

Graduate Theses, Dissertations, and Problem Reports

2000

Determining organic vapor cartridge breakthrough characteristics of JP-8 during aircraft fuel tank entry operations

Kevin W. Culp West Virginia University

Follow this and additional works at: https://researchrepository.wvu.edu/etd

Recommended Citation

Culp, Kevin W., "Determining organic vapor cartridge breakthrough characteristics of JP-8 during aircraft fuel tank entry operations" (2000). *Graduate Theses, Dissertations, and Problem Reports.* 1002. https://researchrepository.wvu.edu/etd/1002

This Thesis is protected by copyright and/or related rights. It has been brought to you by the The Research Repository @ WVU with permission from the rights-holder(s). You are free to use this Thesis in any way that is permitted by the copyright and related rights legislation that applies to your use. For other uses you must obtain permission from the rights-holder(s) directly, unless additional rights are indicated by a Creative Commons license in the record and/ or on the work itself. This Thesis has been accepted for inclusion in WVU Graduate Theses, Dissertations, and Problem Reports collection by an authorized administrator of The Research Repository @ WVU. For more information, please contact researchrepository@mail.wvu.edu.

DETERMINING ORGANIC VAPOR CARTRIDGE BREAKTHROUGH CHARACTERISTICS OF JP-8 DURING AIRCRAFT FUEL TANK ENTRY OPERATIONS

by

Kevin W. Culp

Thesis submitted to the
College of Engineering and Mineral Resources at
West Virginia University
in partial fulfillment of the requirements for the
degree of

Master of Science in Occupational Hygiene and Safety

Warren R. Myers, Ph.D., Chair Paul A. Jensen, Ph.D. Dianne L. McMullin, Ph.D.

Department of Industrial and Management Systems Engineering

Morgantown, WV

Keywords: Respirator, JP-8, fuel, cartridge, breakthrough

ABSTRACT

DETERMINING ORGANIC VAPOR CARTRIDGE BREAKTHROUGH CHARACTERISTICS OF JP-8 DURING AIRCRAFT FUEL TANK ENTRY OPERATIONS

by Kevin W. Culp

This study assessed the service life of organic vapor cartridges exposed to Jet Propulsion Type 8 fuel vapor. Two experiments were conducted that involved exposing 45 cartridges to three challenge concentrations (300, 600, and 1200 parts per million) of fuel vapor and two relative humidity levels (50 and 80 percent). The impact on service life of (1) high relative humidity conditions and (2) prior static exposure to fuel vapor were evaluated.

This study concluded that the 80 percent relative humidity test condition had a statistically significant effect on breakthrough time versus the 50 percent relative humidity condition, reducing service life by as much as 60 percent at the lowest challenge concentration tested. However, this effect was not statistically significant at the highest concentration. Prior exposure to fuel vapor also had a statistically significant impact on service life, but the shift in breakthrough time was minimal and would have a minor impact on cartridge change-out schedule planning.

ACKNOWLEDGMENTS

I'd like to extend a very warm "thank you" to all the wonderful people who contributed to the success of this research. Dr. Paul Jensen, Dr. Warren Myers, and Dr. Dianne McMullin spent countless hours tutoring, guiding, and supporting me, graciously donating their time and resources to the project and to me personally. Gary Fletcher and Kurt Van de Stowe were exceptionally instrumental in helping me understand the "ins and outs" of cartridge testing, and were very accommodating of my initial breakthrough testing efforts in their facilities. Sherman Adams, the most talented glassblower in the world, helped to design and create specialized glassware that was a key part of the vapor generation process. Dr. John Zondlo's creative ideas for vapor generation techniques were golden. Dr. Ernie Moyer, Dr. Steve Berardinelli, Steve Martin, Thomas Jefferson, Lee Hall, Bill Hoffman, Dr. Wakif Iskander, Dr. Gary Winn, Maj Les Smith, SSgt Doug Fritts, Jim Dalton, Diana Schwera, and Laszlo Bejo each provided invaluable technical and physical resource contributions to this project. My wife June never ceases to amaze me with her ability to catch manuscript errors; she spent countless hours reviewing and editing my work. Even more critical was the encouragement June and our little girl, Sarah, gave to me throughout the entire degree program. But most importantly, I want to thank God giving me the desire and ability to learn and for the people He has blessed me with.

TABLE OF CONTENTS

LIST OF FIGURES	
LIST OF TABLES	
GLOSSARY	vii
CHAPTER 1. INTRODUCTION	1
1.1. Use of Jet Propulsion Type 8 (JP-8) jet fuel in the U.S. Air Force	
1.1. USE OF JET PROPULSION TYPE 8 (JP-8) JET FUEL IN THE U.S. AIR FORCE	
1.3. Purpose of study	
CHAPTER 2. REVIEW OF LITERATURE	
2.1. HISTORY AND PREDOMINANCE OF JP-8 JET FUEL	
2.2. PROPERTIES AND HEALTH RISKS OF JP-8	
2.2.1. Chemical Composition	
2.2.2. Toxicology	
2.2.3. Exposure limits	
2.3. OPERATIONAL PARAMETERS AND CONCERNS	
2.3.1. Vapor composition	
2.3.2. Exposure monitoring data	
2.3.3. Respirator use	
2.3.4. Breakthrough testing parameters vs. the workplace environment	
2.4. REGULATORY REQUIREMENTS	
2.5.1. National Institute for Occupational Safety and Health (NIOSH)	
2.5.1. National Institute for Occupational Safety and Health (NIOSH)	
2.5.2. Environmental Protection Agency	
2.6.1. Overview	
2.6.2. Breakthrough testing methods	
2.7. Breakthrough of mixtures	
2.7.1. Overview	
2.7.2. Breakthrough testing methods	
2.8. Vapor generation	
CHAPTER 3. METHODS AND MATERIALS	
3.1. Purpose of study	
3.2. EXPERIMENTAL DESIGN	
3.2.1. Hypotheses 1 and 2	
3.2.2. Hypothesis 3	
3.3. EQUIPMENT CONFIGURATION	
3.3.1. General description	
3.3.2. Temperature, humidity, and air flow rate control	
3.3.3. JP-8 vapor generation	
3.3.4. Measurements	
3.4.1 Pro Conditioning	

3.4.2. Prior exposure	41
3.4.3. Breakthrough tests	
3.5. DATA REDUCTION AND ANALYSIS METHODOLOGY	
CHAPTER 4. RESULTS	48
4.1. Breakthrough testing data	48
4.2. CHARCOAL TUBE SAMPLING RESULTS.	
4.3. CARTRIDGE WEIGHT CHANGE	
4.4. INITIAL OBSERVATIONS	55
4.4.1. Effects of relative humidity and prior exposure (null hypotheses 1 and 2)	
4.4.2. Relationships between breakthrough concentration and time (null hypothesis 3).	
CHAPTER 5. ANALYSIS AND DISCUSSION	59
5.1. EFFECT OF RELATIVE HUMIDITY AND CHALLENGE CONCENTRATION ON BREAKTHROUG	H TIME
(NULL HYPOTHESIS 1)	
5.1.1. Overview	
5.1.2. Normality and homogeneity of variance	
5.1.3. Analysis of Variance (ANOVA)	
5.1.4. Tests for differences between means	
5.2. EFFECTS OF PRIOR EXPOSURE AND CHALLENGE CONCENTRATION (NULL HYPOTHESIS 2)	
5.2.1. Overview	61
5.2.2. Normality and homogeneity of variance	61
5.2.3. Analysis of Variance (ANOVA)	
5.2.4. Tests for differences between means	
5.3. ANALYSIS OF BREAKTHROUGH CONCENTRATION VS. BREAKTHROUGH TIME (NULL HYPE	OTHESIS 3)
5.3.1. Application of the Yoon and Nelson equation	
5.3.2. Modeling of relative humidity effects	
5.4. DEVELOPMENT OF CARTRIDGE SERVICE LIFE GUIDELINES	
5.4.1. General approach	
5.4.2. Predicting breakthrough times for the 50 percent relative humidity condition	
5.4.3. Predicting breakthrough times for the 80 percent relative humidity condition (no	
exposure)5.4.4. Predicting breakthrough times for the 80 percent relative humidity condition (wi	
2.4.4. Predicting breakthrough times for the 80 percent relative humiaity condition (will exposure)	
CHAPTER 6. CONCLUSIONS AND RECOMMENDATIONS	
6.1. SUMMARY OF FINDINGS.	
6.2. CHANGE-OUT SCHEDULE RECOMMENDATIONS.	
6.3. CONSIDERATIONS FOR FUTURE RESEARCH EFFORTS.	
6.3.1. Comparison of sampling methods	
6.3.2. Compositional differences between challenge and breakthrough vapors	
6.3.3. Changes in breakthrough times resulting from extensive prior exposure to fuel vo	
6.3.4. Modeling of relative humidity effects	
6.3.5. Identification of a surrogate compound	
6.4. CLOSING REMARKS	

REFERENCES

APPENDICES

APPENDIX A: MEASURED BREAKTHROUGH CONCENTRATION ON OUTLET SIDE OF CARTRIDGES DURING TESTS

APPENDIX B: MODIFIED NIOSH 1550 METHOD SAMPLING RESULTS

APPENDIX C: CARTRIDGE WEIGHT CHANGE SUMMARY

APPENDIX D: STATISTICAL ASSESSMENT OF RESULTS – SAS/STAT OUTPUT APPENDIX E: CURVE-FITTING ANALYSIS OF GENERALIZED YOON AND

NELSON EQUATION

LIST OF FIGURES

FIGURE 3-1. FACTORIAL DESIGN OF BREAKTHROUGH TESTING RESEARCH	30
FIGURE 3-2. TEST SYSTEM CONFIGURATION.	
FIGURE 3-3. VAPOR GENERATION PORTION OF BREAKTHROUGH TESTING SYSTEM	34
FIGURE 3-4. CUSTOM DISTILLATION HEAD INSERTED INTO TOP OF PACKED COLUMN	37
FIGURE 3-5. CONFIGURATION OF CARTRIDGES INSIDE CHAMBER FOR PRE-CONDITIONING AT 80%	
RELATIVE HUMIDITY	
FIGURE 4-1. ESTIMATED MASS OF WATER AND JP-8 FUEL VAPOR FLOWING THROUGH EACH CARTRIDO	ЗE
PER MINUTE OF BREAKTHROUGH TEST AT 25 °C	50
FIGURE 4-2. TOTAL AVERAGE CARTRIDGE WEIGHT GAINS AT 20% BREAKTHROUGH POINTS FOR EACH	
TEST CONDITION. (ALL CARTRIDGES WERE PRECONDITIONED FOR 6 HOURS AT 80% RELATIVE	
HUMIDITY AND 25 °C.)	51
FIGURE 4-3. MEAN BREAKTHROUGH TIME TO 10% OF JP-8 FUEL VAPOR CHALLENGE CONCENTRATIO	
FIGURE 4-4. SCATTER PLOT OF BREAKTHROUGH TIMES FOR 50% RELATIVE HUMIDITY CONDITION ANI	
PRIOR EXPOSURE TO FUEL VAPOR. ALL CARTRIDGES WERE PRECONDITIONED AT 80% RELATIVE	į.
HUMIDITY AND 25 °C FOR SIX HOURS. PRIOR EXPOSED CARTRIDGES WERE PREVIOUSLY SUBJECT	TED
TO STATIC CONCENTRATIONS OF 1200 PPM FUEL VAPOR FOR EIGHT HOURS AT 80% RELATIVE	
HUMIDITY AND 25 °C.	57
FIGURE 4-5. SCATTER PLOT OF BREAKTHROUGH TIMES FOR 80% RELATIVE HUMIDITY CONDITION ANI	ON C
PRIOR EXPOSURE TO FUEL VAPOR. ALL CARTRIDGES WERE PRECONDITIONED AT 80% RELATIVE	į.
HUMIDITY AND 25 °C FOR SIX HOURS. PRIOR EXPOSED CARTRIDGES WERE PREVIOUSLY SUBJECT	TED
TO STATIC CONCENTRATIONS OF 1200 PPM FUEL VAPOR FOR EIGHT HOURS AT 80% RELATIVE	
HUMIDITY AND 25 °C.	58
FIGURE 4-6. SCATTER PLOT OF BREAKTHROUGH TIMES FOR 80% RELATIVE HUMIDITY CONDITION ANI)
PRIOR EXPOSURE TO FUEL VAPOR. ALL CARTRIDGES WERE PRECONDITIONED AT 80% RELATIVE	Ε
HUMIDITY AND 25 °C FOR SIX HOURS. PRIOR EXPOSED CARTRIDGES WERE PREVIOUSLY SUBJECT	TED
TO STATIC CONCENTRATIONS OF 1200 PPM FUEL VAPOR FOR EIGHT HOURS AT 80% RELATIVE	
HUMIDITY AND 25 °C.	58
FIGURE 5-1. SEMI-LOG PLOT OF A GENERALIZED YOON AND NELSON EQUATION AGAINST MEAN	
BREAKTHROUGH TIMES FOR 50% RELATIVE HUMIDITY TEST CONDITION. ALL CARTRIDGES WER	E
PRECONDITIONED AT 80% RELATIVE HUMIDITY AND 25 °C FOR SIX HOURS	
FIGURE 5-2. SEMI-LOG PLOT OF A GENERALIZED YOON AND NELSON EQUATION AGAINST MEAN	
BREAKTHROUGH TIMES FOR 80% RELATIVE HUMIDITY TEST CONDITION (WITHOUT PRIOR	
EXPOSURE TO FUEL VAPOR). ALL CARTRIDGES WERE PRECONDITIONED AT 80% RELATIVE	
HUMIDITY AND 25 °C FOR SIX HOURS.	65
FIGURE 5-3. SEMI-LOG PLOT OF A GENERALIZED YOON AND NELSON EQUATION AGAINST MEAN	00
BREAKTHROUGH TIMES FOR 80% RELATIVE HUMIDITY TEST CONDITION (WITH PRIOR EXPOSURE	OT 5
FUEL VAPOR). ALL CARTRIDGES WERE PRECONDITIONED AT 80% RELATIVE HUMIDITY AND 25 °	
FOR SIX HOURS. PRIOR EXPOSED CARTRIDGES WERE PREVIOUSLY SUBJECTED TO STATIC	_
CONCENTRATIONS OF 1200 PPM FUEL VAPOR FOR EIGHT HOURS AT 80% RELATIVE HUMIDITY A	ND
25 °C	
FIGURE 5-4. GENERALIZED YOON AND NELSON EQUATION FIT TO MEASURED BREAKTHROUGH DATA	
50% RELATIVE HUMIDITY WITHOUT PRIOR EXPOSURE TO FUEL. COFFECIENTS FOR FOLIATION	

WERE DETERMINED INDIVIDUALLY FOR EACH CHALLENGE CONCENTRATION. ALL CARTRIDGES
WERE PRECONDITIONED AT 80% RELATIVE HUMIDITY AND 25 °C FOR SIX HOURS67
FIGURE 5-5. GENERALIZED YOON AND NELSON EQUATION FIT TO MEASURED BREAKTHROUGH DATA AT
80% RELATIVE HUMIDITY, WITHOUT PRIOR EXPOSURE TO FUEL. COEFFICIENTS FOR EQUATION
WERE DETERMINED INDIVIDUALLY FOR EACH CHALLENGE CONCENTRATION. ALL CARTRIDGES
WERE PRECONDITIONED AT 80% RELATIVE HUMIDITY AND 25 °C FOR SIX HOURS68
FIGURE 5-6. GENERALIZED YOON AND NELSON EQUATION FIT TO MEASURED BREAKTHROUGH DATA AT
80% RELATIVE HUMIDITY, WITH PRIOR EXPOSURE TO FUEL. COEFFICIENTS WERE DETERMINED
INDIVIDUALLY FOR EACH CHALLENGE CONCENTRATION. ALL CARTRIDGES WERE PRECONDITIONED
AT 80% RELATIVE HUMIDITY AND 25 °C FOR SIX HOURS. PRIOR EXPOSED CARTRIDGES WERE
PREVIOUSLY SUBJECTED TO STATIC CONCENTRATIONS OF 1200 PPM FUEL VAPOR FOR EIGHT HOURS
AT 80% RELATIVE HUMIDITY AND 25 °C68
FIGURE 5-7. RATIO BETWEEN BREAKTHROUGH TIMES FOR 80 PERCENT AND 50 PERCENT RELATIVE
HUMIDITY CONDITIONS (WITHOUT PRIOR EXPOSURE TO FUEL VAPOR), WITH LINEAR REGRESSION
FIT. DATA POINTS REPRESENT THE CALCULATED MEAN BREAKTHROUGH TIME RATIOS. ALL
CARTRIDGES WERE PRECONDITIONED AT 80% RELATIVE HUMIDITY AND 25 °C FOR SIX HOURS70
FIGURE 5-8. STRAIGHT-LINE APPROXIMATION OF CARTRIDGE BREAKTHROUGH TIMES BASED ON 95%
LCL ESTIMATES (50 PERCENT RELATIVE HUMIDITY, NO PRIOR EXPOSURE). ALL CARTRIDGES WERE
PRECONDITIONED AT 80% RELATIVE HUMIDITY AND $25~^{\circ}\mathrm{C}$ FOR SIX HOURS AND WERE TESTED WITH
AN AIR FLOW RATE OF 32 LPM THROUGH EACH CARTRIDGE73
FIGURE 5-9. STRAIGHT-LINE APPROXIMATION OF CARTRIDGE BREAKTHROUGH TIMES BASED ON 95%
LCL ESTIMATES (80 PERCENT RELATIVE HUMIDITY, NO PRIOR EXPOSURE). ALL CARTRIDGES WERE
PRECONDITIONED AT 80% RELATIVE HUMIDITY AND $25~^{\circ}\text{C}$ FOR SIX HOURS AND WERE TESTED WITH
AN AIR FLOW RATE OF 32 LPM THROUGH EACH CARTRIDGE74

LIST OF TABLES

•
TABLE 2-1. GENERAL CHEMICAL COMPOSITION OF LIQUID JP-8 FUEL. ²
TABLE 2-2. MAJOR COMPONENTS OF JP-8 JET FUEL VAPOR AT THE LOWER TEMPERATURE LIMIT OF
FLAMMABILITY (LTLF).8
TABLE 2-3. CHANGES IN VALUE OF S ACROSS THE BREAKTHROUGH CURVE
TABLE 2-4. APPROXIMATE RATIO OF WATER MOLECULES TO FUEL VAPOR MOLECULES IN A FIXED
VOLUME OF AIR FOR 50 AND 80 PERCENT RELATIVE HUMIDITY LEVELS, AT 300 AND 1200 PARTS
PER MILLION OF FUEL VAPOR
TABLE 3-1. SYSTEM PARAMETER SETTINGS FOR CARTRIDGE PRE-CONDITIONING WITH 32 LITERS PER
MINUTE OF AIR AT 25 °C AND 80 PERCENT RELATIVE HUMIDITY. TEMPERATURE AND RELATIVE
HUMIDITY SETTINGS ARE EXPRESSED AS APPROXIMATE RANGES OF SETTING PAIRS (A AND B),
SINCE AMBIENT LABORATORY TEMPERATURE CONDITIONS AFFECTED THE TEMPERATURE BEING
DELIVERED TO THE RESPIRATOR TESTING CHAMBER. PERIODIC ADJUSTMENTS WERE MADE TO
ACHIEVE A MONITORED TEMPERATURE OF 25 °C AND RELATIVE HUMIDITY LEVEL OF 80 PERCENT
WITHIN THE CHAMBER
TABLE 3-2. SYSTEM PARAMETER SETTINGS DURING PRIOR EXPOSURE OF CARTRIDGES TO 25 °C AIR AT
80% RELATIVE HUMIDITY AND 1200 PPM JP-8 VAPOR. TEMPERATURE AND RELATIVE HUMIDITY
SETTINGS ARE EXPRESSED AS APPROXIMATE RANGES OF SETTING PAIRS (A AND B), SINCE AMBIEN
LABORATORY TEMPERATURE CONDITIONS AFFECTED THE TEMPERATURE BEING DELIVERED TO THI
RESPIRATOR TESTING CHAMBER. PERIODIC ADJUSTMENTS WERE MADE TO ACHIEVE A MONITORED
TEMPERATURE OF 25 °C AND RELATIVE HUMIDITY LEVEL OF 80 PERCENT WITHIN THE CHAMBER.4
TABLE 3-3. SYSTEM CONFIGURATION SETTINGS USED DURING CARTRIDGE BREAKTHROUGH TESTING.
TEMPERATURE AND RELATIVE HUMIDITY SETTINGS ARE EXPRESSED AS APPROXIMATE RANGES OF
SETTING PAIRS (A & B, AND C & D), SINCE AMBIENT LABORATORY TEMPERATURE CONDITIONS
AFFECTED THE TEMPERATURE BEING DELIVERED TO THE RESPIRATOR CHAMBER. PERIODIC
ADJUSTMENTS WERE MADE TO ACHIEVE A MONITORED TEMPERATURE OF 25 °C AND RELATIVE
HUMIDITY LEVEL OF 50 OR 80 PERCENT WITHIN THE RESPIRATOR TESTING CHAMBER4
TABLE 4-1. SUMMARY TABLE OF CHARCOAL TUBE SAMPLING RESULTS, COMPARING TARGET
CONCENTRATION (MEASURED WITH FOXBORO TVA-1000B PORTABLE FLAME IONIZATION
DETECTOR) TO VALUES MEASURED VIA MODIFIED NIOSH 1550 SAMPLING METHOD4
TABLE 4-2. SUMMARY OF TOTAL MEAN CARTRIDGE WEIGHT GAINS (IN GRAMS) FOR EACH TREATMENT
CONDITION4
TABLE 4-3. MASS FLOWING THROUGH THE CARTRIDGE PER MINUTE AT TESTED CONDITIONS OF
CHALLENGE CONCENTRATION AND RELATIVE HUMIDITY, WITH AIR FLOW RATE SET AT 32 LPM 5
TABLE 4-4. SUMMARY TABLE OF TIME (IN MINUTES) TO VARIOUS BREAKTHROUGH CONCENTRATIONS FO
50 PERCENT RELATIVE HUMIDITY (NO PRIOR EXPOSURE) TEST CONDITION. ALL CARTRIDGES WERE
PRECONDITIONED AT 25 $^{\circ}\text{C}$ and 80 percent relative humidity for Six Hours at an Air flow
RATE OF 32 LPM, AND WERE TESTED AT 25 °C AND A FLOW RATE OF 32 LPM5
TABLE 4-5. SUMMARY TABLE OF TIME (IN MINUTES) TO VARIOUS BREAKTHROUGH CONCENTRATIONS
FOR 80 PERCENT RELATIVE HUMIDITY (NO PRIOR EXPOSURE) TEST CONDITION. ALL CARTRIDGES
WERE PRECONDITIONED AT $25~^{\circ}\text{C}$ and $80~^{\circ}\text{Percent}$ relative humidity for SIX hours at an AIF
FLOW RATE OF 32 LPM, AND WERE TESTED AT 25 °C AND A FLOW RATE OF 32 LPM5
TABLE 4-6. SUMMARY TABLE OF TIME (IN MINUTES) TO VARIOUS BREAKTHROUGH CONCENTRATIONS
FOR 80 PERCENT RELATIVE HUMIDITY (WITH PRIOR EXPOSURE) TEST CONDITION. ALL CARTRIDGES
WERE PRECONDITIONED AT $25~^{\circ}$ C and $80~^{\circ}$ PERCENT RELATIVE HUMIDITY FOR SIX HOURS AT AN AIR
FLOW RATE OF 32 LPM, FOLLOWED BY STATIC EXPOSURE TO 1200 PPM OF FUEL VAPOR AND 80

PERCENT RELATIVE HUMIDITY AT 25 $^{\circ}$ C FOR EIGHT HOURS. THEY WERE THEN TESTED AT 25 $^{\circ}$ C	
AND A FLOW RATE OF 32 LPM.	54
TABLE 5-1. ANALYSIS OF VARIANCE (ANOVA) FOR RELATIVE HUMIDITY AND CONCENTRATION	
TREATMENTS	60
TABLE 5-2. ANALYSIS OF VARIANCE (ANOVA) FOR PRIOR EXPOSURE AND CONCENTRATION	
TREATMENTS	
TABLE 5-3. CURVE-FIT PARAMETERS FOR GENERALIZED YOON AND NELSON EQUATION	67
TABLE 5-4. RATIO BETWEEN 80 PERCENT (WITH NO PRIOR EXPOSURE TO FUEL) AND 50 PERCENT	
RELATIVE HUMIDITY BREAKTHROUGH TIMES FOR FIXED CONCENTRATIONS AND BREAKTHROUGH	
POINTS	
Table 5-5. Simplified estimates of cartridge service life at selected action level for 50%	
RELATIVE HUMIDITY EXPOSURE AND ROOM TEMPERATURE CONDITIONS. IN MOST CASES, THE	
SELECTED ACTION LEVEL WILL BE ½ THE OEL OR TLV (7 OR 25 PPM)	73
TABLE 5-6. SIMPLIFIED ESTIMATES OF CARTRIDGE SERVICE LIFE AT A SELECTED ACTION LEVEL FOR 809	%
RELATIVE HUMIDITY EXPOSURE AND ROOM TEMPERATURE CONDITIONS. IN MOST CASES, THE	
SELECTED ACTION LEVEL WILL BE ½ THE OEL OR TLV (7 OR 25 PPM)	74
Table 6-1(a) through (c). Estimated cartridge service life for pairs of $3M^{TM}$ 7251 organic	
VAPOR CARTRIDGES DURING ACTIVE EXPOSURE TO JP-8 JET FUEL. ESTIMATES ARE BASED ON TH	_
SERVICE LIFE TESTED UNDER LABORATORY CONDITIONS WITH 32 LPM AIRFLOW THROUGH EACH	[
CARTRIDGE (EQUIVALENT TO 64 LPM AIRFLOW THROUGH EACH SET OF CARTRIDGES) AT (A) 300)
PPM, (B) 600 PPM, AND (C) 1200 PPM CHALLENGE CONCENTRATIONS. ALL CARTRIDGES WERE	
PRECONDITIONED AT 80 PERCENT RELATIVE HUMIDITY AND 25 °C FOR SIX HOURS	79
TABLE 6-2. SUMMARY OF WOOD MODEL EQUATION PARAMETERS AND ESTIMATED BREAKTHROUGH	
TIMES (TO 10 PERCENT OF THE CHALLENGE CONCENTRATION) FOR MAJOR COMPONENTS OF JP-8	
FUEL VAPOR. CALCULATIONS ARE FOR A 300 PPM CHALLENGE CONCENTRATION (0.228 TORR)	
UNDER DRY CONDITIONS WITH NO CARTRIDGE PRECONDITIONING, AND THE SATURATION PARTIA	
PRESSURES (ρ_{SAT}) LISTED ARE FOR EACH SUBSTANCE IN PURE FORM	82
TABLE 6-3. PARAMETERS FOR APPLYING THE WOOD MODEL EQUATION TO MAJOR COMPONENTS OF JP	
JET FUEL	82

GLOSSARY

ACGIH. American Conference of Governmental Industrial Hygienists, a professional organization devoted to the administrative and technical aspects of occupational and environmental health.

AFOSH. Air Force Occupational Safety and Health program. By Executive Order 12196, the Department of Defense is responsible for establishing a Safety and Health program that meets or exceeds federal OSHA guidelines. The AFOSH program is the Air Force's implementation of that requirement.

Air Purifying Respirator (APR). A device that allows a worker to breathe ambient air that has been cleaned of hazardous substances. Cartridges or canisters remove the substances through a variety of mechanisms. With organic vapor cartridges, adsorption of the vapors is the primary mechanism used.

Breakthrough. Permeation of a hazardous substance through a respirator cartridge or canister. Breakthrough is typically defined as a fixed concentration or a percentage of the challenge concentration being drawn (or pushed) through the cartridge or canister.

CFR. The Code of Federal Regulations (CFR) is a codification of general and permanent rules (regulations) that have been previously published in the Federal Register. The CFR, which is compiled by the Office of the Federal Register, is divided into 50 titles, which cover broad areas subject to Federal regulation.

Challenge concentration. The amount of vapor present in the air stream being fed through a respirator cartridge or canister. This is usually defined in terms of parts per million (ppm) or milligrams per cubic meter (mg/m³).

Committee on Toxicology (COT). A group within the National Research Council's National Academy of Sciences that is tasked with assessing toxicity associated with hazardous substances.

IERA. Institute for Environmental, Safety, and Occupational Health Risk Analysis. IERA is a U.S. Air Force institution headquartered at Brooks Air Force Base in San Antonio, Texas, providing occupational health and environmental risk support to the Air Force community.

Immediately Dangerous to Life or Health (IDLH). A concentration of a harmful substance in air that poses a threat which would be likely to cause death or immediate or delayed permanent adverse health effects or prevent escape from such an environment.

Jet Propellant Type 8 (JP-8). A type of aviation fuel frequently used in military jet aircraft, similar in composition to Jet-A fuel used in the commercial aviation industry.

LPM. Liters per minute.

mg/m³. Milligrams of a substance per cubic meter of air, an expression of vapor concentration in mass per unit volume. For JP-8 jet fuel, one mg/m³ is approximately equivalent to 0.14 parts per million (ppm).

National Institute for Occupational Safety and Health (NIOSH). A national organization within the U.S. Centers for Disease Control and Prevention that conducts health and safety research, recommends standards, and regulates certification of respiratory protection equipment.

NRC. National Research Council.

Occupational Exposure Limit (OEL). The U.S. Air Force limit for airborne concentrations of a substance for a specific period of time. The term OEL includes all time-weighted averages (OEL-TWA)s, short-term exposure limits (OEL-STELs), and ceilings that apply to a substance. OELs apply to occupational exposures for each individual worker for a single 8-hour work shift, and must be adjusted for longer shifts.

OSHA. Occupational Safety and Health Administration.

Parts per million (ppm). An expression of vapor concentration in air. For JP-8 jet fuel, which has an approximate molecular weight of 170 milligrams (mg), a commonly-accepted conversion factor is about 0.14 ppm for each milligram per cubic meter (mg/m^3) .

Permissible Exposure Limit (PEL). A maximum allowable concentration of a substance in air, established by OSHA as a legal standard. PELs are 8-hour exposure limits for an individual worker over a 40-hour work week.

Preconditioning. A procedure which involves passing temperature- and humidity-controlled air through a cartridge in an attempt to simulate static, shelf exposure to fixed levels of humidity and temperature over an extended period of time. In this study, each cartridge was preconditioned by passing 32 liters per minute of air at 25 °C and 80 percent relative humidity through it for a duration of 6 hours.

Prior exposure. A simulation of workplace static exposure of an organic cartridge's face to high levels of fuel vapor and relative humidity. For this study, prior exposure refers to exposing a cartridge's face to air containing 1200 parts per million (ppm) of fuel vapor and 80 percent relative humidity for an 8-hour duration.

Recommended Exposure Limit (REL). A maximum 10-hour Time-Weighted Average Concentration over a 40-hour work week, set by the National Institute for Occupational Safety and Health (NIOSH). It is intended to be a recommended guideline and is not legally enforceable.

Respirator. A protective device that is designed to provide a safe breathing atmosphere free from harmful concentrations of hazardous substances.

Service Life. The length of time a cartridge may be used to prevent respiratory exposure to a vapor. (Also see "breakthrough".)

Technical Order (T.O.). A document that provides maintenance guidance to U.S. Air Force employees. T.O. 1-1-3 is the primary document referenced during repair of aircraft fuel systems.

Threshold Limit Value (TLV[®]). An exposure guideline set by the American Conference of Governmental Industrial Hygienists (ACGIH) under which most people can work consistently for 8 hours per day over a 40-hour work week with no harmful effects.

USAF. United States Air Force.

WVU. West Virginia University, in Morgantown, West Virginia.

Chapter 1. INTRODUCTION

1.1. Use of Jet Propulsion Type 8 (JP-8) jet fuel in the U.S. Air Force

Throughout the United States, both in the military and in the aviation industry, kerosene-based jet fuels are commonly used as propulsion sources. Activities that require personnel to work around such fuels often expose individuals to vapors that may exceed applicable occupational exposure limits. When engineering and administrative controls cannot adequately maintain levels below these limits, respiratory protection is employed to ensure employees are breathing fresh air sources.

In the United States Air Force (USAF), JP-8 jet fuel is the predominant fuel source for numerous aircraft. Military personnel are frequently exposed to JP-8 vapors when entering aircraft fuel tanks to conduct repairs, during ground refueling activities, storage tank cleaning and maintenance, and other activities where liquid JP-8 may volatilize and produce vapors in a worker's breathing zone. Similar exposures occur in civilian and commercial aviation industry, where similar fuels are used (e.g. Jet-A fuel).

1.2. Respiratory protection

Respirators containing organic vapor cartridges are sometimes used to control airborne exposures to fuel vapors. The cartridges use a carbon-based material which adsorbs vapor (aqueous and organic compounds) present in the air stream. As the cartridge is exposed over time, it eventually becomes saturated to the extent that it can no longer adsorb and remove these compounds from the air stream. When this occurs, organic vapors begin to pass through the cartridge. Consequently, the worker is exposed to an increasing concentration of vapors, which may exceed the applicable Occupational Exposure Limit (OEL) and place the worker at risk. When the concentration of vapors reaches a predetermined value or percentage of the upstream concentration, breakthrough has occurred.

Recent regulations established by the Occupational Safety and Health Administration (OSHA) in Title 29, Code of Federal Regulations (CFR) Part 1910.134 require employers to establish change-out schedules when air purifying respirators are worn to control exposures below the applicable Permissible Exposure Limit (PEL). Warning properties such as odor or irritation may no longer be used as the sole basis for changing cartridges, although they can be used in conjunction with the established change-out schedule.

Unfortunately, many employers do not have access to quantifiable breakthrough data to help them establish effective change-out schedules. Furthermore, most of the data that do exist were based on breakthrough times for single-component substances. Mathematical models that predict breakthrough for single-component substances have limited applicability to substances containing numerous compounds, such as JP-8, a complex mixture of over 300 organic compounds.

Within the USAF, organic vapor cartridges are used to control exposures to JP-8 vapors under two configurations: (1) as a primary means of vapor control (dynamic air flow through the cartridge); and (2) as a back-up, escape only provision, employed only when a supplied airline system fails to provide adequate flow of air. The first configuration is not used frequently in the USAF, but is more often used in the commercial aviation industry. The second configuration is commonly used in the USAF, particularly during worker entry into aircraft fuel tanks. It is important to note that in the second configuration, the worker is not actively breathing through the cartridge, since a Grade D breathing air source is provided. However, the face of the cartridge is exposed to the ambient level of fuel vapor, since the cartridge will become the default source of breathing air to the user should the supplied air system fail.

1.3. Purpose of study

Since there is limited breakthrough data for the use of organic vapor cartridges in controlling worker exposure to environments consisting of complex fuel mixtures such as JP-8, it would be valuable to the USAF and to the aviation industry to address the following:

- How long will a cartridge last when actively used at known concentrations of JP-8 fuel vapor?
- Will relative humidity impact the service life of a cartridge?
- Does static exposure of a cartridge to JP-8 fuel vapor reduce its ability to perform under dynamic conditions, thereby limiting the active service life?

The purpose of this study is to address these identified areas of concern through the use of controlled experimental procedures and methodology to simulate static and dynamic exposure of organic vapor cartridges to known concentrations of JP-8 fuel vapor and conditions of temperature and relative humidity.

Chapter 2. REVIEW OF LITERATURE

2.1. History and predominance of JP-8 jet fuel

Prior to World War II, most of the jet engines used throughout the world used kerosene as a fuel source.¹ The development of high-speed jet aircraft in the late 1940s and early 1950s promulgated research into new aviation fuels that would perform better under high altitude conditions. Various attempts at using different distillation cuts of crude oil eventually led to production of JP-4, a wide-cut fuel composed of a gasoline/kerosene mixture with a flash point near –10 °F. In the mid-1950s, JP-4 was adopted for widespread use in the Air Force and soon became the fuel of choice for use in many of the Air Force's jet engines.¹

Shortly thereafter, the Navy began to use JP-5, a high flash point kerosene that had a minimum flash point of 140°F and was therefore, for safety reasons, more compatible with shipboard use. Experience with both types of fuels in combat during the Vietnam War demonstrated that Air Force aircraft using JP-4 fuel experienced higher combat losses than U.S. Navy aircraft, and a much higher probability of a crash fire than with JP-5. Furthermore, accident rates for ground-based handling of kerosene-based fuels were found to be significantly lower than for wide-cut fuels such as JP-4.1

JP-8 was developed to provide a safer kerosene-based fuel that would be readily available and have a freezing point acceptable to the Air Force (-47 °F). The Air Force began converting from JP-4 to JP-8 in 1979, and completed the conversion by 1994. JP-8 use rapidly became widespread, even being used in the U.S. Army's ground vehicles and equipment, as well as its airplanes and helicopters. JP-8 is now the dominant fuel for use on the battlefield, with the primary exception being the Navy's continued reliance on JP-5 for shipboard use.

2.2. Properties and health risks of JP-8

2.2.1. Chemical Composition

The chemical composition of JP-8 fuel is very similar to Jet-A fuel used in the commercial sector. It is refined from crude or shale oil to a mixture of C_8 through C_{17} hydrocarbons. Table 2-1 contains a summary of the general composition of liquid JP-8 fuel.² The actual composition may vary slightly depending on the source and manufacturer of the product.

Table 2-1. General chemical composition of liquid JP-8 fuel.²

Component	% by volume
C ₈ to C ₉ aliphatic hydrocarbons	9%
C ₁₀ to C ₁₄ aliphatic hydrocarbons	66%
C ₁₅ to C ₁₇ aliphatic hydrocarbons	7%
Aromatic hydrocarbons, typical of cracked gasoline and kerosene (includes	
benzene, alkyl benzenes, toluene, xylene, naphthalenes)	18%

2.2.2. Toxicology

An extensive review of military fuels was conducted by the National Research Council's (NRC) Committee on Toxicology (COT) to establish Permissible Exposure Levels (PELs) for use by the military². Their study considered three types of fuels that were similar in composition (JP-5, JP-8, and Diesel Fuel Marine). The COT review of the literature reported the following toxicological effects:

- 1. *Kidney system:* Renal toxicity tests conducted in rats and mice of both sexes indicate the primary risk is to the male rat, where kidney lesions result following inhalation of vapors. This result is not believed to be applicable to humans since the lesions are unique to male rats.
- 2. *Central Nervous System (CNS):* Studies of workers exposed to fuel vapors indicate acute effects may include dizziness, headaches, nausea, and fatigue. Chronic effects may include neurological symptoms (sleeplessness, depression, headaches, fatigue) and possible impairment of motor skills.
- 3. *Liver:* Tests involving rats, mice, dogs, and monkeys that were exposed intermittently to fuel vapors indicated no pathological change except for a small increase in female rat liver weights.

4. *Carcinogenicity*: Studies of petroleum workers, which consisted largely of refinery workers and service station attendants, demonstrated an increased risk of cancer. However, these studies were not specific to jet fuel exposures, and much of the impact is attributed to benzene, widely believed to be a carcinogen.³ Following their review of this and other epidemiological and toxicological studies, the COT concluded that JP-5 and JP-8 do not pose a carcinogenic risk to humans.

2.2.3. Exposure limits

The Occupational Safety and Health Act (OSH Act) of 1970 exempts federal agencies, including the Department of Defense, from adhering to the requirements set by the Occupational Safety and Health Administration (OSHA). However, the Department of Defense is required by Executive Orders 12196 and 126084 to maintain a safety and health program that meets, at a minimum, the requirements set forth by OSHA. The USAF has created a set of "Air Force Occupational Safety and Health" (AFOSH) standards as part of its safety and health program.

AFOSH Standard 48-8,5 "Controlling Exposure to Hazardous Materials," is the Air Force's governing health standard for controlling exposure to chemicals. AFOSH Standard 48-8 requires Air Force personnel to adhere to the most stringent exposure limit of two primary standards: (1) PELs set by OSHA, and (2) Threshold Limit Values (TLVs®) established by the American Conference of Governmental Industrial Hygienists. When a standard does not exist for a substance in question, the Air Force Surgeon General (AFMOA/SG) may establish an exposure limit by conducting independent studies, relying upon the professional literature, or using another recommended standard such as the "Recommended Exposure Limits" (RELs) set by the National Institute for Occupational Safety and Health (NIOSH).

For JP-8 jet fuel, neither OSHA nor the ACGIH has adopted an exposure limit. At present, the ACGIH⁶ lists in its "Notice of Intended Changes" an 8-hour TLV[®] of 100 mg/m³ (over a 40-hour working week) for diesel and kerosene, with a skin absorption notation and an A3 carcinogenicity category that identifies it as a confirmed animal carcinogen with unknown

relevance to humans. However, since this TLV® has not yet been adopted by the ACGIH, this value is subject to change.

The Air Force has adopted the exposure guidelines given by the Committee on Toxicology. The COT recommended an 8-hour time-weighted average (TWA) PEL of 350 mg/m³ and a Short Term Exposure Limit (STEL) of 1800 mg/m³. Using an average molecular weight of 170 g/mol, this equates to an 8-hour PEL of approximately 50 ppm and a STEL of 250 ppm.

2.3. Operational parameters and concerns

2.3.1. Vapor composition

Most of the components found in JP-8 are low-volatility, high molecular weight carbon chains containing more than 10 carbons each. Because of their low vapor pressures, these compounds tend to remain in liquid form under room temperature conditions. Therefore, fuel vapor is composed primarily of the more volatile substances in the fuel and does not proportionally parallel the composition of liquid fuel.

The vapor pressure of a volatile substance can be represented by Raoult's Law and Dalton's Laws.⁷ This property of mixtures is described through the following equation:

$$P_{total} = (P^{\circ}_{A})(X_{A}) + (P^{\circ}_{B})(X_{B}) + ... + (P^{\circ}_{N})(X_{N})$$

where $P_{total} = Vapor pressure of a solution containing a nonvolatile solute$

 P_A° = Vapor pressure of the solvent, in pure form

 $X_A = Mole$ fraction of component A

 P_B° = Vapor pressure of component B, in pure form

 $X_B = Mole$ fraction of component B

 P_{N}° = Vapor pressure of component N, in pure form

 $X_N = Mole$ fraction of component N

According to this property of mixtures, the vapor pressure of each substance in a mixture would be less than its vapor pressure in pure form. Additionally, the total vapor pressure in a mixture

would be a mole fraction-weighted average of each component's vapor pressure. Consequently, the high percentage of low-volatility compounds in fuel causes the total vapor pressure to be lower than would be expected if the fuel was composed predominantly of low-volatility substances. Naegeli and Childress analyzed JP-8 fuel vapor composition at the Lower Temperature Limit of Flammability (LTLF), the "temperature at which the lower explosion limit (LEL) exists in dry air under conditions of vapor-liquid equilibrium." ⁸ The top 10 components of JP-8 fuel found in their studies are listed in Table 2-2. Additionally, they found the average molecular weight of JP-8 vapor at the LTLF to be 114 g/mol.

Table 2-2. Major components of JP-8 jet fuel vapor at the Lower Temperature Limit of Flammability (LTLF).⁸

Compound in JP-8 jet fuel	Vapor concentration at 35.6 °C (ppm)
Methyl cyclohexane	803
n-Octane	498
n-Nonane	450
m-Xylene	439
Toluene	410
Ethyl cyclohexane	266
cis-1,4-dimethyl cyclohexane	261
n-Heptane	252
Cyclohexane	239
o-Xylene	235

.

For purposes of fuel vapor composition categorization, there are three general classifications of activities which can expose Air Force employees to fuel vapors:

<u>Naturally-ventilated activities</u>. This includes such activities as ground-based aircraft refueling, external servicing of aircraft and storage tanks, and fuel tank entry attendant activities, among others. Activities conducted outside of a confined space where jet fuel is present will often involve exposure to fuel vapors. These activities are usually not controlled with local exhaust ventilation.

- <u>Ventilated confined space fuel tank entry</u>. Personnel frequently enter aircraft fuel tanks to conduct routine and special cleaning and maintenance. Major maintenance is often conducted after personnel completely drain the tank of all liquid fuel and have purged the tank with fresh air. However, it is often difficult or impractical to completely purge the aircraft of <u>all</u> liquid fuel or vapors in a timely manner, and for some repairs it may be unnecessary. Therefore, some level of fuel vapor is frequently present in the tank. The vapor is controlled by blowing air into and actively extracting it from the tank. When doing work on a flightline, it is standard procedure to use a "blow purge" method which simply forces air into the tank through a flexible duct without using a forced extraction method.⁹
- <u>Foam removal</u>. An activity which has been shown to expose workers to high levels of fuel vapor is one that requires removal of a highly porous polyurethane foam, often present in the tank to prevent movement of the fuel and to minimize explosion and fire risks. Highest exposures have typically been measured^{10,11,12,13} during the initial entry into a tank for the purpose of removing this foam, occasionally reaching levels in excess of 10,000 mg/m³.

The vapor composition to which a worker would be exposed may vary somewhat depending upon the task being accomplished. Raoult's and Dalton's Laws describe vapor composition in a state of equilibrium within an enclosed vessel. These laws may describe the vapor composition anticipated during initial opening of a fuel tank and the subsequent removal of foam saturated with liquid fuel. Under actively ventilated confined space conditions, many of the more volatile, low molecular weight compounds would be expected to have been removed from the worker's breathing zone. Composition of vapors under naturally-ventilated conditions would be expected to fall somewhere between the two extremes.

Before entering, personnel ventilate the fuel tank to reduce the vapor concentrations to safe levels. Air Force fuel cell maintenance procedures are defined in Technical Order (T.O.) 1-1-3¹⁴, "Inspection and Repair of Aircraft Integral Tanks and Fuel Cells." T.O. 1-1-3 establishes the safe limit for tank entry to be greater than 19.5% oxygen and less than 10% of the Lower Explosive

Limit (LEL). For JP-8, which has an LEL of between 0.6 and 0.9 percent (or 6000 to 9000 ppm),⁹, this corresponds to a concentration of about 600 ppm. In some cases where an aircraft contains explosion suppression and fire-resistant polyurethane foam, personnel are required to remove the foam before conducting repairs. A special safe entry level for these operations has been set at 20% of the LEL (1200 ppm) during foam removal only. LEL measurements are made using the Bacharach 514M Explosive Meter, which employs a catalytic filament sensor to measure the percentage of the LEL.⁹ Meters are calibrated to methane. Users move the dial to a JP-8 setting when working with JP-8, which corresponds to a conversion factor of approximately 3.0 relative to methane.

When a tank is initially opened, concentrations of fuel vapor frequently exceed safe entry levels. If repairs must be conducted with any fuel remaining in the tank, T.O. 1-1-3 requires personnel to purge the tank before entering. Purging continues throughout the tank entry operation, regardless of the initial vapor concentration.

2.3.2. Exposure monitoring data

Monitoring data from Det 1 HSC/OEMI's jet fuel exposure consultation efforts^{9,13} for numerous fuel tank entry sampling efforts throughout 1997 and 1998 revealed concentrations ranging between 3.85 mg/m³ and 10,295 mg/m³ (< 1 ppm to 1440 ppm). Mean values were reported to be 267 mg/m³ (38 ppm) for all operations (foam and non-foam), which is below the OEL of 350 mg/m³ (50 ppm).

2.3.3. Respirator use

The majority of Air Force fuel systems maintenance shops use 3MTM EasiAir continuous-flow airline respirators equipped with organic vapor (OV) cartridges. Grade D air is provided as the primary breathing source. Organic vapor cartridges are mounted to the respirator and are used only for escape from the fuel tank in the event the primary air source is terminated. In this configuration, cartridges are passively exposed to organic vapors without actively drawing contaminants through the cartridge. The worker then removes respiratory protection equipment

and often allows it to sit for a period of time before using it again. In this configuration, use of the respirator is limited to the conditions acceptable for full facepiece air purifying respirators. Continuous flow and full facepiece air purifying respirators such as this one have an Assigned Protection Factor (APF) of 50, designated by NIOSH in its Respirator Decision Logic 15 reference, and cannot be used in oxygen-deficient or Immediately Dangerous to Life and Health (IDLH) environments.

In some cases, air purifying respirators equipped with organic vapor cartridges may be used for primary protection. In this configuration, the user wears a half-face or full-facepiece respirator without an additional air supply, and draws the entire air source through the cartridges. It is not common practice for Air Force personnel to wear only air purifying respirators during fuel tank entry operations, but they may be used for other operations involving potential exposure to fuel vapor in some situations.

2.3.4. Breakthrough testing parameters vs. the workplace environment

Currently, NIOSH conducts organic vapor cartridge certification breakthrough testing using a single contaminant (carbon tetrachloride) at pre-determined parameters defined in 42 CFR 84.207. If a cartridge lasts at least 50 minutes during this test when exposed to a challenge concentration of 1000 ppm, it passes the certification test.

It is important to recognize that the NIOSH certification process is only designed to ensure organic vapor respirator cartridges meet a minimum breakthrough requirement for carbon tetrachloride. This process is not intended to help the end user establish a cartridge change-out schedule for workplace-specific organic vapors or environmental conditions. It is therefore critical to have available other techniques for estimating the service life of a cartridge under as-used conditions.

Manufacturers frequently conduct other testing on cartridges with single component challenge chemicals under a variety of conditions. While much of this data can be used to help estimate a

cartridge's service life, there are some unique considerations involved in determining the service life of organic cartridges used in a JP-8 vapor environment. These include:

- JP-8 consists of a complex mixture of organic compounds, ranging from the lighter fraction 8-carbon aromatic hydrocarbons to the much less volatile 14-carbon compounds. Singlecompound breakthrough testing may not be an accurate predictor of multiple-compound breakthrough times. Therefore, an understanding of theoretical and actual breakthrough times for JP-8 remain uncertain.
- When used in a back-up configuration, cartridges are passively exposed rather than drawing
 fuel vapors through the cartridges. Passively exposing a cartridge to organic vapors and
 allowing it to remain unused on a shelf for a period of time may allow the vapor to diffuse
 through the cartridge and adversely impact its effective service life during subsequent uses.

2.4. Regulatory requirements

The governing regulation for use of respirators in the workplace is the Occupational Safety and Health Administration's (OSHA) Respiratory Protection Standard, 29 Code of Federal Regulations (CFR) 1910.134.¹⁷

Prior to October 1998, when this portion of the standard was revised, OSHA required users of respirators to define a strategy for identifying when to change out cartridges worn in an air purifying respirator. However, the requirement was not well-defined, and permitted users to rely on warning properties as a primary mechanism for replacing the cartridges if that property could be reliably detected at a concentration lower than the PEL.

The final rule for the new respiratory protection standard changed the requirement in several significant ways. Interpretation of this standard must be made in the context of OSHA Directive CPL 2.0120 and OSHA Instruction CPL 2.103, "Field Inspection Reference Manual (FIRM)," which identify inspection procedures for OSHA compliance officers to follow during enforcement of the Respiratory Protection Standard. According to the standard, when cartridges

or canisters are used to control gas and vapor exposures, they must either be equipped with an End of Service Life Indicator (ESLI), or be used only with the employer's implementation of a cartridge/canister change-out schedule that ensures they are replaced in adequate time to prevent contaminant breakthrough. Some of OSHA's chemical-specific standards dictate change-out schedule requirements applicable to exposures to those substances only. For example, the standards for acrylonitrile (1910.1045), benzene (1910.1028), and vinyl chloride (1910.1017) specify cartridges be replaced at the end of their service life or the end of each shift, whichever occurs first. The butadiene standard (1910.1051) contains a replacement schedule that is based on the exposure concentration, and includes alternate procedures when additional breakthrough testing data is available. Formaldehyde (1910.1048) requires cartridges to be replaced every 3 hours or at the end of the work shift, whichever occurs first. For all other substances where air purifying respirators are worn to control worker exposures, OSHA requires the employer to establish and implement a change-out schedule. Warning properties such as odor or irritation may not be used as the sole basis for changing cartridges, although they can be used in conjunction with the established change-out schedule. The primary reason for this change is the notion that warning properties are unreliable and are therefore inadequate to indicate sorbent exhaustion has occurred.

The preamble to the final rule for the new standard states that employers are "not required to research and analyze experimental breakthrough data", but "may obtain information from sources who have expertise and knowledge that can help the employer to develop reasonable change schedules." CPL 2.0120 provides guidance to assist an employer in creating change-out schedules. A brief summary of the guidelines in CPL 2.0120 follows.

Manufacturer's Objective Data: Cartridge-specific data developed and presented by each
manufacturer may be available through distributors, via the manufacturer's Internet web site,
or verbally via telephone help line. In some cases, manufacturers have developed computer
programs that compute breakthrough times based on known workplace conditions and
cartridge characteristics.

- Experimental Methods: Breakthrough-time data may be determined experimentally in a laboratory using worst-case simulations of workplace conditions. OSHA considers this to be a good approach when compared to other available techniques.
- Mathematical Predictive Modeling: Several types of mathematical equations have been developed based on theoretical assumptions and experimentally-determined breakthrough data. Some mathematical models may require considerable expertise and could involve obtaining proprietary information from each cartridge manufacturer. OSHA believes further development and validation of such models would be of value, and supports further efforts. The "Gerry O. Wood Mathematical Model" is offered as one means for estimating service life.^{18,35}
- Analogous Chemical Structures: With this method, the employer compares the chemical of interest against breakthrough characteristics for chemicals of a similar structure. Similarly, a chemical with known characteristics could be justifiably used as a surrogate for a chemical reasonably believed to migrate through the cartridge more slowly, such as a heavier, less volatile compound in the same chemical series. This approach depends significantly on experimental data and expertise. OSHA considers it to be generally less accurate than other methods and advocates its use when better information is unavailable to the employer.
- Workplace Simulations: Currently under development, several methods propose to test breakthrough under actual conditions of use by drawing workplace air through the cartridge at a normal high work level breathing rate and sampling the air stream on the other side of the cartridge to monitor breakthrough. Such a method could supplement an employer's routine air monitoring program and may be able to better account for changing humidity, temperature, and concentration conditions.
- Rules of Thumb: Experimental data may lead to development of rules of thumb for estimating cartridge and canister service life. For example, the American Industrial Hygiene

Association (AIHA) publication¹⁹, "The Occupational Environment Evaluation and Control," suggests a method for estimating organic vapor cartridge service life. The method assumes a service life of 8 hours at a normal work rate when the chemical's boiling point is greater than 70 °C and the concentration is less than 200 ppm. The 8-hour breakthrough time is reduced by a number of factors presented in the text, including work rate, concentration, and humidity conditions. OSHA expresses some doubt as to the reliability of this method and advocates its use only in concert with another service life prediction method.

Other requirements of OSHA's Respiratory Protection Standard include establishing a workplace-specific respiratory protection program that address selection and use of respirators, facepiece fittesting and medical monitoring, and training. The standard requires initial fit-testing for all users wearing tight-fitting respirators, and at least annually thereafter, when there is a change in the facepiece, or when the worker's physical condition changes such that the respirator fit could be compromised (e.g. significant weight change). The standard also addresses use of respirators in potentially Immediately Dangerous to Life or Health (IDLH) and oxygen-deficient environments, prohibiting the use of air purifying respirators under those conditions.

Since the USAF is required to maintain a safety and health program at least as stringent as that established by OSHA, the general tenets of the Respiratory Protection Standard apply. AFOSH Standard 48-137, Respiratory Protection Program,²⁰ applies these requirements to USAF personnel.

2.5. Cartridge certification protocols

2.5.1. National Institute for Occupational Safety and Health (NIOSH)

Under its responsibility to test and certify respirators, NIOSH developed requirements for testing chemical vapor cartridges and canisters which are defined in 42 CFR 84.207, "Bench tests: gas and vapor tests: minimum requirements." All manufacturers of gas and vapor cartridges must meet these certification requirements before providing a product to the public.

For organic vapor cartridges, testing must be accomplished at a relative humidity of 50±5 percent and a temperature of approximately 25 °C. The challenge vapor is carbon tetrachloride (CCl₄) at a concentration of 1000 ppm; or a lower concentration for organic compounds that produce atmospheres immediately dangerous to life and health at 1000 ppm. Breakthrough has occurred when a concentration of 5 ppm is measured exiting the cartridge.

Two types of tests are completed: one on cartridges as received, without equilibration; and one with cartridges that have been equilibrated to known temperature and humidity conditions.

Non-equilibrated cartridges: After the cartridges are received, they are placed in a sealed bag and
tested within 18 hours. If the cartridges are intended to be used individually (one at a time) in
a respirator, three are tested at 64 LPM each. If designed to be used in pairs, three pairs of
cartridges are tested at 64 LPM (or 32 LPM per cartridge).

Equilibrated cartridges:

- Two cartridges (or pairs) are equilibrated by passing room temperature air at 25 percent relative humidity at a flow rate of 25 LPM for 6 hours. Cartridges must be placed in a sealed bag and tested within 18 hours of equilibration. If the cartridges are intended to be used individually (one at a time) in a respirator, they are tested at 64 LPM each. If designed to be used in pairs, they are tested at 64 LPM (or 32 LPM per cartridge).
- Two cartridges (or pairs) are equilibrated by passing room temperature air at 85 percent relative humidity and a flow rate of 25 LPM for 6 hours. Cartridges must be placed in a sealed bag and tested within 18 hours of equilibration. If the cartridges are intended to be used individually (one at a time) in a respirator, they are tested at 64 LPM each. If designed to be used in pairs, they are tested at 64 LPM (or 32 LPM per cartridge).

The NIOSH criteria requires that cartridges have a minimum tested service life of 50 minutes in order to pass the certification requirements.

2.5.2. Environmental Protection Agency

The Environmental Protection Agency (EPA) has developed some interim guidelines in support of Section 5 of the Toxic Substances Control Act (TSCA), which authorizes the EPA to require the use of respiratory protection for workers exposed to gases or vapors of new chemical substances or those submitted as Premanufacture Notifications (PMNs). The EPA requires use of supplied-air respirators for exposure to new volatile chemicals unless a company can show that a NIOSH-approved organic vapor cartridge-type respirator will effectively remove the contaminant from the worker's breathing zone.

The interim recommendations are predominantly based on the Wood and Ackley protocol²¹ for testing organic vapor canisters and cartridges, and on NIOSH's draft decision logic for respirator selection during PMN uses.²² The interim recommendations break the testing protocol into two phases. Phase I involves eight different tests that represent the worst case environmental conditions. Phase II, which is only required under certain conditions, addresses the desorption characteristics of the cartridge or canister filters at elevated temperatures by including additional tests under conditions of higher temperature.

An overview of the recommended protocol is included below:

- Conduct an initial screening for service life that is based on predictive modeling. If modeling shows that a predicted service life would be shorter than 20 minutes for the substance, the company should consider an alternative to using an air purifying respirator, such as a supplied-air respirator.
- Document that adsorption of the substance will not result in heats of reaction that yield temperatures more than 20°C above the ambient temperature.

- Perform a minimum of eight tests on the cartridges or canisters of interest at a 50 liter per minute flow rate and a temperature of 25±2.5 °C, according to the following parameters:
- Two tests each at concentrations of 10 times, 100 times, and 500 times the proposed exposure limit, with a relative humidity held constant at 80±5 percent.
- Two tests at 500 times the proposed exposure limit, and a relative humidity held constant at 20±5 percent.
- If the cartridge or canister will be used for worker protection at elevated temperatures, defined as 35 °C or higher, conduct two more series of tests (two replicates for each) at 10 and 500 times the proposed exposure limit, at a temperature of 35±2.5 °C and 80±5 percent relative humidity.
- Develop change-out schedules according to service life testing results for the worst case conditions, applying a safety factor of 60% to account for environmental condition variability.

2.6. Breakthrough of homogeneous substances

2.6.1. Overview

In 1976 Nelson and Correia²³ published the conclusions of an extensive study describing fundamental breakthrough characteristics of organic vapors through carbon respirator cartridges. This report was the culmination of over 5 years of research in this area. During that series of studies, Nelson et. al.^{2425:26} tested cartridge breakthrough for 121 types of vapors at various concentrations, humidity levels, and air flow rates, and provided a review of solvent vapor adsorption properties on activated carbon. The authors also compared theoretical breakthrough times using the adsorption isotherm, Mecklenburg, and Wheeler equations, and attempted to develop a simplified empirical expression for predicting breakthrough to 10 percent of the challenge concentration.

Additional research by Yoon and Nelson²⁷, Moyer²⁸²⁹, Wood and Moyer^{30·31}, Wood and Stampfer³², and others have further defined the impacts of exposure conditions on breakthrough time and developed additional predictive models for single contaminant breakthrough estimation. One often-used model is presently known as the "modified Wheeler equation".

The original Wheeler equation was initially derived by Wheeler and Robell³³ to describe catalytic bed poisoning, and was later modified by Jonas and Svirbely³⁴ into the following form:

$$t_b = \frac{W_e}{C_0 Q} \left[W - \frac{\rho_B Q}{k_v} \ln \left[\frac{C_0}{C_x} \right] \right]$$

where

 t_b = breakthrough time in minutes

 W_{i} = adsorption capacity in g/g

 k_n = adsorption rate constant in minutes⁻¹

W = adsorbant weight of carbon in g

 ρ_B = bulk density of the packed bed in g/cm³

Q = air flow rate in cm³/min

 C_g = challenge concentration in g/cm³

 $C_x = \text{exit concentrations of interest in g/cm}^3$

While this equation is commonly used to analyze contaminant breakthrough in carbon beds, it is only valid for small exit concentrations (small fractions of the inlet concentration) since it predicts that the exit concentration will increase exponentially.²⁷

Yoon and Nelson applied a correction term to this model to account for the reversibility of adsorption of the contaminant as the breakthrough concentration (C_x) increases, C_x increases, C_x as follows:

$$t_{b} = \left[\frac{W_{e}W}{C_{0}Q}\right] - \left[\frac{W_{e}\rho_{B}}{k_{v}C_{0}}\right] \ln \left[\frac{C_{0} - C_{x}}{C_{x}}\right]$$

with variables defined as above.

Wood further defined additional terms in this equation, developing models for W_{ϵ} and k_{ν} as shown below:

$$W_{e} = W_{o} d_{L} \exp \left[-b' W_{o} P_{e}^{-1.8} R^{2} T^{2} \left(\ln \left\{ \frac{\rho}{\rho} \right\}_{sat} \right) \right]$$

$$P_e = \left(\frac{n_D^2 - 1}{n_D^2 + 2}\right) \frac{M_W}{d_L}$$

$$\frac{1}{k_V} = \left(\left(\frac{1}{V_L} \right) + 0.027 \right) \left(I + \frac{S}{P_e} \right)$$

where

 $W_{\scriptscriptstyle 0}$ = carbon micropore volume (cm³/g)

 d_L = liquid density of adsorbate (g/cm³)

T = absolute temperature in Kelvin

ho = partial pressure corresponding to the challenge concentration

 $\rho_{\rm\scriptscriptstyle sat}$ = partial pressure (at saturation) of substance

 P_{e} = molar polarization (electron cloud displacement or preferential orientation of dipoles)

R = ideal gas constant of 1.987

 $b' = 3.56 \times 10^{-5}$ (empirically determined)

 $M_W =$ molecular weight

 n_D = refractive index

 $I = \text{calculated constant of } 8.25 \times 10^{-4}.$

S is an empirically-derived coefficient that can be estimated from:

$$S = 0.063 - 0.0058 \ln \left[\left(C_0 - C_y \right) / C_y \right]$$

Note that changes in the value of S, which ultimately impact k_p and modify the slope of the prediction curve, are most significant at the lowest percentages of the breakthrough curve (see Table 2-3). This has a direct relationship on k_p . Since k_p appears in the denominator of the Yoon and Nelson equation, an increase in the value of S will reduce the predicted breakthrough time, t_p .

Table 2-3. Changes in value of S across the breakthrough curve.

% breakthrough	S
1	0.036
5	0.046
10	0.050
20	0.055
30	0.058
40	0.061
50	0.063

The equilibrium adsorption capacity parameter, W_o , tends to be relatively constant across the breakthrough curve (at a fixed temperature) and is relatively insensitive to the challenge concentration except for substances of extremely low volatility. Note also that W_o and k_o are not independent of each other, since they share the molar polarization term, P_o , a constant that is dependent on the polarization characteristics of the challenge substance.

The effects of relative humidity on breakthrough times are currently being studied to better define the response functions. Relative to vapors of most organic compounds, water vapor adsorption by activated carbon is extremely slow. However, at low contaminant concentrations and high humidity levels, the number of water molecules greatly exceeds the number of contaminant molecules, with the water vapor causing a significant reduction in breakthrough time. For example, 100 ppm of a substance such as methylene chloride (molecular weight = 84.9) is equivalent to 2.4×10^{18} molecules in 1 Liter of air. The same volume of air humidified at 80

percent contains approximately 6.1×10^{20} water molecules (11.5 mg^{37}), over 250 times the number of methylene chloride molecules. For JP-8 fuel, using an approximate molecular weight of 170 g/mol, 300 ppm is equivalent to 7.4×10^{18} molecules and 1200 ppm equates to 3.0×10^{19} molecules. The relative ratios of water to fuel vapor molecules would be as shown in Table 2-4.

Table 2-4. Approximate ratio of water molecules to fuel vapor molecules in a fixed volume of air for 50 and 80 percent relative humidity levels, at 300 and 1200 parts per million of fuel vapor.

Relative humidity level	Ratio of water to fuel vapor molecules at 300 ppm fuel vapor	Ratio of water to fuel vapor molecules at 1200 ppm fuel vapor
50 percent	51:1	12:1
80 percent	83:1	20:1

One model published by Wood³⁸ relates the breakthrough time at a reference relative humidity to a humidity level of interest. The equation takes a general form of the following:

$$\frac{t_b(ref)}{t_b} = K + K'RH^n$$

where $t_b(ref)$ is the breakthrough time at a reference relative humidity, t_b is the breakthrough time at the relative humidity level of interest, K and K' are constants that depend on the amount of water vapor in the air relative to saturation, and n represents the number of water molecules that fill the charcoal micropores. This model essentially allows prediction of a breakthrough time at any relative humidity when all other key parameters (e.g. temperature, challenge concentration, and percentage of breakthrough) are held constant. Wood states that in his application of this model to initially dry carbon bed tests, the calculated parameters for this equation did not remain constant between the 10 percent and 50 percent of the challenge concentration penetration points. However, he does not address changes in this ratio that may occur throughout the breakthrough curve (with challenge concentration held constant) for preconditioned carbon beds,

nor does he discuss potential differences in this ratio resulting from changes in the challenge concentration. This model does not describe either of these impacts.

Nelson and Correia²³ observed during their studies that the typical sigmoidal (s-shaped) breakthrough response curve of breakthrough concentration versus time under dry conditions began to elongate as the relative humidity during test conditions was raised above 65%. This effect is even more pronounced when a cartridge has been pre-conditioned at high humidity levels (65 percent or greater), such that the response becomes nearly linear throughout a large portion of the curve.

It is important to note that these equations help to predict the exit concentration over time when parameters for the cartridge, air flow rate, exposure concentration, and specific compound characteristics are known. While some estimates can be made, most models are limited in their ability to account for the effects of relative humidity, temperature, or mixtures of compounds.

In summary, most of the research in this area has led to the following conclusions:

- Higher exposure concentrations will reduce the breakthrough time for a given contaminant.
 Breakthrough time is approximately inversely proportional to challenge concentration at the
 50 percent breakthrough point, with the complete breakthrough curve exhibiting a sigmoidal
 shape and following the reaction-kinetic equation principles of mass conservation and firstorder kinetics.
- Breakthrough time is inversely proportional to flow rate.
- Breakthrough time is reduced by between 1 and 10 percent for every 10° C increase in temperature above a cartridge's test conditions.
- Activated carbon generally has a greater affinity for less volatile substances.

- High relative humidity levels during cartridge use reduce service lives when compared to low relative humidity levels. This effect is especially pronounced at relative humidity levels above 65 percent.
- Preconditioning a cartridge at a low relative humidity has a mild impact on its service life, with
 the test relative humidity having a considerably greater impact than the preconditioning
 humidity. However, preconditioning at high relative humidity levels will cause a significant
 reduction in service life.
- Breakthrough times for cartridges tested under pulsating air flow rates are not significantly different from those tested with a steady-state air flow source.

2.6.2. Breakthrough testing methods

Methods for testing breakthrough for cartridges exposed to single-component substances typically involve producing a constant flow rate of air at fixed temperature and humidity conditions into a mixing chamber.²³ In the chamber, a fixed delivery rate of the substance in question is injected and flash-vaporized. The contaminated air is fed into a cartridge testing chamber, where it flows through the cartridge. Relative humidity, temperature, and concentration are monitored at various points through the system to ensure adequate control and to monitor the system parameters. Detection equipment may vary depending upon the substance being monitored. For organic vapors, infrared (IR) detectors or Flame Ionization Detectors (FIDs) are commonly used.

2.7. Breakthrough of mixtures

2.7.1. Overview

As compared to research published regarding breakthrough data for single-component organic substances, there is a much smaller body of research that has been published to date on organic vapor cartridge service life when exposed to mixtures of two or more substances. Lewis et. al.,³⁹ Grant and Mares,⁴⁰ Myers and Prausnitz,⁴¹ and Jonas and Sansone⁴² have each studied carbon adsorption characteristics gases and hydrocarbons to a limited degree.

More recently, Yoon et. al.^{43,44} tested organic vapor cartridges for mixtures involving acetone and *m*-xylene (binary tests) and various combinations of acetone, cyclohexane, toluene, ethyl acetate, and *m*-xylene (ternary and quaternary tests).

Data from the mixture studies indicate that compounds that are relatively weakly adsorbed by a carbon bed can be displaced by one that has stronger adsorption characteristics. This may, in fact, actually result in a breakthrough concentration for the displaced substance that is greater than its concentration in the challenge mixture. Therefore, the service life of a cartridge becomes highly dependent on the challenge concentration for each component in the mixture, and is measurably influenced as a result of the displacement process. Weakly-adsorbed compounds break through faster than they would as single-component challenges.

Yoon, Nelson, and Lara⁴⁴ have developed a mathematical model that accounts for the rate of adsorption, the capacity of the carbon bed, and the displacement phenomenon that occurs with multi-component substances. Since JP-8 contains over 300 organic compounds, further discussion of their model is beyond the scope of this paper.

2.7.2. Breakthrough testing methods

The breakthrough testing methods used for multi-component substances are similar to those used for single-component substances. Methods involve controlled injection and flash volatilization of each component individually into the air stream, allowing them to mix in a chamber before passing through the cartridge.

2.8. Vapor generation

In most of the studies reported above, vapor generation of single and multiple contaminants is typically accomplished in a manner similar to that for single component breakthrough testing. A typical vapor generation configuration uses multiple motor-controlled syringes to inject and vaporize a known mass of each contaminant into the air stream.

The literature does not reflect significant use of other methods for vapor generation in cartridge breakthrough studies. However, inhalation toxicity studies frequently employ other methods. One such method has been employed for producing known and constant concentrations of fuel vapors during toxicity testing of petroleum- and shale-derived fuels at the Toxic Hazards Research Unit, Wright-Patterson Air Force Base, Ohio. The Air Force⁴⁵ used evaporation towers consisting of a 13-inch long, 1-3/4-inch outside diameter glass cylinder. Each of the towers had a 13-turn, 9-inch long spiral embedded in its wall to contain a heating coil and to lengthen the path of vaporization. The top of each tower reduced to a "T" with one arm for vapor exhaust and the other for connecting the input fuel. The bottom was connected to a double "T" constructed of stainless steel tubing, which was used to drain waste fuel and feed carrier air into the system. Vapor effluent was fed into an enclosed dome where animals were exposed to the fuel vapors. Minor corrections in the vapor concentration were accomplished by changing the air flow in each dome. The primary energy of vaporization came from an electrically heated coil wrapped around the tower, with a lesser portion of the energy supplied with the incoming air.

Although not specifically designed for multiple contaminant generation, Potts and Steiner⁴⁶ reported on a device for volatilizing high-boiling liquids without requiring heat input. Their approach uses a multiple plate, high efficiency, countercurrent distillation column that is maintained at a temperature below ambient. They tested two configurations. The first was a relatively simple system that serves well for experiments of short duration where the desired concentration is close to the saturation level in air. However, this system was highly dependent on the temperature of ambient air surrounding the distillation column, so any fluctuations in air temperature could affect the liquid vapor pressure and cause small fluctuations in the generated concentration. Fluctuations would normally occur over a several-hour period, and it was possible to adjust the air flow rates to compensate accordingly and maintain a constant concentration. However, for longer-term studies, the authors designed a second apparatus that uses a temperature-controlled water jacket to maintain a constant temperature within the distillation column.

According to the authors, one significant advantage of using this system over flash volatilization methods is that in multiple component mixtures, where each component has different vapor pressures, this method would produce a vapor composition that is very similar to that which would be generated from liquid in an open room, as governed by Raoult's Law. Operating the second system for such applications would require a minor modification, allowing for a fresh source of liquid continuously supplied to the top of the column instead of being recirculated. Periodic or continuous emptying of the reservoir would also be necessary.

Chapter 3. METHODS AND MATERIALS

3.1. Purpose of study

The NIOSH protocol for certification of organic vapor cartridges requires the testing of only a single substance, carbon tetrachloride. However, in a work environment, workers are most likely exposed to a different substance, and frequently to multiple substances at the same time. For example, a typical oil-based paint may contain numerous types of solvents (e.g. toluene, xylene, and methyl ethyl ketone), each of which has a different affinity toward carbon and would break through the cartridge at different times.

The OSHA requirement to develop cartridge change-out schedules presents a real dilemma for industry and for the Air Force, since there is a large, undefined number of different chemical combinations to which a worker could be exposed. Cartridge testing already requires considerable resources to assess single chemical breakthrough times. Costs escalate considerably when attempting to address the numerous permutations of multiple chemical exposures possible in the work environment.

To develop change-out schedules for organic vapor cartridges during activities where personnel are exposed to JP-8 jet fuels, the USAF needs to better understand the breakthrough characteristics of the cartridges most commonly used by its employees in an active mode (as primary protective devices) and in a passive mode (as a backup, escape-only provision). Of particular interest is the impact of exposing a cartridge to a static concentration of JP-8 fuel vapor prior to actively drawing air through the cartridge in a dynamic configuration, and the resulting impact on its service life, if any. The emphasis will be placed on cartridges currently in predominant use within the USAF.

Therefore, the focus of this study was to determine those breakthrough times to support development of cartridge change-out schedules during fuel tank entry operations. The hypotheses tested in this study are:

- 1st H₀: Preconditioning, followed by subsequent exposure to high levels of relative humidity, will have no significant impact on the breakthrough time of an organic vapor cartridge dynamically exposed to fuel vapor as compared to a cartridge challenged at a low relative humidity level. The alternative hypothesis, H₁, states that there is a significant impact on breakthrough time resulting from exposure to high levels of relative humidity.
- 2nd H₀: Prior exposure of a cartridge to a high-level, static concentration of fuel vapor and high level of relative humidity for a full work shift will have no significant impact on its breakthrough time when that cartridge is subsequently used under dynamic flow conditions, relative to cartridges without prior exposure. The alternative hypothesis, H₁, states that there would be a significant impact on breakthrough time.
- 3rd H₀: The breakthrough response characteristics of JP-8 through an organic vapor cartridge cannot be adequately modeled by a generalized form of the Yoon and Nelson equation. The alternative hypothesis, H₁, would state that the response function does follow this equation.

3.2. Experimental design

3.2.1. Hypotheses 1 and 2

To test the first two null hypotheses, two experimental models were established in the form of two by three factorial designs. The first model, which examines the impact of relative humidity and concentration on breakthrough time, uses a 3-level treatment of concentration (300, 600, and 1200 parts per million of JP-8, equivalent to 2100, 4200, and 8300 mg/m³, respectively) and a 2-level treatment of test relative humidity (50 percent and 80 percent). The second model uses a 3-level treatment of concentration (same levels as before) and a 2-level "prior exposure" treatment ("yes" or "no") with relative humidity held constant at 80 percent. Five replicates were conducted at each test condition, and the "no prior exposure" treatment at 80 percent relative humidity was shared between the two data sets. All cartridges were preconditioned at 80 percent relative humidity and a temperature of 25 °C. Pre-exposed cartridges were passively exposed in 25 °C air

for 8 hours at 1200 ppm fuel vapor and 80 percent relative humidity. A flow diagram of the cartridge testing procedure is shown in Figure 3-1.

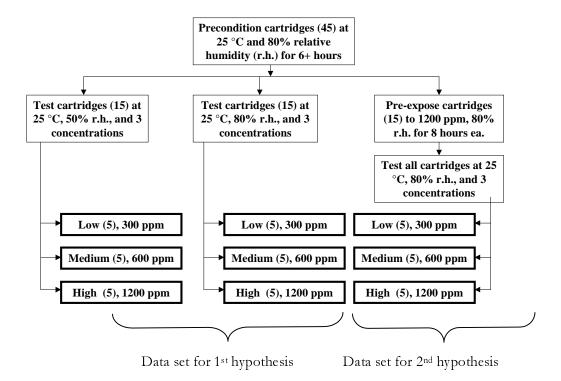


Figure 3-1. Factorial design of breakthrough testing research.

The dependent variable is the breakthrough time to a given fraction of the challenge concentration (e.g. 1%, 5% 10%, 20%) or to a fixed level (e.g. the TLV or OEL).

Although the models could have been combined into one 2 x 2 x 3 experimental design (2 levels of relative humidity, 2 levels of prior exposure, and 3 levels of concentration), time constraints limited the number of tests that could be performed. Therefore, the author chose to measure the impact of prior exposure only at the assumed worst-case condition, the higher relative humidity condition of 80%.

Care was taken throughout the testing to minimize potential systematic error by spacing replicates of each test condition over time throughout the testing period. However, as a result of the amount of time required to achieve system stability before each test, it was impractical to completely randomize the design, and in several instances two or three cartridges were tested under the same environmental conditions in sequence. Analysis of Variance (ANOVA) was still applied to assess the effects of each treatment, recognizing that this design did not meet the strict statistical requirements for using that type of analysis.

For the first null hypothesis, the model statement appears as follows:

$$Y_{iik} = \mu + R_i + C_i + (RC)_{ii} + \varepsilon_{iik}$$

where

 Y_{ijk} = Observation of breakthrough time, in minutes

 R_i = Test relative humidity (2 levels: 50% or 80%)

 C_i = Challenge concentration of JP-8 vapor (3 levels: 300, 600, and 1200 ppm)

 $(RC)_{ii}$ = Interaction between relative humidity and challenge concentration

 $\epsilon_{iik} =$ Experimental error

A model statement for the second null hypothesis is shown below:

$$Y_{iik} = \mu + P_i + C_i + (PC)_{ii} + \varepsilon_{iik}$$

where

 Y_{iik} = Observation of breakthrough time, in minutes

P_i = Prior exposure factor (2 levels: no prior exposure and prior exposure)

C_i = Challenge concentration of JP-8 fuel vapor (300, 600, or 1200 ppm)

(PC)_{ii} = Interaction between prior exposure and challenge concentration treatments

 $\epsilon_{ijk} =$ Experimental error

3.2.2. Hypothesis 3

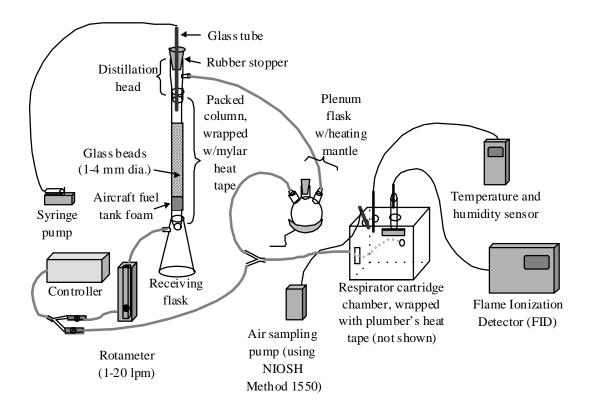
The null hypothesis was tested through regression analysis of the breakthrough times vs. challenge concentrations. No additional data collection was necessary.

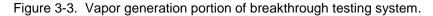
3.3. Equipment configuration

3.3.1. General description

The basic approach for conducting the breakthrough studies involved producing a known and controllable concentration of JP-8 vapor, attempting to vaporize the more volatile components while allowing the less volatile compounds to remain in liquid form. The generated air stream/fuel vapor mix was controlled for temperature and humidity conditions, and subsequently fed into a holding chamber where it was pushed through the organic vapor cartridge. Air flow was exhausted into a ventilated fume hood. The general test system configuration is depicted in the block diagram below (Figure 3-2).

Figure 3-2. Test system configuration.







The vapor generation process involved passing air controlled for temperature, humidity, and flow rate through the bottom of a glass packed column filled with glass beads ranging in diameter between 0.1 cm and 0.4 cm. Jet fuel was injected into the top of the column through a distillation head at a constant flow rate for a given target vapor concentration via a Cole-Parmer 74900 series (S/N 8573) syringe pump (Cole-Parmer Instrument Co., Vernon Hills, IL) equipped with two Hamilton 100-mL Gastight[®] syringes (part number 1100) with teflon leur locks (Hamilton Company, Reno, NV). Fuel entering the column dispersed across the glass beads, increasing the surface area of the liquid fuel and increasing the efficiency of evaporation. Flow rates of fuel injected into the column were set to 1, 2, and 4 mL/min for the 300, 600, and 1200 ppm challenge concentrations, respectively.

As the air flowed counter-currently through the packed column, the concentration of fuel vapor continued to increase until it passed out of the top of the column through the side of the distillation head. The fuel vapor-enriched air was then fed through polyethylene tubing into a plenum flask, which acted as a liquid trap for any condensing fuel (and doubled as a temperature, humidity, and concentration monitoring point when necessary). Liquid that did not evaporate, e.g. the less volatile components, dripped through the bottom of the column and was collected in an Erlenmeyer flask at its base.

The saturated air then entered into a 28-liter Plexiglass[®] chamber. The organic vapor cartridge to be tested was attached to a matching cartridge holder and was immersed into the chamber. Air flowed through the cartridge and exited the other side through a 4-cm inner diameter glass tube.

Adjustments to the fuel vapor concentration entering the chamber were made by mixing the saturated air with fresh air from the air flow controller. A combination of y-splitters and needle valves allow the ratios to be adjusted accordingly to achieve the target challenge concentration of 300, 600, and 1200 ppm.

3.3.2. Temperature, humidity, and air flow rate control

A Miller-Nelson controller (Miller-Nelson Research, Inc., Monterey, CA), model no. HCS-301, S/N 97626, was used to provide a constant flow of temperature and humidity controlled air. Heat losses were encountered; therefore, it was necessary to insulate connecting tubing and to add energy at four different locations: (1) a 250-watt infrared heat lamp was placed 25 cm from the glass needle valve and rotameter to avoid any water vapor condensation within those components; (2) the packed column was wrapped with 1.25 meters of 4 cm-wide Mylar[®] heat tape (maximum power rating of 20 watts per meter); (3) a heating mantle was placed under the 3-neck plenum flask to minimize the potential for fuel and water vapor condensation (maximum power rating of 270 watts); and (4) 2 meters of plumber's heat tape was wrapped around the respirator chamber (power rating unknown). The Mylar[®] heat tape, heating mantle, and plumber's heat tape were each connected to separate variable AC power supplies to enhance controllability at each

position. A water-jacketed temperature control methodology would have allowed less user intervention and more precision, but at greater expense. The methods used provided adequate temperature stability when monitored and adjusted periodically throughout each testing period.

The chamber temperature was maintained at 25±1.5 °C for all tests. Relative humidity was controlled within ±2 percent for both the 50 and 80 percent relative humidity test conditions.

3.3.3. IP-8 vapor generation

The infusion pump, equipped with two 100 mL syringes, provided a constant flow rate of fresh fuel into the packed column. Flow rates were between 1.0 mL/min and 4.0 mL/min, depending on the desired concentration in the cartridge testing chamber.

The packed column and head, along with connection joints on the plenum flask and the Erlenmeyer flask, were custom-constructed by the West Virginia University Chemistry Department's resident glassblower. The column was 58 cm in length and had an inner diameter of 34 mm. It was fitted with a tight-fitting glass joint on the bottom to permit a snug connection with the 3 liter Erlenmeyer flask, which was modified to include a matching joint. The top of the column contained a receiving joint, into which the custom distillation head was inserted. Fuel flowed directly into the top of the packed head via a short glass tube inserted through a rubber stopper. The bottom joint of the packed column, and the joint of the distillation head, were both wrapped with Teflon® tape to ensure no leakage of air, vapor, or liquid occurred and to avoid bonding of the ground glass joints.

The air exited the column through the side of the distillation head and flowed into a 1-liter 3-neck plenum flask. The flask was intended to act as a liquid trap in the event any condensation of fuel or water vapor would result at any time during the initial configuration and active cartridge testing phases, but also added the flexibility to monitor the temperature, humidity, and vapor concentration directly leaving the column and prior to entering the cartridge testing chamber.

Figure 3-4. Custom distillation head inserted into top of packed column.



Concentrations of fuel vapor were maintained within ±5 percent of the target concentration for all test conditions. If the concentration was found to be outside of this range during any breakthrough test, the test was terminated and the data excluded from analysis.

3.3.4. Measurements

3.3.4.1. Temperature and relative humidity

Temperature and relative humidity levels were monitored inside the cartridge testing chamber with a Digital Hygrometer/Thermometer (Control Company, Friendswood, TX). The probe was inserted to a depth of approximately 5 cm into the top of the chamber. Calibration of the instrument's response for relative humidity was verified using a saturated lithium chloride salt solution reference method for the low relative humidity calibration point (12.2 percent at 22 °C), and a saturated sodium chloride salt solution reference method for the high relative humidity level (75.6 percent at 22 °C).

3.3.4.2. Fuel vapor monitoring

Two primary mechanisms were used to measure vapor concentrations within the chamber and on the exit side of the cartridge. Direct reading measurements were taken with a portable Flame Ionization Detector (FID), and time-weighted average measurements were taken using coconut shell solid sorbent charcoal tubes.

Flame Ionization Detector

A Foxboro® TVA-1000B (The Foxboro Company, Foxboro, MA), which is a portable vapor analyzer with a photoionization detector (PID) and FID, was used in the FID monitoring mode to periodically confirm that the challenge concentration inside the chamber had reached the desired steady-state concentration. The same FID was used to monitor breakthrough concentrations. The FID was zeroed by drawing ambient laboratory air through a clean charcoal sampling tube connected to the sampling probe. Calibration was performed using pentane at 7500 ppm (CALGAZTM, from Air Liquide America Corp., Cambridge, MD).

During preliminary testing with this device, several problems and questions were identified concerning the use of this instrument with jet fuel vapors. It was noted that after continuously exposing the instrument to a high level of fuel vapor in the chamber, upon removal from the chamber, the TVA-1000B required in excess of 60 minutes to return to a "zero" reading. Continued testing led to the conclusion that the water trap filter, which was attached to the end of the sampling probe, was adsorbing or absorbing a measurable amount of fuel vapor and desorbing throughout the sampling train during periods of reduced exposure levels. To avoid this problem, an external TSI Portacount[®] HEPA filter, part number 1602066 (TSI, Inc., St. Paul, MN) was added to the tip of the probe and was tested to ensure minimal adsorption occurred. A separate external filter was used at each challenge concentration. However, even with an external filter in place, the instrument still required between 10 and 15 minutes to recover from a high-level exposure to fuel vapor in the chamber. Therefore, it became necessary to ensure the instrument was allowed adequate time to "re-zero" itself after monitoring the chamber concentration.

Charcoal Tube Sampling

NIOSH Method 1550 documents a technique for measuring naphthas, the lighter-fraction components of JP-8 that dominate the composition of fuel vapor near the test temperature conditions. This method uses a 100 mg front / 50 mg back coconut shell charcoal solid sorbent tube with collection flow rates of between 0.01 and 0.2 LPM. It has a working range of 100 to 2000 mg/m³ for a 5 liter air sample. As presented in NIOSH Method 1550, the working range does not adequately cover the higher concentrations measured during this study. Therefore, the author consulted with the NIOSH Method 1550 validation team to determine if using a higher capacity charcoal tube would be an acceptable alteration. The validation team indicated that a 400 mg front / 200 mg back charcoal tube would be acceptable for monitoring higher concentrations, with some modifications to the analysis protocol to account for the additional mass of adsorbate.

The modified NIOSH Method 1550 was used to collect time-weighted average fuel vapor concentrations only within the respirator chamber during breakthrough tests. Sampling was conducted at approximately 30 mL/min using an SKC personal sampling pump with a low-flow rate adapter. The pump was calibrated before and after each test with a BIOS International DryCal DC-2 Flow Calibrator (Base S/N B-757) and an accompanying low flow cell, part number DC-1LC, S/N 1131 (BIOS International, Butler, NJ).

3.3.4.3. Cartridge weights

To determine the mass of water vapor and fuel adsorbed by the carbon, each cartridge was weighed upon removal from its packaging, after preconditioning, after prior exposure to fuel vapor (when applicable), and upon completion of its test for breakthrough. Cartridges were weighed using a Mettler AE 163 Electronic Balance, S/N B96156 (Mettler Toledo, Toledo, OH) with a precision of ± 0.1 mg.

3.4. Test parameters and procedures

3.4.1. Pre-Conditioning

All cartridges were preconditioned at 25 °C and 80 percent relative humidity for a 6-hour period. 32 LPM of air was passed through each cartridge, which were placed (in pairs) within the respirator chamber (Figure 3-5). The air flow tubing from the Miller-Nelson controller fed directly into the respirator chamber at 64 liters per minute. Since the laboratory ambient temperatures were lower than the desired pre-conditioning temperature of 25 °C, the Miller-Nelson controller was adjusted to compensate for heat loss within the air flow tubing. Air exited the Miller-Nelson controller at approximately 32 °C and 53 percent relative humidity, which is equivalent to 25 °C at 80 percent relative humidity.

Figure 3-5. Configuration of cartridges inside chamber for pre-conditioning at 80% relative humidity.



Actual settings for the Miller-Nelson controller were as follows:

Table 3-1. System parameter settings for cartridge pre-conditioning with 32 liters per minute of air at 25 °C and 80 percent relative humidity. Temperature and relative humidity settings are expressed as approximate ranges of setting pairs (A and B), since ambient laboratory temperature conditions affected the temperature being delivered to the respirator testing chamber. Periodic adjustments were made to achieve a monitored temperature of 25 °C and relative humidity level of 80 percent within the chamber.

Parameter	Dial setting
Miller-Nelson controller flow rate setting	64.0
Miller-Nelson controller temperature setting	$32.3^{(A)}$ to $40.0^{(B)}$
Miller-Nelson controller relative humidity setting	47.0 ^(A) to 29.0 ^(B)

Periodic adjustments to the controller temperature and humidity dial positions were made to compensate for changing ambient conditions, particularly during the University's transition from winter to summer HVAC settings. Instead of making major changes to the system temperature and humidity settings, the laboratory ambient temperature was adjusted whenever possible. During a period in which the laboratory air conditioning system was inoperable, testing was postponed until the HVAC system was active again. In all cases, adjustments were made such that pairs of temperature and relative humidity settings yielded a monitored temperature and humidity level of 25 °C and 80 percent relative humidity within the respirator testing chamber, equivalent to a dew point of 21.3 °C.

After pre-conditioning, each cartridge was placed in a sealed Ziploc[®] bag to prevent water weight loss until the prior exposure procedure or breakthrough test began. Elapsed time from cartridge pre-conditioning and testing ranged from 6 hours to 72 hours.

3.4.2. Prior exposure

Pre-exposed cartridges were first pre-conditioned as described above, and were then placed in a cartridge holder that allowed the cartridge face (inlet) to be exposed to fuel vapor and humidified air in the chamber. Cartridge holders were sealed with hot glue on the reverse side to prevent the

outlet side of the cartridge from being exposed to chamber air. These cartridges were then placed in groups of three to five cartridges in the chamber and exposed to 25 °C air at 1200 ppm and 80 percent relative humidity for 8 hours, equivalent to a standard full-shift work exposure.

General parameter settings for each of the control inputs are shown in Table 3-2. Periodic adjustments to the temperature control and relative humidity settings were necessary depending on the changing ambient laboratory temperature conditions and the associated drift in system temperature, humidity, and vapor concentration. In all cases, adjustments were made such that pairs of temperature and relative humidity settings yielded a monitored temperature and humidity level of 25 °C and 80 percent relative humidity within the respirator testing chamber.

Table 3-2. System parameter settings during prior exposure of cartridges to 25 °C air at 80% relative humidity and 1200 ppm JP-8 vapor. Temperature and relative humidity settings are expressed as approximate ranges of setting pairs (A and B), since ambient laboratory temperature conditions affected the temperature being delivered to the respirator testing chamber. Periodic adjustments were made to achieve a monitored temperature of 25 °C and relative humidity level of 80 percent within the chamber.

Parameter	Setting
Miller-Nelson controller: flow rate (LPM)	9.0
Miller-Nelson controller temperature (°C)	$32.3^{(A)}$ to $40.0^{(B)}$
Miller-Nelson controller relative humidity (%)	47.0 ^(A) to 29.0 ^(B)
Fuel flow rate into packed column (mL/min)	1.0
Air flow rate through column (LPM)	4.7
Column heat tape rheostat voltage (Volts)	70
Flask heating mantle rheostat voltage (Volts)	15
Chamber heat tape rheostat voltage (Volts)	30

After prior exposure, each cartridge was stored in a sealed Ziploc® bag awaiting its breakthrough test. Elapsed time between pre-exposure and testing ranged from 6 to 72 hours.

3.4.3. Breakthrough tests

Cartridges were tested at three concentrations (300, 600, and 1200 ppm) and two test relative humidity levels (50 and 80 percent), requiring six sets of operating parameters (see Table 3-3).

Achieving these concentrations at equilibrium conditions usually required between one and two hours of warm-up time. During warm-up, each component was allowed to equilibrate to its desired temperature; the packed column became saturated with liquid fuel, ensuring a steady-state liquid flow rate across the glass beads; and the TVA-1000B was given time to recover to zero following measurement of the chamber concentration.

As mentioned previously, some minor adjustments to the temperature control settings and flow rates were necessary, depending on the changing laboratory temperature conditions and the associated drift in system temperature, humidity, and vapor concentration; for this reason, Table 3-3 expresses the temperature and relative humidity dial positions as pairs of settings. Additionally, the settings indicated on the Miller-Nelson controller indicate approximate air flow feed conditions from the controller itself but do not reflect the actual flow rate through and temperature and relative humidity inside the respirator testing chamber as a result of temperature drops in the system air combined with heat losses throughout the system. To compensate for this, chamber temperature and humidity were continuously verified throughout the duration of each breakthrough test, and air flow through the system was checked periodically by measuring the air flow through an exit port of the respirator chamber with a BIOS International DryCal DC-2 Flow Calibrator, base S/N B-757, and an accompanying high flow cell, part number DC-1HC, S/N 1454 (BIOS International, Butler, NJ).

Table 3-3. System configuration settings used during cartridge breakthrough testing. Temperature and relative humidity settings are expressed as approximate ranges of setting pairs (A & B, and C & D), since ambient laboratory temperature conditions affected the temperature being delivered to the respirator chamber. Periodic adjustments were made to achieve a monitored temperature of 25 °C and relative humidity level of 50 or 80 percent within the respirator testing chamber.

Parameter	50% RH 300 ppm	50% RH 600 ppm	50% RH 1200 ppm	80% RH 300 ppm	80% RH 600 ppm	80% RH 1200 ppm		
Miller-Nelson controller: flow rate (LPM) dial setting	35.1							
Miller-Nelson controller temperature (°C) dial setting	3	33.0 ^(A) to 40.0 ^(B) 33.0 ^(C) to 40.0 ^(D)						
Miller-Nelson controller relative humidity (%) dial setting	27.8 ^(A) to 17.1 ^(B) 47.0 ^(C) to 29.0 ^(D)				0 ^(D)			
Fuel flow rate into packed column (mL/min)	1.0	2.0	4.0	1.0	2.0	4.0		
Air flow rate through packed column (LPM)	4.7	8.8	18.0	4.7	8.8	18.0		
Column heat tape rheostat voltage (Volts)	70							
Flask heating mantle rheostat voltage (Volts)	15							
Chamber heat tape rheostat voltage (Volts)	4							

The breakthrough testing followed the general procedures given below:

- 1. Configure the testing system to the parameters shown in Table 3-3.
- 2. Zero and calibrate the TVA-1000B to 7500 ppm pentane.
- 3. After approximately one hour, begin monitoring the chamber temperature, humidity, and concentration. Perform minor adjustments as needed, waiting 10 to 15 minutes after each adjustment to ensure stability has been achieved.

- 4. Once the system has reached equilibrium, remove TVA probe from the chamber and allow it to re-zero.
- 5. Remove cartridge from the Ziploc[®] bag and place it in the cartridge holder. Open the chamber, put the holder in place, plug the top of the cartridge holder, and seal the chamber opening with rope caulk. Close chamber door and wait 5 to 10 minutes for the chamber to equilibrate.
- 6. Initiate the breakthrough test by removing the cartridge holder plug. Immediately place TVA-1000B probe inside outlet end of cartridge holder and begin TVA data logging; insert charcoal tube into chamber and start sampling pump; and manually log temperature and humidity.
- 7. Monitor chamber concentration, temperature, and relative humidity approximately every hour (or sooner when possible) to ensure stability at the desired challenge concentration. If the concentration or other conditions have changed, modify column air flow rate, system temperature settings, and humidity level as necessary. After monitoring the chamber, remove the TVA-1000B sampling probe and allow it to recover to a reading of less than 5 ppm exposed to ambient laboratory air, then continue monitoring and data logging the breakthrough concentration on the outlet end of the cartridge holder.
- 8. Once the breakthrough concentration reaches 20 percent of the challenge concentration, remove the TVA-1000B probe, terminate data logging, stop sampling pump, remove charcoal tube, and re-plug the cartridge holder.
- 9. Remove cartridge from the chamber and weigh it. Cartridge may be discarded once testing is completed.
- 10. At the end of testing, post-calibrate the sampling pump and cap the charcoal tube. Respan and re-zero the TVA-1000B.

3.5. Data reduction and analysis methodology

Data-logged breakthrough concentrations in the TVA-1000B were transferred via serial cable into the Foxboro data logging software on an Intel-based PC and were subsequently imported into

Microsoft Excel[®] 97 spreadsheet software. Microsoft Excel[®] was then used to restructure logged concentrations data to enable further graphical analysis and to export data sets readable in a PC-based statistical analysis tool, the SAS Institute, Inc.'s SAS/STAT[®] software. A summary chart was developed to identify various breakthrough times for each test, specifically at the 1%, 5%, 10%, and 20% of challenge concentration points; for the current Air Force 8-hour Occupational Exposure Limit of 50 ppm; and for the proposed ACGIH 8-hour Time-Weighted Average TLV[®] of 14 ppm.

The null hypotheses 1 and 2 (effects of relative humidity and prior exposure) were both tested at the 10 percent of challenge concentration breakthrough time. This percentage value was selected since it is the mid-point of the breakthrough range sampled, and is a concentration that has been frequently tested in the literature. Testing the hypotheses first required assessing the distribution normality of the five data points in each cell, and then determining the homogeneity of variance (HOV) for each cell relative to the other five cells in its data set. Normality of breakthrough times was verified using the SAS/STAT® PROC UNIVARIATE procedure, and homogeneity of breakthrough time variance among cells via Levene's test for equality of variance.

Differences in mean breakthrough times were compared between each cell via Tukey's "Honestly Significant Difference" (HSD) test. The Tukey test facilitates a mean breakthrough time comparison between the six cells in each data set (for a total of 15 comparisons). If the interaction between independent variables was found to be significant, a blocked means comparison was accomplished between the six cells (for a total of 9 comparison tests). The Tukey HSD test controls the experimentwise alpha to a constant by reducing the alpha value used in each cell comparison, thereby minimizing the risk of committing a Type I error (at the risk of allowing the Type II error to increase).

Once normality and homogeneity of variance were established, a General Linearized Model (the SAS/STAT® PROC GLM procedure) provided an assessment of the impact of each treatment

(relative humidity, prior exposure, and concentration) on the dependent variable (breakthrough time).

Characterizing the relationship between the challenge concentration and breakthrough time was assessed by examining the Yoon and Nelson equation and the Wood model (see Section 2.6.1) and attempting to empirically fit the data sets to a generalized form of these equations. A generalized form of the Yoon and Nelson equation was declared in a curve fitting software package and tested for fit against the mean 1%, 5%, 10%, and 20% breakthrough points for each treatment.

Microsoft Excel® and Oakdale Engineering's DataFit software (Oakdale Engineering, Oakdale, PA) were used to provide the graphical analysis and regression tools to assess this relationship.

A form of Wood's relative humidity model (see Section 2.6.1) was compared to the 50 and 80 percent relative humidity (no prior exposure) data sets to examine the relationship between them at each challenge concentration and throughout the duration of the breakthrough curve. The mean breakthrough time for the 1%, 5%, 10%, and 20% breakthrough points of the 80 percent relative humidity condition were divided by the equivalent mean breakthrough time of the 50 percent relative humidity condition for each of the three challenge concentrations. This yielded a ratio similar in concept to Wood's relative humidity model. The ratios were then plotted against the breakthrough percentage to identify any trends that result across the breakthrough curve and between challenge concentrations.

Chapter 4. RESULTS

4.1. Breakthrough testing data

Appendix A contains a listing of the concentrations recorded by the TVA-1000B during each cartridge test. A summary of the time required for breakthrough of 1%, 5%, 10%, and 20% of the challenge concentration, and the proposed ACGIH TLV[®] and current Air Force OEL, is presented in Tables 4-4 through 4-6 for each cartridge tested. The tables also include the mean breakthrough times, standard deviations, and the 95th percentile upper and lower confidence limits (2-sided) for each breakthrough point.

4.2. Charcoal tube sampling results

Respirator chamber concentrations of fuel vapor were monitored using a modified version of the NIOSH 1550 Sampling Method for naphthas (see Appendix B). Table 4-1 provides a summary of chamber concentrations measured with the modified NIOSH 1550 Sampling Method, and compares these concentrations to the target concentration. The respirator chamber concentration was monitored with the Foxboro TVA-1000B portable FID at the start and end of each test and intermittently throughout to ensure stability within $\pm 5\%$ of the target concentration.

These results indicate that with the TVA-1000B calibrated to 7500 ppm of pentane gas, a measured concentration of 1 mg/m³ of fuel vapor (via the modified NIOSH 1550 Method) is approximately equivalent to between 0.152 and 0.159 ppm as reported by the TVA-1000B.

The range of concentrations measured at each challenge level is somewhat greater than the $\pm 5\%$ concentration targeted with the TVA-1000B. At 300 ppm, the range spans from 12.6% below to 22.6% above the mean; at 600 ppm, the range covers 11.2% below to 9.8% above the mean concentration; and at 1200 ppm, the range covers from 6.0% below to 12.8% above the mean concentration.

Table 4-1. Summary table of charcoal tube sampling results, comparing target concentration (measured with Foxboro TVA-1000B Portable Flame Ionization Detector) to values measured via modified NIOSH 1550 Sampling Method.

Target concentration (ppm), per TVA-1000B	Mean (mg/m3)	Minimum (mg/m³)	Maximum (mg/m³)	σ	Measured ppm per mg/m³
300	1980	1730	2170	152	0.152
600	3780	3410	4200	200	0.159
1200	7570	7120	8540	360	0.158

Since this method has not been fully validated and compared to TVA-1000B monitoring results, these data will not be used for analysis of cartridge breakthrough times. However, they are available for documentation and possible future analysis.

4.3. Cartridge weight change

A table listing the change in cartridge weight resulting from pre-conditioning to 80 percent relative humidity, prior exposure to fuel vapor and high humidity, and the cartridge testing activities is provided in Appendix C. A summary is provided in Table 4-2 below:

Table 4-2. Summary of total mean cartridge weight gains (in grams) for each treatment condition.

Concentration	50 (no prior)	80 (no prior)	80 (prior)
300	17.3	21.0	21.3
600	19.2	25.7	25.8
1200	23.7	27.3	27.0

Each cartridge test was terminated when 20 percent of the challenge concentration was measured exiting the cartridge. Therefore, the weight gain would be expected to be greater at the high challenge concentrations, and this was the case. Likewise, the higher relative humidity levels of 80 percent yielded a higher total cartridge weight gain when compared to the 50 percent relative humidity test condition.

At 50 percent relative humidity and 25 °C, air contains approximately 11.5 mg/L of water vapor, and contains approximately 18.4 mg/L at 80 percent relative humidity. ³⁷ With these data and the sampling data reported in Section 4.2 above, a table of estimated water and fuel vapor mass flowing through each cartridge per minute was constructed (Table 4-3).

Table 4-3. Mass flowing through the cartridge per minute at tested conditions of challenge concentration and relative humidity, with air flow rate set at 32 LPM.

Challenge concentration		50% relative humidity		ative /
300 ppm	Water:	0.37 g	Water:	0.59 g
	JP-8:	0.07 g	JP-8:	0.07 g
	Total:	0.44 g	Total:	0.66 g
600 ppm	Water:	0.37 g	Water:	0.59 g
	JP-8:	0.14 g	JP-8:	0.14 g
	Total:	0.51 g	Total:	0.73 g
1200 ppm	Water:	0.37 g	Water:	0.59 g
	JP-8:	0.27 g	JP-8:	0.27 g
	Total:	0.64 g	Total:	0.86 g

Figure 4-1. Estimated mass of water and JP-8 fuel vapor flowing through each cartridge per minute of breakthrough test at 25 °C.

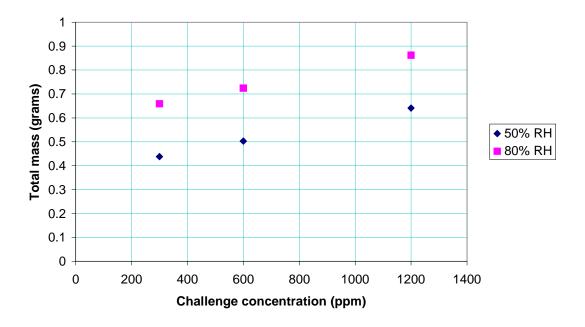


Figure 4-1 shows that based on measured sampling data, as the challenge concentration increases, the mass flow through the cartridge increases with an approximately linear relationship to the challenge concentration, and raising the relative humidity level from 50 percent to 80 percent simply shifts this line upward by a fixed amount.

An examination of total cartridge weight gains also indicates an approximate linear relationship between challenge concentration and weight gain for the 50 percent relative humidity test condition. However, this relationship does not appear to be linear for both 80 percent relative humidity test conditions (Figure 4-2), with the most significant weight change difference occurring between the 300 and 600 ppm challenge concentrations. The reason for this difference is unclear, but could be related to the loss in water weight that may occur as a result of preconditioning cartridges at 80 percent relative humidity and testing them at 50 percent relative humidity.

Figure 4-2. Total average cartridge weight gains at 20% breakthrough points for each test condition. (All cartridges were preconditioned for 6 hours at 80% relative humidity and 25 °C.)

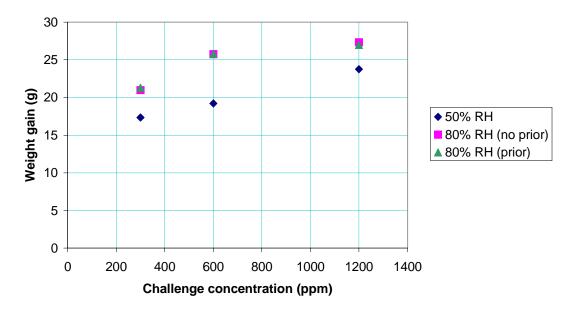


Table 4-4. Summary table of time (in minutes) to various breakthrough concentrations for 50 percent relative humidity (no prior exposure) test condition. All cartridges were preconditioned at 25 °C and 80 percent relative humidity for six hours at an air flow rate of 32 LPM, and were tested at 25 °C and a flow rate of 32 LPM.

300 ppm	Cartridge	<u>1%</u>	<u>5%</u>	<u>10%</u>	<u>20%</u>	TLV	AF OEL
	46	171	204	221	234	203	230
	49	185	206	219	231	205	227
	55	-	216	229	242	214	238
	56	-	219	232	245	217	241
	74	171	226	243	259	224	255
	Mean	176	214	229	242	213	238
	StdDev	8.1	9.2	9.6	11.0	8.7	11.0
	95% LCL	147	200	214	225	199	221
	95% UCL	205	229	244	259	226	255
600 ppm	<u>Cartridge</u>	<u>1%</u>	<u>5%</u>	<u>10%</u>	<u>20%</u>	<u>TLV</u>	AF OEL
	31	78	-	108	124	87	102
	32	75	93	109	126	-	104
	44	74	-	104	123	-	100
	63	-	96	110	128	-	106
	84	73	94	109	127	84	105
	Mean	75	94	108	126	86	103
	StdDev	2.2	1.5	2.3	2.1	2.1	2.4
	95% LCL	70	89	104	122	47	100
	95% UCL	80	100	112	129	124	107
1200 nnm	Contrider	40/	En/	400/	200/	TLV	AE OF!
1200 ppm	<u>Cartridge</u> 36	<u>1%</u> 41	<u>5%</u> 52	10% 59	20% 67	<u>TLV</u> 42	AF OEL 51
	3 0 39	39	32 48	59 52	57	42 40	47
	54	40	52	57	66	41	51
	72	39	48	52	59	40	47
	72 73	44	55	60	68	45	54
	73		55	00	00	40	54
	Mean	41	51	56	63	42	50
	StdDev	2.1	3.0	3.8	5.0	2.1	3.0
	95% LCL	37	46	50	56	38	45
	95% UCL	44	56	62	71	45	55

Table 4-5. Summary table of time (in minutes) to various breakthrough concentrations for 80 percent relative humidity (no prior exposure) test condition. All cartridges were preconditioned at 25 °C and 80 percent relative humidity for six hours at an air flow rate of 32 LPM, and were tested at 25 °C and a flow rate of 32 LPM.

300 ppm	<u>Cartridge</u>	<u>1%</u>	<u>5%</u>	<u>10%</u>	20%	TLV	AF OEL
	35	64	104	135	190	-	167
	47	-	98	139	204	96	187
	48	74	99	138	193	96	177
	64	70	106	149	214	104	196
	65	70	105	144	210	102	188
	Mean	70	102	141	202	100	183
	StdDev	4.1	3.6	5.5	10.4	4.1	11.2
	95% LCL	61	97	132	186	91	165
	95% UCL	78	108	150	219	108	201
600 ppm	<u>Cartridge</u>	<u>1%</u>	<u>5%</u>	<u>10%</u>	<u>20%</u>	<u>TLV</u>	AF OEL
	34	-	76	92	116	68	88
	45	-	67	85	109	57	79
	62	55	72	93	117	63	-
	70	50	69	90	112	58	83
	80	60	78	97	107	68	92
	Mean	55	72	91	112	63	86
	StdDev	5.0	4.6	4.4	4.3	5.3	5.7
	95% LCL	37	65	85	105	55	74
	95% UCL	73	80	98	119	71	97
1200 ppm	Cartridge	<u>1%</u>	<u>5%</u>	10%	<u>20%</u>	TLV	AF OEL
	37	34	45	51	60	35	44
	38	42	51	57	64	43	50
	71	32	42	47	55	33	40
	81	34	44	49	56	35	43
	<i>82</i>	36	45	50	57	37	44
	Mean	36	45	51	58	37	44
	StdDev	3.8	3.4	3.8	3.6	3.8	3.6
	95% LCL	30	40	45	53	31	39
	95% UCL	42	51	57	64	43	50

Table 4-6. Summary table of time (in minutes) to various breakthrough concentrations for 80 percent relative humidity (with prior exposure) test condition. All cartridges were preconditioned at 25 °C and 80 percent relative humidity for six hours at an air flow rate of 32 LPM, followed by static exposure to 1200 ppm of fuel vapor and 80 percent relative humidity at 25 °C for eight hours. They were then tested at 25 °C and a flow rate of 32 LPM.

300 ppm	<u>Cartridge</u>	<u>1%</u>	<u>5%</u>	<u>10%</u>	20%	TLV	AF OEL
	60	-	102	136	184	100	170
	61	-	89	130	190	87	172
	66	57	86	125	194	-	171
	67	-	93	132	205	90	181
	75	-	93	134	175	90	159
	Mean	57	93	131	190	92	171
	StdDev	-	6.0	4.2	11.2	5.7	7.8
	95% LCL	-	83	125	172	80	158
	95% UCL	-	102	138	207	104	183
600 ppm	<u>Cartridge</u>	<u>1%</u>	<u>5%</u>	<u>10%</u>	<u>20%</u>	TLV	AF OEL
	57	43	59	77	101	-	-
	58	45	63	84	111	-	78
	59	41	63	83	106	-	78
	68	45	63	79	101	55	-
	69	49	66	85	110	57	78
	Mean	45	63	82	106	56	78
	StdDev	3.0	2.5	3.4	4.8	1.4	0.0
	95% LCL	40	59	76	98	31	78
	95% UCL	49	67	87	113	81	78
1200 ppm	<u>Cartridge</u>	1%	<u>5%</u>	10%	20%	TLV	AF OEL
1 66	<u>541 (14)</u>	<u>- 70</u>	<u>370</u> 41	49	59	<u></u>	
	52	_	40	48	57	_	-
	<i>76</i>	-	35	42	50	_	33
	77	_	34	43	52	-	32
	<i>78</i>	33	43	48	56	34	41
	-		-	-	-		
	Mean	33	39	46	55	34	35
	StdDev	-	3.9	3.2	3.7	-	4.9
	95% LCL	-	32	41	49	-	18
	95% UCL	-	45	51	61	-	53

4.4. Initial observations

4.4.1. Effects of relative humidity and prior exposure (null hypotheses 1 and 2)

Tables 4-4 and 4-5 form the basis for evaluating the first null hypothesis. A visual examination of these data indicates a strong impact of challenge concentration on breakthrough time, such that a higher challenge concentration results in a considerably shorter time to breakthrough than a lower challenge concentration. It is also evident from the table that there is a reduction in mean breakthrough times when the relative humidity is raised from 50 percent to 80 percent. Another trend that can be seen from this table is that at the high challenge concentration, relative humidity appears to have little impact on the mean breakthrough time yet is more noticeable at lower challenge concentrations. This is indicative of a possible interaction between relative humidity and challenge concentration.

A review of Tables 4-5 and 4-6, which represent the data set used for evaluating the second null hypothesis, provides evidence that challenge concentration has a measurable effect on breakthrough time, with higher concentrations resulting in shorter breakthrough time than lower concentrations. It also appears that prior exposure may slightly reduce breakthrough time.

The impacts of relative humidity and prior exposure can be demonstrated graphically by plotting curves of the mean breakthrough times (at the 10% breakthrough level) vs. the corresponding challenge concentration for each column (Figure 4-3).

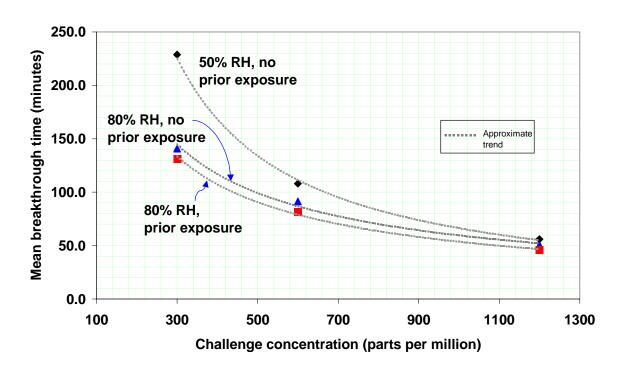


Figure 4-3. Mean breakthrough time to 10% of JP-8 fuel vapor challenge concentration.

4.4.2. Relationships between breakthrough concentration and time (null hypothesis 3)

Independent scatter plots of the breakthrough concentration vs. time to breakthrough were made for each relative humidity and prior exposure treatment. Since there are gaps in the continuity of the data-logged breakthrough concentrations (as a result of intermediate chamber monitoring with the same device), representative points along the breakthrough concentration curve were selected (1%, 5%, 10%, and 20% values of the challenge concentration) where most data points were available for each cartridge. Scatter plots are shown in Figures 4-4 through 4-6.

A cursory examination of Figure 4-4, which shows the response curve at the 50% relative humidity condition, indicates an apparent non-linearity in the breakthrough concentration with respect to time over the entire range of the curve. This plot appears to resemble the lower

portion of a typical sigmoidal response curve often reported in the literature for relative humidity test conditions below 65 percent (see section 2.6.1).

However, the 80 percent relative humidity without prior exposure test condition breakthrough response curve (Figure 4-5) appears to lose the clarity of the sigmoidal response curve, appearing to be linear particularly at the lowest challenge concentration of 300 ppm. This effect is also apparent for the 80 percent relative humidity with prior exposure test condition (Figure 4-6).

Figure 4-4. Scatter plot of breakthrough times for 50% relative humidity condition and no prior exposure to fuel vapor. All cartridges were preconditioned at 80% relative humidity and 25 °C for six hours. Prior exposed cartridges were previously subjected to static concentrations of 1200 ppm fuel vapor for eight hours at 80% relative humidity and 25 °C.

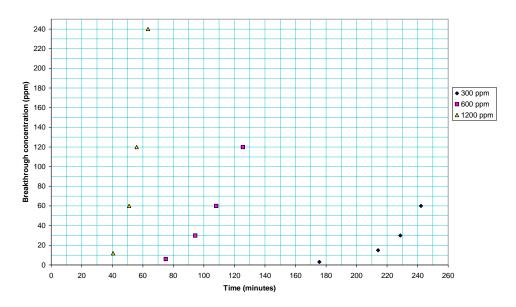


Figure 4-5. Scatter plot of breakthrough times for 80% relative humidity condition and no prior exposure to fuel vapor. All cartridges were preconditioned at 80% relative humidity and 25 °C for six hours. Prior exposed cartridges were previously subjected to static concentrations of 1200 ppm fuel vapor for eight hours at 80% relative humidity and 25 °C.

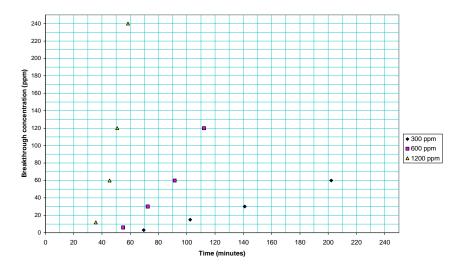
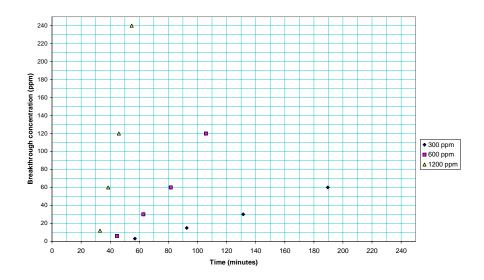


Figure 4-6. Scatter plot of breakthrough times for 80% relative humidity condition and prior exposure to fuel vapor. All cartridges were preconditioned at 80% relative humidity and 25 °C for six hours. Prior exposed cartridges were previously subjected to static concentrations of 1200 ppm fuel vapor for eight hours at 80% relative humidity and 25 °C.



Chapter 5. ANALYSIS AND DISCUSSION

5.1. Effect of relative humidity and challenge concentration on breakthrough time (null hypothesis 1)

5.1.1. Overview

A 2-sided Analysis of Variance (ANOVA) was conducted to assess the impact of relative humidity and challenge concentration on breakthrough time. The ANOVA was completed for the 10 percent of challenge concentration breakthrough time at each of five data points in all six cells within the matrix. Each cell was tested for normality and homogeneity of variance prior to applying an analysis of variance. The source code and data output for the SAS/STAT® ANOVA and means test analysis routines are included in Appendix D.

5.1.2. Normality and homogeneity of variance

It is important to recognize that determining if a five-point data set has a normal distribution is difficult because of the low number of data points. Nevertheless, confirmation of normality lends more credibility to correct application of an ANOVA test.

The PROC UNIVARIATE procedure in SAS/STAT® assesses normality by determining the Shapiro-Wilk statistic, W, which is the "ratio of the best estimator of the variance to the corrected sum of squares estimator of the variance."⁴⁷ A positive normality conclusion requires a large W value (one that is close to the maximum of 1.0) and a large probability (Pr) value (greater than 0.10). In this data set, all cells meet these requirements, so the data within each cell are considered to be normally distributed.

Levene's test for equality of variance was applied to the six cells in this data set.⁴⁸ The calculated F distribution value was 2.4369, which corresponds to an α of 0.06. When α exceeds 0.10, the data sets are considered to be homogenous; however, $\alpha > 0.05$ is sometimes used as a less stringent criterion. The variances for the cells in this data set would be considered homogenous under the latter criterion.

While ANOVA assumes that homogeneity of variance and normality are both present in the data set, the F statistic is considered to be relatively insensitive to violations of these assumptions.⁴⁹ Therefore, this issue will not be addressed further.

5.1.3. Analysis of Variance (ANOVA)

The Analysis of Variance indicates that relative humidity and concentration both had a significant impact on the breakthrough time to 10% of the challenge concentration (P < 0.0001 for each treatment). Additionally, the interaction between relative humidity and concentration was significant (P < 0.0001). A summary of the ANOVA results is presented in Table 5-1.

Table 5-1. Analysis of Variance (ANOVA) for relative humidity and concentration treatments.

Independent variable	Degrees of freedom	Type I Sum of Squares (SS)	Mean Square	F-Value	Pr > F- Value
Relative humidity (RH)	1	10010	10010	340	< 0.0001
Concentration (Conc)	2	89000	44500	1520	< 0.0001
RH X Conc (Interaction)	2	10020	5010	171	< 0.0001

5.1.4. Tests for differences between means

While the Analysis of Variance showed that relative humidity and concentration both have an overall effect on breakthrough time, it does not reveal at which levels of concentration or relative humidity this impact exists. The Tukey "Honestly Significant Difference" (HSD) test was applied to the cell means at each level of concentration and each level of relative humidity. Since there is evidence of interaction between treatment factors, a blocked approach was used. The Tukey HSD test indicated that there was no difference between the 50 and 80 percent relative humidity test conditions at 1200 ppm; all other means were significantly different. In other words, the impact of relative humidity had far less significance at the highest challenge concentration, further evidence of an interaction between relative humidity and concentration. As mentioned previously, this is demonstrated graphically in Figure 4-3, where the breakthrough time curves for

each relative humidity test condition converge at the high challenge concentration and diverge at the lowest.

5.2. Effects of prior exposure and challenge concentration (null hypothesis 2)

5.2.1. Overview

A 2-sided ANOVA was conducted to assess the impact of the prior exposure and challenge concentration treatments on breakthrough time. As before, these runs were completed for the 10 percent of challenge concentration breakthrough time at each of five data points in all six cells within the matrix (see Appendix D). The analysis included an assessment of normality and homogeneity of variance prior to conducting the ANOVA.

5.2.2. Normality and homogeneity of variance

In this data set, all cells met the normality criteria. Data points are therefore considered to be normally distributed at the 10 percent breakthrough times.

Levene's test for equality of variance was applied to the six cells in this data set. The homogeneity of variance test is met at the 0.10α criterion level.

5.2.3. Analysis of Variance (ANOVA)

The Analysis of Variance indicates that prior exposure to high levels of fuel vapor and relative humidity has a significant impact on the breakthrough time to 10% of the challenge concentration (P < 0.0001 for each treatment). However, the interaction between the prior exposure and concentration treatments were reported as insignificant (P = 0.33). A summary of the ANOVA results is presented in Table 5-2.

A further assessment of the concentration x prior exposure factor was conducted to determine if the power $(1 - \beta)$ was sufficient to confidently conclude that there was no significant interaction between the factors. Using an α of 0.05, power was calculated by first determining the ϕ^2_{effect} using the general equation below:

$$\phi_{effect} = \sqrt{\frac{(n)\left[\sum \left(\mu - \mu_i - \mu_j + \mu_{ij}\right)^2\right]}{ab\sigma_{error}^2}}$$

where

n = number of observations in each cell

a = number of levels in factor A

b = number of levels in factor B

 μ = population mean

 μ_i , μ_i = means for treatments A and B (respectively)

 μ_{ij} = mean for the common cell

 σ_{error}^2 is the error variance for the population.

The resulting value of ϕ_{effect} was found to be 0.62. With df_{num} (degrees of freedom in the numerator) of 2 and df_{demm} (degrees of freedom in the denominator) of 24, this equates to a power⁴⁹ of < 0.10. Therefore, the power of this test was insufficient to conclude there was interaction between the variables.

Table 5-2. Analysis of Variance (ANOVA) for prior exposure and concentration treatments.

Independent Variable	Degrees of freedom	Type I Sum of Squares (SS)	Mean Square	F-Value	Pr > F- Value
Prior exposure (Prior)	1	488	488	28.1	< 0.0001
Concentration (Conc)	2	38800	19400	1120	< 0.0001
Prior X Conc (interaction)	2	40.1	20.0	1.15	0.33

5.2.4. Tests for differences between means

While the Analysis of Variance showed that prior exposure and concentration both have an overall effect on breakthrough time, it does not reveal at which level of concentration or prior exposure factor this impact exists. The Tukey HSD comparison of means between each of the

six cells in the matrix revealed there to be a significant difference between all cells except the bottom two, the cartridges tested at a 1200 ppm challenge concentration at both prior exposure levels. In other words, the impact of prior exposure has an insignificant impact at a higher challenge concentration.

5.3. Analysis of breakthrough concentration vs. breakthrough time (null hypothesis 3)

5.3.1. Application of the Yoon and Nelson equation

The Yoon and Nelson equation is re-stated as follows:

$$t_b = -\left[\frac{\rho_B W_e}{C_0 k_y}\right] \ln \left[\frac{C_0 - C_x}{C_x}\right] + \left[\frac{W W_e}{C_0 Q}\right]$$

Recall that as defined in the Wood model, W_e changes slightly with the ratio of the challenge substance's vapor pressure to the saturation partial pressure of that substance for most substances. For example, if the average vapor pressure for JP-8 jet fuel is assumed to be 1.47, at a challenge concentration of 300 ppm, the ratio ρ/ρ_{sat} is 0.23. At 1200 ppm, this ratio is 0.91. Across the range of challenge concentrations tested in this study, per the Wood model, the value of W_e will change by the amount given by $(\ln(0.91))^2/(\ln(0.23))^2=0.004$, or approximately 0.4 percent. It may therefore be treated as a constant.

The k_p parameter is affected predominantly by the value of S, which changes only slightly when the percentage of breakthrough concentration is above 5 percent. If k_p is selected at a mid-point along the tested breakthrough curve (e.g. 10 percent breakthrough), the Yoon and Nelson equation would tend to under-predict the breakthrough time for low breakthrough points (1 and 5 percent) and slightly over-predict at the 20 percent breakthrough point.

Therefore, for the purposes of model comparison and breakthrough prediction, k_n and W_n will be treated as constants. This allows a simplification of the Yoon and Nelson equation to the following form:

$$t_b = -A \frac{1}{C_0} \ln \left[\frac{C_0 - C_x}{C_x} \right] + \frac{B}{C_0}$$

where A and B are curve-fitting constants. This equation is now in the form of y = -mx + b, with x defined as:

$$x = \frac{1}{C_0} \ln \left[\frac{C_0 - C_x}{C_x} \right]$$

A semi-log scatter plot of this x value against the mean breakthrough times should, in theory, demonstrate if this relationship is followed. This was accomplished by fitting the Yoon and Nelson equation to each factorial condition in both experiments. Plots are shown in Figures 5-1 through 5-3.

Figure 5-1. Semi-log plot of a generalized Yoon and Nelson equation against mean breakthrough times for 50% relative humidity test condition. All cartridges were preconditioned at 80% relative humidity and 25 °C for six hours.

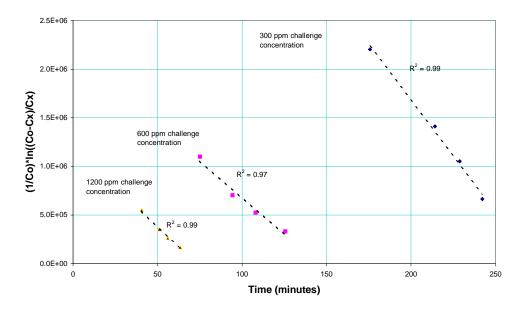


Figure 5-2. Semi-log plot of a generalized Yoon and Nelson equation against mean breakthrough times for 80% relative humidity test condition (without prior exposure to fuel vapor). All cartridges were preconditioned at 80% relative humidity and 25 °C for six hours.

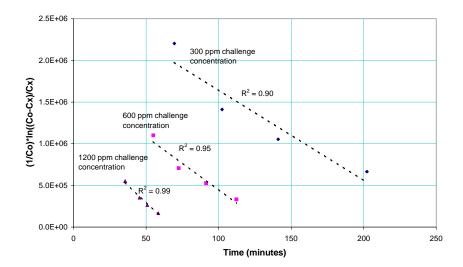
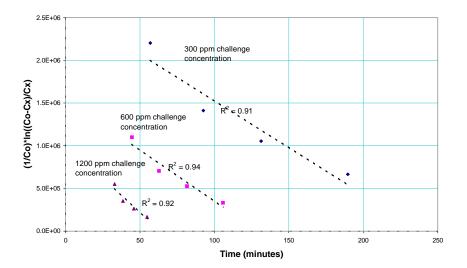


Figure 5-3. Semi-log plot of a generalized Yoon and Nelson equation against mean breakthrough times for 80% relative humidity test condition (with prior exposure to fuel vapor). All cartridges were preconditioned at 80% relative humidity and 25 °C for six hours. Prior exposed cartridges were previously subjected to static concentrations of 1200 ppm fuel vapor for eight hours at 80% relative humidity and 25 °C.



It can be seen from these plots that the 50 percent relative humidity condition appears to follow the form of the Yoon and Nelson equation quite well. Regression squared coefficients (R²), which are indicators of the amount of variation in the dependent variable (the Yoon and Nelson equation) that can be accounted for by the independent variable (challenge concentration),⁴⁹ were 0.99 for the 300 and 1200 ppm challenge concentrations and 0.97 for the 600 ppm challenge concentration. However, the fit for both 80 percent relative humidity test conditions was not as good. Visual examination of these charts indicates a possible non-linearity for both 80 percent relative humidity test conditions, which was also evident in the linear plots of breakthrough concentration vs. time presented in Section 4.4.2.

This finding does appear to be consistent with Nelson and Correia's data set where breakthrough curves for carbon cartridges preconditioned and tested at high humidity levels departed from the typical sigmoidal shape and became more linear in nature except for the extreme portions of the breakthrough curve.²³

Another way of presenting this relationship is to plot the breakthrough time predicted by the generalized Yoon and Nelson equation against the mean breakthrough times as shown in Figures 5-4 to 5-6. To produce these prediction curves, constants A and B were determined individually for each challenge concentration curve using the DataFit curve fitting software tool. The curve fitting was accomplished on the breakthrough times for the 1%, 5%, 10%, and 20% of challenge concentration (see Appendix E), and was based on all cartridges tested at each condition. Optimal curve fit parameters are shown in Table 5-3.

Table 5-3. Curve-fit parameters for generalized Yoon and Nelson equation.

Relative humidity	Prior exposure	Challenge concentration	Α	95% CL (+/-)	В	95% CL (+/-)
50	No	300	4.31E-05	9.05E-06	5.69E-04	2.53E-05
		600	6.49E-05	6.45E-06	6.02E-04	1.88E-05
		1200	5.82E-05	1.17E-05	6.02E-04	3.52E-05
80	No	300	8.44E-05	1.60E-05	5.02E-04	4.66E-05
		600	7.63E-05	1.32E-05	5.55E-04	3.69E-05
		1200	5.82E-05	1.19E-05	5.58E-04	3.59E-05
80	Yes	300	1.01E-04	2.03E-05	5.13E-04	5.03E-05
		600	7.74E-05	1.14E-05	5.23E-04	3.43E-05
		1200	6.76E-05	2.11E-05	5.38E-04	5.24E-05

These plots also confirm that the generalized Yoon and Nelson equation does appear to fit the data well for the 50 percent relative humidity condition. The fit for both 80 percent relative humidity conditions is not as good.

Figure 5-4. Generalized Yoon and Nelson equation fit to measured breakthrough data at 50% relative humidity, without prior exposure to fuel. Coefficients for equation were determined individually for each challenge concentration. All cartridges were preconditioned at 80% relative humidity and 25 °C for six hours.

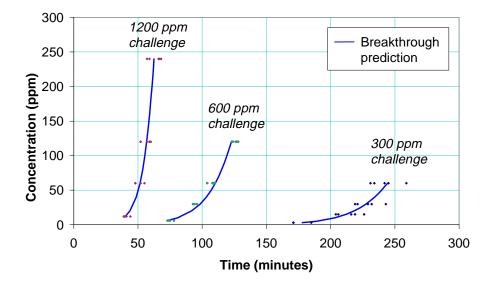


Figure 5-5. Generalized Yoon and Nelson equation fit to measured breakthrough data at 80% relative humidity, without prior exposure to fuel. Coefficients for equation were determined individually for each challenge concentration. All cartridges were preconditioned at 80% relative humidity and 25 °C for six hours.

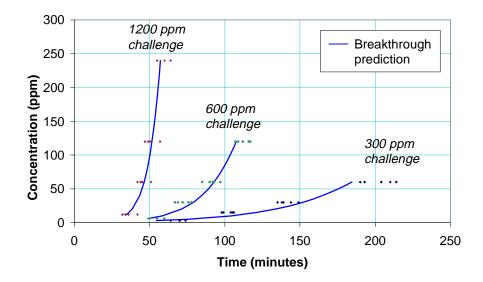
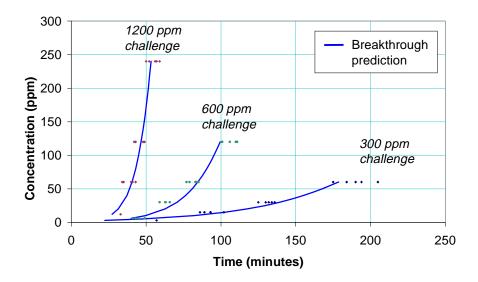


Figure 5-6. Generalized Yoon and Nelson equation fit to measured breakthrough data at 80% relative humidity, with prior exposure to fuel. Coefficients were determined individually for each challenge concentration. All cartridges were preconditioned at 80% relative humidity and 25 °C for six hours. Prior exposed cartridges were previously subjected to static concentrations of 1200 ppm fuel vapor for eight hours at 80% relative humidity and 25 °C.



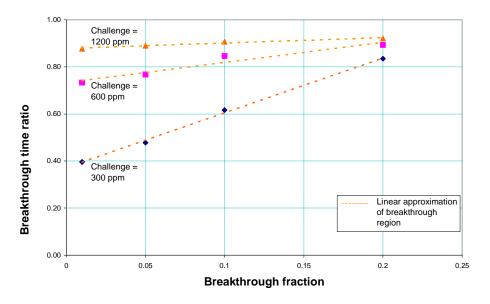
5.3.2. Modeling of relative humidity effects

A test of Wood's relative humidity model was conducted by calculating the ratio of breakthrough times for the 80% and 50% no prior exposure test conditions, with all other parameters held constant. The result of this comparison is presented in Table 5-4 and Figure 5-7.

Table 5-4. Ratio between 80 percent (with no prior exposure to fuel) and 50 percent relative humidity breakthrough times for fixed concentrations and breakthrough points.

Challenge Concentration	Percent breakthrough	Breakthrough time (50% RH)	Breakthrough time (80% RH)	Ratio t ₈₀ /t ₅₀
300	1	176	70	0.40
300	5	214	102	0.48
300	10	229	141	0.62
300	20	242	202	0.83
600	1	75	55	0.73
600	5	94	72	0.77
600	10	108	91	0.85
600	20	126	112	0.89
1200	1	41	36	0.88
1200	5	51	45	0.89
1200	10	56	51	0.91
1200	20	63	58	0.92

Figure 5-7. Ratio between breakthrough times for 80 percent and 50 percent relative humidity conditions (without prior exposure to fuel vapor), with linear regression fit. Data points represent the calculated mean breakthrough time ratios. All cartridges were preconditioned at 80% relative humidity and 25 °C for six hours.



From this information, three observations can be made:

- It appears that at a fixed challenge concentration, the ratio of breakthrough times increases as the breakthrough percentage increases. This effect is quite pronounced at 300 and 600 ppm, but is less visible at the highest concentration of 1200 ppm.
- At low breakthrough concentrations, the breakthrough time ratio increases as the challenge concentration is raised.
- At high breakthrough concentrations (approaching 20 percent of the challenge concentration), the ratio of breakthrough times for each of the challenge concentrations begin to converge.

These findings are consistent with the previous conclusion that there exists an interaction between challenge concentration and relative humidity. The reason for the difference in ratios as the challenge concentration changes is most likely explained by the large number of water molecules present in air at high relative humidity levels relative to the number of organic compound molecules in the air stream. The ratio of water to organic compound molecules is much greater at 300 ppm of fuel vapor, allowing the high concentration of water molecules in the 80 percent relative humidity test condition vapor to have a more profound effect than at 1200 ppm of fuel vapor.³⁶

The difference in ratios that is apparent from the increase in the breakthrough fraction curve may be a result of the longer carbon bed exposure time, allowing the cartridge more time to reach an equilibrium point between water vapor and the organic compounds in JP-8 jet fuel.³⁸ Although not tested during this study, as the breakthrough curve continues beyond the 20 percent point, the ratio would be expected to level off and never completely approach 1.0.

5.4. Development of cartridge service life guidelines

5.4.1. General approach

Ideally, the optimal method to use in developing service life guidelines would be to fit the Yoon and Nelson equation and the Wood model to the entire data set, empirically derive the applicable constants, and predict exposure under any work environment condition of interest. However, as presented in Section 5.3 above, these equations do not appear to accurately describe the full JP-8 fuel vapor breakthrough data set, so a slightly different (and much simpler) approach was taken to enable development of a breakthrough time table for end-user implementation.

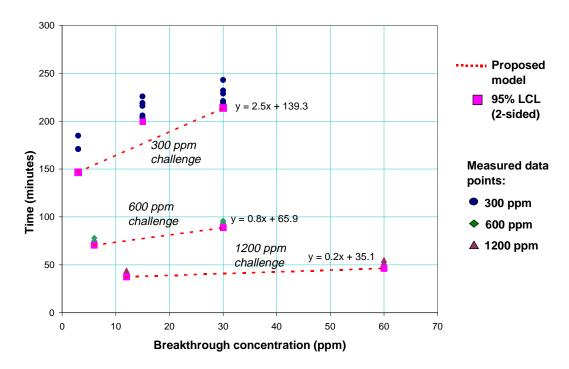
Because of the uncertainty associated with characterizing workplace exposures, it isn't necessary to be able to predict the breakthrough time at any randomly-selected challenge concentration or relative humidity condition. For this reason, a segmented or classification-based approach is appropriate, and the accuracy of a prediction model designed for this purpose must only be good enough to provide adequate worker protection with an adequate safety margin.

For JP-8 jet fuel, which has an OEL of 50 ppm and a proposed TLV® of 14 ppm, the only portion of the breakthrough curve of real interest to the end user is the region of 25 ppm or below, since cartridges should be changed out at ½ of the exposure limit. A straight-line interpolation between the extreme points within this range provided a good approximation of the breakthrough time at any concentration within this range and enabled development of a simple table that can be easily put into use (see Section 6.2). It is important to recognize that the linear models developed in this section only apply to breakthrough concentrations below 30 ppm. If applied above that concentration, these equations will incorrectly predict a service life that is longer than the actual service life.

5.4.2. Predicting breakthrough times for the 50 percent relative humidity condition

For the 50 percent relative humidity test condition, measured breakthrough times for each challenge concentration curve were plotted against breakthrough concentration. For the 1200 ppm challenge concentration, this included breakthrough points through 5 percent breakthrough (or 60 ppm). 30 ppm was selected as the upper end for the 600 and 300 ppm challenge concentrations to allow finer resolution at these levels. The 95% LCL of the mean was then plotted for each set of cartridges, and a straight line was used to connect the 95% LCL for the breakthrough point on the lower end to the 95% LCL on the upper end of each challenge concentration data set. The resulting linear regression equations were then used to interpolate breakthrough times of interest within this region.

Figure 5-8. Straight-line approximation of cartridge breakthrough times based on 95% LCL estimates (50 percent relative humidity, no prior exposure). All cartridges were preconditioned at 80% relative humidity and 25 °C for six hours and were tested with an air flow rate of 32 LPM through each cartridge.



This yields three equations that can be used to estimate breakthrough times for 300, 600, and 1200 ppm challenge concentrations. Equations are summarized in Table 5-5.

Table 5-5. Simplified estimates of cartridge service life at selected action level for 50% relative humidity exposure and room temperature conditions. In most cases, the selected action level will be $\frac{1}{2}$ the OEL or TLV (7 or 25 ppm).

Maximum estimated worker exposure (ppm)	Estimated breakthrough time (in minutes) to a desired action level (AL, in ppm)
300	Time = $(2.5)(AL) + 139$
600	Time = $(0.8)(AL) + 66$
1200	Time = $(0.2)(AL) + 35$

5.4.3. Predicting breakthrough times for the 80 percent relative humidity condition (no prior exposure) A similar approach was used for the 80 percent relative humidity (no prior exposure) test condition. Results are presented in Figure 5-9 and Table 5-6.

Figure 5-9. Straight-line approximation of cartridge breakthrough times based on 95% LCL estimates (80 percent relative humidity, no prior exposure). All cartridges were preconditioned at 80% relative humidity and 25 °C for six hours and were tested with an air flow rate of 32 LPM through each cartridge.

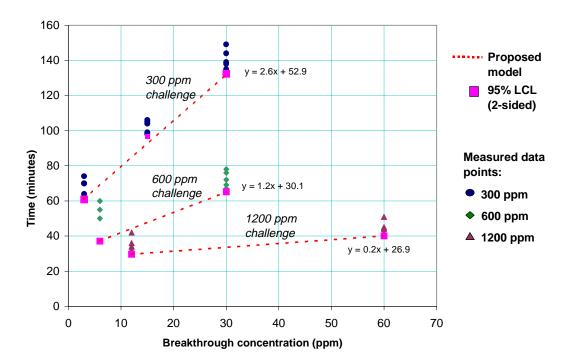


Table 5-6. Simplified estimates of cartridge service life at a selected action level for 80% relative humidity exposure and room temperature conditions. In most cases, the selected action level will be $\frac{1}{2}$ the OEL or TLV (7 or 25 ppm).

Maximum estimated worker exposure (ppm)	Estimated breakthrough time (in minutes)
	to a desired action level (AL, in ppm)
300	Time = $(2.6)(AL) + 53$
600	Time = $(1.2)(AL) + 30$
1200	Time = $(0.2)(AL) + 27$

5.4.4. Predicting breakthrough times for the 80 percent relative humidity condition (with prior exposure)

The Air Force is currently using these cartridges as a back-up provision in the event of an air supply failure, so these cartridges are seldom placed in actual use. Of primary concern is the service life expected from the cartridges if they are needed to aid in escape from an environment containing JP-8 fuel vapor.

The prior exposure test did show a statistically significant reduction in cartridge service life compared to the 80 percent relative humidity without prior exposure condition. However, if the cartridges are only put into active use in a back-up capacity, and are not actively used afterwards, this effect can be ignored. The change is not significant at 1200 ppm, and will not impair the service life needed during the 15 minutes or so that may be needed to exit a fuel tank.

Because of the current use conditions, no prediction model will be proposed for determining breakthrough times of cartridges with prior exposure to fuel vapor. However, it is unclear how much of an impact long-term exposure to fuel vapor may have, since this study terminated exposure at 8 hours. Instead, cartridges used in a back-up configuration should be discarded and replaced on a regular schedule. Since data for exposures exceeding 8 hours is currently unavailable, the professional recommendation of this author is to discard cartridges after 8 hours of cumulative static exposure to fuel vapor, or within one week or less of first use.

Chapter 6. CONCLUSIONS AND RECOMMENDATIONS

6.1. Summary of findings

The research reported in this paper helps to define the service life of the 3MTM 7251 organic vapor cartridge when exposed to concentrations of JP-8 fuel between 300 and 1200 parts per million (ppm). In doing so, this research led to the following conclusions:

- The test relative humidity has a statistically significant impact on a cartridge's service life for cartridges preconditioned at 80 percent relative humidity. When compared to cartridges actively tested at 50 percent relative humidity, the service lives of cartridges tested at 80 percent relative humidity were significantly reduced at challenge concentrations of 300 and 600 ppm, with more than a 50 percent reduction in breakthrough time at 300 ppm. The difference between mean breakthrough times at 1200 ppm was not statistically significant when compared using the Tukey HSD means test.
- The interaction between relative humidity and challenge concentration is significant. Much of
 the current research on the impacts of relative humidity suggest the use of an adjustment
 factor that accounts for the relative humidity level, but not the interaction between relative
 humidity and challenge concentration.
- Exposing the face of a cartridge to JP-8 fuel vapor and high humidity over an 8-hour period without actively drawing vapor through it had a statistically significant impact on a cartridge's service life at some challenge concentrations. This effect was most prominent at 300 ppm, but was not significant at 1200 ppm. For end-user applications, this difference is moderate and will have a minor impact on the cartridge replacement times selected as part of a change-out schedule.
- The interaction between concentration and prior static exposure of a cartridge's face to fuel vapor and high humidity levels is not significant.

- The breakthrough response curve for cartridges tested at 50 percent relative humidity can be modeled well by a general form of the Yoon and Nelson equation, with equation parameters determined empirically. This model is useful for predicting a cartridge's service life at the 50% relative humidity test condition.
- The breakthrough response curve for cartridges tested at 80 percent relative humidity does not appear to follow the shape of the Wood Model equation as well as the 50 percent relative humidity data sets.
- A comparison of breakthrough times between the 80 and 50 percent relative humidity levels (without prior exposure) demonstrates that the ratio does not remain constant throughout the portion of the breakthrough curve tested (1 percent to 20 percent breakthrough), nor is the ratio constant at different challenge concentrations.

6.2. Change-out schedule recommendations

The data collected during this study would not be as meaningful to the aviation community in general unless it can be used to create a cartridge change-out schedule for workers exposed to JP-8 jet fuel. While the equations presented in Section 5.4 are sufficient to estimate cartridge service life at the 50 and 80 percent relative humidity levels, the end user should not be required to calculate breakthrough times. Instead, a change-out table was developed to enable an end-user to quickly determine breakthrough times to ½ of the Air Force OEL or the ACGIH's proposed TLV®. For conditions that vary significantly from the tested conditions (e.g. higher temperatures or humidity levels), the 80 percent relative humidity test condition breakthrough times are reduced by an additional 25 percent to provide an extra margin of safety.

The tables should only be applied when a good characterization of the workplace environment and exposures has been accomplished by an individual trained in such techniques. If there is any question regarding applicability of these recommendations, consult a health or safety professional before entering a potentially hazardous environment. Additionally, the breakthrough times

presented in this table are only applicable to pairs of 3MTM 7251 organic vapor cartridges used in an air purifying respirator.

Application of these tables is a four-step process:

- 1. Assess the maximum exposure anticipated during the task to be accomplished, and characterize the exposure as high (between 600 and 1200 ppm), medium (between 300 and 600 ppm), or low (less than 300 ppm). If anticipated exposures exceed 1200 ppm, an air purifying respirator should not be used in that environment and these tables do not apply. Determination of concentration should initially be accomplished by a health or safety professional, who may recommend a sampling method for local use by fuel systems repair personnel. One possible method that could be employed by repair personnel is to monitor the concentration with an explosive meter and convert the measured percentage of the Lower Explosive Limit (LEL) to a part per million value. For example, assuming an LEL of between 6000 and 9000 ppm, a reading of 10 percent of the LEL would equate to a concentration between 600 ppm and 900 ppm of fuel vapor, which would characterize the exposure as "high". Before using this method, however, some validation work needs to be accomplished to ensure adequate sensitivity, accuracy, and reliability of the selected explosive meter, and to compare its response to other sampling methods (such as the FID used in this study).
- 2. Characterize the relative humidity level as high (80 percent or greater), medium (between 50 and 80 percent), or low (less than 50 percent). If the maintenance procedure is to be accomplished in an environment where the humidity level is not controlled, weather reports may be adequate for estimating the relative humidity level. If conducted indoors, a measurement should be taken with a hygrometer or similar device.
- 3. Select a breakthrough level of concern. This should be ½ of the OEL or the proposed ACGIH TLV[®], depending on the safety factor desired.

4. Look up the breakthrough time in the corresponding table, and ensure the cartridge is changed out before that time elapses. Be sure to allow adequate time to exit the environment before the service life expires.

Table 6-1(a) through (c). Estimated cartridge service life for pairs of 3MTM 7251 organic vapor cartridges during active exposure to JP-8 jet fuel. Estimates are based on the service life tested under laboratory conditions with 32 LPM airflow through each cartridge (equivalent to 64 LPM airflow through each set of cartridges) at (a) 300 ppm, (b) 600 ppm, and (c) 1200 ppm challenge concentrations. All cartridges were preconditioned at 80 percent relative humidity and 25 °C for six hours.

(a) Vapor concentration less than 300 ppm		Breakthrough	time
Desired change-out concentration	Below 50% relative humidity	50-80% relative humidity	Above 80% relative humidity or temp above 85 °F
7 ppm (1/2 of proposed TLV®)	2 ½ hrs	1 hr	45 min.
25 ppm (1/2 of USAF OEL)	3 ¼ hrs	2 hrs	1 ½ hrs.

(b) Vapor concentration 300 to 600 ppm		Breakthrough	time
Desired change-out concentration	Below 50% relative humidity	50-80% relative humidity	Above 80% relative humidity or temp above 85 °F
7 ppm (1/2 of proposed TLV®)	1 hr	35 min.	20 min.
25 ppm (1/2 of USAF OEL)	1 ¼ hrs	1 hr	45 min.

(c) Vapor concentration 600 to 1200 ppm		Breakthrough	time
Desired change-out concentration	Below 50% relative humidity	50-80% relative humidity	Above 80% relative humidity or temp above 85 °F
7 ppm (1/2 of proposed TLV®)	35 min.	30 min.	20 min.
25 ppm (1/2 of USAF OEL)	40 min.	30 min.	20 min.

6.3. Considerations for future research efforts

6.3.1. Comparison of sampling methods

At present, there have been few controlled, side-by-side comparisons between Flame Ionization Detector (FID) direct sampling and the modified NIOSH 1550 charcoal tube adsorbant sampling methods. A better understanding of the relationship between these methods and the relative merits of each would help establish and more accurately document workplace exposures, cartridge breakthrough times, and comparisons to existing occupational exposure limits. For example, an occupational exposure limit of 350 mg/m³ can be converted to parts per million (ppm) by using the existing conversion factors and published molecular weights for JP-8 jet fuel or kerosene (approximately 170 g/mole). However, those values are based on the average molecular weight of all components in liquid fuel and not on the vapor composition, which appears to have a much lower average molecular weight of approximately 114 g/mol.8 Using a part per million conversion factor based on the average molecular weight of the liquid fuel may not accurately represent the actual workplace exposure when compared to the exposure limit.

6.3.2. Compositional differences between challenge and breakthrough vapors

According to the current literature regarding breakthrough of substances containing multiple components, the interaction between components is relatively complex. Substances weakly adsorbed in a carbon bed can be displaced by those with stronger adsorption properties, potentially modifying the composition of the vapor breaking through the cartridge. Consequently, a worker using a respirator for protection against JP-8 may actually be exposed to a subset of substances that is considerably different than the ambient JP-8 vapor when breakthrough begins. Depending on the substances that break through first, and their concentrations, the risks to the worker could be different than if one assumes the compounds breaking through resemble the composition of JP-8. This could be especially important if other

compounds are present in the work environment, such as methyl ethyl ketone (MEK) solvent that might be used in a fuel tank.

6.3.3. Changes in breakthrough times resulting from extensive prior exposure to fuel vapor

This research reported on the change in breakthrough time that results from exposing a cartridge, under static conditions, to high levels of fuel vapor in a controlled, high humidity test environment, and concluded that there does appear to be a slight reduction in breakthrough time after eight hours of exposure. It would be beneficial to understand the impact of repeated cartridge exposure under such conditions, combined with storage of the cartridge over a period of several days or weeks, and the resulting impact on breakthrough times. Modeling of the passive diffusion of fuel vapor that occurs into the carbon and its applicability to existing breakthrough models would be beneficial to the respirator user community.

6.3.4. Modeling of relative humidity effects

The current work that is being done to model the effects of relative humidity levels during preconditioning and test conditions should be applied to the data presented in this report in an attempt to identify whether or not JP-8 follows the typical response characteristics predicted by those models. With this information, it will be possible to better predict the impact of other humidity levels, particularly those higher than the 80% level tested in this study.

6.3.5. Identification of a surrogate compound

Since JP-8 fuel is composed of over 300 organic compounds, it would be beneficial to be able to identify a single compound that could be used in future breakthrough testing to represent JP-8 fuel vapor. By doing this, it may be possible to more easily produce controlled concentrations of a challenge vapor and quickly estimate breakthrough response time for any given cartridge.

Identifying a surrogate compound could be accomplished by first determining the breakthrough times for JP-8 through a dry carbon bed, and then estimating W_e and k_p under dry conditions in a manner similar to that used to curve fit the 50% relative humidity data to the Yoon and Nelson

equation in this report. These values could then be compared to W_e and k_p values calculated through the Wood Model equations for the major components of JP-8⁸ fuel vapor. A list of the applicable properties and parameters for these components is presented in Table 6-2, based on the assumed test values in Table 6-2 and commonly-available chemical property information.³⁷

Table 6-2. Summary of Wood Model equation parameters and estimated breakthrough times (to 10 percent of the challenge concentration) for major components of JP-8 fuel vapor. Calculations are for a 300 ppm challenge concentration (0.228 torr) under dry conditions with no cartridge preconditioning, and the saturation partial pressures (ρ_{sat}) listed are for each substance in pure form.

Compound	Density (g/cc)	ρ (torr)	ρ _{sat} (torr)	MW (g/mol)	n _D	Pe	k _v (min ⁻¹)	W _e (g/g)	Est. time (min.)
Methyl cyclohexane	0.7694	0.228	37	98.19	1.4231	32.50	2154	0.318	250
n-Octane	0.7025	0.228	10	114.2	1.3974	39.19	2424	0.363	258
n-Nonane	0.7176	0.228	3	128.3	1.4054	43.85	2592	0.406	263
m-Xylene	0.8642	0.228	9	106.2	1.4972	35.96	2299	0.440	329
Toluene	0.8669	0.228	21	92.15	1.4961	31.06	2091	0.378	312
Ethyl cyclohexane	0.7880	0.228	13	112.2	1.4330	37.01	2340	0.392	279
cis-1,4-dimethyl cyclohexane	0.7829	0.228	18	112.2	1.4230	36.50	2320	0.376	267
n-Heptane	0.6837	0.228	46	100.2	1.3878	34.6	2242	0.286	224
Cyclohexane	0.7785	0.228	78	84.16	1.4266	27.7	1937	0.245	212
o-Xylene	0.8802	0.228	7	106.2	1.5055	35.8	2292	0.457	341
JP-8 Jet Fuel ²	0.8075	0.228	1.5	170	-	-	-	-	

Table 6-3. Parameters for applying the Wood Model equation to major components of JP-8 jet fuel.

Parameter	Value	Description
W_o	0.597	Carbon micropore volume (cm³/g), from manufacturer
b'	3.56E-05	Empirical coefficient
R	1.987	Ideal gas constant
T	298	Test condition temperature (K)
S	0.036	Empirical constant at 1% breakthrough concentration
V_L	5.93	Linear air flow velocity, cm/sec, based on cross-sectional area of 90
		cm ² (per manufacturer)
	0.00083	Empirical constant
W	44.5	Weight of carbon, from manufacturer
Q	32000	Air flow rate (cm³/min)
$ ho_{B}$	0.436	Bulk density of the packed bed
C _o	300	Challenge concentration, in ppm
C _x	30	Breakthrough concentration, in ppm (10 percent of challenge)

6.4. Closing remarks

There is a vast amount of undiscovered knowledge in the respirator research field, and many opportunities to enhance the safety and health conditions for workers using respirators to provide protection from hazardous substances. It is this author's hope that the work presented in this paper will have a positive impact on workers exposed to jet fuel vapors, and that this work may serve as a launching point for further research to answer much of the complexities that remain.

REFERENCES

.

¹ Air Force Research Laboratory (AFRL/PRSF): History of Aviation Fuel Development in the United States (unpublished internal reference).

² Committee on Toxicology (COT): Permissible Exposure Levels for Selected Military Fuel Vapors, National Research Council, National Academy Press, Washington DC (1996).

³ International Agency for Research on Cancer (IARC): IARC Monographs on the Evaluation of Carcinogenic Risks to Humans. Overall Evaluations of Carcinogenicity: An Updating of IARC Monographs Volumes 1 to 42, Supplement 7. IARC, Lyon, France (1987).

⁴ Executive Order 12196, February 26, 1980, Occupational Safety and Health Programs for Federal Employees (as amended by Executive Order 12608, September 9, 1987).

⁵ Air Force Occupational Safety and Health (AFOSH) Standard 48-8, "Controlling Exposures to Hazardous Materials" (1 Sep 1997).

⁶ American Conference of Governmental Industrial Hygienists (ACGIH): Threshold Limit Values for Chemical Substances and Physical Agents / Biological Exposure Indices. ACGIH, Cincinnati, OH (2000).

⁷ McMurry, J. and R.C. Fay: <u>Chemistry, Second Edition</u>. Upper Saddle River, Jew Jersey: Prentice-Hall, Inc. (1998).

⁸ Naegeli, D.W. and K. H. Childress: Lower Explosion Limits and Compositions of Jet Fuel Vapors. Paper no. WSS/CI 98S-66, presented at Western States Section/Combustion Institute, University of California, Berkeley, March 1998.

⁹ United States Air Force Human Systems Center (HSC), Det 1 HSC/OEMI: "Consultative Letter, AL-OE-BR-CL-1998-0062, Benzene and Jet Fuel Exposures During Aircraft Fuel Systems Maintenance Operations," Detachment 1 HSC/OEMI, 7 May 1998.

¹⁰ United States Air Force Human Systems Center (HSC), Det 1 HSC/OEMI: Survey Reports 1997-224, 228, 231, and 232 (1997)

¹¹ United States Air Force Human Systems Center (HSC), Det 1 HSC/OEMI: Survey Reports 1998-001, 024 to 032 (1998)

¹² United States Air Force Human Systems Center (HSC), Det 1 HSC/OEMI: Survey Report 1998-032 - Exposure to Fuel Vapors During Aircraft Fuel Systems Maintenance Operations, Robins ANG, GA (1998)

¹³ Carlton, G.N. and L.B. Smith: Exposures to Jet Fuel and Benzene During Aircraft Fuel Tank Repair in the U.S. Air Force. Applied Occupational and Environmental Hygiene, 15(6):485-491 (2000).

¹⁴ United States Air Force Materiel Command (AFMC): Technical Order 1-1-3, "Inspection and Repair of Aircraft Integral Tanks and Fuel Cells", WR-ALC/LKJTC, Robins AFB, GA, 30 Nov 1994; with change 6 dated 23 Jan 98.

National Institute for Occupational Safety and Health (NIOSH), "NIOSH Respirator Decision Logic," DHHS (NIOSH) Publication No. 87-108 (1987).

¹⁶ National Institute for Occupational Safety and Health (NIOSH): 42 CFR 84.207, "Bench tests: gas and vapor tests: minimum requirements." (1995).

Occupational Safety and Health Administration (OSHA): 29 CFR 1910.134, Respiratory Protection. http://www.osha-slc.gov/OshStd_data/1910_0134.html (accessed 22 Jan 00).

- ¹⁸ Occupational Safety and Health Administration (OSHA): The Gerry O. Wood Mathematical Model. http://www.osha-slc.gov/SLTC/respiratory advisor/wood table/wood model/wood model.html (accessed 17 June 99).
- ¹⁹ DiNardi, S.R. (ed.): The Occupational Environment Its Evaluation and Control. Fairfax, VA: AIHA Press (1997).
- ²⁰ United States Air Force Occupational Safety and Health (AFOSH) Standard 48-137, "Respiratory Protection Program" (1 Nov 98).
- Wood, G.O. and Ackley, M.W.: A Testing Protocol for Organic Vapor Respirator Canisters and Cartridges. American Industrial Hygiene Association Journal, 50:651-654 (1989).
- ²² Bollinger, N. and C. Coffey: Decision Logic for Organic Vapor Cartridge Respirators for Premanufacture Notification (PMN) Substances. DRAFT (May 25, 1988, unpublished).
- ²³ Nelson, G.O. and A.M. Correia.: Respirator Cartridge Efficiency Studies: VIII. Summary and Conclusions. *American Industrial Hygiene Association Journal* 37:514-525 (1976).
- ²⁴ Nelson, G.O. and C.A. Harder: Respirator Cartridge Efficiency Studies: IV. Effects of Steady-State and Pulsating Flow. *American Industrial Hygiene Association Journal* 33:797-805 (1972).
- ²⁵ Nelson, G.O., C.A. Harder, and B.E. Bigler: Respirator Cartridge Efficiency Studies: VI. Effect of Concentration. *American Industrial Hygiene Association Journal* 37:205 (1976).
- Nelson, G.O., A.M. Correia, and C.A. Harder: Respirator Cartridge Efficiency Studies: VII. Effect of Relative Humidity and Temperature. American Industrial Hygiene Association Journal 37:280 (1976).
- Yoon, Y.H. and J.H. Nelson: Application of Gas Adsorption Kinetics I. A Theoretical Model for Respirator Cartridge Service Life. American Industrial Hygiene Association Journal 45:509-516 (1984).
- ²⁸ Moyer, E. S.: Review of Influential Factors Affecting the Performance of Organic Vapor Air-Purifying Respirator Cartridges. *American Industrial Hygiene Association Journal* 44:46-51(1983).
- Moyer, E.S.: Organic Vapor (OV) Respirator Cartridge Testing Potential Jonas Model Applicability. American Industrial Hygiene Association Journal 48:791-97 (1987).
- Wood, G.O. and E.S. Moyer: A Review of the Wheeler Equation and Comparison of Its Applications to Organic Vapor Respirator Cartridge Breakthrough Data. *American Industrial Hygiene Association Journal* 50:400-407(1989).
- ³¹ Wood, G.O. and E.S. Moyer: A Review and Comparison of Adsorption Isotherm Equations Used to Correlate and Predict Organic Vapor Cartridge Capacities. *American Industrial Hygiene Association Journal* 52:235-242(1991).
- Wood, G.O. and J.F. Stampfer: Adsorption Rate Coefficients for Gases and Vapors on Activated Carbons. *Carbon 31*:195-200 (1993).
- ³³ Wheeler, A. and A.J. Robell: Performance of Fixed-Bed Catalytic Reactors with Poison in the Feed. *J. Catal.* 13:299-305 (1969).

- ³⁹ Lewis, W.K., E.R. Gilliland, B. Chertow, and W.P. Cadagon: Adsorption equilibria: hydrocarbon gas mixtures. *Ind. Eng. Chem* 42:1319-1326 (1950).
- ⁴⁰ Grant, R.J. and M. Mares: Adsorption of binary hydrocarbon gas mixtures on activated carbon. *Ind. Eng. Chem. Fund. 5*:490-498 (1966).
- ⁴¹ Myers, A.L. and J.M. Prausnitz: Thermodynamics of mixed-gas adsorption. Am. Inst. Chem. Eng. J. 11:121-127 (1965).
- ⁴² Jonas, L.A. and E.B. Sansone: Prediction of activated carbon performance for sequential adsorbates. *American Industrial Hygiene Association Journal* 47:509-511 (1986).
- ⁴³ Yoon, Y.H., J.H. Nelson, J. Lara, C. Kamel, and D. Fregeau.: A Theoretical Interpretation of the Service Life of Respirator Cartridges for the Binary Acetone/m-Xylene System. *American Industrial Hygiene Association Journal*, 52(2):65-74 (1991).
- Yoon, Y.H., J.H. Nelson, J. Lara: Respirator Cartridge Service-Life: Exposure to Mixtures. American Industrial Hygiene Association Journal, 57:809-819 (1996).
- ⁴⁵ Leahy, H.F.: AL/OE-TR-1994-0075, Overview of the Vapor Generation and Analysis Parameters of the Petroleum- and Shale-Derived Fuel Studies Conducted in Thomas Dome Exposure Chambers at the Toxic Hazards Research Unit, Wright-Patterson AFB (Dayton), Ohio 1973-1983. United States Air Force Materiel Command, Armstrong Laboratory, Dayton, OH (May 1994).
- ⁴⁶ Potts, W.J. and E.C. Steiner: An apparatus for generation of vapors from liquids of low volatility for use in inhalation toxicity studies. *American Industrial Hygiene Association Journal*, 41:141-145 (1980).
- ⁴⁷ SAS Institute, Inc: SAS OnlineDoc®, Version 8. <u>http://sasdocs.ats.ucla.edu/</u> (accessed 15 Jul 00).
- ⁴⁸ Levene, H. (1960): "Robust Tests for the Equality of Variance," in Contributions to Probability and Statistics, ed. I. Olkin, Palo Alto, CA: Stanford University Press, 278 -292.
- ⁴⁹ Keppel, G.: Design & Analysis A Researcher's Handbook, 2nd edition. Englewood Cliffs, NJ: Prentice-Hall, Inc. (1973).

³⁴ Jonas, L.A. and W.J. Svirbely: The Kinetics of Adsorption of Carbon Tetrachloride and Chloroform from Air Mixtures by Activated Carbon. *J. Catal.* 24:446-459 (1972).

³⁵ Wood, G.O.: Estimating Service Lives of Organic Vapor Cartridges. *American Industrial Hygiene Association Journal 55(1)*:11-15 (1994).

³⁶ Yoon, Y.H. and J.H. Nelson: Effects of humidity and contaminant concentration on respirator cartridge breakthrough. *American Industrial Hygiene Association Journal* 51(4):202-209(1990).

³⁷ Weast, R.C. (ed.): CRC Handbook of Chemistry and Physics. Boca Raton, FL: CRC Press, Inc. (1984).

³⁸ Wood, G.O.: A model for adsorption capacities of charcoal beds: I. Relative humidity effects. American Industrial Hygiene Association Journal 48:622-625(1987).

APPENDIX A

Measured breakthrough concentration on the exit side of cartridges during tests.

The following tables list the time elapsed (in minutes) in the left-hand column and the measured concentration (in parts per million, or ppm) in the neighboring columns underneath each cartridge number. Cartridges are grouped by treatment.

Table A-1. Breakthrough concentrations (in parts per million, or ppm) per test time (in minutes) for cartridges tested at 300 ppm and 50 percent relative humidity, with no prior exposure to fuel vapor.

TIME	46	49	55	56	74
1	8.3	5.2	4.5	1.6	2.2
2	6	3.9	3.9	1.2	2
3	4.7	3.1	3.4	1	1.9
4	3.8	2.6	3.1	0.9	1.7
5	3.2	2.3	2.8	0.8	1.6
6	2.7	2	2.6	0.7	1.5
7	2.4	1.7	2.3	0.6	1.4
8	2.1	1.6	2.2	0.6	1.3
9	1.9	1.5	2	0.5	1.2
10	1.7	1.3	1.9	0.5	1.1
11	1.5	1.2	1.8	0.5	1.1
12	1.4	1.2		0.4	1
13	1.3	1.1		0.4	1
14	1.2	1		0.3	1
15	1.1	1		0.4	0.9
16	1	1		0.3	0.9
17	1	0.9		0.3	0.8
18	0.9	0.9		0.3	0.8
19	0.9	0.9		0.3	0.8
20	0.8	0.8		0.3	0.7
21	0.8	8.0		0.3	0.7
22	0.8	0.8		0.3	0.7
23	0.7	0.8		0.2	0.7
24	0.7	0.7	2.5	0.2	0.6
25	0.7	0.7	2.2	0.2	0.6
26	0.7	0.7	2	0.2	0.6
27	0.6	0.7	1.8	0.2	0.6
28	0.6	0.7	1.7	0.2	0.6
29	0.6	0.7	1.6	0.2	0.5
30	0.6	0.7	1.5	0.2	
31	0.5	0.7	1.4	0.2	
32	0.5	0.6	1.4	0.1	
33	0.5	0.6	1.3	0.2	
34 35	0.5 0.5	0.6	1.2 1.2	0.1	
	0.0	0.6		0.1	
36	0.5	0.6	1.1	0.1	
37	0.5	0.6	1.1	0.1	
38	0.4	0.6	1.1	0.1	
39	0.4	0.6		0.1	
40 41	0.4	0.6	1	0.1	
41		0.6	1	0.1	
42				0.1	
43		0.6	0.9	0.1	
44		0.6	0.9	0.1	
46		0.6	0.9	0.1	

TIME	46	49	55	56	74
47		0.6	0.8	0.1	
48		0.5	0.8	0.1	
49		0.6	0.8	0.1	
50		0.5	0.8	0.1	
51		0.5	0.8	0.1	
52		0.5	0.8	0.1	
53		0.5	0.7	0.1	
54		0.5	0.7	0.1	
55		0.5	0.7	0.1	
56		0.5	0.7	0.1	
57		0.5	0.7	0.1	
58		0.5	0.7	0.1	
59			0.7	0.1	
60			0.7		
61			0.6		
62			0.6		3.2
63			0.6		2.8
64			0.6		2.6
65			0.6		2.3
66			0.6		2.1
67			0.6		1.9
68	0.8		0.6		1.8
69	8.0		0.6		1.6
70	0.7		0.6		1.5
71	0.7		0.6		1.4
72	0.7		0.6		1.3
73	0.6	2			1.3
74	0.6	1.7			1.2
75	0.6	1.5			1.2
76	0.5	1.4			1.1
77	0.5	1.3			1
78	0.5	1.2		1.3	1
79	0.5	1.1		1.1	0.9
80	0.5	1		1	0.9
81	0.5	0.9		0.9	0.9
82	0.5	0.9		0.8	0.9
83	0.4	0.9		0.7	0.8
84	0.4	0.8		0.7	0.8
85	0.4	0.8		0.6	0.8
86	0.4	0.8		0.6	0.8
87	0.4	0.8		0.5	0.8
88	0.4	0.7		0.5	0.8
89	0.4	0.7		0.4	0.7
90	0.4	0.7		0.4	0.7
91	0.4	0.7		0.4	0.7
92	0.4	0.7		0.4	0.7

TIME	46	49	55	56	74
93	0.4	0.6		0.4	0.7
94	0.4	0.7		0.4	0.7
95	0.4	0.6		0.4	0.7
96	0.4	0.6		0.3	0.7
97	0.4	0.6		0.3	0.7
98	0.4	0.6		0.3	0.7
99	0.4	0.6	4.2	0.3	0.7
100	0.4	0.6	3.6	0.3	0.7
101	0.4	0.6	3.1	0.3	0.7
102	0.4	0.6	2.7	0.3	0.7
103	0.4	0.6	2.4	0.3	0.7
104	0.4	0.6	2.2	0.3	0.7
105	0.4	0.6	2	0.3	0.7
106	0.4	0.6	1.9	0.3	0.7
107	0.4	0.6	1.7	0.3	0.7
108		0.6	1.6	0.3	0.7
109		0.6	1.5	0.3	0.7
110		0.6	1.5	0.3	0.7
111		0.6	1.4	0.3	0.7
112		0.6	1.3	0.3	0.7
113		0.6	1.3	0.3	
114		0.6	1.2	0.3	
115		0.6	1.2	0.3	
116		0.6	1.2	0.3	
117		0.6	1.2	0.3	
118		0.6	1.1	0.3	
119		0.6	1.1	0.3	
120		0.6	1.1	0.4	
121		0.6	1.1	0.4	
122			1.1	0.4	
123			1.1	0.4	
124	2.5		1	0.4	
125 126	2.5 2.1		1	0.4	
127	1.9		1	0.4	3.3
128	1.7		1	0.4	2.9
129	1.6		1	0.4	2.6
130	1.5		1	0.5	2.4
131	1.4		1	0.5	2.4
132	1.3		1	0.5	2.2
133	1.3		1	0.5	2.1
134	1.2		1	0.5	1.9
135	1.2		1	0.5	1.9
136	1.2		1	0.6	1.8
137	1.2		1	0.6	1.8
138	1.2		1.1	0.6	1.8
130	1.2		1.1	0.0	1.0

TIME	46	49	55	56	74
139	1.2	2.3	1.1		1.8
140	1.3	2.1	1.1		1.8
141	1.2	1.9	1.1		1.8
142	1.3	1.8	1.1		1.8
143	1.3	1.7	1.1		1.8
144	1.3	1.6	1.1		1.8
145	1.3	1.5	1.1		1.9
146	1.3	1.4	1.2		1.9
147	1.3 1.3	1.4	1.2		1.9
148	1.4	1.4	1.2		1.9
149	1.4	1.4	1.2		1.9
150	1.5	1.4	1.3		2
151	1.5	1.3	1.3		2
152	1.5	1.3	1.3		2
153	1.6	1.4	1.4		2.1
154	1.7	1.4	1.4		2.1
155	1.7	1.4	1.4		2.1
156	1.8	1.4	1.5		2.2
157	1.9	1.4	1.5	1.9	2.2
158	1.9	1.5	1.5	1.8	2.3
159	2	1.5	1.6	1.8	2.2
160	2	1.5	1.6	1.7	2.3
161	2.1	1.5	1.6	1.7	2.4
162	2.2	1.6	1.7	1.8	2.4
163	2.3	1.6	1.8	1.8	2.5
164	2.3	1.6	1.8	1.8	2.5
165	2.4	1.7	1.9	1.8	2.6
166	2.5	1.7	1.9	1.8	2.7
167	2.6	1.7	2	1.9	2.7
168	2.7	1.8	2	2	2.8
169	2.8	1.8	2.1	2	2.9
170	2.9	1.9		2.1	2.9
171	3	1.9		2.1	3
172	3.2	2		2.2	3
173	3.3	2.1		2.3	3.1
174	3.5	2.1		2.4	3.2
175	3.6	2.2		2.4	
176	3.8	2.2		2.5	
177	4	2.3		2.6	
178	4.1	2.4			
179	4.4	2.5			
180	4.6	2.6			
181	4.8	2.7			
182	5	2.8			
183	5.1	2.8	4.4		

TIME	46	49	55	56	74
184	5.3	3	4.4		
185	5.6	3.1	4.5		
186	5.9	3.2	4.5		
187	6.2	3.3	4.7		
188	6.5	7.5	4.8		6.7
189	6.8	7.4	4.9		6.4
190	7.3	7.5	5.1		6.3
191	7.5	7.6	5.2		6.2
192	8	7.9	5.4		6.2
193	8.3	8.1	5.6		6.2
194	8.8	8.4	5.8		6.3
195	9.2	8.8	6.1		6.4
196	9.6	9.1	6.3		6.5
197	10	9.6	6.6		6.6
198	11	10	6.9		6.8
199	11	11	7		6.9
200	12	11	7.2		7.1
201	13	12	7.6	8.7	7.2
202	13	12	7.9	8.4	7.4
203	14	13	8.2	8.4	7.6
204	15	14	8.6	8.4	7.8
205	16	14	9	8.5	8
206	16	15	9.5	8.6	8.2
207		16	9.8	8.9	8.4
208		17	10	9.2	8.7
209		18	11	9.4	9
210		19	11	9.9	9.1
211		20	12	10	9.4
212		21	12	11	9.7
213		22	13	11	10
214		23	14	12	10
215		25	14	12	11
216		26	15	13	11
217	27	27	16	14	12
218	27	29	17	14	12
219	28	31	18	15	12
220	29 30	32	19	16 17	12 13
221		34	20 21	18	13
223	32 34	36 38		19	14
223	35	41	22 23	20	14
225	38	43	24	21	14
226	40	46	25	22	15
227	42	49	27	23	16
228	44	51	29	24	16
220		JI	23	4	10

TIME	46	49	55	56	74
229	46	55	30	25	17
230	49	58	32	27	18
231	52	61	34	29	18
232	54		35	30	19
233	57		37	32	20
234	61		40	34	20
235			42	35	21
236			44	38	22
237			47	39	23
238			49	42	24
239			52	44	25
240			55	47	26
241			58	49	27
242			61	52	28
243			64	53	29
244			67	56	31
245			72	59	32
246			76	63	33
247					35
248					37
249					38
250					40
251					41
252					43
253					46
254					48
255					50
256					52
257					54
258					57
259					59
260					61

Table A-2. Breakthrough concentrations (in parts per million, or ppm) per test time (in minutes) for cartridges tested at 600 ppm and 50 percent relative humidity, with no prior exposure to fuel vapor.

TIME	31	32	44	63	84
1	3.2	4	3.3	3.2	3.7
2	2.9	3.4	2.9	2.9	3.4
3	2.8	3	2.5	2.7	3.2
4	2.6	2.7	2.2	2.6	3
5	2.5	2.4	2	2.4	2.8
6	2.4	2.2	1.8	2.3	2.7
7	2.2	2.1	1.7	2.2	2.5
8	2.1	1.9	1.6	2.1	2.4
9	2	1.8	1.4	2	2.3
10	1.9	1.7	1.3	1.9	2.2
11	1.9	1.6	1.2	1.8	2.1
12	1.8	1.4	1.2	1.7	2
13	1.7	1.4	1.1	1.6	1.9
14	1.7	1.3	1		1.9
15	1.6	1.2	1		1.8
16	1.5	1.2	0.9		1.7
17	1.5	1.1	0.9		1.7
18	1.5	1.1	0.8		1.6
19	1.4	1			1.6
20	1.4	1			1.5
21	1.3	1			1.4
22	1.3	0.9			1.4
23	1.2	0.9			1.4
24	1.2	0.9			1.4
25	1.2	0.8			1.3
26 27	1.2	0.8			1.3 1.2
28	1.1	0.8			
29	1.1	0.8			1.2 1.2
30	1.1	0.8			1.2
31	1.1	0.7			1.1
32		0.7			1.1
33		0.7			1.1
34		0.7			1.1
35		0.7			1.1
36		0.7			1
37		0.7			1
38		0.7		2.2	1
39		0.7		2.1	0.9
40		0.7		1.9	0.9
41			1.5	1.8	-
42			1.4	1.7	
43			1.3	1.6	
44			1.3	1.6	
45			1.3	1.5	
46			1.2	1.5	

TIME	24	22	44	CO	0.4
TIME	31	32	44	63	84
47 48	5.7		1.2	1.4 1.4	
	4.8		1.2		
49	4.2			1.3	
50 51	3.7		1.1	1.3	
51	3.3		1.1	1.3	
52	3		1.1	1.3	
53	2.7		1.2	1.3	
54	2.5		1.2	1.3	
55	2.4	5 0	1.2	1.4	
56	2.3	5.3	1.3	1.4	
57	2.2	4.5	1.3	1.4	
58	2.2	4.1	1.4	1.4	
59	2.1	3.7	1.5	1.5	
60	2.1	3.5	1.6	1.6	
61	2.1	3.3	1.7	1.6	
62	2.1	3.2	1.8	1.7	
63	2.2	3.2	2	1.8	
64	2.2	3.2	2.2	1.9	
65	2.3	3.3	2.4	2.1	
66	2.4	3.4	2.6	2.2	
67	2.5	3.5	2.8	2.4	5.8
68	2.7	3.7	3.1	2.6	5.5
69	2.8	3.9	3.4	2.8	5.4
70	3	4.2	3.7	3.1	5.4
71	3.3	4.5	4.1	3.4	5.5
72	3.5	4.8	4.6		5.7
73	3.8	5.2	5.1		5.9
74	4.2	5.6	5.6		6.2
75	4.5	6.1			6.6
76	4.9	6.7			7.1
77	5.4				7.6
78	6				8.3
79	6.5				9.1
80	7.1				10
81	7.8				11
82	8.6				12
83	9.7				13
84	11				15
85	12				16
86	13			18	18
87	14	23		19	19
88	16	24		20	21
89	17	24		21	22
90	_ 	26	34	22	24
91		27	35	23	26
92		28	36	24	27

TIME	31	32	44	63	84
93		30	38	26	29
94		31	39	27	31
95		33	41	29	32
96		34	43	30	34
97		36	44	32	36
98		38	46	34	38
99		40	48	36	39
100		42	50	38	41
101	49	44	52	39	43
102	50	46	54	41	45
103	50	48	57	43	47
104	52	50	59	45	48
105	54	52	61	47	50
106	56	54	64	49	52
107	57	55	67	52	55
108	60	57	69	54	57
109	62	60	73	56	59
110	65	63	76	58	62
111	69	65	79	61	63
112	72	69	82		65
113	75	72	85		67
114	78	75	88		71
115	81	78	92		74
116	85	81	96		77
117	89	85	100		80
118	93	89	103		83
119	97	92	107		87
120	101	96	109		91
121	105	100	112		94
122	110	104	115	93	98
123	115	107	119	97	102
124	120	112		100	106
125		117		105	110
126		122		109	115
127				114	120
128				119	
129				124	

Table A-3. Breakthrough concentrations (in parts per million, or ppm) per test time (in minutes) for cartridges tested at 1200 ppm and 50 percent relative humidity, with no prior exposure to fuel vapor.

TIME	36	39	54	72	73
1	4.7	4.6	3.6	4.3	3.8
2	4.3	4.1	3.2	3.8	3.3
3	4.1	3.7	2.9	3.4	3
4	3.8	3.4	2.7	3	2.7
5	3.6	3.1	2.4	2.8	2.4
6	3.4	2.9	2.3	2.6	2.2
7	3.3	2.7	2.1	2.4	2
8	3.2	2.5	2	2.2	1.9
9	3.1	2.4	1.9	2.1	1.7
10	2.9	2.2	1.8	2	1.6
11	2.8	2.1	1.7	1.8	1.5
12	2.7	2	1.6	1.8	1.5
13	2.6	1.9	1.5	1.7	1.4
14	2.6	1.8	1.5		
15	2.5	1.7	1.5		
16	2.5	1.6	1.4		
17	2.5	1.6	1.4		
18	2.5	1.5	1.4		
19	2.4	1.4	1.4		
20	2.4	1.4	1.4		
21	2.4	1.4	1.4		
22	2.5	1.4	1.4		
23 24	2.5	1.4 1.4	1.4		
25	2.6	1.5		4.2	
26	2.7	1.6		3.9	
27	2.9	1.7		3.7	
28	3	1.9		3.7	
29	3.2	2.1		3.7	
30	3.4	2.4		3.9	
31	3.7	2.8		4.2	
32	4.1	3.3		4.5	
33	4.5	3.8		5.1	
34	4.9	4.6		5.8	
35	5.5	5.5		6.6	
36	6.2	6.6		7.7	7.3
37	7	7.7		8.9	7.2
38	7.9	9.1	11	10	7.4
39	9	11	12	12	7.7
40	10	13	12	15	8.3
41	12	16	14	18	8.9
42	14	20	15	21	9.7
43	16	24	17	25	11
44	19	29	19	30	12
45	21	35	21	36	14
46	25	42	24	43	16

TIME	36	39	54	72	73
47	29	50	28	50	19
48	33	59	33	60	21
49	38	72	39	72	25
50	45	86	44	85	29
51	52	103	50	99	34
52	58	121	61	114	39
53	63	143	71	127	45
54	71	163	79	143	52
55	79	193	90	160	61
56	89	218	102	178	70
57	97	248	116	196	80
58	106		131	217	91
59	120		144	237	103
60	133		156	260	115
61	149		169		127
62	161		183		141
63	175		199		155
64	189		215		171
65	205		233		186
66	223		248		204
67	244				220
68					239
69					259

Table A-4. Breakthrough concentrations (in parts per million, or ppm) per test time (in minutes) for cartridges tested at 300 ppm and 80 percent relative humidity, with no prior exposure to fuel vapor.

TIME	35	47	48	64	65
1	3.7	2.9	6.8	5.2	3.7
2	3.4	2.5	4.9	4.6	3
3	2.9	2.2	3.8	4.1	2.6
4	2.6	1.9	3	3.7	2.3
5	2.3	1.7	2.5	3.4	2.0
6	2.1	1.5	2.1	3.1	1.8
7	1.9	1.3	1.8	2.8	1.7
8	1.7	1.2	1.5	2.7	1.5
9	1.6	1.1	1.3	2.5	1.4
10	1.5	1	1.2	2.3	1.3
11	1.4	0.9	1	2.2	1.2
12	1.3	0.9	0.9	2.1	1.1
13	1.2	0.8	0.8	1.9	1
14	1.1	0.8	0.8	1.8	1
15	1.1	0.7	0.7	1.8	0.9
16	1	0.7		1.7	0.9
17	1	0.6		1.6	0.8
18	0.9	0.6		1.5	0.8
19	0.9	0.6			0.7
20	0.9	0.5			0.7
21	0.8	0.5			
22	0.8	0.5			
23	0.8	0.4			
24	0.7	0.4			
25	0.7	0.4			
26	0.7	0.4			
27	0.6	0.4			
28	0.6	0.4			
29	0.6	0.4			
30	0.6	0.4			
31		0.4			
32		0.4	2.7		
33		0.4	2.2		
34		0.4	1.9		
35		0.4	1.6		
36		0.4	1.5		
37		0.4	1.3		
38		0.4	1.2		
39		0.4	1.1		
40		0.4	1		
41		0.4	0.9		
42		0.4	0.9		
43		0.4	0.8		
44		0.4	0.8	2.7	
45		0.4	0.7	2.4	
46		0.4	0.7	2.2	

TIME	35	47	48	64	65
47		0.5	0.7	2.1	
48		0.5	0.7	2	
49	1.4	0.5	0.7	1.9	
50	1.3	0.6	0.7	1.8	2
51	1.2	0.6	0.7	1.7	1.8
52	1.2	0.7	0.7	1.7	1.7
53	1.1	0.7	0.7	1.7	1.6
54	1	0.8	0.7	1.6	1.6
55	1.1	8.0	8.0	1.6	1.5
56	1	0.9	0.8	1.6	1.5
57	1	1	0.8	1.6	1.5
58	1	1.1	0.9	1.6	1.5
59	1	1.2	0.9	1.7	1.5
60	1.1	1.3	1	1.7	1.6
61	1.1		1	1.8	1.7
62	1.1		1.1	1.9	1.8
63	1.2		1.2	2	1.9
64	1.2		1.3	2.1	2
65	1.2		1.4	2.2	2.1
66	1.3		1.5	2.3	2.3
67	1.4		1.7	2.5	2.5
68	1.5		1.8	2.6	2.6
69	1.6		2	2.8	2.9
70	1.7		2.2	3.1	3.1
71	1.9		2.4	3.3	3.4
72	2		2.6	3.6	3.7
73	2.2		2.8	3.9	4
74	2.4	7.1	3.1	4.2	4.3
75	2.5	7.2	3.4	4.6	4.7
76	2.8	7.3	3.8	5	5.1
77	3.1	7.6	4.2	5.4	5.6
78	3.3	7.9	4.6	5.8	6
79	3.7	8.3	5.1	6.3	6.5
80	4	8.7	5.6	6.7	6.9
81	4.4	9.1	6.1	6.9	7.2
82	4.8	9.4	6.7	7.2	7.5
83	5.7	9.8	7.3	7.7	7.9
84	6	10	8	8	8.3
85	6.5	11	8.7	8.4	8.6
86	6.9	11	9.4	8.7	8.9
87	7.4	11	10	9.1	9.2
88	8	12	11	9.3	9.5
89	8.7	12	11	9.6	9.8
90		12	12	9.9	10
91		13	12	10	10
92		13	13	11	11

TIME	35	47	48	64	65
93		13	13	11	11
94		13	13	11	11
95		14	14	11	12
96		14	14	12	12
97		15	14	12	12
98		15	15	12	13
99		15	15	13	13
100		16	15	13	13
101		16	16	13	14
102		16		14	14
103		17		14	14
104		17		14	15
105		17		14	15
106	19	18		15	15
107	18	18			
108	18	19			
109	18	19			
110	19	19			
111	19	20			
112	19	20			
113	19	21			
114	19	21			
115	20				
116	20				
117	20				
118	21				
119	21				
120	22		25		
121	22		24		23
122	23		25		23
123	23		25		23
124	23		25	25	23
125	25		25	24	23
126	26		26	24	23
127	27		26	24	23
128	29	29	26	24	24
129	29	28	27	24	24
130	29	28	27	24	24
131	30	28	27	24	25
132	29	28	28	24	25
133	29	28	28	25	25
134	30	28	29	25	26
135	30	29	29	25	26
136	30	29	29	25	27
137	31	30	30	26	27
138	31	30	30	26	27

TIME	35	47	48	64	65
139	31	30	31	26	28
140	32	30	31	27	28
141	32	31	32	27	29
142	33	31	32	28	29
143	33	32	33	28	30
144	34	32	33	28	30
145	34	32	34	29	
146	35	33	34	29	
147	35	33	34	29	
148	35	33	35	30	
149	36	34	35	30	
150	36	34	36	30	
151	36	34	36	31	
152		35	37	31	
153		35	37	32	
154		36	38	32	
155		36	38	32	38
156		37	39	33	37
157		37	39	33	36
158		38	40	34	37
159		38	40	34	37
160		39	41	34	37
161		39	41		38
162		39	42		38
163		40	42		39
164		40	43		39
165		41	43		39
166	48	41	44		40
167	52	41	45		40
168	51	42	45		41
169	52	43	45		41
170	51	43	46		41
171	52	43	46		42
172	52	43	47		42
173	53	43	48		43
174	52	43	48		43
175	51	43	48	40	44
176	51	44		40	44
177	50	44		41	45
178	51	45		41 41	45
179	52 52	45 46		41	46 46
180 181				42	
181	52 53	46 47		42	47 47
183	53 53	47		43	47
				43	
184	54	48		44	48

TIME	25	47	40	64	C.E.
TIME	35	47	48	64	65
185	54	49		44	49
186	56	49		45	49
187	57	50		45	50
188	58	50	57	46	50
189	58	51	58	46	51
190	58	51	59	47	51
191		52	59	48	52
192		53	60	48	52
193		53	60	49	53
194		54		49	53
195		54		50	53
196		55		50	54
197		56		51	55
198		57		51	53
199		58		51	54
200		58		51	54
201		58		51	55
202		59		52	55
203		60		53	56
204		60		53	57
205				54	58
206				55	58
207				55	59
208				56	59
209				56	60
210				57	60
211				58	
212				58	
213				59	
214				60	
215				61	

Table A-5. Breakthrough concentrations (in parts per million, or ppm) per test time (in minutes) for cartridges tested at 600 ppm and 80 percent relative humidity, with no prior exposure to fuel vapor.

TIME	34	45	62	70	80
1	0.2	1	3.3	3.4	3.5
2	0.1	0.9	2.9	3	3.1
3	0.1	0.9	2.5	2.8	2.8
4	0	0.8	2.2	2.5	2.5
5	0	0.7	2	2.3	2.3
6	-0.1	0.7	1.8	2.2	2.1
7	-0.1	0.7	1.6	2	1.9
8	-0.1	0.6	1.5	1.9	1.8
9	-0.1	0.6	1.4	1.8	1.7
10	-0.1	0.6	1.3	1.7	1.5
11	-0.2	0.5	1.2	1.6	1.4
12	-0.2	0.5	1.1	1.5	1.4
13	-0.2	0.5		1.4	1.3
14	-0.2	0.5		1.4	1.2
15	-0.2	0.4		1.3	1.1
16		0.5		1.2	1.1
17		0.4		1.2	1
18		0.4		1.2	1
19		0.4		1.1	1
20		0.4		1.1	0.9
21		0.4		1.1	
22		0.4		1	
23		0.4		1	
24		0.5		1	
25		0.5		1	
26		0.5		1	
27		0.5		1	
28		0.5		1	
29		0.6	4.4	1	
30		0.6	3.7	1.1	
31	1.7	0.6	3.3	1.1	
32	1.4	0.6	2.9	1.1	
33	1.2	0.7	2.6	1.2	
34	1	0.7	2.4	1.2	
35	0.8	0.8	2.2	1.3	
36	0.7	0.9	2.1	1.4	
37	0.6	1	2	1.5	
38	0.6	1.1	1.9	1.7	
39	0.5	1.2	1.9	1.9	
40	0.5	1.3	1.9	2.1	
41	0.5		1.9	2.3	
42	0.5		2	2.5	
43	0.5		2.1	2.8	
44	0.6		2.2	3.2	
45	0.6		2.3	3.6	
46			2.5	3.9	

	1				
TIME	34	45	62	70	80
47			2.7	4.3	4.9
48			2.9	4.8	4.6
49			3.2	5.4	4.3
50			3.5	6.4	4.1
51			3.9	6.9	4
52			4.4	7.7	4
53			4.9	8.8	4
54			5.3	9.6	4.1
55		4.0	6.1	11	4.4
56		13	6.9	12	4.6
57		14	7.7	14	4.9
58		15	8.8	14	5.2
59	2.4	16	9.8	16	5.6
60	8.4	17	11	17	6.2
61	8.3	19	12	19	6.8
62	8.6	20	13	20	7.3
63	9	22	14	22	8.1
64	9.6	25	16	24	8.9
65	10	27	17	24	9.9
66	11	29	19	26	11
67	13	31	21	27	12
68	14	32	22	29	14
69	16	34	24	30	15
70	18	36	26	31	17
71	20	38	28	32	19
72	21	39	30	33	20
73	24	41			22
74	26	42			24
75	27	44			25
76	30	45			27
77	31	47			28
78	33	48			30
79	36	50			31
80	37	52			33
81	39	53			34
82	40	55			36
83	42	56			37
84	44	58		52	38
85	45 47	60		53	40
86	47	61		54	41
87	48	63		55 57	43
88	50	65	F.C.	57	44
89	52	67	56	59	46
90	54 56	70	56	61	47
91	56	72	58	62	49
92	60	74	59	64	50

TIME	34	45	62	70	80
93	65	76	60	65	52
94	70	78	62	67	54
95	71	80	63	70	56
96	72	82	65	73	58
97	74	84	67	75	60
98	75	87	68	77	90
99	75	89	70	79	92
100	77	90	73	82	95
101	78	93	75	84	98
102	81	96	75	87	101
103	82	99	78	90	105
104	84	102	79	93	108
105	86	105	82	95	112
106	89	109	85	99	115
107	92	112	87	102	119
108	94	116	90	106	122
109	97	120	93	109	
110	100		97	112	
111	103		100	116	
112	106		102	120	
113	109		106		
114	112		109		
115	115		113		
116	119		116		
117			119		

Table A-6. Breakthrough concentrations (in parts per million, or ppm) per test time (in minutes) for cartridges tested at 1200 ppm and 80 percent relative humidity, with no prior exposure to fuel vapor.

TIME	37	38	71	81	82
1	4.4	4.8	4.1	3.7	2.2
2	4.1	4.4	7.1	3.3	2.1
3	3.8	4	5.1	3	1.9
4	3.5	3.6	4.6	2.7	1.7
5	3.3	3.4	4.2	2.4	1.6
6	3.1	3.1	3.9	2.3	1.5
7	2.9	2.9	3.6	2.1	1.4
8	2.8	2.7	3.4	2	1.3
9	2.6	2.6	3.3	1.8	1.2
10	2.5	2.5	3.1	1.7	1.1
11	2.5	2.4	3		1.1
12	2.4	2.3	2.9		1.1
13	2.4	2.2	2.8		1
14	2.3	2.1	2.7		1
15	2.3	2.1			1
16	2.4	2			1
17	2.4	2			1
18	2.5	1.9			1
19	2.5	1.9			1.1
20	2.5	1.9			1.1
21	2.6	1.9			1.2
22	2.7	1.9			1.4
23	3	1.9			1.5
24	3.1	1.9			1.7
25	3.3	2			2
26	3.7	2			2.3
27	4.3	2.1			2.7
28	4.9	2.1			3.1
29	5.6	2.3	9.4	8.4	3.7
30	6.5	2.5	10	8.6	4.4
31	7.6	2.7	11	9.1	5.2
32	8.7	3	13	9.7	6.1
33	10	3.3	15	11	7.2
34	11	3.7	17	12	8.7
35	13	4.2	20	14	11
36	16	4.8	24	17	13
37 38	19 21	5.6	28	20	15
39	24	6.4 7.3	33 40	23 27	18 22
40	29	8.3	48	32	27
41	33	9.9	54	38	33
41	39	12	61	44	39
43	44	14	72	52	47
43	50	16	80	62	54
45	56	20	90	74	62
46	66	24			73
40	OO	24	103	85	73

TIME	37	38	71	81	82
47	74	28	116	96	83
48	83	33	128	109	95
49	93	39	140	120	107
50	103	46	153	135	119
51	118	54	168	149	134
52	128	66	183	164	148
53	145	75	199	180	162
54	159	89	217	196	178
55	168	99	237	216	194
56	178	113	257	235	214
57	201	125		255	233
58	219	140			254
59	227	155			
60	250	175			
61		193			
62		201			
63		217			
64		237			
65		253			

Table A-7. Breakthrough concentrations (in parts per million, or ppm) per test time (in minutes) for cartridges tested at 300 ppm and 80 percent relative humidity, with prior static exposure to fuel vapor.

TIME	60	61	66	67	75
1	3.7	4.4	3	2.8	
2	3.2	3.6	2.6	2.1	
3	2.7	3	2.3	1.8	
4	2.4	2.6	2.1	1.5	
5	2.1	2.3	1.8	1.4	
6	1.8	2	1.7	1.2	
7	1.7	1.8	1.5	1.1	
8	1.5	1.6	1.4	1	
9	1.4	1.5	1.3	0.9	
10	1.3	1.3	1.2	0.8	
11	1.2	1.2	1.1	0.8	
12	1.1	1.1		0.7	
13	1	1		0.6	
14	1	1		0.6	
15	0.9	0.9		0.5	
16		0.8		0.5	
17		0.8		0.5	
18		0.8		0.5	
19		0.7		0.4	
20		0.7		0.4	
21		0.6		0.4	
22		0.6		0.4	
23		0.6		0.4	
24		0.5		0.3	
25		0.5		0.4	
26		0.5		0.3	
27		0.5		0.3	
28		0.5		0.3	
29		0.5		0.3	
30		0.5		0.3	
31		0.5		0.3	
32		0.4		0.3	
33		0.4		0.3	
34		0.4		0.3	
35		0.4		0.3	
36		0.5		0.3	
37			1.3	0.3	
38	2.3		1.2	0.3	
39	2.1		1.2	0.3	
40	1.9		1.2	0.3	
41	1.8		1.2	0.4	
42	1.7		1.2	0.4	1.2
43	1.6		1.2		1.3
44	1.6		1.2		
45	1.5		1.3		
46	1.3		1.3		

TIME	60	61	66	67	75
47	1.1		1.4		
48	0.8		1.5		
49	0.6		1.6		
50	0.4		1.7		
51			1.8		
52			2		
53			2.2		
54			2.4		
55			2.6		
56			2.8		
57			3.1	3.6	
58			3.4	3.5	
59			3.8	3.6	
60			4.1	3.7	
61			4.5	3.8	
62			4.9	4	7.8
63			5.3	4.3	7.6
64		4.6	5.7	4.6	7.7
65		4.9	6.2	5	7.7
66		5.3	6.6	5.4	7.8
67		5.6	7	5.8	7.9
68		6	7.4	6.2	8.1
69		6.4	7.8	6.6	8.3
70	4.3	6.8	8	7.1	8.3
71	4.9	7.3	8.2	7.3	8.5
72	5.4	7.8	8.6	7.8	8.7
73	5.9	8.4	8.9	8.2	9
74	6.3	9.1	9.2	8.6	9.3
75	6.7	9.6	9.6	8.9	9.5
76	7	10	9.9	9.3	9.8
77	7.3	11	10	9.7	10
78	7.7	11		10	10
79	8	11		10	11
80	8.3	12		11	11
81	8.5	12		11	11
82	8.8	12		11	11
83	9	13		12	12
84	9.3	13		12	12
85	9.6	13		12	12
86	9.9	14		13	13
87	10	14		13	13
88	10	15		13	13
89	11	15		14	14
90	11	15	18	14	14
91	11		18	15	14
92	12		18	15	15

TIME	60	61	66	67	75
93	12		18	15	15
94	12		18	15	15
95	12		18	16	16
96	13		18	16	16
97	13		19	16	17
98	13		19	16	17
99	14		19	17	17
100	14		20	17	17
101	15		20	17	18
102	15		20	17	18
103		21	21	17	19
104		21	21	17	19
105		21	21	17	20
106		21	22	18	20
107		21	22	18	20
108		21	22	18	21
109		21	23	18	21
110		22	23	18	22
111		22	24	19	22
112		22	24	19	22
113		23	25	19	23
114		23	25	20	23
115		24	26	20	24
116		24	26	21	24
117		25	27		24
118		25	27		25
119		25	28		25
120		26	28		26
121	26	26	28		26
122	26	27	29		26
123	26	27	29		26
124	26	27	30		27
125	26	28	30		27
126	26	28			27
127	27	29			28
128	27	29			28
129	27	30			28
130	28	30		30	28
131	28	30		30	29
132	29			30	29
133	29			30	30
134	29			30	30
135	29			31	39
136	30			31	39
137				31	39
138				32	40

TIME	60	61	66	67	75
139			38	32	40
140			38	32	40
141			38	33	41
142			38	33	41
143			38	34	42
144			39	33	42
145			38	33	43
146			38	34	43
147		39	39	34	44
148		39	39	35	44
149		40	40	35	44
150		40	40	36	44
151		41	41	36	45
152	41	41	41	37	46
153	41	41	41	37	46
154	42	42	42	37	47
155	42	42	42	38	48
156	42	43	43	38	48
157	42	43	43	39	49
158	43	44	44	39	49
159	43	44	44	40	50
160	44	44	43	40	51
161	44	44	44	41	51
162	45	45	42	41	52
163	45	45	46	41	52
164	46	46	47	41	53
165	47	46	47	42	54
166	47	47	48	42	54
167	48	47	48	43	55
168	49	48	49	43	55
169	49	48	49	44	56
170	50	49	50	44	57
171	51	50	50	45	57
172	51	50	51	45	58
173	52	50	51	46	59
174	53	51	52	46	59
175	53	52	52	46	60
176	53	52	53	47	
177	54	53	53	48	
178	55	54	54	48	
179	56	54	54		
180	57	55	55		
181	57	55	55		
182	58	56	55		
183	59	57	55		
184	60	57	55		

TIME	60	61	66	67	75
185	63	58	55		
186		58	55		
187		58	56		
188		58	56		
189		59	57		
190		60	57	54	
191		61	58	54	
192			58	54	
193			59	54	
194			60	54	
195			61	55	
196				55	
197				56	
198				56	
199				57	
200				57	
201				58	
202				58	
203				59	
204				59	
205				60	
206				60	

Table A-8. Breakthrough concentrations (in parts per million, or ppm) per test time (in minutes) for cartridges tested at 600 ppm and 80 percent relative humidity, with prior static exposure to fuel vapor.

TIME	57	58	59	68	69
1	4.1	3.6	2.8		4.4
2	3.8	3.2	2.4	5.5	3.8
3	3.5	2.9	2.2	4.8	3.2
4	3.3	2.6	1.9	4.4	2.8
5	3.1	2.4	1.8	4	2.5
6		2.2	1.6	3.7	2.2
7		2	1.5	3.5	2
8		1.9	1.4	3.3	1.8
9		1.8	1.3	3.1	1.7
10		1.7	1.2	3	1.5
11		1.6	1.1	2.8	1.4
12		1.5	1	2.7	1.3
13		1.4	1	2.6	1.2
14		1.4	0.9	2.6	1.1
15		1.3	0.9	2.5	1.1
16			0.9	2.5	1
17			0.8	2.4	0.9
18			0.8		0.9
19			0.8		0.8
20			0.8		0.8
21			0.8		0.8
22			0.8		0.8
23			0.8		0.7
24			0.8		0.7
25			0.8		0.7
26		4.3	0.8		
27		3.7	0.9		
28		3.3	0.9		
29		3	1		
30		2.8	1		
31	3.7	2.7	1.1		
32	3.5	2.6	1.2		
33	3.5	2.6	1.3		
34	3.4	2.6	1.5		
35	3.5	2.8	1.7		
36	3.6	2.9	1.8		
37	3.7	3	2		
38	3.9	3.2	2.3	6.3	4.5
39	4.1	3.5	2.6	5.9	4.1
40	4.4	3.8	2.9	5.6	3.8
41	4.8	4.2	3.2	5.6	3.7
42	5.2	4.6	3.7	5.5	3.7
43	5.7	5.1	4.2	5.6	3.8
44		5.7	4.7	5.8	4
45		6.3	5.3	6	4.2
46			6.1	6.4	4.5

TIME	57	58	59	68	69
47	31	30	7	6.8	4.9
48			,	7.4	5.4
49				8	5.9
50				8.7	6.6
51				9.5	7.4
52				11	8.2
53				12	9.3
54				13	10
55				15	12
56	26			16	13
57	27			18	15
58	29			20	17
59	30	25	26	22	18
60	31	26	27	24	20
61	32	28	28	26	22
62	33	29	29	28	24
63	34	30	30	30	26
64	36	31	31	32	27
65	37	33	32		29
66	39	34	34		31
67		35	35		
68		36	36		
69		38	38		
70		39	39		
71		40	41		
72		41	42		
73		43	43		
74		44	44		
75 76		46	45		
76	59	48	47	E-2	
77 79	60	49 51	49 51	57 58	
78 79	61 63	51	51	58 60	52
80	64	54	54	61	53
81	66	55	55	63	54
82	68	56	57	65	55
83	70	58	59	67	57
84	73	59	62	70	58
85	75	61	64	72	60
86	77	63	66	74	61
87	79	65	68	76	63
88	81	66	72	79	65
89	84	68	74	82	67
90	87	70	75	84	68
91	89	72	78	87	72
92	92	73	80	90	74

TIME	57	58	59	68	69
93	94	75	83	93	76
94	97	76	85	96	78
95	99	78	88	99	80
96	102	80	90	102	82
97	106	82	92	106	84
98	110	84	95	109	87
99	113	86	98	112	89
100	117	88	101	116	90
101	121	91	104	120	93
102		93	107		96
103		96	110		99
104		99	113		102
105		102	117		105
106		104	119		108
107		107			111
108		110			115
109		114			118
110		117			122
111		121			

Table A-9. Breakthrough concentrations (in parts per million, or ppm) per test time (in minutes) for cartridges tested at 1200 ppm and 80 percent relative humidity, with prior static exposure to fuel vapor.

78 1.3 1.2
1.3 1.2
1.2
1.1
1.1
1
1
1
0.9
0.9
0.9
0.9
0.9
0.9
0.9
1
1.1
1.1
1.4
1.5
1.7
2
2.3
2.7
3.1
3.7
4.4
5.2
6.3
7.5
9.1
11
13
16
19
23
28
33
36 46
54
65
77
90
100

TIME	51	52	76	77	78
47	108	114	187	163	110
48	116	123	206	176	118
49	123	132	223	190	128
50	132	143	245	204	141
51	141	154		220	154
52	152	167		237	170
53	162	179		255	185
54	173	190			201
55	185	205			218
56	199	220			236
57	213	236			257
58	227				
59	240				

APPENDIX B

Modified NIOSH 1550 Method Sampling Results

Results from sampling of JP-8 fuel vapors within the respirator chamber, using the modified NIOSH 1550 Method for naphthas, are presented in the following table.

Table B-1. Modified NIOSH 1550 Method charcoal tube sampling results. Target concentration was measured with the Foxboro TVA-1000B. Conversion of measured concentration charcoal tube sampling results to parts per million (ppm) was accomplished using an average molecular weight of 170 g/mol and a molar gas volume of 24.45 liters.

Sample number	Cartridge number	Target concentration (measured w/TVA-1000B)	Mass collected (mg)	Air volume collected (L)	Measured concentration via NIOSH 1550 (mg/m³)	Measured concentration, converted to ppm
9388-KC30	31	600	15	3.706	4004	582
9388-KC31	32	600	15	3.933	3824	549
9388-KC33	34	600	14	3.545	3879	568
9388-KC34	35	300	12	5.855	2096	295
9388-KC35	36	1200	12	1.591	7247	1085
9388-KC36	37	1200	14	1.807	7737	1114
9388-KC37	38	1200	14	1.966	7162	1024
9388-KC38	39	1200	15	1.719	8540	1255
9388-KC42	44	600	13	3.640	3676	514
9388-KC43	45	600	13	3.370	3843	555
9388-KC44	46	300	13	6.135	2039	305
9388-KC45	47	300	13	6.229	2057	300
9388-KC46	48	300	12	5.875	2089	294
9388-KC47	49	300	14	7.411	1845	272
9388-KC49	51	1200	14	1.833	7430	1098
9388-KC50	52	1200	13	1.765	7592	1059
9388-KC52	54	1200	15	2.020	7540	1068
9388-KC53	55	300	16	7.619	2103	302
9388-KC54	56	300	16	7.578	2138	304
9388-KC55	57	600	13	3.159	4204	592
9388-KC56	58	600	14	3.436	3981	586
9388-KC57	59	600	13	3.306	3878	566
9388-KC58	62	600	14	3.619	3736	556
9388-KC59	60	300	12	5.652	2173	305
9388-KC60	61	300	13	5.895	2146	317
9388-KC61	63	600	13	3.547	3651	527
9388-KC62	64	300	9.6	5.419	1770	255
9388-KC63	65	300	12	6.424	1865	269
9388-KC64	66	300	11	5.882	1824	269
9388-KC65	67	300	11	6.271	1727	252
9388-KC66	68	600	12	3.152	3791	548
9388-KC67	70	600	13	3.508	3606	533
9388-KC68	69	600	12	3.422	3407	504

Table B-1 (continued). Modified NIOSH 1550 Method charcoal tube sampling results.

Sample number	Cartridge number	Target concentration (measured w/TVA-1000B)	Mass collected (mg)	Air volume collected (L)	Measured concentration via NIOSH 1550 (mg/m³)	Measured concentration, converted to ppm
9388-KC69	71	1200	13	1.733	7513	1079
9388-KC70	72	1200	15	1.858	7815	1161
9388-KC71	73	1200	15	2.109	7117	1024
9388-KC72	74	300	15	7.959	1882	271
9388-KC73	75	300	11	5.840	1880	270
9388-KC74	80	600	11	3.638	3576	514
9388-KC75	76	1200	12	1.532	7983	1148
9388-KC76	77	1200	12	1.601	7564	1088
9388-KC77	81	1200	13	1.766	7469	1074
9388-KC78	78	1200	13	1.731	7250	1043
9388-KC79	82	1200	14	1.767	7651	1100
9388-KC80	84	600	14	3.937	3622	521

APPENDIX C

Cartridge weight change summary

The attached table lists the changes in cartridge weight that resulted from each stage preparation and testing. All weights are reported in grams.

Table C-1. Cartridge weight gains during pre-conditioning at 80 percent relative humidity, prior exposure to 1200 ppm JP-8 fuel and 80% relative humidity, and breakthrough tests at challenge conditions. (Tests were terminated at 20 percent breakthrough of the challenge concentration.)

Crtdg num	Conc	RH	Prior	Pkg wt (g)	Pre-conditioning wt gain (g)	Prior exposure wt gain (g)	Breakthrough test wt gain (g)	Total gain (g)
46	300	50	No	76.267	14.372	N/A	2.804	17.176
49	300	50	No	76.058	13.732	N/A	3.054	16.786
55	300	50	No	76.015	14.456	N/A	2.954	17.410
56	300	50	No	76.344	14.313	N/A	3.251	17.564
74	300	50	No	76.147	14.577	N/A	3.214	17.791
31	600	50	No	76.333	13.898	N/A	5.124	19.022
32	600	50	No	76.659	13.902	N/A	5.121	19.023
44	600	50	No	76.743	14.114	N/A	5.249	19.363
63	600	50	No	76.296	14.455	N/A	4.728	19.183
84	600	50	No	76.396	14.166	N/A	5.362	19.528
36	1200	50	No	76.721	15.800	N/A	8.024	23.824
39	1200	50	No	76.659	13.337	N/A	8.971	23.308
54	1200	50	No	76.087	14.738	N/A	8.535	23.273
72	1200	50	No	76.160	14.313	N/A	10.217	24.530
73	1200	50	No	76.261	14.208	N/A	10.558	24.766
35	300	80	No	76.204	13.533	N/A	7.251	20.784
47	300	80	No	76.497	14.513	N/A N/A	7.401	21.914
48	300	80	No	76.826	13.779	N/A N/A	7.457	21.236
64 65	300	80	No No	75.984 76.113	14.578 14.808	N/A N/A	5.477 6.088	20.055
34	600	80	No	76.747	13.497	N/A	11.207	20.896 24.704
45	600	80	No	76.812	14.276	N/A	11.643	25.919
62	600	80	No	75.980	14.601	N/A	11.739	26.340
70	600	80	No	75.970	14.614	N/A	11.145	25.759
80	600	80	No	76.059	14.387	N/A	11.629	26.016
37	1200	80	No	76.281	15.367	N/A	12.286	27.653
38	1200	80	No	76.625	13.867	N/A	12.900	26.767
71	1200	80	No	75.947	14.368	N/A	13.354	27.722
81	1200	80	No	76.186	14.271	N/A	12.451	26.722
82	1200	80	No	75.928	14.697	N/A	13.169	27.866
60	300	80	Yes	76.383	14.682	0.980	5.977	21.639
61	300	80	Yes	76.045	14.385	0.729	6.175	21.289
66	300	80	Yes	76.107	14.351	1.590	5.078	21.019
67	300	80	Yes	75.895	14.312	1.713	5.067	21.092
75	300	80	Yes	76.029	14.226	1.809	5.344	21.379
57	600	80	Yes	76.119	14.526	0.880	10.457	25.863
58	600	80	Yes	76.037	14.399	1.031	10.562	25.992
59	600	80	Yes	76.171	14.722	0.959	10.546	26.227
68	600	80	Yes	76.465	13.842	0.767	10.848	25.457
69	600	80	Yes	76.369	14.109	0.856	10.477	25.442
51	1200	80	Yes	76.074	14.372	1.015	11.195	26.582
52	1200	80	Yes	76.128	14.575	0.810	11.708	27.093
76	1200	80	Yes	76.291	14.231	1.609	10.817	26.657
77	1200	80	Yes	76.141	14.098	1.821	11.529	27.448
78	1200	80	Yes	76.070	14.344	1.000	11.778	27.122

APPENDIX D

Statistical Assessment of Results: SAS/STAT® Output

SAS programs and output for the Analysis of Variance (ANOVA), means tests, homogeneity of variance, and normality assessments are enclosed in this Appendix for hypotheses 1 and 2.

ANOVA and means tests for first hypothesis (RELATIVE HUMIDITY and CONCENTRATION)

```
options linesize=78 pagesize=60 nodate;
title 'Evaluation of Challenge Conc and RH Treatments at 10% Breakthrough';
* Read the full dataset and use only 80% RH data;
data rh;
         infile 'a:\sas\full.dat';
         input fraction cx conc rh prior time;
         if prior = 1 then delete;
        if fraction ^= 0.1 then delete;
* Group the cells for between-cell comparisons;
if (conc=300 \text{ and } rh=50) then cell = 1;
if (conc=600 \text{ and } rh=50) then cell = 2;
if (conc=1200 \text{ and } rh=50) then cell = 3;
if (conc=300 \text{ and } rh=80) then cell = 4;
if (conc=600 \text{ and } rh=80) then cell = 5;
if (conc=1200 and rh=80) then cell = 6;
* Test challenge concentration vs. prior exposure;
proc anova;
        class rh conc;
        model time = rh conc rh*conc;
means conc / tukey;
        means rh / tukey;
* Test cells for homogeneity of variance & normality,
  and significant difference between means;
proc glm;
        class cell;
        model time = cell;
        means cell / hovtest;
proc univariate plot normal;
        var time;
        by rh conc;
* Test differences between means
* (since there is interaction, must use blocked approach)
proc sort;
        by rh;
proc glm;
        class cell;
        model time = cell;
means cell / tukey;
                 by rh;
proc sort;
        by conc;
proc anova;
        class cell;
        model time = cell;
        means cell / tukey;
                 by conc;
proc print;
run;
```

Evaluation of Challenge Conc and RH Treatments at 10% Breakthrough

Analysis of Variance Procedure Class Level Information

Class	Levels	Values
RH	2	50 80
CONC	3	300 600 1200

Number of observations in data set = 30

Analysis of Variance Procedure

Dependent Variab	Dependent Variable: TIME						
Source	DF	Sum of Squares	Mean Square	F Value	Pr > F		
Model	5	109011.8667	21802.3733	742.42	0.0001		
Error	24	704.8000	29.3667				
Corrected Total	29	109716.6667					
	R-Square	C.V.	Root MSE		TIME Mean		
	0.993576	4.809854	5.419102		112.6667		
Source	DF	Anova SS	Mean Square	F Value	Pr > F		
RH CONC RH*CONC	1 2 2	10010.13333 88983.26667 10018.46667	10010.13333 44491.63333 5009.23333	340.87 1515.04 170.58	0.0001 0.0001 0.0001		

Analysis of Variance Procedure

Tukey's Studentized Range (HSD) Test for variable: TIME

NOTE: This test controls the type I experimentwise error rate, but generally has a higher type II error rate than REGWQ.

Alpha= 0.05 df= 24 MSE= 29.36667 Critical Value of Studentized Range= 3.532 Minimum Significant Difference= 6.0522

Tukey Grouping	Mean	N	CONC
А	184.900	10	300
В	99.700	10	600
C	53.400	10	1200

Analysis of Variance Procedure

Tukey's Studentized Range (HSD) Test for variable: TIME

NOTE: This test controls the type I experimentwise error rate, but generally has a higher type II error rate than REGWQ.

Alpha= 0.05 df= 24 MSE= 29.36667 Critical Value of Studentized Range= 2.919 Minimum Significant Difference= 4.084

Means with the same letter are not significantly different.

Tukey Grouping	Mean	N	RH
A	130.933	15	50
В	94.400	15	80

General Linear Models Procedure Class Level Information

Class	Levels	Values
CELL	6	1 2 3 4 5 6

Number of observations in data set = 30

General Linear Models Procedure

Dependent Variabl	Dependent Variable: TIME					
Source	DF	Sum of Squares	Mean Square	F Value	Pr > F	
Model	5	109011.8667	21802.3733	742.42	0.0001	
Error	24	704.8000	29.3667			
Corrected Total	29	109716.6667				
	R-Square	C.V.	Root MSE		TIME Mean	
	0.993576	4.809854	5.419102		112.6667	
Source	DF	Type I SS	Mean Square	F Value	Pr > F	
CELL	5	109011.8667	21802.3733	742.42	0.0001	
Source	DF	Type III SS	Mean Square	F Value	Pr > F	
CELL	5	109011.8667	21802.3733	742.42	0.0001	

General Linear Models Procedure

Levene's Test for Equality of TIME Variance ANOVA of Squared Deviations from Group Means

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
CELL	5	16228.2	3245.6	2.4369	0.0638
Error	24	31965.2	1331.9		

General Linear Models Procedure

Level of		TIME		
CELL	N	Mean	SD	
1	5	228.800000	9.60208311	
2	5	108.000000	2.34520788	
3	5	56.000000	3.80788655	
4	5	141.000000	5.52268051	
5	5	91.400000	4.39317653	
6	5	50.800000	3.76828874	

Evaluation of Challenge Conc and RH Treatments at 10% Breakthrough

98

----- RH=50 -----

Univariate Procedure

Variable=TIME

Moments

N	15	Sum Wgts	15
Mean	130.9333	Sum	1964
Std Dev	75.13936	Variance	5645.924
Skewness	0.50858	Kurtosis	-1.55749
USS	336196	CSS	79042.93
CV	57.3875	Std Mean	19.4009
T:Mean=0	6.748828	Pr> T	0.0001
Num ^= 0	15	Num > 0	15
M(Sign)	7.5	Pr>= M	0.0001
Sgn Rank	60	Pr>= S	0.0001
W:Normal	0.814914	Pr <w< td=""><td>0.0053</td></w<>	0.0053

Quantiles(Def=5)

100% Max 75% Q3	243 221	99% 95%	243 243
50% Med 25% O1	109 59	90% 10%	232 52
0% Min	52	5%	52
		1%	52
Range	191		
Q3-Q1	162		
Mode	52		

Extremes

Lowest	0bs	Highest	0bs
52(14)	219(2)
52(12)	221(1)
57(13)	229(3)
59(11)	232(4)
60(15)	243(5)

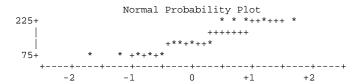
Stem	Leaf	#	Boxplot
2	22334	5	++
1			
1	01111	5	*+*
0	55666	5	++

Multiply Stem.Leaf by 10**+2

----- RH=50 ------

Univariate Procedure

Variable=TIME



Evaluation of Challenge Conc and RH Treatments at 10% Breakthrough 100

Univariate Procedure

Variable=TIME

Moments

N	15	Sum Wgts	15
Mean	94.4	Sum	1416
Std Dev	38.41837	Variance	1475.971
Skewness	0.146423	Kurtosis	-1.55365
USS	154334	CSS	20663.6
CV	40.69743	Std Mean	9.919581
T:Mean=0	9.516531	Pr> T	0.0001
Num ^= 0	15	Num > 0	15
M(Sign)	7.5	Pr>= M	0.0001
Sgn Rank	60	Pr>= S	0.0001
W:Normal	0.87524	Pr <w< td=""><td>0.0405</td></w<>	0.0405

Quantiles(Def=5)

149	99%	149
138	95%	149
92	90%	144
51	10%	49
47	5%	47
	1%	47
102		
87		
47		
	138 92 51 47 102 87	138 95% 92 90% 51 10% 47 5% 1% 102

Extremes

Lowest	Obs	Highest	Obs
47(13)	135(1)
49(14)	138(3)
50(15)	139(2)
51(11)	144(5)
57(12)	149(4)

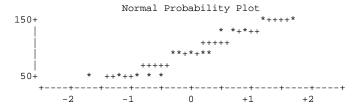
Stem	Leaf	#	Boxplot
14	49	2	
12	589	3	++
10			
8	50237	5	*+*
6			
4	79017	5	++
	+		

Multiply Stem.Leaf by 10**+1

----- RH=80 ------

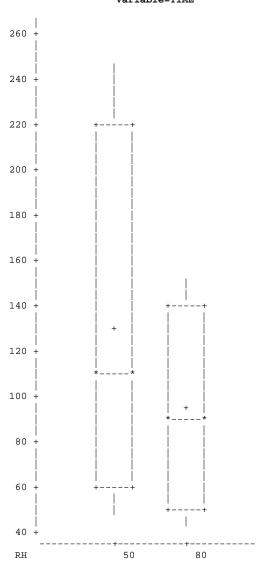
Univariate Procedure

Variable=TIME



Univariate Procedure Schematic Plots

Variable=TIME



----- RH=50 -----

General Linear Models Procedure Class Level Information

CELL 3 1 2 3

Number of observations in by group = 15

----- RH=50 ------

General Linear Models Procedure

Dependent Variable: TIME					
Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	2	78594.13333	39297.06667	1050.72	0.0001
Error	12	448.80000	37.40000		
Corrected Total	14	79042.93333			
	R-Square	C.V.	Root MSE		TIME Mean
	0.994322	4.670739	6.115554		130.9333
Source	DF	Type I SS	Mean Square	F Value	Pr > F
CELL	2	78594.13333	39297.06667	1050.72	0.0001
Source	DF	Type III SS	Mean Square	F Value	Pr > F
CELL	2	78594.13333	39297.06667	1050.72	0.0001
RH=50					

General Linear Models Procedure

Tukey's Studentized Range (HSD) Test for variable: TIME

NOTE: This test controls the type I experimentwise error rate, but generally has a higher type II error rate than REGWQ.

Alpha= 0.05 df= 12 MSE= 37.4 Critical Value of Studentized Range= 3.773 Minimum Significant Difference= 10.318

CELL	N	Mean	Tukey Grouping
1	5	228.800	А
2	5	108.000	В
3	5	56 000	C

----- RH=80 -----

General Linear Models Procedure Class Level Information

CELL 3 456

Number of observations in by group = 15

----- RH=80 -----

General Linear Models Procedure

		Dependent Sum of	Variable: TIME Mean		
Source	DF	Squares		F Value	Pr > F
Model	2	20407.60000	10203.80000	478.30	0.0001
Error	12	256.00000	21.33333		
Corrected Total	14	20663.60000			
	R-Square	C.V.	Root MSE		TIME Mean
	0.987611	4.892799	4.618802		94.40000
Source	DF	Type I SS	Mean Square	F Value	Pr > F
CELL	2	20407.60000	10203.80000	478.30	0.0001
Source	DF	Type III SS	Mean Square	F Value	Pr > F
CELL	2	20407.60000	10203.80000	478.30	0.0001

----- RH=80 -----

General Linear Models Procedure

Tukey's Studentized Range (HSD) Test for variable: TIME

NOTE: This test controls the type I experimentwise error rate, but generally has a higher type II error rate than REGWQ.

Alpha= 0.05 df= 12 MSE= 21.33333 Critical Value of Studentized Range= 3.773 Minimum Significant Difference= 7.793

CELL	N	Mean	Tukey Grouping
4	5	141.000	А
5	5	91.400	В
6	5	50.800	С

----- CONC=300 -----

Analysis of Variance Procedure Class Level Information

Class Levels Values

Number of observations in by group = 10

----- CONC=300 -----

Analysis of Variance Procedure

Dependent Variabl	le: TIME				
Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	19272.10000	19272.10000	314.13	0.0001
Error	8	490.80000	61.35000		
Corrected Total	9	19762.90000			
	R-Square	C.V.	Root MSE		TIME Mean
	0.975166	4.236141	7.832624		184.9000
Source	DF	Anova SS	Mean Square	F Value	Pr > F
CELL	1	19272.10000	19272.10000	314.13	0.0001

----- CONC=300 -----

Analysis of Variance Procedure

Tukey's Studentized Range (HSD) Test for variable: TIME

NOTE: This test controls the type I experimentwise error rate, but generally has a higher type II error rate than REGWQ.

Alpha= 0.05 df= 8 MSE= 61.35 Critical Value of Studentized Range= 3.261 Minimum Significant Difference= 11.423

Tukey Grouping	Mean	N	CELI
A	228.800	5	1
В	141.000	5	4

----- CONC=600 -----

Analysis of Variance Procedure Class Level Information

Class Levels Values

Number of observations in by group = 10

----- CONC=600 -----

Analysis of Variance Procedure

Dependent Variable: TIME							
Source	DF	Sum of Squares	Mean Square	F Value	Pr > F		
Model	1	688.9000000	688.9000000	55.56	0.0001		
Error	8	99.2000000	12.4000000				
Corrected Total	9	788.1000000					
	R-Square	C.V.	Root MSE		TIME Mean		
	0.874128	3.531959	3.521363		99.70000		
Source	DF	Anova SS	Mean Square	F Value	Pr > F		
CELL	1	688.9000000	688.9000000	55.56	0.0001		
		G0NG-600					
		CONC=600					

Analysis of Variance Procedure

Tukey's Studentized Range (HSD) Test for variable: TIME

NOTE: This test controls the type I experimentwise error rate, but generally has a higher type II error rate than REGWQ.

Alpha= 0.05 df= 8 MSE= 12.4 Critical Value of Studentized Range= 3.261 Minimum Significant Difference= 5.1357

Tukey Grouping	Mean	N	CELI
А	108.000	5	2
В	91.400	5	5

----- CONC=1200 -----

Analysis of Variance Procedure Class Level Information

Class Levels Values
CELL 2 3 6

Number of observations in by group = 10

------ CONC=1200 ------

Analysis of Variance Procedure

Dependent Variable: TIME							
Source	DF	Sum of Squares	Mean Square	F Value	Pr > F		
Model	1	67.60000000	67.60000000	4.71	0.0618		
Error	8	114.80000000	14.35000000				
Corrected Total	9	182.40000000					
	R-Square	C.V.	Root MSE		TIME Mean		
	0.370614	7.093894	3.788139		53.40000		
Source	DF	Anova SS	Mean Square	F Value	Pr > F		
CELL	1	67.60000000	67.60000000	4.71	0.0618		
		CONC=1200					
		CONC=1200					

Analysis of Variance Procedure

Tukey's Studentized Range (HSD) Test for variable: TIME

NOTE: This test controls the type I experimentwise error rate, but generally has a higher type II error rate than REGWQ.

Alpha= 0.05 df= 8 MSE= 14.35 Critical Value of Studentized Range= 3.261 Minimum Significant Difference= 5.5247

Tukey Grouping	Mean	N	CELL
A	56.000	5	3
A	50.800	-	6
A	50.800	5	6

OBS	FRACTION	CX	CONC	RH	PRIOR	TIME	CELL
1	0.1	30	300	50	0	221	1
2	0.1	30	300	50	0	219	1
3	0.1	30	300	50	0	229	1
4	0.1	30	300	50	0	232	1
5	0.1	30	300	50	0	243	1
6	0.1	30	300	80	0	135	4
7	0.1	30	300	80	0	139	4
8	0.1	30	300	80	0	138	4
9	0.1	30	300	80	0	149	4
10	0.1	30	300	80	0	144	4
11	0.1	60	600	50	0	108	2
12	0.1	60	600	50	0	109	2
13	0.1	60	600	50	0	104	2
14	0.1	60	600	50	0	110	2
15	0.1	60	600	50	0	109	2
16	0.1	60	600	80	0	92	5
17	0.1	60	600	80	0	85	5
18	0.1	60	600	80	0	93	5
19	0.1	60	600	80	0	90	5
20	0.1	60	600	80	0	97	5
21	0.1	120	1200	50	0	59	3
22	0.1	120	1200	50	0	52	3 3
23	0.1	120	1200	50	0	57	3
24	0.1	120	1200	50	0	52	3
25	0.1	120	1200	50	0	60	3
26	0.1	120	1200	80	0	51	6
27	0.1	120	1200	80	0	57	6
28	0.1	120	1200	80	0	47	6
29	0.1	120	1200	80	0	49	6
30	0.1	120	1200	80	0	50	6

ANOVA and means tests for second hypothesis (PRIOR EXPOSURE and CONCENTRATION)

```
options linesize=78 pagesize=60 nodate;
title 'Evaluation of Challenge Conc and PE Treatment at 10% Breakthrough';
* Read the full dataset and use only 80% RH data;
data prior;
         infile 'a:\sas\full.dat';
         input fraction cx conc rh prior time;
         if rh = 50 then delete;
         if fraction ^= 0.1 then delete;
^{\star} Group the cells for between-cell comparisons;
if (conc=300 and prior=0) then cell = 1;
if (conc=600 and prior=0) then cell = 2;
if (conc=1200 and prior=0) then cell = 3;
if (conc=300 and prior=1) then cell = 4;
if (conc=600 and prior=1) then cell = 5;
if (conc=1200 and prior=1) then cell = 6;
* Test challenge concentration vs. prior exposure;
proc anova;
         class prior conc;
        model time = prior conc prior*conc;
        means conc / tukey;
        means prior / tukey;
* Test cells for homogeneity of variance, normality,
  and significant difference between means;
proc glm;
         class cell;
        model time = cell;
means cell / hovtest tukey;
proc univariate plot normal;
         var time;
        by prior conc;
proc print;
run;
```

Evaluation of Challenge Conc and PE Treatment at 10% Breakthrough

Analysis of Variance Procedure Class Level Information

Class	Levels	Values
PRIOR	2	0 1
CONC	3	300 600 1200

Number of observations in data set = 30

Analysis of Variance Procedure

Dependent Variabl	Dependent Variable: TIME						
Source	DF	Sum of Squares	Mean Square	F Value	Pr > F		
Model	5	39296.56667	7859.31333	452.99	0.0001		
Error	24	416.40000	17.35000				
Corrected Total	29	39712.96667					
	R-Square	C.V.	Root MSE		TIME Mean		
	0.989515	4.609369	4.165333		90.36667		
Source	DF	Anova SS	Mean Square	F Value	Pr > F		
PRIOR CONC PRIOR*CONC	1 2 2	488.03333 38768.46667 40.06667	488.03333 19384.23333 20.03333	28.13 1117.25 1.15	0.0001 0.0001 0.3321		

Analysis of Variance Procedure

Tukey's Studentized Range (HSD) Test for variable: TIME

NOTE: This test controls the type I experimentwise error rate, but generally has a higher type II error rate than REGWQ.

Alpha= 0.05 df= 24 MSE= 17.35 Critical Value of Studentized Range= 3.532 Minimum Significant Difference= 4.6519

Tukey Grouping	Mean	N	CONC
А	136.200	10	300
В	86.500	10	600
C	48.400	10	1200

Analysis of Variance Procedure

Tukey's Studentized Range (HSD) Test for variable: TIME

NOTE: This test controls the type I experimentwise error rate, but generally has a higher type II error rate than REGWQ.

Alpha= 0.05 df= 24 MSE= 17.35 Critical Value of Studentized Range= 2.919 Minimum Significant Difference= 3.1391

Means with the same letter are not significantly different.

Tukey Grouping	Mean	N	PRIOR
А	94.400	15	0
В	86.333	15	1

General Linear Models Procedure Class Level Information

Class	Levels	Values
CELL	6	1 2 3 4 5 6

Number of observations in data set = 30

General Linear Models Procedure

Dependent Variabl	le: TIME				
Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	5	39296.56667	7859.31333	452.99	0.0001
Error	24	416.40000	17.35000		
Corrected Total	29	39712.96667			
	R-Square	C.V.	Root MSE		TIME Mean
	0.989515	4.609369	4.165333		90.36667
Source	DF	Type I SS	Mean Square	F Value	Pr > F
CELL	5	39296.56667	7859.31333	452.99	0.0001
Source	DF	Type III SS	Mean Square	F Value	Pr > F
CELL	5	39296.56667	7859.31333	452.99	0.0001

General Linear Models Procedure

Levene's Test for Equality of TIME Variance ANOVA of Squared Deviations from Group Means

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
CELL Error	5 24	846.6 6601.7	169.3 275.1	0.6156	0.6890

General Linear Models Procedure

Tukey's Studentized Range (HSD) Test for variable: TIME

NOTE: This test controls the type I experimentwise error rate, but generally has a higher type II error rate than REGWQ.

Alpha= 0.05 df= 24 MSE= 17.35 Critical Value of Studentized Range= 4.373 Minimum Significant Difference= 8.1454

Tukey Grouping	Mean	N	CELL
A	141.000	5	1
В	131.400	5	4
C	91.400	5	2
D	81.600	5	5
E E	50.800	5	3
E	46.000	5	6

------ PRIOR=0 CONC=300 -----

Univariate Procedure

Variable=TIME

Moments

N	5	Sum Wgts	5
Mean	141	Sum	705
Std Dev	5.522681	Variance	30.5
Skewness	0.712412	Kurtosis	-0.51545
USS	99527	CSS	122
CV	3.916795	Std Mean	2.469818
T:Mean=0	57.08923	Pr> T	0.0001
Num ^= 0	5	Num > 0	5
M(Sign)	2.5	Pr>= M	0.0625
Sgn Rank	7.5	Pr>= S	0.0625
W:Normal	0.947621	Pr <w< td=""><td>0.7275</td></w<>	0.7275

Quantiles(Def=5)

100% Max	149	99%	149
75% Q3	144	95%	149
50% Med	139	90%	149
25% Q1	138	10%	135
0% Min	135	5%	135
		1%	135
Range	14		
Q3-Q1	6		
Mode	135		

Extremes

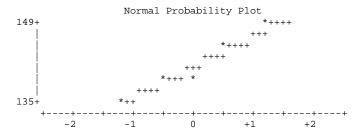
Lowest	Obs	Highest	Obs
135(1)	135(1)
138(3)	138(3)
139(2)	139(2)
144(5)	144(5)
149(4)	149(4)

Stem	Leaf	#	Boxplot
148	0	1	
146			
144	0	1	++
142			
140			+
138	00	2	**
136			
134	0	1	ĺ
	+		•

------ PRIOR=0 CONC=300 -----

Univariate Procedure

Variable=TIME



------ PRIOR=0 CONC=600 -----

Univariate Procedure

Variable=TIME

Moments

N	5	Sum Wgts	5
Mean	91.4	Sum	457
Std Dev	4.393177	Variance	19.3
Skewness	-0.41751	Kurtosis	0.965664
USS	41847	CSS	77.2
CV	4.806539	Std Mean	1.964688
T:Mean=0	46.52138	Pr> T	0.0001
Num ^= 0	5	Num > 0	5
M(Sign)	2.5	Pr>= M	0.0625
Sgn Rank	7.5	Pr>= S	0.0625
W:Normal	0.980238	Pr <w< td=""><td>0.9224</td></w<>	0.9224

Quantiles(Def=5)

100% Max	97	99%	97
75% Q3	93	95%	97
50% Med	92	90%	97
25% Q1	90	10%	85
0% Min	85	5%	85
		1%	85
Range	12		
Q3-Q1	3		
Mode	85		

Extremes

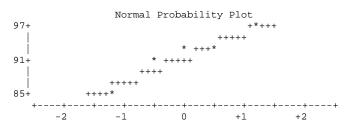
Lowest	0bs	Highest	Obs
85(2)	85(2)
90(4)	90(4)
92(1)	92(1)
93(3)	93(3)
97(5)	97(5)

Stem	Leaf	#	Boxplot
96	0	1	
94			ĺ
92	00	2	++
90	0	1	+++
88			
86			
84	0	1	0

------ PRIOR=0 CONC=600 ------

Univariate Procedure

Variable=TIME



Univariate Procedure

Variable=TIME

Moments

N	5	Sum Wgts	5
Mean	50.8	Sum	254
Std Dev	3.768289	Variance	14.2
Skewness	1.379189	Kurtosis	2.520333
USS	12960	CSS	56.8
CV	7.417891	Std Mean	1.68523
T:Mean=0	30.14425	Pr> T	0.0001
Num ^= 0	5	Num > 0	5
M(Sign)	2.5	Pr>= M	0.0625
Sgn Rank	7.5	Pr>= S	0.0625
W:Normal	0.894664	Pr <w< td=""><td>0.3786</td></w<>	0.3786

Quantiles(Def=5)

100% Max	57	99%	57
75% Q3	51	95%	57
50% Med	50	90%	57
25% Q1	49	10%	47
0% Min	47	5%	47
Range Q3-Q1 Mode	10 2 47	1.9	47

Extremes

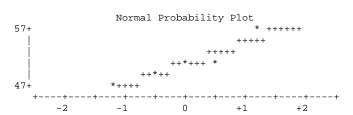
Lowest	0bs	Highest	Obs
47(3)	47(3)
49(4)	49(4)
50(5)	50(5)
51(1)	51(1)
57(2)	57(2)

Stem		#	Boxplot
56	U	1	U
54			
52			
50	00	2	+++
48	0	1	++
46	0	1	
	+		

------ PRIOR=0 CONC=1200 ------

Univariate Procedure

Variable=TIME



------ PRIOR=1 CONC=300 ------

Univariate Procedure

Variable=TIME

Moments

N	5	Sum Wgts	5
Mean	131.4	Sum	657
Std Dev	4.219005	Variance	17.8
Skewness	-0.83091	Kurtosis	0.581366
USS	86401	CSS	71.2
CV	3.21081	Std Mean	1.886796
T:Mean=0	69.64186	Pr> T	0.0001
Num ^= 0	5	Num > 0	5
M(Sign)	2.5	Pr>= M	0.0625
Sgn Rank	7.5	Pr>= S	0.0625
W:Normal	0.961922	Pr <w< td=""><td>0.8204</td></w<>	0.8204

Quantiles(Def=5)

100% Max	136	99%	136
75% Q3	134	95%	136
50% Med	132	90%	136
25% Q1	130	10%	125
0% Min	125	5%	125
		1%	125
Range	11		
Q3-Q1	4		
Mode	125		

Extremes

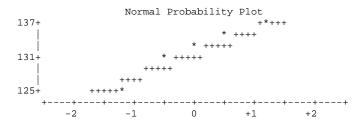
Lowest	0bs	Highest	0bs
125(3)	125(3)
130(2)	130(2)
132(4)	132(4)
134(5)	134(5)
136(1)	136(1)

Stem	Leaf	#	Boxplot
136	0	1	
134	0	1	++
132	0	1	**
130	0	1	+++
128			
126			
124	0	1	ĺ
	+		

------ PRIOR=1 CONC=300 ------

Univariate Procedure

Variable=TIME



------ PRIOR=1 CONC=600 ------

Univariate Procedure

Variable=TIME

Moments

N	5	Sum Wgts	5
Mean	81.6	Sum	408
Std Dev	3.435113	Variance	11.8
Skewness	-0.60689	Kurtosis	-2.03821
USS	33340	CSS	47.2
CV	4.209697	Std Mean	1.536229
T:Mean=0	53.11708	Pr> T	0.0001
Num ^= 0	5	Num > 0	5
M(Sign)	2.5	Pr>= M	0.0625
Sgn Rank	7.5	Pr>= S	0.0625
W:Normal	0.901556	Pr <w< td=""><td>0.4155</td></w<>	0.4155

Quantiles(Def=5)

100% Max	85	99%	85
75% Q3	84	95%	85
50% Med	83	90%	85
25% Q1	79	10%	77
0% Min	77	5%	77
Range Q3-Q1 Mode	8 5 77	± 0	,,

Extremes

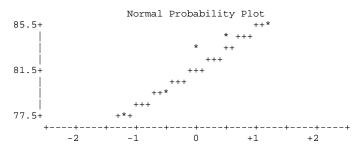
Lowest	Obs	Highest	Obs
77(1)	77(1)
79(4)	79 (4)
83(3)	83(3)
84(2)	84(2)
85(5)	85(5)

Stem	Leaf	#	Boxplot
85	0	1	
84	0	1	++
83	0	1	**
82			
81			+
80			
79	0	1	++
78			
77	0	1	j
	+		

----- PRIOR=1 CONC=600 ------

Univariate Procedure

Variable=TIME



Univariate Procedure

Variable=TIME

Moments

N	5	Sum Wgts	5
Mean	46	Sum	230
Std Dev	3.24037	Variance	10.5
Skewness	-0.58782	Kurtosis	-2.89796
USS	10622	CSS	42
CV	7.044283	Std Mean	1.449138
T:Mean=0	31.74302	Pr> T	0.0001
Num ^= 0	5	Num > 0	5
M(Sign)	2.5	Pr>= M	0.0625
Sgn Rank	7.5	Pr>= S	0.0625
W:Normal	0.817247	Pr <w< td=""><td>0.1095</td></w<>	0.1095

Quantiles(Def=5)

100% Max	49	99%	49
75% Q3	48	95%	49
50% Med	48	90%	49
25% Q1	43	10%	42
0% Min	42	5%	42
Range Q3-Q1 Mode	7 5 48	10	12

Extremes

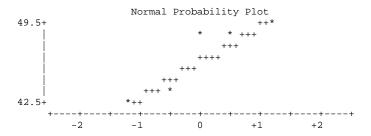
Lowest	Obs	Highest	0bs
42(3)	42(3)
43(4)	43(4)
48(5)	48 (2)
48(2)	48 (5)
49(1)	49 (1)

C 1	T 6		
Stem	Leai	#	Boxplot
49	0	1	
48	00	2	++
47			
46			+
45			į į
44			į į
43	0	1	++
42	0	1	
	+		

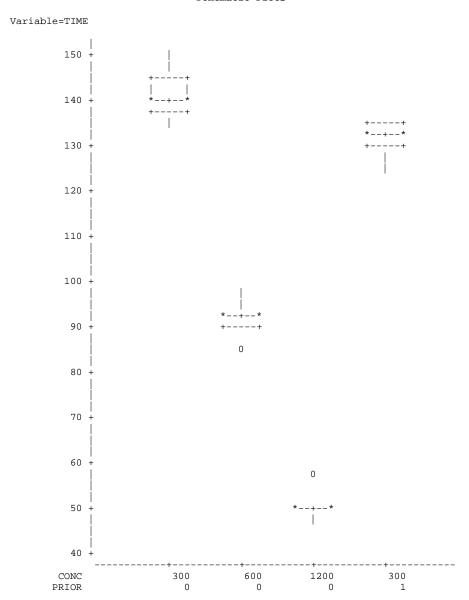
----- PRIOR=1 CONC=1200 ------

Univariate Procedure

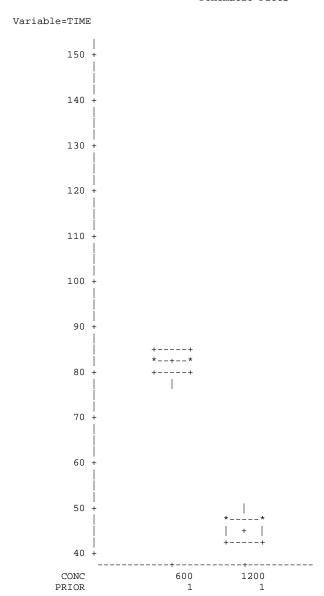
Variable=TIME



Univariate Procedure Schematic Plots



Univariate Procedure Schematic Plots



OBS	FRACTION	CX	CONC	RH	PRIOR	TIME	CELL	
1	0.1	30	300	80	0	135	1	
2	0.1	30	300	80	0	139	1	
3	0.1	30	300	80	0	138	1	
4	0.1	30	300	80	0	149	1	
5	0.1	30	300	80	0	144	1	
6	0.1	60	600	80	0	92	2	
7	0.1	60	600	80	0	85	2	
8	0.1	60	600	80	0	93	2	
9	0.1	60	600	80	0	90	2	
10	0.1	60	600	80	0	97	2	
11	0.1	120	1200	80	0	51	3	
12	0.1	120	1200	80	0	57	3	
13	0.1	120	1200	80	0	47	3	
14	0.1	120	1200	80	0	49	3	
15	0.1	120	1200	80	0	50	3	
16	0.1	30	300	80	1	136	4	
17	0.1	30	300	80	1	130	4	
18	0.1	30	300	80	1	125	4	
19	0.1	30	300	80	1	132	4	
20	0.1	30	300	80	1	134	4	
21	0.1	60	600	80	1	77	5	
22	0.1	60	600	80	1	84	5	
23	0.1	60	600	80	1	83	5	
24	0.1	60	600	80	1	79	5	
25	0.1	60	600	80	1	85	5	
26	0.1	120	1200	80	1	49	6	
27	0.1	120	1200	80	1	48	6	
28	0.1	120	1200	80	1	42	6	
29	0.1	120	1200	80	1	43	6	
30	0.1	120	1200	80	1	48	6	

APPENDIX E

Curve-Fitting Analysis of Generalized Yoon and Nelson Equation

This appendix presents the results of Oakdale Engineering's DataFit software analysis of a generalized form of the Yoon and Nelson equation for each of the nine treatment combinations.

Table E-1. Generalized Yoon and Nelson equation curve fit results for 50 percent relative humidity and 300 ppm fuel vapor test conditions, using breatkthrough times at 1%, 5%, 10%, and 20% of challenge concentration.

Results from project "c:\program files\datafit\50 percent no prior exposure - 300 ppm.dft"

Equation ID: Generalized Yoon and Nelson equation

Model Definition:

 $F1 = X1 * 170 / 24.45 / 1000 / (100)^3$

 $F2 = X2 * 170 / 24.45 / 1000 / (100)^3$

Y = b/F1 - a/F1*ln((F1-F2)/F2)

Number of observations = 18

Number of missing observations = 0

Solver type: Nonlinear

Nonlinear iteration limit = 250

Diverging nonlinear iteration limit =10

Number of nonlinear iterations performed = 4

Residual tolerance = 0.00000000001

Sum of Residuals = -1.02318153949454E-12

Average Residual = -5.6843418860808E-14

Residual Sum of Squares (Absolute) = 1387.22005698173

Residual Sum of Squares (Relative) = 1387.22005698173

Standard Error of the Estimate = 9.31135079144579

Coefficient of Multiple Determination (R^2) = 0.8644270526

Proportion of Variance Explained = 86.44270526%

Adjusted coefficient of multiple determination (Ra 2) = 0.8559537434

Durbin-Watson statistic = 1.59014705060522

Regression Variable Results

Variable	Value	Standard Error	t-ratio	$\operatorname{Prob}\left(t\right)$
a	4.31E-05	4.27E-06	10.10038	0
Ь	0.000569	1.19E-05	47.74563	0

68% Confidence Intervals

Variable	Value	68% (+/-)	Lower Limit	Upper Limit
a	4.31E-05	4.38E-06	3.87E-05	4.75E-05
Ь	0.000569	1.22E-05	0.000557	0.000582

90% Confidence Intervals

Variable	Value	90% (+/-)	Lower Limit	Upper Limit
a	4.31E-05	7.45E-06	3.57E-05	5.06E-05
b	0.000569	2.08E_05	0.000548	0.00059

Variable	Value	95% (+/-)	Lower Limit	Upper Limit	
a	4.31E-05	9.05E-06	3.41E-05	5.22E-05	
b	0.000569	2.53E-05	0.000544	0.000595	
99%	Confidence Int	ervals			
Variable	V alue	99% (+/-)	Lower Limit	Upper Limit	
a	4.31E-05	1.25E-05	3.06E-05	5.56E-05	
b	0.000569	3.48E-05	0.000534	0.000604	
Variance	Analysis				
Source	DF	Sum of Squares	Mean Square	F Ratio	Prob(F)
Regression	1	8845.058	8845.058	102.0176	0
Error	16	1387.22	86.70125		
Total	17	10232.28			

Table E-2. Generalized Yoon and Nelson equation curve fit results for 50 percent relative humidity and 600 ppm fuel vapor test conditions, using breatkthrough times at 1%, 5%, 10%, and 20% of challenge concentration.

Results from project "c:\program files\datafit\50 percent no prior exposure - 600 ppm.dft"

Equation ID: Generalized Yoon and Nelson equation

Model Definition:

 $F1 = X1 * 170 / 24.45 / 1000 / (100)^3$

 $F2 = X2 * 170 / 24.45 / 1000 / (100)^3$

Y = b / F1 - a / F1 * ln((F1 - F2) / F2)

Number of observations = 17

Number of missing observations = 0

Solver type: Nonlinear

Nonlinear iteration limit = 250

Diverging nonlinear iteration limit =10

Number of nonlinear iterations performed = 14

Residual tolerance = 0.00000000001

Sum of Residuals = -1.13463016759852E-08

Average Residual = -6.67429510352068E-10

Residual Sum of Squares (Absolute) = 192.414803586751

Residual Sum of Squares (Relative) = 192.414803586751

Standard Error of the Estimate = 3.58157138312921

Coefficient of Multiple Determination (R^2) = 0.9684462441

Proportion of Variance Explained = 96.84462441%

Adjusted coefficient of multiple determination (Ra 2) = 0.9663426604

Durbin-Watson statistic = 0.881318930486843

Regression Variable Results

Variable	Value	Standard Error	t-ratio	Prob(t)
a	6.49E-05	3.02E-06	21.45645	0
Ь	0.000602	8.81E-06	68.33282	0

68% Confidence Intervals

Variable	Value	68% (+/-)	Lower Limit	Upper Limit
a	6.49E-05	3.11E-06	6.18E-05	6.80E-05
Ь	0.000602	9.06E-06	0.000593	0.000611

90% Confidence Intervals

Variable	Value	90% (+/-)	Lower Limit	Upper Limit
a	6.49E-05	5.30E-06	5.96E-05	7.02E-05
b	0.000602	1.54E_05	0.000587	0.000617

Variable	Value	95% (+/-)	Lower Limit	Upper Limit	
a	6.49E-05	6.45E-06	5.85E-05	7.13E-05	
Ь	0.000602	1.88E-05	0.000583	0.000621	
99%	Confidence Int	ervals			
Variable	Value	99% (+/-)	Lower Limit	Upper Limit	
a	6.49E-05	8.91E-06	5.60E-05	7.38E-05	
Ь	0.000602	2.60E-05	0.000576	0.000628	
Variance	Analysis				
Source	DF	Sum of Squares	Mean Square	F Ratio	Prob(F)
Regression	1	5905.585	5905.585	460.3792	0
Error	15	192.4148	12.82765		
Total	16	6098			

Table E-3. Generalized Yoon and Nelson equation curve fit results for 50 percent relative humidity and 1200 ppm fuel vapor test conditions, using breatkthrough times at 1%, 5%, 10%, and 20% of challenge concentration.

Results from project "c:\program files\datafit\50 percent no prior exposure - 1200 ppm.dft"

Equation ID: Generalized Yoon and Nelson equation

Model Definition:

 $F1 = X1 * 170 / 24.45 / 1000 / (100)^3$

 $F2 = X2 * 170 / 24.45 / 1000 / (100)^3$

Y = B/F1 - A/F1*ln((F1-F2)/F2)

Number of observations = 20

Number of missing observations = 0

Solver type: Nonlinear

Nonlinear iteration limit = 250

Diverging nonlinear iteration limit =10

Number of nonlinear iterations performed = 7

Residual tolerance = 0.00000000001

Sum of Residuals = -1.15463194561016E-11

Average Residual = -5.77315972805081E-13

Residual Sum of Squares (Absolute) = 223.154776748051

Residual Sum of Squares (Relative) = 223.154776748051

Standard Error of the Estimate = 3.52100661702218

Coefficient of Multiple Determination (R^2) = 0.8592749319

Proportion of Variance Explained = 85.92749319%

Adjusted coefficient of multiple determination (Ra^2) = 0.8514568726

Durbin-Watson statistic = 2.76760194875835

Regression Variable Results

Variable	Value	Standard Error	t-ratio	$\operatorname{Prob}\left(t\right)$
A	5.82E-05	5.55E-06	10.48375	0
В	0.000602	1.68E-05	35.88596	0

68% Confidence Intervals

Variable	Value	68% (+/-)	Lower Limit	Upper Limit
A	5.82E-05	5.68E-06	5.25E-05	6.39E-05
В	0.000602	1.72E-05	0.000585	0.000619

90% Confidence Intervals

Variable	Value	90% (+/-)	Lower Limit	Upper Limit
A	5.82E-05	9.62E-06	4.86E-05	6.78E-05
В	0.000602	2 91E_05	0.000573	0.000631

Variable	Value	95% (+/-)	Lower Limit	Upper Limit	
A	5.82E-05	1.17E-05	4.65E-05	6.98E-05	
В	0.000602	3.52E-05	0.000567	0.000637	
99%	Confidence Int	ervals			
Variable	Value	99% (+/-)	Lower Limit	Upper Limit	
A	5.82E-05	$1.60\mathrm{E}\text{-}05$	4.22E-05	7.42E-05	
В	0.000602	4.83E-05	0.000554	0.00065	
Variance	Analysis				
Source	DF	Sum of Squares	Mean Square	F Ratio	Prob(F)
Regression	1	1362.595	1362.595	109.909	0
Error	18	223.1548	12.39749		
Total	19	1585.75			

Table E-4. Generalized Yoon and Nelson equation curve fit results for 80 percent relative humidity and 300 ppm fuel vapor test condition (no prior exposure to fuel), using breatkthrough times at 1%, 5%, 10%, and 20% of challenge concentration.

Results from project "c:\program files\datafit\80 percent no prior exposure - 300 ppm.dft"

Equation ID: Generalized Yoon and Nelson equation

Model Definition:

F1 = X1 * 170 / 24.45 / 1000 / (100)^3

 $F2 = X2 * 170 / 24.45 / 1000 / (100)^3$

Y = b/F1 - a/F1*ln((F1-F2)/F2)

Number of observations = 19

Number of missing observations = 0

Solver type: Nonlinear

Nonlinear iteration limit = 250

Diverging nonlinear iteration limit =10

Number of nonlinear iterations performed = 4

Residual tolerance = 0.00000000001

Sum of Residuals = -2.17140438962815E-09

Average Residual = -1.14284441559376E-10

Residual Sum of Squares (Absolute) = 5496.29933898933

Residual Sum of Squares (Relative) = 5496.29933898933

Standard Error of the Estimate = 17.9808711085671

Coefficient of Multiple Determination (R^2) = 0.8797671468

Proportion of Variance Explained = 87.97671468%

Adjusted coefficient of multiple determination (Ra^2) = 0.872694626

Durbin-Watson statistic = 0.434836427052552

Regression Variable Results

Variable	Value	Standard Error	t-ratio	Prob(t)
a	8.44E-05	7.57E-06	11.15313	0
b	0.000502	2.21E-05	22.73556	0

68% Confidence Intervals

Variable	Value	68% (+/-)	Lower Limit	Upper Limit
a	8.44E-05	7.75E-06	7.67E-05	9.22E-05
Ь	0.000502	2.26E-05	0.000479	0.000524

Variable	Value	90% (+/-)	Lower Limit	Upper Limit
a	8.44E-05	1.32E-05	7.13E-05	9.76E-05
Ь	0.000502	3.84E-05	0.000463	0.00054

95%	Confid	ence	Interva	le

Variable	Value	95% (+/-)	Lower Limit	Upper Limit		
a	8.44E-05	1.60E-05	6.84E-05	0.0001		
Ь	0.000502	4.66E-05	0.000455	0.000548		
99%	6 Confidence Inte	ervals				
Variable	Value	99% (+/-)	Lower Limit	Upper Limit		
a	8.44E-05	2.19E-05	6.25E-05	0.000106		
b	0.000502	6.40E-05	0.000438	0.000566		
Variance	e Analysis					
Source	DF	Sum of Squares	Mean Square	F Ratio	Prob(F)	
Regression	1	40217.49	40217.49	124.3923	0	
Error	17	5496.299	323.3117			
Total	18	45713.79				

Table E-5. Generalized Yoon and Nelson equation curve fit results for 80 percent relative humidity and 600 ppm fuel vapor test condition (no prior exposure to fuel), using breatkthrough times at 1%, 5%, 10%, and 20% of challenge concentration.

Results from project "c:\program files\datafit\80 percent no prior exposure - 600 ppm.dft"

Equation ID: Generalized Yoon and Nelson equation

Model Definition:

F1 = X1 * 170 / 24.45 / 1000 / (100)^3

 $F2 = X2 * 170 / 24.45 / 1000 / (100)^3$

Y = b/F1 - a/F1*ln((F1-F2)/F2)

Number of observations = 18

Number of missing observations = 0

Solver type: Nonlinear

Nonlinear iteration limit = 250

Diverging nonlinear iteration limit =10

Number of nonlinear iterations performed = 11

Residual tolerance = 0.00000000001

Sum of Residuals = -1.55638701926364E-08

Average Residual = -8.64659455146466E-10

Residual Sum of Squares (Absolute) = 738.104492986764

Residual Sum of Squares (Relative) = 738.104492986764

Standard Error of the Estimate = 6.79201964158473

Coefficient of Multiple Determination (R^2) = 0.9037986976

Proportion of Variance Explained = 90.37986976%

Adjusted coefficient of multiple determination (Ra 2) = 0.8977861162

Durbin-Watson statistic = 1.18454365168205

Regression Variable Results

Variable	Value	Standard Error	t-ratio	Prob(t)
a	7.63E-05	6.23E-06	12.26042	0
b	0.000555	1.74E-05	31.90643	0

68% Confidence Intervals

Variable	Value	68% (+/-)	Lower Limit	Upper Limit
a	7.63E-05	6.39E-06	7.00E-05	8.27E-05
Ь	0.000555	1.79E-05	0.000537	0.000573

Variable	Value	90% (+/-)	Lower Limit	Upper Limit
a	7.63E-05	1.09E-05	6.55E-05	8.72E-05
b	0.000555	3.04E-05	0.000525	0.000585

	_			
05%	Conti	donce	Interval	0

Variable	Value	95% (+/-)	Lower Limit	Upper Limit	
a	7.63E-05	1.32E-05	6.31E-05	8.96E-05	
Ь	0.000555	3.69E-05	0.000518	0.000592	
99	% Confidence Inte	rvals			
Variable	Value	99% (+/-)	Lower Limit	Upper Limit	
a	7.63E-05	1.82E-05	5.82E-05	9.45E-05	
b	0.000555	5.08E-05	0.000504	0.000606	
Variano	ce Analysis				
Source	DF	Sum of Squares	Mean Square	F Ratio	Prob(F)
Regression	1	6934.396	6934.396	150.3179	0
Error	16	738.1045	46.13153		
Total	17	7672.5			

Table E-6. Generalized Yoon and Nelson equation curve fit results for 80 percent relative humidity and 1200 ppm fuel vapor test condition (no prior exposure to fuel), using breatkthrough times at 1%, 5%, 10%, and 20% of challenge concentration.

Results from project "c:\program files\datafit\80 percent no prior exposure - 1200 ppm.dft"

Equation ID: Generalized Yoon and Nelson equation

Model Definition:

F1 = X1 * 170 / 24.45 / 1000 / (100)^3

 $F2 = X2 * 170 / 24.45 / 1000 / (100)^3$

Y = b/F1 - a/F1*ln((F1-F2)/F2)

Number of observations = 20

Number of missing observations = 0

Solver type: Nonlinear

Nonlinear iteration limit = 250

Diverging nonlinear iteration limit =10

Number of nonlinear iterations performed = 6

Residual tolerance = 0.00000000001

Sum of Residuals = -1.47082346302341E-12

Average Residual = -7.35411731511704E-14

Residual Sum of Squares (Absolute) = 231.645099858101

Residual Sum of Squares (Relative) = 231.645099858101

Standard Error of the Estimate = 3.58736284955104

Coefficient of Multiple Determination (R^2) = 0.8545810604

Proportion of Variance Explained = 85.45810604%

Adjusted coefficient of multiple determination (Ra 2) = 0.8465022304

Durbin-Watson statistic = 2.41665766459065

Regression Variable Results

U				
Variable	Value	Standard Error	t-ratio	Prob(t)
a	5.82E-05	5.65E-06	10.28496	0
b	0.000558	1.71E-05	32.67887	0

68% Confidence Intervals

Variable	Value	68% (+/-)	Lower Limit	Upper Limit
a	5.82E-05	5.78E-06	5.24E-05	6.39E-05
b	0.000558	1.75E-05	0.000541	0.000576

Variable	Value	90% (+/-)	Lower Limit	Upper Limit
a	5.82E-05	9.81E-06	4.84E-05	6.80E-05
Ь	0.000558	2.96E-05	0.000529	0.000588

95%	Confid	ence	Interva	le

Variable	Value	95% (+/-)	Lower Limit	Upper Limit	
a	5.82E-05	1.19E-05	4.63E-05	$7.00\mathrm{E}\text{-}05$	
Ь	0.000558	3.59E-05	0.000523	0.000594	
99%	6 Confidence Int	ervals			
Variable	Value	99% (+/-)	Lower Limit	Upper Limit	
a	5.82E-05	1.63E-05	4.19E-05	7.44E-05	
b	0.000558	4.92E-05	0.000509	0.000608	
V 7	. A				
v ariance	Analysis				
Source	DF	Sum of Squares	Mean Square	F Ratio	Prob(F)
Regression	1	1361.305	1361.305	105.7803	0
Error	18	231.6451	12.86917		
Total	19	1592.95			

Table E-7. Generalized Yoon and Nelson equation curve fit results for 80 percent relative humidity and 300 ppm fuel vapor test condition (with prior exposure to fuel), using breatkthrough times at 1%, 5%, 10%, and 20% of challenge concentration.

Results from project "c:\program files\datafit\80 percent prior exposure - 300 ppm.dft"

Equation ID: Generalized Yoon and Nelson equation

Model Definition:

F1 = X1 * 170 / 24.45 / 1000 / (100)^3

 $F2 = X2 * 170 / 24.45 / 1000 / (100)^3$

Y = b/F1 - a/F1*ln((F1-F2)/F2)

Number of observations = 16

Number of missing observations = 0

Solver type: Nonlinear

Nonlinear iteration limit = 250

Diverging nonlinear iteration limit =10

Number of nonlinear iterations performed = 4

Residual tolerance = 0.00000000001

Sum of Residuals = -2.8421709430404E-13

Average Residual = -1.77635683940025E-14

Residual Sum of Squares (Absolute) = 3333.48803562005

Residual Sum of Squares (Relative) = 3333.48803562005

Standard Error of the Estimate = 15.4306930582711

Coefficient of Multiple Determination (R^2) = 0.891362257

Proportion of Variance Explained = 89.1362257%

Adjusted coefficient of multiple determination (Ra^2) = 0.8836024182

Durbin-Watson statistic = 0.844554067257592

Regression Variable Results

U				
Variable	Value	Standard Error	t-ratio	$\operatorname{Prob}\left(t\right)$
a	0.000101	9.47E-06	10.71768	0
Ь	0.000513	2.35E-05	21.87854	0
b	0.000513	2.35E-05	21.87854	

68% Confidence Intervals

Variable	Value	68% (+/-)	Lower Limit	Upper Limit
a	0.000101	9.76E-06	9.17E-05	0.000111
b	0.000513	2.42E-05	0.000489	0.000537

Variable	Value	90% (+/-)	Lower Limit	Upper Limit
a	0.000101	1.67E-05	8.48E-05	0.000118
Ь	0.000513	4.13E-05	0.000472	0.000554

95%	Confid	ence	Interva	le

Variable	Value	95% (+/-)	Lower Limit	Upper Limit	
a	0.000101	2.03E-05	8.12E-05	0.000122	
Ь	0.000513	5.03E-05	0.000463	0.000563	
999	% Confidence Into	ervals			
Variable	Value	99% (+/-)	Lower Limit	Upper Limit	
a	0.000101	2.82E-05	7.33E-05	0.00013	
b	0.000513	6.98E-05	0.000443	0.000583	
Variance	e Analysis				
Source	DF	Sum of Squares	Mean Square	F Ratio	$\operatorname{Prob}\left(\!F\!\right)$
Regression	1	27350.95	27350.95	114.8687	0
Error	14	3333.488	238.1063		
Total	15	30684.44			

Table E-8. Generalized Yoon and Nelson equation curve fit results for 80 percent relative humidity and 600 ppm fuel vapor test condition (with prior exposure to fuel), using breatkthrough times at 1%, 5%, 10%, and 20% of challenge concentration.

Results from project "c:\program files\datafit\80 percent prior exposure - 600 ppm.dft"

Equation ID: Generalized Yoon and Nelson equation

Model Definition:

F1 = X1 * 170 / 24.45 / 1000 / (100)^3

 $F2 = X2 * 170 / 24.45 / 1000 / (100)^3$

Y = b/F1 - a/F1*ln((F1-F2)/F2)

Number of observations = 20

Number of missing observations = 0

Solver type: Nonlinear

Nonlinear iteration limit = 250

Diverging nonlinear iteration limit =10

Number of nonlinear iterations performed = 4

Residual tolerance = 0.00000000001

Sum of Residuals = -1.86572890470416E-09

Average Residual = -9.32864452352078E-11

Residual Sum of Squares (Absolute) = 847.992267415797

Residual Sum of Squares (Relative) = 847.992267415797

Standard Error of the Estimate = 6.86372213329618

Coefficient of Multiple Determination (R^2) = 0.9191633842

Proportion of Variance Explained = 91.91633842%

Adjusted coefficient of multiple determination (Ra 2) = 0.9146724611

Durbin-Watson statistic = 0.995707032240142

Regression Variable Results

Variable	Value	Standard Error	t-ratio	Prob(t)
a	7.74E-05	5.41E-06	14.30634	0
b	0.000523	1.63E-05	31.97013	0

68% Confidence Intervals

Variable	Value	68% (+/-)	Lower Limit	Upper Limit
a	7.74E-05	5.53E-06	7.19E-05	8.29E-05
Ь	0.000523	1.67E-05	0.000506	0.000539

Variable	Value	90% (+/-)	Lower Limit	Upper Limit
a	7.74E-05	9.38E-06	6.80E-05	8.68E-05
b	0.000523	2.83E-05	0.000494	0.000551

95%	Confid	ence	Interva	le

Variable	Value	95% (+/-)	Lower Limit	Upper Limit	
a	7.74E-05	1.14E-05	$6.60\mathrm{E}\text{-}05$	8.88E-05	
ь	0.000523	3.43E-05	0.000488	0.000557	
999	∕₀ Confidence Inte	ervals			
Variable	Value	99% (+/-)	Lower Limit	Upper Limit	
a	7.74E-05	1.56E-05	6.18E-05	9.30E-05	
Ъ	0.000523	4.71E-05	0.000476	0.00057	
Varianc	e Analysis				
Source	DF	Sum of Squares	Mean Square	F Ratio	Prob(F)
Regression	1	9642.208	9642.208	204.6714	0
Error	18	847.9923	47.11068		
Total	19	10490.2			

Table E-9. Generalized Yoon and Nelson equation curve fit results for 80 percent relative humidity and 1200 ppm fuel vapor test condition (with prior exposure to fuel), using breatkthrough times at 1%, 5%, 10%, and 20% of challenge concentration.

Results from project "c:\program files\datafit\80 percent prior exposure - 1200.dft"

Equation ID: Generalized Yoon and Nelson equation

Model Definition:

F1 = X1 * 170 / 24.45 / 1000 / (100)^3

 $F2 = X2 * 170 / 24.45 / 1000 / (100)^3$

Y = b/F1 - a/F1*ln((F1-F2)/F2)

Number of observations = 16

Number of missing observations = 0

Solver type: Nonlinear

Nonlinear iteration limit = 250

Diverging nonlinear iteration limit =10

Number of nonlinear iterations performed = 8

Residual tolerance = 0.00000000001

Sum of Residuals = -2.42259545757406E-10

Average Residual = -1.51412216098379E-11

Residual Sum of Squares (Absolute) = 225.882994810731

Residual Sum of Squares (Relative) = 225.882994810731

Standard Error of the Estimate = 4.01677726907255

Coefficient of Multiple Determination (R^2) = 0.7708516411

Proportion of Variance Explained = 77.08516411%

Adjusted coefficient of multiple determination (Ra^2) = 0.7544839012

Durbin-Watson statistic = 1.29520996311729

Regression Variable Results

Variable	Value	Standard Error	t-ratio	Prob(t)
a	6.76E-05	9.86E-06	6.862637	0.00001
b	0.000538	2.44E-05	22.03342	0

68% Confidence Intervals

Variable	Value	68% (+/-)	Lower Limit	Upper Limit
a	6.76E-05	1.02E-05	5.75×-05	7.78E-05
Ь	0.000538	2.52E-05	0.000513	0.000563

Variable	Value	90% (+/-)	Lower Limit	Upper Limit
a	6.76E-05	1.74E-05	5.03E-05	8.50E-05
Ь	0.000538	4.30E-05	0.000495	0.000581

05%	Car	fidan	co L	nterva	le
7570	COL	шаст	ce r	шегуа	IS.

Variable	Value	95% (+/-)	Lower Limit	Upper Limit		
a	6.76E-05	2.11E-05	4.65E-05	8.88E-05		
b	0.000538	5.24E-05	0.000486	0.00059		
99% €	Confidence Inte	rvals				
Variable	Value	99% (+/-)	Lower Limit	Upper Limit		
a	6.76E-05	2.93E-05	3.83E-05	9.70E-05		
Ь	0.000538	7.27E-05	0.000465	0.000611		
Variance A	nalysis					
Source	DF	Sum of Squares	Mean Square	F Ratio	Prob(F)	
Regression	1	759.867	759.867	47.09579	1.00E-05	
Error	14	225.883	16.1345			
Total	15	985.75				