EDGEWOOD

RESEARCH, DEVELOPMENT & ENGINEERING CENTER

U.S. ARMY CHEMICAL AND BIOLOGICAL DEFENSE COMMAND

ERDEC-TR-357

ADSORPTION OF CHLOROFORM
BY THE RAPID RESPONSE SYSTEM FILTER

Christopher Karwacki
Paulette Jones

RESEARCH AND TECHNOLOGY DIRECTORATE

January 1997

1997081407

Aberdeen Proving Ground, MD 21010-5423

Disclaimer

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorizing documents.

DEPARTMENT OF THE ARMY
U.S. Army Edgewood Research, Development and Engineering Center
Aberdeen Proving Ground, Maryland   21010-5423

ERRATUM SHEET

15 December 1997

REPORT NO.   ERDEC-TR-357

TITLE   ADSORPTION OF CHLOROFORM BY THE RAPID
                    RESPONSE SYSTEM FILTER

AUTHORS   Christopher Karwacki, and Paulette Jones

DATE   January 1997

CLASSIFICATION   UNCLASSIFIED

Please remove the front cover from copies of ERDEC-TR-357 sent to
you earlier in 1997 and attach the enclosed replacement cover.
Previously printed covers were inadvertently printed with the
incorrect activity name and logo.

Sandra J. Johnson
SANDRA J. JOHNSON
Chief, Technical Releases Office

REPORT DOCUMENTATION PAGE

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	1997 January	Final, 95 Apr - 95 Jun

4. TITLE AND SUBTITLE
Adsorption of Chloroform by the Rapid Response System Filter

5. FUNDING NUMBERS
PR-10262622A552

6. AUTHOR(S)
Karwacki, Christopher, and Jones, Paulette

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
DIR, ERDEC, ATTN: SCBRD-RTE, APG, MD 21010-5423

8. PERFORMING ORGANIZATION REPORT NUMBER
ERDEC-TR-357

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

Adsorption equilibria and dynamic breakthrough data were measured to determine the adsorption capacity and effect of purge air on the desorption of chloroform from activated carbon simulating the Rapid Response System (RRS) filter. The objectives of this investigation were to (1) estimate the vapor concentrations of chloroform produced in the RRS decontamination process, (2) characterize the breakthrough behavior of chloroform on activated coconut adsorbent used in the RRS filter during feed and purge cycles, and (3) provide an estimate of filter life based on routine RRS decontamination operations. Results of the investigation show chloroform vapor concentrations of approximately 1.3 g/m^3 can result during normal RRS decontamination operations. Under normal operating concentrations, the maximum capacity of the filter is estimated at 925 $g\text{-}min/m^3$ at 1.3 g/m^3 feed concentration and increases to 1732 $g\text{-}min/m^3$ at 10.0 g/m^3. The filter's capacity and useful life are reduced significantly when purged with clean air after exposure to chloroform. Either reducing or eliminating the purge air between operations can increase the filter's useful life from 2 to 7 days.

14. SUBJECT TERMS
Desorption   Chloroform
Adsorption   Rapid Response System filter

15. NUMBER OF PAGES
27

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	SAR

Blank

PREFACE

Acknowledgments

Blank

CONTENTS

FIGURES

TABLES

ADSORPTION OF CHLOROFORM BY THE RAPID RESPONSE SYSTEM FILTER

1. INTRODUCTION

The filtration of contaminated airstreams is one of several critical stages involving the detoxification of nonstockpile materiel performed by the Rapid Response System (RRS). A major concern during routine operations is to maintain adequate engineering controls to prevent releasing hazardous compounds into the environment. One approach is to use a single pass adsorption unit containing activated carbon to remove vapors that can vent from the decontamination vessel. Typical operations may involve the decontamination of mustard and lewisite with organic oxidants in the presence of chloroform and *tert*-butyl alcohol, which are used as solvents.

Of all chemicals used, chloroform, which will be present in significant quantities, may offer the greatest burden to the RRS filter. Chloroform's removal by activated carbon is limited to physical adsorption (no chemical reaction); and, due to its high vapor pressure, the propensity exists for the vapor to desorb from the adsorbent bed during air purge.[1] The extent of desorption is dependent upon the adsorption capacity of the adsorbent, the adsorbed phase loading, temperature of the bed, purge volume, and the presence of other adsorbed materials (i.e., water). The adsorption behavior is primarily governed by the equilibrium concentrations of chloroform adsorbed at some fluid phase concentration. In this investigation, adsorption equilibria and dynamic breakthrough data were measured to determine the effect of purge air on desorption of chloroform from activated carbon. Test conditions were limited to parameters simulating the RRS filter. The effects of concentration, dosage, flow rate, purge volume, and relative humidity (RH) were examined. The influence of other adsorbed chemicals, other than moisture, was not determined.

The objectives of this investigation were to (1) estimate the vapor concentrations of chloroform produced in the RRS decontamination process, (2) characterize the breakthrough behavior of chloroform on activated coconut adsorbent used in the RRS filter during feed and purge cycles, and (3) provide an estimate of filter life based on routine RRS decontamination operations.

2. BACKGROUND

RRS Filter Specifications.

The complete RRS filtration unit is designed to remove particulate and vapor contaminants prior to releasing the airstream to the outside air. Four stages of vapor filtration are used, where the first two filters contain coconut shell-based adsorbent, and the latter contain standard CW agent-compatible adsorbent (Figure 1). The location of the coconut carbon filters was intended to either reduce or delay the loading of nonagent vapors to the CW filters. The CW filters were to adsorb (physical and chemical) agent vapors, because this carbon is the only material with validated performance against this class of vapors. Filters one and two were selected to remove chloroform and initially other nonagent vapors to reduce the loading of these vapors on the NBC filters (numbers three
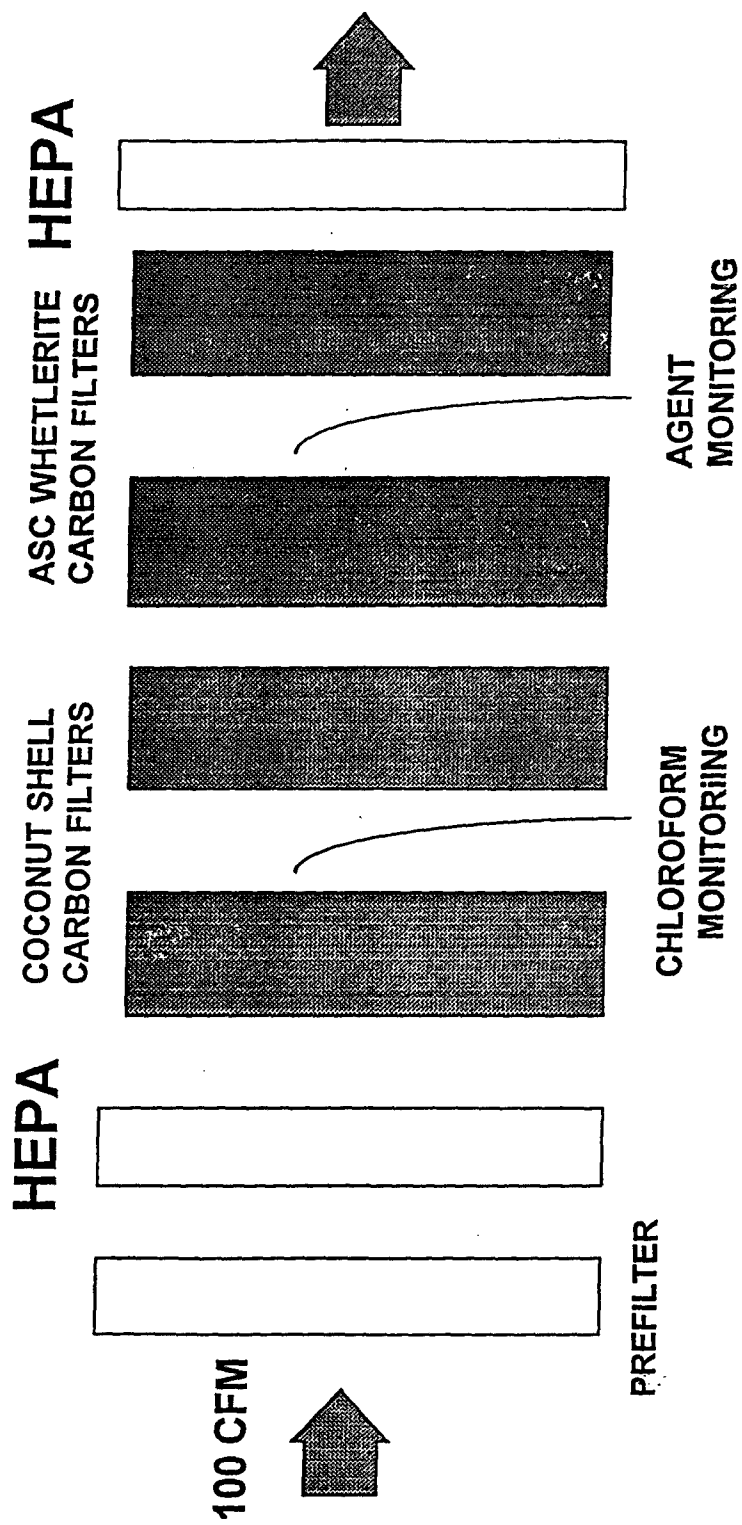
Figure 1. Single Pass Filter Diagram Used in RRS

HEPA

ASC WHETLERITE
CARBON FILTERS

COCONUT SHELL
CARBON FILTERS

HEPA

AGENT
MONITORING

CHLOROFORM
MONITORIING

PREFILTER

100 CFM

and four). The coconut carbon filters may also adsorb agent, with any desorbed material being removed by the CW filters. The coconut filters are the subject of this investigation and were characterized independently of the CW filters. All four filters were designed by Ionex Research Corporation (Broomfield, CO) and are similar in design except for the type of adsorbent used in each filter. The filter selected for the RRS operation is a tray design with two beds separated by the primary airflow (Figure 2). The airflow is split equally to each bed. Specifications of the filter are shown in Table 1. In this investigation, the breakthrough behavior of chloroform through one bed of the filter is simulated in a tube configuration and is discussed in Section 3.3.

3.   EXPERIMENTAL METHODS

3.1   Generated Chloroform Concentrations.

The RRS operation consists of a reactor vessel that uses chloroform as a solvent to decontaminate agent-laden waste. During normal operations, the reactor vessel is the only source where chloroform can escape into the airstream. A secondary source may occur either during reactor filling or by a spill. The latter events are difficult to quantify, yet the overall effect on the filter may be determined from adsorption capacity measurements. The amount of chloroform that can evaporate into the airstream is a function of the surface area of the liquid, the velocity of air across the surface of the liquid, and the temperature of the liquid chloroform. In this investigation, experimental evaporation rates were measured under a range of flows and surface areas. These values were compared to a math model (D2) used to simulate liquid evaporation rates from surfaces. The D2 model is the Department of Army's approved chemical hazard predictor for the Chemical Stockpile Emergency Preparedness Program. The model evaluates the evaporation rate of a chemical based on its molecular weight, molar volume, and vapor pressure when exposed to various wind speeds. The driving force for evaporation is the difference between the mole fractions of chloroform at the chemical-air interface and in the bulk airstream. If the mole fraction of chloroform in the air is assumed to be negligible, the driving force can be approximated by the ratio of the vapor pressure of the chloroform to the atmospheric pressure. The model can simulate evaporation for both ambient conditions with a known wind speed and for still air (<0.2 m/s). The properties of chloroform used in the D2 model are shown in Table 2.

3.2   Isotherms.

Equilibrium capacities for the adsorption of chloroform from bulk nitrogen were measured at 25 °C on coconut and BPL (unimpregnated) activated carbons. The coconut adsorbent was supplied in granular form by Ionex Research Corporation (Broomfield, CO), and sized to 8-16 mesh (U.S. Standard Sieve). The BPL, a product of Calgon Carbon Company (Pittsburgh, PA), is a bituminous coal and was sized to 12-30 mesh.

Figure 3 shows a schematic flow diagram of the isotherm apparatus. The system consisted of a microbalance (CAHN-200), an IR gas analyzer (MIRAN-IA), and a stainless steel bellows pump (Metal Bellows Company, Sharon, MA) for recirculating the gas in a closed-loop configuration. The volume of the system was estimated at 7.0 L by injecting measured quantities of air at reduced pressure. The adsorption measurements consisted of purging the entire system with nitrogen and placing ˜80 mg of sample carbon into the suspended basket. Prior to their use, all samples were oven dried at 110 °C for 3 hr.
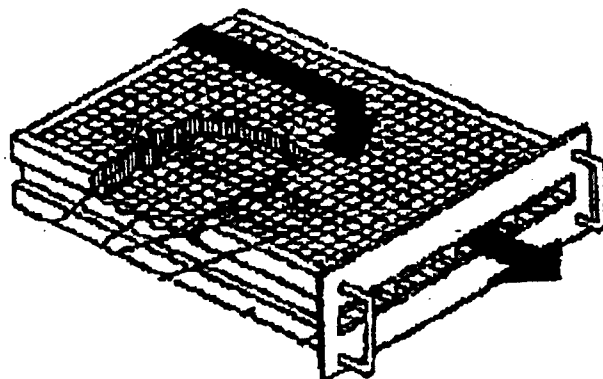
Figure 2. Illustration of RRS Filter Produced by Ionex Research Corporation

Table 1. RRS Filter Specifications

Model	Type II flat bed
Number of Beds	dual beds
Flow Configuration	split flow
Bed Depth	5.1 cm each
Filter Bed Area	3910 cm^2
Flow Rate	150 cfm total (4245 L/min) 75 cfm per bed (2123 L/min)
Bed Airflow Velocity	9.1 cm/s
Residence Time per Bed	0.56 s

Table 2. Properties of Chloroform Used in the D2 Evaporation Rate Model

Molecular Weight, g/mole	119.4
Molar Volume, mL/mole	80.5
Liquid Density, g/mL	1.484
Temperature, °C	25
Atmospheric Pressure, mm Hg	760
Boiling Point, °C	61
Vapor Pressure, mm Hg (Antoine constants)	A = 15.9732 B = 2696.79 C = -46.16
Surface Type	non-porous
Reactor Vessel	assumed square 0.037 m²

Figure 3. Schematic of Isotherm Apparatus

The flow rate of the system was set at 2.5 L/min. A known quantity of chloroform was injected through a septum-sealed port located downstream of the mic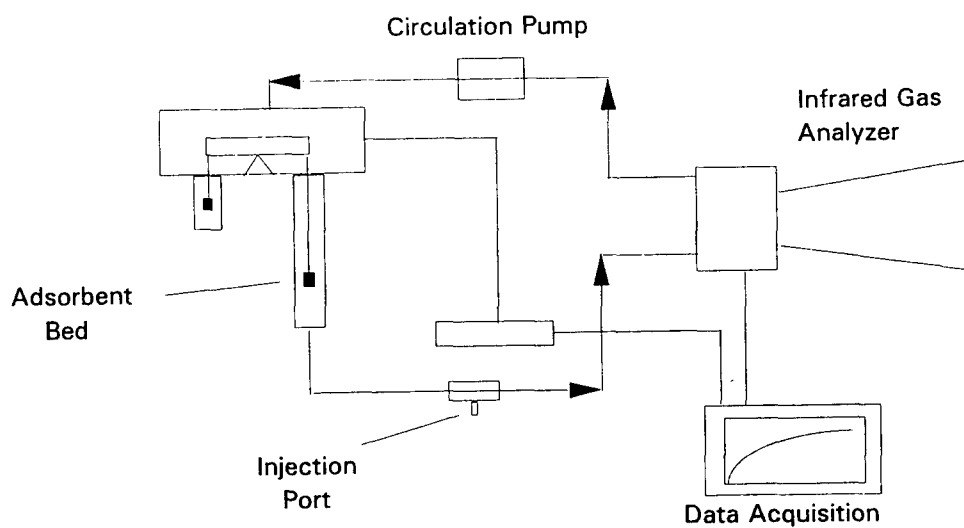robalance. The injected sample circulated through the system while passing across the adsorbent sample. During the equilibrium period, the IR analyzer measured the gas phase concentration while the output of the microbalance showed the weight increase due to adsorption of chloroform. An equilibrium value was recorded when there was no appreciable change in sample weight.

3.3   Dynamic Adsorption.

Chloroform breakthrough simulations of the RRS filter were measured on test beds representing a single RRS filter under continuous and intermittent feed conditions. The test conditions are summarized in Table 3. The continuous challenge tests provided information on the time to breakthrough, simulating long-term exposures at high and low vapor concentrations. A low concentration of 1.3 g/L represented a normal operation, and 10 g/L was selected to represent a sudden release of chloroform, possibly due to a spill.

Table 3. Test Conditions for Intermittent and Continuous Challenges

Bed Diameter	3.1 cm
Bed Area	7.54 cm^2
Bed Depth	5.1 cm
Flow Rate	4.1 L/min
Flow Velocity	9.1 cm/s
Relative Humidity	dry, 50% RH
Breakpoint Concentration	5.0 mg/m^3 (1.0 ppm)
Continuous Feed	130, 260, 390, 520 650, 967, 1732 g-min/m^3 100% breakthrough
Feed Concentration	1.3 and 10.0 g/m^3
Intermittent Feed	1300 g-min/m^3
Feed Concentration	1.3 g/m^3
Exposure Period	100 min
Purge Time (between feed)	14 hr

In an attempt to determine the maximum life of the filter, intermittent challenges of chloroform were run to simulate daily operations. In this investigation, a 100 min/day operation was considered reasonable. This time represented the period when the reactor was open, allowing chloroform to be released into the hood and subsequently passed through the filter. During the test, dry air was purged through the bed continuously. A repeated challenge occurred every 24 hr until a breakthrough concentration of 1.0 ppm at the effluent of the bed was recorded. The elapsed period of the test provided the useful life of the filter prior to replacement.

Dynamic adsorption tests were run on carbon samples containing <2% moisture (as-received) and with carbons equilibrated to 50% RH. The carbon samples were equilibrated overnight in a flowing airstream (through the bed) for 18 hr in a humidification chamber set at 50% RH and 80 °F. To determine the weight gain, the adsorbent was weighed before and after equilibration. Prior to testing, carbon samples were packed into glass tubes of uniform depth (5.1 cm) and diameter (3.0 cm).

A schematic of the dynamic adsorption apparatus is shown in Figure 4. The system included an RH control unit [Miller-Nelson (Monterey, CA) Model HCS-301], a sparger for disseminating the chloroform, a mixing manifold, dual test beds, and a gas chromatograph (GC) [Hewlett Packard (Baltimore, MD) 5890 Series II] for measuring the time-concentration profiles. The chloroform/air mixture was prepared by mixing 39 to 300 mg/min (depending upon the concentration desired) of chloroform with conditioned air (dry or 50% RH) at 30 L/min. Test beds were exposed to specific dosages as summarized in Table 3. At the end of the challenge period, air was purged through the sample beds, and the effluent was monitored until desorption occurred. The concentrations of chloroform upstream and downstream of the test beds were monitored by a GC, equipped with a flame ionization detector and capillary columns (VOCOL™, 105 m length x 0.53 mm o.d., 3.0 μm coating, Supelco 2-5358). Dosages were obtained by integrating the time-concentration plots of chloroform measured at the influent and effluent positions of the test beds.

4. RESULTS AND DISCUSSION

4.1 Glovebox Concentrations.

The values of chloroform concentrations expected to be encountered in the glovebox were estimated by experiment and model. Those values, which range from 70.2 to 158 g/min-m^2 at 25 °C, are shown in Table 4. Model predictions show that the evaporation rate ranged from 99 to 158 g-min/m^2 for airflow velocities at <0.3 m/s to as high as 0.5 m/s.

For the RRS, the actual operational airflow velocity is 0.08 m/s, and the reactor vessel area is 0.037 m^2. Based upon these two parameters, the calculated evaporation rate for chloroform is 129.7 g/min-m^2. The experimental values measured were lower than the model predictions (70.2-88.9 g/min-m^2) and may be due to the higher test velocities and smaller liquid areas of the samples evaluated. Also, intuitively, the 70.2 g/min-m^2 evaporation rate (taken at a velocity of 0.67 m/s and a liquid area of 0.0214 m^2) would have been expected to be higher than the 88.9 g/min-m^2, which was taken at a lower velocity and liquid area. This discrepancy in the experimentally determined evaporation rates should be accepted as being within experimental error.
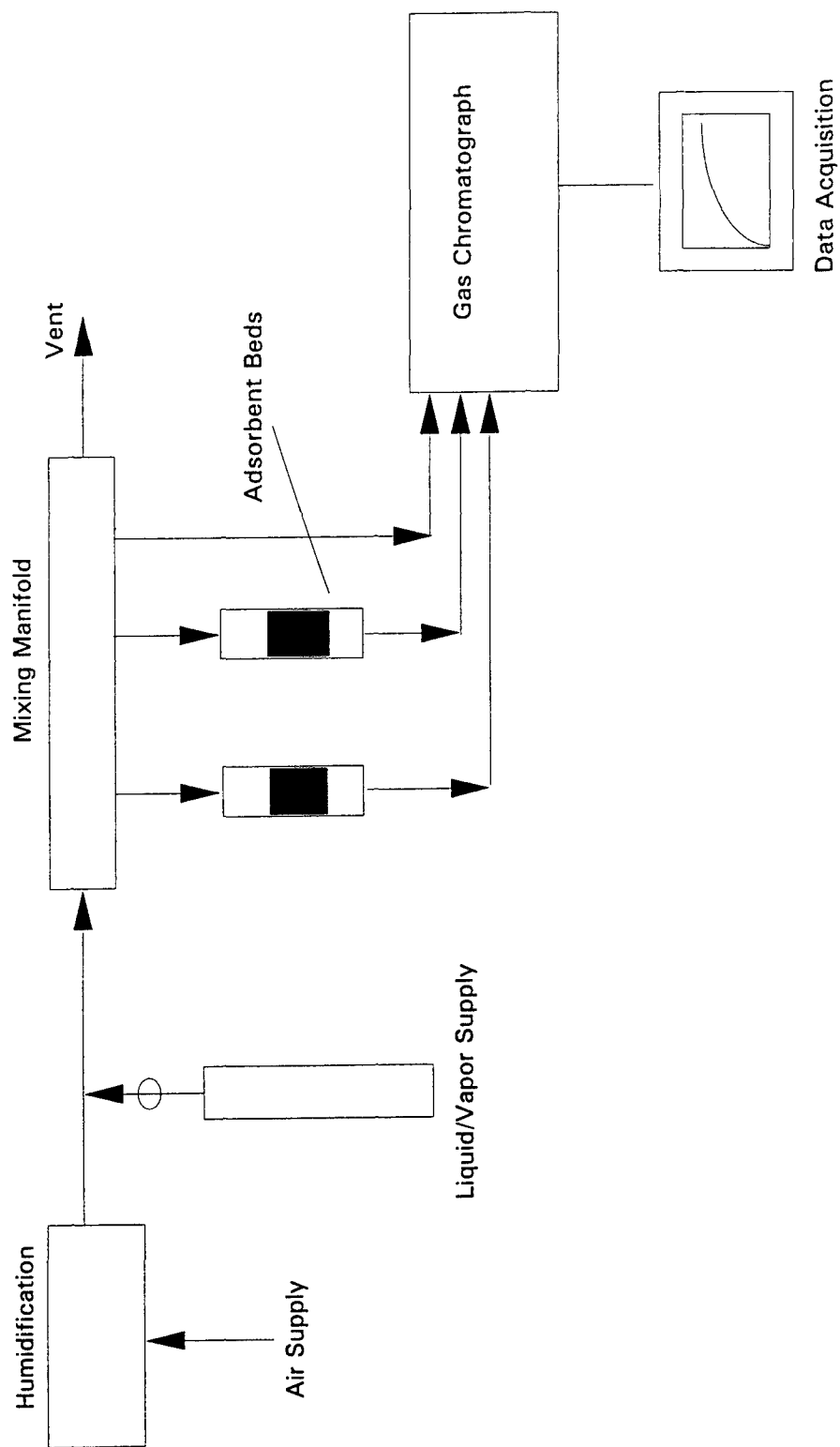
13

Figure 4. Schematic of Dynamic Adsorption Apparatus

14

Table 4. Estimate of Chloroform Concentration (Normal Operation)

Evaporation g/min-m^2	Velocity m/s	Liquid Area m^2
99	<0.3	0.100 model
158	0.5	0.100 model
129.7	0.08*	0.037 model*
88.9	0.35	0.0167 experiment
70.2	0.67	0.0214 experiment

*Actual operating conditions for RRS vessel and airflow velocity

In this study, a conservative value of 100 g/min-m^2 was used for the RRS simulation. Based on this value and the surface area of the reactor vessel (0.037 m^2), an evaporation rate of 3.7 g/min (specific to the RRS vessel) of chloroform was estimated. Given an airflow velocity range of 0.08-0.12 m/s at 100 and 150 cfm, respectively, a vapor concentration of 1.3-0.86 g/m^3 would result for each minute the reactor vessel is open, assuming there is no change in the evaporation rate constant. Note that at airflow velocities less than 0.2 m/s, the D2 model considers the air to be "still wind," and small changes in velocity below this value would not result in a significant change in evaporation rate. Also note that an increase in operating temperature and a reduction in atmospheric pressure will increase the evaporation rate, producing a higher vapor concentration.

A simple relationship of time of operation and dosage to the filter was determined per day and is shown in Table 5. A 100 min/day operation was selected in this study.

Table 5. Filter Dosages as a Function of Operation Time per Day
(Estimate is based on 100 cfm diluent.)

Time min/day	Dose g	Dilution L	Dosage mg-min/m^3
1	3.7	2830	1307
10	37	28300	13074
100	370	283000	130740
500	1855	1415000	653700

4.2   Adsorption Equilibria.

Figure 5 shows the measured isotherms for adsorption of chloroform (0-7.0 mg/L) on coconut carbon (Ionex) and the familiar BPL-grade activated carbon (Calgon Carbon). The shapes of both isotherms are favorable with improved linearity approaching the

15

Henry's law region below 0.1 mg/L ($P_i < 2.0\ Pa$). One sees in Figure 5 that the selectivity of the coconut carbon for chloroform is stronger than it is with BPL. This increased affinity at very low pressures is characteristic of the pore size distribution and surface chemistry unique to each material.
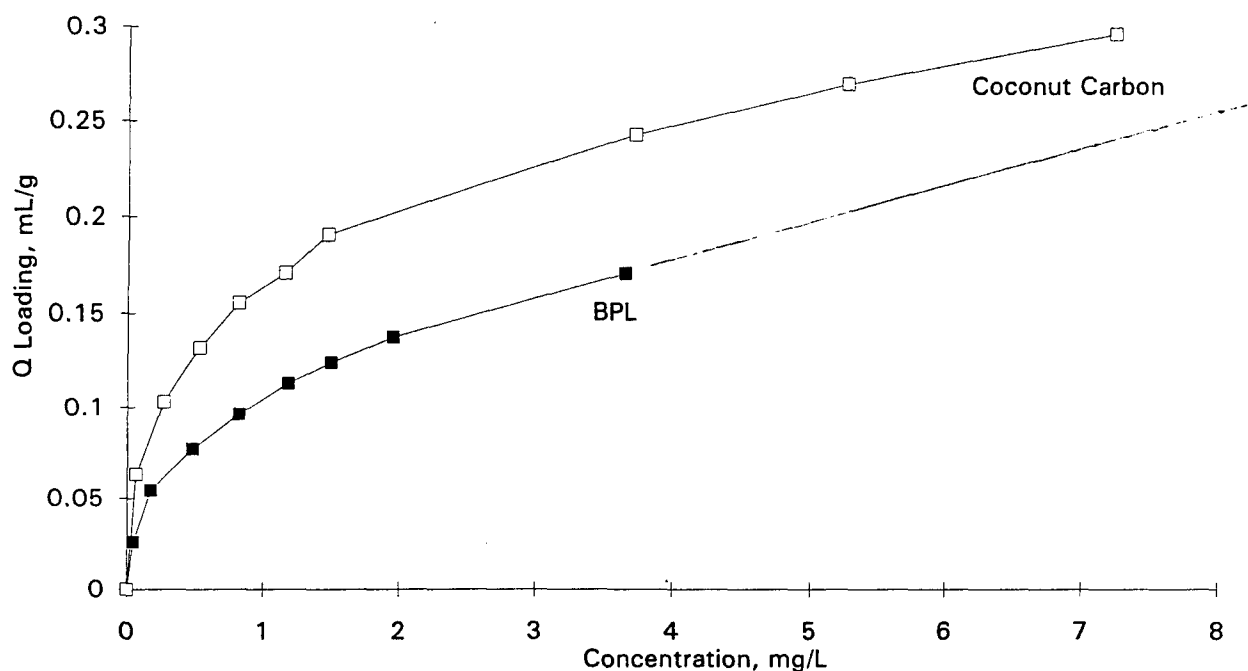

Figure 5. Isotherm of Chloroform on Coconut and BPL Activated Carbons

The slope of the isotherms in the linear region indicates chloroform's affinity for the adsorbent and can be represented by:

$$K_1 = Q_1/P_T X_i \tag{1}$$

where K_1 is the Henry's law constant (mmol/g/Pa) for chloroform and represents the limiting slope at infinite dilution ($P_i \rightarrow O$).[2,3] Q_1 is the amount of chloroform adsorbed (mmol/g) at an equilibrium gas phase mole fraction of x_i from a total pressure of P_T (Pa) and temperature equal to 25 °C. Analysis of this region shows that K_1 is estimated at 0.5675 mmol/g/Pa for the coconut carbon and 0.3190 mmol/g/Pa for the BPL carbon. The increased selectivity for the coconut carbon is most likely due to an increase in the number of micropores of higher energy, although differences in the surface chemistry may also influence the slope of the isotherm in this region.

16

The curved region of the isotherm for the coconut carbon falls between loadings of 0.094 to 0.283 g/g with an exponent equal to 0.36,

$$Q_2/Q_1 = (C_2/C_1)^{0.36} \tag{2}$$

The degree of curvature indicates the relative pore distribution sizes and their respective volumes in the micropore region.[4] A narrow distribution will yield a smaller exponent, n, and be characterized by more rapid curvature. This behavior is typical of nutshell carbons where a greater number of pores fall in a relatively narrow size range and contain a significant micropore volume. Similar analysis of chloroform adsorption on BPL carbon shows a wider pore distribution ($n = 0.50$) and a lower adsorption capacity in the micropore region.

At higher loadings, the isotherm for the coconut carbon once again becomes approximately linear out to the maximum measured concentration of 7.2 mg/L ($P_i = 149.6$ Pa). The adsorption capacity increases to 0.29 mL/g. In this region, adsorption is characterized by chloroform layering as opposed to pore-filling seen at lower pressures.[5] Figure 6 shows a log-log plot of adsorption capacity and relative pressure using the Dubinin-Radushkevich expression for both BPL and coconut carbons. Extrapolation to the y-intercept (*log Q*, mL/g) indicates that 37.7% (0.77 mL/g) of the total micropore volume is occupied at 7.2 mg/L vapor concentration for the coconut carbon. By comparison, BPL's micropore volume is estimated to be 0.24 mL/g at 7.2 mg/L and occupies 48% (0.50 mL/g) of the total micropore volume.
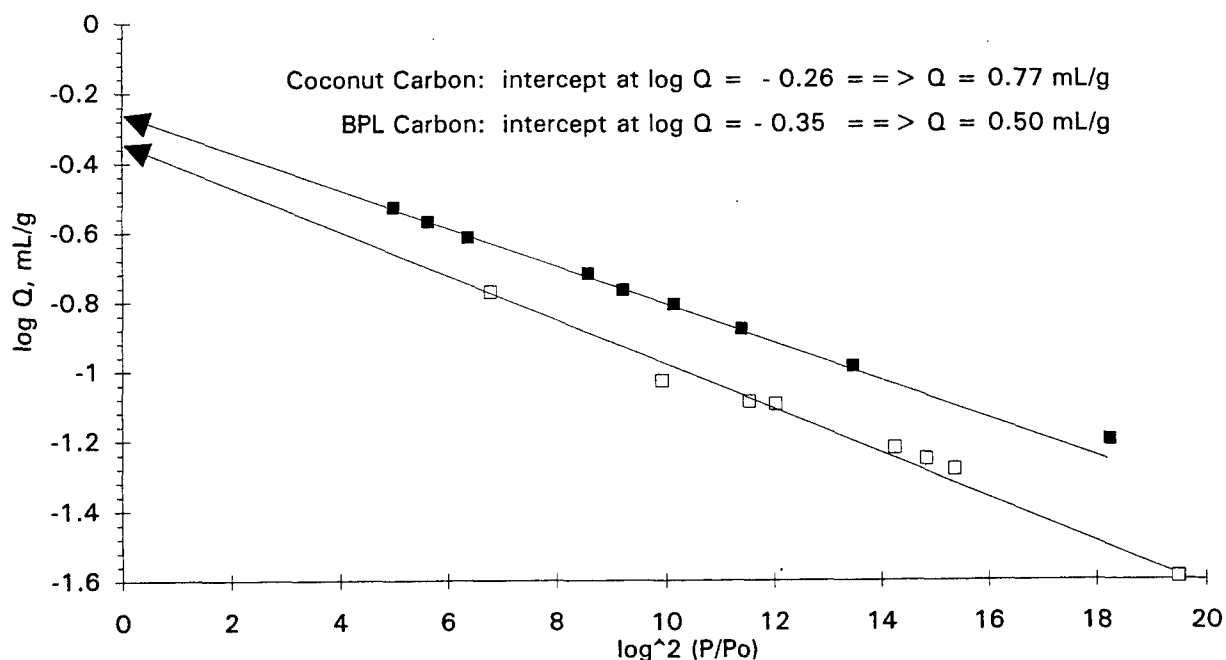

Figure 6. Plot of Micropore Volume Plot of Coconut and BPL Carbons Using the Dubinin-Radushkevich Equation

Based on the above results, it is anticipated that the coconut carbon would perform better than the BPL grade carbon under dynamic adsorption conditions. Yet, neither grade of carbon produces an isotherm that is ideal for adsorption (high uptake) and desorption (high retention/low desorption). In principle, the more favorable an isotherm, the less favorable desorption will become. Therefore, under purge conditions (zero adsorbate), desorption will result as governed by isotherm shape. The advantage of a steep isotherm followed by an extensive plateau (Figure 5) is that desorption can be minimized under reduced vapor concentrations. The coconut carbon, having a higher affinity (initial slope) for chloroform than BPL, also has a greater adsorption capacity. However, in the region up to about 1.5 mg/L vapor concentration, the selectivity (i.e., isotherm slope at low loadings) for chloroform falls rapidly for both carbons yet continues to climb. In this transition, the adsorbed phase loading (slope is decreasing) changes significantly with a change in the vapor phase concentration. During dynamic adsorption, similar changes are anticipated in addition to kinetic factors, resulting in desorption during purge and spreading of the concentration zone.

4.3   Chloroform Breakthrough.

Based upon the physical parameters of the RRS (i.e., reactor size, glove box airflow velocity), a range of challenge concentrations from 1.3 and 10 g/m^3 was established for this testing to simulate RRS operations (Section 4.1). The times to achieve an effluent concentration of 1.0 ppm (5.0 mg/m^3) of chloroform were measured on test beds whose carbon depth and airflow velocity simulated the RRS filter. Total challenge dosages ranging from 390 to 1732 g-min/m^3 of chloroform were evaluated.

All data were recorded under continuous feed except for the lowest dosage (390 g-min/m^3), which was evaluated for both continuous feed and an intermittent feed of three dosages of 130 g-min/m^3 each. Breakthrough time decreased with increasing dosage, as anticipated. At the 10 g/m^3 challenge, the test was run to breakthrough (5.0 mg/m^3) in 173 min. Based upon the flattening shape (decreasing slope) of the chloroform adsorption isotherm, this measurement provided the maximum dosage the bed could withstand under a continuous feed condition, which is equal to 1732 g-min/m^3. At 1.3 g/m^3, the time to breakthrough is increased to 711 min. The measured capacity is reduced to 925 g-min/m^3 because of the changing shape of the isotherm.

Note the effect of purge.volume on time to breakthrough at reduced dosages and the effect it has on spreading the wavefront deeper into the bed. At dosages of 650 and 520 g-min/m^3, breakthrough occurs at 850 and 1200 min, respectively, indicating that the wavefront continued to advance with increasing purge volume. The capacity of the bed is reduced at decreasing dosages under continuous purge conditions. If no spreading occurred (as in the case of strongly adsorbed materials such as mustard), the length of the wavefront would be proportional to the zone length for the maximum dosage less the critical bed depth. At dosages less than capacity, no amount of purge would advance the wave. However, for a chloroform challenge with decreasing dosage and increasing purge volume, the wavefront slowly advances in a manner similar to a chromatogram.

Figure 7 shows that a test under continuous feed at 390 g-min/m^3 (at 1.3-g/m^3 feed) produces breakthrough in 1550 min, with a total purge volume of 5125 L (to breakpoint). Figure 7 also shows the 390 g-min/m^3 dosage test, which consisted of three intermittent challenges of 130 g-min/m^3 each. By comparison to the continuous feed test, the intermittent challenge time to breakthrough is 3655 min for the same total dosage
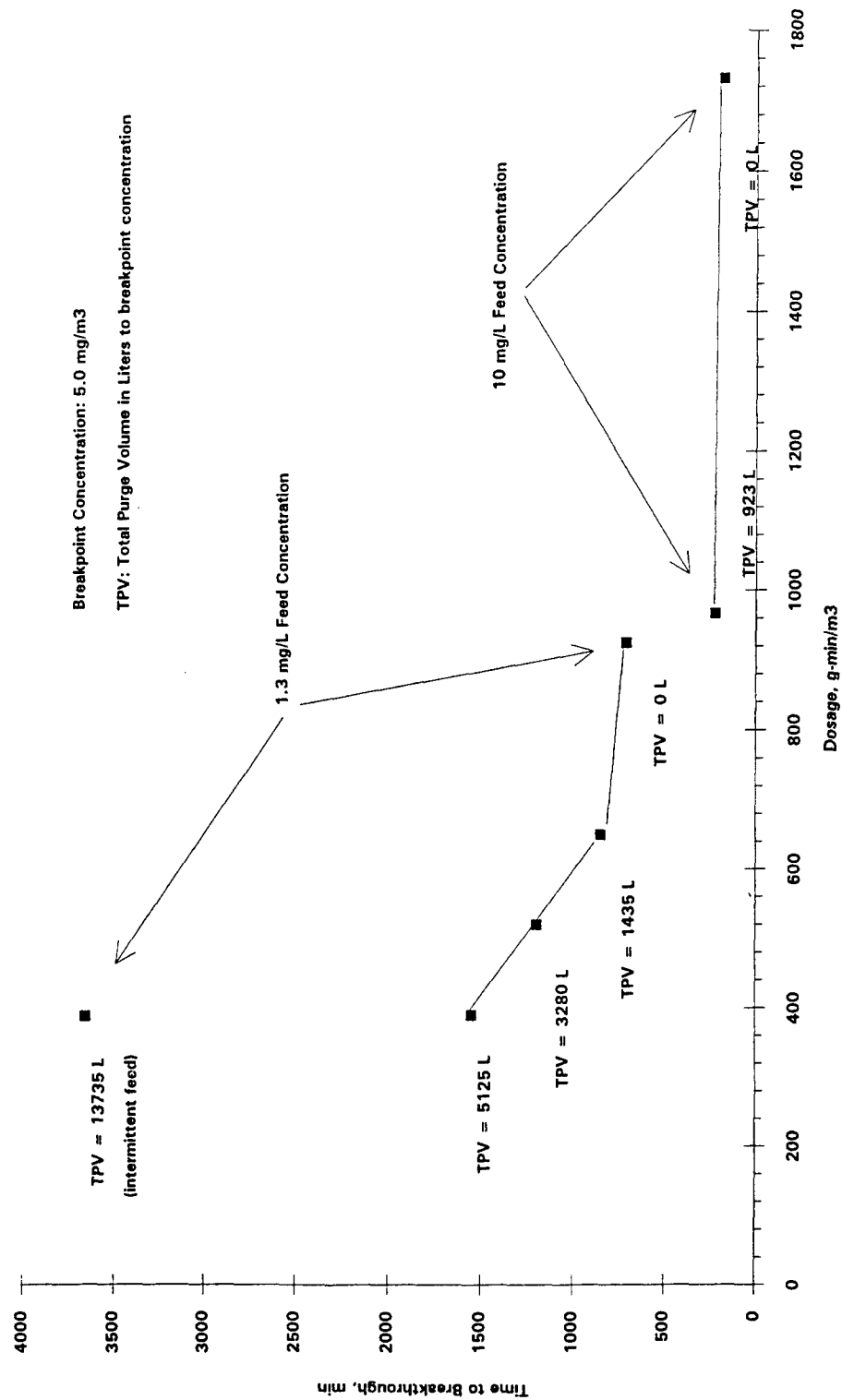
Figure 7. Effect of Chloroform Dosage on Time to Breakthrough on Coconut Carbon (<2% moisture)

(390 g-min/m³). The cumulative purge volume (which includes the purge times between the three individual challenges of 130 g-min/m³) was 13735 L. The specific time intervals associated with the intermittent challenge test are presented in Figure 8. Specifically, the individual challenges were delivered at 1500-min intervals until breakthrough occurred. As discussed in Sections 3.1 and 4.1, this test simulated the most realistic exposure to chloroform during a typical RRS operation.

Overall, the intermittent challenge test had a total purge volume of 13735 L compared to only 5125 L for the continuous challenge test. However, if one compares the purge volume after both carbon beds received the entire 390 g-min/m³ challenge, the intermittent test had a final purge volume (after the third incremental challenge) of only 2895 L versus the previously mentioned purge volume of 5125 L for the continuous challenge test. If the zone lengths were proportional to dosage and not affected by purge volume, then the purge volume (and dosage) to breakthrough would be identical for continuous and intermittent runs. A lower purge volume (to breakthrough) indicates a longer mass transfer zone due to spreading. The reduction in purge volume between the intermittent and continuous tests, from 5125 to 2895 L (the volume following the third intermittent dosage to breakthrough), suggests that spreading occurred beyond the length proportional to the dosage level. Although it appears that the intermittent tests provided a longer operating life, the actual working capacity of the adsorbent bed is reduced.

The above analysis shows that an increase in the useful life of the RRS filter can be obtained by reducing the purge volume between operations. Assuming each RRS neutralization operation generates a 130 g-min/m³ feed, the capacity of the bed under continuous feed is approximately 925 g-min/m³ or seven reactor cycles. If the purge volume is either eliminated or reduced to a minimum between operations, the filter life could be extended from 2 to 7 days.

4.4   Adsorption at 50% RH.

The moisture contents of the carbon samples tested as-received and at 50% RH are shown in Table 6. As anticipated, the weight pick-up of moisture is relatively low (8.2% coconut, 3.8% BPL), reflecting the hydrophobic properties of activated carbons. The higher weight pick-up of the coconut carbon is due to an increase in the number of smaller pores with a higher volume than BPL, as indicated in the chloroform adsorption isotherms.

Table 6. Equilibrium Capacities of Chloroform on Coconut and BPL Adsorbents

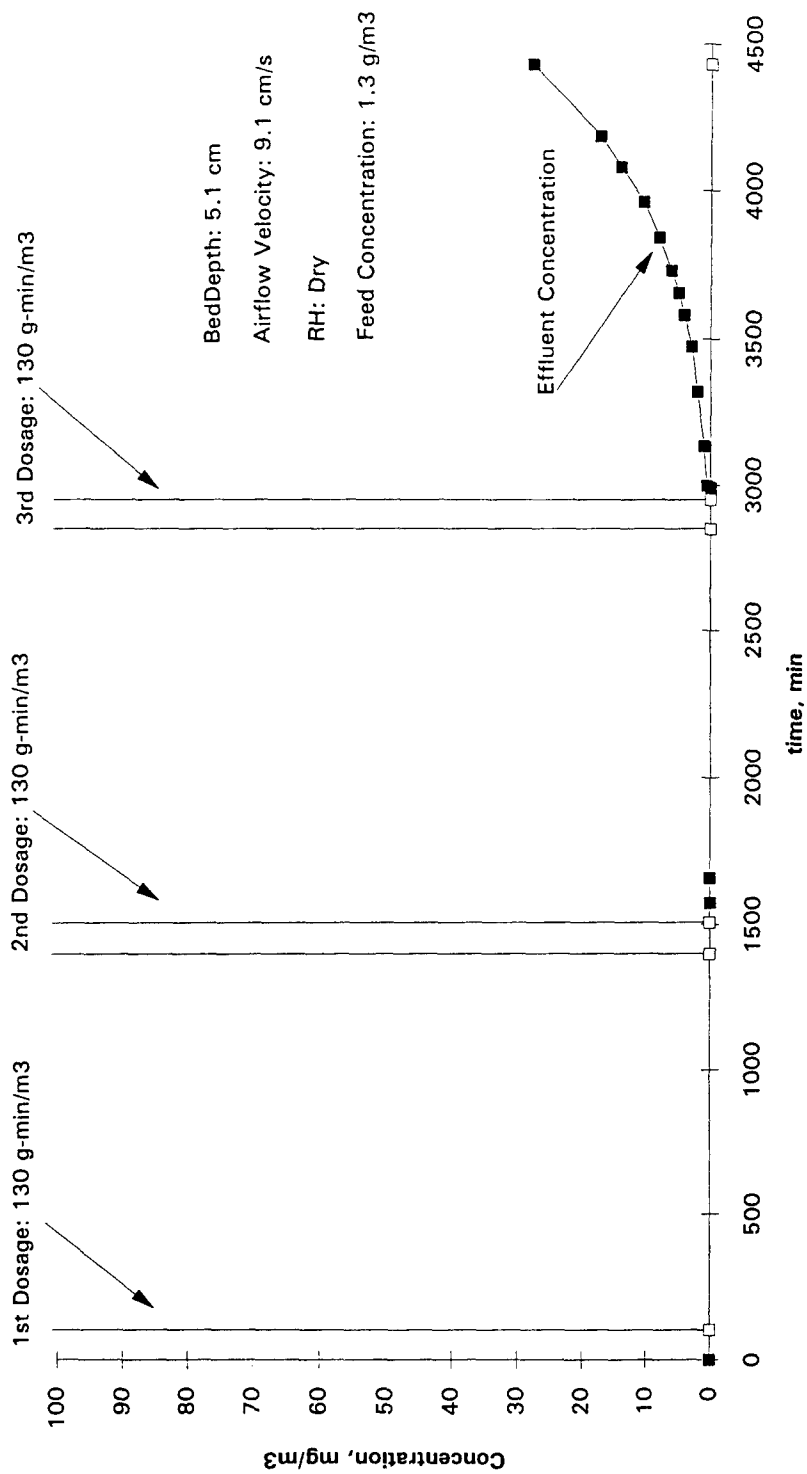|		Q, mL/g	
Adsorbent	Method	Dry	50% RH
Ionex	Dynamic	0.397	0.337
BPL		0.287	0.282
Ionex	Isotherm	0.337	----
BPL		0.297	----

Figure 8. Breakthrough of Chloroform Fed Intermittently on Coconut Carbon (<2% moisture)

In Figure 9, the chloroform breakthrough on dry and moisture-laden carbons is shown under a continuous feed of 10 g/m³. A 25% reduction in breakthrough time is measured for the coconut carbon, resulting in a 43-min loss in filter life. In comparison, the effect of moisture content (50% RH) on breakthrough time is negligible for BPL carbon.

Equilibrium capacities estimated from the stoichiometric centers of complete breakthrough curves (100% feed) support the observed change in breakthrough time with moisture content (Figure 9). Note that the equilibrium capacities for the dry samples are in good agreement with the adsorption isotherm values discussed in Section 4.2. Table 6 shows that a 15% reduction in chloroform capacity is obtained at 50% RH for the coconut carbon.

At lower dosages, the effect of increased moisture is more dramatic on reducing the time to breakpoint (Figure 10). At a dosage of 1000 g-min/m³, the breakpoint is 220 min (dry) and is reduced to 150 min (50% RH). The reduction in filter life is due to the apparent speed of the wavefront as it is increased due to the loss of higher energy sites occupied by moisture.

5. CONCLUSIONS

The following conclusions result from the study conducted:

Chloroform vapor concentrations of approximately 1.3 g/m³ can result during normal RRS decontamination operations. This is based on an evaporation rate of 3.7 g/min from a reactor vessel surface area of 0.037 m², at 25 °C, 1.0 atm pressure and 100 cfm airflow.

The isotherms for BPL and coconut carbons indicate that the coconut carbon has a higher affinity for chloroform (at very low partial pressures) than the BPL carbon. At higher concentrations, the chloroform capacity of the coconut carbon is 0.29 mL/g versus 0.25 mL/g for BPL carbon.

The maximum chloroform capacity of an 8 x 16 mesh coconut carbon RRS filter (as estimated using laboratory tube samples) is 925 g-min/m³ for a continuous challenge of 1.3 g/m³ and 1732 g-min/m³ for a continuous challenge of 10.0 g/m³.

A total dosage of 130 g-min/m³ was used as a reasonable estimate of the dosage likely to be encountered by the RRS filter during daily operations. This value assumes approximately 3 neutralization cycles taking a total of 100 min with a challenge concentration of 1.3 g/m³.

Intermittent challenge testing with chloroform at 1.3 g/m³ was conducted on 8 x 16 mesh coconut carbon at the bed depth and airflow velocity associated with actual RRS filters. Three challenges of 130 g-min/m³ were conducted with continuous air purging between each challenge. The challenge dosages were 1500 min apart. A breakthrough concentration of 5.0 mg/m³ did not occur until after a total purge volume of 13735 L of clean air had passed through the simulated filter. The elapsed time to the break concentration was 3655 min. This test simulated 3 days of RRS neutralization operations.
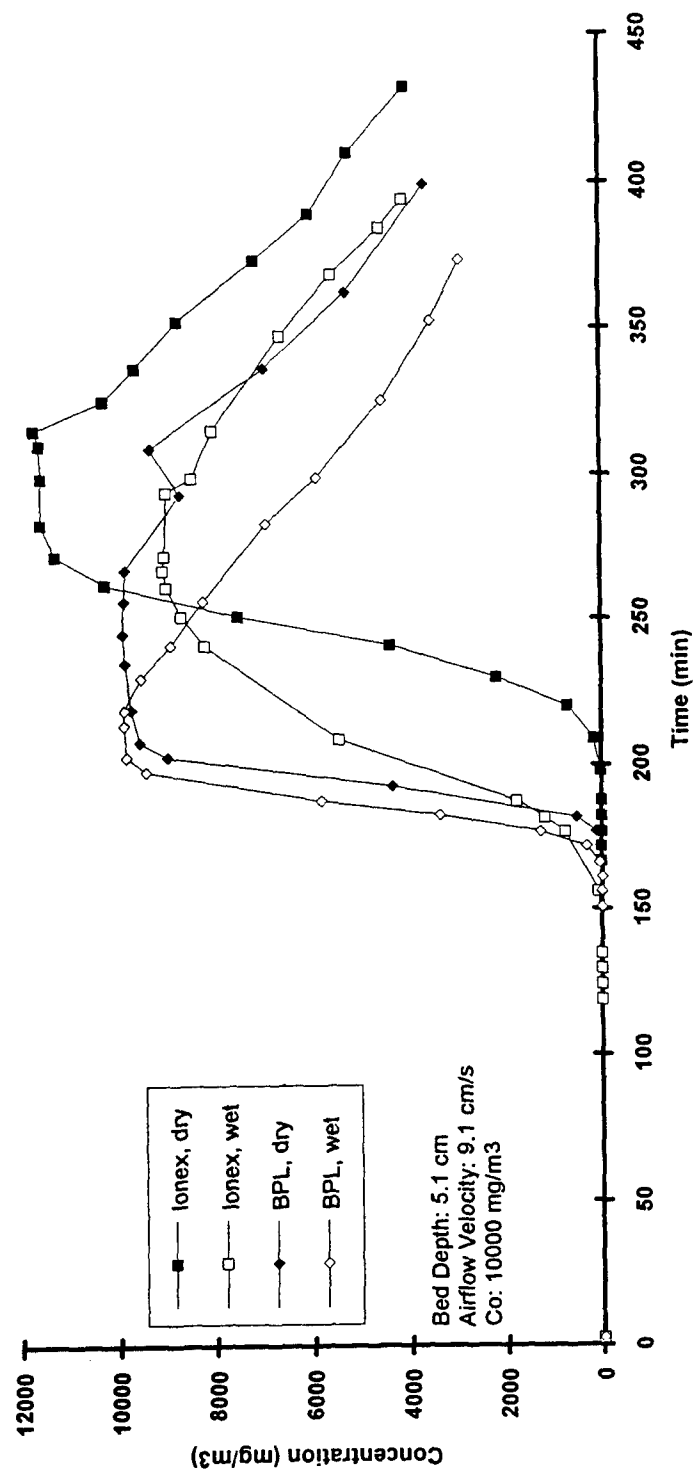
Figure 9. Chloroform Dosage on Time to Breakthrough for 8 x 16 Mesh Coconut Carbon
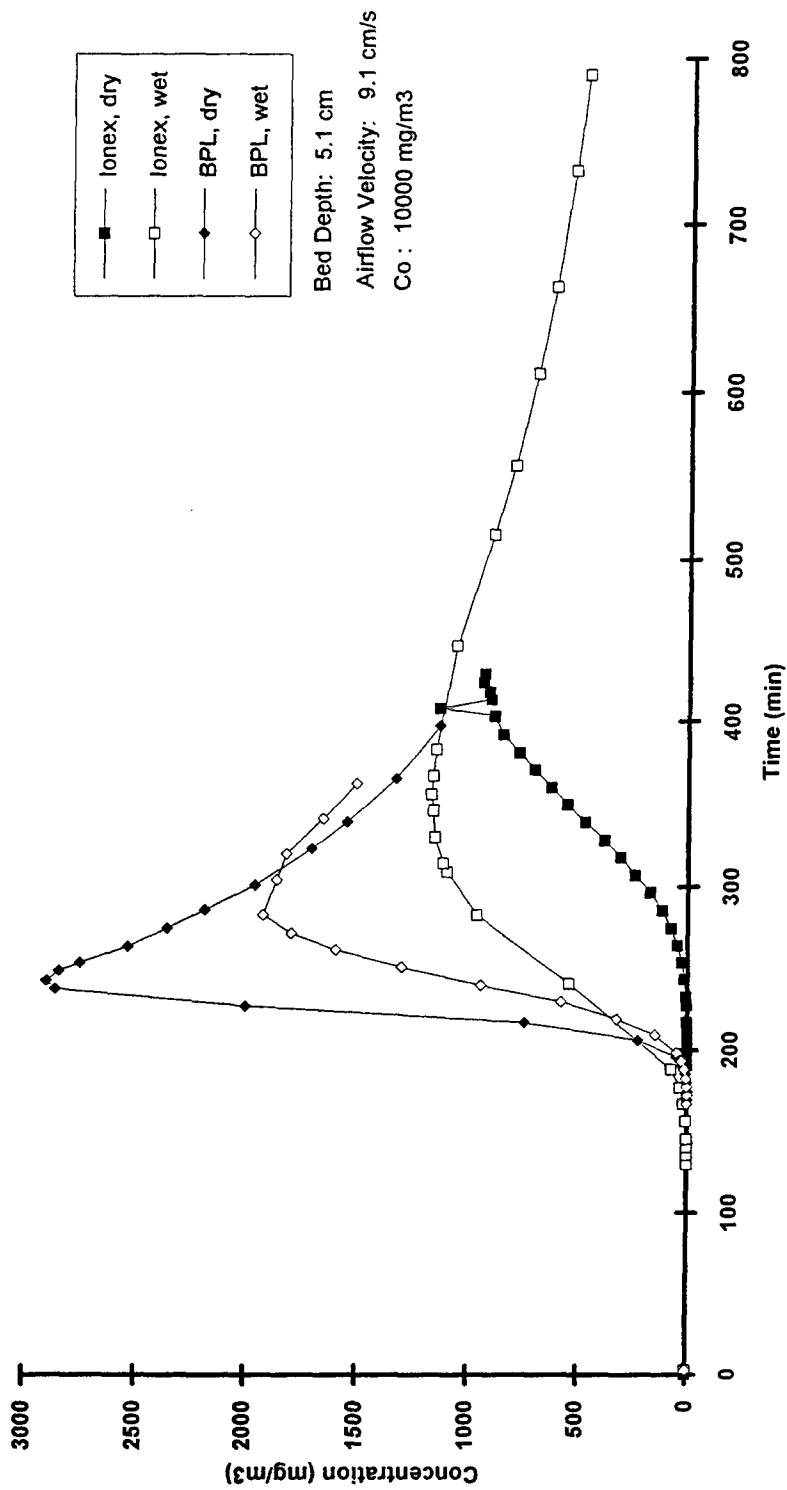
23

Figure 10. Breakthrough of Chloroform Following a 100-Min Dosage on Dry and 50% RH Carbons

24

Based upon the estimated evaporation rates used, the RRS system could theoretically operate for 2+ days conducting neutralization operations with chloroform (100 min total challenge each day at 1.3 g/m^3) before a filter change would be required.

For comparative purposes, continuous challenge testing with chloroform at 1.3 g/m^3 was conducted on 8 x 16 mesh coconut carbon at the bed depth and airflow velocity associated with actual RRS filters. A single challenge of 390 g-min/m^3 was "fed" to the carbon sample. At the conclusion of the challenge, a clean air purge continued until the effluent concentration (break) of 5.0 mg/m^3 was achieved. Breakthrough occurred after 5125 L of clean air had passed through the simulated filter. The elapsed time to the break concentration was 1550 min.

As demonstrated by the differences in carbon performance between the intermittent and continuous filter challenges, the chloroform wavefront continues to migrate across the filter bed during clean air purge. Therefore, for any fixed challenge dosage tested herein, the chloroform will eventually penetrate the 8 x 16 mesh coconut carbon filter bed. Hence, the capacity of the RRS carbon filter is reduced to equal the challenge dosage under continuous purge conditions.

For a chloroform challenge of 10 g/m^3, coconut carbon that was equilibrated to 50% RH showed a 25% reduction in the chloroform filtration performance. This 25% reduction was equivalent to a 43-min loss in filter "life." The effect of moisture content (50% RH) on the breakthrough time of BPL carbon was negligible.

The RRS operations conducted worldwide over a variety of environmental conditions (filtered air relative humidity) will result in a wide variation in coconut filter adsorption performance for chloroform. Insufficient data were taken during this evaluation to quantify filter performance at high relative humidities.

Blank

26

LITERATURE CITED

1. Jonas, L.A. *et al*, "The Effect of Moisture on the Adsorption of Chloroform by Activated Carbon," J. Amer. Ind. Hyg. Assoc., Vol. 46 (1) (1985).

2. Adamson, A.W., Physical Chemistry of Surfaces, 5th Ed., John Wiley and Sons, Incorporated, New York, NY, 1990.

3. Golden, T.C., and Sircar, S., Equilibrium and Kinetics of Adsorption of Freon-12 at Infinite Dilution, AICHE Journal, Vol. 40 (6) (1994).

4. Gregg, S.J., and Sing, K.S-W., Adsorption, Surface Area and Porosity, 2nd Ed., Academic Press, New York, NY, 1982.

5. Ruthven, D.M., Principles of Adsorption and Adsorption Processes, John Wiley & Sons, New York, NY, 1984.

STANDARD B

DEPARTMENT OF THE ARMY
CDR USACBDCOM
ATTN AMSCB CIR M
5232 FLEMING ROAD
APG MD 21010-5423

OFFICIAL BUSINESS