement system, a temperature and pressure gauge, a helium flow system, a vacuum system and a gas chromatograph. A schematic diagram of the experimental system is given in Figure 5.

The microbalance system (Rubotherm, Bochum, Germany) allows for accurate mass measurements ($\pm$ 10 μg) in a highly controlled environment with a wide range of temperature (-80 °C to 250 °C) and pressure (0-300 bar). The microbalance is capable of measuring masses up to 60 g with a reproducibility of $\pm$ 20 μg.   The sorption measurement system is controlled by a computer, which records the mass and temperature of the system at desired intervals over a long range of times (from minutes to months).   With the exception of the Viton sealing ring, all of the internal components of the sorption measurement cell (as shown in Figure 6) are constructed of either titanium or stainless steel, both of which adsorb negligible amounts of carbon tetrachloride, so as not to interfere with accurate measurement of carbon tetrachloride on the particles.   The contact area of the Viton sealing ring with the carbon tetrachloride gas is small and any effects on the desorption rate measured were taken into consideration by performing an empty holder sweep with the Viton ring in place.
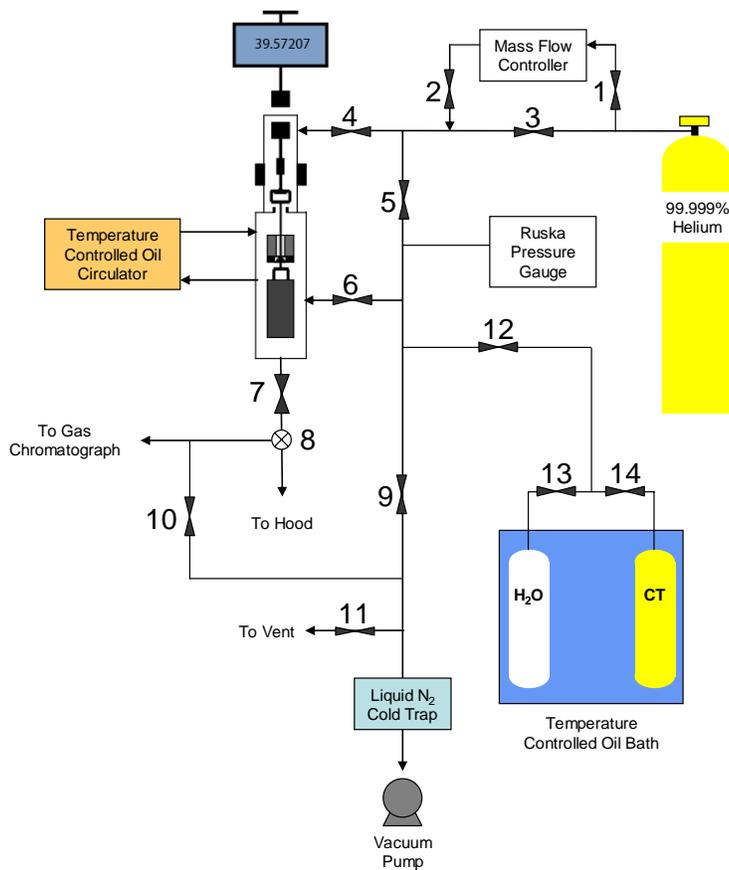
Figure 5. Microbalance measurement system flow chart
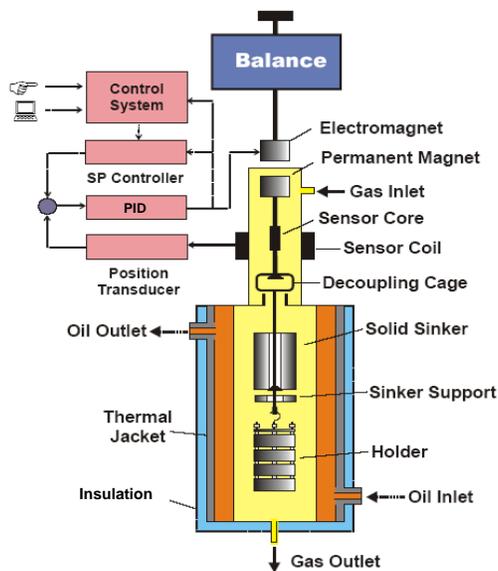
Figure 6. Diagram of sorption measurement cell (from *Marin-Flores (2004)*)

The internal volume of the sorption measurement cell was (100 ± 5) cm^3. The temperature was controlled by oil circulated in the lower thermal jacket and the coupling housing jacket (not shown), by a circulator (TP-6 Heating Circulator, Julabo USA Inc.) which was controlled to +/- 0.01 °C from 20 °C to 300 °C. The cell temperature was measured using a platinum resistance thermometer (Minco S276PD06 (E)) accurate to 0.1 °C and recorded by the computer system.

The mass was measured by a standard microbalance (Mettler AT261) by means of a force transmitted from the holder, which was suspended by the magnetic force between the permanent magnet and the electromagnet (Figure 6). An internal calibration of the Mettler balance was performed when a run begins and ends, as well as every 120 min during a run.

To account for electronic drift over the course of long runs, and to measure the density of the gas in the microbalance, the microbalance has three different measuring positions controlled by the system (Figure 7). In the zero point (ZP) or tare position, both the holder and the solid sinker hang free from the permanent magnet and its attached suspension rod. In measurement position 1 (MP1), the sample holder is suspended by raising the permanent magnet just a few millimeters in order to lift the decoupling cage, while leaving the solid sinker resting on the sinker support. In measurement position 2 (MP2), the permanent magnet is raised a few more millimeters, so that both the sample holder and the solid sinker are suspended. The mass (as measured by the microbalance) for each of these positions was recorded by the computer and stored as a text file. For the current work, MP1 was recorded every 2 min, while ZP and MP2 were measured and

recorded every 10 min. By interpolation, zero-point and buoancy corrections were applied to every measured sample mass point.
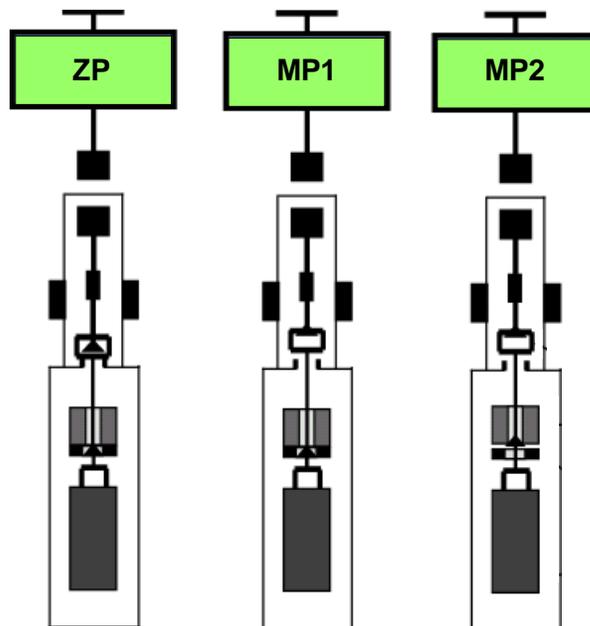
Figure 7. Microbalance measuring positions

The cell pressure was measured using a Ruska quartz spiral gauge (accurate to 0.1 kPa, with a range of 0-1100 kPa), which was connected to the sorption measurement cell via stainless steel tubing. Helium (99.999% minimum molar purity), which was used as a sweep gas, was supplied to the top of the sorption cell from a gas cylinder and regulated by a mass flow controller (LR250, Millipore).

A vacuum system was employed to evacuate the cell and the lines as necessary. A turbo vacuum pump (Trivac PT50, $< 1 \times 10^{-3}$ mbar) is connected to the system via a liquid nitrogen cold trap. The cold trap was used to prevent carbon tetrachloride from

entering the vacuum pump and to prevent hydrocarbons from the pump oil from coming in contact with the porous particles in the microbalance.

The outlet gas from the cell could either be sent to a vent into a fume hood or to a gas chromatograph (HP 5890 Series II) equipped with both a flame ionization detector (FID) and an electron capture detector (ECD). The FID was used to measure carbon tetrachloride concentrations from 1 ppm up to 50,000 ppm, and the ECD was used to measure carbon tetrachloride concentration from 1 ppm down to 10 ppb. The ECD detector and the FID detector (at concentrations less than 5000 ppm) had an error of about 5%. However, for the FID detector at very large concentrations, the error increased to about 9%, due to the long time periods over which the detection peak must be integrated. During a run, the sweep gas exiting the cell continually flowed to the gas chromatograph.

Calibration of the gas chromatograph was done using carbon tetrachloride gas standards. For concentrations less then 1010 ppm, these standards were made by dilution with dry air of a 1010 ppm ± 2% certified carbon tetrachloride gas standard obtained from Scott Specialty Gasses. For concentrations greater then 1010 ppm, gas standards were made from liquid carbon tetrachloride (99.9%). Stainless steel cylinders, equipped with on/off valves at one end, were heated (using an electrical heat tape) to 100 °C for 24 h while being evacuated, to eliminate any volatiles in the cylinders. The cylinders were then cooled to room temperature, they were filled with air at atmospheric pressure, and liquid carbon tetrachloride was injected using a syringe and needle into the stainless steel cylinders through the open valves. The cylinders were then again heated to 100 °C for

24 h to vaporize the carbon tetrachloride. These cylinders were then placed in a 90 °C

hot water bath and connected to the gas chromatograph for analysis. The concentration

of the standard was determined by the following equation:

$$C = \frac{22.4 \cdot 10^6 \cdot \left(\dfrac{T}{273}\right) \cdot \left(\dfrac{760}{P}\right) \cdot \rho_{CT} \cdot v_{CT}}{M \cdot V}$$

where C is the concentration in ppm, T is room temperature in K, P is atmospheric

pressure in mm Hg, ρ_{CT} is the density of liquid carbon tetrachloride at T and P, v_{CT} is the

volume of liquid carbon tetrachloride added to the cylinder, M is the molecular weight of

carbon tetrachloride, and V is the volume of the cylinder. For this study, concentrations

were made from liquid carbon tetrachloride with concentrations ranging from 5000 ppm

to 50000 ppm in 1.00 ± 0.05 L cylinders. Other uncertainties in making these standards

included uncertainties in pressure, temperature, the density of the liquid carbon

tetrachloride and volume of carbon tetrachloride added to the cylinder and sum of these

uncertainties makes up the overall uncertainty. Since very small amounts of liquid

carbon tetrachloride were added to the cylinders to make these samples, a needle and

syringe were used to inject the liquid carbon tetrachloride into the cylinders, with careful

care taken to assure that no air bubbles were present and that all of the carbon

tetrachloride in the syringe was injected into the cylinder. Including these uncertainties

in the standards, the total errors in the gas chromatograph measurements are estimated to

be 10% for the ECD and low FID concentrations and 18% for FID concentrations above

5000 ppm.

Carbon tetrachloride (99.9%, Sigma Aldrich) and water (nanopure, 18 MΩ-cm resistivity) were obtained to use as adsorbates. The carbon tetrachloride was dried using 5 Å molecular sieves prior to being placed in a 75 mL stainless steel cylinder. The water was also placed in a 75 mL stainless steel cylinder. Both the carbon tetrachloride and the water were degassed prior to use. This was done by placing the cylinders in liquid nitrogen for approximately 5 min. While the cylinders were still in the liquid nitrogen, the cylinders were opened to the vacuum system for approximately 5 min. The cylinders were then removed from the liquid nitrogen and heated to near room temperature. This procedure was repeated three times to insure that the liquids were totally degassed. The cylinders were kept submerged in a temperature controlled oil bath   (F83-HP Ultra-Low Refrigerated Circulator, Julabo USA Inc.), controllable to ± 0.01 C.

2.3 Helium Calibration

Helium calibration was performed to determine the mass of sample particles added to the holder. After the sample had been prepared, loaded, and evacuated in the sorption cell, as described above, the cell was pressurized with helium to approximately 10 atm. The system was allowed to come to equilibrium and rest at equilibrium for approximately 30 min. After 30 min, the mass readings in all three positions, the cell temperature and pressure, atmospheric temperature and pressure, and the atmospheric relative humidity were recorded. The pressure in the cell was then reduced by approximately 1 atm. This was repeated until the cell came to atmospheric pressure, and then vacuum was used to obtain the mass of the sample at three sub-atmospheric pressures.

The mass of the solid sinker and the mass of the sample plus the holder were plotted against the density of helium. The y-intercepts of these graphs were used to find the true mass of the solid sinker and the true mass of the holder with the sample. The slopes gave the corresponding volumes, which are needed to make very small buoyancy corrections. To find the mass of the sample, the mass of the holder, which was obtained by helium calibration of the empty holder, was subtracted from the mass of the sample plus holder. A detailed description of these calculations, as well as all of the equations used, is found in *Marin-Flores (2004)*.

2.4 Isotherms

To determine the physical characteristics of the particles, both nitrogen and carbon tetrachloride isotherms have been determined for the T-27, P-47 and the P-55 particles. The nitrogen isotherms were performed by Diana Washington at the Idaho National Engineering and Environmental Laboratory using a Micrometritics Tristar 3000 system at 77 K (*Washington, 2004*). These nitrogen isotherms were reported by *Marin-Flores (2004)*.

Partial carbon tetrachloride isotherms were performed in the current project using the microbalance system. After particles were prepared, loaded into the microbalance and calibrated using helium, as described above, the cell was evacuated for 1 h to ensure all of the helium was removed. The degassed carbon tetrachloride was placed in the temperature controlled oil bath, and the temperature in the bath was set at -35 °C. With the cell set at 25 °C, the particles were exposed to the carbon tetrachloride vapor until sample mass stability was achieved. The measured pressure in the cell, which is

essentially the vapor pressure of carbon tetrachloride at the oil bath temperature, and the measurement point were recorded for analysis after the run. The oil bath temperature was then increased in increments (usually by 2-5 °C) up to 20 °C, each time recording the cell pressure and the measurement point.

To determine if there was hysteresis in the isotherm, the desorption isotherm was measured. This was done by decreasing the temperature in the oil bath incrementally, allowing the cell to come to equilibrium at each point and taking measurements. To obtain the isotherm, the mass of the adsorbed gas per gram of sample was plotted versus the relative pressure of carbon tetrachloride in the cell. The mass of the adsorbed gas was found using the following equation.

$$ m^{ad} = \frac{m_{S+H}^{app} - m_{S+H}^{o} + \rho_{cell} V_{S+H}}{\left(1 - \rho_{cell} \big/ \rho_{AP}\right)} $$

where, m_{S+H}^{app} is the apparent mass of the sample plus holder, m_{S+H}^{o} is the true mass of the sample plus holder, ρ_{cell} is the density of the gas phase in the cell, V_{S+H} is the volume of the sample plus holder, and ρ_{AP} is the density of the adsorbed phase, which is assumed to be the liquid density of carbon tetrachloride. The relative pressure was determined by the ratio of the cell pressure to the vapor pressure of carbon tetrachloride at the temperature of the cell.

To determine the pore size distribution, nitrogen isotherms were previously analyzed by *Marin-Flores (2004)* using the traditional *BJH* method, as well as the method proposed by *Miyata et al (2003)*. The Miyata et al. method accounts for curvature in the properties of a liquid confined in narrow pores and the statistical thickness of the film. These are corrected for using a modified Kelvin equation. Details

of the equations used to find the pore size distributions are found in *Hudson (2003)* and *Marin-Flores (2004).* Partial carbon tetrachloride isotherms were done in this study to determine the volume of carbon tetrachloride adsorbed by the particles studied. Though these were not complete enough to use to determine pore size distribution, work by *Miyata et al. (2003)* and *Naono et al. (1997)* show that when analyzed by proper methods, pore size distributions using nitrogen and carbon tetrachloride isotherms are identical. Therefore, the nitrogen pore size distributions from the isotherm data were assumed to characterize the particles used in the current study.

2.5 Desorption Rate Experiments (Sweeps)

Since helium gas (99.999 %) was used to "sweep" the measurement cell in which these experiments were performed, an experiment was referred to as a sweep. Four different types of sweeps were done using the microbalance system. Carbon tetrachloride sweeps were done with T-27 particles. Empty holder sweeps were done with carbon tetrachloride (from the gas phase only); additionally, sweeps of T-27 and P-45 particles were done using water and carbon tetrachloride + water mixtures as the adsorbates.

To ensure accurate measurements, several factors were kept constant for all of the sweeps. Prior to each measurement, the particles were prepared, and the sample and holder were calibrated with helium as described above. The flow of the sweep gas was kept at 30.0 mL/min. The temperature of the cell was kept at a constant (25 ± 0.1) °C. The cell, prior to the start of a sweep, was pressurized with sweep gas to 1.1 ± 0.1 atm and allowed to come to equilibrium. Additionally, during pressurization, the sweep gas entered the cell via the same inlet as the adsorbate gas. This was done to flush the inlet

line to assure that all adsorbate was in the cell prior to a sweep beginning, thus eliminating the slow bleeding of adsorbate into the cell during a sweep.

When the sweep was started, the exit valve was opened first, allowing the cell pressure to drop to that of the surrounding atmosphere, and then the sweep gas was allowed to flow through the cell. The mass of the sample and holder were measured automatically every 2 min, and all mass readings were recorded by the computer control system. The start of the sweep was determined as the time that the flowing sweep gas entered the cell. Runs were continued until the desorption rates decreased well below 1 x 10^{-5} g / g sample / h. For sweeps involving the measurement of carbon tetrachloride, the gas chromatograph was calibrated at the beginning of every sweep and also once every day that a sample was taken.

Several factors were not controlled in this study: 1) the time from when the cell was closed to the adsorbate until the cell was pressurized with helium (from 30 min – 5 hrs), and 2) the time between when the cell was pressurized and the sweep was started (from 30 min – 15 hrs). These variations could impact the initial spatial distribution of components in the gas phase in the cell at the start of a sweep experiment. The initial spatial distribution of the gas phase component effect the empty holder sweep corrections performed on the carbon tetrachloride and carbon tetrachloride + water sweeps.

2.5.1 Carbon Tetrachloride Sweeps

One carbon tetrachloride sweep was done on the T-27 particles, to compare with prior results. After calibration, the particles were exposed to carbon tetrachloride vapors

from the liquid carbon tetrachloride cell immersed in the oil bath, set at a temperature of 10 °C.

Gas chromatograph measurements were taken at various intervals throughout the run, more closely spaced in the early part of a sweep when exit concentrations were changing rapidly. The sweeps typically lasted approximately 300 h.

2.5.2 Empty Cell Sweeps

Empty holder sweeps were done to determine the amount of carbon tetrachloride versus time swept from the gas phase in the microbalance cell. A helium calibration of the empty holder was done before the sweep to determine the mass of the holder. Then, the temperature controlled oil bath for the liquid carbon tetrachloride sample was set to 10 °C, and the cell was evacuated for 1 h to remove the helium gas. The microbalance cell was then opened to the carbon tetrachloride vapor and allowed to come to equilibrium (approximately 12 h). During this time, the mass of the holder decreased slightly and then became constant.

While the system was coming to equilibrium, the gas chromatograph was calibrated using the full range of standards as described above. Additionally, the gas chromatograph was recalibrated every day that a sample was taken. Gas chromatograph samples were taken every 2 min for the first hour, every 10 min for the second hour, and every 20 min for the third hour. After the third hour, samples were taken periodically for approximately 2 days, until the empty holder sweep experiments were terminated.

To determine the total amount of carbon tetrachloride in the gas phase in the cell, the concentration versus time curve obtained from gas chromatograph data was

integrated. This was compared to calculations done using the ideal gas law to validate the accuracy of the integration. The concentration versus time curves could be used to correct the carbon tetrachloride rate determined by the gas chromatograph during the water-carbon tetrachloride sweeps with particles in the holder.

2.5.3 Water Sweeps

Water sweeps were done on prepared T-27 and P-47 particles. During the final evacuation prior to loading, the temperature controlled oil bath containing the liquid water sample was set to 20 °C. To ensure that no condensation of water vapor occurred in the lines from the water cylinder to the cell, the room temperature was maintained at 25 °C or above.

After evacuation, the particles were exposed to the water vapor for approximately 12 h, until mass stability was achieved. No gas chromatograph measurements were necessary for these water sweeps. The sweep took, on average, 150 h.

2.5.4 Carbon Tetrachloride + Water Sweeps

Competitive desorption sweeps were performed with water and carbon tetrachloride as the adsorbates. Due to the carbon tetrachloride vapor pressure being much higher then that of water, water was loaded onto the particles first, followed by carbon tetrachloride.

The water was loaded onto the particles in much the same way as the water sweeps; however, in order to not completely fill the pores with water, the cell was closed to the water vapor prior to the cell reaching equilibrium. To fill the pores approximately

half way by volume, the microbalance was watched, until the mass adsorbed was approximately half of that adsorbed in the water sweeps.

After the cell was closed to the water vapor, the cell was allowed to come to equilibrium for approximately 12 h. Meanwhile, the temperature of the oil bath was lowered to 10 °C, and the lines from the cell to the carbon tetrachloride cylinder were evacuated using the vacuum system. Then, the cell was opened to carbon tetrachloride vapors for approximately 12 h, the sample mass increasing and becoming stable during this period. During this time, the gas chromatograph was calibrated using carbon tetrachloride standards previously prepared.

From the microbalance measurements, combined with cell temperature, cell pressure, and gas-phase density (using the solid sinker apparent mass), the amount of water and carbon tetrachloride in the adsorbed and gas phases can be calculated. An example calculation for one of the sweeps is shown in Appendix 1.

After equilibrium was achieved, the cell was pressurized to approximately 1.1 atm with helium, and the sweep started as for the water runs. Gas chromatograph samples were taken at 1 min, then every 2 min for the two hours, every 10 min for the third hour, and every 20 min for the fourth hour. After the fourth hour, samples were taken randomly for the remainder of the run, with at least two samples taken per day. This sweeps took about 125 h for the T-27 particles and about 200 h for the P-47 particles.

The desorption rates for carbon tetrachloride from the particles were calculated using the gas chromatograph results, corrected by subtracting the empty cell rates. The total desorption rates were calculated using the data from the microbalance, and the

desorption rates for water were calculated as the difference between the total desorption

rates and the carbon tetrachloride rates.

Chapter 3

Results and Discussion

3.1   Isotherms

Carbon tetrachloride adsorption and desorption equilibrium points were measured for the T-27 particles and compared to previous nitrogen and carbon tetrachloride isotherms obtained by *Hudson (2003)*. While the whole isotherm was not obtained, the upper branch of the isotherm was measured to estimate the pressures needed to fully load the pores for the sweep experiments. A plot of actual liquid volume adsorbed (pore volume) versus relative pressure is shown in Figure 8. The current data were shown to be in very good agreement (± 3%) with Hudson's data.
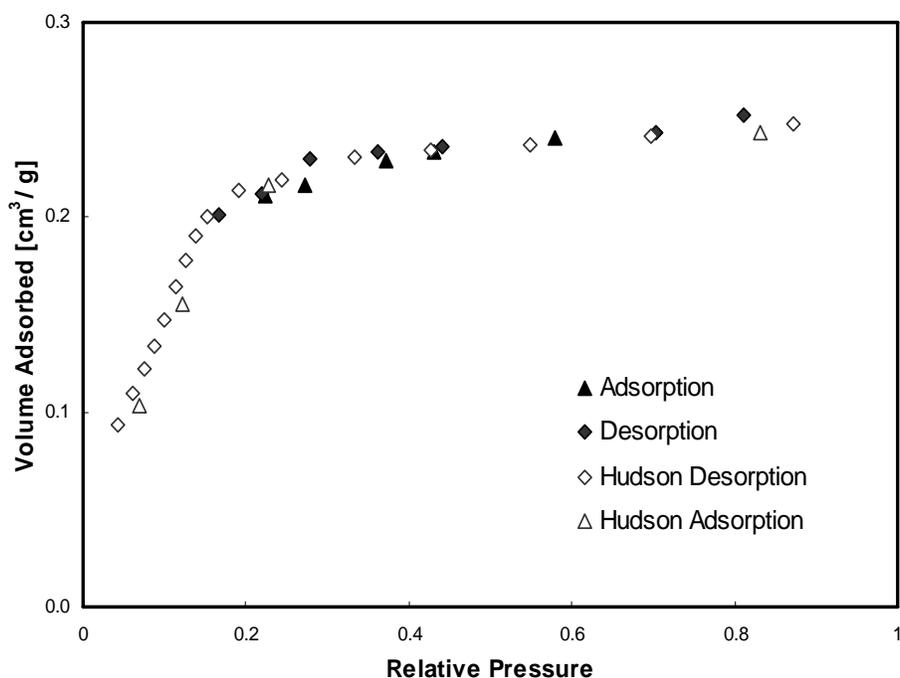
Figure 8. Comparison of CCl₄ isotherm data for T-27 particles at 25 °C with data measured by *Hudson (2003).*

Based on the work done by *Hudson (2003)* and *Marin-Flores (2004)*, pore size distributions calculated from carbon tetrachloride and nitrogen isotherms are in close agreement for ordered silica particles. The most thorough study of all particles used in this work was done using nitrogen as an adsorbent as reported by *Marin-Flores (2004)*. A table of peak pore sizes and pore volumes from that work calculated using the traditional BJH method and a method proposed by *Miyata et al. (2003)* is found in Table 1.

Table 1. Peak pore sizes (nm) and pore volumes as found by *Marin-Flores (2004)*

Particle	Adsorption branch		Desorption branch		Pore Volume (cm^3/g)		
	BJH	Miyata	BJH	Miyata	Meso	Micro	Total
T-27	2.0	2.7	2.1, 3.9	2.7, 4.6	0.13	0.27	0.40
P-47	4.0	4.7	3.5	4.2	0.20	0.15	0.35
P-55	6.8	7.6	3.6, 4.8	4.3, 5.5	0.47	0.30	0.77

Limited carbon tetrachloride isotherms were measured for P-47 and P-55 particles. While these data was not substantial enough to completely characterize the particles, there was sufficient data on the upper branch of the isotherm to determine the relative pressure needed to fill the pores for the subsequent sweeps. These are shown in Figures 9 and 10.
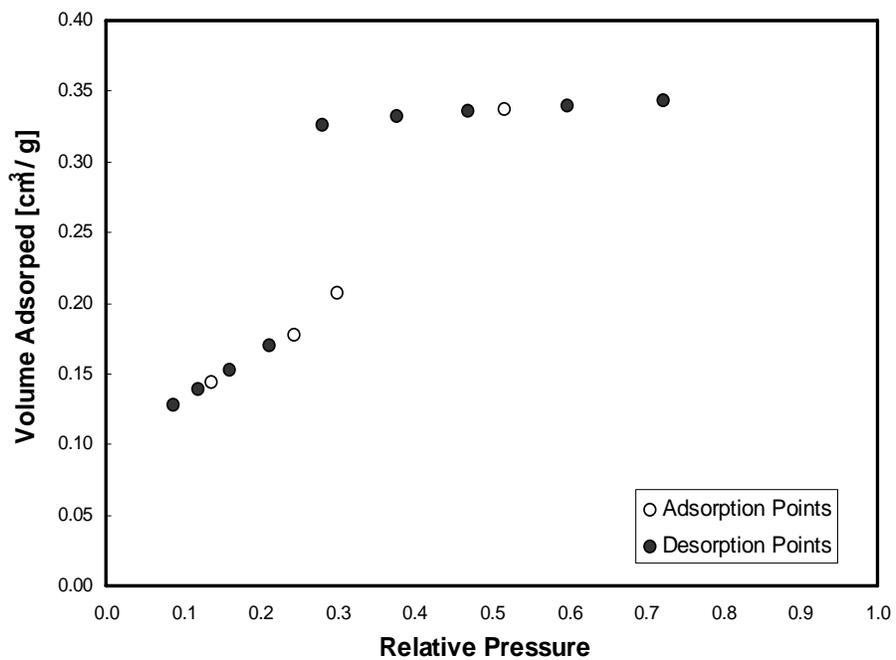
Figure 9. Partial CCl$_4$ isotherm for P-47 particles at 25 °C
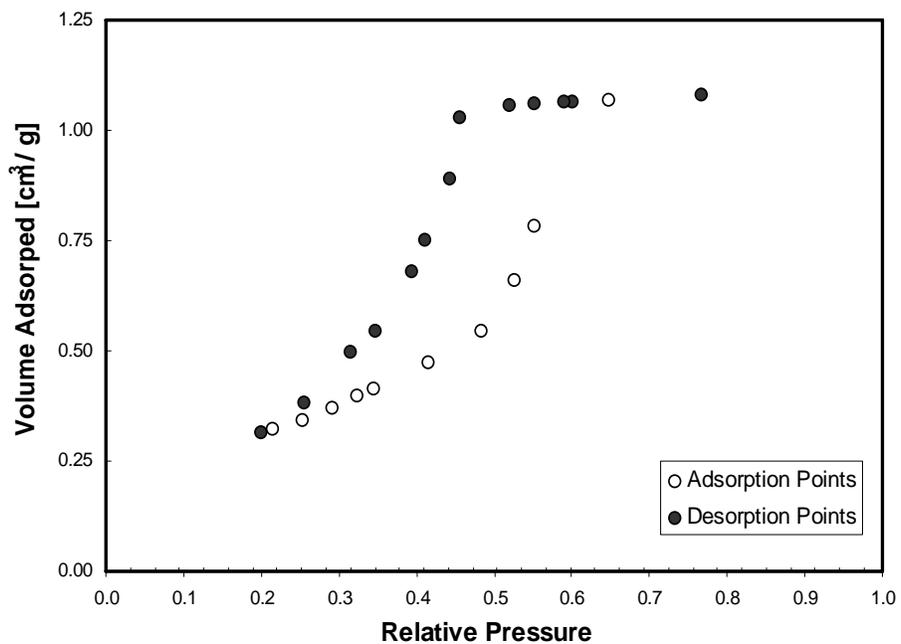
Figure 10. Partial CCl$_4$ isotherm for P-55 particles at 25 °C

It was found that the pore volume for the T-27 calculated with carbon tetrachloride (about 0.25 cm^3/g) was lower than when calculated using nitrogen (0.30 cm^3/g from Hudson and 0.40 from Marin-Flores), and the P-55 pore volume was higher for carbon tetrachloride (1.10 cm^3/g) than from the nitrogen isotherm (0.77 cm^3/g). It is unknown why these pore volumes differ so greatly. It should be noted that the same amounts of carbon tetrachloride were loaded (at similar pressures) onto the T-27 particles prior to helium sweeps in all three studies.

3.2   Desorption Rate Experiments (Sweeps)

3.2.1   Carbon Tetrachloride Sweeps

A carbon tetrachloride sweep was performed using T-27 particles to insure that current measurement techniques agreed with the prior carbon tetrachloride sweeps performed by *Marin-Flores (2004)*. A comparison of Marin-Flores' data and the measurements made using the current study are shown in Figure 11.
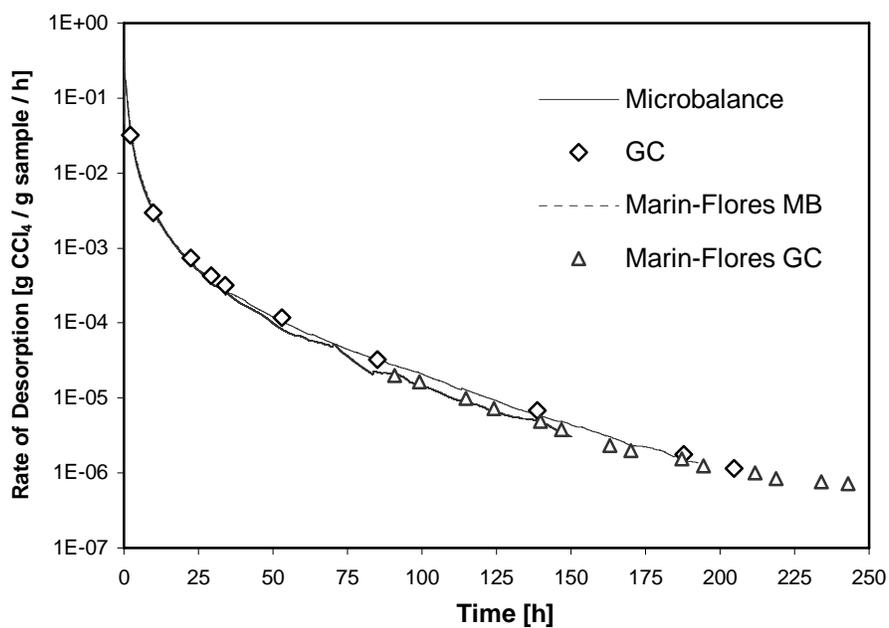
Figure 11. Rate vs. time data for CCl$_4$ sweep with T-27 particles

The current data and that reported by *Marin-Flores* were within 15% of each other for the first 50 h of the sweep. At times near 100 h, the difference becomes as much as 50%, however, the curves seem to remerge at longer times, and the significance of the differences is small with respect to the mass leaving the particles. This is seen on the rate vs. mass adsorbed curves found in Figure 12.
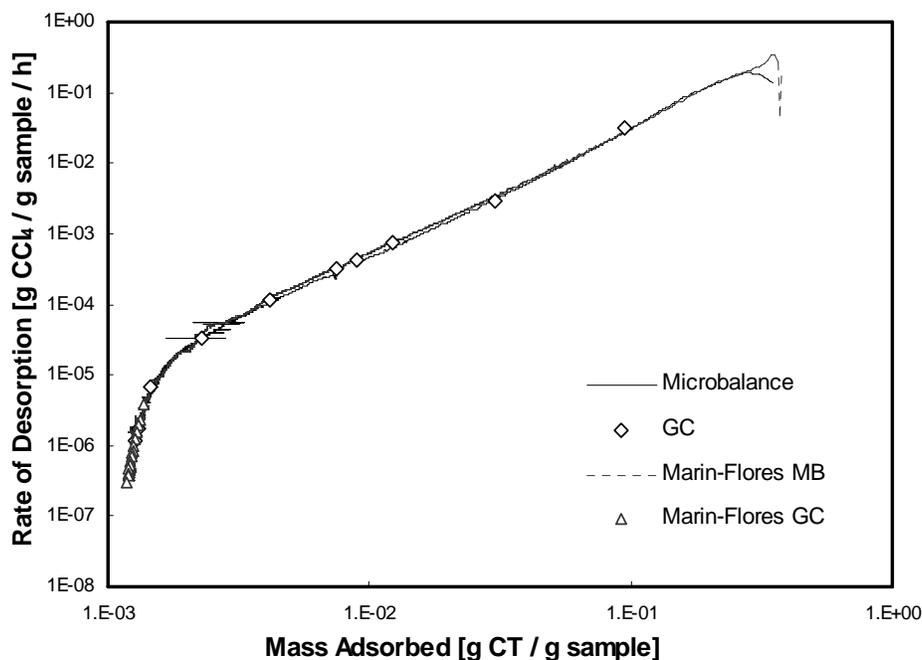
Figure 12. Rate vs. mass adsorbed data for CCl₄ sweep with T-27 particles

For the current work, the final mass adsorbed was 1.3 mg CT/g sample, compared to a residual mass adsorbed reported by *Marin-Flores* of 1.2 mg CT/g sample. This represents an increase of 8 %, which is within the standard error of the gas chromatograph of 10%. Thus, the two experiments agree well within their combined uncertainty.

3.2.2 Empty Holder Sweeps

Empty holder sweeps were done to determine the release rates of carbon tetrachloride from the gas phase of the microbalance cell under standard operating conditions (atmospheric pressure (about 0.92 atm) and 25 °C). Prior to the sweep, a helium calibration was performed to determine the true mass and volume of the empty

holder that would be used in all desorption rate calculations during this study. The results of this calibration are shown in Figure 13. The empty holder was determined to have a true mass of 39.56982 g and had a volume of 5.000 cm^3. This correlates well with values reported by both *Marin-Flores* (39.57090 g and 5.008 cm^3) and *Hudson* (39.57207 g and 4.960 cm^3). Slight differences in mass could be due to replacement of the individual bed screens.
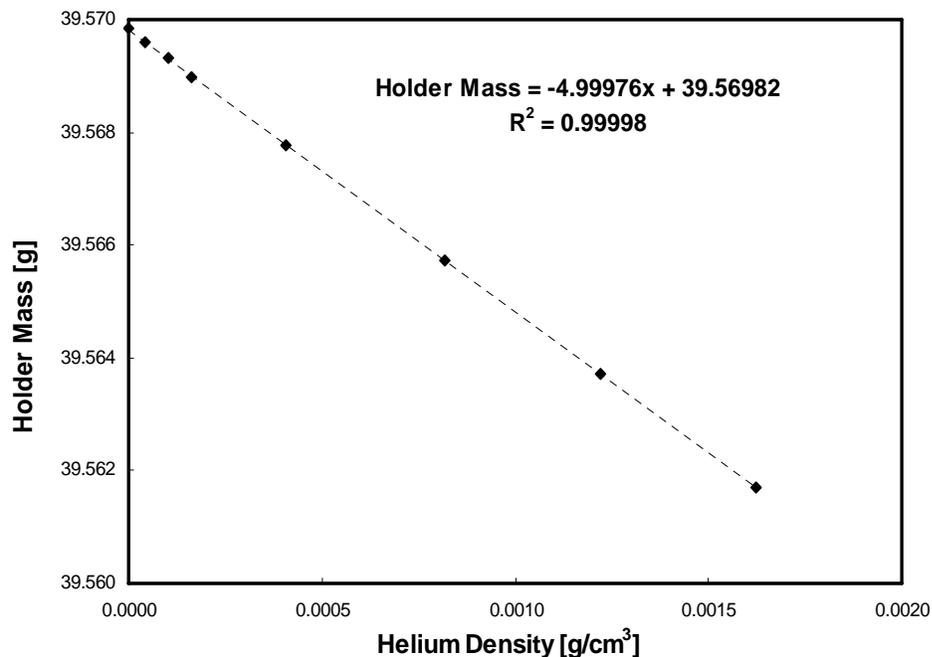
Figure 13. Helium calibration results for the empty cell sweep.

After the helium calibration, the previously evacuated microbalance cell (containing the empty holder) was filled with carbon tetrachloride vapor. The cell was then pressurized with helium, vented to atmospheric pressure, swept with helium at

30 cm^3/min and the concentration of the exiting gas was measured at selected times with a gas chromatograph. This experiment was performed in triplicate. The results of all three sweeps are the found in Figure 14.
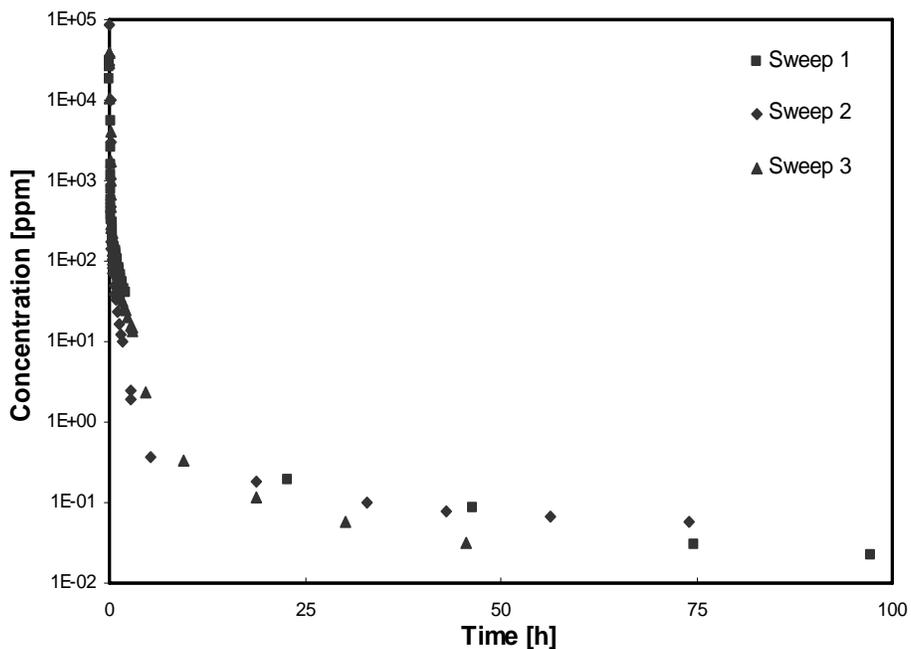
Figure 14. Empty holder sweep exit concentrations

To determine the amount of carbon tetrachloride that exited from the cell during a sweep, the time vs. concentration curve for each run was integrated using Simpson's rule. This was compared to the amount of carbon tetrachloride expected in the cell as estimated using the ideal gas law. These values are reported in Table 2.

Table 2. Calculated amounts of CCl₄ in gas phase of microbalance cell

Method	Amount of CCl$_4$ [g]
Sweep 1	4.45E-02
Sweep 2	4.37E-02
Sweep 3	4.33E-02
Average	4.39E-02
Ideal Gas Law	4.36E-02

For all of the sweeps, the amount of carbon tetrachloride calculated in the gas phase agreed to within 2.1 % with the calculation based on the cell volume, temperature and pressure (ideal gas law). The uncertainty in the ideal gas law value is 5 %, due to uncertainty in cell volume. Assuming all the carbon tetrachloride was swept from the cell, this can be taken as a validation of the accuracy of the gas chromatograph measurement calculations. An average of all three sweeps was subtracted from the measured amounts of carbon tetrachloride during sweep experiments with particles in the cell, to get corrected desorption rates of carbon tetrachloride from the particles.

3.2.3 Water Sweeps

Water sweeps were done on both the T-27 and the P-47 particles. Two sweeps were performed with each particle. For all sweep experiments, at least 90% of the initial water mass was desorbed from the particles. A summary of these results is found in Table 3. The volume of water adsorbed (in terms of liquid volume) was much lower than

the volume of carbon tetrachloride adsorbed for both sets of particles. The significance of this is discussed in a subsequent section.

The amount of water retained at the end of an experiment, when the rate became extremely low, appears to be nearly the same for these two types of particles. It was not possible to determine with certainty that the mass that remained at the end of a sweep was pure water. However, all precautions were taken to ensure that only water was adsorbed on the particles, and the calculated results assume that only the water measured in the loading phase was adsorbed to the particles.

Table 3. Summary of H_2O sweep results

Particles	Amount of H_2O adsorbed [g H_2O / g sample]	Amount of H_2O remaining [g H_2O / g sample]	% of initial mass
T-27 1st Sweep	0.20127	0.01436	7.14
T-27 2nd Sweep	0.18248	0.01381	7.57
P-47 1st Sweep	0.16651	0.01639	9.84
P-47 2nd Sweep	0.12839	0.01152	8.97

3.2.3.1 T-27 Particle Results

Two sweeps of T-27 particles loaded with water were performed, each time using freshly prepared particles. Figures 15 and 16 display the results for these two water sweeps. The gaps in the data represent computer outages where no data were obtained from the microbalance.

In the first sweep, 0.88072 g of particles was loaded into the microbalance. After being exposed to water vapor, the particles adsorbed 0.20127 g H_2O/g sample. After 200 h, the amount of water still on the particles was 0.01436 g H_2O/g sample or 7.14% of the initial amount adsorbed. The sweep was stopped at 200 h because the microbalance results become unsteady when the desorption rate is significantly less than 1×10^{-5} g /g sample/h.

The second sweep of T-27 particles started with a mass of 0.79672 g of particles loaded into the microbalance, and, after being exposed to water vapor and allowed to come to equilibrium, the particles adsorbed 0.18248 g H_2O/g sample. The particles were swept for 190.85 h and had 0.01381 g H_2O/g sample remaining of the particles which represents 7.57% of the initial water mass.

Both of the sweeps exhibited very fast desorption and rapid drops in desorption rate in the first 20-25 hr of the sweep, followed by a more gradual decrease in desorption rate versus time for the remainder of the sweep. The latter part of the desorption rate curves are nearly exponential in form, with a significant fraction of the initial water remaining on the particles when the rate becomes negligibly small. Perhaps this is best shown on the plots of desorption rate versus mass adsorbed, where there are clearly residual amounts of water remaining on the particles. It should be noted that the residual masses of water on these particles are about an order of magnitude larger than those measured by *Marin-Flores (2004)* and in the present work (Figure 12) for carbon tetrachloride on the same particles.
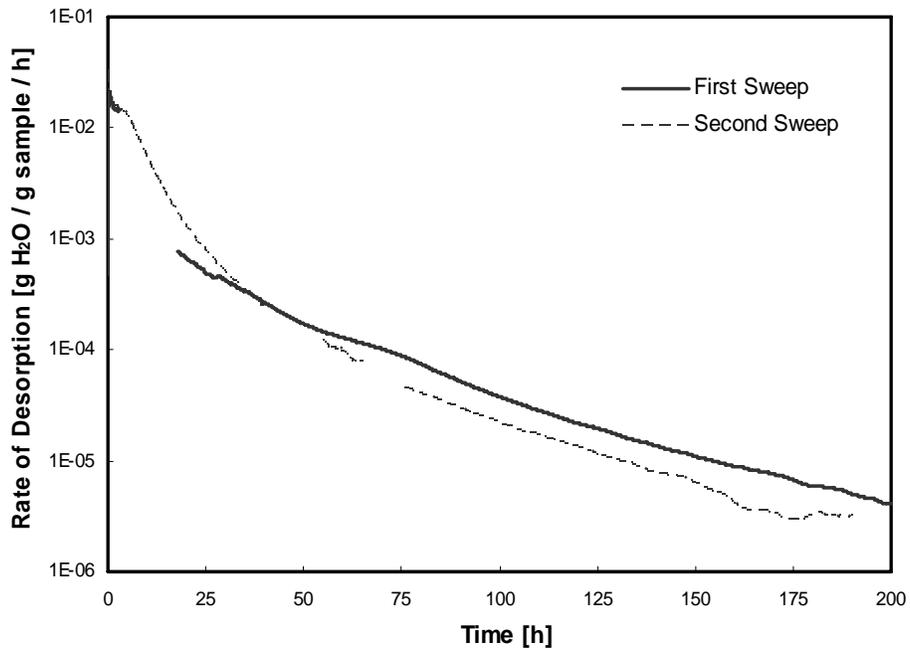
Figure 15. H$_2$O desorption rate vs. time curves for the first and second sweep of T-27 particles
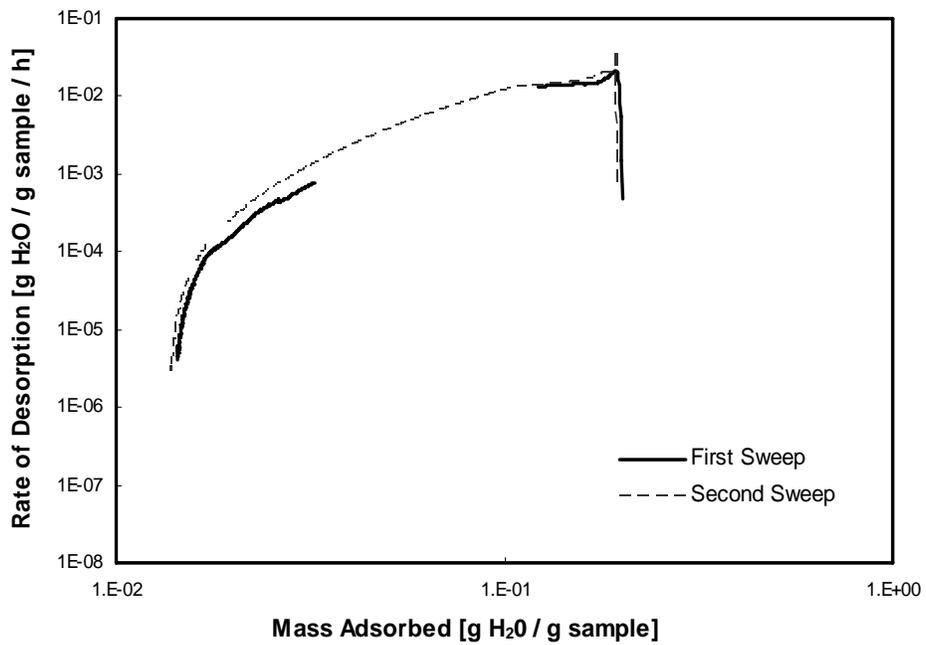
Figure 16. H$_2$O desorption rate vs. mass adsorbed curves for the first and second sweep of T-27 particles

46

3.2.3.2 P-47 Particle Results

Two sweeps of P-47 particles loaded with water were done. The results of these sweeps are shown in Figures 17 and 18. Both sweeps show fast desorption rates in the first 25 h, followed by slow desorption throughout the remainder of the sweep. The water desorption rate is nearly exponentially decreasing with time throughout each run. Again, 12-16 mg/g sample of water remains on the particles when the desorption rates become negligibly small.

The first sweep of P-47 particles was performed with 0.16651 g H_2O/g sample adsorbed on 0.86471 g of particles. The particles were swept for 125 h and resulted in a mass remaining of 0.01639 g/g sample or 9.84% of the initial mass.

The second sweep of the P-47 particles started with 0.84205 g of sample in the microbalance and 0.12839 g H_2O/g sample was adsorbed to the particles. After a sweep of helium gas for 125 h, the mass of water remaining on the particles was 0.01152 g/g sample which represents 8.97% of the initial mass of water on the particles.

It was hypothesized that the since the pore volume of the T-27 particles is greater than the P-47, a greater mass of water initially adsorbed to the T-27 particles was expected. However, since the pore surface area of the P-47 particles is much less than that of the T-27 particles, it was expected that more water would be left on the T-27 particles than that the P-47 particles.

While the amount of water adsorbed onto the T-27 particles was greater than that of the P-47 particles, the amount of water remaining on the particles was nearly the same. Thus, the percentage of the initial mass remaining was slightly greater for the P-47 particles, thus disproving the above hypothesis.
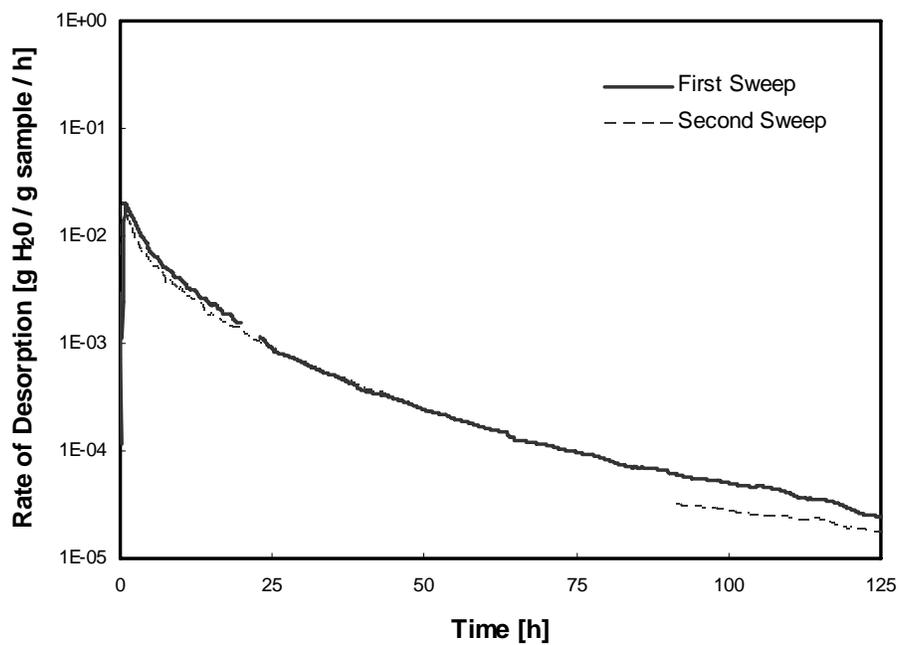
Figure 17. H$_2$O desorption rate vs. time curves for the first and second sweep of P-47 particles
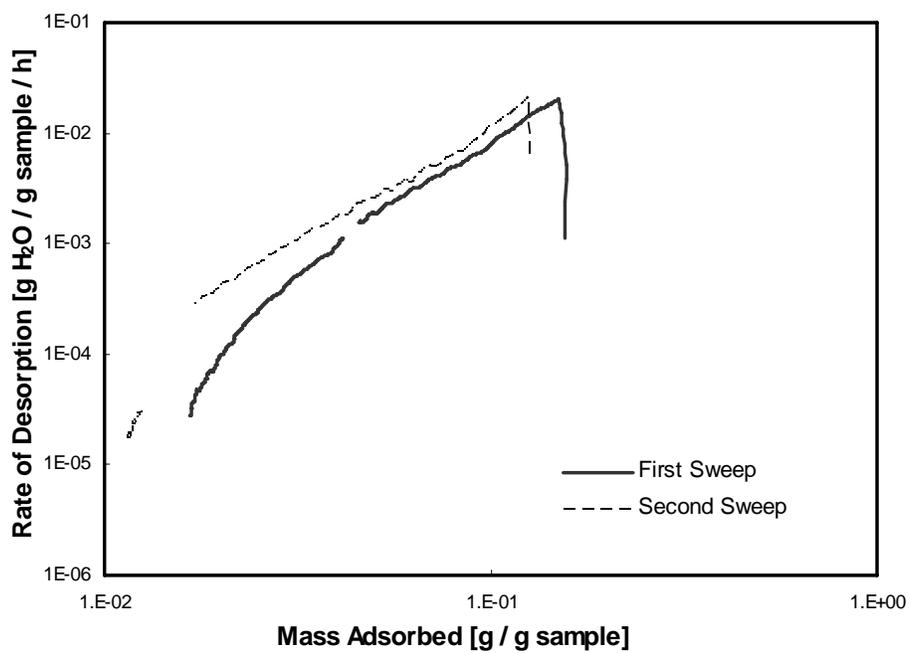
Figure 18. H$_2$O desorption rate vs. mass adsorbed curves for the first and second sweep of P-47 particles

48

3.2.4   Carbon Tetrachloride + Water Sweeps

Sweeps were performed on both T-27 and P-47 particles. Two sweeps of each type of particles were done, each time using a different water/carbon tetrachloride ratio. New, freshly prepared particles were used for each sweep.   The initial cell pressure (predominantly carbon tetrachloride in the gas phase) was the same for all carbon tetrachloride + water sweep experiments. A summary of these results is shown in Table 4. Each sweep was analyzed by comparing rates of desorption with time and mass adsorbed to the particles.

Table 4. Summary of CCl_4 + H_2O desorption sweeps

Particles	Mass adsorbed		Mass remaining	% of initial mass
	[g H_2O / g sample]	[g CCl_4 / g sample]		
T-27 1st Sweep	0.05257	0.23149	0.00592	2.08
T-27 2nd Sweep	0.07441	0.14431	0.00737	3.37
P-47 1st Sweep	0.03923	0.30047	0.00381	1.12
P-47 2nd Sweep	0.11764	0.16876	0.01084	3.79

The total desorption rates were obtained from microbalance readings. The carbon tetrachloride rates were determined by gas chromatograph measurements, and the water rates were calculated as the difference between the total rate and the carbon tetrachloride rate.

To correct the gas chromatograph measurements for the carbon tetrachloride in the initial gas phase, the average empty cell sweep values were subtracted from the gas chromatograph carbon tetrachloride rate at similar sweep times. The sweeps were not corrected for water in the initial gas phase. Calculations (an example is shown in

Appendix 1) showed that only 1-2 mg of water vapor existed in the initial gas phase. This amount of water had a very small effect on the sweeps.

3.2.4.1 Rate vs. Time Curves

The first sweep of T-27 particles, the results of which are found in Figure 19, was done with 0.97666 g of particles. A 19 wt % water mixture by mass was produced on the particles, by loading them with 0.05257 g H_2O/g sample and 0.23149 g CCl_4/g sample. The particles were desorbed for 109.5 h
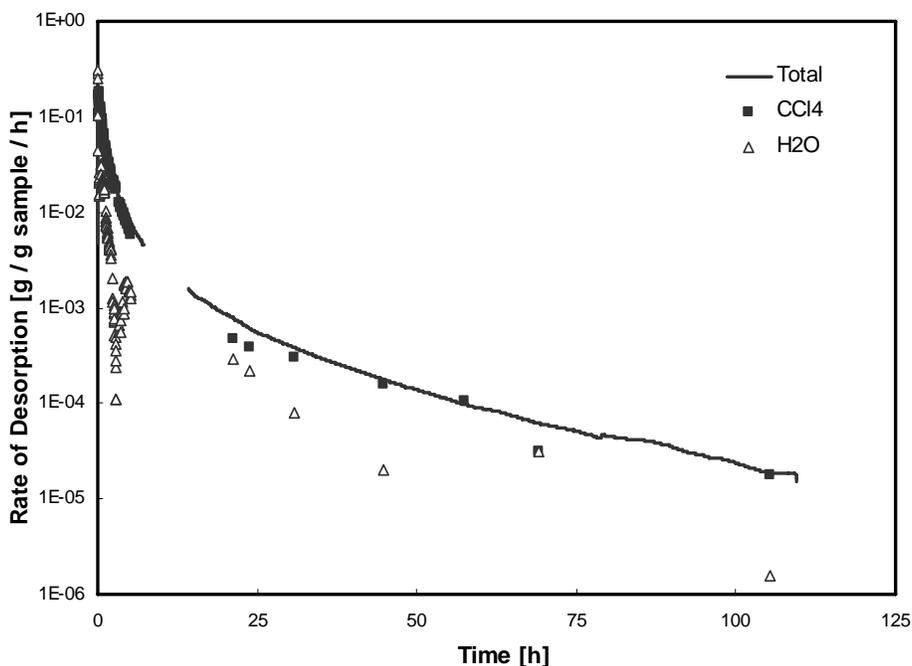
Figure 19. H_2O, CCl_4, and total desorption curves for the first sweep of T-27 particles with 19 wt% H_2O

For the first sweep, the initial water rates appear higher than both the total rate and the carbon tetrachloride rate, however, this is very brief (less then 30 min) and the water rate drops off quickly before briefly rising again at 5 h. The results for the first 30

min are likely spurious, as there is no reason to believe there should be high initial water desorption rates for this experiment. Except for the first 30 min of the sweep, the water rate is always lower than the carbon tetrachloride rate, although the water rate becomes a significant fraction of the total rate for an intermediate period from 10 h to 20 h. Ignoring the initial water rates, the total rate seems to be always controlled by the carbon tetrachloride rate, with the water rate having no impact other than a small one for the intermediate period.

The second sweep of T-27 particles was performed using 0.96162 g of particles upon which 0.07441 g H_2O/g sample and 0.14431 g CCl_4 /g sample were loaded, producing a 34 wt % water mixture on the particles. Helium was passed over the particles at 30 sccm for 126 h. The results are shown in Figure 20.
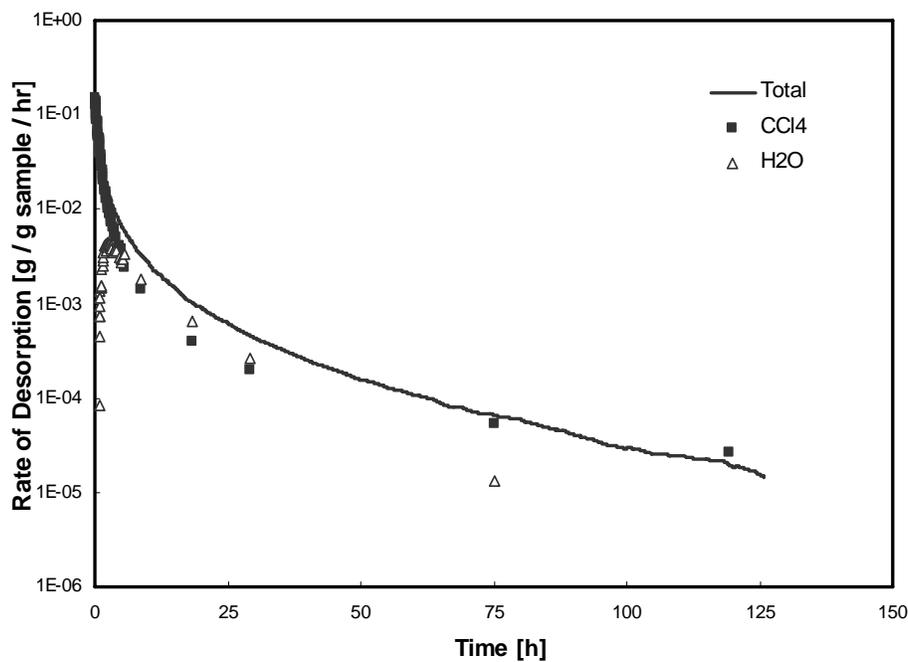
Figure 20. H_2O, CCl_4, and total desorption curves for the second sweep of T-27 particles with 34 wt% H_2O

This sweep of the same particles yielded similar total desorption rates but varied greatly in the carbon tetrachloride and water desorption rates. The carbon tetrachloride measurements were found to track the total desorption rate as recorded by the microbalance for the first few hours of the sweep. Then, the carbon tetrachloride rates became less than the total rate, and there is an increase in the water desorption rate to a maximum of 4 x 10^{-3} g/g sample/hr at 3 h. Like the first sweep, water rate becomes comparable with the carbon tetrachloride rate during an intermediate time period (about 5 to 25 h), but the water rate drops off significantly after approximately 25 h. During this intermediate time period, it seems that the total rate is at least partially controlled by the water rate, whereas, for all other time periods, the total rate is controlled by the carbon tetrachloride rate. This is consistent with the first run, because more water was present in this second run, and the water rate had greater influence during the intermediate period. Also, it makes sense that the water comes off the particles after the bulk of the carbon tetrachloride, since it was adsorbed onto the particles first.

The first sweep of P-47 particles was done using 0.91709 g particles which were loaded with 0.03923 g H_2O/g sample and 0.30047 g CCl_4/g sample, producing a 12 wt% water mixture based on mass. These particles were desorbed with helium sweep gas for 197.8 h. The results of this sweep are shown in Figure 21.
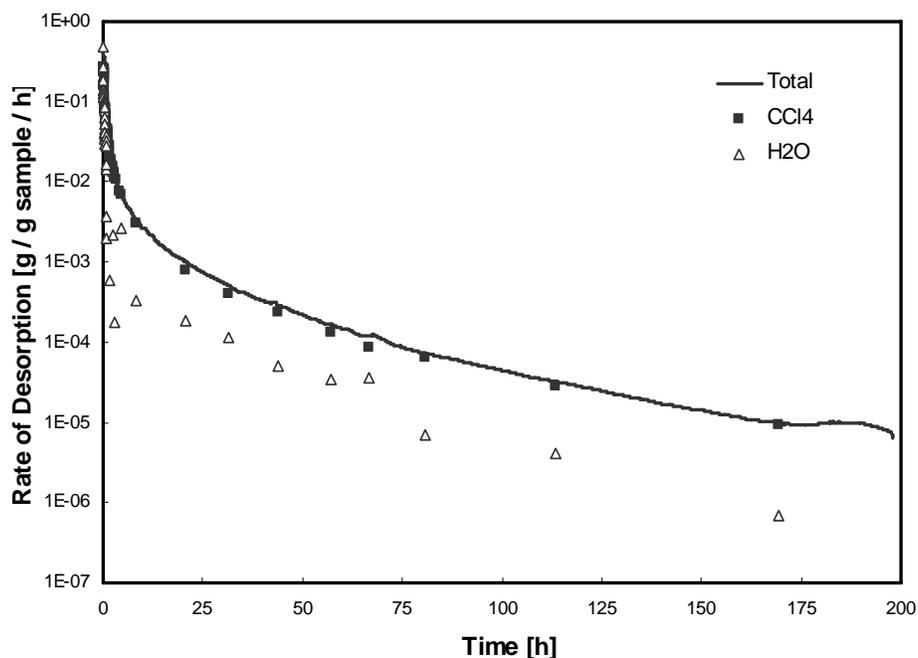
Figure 21. H_2O, CCl_4, and total desorption curves for the first sweep of P-47 particles with 12 wt% H_2O

For this run, high initial water rates are again observed (probably spurious), however, the water rate drops rapidly to values significantly below carbon tetrachloride rates, and remain low throughout the run. The carbon tetrachloride rates are very close to the total rate for the entire run, suggesting that the total rate is controlled by the carbon tetrachloride rate. This makes sense, as the amount of water initially adsorbed onto the particles was low.

A second sweep was done using 0.93360 g of the P-47 particles. These particles adsorbed 0.11764 g H_2O/g sample and 0.16876 g CCl_4/g sample, resulting in a 45 wt% water composition by mass. The desorption results for this run are shown in Figure 22.
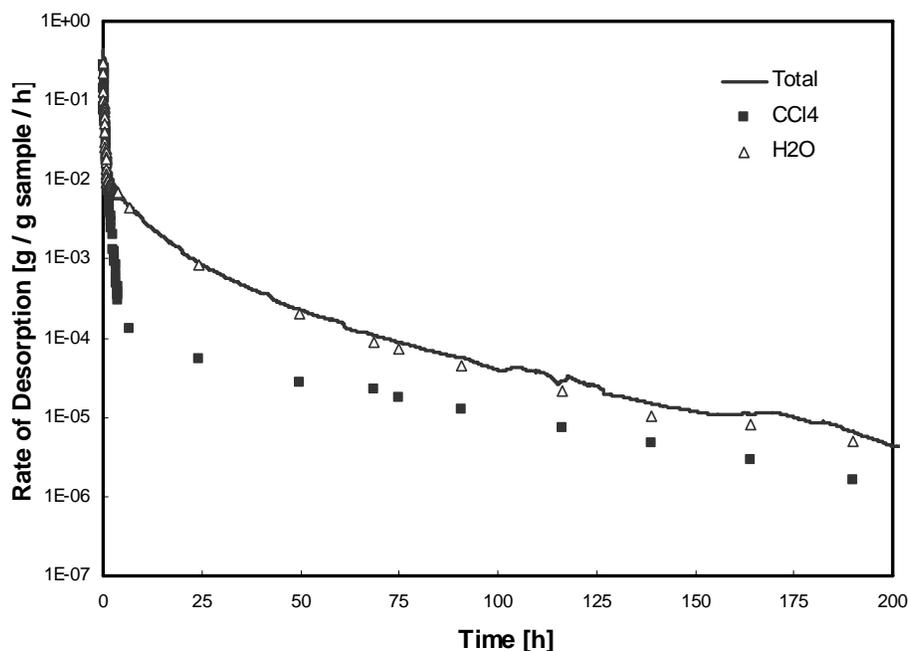
Figure 22. H$_2$O, CCl$_4$, and total desorption curves for the second sweep of P-47 particles with 45 wt% H$_2$O

This sweep differs from all other sweeps in that the water rate appears to control the overall rate for much of the run. The carbon tetrachloride rate is higher than the water rate only during the first two hours of the sweep. This is better illustrated in Figure 23, where the data for the first 5 h of the sweep are shown. Except for the first 20 min, during the first two hours, the carbon tetrachloride rate closely follows the total rate curve, however after two hours, it crosses the water rate curve and the water rate follows the total rate. The high water rates in the first 20 min are likely spurious as there is no reason to believe that the water rates during this time would be higher than the carbon tetrachloride rates. These initial water rates could be due to ignoring the 1-2 mg of water in the gas phase, which must come out early in the sweep. This suggests that during the first 2 h of the sweep, that the rate is controlled by the release of carbon tetrachloride;

however, after 2 hours, the release of water controls the total rate. There appears to be

slow convergence of the two rates at long times (Figure 22), with the carbon tetrachloride

rate starting to again have some impact on the total rate.
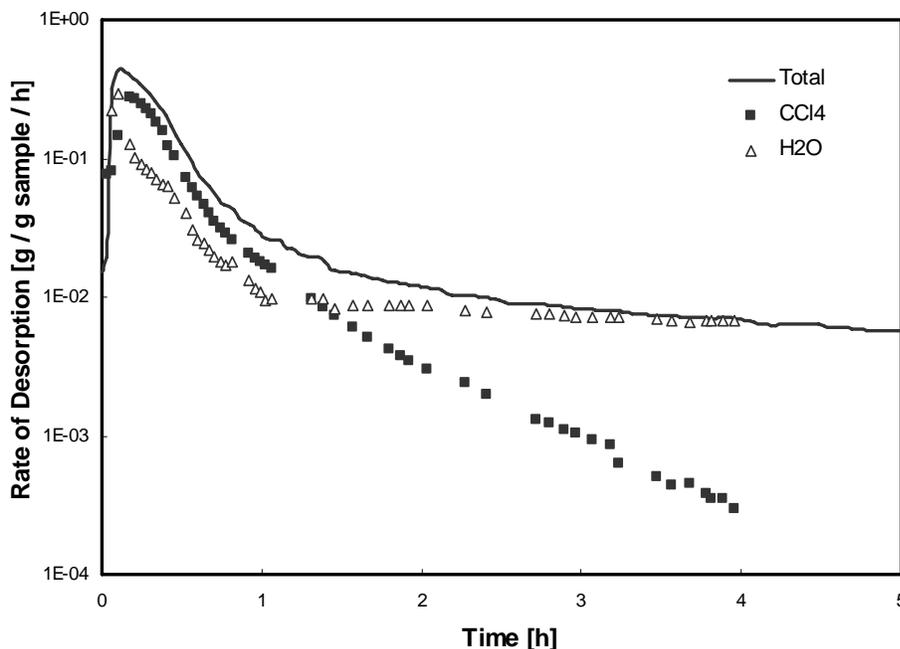
Figure 23. H$_2$O, CCl$_4$, and total desorption curves for the first 5 hours of the second P-47 sweep

3.2.4.2 Rate vs. Mass Adsorbed Curves

To understand how the rates varied based on the mass remaining on the particles,

the carbon tetrachloride, water and total rates were plotted against the mass adsorbed.

The total rate was plotted against the total mass adsorbed (as measured by the

microbalance), and the carbon tetrachloride and water rates were plotted against mass of

carbon tetrachloride adsorbed and mass of water adsorbed, respectively, as calculated by

integration of the individual species rate versus time data.

The first T-27 sweep resulted in a final mass of 0.00592 g/g sample. This is 2.08% of the total initial mass loaded onto the particles. The results are show in Figure 24. In this sweep, the carbon tetrachloride mass adsorbed appears to be greater than the total mass adsorbed, and the water mass adsorbed becomes very small and finally goes negative. The carbon tetrachloride points follow the total line in the early part of the run, which is probably correct. However, the overly large residual carbon tetrachloride amount and the large shift of the water points to the left are both due to the "apparent" large water desorption rates in the first few minutes of the run. These are likely not real. If it is assumed that carbon tetrachloride is the only species coming off initially, then the integrations will yield a switch to large water residuals and small carbon tetrachloride residuals, probably closer to the true situation. Thus, relatively small uncertainties in the measurements for the initial few points can cause large changes in predicted residual amounts adsorbed on the particles.
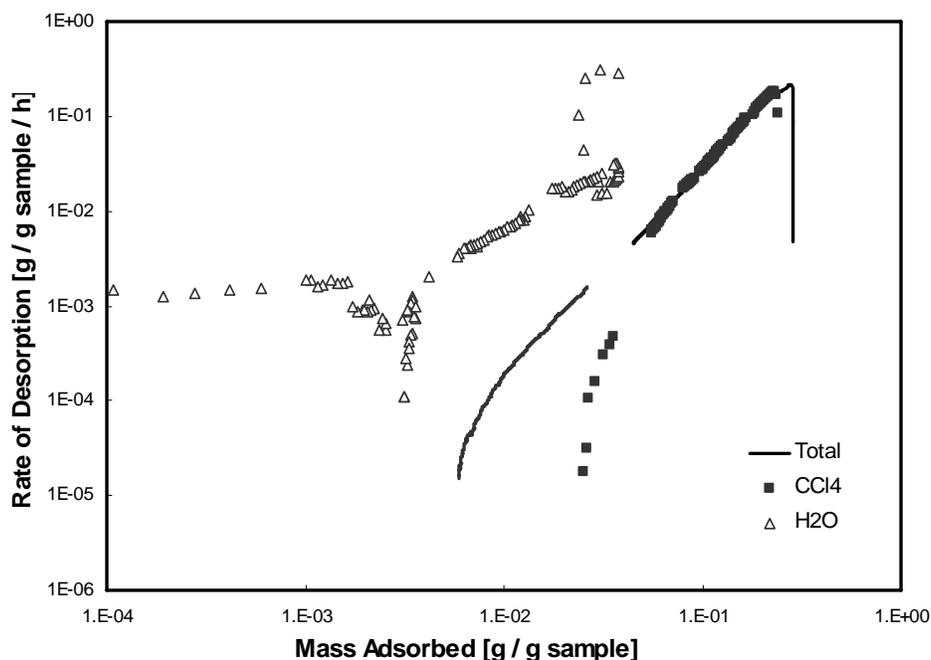
Figure 24. Total and component desorption curves for the first T-27 sweep, where total desorption rate is plotted vs, total mass adsorbed and component desorption rates are plotted vs. component masses adsorbed.

The second sweep of T-27 particles is found in Figure 25. After the run was complete, 0.00737 g/g sample was left on the particles, which was 3.37% of the total mass initially adsorbed. At least in a qualitative sense, this graph seems reasonable. At the start of the run, when the total rates are completely controlled by carbon tetrachloride desorption, and a good portion of the mass adsorbed is this species, the carbon tetrachloride points are near the total line. Late in the run, most of the carbon tetrachloride is likely gone, and the water points more closely approximate the total line.
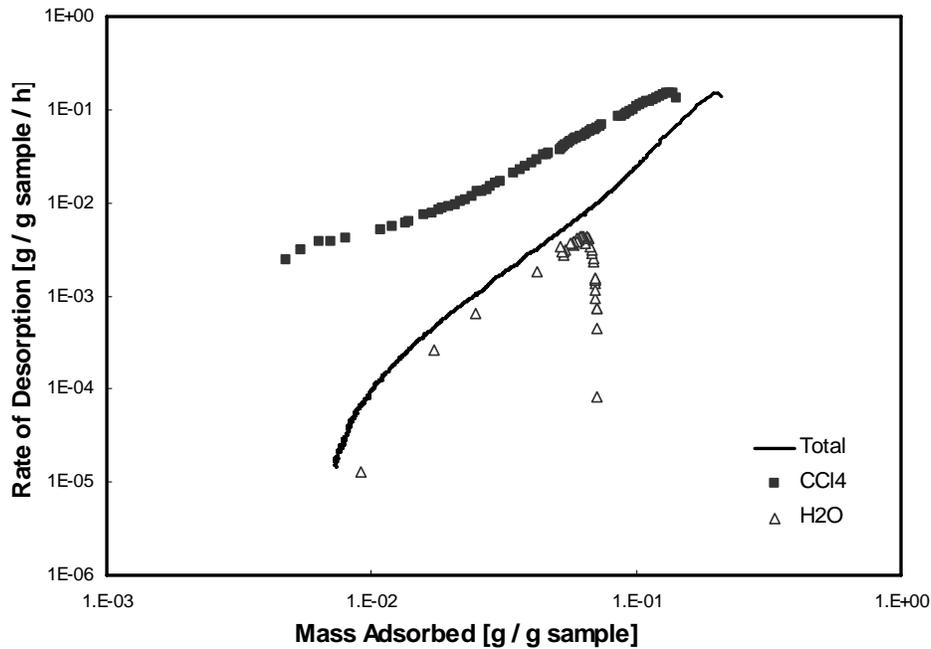
Figure 25. **Total and component desorption curves for the second T-27 sweep, where total desorption rate is plotted vs, total mass adsorbed and component desorption rates are plotted vs. component masses adsorbed.**

At the end of the first P-47 sweep, 0.00381 g/g sample remained on the particles or 1.12% of the total initial mass loaded onto the particles. This is seen in Figure 26. As with the first   T-27 sweep, this sweep yielded water points that are highly uncertain and carbon tetrachloride rates that closely follow the total rate. However, unlike for the T-27 particles, the carbon tetrachloride rates also go negative. For most of the sweep, the water mass adsorbed was calculated to be negative. These problems for residual carbon tetrachloride, and water throughout the run, are again traceable to early measurement uncertainties, where there is again an "apparent" early water desorption surge, which is not physically reasonable, since there is very little water initially on these particles, and it was put onto the particles first. It should be recalled that the water rates come from

differences between the microbalance rates and the GC rates, and there are large

uncertainties during the first few minutes of a run.
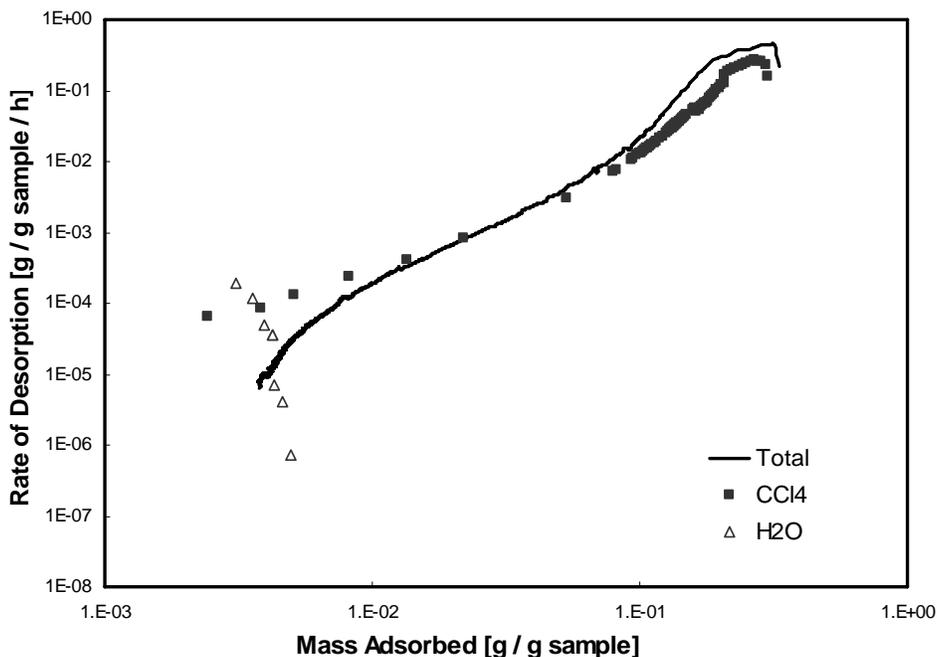
Figure 26. Total and component desorption curves for the first P-47 sweep, where total desorption rate is plotted vs, total mass adsorbed and component desorption rates are plotted vs. component masses adsorbed.

There was 0.01084 g/g sample remaining on the second sweep of the P-47

particles, or 3.79% of the total mass adsorbed, after 200 h. The desorption vs. mass

adsorbed points are shown in Figure 27. This also shows the water mass adsorbed

becoming negative and the carbon tetrachloride residual mass being much greater then

that calculated for the total mass remaining on the particles, neither of which is possible.
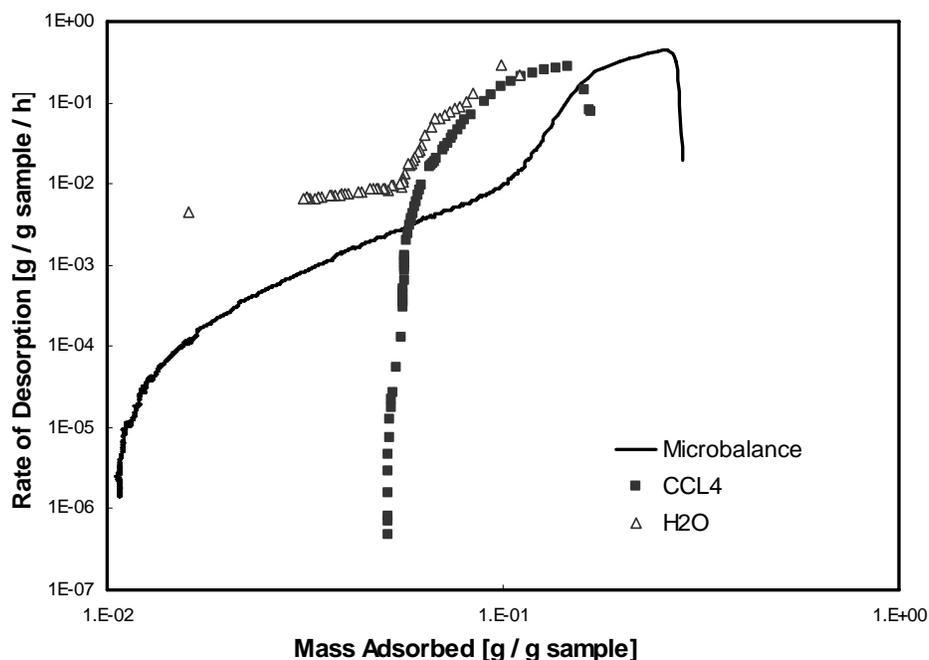
Figure 27. Total and component desorption curves for the second P-47 sweep, where total desorption rate is plotted vs, total mass adsorbed and component desorption rates are plotted vs. component masses adsorbed.

3.3   Sources of Error

The calculations of the mass of each species adsorbed onto the particles are severely impacted by several experimental errors that exist in the measurement methodology. First, the time that experiment starts is difficult to determine with precision, since there are many different valves to turn, and they cannot all be turned at the same time. The microbalance takes measurements every two minutes, and it is nearly impossible to coordinate these measurements with the start of a sweep. This has been a reported problem in previous studies (*Hudson 2003, Marin-Flores 2004*). Marin-Flores was able to correlate the time that a sample was taken to the time that it exited the microbalance, however, errors of even   ± 1 min would not have been evident in this

prior work. For the current study, during the first hour, the desorption rates are very high and thus an error of only a few seconds has measurable effects on the final mass adsorbed values. The error is estimated to be approximately ± 10 s. for the initial start time. This time error seems to have a relatively small effect on the final amount adsorbed, only changing the value by ±15 %, but there are other contributions to this timing error that cannot be quantified.

One significant contribution to the timing error is the nature of gas flow during the initial few minutes of the sweep. The pressure difference between the atmosphere and the cell varied by approximately 0.1 – 0.25 atm. This correlates to an initial loss of 11.1-27.8 cm^3 of gas from the cell when the cell in initially vented before the start of a sweep. According to empty holder data, this is essentially all carbon tetrachloride. The volume of the line from the cell for the gas chromatograph was estimated at 30 cm^3, and the first gas chromatograph measurement does not occur until the sweep gas has been running at a rate of 30 sccm for 1 min. Therefore, this initial surge of carbon tetrachloride does not get measured by the gas chromatograph.

The composition of the gas in the line to the gas chromatograph is also questionable for the first few minutes of the sweep. This arises from the laminar flow (Reynold's number of 5 at 25 °C and 0.95 atm) of helium observed in the line. Initially, this line is filled with air, however when the sweep is started, the mixing characteristics of the line are uncertain, complicating the correlation of the time lag from the time a sample was taken to the state the system was in when the gas exited the cell.

Mixing in the sample loop of the gas chromatograph could also lead to inaccuracies in the measurements. The sample loop of the gas chromatograph was 1.0

mL. The time that the valve was opened to fill the sample loop was 5.0 ± 0.5 s. Since the rates at the beginning of the run are changing rapidly, the concentration of the sample loop may not accurately represent the concentration that exited the microbalance 1 min earlier.

Another source of error seems to be much more significant. This error comes from the variation in the gas chromatograph readings. Due to the very high concentrations being measured, the gas chromatograph concentrations can be in error by as much as 18 %. When variations of this magnitude are propagated through the calculations, the result is a change in the final mass value of ± 60 mg/g sample.   This is larger than the total residual mass for any of the sweep experiments.

Unfortunately, the gas chromatograph was limited to taking samples every 1.5 min and the microbalance was only able to measure the mass every 2 min. These time lags become quite significant during the first hour of the sweep.

As an example of the impact that these errors have on the first few minutes of the sweep, the second P-47 water + carbon tetrachloride sweep data were recalculated, this time assuming that only carbon tetrachloride was coming off the particles during the first 20 min of the sweep. That is, the "spurious" water surge discussed above was ignored in the calculations. The desorption rate versus time was then replotted and is shown in Figure 28. When this assumption is made, the carbon tetrachloride mass adsorbed points shift drastically to the left, while the water points shift slightly to the right with many more points becoming positive.

When the first 20 min of the sweep are assumed to involve only release of carbon tetrachloride, the mass adsorbed for similar rates are much more plausible. The carbon

tetrachloride rates are near the total desorption rates for large mass adsorbed values, while the water rates follow the total rates for the remainder of the sweep.
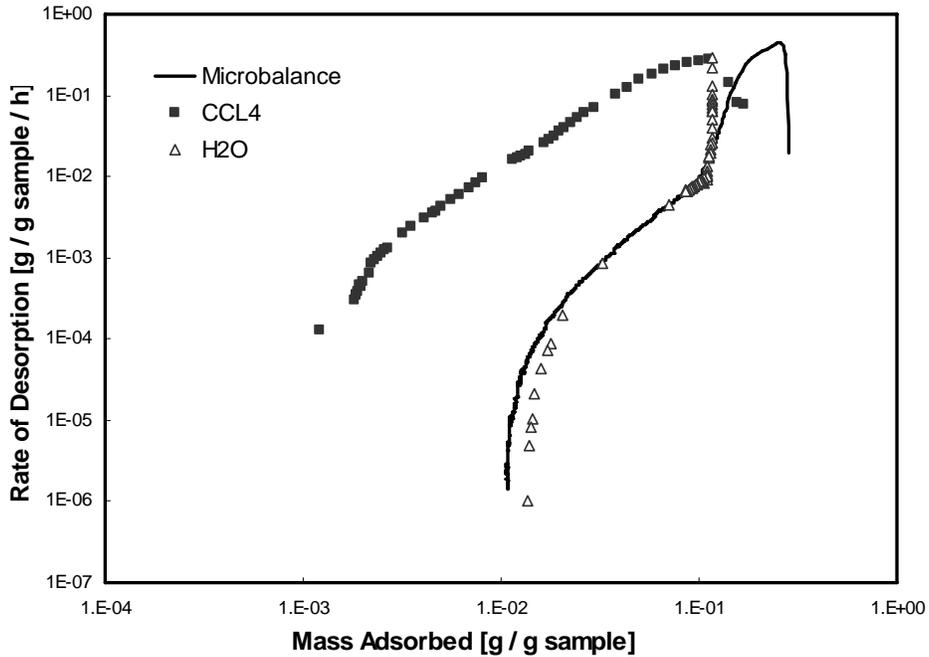
Figure 28. Desorption rate vs. mass adsorbed for the second P-47 sweep assuming that during the first 20 min of the sweep only carbon tetrachloride is being released.

However, even with these large errors, several further important observations can be made on trends displayed through these runs. These observations were made using the total desorption rate versus time curves, which are the most reliable data that were collected.

3.4   Comparisons Using Only Microbalance Data

Due to the various water/carbon tetrachloride ratios that existed during the T-27 and P-47 sweeps, further comparisons of all carbon tetrachloride + water sweeps were done based on pore size and initial water mass. In comparing the particles, it is of interest to note the differences in volumes adsorbed onto the particles for the pure carbon tetrachloride, pure water and carbon tetrachloride + water sweeps. A summary of these differences is found in Table 5.

Table 5. Summary of volumes adsorbed of H_2O, CCl_4 and CCl_4 + H_2O mixtures for T-27 and P-47 particles

Particles	Pure CCl_4 [cm^3/g sample]	Pure H_2O [cm^3/g sample]	CCl_4 + H_2O [cm^3/g sample]	
			Sweep 1	Sweep 2
T-27 Sweep	0.248	0.192	0.198	0.165
P-47 Sweep	0.343	0.147	0.228	0.223

It is interesting to note that the volume of water (as a liquid volume) absorbed on the particles is much less than the volume of carbon tetrachloride (as a liquid volume). While the T-27 volumes differ by 22.5 %, the P-47 volumes differ by 57.2 %. The impact on pore volume of exposing the particles to water seems to persist for the mixtures on the T-27 particles, whereas, intermediate pore volumes were observed for mixtures on the P-47 particles. A possible reason for the decrease in pore volumes is the transition of the freshly prepared particles from a hydrophobic state to a more hydrophilic state, as observed by *Riley et al. (2001)*. It could also be, that for some unknown reason,

a substantial amount of pore volume is susceptible to blockage by water for the P-47 particles and to a lesser degree for T-27 particles.

This reduction in pore volume for T-27 particles was not seen by *May (2003)*. May noted a slight increase in the volumes of pure water and carbon tetrachloride + water mixtures adsorbed over volumes of pure carbon tetrachloride. This difference may be due to an increased exposure to laboratory air in the prior work. Also, the same particles were used for all experiments in the May study, whereas, fresh particles were used for each experiment in the current study.

This is further illustrated by comparing adsorbed volumes of the carbon tetrachloride + water mixtures. The first and second sweeps were loaded with 19 and 34 wt% H_2O respectively, and a corresponding decrease (20.2% and 33.5 % respectively) in the volume adsorbed is observed. This would seem to be a logical result due to an increase of pore blockage by additional water, however, the volume of pure water adsorbed on the particles is nearly the same as the volume of carbon tetrachloride and water for the first sweep but much less than the volume adsorbed for the second sweep. Such was not the case for the P-47 particles. Similar volumes (0.228 and 0.223 cm^3/g sample) were adsorbed for vastly different water/carbon tetrachloride ratios (12 and 45 wt% H_2O), and much higher than for pure water. These data are inconclusive in describing the filling mechanisms of these particles and merits further research.

3.4.1   Pore Size

The T-27 carbon tetrachloride + water sweeps and the pure water sweeps were compared to the pure carbon tetrachloride sweeps performed by *Marin-Flores (2004).* The results of this comparison are shown in Figure 29.
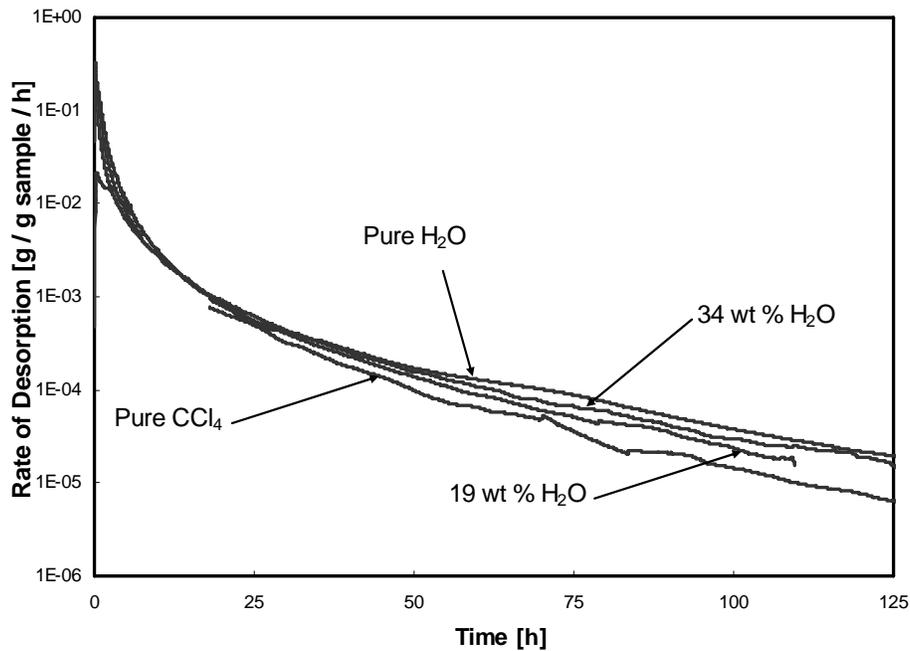
Figure 29.   Comparison of overall desorption rates for CCl$_4$ + H$_2$O sweeps, H$_2$O sweeps and CCl$_4$ sweeps performed on T-27 particles

For the first 5 h of the sweep, the rates of the pure carbon tetrachloride and the mixtures were higher than the water rate. During an intermediate time frame (about 5 h – 25 h) all four rates exhibit similar desorption rates, after which time the rates cross and the water rate becomes larger than the pure carbon tetrachloride rates and the mixtures for the duration of the run. At large times, some divergence begins to appear, however, the divergence is not very large (approximately 6 x 10^{-6} - 2 x 10^{-5} g/g sample/h).

The P-47 pure water and carbon tetrachloride + water sweeps were compared to pure carbon tetrachloride sweeps performed by *Marin-Flores (2004)*. The results of this comparison are shown in Figure 30.
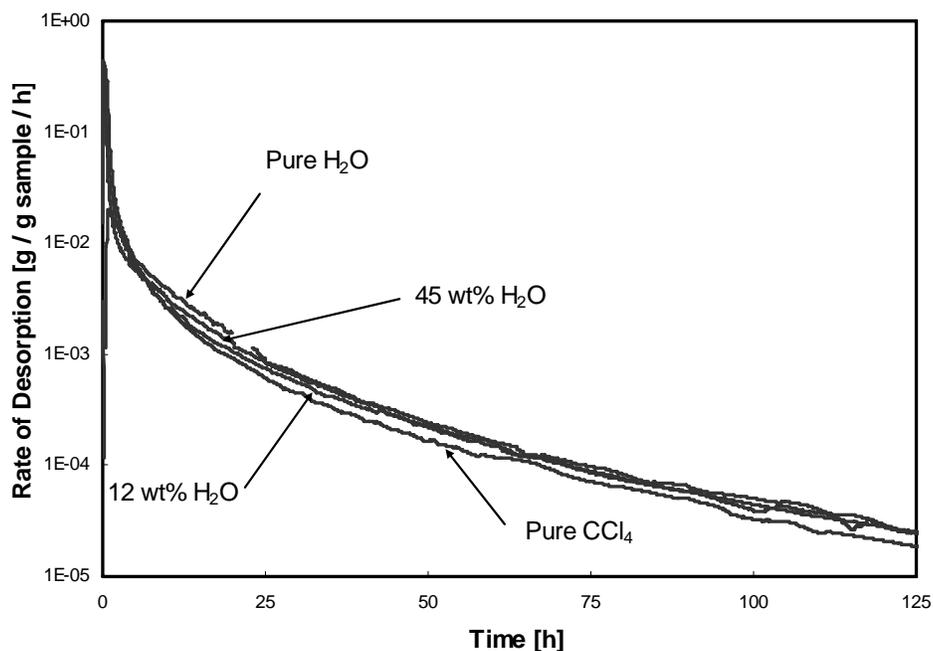
Figure 30. Comparison of overall desorption rates for CCl$_4$ + H$_2$O sweeps, H$_2$O sweeps and CCl$_4$ sweeps performed on P-47 particles

Like the T-27 particles, for the P-47 particles, the total desorption rates for the pure carbon tetrachloride and the mixtures were higher than the pure water rates during the first hours of the sweep and crossed over, with the water rate being larger, after 5 h. A very small distribution of desorption rates was observed throughout the entire sweep for all compositions, i.e., the total desorption rates for all adsorbates were nearly the same.

Marin-Flores (2004) found, by comparing desorption rates of pure carbon tetrachloride versus time for T-27 and P-47 particles, that the rates of the T-27 particles were always lower than the rates of P-47 particles (at equivalent desorption times). In the

current work, the water and the carbon tetrachloride + water rates agree with that finding. In all cases, the T-27 particles exhibited lower desorption rates when compared to P-47 particles at similar sweep times

3.4.2 *Initial Water Composition on Particles*

The rate of desorption verses mass adsorbed to the particles were compared for T-27 and P-47 particles using the water and carbon tetrachloride + water data from this study and the carbon tetrachloride studies done by *Marin-Flores (2004)*. The T-27 comparison is shown in Figure 31, while the P-47 data are found in Figure 32.

Both the T-27 and the P-47 particles display a significant trend for the amount of mass remaining on the particles based on the amount of water initially loaded onto the particles. Both types of particles show that the higher the initial water concentration, the higher the mass remaining on the particles. For the carbon tetrachloride + water mixtures, the desorption profiles are very similar to pure carbon tetrachloride at large masses adsorbed (early in the sweeps) but quickly deviate from these profiles after a large amount of mass has been desorbed, and the desorption profiles appear to move closer to those for pure water.
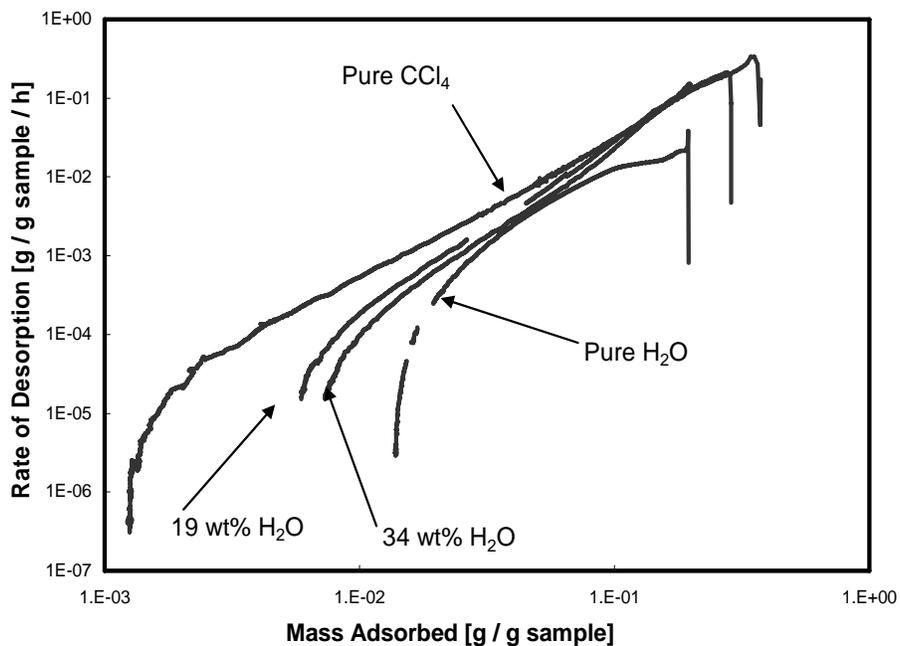
Figure 31. Comparison of overall desorption rates for CCl_4 + H_2O sweeps, H_2O sweeps and CCl_4 sweeps vs. mass adsorbed for T-27 particles
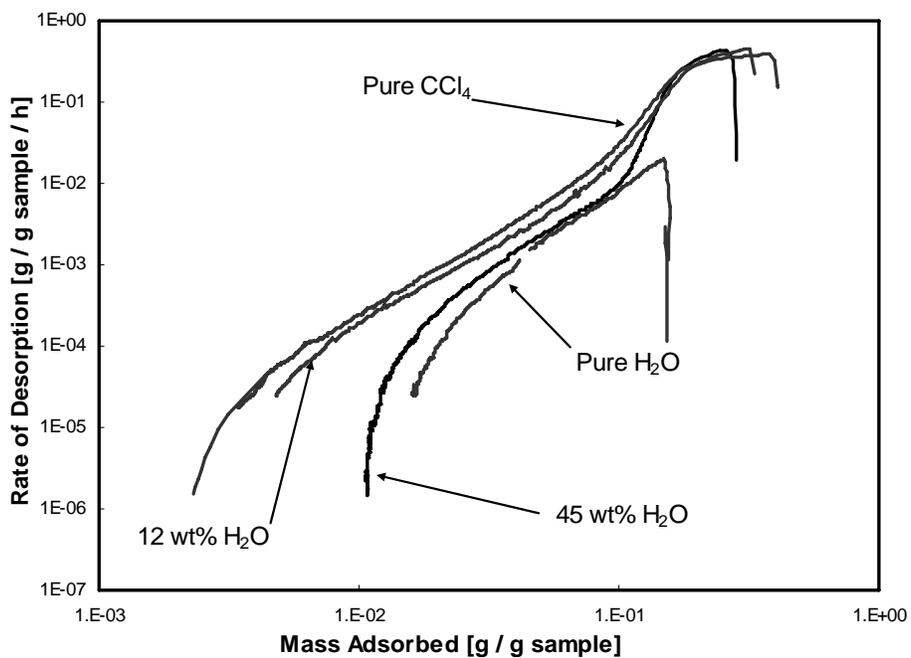
Figure 32. Comparison of overall desorption rates for CCl_4 + H_2O sweeps, H_2O sweeps and CCl_4 sweeps vs. mass adsorbed for P-47 particles

69

These results suggest that the mass remaining at the end of the carbon tetrachloride + water sweeps is weighted toward higher concentrations of water. There may be significant amounts of carbon tetrachloride still on the particles, especially at low initial water mass initially adsorbed, however, it seems that the majority of the residual mass is water when the initial mass adsorbed has equivalent amounts of each species. Furthermore, these comparisons seem to suggest that pore size has a more significant effect than the water/carbon tetrachloride composition ratio during the bulk of the desorption process, however, the water/carbon tetrachloride ratio appears to control the amount (and presumably the composition) of mass remaining on the particles after being swept.

Conclusions

Equilibrium isotherms and desorption rates have been measured for prepared mesoporous silica particles with narrow pore size distributions using two different surfactants, Tween 40 (T-27 particles) and Pluronic 123 (P-47 and P-55 particles). Partial carbon tetrachloride isotherms have been measured for all three particles. The new carbon tetrachloride measurements for T-27 were shown to be in good agreement with those previously reported for these particles, indicating continuity of evolving measurement techniques. In a prior study, nitrogen isotherms were determined for all three particles. Although nitrogen and carbon tetrachloride isotherms yield similar pore size distributions, pore volumes measured in the current work were found to be significantly different. The reasons are not known, but they may relate to the drastically different temperatures used in these two adsorption equilibrium experiments, or to differences in effective volumes for these two species in small pores. Pore volumes determined when loading water on these particles were found to be significantly smaller than for carbon tetrachloride at the same temperature.

The same microbalance system used in previous studies, with new gas chromatograph techniques, was used to perform desorption rate studies on the T-27 and P-47 particles, using pure water, pure carbon tetrachloride and various carbon tetrachloride + water mixtures as adsorbates at 25 °C and atmospheric pressure. Dry helium was used as the sweep gas. A pure carbon tetrachloride sweep was done on T-27 using the modified experimental setup, and was found to be in good agreement with previous results. Since carbon tetrachloride sweeps were run in the prior study for all

three types of particles, new pure carbon tetrachloride sweeps were not performed on the other particles.

Empty holder sweeps were done with carbon tetrachloride to determine exit rates from the gas phase, and to estimate total gas phase amount of this species by integration of the exit rate curves. An average total mass from three different empty holder sweeps agreed within 2.1 % with the total mass calculated by the ideal gas law, using an estimated volume for the cell. This agreement is well within the 5 % estimated uncertainty in the cell volume

Pure water and carbon tetrachloride + water sweeps were measured for T-27 and P-47 particles. When the T-27 and P-47 desorption rate versus time curves were compared with each other, the effect of pore size was not large, although the desorption rates were somewhat lower for the smaller pore particles at the same sweep times. Prior work has shown that the reverse is true when the rates are compared at the same mass adsorbed. Pore size seemed to have little effect on the total residual mass on the particles at the end of a sweep. The percentage of initial water on the particles had a pronounced affect on the residual mass. The residual mass increased as the initial amount of water on the particles increased, changing by an order of magnitude between pure carbon tetrachloride and pure water. While no analyses were done of the mass remaining on the particles, the distribution of mixture curves between those for the components suggests that the majority of the mass remaining on the particles was water.

From the mixture sweeps, individual carbon tetrachloride and water desorption rates were determined with reasonable accuracy, except for a short time period at the beginning of the sweep, when desorption rates are extremely high. Due to several

experimental uncertainties, including difficulties in synchronizing microbalance and gas chromatograph measurements, as well as uncertainties in chromatograph results at high carbon tetrachloride concentrations, the integrated individual masses of carbon tetrachloride and water remaining on the particles were highly uncertain. The carbon tetrachloride desorption rates controlled the total desorption rates during the first part of all sweep experiments. For a range of intermediate times, the rates of the two species were comparable. At long times, the carbon tetrachloride rates were significantly larger than for water , except for the second P-47 sweep, in which the initial water content was large. For this run, the long time water rates were larger than for carbon tetrachloride, although they seemed to be converging near the end of the run. It should be noted that the rates at these long times were very small, and not having significant impact on the residual mass on the particles.

Future Work

The results of this study show that water and carbon tetrachloride desorption rates can be simultaneously measured, however, new analytical techniques need to be developed in order to measure the very high carbon tetrachloride desorption rates that occur during the first 2 h of the experiment. Alternatively, and perhaps a better approach, a quantitative technique needs to be developed to analyze the mass remaining on the particles. This may be accomplished by dissolving the particles in a very high concentration sodium hydroxide solution. A liquid/liquid extraction could then be performed and the solvent analyzed for carbon tetrachloride. Additionally, desorptions using different water-carbon tetrachloride ratios (especially at very high and very low water ratios), as well as desorptions using different particles, should be done to further elucidate the findings of this study. An investigation into the reasons different volumes of water and carbon tetrachloride are loaded onto the particles might help clarify the desorption mechanisms. Also, the order of carbon tetrachloride and water loading could be reversed to see what effect a water layer over the carbon tetrachloride would have on the desorption characteristics of both compounds.

Bibliography

Armstrong, J. E.; E. O. Frind; R. D. McClellan. *Water Resources Research* **1994**, 30, 355-368.

Barrett, L. G.; Joyner, L. G.; Halenda, P. P. *Journal of the American Chemical Society* **1951**, *73*, 373-380.

Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T.-W.; Olson, D.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. *Journal of the American Chemical Society* **1992**, *114*, 10834-10843.

Burgos, N.; M. Paulis; M. M. Antxustegi; M. Montes. *Applied Catalysis B: Environmental* **2002**, *38*, 251 - 258.

Branton, P. J.; Hall, P. G.; Sing, K. S. W. *Characterization of Porous Solids IV*; Mays, T. J.; Rouquerol, J.; Rodriguez-Reinoso, F.; Sing, K. S. W.; Unger, K. K., Eds.; Royal Society of Chemistry: London, **1997**.

Carrott, l. M. M. L. R.; Candeias, A. J. E.; Carrott, P. J. M.; Ravikovitch, P. I.; Neimark, A. V.; Sequeira, A. D. *Microporous and Mesoporous Materials* **2001**, *47*, 323 - 337.

Carrott, l. M. M. L. R.; Carrott, P. J. M.; Candeias, A. J. E.; Unger, K. K.; Sing, K. S. W. *Fundamentals of Adsorption 6*; Meunier, F., Ed.; Elsevier: Paris, **1998.**

Chiou, C. T. and T. D. Shoup. *Environmental Science and Technology* **1985**, *19*, 1196.

de Fouw, J. *Carbon Tetrachloride*; World Health Organization: Geneva, **1999**.

EPA, Environmental Protection Agency, United States of America. *510-B-94-003*, 1994.

Farrell, J.; Grassian, D.; Jones, M. *Environmental Science and Technology* **1999**, *33*, 1237 - 1243.

Farrell, J. and M. Reinhard. *Environmental Science and Technology* **1994**, *28*, 53 - 62.

Galarneau, A.; Desplantier, D.; Dutartre, R.; DiRenzo, F. *Microporous and Mesoporous Materials* **1999**, *27*, 297.

Goyne, K. W.; Chorover, J.; Zimmerman, A. R.; Komarneni, S.; Brnatley, S. L. *Journal of Colloid and Interface Science* **2004**, *272*, 10 - 20.

Hakuman, M. and H. Naomo. *Journal of Colloid and Interface Science* **2001**, *241*, 127 - 141.

Harter, T. and J. W. Hopmans, 2004. Role of Vadose Zone Flow Processes in Regional Scale Hydrology: Review, Opportunities and Challenges. In: Feddes,R.A., G.H. de Rooij and J.C. van Dam, Unsaturated Zone Modeling: Progress, Applications, and Challenges. Kluwer, 2004

Hudson, J.; Master's Thesis, Washington State University: Department of Chemical Engineering, 2003.

Inagaki, S.; Y. Fukushima. *Microporous and Mesoporous Materials* **1998***, 21, 667-672*

Johnston, C. T.; Tipton, T.; Trabue, S., Erickson; Stone, D. *Environmental Science and Technology* **1992**, *26*, 382-390.

Kawi, S. and M. Te. *Catalysis Today* **1998**, *44*, 101 - 109.

Koyano, K. A.; Tatsumi, T.; Tanaka, Y.; Nakata, S. *Journal of Physical Chemistry B* **1997**, *101*, 9436 - 9440.

Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710 - 712.

Lukens, W. W.; Schmidt-Winkel, P.; Zhao, D.; Feng, J.; Stucky, G. D. *Langmuir* **1999**, *15*, 5403.

May, T. O., Master's Thesis, Washington State University: Department of Chemical Engineering, 2003.

Marin-Flores, O., Master's Thesis, Washington State University: Department of Chemical Engineering, 2004.

Miyata, T.; Endo, A.; Ohmori, T.; Akiya, T; Nakaiwa, M.J. *Journal of Colloid and Interface Science.* **2003,** *262*, 116-125

Naono, H.; Hakuman, M.; Shiono, T.J. *Journal of Colloid and Interface Science.* **1997**. *186,* 360-368

Oh, J. S.; W. G. Shin; J. W. Lee; J. H. Kim; H. Moon; G. Seo. *Journal of Chemical Engineering Data.* **2003**, *48*, 1458-1462

O'Melia, B. C.; Parson, D. R. In *Volatile Organic Compounds in the Environment*; Wang, W.; Schnoor, J. L; Doi, J. Eds.: ASTM, **1996**.

O'Neill, M. W.; Symons, J. M.; Lazaridou, M. E.; Park, J. B. *Environmental Progress* **1993**, *12*, 12-23

Ong, S. K. and L. W. Lion. *Water Research* **1991**, *25*, 29-36.

Peng, D. and N. H. Dural. *Journal of Chemical Engineering Data* **1998**, *43*, 283-288

Pennell, K. D.; Rhue, R. D.; Rao, P. S. C.; Johnston, C. T. *Environmental Science and Technology* **1992**, *26*, 756-763

Pignatello, J. J. and B. Xing, *Environmental Science and Technology* **1996**, *30*, 1-11.

Poe, S. H.; Valsaraj, K. T.; Thibodeaux, L. J.; Springer, C. *Journal of Hazardous Materials* **1988**, 19, 17.

Ravikovitch, P. I.; Wie, D.; Chueh, W. T.; Haller, G. L.; ; Neimark, A. V. *Journal of Physical Chemistry B* **1997**, *101*, 3671.

Riley, R. G.; Thomson, C. J.; Huesemann, M. H.; Wang, Z.; Peyton, B.; Fortman, T.; Truex, M. J.; Parker, K. E.. *Environmental Science and Technology* **2001**, *35*, 3707 - 3712.

Rockhold, M.; The Geological Society of America 2003 Annual Meeting, **2003**.

Rouquerol, F.; Rouquerol, J.; Sing, K. *Adsorption by Powders & Porous Solids: Principles, Methodology and Applications*; Academic Press: San Diego, **1999**.

Thibaud, C.; Erkey, C.; Akgerman, A.. *Environmental Science and Technology* **1993**, *27*, 2373-2380.

Wang, W.; Schnoor, J. L; Doi, J. *Volatile Organic Compounds in the Environment*; Wang, W.; Schnoor, J. L; Doi, J. Eds.; ASTM: West Conshohocken, PA, **1996**

Werth, C. J. and M. Reinhard. *Environmental Science Technology* **1997**, *31*, 689-696.

Zhao, D.; Q, H.; J. Feng; B. F. Chmelka; G. D. Stucky. *Journal of the American Chemical Society* **1998**, *120*, 6024 - 6036.

APPENDIX 1

Calculation of Gas and Solid Phase Compositions
for Water + Carbon Tetrachloride Loading

Water is initially loaded onto the particles and the cell is allowed to come to equilibrium. The density of the vapor phase is calculated by the ideal gas law :

$$\rho_{ideal}^{vap} = \frac{MW_{H_2O} * P_{cell}}{R*T} \qquad [A.1]$$

where MW_{H_2O} is the molecular weight of water, P_{cell} is the pressure in the microbalance cell as measured by the Ruska gauge, R is the gas constant and T is the temperature of the cell. The mass of water in the gas phase can then the calculated :

$$m_{H_2O}^{vap} = \rho_{ideal}^{vap} * V_{cell} \qquad [A.2]$$

where V_{cell} is the volume of the cell. The mass of water adsorbed onto the particles is calculated as follows:

$$m_{H_2O}^{ads} = \frac{m_{HS} - m_{HS}^o + \rho_{ideal}^{vap} V_{HS}}{\left(1 - \rho_{ideal}^{vap} \middle/ \rho_{AP}\right)} \qquad [A.3]$$

where m_{HS} is the measured mass of the holder + sample, m_{HS}^o is the true mass of the holder + sample obtained from helium calibration, V_{HS} is the volume of the holder + sample and ρ_{AP} is the density of the adsorbed phase, taken here to be pure liquid water.

The total mass of water in the cell is the summation of the mass of water in the vapor and adsorbed phases.

$$m_{H_2O}^{total} = m_{H_2O}^{vap} + m_{H_2O}^{ads} \qquad \text{[A.4]}$$

The next measurements are taken after the carbon tetrachloride has been loaded onto the particles and the cell has come to equilibrium again. The density of this gas phase is calculated using the true mass and volume of the solid sinker (m_{SS}°, V_{SS}), as found during helium calibration of the sample, and the apparent solid sinker mass (m_{SS}^{app}) measured during the run:

$$\rho^{vap} = \frac{m_{SS}^{\circ} - m_{SS}^{app}}{V_{SS}} \qquad \text{[A.5]}$$

Using the gas phase density, an average molecular weight of the gas phase is calculated:

$$MW^{vap} = \frac{\rho^{vap} * R * T}{P_{cell}} \qquad \text{[A.6]}$$

The vapor phase mole factions of water and carbon tetrachloride can then be found:

$$y_{H_2O} = \frac{MW_{CCl_4} - MW^{vap}}{MW_{CCl_4} - MW_{H_2O}} \qquad \text{[A.7]}$$

$$y_{CCl_4} = 1 - y_{H_2O} \qquad \text{[A.8]}$$

From the mole fractions of carbon tetrachloride and water, the mass of the carbon tetrachloride and water in the vapor phase are calculated:

$$m_{H_2O}^{vap\,*} = \frac{y_{H_2O} * P_{cell} * V_{cell} * MW_{H_2O}}{R * T} \qquad [A.9]$$

$$m_{CCl_4}^{vap\,*} = \frac{y_{CCl_4} * P_{cell} * V_{cell} * MW_{CCl_4}}{R * T} \qquad [A.10]$$

The mass of water in the vapor phase, in all cases, was always found to be much smaller than the mass of carbon tetrachloride (1- 2 mg H_2O vs. 33-35 mg CCl_4).

The mass of the water adsorbed to the particles after the carbon tetrachloride was added is calculated as follows:

$$m_{H_2O}^{ads\,*} = m_{H_2O}^{total} - m_{H_2O}^{vap\,*} \qquad [A.11]$$

The total mass on the particles can be calculated using the final microbalance readings, and the total mass of carbon tetrachloride adsorbed can be found :

$$m_{total}^{ads\,*} = \frac{m_{HS} - m_{HS}^o + \rho^{vap} V_{HS}}{\left(1 - \rho^{vap} \big/ \rho_{AP}\right)} \qquad [A.12]$$

$$m_{CCl_4}^{ads\,*} = m_{total}^{ads\,*} - m_{H_2O}^{ads\,*} \qquad [A.13]$$

where ρ_{AP} is the density of the adsorbed phase, taken here to be additive volumes of pure liquid carbon tetrachloride and pure liquid water. For all cases the change in the amount of water adsorbed to the particles did not change more than 1%, which is less then the error in the calculations.

As an example, the second sweep of the P-47 sweep was loaded with water at 25 °C, with an equilibrium pressure of 0.0231 atm. This yields a mass of 2 mg H_2O in the gas phase and 177 mg H_2O adsorbed to the particles.

After carbon tetrachloride was added, the temperature remained at 25 °C, and the new equilibrium pressure was 0.0695 atm. The density of the gas was 0.00034 g/cm^3 as measured by the microbalance. The average molecular weight was calculated as 120 g/mol, with 0.25 being the mole fraction of water in the gas phase. The masses of water and carbon tetrachloride in the vapor phase were found to be 2 mg and 33 mg, respectively. Since the water mass was much smaller than that of carbon tetrachloride, the water in the gas phase was assumed to have no effect on the desorption rates during the sweep. The mass of water adsorbed to the particles was 175 mg and the mass of carbon tetrachloride was found to be 195 mg. The mass percent of water was found to be 45 % water.