



# EDGEWOOD

CHEMICAL BIOLOGICAL CENTER

U.S. ARMY RESEARCH, DEVELOPMENT AND ENGINEERING COMMAND

ECBC-TR-658

**A RESIDUAL LIFE INDICATOR (RLI)  
FOR PHYSICAL ADSORPTION CAPACITY  
OF NUCLEAR, BIOLOGICAL, AND CHEMICAL FILTERS**

**PART III**

**A NOVEL RLI DESIGN FOR COLLECTIVE PROTECTION  
DEMONSTRATED USING BREAKTHROUGH AND  
CHEMICAL PULSE DATA**



David Friday  
Marc Shrewsbury  
Scott Deibert

HUNTER APPLIED RESEARCH CENTER  
Edgewood, MD 21040

Gregory W. Peterson

RESEARCH AND TECHNOLOGY DIRECTORATE

November 2008

Approved for public release;  
distribution is unlimited



# 20081230007

ABERDEEN PROVING GROUND, MD 21010-5424

## 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.

# REPORT DOCUMENTATION PAGE

*Form Approved*  
OMB No. 0704-0188

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 this 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 Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. **PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.**

<b>1. REPORT DATE (DD-MM-YYYY)</b> XX-11-2008		<b>2. REPORT TYPE</b> Final		<b>3. DATES COVERED (From - To)</b> Jun 2006 - Nov 2007	
<b>4. TITLE AND SUBTITLE</b> A Residual Life Indicator (RLI) for Physical Adsorption Capacity of Nuclear, Biological, and Chemical Filters, Part III, A Novel RLI Design for Collective Protection Demonstrated Using Breakthrough and Chemical Pulse Data				<b>5a. CONTRACT NUMBER</b> 5E22A	
				<b>5b. GRANT NUMBER</b>	
				<b>5c. PROGRAM ELEMENT NUMBER</b>	
<b>6. AUTHOR(S)</b> Friday, David; Shrewsbury, Marc; Diebert, Scott (HARC); and Peterson, Gregory W. (ECBC)				<b>5d. PROJECT NUMBER</b> BA05PRO102	
				<b>5e. TASK NUMBER</b>	
				<b>5f. WORK UNIT NUMBER</b>	
<b>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)</b> DIR, ECBC, ATTN: AMSRD-ECB-RT-PF, APG, MD 21010-5424 Hunter Defense Technologies, Applied Research Center 2109 Emmorton Park Road, Suite 120, Edgewood, MD 21040				<b>8. PERFORMING ORGANIZATION REPORT NUMBER</b> ECBC-TR-658	
<b>9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)</b> Defense Threat Reduction Agency 8725 John J. Kingman Road, Room 3226 Fort Belvoir, VA 22060-6201				<b>10. SPONSOR/MONITOR'S ACRONYM(S)</b> DTRA	
				<b>11. SPONSOR/MONITOR'S REPORT NUMBER(S)</b>	
<b>12. DISTRIBUTION / AVAILABILITY STATEMENT</b> Approved for public release; distribution is unlimited.					
<b>13. SUPPLEMENTARY NOTES</b>					
<b>14. ABSTRACT</b> We start by simulating the condition of a fielded filter by selecting representative threat vapors and representative contaminant vapors. We assume that only contaminants that are moderately and strongly adsorbed can affect the residual life. A simulated contaminated filter is configured using contaminated carbon at the bed inlet and fresh carbon at the bed outlet. Breakthrough experiments are then completed using an organic to simulate the threat vapor. These data define "residual life" based on relative humidity (RH), threat vapor, contaminant chemical, and the extent of bed contamination. Using a novel residual life indicator approach that employs dual satellite beds, one sampling the filter air inlet and one sampling the filter outlet, chemical pulse tests are conducted. Simulated contaminated beds are tested at different RHs. The difference between the reference bed effluent concentration profile and the contaminated bed effluent concentration profile is correlated to the residual life using a simple algorithm.					
<b>15. SUBJECT TERMS</b> Acetone Organic contamination Pulse testing Physical adsorption capacity Residual life indicator (RLI)					
<b>16. SECURITY CLASSIFICATION OF:</b>			<b>17. LIMITATION OF ABSTRACT</b>	<b>18. NUMBER OF PAGES</b>	<b>19a. NAME OF RESPONSIBLE PERSON</b>
<b>a. REPORT</b>	<b>b. ABSTRACT</b>	<b>c. THIS PAGE</b>			<b>19b. TELEPHONE NUMBER (include area code)</b>
U	U	U	UL	49	Sandra J. Johnson 410-436-2914

Blank

## PREFACE

The work described in this report was authorized under Project No. BA05PRO102. This work was started in June 2006 and completed in November 2007.

The use of either trade or manufacturers' names in this report does not constitute an official endorsement of any commercial products. This report may not be cited for the purposes of advertisement.

This report has been approved for public release. Registered users should request additional copies from the Defense Technical Information Center; unregistered users should direct such requests to the National Technical Information Service.

Blank

## CONTENTS

1.	INTRODUCTION .....	1
1.1	Background .....	1
1.2	Classification of Threat Vapors for RLI Purposes.....	2
1.3	Approach to Estimating Residual Life of a Filter .....	2
2.	BREAKTHROUGH TESTING.....	3
2.1	Simulated Contaminated Filter .....	3
2.2	Breakthrough Apparatus and Procedure .....	4
2.3	Breakthrough Test Results .....	5
2.3.1	Hexane Challenge/Octane Contaminant .....	7
2.3.1.1	Effect of RH .....	7
2.3.1.2	Effect of Contaminant Loading .....	8
2.3.1.3	Effect of Contaminated Bed Fraction .....	8
2.3.2	Hexane Challenge/Dodecane Contaminant .....	10
2.3.2.1	Effect of RH .....	10
2.3.2.2	Effect of Contaminant Loading .....	10
2.3.2.3	Effect of Contaminated Bed Fraction .....	11
2.3.3	Nonane Challenge/Octane Contaminant.....	13
2.3.4	Nonane Challenge/Dodecane Contaminant .....	14
2.3.4.1	Effect of RH.....	14
2.3.4.2	Effect of Contaminant Loading .....	14
2.3.4.3	Effect of Contaminated Bed Fraction .....	15
2.4	Summary of Breakthrough Results.....	16
3.	PULSE TESTING.....	18
3.1	Pulse Testing Concept and Approach .....	18
3.2	Pulse Testing System Apparatus and Procddure.....	19
3.2.1	Apparatus .....	19
3.2.2	Bed Preparation.....	20
3.2.3	Test Procedure .....	21
3.3	Pulse Test Results .....	21
3.3.1	Testing Overview and Experiment Summary .....	22
3.3.2	Octane Contaminant Results.....	22
3.3.2.1	15% RH.....	23
3.3.2.2	50% RH.....	25
3.3.2.3	80% RH.....	26
3.3.3	Dodecane Contaminant Results .....	28
3.3.3.1	15% RH.....	28
3.3.3.2	50% RH.....	29
3.3.3.3	65% RH.....	31

3.3.3.4	80% RH.....	31
3.4	Pulse Testing Summary .....	33
4.	RLI CORRELATION.....	33
5.	SUMMARY .....	38
	LITERATURE CITED .....	41

## FIGURES

2.1	Bed Configuration for Simulated Containment Filter .....	4
2.2	Test System Schematic .....	5
2.3	Hexane Challenge with Octane Contaminant at 15% RH .....	9
2.4	Hexane Challenge with Octane Contaminant at 50% RH .....	9
2.5	Hexane Challenge with Octane Contaminant at 80% RH .....	10
2.6	Hexane Challenge with Dodecane Contaminant at 15% RH.....	11
2.7	Hexane Challenge with Dodecane Contaminant at 50% RH.....	12
2.8	Hexane Challenge with Dodecane Contaminant at 80% RH.....	12
2.9	Nonane Challenge with Octane Contaminant at 15% RH.....	13
2.10	Nonane Challenge with Octane Contaminant at 80% RH.....	14
2.11	Nonane Challenge with Dodecane Contaminant at 15% RH .....	15
2.12	Nonane Challenge with Dodecane Contaminant at 80% RH .....	16
3.1	RLI Pulse Apparatus P&ID .....	20
3.2	Results for 0.1 g/g Octane Loading at 15% RH Using PFCB .....	24
3.3	Results for 0.2 g/g Octane Loading at 15% RH Using PFCB .....	24
3.4	Results for 0.1 g/g Octane Loading at 50% RH Using PFCB .....	25
3.5	Results for 0.2 g/g Octane Loading at 50% RH Using PFCB .....	26
3.6	Results for 0.1 g/g Octane Loading at 80% RH Using R123 .....	27
3.7	Results for 0.2 g/g Octane Loading at 80% RH Using R123 .....	27
3.8	Results for 0.1 g/g Dodecane Loading at 15% RH Using PFCB.....	28
3.9	Results for 0.2 g/g Dodecane Loading at 15% RH Using PFCB.....	29
3.10	Results for 0.1 g/g Dodecane Loading at 50% RH Using PFCB.....	30

3.11	Results for 0.2 g/g Dodecane Loading at 50% RH Using PFCB.....	30
3.12	Results for 0.2 g/g Dodecane Loading at 65% RH Using PFCB.....	31
3.13	Results for 0.1 g/g Dodecane Loading at 80% RH Using R123.....	32
3.14	Results for 0.2 g/g Dodecane Loading at 80% RH Using R123.....	32

## TABLES

2.1	Simulant and Agent Properties .....	6
2.2	Contaminant Properties.....	6
2.3	Complete List of Breakthrough Experiments .....	7
2.4	Estimated Breakthrough Times Using MTZ that is 35% of Bed.....	18
3.1	Pulse Gas Properties .....	22
3.2	Complete List of Pulse Experiments .....	22
4.1	Summary of PFCB with Octane as Contaminant .....	35
4.2	Summary of PFCB with Dodecane as Contaminant.....	35
4.3	Summary of 80% RH Experiments Using R123 .....	36
4.4	Break Time, Mass Ratio Comparison with Octane as Contaminant .....	37
4.5	Break Time, Mass Ratio Comparison with Dodecane as Contaminant.....	37

# A RESIDUAL LIFE INDICATOR (RLI) FOR PHYSICAL ADSORPTION CAPACITY OF NUCLEAR, BIOLOGICAL, AND CHEMICAL FILTERS

## PART III

### A NOVEL RLI DESIGN FOR COLLECTIVE PROTECTION DEMONSTRATED USING BREAKTHROUGH AND CHEMICAL PULSE DATA

#### 1. INTRODUCTION

##### 1.1 Background

Estimating the remaining filtration capacity of a filter has been investigated for more than 20 years. Typically, these efforts have been divided into two types of indicators, namely, (1) end-of-service life and (2) residual filter life end. An end-of-service life indicator (ESLI) refers to a method of detecting a toxic chemical eluting through a filter during a chemical event. In collective protection (ColPro) applications, this may not be as useful as determining the residual life prior to a chemical event since filter change-out during that event is not practical (or possibly even feasible). A typical example of an ESLI is a device that changes color when exposed to a given chemical or group of chemicals. We will discuss the problems with this in the next paragraphs. Is an ESLI that responds specifically to cyanogen chloride (CK) or Sarin (GB) really useful? At what concentration does the sensor respond? What is the protocol following a sensor response? How many potential threats do NOT respond to the detector? Given all of these questions, what is the real value of an ESLI that responds to one or two chemicals?

The filter "residual life" is the remaining filtration capacity of filter and whether it should be subjected to a chemical event is the focus of this report. Specifically, we will demonstrate how ambient contaminants can degrade filter capacity during peacetime operations. Many previous efforts have been conducted to estimate the residual life of filters.<sup>1-9</sup> While most of them produced little or no useful results, even those efforts that did provide some valuable insight into a residual life indicator (RLI) failed to answer the fundamental question: what is the residual life of the filter with respect to specific challenge gas or gases? This work attempts to address this question in its entirety by first addressing only those gases that are affected by adsorbed contaminants.

Assessing the residual life of collective protection filters is particularly important, since unlike individual protection filters, it is much more difficult and expensive to change them. In fact, the current military requirement for individual protection is to have the capability to change filters in a chemically contaminated environment. This is clearly not possible for collective protection filters. Current change-out doctrine for collective protection filters is based solely on time-in-service. Using this approach, it is very likely that good filters are changed too early (increasing life cycle cost) and poor filters remain in service too long (potential protection risk).

## 1.2 Classification of Threat Vapors for RLI Purposes

Generally speaking, one can divide threat vapors into two categories in terms of removal mechanisms by ASZM-TEDA: (1) those vapors removed primarily by physical adsorption [e.g. GB and Distilled Mustard (HD)] and (2) those vapors that require subsequent chemical reaction to prevent elution into the product [e.g. CK, hydrogen cyanide (AC), and phosgene (CG)]. Toxic Industrial Chemical (TIC) vapors can also be classified in this manner. Gases from both categories can be adversely affected by adsorbed contaminants as shown by Peterson et al.<sup>10</sup> Gases such as CK and AC that require chemical reaction can also be adversely affected by a reduction in impregnant activity. Both high water loadings (caused by exposure to high RHs) as well as reactive ambient contaminant gases such as NO<sub>x</sub>, SO<sub>x</sub>, etc., can reduce impregnant reactivity.

## 1.3 Approach to Estimating Residual Life of a Filter

Based on the two-category concept, we have divided our RLI effort into two parts: Part 1, determine the effect of adsorbed contaminants on filter protection performance, and Part 2, determine the effect of loss of impregnant activity on the filter performance. This report details the efforts undertaken to complete Part 1. The loss of filter life due to impregnant degradation will be the focus of a follow-on effort.

A critical component of the RLI approach is that the remaining filter life can only be estimated knowing the current state of the filter. That means that all of the adsorbed constituents (contaminants) that can adversely affect the ability of the threat vapor to adsorb must be characterized. The only method to accomplish this task is to sample the adsorption capacity of all the ASZM-TEDA carbon in the entire filter. The best method to accomplish this task is to use a weakly adsorbed (non-destructive) probe gas that does not react with the impregnants. That is the approach used in this effort.

The RLI correlation is developed in two parts. We start by simulating the condition of a fielded filter (Section 2). We assume that only contaminants that are moderately and strongly adsorbed can affect the residual life since weakly adsorbed gases elute quickly through the filter and can easily be displaced by water and most threat gases. We configure a simulated contaminated filter using contaminated carbon at the bed inlet and fresh carbon at the bed outlet. Breakthrough experiments are then completed using an organic to simulate the threat vapor.

In Section 3, we configure the same simulated contaminated beds used in the breakthrough study described in the previous paragraph. This time, these beds are challenged with pulses of perfluorocyclobutane (PFCB) or 1,1-dichloro-2,2,2-trifluoroethane (R123). Our approach uses two beds, a contaminated bed and a reference bed made up of only fresh carbon. Both beds sample the same RH, assuming that the filter effluent RH is nearly the same as the filter influent RH, or in other words, the ambient RH air does not change rapidly. Both beds will have almost the same moisture content, resulting in a method that allows us to “subtract out” the effect of adsorbed water on the pulse gas result.

In Section 4, we correlate the results from the breakthrough studies of Section 2 with the pulse studies performed in Section 3. A relationship is developed that relates the difference between the contaminated bed pulse and the reference bed pulse.

## 2. BREAKTHROUGH TESTING

In this section, breakthrough experiments are conducted to simulate the behavior of a contaminated filter when exposed to a chemical threat. With this approach, we can then establish a true filter residual life based upon the remaining filter capacity as determined by the breakthrough data. Several critical parameters that affect filter residual life are explored. These include the following:

- The fraction (%) of the filter that is contaminated - 25 and 75% of the total bed depth
- The strength of adsorption of the contaminant - octane and dodecane
- The loading (adsorbed phase concentration) of the contaminant - 0.1 g/g and 0.2 g/g

The strength of adsorption of contaminants needs further explanation. Simply put, the stronger the chemical is adsorbed, the more difficult it is to displace. This means that a very strongly adsorbed vapor will not be displaced by even strongly adsorbed threat vapors such as Sarin (GB) or Distilled Mustard (HD). Octane is a strongly adsorbed chemical, but is not nearly as strongly adsorbed as dodecane. Generally speaking of carbon adsorbents, chemicals with higher boiling points are more strongly adsorbed than those with lower boiling points.

### 2.1 Simulated Contaminated Filter

Shown below in Figure 2.1 is a schematic of the "contaminated" filter concept. This concept is critical to the correct interpretation of residual life. This concept assumes that the contaminants that affect residual life will generally be confined to the inlet of the filter. This is consistent with the fact that chemicals that can effectively prevent the threat vapors from adsorbing will themselves be strongly adsorbed; thus, they will not easily elute through the filter. Therefore, these contaminant vapors will tend to adsorb primarily at the filter inlet.

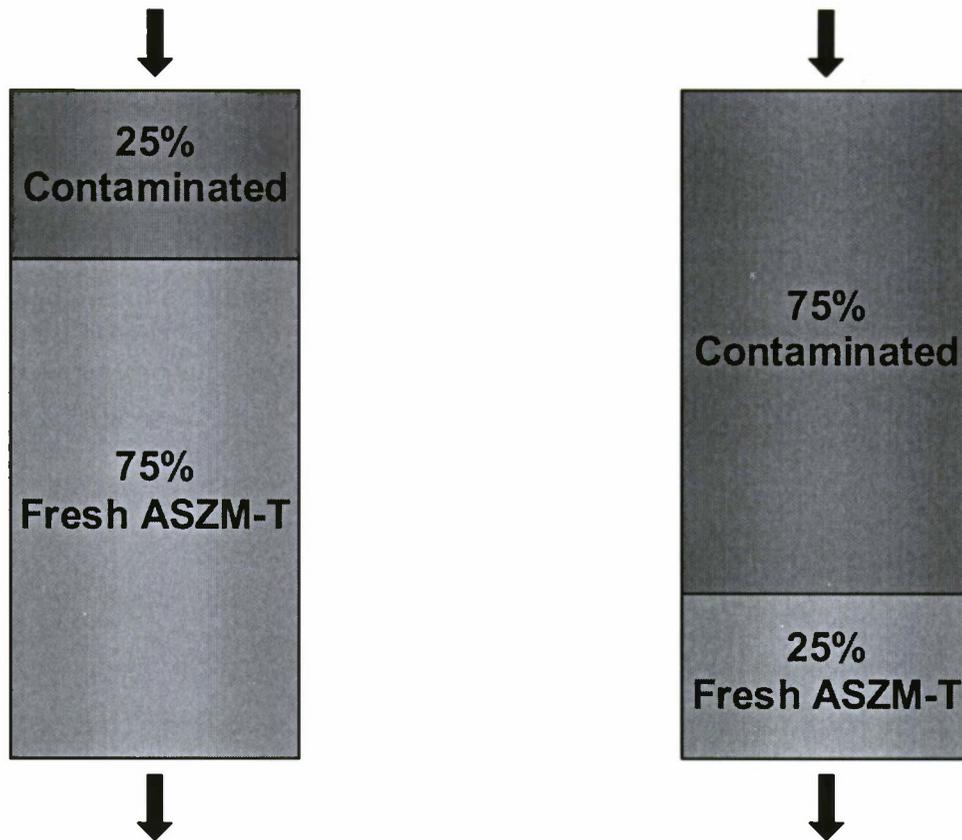


Figure 2.1 Bed Configuration for Simulated Contaminated Filter

## 2.2 Breakthrough Apparatus and Procedure

The beds used in these experiments are 4.1 cm in diameter. The volumetric flow rate is set at 18.6 L/min at ambient temperature to simulate the air velocity through a M98 filter. The bed depth is 5.5 cm slightly greater than a M98. The challenge concentration used in all experiments is 4,000 mg/m<sup>3</sup>. Figure 2.2 illustrates the system used in the experiments.

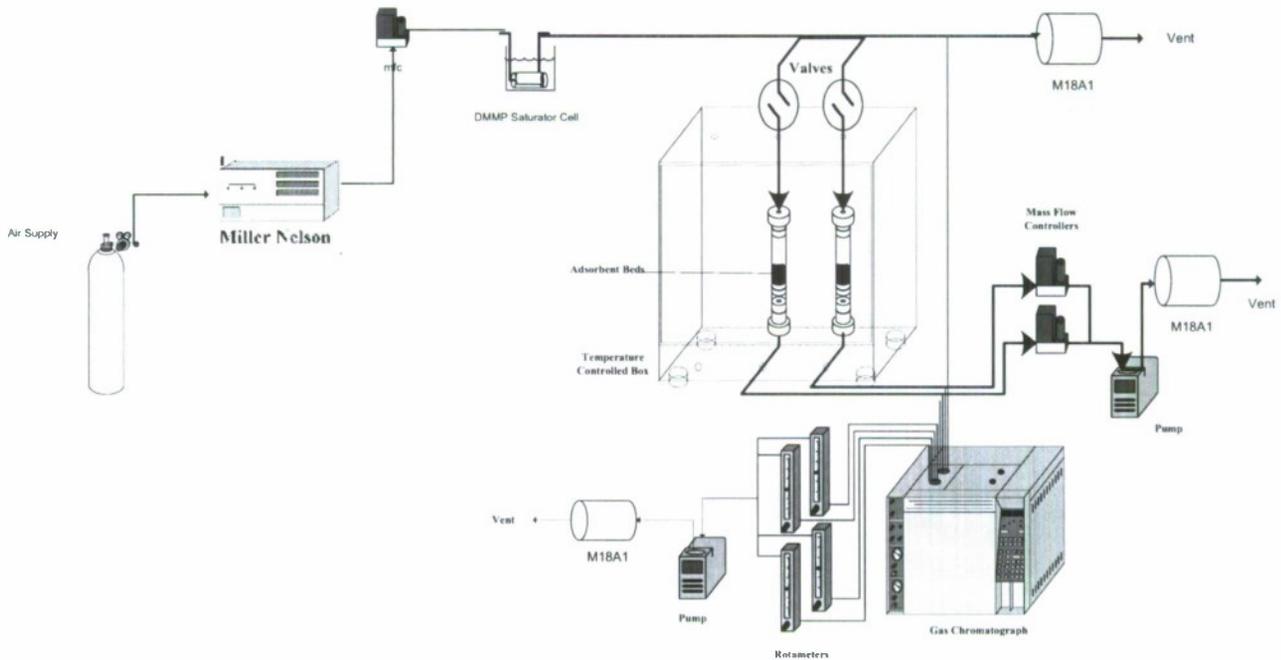


Figure 2.2 Test System Schematic

Breakthrough testing was conducted on a push-pull-vented test apparatus at a temperature of approximately 25 °C. Glass test tubes with an inside diameter of approximately 4.1 cm were packed using a snowstorm method through a 30 in. drop tube. The challenge was delivered by flowing air through saturated vapor in a temperature controlled glass cell and diluting with clean humidified air. The feed and effluent streams were monitored with a Hewlett Packard 5890 Series II gas chromatograph equipped with a flame ionization detector (GC/FID).

### 2.3 Breakthrough Test Results

Breakthrough testing is performed to demonstrate the effect of RH, the adsorption strength of the adsorbed contaminant, and the adsorption strength of the threat vapor. Two different threat vapor simulants are used, each with a different adsorption strength. We consider the effect of adsorbed water on the breakthrough behavior as well. This will be important in the pulse vapor analysis described in the next section. So, the breakthrough testing consists of the following parameters:

- Two threat vapor simulants – hexane and nonane
- Two contaminants – octane and dodecane
- Two contaminant loadings – 0.1 g/g and 0.2 g/g by weight
- Three RHs – 15, 50, and 80%

Given below in Tables 2.1 and 2.2 are several important physical properties of the simulants and contaminants used in the breakthrough experiments. A critical parameter that is related to adsorption strength is the boiling point. Note that the stronger adsorbed simulant (nonane) has a higher boiling point than the weaker adsorbed contaminant (octane). One would expect that nonane would be able to compete favorably for adsorption space.

Table 2.1 Simulant and Agent Properties

Property	n-Hexane	Nonane	Values for GB
CAS	110-54-3	111-84-2	107-44-8
Molecular Weight	86.2 g/mol	128.3 g/mol	140.08 g/mol
Boiling Point	68.9 °C	150.6 °C	150 °C
Vapor Pressure @ 20 °C	124 mmHg	3 mmHg	2.48 mmHg
Water Solubility @ 20 °C	0.002 wt.%	Insoluble	Miscible
Liquid Density	0.66 g/mL	0.72 g/mL	1.09 g/mL
8-hr TWA	50 ppm	None	0.00003 mg/m <sup>3</sup>
IDLH	1100 ppm	Not determined	0.1 mg/m <sup>3</sup>

\*Calculated at 25 °C

Table 2.2 Contaminant Properties

Property	Octane	Dodecane
CAS	11-65-9	112-40-3
Molecular Weight	114.2 g/mol	170.34 g/mol
Boiling Point	125.6°C	216°C
Vapor Pressure @ 20°C	10 mmHg	0.3 mmHg
Water Solubility @ 20°C	0.00007 wt.%	Insoluble
Liquid Density @ 20°C	0.70 g/mL	0.75 g/mL
8-hr TWA	500 ppm	Unknown
IDLH	1000 ppm	Unknown

Given below in Table 2.3 is the complete list of breakthrough experiments. The far right column refers to the figure number where that result is plotted. We have decided to organize all the breakthrough experiments by the threat vapor simulant-contaminant pair.

Table 2.3 Complete List of Breakthrough Experiments

Challenge Vapor	Contaminant	Contaminant Bed Fraction (%)	Contaminant Loading (g/g)	RH (%)	Figure #
Hexane	Octane	0, 25,75	0.1	15	2.2
Hexane	Octane	25,75	0.2	15	2.2
Hexane	Octane	0, 25,75	0.1	50	2.3
Hexane	Octane	25,75	0.2	50	2.3
Hexane	Octane	0, 25,75	0.1	80	2.4
Hexane	Octane	25,75	0.2	80	2.4
Hexane	Dodecane	0, 25,75	0.1	15	2.5
Hexane	Dodecane	25,75	0.2	15	2.5
Hexane	Dodecane	0, 25,75	0.1	50	2.6
Hexane	Dodecane	25,75	0.2	50	2.6
Hexane	Dodecane	0, 25,75	0.1	80	2.7
Hexane	Dodecane	25,75	0.2	80	2.7
Nonane	Octane	0, 25,75	0.1	15	2.8
Nonane	Octane	25,75	0.2	15	2.8
Nonane	Octane	0, 25,75	0.1	80	2.9
Nonane	Octane	25,75	0.2	80	2.9
Nonane	Dodecane	0, 25,75	0.1	15	2.10
Nonane	Dodecane	25,75	0.2	15	2.10
Nonane	Dodecane	0, 25,75	0.1	80	2.11
Nonane	Dodecane	25,75	0.2	80	2.11

### 2.3.1 Hexane Challenge/Octane Contaminant

This system would represent a less strongly adsorbed threat vapor (hexane) with a moderately adsorbed contaminant vapor (octane). Shown in Figures 2.3 through 2.5 are the results for each contaminated bed configuration at the three different RHs: 15, 50 and 80%. In every experiment, both beds were allowed to equilibrate at the test RH prior to introducing the challenge chemical.

The following discussion compares the results of Figures 2.3 through 2.5.

#### 2.3.1.1 Effect of RH

Clean Bed (Baseline) – The breakthrough times (based on approximately half of the feed concentration) at 15 and 50% RH (Figures 2.3 and 2.4) are about the same - about 105 min. However, the breakthrough time and the shape of the breakthrough curve for 80% RH, as shown in Figure 2.4, is entirely different. This is because hexane is adversely affected by adsorbed water at 80% RH. The hexane begins to breakthrough at about 30 min but rises only to about half of the challenge concentration at 40 min. For the next 60 min or so, it rises slowly towards the feed concentration.

Contaminated Beds – Visual observation shows that the results at 15 and 50% RH are almost the same. The only difference appears to be a slight effect of octane loading at 50% RH where the breakthrough of the 0.2 g/g loaded bed occurs at about 75 min and the 0.1 g/g loaded bed occurs at about 90 min. The results at 80% RH are very different. The trend observed for the 15 and 50% RH runs is the same, but the times are compressed. The shapes of all of the breakthrough curves at 80% RH are also different. For example, the baseline experiment appears to rise up to around 2000 mg/m<sup>3</sup> at around 40 min and then gradually increase towards the challenge concentration of 4000 mg/m<sup>3</sup>. This is caused by a multi-component adsorption effect between adsorbed water and hexane.

#### 2.3.1.2 Effect of Contaminant Loading

Visual observation shows that the results at 15 and 50% RH are almost the same. The only difference appears to be a slight effect of octane loading at 50% RH where the breakthrough of the 0.2 g/g loaded bed occurs at about 75 min and the 0.1 g/g loaded bed occurs at about 90 min. The results at 80% RH are very different. The trend observed for the 50% RH run is the same, but the times are compressed. The shape of all the curves at 80% RH matches the shape for the baseline run. These results are consistent since adsorbed water is itself a “contaminant” for hexane.

#### 2.3.1.3 Effect of Contaminated Bed Fraction

The difference in breakthrough times between the 25 and 75% contaminated beds at 15% RH are different depending upon the loading. At 0.1 g/g octane loading, the difference between the 25 and 75% contaminated beds is about 20 min. At 0.2 g/g loading, the difference between the 25 and 75% contaminated beds is greater, about 35 min. The same trend is observed at 50% RH (25 min and 40 min, respectively), although there is not as large of a difference observed in the 0.1 g/g loaded beds. At 80% RH, it is difficult to determine a difference in results as a function of loading, although the general trend from baseline as the longest break time is still the same. The following is the order from longest to shortest breakthrough time:

1. Baseline
2. 0.1 g/g loading, 25% contaminated bed
3. 0.2 g/g loading, 25% contaminated bed
4. 0.1 g/g loading, 75% contaminated bed
5. 0.2 g/g loading, 75% contaminated bed

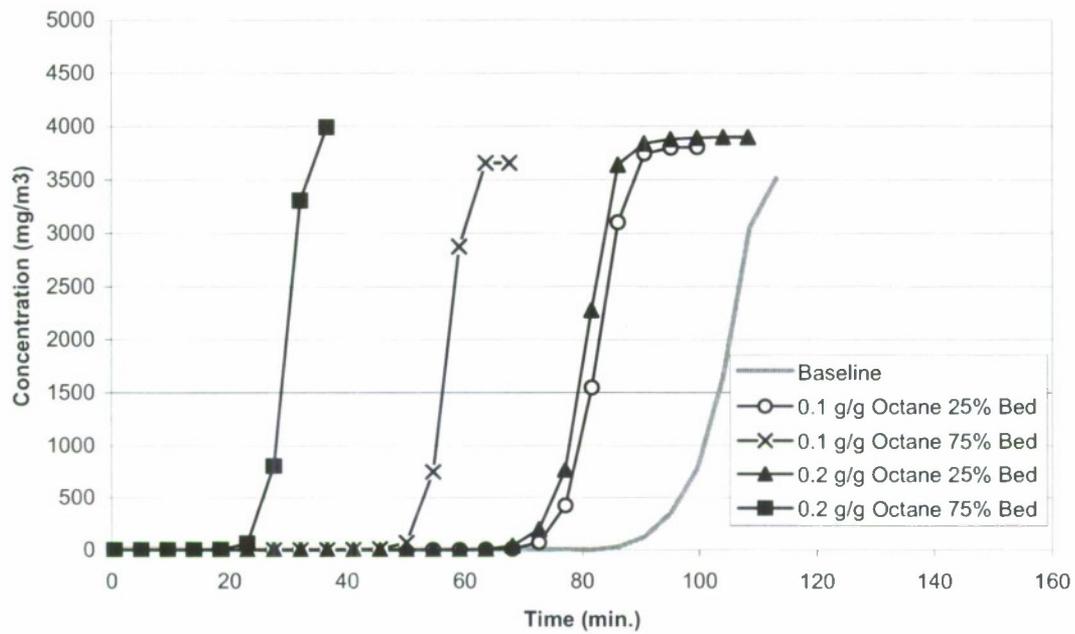


Figure 2.3 Hexane Challenge with Octane Contaminant at 15% RH

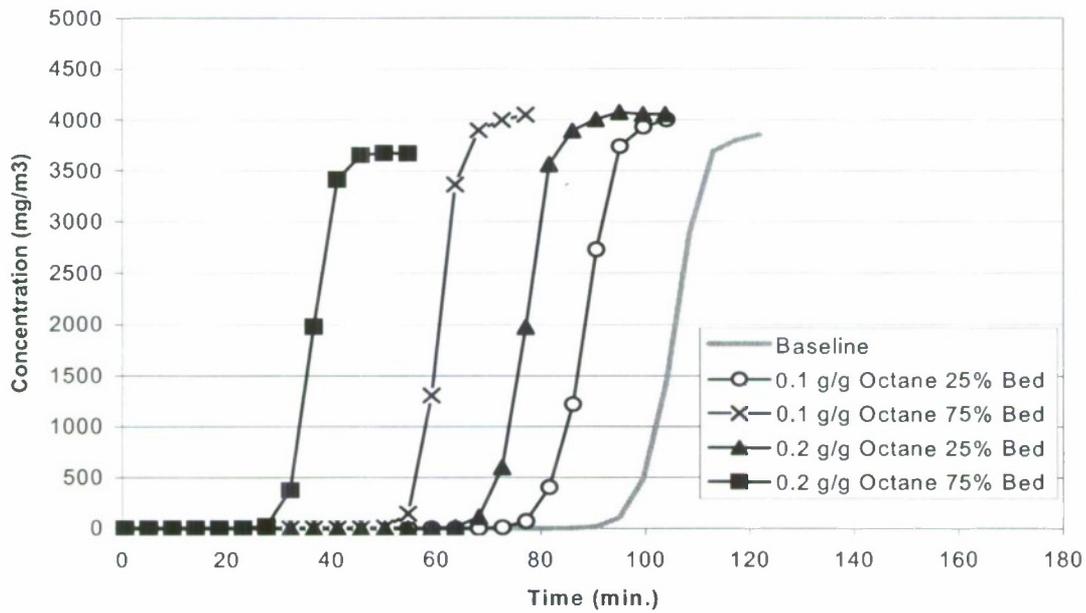


Figure 2.4 Hexane Challenge with Octane Contaminant at 50% RH

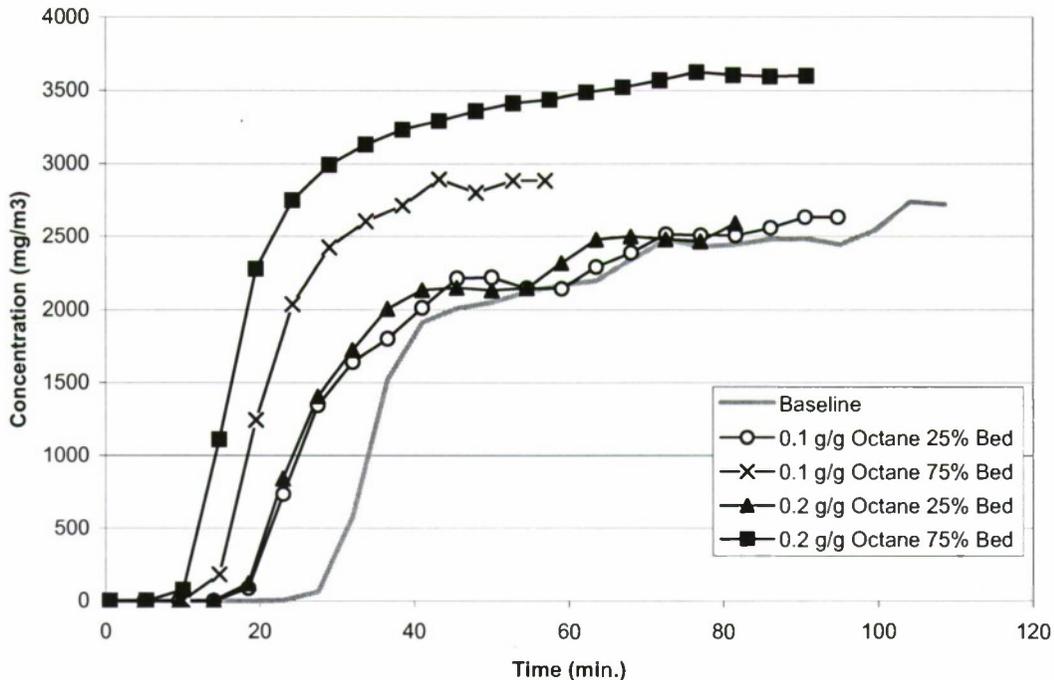


Figure 2.5 Hexane Challenge with Octane Contaminant at 80% RH

### 2.3.2 Hexane Challenge/Dodecane Contaminant

In these tests, we will examine the effect of a more strongly adsorbed contaminant (dodecane) on the less strongly adsorbed threat vapor simulant (hexane). Figures 2.6 through 2.8 show the results for the hexane-dodecane system at 15, 50, and 80% RH.

#### 2.3.2.1 Effect of RH

Clean Bed (Baseline) – The breakthrough times at all RH used in this study are the same data shown in Figures 2.3 through 2.5.

Contaminated Beds – These results are almost identical to those measured for the hexane-octane system. Here is a slight difference, however. The 0.1 g/g dodecane experiments breakthrough later than their 0.1 g/g octane counterparts. This is almost assuredly due to the fact that the octane loading is actually higher than 0.1 g/g or the dodecane loading is lower than 0.1 g/g. From an adsorption strength point of view, this would not make sense.

#### 2.3.2.2 Effect of Contaminant Loading

Once again the results and trends are very similar to those observed for the hexane-octane system.

### 2.3.2.3 Effect of Contaminated Bed Fraction

The difference in breakthrough times between the 25 and 75% contaminated beds at 15% RH are different depending upon the loading. At 0.1 g/g dodecane loading, the difference between the 25 and 75% contaminated beds is about 25 min. At 0.2 g/g loading, the difference between 25 and 75% contaminated beds is greater, about 50 min. The same trend and virtually the same differences are observed at 50% RH. At 80%RH, as with the hexane-octane system, it is difficult to determine a difference in results as a function of loading, although the general trend from baseline as the longest break time is still the same. From longest to shortest breakthrough time the order remains

1. Baseline
2. 0.1 g/g loading, 25% contaminated bed
3. 0.2 g/g loading, 25% contaminated bed
4. 0.1 g/g loading, 75% contaminated bed
5. 0.2 g/g loading, 75% contaminated bed

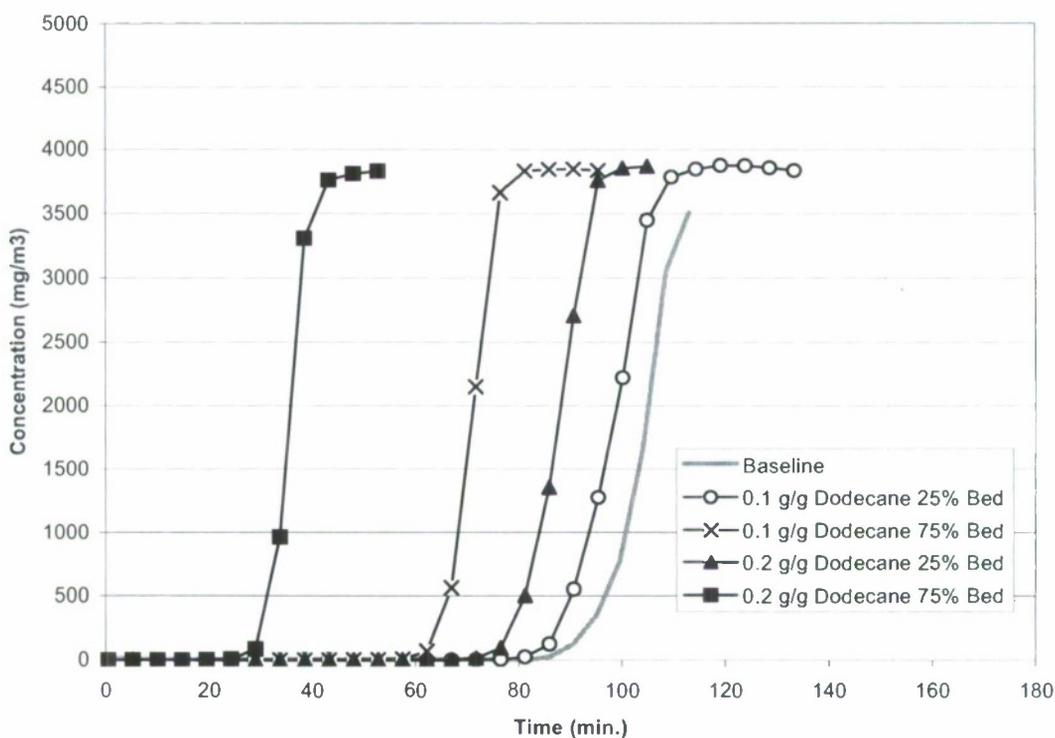


Figure 2.6 Hexane Challenge with Dodecane Contaminant at 15% RH

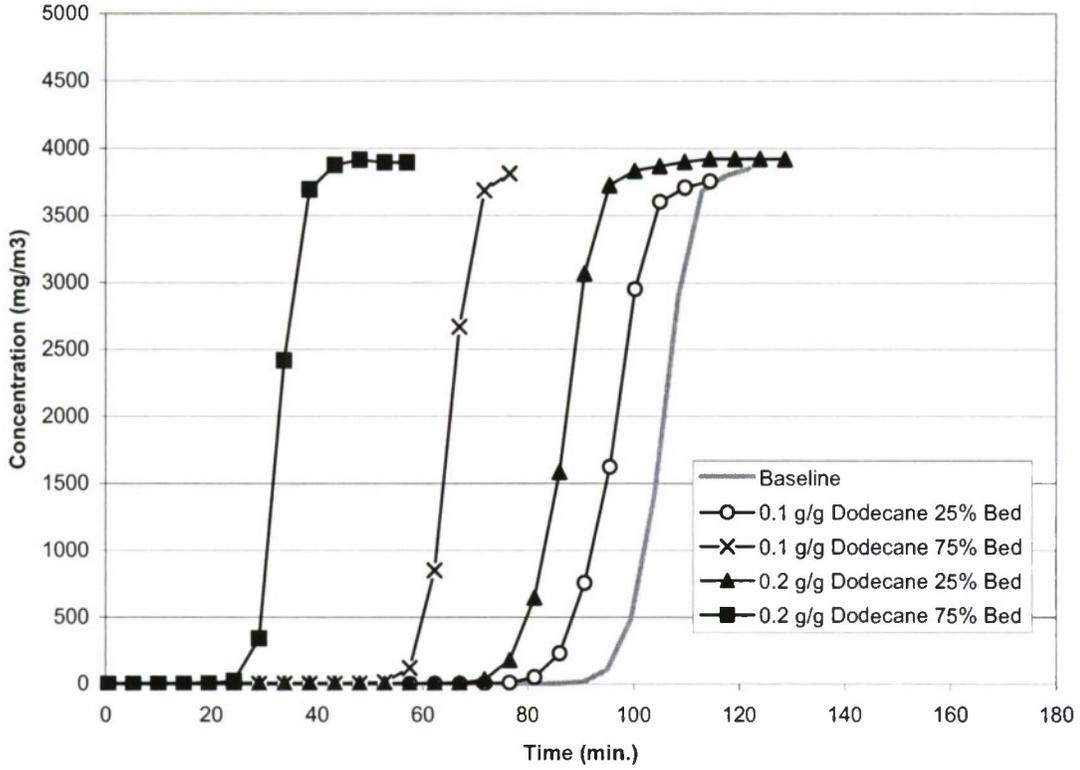


Figure 2.7 Hexane Challenge with Dodecane Contaminant at 50% RH

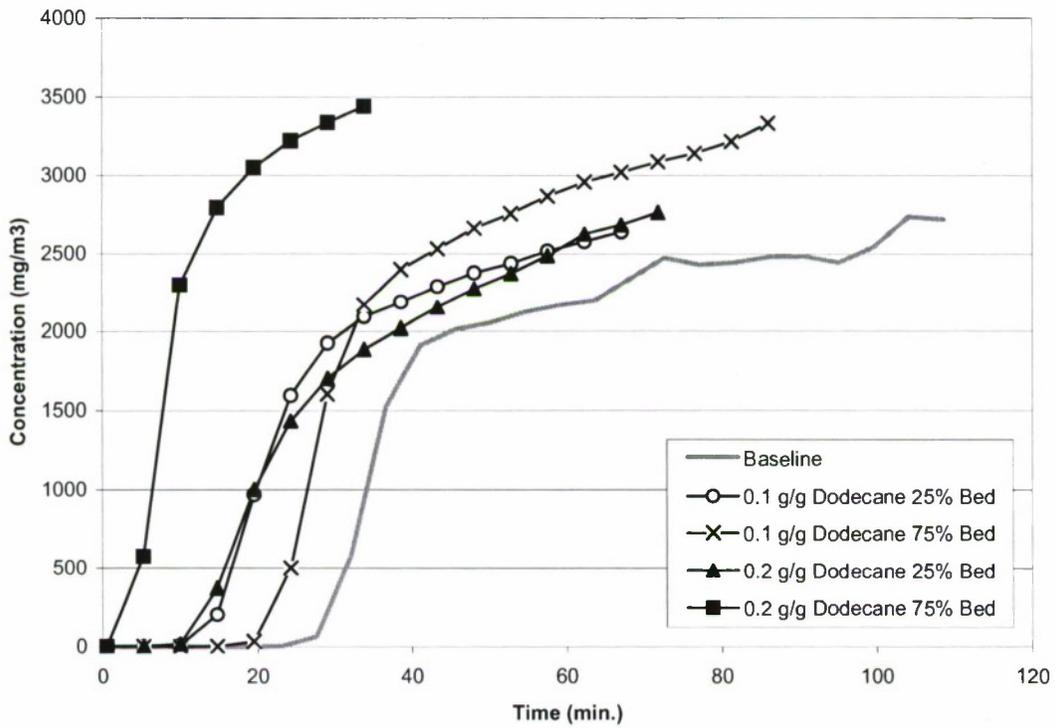


Figure 2.8 Hexane Challenge with Dodecane Contaminant at 80% RH

### 2.3.3 Nonane Challenge/Octane Contaminant

This system represents a more strongly adsorbed threat vapor with a less strongly adsorbed contaminant vapor. Shown in Figures 2.9 and 2.10 are the results at 15 and 80% RH. The 50% RH experiments were not conducted since the 80% RH experiment (Figure 2.10) shows very little effect of moisture.

These results can be summarized simply. Whereas the more weakly adsorbed simulant (hexane) is greatly affected by moisture, the more strongly adsorbed simulant (nonane) is able to effectively displace moisture due to preferential adsorption. Therefore, nonane breakthrough is affected more by the more strongly adsorbed contaminant (dodecane) loading than moisture content and RH.

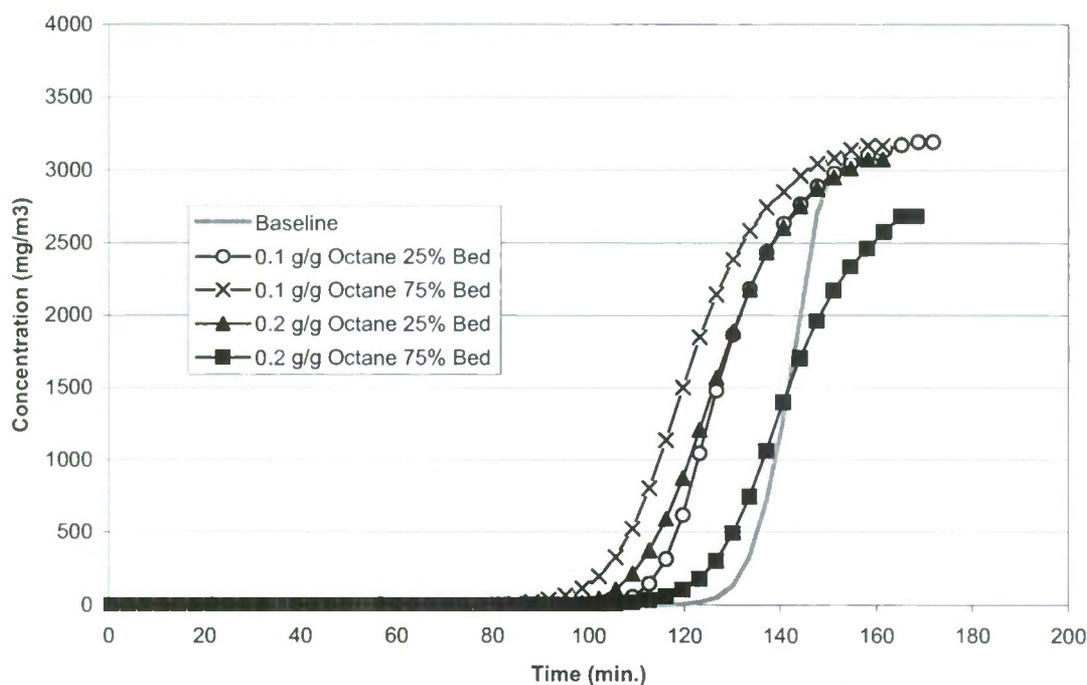


Figure 2.9 Nonane Challenge with Octane Contaminant at 15% RH

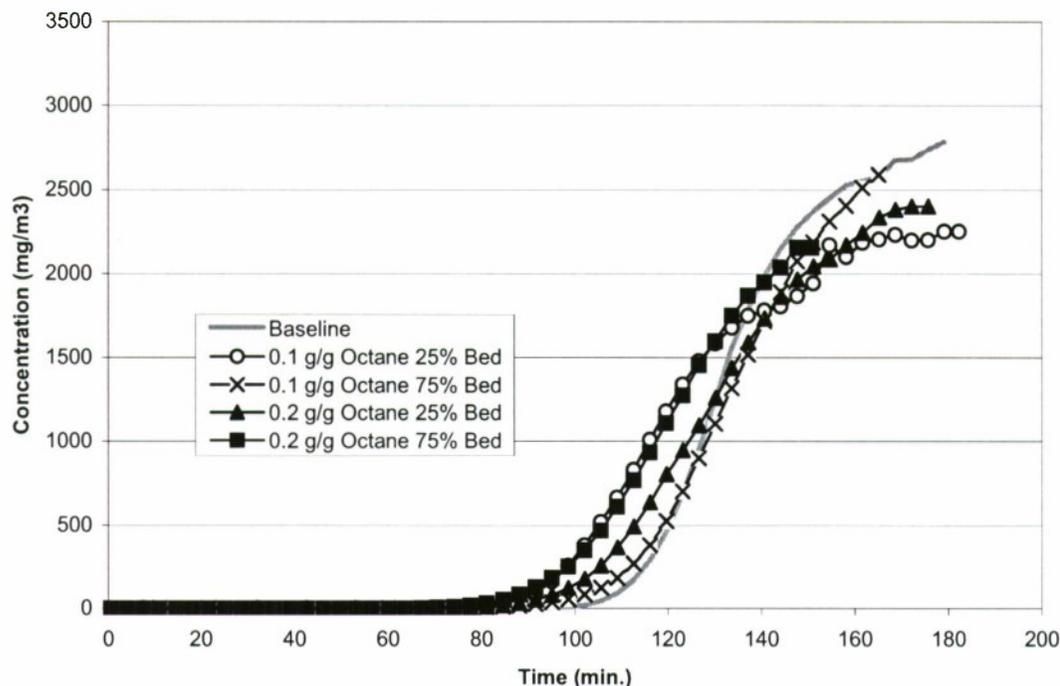


Figure 2.10 Nonane Challenge with Octane Contaminant at 80% RH

### 2.3.4 Nonane Challenge/Dodecane Contaminant

This system represents the more strongly adsorbed threat vapor (nonane) with the more strongly adsorbed contaminant (dodecane). The results for this pair are shown in Figures 2.11 and 2.12.

#### 2.3.4.1 Effect of RH

Clean Bed (Baseline) – As in Section 2.3.3, there is a slight effect of adsorbed water. The breakthrough time at 15% RH is about 160 min, and the breakthrough time at 80% RH is about 140 min.

Contaminated Beds – Visual observation shows that the results at 15 and 80% RH are quite different. At 15% RH and 0.1 g/g dodecane loading, the difference in the break times for the 25 and 75% contaminated beds is about 50 min. While at 80% RH and 0.1 g/g dodecane loading, the difference in the break times for the 25 and the 75% contaminated beds is about 30 min.

#### 2.3.4.2 Effect of Contaminant Loading

The effect of contaminant loading at 15% RH is not large. At 0.1 g/g and 0.2 g/g dodecane loading, the difference is only about 8 min. Another interesting observation is that the 100% contaminated bed of 0.2 g/g loaded dodecane has a breakthrough time of about

25 min. This means that the remaining adsorption space, even where dodecane is adsorbed, is being utilized, at least to some extent, by the nonane.

### 2.3.4.3 Effect of Contaminated Bed Fraction

The difference in breakthrough times between the 25 and 75% contaminated beds at 15% RH, for both the 0.1 and the 0.2 g/g dodecane loadings is almost identical, about 50 min. At 80% RH, the difference for the 0.2 g/g dodecane loading is about 20 min greater – 30 min for the 0.1 g/g dodecane loading and 50 min for the 0.2 g/g dodecane loading.

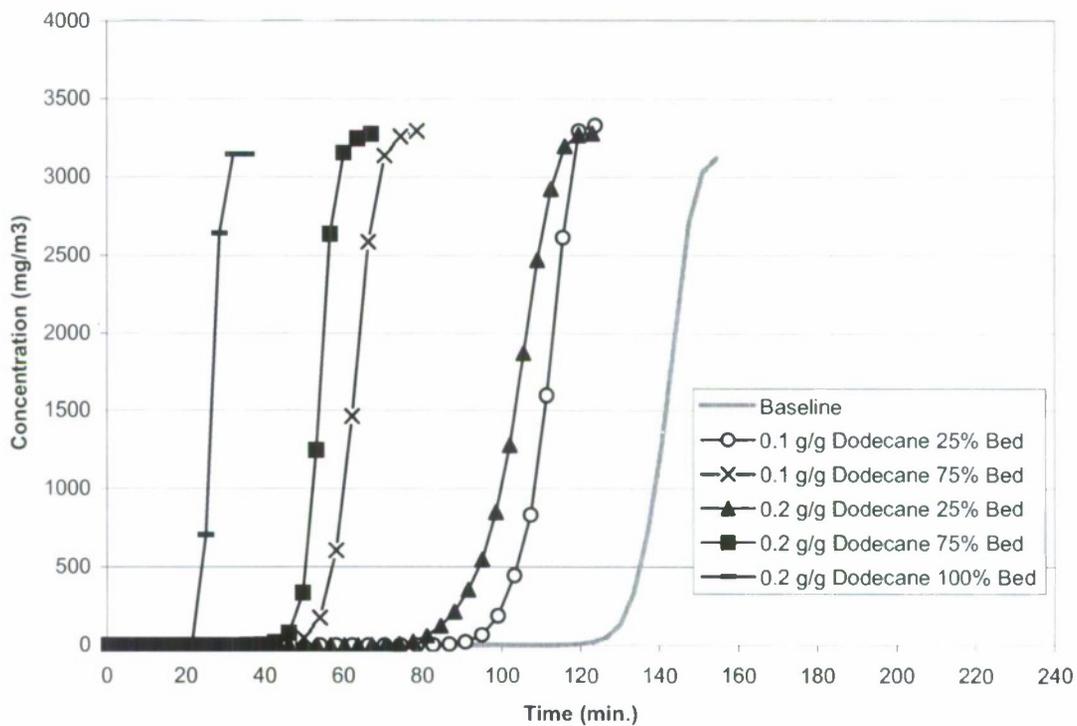


Figure 2.11 Nonane Challenge with Dodecane Contaminant at 15% RH

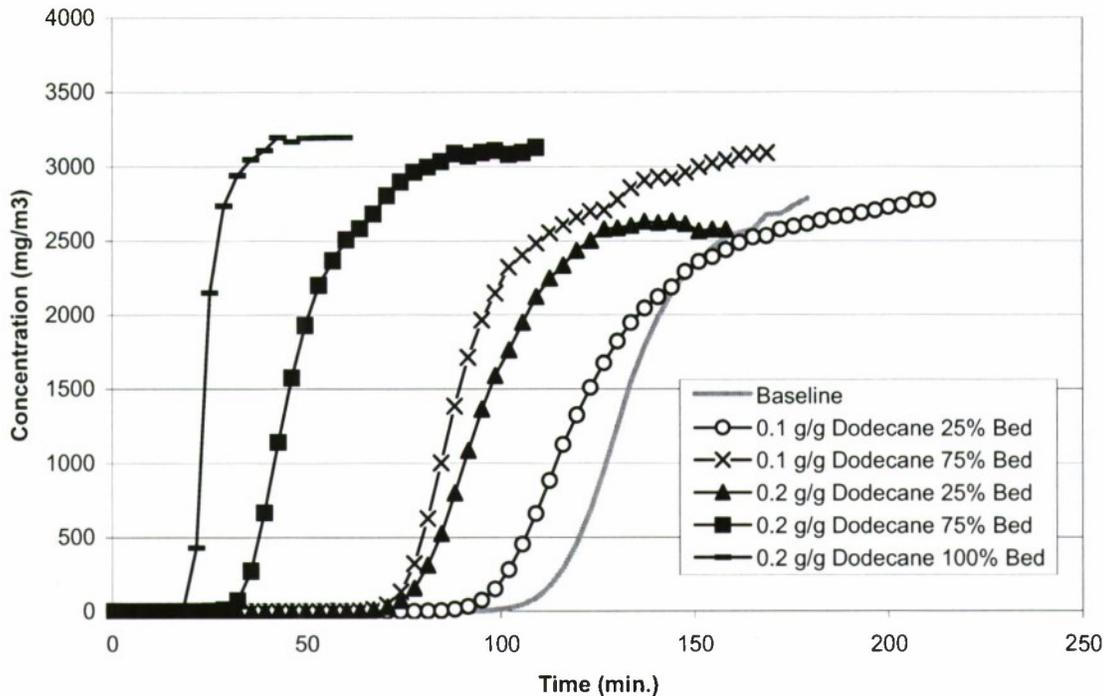


Figure 2.12 Nonane Challenge with Dodecane Contaminant at 80% RH

#### 2.4 Summary of Breakthrough Results

The breakthrough results confirm the complexity of a true RLI. It is shown that the breakthrough time (filter life) is dependent on a number of parameters such as RH, adsorption strength of the contaminant, and the loading of the contaminant. The sensitivity that each of these parameters has on breakthrough behavior is critically dependent on the adsorption behavior of the threat chemical.

If hexane is representative of the threat vapor:

- A contaminant that adsorbs as strongly as octane can prevent hexane from adsorbing (although not completely).
- A contaminant that is very strongly adsorbed such as dodecane can almost completely exclude hexane at 0.2 g/g loading.
- Adsorbed water can greatly affect residual life.

If nonane is representative of the threat vapor:

- Octane has a small effect on breakthrough time. Nonane can displace and/or adsorb the remaining adsorption volume, even at a 0.2 g/g octane loading.
- Adsorbed water has only a small negative impact.
- Dodecane is a representative contaminant and can adversely affect breakthrough times.

Therefore, an RLI must consider both the contaminant and the threat vapor. The implication is that less strongly adsorbed vapors such as CK will be affected to an even greater extent than hexane. Therefore, the following conclusions must be taken into consideration:

- The threat vapor adsorption strength must be considered in the RLI test.
- The contaminant loading and adsorption strength relative to the threat vapor can drastically change the true filter residual life.
- A safe-sided approach is to assume the worst situation, that is hexane threat simulant and dodecane adsorbed contaminant

In order to convert the data measured here in Section 2.0 to filter life, it is necessary to consider the effects of mass transfer. The breakthrough time in these experiments is determined at half of the challenge concentration, about  $2,000 \text{ mg/m}^3$ . This is close to the stoichiometric center of a single transition wave, and the adsorption capacity can easily be calculated from the value. The calculated capacity cannot be directly correlated to the residual life since the mass transfer zone (MTZ) has not been taken into account. The MTZ is the length of bed where the adsorption wave transitions from the challenge concentration down to the breakthrough concentration. For an M98, that constitutes about 35% of the bed. For the following breakthrough experiments, one can estimate the bed "residual life" by subtracting about 35% of time off the stoichiometric center breakthrough time of a clean bed. Thus, a breakthrough time of 100 min would imply a residual life of about 65 min. A breakthrough time of 35 min from a contaminated bed would imply instant break, thus a residual life of zero.

Given below in Table 2.4 are the stoichiometric times (time where  $2,000 \text{ mg/m}^3$  is measured in the effluent) and estimated breakthrough times using an MTZ that is 35% of the bed. The clean bed stoichiometric time breakthrough is multiplied by 0.65 to get the estimated breakthrough time for a clean bed. If we assume that the MTZ is not affected by RH, then every clean bed result can be multiplied by 0.35 to get the "offset" time. The "offset" time is the amount of protection "consumed" the MTZ, and it is subtracted from the stoichiometric time to get the estimated breakthrough time.

For example, for hexane to beds with  $0.1 \text{ g/g}$  octane loading, the clean bed time is 105 min. The estimated breakthrough is  $0.65 \times 105 = 68 \text{ min}$ , while the "offset" time at 15% RH is  $0.35 \times 105 = 37 \text{ min}$ . We round to the nearest 5 min to get 70 and 35 min, respectively. So, the estimated breakthrough time for the 25% contaminated bed is  $80 - 35 = 45 \text{ min}$ , and the estimated breakthrough time for the 75% contaminated bed is  $55 - 45 = 10 \text{ min}$ .

Table 2.4 Estimated Breakthrough Times Using MTZ that is 35% of Bed

Challenge Vapor	Contaminant	Bed Fraction (%)	Loading (g/g)	RH (%)	Stoichiometric Center Times (min)	Breaktime Estimates Using MTZ (min)
Hexane	Octane	0, 25,75	0.1	15	105, 80,55	70,45,20
Hexane	Octane	25,75	0.2	15	80,30	45, instant
Hexane	Octane	0, 25,75	0.1	50	105,90,60	70,55,25
Hexane	Octane	25,75	0.2	50	75,35	40, instant
Hexane	Octane	0, 25,75	0.1	80	40,35,20	25,20,5
Hexane	Octane	25,75	0.2	80	35,15	20, instant
Hexane	Dodecane	0, 25,75	0.1	15	105,95,70	70,60,35
Hexane	Dodecane	25,75	0.2	15	85,35	50, instant
Hexane	Dodecane	0, 25,75	0.1	50	105,95,60	70,60,25
Hexane	Dodecane	25,75	0.2	50	85,35	50, instant
Hexane	Dodecane	0, 25,75	0.1	80	35,30,30	20,15,15
Hexane	Dodecane	25,75	0.2	80	35,10	20, instant
Nonane	Octane	0, 25,75	0.1	15	140, 125,120	90,75,70
Nonane	Octane	25,75	0.2	15	130, 145	80,95
Nonane	Octane	0, 25,75	0.1	80	135,140,140	85,90,90
Nonane	Octane	25,75	0.2	80	140,135	90,85
Nonane	Dodecane	0, 25,75	0.1	15	140,110,60	90,60,10
Nonane	Dodecane	25,75	0.2	15	100,30	50, instant
Nonane	Dodecane	0, 25,75	0.1	80	140,130,90	90,80,45
Nonane	Dodecane	25,75	0.2	80	110,50	60, instant

For every system where 75% of the bed is contaminated with a 0.2 g/g loading, there is instant break, except for the nonane feed to octane contaminated beds system where nonane is virtually unaffected by adsorbed octane.

### 3. PULSE TESTING

In Section 2, data were measured that correlate directly to the remaining filter life. Several different parameters were investigated to better understand the true meaning of residual life. In this section, we will probe each of the bed configurations tested in Section 2 using a non-destructive chemical vapor pulse.

#### 3.1 Pulse Testing Concept and Approach

The satellite beds are probed using a non-destructive gas, typically referred to as a chemical pulse method. The basic requirements of the probe gas are that it is weakly adsorbed, non-toxic, non reactive, and easily detectable. Even though the probe gas is weakly adsorbed, the carbon will still retain it for a measurable period of time. As the bed becomes filled with

contaminants, the retention time of the chemical pulse will be reduced. In addition, based on basic fundamentals of adsorption/chromatography science, the peak (maximum) chemical concentration will rise as the level of bed contamination increases.

The two major problems with a chemical pulse method to determine the filter residual are listed below:

1. A large amount of test chemical may be required, especially for large filter installations that employ a large number of M98's.
2. Any non-destructive pulse chemical will almost certainly be adversely affected by adsorbed water. Thus, adsorbed water will be interpreted as a potential contaminant (the estimated filter residual life will be lower) when we already know that most agents are not adversely affected by adsorbed water.

The RLI approach overcomes these two shortcomings by using (1) a satellite cartridge that samples the inlet air to mimic the environmental history of the filter or filter system and (2) a second satellite filter at the filter outlet to serve as a reference for RH.

### 3.2 Pulse Testing System Apparatus and Procedure

The system is designed to make sure a precise mass of pulse chemical is introduced into each bed for each test. This is critical in order to accurately assess the pulse test results since even a 0.1 g/g increase in mass delivered could produce a result that is interpreted as a leak.

#### 3.2.1 Apparatus

An infrared analyzer (MIRAN 1A) is used to detect the bed probe chemical. It is set to a wavelength of 10.3 microns, a path length of 20.25 m, and an absorbance sensitivity of .1X to detect the probe chemical. The air mixing chamber supplies humidified air to the test beds, and has a volume of 4.5 L. The dew point hygrometer samples the humidified air from the mixing chamber to determine RH.

Rotameters are used to control the flow rate through the sample beds. Their range is 0 to 23 L/min, and for this test, they are set at 7.8 L/min to meter the correct velocity (25.4 cm/s) through the bed.

The beds are 1-in. diameter and are made from stainless steel. A spring and a porous top plate are used to keep the carbon particles from fluidizing during the test. Bed depth should be sized to mimic the filters in the filter bank. For this test, the beds used are 5.6 cm in depth and tested at an air flow velocity of approximately 25.5 cm/s.

Solenoid valves are used to control the flow of probe chemical through the test system. The valves are ¼ in., 2-way valves. Bed selection valves are used to select the bed to be tested. These valves are ¼ in., 3-way valves.

Type T thermocouples are used to measure the air temperature in the test system.

A mass flow controller is used to control the flow rate through the probe chemical reservoir (volume = 20 mL) during the test. It is set at 40 mL/min. It is rated at 0 to 100 mL/min.

Figure 3.1 shows a piping and instrumentation diagram (P&ID) of the RLI pulse apparatus.

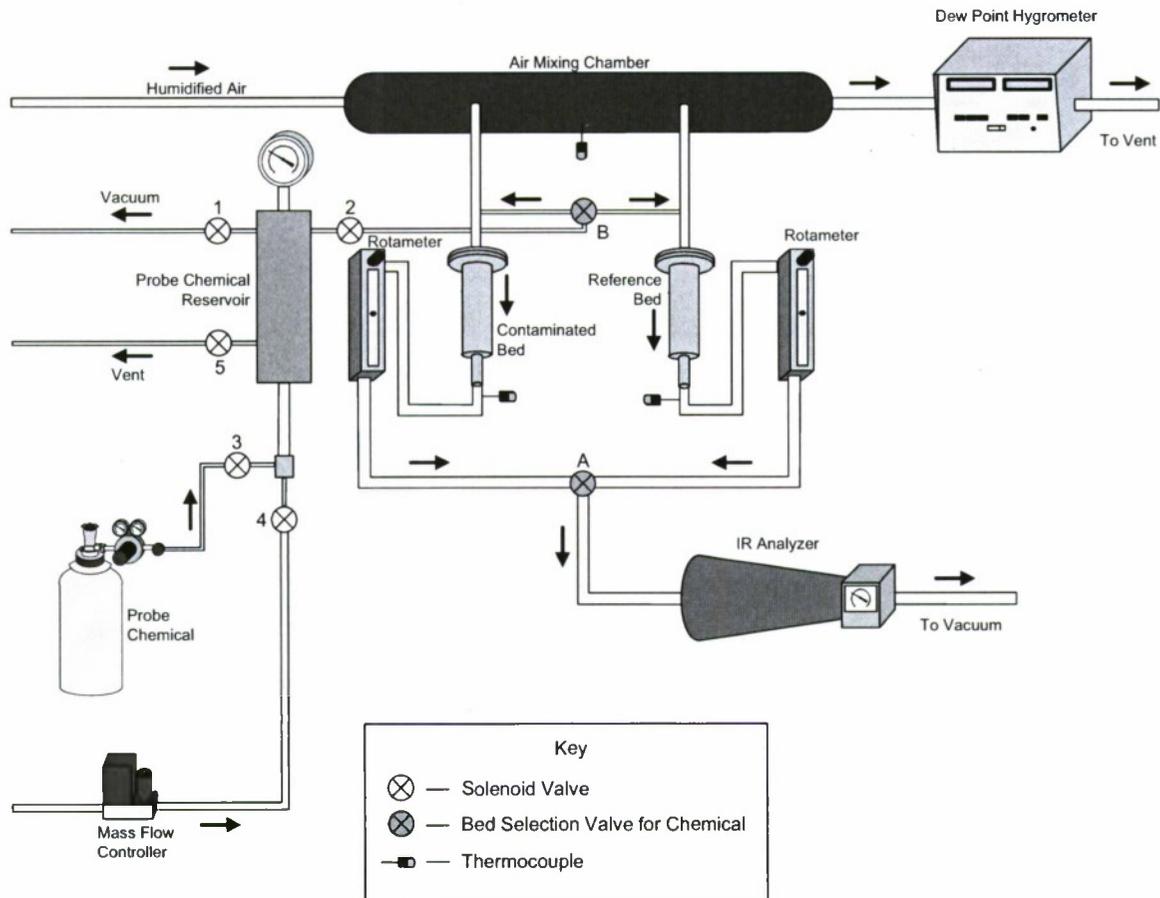


Figure 3.1 RLI Pulse Apparatus P&ID

### 3.2.2 Bed Preparation

1. Fill the reference bed to 5.6 cm with ASZM-T carbon. Measure bed depth with a small metric ruler.
2. For the 25% contaminated bed, fill to 4.1 cm with ASZM-T carbon. For the 75% contaminated bed, fill to 4.1 cm with ASZM-T carbon. Use fresh ASZM-T to make up the rest of the bed for a total bed depth of 5.6 cm.
3. Before conducting the test, make sure beds are fully equilibrated to the desired RH. This will take at least 2 hr for the 80% RH tests.

### 3.2.3

#### Test Procedure

1. Open valve 1 to vacuum down the probe chemical reservoir to 28 in. of Hg (vacuum) to purge the reservoir. Once the gauge reads 28 in., close valve 1. (Valves 2, 3, 4, and 5 should remain closed.)
2. Open valve 3 to fill the reservoir with the probe chemical until the gauge reads 0 in. (ambient pressure). Once the gauge reads 0 in., close valve 3. Open valve 1 to vacuum the reservoir back down to 28 in., purging any air out of the reservoir, and then close valve 1. (Valves 2, 4, and 5 should remain closed.)
3. Open valve 3 once again to fill the reservoir with the probe chemical until the gauge reads 12 in. (vacuum) for the 15 and 50% RH tests (PFCB) or until the gauge reads 6 in. (R123) for the 80% RH tests. Then close valve 3. (Valves 1, 2, 4, and 5 should remain closed.)
4. Use the bed selection valves A and B to configure the correct flow path for the first bed to be tested. Simultaneously open valves 2 and 4 and set the mass flow controller to 40 mL/min. to start the test.
5. The response from the Miran 1A is sent to an SCXI data acquisition system. This, in turn, is being accessed and controlled using a PC. Data are recorded continuously using Labview software. Monitor the IR analyzer for a response on the meter to see that the probe chemical is being detected. The reading on the meter should peak and then fall back to zero. When the reading reaches zero, the test is complete. When the test is completed, set the mass flow controller back to 0 and close valves 2 and 4. (Valves 1, 3, and 5 should remain closed.)
6. Repeat test procedure steps 1 through 4 for the remaining bed.

### 3.3

#### Pulse Test Results

Pulse testing is performed using the same contaminated bed configurations tested in Section 2. Two pulse gases are used depending upon the RH. PFCB is used for the 15 and 50% tests. R123 must be used at 80% RH, because the PFCB is almost totally displaced by water, i.e., very little adsorption occurs, even in the reference bed. An additional set of tests is performed at 65% RH using dodecane as the contaminant to demonstrate the likely maximum RH where PFCB can be used as the probe chemical. Properties of the test gases are presented in Table 3.1, and the experiments performed are summarized in Table 3.2.

Table 3.1 Pulse Gas Properties

Property	PFCB	R123
Molecular Weight	200.04 g/mol	152.93 g/mol
Boiling Point	-5.6 °C	27.8 °C
Water Solubility @ 20 °C	Insoluble	0.21 wt%
Liquid Density @ 20 °C	1.5 g/mL	1.48 g/mL

### 3.3.1 Testing Overview and Experiment Summary

Table 3.2 Complete List of Pulse Experiments

Challenge Vapor	Contaminant	Contaminant Bed Fraction (%)	Contaminant Loading (g/g)	RH (%)	Figure #
PFCB	Octane	25,75	0.1	15	3.2
PFCB	Octane	25,75	0.2	15	3.3
PFCB	Octane	25,75	0.1	50	3.4
PFCB	Octane	25,75	0.2	50	3.5
R123	Octane	25,75	0.1	80	3.6
R123	Octane	25,75	0.2	80	3.7
PFCB	Dodecane	25,75	0.1	15	3.8
PFCB	Dodecane	25,75	0.2	15	3.9
PFCB	Dodecane	25,75	0.1	50	3.10
PFCB	Dodecane	25,75	0.2	50	3.11
PFCB	Dodecane	25,75	0.1	65	3.12
R123	Dodecane	25,75	0.2	80	3.13
R123	Dodecane	25,75	0.1	80	3.14

### 3.3.2 Octane Contaminant Results

The results of pulse tests conducted at 15, 50, and 80% RH using octane as the contaminant are summarized in this section. There are two plots for each RH; one plot displays the results for the 0.1 g/g octane loading and the other plot displays the 0.2 g/g octane loading results. Every plot shown consists of two pairs of experiments (four in total): the reference bed and 25 and 75%, respectively, of the contaminated bed. Every reference bed experiment is different, since even at the same target RH, there may be a slight difference in the actual RH.

Each of these pulse experiments can be compared to a corresponding breakthrough experiment. In the following discussion, the breakthrough reference plots will be noted and used for comparison.

### 3.3.2.1 15% RH

Shown below in Figures 3.2 and 3.3 are the pulse results at 15% RH. In each figure, there are two test "pairs": a 25% contaminated bed with its corresponding reference run and a 75% contaminated bed with its reference run. A reference test is performed with every contaminated bed test to account for any deviation in RH and temperature that might occur. The difference between the reference and contaminated beds should be proportional or related to loss of adsorption capacity.

The peak concentration and peak time are used to analyze the test results. An increase in peak concentration will usually occur with a decrease in peak time. This is consistent with the well-characterized behavior of chemical vapors on chromatographic columns. As the adsorption capacity increases, the peak time increases. With the increase in adsorption capacity typically one will see a decrease in the peak concentration. This behavior is directly related to the favorable shape of the adsorption isotherm (concave down). Therefore, the shorter peak times and higher the peak concentrations relative to the reference bed correlate to less adsorption capacity, and therefore a shorter residual life.

Figure 3.2 shows the results for the 0.1 g/g octane loading. For the 25% contaminated bed, there is a measurable difference from the reference (pink and red lines). The peak concentration increases from about 10 to about 15 ppm. For the 75% bed, the peak concentration is about 55 ppm, an increase of about 45 ppm, and the peak time has shifted back almost 40 min from the reference. Clearly this is indicative of a large amount of capacity loss when going from a 25 to a 75% contaminated bed. Generally speaking, this is the same relative trend that is observed in the breakthrough testing.

When comparing Figures 3.2 and 3.3, notice that the peak concentrations for the contaminated beds at 0.2 g/g octane loading are considerably higher than those at 0.1 g/g. This is especially noticeable for the 75% contaminated bed where the increase in peak concentration is from 55 (0.1 g/g loading) to 250 ppm (0.2 g/g loading). This is clearly indicative of PFCB co-adsorbing in the available adsorption sites. For example, at lower loadings (0.1 g/g), more PFCB adsorbs due to more available pore volume, resulting in lower peak elution concentrations.

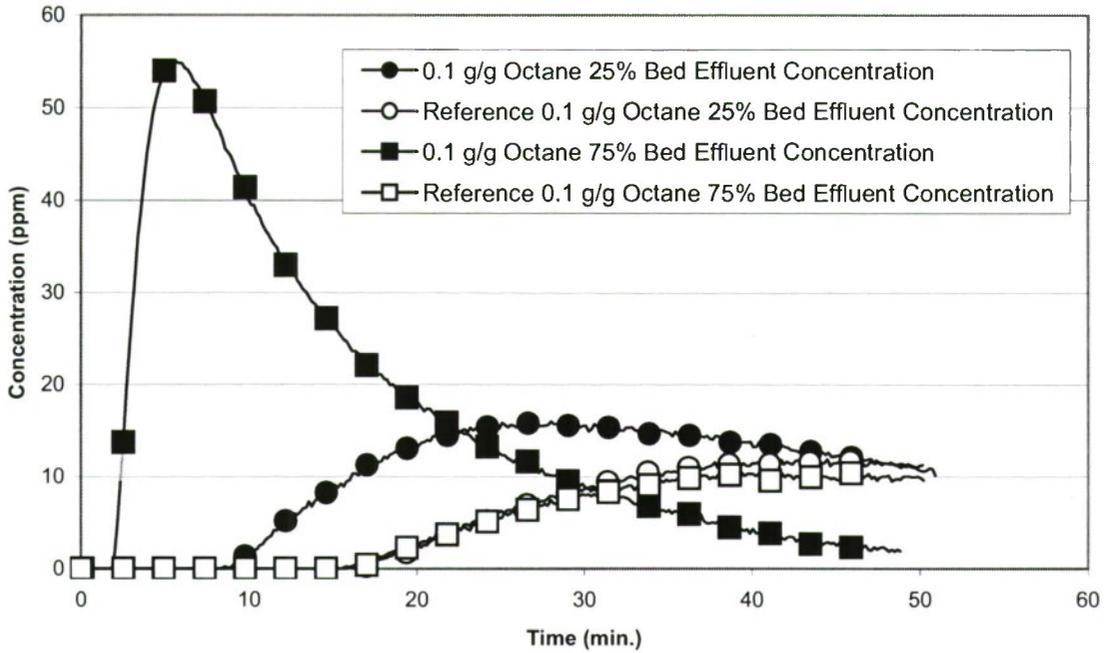


Figure 3.2 Results for 0.1 g/g Octane Loading at 15% RH Using PFCB

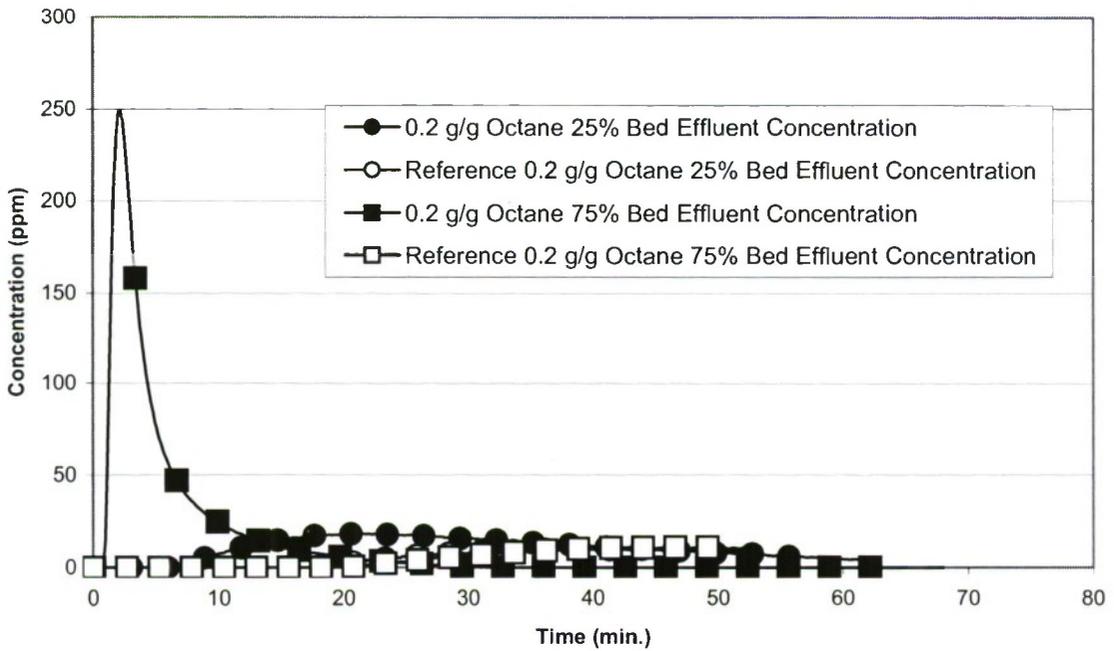


Figure 3.3 Results for 0.2 g/g Octane Loading at 15% RH Using PFCB

3.3.2.2 50% RH

Shown below in Figures 3.4 and 3.5 are the pulse results at 50% RH. There are several key features to highlight. First, the same trend observed at 15% RH is seen at 50% RH. There is a large difference between the 25 and 75% bed results. Second, the effect of adsorbed water is seen in the reference results as well as in the contaminated bed results. For example, the reference at 15% RH from Figure 3.2 has a peak concentration of about 10 ppm at about 40 min, while the reference bed at 50% RH has a peak time of about 35 ppm at about 17 min. In addition, the peak concentrations of the contaminated beds are much higher than their 15% RH counterparts. For example, the 75% contaminated bed with 0.1 g/g octane loading at 50% RH has a peak concentration of 170 ppm compared to 55 ppm at 15% RH.

As with the 15% RH tests, the peak concentrations also increase as the octane loading is increased.

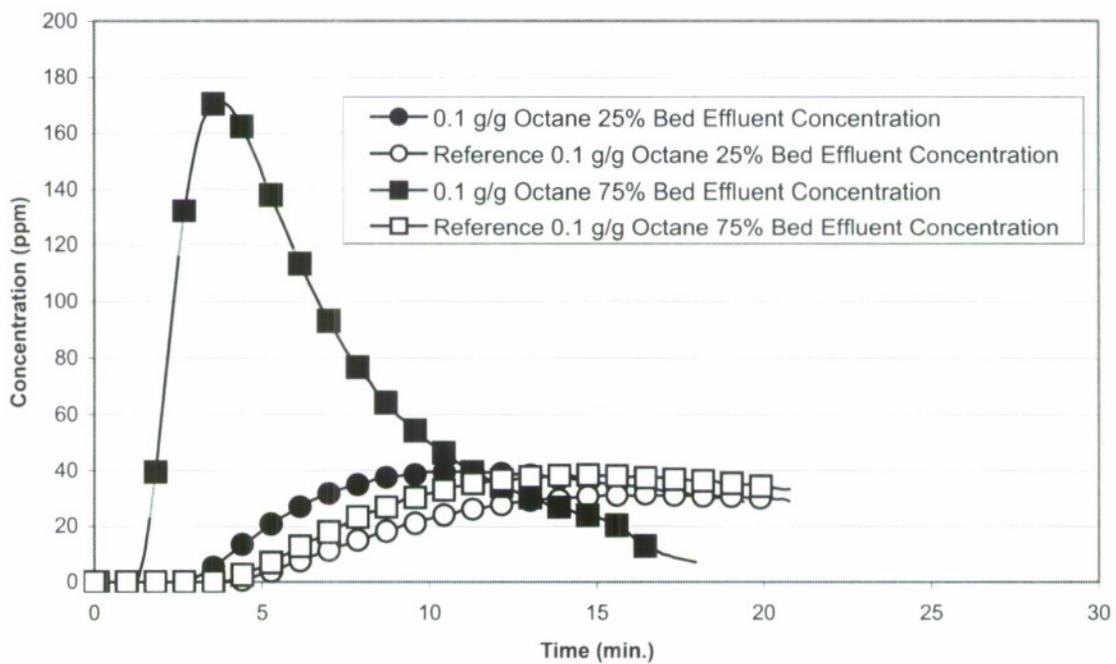


Figure 3.4 Results for 0.1 g/g Octane Loading at 50% RH Using PFCB

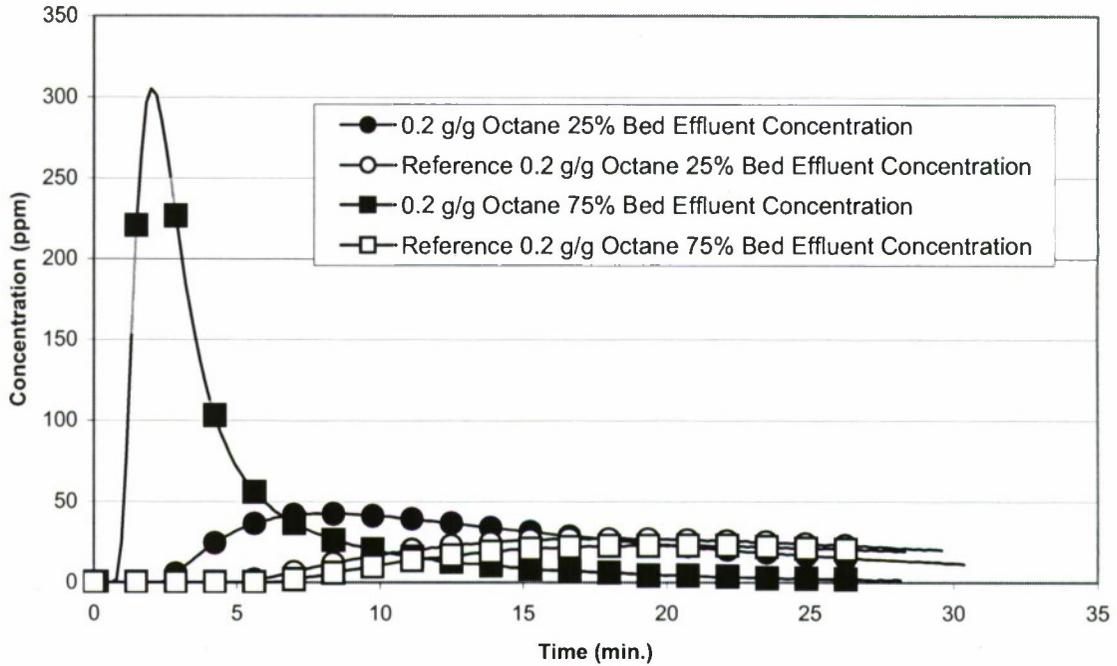


Figure 3.5 Results for 0.2 g/g Octane Loading at 50% RH Using PFCB

### 3.3.2.3 80% RH

At 80% RH, PFCB is not viable, since very little PFCB adsorbs on clean carbon. Therefore, a more strongly adsorbed pulse chemical, R123, is required.

Shown below in Figures 3.6 and 3.7 are the pulse results at 80% RH. These results are very different from the results for PFCB at the lower RH. First, the peak elution times are almost the same for all three beds: reference, 25 and 75% contaminated. Second, the peak times occur very early, all within 5 min or so. However, the trend still holds. The largest peak concentration is seen with the 75% contaminated bed for both octane loadings.

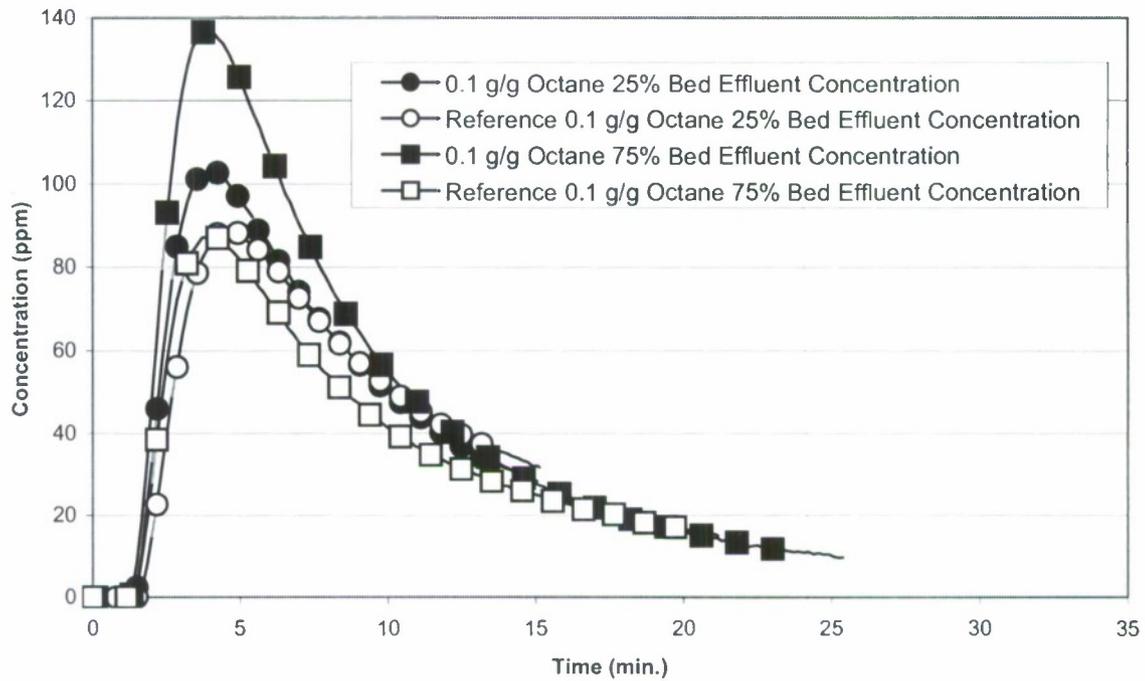


Figure 3.6 Results for 0.1 g/g Octane Loading at 80% RH Using R123

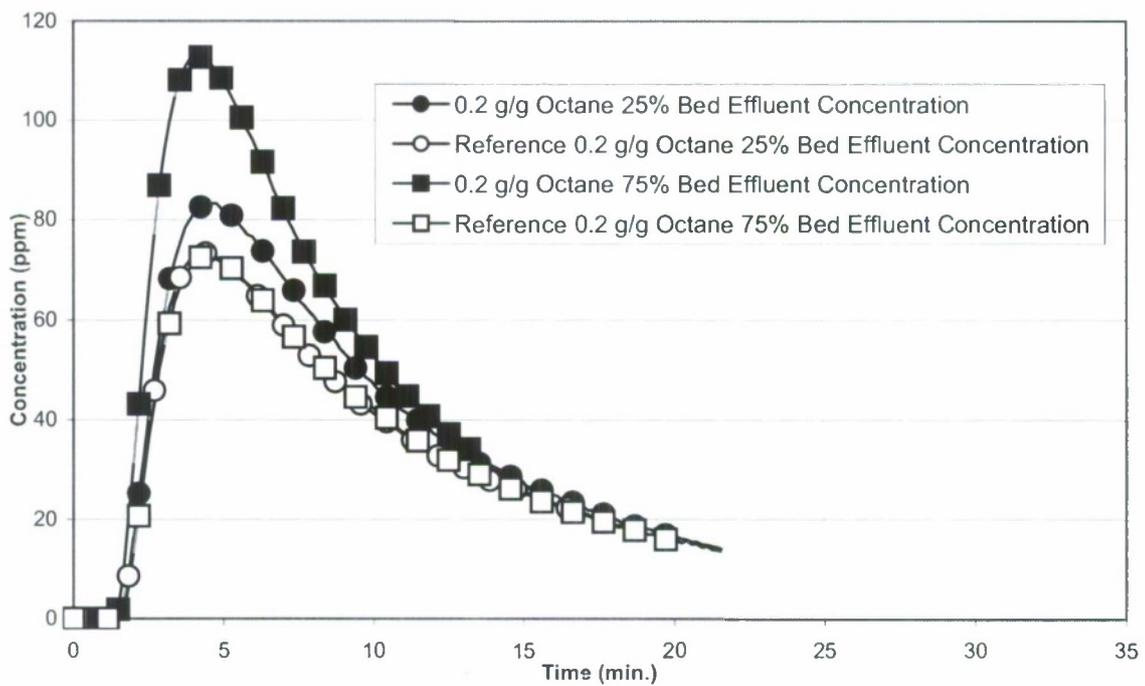


Figure 3.7 Results for 0.2 g/g Octane Loading at 80% RH Using R123

### 3.3.3 Dodecane Contaminant Results

#### 3.3.3.1 15% RH

Shown in Figures 3.8 and 3.9 are the results using dodecane as the contaminant at 15% RH. These results are similar to those observed for octane indicating that octane and dodecane have about the same effect on PFCB. In other words, any vapor equal to or greater than octane in adsorption strength will generate the same RLI result with PFCB. .

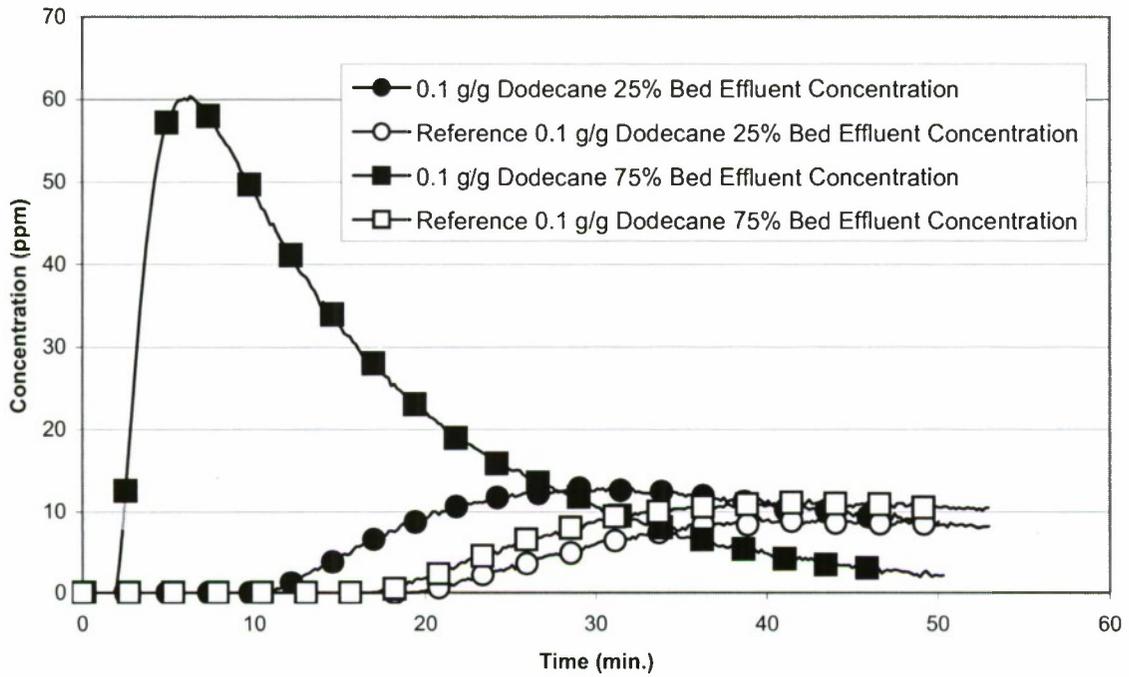


Figure 3.8 Results for 0.1 g/g Dodecane Loading at 15% RH Using PFCB

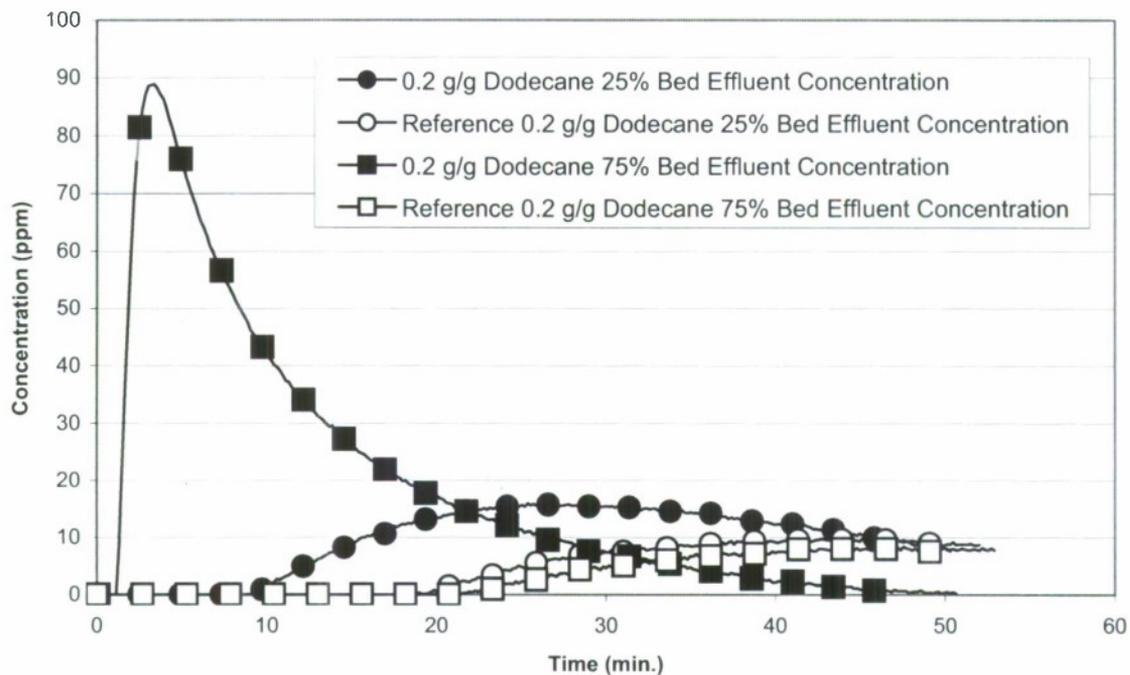


Figure 3.9 Results for 0.2 g/g Dodecane Loading at 15% RH Using PFCB

### 3.3.3.2 50% RH

Shown in Figures 3.10 and 3.11 are the results using dodecane as the contaminant at 50% RH. These results are similar to those observed for octane showing that the change in RH does not change the fact that any vapor more strongly adsorbed than octane will produce the same result.

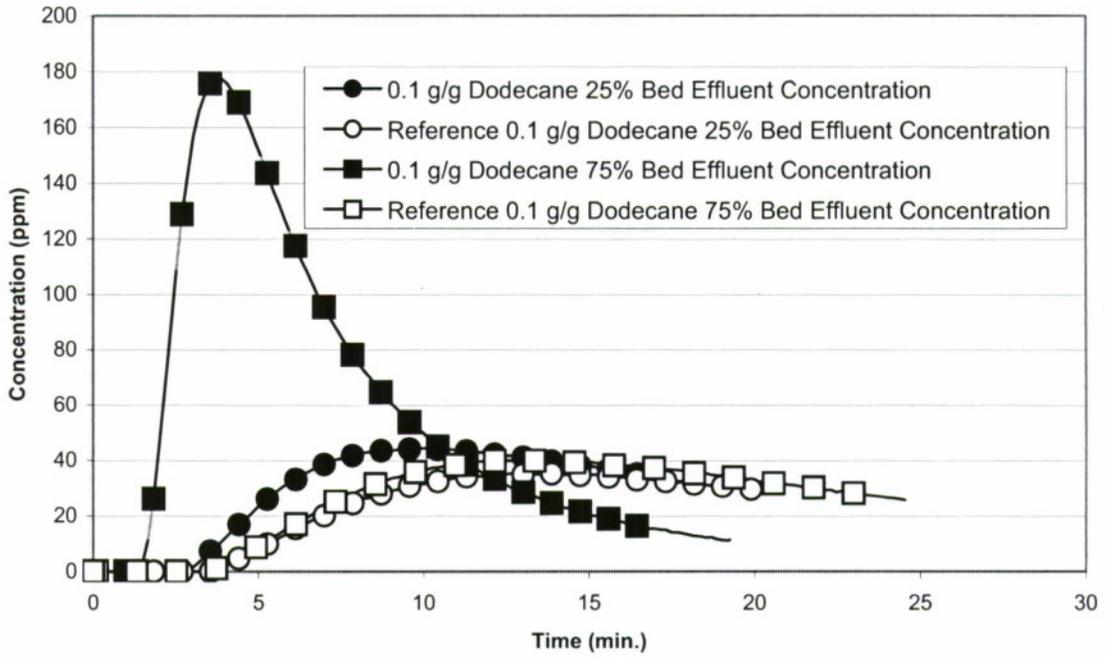


Figure 3.10 Results for 0.1 g/g Dodecane Loading at 50% RH Using PFCB

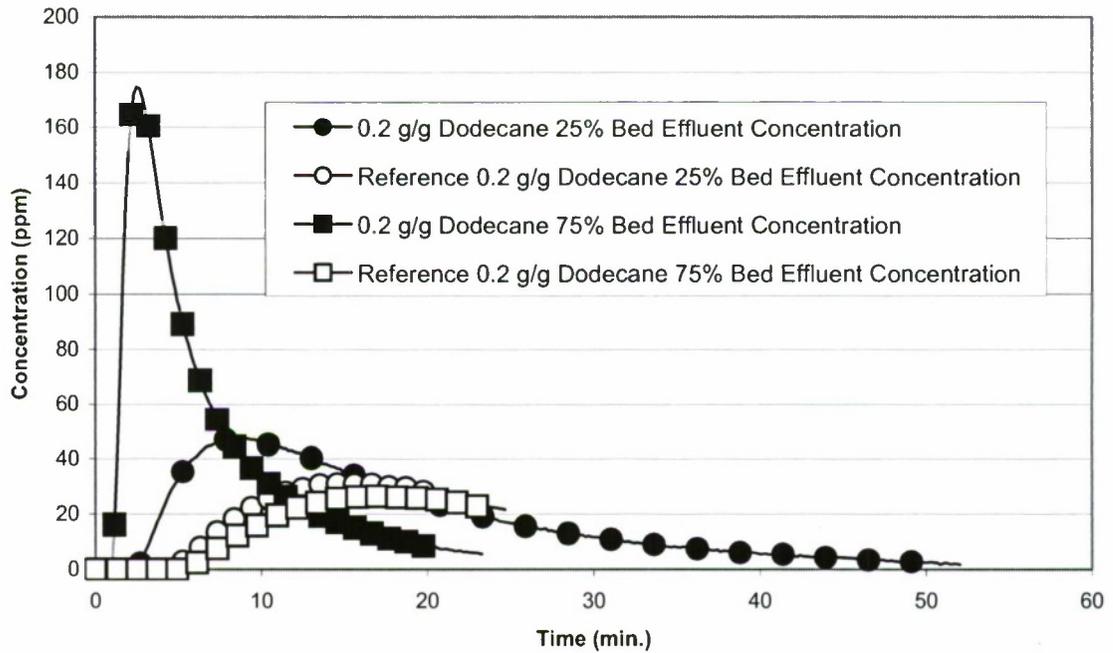


Figure 3.11 Results for 0.2 g/g Dodecane Loading at 50% RH Using PFCB

### 3.3.3.3 65% RH

Shown in Figure 3.12 are the results using dodecane with a 0.2 g/g loading at 65% RH. These experiments were conducted to identify the RH limit where PFCB can be effectively used as an indicator.

While these results do show the same trend as described previously and can likely be used to estimate the residual life, PFCB clutes through the bed quickly (short peak times) and at relatively high concentrations. At 65% RH, we are very close to the usable limit of PFCB, since a reliable indicator must be able to differentiate between the reference and the contaminated bed. If the reference bed has a very low adsorption capacity, then quantifying the difference between reference and contaminated beds is more difficult.

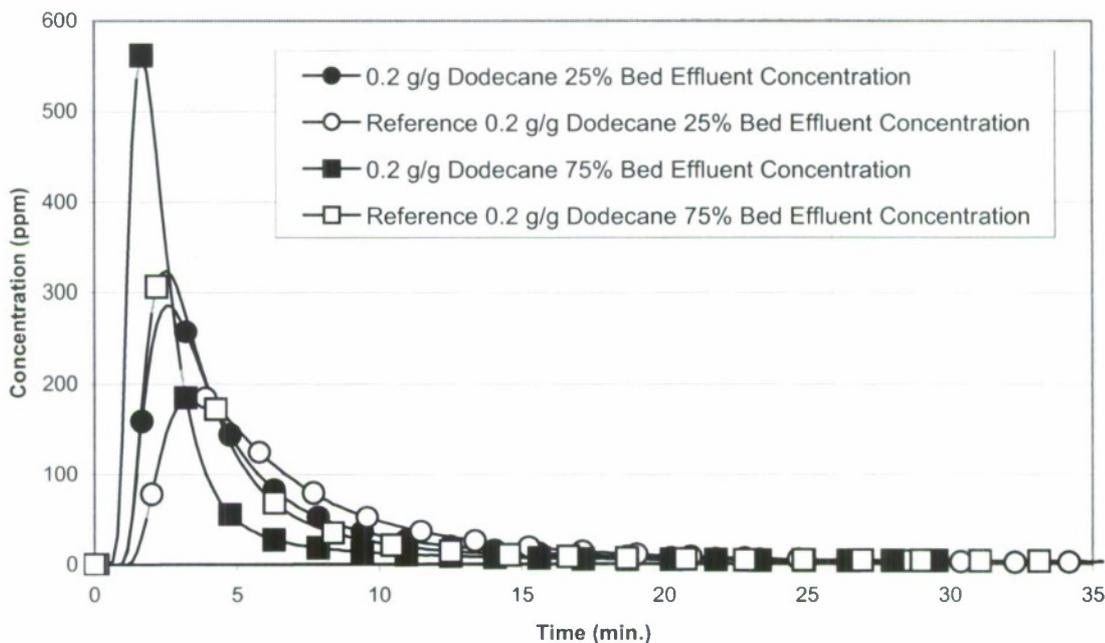


Figure 3.12 Results for 0.2 g/g Dodecane Loading at 65% RH Using PFCB

### 3.3.3.4 80% RH

Shown in Figures 3.13 and 3.14 are the results using dodecane as the contaminant at 80% RH. The pulse chemical used was R123. These results are similar those observed for octane.

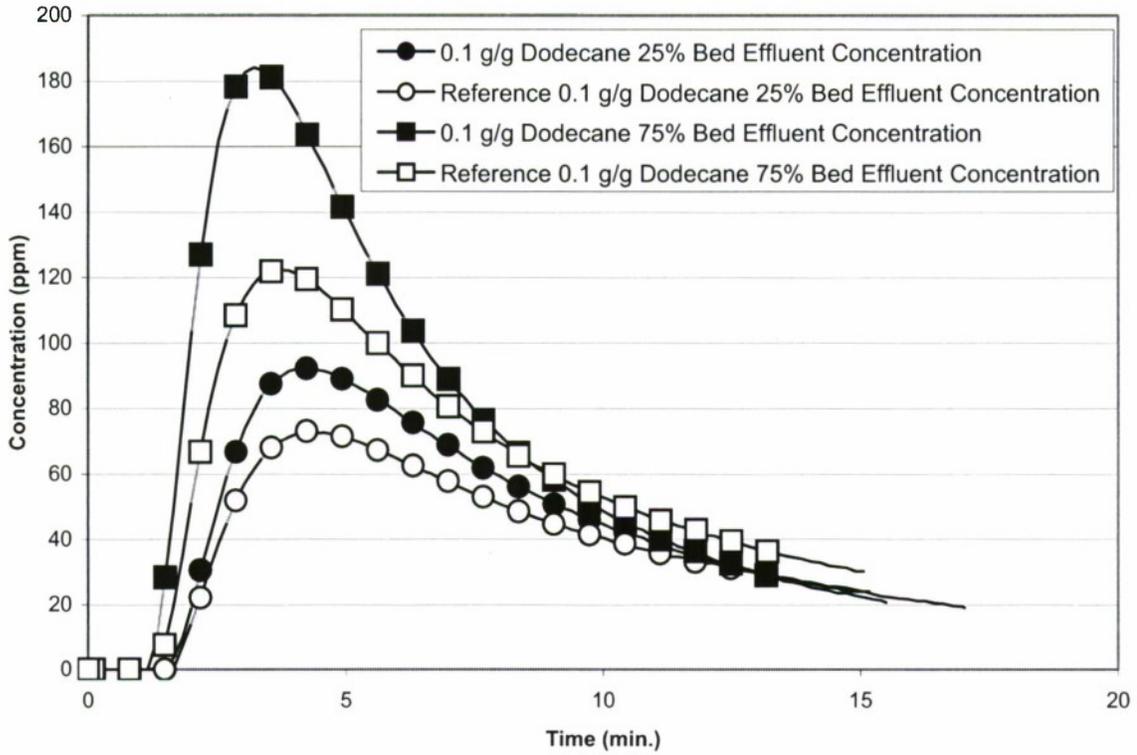


Figure 3.13 Results for 0.1 g/g Dodecane Loading at 80% RH Using R123

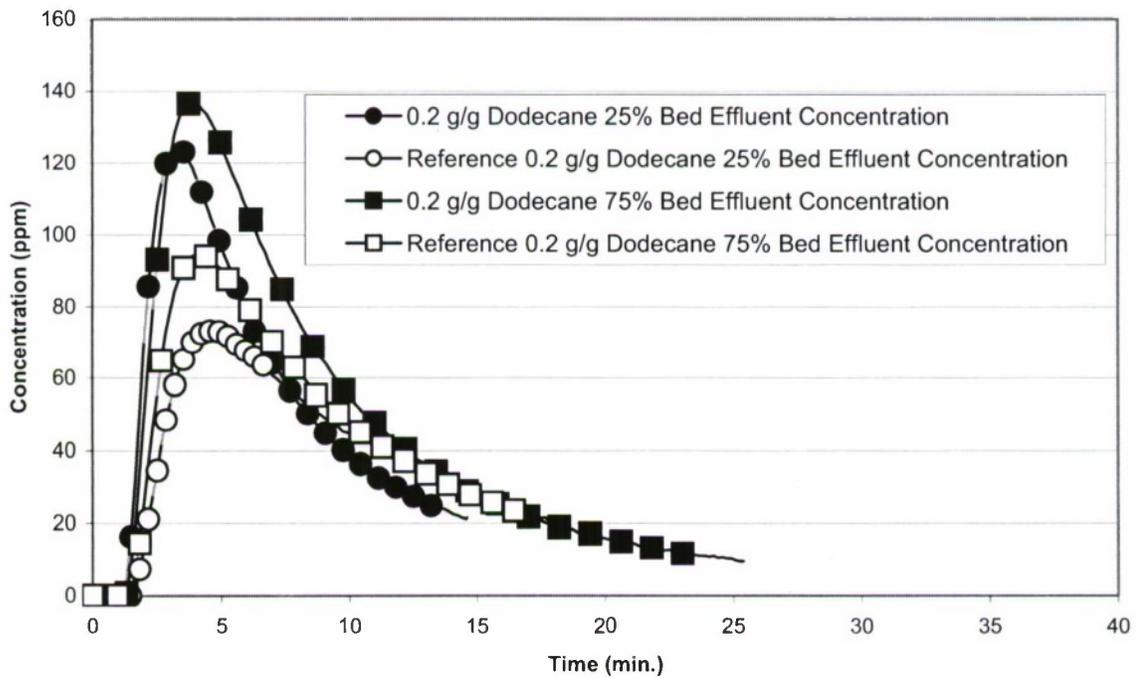


Figure 3.14 Results for 0.2 g/g Dodecane Loading at 80% RH Using R123

### 3.4 Pulse Testing Summary

The following are some key conclusions drawn from these pulse tests:

- The effect of RH is dramatic when using PFCB. Compare reference beds, for example, at 15 and 50% RH where the peak time goes from 40 to about 17 min. This is a major problem that has confronted attempts to develop an RLI in the past. The reference bed approach allows one to "subtract" the effect of RH.
- PFCB pulse tests are similar between dodecane and octane. Therefore, PFCB will give us a weakly adsorbed vapor response (safe sided).
- The limit where PFCB is effective is close to 65% RH.
- The relative response of R123 to contaminated bed changes is much smaller than that of PFCB, but it appears to be great enough to provide a measurable difference.

### 4. RLI CORRELATION

As we have shown from the breakthrough results and the pulse test results, RH (water adsorption) can dramatically change the relationships between variables. In addition, we have seen that the adsorption behavior of the threat vapor and the contaminant can also have a measurable effect on the breakthrough time.

A qualitative review of the pulse gas results at each RH show that the general trend from 25 to 75% contaminated remains consistent. At the higher RHs, the reference bed allows much more PFCB to penetrate earlier so that the difference between the reference and contaminated beds is much less. This in turn diminishes the resolution in the test, e.g., it becomes much more difficult to determine if the residual life is 70 or 30% of the original filter life. The resolution issue is especially true for the R123 results.

In terms of the procedure to be followed in operational situations for the dual-probe chemical system, the reference bed would be tested first using PFCB. If the peak concentration is below a preset value and the peak time is greater than a preset value, then PFCB can be used to probe the contaminated bed. Otherwise, R123 must be used for both beds. For example, in this work, a maximum PFCB concentration for the reference might be set at 200 ppm and a minimum peak retention time would be set at 3 min (see Figure 3.12). Clearly another alternative could be to keep the RH for both the reference and contaminated beds below 60% or so. This could be accomplished by heating the air entering the satellite beds to approximately 35 °C.

## RLI Estimation Algorithm

An algorithm that provides a reasonable correlation for residual life is as follows:

1. Find the reference peak time.
2. Integrate the reference effluent concentration from time = 0 to the peak time.
3. Integrate the corresponding contaminated effluent concentration from time = 0 to the peak time.
4. Compute the ratio of the two numbers (contaminated mass/reference mass).
5. Calculate the residual life by applying the MTZ effect.

As an example, let us examine how this would work for a 0.1 g/g bed contaminated with octane at 15% RH. Refer to Figure 3.2. The peak time for the reference is about 40 min. If we integrate under the effluent concentration curve for the 25% contaminated bed up to 40 min, we get 24 mg. Performing the same integration for the reference concentration curve up to 40 min results in an integrated mass of 8 mg.

A qualitative observation of the 15 and 50% RH reference bed results for all of the experiments shown in the plots in Section 3.0 is the large difference in reference bed results. We should be able to use the large change to scale our results based on the implied RH of the reference bed result. For example, if the mass and peak time for 15% RH results were kept as a baseline then the mass ratio could be scaled using this information. In this case, if we multiply the 50% RH results by 1.5 the mass ratios between 15 and 50%RH, the experiments are much closer.

Tables 4.1 and 4.2 summarize the correlated results for PFCB using octane and dodecane as the contaminant.

The next to last column is generated by integrating the effluent breakthrough curve up to the peak time. The last column is the ratio of the effluent mass of chemical between the contaminated and the reference bed. It is that value we propose to use to correlate to residual life.

From inspection, integrated ratio numbers below about 2.5 correspond to about 25% contaminated beds. Numbers above 6 or so correspond to the 75% contaminated beds. From a residual life perspective, if one assumes that about a quarter of the bed is mass transfer zone, then 25% contaminated bed will result in a 33% loss of protection time and a 75% contaminated bed will result in an almost immediate breakthrough.

Table 4.1 Summary of PFCB with Octane as Contaminant

Contaminant	Bed Loading (g/g)	Bed (%)	RH (%)	Peak Time (min)	Peak Conc (ppm)	Integrated Mass at Ref. Peak Time (mg)	Integrated Ratio Contam/Ref.
Octane	0.1	25	15	25	16	24	3.0
Reference	0	0	15	36	11	8	
Octane	0.1	75	15	5.6	55	70	9.2
Reference	0	0	15	36	10	8	
Octane	0.1	25	50	9.6	38	28	2.0
Reference	0	0	50	15	31	14	
Octane	0.1	75	50	3.7	171	99	5.7
Reference	0	0	50	14	38	18	
Octane	0.1	25	15	20	18	35	3.5
Reference	0	0	15	40	10	10	
Octane	0.2	75	15	2.2	249	88	13.2
Reference	0	0	15	38	10	7	
Octane	0.2	25	50	6.6	53	34	2.8
Reference	0	0	50	13	32	12	
Octane	0.2	75	50	2	305	86	8.5
Reference	0	0	50	17	22	10	

Table 4.2 Summary of PFCB with Dodecane as Contaminant

Contaminant	Loading (%)	Bed (%)	RH (%)	Peak Time (min)	Peak Conc (ppm)	Integrated Mass at Ref. Peak Time (mg)	Integrated Ratio Contam/Ref.
Dodecane	0.1	25	15	27	12	19	2.78
Reference	0	0	15	38	9	6	
Dodecane	0.1	75	15	6	60	86	7.88
Reference	0	0	15	36	10	8	
Dodecane	0.1	25	50	9.2	44	25	1.59
Reference	0	0	50	13	35	15	
Dodecane	0.1	75	50	3.8	16	93	3.93
Reference	0	0	50	13	40	18	
Dodecane	0.2	25	15	25	16	29	2.82
Reference	0	0	15	40	9	9	
Dodecane	0.2	75	15	3	89	92	10.31
Reference	0	0	15	41	8	6	
Dodecane	0.2	25	50	8	47	37	2.25
Reference	0	0	50	15	31	15	

Table 4.2 Summary of PFCB with Dodecane as Contaminant (Continued)

Contaminant	Loading (%)	Bed (%)	RH (%)	Peak Time (min)	Peak Conc (ppm)	Integrated Mass at Ref. Peak Time (mg)	Integrated Ratio Contam/Ref.
Dodecane	0.2	75	50	2.7	174	80	5.56
Reference	0	0	50	15	26	11	
Dodecane	0.2	75	65	1.6	562	54	2.09
Reference	0	0	65	2.5	323	22	
Dodecane	0.2	25	65	2.5	286	37	1.91
Reference	0	0	65	3.5	189	18	

Shown in Table 4.3 are the results for all of the 80% experiments using R123. These results are not as consistent as the results for the PFCB. For example, consider the integrated mass ratio values

Table 4.3 Summary of 80% RH Experiments Using R123

Contaminant	Loading (%)	Bed (%)	RH (%)	Peak Time (min)	Peak Conc (ppm)	Integrated Mass at Ref. Peak Time (mg)	Integrated Ratio Contam/Ref.
Octane	0.1	25	80	3.9	103	5.8	2.3
Reference	0	0	80	4.4	89	2.5	
Octane	0.1	75	80	3.9	137	11.9	2.5
Reference	0	0	80	4.1	87	4.7	
Octane	0.2	25	80	4.4	83	4.3	1.2
Reference	0	0	80	4.4	73	3.6	
Octane	0.2	75	80	4.1	113	9	2.7
Reference	0	0	80	4.4	73	3.3	
Dodecane	0.1	25	80	4.2	92	5	1.7
Reference	0	0	80	4.2	73	3	
Dodecane	0.1	75	80	3.1	184	24	3.0
Reference	0	0	80	3.8	123	8	
Dodecane	0.2	25	80	3.4	124	15	3.8
Reference	0	0	80	4.8	74	4	
Dodecane	0.2	75	80	3.9	137	13	2.6
Reference	0	0	80	4.2	95	5	

Given in Tables 4.4 and 4.5 below are integrated mass ratios along the estimated breakthrough times from Table 2.4.

Table 4.4 Break Time, Mass Ratio Comparison with Octane as Contaminant

Octane Loading (%)	Bed (%)	RH (%)	Integrated Mass Ratio Contam/Ref.	Estimated Hexane Break Time (min)	Hexane Residual Life (%)	Estimated Nonane Break Time (min)	Nonane Residual Life (%)
0.1	25	15	3.0	45	43	75	54
0.1	75	15	9.2	20	19	70	50
0.1	25	50	2.0	55	52		
0.1	75	50	5.7	25	24		
0.1	25	80	2.3	20	18	90	64
0.1	75	80	2.5	5	4	90	64
0.2	25	15	3.5	45	43	80	57
0.2	75	15	13.2	Instant	None	95	68
0.2	25	50	2.8	40	38		
0.2	75	50	8.5	Instant	None		
0.2	25	80	1.2	20	18	90	64
0.2	75	80	2.7	Instant	None	85	61

Table 4.5 Break Time, Mass Ratio Comparison with Dodecane as Contaminant

Dodecane Loading (%)	Bed (%)	RH (%)	Integrated Mass Ratio Contam/Ref.	Estimated Hexane Break Time (min)	Hexane Residual Life (%)	Estimated Nonane Break Time (min)	Nonane Residual Life (%)
0.1	25	15	2.8	60	57	60	43
0.1	75	15	7.9	35	33	10	7
0.1	25	50	1.6	60	57	n/a	n/a
0.1	75	50	3.9	25	24	n/a	n/a
0.1	25	80	1.7	15	14	80	57
0.1	75	80	3.0	15	14	45	32
0.2	25	15	2.8	50	48	50	36
0.2	75	15	10.3	Instant	None	Instant	None
0.2	25	50	2.3	50	48	n/a	n/a
0.2	75	50	5.6	Instant	None	n/a	n/a
0.2	25	80	3.8	20	13	60	43
0.2	75	80	2.6	Instant	None	Instant	None

## 5. SUMMARY

In this report, we have quantified the effect of heavy ambient contaminants on agent simulant breakthrough and developed a chemical vapor pulse method to determine the residual capacity, or residual life, of in-service ColPro filters. Many conclusions have been drawn from the data collected in this report.

In quantifying the effects of heavy contaminants on agent simulant breakthrough, we reached the following conclusions:

1. If hexane is a representative of the threat vapor (a moderate-to-high vapor pressure TIC), then
  - A contaminant that adsorbs as strongly as octane can prevent hexane from adsorbing, although not completely.
  - A contaminant that is very strongly adsorbed, such as dodecane, can almost completely exclude hexane at 0.2 g/g loading.
  - Adsorbed water can greatly affect residual life.
2. If nonane is a representative of the threat vapor (a low vapor pressure nerve agent), then
  - Octane has a small effect on the breakthrough time. Nonane can displace and/or adsorb in the remaining adsorption volume, even at a 0.2 g/g octane loading.
  - Adsorbed water has only a small negative impact.
  - Dodecane as a representative contaminant can adversely affect breakthrough times.

Some key conclusions from the pulse tests are

- The effect of RH is dramatic when using PFCB. Compare reference beds, for example, at 15 and 50% RH where the peak time goes from 40 to about 17 min. High RH has been the major hindrance to developing an RLI in the past. The reference bed approach allows one to subtract the effect of RH.
- PFCB pulse tests are similar between dodecane and octane. Therefore, PFCB will give us a weakly adsorbed vapor response (safe-sided).
- The limit where PFCB is effective at probing the carbon bed for contaminants is approximately 65% RH.

- The relative response of R123 to a contaminated bed is much smaller than that of PFCB, but appears to be great enough to provide a measurable difference.

A method has been developed to correlate vapor pulse response to the remaining life of in-service filters. Major conclusions are listed below:

- The dual satellite bed approach to “subtract out” the effects of adsorbed water has been shown to be effective
- The pulse results using the mass ratio calculation correlate well to the estimate breakthrough times for most of the test conditions investigated.
- Results for R123 at 80% RH are not as reliable as the results for PFCB at 15 and 50% RH. A reasonable approach in future development would include keeping the satellite beds at an elevated temperature to maintain a RH below 60% or so.
- The RLI concept proposed here has been fully evaluated and it is ready for technology transition to an engineering prototype.

Blank

## LITERATURE CITED

1. Favas, George. *End of Service Life Indicator (ESLI) for Respirator Cartridges. Part I. Literature Review*; DSTO-TN-0657; Defence Science and Technology Organisation: Canberra, Australia, 2005.
2. Lawhon, S.J.; Richardson, A.W.; Hofacre, K.C.; Gardner, P. *Development and Design of a Colorimetric End-of-Service-Life Indicator*; ECBC-CR-065; U.S. Army Edgewood Chemical Biological Center: Aberdeen Proving Ground, MD, 2003; UNCLASSIFIED Report (AD B298 053).
3. Mix, T.W.; McDonald, T.C. *A Vapor Challenge Method of Measuring the Residual Life of Gas Filters*; CRDEC-CR-086; U.S. Army Chemical Research Development and Engineering Center: Aberdeen Proving Ground, MD, 1990; UNCLASSIFIED Report (AD A227 711).
4. Smith, M.E. *The Adsorption of Pulses of Vapour through Charcoal Beds*, Master of Philosophy Thesis, Chemical Defence Establishment: Porton Down, Salisbury, Wiltshire, England, 1983.
5. Hammarstrom, J.; Bac, N.; Sacco, A., Jr. *Residual Life Method for Determining Gas Protection of ASC Whetlerite Carbon Beds*; ARCSL-CR-83046; U.S. Army Chemical Systems Laboratory: Aberdeen Proving Ground, MD, 1983; UNCLASSIFIED Report (AD B079 938).
6. Kladnig, W.F.; Weiss, A.H. *Residual Protective Life of Carbon Beds*; Quarterly Progress Report #9; Worcester Polytechnic Institute: New England, 1978.
7. Van Dongen, R.H. *Non-Destructive Test of Charcoal Filters. Part III. Characteristics of the elution peaks of ethane and propane on partially spent charcoal filters of various moisture content*. TNO: Brussels, 1975.
8. Wheat, J.A.; Hyde, J.C. *Estimation of the Residual Adsorption Capacity of Charcoal Filters*; Report No. 663; Defence Research Establishment: Ottawa, 1972.
9. Karwacki, C.J.; Morrison, R.W. *Adsorptive Retention of Volatile Vapors for Nondestructive Filter Leak Testing*. *Ind. Eng. Chem. Res.* **1998**, *37*, 3470-3480.
10. Peterson, G. W.; Jones, P.; Keller, J.; Weller, E. *Contaminant-Induced Degradation of ASZM-TEDA Reactivity*. ECBC-TR-629; U.S. Army Edgewood Chemical Biological Center: Aberdeen Proving Ground, MD, 2008; UNCLASSIFIED Report (AD B341 218).