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The analytical determination of the uniqueness and persistence of the volatile components of human scent using optimized collection methods

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THE ANALYTICAL DETERMINATION OF THE UNIQUENESS AND PERSISTENCE OF THE VOLATILE COMPONENTS OF HUMAN SCENT USING OPTIMIZED COLLECTION METHODS

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by

Allison Marsh Curran

2005

To: Interim Dean Mark Szuchman
College of Arts and Sciences

This dissertation, written by Allison Marsh Curran, and entitled The Analytical Determination of the Uniqueness and Persistence of the Volatile Components of Human Scent Using Optimized Collection Methods, having been approved in respect to style and intellectual content, is referred to you for judgment.

We have read this dissertation and recommend that it be approved.

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Florida International University, 2005

DEDICATION

This dissertation is dedicated to my family; my parents Beverly and Mark Curran, my brother Mark, and sister Alicia for their love and support.

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ABSTRACT OF THE DISSERTATION

THE ANALYTICAL DETERMINATION OF THE UNIQUENESS AND PERSISTENCE OF THE VOLATILE COMPONENTS OF HUMAN SCENT USING OPTIMIZED COLLECTION METHODS

by

Allison Marsh Curran

Florida International University, 2005

Miami, Florida

Professor Kenneth G. Furton, Major Professor

The Locard exchange principle proposes that a person can not enter or leave an area or come in contact with an object, without an exchange of materials. In the case of scent evidence, the suspect leaves his scent in the location of the crime scene itself or on objects found therein. Human scent evidence collected from a crime scene can be evaluated through the use of specially trained canines to determine an association between the evidence and a suspect. To date, there has been limited research as to the volatile organic compounds (VOCs) which comprise human odor and their usefulness in distinguishing among individuals. For the purposes of this research, human scent is defined as the most abundant volatile organic compounds present in the headspace above collected odor samples.

An instrumental method has been created for the analysis of the VOCs present in human scent, and has been utilized for the optimization of materials used for the collection and storage of human scent evidence. This research project has identified the volatile organic compounds present in the headspace above collected scent samples from different

individuals and various regions of the body, with the primary focus involving the armpit area and the palms of the hands. Human scent from the armpit area and palms of an individual sampled over time shows lower variation in the relative peak area ratio of the common compounds present than what is seen across a population. A comparison of the compounds present in human odor for an individual over time, and across a population has been conducted and demonstrates that it is possible to instrumentally differentiate individuals based on the volatile organic compounds above collected odor samples.

TABLE OF CONTENTS

CHAPTER PAGE

1. INTRODUCTION 1
   1.1. Research Introduction 1
   1.2. History and Legal Aspects of Human Scent 1
   1.2.1. Varieties of Human Scent Identification Canines 2
   1.2.2. Human Scent & the Law 3
   1.3. Production of Human Scent 8
   1.3.1. Creation of Human Body Odor 8
   1.3.2. The Skin 9
   1.3.3. Apocrine Glands 10
   1.3.4. Eccrine Glands 10
   1.3.5. Sebaceous Glands 11
   1.3.6. Axillary Region of Body 12
   1.3.7. Microbiology of Odor Production 13
   1.3.8. Generation of Volatile Fatty Acids (VFAs) 16
   1.4. Chemical Composition of Human Scent 18
   1.4.1. Components of Human Sweat 18
   1.4.2. Components of Fingerprint Residue 23
   1.4.3. Headspace Analysis of Human Odor 24
   1.5. Variability of Human Scent 26
   1.5.1. Genetic Basis for Individualizing Human Odor 26
   1.6. Persistence and Stability 27
   1.6.1. Survivability and Durability of Human Scent 27
   1.7. Collection of Human Scent as Evidence 31
   1.7.1. Methods for Human Scent Collection 31
   1.7.2. Collection Materials 34
   1.7.3. Fiber Properties 36
   1.8. Canines and Human Scent 42
   1.8.1. Scent Matching Abilities 42
   1.8.2. Factors Effecting Canine Matching Ability 45
   1.8.3. Tracking Canines 45
   1.8.4. Trailing / Scent Article Canines 46
   1.8.5. Human Scent Line-up Canines 49
   1.9. Theory of Instrumental Techniques 51
   1.9.1. Solid Phase Micro-extraction (SPME) 51
   1.9.2. Supercritical Fluid Extraction 54
   1.10. Data Handling 56
   1.11. Research Goals 59

2. METHODOLOGY 61
   2.1. Materials 61
   2.1.1. Absorber Materials 61

2.1.2. Cleanser Materials 61
2.1.3. Storage Materials 62
2.1.4. Odor Sampling Materials 63
2.1.5. Laboratory Materials 63
2.2. Instrumental Methods 65
2.3. Comparison of ACS and SPME for the Extraction of Human Scent 65
2.3.1. Materials 65
2.3.2. Methods 65
2.4. Solid Phase Microextraction (SPME) Optimization 66
2.4.1. Materials 66
2.4.2. Methods 66
2.5. Evaluation of Different Absorbent Collection Mediums: 67
2.5.1. Materials 67
2.5.2. Headspace Analysis Method 67
2.5.3. Scanning Electron Microscope (SEM) and Field Emission Scanning Electron Microscope (FESEM) Imaging of Surface Characteristics of Absorbers 68
2.6. Analysis of Body Odor Collected From Individuals 68
2.6.1. Comparison of Foot Odor Among Individuals 68
2.6.2. Comparison of Odor Collected From Different Body Regions 69
2.6.3. Comparison of Armpit Odor from the Left and Right Side of an Individual 70
2.6.4. Comparison of Armpit Sampling Techniques: Worn vs. Wiped 72
2.7. Comparison of Odor Profiles Obtained from the Armpit Area of Two Males 73
2.7.1. Materials 73
2.7.2. Sampling 74
2.7.3. Extraction and Analysis of Armpit Samples (SPME-GC/MS) 75
2.8. Creation of a Method for Producing Analytically Clean Absorber Materials 75
2.8.1. Materials 75
2.8.2. Gravity and Steam Re-sterilization 76
2.8.3. Soxhlet Extraction 77
2.8.4. Supercritical Fluid Extraction 77
2.8.5. SPME-GC/MS Analysis 78
2.9. Evaluation of Storage Materials Commonly Used to Collect Human Scent 79
2.9.1. Materials 79
2.9.2. Procedure 79
2.10. Evaluation of Compounds Present in the Headspace of Different Cleansers 80
2.10.1. Materials 81
2.10.2. Methods 81
2.11. Determination of the Optimal Extraction Time for Armpit and Hand Odor Samples 82

2.11.1. Materials 82
2.11.2. Armpit Sampling Procedure 82
2.11.3. Hand Sampling Procedure 83
2.11.4. SPME-GC/MS Analysis 83
2.12. Evaluation of the Effect of Washing the Hands Prior to Sampling 84
2.12.1. Materials 84
2.12.2. Methods 84
2.12.3. Extraction and Analysis of Hand Odor Samples (SPME-GC/MS) 85
2.12.4. Approximation of the Amount of Volatile Organic Compounds Extracted by Headspace SPME 86
2.13. Population Anlysis of the Volatile Organic Compounds Present Above Collected Odor Samples 86
2.13.1. Evaluation of the Compounds Present in Armpit Odor among Ten Individuals 86
2.13.2. Evaluation of the Components of Hand Odor among Sixty Individuals 88
2.14. Evaluation of Odor Profiles of Individuals Over Time 90
2.14.1. Materials 90
2.14.2. Method for Armpit Sampling 91
2.14.3. Method for Hand Odor Sampling 91
2.15. Persistance of Collected Human Scent 92
2.15.1. Scent Weight Dissipation 92
2.15.2. Solid Phase Micro-extraction of Collected Hand Odor Samples Over Time 94

3. RESULTS & DISCUSSION 97
3.1. Comparison of ACS and SPME for the Extraction of Human Scent 97
3.2. Solid Phase Micro-extraction (SPME) Optimization 97
3.2.1. Fiber Chemistries 97
3.3. Evaluation of Different Absorbent Collection Mediums: 100
3.3.1. Headspace Evaluation 100
3.3.2. SEM Imaging for Surface Characteristics 102
3.4. Analysis of Odor Collected From Individuals 106
3.4.1. Comparison of Foot Odor Compounds Among Individuals 106
3.4.2. Comparison of Odor Collected from Different Regions of the Body 108
3.4.3. Comparison of Armpit Odor Collected from the Right and Left Side of Male 4 109
3.4.4. Comparison of Sampling Techniques: Wiped vs. Worn Gauze 113
3.4.5. Comparison of Armpit Odor Between Two Unrelated Males: 115
3.5. Creation of a Pre-Treatment for Producing Analytically Clean Absorbers 121
3.5.1. Steam and Gravity Re-sterilization 121
3.5.2. Soxhlet Extraction 122

3.5.3. Supercritical Fluid Extraction 122
3.6. Evaluation of Storage Materials Commonly Used to Collect Human Scent 131
3.7. Evaluation of Compounds Present in the Headspace of Different Cleansers 131
3.8. Determination of the Optimal Extraction Time for Armpit and Hand Odor Samples 135
3.9. Evaluation of the Effect of Washing the Hands Prior to Sampling 138
3.10. Population Anlysis of the Volatile Organic Compounds Present Above Collected Odor Samples 144
3.10.1. Evaluation of the Compounds Present in Armpit Odor among Ten Individuals 144
3.10.2. Evaluation of the Components of Hand Odor among Sixty Individuals 152
3.10.3. Comparison of Armpit and Hand Odor Profiles 161
3.11. Evaluation of Odor Profiles for Individuals over Time 165
3.11.1. Armpit Region Samples 165
3.11.2. Hand Odor 173
3.12. Persistance of Human Scent 209
3.12.1. Scent Weight Dissipation Study 209
3.12.2. Solid Phase Micro-extraction of Collected Hand Odor Samples over Time 213

4. CONCLUSIONS 220

5. FUTURE WORK 223

REFERENCES 225

APPENDICES 235

VITA 279

LIST OF TABLES

TABLE PAGE

Table 1: U.S. Court Cases and Their Effect on Canine Scent Evidence 6

Table 2: Aldehydes Formed by Oxidative Degradation of Sebaceous Components.....25

Table 3: Examples of Objects from which DNA Profiles Were Successfully Extracted 30

Table 4: Examples of Articles Used for Human Scent Identification Line-ups in the Netherlands.....33

Table 5: Examples of Articles from which Human Scent is Colleted by the FBI as Human Scent Evidence 34

Table 6: Amino Acid Composition of Silk and Wool Fibers 38

Table 7: Properties of Natural and Synthetic Fibers.....39

Table 8: Common Industrial Treatment and Finishing Processes of Natural Fibers.....42

Table 9: Average Humidity and Temperature for Samplings of Male 1 and Male 2 75

Table 10: Comparison of Compounds Extracted Between ACS and SPME of Worn Socks 98

Table 11: Comparison of Performance of Different Fiber Chemistries on Extracting Human Compounds 100

Table 12: Average Number of Headspace Compounds Present in Absorbent Materials.....101

Table 13: Compounds Extracted in the Headspace of Absorbent Materials Which Have Been Previously Reported in Human Secretions.....101

Table 14: Properties of Sorbents.....102

Table 15: Comparison of Human Odor Compounds Extracted Among Five Individuals.....108

Table 16: Comparison of Human Compounds Extracted in Odor Collected From Six Different Regions of the Body for Female 3 110

Table 17: Comparison of the Human Compounds Extracted in the Right and Left Armpit for Male 4 112

Table 18: Comparison of Human Compounds Extracted in Wiped and Worn Gauze....114

Table 19: Volatile Compounds Extracted Intraday, Male 4....116

Table 20: Relative Ratios of Common Compounds Found Through Intraday Sampling (S1, S2) for Male 4....117

Table 21: Volatile Compounds Extracted Interday, Male 4....119

Table 22: Common Volatile Compounds Extracted Between Male 4 (W1, W3S1, W3S2)....120

Table 23: A Comparison of the Common Volatile Compounds Extracted Between Male 4 (average) and Male 2....120

Table 24: Volatile Compounds which are Uncommon between Male 4 and Male 2....121

Table 25: Average Number of Compounds Contributed by the Storage Material to Analytically Clean Absorbers....132

Table 26: Comparison of Human Compounds Extracted from the Headspace of Fragrance-free Soaps Made From Animal Fat and Olive Oil....134

Table 27: Human Compounds Extracted Among Six Subjects both Pre and Post Washing in Hand Odor....140

Table 28: Response Factor for Standards in Relation to Nano-gram Amounts....143

Table 29: Compounds Extracted from Male 2 (M2), Male 4 (M4), Male 5 (M5), Male 6 (M6), Male 7 (M7), Female 2 (F2), Female 4 (F4), Female 5 (F5), Female 6 (F6), and Female 7 (F7)....147

Table 30: Frequency of Occurrence of the Sixty-four Human Compounds Extracted from the Armpit Odor of Ten Subjects....149

Table 31: Human Compounds Extracted in Hand Odor among Sixty Individuals....156

Table 32: Vapor Pressure Values for the Sixty-three Human Compounds in Hand Odor....158

Table 33: Comparison of VOCs in Collected Armpit (A) and Hand (H) Odor Samples....164

Table 34: Twenty-two VOCs Extracted Across Three Weekly Samplings of Armpit Odor....167

Table 35: Linear Correlation Coefficients for the Peak Areas of the Common Compounds 167

Table 36: Human Compounds Extracted Between Four Weekly Samplings of Armpit Odor 170

Table 37: Spearman Correlations of the Hand Odor of the Six Subjects against the Population Utilizing All Odor Components Determined 176

Table 38: Common Compounds Among Intraday Sampling of Hand Odor for Male 2 177

Table 39: Correlation Coefficients for Intraday Samplings of Male 2 177

Table 40: Common Compounds Among Intraday Sampling of Hand Odor for Male 4 178

Table 41: Correlation Coefficients for Intraday Samplings of Male 4 178

Table 42: Common Compounds Among Intraday Samplings of Hand Odor for Female 2 179

Table 43: Correlation Coefficients for Intraday Samplings of Female 2 179

Table 44: Common Human Compounds Extracted in Hand Odor through Intra-day Sampling of Female 5 180

Table 45: Correlation Coefficients for Intra-day Samplings of Female 5 180

Table 46: Common Compounds Extacted Among Intra-day Samplings of F6 181

Table 47: Correlation Coefficients for Intra-day Samplings of Female 6 181

Table 48: Common Human Compounds Extracted Among Intraday Samplings of Female 7 182

Table 49: Correlation Coefficients for Multiple Samplings of Hand Odor for Female 7 182

Table 50: Linear Correlation Results of Primary Odor Components Across the Six Subjects and Replicates 183

Table 51: Comparison of the Primary Odor Components for Male 2 and Female 6 189

Table 52: Comparison of the Primary Odor Components for Male 2 and Female 6 190

Table 53: Spearman Ranking Correlation Results of Primary Odor Components Across the Six Individuals and Replicates 191

Table 54: Spearman Correlation of the Hand Odor of the Six Subjects against the Population Utilizing the Twenty Primary Odor Components....197

Table 55: Principle Component Analysis Summary....201

Table 56: Common VOCs Extracted Among Inter-day Samplings of Hand Odor for F 4....203

Table 57: Spearman Ranking Correlation Coefficients for Inter-day Samplings of Hand Odor of Female 4....203

Table 58: Common Compounds Extracted Among Inter-day Samplings of Hand Odor for Female 7....204

Table 59: Spearman Ranking Correlation Coefficients for Inter-day Hand Odor Samples of Female 7....204

Table 60: Common Compounds Extracted Among Inter-day Samplings of Hand Odor for Male 4....205

Table 61: Spearman Rank Correlation Coefficients for Interday Hand Odor Samples of Male 4....205

Table 62: Spearman Ranking Correlation Coefficients for Inter-day Sampling Among Individuals....206

Table 63: Gauze Masses Reported in Milligrams....210

Table 64: Glass Slide Covers Masses Reported in Milligrams....211

Table 65: Bead Set Masses Reported in Milligrams....211

Table 66: Human Compounds Present in the Headspace of a Collected Hand Odor Sample of Female 7 over Time....216

Table 67: Human Compounds Present in the Headspace of a Collected Hand Odor Sample of Female 5 over Time....218

LIST OF FIGURES

FIGURE PAGE

Figure 1: Scent Transfer Unit 100 (STU-100) 7

Figure 2: Human Thermal Plume, with permission Prof. Gary Settles, Penn State 9

Figure 3: Proposed Scheme for the Release of Odiferous Acids by the Skin 15

Figure 4: Olfactory Evaluation of Short-chain Fatty Acid Solutions 20

Figure 5: Natural Protein Structure 37

Figure 6: Natural Cotton (Cellulose) Structure 37

Figure 7: Specialized Bloodhounds Working a Location Check 48

Figure 8: Historical Methods of Human Scent Line-ups as Depicted in a Dutch Newspaper, with permission, Copyright: Netherlands National Police Agency 50

Figure 9: Modern Human Scent Line-up Process at the Netherlands National Police Agency, with permission, Copyright: Netherlands National Police 50

Figure 10: Headspace Extraction Using SPME 52

Figure 11: ACS vs. SPME for the Extraction of Foot Odor from Worn Socks 99

Figure 12: SEM and FESEM Images of DUKAL Brand and Johnson & Johnson Gauze 103

Figure 13: SEM and FESEM Images of Johnson & Johnson and Hungarian Cotton 104

Figure 14: SEM and FESEM Images of King's Cotton and Polish Cotton 105

Figure 15: Comparison of Headspace Chromatograms Produced from Collected Foot Odor 107

Figure 16: Comparison of Headspace Extractions Among Six Different Body Regions of Female 3 111

Figure 17: Comparison of the Headspace Extractions of Odor Collected from the Right and Left Armpit of Male 4 112

Figure 18: Semi-Quantitative Comparison of the Relative Peak Area Ratios of the Human Compounds Extracted in the Left and Right Armpit of Male 4 112

Figure 19: Comparison of Armpit Odor Profiles Obtained from the Left Armpit of Male 2 Through Different Sampling Techniques 113

Figure 20: Chromatograms Produced From Intraday Analysis, Male 4 115

Figure 21: Expanded Chromatograms Produced from Different Individuals, M2 and M4 118

Figure 22: Comparison of the Abundances of Human Compounds Present Initially and After Re-sterilization using Vacuum Pressurized Steam 124

Figure 23: Comparison of the Abundances of Human Compounds Present Initially and After Re-sterilization using Gravity Steam 124

Figure 24: Comparison of Methanol and Chloroform Soxhlet Extractions of Sorbent Materials 125

Figure 25: Removal Rates for the Extraction of Nonanal and Decanal at Different Static Extraction Times 125

Figure 26: Removal Rates for the Extraction of Nonanal and Decanal at Different Temperatures 127

Figure 27: Removal Rates for the Extraction of Nonanal and Decanal Using Different Modifiers 129

Figure 28: Comparison of DUKAL Sterile Gauze before and After SFE Treatment 130

Figure 29: Comparison of IMCO Brand Sterile Gauze before and After SFE Treatment 130

Figure 30: Comparison of King's Cotton before and after SFE Treatment 130

Figure 31: Comparison of Storage Effects on Analytically Clean Absorbent Materials at Five Weeks 133

Figure 32: Comparison of Fragrance Free Soaps Made from Animal Fat and Those which are Olive Oil Based 134

Figure 33: Number of Compounds Extracted vs. Time in Armpit Odor 136

Figure 34: Abundances of Common Human Compounds Extracted vs. Time in Armpit Odor 136

Figure 35: Number of Compounds Extracted vs. Time in Hand Odor 137

Figure 36: Abundance of Common Human Compounds vs. Time in Hand Odor 137

Figure 37: Comparison of the Common Human Compounds Extracted in Both Pre and Post Washed Hand Odor Samples across Three Males 141

Figure 38: Comparison of the Common Human Compounds Extracted in Both Pre and Post Washing Samples of Hand Odor across Three Female 142

Figure 39: Calibration Curve for 2-Furancarboxaldehyde 143

Figure 40: Comparison of Odor Profiles from Male 2 (M2), Male 4 (M4), Male 5 (M5), and Male 6 (M6) After 30min of Exercise 146

Figure 41: Comparison of Odor Profiles from Female 2 (F2), Female 4 (F4), Female 5 (F5), and Female 6 (F6) After 30min of Exercise 146

Figure 42: Inter-person Comparison of the Relative Peak Area Ratios of All Human Compounds Extracted in Armpit Odor among Ten Subjects 151

Figure 43: Hand Odor Profiles Produced from Male Subjects 152

Figure 44: Hand Odor Profiles Produced from Female Subjects 153

Figure 45: Relative Peak Area Ratios of the Human Compounds Extracted in Hand Odor across Thirty Men 162

Figure 46: Relative Peak Area Ratios of the Human Compounds Extracted in Hand Odor across Thirty Females 163

Figure 47: Comparison of the Relative Peak Area Ratios of the Common Compounds Extracted in Male 4 and Male 2 Across Three Weekly Samplings 168

Figure 48: Ratio Patterns for the Relative Peak Areas of the Twenty-two Common Compounds Extracted Among Three Weekly Samplings of Male 2 & Male 4 Across Ten Subjects 169

Figure 49: Comparison of the Common Human Compounds Extracted Between Four Weekly Samplings of Armpit Odor of Females 4, 5, and 7 172

Figure 50: Common Compounds Among Intraday Samplings of Hand Odor for Male 2 177

Figure 51: Compounds Among Intraday Samplings of Hand Odor for Male 4 178

Figure 52: Common Compounds Among Intraday Samplings of Hand Odor for Female 2 179

Figure 53: Intraday Comparison of the Common Human Compounds Extracted in Hand Odor of Female 5 180

Figure 54: Intraday Comparison of the Common Compounds Extracted in Hand Odor for Female 6 181

Figure 55: Intraday Comparison of the Common Compounds for Female 7 182

Figure 56: Comparison of the Human VOCs Between Male 2 and Female 6 189

Figure 57: Comparison of the Human VOCs Between Male 4 and Female 7 190

Figure 58: Data Array Comparison of Male 2 Sampling 2 and Female 6 Sampling 2 199

Figure 59: Ranked Array Comparison for Male 2 Sampling 2 and Female 6 Sampling 2 199

Figure 60: Three Dimensional Principle Component Projection Plot of PCs 1, 2, and 3 202

Figure 61: Comparison of Inter-day Hand Odor Samplings of Female 4 203

Figure 62: Comparison of Inter-day Hand Odor Samplings of Female 7 204

Figure 63: Comparison of Inter-day Hand Odor Samplings of Male 4 205

Figure 64: Scent Weight Dissipation from Gauze Pads 212

Figure 65: Scent Weight Dissipation from Slide Covers 212

Figure 66: Comparison of the Relative Ratio Patterns of the Common Human Compounds Extracted in a Collected Hand Odor Sample of Female 7 over Time 217

Figure 67: Comparison of the Relative Ratio Patterns of the Common Human Compounds Extracted in a Collected Hand Odor Sample of Female 5 over Time 219

1. INTRODUCTION

1.1. Research Introduction

The Locard exchange principle proposes that a person can not enter or leave an area or come in contact with an object, without an exchange of materials. In the case of scent evidence, the suspect leaves his scent in the location of the crime scene itself or on objects found therein. Human scent evidence collected from a crime scene can be evaluated through the use of specially trained canines to determine an association between the evidence and a suspect. To date, there has been limited research as to the volatile organic compounds which comprise human odor and their usefulness in distinguishing between individuals. In addition, the collection and preservation materials employed for human scent evidence have yet to be evaluated and optimized. The scarcity of scientific background pertaining to human odor and scent collection methods has led to successful legal challenges as to the use of canine human scent discriminations for investigative purposes. This research project seeks to provide scientific and instrumental support to the biological methods being employed by law enforcement agencies using human scent evidence for canine discriminations.

1.2. History and Legal Aspects of Human Scent

Evidence of canines used for tracking in forensic investigations can be found as far back as Ancient Greece, where a satire by Sophocles (496-406B.C.) was entitled *Inchneutai (The Tracking Dogs)* and describes the use of canines to track a robber and a stolen herd. Tracking dogs were also depicted in the time of the Roman Empire as described by

Plinius (A.D. 23-79) as one of the six categories of dogs in his *Naturalis Historia*. In the 1460's, Heinrich Mynsinger describes in a literary work how canines were trained to track the trail of a thief [1].

The ability of canines to discriminate human scent has been documented as early as 1887 [2]. George J. Romanes contributed many fundamental observations as to the ability of dogs to scent discriminate among humans such as the human body leaves an individual odor which a dog can distinguish, individual odors can be determined at great distances and under different environmental stresses, and that canines are not deterred from scent discrimination by fragrances.

1.2.1. Varieties of Human Scent Identification Canines

It is relevant to note that there is a difference between canines which are used to track human scent, trail human scent, and those which are trained for scent identifications. Tracking canines are trained to utilize both human scent and environmental disturbances to locate the track of an individual, but are not given an initial scent to follow. Trailing canines are scented on an object and then asked to determine if the scent of the individual can be detected in an area (uncontrolled environmental conditions) and follow it to the source or until the trail ends. Human scent identification canines are presented with an individual's scent collected from a crime scene and then asked to match the odor from a selection of scents under semi-controlled environmental conditions [3].

1.2.2. Human Scent & the Law

The ability of canines to locate items of forensic interest such as controlled substances and explosives has long been accepted in the law enforcement community [4]. More recently, canines are being employed to identify an individual based upon his or her scent collected from a crime scene. The idea that people can be distinguished based on their odor is not a new concept; tracking, trailing and scent identification lineup canines have been used successfully for decades. A canine scent identification indicates an association between the suspect and the scent evidence.

In the United States, a canine alert is admitted as expert witness testimony by the dog's handler. *Daubert v. Merrell Dow Pharmaceuticals, Inc.* [5] determines the standard for the admission of expert testimony in federal and many state trials and has legal implications on canine alerts. Under this standard, the trial judge is responsible for ensuring that the evidence is relevant and reliable. When determining reliability, the judge considers whether the technique can and has been tested, has been subjected to peer review and publication, the known or potential error rate, and if the technique has gained general acceptance. Due to the lack of supporting science, suspects identified in a scent lineup or successfully tracked by canines could not be introduced as evidence in trial until recently.

The reliability of canine detection has been questioned [6]; the lack of standardized training, knowledge of the system that dogs use for scent recognition as well as information about what substances the canines are using for the alert has led to mixed

legal decisions of whether canine scent discriminations satisfy the expert witness qualifications of Daubert [7,8]. Presently, instrumental validation is not an option for human scent identifications due to the lack of scientific and technical research for utilizing human scent as a biometric measurement.

For a scent identification to be admitted as evidence in a U.S. court of law, it must satisfy the Kelly/Frye or Federal rules of evidence. In 1923, *Frye v. United States* [9] ruled that scientific evidence is admissible in court if the technique used has general acceptance in its field. The Kelly rule, resulting from the *People v. Kelly* [10], applies to new scientific techniques, especially in cases involving novel devices or processes. First, the technique must be considered reliable in the scientific community. Second, the witness testifying about the technique must be a qualified expert on the subject. Third, there must be proof that the person performing the test used correct scientific procedures.

The most recent U.S. court ruling pertaining to canines and human scent was a Kelly hearing conducted in late 2004, prior to the prosecution of the *State of California V. Benigno Salcido* [11], GA052057, an attempted murder case. The courts questioned the reliability of the Scent Transfer Unit-100 (STU-100), a scent collection device; whether human scent is unique; how long scent will remain at a location; how long scent captured on a gauze pad will remain and a number of other issues. In this case, the odor was collected from the inside of an open window and a bloody knife at the crime scene using the STU-100 which uses dynamic air flow to trap the odor on sterile gauze. The collected odor was presented to a specialized bloodhound and the canine led investigators

from outside the rear door of the victim's house to a nearby residence. Later, collected odor was presented to the bloodhound at the police station where it trailed through the hallways and identified an occupant of the previously identified house. A study published by Curran et al. [3] was used as an exhibit by the People in support of its position, and expert witness testimony was provided by Dr. Kenneth Furton (Florida International University), Dr. Brian Eckenrode (FBI) and SSA Rex Stockham (FBI). In its ruling on March 11, 2005, the court agreed with the People and ruled that the STU-100 and human scent discrimination by canine can be admitted into court as evidence if the person utilizing the technique used the correct scientific procedures, the training and expertise of the dog-handler team is proven to be proficient, and the methods used by the dog handler are reliable.

Prior to *People v. Salcido,* United States courts have varied opinions pertaining to the admissibility of human scent identification as evidence. In *Tomlinson v. State of Florida* [12], canine tracking evidence was admissible because the dog immediately took the track and followed it to a pair shoes, and was reinforced by a visible track made by a shoe matching the pair found by the canines. In *State of Arizona v. Roscoe* [13], human scent evidence was admitted as expert witness testimony after the court ruled that the Frye test was inapplicable. *United States v. McNiece* [14] held that courts did not need to apply the strict Frye ruling to scent evidence; however, some courts support applying the Frye test. *California v. Ryan Willis* [15], held that dog scent identification evidence was improperly admitted to the courtroom as per the rules set forth by the Frye and Kelly cases. In *Winston v. State* (Tex. App. 2002), an appellate court noted that 37 states and

the District of Columbia admit scent trailing evidence to prove the identity of the accused. "For purposes of judging the reliability of evidence based on a dog's ability to distinguish between scents," the court wrote, "we believe there is little distinction between a scent lineup and a situation where a dog is required to track an individual's scent over an area traversed by multiple persons." A California appellate court criticized this approach as too simplistic in *People v. Mitchell* [16], and stated its concern about "the absence of any evidence that every person has a scent so unique that it provides an accurate basis for a scent identification lineup." *People v. Salcido* has set a new standard for admitting canine human scent identifications as evidence in court, and Table 1 demonstrates the effect of several court rulings pertaining to the use of canine evidence.

Table 1: U.S. Court Cases and Their Effect on Canine Scent Evidence

COURT CASE	YEAR	RESULTING EFFECT
People v. Craig 86 Cal.App.3d 905	1978	The reliability of a canine-handler team must be determined on a case by case basis.
People v. Malgren 139 Cal.App.3d 234	1983	Jury instruction is required when using canine evidence.
People v. Gonzalez 218 Cal.App.3d 403	1990	Corroborating evidence is required when using canine human scent identifications.
People v. Mitchell 110 Cal. App. 4th 772	2003	Fist case involving the STU-100. Scientific evidence pertaining to the degradation of human scent and the question of whether the scent would remain in the STU after it was cleaned with alcohol is expressed.
People v. Salcido, ____Cal. App. 2nd ____	2005	Human scent discrimination by canines can be admitted into court as evidence if the person utilizing the technique used the correct scientific procedures, the training and expertise of the dog-handler team is proven to be proficient, and the methods used by the dog handler are reliable. The STU-100 was also determined to be a viable instrument.

The use of the Scent Transfer Unit-100 or STU-100 (Figure 1) for human scent collection has been controversial in several court proceedings in California, including *California vs. Flores* (2000) and *California vs. Willis* [15]. The STU-100 is essentially a portable vacuum which uses air flow through sterile gauze to trap the scent. Contamination issues pertaining to whether the STU-100 by design causes cross contamination of sequential samplings have arisen. The STU-100 is made of plastic and the standard protocol for cleaning involves wiping with isopropanol swabs. The FBI and the Southern California Bloodhound Handlers Coalition (SCBHC) examined the potential for the STU-100 to produce cross-contaminated scent pads after cleaning with scent transferred from an article of evidence. It was determined that when standard STU-100 cleaning protocols are used, either no scent cross-contamination occurs from one pad to the next or the contamination is below the detectable threshold of the trained canine [17].

Figure 1: Scent Transfer Unit 100 (STU-100)

1.3. Production of Human Scent

1.3.1. Creation of Human Body Odor

The production of human scent is a complicated process that is yet to be fully understood. It is known that the epidermis (outer) layer of the skin constantly sheds epithelial cells into the environment. The surface of the skin contains about two billion cells, of which 1/30 are being shed daily (approximately 667 cells per second). The average lifespan of an epithelial cell is approximately 36 hours. Dead cells which are shed from the surface of the skin are referred to as "rafts" which are approximately 14 microns in size and weigh approximately 0.07 micrograms. The "raft" is composed of one or more dead cells, approximately four microbial bacteria, and body secretions. All three components of the "raft" are said to be characteristic to the individual. Each "raft" is also said to be surrounded by a vapor cloud which results from bacterial action upon the cells [18]. Studies conducted by Harold E. Lewis at the National Institute for Medical research in London have shown that there is a current of warm air which surrounds the human body [19]. The current of warm air is approximately one third to one half inch thick and it travels up and over the body at a rate of 125 feet per minute (Figure 2). Analysis of the air current showed that it contained four to five times as many germs as the air in the rest of the sampling room. The germs come from the bacteria that are shed off with dead skin cells, larger flakes of skin fall to the ground but smaller ones are drawn up into the current. These currents can also be visualized running along the outside of clothing. The warm air currents are said to carry the "rafts" from the body into the surrounding area allowing for the deposit of human scent in the environment.

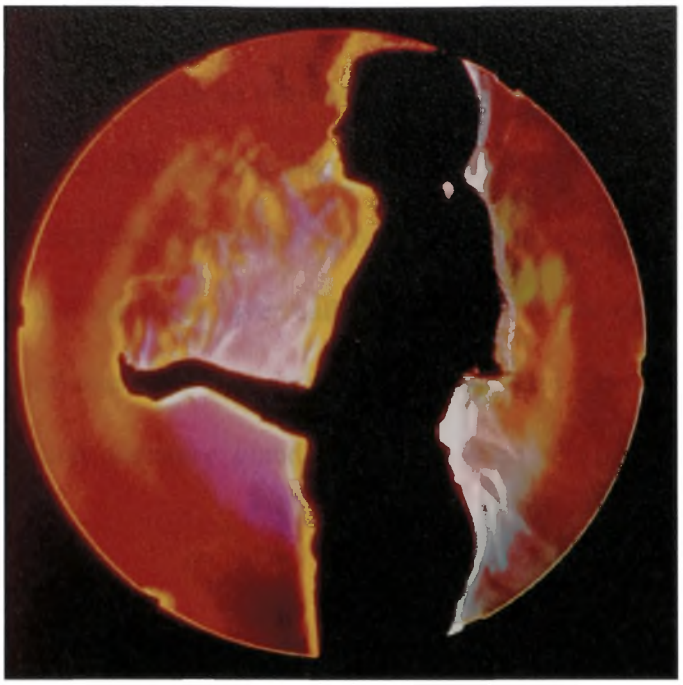


Figure 2: Human Thermal Plume, with permission Prof. Gary Settles, Penn State

The idea that human scent is produced through bacterial action on dead skin cells and secretions is the most common depiction of the creation of human odor. Other studies have suggested that odor is formed very quickly, supporting the idea that odor production is due to simple bond cleavage as opposed to a complex bacterial action [20]. Comparisons of the extracts of axillary sweat collected from both males and females showed qualitative similarities in the volatile organic acids present, suggesting a similar origin and mechanism for odor production in men and women [21].

1.3.2. The Skin

The human skin serves several functions, including the regulation of body temperature and excretion. Perspiring is the process of secreting a fluid onto the body's surface

through sweat glands and is a means to regulate body temperature. Approximately 1% of human body weight is necessary to be evaporated in the form of sweat to prevent a 10°C rise in body temperature. Perspiration also eliminates lactic acid, which is produced through muscular activity [22]. The skin can be divided into two layers: the outer layer called the epidermis and the inner layer called the dermis. The dermis layer contains most of the specialized excretory and secretory glands. The dermis layer of the skin contains up to 5 million secretory glands including eccrine, apocrine and sebaceous glands [23].

1.3.3. Apocrine Glands

The apocrine glands are found primarily in the axillary regions (i.e. armpits and genital areas). The apocrine glands in humans are similar to the apocrine/sebaceous gland in animals and thus traditionally have been considered human scent glands. They are a secondary sexual characteristic, becoming active at puberty and respond primarily to emotional stress. In animals, these glands serve definite social functions, comprising a complex system of chemical messages (pheromones) that provoke specific types of behaviors [24]. Pure apocrine secretions are both odorless and sterile when first appearing on the skin's surface [25]. Apocrine secretion is known to contain steroid sulfates, cholesterol, and proteins [26].

1.3.4. Eccrine Glands

The eccrine glands can be found throughout the body, with the highest densities found in the palms of the hands and the soles of the feet. In a normal individual, eccrine glands

are capable of secreting up to 2 to 4 L of fluid per hour. Pure eccrine secretions have been shown to be white in appearance [25], and typically composed of 98% water, but it also contains various organic and inorganic components [23]. Eccrine sweat originates in the extracellular fluid and, therefore, reflects the chemistry of blood plasma [26]. The volatile components of blood have been identified (Appendix B) and include alcohols, aldehydes, and alkanes [27,28]. The components of human breath have also been determined (Appendix B) and contain both aldehydes and alkanes [28,29,30] and the headspace of urine has also been evaluated (Appendix B) for the composition of VOCs [28].

1.3.5. Sebaceous Glands

The sebaceous glands are usually located in body regions where hair is present, including the face and scalp. Sebaceous glands produce secretions called sebum, which consists of glycerides, free fatty acids, wax esters, squalene, and cholesterol. A wide variety of organic compounds can be found in the sebum, which can be influenced by an individual's diet and genetics. The hydrolysis of human sebum results in the formation of a mixture of fatty acids, and the amount of free fatty acids in sebum can vary but averages between 15-25% [23]. Investigations into the biochemical uniqueness of skin lipids have suggested that slight differences in the overall composition of the sebaceous fatty acid mixture could lead to unique individual odors in humans [31].

1.3.6. Axillary Region of Body

The human axillary (armpit) region is the area of the body where the largest collection of secretion glands in both size and number are located. Apocrine, eccrine, and sebaceous glands, which are the major glands responsible for the secretion of sweat, are all present in the axillary region of the body. A number of factors make the axillary region a good odor producing area in the human body: (1) the contents of the apocrine gland secretions may serve as bacterial substrates; (2) moisture is available from the eccrine glands; (3) there is a resident population of bacteria to transform non-odorous to odorous substances; and (4) the presence of axillary hair may aid in the dispersion of the odor [32]. The occurrence of hair in the axillary region greatly increases odor, as it acts as a collection site for axillary secretions, debris and bacteria. Shaving and washing of the axillary area have shown to eliminate odor for more than 24 hours [25]. The axilla has a stable microbial population of both aerobic and anaerobic organisms, at densities between 500,000/cm^2 and 1,000,000/cm^2. The amount of bacteria present in the axilla from day to day does not vary significantly. The microflora have been determined to be qualitatively and quantitatively the same in both the right and left axilla of an individual and are not effected by handedness or sex [33].

Studies on body secretions conducted using humans as odor judges have shown that axillary odor is caused by *in vivo* bacterial action upon apocrine secretions. The microbes present on the skin and considered possible participants in the creation of human odor are Corynebacterium, Micrococcus, Pityrosparum, Sarcina, and Staphylcoccus. Apocrine sweat when stored at room temperature and in the presence of

micro-organisms will produce the characteristic axillary malodor within a few hours after collection. However, apocrine sweat stored without micro-organisms will not produce the characteristic axillary odor when stored at room temperature up to 14 days after collection. Apocrine secretions when stored at 0 °C produce no odor with or without the micro-organisms. Eccrine secretions, both sterile and unsterile, produced no perceivable malodor when incubated. The addition of bacteria and of contaminants such as keratin, sebum, apocrine sweat and hair to eccrine secretions is necessary for the production of any odor; however, the resulting odor is unlike axillary malodor [25].

1.3.7. Microbiology of Odor Production

Microbial biotransformation of naturally occurring odorless secretions into volatile odorous molecules is said to generate human body odor. Odors radiate from the surface of the skin, in particular from the axillary region where large populations of microorganisms bloom on secretions from the apocrine, eccrine and sebaceous glands. The involvement of bacteria in the production of these odors has been demonstrated and the presence of specific bacteria (such as *Staphylococcus epidermis* and *Corynebacteria*) has been correlated both *in vivo* and *in vitro* with the odor characteristic of the axillary region [24]. Studies into the relationship between axillary odor and the microbiology of the axilla have produced definitive results and conclusions as to the involvement of *Corynebacteria* in the creation of axillary odor [33]. Comparison of the bacterial composition of subjects determined to have intense axillary odor and those with absent or faint odor and it was shown that both lipophilic and large-colony diptheroids (*Corynebacterium*) were more frequent and more numerous in subjects with axillary

odor. Of the different types of the bacteria incubated with apocrine sweat on the forearm of the subjects, only *Corynebacterium* produced the characteristic axillary malodor.

A more recent study into the biochemical mechanisms of human axillary odor formation has determined a structure for the precursors for human body odorants and isolated a bacterial enzyme involved in their cleavage (Figure 3). In this study, 3-methyl-2-hexenoic acid, the major contributor to axillary malodor as determined by Zeng et al. 1991, was determined in hydrolyzed axilla secretions along with the chemically related compound 3-hydroxy-3-methylhexanoic acid. LC/MS analysis of these acids suggested that they are covalently linked to a glutamide residue in fresh axilla secretions. The organic extracts obtained from the axilla secretions prior to undergoing hydrolysis were almost odorless, supporting the findings of Shelley et al 1953. Strong odor was produced only after hydrolysis and re-acidification, indicating that the volatiles are mainly present in the collected secretions as covalently linked, water soluble precursors. The natural precursors of both acids were purified from non-hydrolyzed axilla secretions. Axilla bacteria belonging to *Corynebacteria* were found to release these acids from the neutral, odorless precursors *in vitro*. The determination that bacteria, but only *Corynebacteria*, cleave the precursor supports the finding by Leyden et al. 1981 that a dense population of coryneforms is necessary for strong odor formation. A Zn^{2+} dependent aminoacylase, which was determined to mediate the cleavage, was purified from *Corynebacteria stratium* and this enzyme has been shown to be highly specific for glutamine residue. It has been postulated that body odor formation originates from common catabolic pathways of the skin bacteria and thus is a by-product of bacteria metabolism of

unspecific skin secretions. The nature of the identified glutamine bound acids provides another theory: the compounds are synthesized specifically to exert their action once secreted in the axilla region. The benefits of the secretion of the precursor instead of direct secretion of the acids could lie in the fact that a precursor leads to the controlled release of the acids making the odor more long lasting [34].

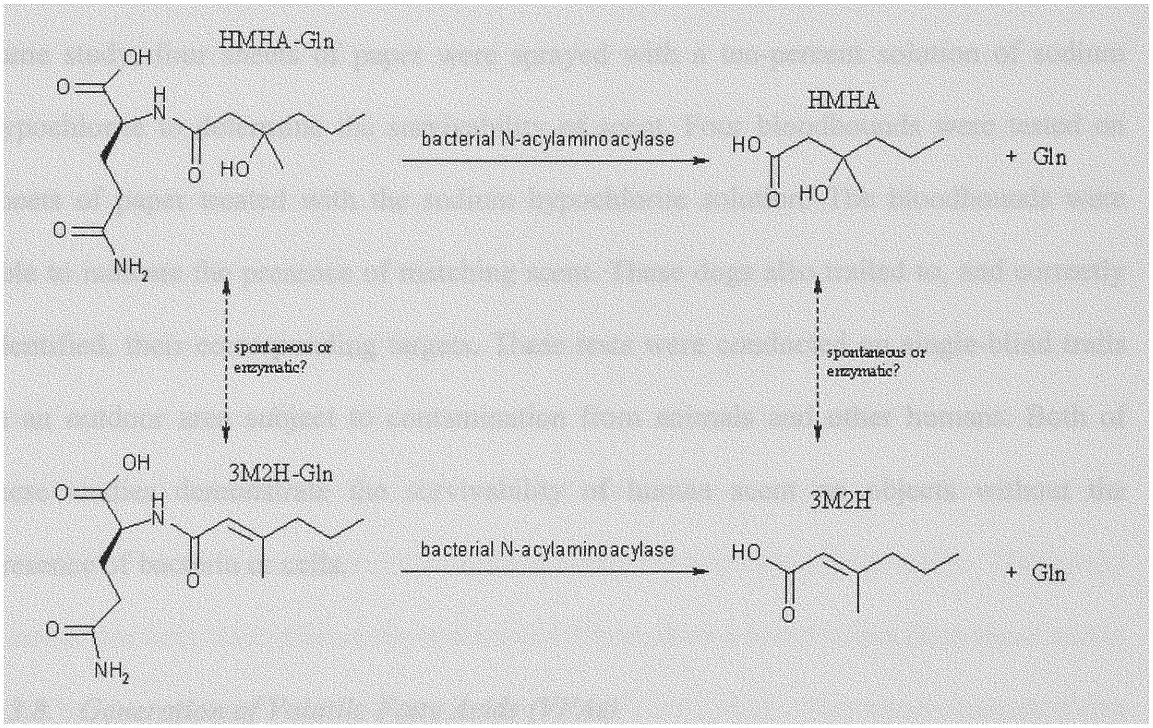


Figure 3: Proposed Scheme for the Release of Odiferous Acids by the Skin

Although microbial biotransformation of human secretions into volatile odorous molecules is said to generate human body odor, it has been shown through canine

evaluation that bacteria, as well as cells, are not necessary to sustain human odor after it has been created. The FBI and the SCBHC have shown the ability of bloodhounds to discriminate when scented from objects which have been irradiated to remove possible contamination with biological agents [17]. In this study the scent samples were irradiated for one hour with average doses of 40.7 kGy and 39.5 kGy and in six trials, the bloodhounds were able to be scented from the irradiated objects and correctly trail and match the scent to the target corresponding to the scent pad. In another portion of the same study, four sheets of paper were sprayed with a ten-percent solution of sodium hypochlorite to determine the survivability of scent. Four bloodhounds were tested on sheets of paper treated with the sodium hypochlorite solution. The bloodhounds were able to indicate the presence of matching scent. These dogs also trailed to, and correctly identified, their corresponding targets. These tests were conducted on single-blind trails in an outdoor area subject to contamination from animals and other humans. Both of these studies demonstrate the survivability of human scent on objects without the presence of bacteria or cells.

1.3.8. Generation of Volatile Fatty Acids (VFAs)

It is generally accepted that short-medium chain (C_2-C_{12}) volatile fatty acids (VFAs) contribute to axillary malodor. A potential route to VFAs in the axilla is through the bio transformation of longer chain (C_{14}-C_{30}), structurally unusual (methyl branched and or odd carbon number) fatty acids present in the sebum [31].

In an *in vitro* study on the formation of VFAs from bacterial action, the fermentation of representative axillary *Propionibacterium* (P. avidum and P. acnes) and *Staphylococcus* species (S. epidermidis) were combined with substrates such as glycerol and lactic acid, which are readily available in the axillary region. Interaction of P.avidum with both substrates resulted in the generation of significant quantities of propionic acid (C_3) and acetic acid (C_2) was also produced from interaction with lactic acid. P. acnes also produced significant levels of both propionic and acetic acid through interaction with lactic acid; however, interaction with glycerol produced no acetic acid and only a small quantity of propionic acid. The Staphylococcus bacteria metabolized both glycerol and lactic acid producing large amounts of both acetic and propionic acid. These results indicate that the fermentation pathways by cutaneous propionibacteria and staphylococci produce short chain (C_2-C_3) VFAs on axillary skin. In another experiment within the same study, representative *Staphylococcus, Corynebacterium,* and *Propionibacterium* species were incubated for up to 72 hours with valine, leucine, and isoleucine to evaluate their ability to generate metabolites of these branched aliphatic amino acids. The results showed that only *Staphylococcus* species can form odorous metabolites from these amino acids producing significant levels of branched VFAs (C_4-C_5). The results indicated that VFA production by *Staphylococcus* increases significantly with increasing oxygen availability, growth was also optimal under aerobic conditions, and these two observations imply that biotransformation activity is linked to overall metabolic activity [35].

1.4. Chemical Composition of Human Scent

1.4.1. Components of Human Sweat

There is a limited understanding of how the body produces the volatile organic compounds present in human odor. Most of the relevant scientific research pertaining to human scent has evaluated the contents of axillary (armpit) and plantar (foot) sweat. Comparatively little work has been done to determine the VOCs present in human odor. Knowing the contents of human sweat may not accurately represent the nature of what volatile compounds are present in the headspace above such samples which constitute the odor.

Axillary odor has been shown to consist of at least four androst-16-enes (androstenone, androstadienol, androstenol, and androstadienone) and isovaleric acid as determined through analysis of axillary secretions. The androst-16-enes and isovaleric acid provide the musky, urinous, and sweaty odors associated with axillary odor. The androst-16-enes are mammalian pheromones which are directly involved in the mating behavior of the pig [36]. Axillary secretions have also been determined to contain sulfanylalkanols (Appendix A) including: 3-methyl-3-sulfanylhexan-1-ol [37,38], 3-sulfanylhexan-1-ol, 2-methyl-3-sulfanylbutan-1-ol, and 3-sulfanylpentan-1-ol [38].

Compounds present in both male [20] and female [21] axillary secretion extracts that contained the characteristic malodors present in the axillary region have been isolated and identified (Appendix A). These analyses showed the presence of several C_6-C_{10} straight chains, branched, and unsaturated acids, and the major odor-causing compound was

determined to be (E)-3-methyl-2-hexenoic acid. Other important odor contributors were terminally unsaturated acids, 2-methyl C_6-C_{10} acids and 4-ethyl C_5-C_{11} acids. Comparison of the male and female extracts showed qualitative similarities. Through these results five observations were made pertaining to axillary odor: (1) branched and unsaturated compounds seem to have a high odor impact, (2) (E)-3-methyl-2-hexenoic acid (saturated and branched) is a major contributor to axillary odor, (3) the Z isomer has a high odor impact, but is present at one tenth the concentration of the E isomer, (4) the chain length and branching of the acids found suggest that the precursors for the acids are probably not amino acid-like in composition, and (5) odor occurs quickly, which suggests that odor may be cause by simple bond cleavage and not by complex bacterial action.

Short-chain fatty acids have also been extracted from sweat samples obtained from feet [39]. Samples were collected from subjects wearing pre-extracted socks and exercising for 30 minutes. Extracts from the socks were obtained through a 6-hour Soxhlet extraction with ethyl ether, treated with 2ml of a 0.5% p-toluene sulfonic acid methanol solution, and then analyzed using a GC/MS. Short-chain fatty acids were found in all of the samples, but in greater amounts in subjects that claimed to have strong foot odor. Iso-valeric acid was found only in the subjects who claimed to have strong foot odor. Olfactory evaluation by humans of 1000 ppm solutions of short chain acids (C2-C9) showed that each short chain fatty acid resembled either foot or axillary odor (Figure 4). Short chain acids that resembled axillary odor tended to be higher in carbon number than those that resembled foot odor.

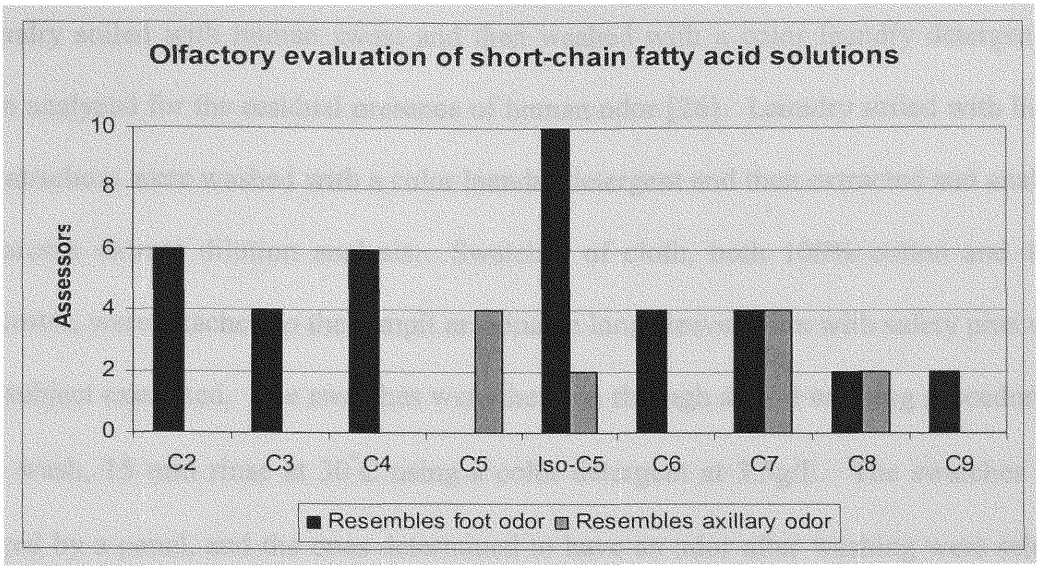


Figure 4: Olfactory Evaluation of Short-chain Fatty Acid Solutions

Investigations into the compounds emitted by humans that attract the Yellow Fever Mosquito have provided insight into the compounds present in human odor. Samples were collected using glass beads that were rolled between fingers. The beads were then loaded into a GC and cryofocused by liquid nitrogen at the head of the column before analysis with GC/MS. The results showed more than 300 observable compounds [40]. In a later study conducted by Bernier, et al., 346 compound peaks were observed [41] and of the compounds detected, 43 were unidentifiable while 303 were identified by standard or identified tentatively by library and spectral interpretation. Of the 303 compounds identified, 26 were confirmed to be of background origin, leaving 277 compounds identified as components of human skin emanations (Appendix A). Through this method, comparisons of the compounds found in different individuals [42] revealed qualitative similarities along with quantitative differences.

Laundry soiled with human sweat and then washed with a color laundry detergent has been analyzed for the residual presence of human odor [26]. Laundry soiled with human sweat/sebum were washed with a color laundry detergent and then extracted and analyzed by aroma extract dilution analysis. Swatches of cloth, both 100% cotton and 100% polyester, were attached to the armpit area inside long sleeve shirts with safety pins while the subject exercised. The swatches were then run through a mild washing procedure: 20 min wash, 15 min rinse at 30°C using a color detergent at 3.5g/L. The swatches were judged by a panel, and the ones determined to have an odor after washing were selected for analytical analysis. Esters (ethyl-2-methylproponate and ethylbutonate), ketones (1-hexen-3-one and 1-octen-3-one) and in particular, aldehydes[(Z)-4-heptenal, octanal, (E)-2-octenal, methional, (Z)-2-nonenal, (E,Z)-2,6-nonadienal, (E,Z)-2,4-nonadienal, (E,E)-2,4-decadienal, and 4-methoxybenzaldehyde] were identified as primary odorants in the swatches post-washing (Appendix A). However, organic acids, which are considered to be the dominant characteristic odorants in human axillary sweat, were not present in the extracts of residual odor.

Research has been carried out to determine the applicability of pattern recognition in the analysis and interpretation of gas chromatograms produced from the analysis of human sweat [43]. This study utilized a recirculating system to load the sweat head-space into the Tenax concentrating traps; the samples were then desorbed from the Tenax traps and analyzed by GLC-FID. The GC-FID was interfaced with an ATARI ST 1040 computer with a pattern matching program. The alignment coefficients, profile correlations, Euclidian distances, and box car distances were all determined using the program. The

analysis was conducted on two sets of twins who were shown to be identical through DNA profiling. One pair of twins were teenage boys and the other adult women. Sweat samples were collected by pinning squares of cotton fabric to the armpit area of a T-shirt, which was worn for eight hours. The results showed there was a difference between the twin matches and the unrelated matches across all four parameters. The largest difference was found in the profile correlation, indicating that identity signals may be shown by differences in the concentrations of certain ranges of volatiles. The difference in alignment coefficients indicates that some of the identity signal depends on an absence or presence of certain compounds. The differences in the Euclidian and box car distances indicate that variation in the amounts of certain compounds present is an important factor in individual scent profiling. This study demonstrated that human scent identity is determined by both qualitative and quantitative differences in sweat volatiles,yet no attempt was made to identify the compounds present.

Previous attempts have been made to characterize the human odor, which a dog uses to match scent. One such study was done evaluating armpit odor using a gas chromatograph equipped with a Tenax Trap [44]. Armpit odor was collected over 12 hours using polyester squares and, after collection, the samples were evaluated and fractionated into four sections using a gas chromatograph. The odor of twins was evaluated through presentation of the fractions to scent discrimination canines that were scented from the whole scent and it was shown that although chromatographically fraction 3 of the twins was similar, the dogs could make a distinction between the twins. When presented with fraction 2 alone, the dogs could not make the distinction between

the twins. The chromatograms for fraction 2 were also determined to be chromatographically similar. When the twin's samples were presented as a whole, however, the dogs could not distinguish between either of the twins. Another study confirms the differences in underarm sweat between European and Japanese males and females [45]. The experiment involved the collection of scent through pinning a polyester pad on the inside of a volunteer's vest and then evaluating the sample utilizing a gas chromatograph. The chromatograms produced from the different individuals with differing ethnic backgrounds were qualitatively different, yet no attempt was made to identify the compounds present.

1.4.2. Components of Fingerprint Residue

Fingerprint residue has been evaluated to determine the chemical compounds that are present. A variety of qualitative methods were used to determine differences in the composition of child and adult fingerprint residues [46]. Participants in the first of these studies were children who were asked to touch the interior of cars, later processed for fingerprints. The second qualitative study involved both children and adults holding recently fabricated and cleaned plastic bottles, both of which were analyzed after being held for fingerprints. These studies show that adult fingerprints differ from child fingerprints in both composition and duration of presence after contact. Compositions of the fingerprint residues of adults have been determined through gas chromatographic analysis (Appendix A) and fatty acids [23,47], cholesterol [47], and squalene [48] were determined to be components of fingerprint residue. It has been shown that fingerprint residue components can be separated by thin-layer chromatography (TLC) [49] and

visibly-excited fluorescent components are also present that can also be separated by TLC [50]. In addition to the fluorescent components already present, another visibly-excited fluorescent component in latent fingerprint residue can be induced by gaseous electrical discharge [51].

1.4.3. Headspace Analysis of Human Odor

Although the composition of human secretions and fingerprint residues have been evaluated for their chemical composition, comparatively little work has been done to determine the compounds present in human odor. Knowing the contents of human sweat may not accurately represent the nature of what compounds are actually present in the headspace above such samples which would comprise human scent.

Human odor components have previously been studied through headspace gas chromatography / mass spectrometry (GC/MS) for compounds specific to age [52]. Subjects studied were between 26-75 years of age and sampled themselves by wearing a pre-treated cotton shirt to bed for three consecutive nights. A rectangular section of the shirt (20 X 30 cm) was cut and sealed in a bag and the air in the bag was pumped into the GC at 23°C for a period of 18 hours. Compounds determined to be present in human odor included hydrocarbons, alcohols, acids, ketones, and aldehydes (Appendix A). Investigations into the creation of the various aldehydes present in human odor determined that their production is a result of oxidative degradation of sebaceous secretion components Table 2. Specifically, 2-nonenal is produced through oxidative degradation of ω7 monosaturated fatty acids, such as palmitoleic acid and vaccenic acid,

with the production potentially accelerated by lipid peroxides such as squalene HPO (Figure 4). This study also presented 2-nonenal as a compound that is only present in the odor of individuals over 40 years of age

Table 2: Aldehydes Formed by Oxidative Degradation of Sebaceous Components

Components Tested	Aldehydes Detected by GC/MS
Cholesterol	Not detected
Squalene	2-methyl-2-butenal
Fatty Acids:	
Palmitoleic Acid	Hexanal, Heptanal, 2-Octenal, 2-Nonenal
Vaccenic Acid	Hexanal, Heptanal, 2-Octenal, 2-Nonenal
Oleic Acid	Nonanal, Pentanal
Linoleic Acid	Hexanal

Solid Phase Micro-extraction (SPME) in conjunction with GC/MS has been used previously to identify volatile components that are responsible for odor produced from human skin [53.] The SPME fibers used were DVB/Carboxen on PDMS 50/30um and the analysis was done using a dual column GC (non-polar DB-1 and polar DB-Wax). Direct sampling of the forearm was done using a 6cm glass tube with a septum at one end that was placed over the skin. The SPME fiber was introduced through the septa and exposed to the headspace above the skin for 45 minutes. The test subjects for this study were 50 females between 18 and 60 years of age. Several different classes of compounds, including: shorter and longer chain hydrocarbons, short chain aldehydes, and a branched ketone, were identified in the headspace from human skin (Appendix A). 88% of the

subjects showed the presence of short chain aldehydes, such as: octanal, nonanal, and decanal. Hydrocarbons of longer chain lengths were found in 96% of the subjects, such as: tetradecane, pentadecane, and hexadecane. The abundances of these compounds varied between individuals, and some subjects exhibited specific volatile compounds such as: 6-methyl-5-hepten-2-one, and hydrocarbons of shorter chain lengths including decane. Human odors have also been sampled through SPME-GC/MS using a novel sampling chamber in attempt to determine the possible existence of biomarkers in human emanations [54].

1.5. Variability of Human Scent

1.5.1. Genetic Basis for Individualizing Human Odor

The genetic basis for individualizing body odors has been studied extensively in genetically engineered mice which differ in respect to the genes present in the major histocompatibility complex (MHC) [55,56,57,58,59,60]. Individual body scents of mice can be altered by modification of a single gene within the MHC [60]. Alterations to the individual body scents of mice result in changes in the concentrations of the volatile components found in the urine [61,62]. The MHC is a group of genes connected to the immune system, and has been shown to play a role in both maternal and kin recognition in mice [58]. In humans, the major histocompatibility complex is referred to as the HLA, which is short for human leucocyte antigens [63]. The MHC consists of polymorphic genes which contain extreme nucleotide diversity as high as 8.6%, as compared to the nucleotide diversity of the human genome which has been estimated to be between 0.08% and 0.2% [64]. Experiments utilizing trained rats have shown that urine odors of defined

HLA-homozygous groups of humans can be distinguished [63]. Electronic nose technology has also shown the ability to discriminate between urine and serum from HLA-homozygous groups of individuals [65]. The pathway through which the MHC influences odors is not known. A model integrating different hypotheses suggests that soluble MHC proteins play a central role in the production of MHC associated odors [66]. The soluble MHC proteins travel into the serum, both intact molecules and degraded moieties of the proteins have been found in the urine and in the sweat, and it is suggested that, through bacterial action, they are transformed into odorous substances.

1.6. Persistence and Stability

1.6.1. Survivability and Durability of Human Scent

A study conducted by the Federal Bureau of Investigation (FBI) in conjunction with members of the Southern California Bloodhound Handlers Coalition (SCBHC) has shown that scent collected from bomb fragments can be a useful tool in explosive device investigations [67]. After the explosive device was detonated, scent was collected and stored on gauze pads from the fragments using the STU-100. The bloodhounds were then presented with the scent and correctly identified matching scent from the builders of the device 60-100% of the time with no false positives. An additional feasibility study conducted by the FBI [68] has again demonstrated the ability of human scent to survive the extreme mechanical and thermal affects associated with the explosion and burning through the ability of canines to correctly identify individuals using scent collected from exploded pipe bomb fragments.

In a another feasibility study previously described in Section 1.3.7, the FBI and the SCBHC have shown the ability of bloodhounds to discriminate when scented from objects which have been irradiated to remove possible contamination with biological agents [17]. In this study, the scent samples were irradiated for one hour with average doses of 40.7 kGy and 39.5 kGy and, in six trials, the bloodhounds were able to be scented from the irradiated objects and correctly trail and match the scent to the target corresponding to the scent pad. In another portion of the same study, four sheets of paper were sprayed with a ten-percent solution of sodium hypochlorite upon which four bloodhounds were tested and able to indicate the presence of matching scent. Both of these studies demonstrate the survivability of human scent in real world situations.

DNA profiles can be extracted from the surface of briefly handled objects such as a telephone, pens and briefcase handles [69]. Table 3 lists casework examples of objects from which DNA profiles were successfully extracted from the Royal Canadian Mounted Police Forensic Laboratory in Regina, Saskatchewan [70]. The quantity of DNA recovered from a fingerprint on an object after a single contact ranges between 0.04-0.2 ng and varies between individuals. Hand washing has been shown to reduce the amount of DNA deposited in fingerprints [71]. A successful DNA profile can be obtained from touching a piece of paper for sixty seconds as well as for two seconds which indicates that the successful extraction of a DNA profile is not dependent on the duration of contact [72]. The shedder status of an individual can contribute to the amount of DNA deposited in fingerprint residues. The threshold levels that discriminate between a "good shedder" and a "poor shedder" have yet to be determined. It has been demonstrated that

some individuals referred to as "good shedders" can deposit a full DNA profile after contact with a surface for ten seconds where as others referred to as "poor shedders" deposit very little DNA even up to two hours after hand washing [73,74]. Hand washing does not affect the ability of "good shedders" to deposit a full DNA profile; however, a "poor shedder" requires a time period of up to six hours before a full profile can be obtained after contact with an object [74]. The ability to extract DNA profiles from briefly handled objects supports the use of briefly handled objects for human scent discriminations, in view of the fact that skin cells are said to be a carrier medium for the deposit of human scent in the environment.

Fingerprint residues deposited on adhesive tape after processing using an alternate light source, cyanoacrylate fuming, and staining with BY-40 followed by crystal violet can still produce and extractable and analyzable DNA profile for six STR loci [75]. DNA profiles have also been successfully extracted from pipe bomb fragments after deflagration [76] and from expended cartridge casings and bullets [77]. The determinations that DNA profiles can be extracted from human fingerprint residues following various developing processes and environmental stresses demonstrate the potential survivability of skin cells and, thus, possibly human scent on these sources and the potential for a scent-discriminating canine to identify a human odor from these types of items.

Table 3: Examples of Objects from which DNA Profiles Were Successfully Extracted

OBJECTS SEPARATED BY DNA SOURCE	
HANDS	
Arm-rest (automobile)	Hash-like Ball (1cm diameter & hand rolled)
Baseball cap (brim)	Hold-up Note
Binder Twine	Ignition Switch
Bottle Cap	Keys
Chocolate Bar (handled end)	Knife Handles
Cigarette Lighter (disposable/striker and body)	Paper (hand folded [3 folds in paper for handling])
Cigarette Paper	Pen (bank robbery-roped pen owned by bank)
Control Levers (for signal lights etc-automobile)	Plastic Bag Handles
Dime	Pry Bar with Shoulder Straps
Door Bell	Remote Car Starter
Door Pull	Rope
Drug Syringe Barrel Exterior	Screwdriver Handle
Electrical Chord	Seat Belt Buckle (automobile)
Expended .22 caliber cartridges and rifle trigger, scope, stock and barrel	Shoe Laces
Fingerprint (single)	Steering Wheels
Gauze and Tape (used to cover fingertips)	Tape on Club Handle (not only the exposed surface but also initial start under layers of tape)
Gloves (interior[fingertips and cloth] and exterior)	Toy Gun
Hammer (head and handle)	Wiener
MOUTH & NOSE	
Apple Core (bite marks)	Lipstick (top surface and outer surface of lipstick case)
Balaclava (knitted cap)	Nasal Secretions (tissue)
Bite Marks	Peach Struddle
Bottle Top	Pop Cans/Bottles
Buccal Stick Only (swab entirely cut off previously)	Ski Coat Collar
Cake (bite mark)	Salami (bite mark)
Cheese Cake (bite mark)	Stamps
Chicken Wing	Straws (from drinking glass)
Chocolate Bar (bite mark)	Telephone Receiver
Cigarette Butts	Tooth

Envelopes	Toothbrush
Glass Rim	Toothpick
Gum	Vomit (bile-like sputum/liquid)
Ham (bite mark)	Welding Goggles (rim of eye/nose area)
GENERAL BODY	
Baseball cap (swab of inside of rim)	Head-rest (automobile)
Bullet hole in Gyproc Wall and Bullet	Paraffin Embedded in Tissue
Buried Remains	Razor (disposal type/blade and plastic cap)
Burned Remains	Tissue Paper Wiping of Underarms of Shirt-(sweat)
Chain (approx 60 cm of end of automobile chain-blood found but alleged to have been used to drag body)	Socks
Hair	Toilet-knife found in toilet trap)
Hair Comb (for head hair)	Urine in Snow
SEXUAL	
Automatic Machine Washed Blue Jeans (crotch for semen)	Water-"S" Trap of Shower
Inside Undershorts	Inside Edge of Fly of Undershorts
	Pubic Hair Comb (from sexual assault kit-white cotton fiber material)
EYES	
Contact Lens Fragments (from vacuum cleaner bag)	Eyeglasses (ear and nose pieces)
	Tears (on tissue)

1.7. Collection of Human Scent as Evidence

1.7.1. Methods for Human Scent Collection

There are two main methods for the collection of human scent for the purpose of scent identification. The direct method is collecting the handled object which can be presented to the canine, and the indirect method is collecting the odor on an absorber from an object or an individual and then presenting the absorber to the canine. Police agencies in the

Hungarian People's Republic collect human scent from objects by placing an "odor collecting cloth" in contact with the object for 20-25 minutes [78]. After the time allotment has passed, the cloths are removed using deodorized tweezers, folded so that the surface which was in contact with the object is on the inside, and sealed inside a glass jar. A scent collection tool called the Scent Transfer Unit-100 (STU-100) was developed to aid law enforcement in the collection of human scent from both people and objects utilizing sterile gauze absorbers [79]. The STU-100, as described in Section 1.2.2, can be used for both contact (placing the object directly on the gauze) and non-contact scent collection (placing the STU-100 directly over the object). There are many variations to the process of collection of scent on an absorber ranging from wiping the object or surface, placing the absorber in contact with the object or surface, or utilizing the STU-100. At a crime scene, any object that may have been touched by the suspect can be collected as scent evidence. Items that are commonly collected for human scent evidence purposes include clothing, lighters, and tools; however, some items are too large to collect and indirect collection of scent is used such as car seats, doors and windows. Table 4 lists items commonly collected for use in scent identification line-ups by the Dutch National Police, and Table 5 lists items commonly collected by the FBI as human scent evidence. These items bear striking similarities to the objects from which DNA profiles can be successfully extracted as listed in Table 3. The fact that DNA profiles have been extracted from handling these types of objects proves that it is reasonable that human scent can be present on these objects as DNA comes from cells and skin cells are said to carry human scent.

Table 4: Examples of Articles Used for Human Scent Identification Line-ups in the Netherlands

SCENT SAMPLES FROM OBJECTS THAT ARE TOO BIG TO SECURE:
Car seats
Steering wheels,
Gear shift knobs
Hand brake
Seats & handles motorbikes
Door, safe, cupboard, wheelbarrow handles
Windows
OBJECTS THAT CAN BE SECURED AS A WHOLE, OR FROM WHICH SCENT SAMPLES ARE TAKEN:
Clothing (gloves, caps, coats, sweaters, socks, T-shirt)
Tools (screwdrivers, crowbar, cutting tools etc)
Knives (from very large to tiny multi-purpose tools)
Guns (different kinds)
Torches
Electric plugs and cables (left over after robbery of big item)
Bags (all sizes), backpacks, especially handles of these
Keys & locks
Stones (different sizes & kinds, used to break windows)
Jewelry boxes
Jewelry, watches
Sunglasses
Car radio's
Mobile phones
Purses
Paper (money, envelopes, paper napkins)

Table 5: Examples of Articles from which Human Scent is Colleted by the FBI as Human Scent Evidence

Items from which scent is collected using the stu-100 as human scent evidence
Throw Rug
Clothing
Telephone
Iron
Keys
Vaginal Swab
Bomb parts- wire, metal, plastic, glass
Door Knob
Steering Wheel
Railroad spike
Paper
Mail
Bullets
Cartridge Casings
Rocks
Human Body Parts (deceased)

1.7.2. Collection Materials

Materials used for the collection of human scent have yet to be optimized or standardized. Each agency uses a different type of absorbent medium varying in sterility to collect human scent evidence. For example, the FBI uses Johnson & Johnson sterile gauze (Appendix B) while the Dutch National police utilize King's Cotton (Appendix C) which is a non-sterile medium. The analysis of human scent through both canine and instrumental means vary in the type of materials used and provide no reasoning for the choice of collection material employed. Some canine human scent research refers to a type of "odor collecting cloth" [78], yet does not specify the composition of the material. Other canine work has utilized t-shirts [91] and handkerchiefs [90] for odor collection

with no specification on composition. Polyester materials have been used for the collection and analysis of human scent by canines [45] and instrumental methods [44]. Cotton is the most widely reported type of material used for human odor collection for both canines [86,92] and instruments [43]. Nevertheless, no mention of the percent composition or sterilness of the fabrics are listed. Employing the STU-100 for human scent collection requires the use of cotton, 5X9-inch, sterile gauze pads [17,67,97] again with no reasoning supplied for the choice of material. Canines have shown the natural ability to discriminate between odors in the presence of a high background; whereas, instrumental analysis requires a significantly lower background.

Sterilization is the process that is intended to kill or remove all types of micro-organisms. In general, there are three principal sterilization methods used for most surgical dressing materials: (1) physical (dry heat or saturated steam), (2) chemical (ethylene oxide gas or chemical liquids), and (3) radiation sterilization. Steam sterilization is commonly referred to as autoclaving which relies on the use of steam above 100°C. Traditionally, gravity (downward-displacement) autoclaves have been utilized for the sterilization of dressings; however, high-vacuum porous-load steam sterilizers are now the method of choice. Essential requirements are for total removal of air from load and the prevention of excessive condensation within the dressing pack during the cycle. The nature of the packing must allow complete steam penetration into the dressing, as well as post-sterilization drying [80]. Ethylene oxide gas is effective against all type of micro-organisms. The biocidal action of this gas is considered to be alkylation of nucleic acids. It is non-corrosive and safe for most plastic and polyethylene materials. The operating

pressures and temperatures (45-60°C and 10-12 psi) of ethylene oxide sterilizers are considerably less than for steam units [81]. A last resource for sterilization treatment lies gamma radiation. Gamma radiation efficiently kills microorganisms throughout the product and packaging with very little temperature effect. The advantages of gamma radiation lie in the precise dosing, rapid processing, uniform dose distribution, system flexibility, and the immediate availability of product after processing. Biologically sterile, however, may not equate to analytically clean, and thus the collection medium may prove to be a limiting factor for the instrumental identification of the compounds present in a human odor profile and thus an optimization of these materials is required.

1.7.3. Fiber Properties

Different fiber chemistries produce differing properties to the various fiber classes. Natural fiber products are considerably more complex than man-made fires and exhibit a greater diversity in surface chemistry, which may be exploited to optimize the absorptive potential of the textile gauze. Natural protein fibers are polyamidic in nature (Figure 5). Silk is predominantly aliphatic in its side-chains and the acid and hydroxyl side chain groups are observed more often than the basic groups. Wool exhibits a more even spread of chemistries, although glutamic acid is one of the most abundant side chains (Table 6). Cellulose fibers (cottons) have a large number of hydroxyl groups, resulting in increased absorbency and affiliation for polar species via hydrogen-bonding (Figure 6). This is detailed in more depth in Table 1 [82]. Depending on which types of compounds the canines are using to distinguish between people, the functional groups present on the

surface of the material may lead to an increased ability to collect human scent from handled objects and people.

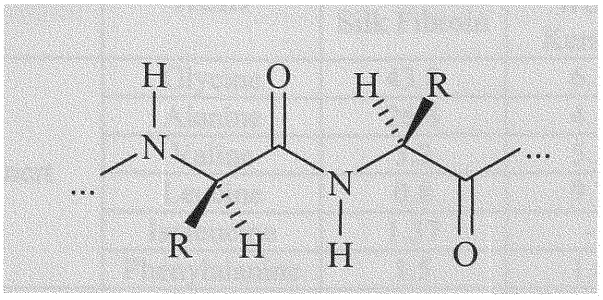


Figure 5: Natural Protein Structure

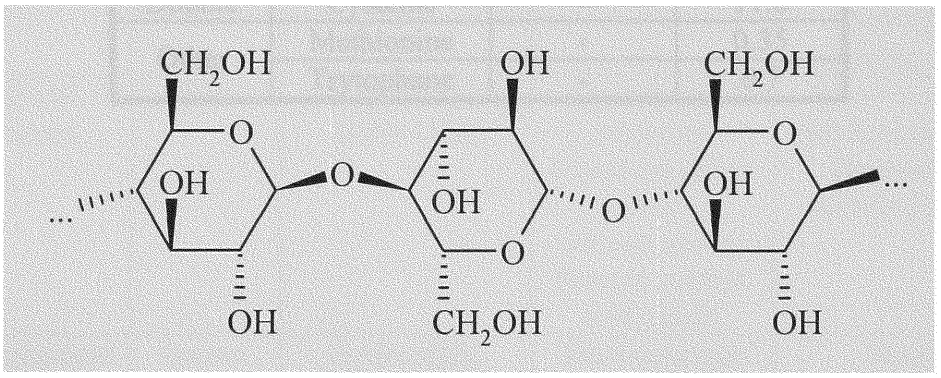


Figure 6: Natural Cotton (Cellulose) Structure

Table 6: Amino Acid Composition of Silk and Wool Fibers

TYPE	AMINO ACID	MASS PERCENT OF AMINO ACID	
		Silk Fibroin	Wool Keratin
Inert	Glycine	43.8	6.5
	Alanine	26.4	4.1
	Valine	3.2	5.5
	Leucine	0.8	9.7
	Isoleucine	1.37	-
	Phenylalanine	1.5	1.6
Acidic	Aspartic Acid	3.0	7.27
	Glutamic Acid	2.03	16.0
Basic	Lysine	0.88	2.5
	Arginine	1.05	8.6
	Histidine	0.47	0.7
Hydroxyl	Serine	12.6	9.5
	Threonine	1.5	6.6
	Tyrosine	10.6	6.1
Ring	Proline	1.5	7.2
Double	Cysteine	-	11.8
Other	Methionine	-	0.35
	Trytophane	-	0.7

Table 7: Properties of Natural and Synthetic Fibers

SOURCE	FIBER TYPE	ABSORBENCY	STRENGTHS	WEAKNESSES
Natural Cellulosic	Cotton	Hydrophilic (MR=7.5%)	Resists alkali damage High temperature resistance Conducts heat & electricity	Prone to acid damage Susceptible to mildew and mold
Natural Cellulosic	Flax	Hydrophilic (MR=12%)	Resists alkali and organic solvent High absorbency Good conductor of heat	Poor resiliency and stiffness
Natural Protein	Wool	Hygroscopic (MR=16%)	Highly absorbent Resists acid damage	Prone to alkali and heat damage Poor heat conductor Harmed by oxidizing agents
Natural Protein	Silk	Hygroscopic (MR=11%)	Good thermal retention Flame retardant (self extinguishing) Resists mildew and mould	Prone to alkali and heat damage Harmed by oxidizing agents
Manufactured Cellulosic	Rayon	Hydrophilic (MR=13%)	Heat resistant below combustion temperature	Weak Flammable
Manufactured Cellulosic	Acetate	Hydrophilic (MR=6%)	Resistant to ultraviolet Resistant to mildew and mould	Heat sensitive Dissolves in organic solvent
Synthetic	Nylon	Hydrophobic (MR=3.5%)	Strong and lightweight Resists alkali and chlorine bleach	Heat sensitive Susceptible to static build-up Flammable Prone to damage

			Olephilic	
Synthetic	Acrylic	Hydrophobic (MR=1.5%)	Resistant to ultraviolet Resistant to most chemicals Flame retardant (modacrylic)	Susceptible to static build-up Heat sensitive
Synthetic	Olefin	Hydrophobic (MR=0.01%)	Strong and lightweight Inert to most chemicals Olephilic	Very heat sensitive Sensitive to ultraviolet Poor surface texture retention
Synthetic	Polyester	Hydrophobic (MR=0.4%)	Excellent resistance to ultraviolet Resistant to most chemicals Olephilic Good wicking	Susceptible to static build-up
Synthetic	PTFE	Hydrophobic (MR<0.01%)	Very chemically inert Excellent resistant to ultraviolet Resists high temperature Flame retardant (self extinguishing)	Heavy Low strength Non-stick (Teflon®)
Mineral / Inorganic	Glass	Hydrophobic (MR<0.01%)	Strong Flame resistant Resistant to chemicals and ultraviolet	Poor flex abrasion resistance Skin irritant Heavy
Mineral / Inorganic	Metallic	Hydrophobic (MR<0.01%)	High electrical conductivity (reduced static build-up)	Poor flex abrasion resistance

The (water) absorbency of a textile fiber is expressed as a percentage by what is known as moisture regain (MR), the ability of a fiber to absorb moisture with respect to its dry weight. Values range from hydrophobic fibers, such as glass wool (MR<0.01%) and polyester (MR=0.4%) through hydrophilic fibers such as cotton (MR=7.5%) to rayon (MR=13%), and hygroscopic fibers such as wool (MR=16%). Certain synthetic fibers with a high degree of hydrophobicity, such as nylons and olefins, are also reported as olephilic, or having a tendency to attract and adsorb oils and fats. The pores within a fabric heavily influence the moisture and air transfer properties of the material. If the collection of human scent is more of a physical interaction with the material than a chemical one, then the MR and the porosity will have an effect on the collection and retention ability of the medium. The porosity of a material is defined as the ratio of airspace to the total volume of the fabric, and is expressed as a percentage as a function of the fabric's density and dimensions;

$$P = \frac{(A \times T - W/D)}{A \times T} \times 100\% \qquad \textbf{Equation 1}$$

Where P = porosity of the fabric, A = area of the specimen in cm^2, T = thickness of the specimen in cm, W = weight of the specimen in g, and D = density of the fiber in g/cm^3 [83].

Natural fiber products often require several industrial treatment processes to improve the appearance and quality of the fibers. Whereas, in the textile industry, the look and finish

is more important, this research seeks to optimize the materials used for the collection of human scent, and so, accordingly, the most appropriate materials may be natural fibers in their raw state. Table 8 lists some of the more common finishing processes for natural fibers, detailing the effects of the treatment as well as the treatment itself. A prime example is Mercerization of cotton to improve strength and luster; this process also increases the absorbency of the fiber but changes its surface geometry [84].

Table 8: Common Industrial Treatment and Finishing Processes of Natural Fibers

FIBER	PROCESS	EFFECT
Wool	Carbonizing	Acid treatment to remove cellulosic impurities
	Fulling	Washing in soap solution to produce a controlled shrinkage
Silk	Degumming	Repeated scouring in soap solution to remove sericin (gummy non-fibrous impurity)
	Weighting	Addition of metallic salt to compensate for weight loss during degumming
Cotton	Mercerization	Treatment with NaOH under tension to improve strength, luster and absorbency
	Durable Press	Treatment with a resin solution and curing to develop cross-linkages between cellulose chains
	Acid Finish	Treatment with acid to produce transparent aesthetic effect, at expense of damage to cotton fiber

The chemical nature of the fiber is also responsible for the behavior of the fiber under various chemical and environmental conditions. Some fibers are stable in basic solution yet are prone to acid damage (cellulose); whereas, other fibers are more stable in acid than base (wool & silk). Other factors worthy of consideration are stability under UV

light, heat resistance and flammability, and electrical properties. Table 7 lists the absorbency of various fibers from each class, and details many of the strengths and weaknesses of fibers that must be considered [84].

1.8. Canines and Human Scent

1.8.1. Scent Matching Abilities

The ability of dogs to match odor collected from different parts of the body has also been evaluated by several groups producing differing results. Dutch police dogs were shown to be able to match scent collected from hands to scent collected from the crook of the elbow from the same individual 32% of the time, which is greater than 16.7% due to chance alone. These dogs also showed the ability to match odor collected from the hands to scent collected from pants pockets of the same individual [85]. Studies in the United Kingdom have also shown that dogs possess the ability to match scent to that of an individual taken from various places of the body with a success rate above 80% where that due to chance was 16.7% [86]. However, a study conducted in the United States by Brisbin and Austadt have produced contrasting results.

In this evaluation of the ability of canines to match odor collected from different parts of the body [87], odors were collected using forceps and metal bars. The canines were trained to distinguish between individuals based on hand odor. In the first part of the experiment, the canines were successful in matching a hand odor sample to the correct scent in an array of hand scented objects. In the second part of the experiment, the dogs were required to match hand odor to objects scented by the crook of the elbow by

different individuals. The canines were only successful in the identifications 57.9% of the time which was not statistically different from chance. The authors concluded that the inability of the canines to correctly match hand odor and elbow odor brings into question dogs' ability to generalize an individual's odor signature and cross match samples taken from different parts of the body. In a Short Communication [88], issues concerning the lack of controls leading to ambiguous scent matching and appropriate training for the canines used in the Brisbin and Austadt experiment were stated. In a reply to the Short Communication, Brisbin and Austadt [89] clarified their conclusions. The authors stated that the ambiguity present in the scent matching was intentional to evaluate whether canines that have been trained to match odor from a specific part of the body will automatically generalize odors when faced with odors from different areas of the body. Justification for the ambiguity was that a strict interpretation of the individual odor theory would suggest that canines have the ability to automatically generalize odors. The canines did not demonstrate the automatic ability to generalize odors leading the authors to make statements about the importance of correct training procedures for scent identification canines and the authors believe that with appropriate training dogs may be able to generalize odors successfully.

The ability of canines to differentiate between twins has been investigated yet the results are ambiguous. A study by Kalmus [90] showed that, when dogs are presented with a scent matching scenario, it was not possible for canines to distinguish between identical twins. However, when the canines were presented with a tracking scenario, greater success was achieved. These results may not accurately reflect the ability of canines to

scent discriminate between the odors of identical twins due to the fact that, in a tracking scenario, environmental factors on the track may have cued the dog. Another study by Hepper [91] demonstrated that dogs have the ability to distinguish between twins who are non-identical (ages 3 to 5 months) and live under the same environmental conditions, i.e. soaps, food, clothing etc. and identical twins (ages 34 and 50 years) which live under different environmental conditions. In the same study, canines were unable to differentiate between identical twins which live under the same environmental conditions.

1.8.2. Factors Effecting Canine Matching Ability

There are many factors that directly affect a dog's performance in scent identifications. The extent of training determines a canine's ability to correctly cross-match scent [87,85,86,92,93]. Canines are more accurate when they are willing to work [92]. Canines perform better when asked to identify scent from people they are familiar [85]. The method in which scent is collected affects the quality of the scent [92]. Washing before scenting significantly decreases a dog's ability to correctly identify scent [94]. In addition, the experimental setup affects a dog's performance [92]. Therefore, without standard training and testing procedures, canine's potential error rate is variable and may be very high.

1.8.3. Tracking Canines

Tracking canines are trained to utilize both human scent and environmental disturbances to locate the track of an individual, but are not given an initial scent to follow [3].

Occasionally tracking canines are said to follow the freshest track in the area to which it is presented, this behavior is described as air scenting. [95]. Air scenting canines are said to follow the trail of an individual with their head up in the air and are considered to be following the scent rafts of an individual being carried by air currents. Tracking dogs are said to follow the trail with their head down and noses on the path and follow very closely the footsteps of the individual. The characterizations of air scenting versus tracking are based on the behavior of the canines while following the odor trail. There are two general terms for the types of odor a canine uses to detect and follow an odor: individual scent (utilized by trailing, and scent article canines) and contact or disturbance odor. Since a tracking canine is not giving an initial scent to follow, the type of odor utilized is contact or disturbance odor which is imparted to the environment. As an individual moves through an environment surface characteristics are influenced, vegetation and insects are crushed etc. and an odor is released based on these contacts [96].

Recent studies have shown that canines require the presence of an odor cue to successfully determine the direction an individual walked, without the presence of these odor cues, utilizing only the environmental disturbances the canines were unable to correctly determine directionality. It has also been shown that canines need at least five footsteps to determine a change in direction of the path a person walked and ~1-2 seconds for the odor information in footsteps to change to provide enough information for canines to perceive the change [96].

1.8.4. Trailing / Scent Article Canines

There are two types of bloodhounds used in the United States for human scent discrimination: traditional and specialized. Traditional bloodhounds search for matching scent at the beginning of the trail by pacing back and forth, this behavior is then left up to the interpretation of the handler to determine the presence of a matching scent. Specialized bloodhounds provide a yes or no response to the handler at the start of a trail to indicate the presence or absence of matching scent. If matching scent is present in the environment the bloodhound trails, whereas, if no matching scent is present the bloodhound refuses to trail. Because these specially trained bloodhounds provide a yes or no response the canines can be used to aid in criminal investigations. When investigators develop a list of suspects, the specially trained bloodhound-handler team is brought to a location recently visited by the person to conduct a suspect-location check (Figure 7). The canine is presented with a scent sample which was collected from the crime scene; a positive response indicates to the investigator that additional efforts should be exerted to determine the reason that the dogs matched scent from the evidence to the location. This type of positive-scent match is often associated to a resident or frequent visitor to that location whereas a negative response during a location check provides evidence to eliminate the suspect from the investigation [68]. A copy of the standard operating procedure for the Federal Bureau of Investigation's Specialized Blood Hounds can be found in Appendix B.

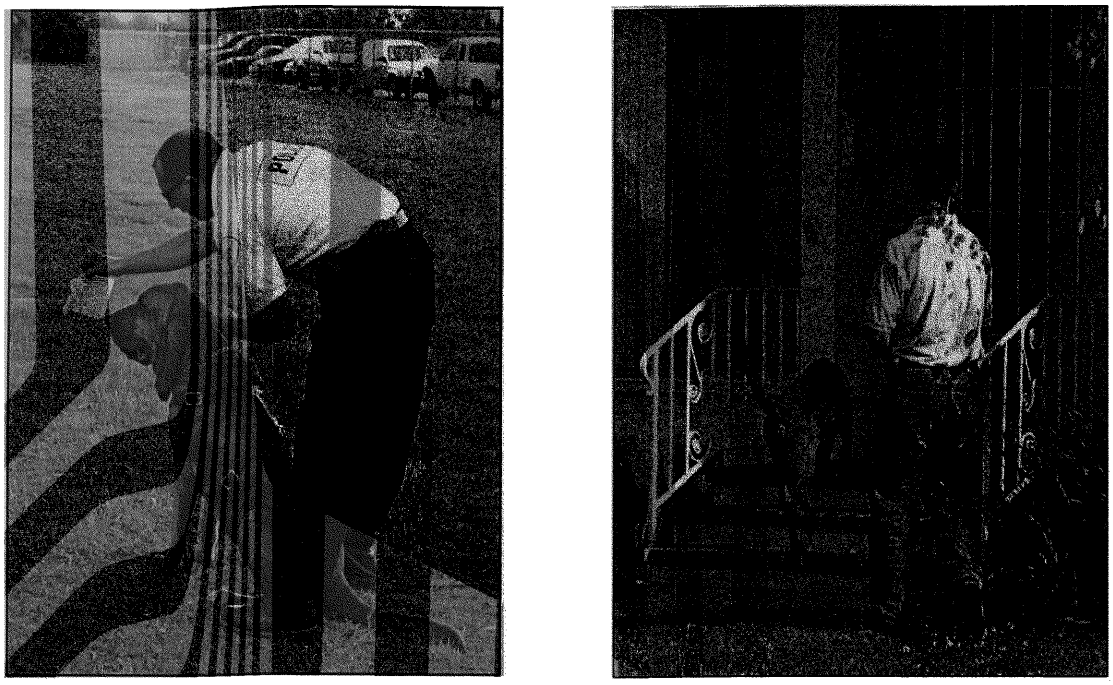


Figure 7: Specialized Bloodhounds Working a Location Check

Limited research has been conducted into the ability of traditionally trained bloodhounds to discriminate the scent of individuals through trailing [97]. In one study, scent was sampled from different areas of the body using a STU-100. The bloodhounds were then presented with trails that varied in cross-contamination from incidental human scent and weather conditions. The search areas utilized in this study included both urban and suburban environments to simulate searches commonly undertaken in criminal investigations. The STU-100 was introduced as a collection device for human scent, and through use of this instrument, the bloodhounds were able to follow the trails to an effective conclusion for investigative purposes.

1.8.5. Human Scent Line-up Canines

A "human scent lineup" is an identification based on a canine matching the human scent collected from a crime scene to a possible suspect. Successful human scent line-ups began in the Netherlands in the mid-1900's, where dogs were asked to smell objects from crime scenes and select the matching odor from objects worn by suspected individuals. Figure 8 is a Dutch artist's rendering a human scent line-up sometime between World War I and World War II. The canine, Albert, is being asked to smell a razor blade used to murder a director of a factory and match it to the caps of different individuals who work in the factory. Today the process for conducting a "human scent line-up" in the Netherlands begins when scent evidence is collected at a crime scene, packaged, and preserved. When a suspect is taken into custody he or she may be asked to submit to a "human scent lineup". The suspect then holds a metal bar in his hands for a period of time, and this metal bar is collected. This metal bar from the suspect along with metal bars that have been held by other individuals and collected at random throughout the population are set up in a sterile room, where the law enforcement certified canine is then exposed to the scent evidence, and allowed to work the line-up of metal bars independently (Figure 9). The order of presentation of the metal bars is determined by rolling dice which correspond to differing placement patterns. The canines are trained and work by a primary reward system, when the dog makes a correct identification the bars is released and the canine is allowed to play with the bar. A scent identification indicates an association between the suspect and the scent evidence. A copy of the standard operating procedure for the Netherlands National Police Human Scent line-ups can be found in Appendix C.

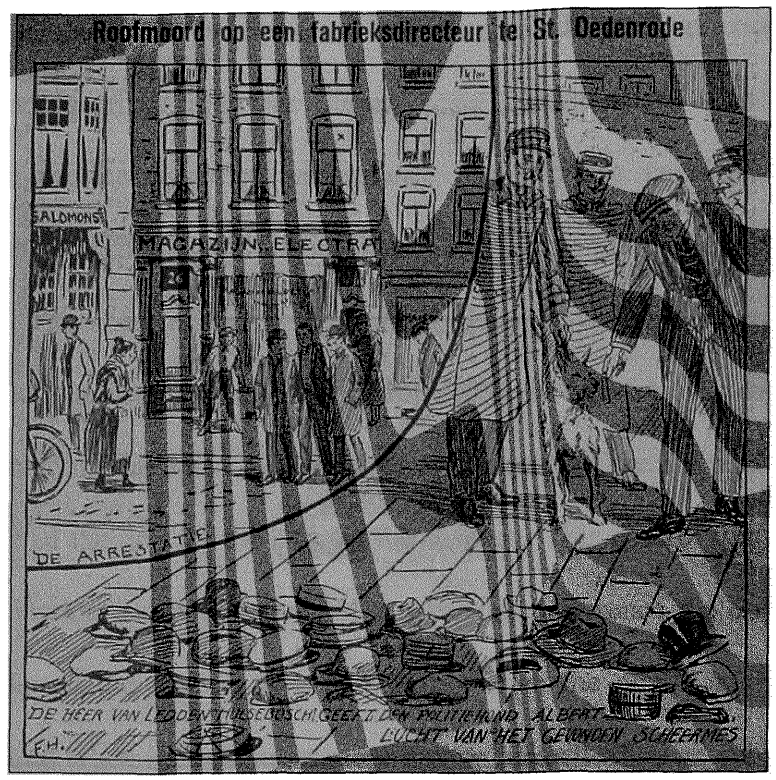


Figure 8: Historical Methods of Human Scent Line-ups as Depicted in a Dutch Newspaper, with permission, Copyright: Netherlands National Police Agency

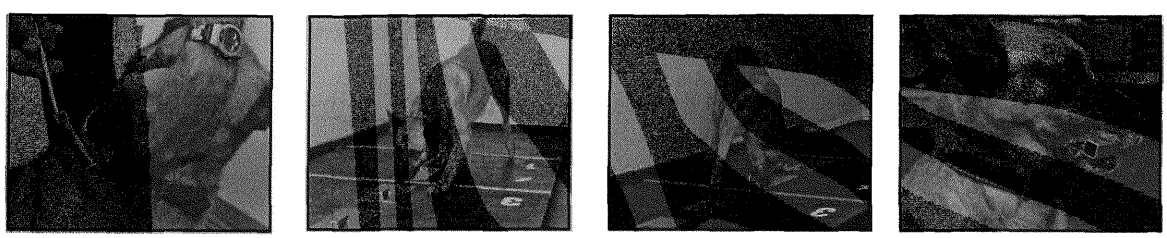


Figure 9: Modern Human Scent Line-up Process at the Netherlands National Police Agency, with permission, Copyright: Netherlands National Police

The experimental design for human scent identifications differs from country to country. Different experimental designs for human scent identification were evaluated and compared [98] on the basis of performance and forensic considerations. It was determined that the experimental set-up does significantly affect the outcomes of scent identifications. The implementation of a control trial as a type of calibration for the dogs proved to provide the best results. The "performance check set-up" shows that the odors in the array, including the odor of the suspect, are neutral for the dog and that there is no prior preference of the dog for the odor of the suspect. This control trial provides that a positive identification is not the result of a particular preference the dog may have, or because the odor of the suspect is very different from the others in the array, which should be required when introducing a scent line-up identification as evidence in a court of law. An assessment of the reliability of scent identifications utilizing this method has been conducted [92] and it has proven to be a useful forensic tool with a high degree of reliability.

1.9. Theory of Instrumental Techniques

1.9.1. Solid Phase Micro-extraction (SPME)

Solid Phase Microextraction (SPME) was developed by Janusz Pawlisyn to address the need for rapid sample preparation in both the laboratory and in the field. This extraction technique is sensitive, selective, and field portable. SPME can be used to sample different mediums, including liquids and gases. There are different types of SPME sampling methods, the one that will be utilized in this research project will be a fused-silica extraction. The silica fiber can have various coatings with varying degrees of

polarity, or the fiber can have a mixture of phases essentially making it applicable to both polar and non-polar analytes. The amount of analyte extracted from the sample is partially dependent on the analyte's affinity to the fiber's coating; making fiber optimization studies an important factor in the extraction. The headspace of the sample is described as the phase above the sample. For headspace extraction to occur the sample must be placed in a sealed container, the fiber is then exposed to the gaseous area above the sample for a certain amount of time, retracted, and then the analytes can be desorbed from the fiber (Figure 10) [99].

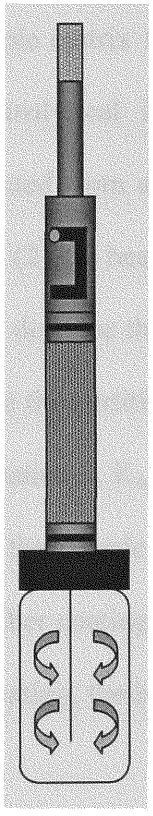


Figure 10: Headspace Extraction Using SPME

Solid Phase Micro-extraction (SPME) utilizes a thin, solid rod composed of fused silica coated with an absorbent polymer. The fiber is protected by a metal sheath, which covers the fiber when it is not in use and this assembly is then placed in a fiber holder. The SPME extraction technique consists of two processes: analytes partitioning between the sample, and the fiber coating and the concentrated analytes desorbing from the fiber into an analytical instrument. Different types of sorbents will extract different types of analytes, and accordingly different types of SPME phases have been created.

Solid phase micro-extraction is a two step extraction process, the partitioning of anlatyes between the fiber coating and the sample matrix followed by desorption of the analytes from the stationary pahse into an analytical instrument. SPME is an equilibrium technique and when a sample is extracted from a sealed vial a three-phase equilibrium exists: (1) the sample to the headspace, (2) the headspace to the fiber, and (3) the fiber to the sample [100]. The equations which describe the equilibrium between the three phases can be seen below. In Equation 2, K_{fh} is the partition coefficient of an anltye between the fiber coating and the headspace. In Equation 3, K_{hs} is the partitioning coefficient between an analyte between the headspace and the sample. In Equation 4, K_{fs} is the partitioning coefficient of an analyte between the fiber coating and the sample. C_f, C_h, and Cs are the concentrations of analyte in the fiber coating, the headspace and the sample, respectively.

$$K_{fh} = C_f / C_h \qquad \textbf{Equation 2}$$

$$K_{hs} = C_h / C_s \qquad \textbf{Equation 3}$$

$$K_{fs} = C_{f/} C_s \qquad \textbf{Equation 4}$$

As result of the aforementioned equilibrium relationships the amount of analyte absorbed by the fiber coating during headspace extraction can be described as follows in Equation 5:

$$N_f = K_{fs}V_fV_sC_o / K_{fs}V_f + K_{hs}V_h + V_s \qquad \textbf{Equation 5}$$

The procedure for headspace sampling using SPME is rather simple. First, the sample is sealed in a closed container with headspace and equilibrium is established between the sample and the headspace. Next, the SPME fiber is inserted into the headspace of the container (there is no contact between the sample and the fiber). The fiber is exposed inside the container for a determined amount of time (until equilibrium is reached). The fiber is then retracted and removed from the vial. The fiber can then be inserted into an inlet of an analytical instrument and heated to promote desorption of the analytes. In a heated GC inlet as the temperature increases, the coating/gas partition coefficients decrease and the fiber coating's ability to retain analytes quickly diminishes [100].

1.9.2. Supercritical Fluid Extraction

When a substance is heated above its critical temperature (Tc) and compressed above its critical pressure (Pc), a single phase is formed and referred to as a supercritical fluid. At

this point, the fluid cannot be liquefied regardless of an increase of pressure. Supercritical fluids portray gas-like diffusivity, low viscosity and zero surface tension. These unique properties allow supercritical fluids to quickly infiltrate into complex sample matrices thereby providing faster extraction rates. For analytical SFE the temperatures normally used fall in the 30-150°C range, which means that the supercritical fluid must be within this range [101]. The best operational extraction parameters for the compounds of interest within a particular sample matrix can be determined by modifying such parameters as pressure, temperature, density, flow rate, and employing the use of modifiers [102]. In contrast to traditional extraction methods such as Soxhlet and steam distillations, SFE methodology eliminates the use of large quantities of hazardous solvents and the costs for their disposal [103].

Carbon dioxide is the primary fluid used in most SFE applications because it has low critical points (T_c = 31.3°C, P_c = 1070psi), both non-toxic and non-flammable, and inexpensive. The drawback to using carbon dioxide lies in the fact that it is a non-polar solvent and thus has limitations when used to extract polar analytes. The addition of a polar solvent, referred to as a modifier, can increase the solvent strength/selectivity of the CO_2.

Supercritical fluid extraction can be divided into two basic categories: the off-line mode and the on-line mode. The off-line mode refers to running an extraction method where the extracted analytes are collected in a device independent of the measurement instrument. The on-line mode involves the extraction technique as well as another

analytical technique such as GC/MS. The on-line mode produces a more concentrated extract to the analytical instrument being utilized and gives the sample less interaction with the environment [104]. Analytical SFE has been applied to a range of different industries. Some of these include food/flavors [103,105,106,107], environmental analysis [108,109, 110], textile finishing [111,112], and pharmaceutical/forensic applications [113,114,115].

1.10. Data Handling

Human odor profiles contain a varying number of compounds depending on the subject being analyzed. Due to the fact that several variables are being measured within each person and among the populations, these analyses yield multivariate data. Multivariate data can be used for differentiation between samples where each is characterized by a set of measurements, or in this case subjects, where each individual's odor profile is characterized by a set of volatile compounds. There are many different methods available for handling multivariate data, including: principle component analysis (PCA) and the Spearman rank correlation-coefficient. PCA is used to reduce a data set and reveal groups within the data, and has been utilized previously [54] to determine seasonal differences in VOCs released by people. A correlation value demonstrates the strength of a relationship between two or more variables. Pattern recognition software may also be a viable means for comparing chromatograms of odor profiles, as has been used previously [43] and described in Section 1.4.1.

Principle component analysis (PCA) is a linear combination method used to reduce a complex data set, from the initial n-dimensional space to a few dimensions. PCA is performed with no information on the classification of the samples, and is based solely on the variance of the data set [116]. PCA involves a mathematical procedure that transforms a number of possibly correlated variables into a smaller number of uncorrelated variables called principal components. Principle components are linear combinations of the original variables, which result in the first principal component accounting for as much of the variability in the data as possible, and each following component accounting for as much of the remaining variability as possible. PCA is used to reduce the dimensionality of a data set and to reveal cluster, common traits within the data [117].

Correlation tests are used to determine relationships between two or more variables. Many correlation determinations require an assumption that the variables have a normal distribution, since that assumption cannot be made in the case of a component of an odor profile nonparametric methods of correlation are required. One of the most used nonparametric methods of measuring correlation is the Spearman rank correlation coefficient. An important concept in nonparametric correlation is assigning an integer value to each variable measured, which is determined by its rank, or size, among the other measurements in the array. One drawback is there is a potential loss of information in replacing the original numbers with ranks. The Spearman correlation is carried out using the ranked arrays of data, which uses a measure of the linear relationship between

two arrays which can be seen from Equation 2, where d is the distance between the ranks and n is the number of variables.

$$r_s = 1 - \frac{6\sum d^2}{n(n^2 - 1)}$$ **Equation 6**

The resulting correlation coefficient will have a value between -1 and +1. A correlation of -1 or +1 will occur if the relationship between the two arrays is linear, whereas a correlation close to zero means there is no linear relationship between the ranks in the array. A confidence interval can then be calculated to determine the significance of the correlations [117].

The null hypothesis which is usually denoted as H_o is the hypothesis which is being tested through the data analysis. In the case of the comparison of odor profiles among a population using the Spearman's rank correlation, the null hypothesis would be that there is not a correlation between the samples and the H_a or alternative hypothesis is that there is a correlation between the samples. The probability of observing a result by chance is usually expressed as a p-value. In any study looking for differences between groups or associations between variables, the likelihood or probability (p) of observing a certain result by chance can be calculated using the t-test. It is not a usual occurrence that an observable difference is true 100% of the time; therefore it is acceptable if a 99% or 95% confidence can be obtained. At a 95% confidence level, there is a less than 5% likelihood that the observed difference occurred by chance, or that the null hypothesis will be

rejected even though it is true. The rejection of a null hypothesis when it is true is called a Type I error; Type 2 errors can also occur and result from retaining the null hypothesis even when it is false [117].

Pattern recognition determinations has been applied to chromatographic peak patterns [43], however, this method may not be the optimal comparison for the peak ratios in human odor. In chromatography peak shape can vary depending on the amount of analyte traveling through the column [118]. The functionality of an analyte may also alter the shape of a resulting peak, for example, acidic compounds generally do not produce Gaussian shaped peaks as interactions may occur between the analyte and the column.

1.11. Research Goals

This research centers on providing scientific analysis of the methods being employed by law enforcement agencies using canines for human scent discriminations. The creation of an instrumental method for the analysis of the volatile organic compounds present in human scent will be applied to the optimization of materials used for the collection and storage of human scent evidence. In addition, a method comparison will be carried out between different techniques for producing analytically clean sorbents for use in human scent collection, including: autoclaving, soxhlet extraction and supercritical fluid extraction. The persistence of human scent when exposed to the environment and within a closed system will also be evaluated. Additionally, a comparison of the volatile organic compounds present in human scent collected from the armpit region and palms of an

individual will lead to determinations as to the types of compounds present in the headspace above secretions produced from different combinations of human secretory glands. A comparison of the compounds present in human odor for an individual over time, and across a population will also be conducted in an attempt to evaluate whether it is possible to differentiate individuals based on the volatile organic compounds above collected odor samples.

2. METHODOLOGY

2.1. Materials

2.1.1. Absorber Materials

The ten different brands of absorbers used in this study include: CKF Super Absorber Cotton Roll (Absorbent Concepts, N. Carolina, USA), DUKAL brand, 100% cotton, sterile, 2X2, 8ply, gauze sponges (DUKAL Corporation, Syosset, NY), Johnson & Johnson sterile small pads 2x2in and 5X9in. sterile dressing (Johnson&Johnson Consumer Company, Inc, Skillman, NJ), Eckerd Sterile Pads (Eckerd Drug Company, Clearwater,FL), IMCO sterile gauze sponges, 2X2in (Independent Medical Co-op, Inc. Daytona Beach, FL), Nexcare Sterile Pads (3M Health Care, St. Paul, MN), Kings Cotton, Hungarian Adsorbers, and Polish absorbers (Dutch National Police). The glass beads were 3 mm, Spherical Soda Lime, Solid Glass Beads (Fisher Scientific, Pittsburg, PA, USA) and the slide covers used were Microscope Glass Slides (Fisher Scientific, Pittsburg, PA, USA).

2.1.2. Cleanser Materials

The twenty-five different types of cleanser used in this study include: Dove unscented moisturizing soap (Unilever, Greenwich, CT), Dove unscented moisturizing body wash (Unilever, Greenwich, CT), Natural, Clear Olive Oil Soap from Life of the Party (North Brunswick, NJ, USA), Natural, Avocado and Cucumber Soap from Life of the Party (North Brunswick, NJ, USA), Dial Pure and Natural, Hypoallergenic bar soap (Dial Corporation, Scottsdale, AZ, USA), Imperial Leather, fresh shower gel (Cussons, Stockport, England), Softsoap Gel, hand soap, antibacterial with moisturizers (Colgate

Palmolive, NY, USA), Olay Beauty Bar, sensitive skin (Proctor & Gamble, Cincinnati, OH, USA), Irish Spring, original deodorant soap (Colgate Palmolive NY, USA), Irish Spring deodorant soap "Icy Blast" (Colgate Palmolive, NY, USA), Irish Spring Micro-clean hand soap (Colgate Palmolive NY, USA), Aveeno, positively radiant cleanser (Johnson & Johnson, Skillman NJ, USA), Vive for Men, Double Action Face Wash (BDF, Wilton, CT, USA), Softsoap Naturals, moisturizing body wash milk and lavender (Colgate Palmolive, NY, USA), Softsoap hand soap, antibacterial, clear with light moisturizers (Colgate Palmolive, NY, USA), Ultra Palmolive Antibacterial, hand soap, with Orange Extracts, (Colgate Palmolive NY, USA), Equate Antibacterial Clear Liquid Soap gentle & mild w/light moisturizers (Vi-Jon Laboratories, Inc. St. Louis, USA), Betres Oatmeal Sensitive Skin (Healthtex Distributors Inc, Miami, FL, USA), Betres Loofah Exfoliant Soap (Healthtex Distributors Inc. Miami, FL, USA), Passion Fruit Organic Soap (Country Rose Soap, Canada), Lavender + Lime Organic Soap (Country Rose Soap, Canada), Emu Oil Soap (Country Rose Soap, Canada), Lemon Orchard Organic (Country Rose Soap, Canada), Liquid Castille Olive Oil Soap (Country Rose Soap, Canada), and Cristallino Olor a Fresa con Cremogen y Glicerina (Hada s.a. Manizales, Colombia).

2.1.3. Storage Materials

Ziploc, Freezer Guard Seal, Pint Size, 7.0"X5.25", (SC Johnson & Sons Inc., Racine, WI, USA). Kapak Heavy Duty SealPAK Pouches, PET//LLDPE, 4.5mils thick, 6.5"X8" (Kapak Corporation, Minneapolis, MN, USA). Kapak Aluminized Pouches, tri-layer polymer chemistry featuring an aluminum film, 6.5"X8", Job# J9539, Lane#2, Box# 056

(Kapak Corporation, Minneapolis, MN, USA). Polyethylene Pouches, 3"X3", 2mil thick, Item# 01-0303-2 (Veripak, Atlanta, GA, USA). The vials used in this study were 10-ml glass, clear, screw top vials with PTFE/Silicone septa (SUPELCO, Bellefonte, PA, USA).

2.1.4. Odor Sampling Materials

The unscented soap used in this study was Dove unscented moisturizing soap (Unilever, Greenwich, CT). The olive oil soap used was Natural, Clear Olive Oil Soap from Life of the Party (North Brunswick, NJ, USA). The vials used in this study were 10-ml glass, clear, screw top vials with PTFE/Silicone septa (SUPELCO, Bellefonte, PA, USA).

2.1.5. Laboratory Materials

SPME fibers used included Carbowax / Divinylbenzene (orange), Polydimethylsiloxane (red), Polydimethylsiloxane / divinylbenzene (blue), Carboxen / Polydimethylsiloxane (black), and Divinylbenzene / Carboxen on Polydimethylsiloxane (DVB/CAR on PDMS) (grey) 50/30um fibers (SUPELCO, Bellefonte, PA, USA). Steel paint cans, quart size, All American Containers (Miami, FL, USA), Activated Charcoal Strips (ACS), Diffusive Flammable Liquid Extraction (DFLEX, Cromwell, Connecticut, USA), Stopper Sleeve, 11mm, natural red rubber, Lot # 1085967-01, Case #075 (Wheaton, Millville, New Jersey, USA). The extraction solvent for the pre-treatment of the gauze pads by supercritical fluid extraction was supercritical grade carbon dioxide (Air Products, Allentown, PA, USA). The methanol used as the modifier for the pre-treatment of the gauze pads was HPLC grade (Fisher Scientific, Pittsburgh, PA, USA). The other solvents used throughout this study include: octanal, 99%, Batch#: 02508MB (Sigma

Aldrich, St Louis, MO, USA), trans-2-nonenal, 97%, Batch#: 09823DC (Sigma Aldrich, St Louis, MO, USA), E,E-2,4-nonadienal, 85+%, Batch #: 06701KO (Sigma Aldrich, St Louis, MO, USA), trans-2-octenal, 94%, Batch #: 05529EO (Sigma Aldrich, St Louis, MO), USA), acetophenone, 99%, Batch #: 07404KC (Sigma Aldrich, St Louis, MO, USA), octanoic acid, 98+% Batch #: 00622JC (Sigma Aldrich, St Louis, MO, USA), benzyl alcohol, anhydrous, 99.8%, Batch #: 03453EC (Sigma Aldrich, St Louis, MO, USA), phenethyl alcohol, 99+%, Batch #: 09131EI (Sigma Aldrich, St Louis, MO, USA), 6-methyl-5-hepten-2-one, 99%, Batch #: 06723DU (Sigma Aldrich, St Louis, MO, USA), heptanal, 95%, Batch #: 14611LB (Sigma Aldrich, St Louis, MO, USA), a-pinene, 99%, Batch #: 00228JI (Sigma Aldrich, St Louis, MO, USA), nonanoic acid, 96%, Batch #: 10021LQ (Sigma Aldrich, St Louis, MO, USA), undecyclic aldehyde, 97%, Batch #: 10226JA (Sigma Aldrich, St Louis, MO, USA), geranylacetone, 96%, Batch #: 08911TA (Sigma Aldrich, St Louis, MO, USA), heptanoic acid, 99%, Batch #: 16130TA (Sigma Aldrich, St Louis, MO, USA), pentadecanoic acid, 99+%, Batch #: 00713LU (Sigma Aldrich, St Louis, MO, USA), phenol, 99+%, Batch #: 11001DC (Sigma Aldrich, St Louis, MO, USA), decanal, minimum 99%, Batch #: 034K1410 (Sigma Aldrich, St Louis, MO, USA), 2-furaldehyde, 99%, Batch #: 03920KB (Sigma Aldrich, St Louis, MO, USA), nonanal, 95%, Batch #: 05223DC (Sigma Aldrich, St Louis, MO, USA), dodecane, anhydrous, 99+%, Batch #: 00654LC (Sigma Aldrich, St Louis, MO, USA), undecane, 99%, Batch #: JV 02708HV (Sigma Aldrich, St Louis, MO, USA), tridecane, 99+%, Batch #: 05419CC (Sigma Aldrich, St Louis, MO, USA), pentadecane, 99+%, Batch #: 15009DB (Sigma Aldrich, St Louis, MO, USA), and hexadecane, 99%, Batch #: 03345PS (Sigma Aldrich, St Louis, MO, USA).

2.2. Instrumental Methods

The instrumentation used for the separation and analysis of the analytes was an Agilent 6970 GC / 5973 MSD. The column used was a HP5-MS, 30 meter, 0.25 μm, 0.25 mm with helium as the carrier gas (flow rate: 1.0 mL/min). The general volatiles method for the GC/MS began when analytes were desorbed in the injection port of the GC with an inlet temperature of 250°C. The GC method begins with an initial oven temperature of 40°C for 5 min., then ramped at 10°C/min until the temperature reaches 300°C, and held at 300°C for 2 min. (total run time: 33 min.). The mass spectrometer used was an HP 5973 MSD with a quadrapole analyzer in full scan mode (range: 50-550). The equipment used was an ISCO Model 260D Syringe Pump with an SFX 2-10 Extractor. The Scanning Electron Microscope (SEM) used was a JEOL JSM 5900LV from and the Field Emission Scanning Electron Microscope used was a JOEL JSM-6330F.

2.3. Comparison of ACS and SPME for the Extraction of Human Scent

2.3.1. Materials

Steel paint cans, quart size, All American Containers (Miami, FL, USA), Activated Charcoal Strips (ACS), Diffusive Flammable Liquid Extraction (DFLEX, Cromwell, Connecticut, USA), Stopper Sleeve, 11mm, natural red rubber, Lot # 1085967-01, Case #075 (Wheaton, Millville, New Jersey, USA).

2.3.2. Methods

The scent was analyzed from socks that had been worn by Male 1 for nine hours on three consecutive days. The six socks were each sealed in a quart sized paint can; to allow for

the SPME extraction a rubber septa was implanted into the lid of each can. Three of the socks were analyzed through ACS-GC/MS and three through SPME-GC/MS. The ACS and SPME extractions were both done for 15 hours and then analyzed. The ACS strips were eluted by soaking the strip in 100 uL of methylene chloride for 30 minutes followed by centrifugation. A DVB/Carboxen on PDMS StableFlex fiber was used for the SPME extraction as it will extract both polar and non-polar compounds. Prior to wear each sock was analyzed using the same method for background purposes. The GC/MS method used has been previously described in Section 2.2.

2.4. Solid Phase Microextraction (SPME) Optimization

2.4.1. Materials

The fiber chemistries evaluated include: carbowax/divinylbenzene (alcohols and polar compounds), Polydimethylsiloxane (nonpolar, semi-volatiles), polydimethylsiloxane/divinylbenzene (volatiles, amines, nitroaromatics), carboxen/polydimethylsiloxane (gases, low molecular weight), and divinylbenzene/carboxen on polydimethylsiloxane (flavors, volatiles, semi-volatiles).

2.4.2. Methods

Male 1 wore five pieces of DUKAL gauze between the foot and sock for ten hours. Each piece of gauze was then placed into a vial and extracted overnight using the orange (Carbowax / Divinylbenzene), red (Polydimethylsiloxane), blue (Polydimethylsiloxane / divinylbenzene), black (Carboxen / Polydimethylsiloxane), and grey (Divinylbenzene / Carboxen on Polydimethylsiloxane) fibers. The exposure time utilized was 15 hours, and

the GC/MS method used was the general volatiles method used was detailed earlier in Section 2.2.

2.5. Evaluation of Different Absorbent Collection Mediums:

2.5.1. Materials

The ten different brands of absorbers used in this study include: CKF Super Absorber Cotton Roll (Absorbent Concepts, N. Carolina, USA), DUKAL brand, 100% cotton, sterile, 2X2, 8ply, gauze sponges (DUKAL Corporation, Syosset, NY) Johnson & Johnson sterile small pads 2x2in and 5X9in. sterile dressing (Johnson&Johnson Consumer Company, Inc, Skillman, NJ), Eckerd sterile pads, 2X2in. (Eckerd Drug Company, Clearwater, FL), IMCO sterile gauze sponges, 2X2in (Independent Medical Co-op, Inc. Daytona Beach, FL), Nexcare sterile pads, 2X2in. (3M Health Care, St. Paul, MN), Kings Cotton, Hungarian Adsorbers, and Polish absorbers (Dutch National Police).

2.5.2. Headspace Analysis Method

In triplicate, each type of absorber was placed into a 10-ml glass, clear, screw top vial with PTFE/Silicone septa (SUPELCO, Bellefonte, PA, USA). Divinylbenzene / Carboxen on Polydimethylsiloxane (DVB/CAR on PDMS) 50/30um fibers (SUPELCO, Bellefonte, PA, USA) were used to extract the compounds present in the headspace above the absorbers contained within the vials. The extractions were done at 15 hours as that has been previously determined to be the optimal extraction time for evaluating collected armpit odor samples. The GC/MS method used for the separation and analysis has been described earlier in Section 2.2.

2.5.3. Scanning Electron Microscope (SEM) and Field Emission Scanning Electron Microscope (FESEM) Imaging of Surface Characteristics of Absorbers

DUKAL, Johnson & Johnson (both 2X2 and STU-100), Polish absorber, Hungarian absorber, and King's Cotton absorbers were cut into a small piece of material. The small pieces were then placed onto an aluminum stub with carbon adhesive. For SEM imaging, the mounted samples were placed into a SPI MODULE Sputter Coater and the gauzes were then coated with gold-palladium. The JOEL JSM-5910LV SEM was then used to image each piece of material at 25X magnification. For FESEM imaging the mounted samples were placed into a PELCO SC-7 Auto Sputter and coated with gold. The JOEL JSM-6330F FESEM was then used to image each piece of material at 500X and 2000X magnification.

2.6. Analysis of Body Odor Collected From Individuals

2.6.1. Comparison of Foot Odor Among Individuals

Materials

All gauze used in this study were DUKAL brand, 100% cotton, sterile, 2X2, 8ply, gauze sponges (DUKAL Corporation, Syosset, NY). The sterile gauze was not subjected to any additional sterilization processes. The vials used in this study were 10-ml glass, clear, screw top vials with PTFE/Silicone septa (SUPELCO, Bellefonte, PA, USA). Prior to use, the glass vials and septa were rinsed with acetone and baked at 210 °C for 48 hours to remove volatile compounds present initially in the vials.

Foot Odor Sampling

The sterile gauze was sealed in 10 mL glass vials, extracted and analyzed to determine which compounds were present initially on the gauze, these compounds present were noted prior to use for background purposes. Five subjects, three females and two males (F1, F2, F3, M2, and M3) wore a piece of DUKAL gauze between their foot and their sock for a period of 9hrs. The gauze was then removed by the subject and returned to the 10-mL glass vial.

Analysis by SPME-GC/MS

The collected body region samples were allowed to sit for 24hours and then extracted using SPME. DVB/Carboxen on PDMS 50/30um fibers (Supelco, Bellefonte, PA, USA) were used to extract the volatile organic compounds from the headspace of the vials containing the gauze. The exposure was done at room temperature for 15 hours. All samples were run using the previously described general volatiles method in Section 2.2.

2.6.2. Comparison of Odor Collected From Different Body Regions

Materials

All gauze used in this study were DUKAL brand, 100% cotton, sterile, 2X2, 8ply, gauze sponges (DUKAL Corporation, Syosset, NY). The sterile gauze was not subjected to any additional sterilization processes. The vials used in this study were 10-ml glass, clear, screw top vials with PTFE/Silicone septa (SUPELCO, Bellefonte, PA, USA). Prior to use, the glass vials and septa were rinsed with acetone and baked at 210 °C for 48 hours to remove volatile compounds present initially in the vials.

Body Region Sampling

The sterile gauze and corresponding safety pin were sealed into a 10 mL glass vial, extracted and analyzed to determine which compounds were present initially on the gauze, these compounds present were noted prior to use for background purposes. Six pieces of gauze were placed in six different regions of the body of Female 3: behind the knee, bottom of the foot, the armpit, the wrist, the crook of the elbow, and the side of the waist. All pieces of gauze except the gauze in the sock were attached to the subject's clothing using safety pins. The gauze which sampled odor obtained from the bottom of the foot was placed between the pad of the foot and the subject's sock. The gauzes were worn for 9 hours and then removed by the subject and placed back into the original 10mL glass vials along with the corresponding safety pins.

Analyses

The collected body region samples were allowed to sit for 24 hrs and then extracted using SPME. DVB/Carboxen on PDMS 50/30um fibers (Supelco, Bellefonte, PA, USA) were used to extract the volatile organic compounds from the headspace of the vials containing the gauze. The exposure was done at room temperature for 15 hours. All samples were run using the previously described general volatiles method in Section 2.2.

2.6.3. Comparison of Armpit Odor from the Left and Right Side of an Individual

Materials

All gauze used in this study were DUKAL brand, 100% cotton, sterile, 2X2, 8ply, gauze sponges (DUKAL Corporation, Syosset, NY). The sterile gauze was not subjected to any

additional sterilization processes. The unscented soap used in this study was Dove unscented moisturizing soap (Unilever, Greenwich, CT). The vials used in this study were 10-ml glass, clear, screw top vials with PTFE/Silicone septa (SUPELCO, Bellefonte, PA, USA). Prior to use, the glass vials and septa were rinsed with acetone and baked at 210 °C for 48 hours to remove volatile compounds present initially in the vials.

Sampling

The sterile gauze and corresponding safety pin were sealed into a 10 mL glass vial, extracted and analyzed to determine which compounds were present initially on the gauze, these compounds present were noted prior to use for background purposes. Male 4 was required to use fragrance free soap and to discontinue the use of deodorant, lotions and perfumes for 48 hours before sampling to minimize the influence of the "tertiary odors" present. A piece of gauze was fastened with a safety pin to the left and right armpit area of Male 4's shirt and worn for 9 hours. After the sampling time was complete the gauze was removed by the subject and placed back into the original 10mL glass vials.

Analyses

The collected armpit samples were allowed to sit for 24 hours and then extracted using SPME. DVB/Carboxen on PDMS 50/30um fibers (Supelco, Bellefonte, PA, USA) were used to extract the volatile organic compounds from the headspace of the vials containing

the gauze. The exposure was done at room temperature for 15 hours. All samples were run using the previously described general volatiles method in Section 2.2.

2.6.4. Comparison of Armpit Sampling Techniques: Worn vs. Wiped

Materials

All gauze used in this study were DUKAL brand, 100% cotton, sterile, 2X2, 8ply, gauze sponges (DUKAL Corporation, Syosset, NY). The sterile gauze was not subjected to any additional sterilization processes. The unscented soap used in this study was Dove unscented moisturizing soap (Unilever, Greenwich, CT). The vials used in this study were 10-ml glass, clear, screw top vials with PTFE/Silicone septa (SUPELCO, Bellefonte, PA, USA). Prior to use, the glass vials and septa were rinsed with acetone and baked at 210 °C for 48 hours to remove volatile compounds present initially in the vials.

Sampling

The sterile gauze were sealed into a 10 mL glass vial, extracted and analyzed to determine which compounds were present initially on the gauze, these compounds present were noted prior to use for background purposes. Male 2 was required to use fragrance free soap and to discontinue the use of deodorant, lotions and perfumes for 48 hours before sampling to minimize the influence of the "tertiary odors" present. A piece of gauze was fastened with a safety pin to the left armpit area of Male 2's shirt and worn for 9 hours. After the sampling time was complete the gauze was removed by the subject and placed back into the original 10 mL glass vials. The following day Male 2 exercised

for 1 hour and then wiped the left armpit area with a piece of sterile gauze, and then returned the gauze to the original 10 mL glass vial.

Analyses

The collected armpit samples were allowed to sit for 24 hours and then extracted using SPME. DVB/Carboxen on PDMS 50/30um fibers (Supelco, Bellefonte, PA, USA) were used to extract the volatile organic compounds from the headspace of the vials containing the gauze. The exposure was done at room temperature for 15 hours. All samples were run using the previously described general volatiles method in Section 2.2.

2.7. Comparison of Odor Profiles Obtained from the Armpit Area of Two Males

2.7.1. Materials

All gauze used in this study were DUKAL brand, 100% cotton, sterile, 2X2, 8ply, gauze sponges (DUKAL Corporation, Syosset, NY). The sterile gauze was not subjected to any additional sterilization processes. The unscented soap used in this study was Dove unscented moisturizing soap (Unilever, Greenwich, CT). The vials used in this study were 10-ml glass, clear, screw top vials with PTFE/Silicone septa (SUPELCO, Bellefonte, PA, USA). Prior to use, the glass vials and septa were rinsed with acetone and baked at 210 °C for 48 hours to remove volatile compounds present initially in the vials.

2.7.2. Sampling

The sterile gauze was sealed in 10 mL glass vials, extracted and analyzed to determine which compounds were present initially on the gauze, these compounds present were noted prior to use for background purposes. The only contact the researcher had with the sterile gauze is when the gauze is sealed initially in the glass vials. In order to reduce contamination powderless latex gloves were worn and contact between the gloves and the gauze was kept to a minimum. Gloves were changed between each piece of gauze that was handled. Two unrelated, twenty-four year old males were evaluated through this study. Subjects used were required to use fragrance free soap and to discontinue the use of deodorant, lotions and perfumes for 48 hours before sampling to minimize the influence of the "tertiary odors" present. In this study, no attempt was made to control the diet of the subjects being sampled. Each subject exercised outdoors for a period of 1 hour wearing a tank top to eliminate compounds present due to the influence of clothing. Each subject then sampled themselves, using a 2 X 2 sterile gauze pad to wipe the armpit area, collect their own sweat, and then re-seal the sample back into the 10 mL glass vial. All samples were stored in the 10 mL vials at room temperature. Subjects were sampled on different days and at different times throughout the same day to evaluate the stability and reproducibility of the resulting scent profile. For intraday sampling the first sample was taken in the morning and the second sample was taken 10 hours later. Interday samplings were all taken prior to 12:00pm. The average humidity and temperature for the days sampling occurred are listed below in Table 9.

Table 9: Average Humidity and Temperature for Samplings of Male 1 and Male 2

SUBJECT	DATE	AVERAGE TEMP. (°F)	AVERAGE HUMIDITY (%)
Male 4, Week 1	4/07/2004	73	63
Male 4, Week 3	4/18/2004	73	62
Male 2	4/10/2004	80	76

2.7.3. Extraction and Analysis of Armpit Samples (SPME-GC/MS)

Each sample was analyzed individually as received. The samples were collected from Male 4 and Male 2, allowed to sit for 24 hours, and then extracted using SPME. DVB/Carboxen on PDMS 50/30um fibers (Supelco, Bellefonte, PA, USA) was used to extract the volatile organic compounds from the headspace of the vials containing the gauze. The exposure was done at room temperature for 15 hours. The GC/MS method has been previously described in Section 2.2.

2.8. Creation of a Method for Producing Analytically Clean Absorber Materials

2.8.1. Materials

DUKAL Sterile Gauze Sponges 2x2, 8-Ply (Dukal Corporation, Hauppauge, NY), Johnson & Johnson Sterile Small Pads 2x2in (Johnson&Johnson Consumer Company, Inc, Skillman, NJ), Eckerd Sterile Pads (Eckerd Drug Company, Clearwater,FL), Nexcare Sterile Pads (3M Health Care, St. Paul, MN), Kings Cotton, Hungarian Adsorbers (Dutch National Police), and sterile eye pad (Kendall Curity, Tyco Health Care Group, Mansfield, MA, USA). Extraction solvents: supercritical grade carbon dioxide (Airgas, Radnor, PA). HPLC grade methanol (Fischer Scientific, Pittsburgh, PA), chloroform

(Fischer Scientific, Pittsburgh, PA), and deionized water. Vials utilized were 10mL clear screw top glass vials with PTFE/Silicone septa (Supelco, Bellefonte, PA) and the solid phase micro-extraction fibers used were Divinylbenzene/Carboxen on PDMS fibers (Supelco, Bellefonte, PA).

2.8.2. Gravity and Steam Re-sterilization

In order to determine whether re-sterilizing gauze pads is an effective route for the removal of compounds initially present on the gauze pad each piece of sterile eye pad (Kendall Curity, Tyco Health Care Group, Mansfield, MA, USA) was cut in half, one piece was placed in a 10mL glass vial and the other was run through either a steam or gravity sterilizer.

The 250 gravity cycle is a 30 minute cycle with a 30 minute dry time. The air in the chamber is removed by introducing steam in the top of the sterilizer chamber which displaces the air out a drain at the bottom of the sterilizer. There is a gauge in the drain that senses when steam starts to enter it. When the steam is sensed by the gauge, the sterilization time begins.

The prevac cycle (vacuum pressurized) is a four minute cycle at 270 °F which starts after the pulsing cycle removes the air from the chamber. The steam enters the chamber from the top and air is removed out the bottom. There is a gauge that monitors when the steam has replaced the air and the sterilization cycle begins. It is a shorter cycle because of the increase in temperature and the efficiency of the steam removal. The dry time for the

prevac cycle is 30 minutes. Dry time is based on ability to get items dry and can vary from 10 minutes to whatever it takes. Variables in the load, such as metal mass, wrapping material, density, etc. affect the dry time. The water is not re-circulated in the sterilizers. They are cleaned weekly with a product called AMSCRUB.

2.8.3. Soxhlet Extraction

In triplicate, a piece of DUKAL gauze ~0.36g was extracted with 200 mL for 9 hours using either methanol or chloroform HPLC grade solvents (Fischer Scientific, Pittsburgh, PA). After the soxhlet extractions were completed, the gauze was placed inside a baked out glass beaker and cover with foil for 24 hours to allow for solvent evaporation, then re-placed inside the 10 mL glass vial for SPME-GC/MS analysis.

2.8.4. Supercritical Fluid Extraction

SFC grade carbon dioxide (Airgas, Radnor, PA) was pressurized by an ISCO Model 260D Syringe Pump attached to an ISCO SFX 2-10 Supercritical Fluid Extractor (ISCO, Lincoln, Nebraska). For the development of the optimal SFE conditions DUKAL brand gauze was used exclusively, as its composition was 100% cotton whereas other materials studied ranged in their composition. A piece of gauze weighing ~0.36g was placed inside a 10 mL SFE cell (ISCO, Lincoln, Nebraska). During the evaluation of the addition of modifiers on extraction efficiency, a modifier was added directly to the extraction cell by pipeting 500 µL onto the gauze pad in the extraction cell. The extraction temperature (36°C, 130°C, and 150°C) within the cell was controlled through use of an ISCO SFE Temperature Controller contained within the SFE Extractor, and an

ISCO Restrictor Temperature Controller was used to maintain temperatures during the dynamic aspect of the extractions. The effect of various pressures on the extraction efficiencies was also evaluated at pressures that included both 2500 and 4500psi. Various static/dynamic time combinations were evaluated including 30/10min and 45/10min. Extraction analytes were not collected or evaluated post extraction. After the extractions the gauzes were removed from the extraction cell, placed inside a 10 mL vial (Supelco, Bellefonte, PA), and headspace analysis was then conducted using SPME-GC/MS as described later in the text. To evaluate of the ruggedness of the optimal SFE conditions, varying sizes and types of materials were run through the SFE and the amount of modifier was scaled-up based on a weight ratio of 500 μL to ~0.36g.

2.8.5. SPME-GC/MS Analysis

Prior to extraction, all materials were placed inside a 10 mL screw-top vial (Supelco, Bellefonte, PA) and a headspace analysis via SPME-GC/MS was conducted utilizing Divinylbenzene/Carboxen on PDMS fibers (Supelco, Bellefonte, PA). The fiber type was chosen in accordance with the optimal fiber for the extraction for human odor samples and the exposure time utilized was fifteen hours, which was determined to be the optimal extraction time for collected armpit odor samples in Section 3.8. All SPME exposures were conducted at room temperature. After extraction, despite the method employed, each gauze pad was then re-placed inside the glass vial used initially for analysis and re-evaluated through the same SPME-GC/MS method. The GC/MS method used has been described previously in Section 2.2.

2.9. Evaluation of Storage Materials Commonly Used to Collect Human Scent

2.9.1. Materials

DUKAL brand, sterile, 2 X 2, 8ply, 100% cotton gauze sponges (DUKAL Corporation, Syosset, NY, USA). 10-ml glass, clear, screw top vials with PTFE/Silicone septa (SUPELCO, Bellefonte, PA, USA). Supercritical grade carbon dioxide (Air Products, Allentown, PA, USA). HPLC grade methanol (Fisher Scientific, Pittsburgh, PA, USA). Ziploc, Freezer Guard Seal, Pint Size, 7.0"X5.25", (SC Johnson & Sons Inc., Racine, WI, USA). Kapak Heavy Duty SealPAK Pouches, PET//LLDPE, 4.5mils thick, 6.5"X8" (Kapak Corporation, Minneapolis, MN, USA). Kapak Aluminized Pouches, tri-layer polymer chemistry featuring an aluminum film, 6.5"X8", Job# J9539, Lane#2, Box# 056 (Kapak Corporation, Minneapolis, MN, USA). Polyethylene Pouches, 3"X3", 2mil thick, Item# 01-0303-2 (Veripak, Atlanta, GA, USA). Divinylbenzene / Carboxen on Polydimethylsiloxane (DVB/CAR on PDMS) 50/30um fibers (SUPELCO, Bellefonte, PA, USA). Maxi Seal, electric heat sealer, Model: MS-8, Power: 310W, Voltage: 120V, Frequency: 60Hz (Premium Balloon Accessories, USA)

2.9.2. Procedure

Prior to use, gauzes were cleaned using a methanol modified supercritical fluid extraction described in Section 3.5.3, placed into 10-ml glass, clear, screw top vials with PTFE/Silicone septa, extracted using Divinylbenzene / Carboxen on Polydimethylsiloxane (DVB/CAR on PDMS) for 15 hours, and then analyzed by gas chromatography / mass spectrometry using the method as described in Section 2.2 to ensure analytical cleanliness. In triplicate, a piece of treated gauze was sealed into each

of the five types of storage materials which include: 10-ml glass, clear, screw top vials with PTFE/Silicone septa, Ziploc, Freezer Guard Seal, Pint Size bags, KPAK Heavy Duty SealPAK Pouches, KPAK Aluminized Pouches, and polyethylene pouches. A heat sealer was used to seal both the KPAK Heavy Duty SealPak and Aluminized pouches as well as the polyethylene, where as the Ziploc, Freezer Guard bags were sealed using the zipper at the top of the bag. These pouches were then allowed to sit for one, two, and five weeks. At the end of the time periods each piece of gauze was removed from its respective storage material and placed back into its original vial using tweezers previously rinsed with a bleach solution and dried. Each stored gauze pad was then re-evaluated using the same SPME-GC/MS method.

2.10. Evaluation of Compounds Present in the Headspace of Different Cleansers

The occurrence of secondary transfer of DNA between people and objects has been observed [119]. The presence of cells are necessary for the recovery of DNA profiles, as an individual comes into contact with an object, there is a transfer of materials and in this case, the transfer of skin cells containing DNA. Skin cells are also considered a substrate/medium for human odor. In order to remove the possibility that the odors analyzed for an individual are a combination of more than one individual through a secondary transfer of cells, it is necessary to incorporate washing of the hands into the sampling strategy.

It has been observed that soaps which claim to be fragrance free appear to have an odor when presented to the human nose. In addition, there is a concern that soaps made from

animal fat may contain components reported to be present in human odor as they are created from a biological material. Studies into fatty acid soap residue on human skin [120] have shown that there is a linear increase of residue with soaping time, and a similar increase with the concentration of calcium in the water (because of the formation of insoluble calcium salts with the acids). These studies have also shown that the increased absorption can be counterbalanced with the increase of rinsing time/decrease of soaping time. A headspace evaluation of the compounds present in the headspace above various brands of soaps and body washes as well as soaps made from differing substrates has been conducted.

2.10.1. Materials

The twenty-five different cleansers evaluated were periously listed in Section 2.1.2. The vials used in this study were 10-ml glass, clear, screw top vials with PTFE/Silicone septa (SUPELCO, Bellefonte, PA, USA).

2.10.2. Methods

In triplicate, an allotment of cleanser materials was placed in a 10ml glass vial. The headspace of each vial containing the cleanser was extracted using DVB/CAR on PDMS 50/30um fibers (SUPELCO, Bellefonte, PA, USA) which were exposed for 5 minutes. The GC/MS method used has been described previously in Section 2.2.

2.11. Determination of the Optimal Extraction Time for Armpit and Hand Odor Samples

2.11.1. Materials

All gauze used were DUKAL brand, 100% cotton, sterile, 2X2, 8ply, gauze sponges (DUKAL Corporation, Syosset, NY, USA) and were treated through the SFE method described in Section 3.5.3 and analyzed through SPME-GC/MS prior to use to ensure analytical cleanliness. The soap used was Natural, Clear Olive Oil Soap from Life of the Party (North Brunswick, NJ, USA). The vials used to hold the gauze were 10ml glass, clear, screw top vials with PTFE/Silicone septa (SUPELCO, Bellefonte, PA, USA). The extraction solvent used was supercritical grade carbon dioxide (Air Products, Allentown, PA, USA).

2.11.2. Armpit Sampling Procedure

A male subject (Male 6) and a female subject (Female 2) were required to use the olive oil soap and directed to shower at least twice using the provided soap during the 48 hour period prior to sampling. The subjects were also instructed to discontinue the use of deodorants, lotions, and perfumes for at least 48 hours before sampling to minimize the influence of "tertiary odors" present. No attempt was made to control the diet of the subjects being sampled. Each subject exercised outdoors for a period of 100min while wearing a tank top in order to minimize the influence of compounds present due to the influence of clothing. Subjects sampled themselves with a pre-treated 2 X 2 sterile gauze pad each 20 minutes for a total of five samples collected for each subject. The subjects were instructed to wipe the armpit area to collect their own sweat and then re-

seal the sample back into the 10 ml glass vial. All samples were stored in the 10 ml vials at room temperature, and allowed to sit for approximately 24 hours prior to extraction. These storage conditions were chosen to simulate the conditions under which odor is collected for canine evaluation purposes, and no attempt was made to control microbial interactions with the substrate as it may make contributions to the overall odor profile.

2.11.3. Hand Sampling Procedure

Five samples each were collected from Male 6 and Female 2 consecutively following a set sampling procedure. Subjects were required to wash hands and forearms using olive oil soap for 30 seconds and rinse with cool water for two minutes, air dry for two minutes, and rub the palms of hands over forearms for five minutes followed by ten minutes of holding gauze between the palms of the hands. Each subject sampled themselves, using a pre-treated 2 X 2 sterile gauze pad, and then re-sealing the sample back into the 10 ml glass vial. All samples were stored in the 10 ml vials at room temperature. The scent samples were allowed to sit for approximately 24 hours prior to extraction.

2.11.4. SPME-GC/MS Analysis

DVB/CAR on PDMS 50/30um fibers (SUPELCO, Bellefonte, PA, USA) were used to extract the VOCs from the headspace of the vials containing the gauze, it was previously determined to be the best fiber chemistry. During optimization, the odor exposures were done at room temperature on multiple samples from Male 1 for 3, 6, 12, and 15 hours for

armpit odor and 12, 15, 18, 21, 24 hours for hand odor. All samples were run using the GC/MS method previously described in Section 2.2.

2.12. Evaluation of the Effect of Washing the Hands Prior to Sampling

2.12.1. Materials

Gauze pads used were DUKAL brand, 100% cotton, sterile, 2 X 2, 8 ply, gauze sponges (DUKAL Corporation, Syosset, NY, USA) and treated prior to use through the SFE method described in Section 3.5.3 and these materials were analyzed by SPME-GC/MS to ensure analytical cleanliness. The vials used to hold the gauze were 10-ml glass, clear, screw top vials with PTFE/Silicone septa (SUPELCO, Bellefonte, PA, USA). The soap used was Natural, Clear Olive Oil Soap from Life of the Party (North Brunswick, NJ, USA). The extraction solvent for the pre-treatment of the gauze pads by supercritical fluid extraction was supercritical grade carbon dioxide (Air Products, Allentown, PA, USA). The methanol used as the modifier for the pre-treatment of the gauze pads was HPLC grade (Fisher Scientific, Pittsburgh, PA, USA).

2.12.2. Methods

Six subjects were evaluated: three males and three females ranging in age from 21-28 years old. Each subject was sampled twice, the first sample was collected without washing and the second was collected immediately following the first utilizing the washing sampling procedure. The protocol for the first sampling (which did not include washing) was as follows: a pre-treated 2 X 2 sterile gauze pad was removed from the 10 ml glass vial using tweezers previously rinsed with a 10% bleach solution and placed in

the palms of the subject's hands, the subjects then sampled themselves by holding the pre-treated gauze between the palms of their hands, walking outdoors for ten minutes and then re-sealing the sample back into the 10 ml glass vial. The protocol for the second sampling (which included washing) was as follows: thirty seconds of washing the hands and forearms with olive oil based soap, two minutes of rinsing the areas with cool water, two minutes of air drying, and followed by five minutes of rubbing the palms of the hands over the forearms. A pre-treated 2 X 2 sterile gauze pad was then removed from the 10 ml glass vial using tweezers previously rinsed with a 10% bleach solution and placed in the palms of the subject's hands. The subjects then sampled themselves by holding the pre-treated gauze between the palms of their hands, walking outdoors for ten minutes and then re-sealing the sample back into the 10 ml glass vial. All samples were stored in the 10 ml vials at room temperature, and allowed to sit for approximately 24 hours prior to extraction. These storage conditions were chosen to simulate the conditions under which odor is collected for canine evaluation purposes, and no attempt was made to control microbial interactions with the substrate as it may make contributions to the overall odor profile.

2.12.3. Extraction and Analysis of Hand Odor Samples (SPME-GC/MS)

DVB/CAR on PDMS fibers were used to extract the volatile organic compounds from the headspace of the vials containing the scented gauze. Exposures were conducted at room temperature for 21 hours, which was previously determined in Section 3.8 to be the optimal extraction time for hand odor samples. The GC/MS instrumentation and method listed previously in Section 2.2 was used for the analysis of all twelve samples studied

here. All gauzes were pre-treated using SFE and extracted using the SPME-GC/MS method prior to use to assure their analytical cleanliness.

2.12.4. Approximation of the Amount of Volatile Organic Compounds Extracted by Headspace SPME

A 1000ppm standard solution was created which contained eight compounds, including 2-furancarboxaldehyde, nonane, 5-methyl-6-hepten-2-one, benzyl alcohol, nonanal, dodecane, decanal, and 6,10-dimethyl-5,9-undecadiene-2-one. Serial dilutions were conducted using the standard solution to create standards of 500, 100, 50, 25, and 10ppm concentrations. These solutions were then injected into the GC/MS with the aid of an autosampler (7683 Series Injector, Hewlet Packard) and a liquid injection liner. The same instrumental conditions were employed as listed in Section 2.2, and ten replicates of each solution were run.

2.13. Population Anlysis of the Volatile Organic Compounds Present Above Collected Odor Samples

2.13.1. Evaluation of the Compounds Present in Armpit Odor among Ten Individuals

Materials

Gauze pads used were DUKAL brand, 100% cotton, sterile, 2 X 2, 8ply, gauze sponges (DUKAL Corporation, Syosset, NY, USA) and were treated prior to use through the SFE method described in Section 3.5.3 and analyzed through SPME-GC/MS to ensure analytical cleanliness. The vials used to hold the gauze were 10-ml glass, clear, screw

top vials with PTFE/Silicone septa (SUPELCO, Bellefonte, PA, USA). The extraction solvent for the pre-treatment of the gauze pads by supercritical fluid extraction was supercritical grade carbon dioxide (Air Products, Allentown, PA, USA). The methanol used as the modifier for the pre-treatment of the gauze pads was HPLC grade (Fisher Scientific, Pittsburgh, PA, USA). The soap used by the subjects to wash all areas of the body was Natural, Clear Olive Oil Soap from Life of the Party (North Brunswick, NJ, USA).

Method for Armpit Sampling

Ten subjects were evaluated: five males M2, M4, M5, M6 and M7 and five females F2, F4, F5, F6, and F7. Male 5 was 17 years of age and Male 6 was 22 years of age. Female 4 and Female 5 were both 21 years of age and Female 7 was 23 years of age. Male 2, Male 4, Female 2, and Female 6 were 24 years of age, while Male 7 was 28 years old. It is relevant to note that F6 and F7 are sisters who live in the same household. Subjects were required to use the olive oil soap and directed to shower at least twice using the provided soap during the 48 hour period prior to sampling. The subjects were also instructed to discontinue the use of deodorants, lotions, and perfumes for at least 48 hours before sampling to minimize the influence of "tertiary odors" present. No attempt was made to control the diet of the subjects being sampled. Each subject exercised outdoors for a period of 30 minutes while wearing a tank top in order to minimize the influence of compounds present due to the influence of clothing. Subjects sampled themselves with a pre-treated 2 X 2 sterile gauze pad. The subjects were instructed to wipe the armpit area to collect their own sweat and then re-seal the sample back into the 10 ml glass vial. All

samples were stored in the 10 ml vials at room temperature, and allowed to sit for approximately 24 hours prior to extraction. These storage conditions were chosen to simulate the conditions under which odor is collected for canine evaluation purposes, and no attempt was made to control microbial interactions with the substrate as it may make contributions to the overall odor profile. The climatic conditions present during the samplings included an average temperature of 73 °F and an average humidity of 77%.

Extraction and Analysis of Odor Samples (SPME-GC/MS)

Divinylbenzene / Carboxen on Polydimethylsiloxane (DVB/CAR on PDMS) 50/30um fibers (SUPELCO, Bellefonte, PA, USA) were used to extract the volatile organic compounds from the headspace of the vials containing the gauze. The exposure for armpit samples was done at room temperature for 15 hours that was previously determined to be the best extraction time based on number and abundance of compounds seen. The GC/MS method has been described earlier in Section 2.2.

2.13.2. Evaluation of the Components of Hand Odor among Sixty Individuals

Materials

Supercritical fluid extraction (SFE) using methanol modified carbon dioxide was used as a pretreatment for the gauze that creates an analytically clean collection medium and the method is described in Section 3.5.3. Gauze pads were DUKAL brand, sterile, 2 X 2, 8ply, gauze sponges (DUKAL Corporation, Syosset, NY, USA). The vials used to hold the gauze were 10-ml glass, clear, screw top vials with PTFE/Silicone septa (SUPELCO, Bellefonte, PA, USA). The extraction solvent for the pre-treatment of the gauze pads by

supercritical fluid extraction was supercritical grade carbon dioxide (Air Products, Allentown, PA, USA). The methanol used as the modifier for the pre-treatment of the gauze pads was HPLC grade (Fisher Scientific, Pittsburgh, PA, USA). The soap used by the subjects to wash the hands and forearms was Natural, Clear Olive Oil Soap from Life of the Party (North Brunswick, NJ, USA).

Method for Hand Odor Sampling

Sixty subjects were evaluated: thirty males and thirty females ranging in age from 17-28 years old. The sampling protocol was as follows: 30 seconds of washing the hands and forearms with olive oil based soap, 2 min of rinsing the areas with cool water, 2 min of air drying, and followed by 5 min of rubbing the palms of the hands over the forearms. A pre-treated 2 X 2 sterile gauze pad was then removed from the 10 ml glass vial using tweezers previously rinsed with a 10% bleach solution and placed in the palms of the subject's hands. The subjects then sampled themselves by holding the pre-treated gauze between the palms of their hands, walking outdoors for 10 min and then re-sealing the sample back into the 10 ml glass vial. All samples were stored in the 10 ml vials at room temperature, and allowed to sit for approximately 24 hrs prior to extraction. These storage conditions were chosen to simulate the conditions under which odor is collected for canine evaluation purposes, and no attempt was made to control microbial interactions with the substrate as it may make contributions to the overall odor profile. The climatic conditions present during the samplings included an average temperature of 80 °F and an average humidity of 76%.

DVB/CAR on PDMS fibers were used to extract the volatile organic compounds from the headspace of the vials containing the scented gauze. Exposures were conducted at room temperature for 21 hours, which was previously determined in Section 3.8 to be the optimal extraction time for hand odor samples. The GC/MS instrumentation and method listed previously in Section 2.2 was used for the analysis of all sixty samples studied here. All gauzes were pre-treated using SFE and extracted using the SPME-GC/MS method prior to use to assure their analytical cleanliness.

2.14. Evaluation of Odor Profiles of Individuals Over Time

2.14.1. Materials

Gauze pads used were DUKAL brand, 100% cotton, sterile, 2 X 2, 8 ply, gauze sponges (DUKAL Corporation, Syosset, NY, USA) and treated prior to use through the SFE method described in Section 3.5.3 and these materials were analyzed by SPME-GC/MS to ensure analytical cleanliness. The vials used to hold the gauze were 10-ml glass, clear, screw top vials with PTFE/Silicone septa (SUPELCO, Bellefonte, PA, USA). The soap used was Natural, Clear Olive Oil Soap from Life of the Party (North Brunswick, NJ, USA). The extraction solvent for the pre-treatment of the gauze pads by supercritical fluid extraction was supercritical grade carbon dioxide (Air Products, Allentown, PA, USA). The methanol used as the modifier for the pre-treatment of the gauze pads was HPLC grade (Fisher Scientific, Pittsburgh, PA, USA).

2.14.2. Method for Armpit Sampling

Three unrelated male subjects were evaluated: M4, M2, and M5. Subjects were required to use the olive oil soap and directed to shower at least twice using the provided soap during the 48 hour period prior to sampling. The subjects were also instructed to discontinue the use of deodorants, lotions, and perfumes for at least 48 hours before sampling to minimize the influence of "tertiary odors" present. No attempt was made to control the diet of the subjects being sampled. Each subject exercised outdoors for a period of thirty minutes while wearing a tank top in order to minimize the influence of compounds present due to the influence of clothing. Subjects sampled themselves with a pre-treated 2 X 2 sterile gauze pad. The subjects were instructed to wipe the armpit area to collect their own sweat and then re-seal the sample back into the 10 ml glass vial. All samples were stored in the 10 ml vials at room temperature, and allowed to sit for approximately 24 hours prior to extraction. These storage conditions were chosen to simulate the conditions under which odor is collected for canine evaluation purposes, and no attempt was made to control microbial interactions with the substrate as it may make contributions to the overall odor profile. Samples were collected on a weekly interval and the average climatic conditions present during the samplings included an average temperature of 73 °F and an average humidity of 77%.

2.14.3. Method for Hand Odor Sampling

Six subjects were evaluated intra-day: two males and four females ranging in age from 17-28 years old. Two females and one male were evaluated through inter-day sampling. The sampling protocol was as follows: thirty seconds of washing the hands and forearms

with olive oil based soap, two minutes of rinsing the areas with cool water, two minutes of air drying, and followed by five minutes of rubbing the palms of the hands over the forearms. A pre-treated 2 X 2 sterile gauze pad was then removed from the 10 ml glass vial using tweezers previously rinsed with a 10% bleach solution and placed in the palms of the subject's hands. The subjects then sampled themselves by holding the pre-treated gauze between the palms of their hands, walking outdoors for ten minutes and then re-sealing the sample back into the 10 ml glass vial. All samples were stored in the 10 ml vials at room temperature, and allowed to sit for approximately 24 hours prior to extraction. These storage conditions were chosen to simulate the conditions under which odor is collected for canine evaluation purposes, and no attempt was made to control microbial interactions with the substrate as it may make contributions to the overall odor profile. Samples were collected both intra-day and interday, and the average climatic conditions present during the samplings included an average temperature of 73 °F and an average humidity of 77%.

2.15. Persistance of Collected Human Scent

2.15.1. Scent Weight Dissipation

Materials

Several different absorbent mediums were evaluated in this study. All gauze used in this study were DUKAL brand, 100% cotton, sterile, 2X2, 8ply, gauze sponges (DUKAL Corporation, Syosset, NY). The sterile gauze was not subjected to any additional sterilization processes. The glass beads were 3mm, Spherical Soda Lime, Solid Glass Beads (Fisher Scientific, Pittsburg, PA, USA). Microscope Glass Slides (Fisher

Scientific, Pittsburg, PA, USA) were also compared as potential scent storage mediums. A Metler AE 240 Analytical Balance was used to determine the mass of each gauze and glass slide cover sample, and an analytical microbalance (CAHN C-33, serial number: 77536, San Diego, CA, USA) was used for the glass beads. Samples were stored in sterile plastic specimen dishes.

Method

Each absorbent material sample was subjected to similar treatment to ensure accuracy of results. Female 1, Female 2, and Male 1 were asked to rinse their hands vigorously in deionized water for five minutes, and then asked to wait five minutes before handling an absorbent medium. For the gauze samples, subjects were asked to roll the gauze between their hands for five minutes. The glass bead samples were collected by asking the subjects to roll the beads between their hands for five minutes. The glass slide covers could not be rolled, so the subjects were asked to hold the slide covers firmly between the forefinger and thumb for five minutes.

After the five minutes of scenting had elapsed, the objects were allowed to sit for fifteen minutes to cool, and then weighed again. Mass by difference was used to determine the initial scent weights present on the gauze, slide covers and beads. The scented materials along with non-scented representative reference materials were left open to the atmosphere in uncovered plastic containers inside an open cardboard box within an air-conditioned room and weighed for eighty-four days. The reference materials were used to account for environmental changes such as humidity, and any weight changes in the

reference materials were subtracted from the weights of the scented materials. Since the reference materials were stored under the same conditions as the scented materials, the environmental factors affecting the weights of the scented materials equally affected the reference materials. All changes in weight of the reference materials can be attributed to environmental factors, as it was handled with powderless latex gloves while being weighed on a clean analytical balance. Gloves were discarded after each weighing.

Each sample was placed in a separate plastic bowl, which was then placed in a large cardboard box left open to the environment. In addition to the three samples collected from three different people, a blank sample was included in the box to correct for environmental factors during the experiment. Despite attempts to avoid the influence of environmental factors by placing the experiment box in a secluded area, some variation is inevitable. The blank samples can be considered 'of constant weight', so any variation in these samples is strictly from environmental factors.

2.15.2. Solid Phase Micro-extraction of Collected Hand Odor Samples Over Time

Materials

Supercritical fluid extraction (SFE) using methanol modified carbon dioxide was used as a pretreatment for the gauze that creates an analytically clean collection medium and the method is described in Section 3.5.3. Gauze pads were DUKAL brand, sterile, 2 X 2, 8ply, gauze sponges (DUKAL Corporation, Syosset, NY, USA). The vials used to hold the gauze were 10-ml glass, clear, screw top vials with PTFE/Silicone septa (SUPELCO, Bellefonte, PA, USA). The extraction solvent for the pre-treatment of the gauze pads by

supercritical fluid extraction was supercritical grade carbon dioxide (Air Products, Allentown, PA, USA). The methanol used as the modifier for the pre-treatment of the gauze pads was HPLC grade (Fisher Scientific, Pittsburgh, PA, USA). The soap used by the subjects to wash the hands and forearms was Natural, Clear Olive Oil Soap from Life of the Party (North Brunswick, NJ, USA).

Method for Hand Odor Sampling

Hand odor samples Female 5 and Female 7 were evaluated after colletion over a time period of twenty-eight days. The sampling protocol was as follows: thirty seconds of washing the hands and forearms with olive oil based soap, two minutes of rinsing the areas with cool water, two minutes of air drying, and followed by five minutes of rubbing the palms of the hands over the forearms. A pre-treated 2 X 2 sterile gauze pad was then removed from the 10 ml glass vial using tweezers previously rinsed with a 10% bleach solution and placed in the palms of the subject's hands. The subjects then sampled themselves by holding the pre-treated gauze between the palms of their hands, walking outdoors for ten minutes and then re-sealing the sample back into the 10 ml glass vial. All samples were stored in the 10 ml vials at room temperature, and allowed to sit for approximately 24 hours prior to extraction. These storage conditions were chosen to simulate the conditions under which odor is collected for canine evaluation purposes, and no attempt was made to control microbial interactions with the substrate as it may make contributions to the overall odor profile. The climatic conditions present during the samplings included an average temperature of 80 °F and an average humidity of 76%.

Extraction and Analysis of Hand Odor Samples (SPME-GC/MS)

DVB/CAR on PDMS fibers were used to extract the volatile organic compounds from the headspace of the vials containing the scented gauze. Exposures were conducted at room temperature for 21 hours, which was previously determined in Section 3.8 to be the optimal extraction time for hand odor samples. The GC/MS instrumentation and method listed previously in Section 2.2 was used for the analysis of all sixty samples studied here. All gauzes were pre-treated using SFE and extracted using the SPME-GC/MS method prior to use to assure their analytical cleanliness.

3. RESULTS & DISCUSSION

3.1. Comparison of ACS and SPME for the Extraction of Human Scent

SPME proved to be superior not only in the abundance of compounds extracted but also the number of compounds extracted as can be seen from Table 10. As can be seen from Figure 11, parallel comparison of activated charcoal strip and solid phase micro-extraction reveal SPME to be the more sensitive and better suited extraction technique for the analysis of human scent. Also, due to the presence of a high background and the size of the socks, a smaller less compound heavy collection material would be more ideal for use as a collection medium.

3.2. Solid Phase Micro-extraction (SPME) Optimization

3.2.1. Fiber Chemistries

The fiber chemistries evaluated include: carbowax/divinylbenzene (alcohols and polar compounds), Polydimethylsiloxane (nonpolar, semi-volatiles), polydimethylsiloxane/divinylbenzene (volatiles, amines, nitroaromatics), carboxen/polydimethylsiloxane (gases, low molecular weight), and divinylbenzene/carboxen on polydimethylsiloxane (flavors, volatiles, semi-volatiles). Table 11 displays the human compounds which were extracted in the headspace of the scented gauze using the different fiber chemistries of DVB/CAR/PDMS, CAR/PDMS, and PDMS/DVB. Table 11 does not list PDMS or CW/DVB as they did not extract any human compounds from the headspace. The two fiber types which preformed the best were the carboxen/polydimethylsiloxane (CAR/PDMS) and the divinylbenzene/carboxen on polydimethylsiloxane (DVB/CAR/PDMS), which respectively extracted two and

seven previously reported human compounds. DVB/CAR/PDMS has revealed itself as the optimal fiber type for the extraction of human compounds from collected scent samples by extracting the largest number of compounds.

Table 10: Comparison of Compounds Extracted Between ACS and SPME of Worn Socks

	Sampling Method					
Human Compounds Extracted	**ACS S1**	**ACS S2**	**ACS S3**	**SPME S1**	**SPME S2**	**SPME S3**
1,3,5,7-Cyclooctatetraene					X	
1,6-Octadien-3-ol, 3,7-dimethyl-				X		
1-Pentadecene				X		X
2-Decanone						X
2-Hexanone						X
4-Heptanone						X
5,9-Undecadien-2-one, 6,10-dimethyl-				X	X	X
6-methyl-5-hepten-2-one	X	X	X			
Acetic acid, phenylmethyl ester					X	
Acetophenone				X	X	X
Benzene, 1,2,4-trimethyl-					X	
Benzene, 1-methyl-2-(1-methylethyl)-						X
Disulfide, dimethyl				X		X
Eicosane				X	X	X
Heneicosane	X		X			
Naphthalene				X		
Phenol				X	X	X
Pyrazine						X
Pyrazine, trimethyl-	X					
Trisulfide, dimethyl			X	X		X
Total Number of Other Compounds Extracted	**8**	**8**	**10**	**25**	**32**	**30**

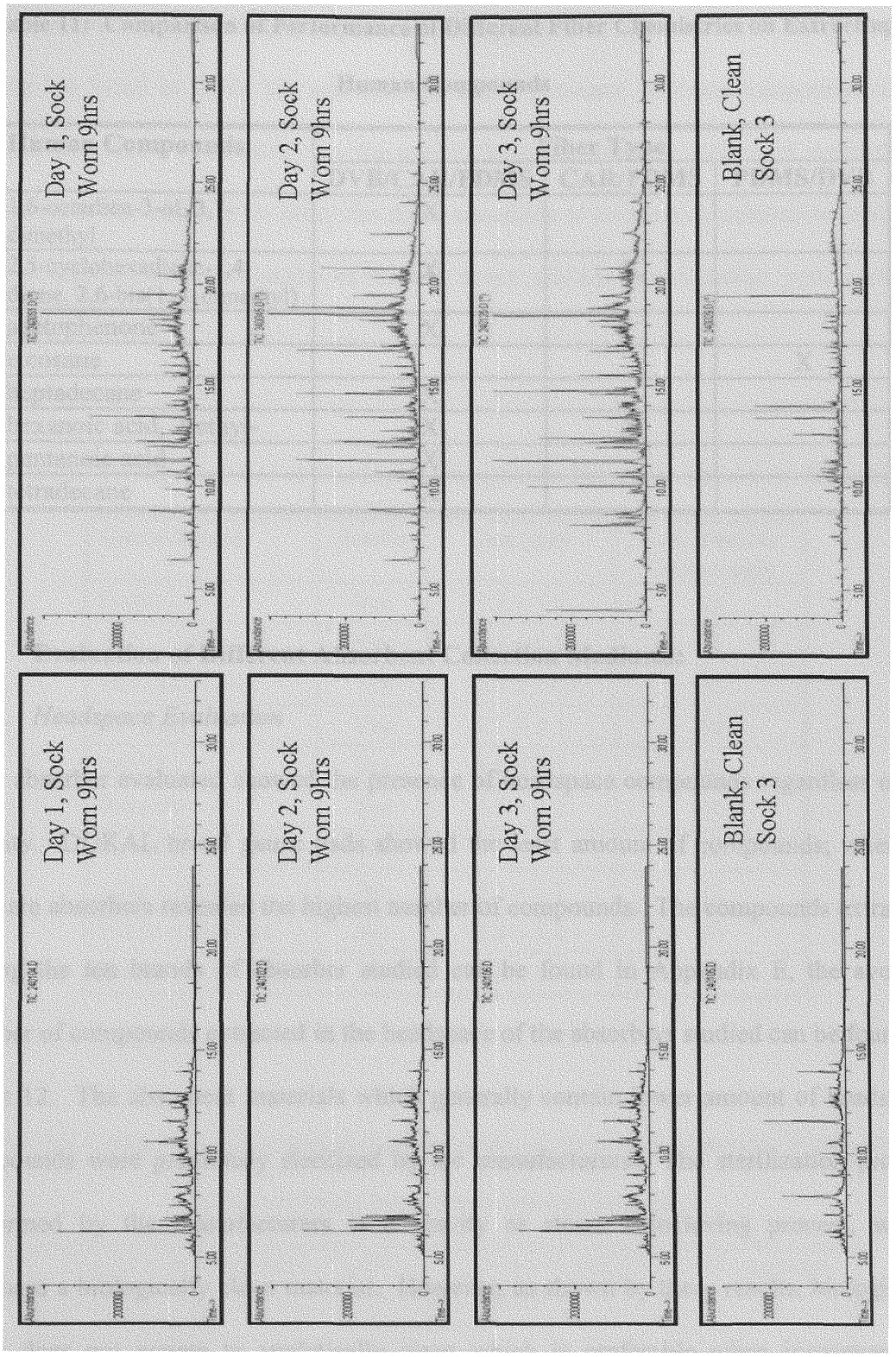


Figure 11: ACS vs. SPME for the Extraction of Foot Odor from Worn Socks

Table 11: Comparison of Performance of Different Fiber Chemistries on Extracting Human Compounds

Human Compounds	Fiber Type		
	DVB/CAR/PDMS	CAR/PDMS	PDMS/DVB
1,6-octadien-3-ol, 3,7-dimethyl	X		
2,5-cyclohexadiene-1,4-dione, 2,6-bis(1, 1-dimethyl)	X	X	
acetophenone	X		
eicosane			X
heptadecane	X		
hexanoic acid, 2-ethyl-	X	X	
pentanoic acid	X		
tetradecane	X		

3.3. Evaluation of Different Absorbent Collection Mediums:

3.3.1. Headspace Evaluation

Each absorber evaluated showed the presence of headspace compounds regardless of its sterility. DUKAL brand gauze pads showed the least amount of compounds; whereas, Nexcare absorbers revealed the highest number of compounds. The compounds extracted among the ten brands of absorber studied can be found in Appendix E, the average number of compounds extracted in the headspace of the absorbers studied can be found in Table 12. The absorbent materials which generally contain lower amount of headspace compounds were previously sterilized by the manufacturers. The sterilization process preformed by the manufacturers is a gravity or steam autoclaving process, which produces a biologically clean material. However, as shown by these results, biologically clean does not equate to analytically clean which is preferable when instrumentally analyzing human scent. Many of the compounds extracted in the headspace of these

absorbers have been previously reported as components of human secretions (Appendix D) and are listed in Table 13, and thus the initial presence of these compounds in the material is a serious limitation for the use of these materials as collection mediums of human scent for analysis. In order for these absorbers to be used as collection materials for the instrumental evaluation of human scent addition sterilization processes are necessary.

Table 12: Average Number of Headspace Compounds Present in Absorbent Materials

Gauze Brand	Sterile	Size (cm)	Ave. Number Compounds
Dukal	Yes	5.1 x 5.1	12
J&J	Yes	5.1 x 5.1	17
J&J (STU-100)	Yes	12.7 x 22.9	43
Nexcare	Yes	5.1 X 5.1	58
IMCO	Yes	5.1 X 5.1	45
Eckerds	Yes	5.1 x 5.1	19
Cotton Roll	No	N/A	38
King's Cotton	No	5.1 x 5.1	22
Polish Absorbers	No	5.1 x 5.1	35
Hungarian Cotton	No	5.1 x 5.1	29

Table 13: Compounds Extracted in the Headspace of Absorbent Materials Which Have Been Previously Reported in Human Secretions

Examples of Compounds PRESENT IN HUMAN SECRETIONS Extracted from ABSORBERS		
Nonanal	Tetradecane	Undecanal
Decanal	Heptadecane	Cyclotetradecane
Hexadecane	Phenol	Nonadecane
2-ethyl-hexanoic acid	Benzyl alcohol	2-butoxy-ethanol

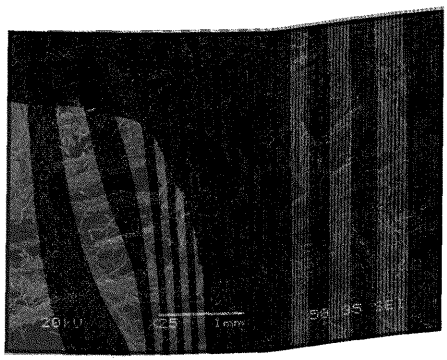
3.3.2. SEM Imaging for Surface Characteristics

Table 14 lists the various absorber brands evaluated through this study along with their fiber composition initial sterilization methods used prior to distribution. As can be seen from Figure 12, Figure 13, Figure 14 at 25X magnification each of the absorbers studied showed different surface characteristics. Various weaving techniques produce differing pore sizes which can be seen among the six types of absorbers. The pore size of an absorber may affect its ability to collect and retain human scent. The hypothesis that human scent is deposited into the environment through rafts carrying skin cells suggests that the pore size of a collection material may prove to be a limiting factor in effective human scent collection and retention over time. The magnifications of 500X and 2000X also demonstrate the differences between the fiber types used within the various gauzes.

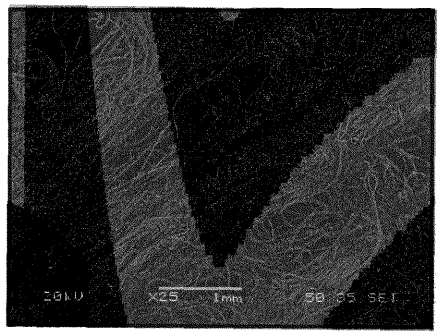
Table 14: Properties of Sorbents

Brand Name	**Textile Material**	**Initial Sterilization Method**
Dukal	100% Cotton	Gamma Radiation
Eckerd	70% Rayon, 30% polyester-cotton mix	Ethylene Oxide
Nexcare	Polypropylene/wood fiber	Ethylene Oxide
Johnson & Johnson	Rayon/polyester/cellulose	Autoclave / Gamma Radiation
King's Cotton	100% Cotton	None

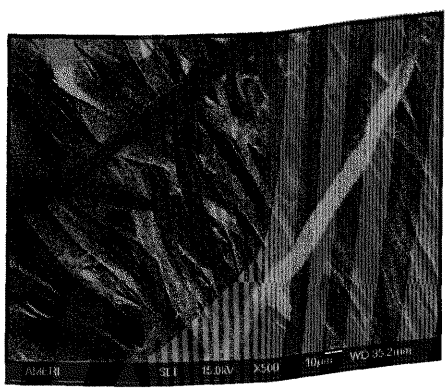
Dukal Brand (25X)



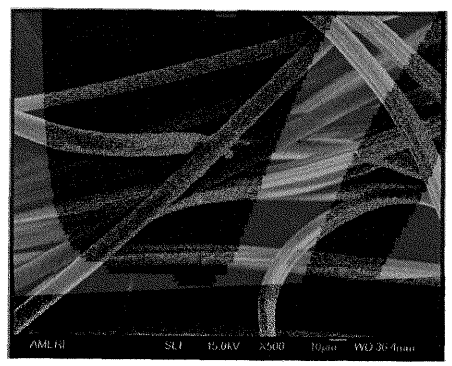
Johnson & Johnson (2X2) (25X)



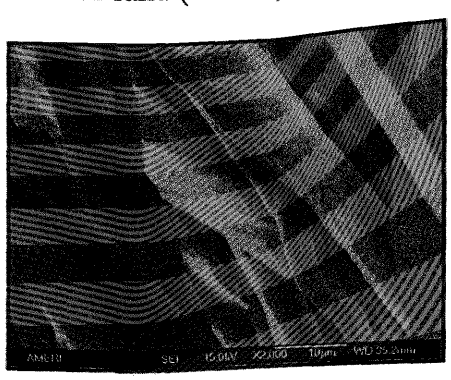
Dukal Brand (500X)



Johnson & Johnson (2X2) (500X)



Dukal Brand (2000X)



Johnson & Johnson (2X2) (2000X)

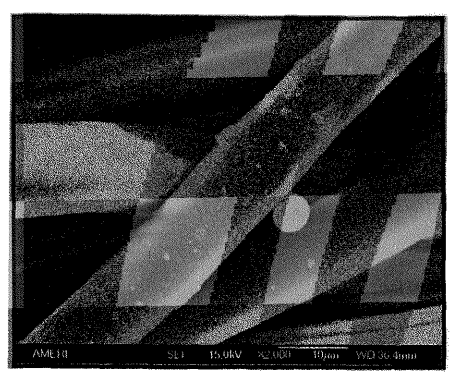
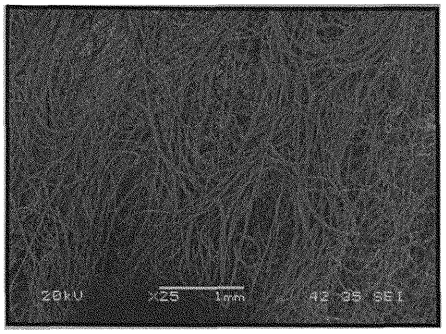


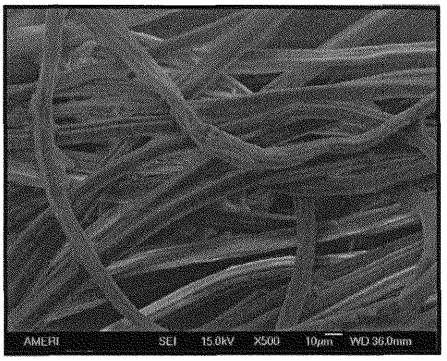
Figure 12: SEM and FESEM Images of DUKAL Brand and Johnson & Johnson Gauze

Johnson & Johnson (STU-100) (25X)

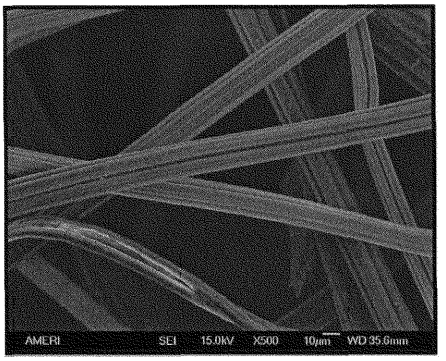


Hungarian Cotton (25X)

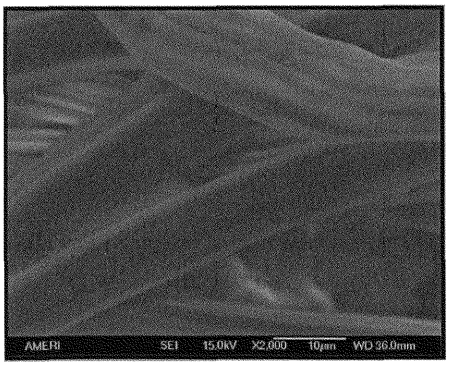
Johnson & Johnson (STU-100) (500X)



Hungarian Cotton (500X)



Johnson & Johnson (STU-100) (2000X)



Hungarian Cotton (2000X)

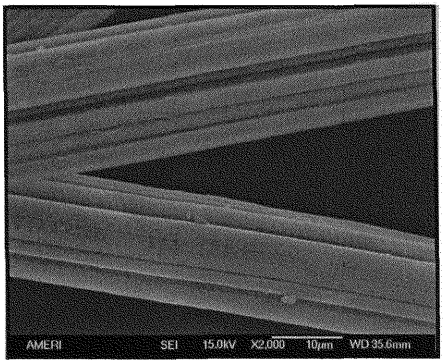
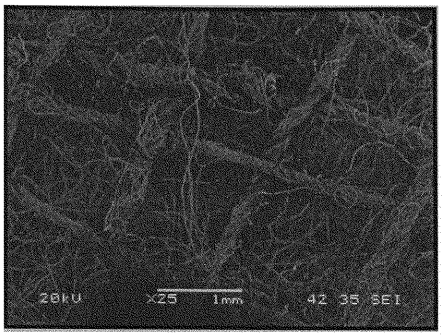
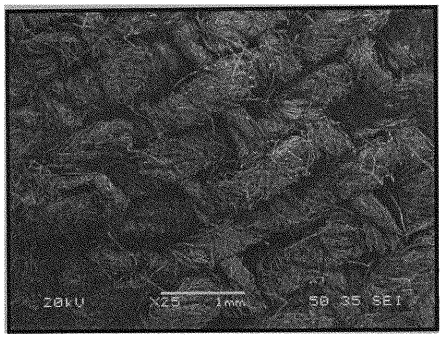


Figure 13: SEM and FESEM Images of Johnson & Johnson and Hungarian Cotton

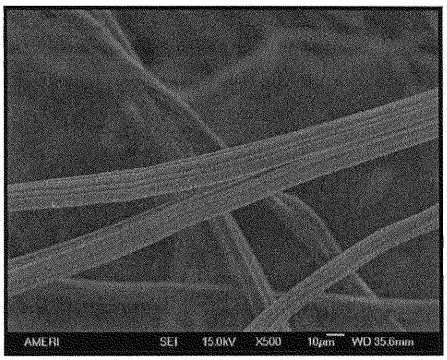
Polish Cotton (25X)



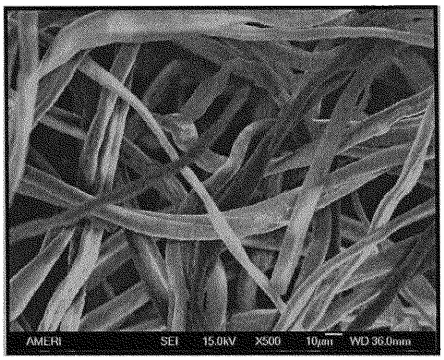
King's Cotton (25X)



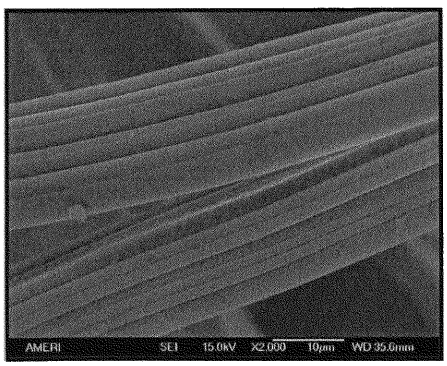
Polish Cotton (500X)



King's Cotton (500X)



Polish Cotton (2000X)



King's Cotton (2000X)

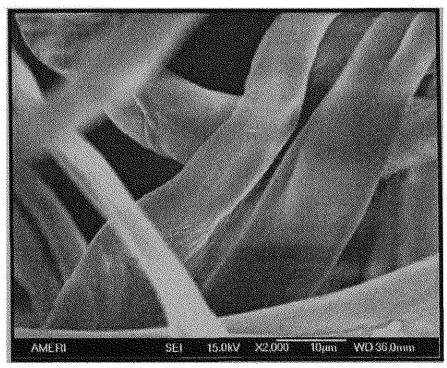


Figure 14: SEM and FESEM Images of King's Cotton and Polish Cotton

3.4. Analysis of Odor Collected From Individuals

3.4.1. Comparison of Foot Odor Compounds Among Individuals

Figure 15 displays the chromatograms produced from the headspace extraction of foot odor collected from the five subjects (F1, F2, F3, M2, and M3). As can be seen, there are similar compounds extracted among the individuals and some compounds which differ. Table 15 displays the human compounds extracted in the headspace of the collected foot odor samples of the subjects. Napthalene was extracted in all of the subjects studied, while 3,7-dimethyl-1,6-octadien-3-ol, 6-methyl-5-hepten-2-one, acetic acid-phenylmethyl ester, acetophenone, octanoic acid, phenol, and phenylethyl alcohol were seen in four of the subjects. Eicosane was extracted in three of the individuals, however, 1-hexadecene, 1-pentadecene, 1-tetradecene, (E)-2-decenal, and 6, 10-dimethyl- 5,9-undecadien-2-one, dodecanoic acid-ethyl ester were all extracted in only one of the subjects. The compounds listed in Table 15 are human compounds but sampling through this method places the collection material under the influence of not only the foot sweat, but also the contributions from socks and shoes. Due to the possibility that these compounds are present due to outside sources, sampling foot odor through this method is not an absolute method of human odor detection.

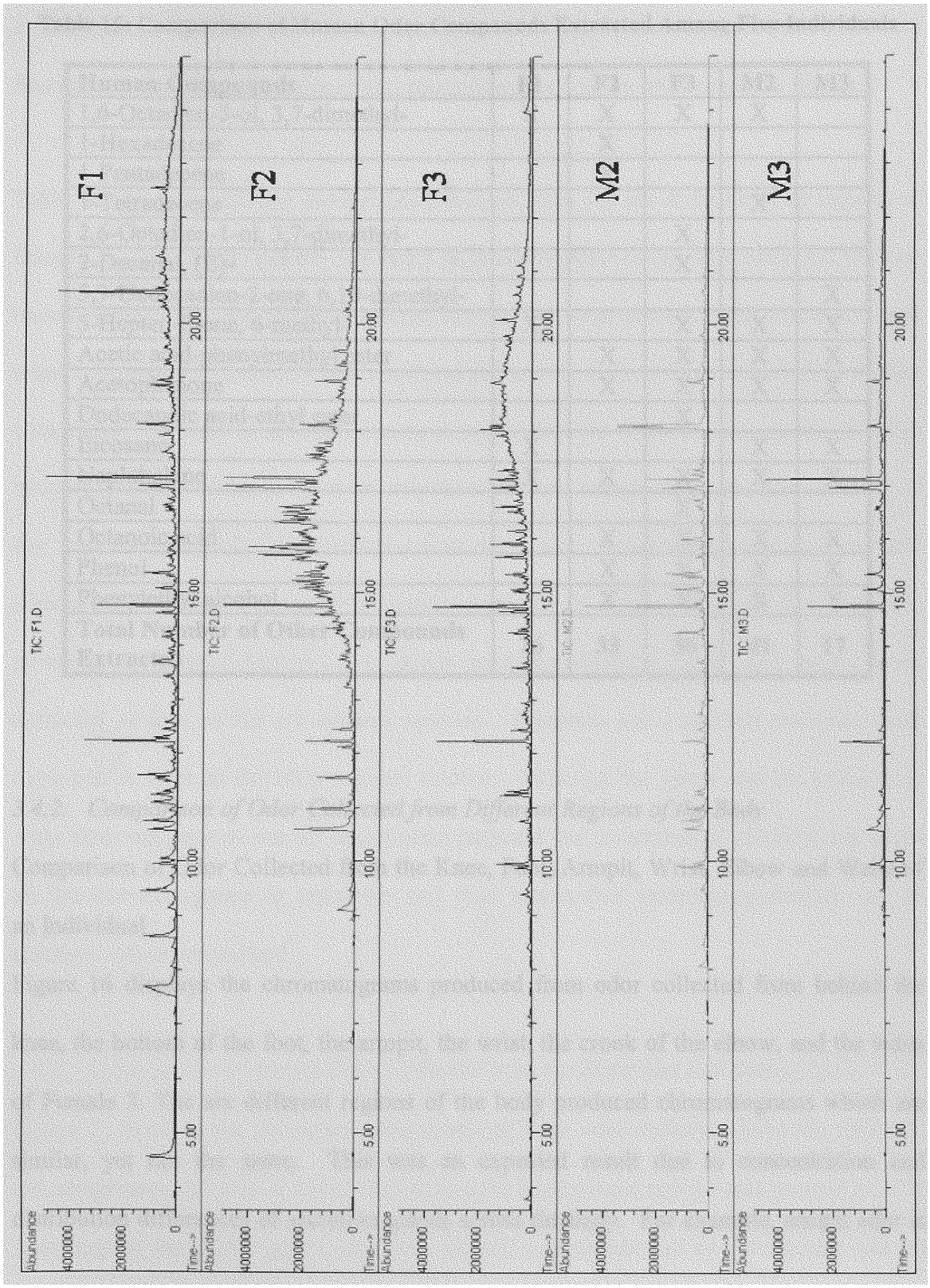


Figure 15: Comparison of Headspace Chromatograms Produced from Collected Foot Odor

Table 15: Comparison of Human Odor Compounds Extracted Among Five Individuals

Human Compounds	F1	F2	F3	M2	M3
1,6-Octadien-3-ol, 3,7-dimethyl-	X	X	X	X	
1-Hexadecene		X			
1-Pentadecene		X			
1-Tetradecene				X	
2,6-Octadien-1-ol, 3,7-dimethyl-			X		
2-Decenal, (E)-			X		
5,9-Undecadien-2-one, 6,10-dimethyl-					X
5-Hepten-2-one, 6-methyl-	X		X	X	X
Acetic acid-phenylmethyl ester		X	X	X	X
Acetophenone		X	X	X	X
Dodecanoic acid-ethyl ester			X		
Eicosane	X			X	X
Naphthalene	X	X	X	X	X
Octanal			X		
Octanoic acid		X	X	X	X
Phenol		X	X	X	X
Phenylethyl alcohol		X	X	X	X
Total Number of Other Compounds Extracted	**26**	**33**	**36**	**41**	**17**

3.4.2. Comparison of Odor Collected from Different Regions of the Body

Comparison of Odor Collected from the Knee, Foot, Armpit, Wrist, Elbow and Waist of an Individual

Figure 16 displays the chromatograms produced from odor collected from behind the knee, the bottom of the foot, the armpit, the wrist, the crook of the elbow, and the waist of Female 3. The six different regions of the body produced chromatograms which are similar, yet not the same. This was an expected result due to concentration and distribution differences of secretion glands across the body. For example, armpit odor is

a combination of Apocrine, eccrine, and sebaceous gland secretions, whereas hand and foot odor is only a combination of secretions from the eccrine and sebaceous glands.

Table 16 shows the human compounds extracted from the six different body regions of Female 3. The gauze placed in contact with the bottom of the foot extracted thirteen human compounds, the armpit produced twelve, the wrist produced ten, the elbow and waist both resulted in seven human compounds, and the knee only produced three human compounds. A total of nineteen human compounds were extracted among the different body regions of Female 3, however only three of these compounds were present in all of the regions sampled: 3,7-dimethyl-1,6-octadien-3-ol, 3,7-dimethyl-6-octen-1-ol, and octadecane. There were no compounds extracted in five of the six body regions, however, 6-methyl-5-hepten-2-one, acetic acid-phenylmethyl ester, and cedrol were extracted in four of the six regions sampled. Eicosane and 1-pentadecene were both extracted in three of the body regions studied. Although the gauze and the safety pins were analyzed prior to use for background purposes the influences of clothing and shoes on the chromatograms is unknown and thus makes this sampling procedure not an absolute collection method.

3.4.3. Comparison of Armpit Odor Collected from the Right and Left Side of Male 4

Figure 17 displays the chromatograms produced from odor collected from the right and left armpit area of Male 4. After considering the background compounds present prior to sampling on the sterile gauze pads, the human compounds can be determined and are listed in Table 17. All of the human compounds extracted were present in both the right

and left armpit of Male 4. Figure 18 shows the relative peak area ratios of the seven human compounds extracted from the right and left armpit samples. As Figure 18 shows, the ratio pattern is similar between the left and right armpit of Male 4.

Table 16: Comparison of Human Compounds Extracted in Odor Collected From Six Different Regions of the Body for Female 3

Human Compounds Extracted	Body Part Where Gauze Was Worn					
	Sock	Armpit	Wrist	Elbow	Waist	Knee
1,6-Octadien-3-ol, 3,7-dimethyl-	X	X	X	X	X	X
1-Pentadecene	X	X			X	
2-Furancarboxaldehyde			X			
5,9-Undecadien-2-one, 6,10-dimethyl-		X				
5-Hepten-2-one, 6-methyl-	X	X	X		X	
6-Octen-1-ol, 3,7-dimethyl-	X	X	X	X	X	X
Acetic acid-phenylmethyl ester	X	X	X		X	
Acetophenone	X					
Benzene, 1,3,5-trimethyl-			X	X		
Cedrol	X	X	X	X	X	
Dodecane	X	X				
Dodecanoic acid	X					
Eicosane		X	X	X		
Heneicosane		X				
Heptanal	X					
Octadecane	X	X	X	X	X	X
Pentadecane	X			X		
Phenylethyl Alcohol	X	X				
Thiazolidine			X			

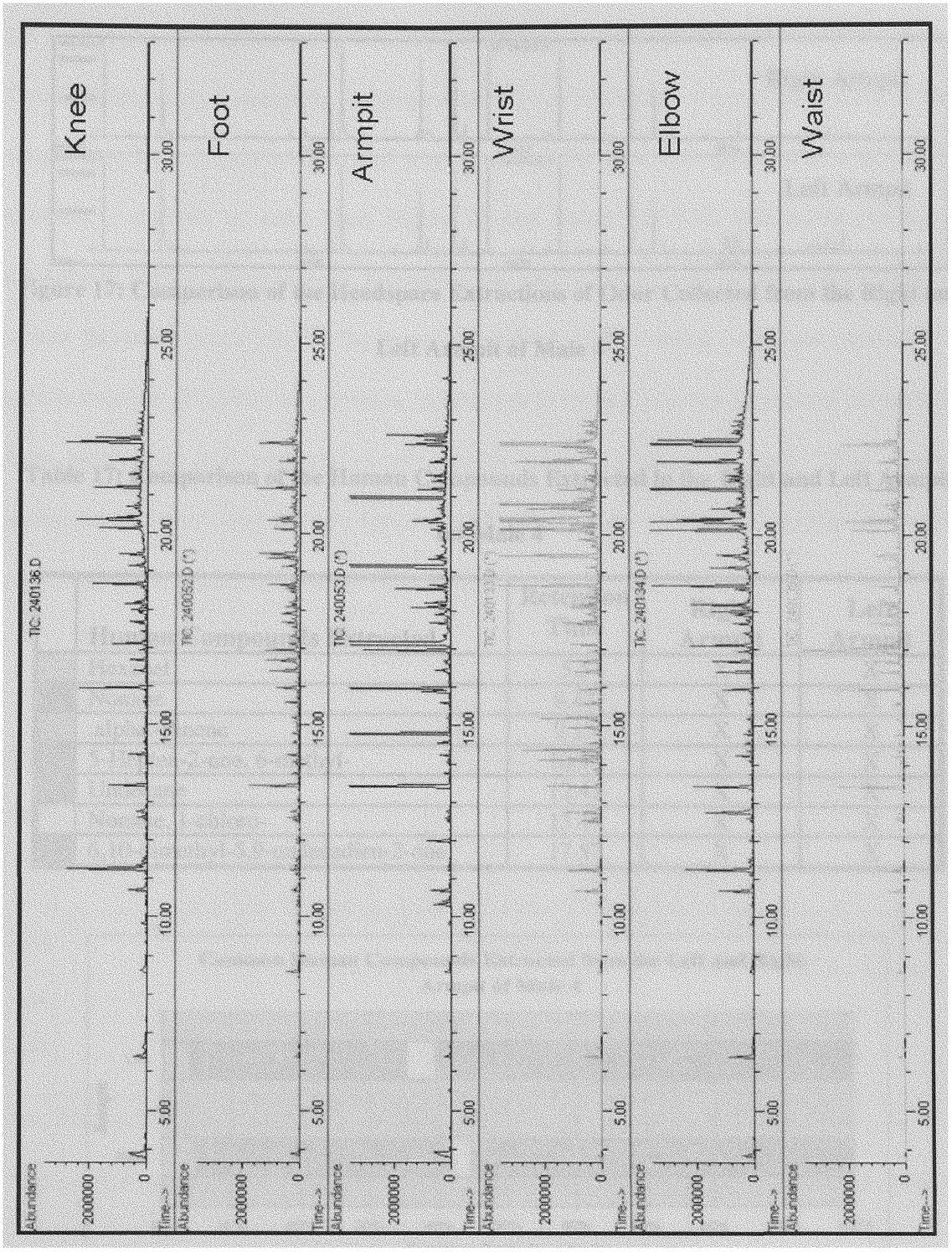


Figure 16: Comparison of Headspace Extractions Among Six Different Body Regions of Female 3

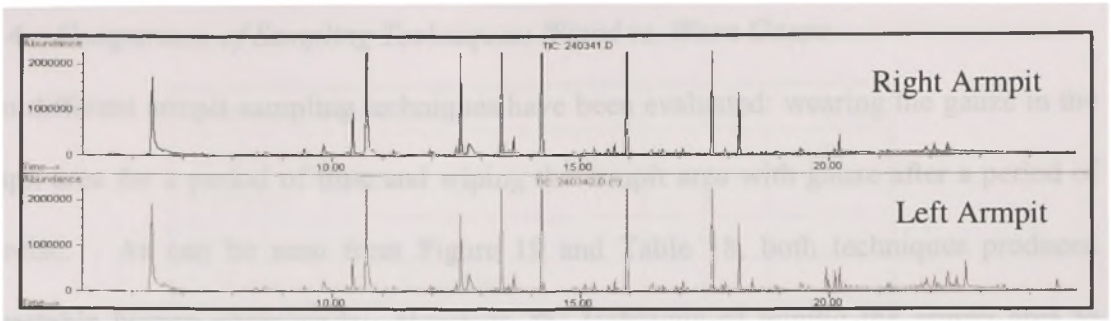


Figure 17: Comparison of the Headspace Extractions of Odor Collected from the Right and Left Armpit of Male 4

Table 17: Comparison of the Human Compounds Extracted in the Right and Left Armpit for Male 4

	Human Compounds Extracted	Retention Time	Right Armpit	Left Armpit
	Hexanal	5.5	X	X
	Nonane	8.43	X	X
	.alpha.-Pinene	9.13	X	X
	5-Hepten-2-one, 6-methyl-	10.33	X	X
	Undecane	12.43	X	X
	Nonane, 1-chloro-	13.49	X	X
	6,10-dimethyl-5,9-undecadien-2-one	17.57	X	X

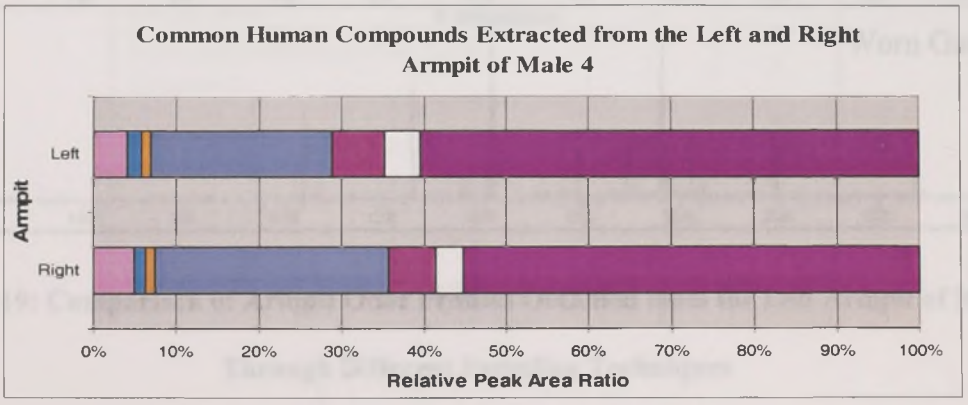


Figure 18: Semi-Quantitative Comparison of the Relative Peak Area Ratios of the Human Compounds Extracted in the Left and Right Armpit of Male 4

3.4.4. Comparison of Sampling Techniques: Wiped vs. Worn Gauze

Two different armpit sampling techniques have been evaluated: wearing the gauze in the armpit area for a period of time and wiping the armpit area with gauze after a period of exercise. As can be seen from Figure 19 and Table 18, both techniques produced extractable human compounds. However, the technique of wiping the armpit area to collect the odor proved to be the superior method. The wiping technique produced a greater number of human compounds, in addition to having less environmental influences from safety pins and clothing as are present when the gauze is worn. The wiping technique also provided a more concentrated sample than wearing the gauze as can be seen from the abundance levels in Figure 19.

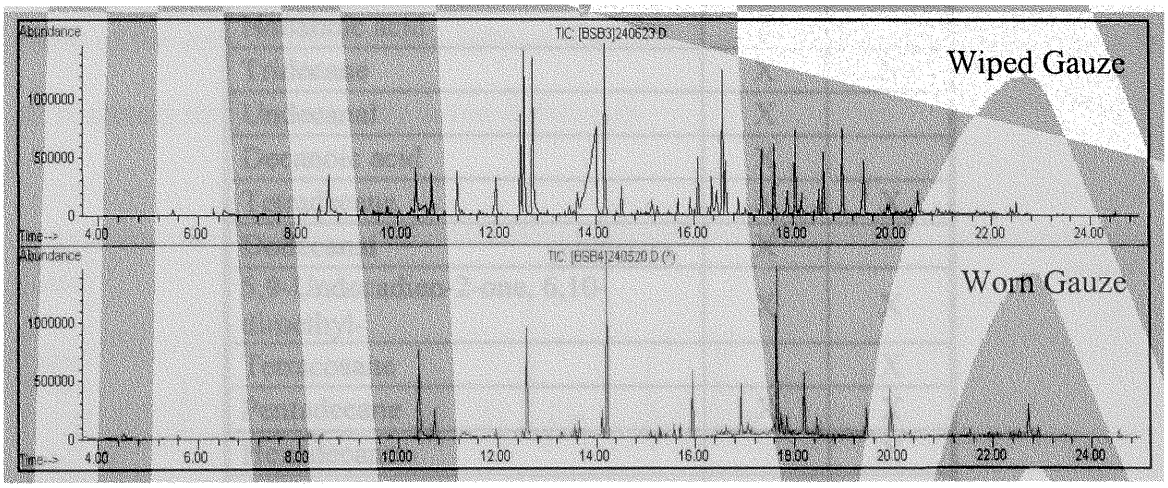


Figure 19: Comparison of Armpit Odor Profiles Obtained from the Left Armpit of Male 2 Through Different Sampling Techniques

Table 18: Comparison of Human Compounds Extracted in Wiped and Worn Gauze

Human Compounds	Wiped	Worn
Toluene		X
Hexanal	X	
Phenol	X	
5-Hepten-2-one, 6-methyl-	X	X
Hexanoic acid	X	
Octanal		X
1-Hexanol, 2-ethyl-	X	
Benzyl Alcohol	X	
1-Hexanol, 2-ethyl-		X
1,6-Octadien-3-ol, 3,7-dimethyl-	X	
Phenylethyl Alcohol	X	
2-Nonenal, (E)-	X	
Acetic acid, phenylmethyl ester	X	
Nonane, 1-chloro-		X
Octanoic Acid	X	
Dodecane		X
6-Octen-1-ol, 3,7-dimethyl-, (R)-	X	
Nonanoic acid	X	
Tridecane	X	X
Undecanal	X	
Decanoic acid	X	
Tetradecane	X	X
Dodecanal	X	
5,9-Undecadien-2-one, 6,10-dimethyl-	X	X
Tetracosane		X
Pentadecane	X	X
Hexadecane		X
Heptadecane	X	

3.4.5. Comparison of Armpit Odor Between Two Unrelated Males: Intraday Analysis of Male 4

Figure 20 shows the chromatograms produced from intraday sampling and analysis of Male 4. Male 4 was sampled once in the morning (Sampling 1) and then again ten hours later (Sampling 2). Figure 20 is shown with the siloxane peaks removed; these peaks are attributed to the SPME fiber coating and the column. Table 19 lists the previously reported compounds which were extracted in both samplings. Sampling 1 produced a higher abundance of compounds than Sampling 2, and cyclotetradecane, hexanal, and nonanoic acid were only seen in Sampling 1. Table 20 shows the relative peak ratios of the common compounds relative to (E)-2-nonenal extracted from the same individual at different times on the same day. (E)-2-nonenal was chosen as the compound which the ratios are relative to because it is extracted in all of the samples presented here. The ratios of the common compounds between the same individual on the same day appear to be relatively similar, with only minor differences.

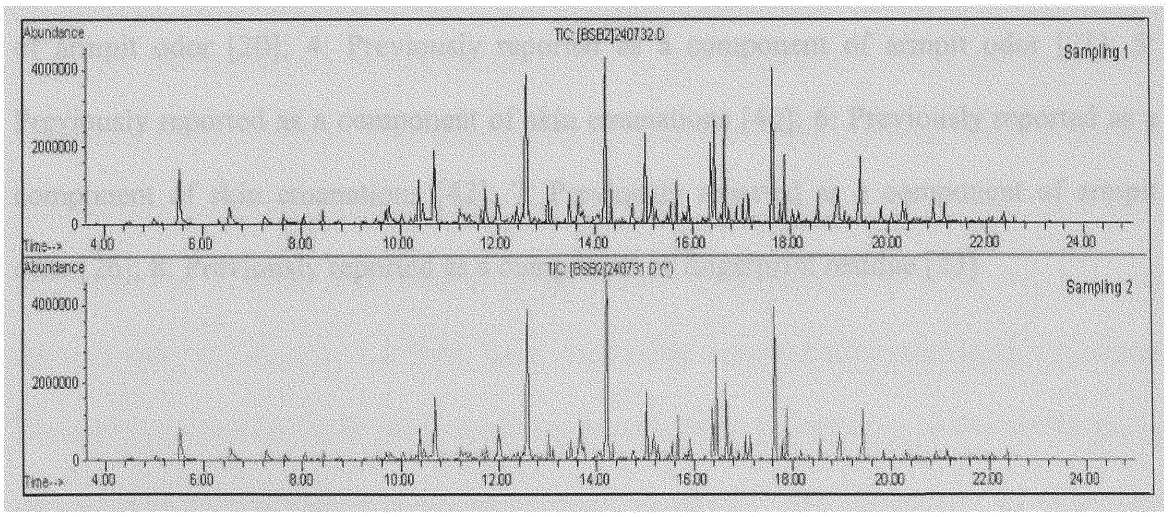


Figure 20: Chromatograms Produced From Intraday Analysis, Male 4

Table 19: Volatile Compounds Extracted Intraday, Male 4

Compound Name	M. W.	Sampling 1	Sampling 2
(E)-2-nonenal[7]	140	X	X
(E)-2-octenal[7]	126	X	X
(E,E)-2,4-nonadienal[1,6,7]	138	X	X
(E,E)-2,4-decadienal[7]	152	X	X
3,7-dimethyl-2,6-octadienal[1]	152	X	X
6,10-dimethyl-5,9-undecadien-2-one[1]	194	X	X
Benzaldehyde[1,6]	106	X	X
benzyl alcohol[1,4]	108	X	X
Cyclotetradecane[1]	196	X	
Dodecanoic Acid[1,3,5,6]	200	X	X
Heptadecane[1,2]	240	X	X
Heptanal[1,5,6]	114	X	X
Hexanal[5,7]	100	X	
Nonanoic Acid[1,3,4]	158	X	
Octadecane[1]	254	X	X
Toluene[1,6]	92	X	X
Undecanal[5]	170	X	X

1: Previously reported as a component in human skin emanation [41]; 2: Previously reported as a volatile component of the skin [53]; 3: Previously reported as a component of armpit odor [20]; 4: Previously reported as a component of armpit odor [21]; 5: Previously reported as a component of skin emanations [40]; 6: Previously reported as a component of skin emanations [42]; 7: Previously reported as a component of armpit odor [26]; 8: Previously reported as a component of fingerprint residue [23].

Table 20: Relative Ratios of Common Compounds Found Through Intraday Sampling (S1, S2) for Male 4

	Compound	Peak Ratio (S1)	Peak Ratio (S2)
1	(E)-2-nonenal	1.0000	1.0000
2	(E)-2-octenal	1.0205	0.6842
3	(E,E)-2,4-nonadienal	0.9683	0.7200
4	(E,E)-2,4-decadienal	0.3247	0.2914
5	3,7-dimethyl-2,6-octadienal	1.6698	2.5324
6	6,10-dimethyl-5,9-undecadien-2-one	5.1980	6.7795
7	benzaldehyde	1.1034	0.4013
8	benzyl alcohol	0.4492	0.5847
9	dodecanoic acid	2.6417	2.4870
10	heptadecane	0.3107	0.3302
11	heptanal	0.7935	0.6783
12	octadecane	0.1931	0.1891
13	toluene	0.0810	0.0850
14	undecanal	1.1646	1.5836

Interday Analysis and Individual Comparison: Male4 and Male 2

Figure 21 shows the chromatograms produced from interday analysis of the same individual, the initial sampling used for intraday analysis is compared to another sampling conducted two weeks earlier (Male 4, W3 and Male 4, W1) and to another individual Male 2. Figure 21 is shown with the siloxane peaks removed; these peaks are attributed to the SPME fiber coating and the column. Peaks seen at 12.59 and 14.24 min. correspond to nonanal and decanal respectively. Both nonanal [40, 41, 42, 53] and decanal [40, 41, 42, 53, 23] have been previously reported as components of human emanations, however, both compounds are present prior to sampling in the sterile gauze and so will be counted only for background purposes. The abundance of these two compounds will be disregarded and, so, Figure 21 shows the chromatograms expanded to

highlight the main compounds seen, which results in an off-scale nonanal peak. Some common compounds can be seen between the individuals along with some unique compounds. Table 21 lists the previously reported common compounds extracted between Week 1 and Week 3 (Sampling 1 and Sampling 2) for Male 4. Table 22 shows the relative peak ratios of the previously reported common compounds between Male 4(W1, W3(S1), W3(S2)) and Male 2 relative to (E)-2-nonenal. As can be seen from Table 23, although there is some variation present within the same individual, the ratio pattern is still distinguishable between individuals with significantly greater variation in the ratios of components observed between individuals tested than that seen for one individual. Table 24 also lists the compounds between Male 4 and Male 2 which are uncommon between the individuals. A combination of the relative ratios of the common compounds between the individuals along with the presence of some unique compounds allows for the chromatographic distinction between individuals.

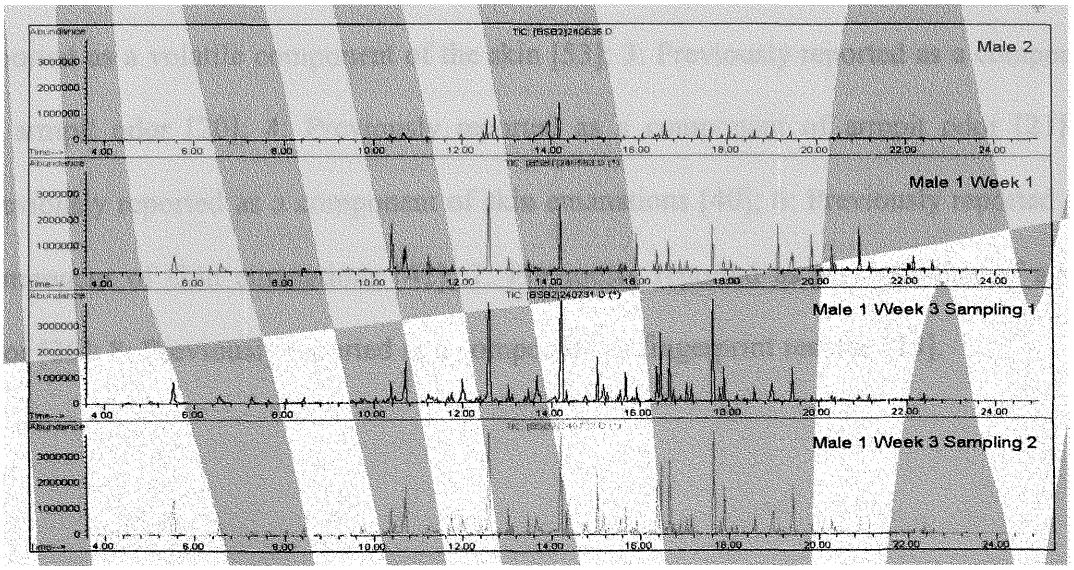


Figure 21: Expanded Chromatograms Produced from Different Individuals, M2 and M4

Table 21: Volatile Compounds Extracted Interday, Male 4

Compound Name	M.W.	Wk 1	Wk 3 S 1	Wk 3 S 2
(E)-2-nonenal[7]	140	X	X	X
(E)-2-octenal[7]	126	X	X	X
(E,E)-2,4-nonadienal[1,6,7]	138		X	X
(E,E)-2,4-decadienal[7]	152		X	X
3,7-dimethyl-2,6-octadienal[1]	152		X	X
6,10-dimethyl-5,9-undecadien-2-one[1]	194	X	X	X
6-methyl-5-hepten-2-one[1,2,6]	126	X		
Benzaldehyde[1,6]	106	X	X	X
benzyl alcohol[1,4]	108	X	X	X
Cyclotetradecane[1]	196	X	X	
Dodecanoic Acid[1,3,5,6]	200	X	X	X
Heptadecane[1,2]	240	X	X	X
Heptanal[1,5,6]	114		X	X
Hexanal[5,7]	100		X	
Nonane[1,6]	128	X		
Nonanoic Acid[1,3,4]	158	X	X	
Octadecane[1]	254	X	X	X
Phenol[1,3,4]	94	X		
Toluene[1,6]	92		X	X
Undecanal[5]	170	X	X	X

1: Previously reported as a component in human skin emanation [41]; 2: Previously reported as a volatile component of the skin [53]; 3: Previously reported as a component of armpit odor [20]; 4: Previously reported as a component of armpit odor [21]; 5: Previously reported as a component of skin emanations [40]; 6: Previously reported as a component of skin emanations [42]; 7: Previously reported as a component of armpit odor [26]; 8: Previously reported as a component of fingerprint residue [23].

Table 22: Common Volatile Compounds Extracted Between Male 4 (W1, W3S1, W3S2)

	Compound	Peak Ratio M4 (W1)	Peak Ratio M4 (W3) S1	Peak Ratio M4 (W3) S2	AVE. Peak Ratio M1	Stand. Dev.	R.S.D
1	(E)-2-nonenal	1	1	1	1	0	0
2	6,10-dimethyl-5,9-undecadiene-2-	4.0209	6.7795	5.1980	5.3328	1.3842	25.95
3	Benzyl alcohol	0.6440	0.5847	0.4492	0.5593	0.0998	17.84
4	Dodecanoic acid	1.3175	2.4870	2.6417	2.1487	0.7240	33.69
5	Heptadecane	0.3300	0.3302	0.3107	0.3236	0.0112	3.461
6	Octadecane	0.2574	0.1891	0.1931	0.2132	0.0383	17.96
7	Undecanal	0.6456	1.5836	1.1646	1.1312	0.4699	41.54

Table 23: A Comparison of the Common Volatile Compounds Extracted Between Male 4 (average) and Male 2

	Compound	Avg. Peak Ratio (M4)	Peak Ratio (M2)	M2/M1 Ratio
1	(E)-2-nonenal	1	1	1
2	6,10-dimethyl-5,9-undecadien-2-one	5.3328	13.5840	2.5472
3	Benzyl alcohol	0.5593	2.1466	3.8378
4	Dodecanoic Acid	2.1487	4.9138	2.2868
5	Heptadecane	0.3236	6.4197	19.8381
6	Octadecane	0.2132	0.9252	4.3404
7	Undecanal	1.1312	3.7387	3.3049

Table 24: Volatile Compounds which are Uncommon between Male 4 and Male 2

Compound Name	M. W. (g/mol)	Formula	M 4	M 2
Alcohols	---	---	---	---
3,7-dimethyl-6-octen-1-ol[1]	156	$C_{10}H_{20}O$		X
Phenol[1,3,4]	94	C_6H_6O		X
Phenylethyl alcohol[1]	122	$C_8H_{10}O$		X
Aldehydes	---	---	---	---
(E)-2-octenal[7]	126	$C_8H_{14}O$	X	
(E,E)-2,4-decadienal[7]	152	$C_{10}H_{16}O$	X	
(E,E)-2,4-nonadienal[1,6,7]	138	$C_9H_{14}O$	X	
3,7-dimethyl-2,6-octadienal[1]	152	$C_{10}H_{16}O$	X	
Benzaldehyde	106	C_7H_6O	X	
Aliphatics/Aromatics	---	---	---	---
Cyclotetradecane[1]	196	$C_{14}H_{28}$	X	
Octadecane[1]	254	$C_{18}H_{38}$	X	
Pentadecane[1,2]	212	$C_{15}H_{32}$		X

1: Previously reported as a component in human skin emanation [41]; 2: Previously reported as a volatile component of the skin [53]; 3: Previously reported as a component of armpit odor [20]; 4: Previously reported as a component of armpit odor [21]; 5: Previously reported as a component of skin emanations [40]; 6: Previously reported as a component of skin emanations [42]; 7: Previously reported as a component of armpit odor [26]; 8: Previously reported as a component of fingerprint residue [23].

3.5. Creation of a Pre-Treatment for Producing Analytically Clean Absorbers

3.5.1. Steam and Gravity Re-sterilization

Headspace evaluation of each half of the absorbers pre and post re-sterilization using either steam or gravity sterilization resulted in a reduced amount of human compounds

present initially on the absorber. Figure 23 and Figure 23 compares the peak heights of human compounds present initially in the eye pad and after re-sterilization. As can be seen from the graphs, re-sterilizing absorber materials using steam or gravity techniques does not result in a chromatographically clean absorber material.

3.5.2. Soxhlet Extraction

The nine hour Soxhlet extractions using either methanol or chloroform did not result in complete removal of the aldehydes from the sorbent material, as can be seen in Figure #. For example, utilizing the methanol solvent, nonanal had an average removal rate of 91.71% and decanal had an average removal rate of 63.35%. In addition to the fact that complete removal of the aldehydes was not achieved, Soxhlet extraction process also entails a long total extraction time as the solvent process is nine hours in length and then, as the material is wet, an additional twenty-four hours is necessary to allow for the solvent to evaporate from the sorbent. Furthermore, Soxhlet extractions require the use and disposal of large amounts of solvent which add to the cost of the process and thus Soxhlet extraction is not an ideal means to pre-treat sorbent materials.

3.5.3. Supercritical Fluid Extraction

Static Extraction Time:

The compounds targeted for removal contain compound classes that are both polar and non-polar; due to this fact the ability of pure CO_2 may not be adequate for complete removal of the polar compounds as CO_2 has high solubility for non-polar analytes. The use of modifiers requires a static step followed by a dynamic step, and the removal rates

of the polar compounds are usually limited by solubility considerations, static/dynamic extraction times of 30/10 min and 45/10 min at (130°C and 4500 psi) were evaluated without the presence of the modifiers. While the extended exposure to the carbon dioxide solvent proved to remove 100% target long chain alkanes such as dodecane, tridecane, hexadecane, and heptadecane; the removal of the aldehydes was not as successful. The longer static extraction time demonstrated minimal extraction recoveries when compared to the shorter extraction period for the polar compounds as can be seen in Figure 25. Nonanal, for example, had a removal rate of 68.11% at 30 minutes compared to 63.30% at the 45 minute period. Furthermore, decanal, another key human scent aldehydes component portrayed a relatively high 92.32% removal rate at the 30 minute static extraction period compared to a lower 66.70% removal rate at the prolonged static extraction time. These results reinforce the fact that the 45 minute extraction provides minimal extraction recoveries and, thus, low removal rates of target human scent volatile organic compounds found within sorbent material evaluated.

The complete removal of the non-polar compounds, yet the persistence of the polar compounds through both extraction times evaluated means that there is a solubility impediment in the complete removal of the aldehydes from the sample matrix. The application of polar modifiers to the extraction cell can enhance the solubility of the polar compounds of interest and thus help to achieve a complete removal of all compounds from the matrix.

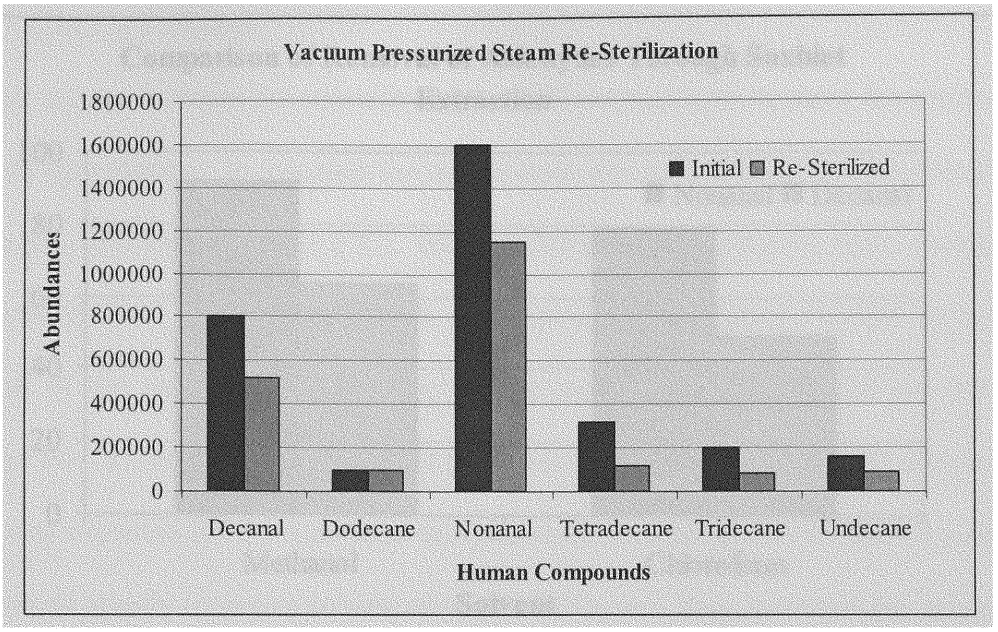


Figure 22: Comparison of the Abundances of Human Compounds Present Initially and After Re-sterilization using Vacuum Pressurized Steam

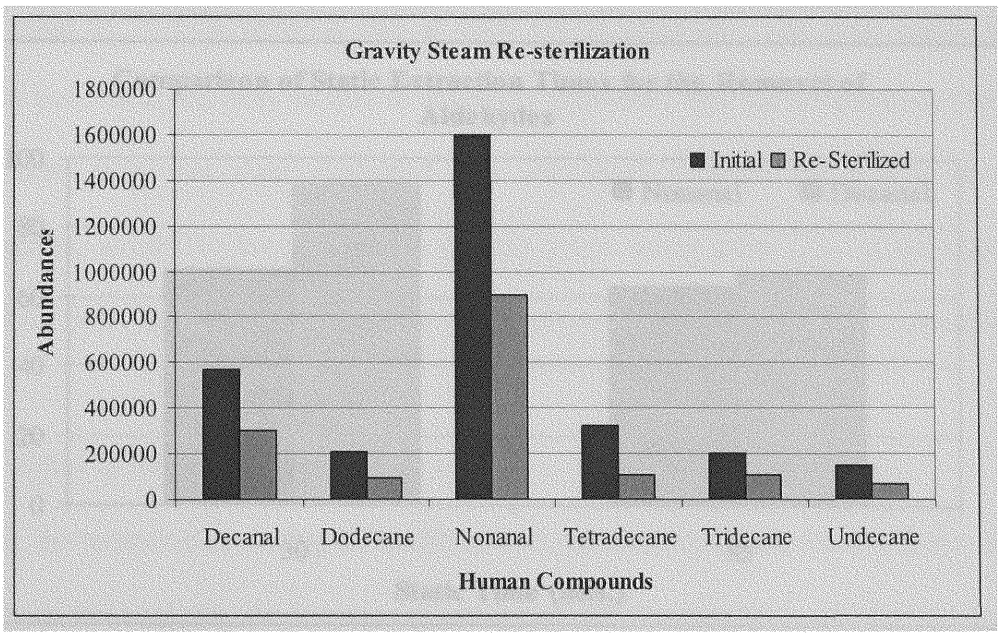


Figure 23: Comparison of the Abundances of Human Compounds Present Initially and After Re-sterilization using Gravity Steam

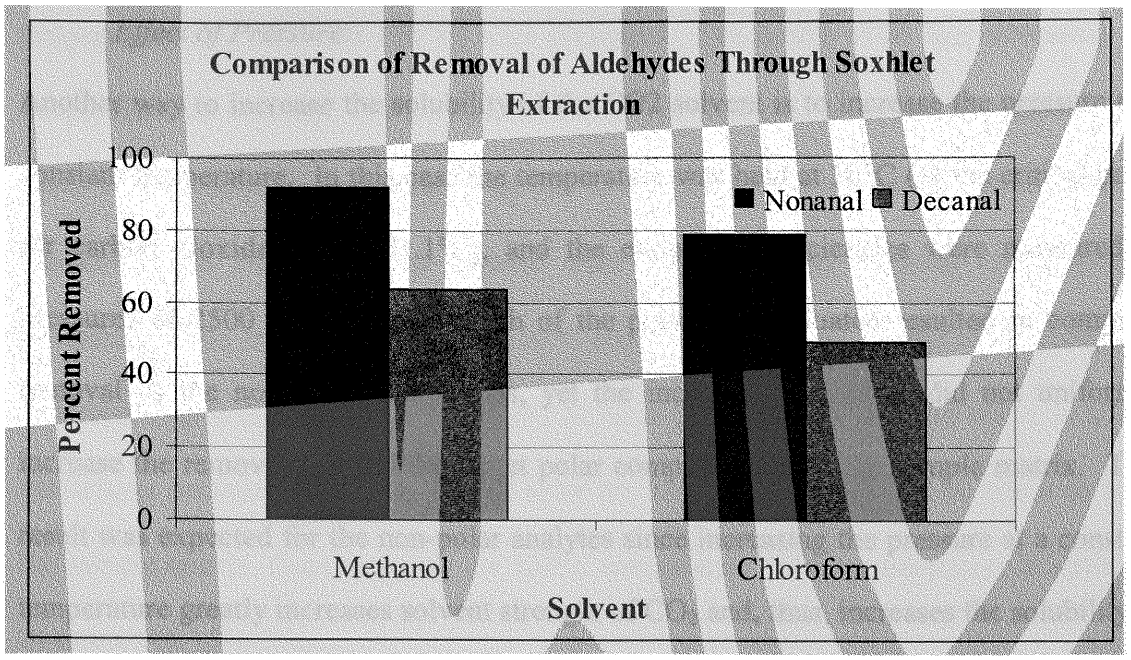


Figure 24: Comparison of Methanol and Chloroform Soxhlet Extractions of Sorbent Materials

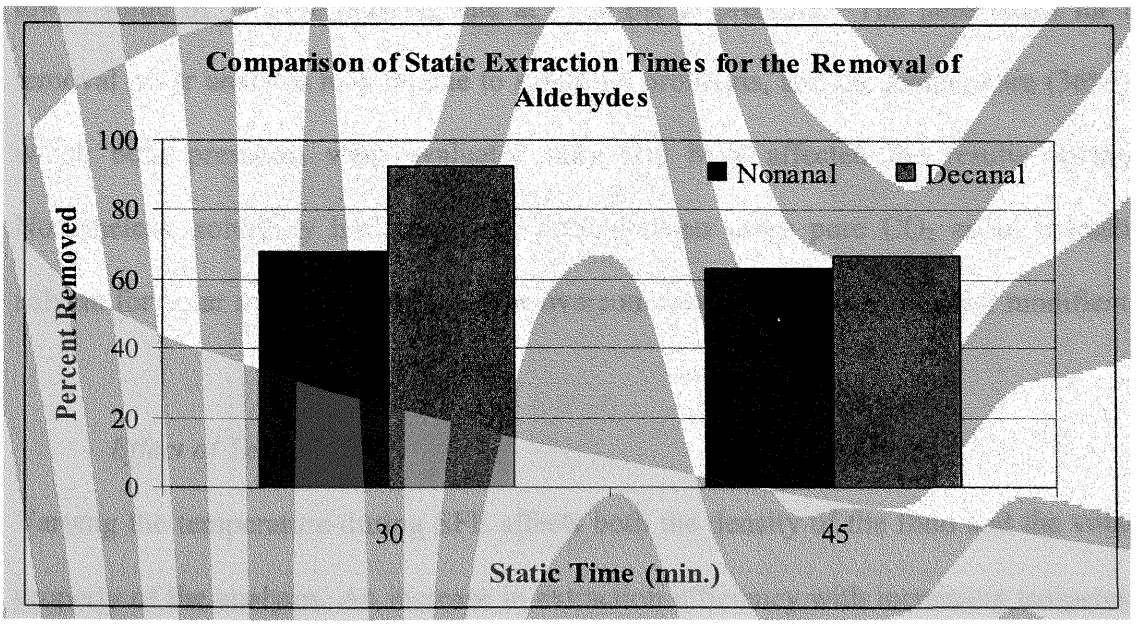


Figure 25: Removal Rates for the Extraction of Nonanal and Decanal at Different Static Extraction Times

Effect of Pressure:

Another way to increase the solubility of the CO2 solvent is to increase the pressure at a constant temperature. In this case the temperature was held at 36°C (as the critical point for carbon dioxide gas is 31.1°C), and the extraction efficiencies were measured at pressures of 2500 and 4500psi. Both of the pressures evaluated resulted in complete removal of the non-polar compounds, yet the increase in pressure did not uniformly increase the removal rates of the target polar compounds from the sample matrix. This result was expected for the non-polar analytes since increasing the pressure at a constant temperature greatly increases solvent strength of CO_2 and, thus, increases the solubility of most analytes found within the sample matrix. Nonanal portrayed a 96.60% removal rate at the lower pressure of 2500psi while dropping to a removal rate of 78.03% at the higher pressure. Decanal was found to be removed 91.58% at the lower pressure compared to a lower value of 76.77% removal rate at 4500 psi of pressure. The poor result for the removal polar analytes may be due to solubility problems, and the temperature (36°C) at which both pressures were evaluated may also have affected the results obtained. Nonetheless, solubility limitations are present when using pure CO_2 as an extraction solvent for polar analytes, which may be overcome with the addition of polar modifiers.

Effect of Temperature:

Varying the temperature during SFE affects both the density of the fluid and the volatile property of the analytes. An increase in extraction efficiency with increasing temperature is dependent on molecular weight as well as the vapor pressure of the analytes. Again utilizing the static/dynamic time of 30/10min along with a pressure of 4500psi, three

temperatures (36, 130, and 150°C) were evaluated. The results show that increasing the temperature up through 150°C was beneficial for nonanal, however, decanal yielded much better results at a temperature of 130°C vs. 150°C. As seen in Figure 26, a lower temperature of 36°C provided nonanal with a much higher removal rate (78.03%) compared to the amount removed at 130°C (68.11%). Decanal, on the other hand, was observed to give the best removal rate (92.32%) at the 130°C temperature value. In all the extractions performed, decanal proved to be the hardest target VOC to be removed from the sample matrix, thereby giving the 130°C temperature value an advantage to optimize its extraction efficiency.

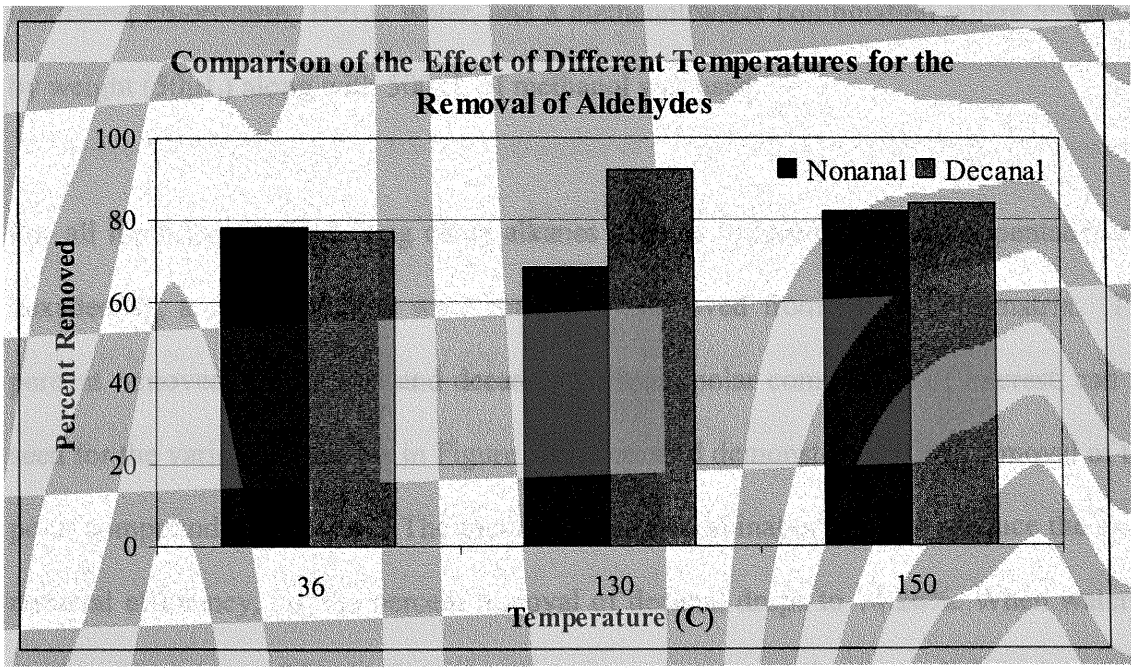


Figure 26: Removal Rates for the Extraction of Nonanal and Decanal at Different Temperatures

Effect of Modifiers:

Due to the non-polar characteristics of the CO_2, there is an inherent limited ability to dissolve polar analytes from the matrix. The use of modifiers enhance the extraction when the solubilities of the target analytes is not sufficient to yield reasonable extraction rates (solubility hindrances), and can also enhance the rate of kinetic/desorption process resulting in a greater interaction with the sample matrix. Thus, a study was conducted to evaluate the effect of different modifiers and their relation to extraction efficiencies of target compounds found in sorbent materials. The extractions performed with each modifier at a static/dynamic timeframe of 30/10min were conducted at a fixed pressure and temperature of 4500 psi, 130°C respectively. The modifiers were all spiked directly onto the gauze while inside the extraction cell and the solvents evaluated included methanol, chloroform, HPLC water, and a methanol/water combination where 5% water by weight (50μL) along with 500μL of methanol was used.

For all modifiers studied, long chain alkanes such as tridecane, undecane, pentadecane, hexadecane, and heptadecane were completely removed from the sample matrix. The percent removed for nonanal and decanal, the main polar compounds of interest, can be seen for the various modifiers in Figure 27. Methanol demonstrated 100% removal of the polar compounds of interest. The methanol/water combination did not produce the same removal efficiency, i.e. the percent removal of decanal drops to 74.26%. When water is used as the only modifier in the extraction, the removal rates improve slightly than those of the MeOH/water mixture modified samples. This indicates that the combination of water which is in a different location in Snyder's triangle than methanol a less basic

solvent when X_D values are compared reduces the extraction capability of the modifier. Chloroform (more similar to water when located in Snyder's triangle) generated a lower removal percentage for decanal (77.90%) compared to nonanal (93.31%).

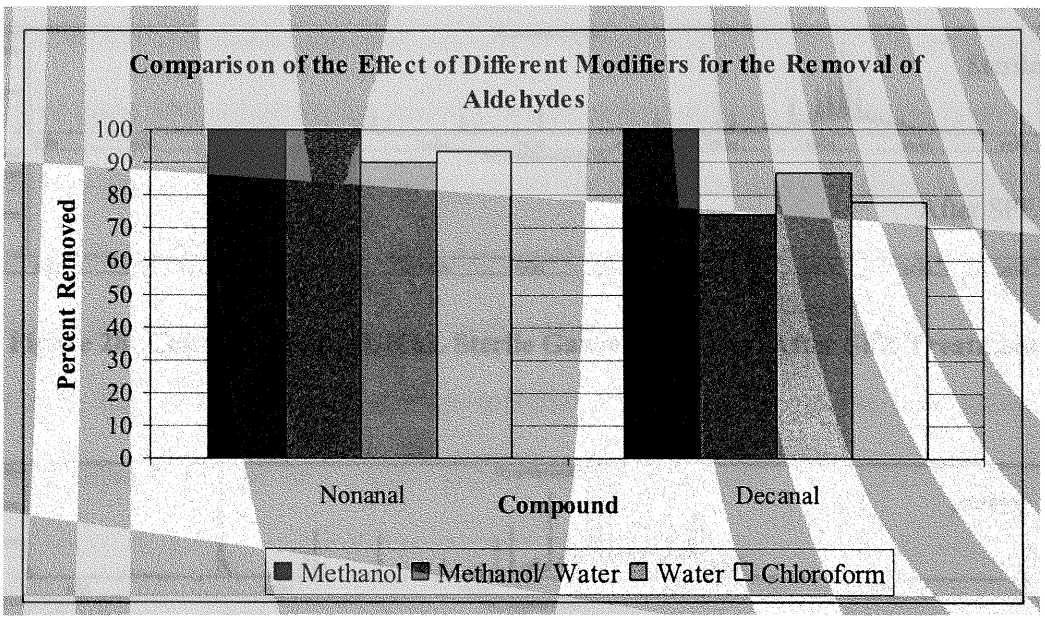


Figure 27: Removal Rates for the Extraction of Nonanal and Decanal Using Different Modifiers

In order to test the ruggedness of the methanol-modified SFE parameters, varying sizes, thicknesses, and types of materials were run through the SFE, and the amount of modifier was scaled-up based on a weight ratio of 500 μL to ~0.36g. The scaling up of the amount of methanol added to the extraction cell resulted in the complete removal of all of the compounds of interest, producing an analytically clean sorbent material, as can be seen in Figure 28, Figure 29, and Figure 30. The SFE parameters for achieving an analytically clean absorber material have been determined to include the direct spiking of methanol

modifier (amount determined by using the ratio of 500 μL to ~0.36g), thirty minutes of static extraction with a pressure of 4500 psi at 130 °C followed by a ten minute dynamic extraction.

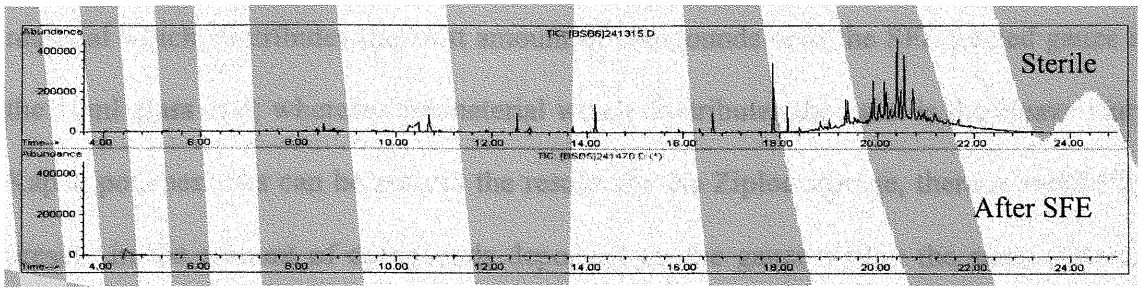


Figure 28: Comparison of DUKAL Sterile Gauze before and After SFE Treatment

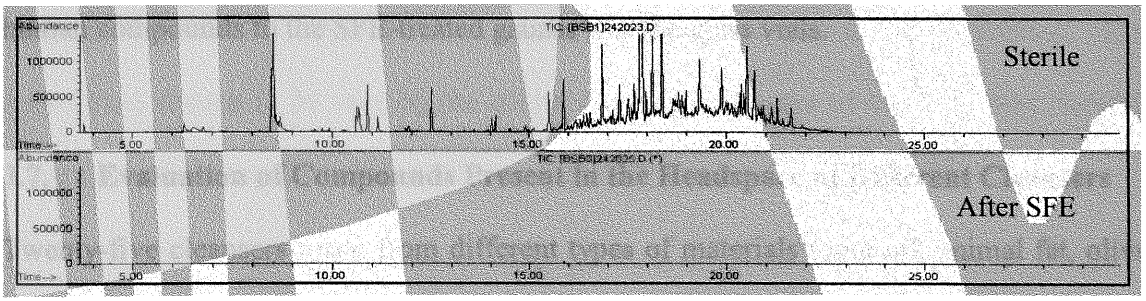


Figure 29: Comparison of IMCO Brand Sterile Gauze before and After SFE Treatment

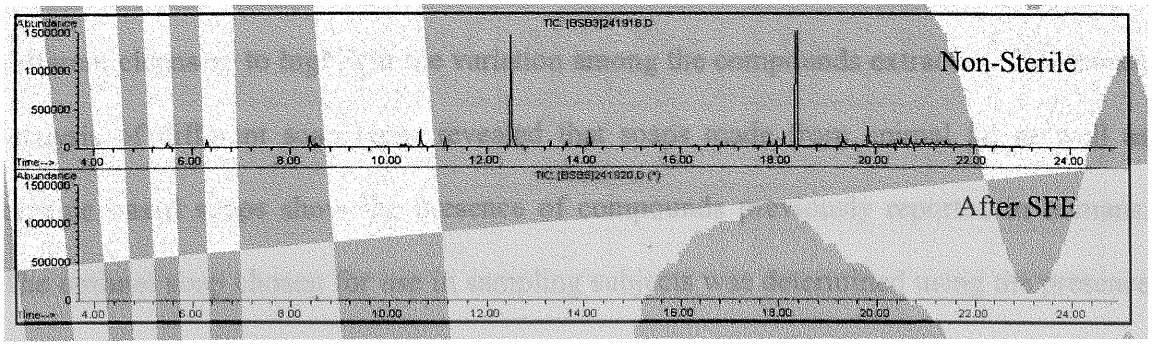


Figure 30: Comparison of King's Cotton before and after SFE Treatment

3.6. Evaluation of Storage Materials Commonly Used to Collect Human Scent

Figure 31 shows the chromatograms produced from storage of SFE-treated gauze in glass vials, polyethylene pouches, Ziploc Freezer Guard bags, Aluminized Kapak, and Heavy Duty Kapak pouches for the five week period. As shown in Table 25, the storage material which contributes the least amount of compounds onto the SFE treated gauze is the 10ml glass vial; whereas, the material which contributes the most is the Heavy Duty Kapak pouches. As can be seen in the results for the Ziploc storage, there is variability present in the amount of compounds deposited on the gauze within the same material over time, these variations may be due to the manufacturing process as all the Ziploc bags were from the same box. The storage material which contributed the least amount of human compounds to the SFE-treated gauzes was the glass vials.

3.7. Evaluation of Compounds Present in the Headspace of Different Cleansers

Twenty-five cleansers made from different types of materials (emu oil, animal fat, olive oil, glycerin, and various organic materials), both fragrance-free and scented, were evaluated through headspace SPME-GC/MS to determine which compounds were present. Appendix E lists the compounds extracted among a selection of the twenty-five different cleansers to highlight the variation among the compounds extracted. Headspace analysis of different soap types revealed that soaps made from animal fat as well as organic based soaps show the presence of compounds previously reported in humans. The optimal soap chosen for use in sampling subjects was determined using the presence of commonly reported compounds in humans in the headspace of soaps as the criteria for exclusion. Figure 32 demonstrates a comparison of the headspace four fragrance-free

soaps, two made from an animal fat base and two made from an olive oil base. The comparison shown here is done with fragrance-free cleansers to minimize the extraneous odor compounds present. Table 26 shows a summary of the human compounds commonly seen in the headspace of fragrance-free soaps made from animal fat as compared to those made from olive oil. Olive oil based fragrance-free soaps did not contain the presence of any human compounds; whereas, animal fat based fragrance-free soaps did show the presence of many types of human compounds. The peaks seen in the chromatograms for olive oil based soaps are siloxane and propylene glycol, due to the column/fiber coating and the soap base respectively. In order to eliminate the possibility that the odor profile has influences from the type of soap being used for washing the body, olive oil based, fragrance-free soaps will be used in the sampling scheme. The soap brand chosen to be used by the subjects to wash all areas of the body was Natural, Clear Olive Oil Soap from Life of the Party (North Brunswick, NJ, USA).

Table 25: Average Number of Compounds Contributed by the Storage Material to Analytically Clean Absorbers

Storage Material	Ave. Num. Compounds			Ave. Num. Human		
	Wk 1	Wk 2	Wk 5	Wk 1	Wk 2	Wk 5
10mL glass vial	3	2	6	1	0	1
Polyethylene	19	24	11	6	7	2
Ziplock Freezer Guard	40	19	15	9	3	3
Aluminum KPAK	93	85	88	6	3	2
Clear KPAK	116	116	107	7	8	6

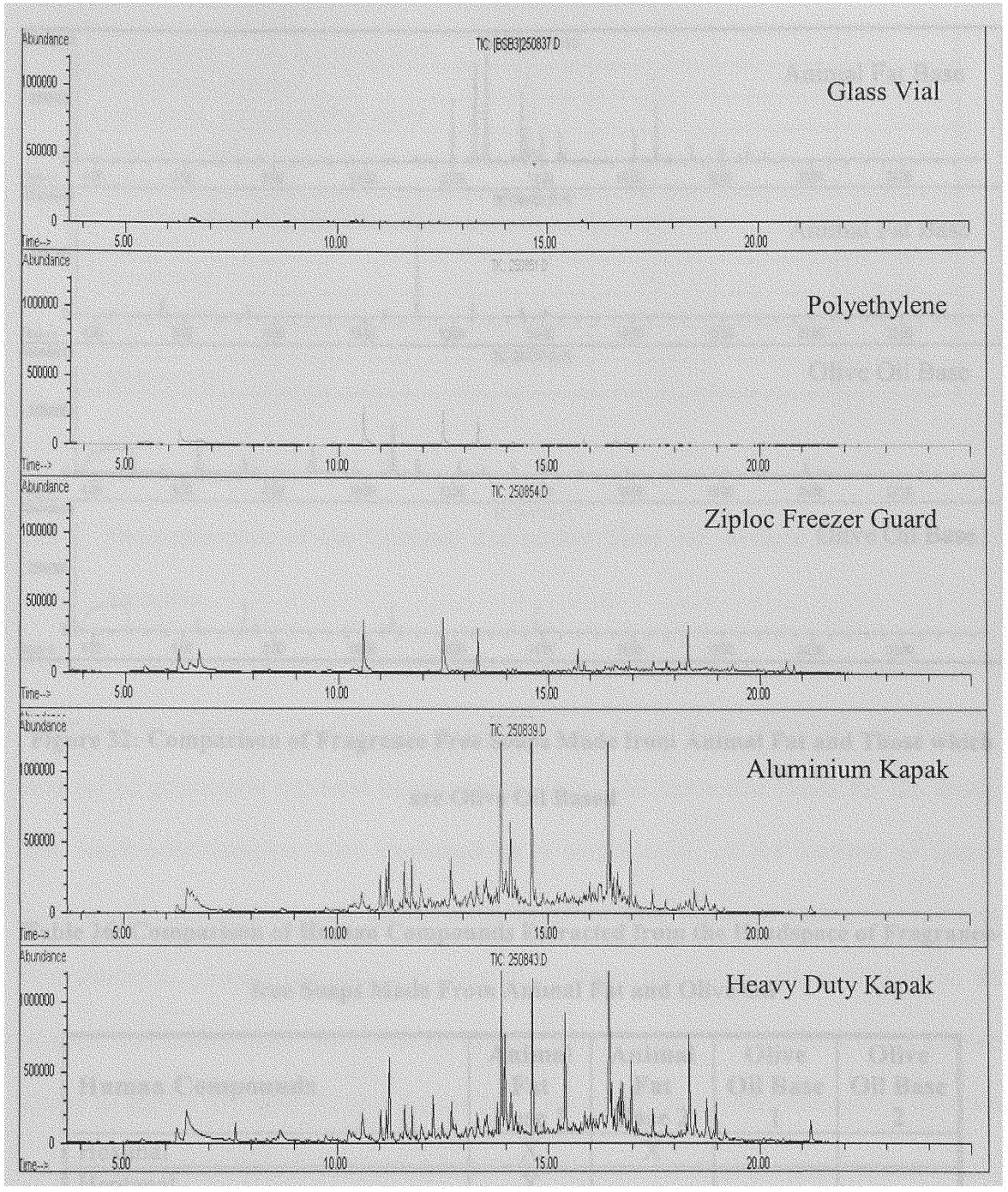


Figure 31: Comparison of Storage Effects on Analytically Clean Absorbent Materials at Five Weeks

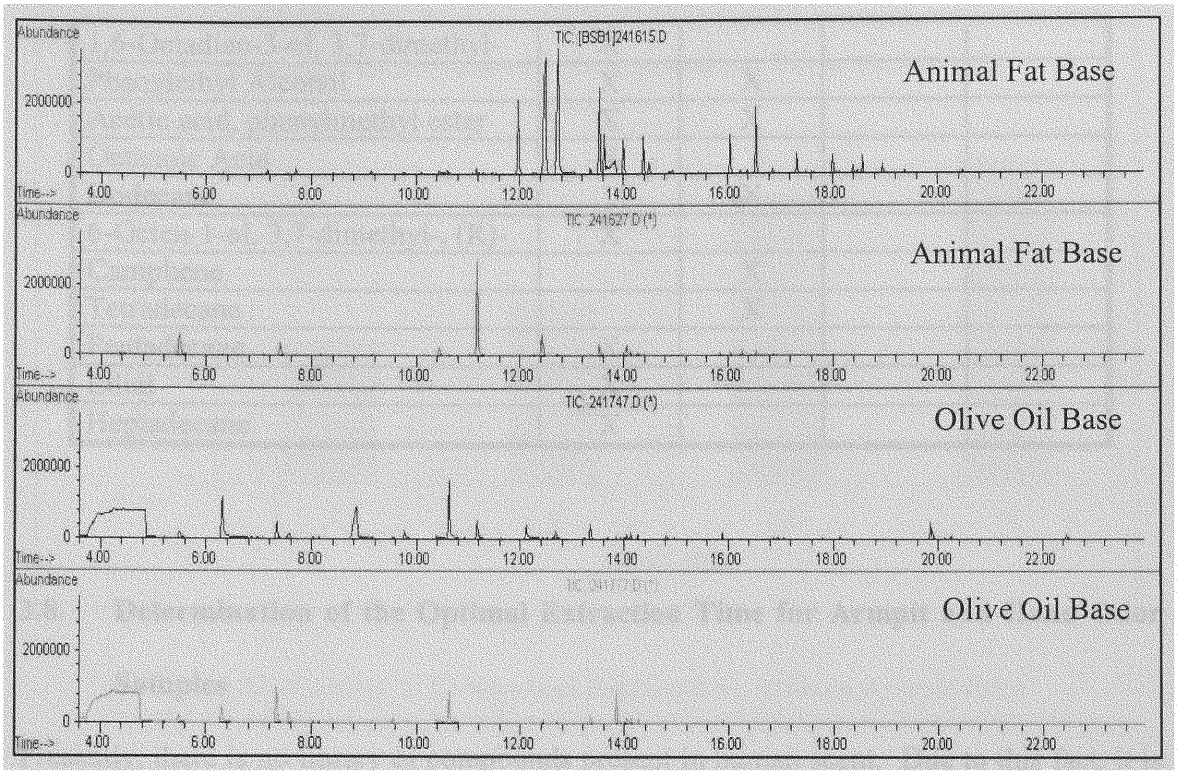


Figure 32: Comparison of Fragrance Free Soaps Made from Animal Fat and Those which are Olive Oil Based

Table 26: Comparison of Human Compounds Extracted from the Headspace of Fragrance-free Soaps Made From Animal Fat and Olive Oil

Human Compounds	Animal Fat Base 1	Animal Fat Base 2	Olive Oil Base 1	Olive Oil Base 2
Hexanal	X	X		
Heptanal	X			
.alpha.-Pinene	X	X		
Benzaldehyde	X			
Hexanoic acid	X			
Benzene, 1-methyl-2-(1-methylethyl	X			
D-Limonene	X			
Benzyl Alcohol	X			

1,6-Octadien-3-ol, 3,7-dimethyl-	X			
Phenylethyl Alcohol	X	X		
Acetic acid, phenylmethyl ester	X	X		
Octanoic Acid	X			
Dodecane		X		
6-Octen-1-ol, 3,7-dimethyl-, (R)-	X			
Camphene		X		
Tetradecane		X		
Pentadecane	X			
Lilial	X			
Heptadecane	X			

3.8. Determination of the Optimal Extraction Time for Armpit and Hand Odor Samples

Presently, there is no library of compounds present in human scent. Due to this fact, it is necessary to consider not only the abundances of compounds extracted, but also the number of previously reported human compounds. The extraction times for the armpit and hand odor samples were evaluated on a combination of the number of human compounds extracted as well as the abundances of four common human compounds, benzaldehyde, phenol, nonanal, and decanal. Fifteen hours was determined to be the optimal extraction time for collected armpit odor through the evaluation parameters stated as shown in Figure 33 and Figure 34. Twenty-one hours was determined to be the optimal extraction time for collected hand odor through the evaluation parameters stated as shown in Figure 35 and Figure 36.

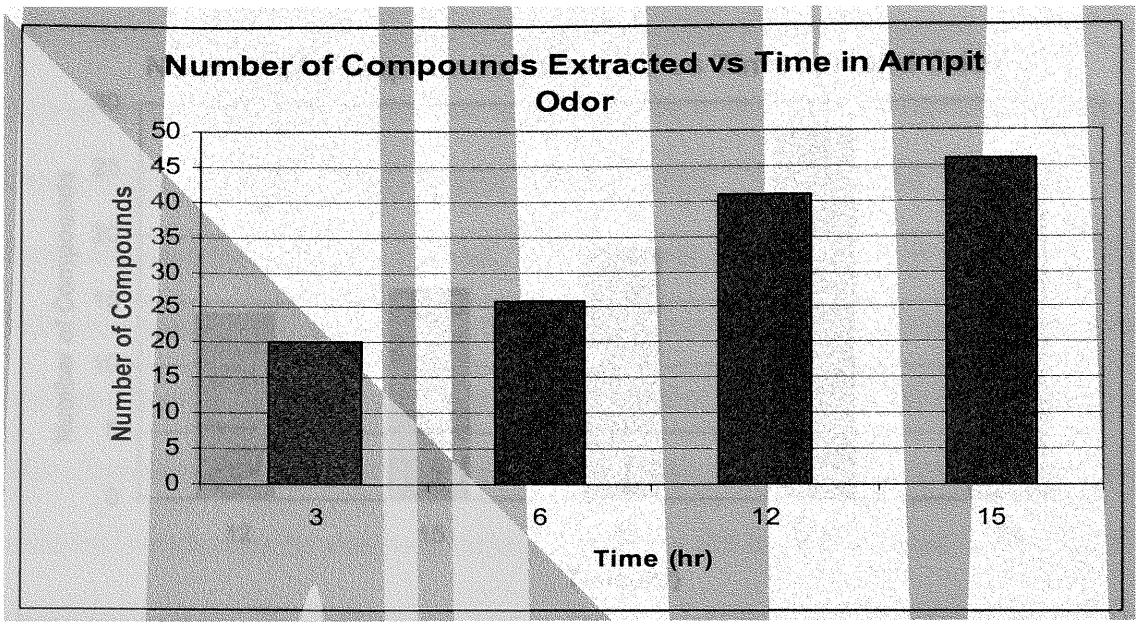


Figure 33: Number of Compounds Extracted vs. Time in Armpit Odor

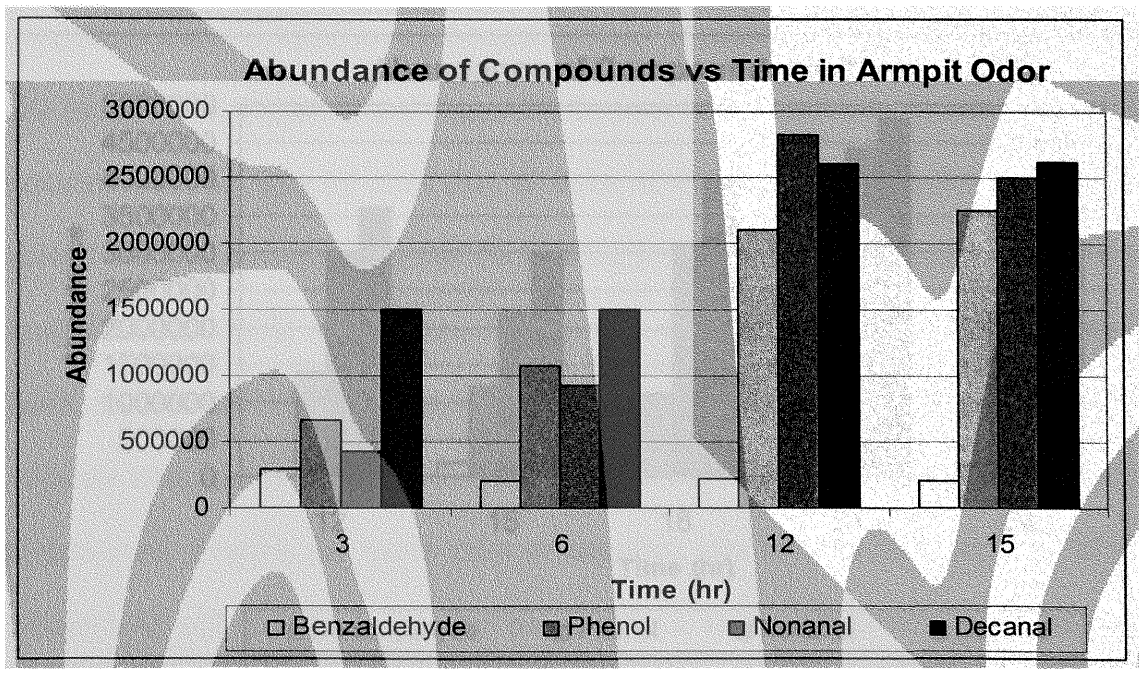


Figure 34: Abundances of Common Human Compounds Extracted vs. Time in Armpit Odor

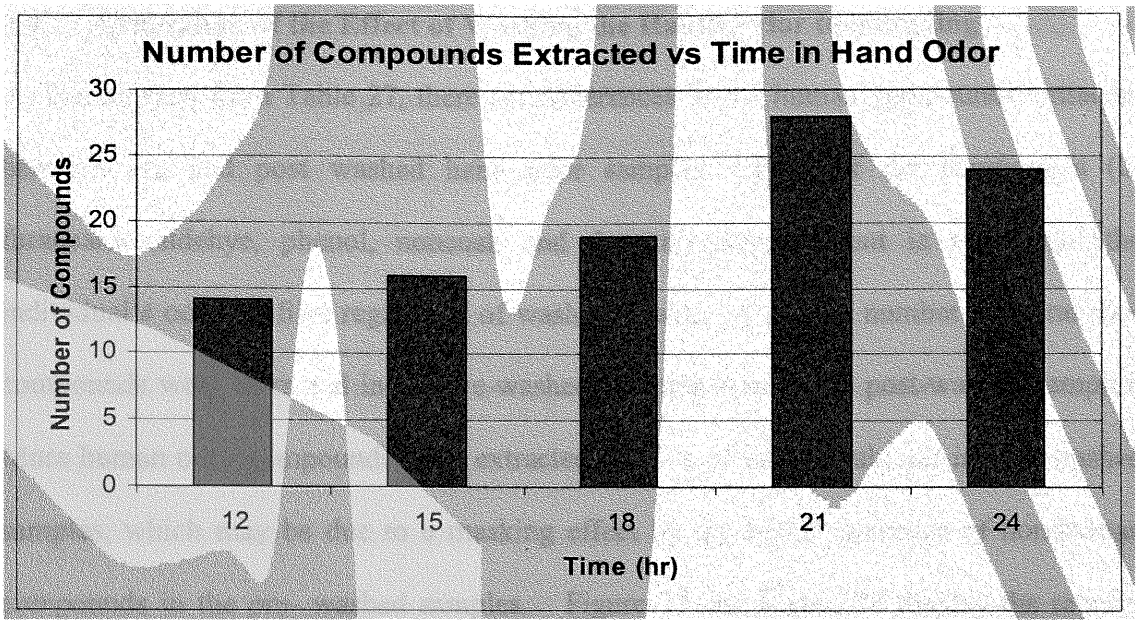


Figure 35: Number of Compounds Extracted vs. Time in Hand Odor

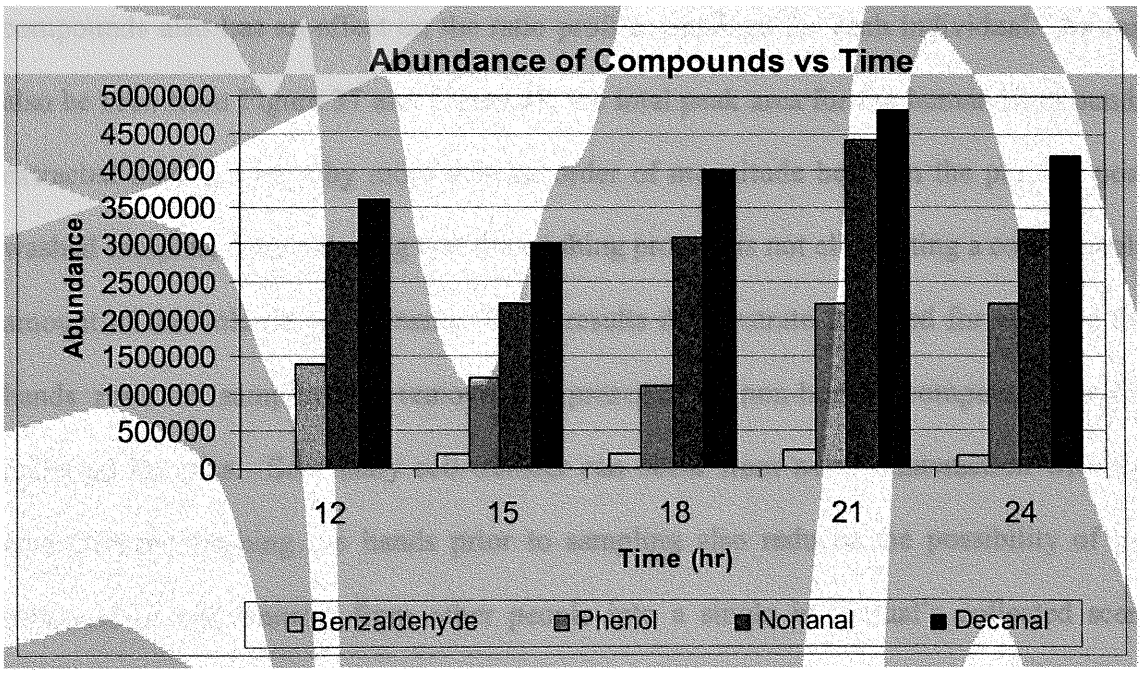


Figure 36: Abundance of Common Human Compounds vs. Time in Hand Odor

3.9. Evaluation of the Effect of Washing the Hands Prior to Sampling

As can be seen from Table 27, there are differences in the human compounds extracted between pre and post washed hand odor samples. Four of the compounds (2-furancarboxaldehye, phenol, nonanal, and decanal) were present in all six of the individual's odor profiles regardless of washing status. A greater number of extraneous compounds were extracted in the pre-washed samples than in the post-washed samples. More human odor compounds were extracted for five of the six subjects in post-washed samples, which may be due to a masking effect by the higher presence of non-human compounds in the pre- washed samples. Figure 37 and Figure 38 display the relative ratios of the common human compounds extracted for the male and female subjects between the pre and post washed samples, respectively. The presence of the extraneous compounds also has an effect on the ratio profiles obtained for each individual. As can also be seen from Figure 37 and Figure 38, the total peak area for the human compounds extracted does not vary by more than an order of magnitude between the pre and post washed samples, demonstrating that the washing process is not eliminating a considerable amount of the volatile components. These results demonstrate the need for washing the hands prior to sampling to remove the presence of non-human compounds in the collected samples. Secondary cell transfer can occur from normal interaction with the environment, washing the hands prior to sampling also reduces the possibility of the influence of cell transfer from other people into a single individual's collected scent sample.

Table 28 displays the response factor values for each of the eight standard compounds evaluated in terms of nano-grams of analyte. The amount of nano-grams was determined through consideration of the concentration of solution in parts per million (1 ppm = 1 ng/μl) and an injection amount of 2 μl. Peak area v. amount plots were constructed using the data collected which resulted in calibration curves, an example of which can be seen in Figure 39. Through the use of an average response factor it is possible to approximate the amount of volatile organic compounds extracted by the SPME fiber, as the slope of the tredline is the response factor for each compound. This study utilizes direct sampling of human odor and through contact results in the collection of biological elements, such as secretions, skin cells and bacteria on the sorbent medium. An absolute mechanism or pathway for the creation of human scent by the human body has yet to be determined; one theory is that human odor is created by bacterial interaction with human secretions which transforms non-odorous substances into odorous substances and releases them into the enviornment. The actions of bacteria on the secretions and skin cells may affect the volatile organic compounds present in the headspace above the collection material. Until the mechanism for the generation of human odor has been definitively detrermined and the role which bacterial action plays in the release VOCs after removal from the body was been established, the amount of VOCs extracted by the SPME fiber cannot be related back to the amount present on the fiber or on the collection material.

Table 27: Human Compounds Extracted Among Six Subjects both Pre and Post Washing in Hand Odor

	M2		M4		M5		F2		F7		F31	
Washing Status	**Pre**	**Post**	**Pre**	**Post**	**Pre**	**Post**	**Pre**	**Post**	**Pre**	**Post**	**Pre**	**Post**
Compound Name												
Butanoic acid	X											X
2-Furancarboxaldehyde	X	X	X	X	X	X	X	X	X	X		X
Phenol	X	X	X	X	X	X	X	X	X	X	X	X
1,6-Octadien-3-ol, 3,7-dimethyl-	X										X	X
Nonanal	X	X	X	X	X	X	X	X	X	X	X	X
Octanoic acid, methyl ester	X		X				X				X	
Octanoic Acid											X	
Decane												X
Dodecane		X		X		X		X		X		
Decanal	X	X	X	X	X	X	X	X	X	X	X	X
Nonanoic acid-methyl ester				X				X			X	X
Hexanedioic acid-dimethyl ester	X	X	X	X		X	X	X		X	X	X
Tridecane		X						X		X		
Eicosane		X		X				X				
Tetradecane	X	X	X				X			X	X	X
6,10-dimethyl-5,9-Undecadien-2-one							X	X			X	X
Dodecanoic acid-methyl ester	X											
Tridecanoic acid-methyl ester	X											
Tetradecanoic acid-methyl ester	X											
Total Number of Human Compounds	**13**	**9**	**7**	**8**	**4**	**6**	**8**	**10**	**4**	**8**	**10**	**11**
Total Number of Other Compounds	**13**	**11**	**4**	**2**	**9**	**4**	**4**	**3**	**3**	**5**	**8**	**5**

Figure 37: Comparison of the Common Human Compounds Extracted in Both Pre and Post Washed Hand Odor Samples across Three Males

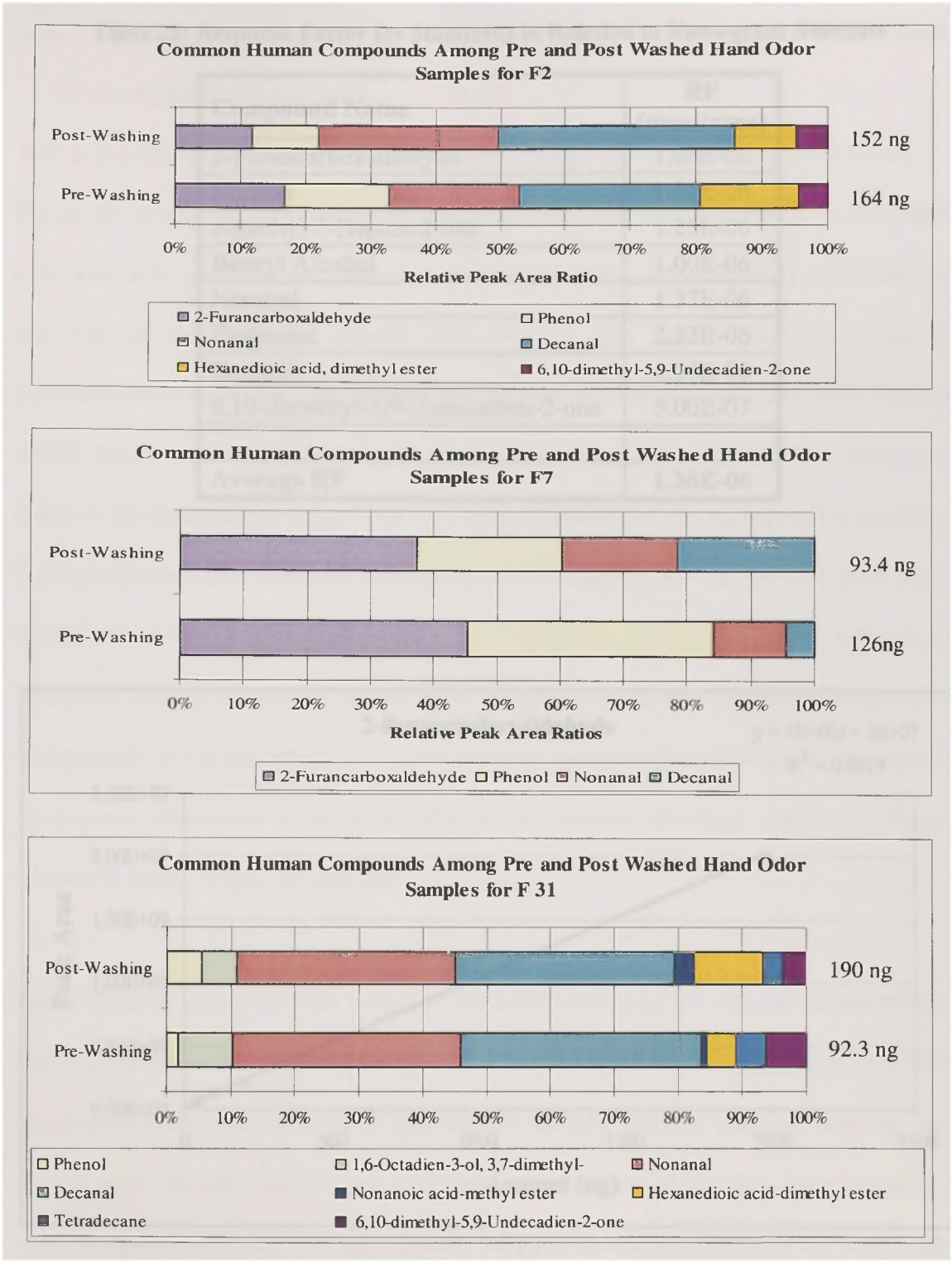


Figure 38: Comparison of the Common Human Compounds Extracted in Both Pre and Post Washing Samples of Hand Odor across Three Female

Table 28: Response Factor for Standards in Relation to Nano-gram Amounts

Compound Name	RF (mass/area)
2-Furancarboxaldehyde	1.00E-06
Nonane	1.87E-06
6-methyl-5-Hepten-2-one	1.25E-06
Benzyl Alcohol	1.00E-06
Nonanal	1.37E-06
Dodecane	2.32E-06
Decanal	1.55E-06
6,10-dimethyl-5,9-Undecadien-2-one	5.00E-07
Average RF	**1.36E-06**

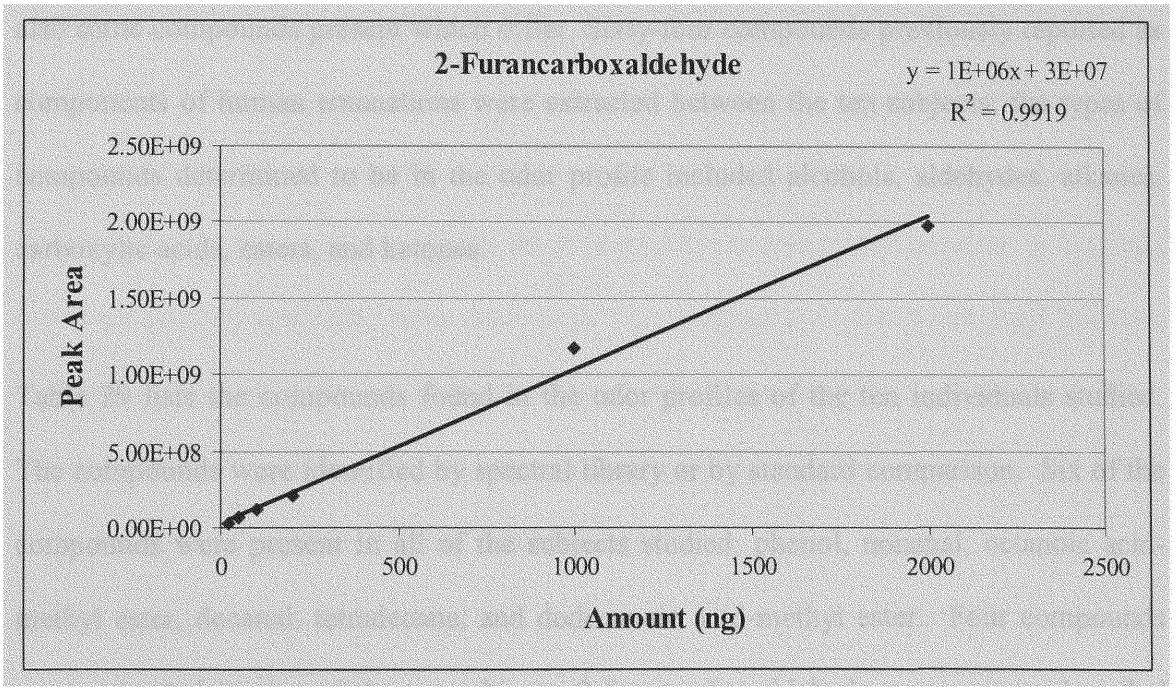


Figure 39: Calibration Curve for 2-Furancarboxaldehyde

3.10. Population Anlysis of the Volatile Organic Compounds Present Above Collected Odor Samples

3.10.1. Evaluation of the Compounds Present in Armpit Odor among Ten Individuals

Figure 40 shows the chromatograms produced from four of the different male subjects (M2, M4, M5, and M6) and Figure 41 demonstrates the chromatograms produced from the four of the different females (F2, F4, F5, and F6). Figure 40 shows the chromatograms expanded to highlight the profiles produced among the male subjects, which results in off-scale decanal, dodecanoic acid-methyl ester, and dodecanoic acid peaks in the chromatogram for Male 4. Figure 41 shows the chromatograms expanded to highlight the profiles produced among the female subjects. As can be seen from Figure 40 and Figure 41, there are some common compounds present among the subjects and also some compounds present which differ. Sixty-four compounds previously reported as components of human emanations were extracted between the ten subjects; the types of compounds determined to be in the odor profile included alcohols, aldehydes, alkanes, carboxylic acids, esters, and ketones.

Table 29 lists the compounds found in the odor profiles of the ten individuals studied. The compounds were identified by spectral library or by standard comparison. Six of the compounds were present in all of the subjects studied: phenol, nonanal, octanoic acid-methyl ester, decanal, tetradecane, and dodecanoic acid-methyl ester. Four compounds were extracted in nine of the ten subjects: 2-furancarboxaldehyde, nonanoic acid-methyl ester, 6,10-dimethyl-5,9-undecadien-2-one, and tetradecanoic acid-methyl ester. Hexanal, 1,2,4-trimethyl-benzene, benzyl alcohol, 2,4-dimethyl-hexane, acetophenone,

phenylethyl alcohol, 1-chloro-nonane, 2-decanone, tetracosane, caryophyllene, tetradecanoic acid, and oleic acid were present in only one of the subjects. Propanedioic acid-methyl ester and octanal were both extracted in some of the males studied, yet were not present in any of the female profiles. 1-methyl-2-(1-methylethyl)-benzene was extracted in some of the female subjects, yet was not present in any of the male profiles.

The frequency of the occurrence of the human compounds extracted in armpit odor among the ten individuals are listed in Table 30. As can be seen from Table 36, across the ten subjects there are fifteen high frequency compounds (100-67% presence), nineteen medium frequency compounds (66-33% presence), and thirty-one low frequency compounds (32-1% presence) among the population. It is uncertain whether scent identity lies within the ratio patterns of the common compounds between individuals, the presence of compounds which have a high variation between people, or whether it is a combination of the two factors. As was previously described in Section 3.4.5, and demonstrated in Figure 48 and Figure 49, it is possible to distinguish between individuals based on relative peak area ratio patterns of the common compound extracted between multiple samplings of individuals, and Figure 42 demonstrates the greater variability between the odor profiles obtained among individuals when the human compounds which differ between individuals, are also considered [121].

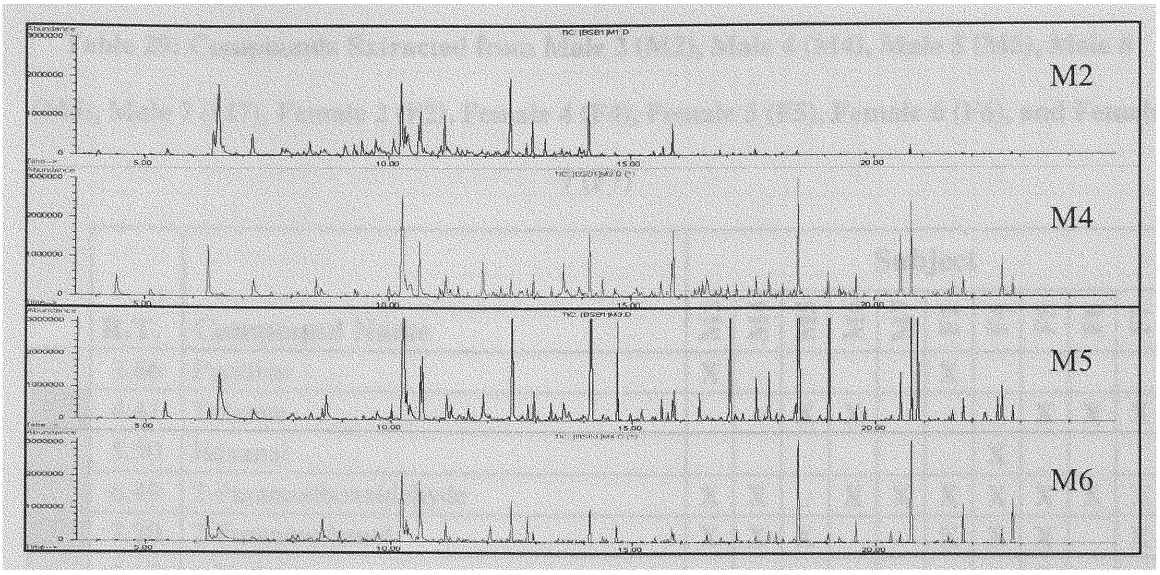


Figure 40: Comparison of Odor Profiles from Male 2 (M2), Male 4 (M4), Male 5 (M5), and Male 6 (M6) After 30min of Exercise

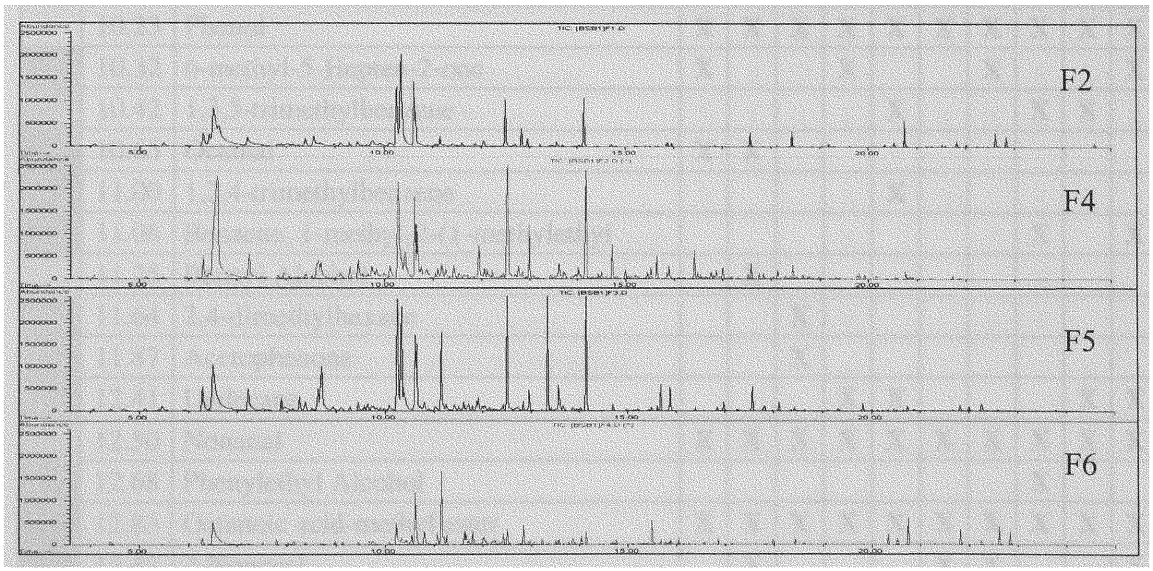


Figure 41: Comparison of Odor Profiles from Female 2 (F2), Female 4 (F4), Female 5 (F5), and Female 6 (F6) After 30min of Exercise

Table 29: Compounds Extracted from Male 2 (M2), Male 4 (M4), Male 5 (M5), Male 6 (M6), Male 7 (M7), Female 2 (F2), Female 4 (F4), Female 5 (F5), Female 6 (F6), and Female 7 (F7)

R.T.	Compound Name	Subject									
		M2	M4	M5	M6	M7	F2	F4	F5	F6	F7
3.86	Pyridine	X					X				
4.41	Toluene			X	X				X	X	X
5.50	Hexanal							X			
6.49	2-Furancarboxaldehyde	X	X		X	X	X	X	X	X	X
7.20	2-Furanmethanol	X	X	X			X	X	X		X
8.12	p-Xylene								X		
8.32	Nonane				X	X			X	X	
8.36	Heptanal		X			X				X	
8.96	Hexanoic acid-methyl ester	X			X			X	X	X	
9.07	Propanedioic acid-dimethyl ester		X	X		X					
9.12	.alpha.-Pinene								X	X	X
9.72	Benzaldehyde	X	X				X				
10.09	Furancarboxylic acid-methyl ester	X				X	X	X			
10.23	Phenol	X	X	X	X	X	X	X	X	X	X
10.32	6-methyl-5-Hepten-2-one	X			X			X			X
10.42	1,3,5-trimethylbenzene					X			X	X	
10.65	Octanal	X	X								
11.00	1,2,4-trimethylbenzene					X					
11.06	Benzene, 1-methyl-2-(1-methylethyl								X		X
11.25	Benzyl Alcohol		X								
11.64	2,4-dimethylhexane			X							
11.87	Acetophenone			X							
12.41	Undecane				X	X				X	X
12.50	Nonanal	X	X	X	X	X	X	X	X	X	X
12.68	Phenylethyl Alcohol								X		
12.83	Octanoic acid-methyl ester	X	X	X	X	X	X	X	X	X	X
13.42	2-Nonenal		X				X	X			X
13.49	1-chlorononane							X			
13.51	Acetic acid-phenylmethyl ester		X						X		
13.59	Nonanol					X	X				
13.85	Naphthalene				X				X	X	X
13.93	2-Decanone					X					

	14.02	Dodecane	X		X		X	X	X	X	X	X
	14.13	Decanal	X	X	X	X	X	X	X	X	X	X
	14.40	Nonanoic acid-methyl ester	X	X	X	X	X	X	X	X		X
	14.68	Hexanedioic acid-dimethyl ester	X			X		X	X			
	14.98	2-Decenal, (E)-		X				X				
	15.23	Tetracosane										X
	15.49	Tridecane	X		X	X		X		X		X
	15.62	Undecanal		X	X			X				X
	15.62	Tetradecanal	X	X	X			X				
	15.83	Decanoic acid-methyl ester		X	X	X		X	X	X	X	
	16.76	1-Pentadecene			X			X		X		
	16.85	Tetradecane	X	X	X	X	X	X	X	X	X	X
	16.99	Diphenyl ether								X		X
	17.17	Undecanoic acid-methyl ester		X	X	X		X		X		
	17.56	6,10-dimethyl-5,9-Undecadien-2-one	X	X	X	X	X	X	X			X
	17.79	Eicosane		X		X			X	X		X
	18.36	9-Octadecenoic acid-methyl ester		X						X		
	18.43	Dodecanoic acid-methyl ester	X	X	X	X	X	X	X	X	X	X
	18.87	Dodecanoic acid		X						X		
	19.33	Hexadecane	X		X			X		X		X
	19.61	Tridecanoic acid-methyl ester		X	X	X		X	X	X	X	
	20.45	Heptadecane		X	X	X		X				X
	20.53	7-Hexadecenoic acid-methyl ester		X	X	X			X	X	X	
	20.74	Tetradecanoic acid-methyl ester	X	X	X	X		X	X	X	X	X
	21.11	Tetradecanoic acid		X								
	21.42	Methyl 9-methyltetradecanoate	X			X		X		X	X	
	21.51	12-methyltetradecanoic acid-methyl ester				X			X			
	21.65	Oleic Acid								X		
	21.80	Pentadecanoic acid-methyl ester			X	X			X	X		
	22.46	14-methyl-pentadecanoic acid-methyl ester				X					X	
	22.83	Hexadecanoic acid-methyl ester	X	X	X	X			X	X	X	X

Table 30: Frequency of Occurrence of the Sixty-four Human Compounds Extracted from the Armpit Odor of Ten Subjects

	Frequency of Occurrence			Percentage of Occurrence (%)		
Compound Name	**Males**	**Females**	**Total**	**Males**	**Females**	**Total**
Pyridine	1	1	2	20	20	20
Toluene	2	3	5	40	60	50
Hexanal	0	1	1	0	20	10
2-Furancarboxaldehyde	4	5	9	80	100	90
2-Furanmethanol	3	4	7	60	80	70
p-Xylene	0	1	1	0	20	10
Nonane	2	2	4	40	40	40
Heptanal	2	1	3	40	20	30
Hexanoic acid-methyl ester	2	3	5	40	60	50
Propanedioic acid-dimethyl ester	3	0	3	60	0	30
.alpha.-Pinene	0	3	3	0	60	30
Benzaldehyde	2	1	3	40	20	30
Furancarboxylic acid-methyl ester	2	2	4	40	40	40
Phenol	5	5	10	100	100	100
5-Hepten-2-one, 6-methyl-	2	2	4	40	40	40
Benzene, 1,3,5-trimethyl-	1	2	3	20	40	30
Octanal	2	0	2	40	0	20
Benzene, 1,2,4-trimethyl-	1	0	1	20	0	10
Benzene, 1-methyl-2-(1-methylethyl	0	2	2	0	40	20
Benzyl Alcohol	1	0	1	20	0	10
Hexane, 2,4-dimethyl-	1	0	1	20	0	10
Acetophenone	1	0	1	20	0	10
Undecane	2	2	4	40	40	40
Nonanal	5	5	10	100	100	100
Phenylethyl Alcohol	0	1	1	0	20	10
Octanoic acid-methyl ester	5	5	10	100	100	100
2-Nonenal, (E)-	1	3	4	20	60	40
Nonane, 1-chloro-	0	1	1	0	20	10
Acetic acid-phenylmethyl ester	1	1	2	20	20	20
Nonanol	1	1	2	20	20	20
Naphthalene	1	3	4	20	60	40
2-Decanone	1	0	1	20	0	10
Dodecane	3	5	8	60	100	80

Decanal	5	5	10	100	100	100
Nonanoic acid-methyl ester	5	4	9	100	80	90
Hexanedioic acid-dimethyl ester	2	2	4	40	40	40
2-Decenal, (E)-	1	1	2	20	20	20
Tetracosane	0	1	1	0	20	10
Tridecane	3	3	6	60	60	60
Undecanal	2	2	4	40	40	40
Tetradecanal	3	1	4	60	20	40
Decanoic acid-methyl ester	3	4	7	60	80	70
1-Pentadecene	1	2	3	20	40	30
Tetradecane	5	5	10	100	100	100
Diphenyl ether	0	2	2	0	40	20
Undecanoic acid-methyl ester	3	2	5	60	40	50
Caryophyllene	1	0	1	20	0	10
5,9-Undecadien-2-one, 6,10-dimethy	5	3	8	100	60	80
Eicosane	2	3	5	40	60	50
9-Octadecenoic acid (Z)-, methyl ester	1	1	2	20	20	20
Dodecanoic acid-methyl ester	5	5	10	100	100	100
Dodecanoic acid	1	1	2	20	20	20
Hexadecane	2	3	5	40	60	50
Tridecanoic acid-methyl ester	3	4	7	60	80	70
Heptadecane	3	2	5	60	40	50
7-Hexadecenoic acid-methyl ester	3	3	6	60	60	60
Tetradecanoic acid-methyl ester	4	5	9	80	100	90
Tetradecanoic acid	1	0	1	20	0	10
Methyl 9-methyltetradecanoate	2	3	5	40	60	50
Tetradecanoic acid, 12-methyl-	1	1	2	20	20	20
Oleic Acid	0	1	1	0	20	10
Pentadecanoic acid-methyl ester	2	2	4	40	40	40
Pentadecanoic acid, 14-methyl-	1	1	2	20	20	20
Hexadecanoic acid-methyl ester	4	4	8	80	80	80

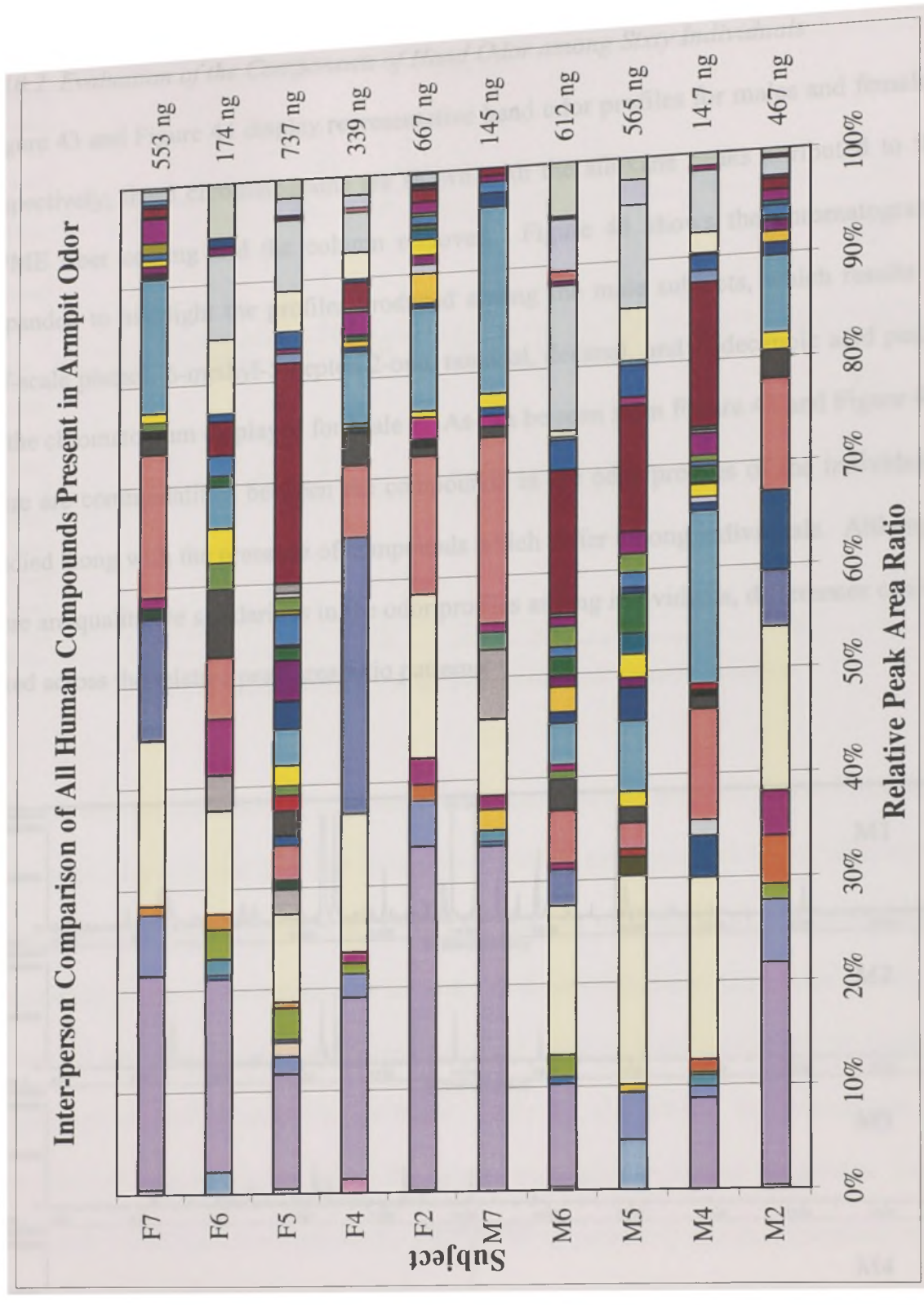


Figure 42: Inter-person Comparison of the Relative Peak Area Ratios of All Human Compounds Extracted in Armpit Odor among Ten Subjects

3.10.2. Evaluation of the Components of Hand Odor among Sixty Individuals

Figure 43 and Figure 44 display representative hand odor profiles for males and females, respectively; these chromatograms are shown with the siloxane peaks attributed to the SPME fiber coating and the column removed. Figure 43 shows the chromatograms expanded to highlight the profiles produced among the male subjects, which results in off-scale phenol, 6-methyl-5-hepten-2-one, nonanal, decanal, and dodecanoic acid peaks in the chromatogram displayed for Male 1. As can be seen from Figure 43 and Figure 44, there are commonalities between the compounds in the odor profiles of the individuals studied along with the presence of compounds which differ among individuals. Although there are qualitative similarities in the odor profiles among individuals, differences can be noted across the relative peak area ratio patterns.

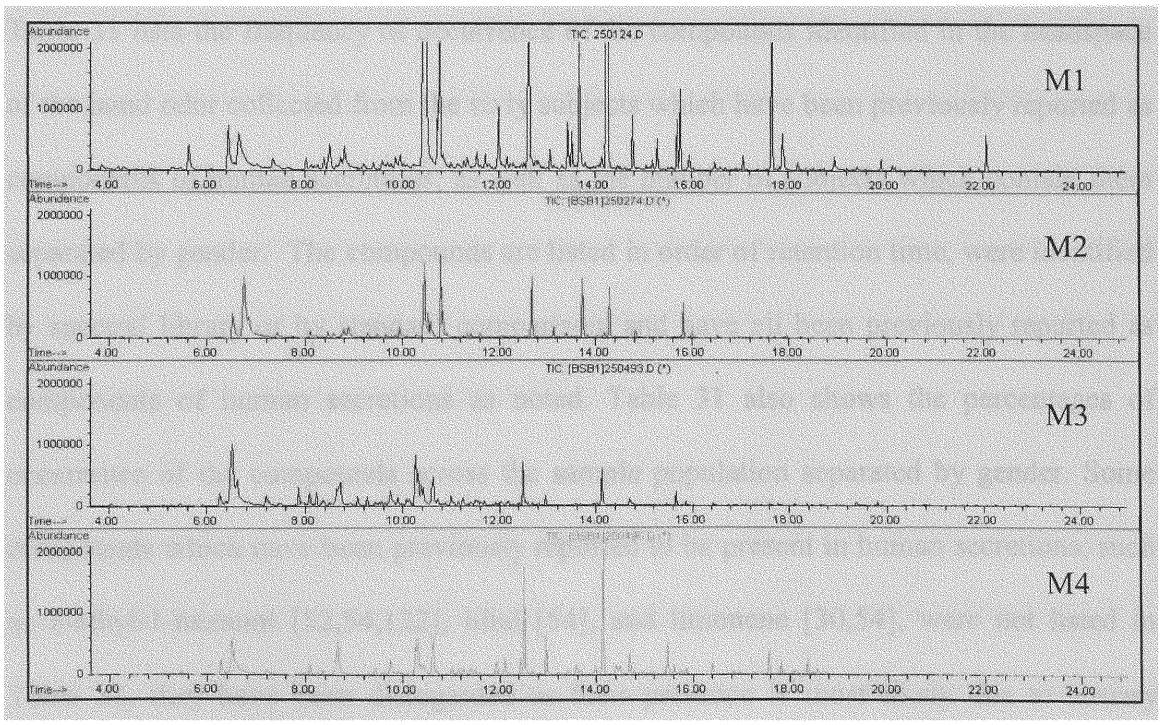


Figure 43: Hand Odor Profiles Produced from Male Subjects

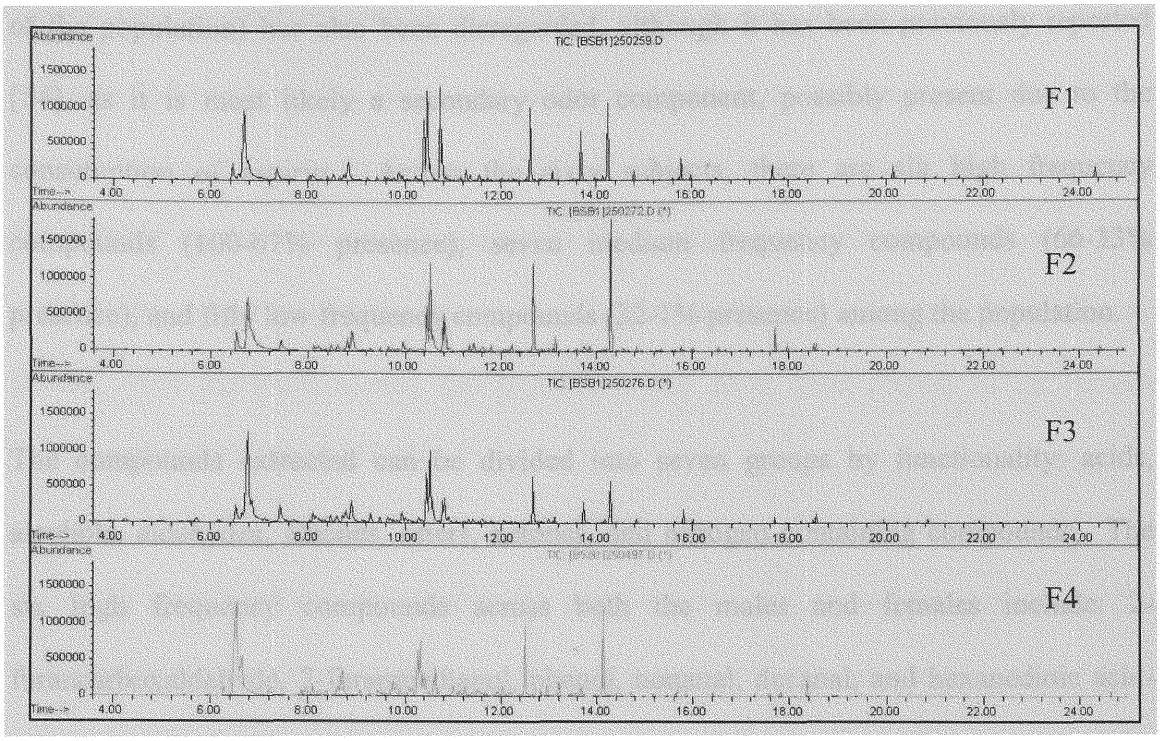


Figure 44: Hand Odor Profiles Produced from Female Subjects

Table 31 lists the frequency of occurrence of the compounds identified in the headspace of the hand odor collected from the sixty subjects which have been previously reported as components of human secretions, as well as the number of subjects which contain them separated by gender. The compounds are listed in order of retention time, were identified by spectral library or by standard comparison, and have all been previously reported as components of human secretions as noted. Table 31 also shows the percentages of occurrence of the compounds across the sample population separated by gender. Some compounds which have been previously reported to be present in human secretions, such as 2-ethyl-1-hexanol [52,54,122], lilial [54], and limonene [30,54], were not listed in Table 31, they have been disregarded as their presence is most likely due to tertiary odors, i.e. skin lotion, perfumes, clothing, etc. Methyl salicylate (present in less than 5%

of the population) has also been disregarded, although it has been previously reported [54], as it is most likely a secondary odor component, possibly present due to the consumption of aspirin. Across the sixty subjects, there are six high frequency compounds (100-67% presence), seven medium frequency compounds (66-33% presence), and fifty low frequency compounds (32-1% presence) among the population.

The compounds extracted can be divided into seven groups by functionality: acids, alcohols, aldehydes, alkanes, esters, ketones, and nitrogen containing compounds. The six high frequency compounds across both the males and females include: 2-furancarboxaldehyde, 2-furanmethanol, phenol, nonanal, decanal, and hexanedioic acid-dimethyl ester. Of these compounds, nonanal and decanal were previously reported as high frequency compounds in the headspace above the forearm skin of females [53]. The seven medium frequency compounds across the males and the females include: propanedioic acid-dimethyl ester, 6-methyl-5-hepten-2-one, octanoic acid-methyl ester, dodecane, undecanal, 6,10-dimethyl-5,9-undecadiene-2-one, and tetradecane. Tetradecane was also previously reported as a high frequency compound present in the headspace above the forearm skin of females; however, 6-methyl-5-hepten-2-one was mentioned as a low frequency compound [53].

Fifteen of the sixty-three compounds extracted were aldehydes which are present in human odor as a result of oxidative degradation of sebaceous secretion components [52]. E-2-nonenal was extracted in 25% of the total population whose ages ranged from 17-28 years of age, which is in agreement with previous studies of the volatile components of

armpit odor conducted by the authors [3,126,121] yet diverges from the possibility of utilizing E-2-nonenal as a compound which increases with age and as a possibleodor marker for individuals over the age of 40 [52]. A preliminary study by the authors into the volatile organic compounds present in the headspace of collected hand odor from children has also revealed the presence of E-2-nonenal [123]. Hexanal, heptanal, and phenol were extracted among the population and have been shown to be volatile components of the blood [27,28].

It can be postulated that the fresher the scent sample, the higher the probability that compounds with greater volatility are present as compared to aged samples where these types of compounds may have dissipated. This has been supported anecdotally from the behavior of bloodhounds when following a scent trail [124]. A fresh trail is followed with the head in an upright position suggesting that more volatile compounds are being utilized; whereas, an old trail is followed with the nose to the ground suggesting that less volatile compounds are being utilized. The ability of human scent line-up canines to match odor which has been collected and stored in a glass jar for more than seven years suggests that a steady state is created within the container which limits dissipation of the odor components [93]. The samples collected for this study were also stored in a glass container and the high and medium frequency compounds extracted among the population studied have vapor pressures that fall in the semi-volatile range as compared to some of the low frequency compounds, as can be seen in Table 32. Canines have the demonstrated the ability to smell TNT (v.p.=$3.0*10^{-6}$ torr) and TNT can also be readily extracted through headspace SPME [125], it is reasonable to assume that all forty-five

compounds listed with vapor pressures equal to or greater than 10^{-6} torr can also be detected by canines. It is possible that a product of the long exposure times of the SPME fiber to the headspace inside the vial containing the scent sample is the extraction compounds with low vapor pressures are appearing in the odor profiles.

Table 31: Human Compounds Extracted in Hand Odor among Sixty Individuals

			Frequency of Occurrence			Percentage of Occurrence (%)		
	R.T.	Compound Name	Males	Females	Total	Males	Females	Total
	3.86	Pyridine	1	0	1	3.33	0.00	1.67
	4.41	Toluene	0	1	1	0.00	3.33	1.67
	4.74	2-Butenal, 2-methyl-	2	2	4	6.67	6.67	6.67
	5.32	Octane	1	0	1	3.33	0.00	1.67
	5.50	Hexanal	0	1	1	0.00	3.33	1.67
	6.49	2-Furancarboxaldehyde	29	30	59	96.67	100	98.33
	7.20	2-Furanmethanol	24	25	49	80.00	83.33	81.67
	7.78	Benzene, 1,3-dimethyl-	0	2	2	0.00	6.67	3.33
	8.12	p-Xylene	2	2	4	6.67	6.67	6.67
	8.32	Nonane	6	6	12	20.00	20.00	20.00
	8.36	Heptanal	6	2	8	20.00	6.67	13.33
	9.07	Propanedioic acid-dimethyl ester	17	17	34	56.67	56.67	56.67
	9.75	Benzene, 1-ethyl-2-methyl-	3	0	3	10.00	0.00	5.00
	9.87	Benzaldehyde	6	3	9	20.00	10.00	15.00
	9.89	Benzene, 1,3,5-trimethyl-	4	5	9	13.33	16.67	15.00
	10.09	Furancarboxylic acid-methyl ester	2	3	5	6.67	10.00	8.33
	10.15	Benzene, 1-ethyl-3-methyl-	0	2	2	0.00	6.67	3.33
	10.23	Phenol	30	30	60	100	100	100
	10.34	5-Hepten-2-one, 6-methyl-	8	16	24	26.67	53.33	40.00
	10.78	Octanal	4	6	10	13.33	20.00	16.67
	11.00	1,2,4-Trimethylbenzene	0	1	1	0.00	3.33	1.67
	11.10	Thiazolidine	1	1	2	3.33	3.33	3.33
	11.25	Benzyl Alcohol	3	6	9	10.00	20.00	15.00
	11.60	Benzene, 1,2,3-trimethyl-	1	2	3	3.33	6.67	5.00
	12.13	1-Octanol	1	2	3	3.33	6.67	5.00
	12.41	Undecane	4	2	6	13.33	6.67	10.00
	12.45	1,6-Octadien-3-ol, 3,7-dimethyl-	5	7	12	16.67	23.33	20.00
	12.50	Nonanal	30	30	60	100	100	100

	12.68	Phenylethyl Alcohol	0	3	3	0.00	10.00	5.00
	12.83	Octanoic acid-methyl ester	5	15	20	16.67	50.00	33.33
	13.42	2-Nonenal, (E)-	7	8	15	23.33	26.67	25.00
	13.47	Nonane, 1-chloro-	0	1	1	0.00	3.33	1.67
	13.59	Nonanol	1	1	2	3.33	3.33	3.33
	13.85	Naphthalene	2	1	3	6.67	3.33	5.00
	13.93	2-Decanone	2	0	2	6.67	0.00	3.33
	14.02	Dodecane	8	12	20	26.67	40.00	33.33
	14.13	Decanal	30	30	60	100	100	100
	14.40	Nonanoic acid-methyl ester	7	12	19	23.33	40.00	31.67
	14.66	6-Octen-1-ol, 3,7-dimethyl-, (R)-	0	1	1	0.00	3.33	1.67
	14.70	Hexanedioic acid, dimethyl ester	18	26	44	60.00	86.67	73.33
	14.98	2-Decenal, (E)-	1	4	5	3.33	13.33	8.33
	15.49	Tridecane	9	8	17	30.00	26.67	28.33
	15.62	Undecanal	9	14	23	30.00	46.67	38.33
	15.68	Eicosane	0	2	2	0.00	6.67	3.33
	15.76	Tetradecanal	2	3	5	6.67	10.00	8.33
	15.83	Decanoic acid, methyl ester	1	4	5	3.33	13.33	8.33
	16.44	.beta.-Pinene	1	1	2	3.33	3.33	3.33
	16.50	2-Octenal, (E)-	4	5	9	13.33	16.67	15.00
	16.58	Decanoic acid	0	1	1	0.00	3.33	1.67
	16.85	Tetradecane	10	15	25	33.33	50.00	41.67
	17.08	Dodecanal	2	0	2	6.67	0.00	3.33
	17.56	6,10-dimethyl-5,9-Undecadien-2-one	19	20	39	63.33	66.67	65.00
	18.10	Pentadecane	0	1	1	0.00	3.33	1.67
	18.37	Tridecanal	2	1	3	6.67	3.33	5.00
	18.43	Dodecanoic acid, methyl ester	7	5	12	23.33	16.67	20.00
	18.87	Dodecanoic acid	6	7	13	20.00	23.33	21.67
	19.33	Hexadecane	0	1	1	0.00	3.33	1.67
	20.36	Cyclotetradecane	0	4	4	0.00	13.33	6.67
	20.45	Heptadecane	0	3	3	0.00	10.00	5.00
	20.53	7-Hexadecenoic acid, methyl ester	0	1	1	0.00	3.33	1.67
	20.74	Tetradecanoic acid, methyl ester	3	1	4	10.00	3.33	6.67
	22.83	Hexadecanoic acid, methyl ester	0	3	3	0.00	10.00	5.00
	23.76	Cyclohexadecane	0	1	1	0.00	3.33	1.67

Table 32: Vapor Pressure Values for the Sixty-three Human Compounds in Hand Odor

Frequency (H/M/L)	Compound Name	Vapor Pressure (torr)	Molecular Weight (g/mol)
Acid			
L	Dodecanoic Acid	8.991E-07[a]	200.32
L	Decanoic acid	1.338E-16[a]	172.27
Alcohol			
H	2-Furanmethanol	6.098E-01[a]	98.10
H	Phenol	2.199E-02[a]	94.11
L	3,7-dimethyl-1,6-octadien-3-ol	7.303E-03[a]	154.25
L	Benzyl alcohol	6.379E-03[a]	108.14
L	Phenylethyl alcohol	6.246E-03[a]	122.17
L	1-octanol	4.911E-03[a]	130.23
L	3,7-dimethyl-6-octen-1-ol	3.086E-03[a]	156.00
L	Nonanol	8.088E-04[a]	144.25
Aldehyde			
L	2-methyl-2-butenal	1.705[a]	84.12
H	2-Furancarboxaldehyde	1.870E-01[a]	96.09
L	Heptanal	1.829E-01[a]	114.19
L	Benzaldehyde	6.011E-02[a]	106.12
L	Hexanal	5.310E-02[b]	100.16
L	Octanal	4.339E-02[b]	128.21
H	Nonanal	3.330E-02[b]	142.24
H	Decanal	9.570E-03[a]	156.27
M	Dodecanal	1.792E-03[a]	184.32
L	Tetradecanal	3.445E-04[a]	212.37
L	E-2-decenal	Not Available	126.20
L	(E)-2-nonenal	Not Available	140.22
M	Undecanal	Not Available	154.25
L	(E)-2-octenal	Not Available	170.29
L	Tridecanal	Not Available	198.35
Aliphatic/Aromatic			
L	Toluene	2.822a	92.14
L	Octane	1.037a	114.23
L	1-Chlorononane	1.037a	162.70
L	p-Xylene	6.595E-01[a]	106.17
L	Nonane	2.532E-01[a]	128.26
L	Benzene, 1-ethyl-3-methyl-	2.086E-01[a]	120.19
L	Benzene, 1-ethyl-2-methyl-	1.759E-01[a]	120.19
L	Benzene, 1,3,5-trimethyl-	1.710E-01[a]	120.19
L	Benzene, 1,2,3-trimethyl-	1.039E-01[a]	120.19
L	.beta.-Pinene	4.328E-02[b]	136.24

L	1,2,4-Trimethylbenzene	4.011E-02[b]	120.19
L	Undecane	2.583E-02[a]	156.31
L	Naphthalene	1.739E-02[a]	128.17
M	Dodecane	7.203E-03[a]	170.34
L	Pentadecane	6.379E-03[a]	212.42
L	Tridecane	2.008E-03[a]	184.36
L	Tetradecane	5.354E-04[a]	198.39
L	Hexadecane	3.616E-05[a]	226.44
L	Heptadecane	5.123E-06[a]	240.47
L	Cyclotetradecane	Not Available	196.00
L	1,3-dimethyl-benzene	Not Available	106.17
L	Eicosane	Not Available	224.43
L	Cyclohexadecane	Not Available	282.55
Ketones			
M	6-methyl-5-hepten-2-one	Not Available	126.20
M	6,10-dimethyl-5,9-undecadien-2-one	Not Available	156.27
L	2-Decanone	Not Available	194.32
Esters			
M	Propanedioic acid, dimethyl ester	3.254E-02[a]	132.00
M	Octanoic acid, methyl ester	2.427E-02[a]	158.24
L	Decanoic acid, methyl ester	3.055E-03[a]	186.29
H	Hexanedioic acid, dimethyl ester	1.506E-03[a]	174.00
L	Dodecanoic acid, methyl ester	5.466E-04[a]	214.35
L	Tetradecanoic acid, methyl ester	1.304E-04[a]	242.40
L	Hexadecanoic acid, methyl ester	2.598E-05[a]	270.45
L	Furancarboxylic acid, methyl ester	Not Available	126.00
L	Nonanoic acid, methyl ester	Not Available	172.27
L	7-hexadecenoic acid, methyl ester	Not Available	268.00
Amines/Amides			
L	Pyridine	2.051[a]	79.10
L	Thiazolidine	Not Available	89.16

*Note: (a) Vapor pressures calculated using the Antoine Equation from Knovel Critical Tables, (b) Extrapolated from data found in the Handbook of Chemistry & Physics (www.hbcpnetbase.com)

Figure 45 and Figure 46 demonstrate the relative ratios of the human compounds extracted in the headspace above the collected hand odor samples for the population separated by gender. The colors which correspond to the compounds are noted in Table 31. As can be seen from the color coded odor charts, differences in the ratio patterns between subjects are evident even for the high frequency compounds among individuals.

It is uncertain whether scent identity lies within the ratio patterns of the common compounds between individuals, the presence of compounds which have a high variation between people, or whether it is a combination of the two factors. The author has published that it is possible to distinguish VOCs from collected armpit samples between individuals based on relative peak area ratio patterns of the common compound extracted between multiple samplings of individuals, and that greater variability between the odor profiles among individuals can be achieved when the human compounds which differ between individuals, are also considered [126].

The hand odor profiles evaluated were produced from a combination of sebaceous and eccrine secretions, without the influence of the apocrine glands as seen in armpit odor. The ability of canines to distinguish the odors of humans over long periods of time [93] suggest that human scent is stable over time, or that portions of an individual's odor profile are stable even though elements of the odor may change. Alterations to portions of the odor of an individual may occur due to the influence of illness, the onset of puberty, the menstrual cycle in females, etc. Many of these factors directly affect the apocrine gland. The secretions obtained from the eccrine and sebaceous glands are less likely to be influenced by these changes, thereby more likely to produce the stable odor of an individual. Trailing canines have shown the ability to follow human odor which is left as an individual passes through the environment, the odor deposited by traversing an area is the overall odor of the individual. Apocrine glands are also centralized to the armpit and genital regions of the body, whereas eccrine and sebaceous glands, which are

also present in the aforementioned regions, are distributed over the body as a whole and thereby may play a greater role in the overall body odor of an individual.

3.10.3. Comparison of Armpit and Hand Odor Profiles

Eight of the ten subjects discussed in Section 3.10.1, also participated in the hand odor population study. For each of these subjects, four females and four males, the volatile organic compounds determined in the odor collected from the armpit region and from the palms of the hands have been compared and are shown in Table 33. The odor profile produced from the hands and the armpit area of a single individual are similar; however, differences can be noted. This was an expected result due to the fact that these two regions of the body contain different types of sweat glands. The hand odor profiles were produced from a combination of sebaceous and eccrine secretions, whereas the armpit odor profiles were produced from a combination of sebaceous, eccrine, and apocrine secretions. Collected hand secretions are also less concentrated than armpit secretions that have been collected after physical activity. Qualitative similarities exist between the compounds present in the odor profiles produced for the hands and the armpit region for an individual.

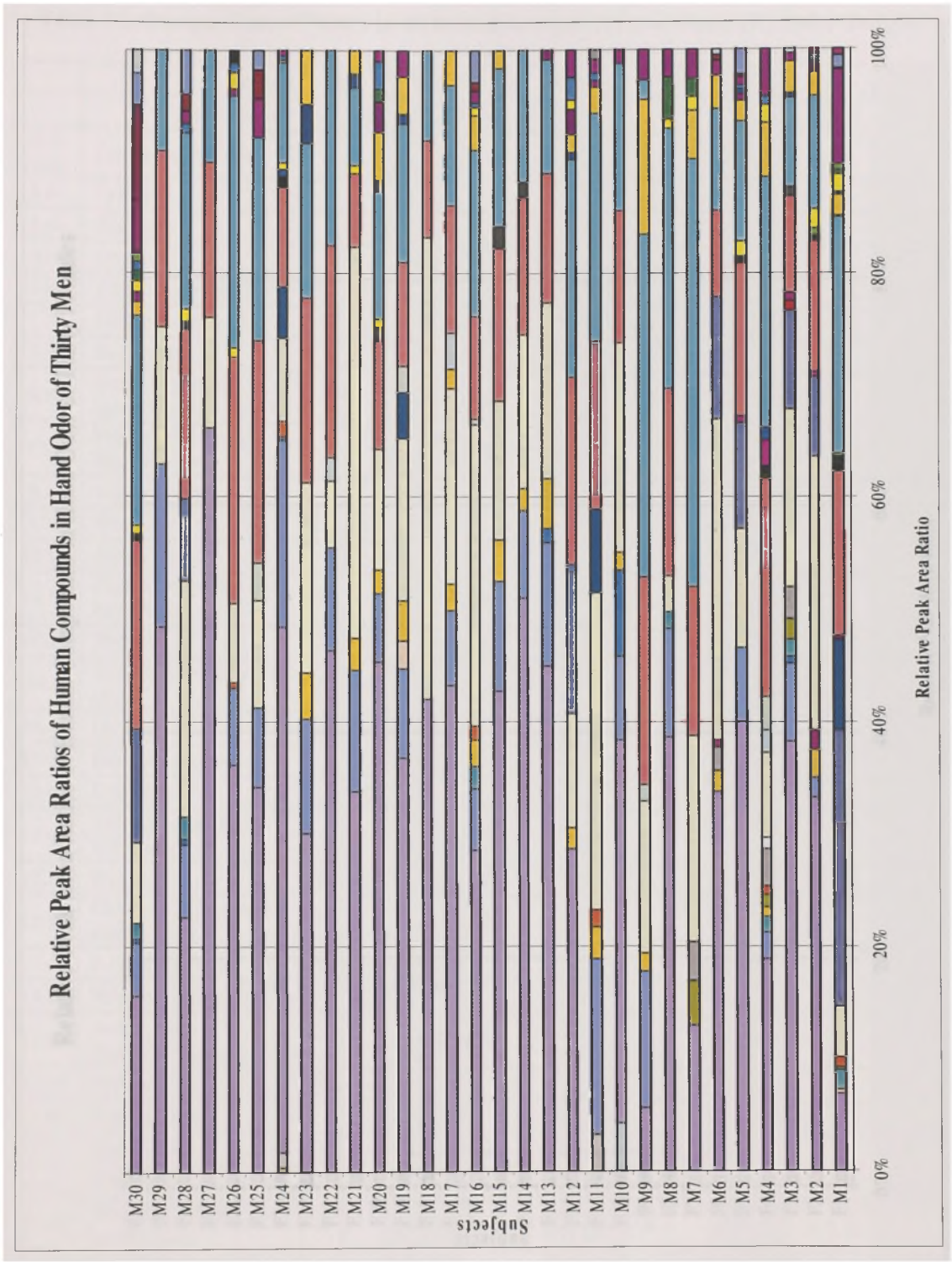


Figure 45: Relative Peak Area Ratios of the Human Compounds Extracted in Hand Odor across Thirty Men

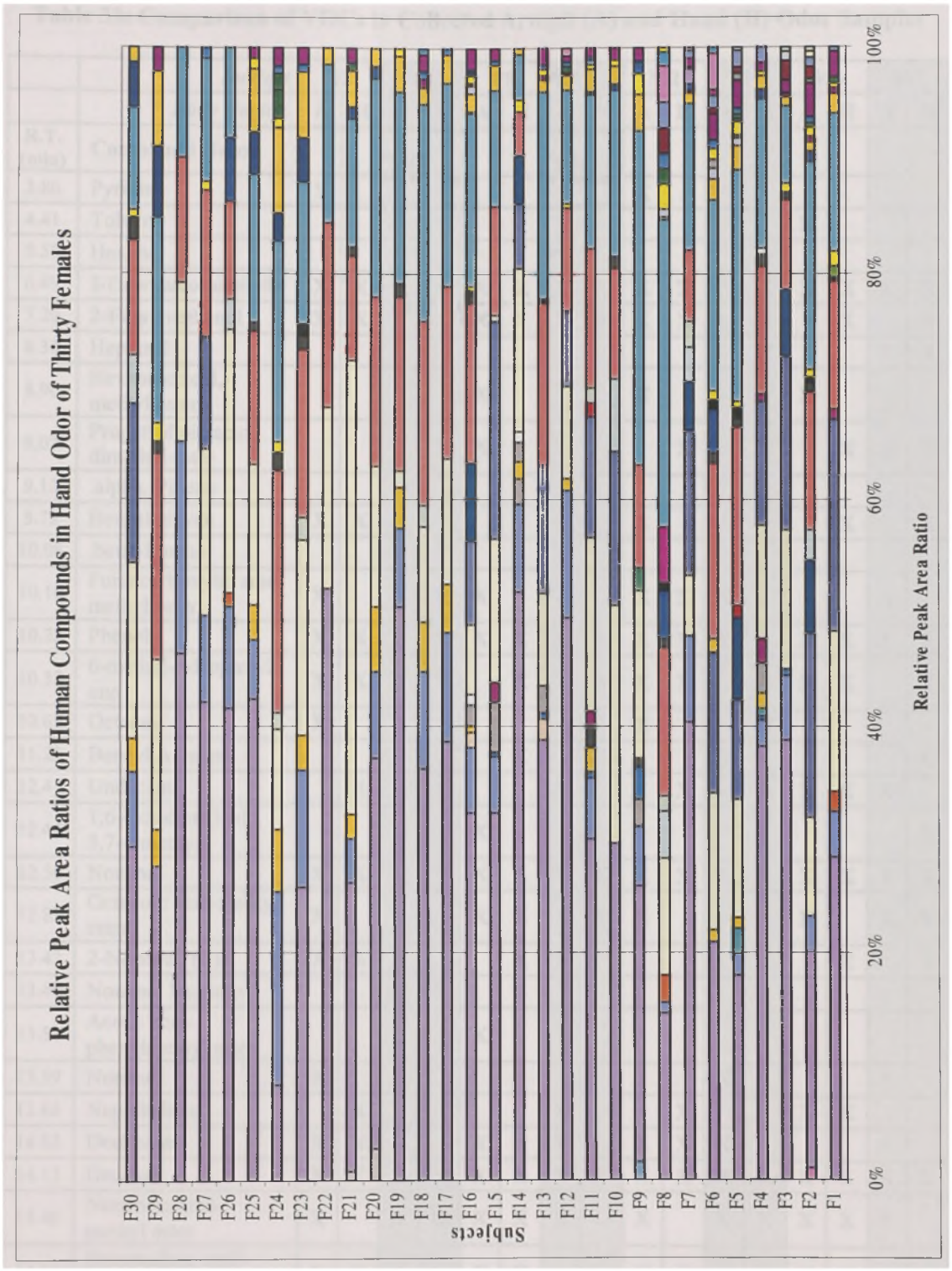


Figure 46: Relative Peak Area Ratios of the Human Compounds Extracted in Hand Odor across Thirty Females

Table 33: Comparison of VOCs in Collected Armpit (A) and Hand (H) Odor Samples

	Subject	F2		F4		F5		F7		M2		M4		M6		M7	
	Body Region	A	H	A	H	A	H	A	H	A	H	A	H	A	H	A	H
R.T. (min)	Compound Name																
3.86	Pyridine	X								X							
4.41	Toluene							X						X			
5.50	Hexanal			X													
6.49	2-Furancarboxaldehyde	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
7.20	2-Furanmethanol	X	X	X	X	X	X	X	X	X	X	X	X		X		X
8.36	Heptanal				X								X			X	X
8.96	Hexanoic acid,-methyl ester			X		X				X				X			
9.07	Propanedioic acid-dimethyl ester				X	X					X				X	X	X
9.12	.alpha.-Pinene							X									
9.72	Benzaldehyde	X	X							X					X		X
10.08	.beta.-Pinene							X									
10.10	Furancarboxylic acid-methyl ester	X		X	X	X				X	X	X				X	
10.23	Phenol	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
10.32	6-methyl-5-Hepten-2-one	X	X	X	X		X	X	X	X	X		X	X	X		X
10.65	Octanal	X								X							
11.25	Benzyl Alcohol						X					X					X
12.41	Undecane		X		X			X			X		X	X	X	X	
12.44	1,6-Octadien-3-ol, 3,7-dimethyl-					X											X
12.50	Nonanal	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
12.83	Octanoic acid-methyl ester	X		X	X	X	X	X	X	X			X	X		X	X
13.42	2-Nonenal, (E)-	X	X	X			X	X							X		X
13.49	Nonane, 1-chloro-			X	X												
13.51	Acetic acid-phenylmethyl ester					X											
13.59	Nonanol	X										X				X	
13.86	Naphthalene		X					X			X			X	X		
14.02	Dodecane	X	X	X		X	X	X	X	X	X	X				X	
14.13	Decanal	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
14.40	Nonanoic acid-methyl ester	X		X	X	X	X	X		X		X	X	X	X	X	
14.68	Hexanedioic acid-dimethyl ester	X	X	X	X	X	X		X	X	X		X	X	X		X
14.98	2-Decenal, (E)-	X										X					
15.49	Tridecane	X	X			X	X	X	X	X	X	X		X	X		
15.62	Undecanal	X	X		X	X	X	X				X			X		X

15.62	Tetradecanal	X								X	X	X					
15.83	Decanoic acid-methyl ester	X		X		X	X							X			
16.85	Tetradecane	X		X		X	X	X		X		X		X		X	X
17.17	Undecanoic acid-methyl ester	X				X						X		X			
17.56	6,10-dimethyl-5,9-Undecadien-2-one	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
18.36	9-Dodecenoic acid-methyl ester					X											
18.43	Dodecanoic acid-methyl ester	X		X		X	X	X	X	X		X		X	X	X	
18.87	Dodecanoic acid		X		X	X	X					X			X		
19.29	10-methyl-Dodecanoic acid-methyl ester			X								X		X			
19.33	Hexadecane	X				X		X		X		X					
19.61	Tridecanoic acid-methyl ester	X		X		X						X		X			
20.45	Heptadecane	X				X		X				X		X			
20.53	7-Hexadecenoic acid,-methyl ester			X		X	X					X		X			
20.74	Tetradecanoic acid-methyl ester	X		X		X		X	X	X		X	X	X			
21.42	Methyl 9-methyltetradecanoate	X				X				X				X			
21.51	12-methyl-Tetradecanoic acid-methyl ester			X								X					
21.65	Oleic Acid					X											
21.80	Pentadecanoic acid,-methyl ester			X		X								X			
22.83	Hexadecanoic acid-methyl ester			X		X	X	X	X	X		X		X			

3.11. Evaluation of Odor Profiles for Individuals over Time

3.11.1. Armpit Region Samples

Twenty-two human compounds were extracted between three weekly samplings of Male 2 and three weekly samplings of Male 4, as listed in Table 34. Of the twenty-two human compounds extracted between the two individuals, five were common between Male 2 and Male 4: 2-furanmethanol, furancarboxylic acid-methyl ester, phenol, nonanal, and

decanal. The ratio pattern comparison of the common compounds among multiple samplings of an individual can be shown in a semi-quantitative fashion. For human scent to be used as a biometric measurement, it is important to show that the variability between samplings of one individual is not greater than the variability seen among individuals. Figure 47 shows the intra-person variability between three weekly samplings of Male 2 and Male 4 based on the relative ratios of the peak areas of the twenty-two common compounds extracted in all three samplings of each subject. As has been previously described elsewhere [3] and is shown here graphically in Figure 47, the relative peak area ratio patterns of the common compounds extracted for the same individual over time demonstrate good reproducibility. Figure 47 also shows the total peak area for these compounds across the three samplings of Male 2 and Male 4. Male 4 appears to have better reproducibility than Male 2; however, the area values are also more similar. Table 35 displays the correlation coefficients determined between the three weekly samplings of Male 2 and Male 4, greater correlation can be seen between the arrays of peak areas for the common compounds sampled for Male 4 than for Male 2. Male 4 also followed exactly the same exercise routine for each of the three samplings, while Male 2 did different activities for the 30min exercise period across the three samplings. Male 2 shows a greater variability in the total peak area for the common compounds as well as a greater variability among the resulting ratio patterns which may be due to the regiment of exercise. As can also be seen from Table 35, the peak area arrays for the common human compounds extracted among three weekly samples for an individual have significantly higher correlation (≥ 0.93) than when compared between subjects (≤ 0.45). Figure 48 demonstrates the variability of the relative peak area ratio

patterns for these twenty-two common compounds among ten individuals. Through this semi-quantitative method of analysis, it is possible to establish that multiple samplings of one individual over time do not contain as much variation as that seen amongst a population [126].

Table 34: Twenty-two VOCs Extracted Across Three Weekly Samplings of Armpit Odor

R.T.	Compound Name	M2	M4
6.50	2-Furancarboxaldehyde	X	
7.20	2-Furanmethanol	X	X
9.72	Benzaldehyde	X	
10.09	Furancarboxylic acid-methyl ester	X	X
10.23	Phenol	X	X
11.25	Benzyl Alcohol		X
12.50	Nonanal	X	X
13.59	Nonanol		X
14.04	Dodecane	X	
14.13	Decanal	X	X
14.40	Nonanoic acid-methyl ester		X
14.98	(E)-2-Decenal		X
15.49	Tridecane		X
15.62	Undecanal		X
16.85	Tetradecane		X
17.56	6,10-dimethyl-5,9-Undecadien-2-one		X
18.43	Dodecanoic acid-methyl ester		X
15.62	Tetradecanal		X
19.61	Tridecanoic acid-methyl ester		X
20.45	Heptadecane		X
20.74	Tetradecanoic acid-methyl ester		X
22.83	Hexadecanoic acid-methyl ester		X

Table 35: Linear Correlation Coefficients for the Peak Areas of the Common Compounds

Linear Correlation Coefficient Matrix						
	M2 (W1)	M2 (W2)	M2 (W3)	M4 (W1)	M4 (W2)	M4 (W3)
M2 (W1)	1	0.9347	0.9638	0.4344	0.4509	0.4084
M2 (W2)	0.9347	1	0.9595	0.1690	0.1660	0.1483
M2 (W3)	0.9638	0.9595	1	0.3452	0.3712	0.3299
M4 (W1)	0.4344	0.1690	0.3452	1	0.9746	0.9860
M4 (W2)	0.4509	0.1660	0.3712	0.9746	1	0.9817
M4 (W3)	0.4084	0.1483	0.3299	0.9860	0.9817	1

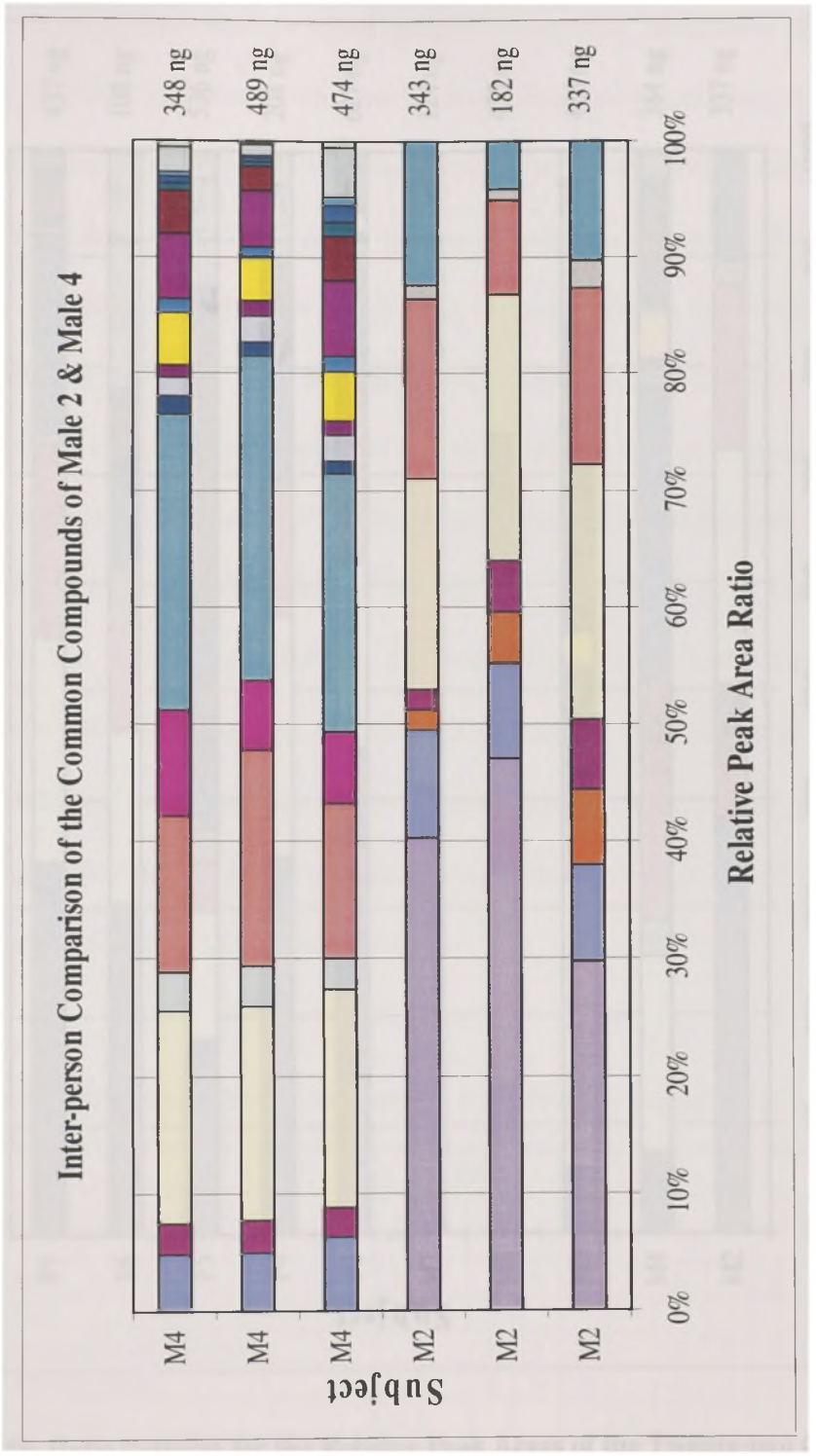


Figure 47: Comparison of the Relative Peak Area Ratios of the Common Compounds Extracted in Male 4 and Male 2 Across Three Weekly Samplings

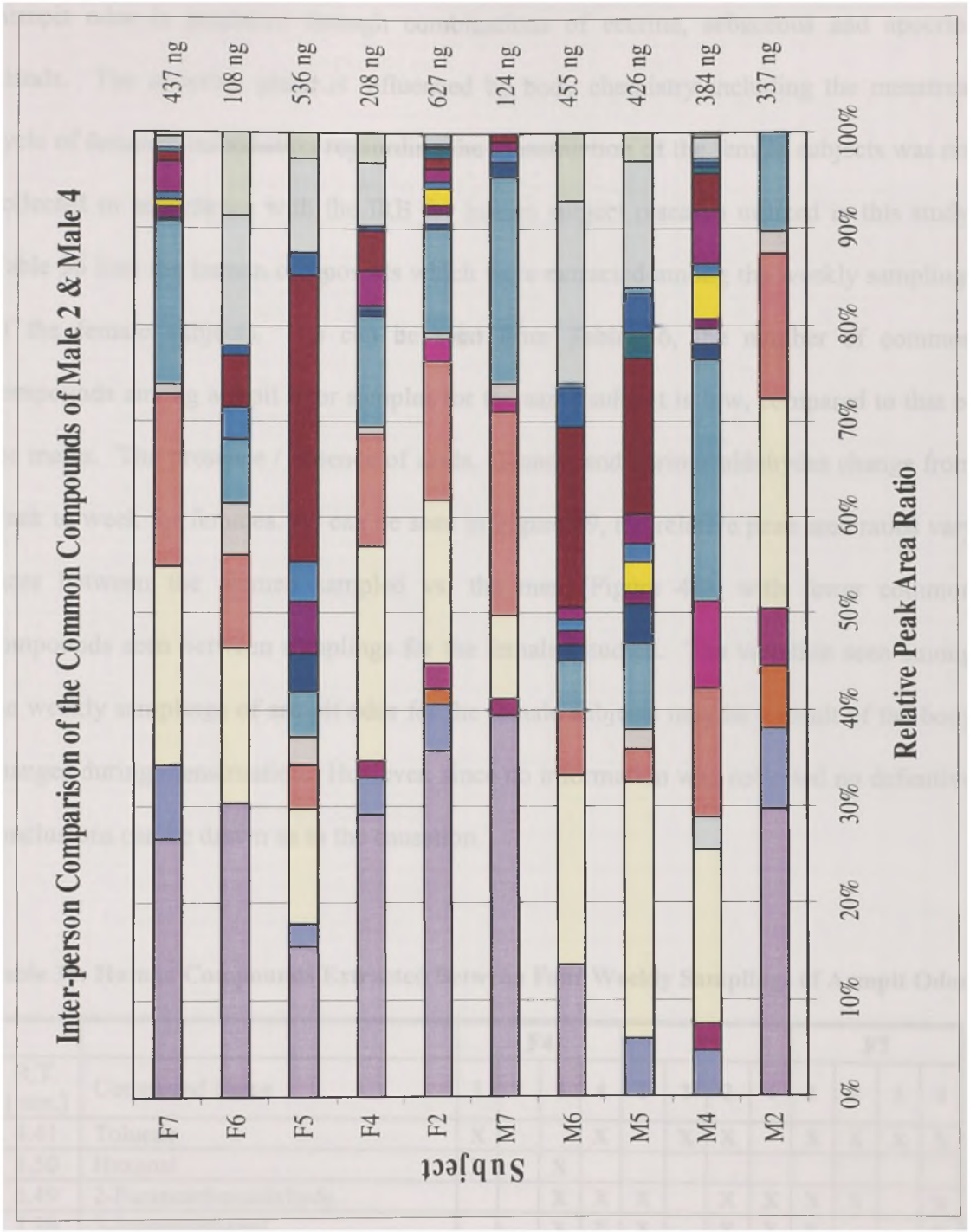


Figure 48: Ratio Patterns for the Relative Peak Areas of the Twenty-two Common Compounds Extracted Among Three Weekly Samplings of Male 2 & Male 4 Across Ten Subjects

Armpit odor is produced through combinations of eccrine, sebaceous and apocrine glands. The apocrine gland is influenced by body chemistry including the menstrual cycle of females; information regaurding the menstruation of the female subjects was not collected in accordance with the IRB for human subject research utilized in this study. Table 36 lists the human compounds which were extracted among the weekly samplings of the female subjects. As can be seen from Table 36, the number of common compounds among armpit odor samples for the same subject is low, compared to that of the males. The presence / absence of acids, alkanes, and various aldehydes change from week to week for females. As can be seen in Figure 49, the relative peak area ratios vary more between the women sampled vs. the men (Figure 48), with fewer common compounds seen between samplings for the females studied. The variation seen among the weekly samplings of armpit odor for the female subjects may be a result of the body changes during menstruation. However, since no information was collected no definitive conclusions can be drawn as to the causation.

Table 36: Human Compounds Extracted Between Four Weekly Samplings of Armpit Odor

		F4				F5				F7			
R.T. (min.)	Compound Name	1	2	3	4	1	2	3	4	1	2	3	4
4.41	Toluene	X			X		X	X		X	X	X	X
5.50	Hexanal	X		X									
6.49	2-Furancarboxaldehyde			X	X	X		X	X	X	X		X
7.20	2-Furanmethanol			X	X	X		X	X	X			X
8.12	p-Xylene	X					X	X		X		X	
8.32	Nonane		X		X		X	X		X	X	X	
8.36	Heptanal	X								X		X	
8.96	Hexanoic acid-methyl ester		X	X		X		X		X	X		
9.07	Propanedioic acid-dimethyl ester				X	X							

9.12	.alpha.-Pinene	X	X				X	X		X		X	X
10.09	Furancarboxylic acid-methyl ester			X		X							
10.23	Phenol	X	X	X	X	X		X	X	X	X	X	X
10.32	6-mthyl-5-Hepten-2-one	X		X					X	X	X	X	X
10.58	Decane						X						
12.41	Undecane	X	X				X			X	X	X	X
12.50	Nonanal	X	X	X	X	X		X	X	X	X	X	X
12.68	Phenylethyl Alcohol							X					
12.83	Octanoic acid-methyl ester		X	X		X		X	X	X	X		X
13.42	2-Nonenal, (E)-			X					X				X
13.49	Nonane, 1-chloro-			X									
13.51	Acetic acid-phenylmethyl ester					X		X					
13.85	Napthalene							X		X			X
14.02	Dodecane	X	X	X	X	X	X	X	X	X			X
14.13	Decanal	X	X	X	X	X	X	X	X	X	X	X	X
14.40	Nonanoic acid-methyl ester			X	X		X	X	X				X
14.68	Hexanedioic acid-dimethyl ester			X		X			X				
15.49	Tridecane	X			X	X	X	X	X	X			X
15.62	Undecanal					X			X				X
15.83	Decanoic acid-methyl ester			X		X		X	X				
16.85	Tetradecane			X	X	X		X	X	X			X
17.17	Undecanoic acid-methyl ester					X		X					
17.56	6,10-dimethyl-5,9-undecadien-2-one			X		X			X				X
17.79	Eicosane			X				X					X
18.36	9-Octadecenoic acid-methyl ester							X					
18.43	Dodecanoic acid-methyl ester	X		X		X		X	X	X	X	X	X
18.87	Dodecanoic acid	X				X		X	X				
19.33	Hexadecane					X		X		X			X
19.61	Tridecanoic acid-methyl ester			X		X		X					
20.45	Heptadecane					X				X			X
20.53	7-Hexadecenoic acid-methyl ester	X		X		X	X	X	X			X	
20.74	Tetradecanoic acid-methyl ester	X	X	X		X	X	X		X	X	X	X
21.42	Methyl 9-methyltetradecanoate					X	X	X			X		
21.51	Tetradecanoic acid, 12-methyl-, methyl ester			X									
21.65	Oleic Acid					X		X					
21.80	Pentadecanoic acid-methyl ester	X		X		X		X				X	
22.46	14-methyl-Pentadecanoic acid-methyl ester						X						
22.83	Hexadecanoic acid-methyl ester	X	X	X		X		X	X	X	X	X	X

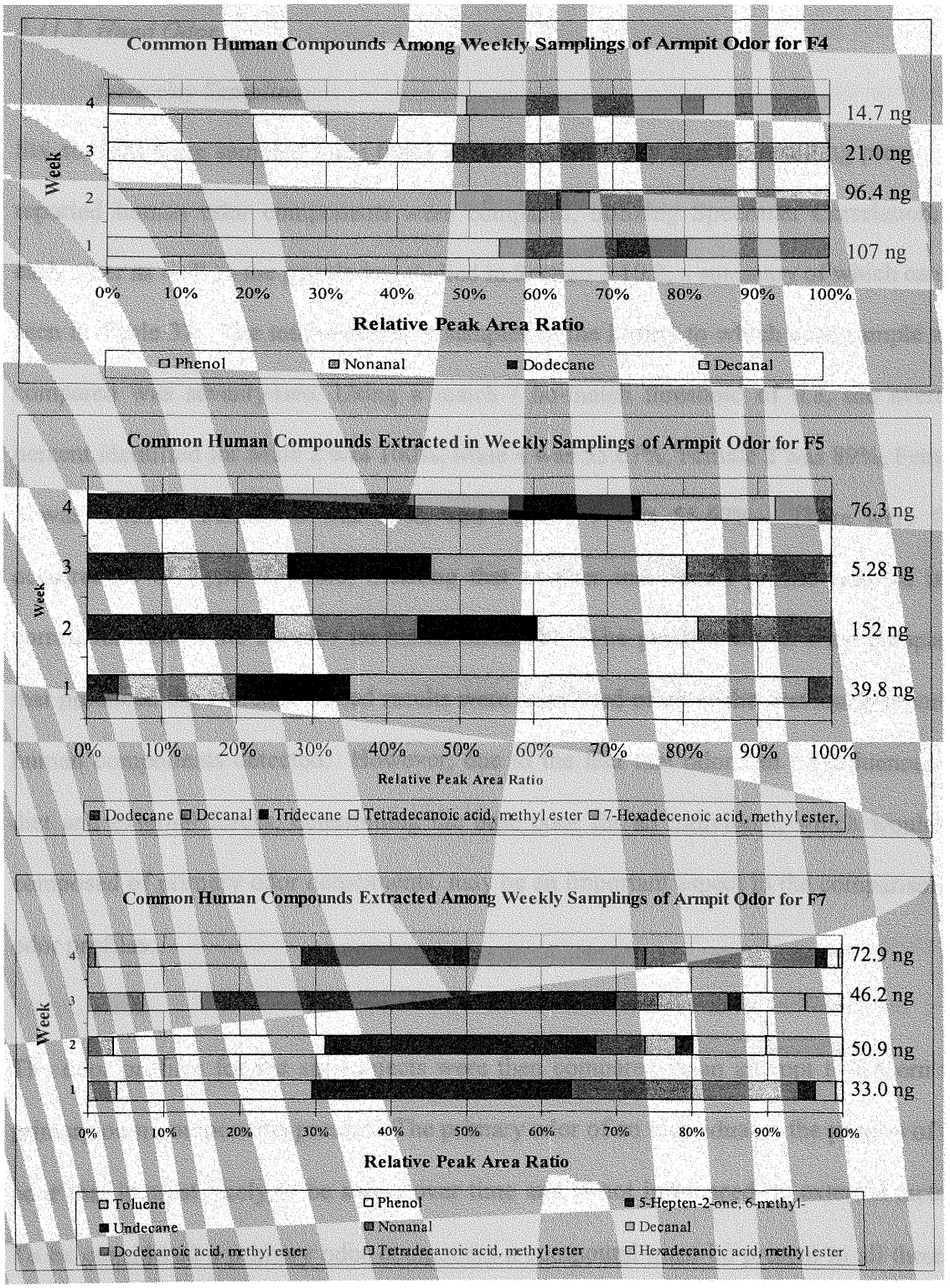


Figure 49: Comparison of the Common Human Compounds Extracted Between Four Weekly Samplings of Armpit Odor of Females 4, 5, and 7

3.11.2. Hand Odor

Intra-day Sampling

Six subjects were sampled three times within the same day and the resulting previously reported human odor components were compared, utilizing Spearman Correlation, to each other as well as the population studied in Section 3.10.2, a summary of which can be seen in Table 37. The total number of samples in the library to which each sample was compared was seventy-two. Using a match / no-match threshold of 0.8, the average percent identified for Male 2 was 100%, Male 4 was 55.67%, Female 2 was 89%, Female 5 was 55.67%, Female 6 was 33%, and Female 7 was 55.67%. There were five occurrences of Type II errors, meaning that another individuals profile resulted in a correlation above the match / no-match threshold. The profiles which were compared that produced the aforementioned results were composed of all of the previously reported human components detected. However, due to the fact that odor can be influenced by diet and external forces, determining the base odor for an individual, which would be composed of primary odor constituents, may be an important aspect in the comparison of odor profiles.

The odor profiles for the six subjects were then compared in an attempt to discern the primary odor components present. The primary odor of an individual is the portion of the odor that is most likely to be stable over time and is not influenced by external factors. To be considered a primary odor component a compound must be present in all three of the samplings for that individual and may differ among subjects. The number of these compounds determined to be primary odor components for the subjects studied ranged

from five to fifteen, with a total of twenty different compounds among the population. The primary odor components for each subject were then compared among the samplings and a linear correlation coefficient was determined, which ranged from 0.9119 to 0.9969 among the individuals within the population. The results for Male 2 can be seen in Table 38, Table 39, and Figure 50; the results for Male 4 can be seen in Table 40, Table 41, and Figure 52; the results for Female 2 can be seen in Table 42, Table 43, and Figure 52; the results for Female 5 can be seen in Table 44, Table 45, and Figure 53; the results for Female 6 can be seen in Table 46, Table 47, and Figure 54; the results for Female 7 can be seen in Table 48, Table 49, and Figure 55.

A searchable library was created in-house using the primary odor components determined among the multiple samplings of each subject. Each sampling for each subject was then searched against the library to determine both the linear and Spearman Rank correlation of each subject to the population using an in-house created automated Excel macro program. The results of these comparisons can be seen in Table 50 and Table 53, where the correlations of each search are listed in descending order. Using the linear correlation method each subject correlated the highest to the intraday samples collected from themselves, using a match / no-match threshold of 0.90, each subject can be differentiated from the others in the library. However, Male 2 sampling 2 has a high linear correlation to Female 6 sampling 2, when considering the ratio patterns of the primary odor components as seen in Figure 56, these subjects visually differ in the number and relative amounts of the VOCs present in their primary odor. The multiple samplings of Male 4 also correlates linearly to the multiple samplings of Female 7, yet, when considering the

ratio patterns of the primary odor components as seen in Figure 57 and Table 52 these subjects visually differ in the number and relative amounts of the VOCs present in their primary odor.

The volatile organic compounds extracted above collected odor sample are difficult to accurately compare in a quantitative fashion. A Spearman Ranking correlation is a semi-quantitative data analysis technique of analyzing non-parametric data sets. Through this method, each primary odor component in each array is assigned an integer ranking based on the size of the peak areas relative to others within the profile. The comparison is based on the pattern of the compounds within a sample with respect to the size of the peak area. The Spearman Ranking Correlation results obtained from comparison amoung the six subjects, as shown in Table 53, present a more accurate representation of the comparison of the compounds determined in the odor profiles. The match / no-match criteria set at 0.8 demonstrated two occurrences of Type I error between the six subjects as seen for Female 6 where two of the replicate's correlation coefficients lie below the threshold and no occurrence of Type II errors. There are no significant correlations between the six different subjects studied, but ranged from 0.6678 to -0.4926.

The multiple samplings of the six subjects were then again compared to the population from Section 3.10.2 using only the twenty compounds determined to be present in the primary odor of the six individuals, the results of which can be seen in Table 54. The total number of samples in the library to which each sample was compared was seventy-two. Using a match / no-match threshold of 0.8, the average percent identified for Male 2

was 100%, Male 4 was 100%, Female 2 was 100%, Female 5 was 100%, Female 6 was 78%, and Female 7 was 100%. There were six occurrences of Type II errors, meaning that another individuals profile resulted in a correlation above the match / no-match threshold. The results suggest that determining the primary odor constituents for subjects through collecting multiple samples not only provides a means to limit the consideration of secondary and tertiary odor influences, but also provides a useful method for the possible instrumental distinction between subjects.

Table 37: Spearman Correlations of the Hand Odor of the Six Subjects against the Population Utilizing All Odor Components Determined

Subject	Replicates		% Identified	Confused With
	Yes	No		
M2,1	3	0	100	0
M2,2	3	0	100	0
M2,3	3	0	100	0
M4,1	1	2	33	0
M4,2	2	1	67	F21
M4,3	2	1	67	0
F2,1	2	1	67	0
F2,2	3	0	100	0
F2,3	2	1	67	0
F5,1	2	1	67	0
F5,2	2	1	67	0
F5,3	1	2	33	0
F6,1	1	2	33	M7
F6,2	1	2	33	0
F6,3	1	2	33	0
F7,1	1	2	33	0
F7,2	2	1	67	M14
F7,3	2	1	67	M14, M23

Table 38: Common Compounds Among Intraday Sampling of Hand Odor for Male 2

	R.T. (min)	Compound Name		R.T. (min)	Compound Name
	6.49	2-Furancarboxaldehyde		14.13	Decanal
	10.23	Phenol		14.40	Nonanoic acid-methyl ester
	12.50	Nonanal		14.68	Hexanedioic acid-dimethyl ester
	12.83	Octanoic acid-methyl ester		17.56	6,10-dimethyl-5,9-Undecadien-2-one
	14.02	Dodecane			

Table 39: Correlation Coefficients for Intraday Samplings of Male 2

Correlations			
Sampling	1,2	1,3	2,3
Linear Correlation Coefficient	0.9581	0.9588	0.9716

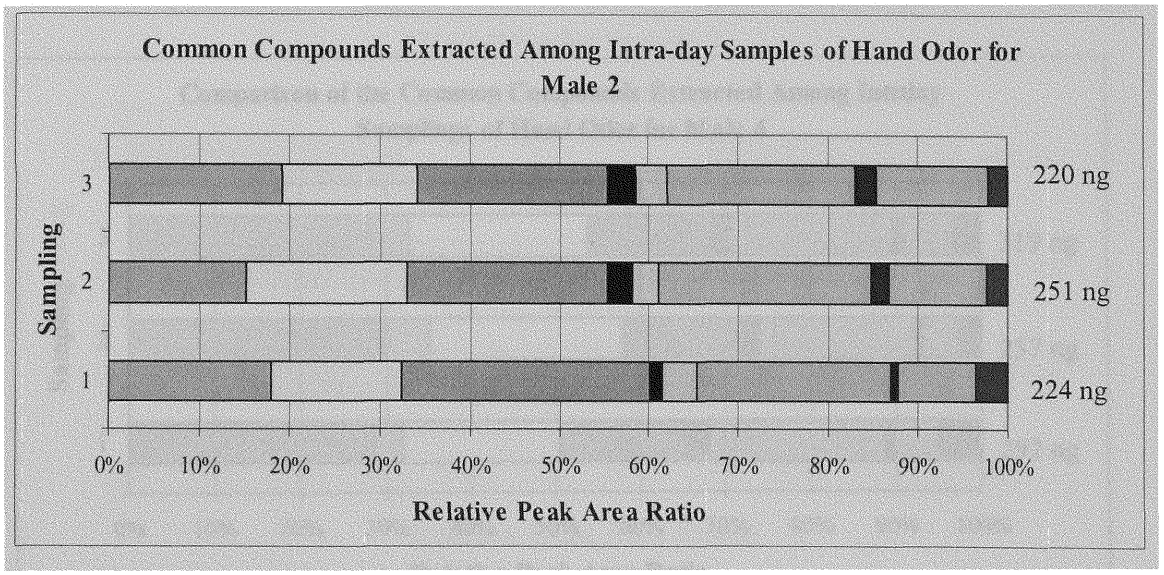


Figure 50: Common Compounds Among Intraday Samplings of Hand Odor for Male 2

Table 40: Common Compounds Among Intraday Sampling of Hand Odor for Male 4

	R.T. (min.)	Compound Name		R.T. (min.)	Compound Name
	6.49	2-Furancarboxaldehyde		14.13	Decanal
	9.07	Propanedioic acid-dimethyl ester		14.40	Nonanoic acid-methyl ester
	10.23	Phenol		14.68	Hexanedioic acid-dimethyl ester
	12.50	Nonanal		16.85	Tetradecane
	12.83	Octanoic acid-methyl ester		17.56	6,10-dimethyl-5,9-Undecadien-2-one
	14.02	Dodecane			

Table 41: Correlation Coefficients for Intraday Samplings of Male 4

Correlations			
Sampling	1,2	1,3	2,3
Linear Correlation Coefficient	0.9831	0.9905	0.9969

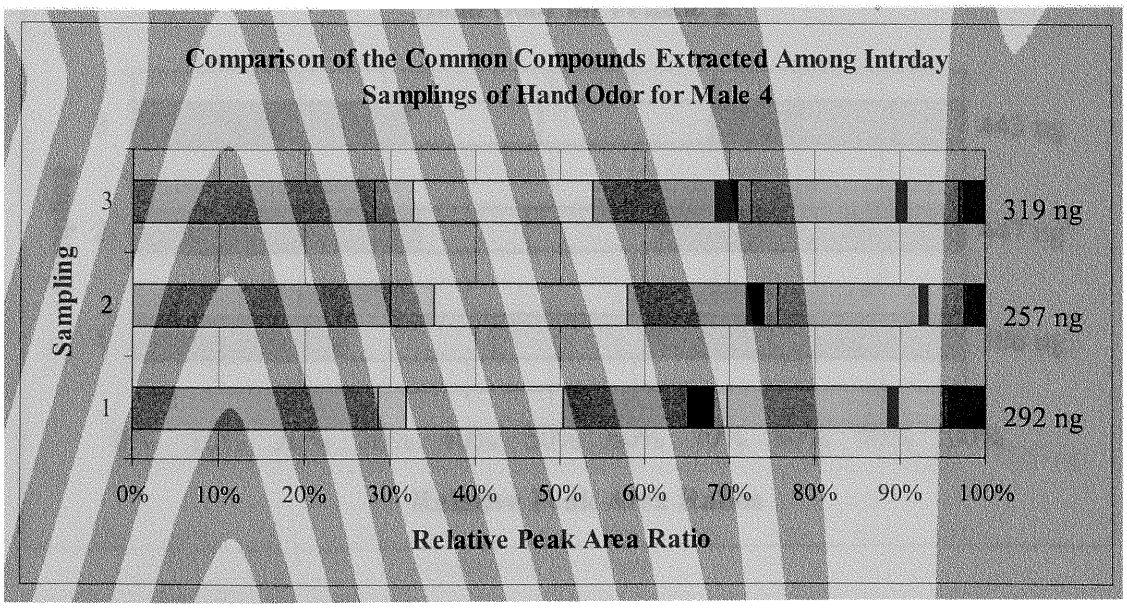


Figure 51: Compounds Among Intraday Samplings of Hand Odor for Male 4

Table 42: Common Compounds Among Intraday Samplings of Hand Odor for Female 2

R.T. (min)	Compound Name	R.T. (min)	Compound Name
6.49	2-Furancarboxaldehyde	14.13	Decanal
10.23	Phenol	14.68	Hexanedioic acid-dimethyl ester
11.25	Benzyl Alcohol	16.85	Tetradecane
12.50	Nonanal		

Table 43: Correlation Coefficients for Intraday Samplings of Female 2

Correlations			
Sampling	1,2	1,3	2,3
Linear Correlation Coefficient	0.9119	0.9210	0.9507

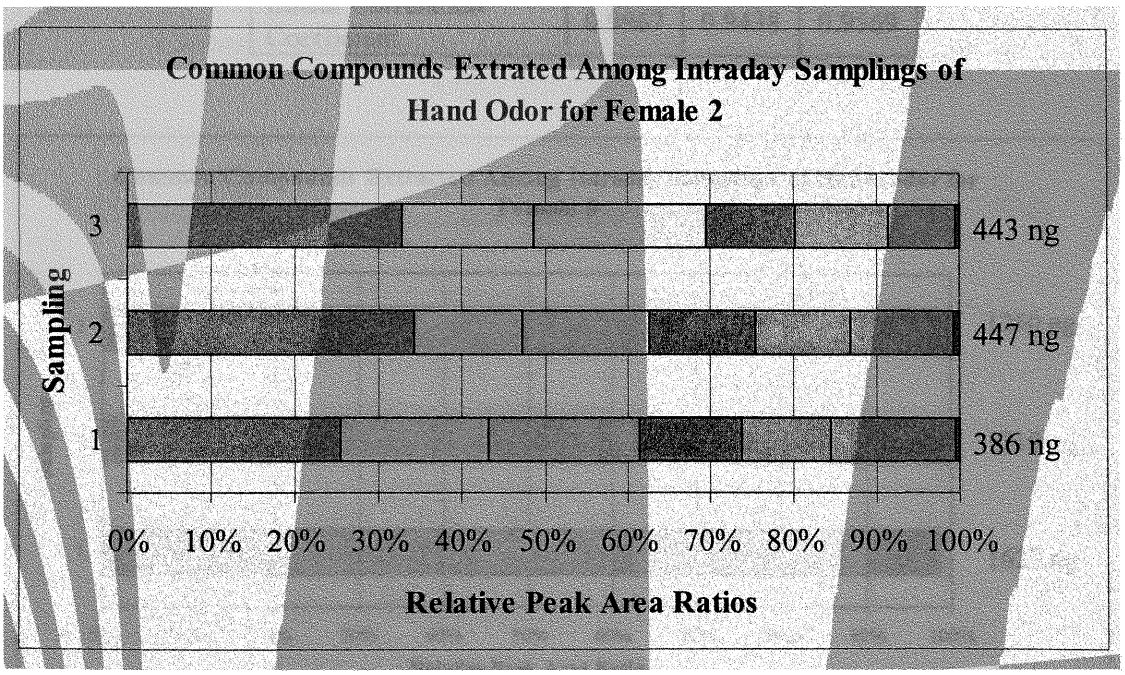


Figure 52: Common Compounds Among Intraday Samplings of Hand Odor for Female 2

Table 44: Common Human Compounds Extracted in Hand Odor through Intra-day Sampling of Female 5

	R.T. (min)	Compound Name		R.T. (min)	Compound Name
	3.86	Pyridine		13.42	2-Nonenal, (E)-
	4.74	2-Butenal, 2-methyl-		14.13	Decanal
	5.65	Butanoic acid		14.68	Hexanedioic acid-dimethyl ester
	6.49	2-Furancarboxaldehyde		15.49	Tridecane
	7.20	2-Furanmethanol		16.85	Tetradecane
	8.32	Nonane		17.56	6,10-dimethyl-5,9-Undecadien-2-one
	9.72	Benzaldehyde		18.87	Dodecanoic acid
	12.50	Nonanal			

Table 45: Correlation Coefficients for Intra-day Samplings of Female 5

Correlations			
Sampling	1,2	1,3	2,3
Linear Correlation Coefficient	0.9967	0.9438	0.9569

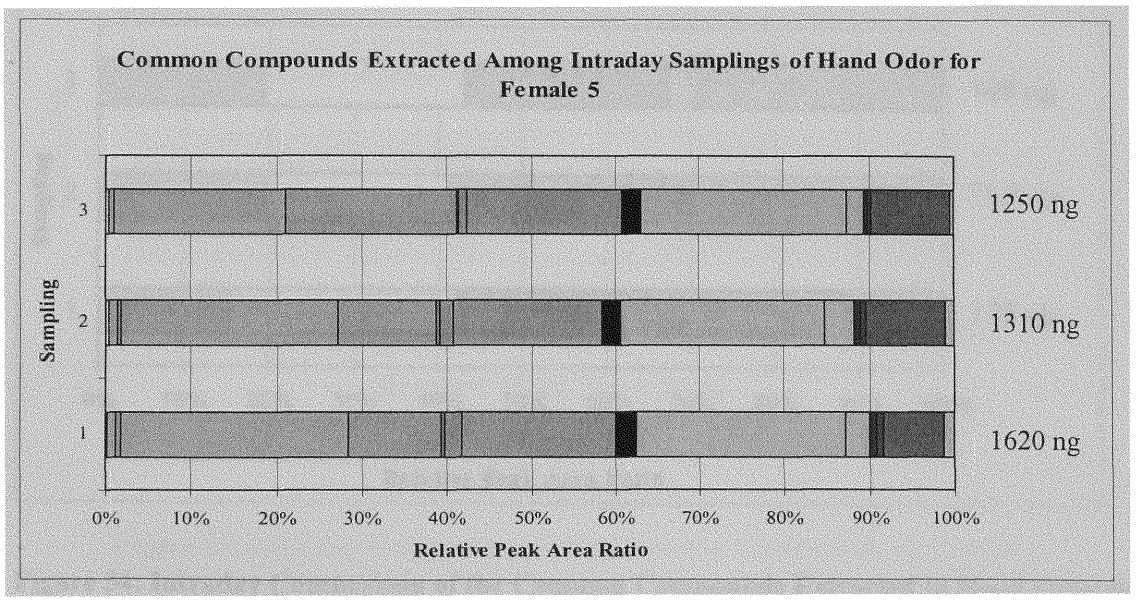


Figure 53: Intraday Comparison of the Common Human Compounds Extracted in Hand Odor of Female 5

Table 46: Common Compounds Extacted Among Intra-day Samplings of F6

	R.T. (min)	Compound Name		R.T. (min)	Compound Name
	6.49	2-Furancarboxaldehyde		14.02	Dodecane
	10.23	Phenol		14.13	Decanal
	12.50	Nonanal			

Table 47: Correlation Coefficients for Intra-day Samplings of Female 6

Correlations			
Sampling	1,2	1,3	2,3
Linear Correlation Coefficient	0.9426	0.9669	0.9679

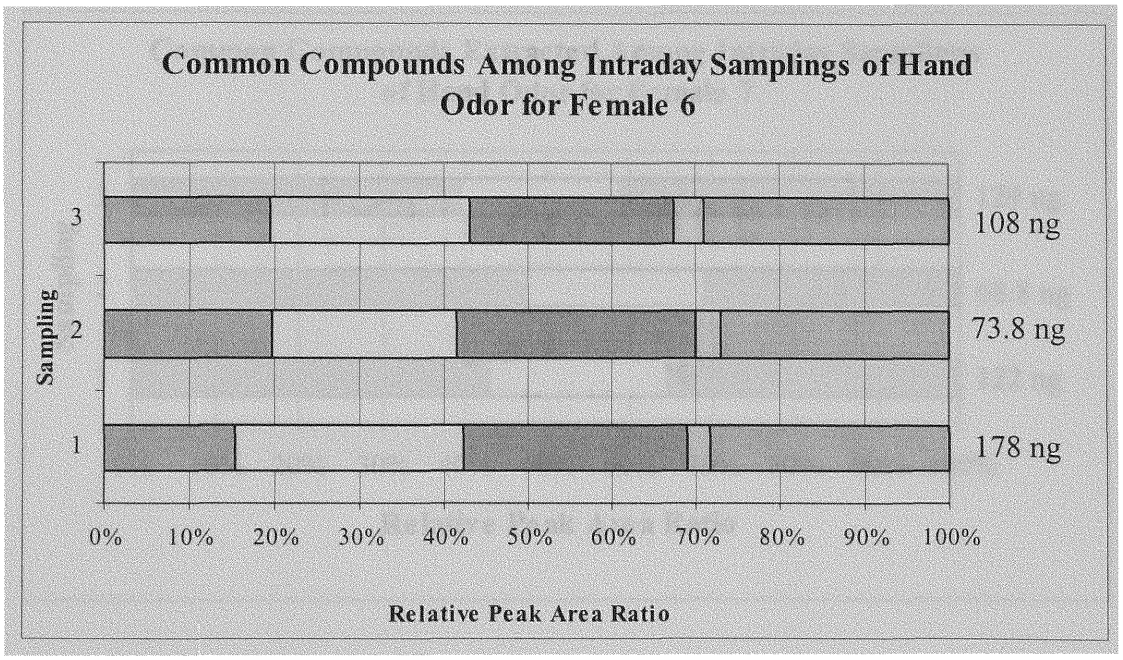


Figure 54: Intraday Comparison of the Common Compounds Extracted in Hand Odor for Female 6

Table 48: Common Human Compounds Extracted Among Intraday Samplings of Female 7

	R.T. (min)	Compound Name		R.T. (min)	Compound Name
	6.49	2-Furancarboxaldehyde		14.13	Decanal
	10.23	Phenol		14.68	Hexanedioic acid-dimethyl ester
	12.50	Nonanal			

Table 49: Correlation Coefficients for Multiple Samplings of Hand Odor for Female 7

Correlations			
Sampling	1,2	1,3	2,3
Linear Correlation Coefficient	0.9859	0.9925	0.9808

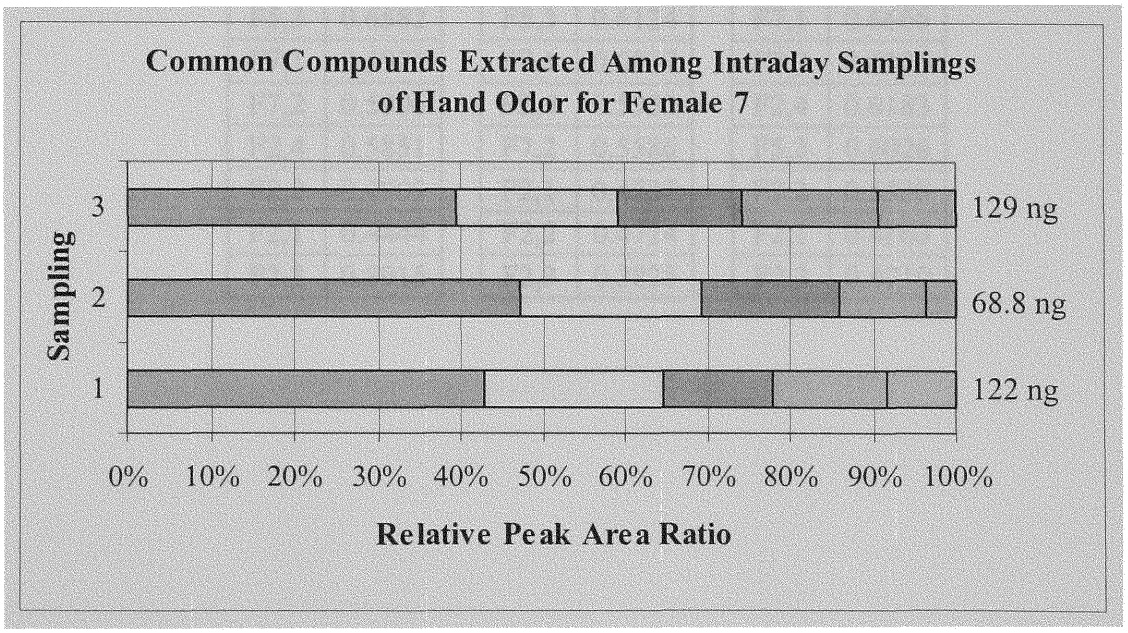


Figure 55: Intraday Comparison of the Common Compounds for Female 7

Table 50: Linear Correlation Results of Primary Odor Components Across the Six Subjects and Replicates

M2,1	
M2,1	1
M2,2	0.9566
M2,3	0.9535
F6,2	0.8895
F6,3	0.8506
F6,1	0.8407
F5,1	0.7480
M4,1	0.7459
F5,2	0.7348
M4,3	0.7229
M4,2	0.6962
F7,3	0.6615
F5,3	0.6582
F7,1	0.5970
F7,2	0.5906
F2,4	0.5851
F2,2	0.4909
F2,1	0.4444
F2,3	0.3915

M2,2	
M2,2	1
M2,3	0.9580
M2,1	0.9566
F6,2	0.9031
F6,1	0.8966
F6,3	0.8957
M4,1	0.7658
M4,3	0.7534
M4,2	0.7230
F5,1	0.6970
F5,2	0.6845
F7,3	0.6672
F5,3	0.6124
F7,1	0.6007
F2,4	0.5933
F7,2	0.5586
F2,1	0.4737
F2,2	0.4724
F2,3	0.3825

M2,3	
M2,3	1
M2,2	0.9580
M2,1	0.9535
F6,2	0.8109
F6,3	0.7942
F6,1	0.7704
M4,1	0.7567
M4,3	0.7416
F7,3	0.7226
M4,2	0.7138
F5,1	0.7102
F5,2	0.6950
F7,1	0.6666
F7,2	0.6326
F2,4	0.6183
F5,3	0.6026
F2,2	0.5328
F2,1	0.4863
F2,3	0.4210

Table 50: Linear Correlation Results of Primary Odor Components Across the Six Subjects and Replicates

M4,1	
M4,1	1
M4,3	0.9905
M4,2	0.9831
F7,3	0.9678
F7,1	0.9510
F7,2	0.9319
F6,3	0.8664
F6,2	0.8548
F2,4	0.8414
F6,1	0.8106
F2,2	0.8019
F5,1	0.7861
F5,2	0.7709
M2,2	0.7658
M2,3	0.7567
M2,1	0.7459
F2,3	0.7414
F2,1	0.7201
F5,3	0.6486

M4,2	
M4,2	1
M4,3	0.9969
M4,1	0.9831
F7,3	0.9608
F7,1	0.9579
F7,2	0.9460
F6,3	0.8409
F2,4	0.8316
F6,2	0.8248
F2,2	0.7959
F6,1	0.7955
F2,3	0.7526
F2,1	0.7327
M2,2	0.7230
M2,3	0.7138
F5,1	0.7073
M2,1	0.6962
F5,2	0.6880
F5,3	0.5683

M4,3	
M4,3	1
M4,2	0.9969
M4,1	0.9905
F7,3	0.9685
F7,1	0.9585
F7,2	0.9394
F6,3	0.8560
F2,4	0.8432
F6,2	0.8420
F6,1	0.8099
F2,2	0.8010
M2,2	0.7534
F2,3	0.7459
M2,3	0.7416
F2,1	0.7399
F5,1	0.7278
M2,1	0.7229
F5,2	0.7098
F5,3	0.5896

Table 50: Linear Correlation Results of Primary Odor Components Across the Six Subjects and Replicates

F2,1	
F2,1	1
F2,4	0.9269
F2,3	0.9210
F2,2	0.9119
M4,3	0.7399
M4,2	0.7327
M4,1	0.7201
F7,1	0.7101
F7,2	0.6954
F7,3	0.6849
F5,1	0.5106
F5,2	0.4927
M2,3	0.4863
M2,2	0.4737
M2,1	0.4444
F5,3	0.3669
F6,2	0.3576
F6,3	0.3548
F6,1	0.3138

F2,2	
F2,2	1
F2,4	0.9745
F2,3	0.9507
F2,1	0.9119
F7,2	0.8515
F7,1	0.8504
F7,3	0.8356
M4,1	0.8019
M4,3	0.8010
M4,2	0.7959
F5,1	0.6518
F5,2	0.6305
M2,3	0.5328
M2,1	0.4909
F5,3	0.4818
M2,2	0.4724
F6,2	0.4090
F6,3	0.3952
F6,1	0.3062

F2,3	
F2,3	1
F2,2	0.9507
F2,1	0.9210
F2,4	0.9171
F7,2	0.7635
M4,2	0.7526
F7,1	0.7463
M4,3	0.7459
M4,1	0.7414
F7,3	0.7130
F5,1	0.5707
F5,2	0.5483
M2,3	0.4210
F5,3	0.4115
M2,1	0.3915
M2,2	0.3825
F6,3	0.3566
F6,2	0.3557
F6,1	0.2807

Table 50: Linear Correlation Results of Primary Odor Components Across the Six Subjects and Replicates

F5,1	
F5,1	1
F5,2	0.9967
F5,3	0.9438
M4,1	0.7861
M2,1	0.7480
F6,2	0.7450
F7,3	0.7435
M4,3	0.7278
F6,3	0.7264
M2,3	0.7102
M4,2	0.7073
M2,2	0.6970
F7,1	0.6957
F7,2	0.6855
F2,4	0.6663
F6,1	0.6532
F2,2	0.6518
F2,3	0.5707
F2,1	0.5106

F5,2	
F5,2	1
F5,1	0.9967
F5,3	0.9568
M4,1	0.7709
M2,1	0.7348
F6,2	0.7248
F7,3	0.7200
M4,3	0.7098
F6,3	0.7066
M2,3	0.6950
M4,2	0.6880
M2,2	0.6845
F7,1	0.6718
F7,2	0.6598
F2,4	0.6463
F6,1	0.6354
F2,2	0.6305
F2,3	0.5483
F2,1	0.4927

F5,3	
F5,3	1
F5,2	0.9568
F5,1	0.9438
M2,1	0.6582
F6,2	0.6575
M4,1	0.6486
F6,3	0.6388
M2,2	0.6124
M2,3	0.6026
M4,3	0.5896
F6,1	0.5846
F7,3	0.5711
M4,2	0.5683
F7,1	0.5201
F7,2	0.5106
F2,4	0.5091
F2,2	0.4818
F2,3	0.4115
F2,1	0.3669

Table 50: Linear Correlation Results of Primary Odor Components Across the Six Subjects and Replicates

F6,1	
F6,1	1
F6,3	0.9664
F6,2	0.9425
M2,2	0.8966
M2,1	0.8407
M4,1	0.8106
M4,3	0.8099
M4,2	0.7955
M2,3	0.7704
F5,1	0.6532
F5,2	0.6354
F5,3	0.5846
F2,4	0.4617
F7,3	0.4039
F7,2	0.3616
F7,1	0.3470
F2,1	0.3138
F2,2	0.3062
F2,3	0.2807

F6,2	
F6,2	1
F6,3	0.9679
F6,1	0.9425
M2,2	0.9031
M2,1	0.8895
M4,1	0.8548
M4,3	0.8420
M4,2	0.8248
M2,3	0.8109
F5,1	0.7450
F5,2	0.7248
F5,3	0.6575
F2,4	0.5416
F7,3	0.5180
F7,2	0.4800
F7,1	0.4508
F2,2	0.4090
F2,1	0.3576
F2,3	0.3557

F6,3	
F6,3	1
F6,2	0.9679
F6,1	0.9664
M2,2	0.8957
M4,1	0.8664
M4,3	0.8560
M2,1	0.8506
M4,2	0.8409
M2,3	0.7942
F5,1	0.7264
F5,2	0.7066
F5,3	0.6388
F2,4	0.5327
F7,3	0.5197
F7,2	0.4682
F7,1	0.4587
F2,2	0.3952
F2,3	0.3566
F2,1	0.3548

Table 50: Linear Correlation Results of Primary Odor Components Across the Six Subjects and Replicates

F7,1	
F7,1	1
F7,3	0.9925
F7,2	0.9859
M4,3	0.9585
M4,2	0.9579
M4,1	0.9510
F2,4	0.8762
F2,2	0.8504
F2,3	0.7463
F2,1	0.7101
F5,1	0.6957
F5,2	0.6718
M2,3	0.6666
M2,2	0.6007
M2,1	0.5970
F5,3	0.5201
F6,3	0.4587
F6,2	0.4508
F6,1	0.3470

F7,2	
F7,2	1
F7,1	0.9859
F7,3	0.9808
M4,2	0.9460
M4,3	0.9394
M4,1	0.9319
F2,4	0.8614
F2,2	0.8515
F2,3	0.7635
F2,1	0.6954
F5,1	0.6855
F5,2	0.6598
M2,3	0.6326
M2,1	0.5906
M2,2	0.5586
F5,3	0.5106
F6,2	0.4800
F6,3	0.4682
F6,1	0.3616

F7,3	
F7,3	1
F7,1	0.9925
F7,2	0.9808
M4,3	0.9685
M4,1	0.9678
M4,2	0.9608
F2,4	0.8777
F2,2	0.8356
F5,1	0.7435
M2,3	0.7226
F5,2	0.7200
F2,3	0.7130
F2,1	0.6849
M2,2	0.6672
M2,1	0.6615
F5,3	0.5711
F6,3	0.5197
F6,2	0.5180
F6,1	0.4039

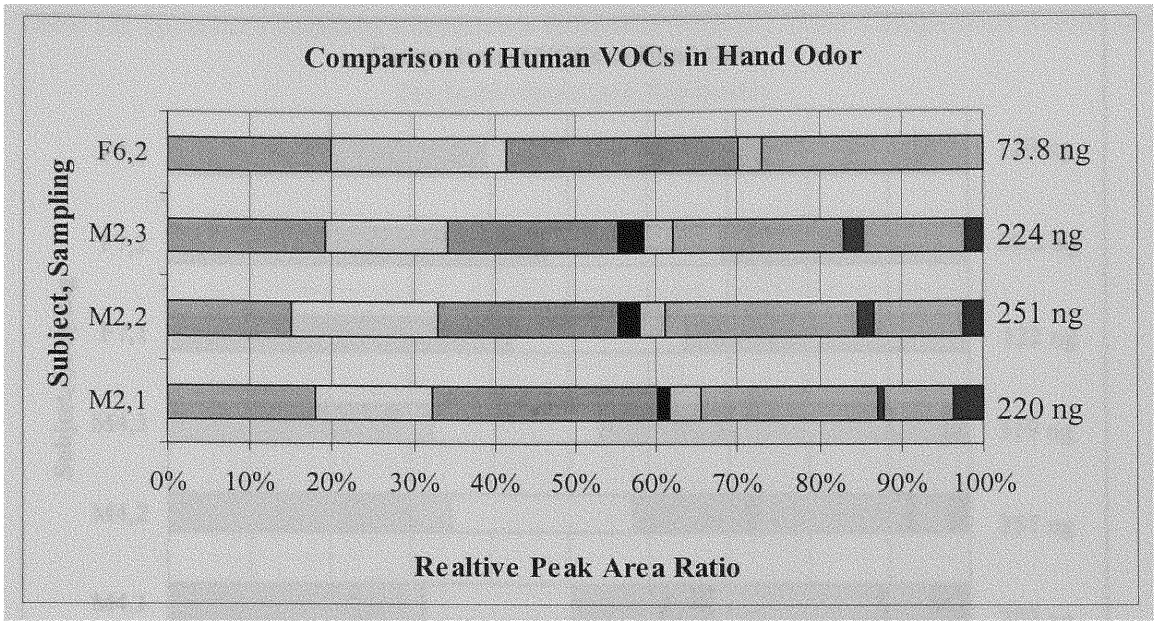


Figure 56: Comparison of the Human VOCs Between Male 2 and Female 6

Table 51: Comparison of the Primary Odor Components for Male 2 and Female 6

	R.T. (min)	Compound Name	M2,1	M2,2	M2,3	F6,2
	6.49	2-Furancarboxaldehyde	X	X	X	X
	10.23	Phenol	X	X	X	X
	12.50	Nonanal	X	X	X	X
	12.83	Octanoic acid-methyl ester	X	X	X	
	14.02	Dodecane	X	X	X	X
	14.13	Decanal	X	X	X	X
	14.40	Nonanoic acid-methyl ester	X	X	X	
	14.68	Hexanedioic acid-dimethyl ester	X	X	X	
	17.56	6,10-dimethyl-5,9-Undecadien-2-one	X	X	X	

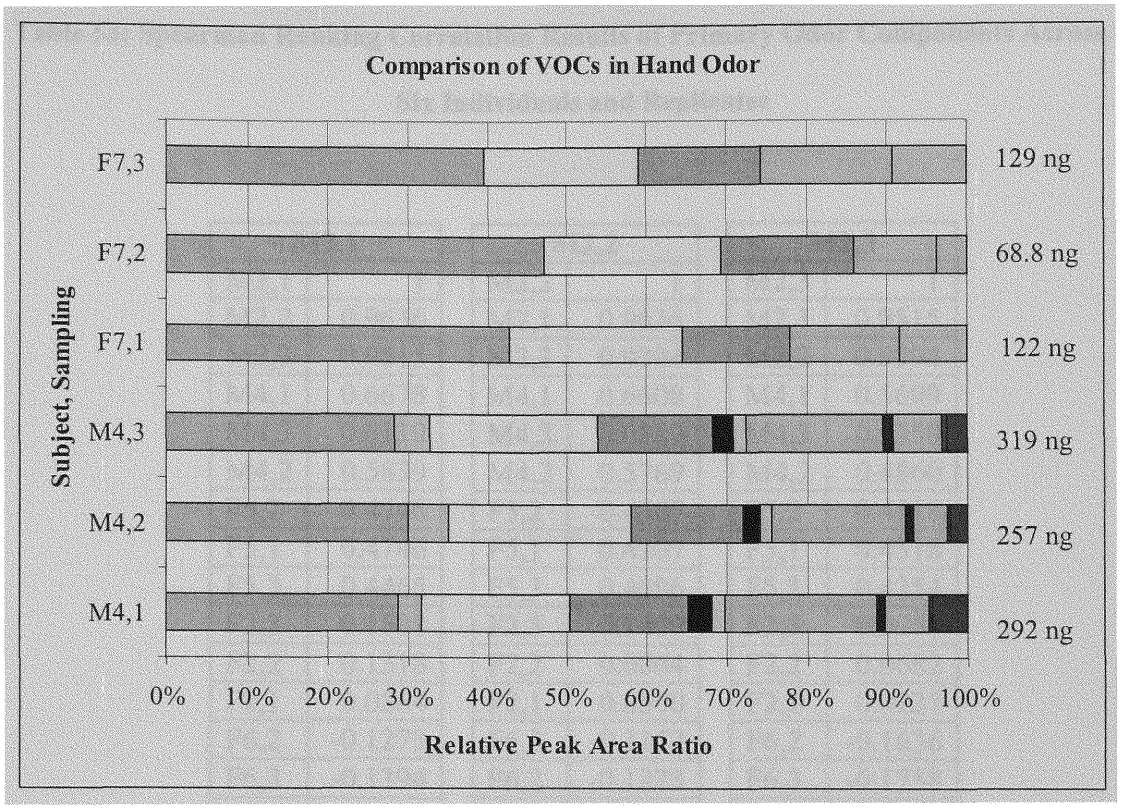


Figure 57: Comparison of the Human VOCs Between Male 4 and Female 7

Table 52: Comparison of the Primary Odor Components for Male 2 and Female 6

	R.T. (min.)	Compound Name	M4 1	M4 2	M4 3	F7 1	F7 2	F7 3
	6.49	2-Furancarboxaldehyde	X	X	X	X	X	X
	9.07	Propanedioic acid-dimethyl ester	X	X	X			
	10.23	Phenol	X	X	X	X	X	X
	12.50	Nonanal	X	X	X	X	X	X
	12.83	Octanoic acid-methyl ester	X	X	X			
	14.02	Dodecane	X	X	X			
	14.13	Decanal	X	X	X	X	X	X
	14.40	Nonanoic acid-methyl ester	X	X	X			
	14.68	Hexanedioic acid-dimethyl ester	X	X	X	X	X	X
	16.85	Tetradecane	X	X	X			
	17.56	6,10-dimethyl-5,9-Undecadien-2-one	X	X	X			

Table 53: Spearman Ranking Correlation Results of Primary Odor Components Across the Six Individuals and Replicates

M2,1	
M2,1	1
M2,2	0.9636
M2,3	0.9515
M4,1	0.6678
M4,3	0.6119
M4,2	0.5839
F5,2	0.4746
F5,1	0.4746
F5,3	0.4465
F2,3	0.1591
F2,2	0.1318
F2,1	0.0864
F6,2	-0.1273
F6,3	-0.1394
F6,1	-0.1758
F7,2	-0.2000
F7,3	-0.2121
F7,1	-0.2121

M2,2	
M2,2	1
M2,1	0.9636
M2,3	0.9394
M4,1	0.6608
M4,3	0.6189
M4,2	0.5769
F5,2	0.4307
F5,1	0.4307
F5,3	0.4096
F2,3	0.1409
F2,2	0.0864
F2,1	0.0500
F6,3	-0.1152
F6,2	-0.1273
F6,1	-0.1273
F7,3	-0.2121
F7,1	-0.2121
F7,2	-0.2242

M2,3	
M2,3	1
M2,1	0.9515
M2,2	0.9394
M4,1	0.5699
M4,3	0.5350
M4,2	0.4860
F5,2	0.4518
F5,1	0.4518
F5,3	0.4254
F2,3	0.0955
F2,2	0.0682
F2,1	0.0227
F6,2	-0.1636
F6,3	-0.1758
F6,1	-0.2242
F7,2	-0.2485
F7,3	-0.2606
F7,1	-0.2606

Table 53: Spearman Ranking Correlation Results of Primary Odor Components Across the Six Individuals and Replicates

M4,1	
M4,1	1
M4,3	0.9545
M4,2	0.9364
M2,1	0.6678
M2,2	0.6608
M2,3	0.5699
F5,2	0.5143
F5,1	0.5128
F5,3	0.4722
F2,3	0.1818
F2,2	0.1469
F2,1	0.1399
F7,3	-0.2409
F7,1	-0.2409
F7,2	-0.2591
F6,1	-0.3227
F6,3	-0.3318
F6,2	-0.3500

M4,2	
M4,2	1
M4,3	0.9818
M4,1	0.9364
M2,1	0.5839
M2,2	0.5769
M2,3	0.4860
F5,2	0.4617
F5,1	0.4602
F5,3	0.4195
F2,3	0.1678
F2,2	0.1399
F2,1	0.1259
F7,3	-0.2409
F7,1	-0.2409
F7,2	-0.2500
F6,1	-0.3318
F6,3	-0.3500
F6,2	-0.3591

M4,3	
M4,3	1
M4,2	0.9818
M4,1	0.9545
M2,2	0.6189
M2,1	0.6119
M2,3	0.5350
F5,2	0.4602
F5,1	0.4586
F5,3	0.4165
F2,3	0.1748
F2,2	0.1538
F2,1	0.1469
F7,3	-0.2318
F7,1	-0.2318
F7,2	-0.2409
F6,1	-0.3318
F6,3	-0.3500
F6,2	-0.3591

Table 53: Spearman Ranking Correlation Results of Primary Odor Components Across the Six Individuals and Replicates

F2,1	
F2,1	1
F2,2	0.9643
F2,3	0.8571
M4,3	0.1469
M4,1	0.1399
M4,2	0.1259
F7,2	0.0893
M2,1	0.0864
F7,3	0.0536
F7,1	0.0536
M2,2	0.0500
M2,3	0.0227
F6,1	-0.0595
F6,2	-0.0833
F6,3	-0.1071
F5,2	-0.1446
F5,1	-0.1446
F5,3	-0.1912

F2,2	
F2,2	1
F2,1	0.9643
F2,3	0.8929
F7,2	0.1607
M4,3	0.1538
M4,1	0.1469
M4,2	0.1399
M2,1	0.1318
F7,3	0.0893
F7,1	0.0893
M2,2	0.0864
M2,3	0.0682
F6,2	0.0357
F6,1	0.0119
F6,3	-0.0119
F5,2	-0.1373
F5,1	-0.1373
F5,3	-0.1838

F2,3	
F2,3	1
F2,2	0.8929
F2,1	0.8571
F7,3	0.1964
F7,1	0.1964
M4,1	0.1818
F6,1	0.1786
M4,3	0.1748
M4,2	0.1678
F7,2	0.1607
M2,1	0.1591
M2,2	0.1409
F6,3	0.1310
F6,2	0.1071
M2,3	0.0955
F5,2	-0.1250
F5,1	-0.1250
F5,3	-0.1618

Table 53: Spearman Ranking Correlation Results of Primary Odor Components Across the Six Individuals and Replicates

F5,1	
F5,1	1
F5,2	0.9929
F5,3	0.9214
M4,1	0.5128
M2,1	0.4746
M4,2	0.4602
M4,3	0.4586
M2,3	0.4518
M2,2	0.4307
F2,3	-0.1250
F2,2	-0.1373
F2,1	-0.1446
F6,3	-0.2145
F6,2	-0.2169
F6,1	-0.2463
F7,3	-0.4544
F7,1	-0.4544
F7,2	-0.4574

F5,2	
F5,2	1
F5,1	0.9929
F5,3	0.9321
M4,1	0.5143
M2,1	0.4746
M4,2	0.4617
M4,3	0.4602
M2,3	0.4518
M2,2	0.4307
F2,3	-0.1250
F2,2	-0.1373
F2,1	-0.1446
F6,3	-0.2145
F6,2	-0.2169
F6,1	-0.2463
F7,3	-0.4544
F7,1	-0.4544
F7,2	-0.4574

F5,3	
F5,3	1
F5,2	0.9321
F5,1	0.9214
M4,1	0.4722
M2,1	0.4465
M2,3	0.4254
M4,2	0.4195
M4,3	0.4165
M2,2	0.4096
F2,3	-0.1618
F2,2	-0.1838
F2,1	-0.1912
F6,3	-0.2218
F6,2	-0.2292
F6,1	-0.2512
F7,3	-0.4838
F7,1	-0.4838
F7,2	-0.4926

Table 53: Spearman Ranking Correlation Results of Primary Odor Components Across the Six Individuals and Replicates

F6,1	
F6,1	1
F6,3	0.9000
F6,2	0.7000
F7,3	0.5429
F7,1	0.5429
F7,2	0.4286
F2,3	0.1786
F2,2	0.0119
F2,1	-0.0595
M2,2	-0.1273
M2,1	-0.1758
M2,3	-0.2242
F5,2	-0.2463
F5,1	-0.2463
F5,3	-0.2512
M4,1	-0.3227
M4,3	-0.3318
M4,2	-0.3318

F6,2	
F6,2	1
F6,3	0.9000
F6,1	0.7000
F7,2	0.4286
F7,3	0.3714
F7,1	0.3714
F2,3	0.1071
F2,2	0.0357
F2,1	-0.0833
M2,2	-0.1273
M2,1	-0.1273
M2,3	-0.1636
F5,2	-0.2169
F5,1	-0.2169
F5,3	-0.2292
M4,1	-0.3500
M4,3	-0.3591
M4,2	-0.3591

F6,3	
F6,3	1
F6,2	0.9000
F6,1	0.9000
F7,3	0.4286
F7,1	0.4286
F7,2	0.3714
F2,3	0.1310
F2,2	-0.0119
F2,1	-0.1071
M2,2	-0.1152
M2,1	-0.1394
M2,3	-0.1758
F5,2	-0.2145
F5,1	-0.2145
F5,3	-0.2218
M4,1	-0.3318
M4,3	-0.3500
M4,2	-0.3500

Table 53: Spearman Ranking Correlation Results of Primary Odor Components Across the Six Individuals and Replicates

F7,1	
F7,3	1
F7,1	1
F7,2	0.9000
F6,1	0.5429
F6,3	0.4286
F6,2	0.3714
F2,3	0.1964
F2,2	0.0893
F2,1	0.0536
M2,2	-0.2121
M2,1	-0.2121
M4,3	-0.2318
M4,2	-0.2409
M4,1	-0.2409
M2,3	-0.2606
F5,2	-0.4544
F5,1	-0.4544
F5,3	-0.4838

F7,2	
F7,2	1
F7,3	0.9000
F7,1	0.9000
F6,2	0.4286
F6,1	0.4286
F6,3	0.3714
F2,3	0.1607
F2,2	0.1607
F2,1	0.0893
M2,1	-0.2000
M2,2	-0.2242
M4,3	-0.2409
M2,3	-0.2485
M4,2	-0.2500
M4,1	-0.2591
F5,2	-0.4574
F5,1	-0.4574
F5,3	-0.4926

F7,3	
F7,3	1
F7,1	1
F7,2	0.9000
F6,1	0.5429
F6,3	0.4286
F6,2	0.3714
F2,3	0.1964
F2,2	0.0893
F2,1	0.0536
M2,2	-0.2121
M2,1	-0.2121
M4,3	-0.2318
M4,2	-0.2409
M4,1	-0.2409
M2,3	-0.2606
F5,2	-0.4544
F5,1	-0.4544
F5,3	-0.4838

Table 54: Spearman Correlation of the Hand Odor of the Six Subjects against the Population Utilizing the Twenty Primary Odor Components

Subject	Replicates		% Identified	Confused With
	Yes	No		
M2,1	3	0	100	F13
M2,2	3	0	100	0
M2,3	3	0	100	0
M4,1	3	0	100	F3
M4,2	3	0	100	F3, F21
M4,3	3	0	100	F3
F2,1	3	0	100	0
F2,2	3	0	100	0
F2,3	3	0	100	0
F5,1	3	0	100	0
F5,2	3	0	100	0
F5,3	3	0	100	0
F6,1	2	1	67	M7
F6,2	2	1	67	0
F6,3	3	0	100	0
F7,1	3	0	100	0
F7,2	3	0	100	0
F7,3	3	0	100	0

The relationship seen through linear correlation between M2 sampling 2 and F6 sampling 2, as well as between Male 4 and Female 7, does not exist when using the Spearman Ranking method. This is due to magnitudal differences between the components within the profiles. For example, there are nine compounds total between M2 and F6, however, F6 only shows the presence of five of these compounds. As shown in Figure 58 and Figure 59, the missing values contribute in a greater fashion to the Spearman Ranking

correlation value than in the linear correlation due to the scale of the values being compared. The presence / absence of the primary odor components between subjects must be considered and given the same weight as the common compounds between subjects, thus the Spearman Ranking correlation results in a truer representation of the relationships between the samples.

Principle component analysis (PCA) was also conducted on the six subject multiple samplings data set. Table 55 displays a summary of results for PCA of the data set, including the Eigenanlysis of the correlation matrix and the resulting principle components. The analysis resulted in a total of fifteen principle components, of which nine are shown here. Each Eigenvalue gives the amount of variance in the data set which is explained by the principle component. As can be seen from Table 55, the first three principle components account for approximately 94.68% of the total variation, and thus these values were plotted in Figure 60. Groupings can be noted amoung the multiple samples collected from the same individual. Female 5's three samplings group together, as well as Male 4, Female 2, and Female 7. The multiple samplings of Female 6 and Male 2, however, produce overlapping groupings which is in agreement with the results of the linear correlations. Female 7 and Male 4, however, do not group together, which does not agree with what was determined through linear correlation.

These results show that through multiple samplings of an individual, determination of the common components in each sampling which are most likely to be elements of the

primary odor for the subject, and comparison of these VOCs across a population it is possible to narrow the field of possible matches of the profiles in question.

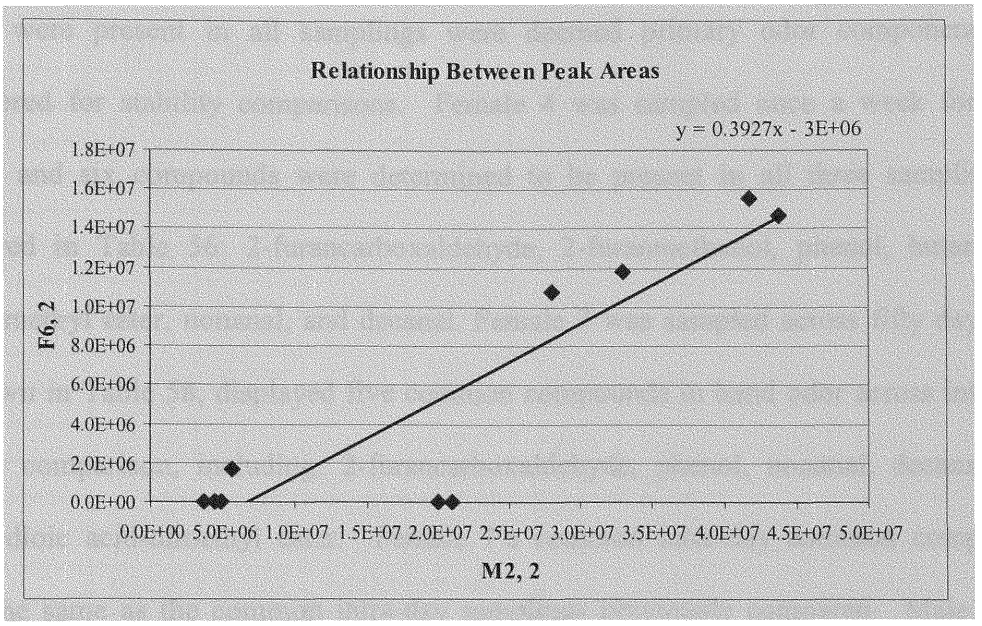


Figure 58: Data Array Comparison of Male 2 Sampling 2 and Female 6 Sampling 2

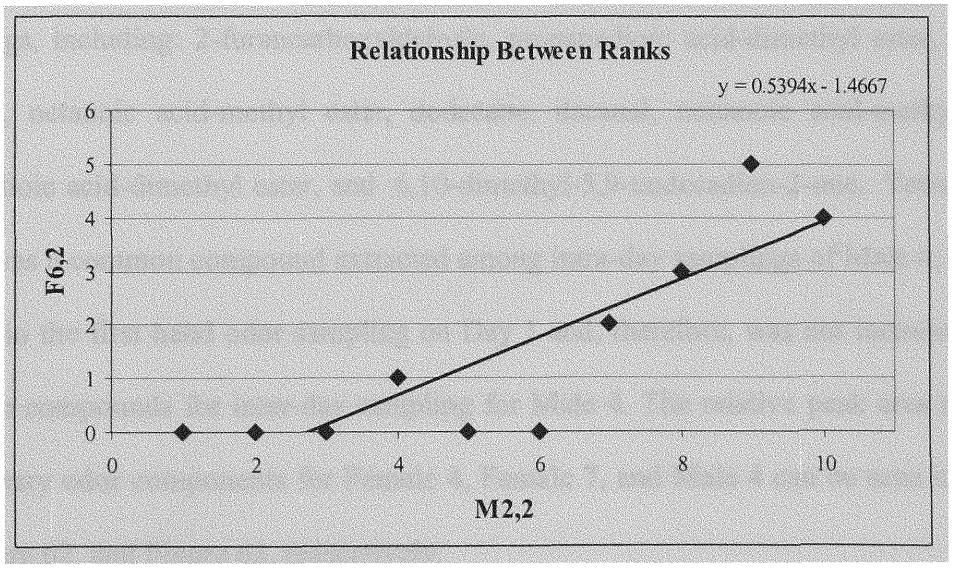


Figure 59: Ranked Array Comparison for Male 2 Sampling 2 and Female 6 Sampling 2

Inter-day Sampling

Hand odor was collected from three subjects (Female 4, Female 7 and Male 4) across multiple days to evaluate the stability of the volatile components over time. Compounds which were present in all samplings were deemed primary odor components and considered for stability comparisons. Female 4 was sampled once a week for three weeks, and six compounds were determined to be present in all three samplings as displayed in Table 56: 2-furancarboxaldehyde, 2-furanmethanol, phenol, butanedioic acid-dimethyl ester, nonanal, and decanal. Female 7 was sampled across fifty days and, as shown in Table 58, displayed five common compounds in hand odor across inter-day sample comparison, including: 2-furancarboxaldehyde, phenol, nonanal, decanal, and hexanedioic acid-dimethyl ester. Female 7's common inter-day common compounds were the same as the common intra-day samplings previously compared. Male 4 was sampled twice in one day and then three times within the same day, twenty-four days later. Male 4, as shown in Table 60, exhibited ten common compounds among the samplings, including: 2-furancarboxaldehyde, propanedioic acid-dimethyl ester, phenol, nonanal, octanoic acid-methyl ester, dodecane, decanal, nonanoic acid-methyl ester, hexanedioic acid-dimethyl ester, and 6,10-dimethyl-5,9-undecadien-2-one. Tetradecane, which was a common compound extracted among intra-day samplings of Male 4, was not present in the first hand odor sampling on Day 1 and, therefore, was not included in the common compounds for inter-day sampling for Male 4. The relative peak area ratios of the primary odor components for Female 4, Female 7, and Male 4 can be seen in Figure 61, Figure 62, and Figure 63, respectively.

Table 55: Principle Component Analysis Summary

Eigenvalue	14.3074	1.6580	1.0767	0.4878	0.3170	0.0680	0.0371	0.0240	0.0173
Percent	79.4856	9.2110	5.9816	2.7099	1.7613	0.3779	0.2063	0.1331	0.0959
Cum Percent	79.4856	88.6967	94.6782	97.3882	99.1495	99.5274	99.7337	99.8668	99.9628
	PC1	**PC2**	**PC3**	**PC4**	**PC5**	**PC6**	**PC7**	**PC8**	**PC9**
M2,1	0.2350	0.2409	-0.1946	0.2786	-0.2522	0.3640	0.0696	0.2475	-0.4693
M2,2	0.2349	0.2199	-0.2756	0.2560	-0.1870	-0.2511	-0.0007	-0.1332	0.1388
M2,3	0.2345	0.1650	-0.2028	0.3297	-0.4615	-0.0826	-0.0045	0.0937	0.3774
M4,1	0.2586	-0.0573	-0.0212	-0.2223	-0.0489	-0.2955	-0.3419	0.1754	-0.1774
M4,2	0.2529	-0.1227	-0.0859	-0.2993	-0.0351	-0.2535	0.0210	0.3571	-0.0670
M4,3	0.2557	-0.0995	-0.0839	-0.2455	-0.0516	-0.3437	-0.0744	0.1500	-0.2267
F2,1	0.2194	-0.3362	-0.0248	0.4353	0.2550	-0.2708	0.2080	-0.2902	-0.2957
F2,2	0.2312	-0.3206	0.1408	0.2817	0.0707	0.1084	-0.1457	-0.1265	-0.1627
F2,3	0.2186	-0.3664	0.1072	0.2946	0.2958	0.1615	-0.1228	0.4889	0.4167
F5,1	0.2224	0.2372	0.4214	0.0124	-0.0110	0.1448	-0.3667	-0.1418	0.0773
F5,2	0.2182	0.2517	0.4410	0.0237	-0.0078	-0.0039	-0.2954	-0.0425	-0.1198
F5,3	0.1913	0.3502	0.4781	0.0364	0.1468	-0.2501	0.6255	0.1542	0.0533
F6,1	0.2329	0.1964	-0.3066	-0.1285	0.3927	0.0326	0.1500	-0.0943	0.0856
F6,2	0.2439	0.1915	-0.2026	-0.1014	0.3065	0.3365	-0.0162	-0.0996	-0.2178
F6,3	0.2434	0.1760	-0.2210	-0.1424	0.3322	0.0678	-0.1306	-0.1087	0.3368
F7,1	0.2459	-0.2293	0.0618	-0.2140	-0.2315	0.0574	0.1701	-0.2763	0.2092
F7,2	0.2405	-0.2385	0.0812	-0.2719	-0.2240	0.4586	0.3318	0.1406	-0.0110
F7,3	0.2531	-0.1733	0.0577	-0.1565	-0.2016	0.0244	0.0292	-0.4688	0.0892

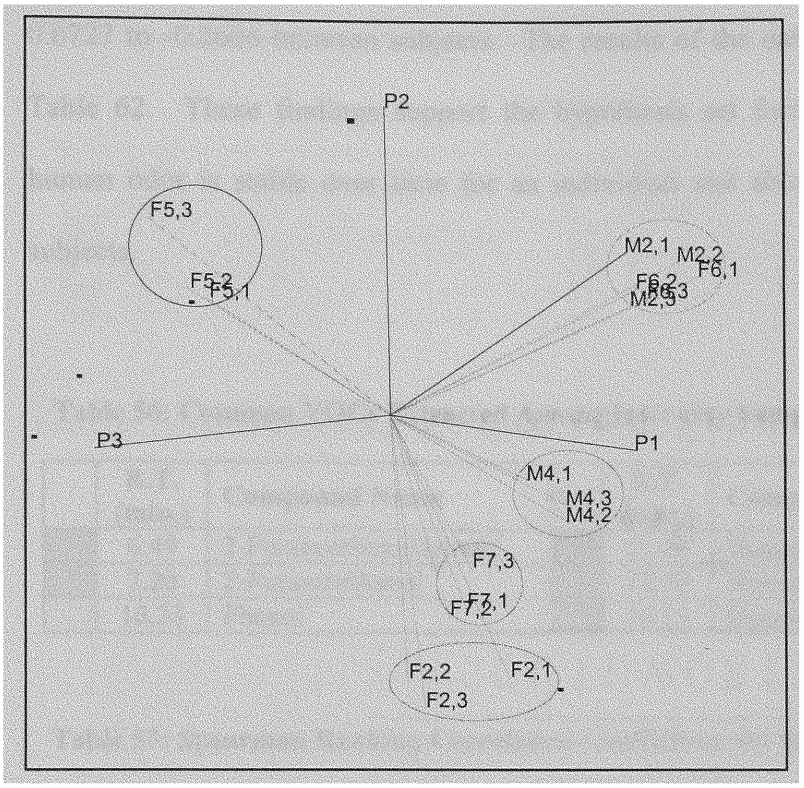


Figure 60: Three Dimensional Principle Component Projection Plot of PCs 1, 2, and 3

Spearman rank correlation analysis was conducted to compare the multiple inter-day samplings for each individual to the multiple intra-day samplings for the subjects previously described. The four inter-day samplings of Female 4 had a correlation range of 1 to 0.7714 (Table 57). The sampling for Female 4 were not collected in the same way as all other hand odor samplings, the gauze was rolled between the palms of the hand instead of being held, so no correlations were run between these samples and the population. The seven hand odor samples for Female 7 collected across fifty days had a correlation range of 1 to 0.7 (Table 59) compared to the range of 0.5429 to -0.4926 between subjects. The five hand odor samples for Male 4 collected across twenty-four days had a correlation range of 0.9758 to 0.9152 (Table 61) compared to the range of

0.6727 to -0.2606 between subjects. The results of the data anlysis are summarized in Table 62. These findings support the hypothesis set forth through canine work that human odor is stable over time for an individual and able to be differentiated among subjects.

Table 56: Common VOCs Extracted Among Inter-day Samplings of Hand Odor for F 4

R.T. (min.)	Compound Name	R.T. (min.)	Compound Name
6.49	2-Furancarboxaldehyde	11.26	Butanedioic acid-dimethyl ester
7.20	2-Furanmethanol	12.50	Nonanal
10.23	Phenol	14.13	Decanal

Table 57: Spearman Ranking Correlation Coefficients for Inter-day Samplings of Hand Odor of Female 4

	F4,1	F4,2	F4,3
F4,1	1	0.7714	1
F4,2	0.7714	1	0.7714
F4,3	1	0.7714	1

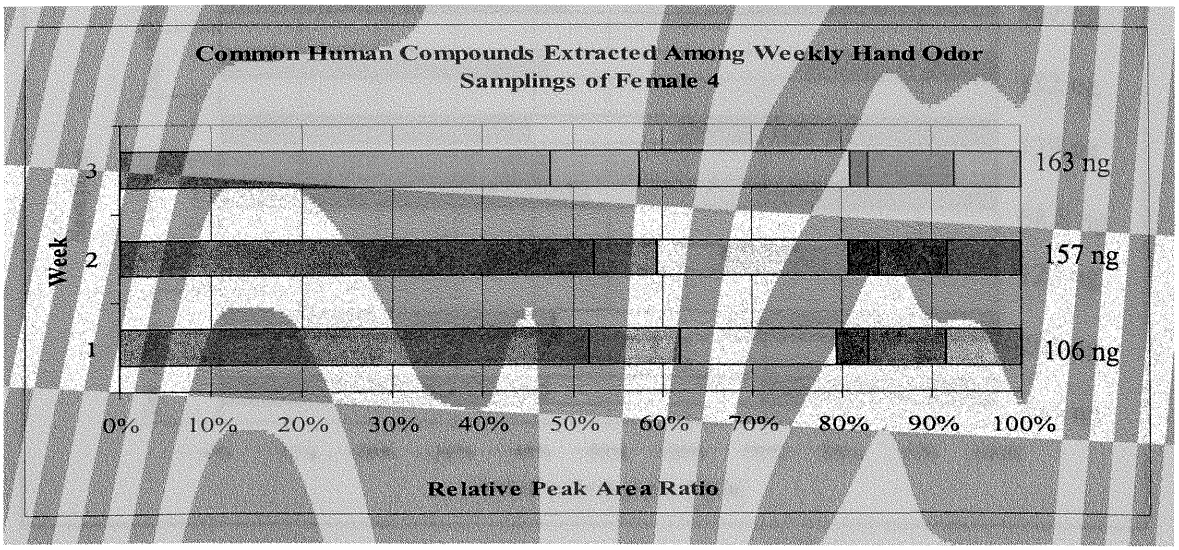


Figure 61: Comparison of Inter-day Hand Odor Samplings of Female 4

Table 58: Common Compounds Extracted Among Inter-day Samplings of Hand Odor for Female 7

R.T. (min)	Compound Name	R.T. (min)	Compound Name
6.49	2-Furancarboxaldehyde	14.13	Decanal
10.23	Phenol	14.68	Hexanedioic acid-dimethyl ester
12.50	Nonanal		

Table 59: Spearman Ranking Correlation Coefficients for Inter-day Hand Odor Samples of Female 7

	F7,1	F7,15	F7,23,1	F7,23,2	F7,23,3	F7,48	F7,50
F7,1	1	1	1	0.9	1	0.7	1
F7,15	1	1	1	0.9	1	0.7	1
F7,23,1	1	1	1	0.9	1	0.7	1
F7,23,2	0.9	0.9	0.9	1	0.9	0.9	0.9
F7,23,3	1	1	1	0.9	1	0.7	1
F7,48	0.7	0.7	0.7	0.9	0.7	1	0.7
F7,50	1	1	1	0.9	1	0.7	1

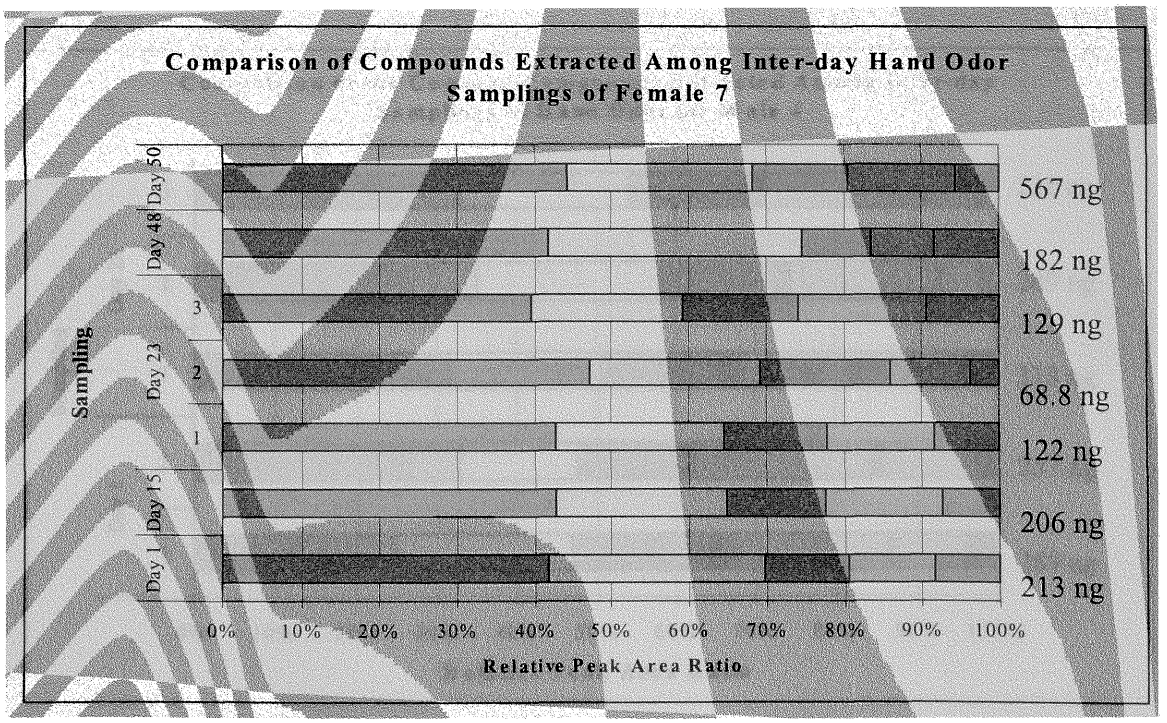


Figure 62: Comparison of Inter-day Hand Odor Samplings of Female 7

Table 60: Common Compounds Extracted Among Inter-day Samplings of Hand Odor for Male 4

	R.T. (min.)	Compound Name		R.T. (min.)	Compound Name
	6.49	2-Furancarboxaldehyde		14.02	Dodecane
	9.07	Propanedioic acid-dimethyl ester		14.13	Decanal
	10.23	Phenol		14.40	Nonanoic acid-methyl ester
	12.50	Nonanal		14.68	Hexanedioic acid-dimethyl ester
	12.81	Octanoic acid-methyl ester		17.65	6,10-dimethyl-5,9-Undecadien-2-one

Table 61: Spearman Rank Correlation Coefficients for Interday Hand Odor Samples of Male 4

	M4,1,1	M4,1,2	M4,24,1	M4,24,2	M4,24,3
M4,1,1	1	0.9515	0.9273	0.9758	0.9758
M4,1,2	0.9515	1	0.9515	0.9636	0.9636
M4,24,1	0.9758	0.9515	1	0.9152	0.9394
M4,24,2	0.9758	0.9636	0.9152	1	0.9758
M4,24,3	0.9273	0.9636	0.9394	0.9758	1

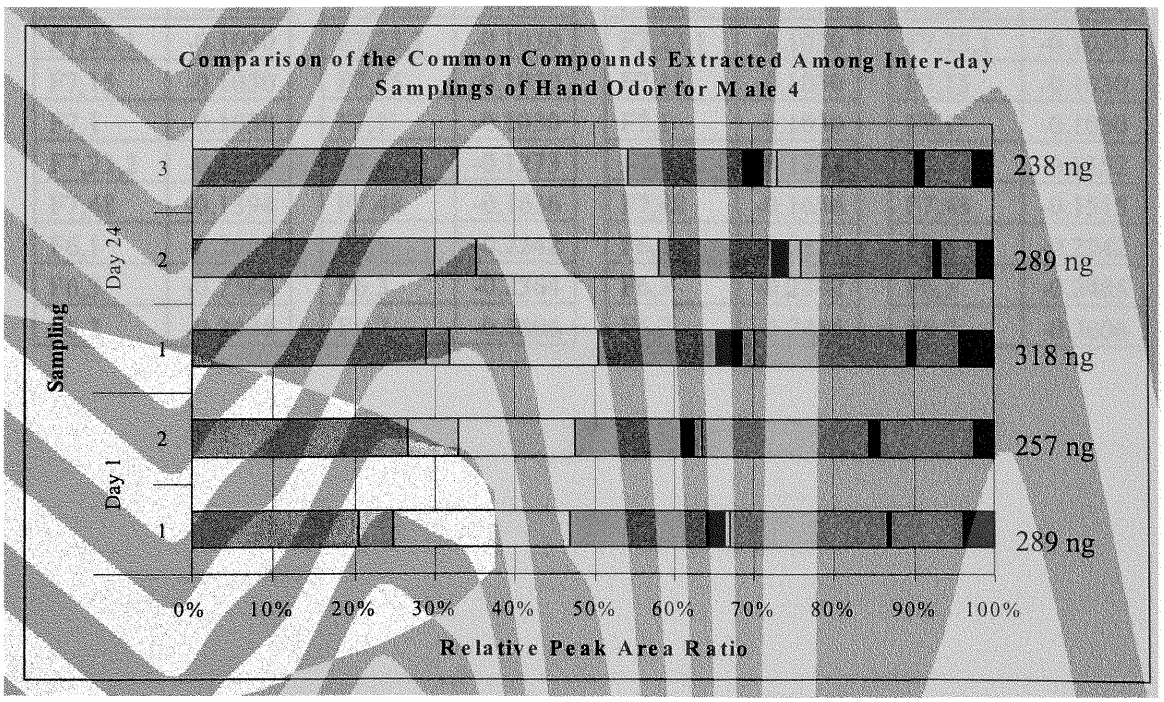


Figure 63: Comparison of Inter-day Hand Odor Samplings of Male 4

Table 62: Spearman Ranking Correlation Coefficients for Inter-day Sampling Among Individuals

M4,1,1	
M4,1,1	1
M4,24,3	0.9758
M4,24,2	0.9758
M4,1,2	0.9515
M4,24,1	0.9273
M2,2	0.6091
M2,1	0.6000
M2,3	0.4727
F5,2	0.4429
F5,1	0.4429
F5,3	0.4083
F2,3	0.2682
F2,2	0.2409
F2,1	0.2318
F7,50	-0.1030
F7,23,3	-0.1030
F7,23,1	-0.1030
F7,15	-0.1030
F7,1	-0.1030
F7,23,2	-0.1152
F7,48	-0.1394
F6,1	-0.2000
F6,3	-0.2364
F6,2	-0.2485

M4,1,2	
M4,1,2	1
M4,24,3	0.9636
M4,24,2	0.9636
M4,24,1	0.9515
M4,1,1	0.9515
M2,1	0.6000
M2,2	0.5909
M2,3	0.5000
F5,2	0.4865
F5,1	0.4865
F5,3	0.4504
F2,3	0.2773
F2,2	0.2318
F2,1	0.2227
F7,50	-0.1030
F7,23,3	-0.1030
F7,23,1	-0.1030
F7,15	-0.1030
F7,1	-0.1030
F7,23,2	-0.1273
F7,48	-0.1636
F6,1	-0.2242
F6,3	-0.2364
F6,2	-0.2606

M4,24,1	
M4,24,1	1
M4,1,2	0.9515
M4,24,3	0.9394
M4,1,1	0.9273
M4,24,2	0.9152
M2,1	0.6727
M2,2	0.6636
M2,3	0.5545
F5,2	0.5030
F5,1	0.5030
F5,3	0.4669
F2,3	0.2864
F2,2	0.2409
F2,1	0.2318
F7,50	-0.1030
F7,23,3	-0.1030
F7,23,1	-0.1030
F7,15	-0.1030
F7,1	-0.1030
F7,23,2	-0.1273
F7,48	-0.1636
F6,1	-0.2121
F6,3	-0.2242
F6,2	-0.2485

M4,24,2	
M4,24,2	1
M4,24,3	0.9758
M4,1,1	0.9758
M4,1,2	0.9636
M4,24,1	0.9152
M2,1	0.5636
M2,2	0.5545
F5,2	0.4504
F5,1	0.4504
M2,3	0.4455
F5,3	0.4143
F2,3	0.2682
F2,2	0.2318
F2,1	0.2136
F7,50	-0.1030
F7,23,3	-0.1030
F7,23,1	-0.1030
F7,15	-0.1030
F7,1	-0.1030
F7,23,2	-0.1152
F7,48	-0.1515
F6,1	-0.2242
F6,3	-0.2485
F6,2	-0.2606

Table 62: Spearman Ranking Correlation Coefficients for Inter-day Sampling Among Individuals

M4,24,3	
M4,24,3	1
M4,24,2	0.9758
M4,1,1	0.9758
M4,1,2	0.9636
M4,24,1	0.9394
M2,2	0.6091
M2,1	0.6000
M2,3	0.5091
F5,2	0.4489
F5,1	0.4489
F5,3	0.4113
F2,3	0.2773
F2,2	0.2500
F2,1	0.2409
F7,50	-0.0909
F7,23,3	-0.0909
F7,23,1	-0.0909
F7,15	-0.0909
F7,1	-0.0909
F7,23,2	-0.1030
F7,48	-0.1273
F6,1	-0.2242
F6,3	-0.2485
F6,2	-0.2606

F7,1	
F7,50	1
F7,23,3	1
F7,23,1	1
F7,15	1
F7,1	1
F7,23,2	0.9000
F7,48	0.7000
F6,1	0.5429
F6,3	0.4286
F6,2	0.3714
F2,3	0.1964
F2,2	0.0893
F2,1	0.0536
M4,24,3	-0.0909
M4,24,2	-0.1030
M4,24,1	-0.1030
M4,1,2	-0.1030
M4,1,1	-0.1030
M2,2	-0.2121
M2,1	-0.2121
M2,3	-0.2606
F5,2	-0.4544
F5,1	-0.4544
F5,3	-0.4838

F7,15	
F7,50	1
F7,23,3	1
F7,23,1	1
F7,15	1
F7,1	1
F7,23,2	0.9000
F7,48	0.7000
F6,1	0.5429
F6,3	0.4286
F6,2	0.3714
F2,3	0.1964
F2,2	0.0893
F2,1	0.0536
M4,24,3	-0.0909
M4,24,2	-0.1030
M4,24,1	-0.1030
M4,1,2	-0.1030
M4,1,1	-0.1030
M2,2	-0.2121
M2,1	-0.2121
M2,3	-0.2606
F5,2	-0.4544
F5,1	-0.4544
F5,3	-0.4838

F7,23,1	
F7,50	1
F7,23,3	1
F7,23,1	1
F7,15	1
F7,1	1
F7,23,2	0.9000
F7,48	0.7000
F6,1	0.5429
F6,3	0.4286
F6,2	0.3714
F2,3	0.1964
F2,2	0.0893
F2,1	0.0536
M4,24,3	-0.0909
M4,24,2	-0.1030
M4,24,1	-0.1030
M4,1,2	-0.1030
M4,1,1	-0.1030
M2,2	-0.2121
M2,1	-0.2121
M2,3	-0.2606
F5,2	-0.4544
F5,1	-0.4544
F5,3	-0.4838

Table 62: Spearman Ranking Correlation Coefficients for Inter-day Sampling Among Individuals

F7,23,2	
F7,23,2	1
F7,50	0.9000
F7,48	0.9000
F7,23,3	0.9000
F7,23,1	0.9000
F7,15	0.9000
F7,1	0.9000
F6,2	0.4286
F6,1	0.4286
F6,3	0.3714
F2,3	0.1607
F2,2	0.1607
F2,1	0.0893
M4,24,3	-0.1030
M4,24,2	-0.1152
M4,1,1	-0.1152
M4,24,1	-0.1273
M4,1,2	-0.1273
M2,1	-0.2000
M2,2	-0.2242
M2,3	-0.2485
F5,2	-0.4574
F5,1	-0.4574
F5,3	-0.4926

F7,23,3	
F7,50	1
F7,23,3	1
F7,23,1	1
F7,15	1
F7,1	1
F7,23,2	0.9000
F7,48	0.7000
F6,1	0.5429
F6,3	0.4286
F6,2	0.3714
F2,3	0.1964
F2,2	0.0893
F2,1	0.0536
M4,24,3	-0.0909
M4,24,2	-0.1030
M4,24,1	-0.1030
M4,1,2	-0.1030
M4,1,1	-0.1030
M2,2	-0.2121
M2,1	-0.2121
M2,3	-0.2606
F5,2	-0.4544
F5,1	-0.4544
F5,3	-0.4838

F7,48	
F7,48	1
F7,23,2	0.9000
F7,50	0.7000
F7,23,3	0.7000
F7,23,1	0.7000
F7,15	0.7000
F7,1	0.7000
F6,2	0.2000
F2,2	0.1964
F2,1	0.1607
F6,1	0.1429
F2,3	0.0893
F6,3	0.0857
M4,24,3	-0.1273
M4,1,1	-0.1394
M4,24,2	-0.1515
M4,24,1	-0.1636
M4,1,2	-0.1636
M2,1	-0.2485
M2,2	-0.2848
M2,3	-0.2970
F5,2	-0.4691
F5,1	-0.4691
F5,3	-0.5103

F7,50	
F7,50	1
F7,23,3	1
F7,23,1	1
F7,15	1
F7,1	1
F7,23,2	0.9000
F7,48	0.7000
F6,1	0.5429
F6,3	0.4286
F6,2	0.3714
F2,3	0.1964
F2,2	0.0893
F2,1	0.0536
M4,24,3	-0.0909
M4,24,2	-0.1030
M4,24,1	-0.1030
M4,1,2	-0.1030
M4,1,1	-0.1030
M2,2	-0.2121
M2,1	-0.2121
M2,3	-0.2606
F5,2	-0.4544
F5,1	-0.4544
F5,3	-0.4838

3.12. Persistance of Human Scent

3.12.1. Scent Weight Dissipation Study

The data collected in the weight dissipation study is shown in Table 63, Table 64, and Table 65. From these data, the mass of the scent present on the media can be calculated by subtracting the initial mass, then adding a correctional factor determined from the differences in the blank mass. The formula used for calculating scent mass present on a sample medium is:

Scent mass = observed mass – initial mass – (observed mass of blank – initial mass of blank)

Figure 64 and Figure 65 demonstrate the trends of scent mass difference plotted versus time for the gauze and slide cover medium respectively. It is readily apparent that the scent collected on the gauze decreased over time, and began leveling off as the scent weight approached zero. While other factors may affect the mass of the gauze, as shown by the variation of the blank sample, the overall decrease in mass shows that environmental factors have a limited impact on the storage capabilities of the gauze. The initial weights of the "scent" for Female 1, Female 2, and Male 1 were 0.69 mg, 2.52 mg, and 3.16 mg, respectively. After eighty-four days of weighing, there was still weight present on the gauze scented by Male 1 and Female 2. It is expected that the mass of odiferous compounds would decrease over time since these compounds must diffuse into the air to produce a detectable scent; thus, the amount of these compounds on the source object must decrease over time. The scent masses recorded on the glass beads indicate

that environmental factors are more significant than actual scent weight, prohibiting glass beads from being a potential scent collection medium. The reason for the increase in mass is not certain, but the slides must be acquiring mass from environmental factors, which may or may not include contaminants that would alter the scent stored on the slide. Of the materials examined in this study, gauze has the most potential as a scent collection medium as demonstrated by the retention of a measurable quantity of scent for several months.

Table 63: Gauze Masses Reported in Milligrams

GAUZE	Blank	Gauze 1 (G1)	Gauze 2 (G2)	Gauze 3 (G3)	Correction factor	Scent wt G1	Scent wt G2	Scent wt G3
Initial mass	597.73	605.08	596.52	606.06	0.00	0.00	0.00	0.00
After scenting		605.77	599.68	608.58	0.00	0.69	3.16	2.52
Day								
1	598.06	606.10	598.85	607.94	0.33	0.69	2.00	1.55
2	597.25	605.33	597.83	607.38	-0.48	0.73	1.79	1.80
3	598.11	606.18	598.83	607.93	0.38	0.72	1.93	1.49
7	597.15	605.30	597.77	606.93	-0.58	0.80	1.83	1.45
8	597.90	605.77	598.45	607.43	0.17	0.52	1.76	1.20
9	598.35	606.69	599.42	608.62	0.62	0.99	2.28	1.94
15	597.66	605.37	597.73	607.23	-0.07	0.36	1.28	1.24
22	598.06	605.87	598.30	607.41	0.33	0.46	1.45	1.02
29	598.83	606.81	599.17	608.54	1.10	0.63	1.55	1.38
36	597.50	605.42	597.43	606.61	-0.23	0.57	1.14	0.78
43	598.52	606.37	598.40	607.61	0.79	0.50	1.09	0.76
50	599.66	607.44	599.39	608.68	1.93	0.43	0.94	0.69
57	598.46	606.11	597.97	607.36	0.73	0.30	0.72	0.57
63	598.49	606.12	598.19	607.63	0.76	0.28	0.91	0.81
70	598.63	606.58	598.38	607.56	0.90	0.60	0.96	0.60
78	600.92	608.76	600.36	609.68	3.19	0.49	0.65	0.43
84	601.24	608.55	600.35	610.07	3.51	-0.04	0.32	0.50

Table 64: Glass Slide Covers Masses Reported in Milligrams

	Blank	Slide 1	Slide 2	Slide 3	Correction factor	Scent wt S1	Scent wt S2	Scent wt S3
Initial mass	4772.52	4576.40	4841.68	4974.43				
After scenting		4576.69	4841.75	4974.85	0.00	0.29	0.07	0.42
Day 1	4772.54	4576.69	4841.80	4974.89	0.02	0.31	0.14	0.48
2	4772.59	4576.70	4841.78	4974.83	0.07	0.37	0.17	0.47
3	4772.63	4576.76	4841.78	4974.82	0.11	0.47	0.21	0.50
7	4772.63	4576.73	4841.80	4974.83	0.11	0.44	0.23	0.51
8	4772.63	4576.70	4841.79	4974.85	0.11	0.41	0.22	0.53
9	4772.55	4576.73	4841.80	4974.85	0.03	0.36	0.15	0.45
15	4772.67	4576.76	4841.84	4974.83	0.15	0.51	0.31	0.55
22	4772.68	4576.74	4841.85	4974.90	0.16	0.50	0.33	0.63
29	4772.65	4576.67	4841.82	4974.94	0.13	0.40	0.27	0.64
36	4772.61	4576.74	4841.88	4974.92	0.09	0.43	0.29	0.58
43	4772.68	4576.80	4841.85	4974.87	0.16	0.56	0.33	0.60
50	4772.73	4576.84	4841.91	4974.96	0.21	0.65	0.44	0.74
57	4772.67	4576.79	4841.86	4975.11	0.15	0.54	0.33	0.83
63	4772.71	4576.84	4841.90	4974.82	0.19	0.63	0.41	0.58
70	4772.71	4576.85	4841.96	4974.86	0.19	0.64	0.47	0.62
78	4772.72	4576.89	4841.97	4974.89	0.20	0.69	0.49	0.66
84	4772.77	4576.86	4841.95	4974.91	0.25	0.71	0.52	0.73

Table 65: Bead Set Masses Reported in Milligrams

	Blank	Set 1	Set 2	Set 3	Correction factor	Scent wt S1	Scent wt S2	Scent wt S3
Initial mass	136.735	136.228	137.675	137.898				
After scenting		136.233	137.685	137.905	0.000	0.005	0.010	0.007
Day 1	136.746	136.228	137.677	137.901	0.011	-0.011	-0.009	-0.008
2	136.753	136.232	137.686	137.905	0.018	-0.014	-0.007	-0.011
3	136.765	136.234	137.684	137.908	0.030	-0.024	-0.021	-0.020
7	136.746	136.235	137.678	137.897	0.011	-0.004	-0.008	-0.012
8	136.749	136.233	137.676	137.899	0.014	-0.009	-0.013	-0.013
9	136.745	136.230	137.675	137.901	0.010	-0.008	-0.010	-0.007
15	136.759	136.229	137.718	137.909	0.024	-0.023	0.019	-0.013
22	136.747	136.229	137.669	137.901	0.012	-0.011	-0.018	-0.009
29	136.746	136.226	137.679	137.897	0.011	-0.013	-0.007	-0.012
36	137.055	136.164	137.711	137.932	0.320	-0.384	-0.284	-0.286
43	136.738	136.22	137.677	137.894	0.003	-0.011	-0.001	-0.007
50	136.739	136.223	137.67	137.892	0.004	-0.009	-0.009	-0.010
57	136.744	136.221	137.672	137.891	0.009	-0.016	-0.012	-0.016
63	136.745	136.222	137.671	137.894	0.010	-0.016	-0.014	-0.014
70	136.764	136.221	137.671	137.893	0.029	-0.036	-0.033	-0.034
78	136.738	136.224	137.683	137.89	0.003	-0.007	0.005	-0.011

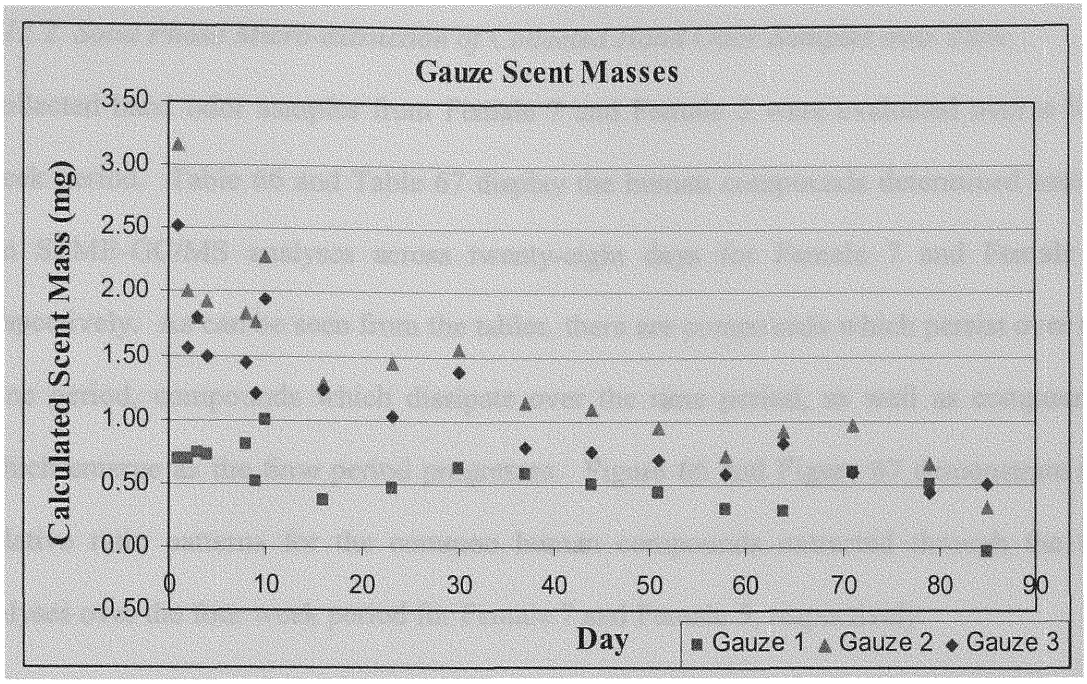


Figure 64: Scent Weight Dissipation from Gauze Pads

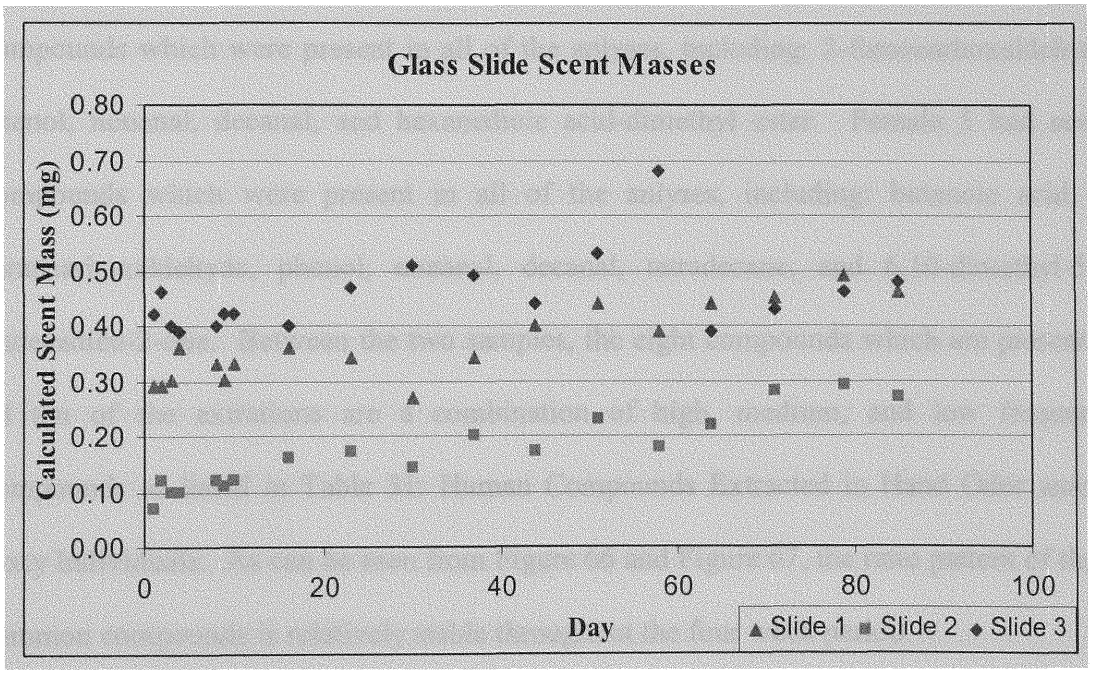


Figure 65: Scent Weight Dissipation from Slide Covers

3.12.2. Solid Phase Micro-extraction of Collected Hand Odor Samples over Time

Collected hand odor samples from Female 7 and Female 5 were evaluated over a four week period. Table 66 and Table 67 display the human compounds determined among ten SPME-GC/MS analyses across twenty-eight days for Female 7 and Female 5, respectively. As can be seen from the tables, there are compounds which persist over the time period, compounds which dissipate over the time period, as well as compounds which emerge as the time period progresses. Figure 66 and Figure 67 demonstrate the relative ratio patterns for the common human compounds extracted through the ten anlyses over the four week period for Female 7 and Female 5, respectively.

The first extraction of the hand odor sample for Female 7 contains fourteen human odor compounds and the first extraction for Female 5 contains sixteen. Female 7 had five compounds which were present in all of the anlyses, including: 2-furancarboxaldehyde, phenol, nonanal, decanal, and hexanedioic acid-dimethyl ester. Female 5 had seven compounds which were present in all of the anlyses, including: butanoic acid, 2-furancarboxaldehyde, phenol, nonanal, decanal, tetradecane, and 6,10-dimethyl-5,9-undecadien-2-one. Between the two samples, the eight compounds which are present in all ten of the extrations are a combination of high, medium, and low frequency compounds as listed in Table 31: Human Compounds Extracted in Hand Odor among Sixty Individuals. As can be seen from Figure 66 and Figure 67, the ratio pattern of these common compounds is relatively stable throughout the four week period.

The analysis of Female 7 shows pyridine, tridecane, and tetradecane were only shown to be present in the first extraction. 2-Furanmethanol disappeared after day seven and propanedioic acid-methyl ester after day five. Butanoic acid was present in all of the extractions except on day twenty-one, which may be due to a problem with the SPME fiber as high amounts of siloxane were also seen during this extraction. The analysis of Female 5 shows the presence of pyridine and 10-methyl-undecanoic acid-methyl ester in only the first extraction and 2-furanmethanol disappears after day three. It is not clear whether these compounds are no longer present in the headspace or if their concentration has fallen below the ability of the SPME fiber to extract.

The analyses conducted on day six and day seven for both subjects show an increase in the number of compounds extracted. Most apparent on day six and seven in the profile of Female 7, is the appearance of many aliphatic/aromatic which are not seen during any other analyses over the time period. This may indicate some sort of a change happening at this time interval after collection inside the vial, and may also be occurring in the scented gauze pads left open to the environment as shown previously in Figure 64. Experiments utilizing canine evaluations of aged materials [93] demonstrated a drop in performance when the canines were using materials that were aged between 1-2 weeks. After an initial significant decrease in performance, the canines were able to distinguish materials aged longer than two weeks with greater ability. This study suggests that when collected odor is stored within a glass container evaporation of the components is limited, and after an initial stabilization period, a steady state is reached which would explain the leveling off in performance of the canines. The evaluation of the composition of latent

fingerprints over time has also shown that the majority of the changes in composition occur within the first week [23]. The results shown here also suggest that the majority of the changes in headspace composition occur within the first seven days after collection.

The changes in collected odor may be due to the biological elements present on the materials after human contact. When evaluating odor which was obtained through direct contact, human secretions, skin cells, and bacteria may all be contained within the collection material. These biological constituents play a role in the creation of human odor when present on the body, removing them from such a moist, warm environment may alter their behavior and hence the compounds released. It may be possible through freezing the material, or storing it at lower temperatures to reduce the biological activity inside the closed system, thus reducing the alterations to the resulting volatile organic compounds. Another means for reducing the biological activity within the container is removing the biological components entirely through gamma radiation of the material after collection. Experiments utilizing canine evaluations after gamma radiation of scented materials [17] have already shown that biological components in the collection materials are not necessary for sustaining the collected odor. It is possible that, after collection of human scent, if the materials are irradiated to remove all biological elements, then the collection material will only contain the chemical constituents and therefore will vary less over time during storage.

Table 66: Human Compounds Present in the Headspace of a Collected Hand Odor Sample of Female 7 over Time

		Days Since Collection									
R.T. (min.)	**Compound Name**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**14**	**21**	**28**
3.86	Pyridine	X									
4.41	Toluene					X	X	X			X
4.67	2-Butenal, 2-methyl-	X									
5.67	Butanoic acid	X	X	X	X	X	X	X	X		X
6.49	2-Furancarboxaldehyde	X	X	X	X	X	X	X	X	X	X
7.20	2-Furanmethanol	X	X	X	X	X	X	X			
7.48	Benzene, 1,3-dimethyl-							X			X
8.12	p-Xylene					X	X	X			
8.32	Nonane	X	X	X		X	X	X			
9.07	Propanedioic acid-dimethyl ester	X	X	X	X	X					
9.89	Benzene, 1,3,5-trimethyl-						X	X			
10.13	Benzene, 1-ethyl-2-methyl-						X	X			
10.23	Phenol	X	X	X	X	X	X	X	X	X	X
10.56	Decane						X	X			
12.41	Undecane						X	X			
12.50	Nonanal	X	X	X	X	X	X	X	X	X	X
14.02	Dodecane						X	X			
14.13	Decanal	X	X	X	X	X	X	X	X	X	X
14.68	Hexanedioic acid-dimethyl ester	X	X	X	X	X	X	X	X	X	X
15.49	Tridecane	X									
16.85	Tetradecane	X									
17.65	6,10-dimethyl-5,9-Undecadien-2-one	X	X	X		X	X		X		

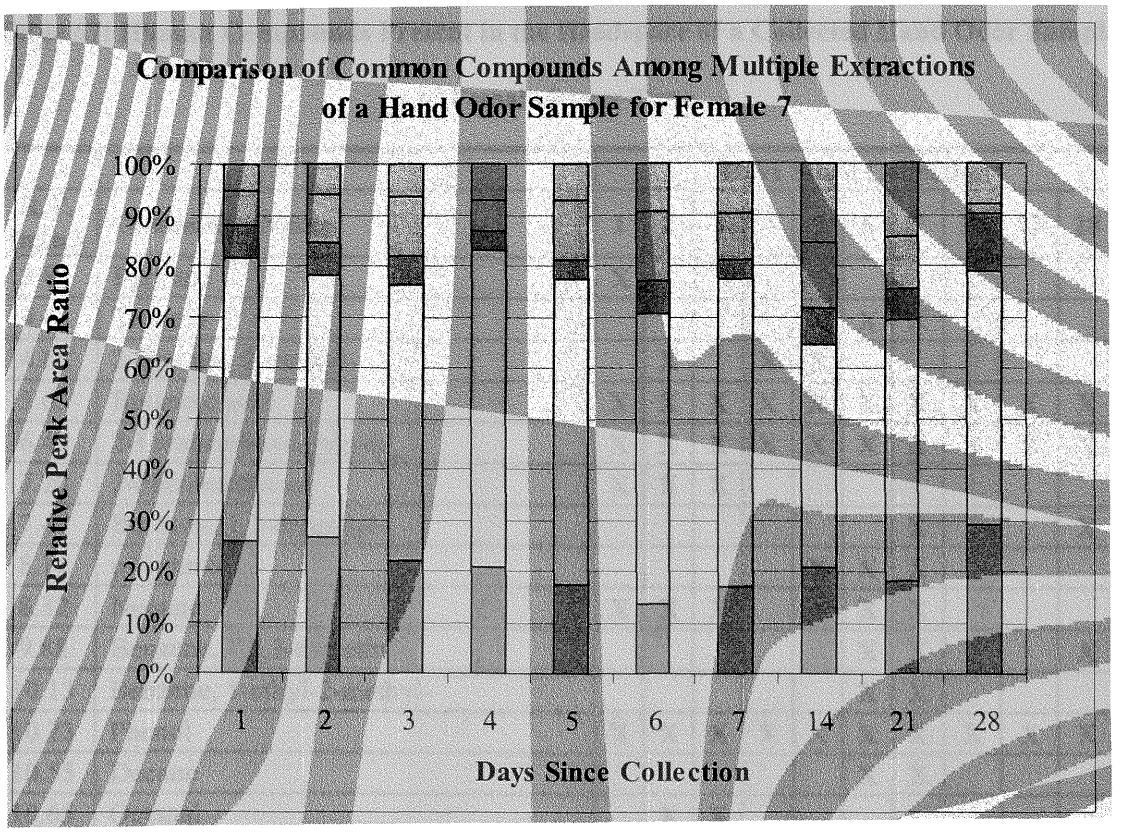


Figure 66: Comparison of the Relative Ratio Patterns of the Common Human Compounds Extracted in a Collected Hand Odor Sample of Female 7 over Time

Table 67: Human Compounds Present in the Headspace of a Collected Hand Odor Sample of Female 5 over Time

		Days Since Collection									
R.T. (min.)	**Compound Name**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**14**	**21**	**28**
3.89	Pyridine	X									
4.41	Toluene					X	X	X			
4.68	2-Butenal, 2-methyl-		X		X	X					
5.63	Butanoic acid	X	X	X	X	X	X	X	X	X	X
6.49	2-Furancarboxaldehyde	X	X	X	X	X	X	X	X	X	X
7.20	2-Furanmethanol	X	X	X							
7.47	Benzene, 1,3-dimethyl-							X			X
8.12	p-Xylene					X	X	X			
8.32	Nonane	X	X	X		X	X	X			
9.88	Benzene, 1,2,3-trimethyl-						X	X			X
10.13	Benzene, 1-ethyl-2-methyl-						X	X			
10.23	Phenol	X	X	X	X	X	X	X	X	X	X
10.55	Decane						X	X			
10.65	Octanal		X	X							
12.41	Undecane	X				X	X	X			X
12.50	Nonanal	X	X	X	X	X	X	X	X	X	X
12.83	Octanoic acid-methyl ester	X	X								
13.42	2-Nonenal, (E)-	X									
14.02	Dodecane						X	X	X		
14.13	Decanal	X	X	X	X	X	X	X	X	X	X
14.68	Hexanedioic acid-dimethyl ester	X	X	X	X	X	X	X		X	X
15.49	Tridecane	X	X		X	X	X	X		X	X
15.62	Undecanal			X		X					
15.62	Tetradecanal				X	X	X	X			
16.85	Decanoic acid			X		X					
16.94	Tetradecane	X	X	X	X	X	X	X	X	X	X
17.65	6,10-dimethyl-5,9-Undecadien-2-one	X	X	X	X	X	X	X	X	X	X
17.79	Eicosane								X	X	
18.43	Dodecanoic acid-methyl ester					X	X	X			X
18.69	Undecanoic acid, 10-methyl-, methyl ester	X									
18.87	Dodecanoic acid					X					

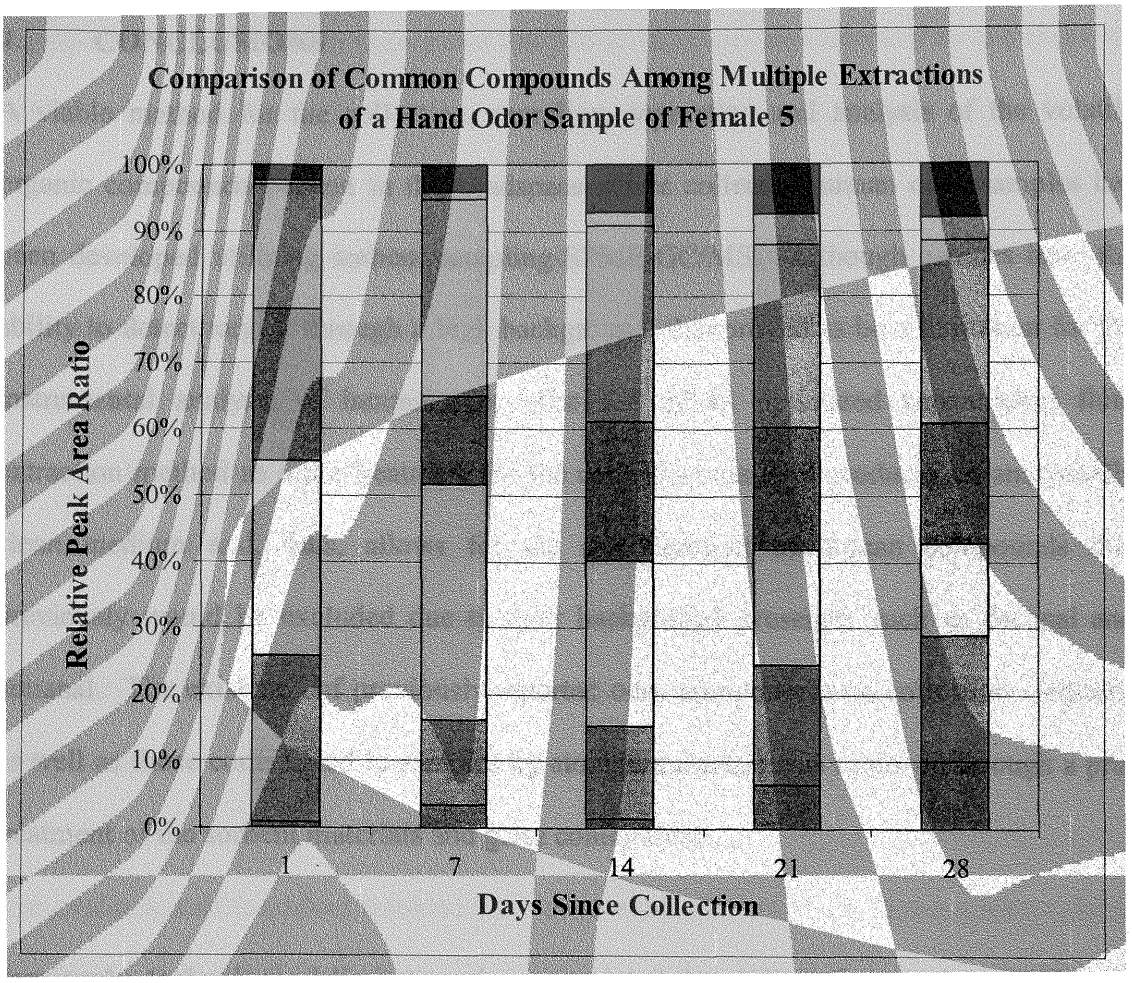


Figure 67: Comparison of the Relative Ratio Patterns of the Common Human Compounds Extracted in a Collected Hand Odor Sample of Female 5 over Time

4. CONCLUSIONS

A viable method for the collection, sampling, separation and analysis of the volatile organic compounds present in the headspace above collected human odor samples has been developed utilizing sorbent sampling-SPME-GC/MS. Although canines have the ability to detect targets through a high background, this proved to be a limitation for the instrumental analysis of human odor. The use of an optimized supercritical fluid extraction method as a pre-treatment for the collection material produces an analytically clean medium and, thus, allows for the consideration of human compounds that previously would be excluded due to their background presence, such as decanal and nonanal. The existence of previously reported odor components on collection mediums as well as those contributed to samples by storage materials was removed through a pre-treatment of the sorbent materials and glass containment.

Previously, technological limitations have restricted the ability of researchers to identify the chemical components that comprise human odor or to use the information to chemically distinguish between individuals. Odor profiles collected from the same region of the body among individuals can be evaluated through comparison of the relative ratios of the odor compounds extracted. It has been shown to be possible to distinguish between the individuals studied here using the relative ratio comparisons of common compounds extracted among individuals. However, examination of additional compounds provides greater discrimination ability. Using this semi-quantitative method of analysis it is also possible to establish that multiple samplings of one individual over time do not contain as much variation as that seen amongst a population. These results

support the individual odor theory that has previously been demonstrated by the ability of canines to accurately discriminate between individuals based on their odor.

The evaluation of the odors released from collected armpit secretions across a ten subject population has allowed for determinations to be made about the abundances of components of human scent collected from the armpit. The seven different types of compounds determined to be present in a human armpit odor profile included acids, alcohols, aldehydes, alkanes, esters, ketones, and nitrogen containing compounds. Across the ten subjects and sixty-five human compounds extracted, there was a high degree of variability observed with fifteen high frequency compounds, nineteen medium frequency compounds, and thirty-one low frequency compounds among the population.

The evaluation of the odors released from collected hand secretions across a sixty subject population has allowed for determinations to be made about the abundances of components of human scent collected from the hands. The seven different types of compounds determined to be present in a human hand odor profile included acids, alcohols, aldehydes, alkanes, esters, ketones, and nitrogen containing compounds. Across the sixty subjects and sixty-three human compounds extracted, there was a sufficient degree of variability observed with six high frequency compounds, seven medium frequency compounds, and fifty low frequency compounds to allow all subjects in the population to be differentiated.

Additionally, there appears to be a relatively long persistence of the human scent compounds in a controlled environment with measurable amounts still present in an open container nearly three months after being deposited on sterile gauze. The volatile organic compounds present in the headspace above collected odor samples change over time when inside a closed system. However, some compounds remain in the headspace four weeks after collection and the ratio pattern of these components is relatively stable over the time period studied.

Finally, an automated program for comparing odoor profile data has been developed which is capable of identifying the human odor components, comparing the results of multiple samples to determine commonalities, ranking the odor components according to size of peak area, and then correlating the ranks between samples. These comparisons, which are based on determining the primary odor components of an individual through multiple samplings and a match / no-match criteria of 0.8, are the first of their kind.

The present results support the central hypothesis that there is a primary odor that is sufficiently consistant for individuals and sufficiently variable among individuals to allow for the instrumental differentiation of subjects based on volatile human scent compounds.

5. FUTURE WORK

Although the headspace SPME-GC/MS analysis method described here can be used for the analysis of the volatile organic compounds present above collected odor samples, this process could be better optimized for target human VOCs. The SPME-GC/MS method created could be further optimized by using single ion monitoring to improve sensitivity to the volatile organic compounds that have been identified to be present in the headspace of collected odor samples. It also may be possible to attain greater peak resolution by optimizing the temperature ramp of the gas chromatograph during analyte separation.

Further studies need to be conducted into determining the optimal storage conditions for collected human scent samples. Storage conditions, including: light and dark effects, as well as temperatures (-80 ^{0}C and room temperature) should be evaluated. Determining the effects of each of these conditions on the odor profiles will aid in determining the optimum storage condition for collected scent samples. The effect of removing the biological components from collected scent samples prior to storage should also be considered.

It is also necessary to optimize a procedure to collect human traces from objects to provide further maintain that the methods used to collect human scent evidence are scientifically sound. Experiments should be conducted using a variety of sampling methods; contact and non-contact with and without dynamic air flow. The metal bars that are utilized by the Netherlands National Police to conduct human scent line-ups could be utilized as a stable medium as they are constructed from stainless steel and it is know that

canines can utilize the amount of odor which they retain. The active scent transfer should be conducted using the Scent Transfer Unit (STU-100), as this is the device used by the FBI to collect human scent evidence and it is know that canines can utilize the amount of odor that is trapped on the resulting sorbent material. Time optimization experiments will also be conducted to determine the optimum time needed for the transfer of VOCs for each of the different sampling methods.

It is important to determine whether the canines are utilizing the VOCs determined through SPME-GC/MS of collected human scent. It is possible, using an odor detection port attachment for the GC/MS, to collect the VOCs as they pass from the GC into the MS. This device can be used to collect the sample for canine comparison with the collected odor sample. The ODP can also be used to fractionate the chromatogram, and these fractions could then be presented to human scent canines to further refine which compounds are being used to distinguish individuals. Canine field trials to determine what the dogs are using to differentiate individuals would also provide a new dimension to the work.

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APPENDICES

A Compounds Previously Reported in Humans 236

B FBI Specialized Bloodhounds SOP 252

C Netherlands National Police Human Scent Line-up SOP 256

D Comparison of the Headspace Compounds Present in Various Absorbers 269

E Comparison of the Headspace Compounds Present in Various Cleansers 275

B Compounds Previously Reported in Humans

The following 521 compounds have been previously reported by various different research groups to be present in humans:

Compound Name (By Functional Group)	Reference
Alcohols	
1-butanol	52
1-decanol	52
1-hepten-3-ol	41, 42
1-hexanol	52
1-hexen-3-ol	41
1-octen-3-ol	41
1-propanol	30
1-tetradecanol	20, 21, 41
2-(2H-benzotriazol-2-yl)-4-methylphenol	41
2-(hydroxymethyl)-2-methyl-1,3-propanediol	41
2-butanol	41
2-decanol	41
2-ethyl-1-butanol	30
2-ethylhexanol	52, 54
2-heptadecanol	41
2-hexadecanol	41, 42
2-hexen-1-ol	41
2-methoxyphenol	26
2-methyl-3-octenol	41
2-methyl-3-pentanol	41
2-octen-1-ol	41
2-phenylethanol	26
2-propanol	30
3,7-dimethyl-2,6-octandiol	54
3,7-dimethyl-6-octanol	54
3,7-dimethyl-6-octen-1-ol	41
3-methyl-4-penten-2-ol	41
4-hexen-1-ol	41, 42
5-methyl-2-isopropyl-cyclohexanol	54
amyl alcohol	52
benzyl alcohol	3, 21, 41, 54, 121, 126

cedrol	54
cholest-5-en-3-ol	41
cyclobutanol	30
decenol, substituted	41
dodecenol	41
ethanol	27, 28, 30
ethylene glycol	41
glycerol	41, 40, 42
hexadecanol	20, 21, 52
methional	26
methylpentanol	42
nonenol	41
octadecanol	52
octanol	52
p-cresol(4-methylphenol)	26
phenol	3, 20, 21, 23, 26, 28, 41, 121, 126
phenylethyl alcohol	41, 54
tridecanol	41
trimethyl-silanol	30
Aldehydes	
(E)-2-nonenal	3, 26, 52, 121, 126
(E)-2-octenal	3, 26
(E)-4,5-epoxy-(E)-2-decenal	26
(E,E)-2,4-decadienal	26
(E,E)-2,4-nonadienal	3, 26
(E,Z)-2,4-decadienal	26
(E,Z)-2,4-nonadienal	26
(E,Z)-2,6-nonadienal	26
(Z)-2-nonenal	26, 52
(Z)-4-heptenal	26
2,2-dimethylhexanal	41
2,4-nonadienal	41, 42
2-methyl-2-butenal	41
2-methylbutanal	41
2-methylhexadecanal	41
3-methylbutanal	40
2-methylpropanal	41, 42
3,7-dimethyl-1,6-octadien-3-ol	126
3,7-dimethyl-2,6-octadienal	3, 41
3-hydroxy-4-methylbenzaldehyde	41

3-methylpentanal	41, 42
4-methoxybenzaldehyde	26
4-phenylmethoxybenzaldehyde	41
acetaldehyde	28
benzaldehyde	3, 27, 41, 42, 54, 121, 122, 126
butanal	40
decanal	41, 40, 52, 53, 54, 121, 122, 126
decanaldehyde	23
dodecanal	41
2-furancarboxaldehyde (furfural)	121, 126
heptanal	3, 27, 29, 41, 40, 42, 52, 121, 126
hexanal	3, 26, 27, 29, 30, 40, 52, 121, 126
lilial	54
nonanal	30, 40, 41, 42,52, 53, 54, 121, 122, 126
octanal	26, 40, 41, 52, 53, 54, 121, 126
pentanal	40,30
propanal	41
phenylacetaldehyde	40
trans-2-heptanal	30
tetradecanal	121, 126
undecanal	3, 40, 121, 126
Aliphatics/Aromatics	
1,1,2-trimethyl-cyclohexane	30
1,2,3-trimethyl-benzene	30
1,2,3-trimethyl-cyclopentane	30
1,2,4-trimethyl-benzene	29, 30
1,2-dimethyl-3-(1-methylethyl)-cyclopentane	30
1,2-dimethyl-benzene	30
1,2-dimethyl-cyclohexane	30
1,2-pentadiene	30
1,3,5,7-cyclooctene	54
1,3,5-trimethyl-benzene	30
1,3-dimethyl-benzene	30
1,4-dimethylbenzene	29, 30, 41
1,5-dimethyl-cyclopentene	30
1-ethyl-2-methyl-benzene	30
1-heptene	29

1-methyl-2-(1-methylethyl)-benzene	30
1-methyl-2-ethyl-benzene	122
1-methyl-2pentyl-cyclopropane	29
1-methyl-3-[1-methylethyl]-benzene	27
1-methylethenyl-benzene	29, 30
1-methylethyl-benzene	30
1-methyl-naphthalene	122
1-octene	52
1-phenyl-1-butene	27
2,2,3,3-tetramethyl-butane	28
2,2,4-trimethyl-heptane	30
2,2,4-trimethyl-hexane	30
2,2-dimethyl-hexane	28
2,3-dimethyl-butane	30
2,3-dimethyl-hexane	28
2,4-dimethyl-1-heptene	30
2,4-dimethyl-heptane	28, 29, 30
2,4-dimethylhexane	41
2,6-dimethyl-1-heptene	41
2,6-dimethyl-octane	30
2,7-dimethyl-1-octene	41
2-B-pinene	30
2-deutero-2-methyl-propane	30
2-ethyl-1,4-dimethyl-benzene	30
2-methoxy-2-methyl-propane	30
2-methyl-1-butene	30
2-methyl-1-heptene	41, 42
2-methyl-1-hexene	41
2-methyl-2-dodecene	41, 42
2-methyl-2-undecene	41
2-methyl-butane	30
2-methyl-dodecane	54
2-methyl-heptane	29, 30
2-methyl-hexadecane	54
2-methyl-hexane	28, 30
2-methyl-pentane	28, 30, 122
2-methyl-1-pentene	28,

2-nonene	42
2-octene	41, 42
3,4-dimethyl-1-pentene	30
3,4-nonadiene	41
3,5-dimethyl-heptane	30
3-dodecene	54
3-ethyl-1,4-hexadiene	41
3-ethyl-2,2-dimethyl-pentane	30
3-methyl-5-undecene	41
3-methyl-heptane	30
3-methyl-hexane	28, 30
3-methyl-nonane	30
3-methyl-octane	29, 30
3-methyl-pentane	30
3-octene	27, 41
4,4'-dimethyl-1,1'-biphenyl	41
4-ethyl-1,2-dimethyl-benzene	27
4-ethyl-3-heptene	41
4-methyl-1-pentene	30
4-methyl-2-pentene	41
4-methyl-4-undecene	41
4-methyl-decane	30
4-nonene	41
4-octene	41
5-decene	41
9-octadecane	41
a-pinene	27, 28, 54, 121, 126
a-terpinolene	30
benzene	27
benzonitrile	122
camphene	54
caryophyllene	54
cholesta-3,5-diene	41
cholesterol	23, 42, 47, 48
cis-1,3-pentadiene	30
cis-1-ethyl-4-methyl-cyclohexane	30
cyclohexadecane	41

cyclohexane	29
cyclotetradecane	3, 41
cyclopentadecane	54
decane	29, 30, 41, 53, 52
diethyl-benzene	27
dimethylpentadiene	41
d-limonene	30, 54
docosane	41, 42
dodecane	30, 52, 54, 121, 126
eicosane	54
ethyl-benzene	27, 30, 41, 122
ethyl-cyclohexane	30
heneicosane	41
heptadecane	3, 41, 121, 126
heptane	30, 42, 122
hexadecane	41, 53, 54, 121, 126
hexadecene	41, 54
hexane	28, 30
isooctane	30
isoprene	28, 29, 30
menthane	41,42
methyl cyclopentane	27, 29, 30
methylbenzene	30
methyl-cyclohexane	30
methyldodecene	41
methylheptadecane	41
naphthalene	26, 121, 122, 126
N-menth-6-ene	41
N-octan-3-ene	30
nonane	30,41,42, 121, 126
octadecane	3, 41
octane	30,41
pentacosane	41,42
pentadecane	41, 53, 54
pentadecene	54
pentane	30
pentene	41

propylbenzene	29, 30, 41
R-1-methyl-4-(1-methylethenyl)-cyclohexene	30
squalene	23, 41, 42, 47, 48
styrene	27, 29, 41, 42
tetracosane	41
tetradecane	41, 53, 54, 121, 126
tetradecene	41
toluene	3, 27, 28, 41,42, 121, 122, 126
triacontene, branched	41
tricosane	41,42
tridecane	54, 121, 126
trimethyl-1,4-heptadiene	41
trimethyl-3-methylenehexadecane	41,42
undecadiene	41
undecane	29, 30, 54, 121, 122, 126
unedecane	52
xylene	27, 28, 30
Amides/Amines/Related	
1,3-butanediamine	41, 42
1,4-benzenedicarbonitrile	41
2-cyano-acetamide	30
2-piperidone	21
ammonia	23
benzothiazole	122
butanamine	42
methenamine	122
N,N-bis(2-hydroxyethyl)dodecanamide	41
N,N-didodecyl formamide	41
N,N-diethyl-3-methylbenzamide (DEET)	41
N,N-dimethyl-1,2-ethanediamine	41
N,N-dimethyl-1-dodecanamine	41, 42
N,N-dimethyl-1-heptadecanamine	41
N,N-dimethyl-1-hexadecanamine	41, 42
N,N-dimethyl-1-octadecanamine	41, 42
N,N-dimethyl-1-pentadecanamine	41
N,N-dimethyl-1-tetradecanamine	41, 42
N,N-dimethyl-1-tridecanamine	41, 42

N,N-dimethyl-3-benzyloxypropylamine	41
N,N-dimethyl-3-butoxypropylamine	41
N-ethylcyclopentamine	41
N-methyl-methanamine	30
N-methyl-N-nitroso-1-dodecanamine	41
propanamide	30, 41, 42
Carboxylic Acids	
(E)-3-methyl-2-hexenoic acid	20,21
(E)-3-methyl-2-octenoic acid	21
(E)-3-methyl-2-pentenoic acid	21
(E)-3-methyl-3-hexenoic acid	34
(Z)-3-methyl-2-hexenoic acid	20, 21, 34
10-undecenoic acid	21
11-phenoxyundecanoic acid	41
2-butenoic acid	41
2-ethylhexanoic acid	20
2-hexenoic acid	21
2-methyl-2-butenoic acid	41
2-methyldecanoic acid	20, 21
2-methylheptanoic acid	20
2-methylhexanoic acid	20, 21
2-methylnonanoic acid	20, 21
2-methyloctanoic acid	20, 21
2-methylpropionic acid	39
2-propenoic acid	41
3-ethylheptanoic acid	26
3-hydroxy-3-methylhexanoic acid	34
3-methyl-2-hexenoic acid	34
3-methyl-2-pentenoic acid	41
3-methyl-butanoic acid	26, 39
3-methylhexanoic acid	20, 21
3-methylpentanoic acid	26, 41
4-ethyldecanoic acid	20, 21
4-ethylheptanoic acid	20, 21
4-ethylnonanoic acid	20, 21
4-ethyloctanoic acid	20, 21, 26
4-ethylpentanoic acid	20, 21

4-hydroxy-3-methoxybenzoic acid	41, 42
4-hydroxybenzoic acid	41
4-methyloctanoic acid	26
7-octenoic acid	20, 21
9,12-ocadecadienoic acid	41
9-decenoic acid	20, 21
9-hexadecenoic acid	41
9-octadecenoic acid	41, 42
acetic acid	26, 41, 52
benzoic acid	21, 41
butanoic acid	26, 52
decanoic acid	20, 21, 39, 40, 41
decanoic acid	20
dodecanoic acid	3, 40, 41, 42, 121, 126
heptadecanoic acid	40, 41, 42
heptadecenoic acid	40, 41
heptanedioic acid	41
heptanedioic acid	41
heptanoic acid	20, 21, 26, 39, 41
hexadecanoic acid	40, 41, 42
hexadecenoic acid	40
hexanedioic acid	41, 40
hexanoic acid	20, 21, 26, 39, 41, 126
lactic acid	23, 40, 41
lauric acid	23
methyl tridecanoic acid	41
methyldodecanoic acid	41
methylheptadecanoic acid	41
methylhexadecanoic acid	41
methylpentadecanoic acid	41, 42
methyltetradecanoic acid	41, 42
methyltridecanoic acid	42
myristic acid	23, 47
nonandioic acid	23
nonanoic acid	3, 20, 21, 23, 39, 41
octadecadienoic acid	40
octadecanoic acid	40, 41, 42

octadecenoic acid	40
octanoic acid	20, 21, 26, 39, 41, 48
oleic acid	23, 47, 48, 126
palmitic acid	23, 47, 48
palmitioleic acid	47
palmitoleic acid	23, 47, 48
pentadecanoic acid	41, 40, 42, 47
pentadecenoic acid	41
pentanoic acid	26
propanoic acid	41
stearic acid	23, 47, 48
tetradecanoic acid	41, 40, 47, 48, 121, 126
tetradecenoic acid	41
tridecanoic acid	41
undecanoic acid	41, 20, 21
Esters	
13-methylpentadecanoic acid, methyl ester	41, 42
14-methylpentadecanoic acid, methyl ester	41, 42
15-methylheptadecanoic acid, methyl ester	41
1-methyl-2-propenoic butyl ester	27
2,4-dihydroxy-3,6-dimethylbenzoic acid, methyl ester	41
2-butenoic acid, butyl ester	41,42
2-hydroxybenzoic acid, phenylmethyl ester	41,42
3-hydroxybenzoic acid, methyl ester	41
4-hydroxybenzoic acid, propyl ester	41,42
7-hexadecenoic acid, methyl ester	121, 126
9-dodecenoic acid, methyl ester	126
9-hexadecanoic acid octadecyl ester	47
9-hexadecenoic acid eicosyl ester	47
9-hexadecenoic acid hexadecyl ester	47
9-hexadecenoic acid methylester	21
9-hexadecenoic acid octadecyl ester	47
9-hexadecenoic acid tetradecyl ester	47
acetic acid, butyl ester	30
acetic acid, phenylmethyl ester	121, 126
butanoic acid, methyl ester	41
cyclopentanetridecanoic acid, methyl ester	121, 126

decanoic acid, methyl ester	121, 126
dodecanoic acid, 10-methyl, methyl ester	121, 126
dodecanoic acid, methyl ester	121, 126
ethyl acetate	27
ethylbutanoate	26
ethylmethylpropanoate	26
ethylpentanoate	26
furancarboxylic acid, methyl ester	121, 126
heptadecanoic acid, methyl ester	41, 21
heptanedioic acid, dibutyl ester	41
hexadecanoic acid, butyl ester	41
hexadecanoic acid, methyl ester	41, 121, 126
hexanedioic acid, dimethyl ester	121, 126
hexanedioic acid, ester	41
hexanedioic acid, ester branched	41
hexanedioic acid, mono(2-ethylhexyl) ester	41, 42
hexanedioic acid, octyl ester	41
hexanoic acid, methyl ester	121
hydroxybutanoic acid, ethyl ester	41
isobornyl propionate	54
methyl palmitate	47
methyl salicylate	54
methyl stearate	47
methyl-3-methyl-2-butenoate	26
methyl 9-methyltetradecanoate	121, 126
methylhexadecanoate	40
methylhexadecanoic acid, methyl ester	41, 42
methyltridecanoic acid, ethyl ester	42
nonanoic acid, methyl ester	41, 121, 126
octadecanoic acid, methyl ester	41
octadecanoic acid, phenyl ester	41
octadecenoic acid, methyl ester	41, 42
octanoic acid, methyl ester	121, 126
palmitic acid methylester	21
pentadecanoic acid, methyl ester	121, 126
pentanedioic acid, ester	41,42
pentanedioic acid, mono(2-ethylhexyl) ester	41,42

propanedioic acid, dimethyl ester	121, 126
tetracosanoic acid, methyl ester	41
tetradecanoic acid, methyl ester	121, 126
tetradecanoic acid, undecyl ester	41
tridecanoic acid, methyl ester	41, 121, 126
undecanoic acid, methyl ester	121, 126
Z-2-butanoic acid, methyl ester	27
Ethers	
diphenyl ether	54
vinyl isopropyl ether	27
Halides/related	
1,6-dichloro-1,5-cyclooctadiene	41
1-chloro-4-(4-methyl-4-pentyl) benzene	41
1-chlorododecane	41
1-chloroheptane	41
1-chlorohexadecane	41
1-chlorohexane	41, 42
1-chlorononane	41, 42, 121, 126
1-chloropentadecane	41
1-chlorotetradecane	41, 42
2,3-dichlorobenzeneamine	41
2-chloro-1-methylethylbenzene	41
3-chlorobenzeneamine	41
benzylchloride	41
carbon tetrachloride	122
chloride	23
chloro-benzene	30
chloroform	122
chloromethane	28
dichlorodifluoroethane	122
dichlorodifluoromethane	122
dichloromethane	27, 30
methyl iodide	41
methyliodide	42
tetrachloro-ethene	30, 122
trichloro-ethene	30, 122
trichlorofluoro-methane	29, 122

Heterocyclics	
1,2,3,4-tetrahydroquinoline	41
1,5-dimethyl-1H-pyrazole	41
1H-indole	41, 42
1-methylpiperazine	41
1-phenyl-3-(1-piperidinyl)-2-buten-1-one	41
1-piperidineethanol	41
2,3,4-trimethylquinoline	41
2,3-dihydro-1H-indene	30
2,3-dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one	41
2,3-dihydro-3,5-methoxy-6-methyl-4H-pyran-4-one	42
2,3-dihydro-4-methylfuran	41, 42
2,5-dihydro-1-nitroso-1H-pyrrole	30
2,5-dimethylpiperazine	41
2,6-dimethylpyrazine	41
2-ethylpiperazine	41
2-ethylpiperidine	41
2-furanmethanol	41, 121, 126
2H-1-benzopyran-2-one	41
2-methoxy-5-methylthiophene	41
2-methoxy-6-methyl-4H-pyran-4-one	41
2-methyl-1H-pyrrole	41
2-methylfuran	30, 41
2-methylisothiazole	41, 42
2-methylpyridine	41
3(1-methyl-2-pyrrolidinyl)pyridine (nicotine)	41, 42
3-acetyl-6-methyl-2H-pyran-2,4(3H)dionethiazolidine	41
3-ethyl-2,5-dimethylpyrazine	41
3-methyl-1H-pyrrole	41
3-methylfuran	41
3-pyridinamine	41
4(1H)-pyridinone	41
4,5-dihydro-2-methyl-1H-imidazole	41
4-methyl-2-pyridinamine	41
4-piperidinemethanamine	41

4-pyridinamine	41, 42
5-methyl-2(5H)thiophenone	41
5-methyl-2-methylthio-4(1H)-pyrimidinone	41
6-amino-3-pyridine carboxylic acid	41
benzofuran	41
dihydro-5-tetradecyl-2(3H)-furanone	41
indole, substituted	41
oxazole	41, 42
piperazine	30
pyrazine	41
pyridine	41, 42, 121, 126
thiazolidine	41
trimethylpyrazine	41
Ketones	
1-hexen-3-one	26
1-octen-3-one	26
2,5-octanedione	27
2-aminoacetophenone	26
2-butanone	28
2-decanone	41, 42
2-hexanone	41
2-methoxy-2-octen-4-one	41
2-nonen-4-one	41
2-pentanone	28, 30, 41, 42
3-hydroxyandrostan-11,17-dione	41
3-pentanone	41, 42
4-methyl-2-pentanone	30, 52
4-heptanone	28
6,10-dimethyl-5,9-undecadien-2-one	3, 41, 121, 126
6-methyl-3,5-heptadien-2-one	41
6-methyl-5-hepten-2-one	3, 41, 42, 52, 53, 121, 126
acetone	27, 28, 30
acetophenone	54
butanone	41, 42
Sulfides	
carbon disulfide	41, 122
dimethyl disulfide	30, 41, 122

dimethylsulfone (C2H6SO2)	20, 21
dimethyltrisulfide	26, 122
Thio/Thioesters/Sulfonyls	
1,1'-sulfonylbis[4-chlorobenzene]	41
1-methylthiobutane	41
1-methylthiopropane	30
1-thiododecane	41
2-methyl-3-sulfanylbutan-1-ol	34
2-thiopropane	41
3-(methylthio)-1,2-propanediol	41
3-(methylthio)-1-propene	30
3-methyl-3-sulfanylhexan-1-ol	34, 37
3-methylthietane	41
3-sulfanylhexan-1-ol	34
3-sulfanylpentan-1-ol	34
acetylthiocarbamic acid, methyl ester	41
cis-1-(methylthio)-1-propene	30
methanesulfonylchloride	41
o-(2-butenylthio)phenol	41
thiocarbamic acid, butyl ester	41
thiomethane	41
trans-1-(methylthio)-1-propene	30
Urea/related	
methylurea	41
N,N-dimethylthiourea	41
tetramethyl thiourea	54
thiourea	41
urea	41, 42
Miscellaneous	
1,2,3-trimethoxypropane	41
1,3-dimethoxybutane	41
1H-pyrrole	28
1-isocyanato-3-methylbenzene	41
a-thujene	30
C10-lactone	20, 21
C8-lactone	20, 21
C9-lactone	20, 21

calcium	23
heptadienal	42
methyl palmitoleate	47
methylundecene	42
oleyl oleate	48
potassium	23
pyrolidine	30
sodium	23
Soloton	26
sulfur	23
sulfur dioxide	122

C FBI Specialized Bloodhounds SOP

The following pages include the standard operating procedure for the Federal Bureau of Investigation's Specialized Blood hounds whom work in the Human Scent Evidence Team (HSET).

Human Scent Evidence Collection

PRINCIPLE

Human scent evidence can exist on items of evidence which have come in direct or indirect contact with a person(s). If collected properly with it's integrity preserved (ie, with proper containment and storage and a thoroughly maintained listing of all personnel who have come into contact with the evidence), human scent evidence can retain it's viability for considerable periods of time.

The collection of human scent evidence pads and their utilization by trained human scent discriminating canines can assist investigators in efforts to identify likely suspects or in the recovery of additional evidence.

SCOPE

This scent collection procedure is used by members of the Laboratory for the gathering of human scent evidence as secondary evidence to be provided to the field for future use by trained human scent discriminating canines.

SPECIMEN

The articles components used to construct the fuzing system should be appropriately packaged so as to preclude the possibility of being damaged or contaminated.

MATERIALS

Eye protection
Tyvek laboratory coat
Latex or Nitrile gloves
Note pad
Pen and marking materials
Secondary Human Scent Evidence Log
Scent Transfer Unit (STU)
Alcohol swabs or cotton balls and alcohol
Johnson + Johnson brand 5" x 9" SURGIPAD* Combine Dressings, number 2145 (Scent Pad)
6 1/2" x 8" or equivalently sized nylon heat sealed bags
Labels
Camera (film or digital)

CALIBRATION

No calibration of the Scent Transfer Unit is required.

PROCEDURE

If feasible, human scent evidence should be collected prior to other Laboratory examinations. Multiple pads must be created from a cross section of evidence submitted. Prior to handling any evidence the collector should wear a new tyvek laboratory coat and new latex or nitrile gloves.

Although the collection process is non-destructive, the specimens should be examined for any trace evidence that could be of probative value. This evidence could include, but not be limited to the following: Hairs, fibers, blood, paint, or other particles.

> If anything of questionable value is found, the examiner should consider contacting the submitting agency to determine if this material is of value and whether it should be preserved.
>
> If it is to be examined or preserved, contact the appropriate unit and determine if they should remove the material prior to conducting the collection procedure. Note: Document the presence of the material by means of notes, sketches, or photographs before it is removed.

List all individuals who come into direct contact with the items being examined. Plug the STU into the previously charged battery source and set up the collection unit. Put on a pair of latex or nitrile gloves. With the vacuum running, clean the intake of collection unit, pad holder, and bracket with an alcohol swab or cotton balls and alcohol. Run the unit until the alcohol has evaporated. Place a Johnson + Johnson brand 5" x 9" SURGIPAD* Combine Dressing, number 2145 on the intake/pad holder of the collection unit, and lock the pad in with the bracket. Place the evidence item directly onto the pad or collection unit bracket. Larger items may be vacuumed by picking up the STU and moving it around the evidence item. If the evidence items are such that removing them from the evidence packaging may cause them to be lost, the collection unit may be introduced into the opening of the package. Turn on the STU collection unit and allow scent collection to occur for 1 min. Record the time of collection, collector's name, the number of the pad in the series (ie, 1 of 3, 2 of 3, etc.), case number, Laboratory number, item number and item description onto the label. If feasible, photograph the collection process. Remove the pad and place it in a 6 1/2" x 8" or equivalently sized nylon heat sealed bag and heat seal the bag's enclosure. Apply the label to the bag. Place the heat sealed bag into a second 6 1/2" x 8" or equivalently sized nylon heat sealed bag and seal the second bag. The bags can be further secured within a paint can. If the scent pads are to be stored for long periods of time, they should be refrigerated or frozen.

The above-described procedures will be repeated until at least (3) scent pads are collected per item of evidence selected. Gloves must be changed between the vacuuming of different evidence items.

LIMITATIONS

Occasions may arise wherein subject search items (K) are packed within the same shipping containers as crime scene search items (Q), creating cross contamination of scent. Additionally, contact with the contributor may reveal issues about scent contamination from the crime scene. If the Laboratory determines that scent cross contamination has occurred, it should be documented in the case activity log, and no scent pads should be made.

SAFETY

Protective tyvek laboratory coats must be worn when handling specimens for scent collection.

Protective latex or nitrile gloves must be worn when handling specimens.

Gloves and tyvek laboratory coats will assist in minimizing the transfer of the collector's scent onto the scent pad.

Gloves and tyvek laboratory coats will prevent exposure of the examiner to possible hazardous material on the items.

Gloves and tyvek laboratory coats will prevent the DNA of the examiner from being transferred to the items.

Safety protocols, contained within the Safety Manual, should be observed at all times.

REFERENCES

The STU instructional video tape.

Approved: _____
Title: _____
Date: _____

D Netherlands National Police Human Scent Line-up SOP

The following pages include the standard operating procedure for the KLPD's canine human scent line-ups.

DESCRIPTION OF THE PROTOCOL

OF A

SCENT IDENTIFICATION LINEUP

AS FOLLOWED IN

THE NETHERLANDS

SINCE AUGUST 1997

Translated from Dutch version

KLPD, Canine Department

Definitions

Certificate:	defined in article 9 of the "Regeling politiespeurhonden" (officially published guidelines). On this certificate (valid for 2 years) the kind of scent-carriers the dogs works with, the presentation method of these scent carriers, the response of the dog and his reward are annotated;
Corpus delicti:	object or scent sample taken from an object, originating form the scene of a crime, that has been accounted for in an official report ("proces verbaal"). The object has to be handled according to the official guidelines (Forensic Technical norms 324.01 and 326.01);
Control object:	object given to the control person for this lineup by the dog handler or helper. This object is preferably of the same kind of material (but not necessarily identical) as the corpus delicti;
Control person:	person who is described as such in the "proces verbaal" (official report) and whose name is noted in the scent identification lineup registration system. The odour of this person is used to test the ability of the dog to perform scent identification lineups;
Foils:	adult persons who do not belong to the suspects environment and who are not (as far as known) involved in the crimes the suspect is being held for. These people participate in the scent identification lineup with their odours;
Suspect:	person who is being suspected of this particular crime. In each lineup there may be only one suspect;

Scent-carrier: material on which the scent of the suspect, the control person and the foils is collected for the lineup. All carriers for a lineup must be identical and not individually marked. Carriers may differ between dogs, for each dog the kind of carrier is annotated on its certificate. The most common kind of scent carrier is a stainless steel tube of 10cm length;

Presentation method: the way in which the scent carriers are presented to the dog, for each dog this is annotated on its certificate. The most common method is to present the stainless steel tubes on a platform where they can be clamped into place;

Sequence scheme: there are 36 different sequence schemes in which the scent identification lineups can be presented. These numbered schemes are the same all over the country (characteristic of these schemes is that they maximise the chance that the dog smells the scent of the suspect in step one or two of the protocol);

Helper: police officer and co-signer of the "proces verbaal" (official report), who is certified for this task. He throws the dice for determining the sequence scheme, he sets up the lineup, he terminates the lineup procedure if the dog gives an incorrect or no response (here he responds after the handlers signal of his dogs response), and if the method calls for it, he also releases the reward for the dog. The helpers name is given in the "proces verbaal" (official report);

Response: reaction the dog gives when he finds a matching odour: for each dog his characteristic response (bite, scratch, sit, lie down) is annotated on the certificate, the handler signals when his dog shows this response;

Reward: after a correct response the dog is given a fixed reward, this is also annotated on the certificate. The most common reward is being allowed to retrieve the matching stainless steel tube from the platform.

Preparation of material for a scent identification lineup.

The preparation of material for a scent identification lineup must be done by a helper or by a dog handler certified for the scent identification task.

The following is needed:

- corpus delicti in closed package accounted for in a "proces verbaal" (official report);
- 1 suspect;
- 6 foils;
- 14 identical scent carriers;
- 1 control object;
- 7 x packaging for scent carriers;
- 1x packaging for control object

The 7 people each hold two scent carriers in their hands for 5-10 minutes. It is not necessary to wash hands prior to handling the scent carriers, since the lineup procedure caters for a check on the attractiveness of the odour of the suspect for the dog. One of the foils is defined as the control person, and this person keeps the control object in his

pocket for the duration of the handling of the scent carriers. This control person is described in the "proces verbaal" of the scent identification lineup, and his name is registered for the scent identification lineup registration system. When the carriers have been scented long enough they are collected. The control object is collected separately. The carriers and the control object are coded on the packaging: "A" for the carriers and the object of the control person, "B" to "F" for the other foils, and "X" for the suspect. The handler/helper notes the names that go with each code for the registration system, although these names will not be mentioned in the "proces verbaal" (privacy argument). The gender and race of the people involved are also noted for registration purposes.

If the scent carriers of the suspect are scented in a different way, the scent carriers of the other 6 people also need to be scented in this same way (this can happen when a suspect refuses to hold the carriers in his hands). This needs to be reported in the "proces verbaal".

Preparation of a scent identification lineup.

The odours are presented according to one of the 36 different sequence schemes (see supplement). These have been coded by two figures (each figure between 1 and 6). The sequence is determined by the helper, who throws a dice twice. The helper installs the scent carriers in two rows according to this sequence (if necessary, successively), according to the presentation method required for the dog who will perform the lineup. The dog handler and his dog are absent during the preparation of the lineup: the handler does not know the position of the different scents and testifies to this in the "proces verbaal".

Performing the lineup (also see fig. 1).

The dog handler may terminate a lineup at any point. The result of this is a disqualification.

Step 1. The helper chooses such a position, that the dog can not see him when he is searching in the row. The handler approaches the first row with his dog. He lets the dog smell at the control object, and lets his dog search freely in the row with scent carriers to find the matching odour. When the dog clearly responds (as described in his certificate), the handler signals. If this response is directed to the scent of the control person, the helper in turn signals the handler (this may also be: "no signal"). The handler may then reward the dog, or let the helper release a reward. After this the procedure continues with step 2. If the dog responds to another odour than that of the control person and thus makes an incorrect choice, and the handler signals, this means that the dog is disqualified. This "disqualification" is reported in the "proces verbaal". If the dog does not respond to any odour and has smelled all the carriers, the handler recalls his dog and this also leads to a disqualification. If the dog does not work systematically and as a result misses one or more carriers but has smelled the others several times this is also a disqualification. In step 1 only may the dog be given scent of the control object a second time.

Step 2. If the dog has responded correctly to the carrier scented by the control person in row 1, the handler may take his dog to row 2 where the procedure described above (step 1) is repeated. An incorrect or no response at all in this row also leads to disqualification. After a correct response the procedure continues with step 3. The dog may only smell at the control object once in step 2.

Step 3. When the dog has responded to the odour of the control person in both rows, the handler must evaluate the behaviour of his dog in both rows. If the handler concludes that his dog has shown special interest for one of the odours in a row, he must let the helper know. If this odour belongs to the suspect, the dog is disqualified for the remainder of the lineup. If the odour did not belong to the suspect, the lineup may continue. The handler must report in his "proces verbaal" that the dog had responded to the odour of the control person in both rows, and had not shown special interest for the odour of the suspect. The procedure continues with step 4. The helper removes the scent carriers with the scent of the control person (if these are still present in the rows).

Step 4. The handler returns to the first row with his dog, which now consists of 6 odours. He lets the dog smell at the corpus delicti. The dog again searches freely in the row for the matching odour. If the dog responds to one of the odours, the handler gives his signal. If this is the odour of the suspect, the helper signals back and the dog is rewarded in the usual manner. The procedure then continues with step 5. If the dog responds to the odour of one of the foils, the helper lets the handler know this is wrong and the lineup is terminated. The conclusion of this lineup as reported in the "proces verbaal" and in the registration system is "incorrect procedure". If the dog does not respond to any of the odours but has smelled all of them, the conclusion that will be reported is "no odour similarity". If the dog does not respond to any of the odours but has not smelled all of them, the conclusion is also "no odour similarity". If, however, it turns out that the dog has systematically not smelled the odour of the suspect, a special note must be made of this in the report. The handler may only present the corpus delicti to the dog to smell once.

Step 5. If the dog has responded to the odour of the suspect based on the odour of the corpus delicti in the first row and has been rewarded (not excessively), the handler takes his dog to the second row and this last part of the procedure is repeated. The handler lets his dog smell at the corpus delicti once again, and lets the dog search in this second row for the matching odour. If the dog again responds to the odour of the suspect, the conclusion of the lineup is "odour similarity between object and suspect". If the dog responds to a foil in this row, the final conclusion is "incorrect procedure". If the dog does not respond to any of the odours in this row, the final conclusion is "no odour similarity".

Step:	**row nr:**	**starter object**	**choice dog**	**result**
1	row 1	control object (odour A)	A (control person)	continue with 2
			B,C,D,E,F or X(susp)	**disqualified**
			no response	**disqualified**
2	row 2	control object (odour A)	A (control person)	continue with 3
			B,C,D,E,F or X(susp)	**disqualified**
			no response	**disqualified**
3	rows 1&2		no interest for odour of X (suspect)	continue with 4
			interest for dour of X	**disqualified**

			(suspect)	
4	row 1	corpus delicti	X (suspect)	continue with 5
			B,C,D,E or F	**incorrect procedure**
			no response	**no odour similarity**
5	row 2	corpus delicti	X (suspect)	**odour similarity**
			B,C,D,E or F	**incorrect procedure**
			no response	**no odour similarity**

Fig. 1. Overview scent identification lineup procedure.

Registration of result

The official report ("proces verbaal", written under oath of office) made of a scent identification lineup contains a description of the way in which the material was prepared, a description of the control person, the control object and how long this was scented, a report on whether the suspect participated freely in the scent collection or if the odours were collected in a different way, information on the helper, the sequence scheme used, information on each of the steps of the procedure and the result of each step. The

handler declares that his dog is unfamiliar with the control person, that he was unaware of the position of any of the odours in the lineup, and that he did not see his dog pay any special attention to the odour of the suspect in steps 1 and 2. This report is co-signed by the helper(s) involved.

Besides this official report, information is put into the scent identification registration system either by filling in a form or using the software package developed for this purpose. This registration should be used by the direct chief for a continuous quality control on the dog.

Additional points.

Place where the lineup is performed: this should be a familiar place for the dog, preferably in quiet surroundings with a fairly stable temperature regime and a place where the dog is commonly trained. It is important to create a fixed place (room) for this purpose, this may become compulsary when these guidelines are reviewed.

Public: As few people as possible should be present at a scent identification lineup. Those who are there should position themselves in such a way that nor the dog, nor the handler can see them during the lineup.

Registration: it is advised to videotape the scent identification lineups. Besides the official report, registration for purposes of quality control should also take place.

More than one suspect: each scent identification lineup may only contain the odour of a single suspect. If there are more suspects, a separate lineup has to be prepared for each suspect. If these are performed with the same dog, all the other odours (the foils and the control person) must be different for each lineup.

More than one corpus delicti: if there are several corpus delicti and a single suspect, a second lineup may be performed with the same dog if the result of the first lineup was a "no odour similarity" (this is not allowed after a "odour similarity", a "disqualification" or an "incorrect procedure"). Then it is important that all the scents in the lineup are the same as in the earlier lineup, but on fresh carriers. If a dog has been disqualified because he showed interest for the odour of the suspect, or if he has found an "odour similarity" between an object and a suspect, he may not be confronted with this suspects odour in scent identification lineups for 14 days. In these 14 days the dog should have at least 2 correct training sessions.

Re-use of corpus delicti: a single corpus delicti may be used for several lineups. It can be used for a second lineup with the same dog, or for a lineup with a second dog. The different lineups have to be performed within 8 hours after the corpus delicti was first unsealed. The dogs who are presented with a "used" corpus delicti have to be used to this.

E Comparison of the Headspace Compounds Present in Various Absorbers

The following pages include the compounds seen in triplicate headspace analysis of various absorbent materials.

	Nexcare gauze	Eckerd gauze	CKF Super Absorber Cotton	Johnson and Johnson 2x2	Johnson and Johnson 5x7	DUKAL gauze	IMCO 2x2	King's Cotton	Hungarian cotton	Polish absorber
Initially Sterile (Yes/No)	Y	Y	N	Y	Y	Y	Y	N	N	N
(+)-.alpha.-terpineol			X							
(E)-2-decenal									X	
(E)-2-heptenal					X					
(E)-2-nonenal								X		
(Z)-7-tetradecene					X					
.alpha. Isomethyl ionone		X								
[(dodecyloxy)methyl]-oxirane			X							
2-methyl propanoic acid				X		X				
1,1,4,4,7,7-hexamethyl-cyclononane		X								
1,1-dodecanediol, diacetate										X
1,2,3-trimethyl benzene						X				X
1,2,4,5-tetramethyl benzene	X									
1,2,4-Methenoazulene, decahydro-1,							X			
1,2,4-trimethyl benzene	X					X				
1,2-dichloro benzene	X									
1,3,5-trimethyl benzene	X				X		X			X
1,3-dimethyl benzene	X				X					
1,4-dichloro benzene				X	X					X
1,5,4-dibromo tetrapentacontane										X
1,7,11-trimethyl cyclotetradecane		X					X			

10-methylnonadecane	X						X			
13,17,21-trimethylheptatriacontane									X	
17-pentatriacontene	X									
1-chloro heptacosane					X					X
1-dodecene	X									
1-ethyl-2,3-dimethyl benzene	X									
1-heptadecene							X			X
1-methyl-2-(1-methylethyl) benzene	X									
1-methyl-2-pyrrolidinone										X
1-methyl-4-(1-methylethyl) benzene	X									
1-methyldecahydronaphthalene			X							
1-nonene								X		X
1-octadecene										X
1-octanol							X		X	
1-pentadecene				X			X		X	X
1-pentyl-2-propyl cyclopentane	X		X							
1-propylpentachlorotriphosphazene								X		
1-tetradecene	X	X	X	X						
2-(2-methoxyethoxy) ethanol									X	
2(3H)-Furanone, dihydro-5-methyl-							X			
2-(dodecyloxy) ethanol	X									
2,2,4-trimethyl-pentanoic acid		X								X
2,2'-diethyl-1,1'-biphenyl						X	X			X
2,4-bis(1,1-dimethylethyl) phenol									X	
2,5-cyclohexadiene-1,4-dione			X							X
2,6-cyclohexadiene-1,4-dione	X	X	X	X	X		X	X	X	X
2,6,10,14-tetramethyl hexadecane		X				X		X	X	X
2,6,10,14-tetramethyl pentadecane		X				X	X	X	X	X
2,6,10-trimethyl dodecane			X			X	X			
2,6,10-trimethyl pentadecane		X		X					X	X
2,6,10-trimethyl tetradecane										X
2,6,11,15-tetramethyl hexadecane	X									
2,6,11-trimethyl dodecane	X				X					
2,6-bis(1,1-dimethylethyl) phenol		X					X			
2,6-bis-cyclohexadien-1-one		X								
2,6-diisopropylnaphthalene				X				X	X	X
2,6-dimethyl heptadecane	X									
2,6-dimethyl undecane	X									

2,6-dimethyl-7-octen-2-ol	X	X		X						
2,9-dimethyl undecane	X									
2-butoxy ethanol	X	X	X	X	X	X	X	X	X	X
2-dodecen-1-yl(-) succinic anhydride										X
2-ethenyl-1,4-dimethyl benzene	X									
2-ethyl-1-hexanol	X		X	X	X	X	X		X	X
2-ethyl-2-methyl propanoic acid									X	
2-Furanmethanol							X			
2-hydroxy benzaldehyde	X							X		
2-methyl decane			X							
2-methyl tricosane			X							
2-n-butylacrolein					X					
2-pentadecanol									X	
2-Propanol, 1-(2-methoxypropoxy)-							X			
2-propoxy ethanol										X
2-Pyridinecarboxaldehyde							X			
3,5,24-trimethyl tetracontane	X		X							
3,5,3',5'-tetramethylbiphenyl								X		
3,7-dimethyl-1,6-octadien-3-ol		X		X						
3-cyclohexene-1-methanol, .alpha.		X		X						
3-heptanone					X					
3-methyl decane			X							
3-methyl pentadecane										X
3-methyl tridecane			X							
3-methyl undecane	X									
3-methyl-5-(1-methylethyl) phenol	X									
3-Penten-2-one, 4-methyl-						X				
3-phenoxy-1-propanol		X								X
4-cyanocyclohexene								X		X
4-cyclohexyl dodecane				X						
4-cyclohexyl tridecane		X								
4-ethyl-1,2-dimethyl benzene	X									
4-methyl decane			X							
4-methylcarbazole				X						
5-methyl-2-(1-methyl) cyclohexanone	X	X	X	X						
5-methyl-2-(1-methyl) cyclohexanol	X		X	X				X		
5-propyl tridecane										X
6,10-dimethyl-5,9-undecadien-2-one								X		X

6-Tridecene							X			
9-octyl heptadecane									X	
acetic acid, phenylmethyl ester	X	X								
acetophenone	X	X					X			X
benzaldehyde		X		X						
Benzene, (1-butylheptyl)-						X				
Benzene, (1-butylhexyl)-						X				
Benzene, (1-butyloctyl)-						X				
Benzene, (1-ethyldecyl)-						X				
Benzene, (1-pentylheptyl)-						X				
Benzene, (1-propylnonyl)-						X				
Benzene, 1,3,5-tris(1-methylethyl)							X			
Benzene, 1,3-bis(1,1-dimethylethyl							X			
benzophenone				X						
benzyl alcohol	X							X	X	
Butanoic acid, butyl ester						X				
Butylated Hydroxytoluene						X	X			
camphor	X			X						
caprolactam					X					
cis-2,6-dimethyl-2,6-octadiene				X						
cyclododecane	X									
Cyclohexadecane							X			
Cyclohexane, 1-(1,5-dimethylhexyl)							X			
Cyclopentadecane							X			
cyclotetradecane	X			X						
decanal	X			X	X	X	X	X	X	X
decane	X		X	X						
Decane 3-cyclohexyl-, 3-cyclohexyl							X			
diisopropylnaphthalene								X		
dimethyl phthalate								X		
D-Limonene	X			X						
docosane									X	
dodecane	X			X			X		X	
dotriacontane		X								
eicosane	X	X				X	X		X	
furfural				X	X					
heptadecane	X	X		X	X	X	X	X	X	X
Heptadecane, 3-methyl-							X			

heptanal	X								X	X
heptanoic acid									X	
hexadecane						X	X	X	X	X
hexadecyl oxirane								X	X	
hexanal	X	X	X	X	X				X	
hexanoic acid									X	
Hexanoic acid, 2-ethyl-							X			
hexatriacontane	X			X						
isobornyl acetate	X	X	X	X						
Limonene				X						
methyl salicylate	X	X	X	X						
N,N-dibutyl formamide			X			X				
N,N-diethyl formamide										X
naphthalene	X	X		X	X					
Naphthalene, 1-methyl-							X			
Naphthalene, 2,3-dimethyl-							X			
nonadecane					X					
Nonadecane, 9-methyl-							X			
nonanal	X	X	X	X	X	X	X	X	X	X
nonane								X		
octadecane		X	X	X		X				X
octanal	X		X		X			X		X
pentacosane									X	
pentadecane	X	X	X	X	X	X	X	X	X	X
pentyl cyclopropane									X	X
phenol				X	X	X	X	X	X	X
tetrachloroethylene					X					
Tetracosane							X			
tetradecanal						X				X
tetradecane	X	X	X	X	X	X	X	X	X	X
tetradecyl oxirane										X
tetratriacontane									X	X
toluene						X		X	X	
tridecanal								X		X
tridecane	X	X	X	X		X	X	X		
Tridecane, 4-methyl-							X			
Tridecane, 5-methyl-							X			
Tridecane, 5-propyl-							X			

Tridecane, 7-hexyl-							X			
tritetracontane		X	X				X			X
undecanal						X		X	X	X
undecane			X		X				X	

F Comparison of the Headspace Compounds Present in Various Cleansar Materials

The following pages include the human compounds extracted in the headspace analysis of various types of cleanser materials including soaps made from a base of animal, organic, and glycerin materials.

Animal Fat Based Cleanser Materials														
Soap Characteristics	Olay Beauty Bar Sensitive	Irish Spring Original Deodorant	Aveeno Johnson & Johnson	Dove Body Wash Unscented	Dove Unscented Bar Soap	Dial Natural Hypoallergenic	Softsoap Naturals Moisturizing	Softsoap Handsoap Antibacterial	Regular Ivory Soap	Zest Aqua Pure	Radox Herbal Bath	Irish Spring Sport Antibacterial	Equate Antibacterial	Emu Oil Soap
Added Frangrance (Yes/No)	Y	Y	Y	N	N	Y	Y	Y	Y	Y	Y	Y	Y	Y
Human Compounds														
.alpha.-Pinene	X	X	X	X	X			X	X		X	X	X	X
1,6-Octadien-3-ol, 3,7-dimethyl-	X	X	X		X	X	X	X		X	X	X		X
1-Octene														
5-Hepten-2-one, 6-methyl-	X							X						X
6-Octen-1-ol, 3,7-dimethyl- , (R)-	X				X			X		X				
Acetic acid-phenylmethyl ester	X		X	X	X			X		X	X	X		
Benzaldehyde	X				X		X	X			X			
Benzene, 1,3-dimethyl-					X			X						
Benzene, 1-methyl-2-(1-methylethyl)					X									
Benzyl Alcohol					X					X				
Camphene	X	X	X	X			X		X	X		X		X
Caryophyllene		X					X	X			X	X		X
Decanal		X										X		
Decane			X								X			X
Decanoic acid-methyl ester											X			
Diphenyl ether									X					
D-Limonene		X			X				X			X		
Docosane							X							
Dodecane	X		X	X			X	X		X	X			

Eicosane							X							
Heneicosane							X							
Heptadecane					X		X							
Heptanal					X									
Hexadecane								X						
Hexanal	X			X	X									X
Hexanoic acid					X									
Hexanoic acid-methyl ester											X			
Lilial	X				X						X			
Nonane														
Octadecane							X							
Octanoic Acid					X									
Octanoic acid-methyl ester											X			
Pentadecane					X		X							
Phenylethyl Alcohol	X			X	X	X		X		X	X	X		
Tetradecane	X		X	X			X	X		X	X			
Toluene														
Tridecane							X				X			
Undecane							X				X			

Organic and Glycerin-Based Cleanser Materials									
	Organic							Glycerin	
Soap Characteristics	Natural Avocado and Cucumber	Natural Clear Olive Oil	Liquid Castille Olive Oil	Lemon Orchard Organic	Lavender and Lime Organic	Passion Fruit Organic	Betres Oatmeal Sensitive	Cristallino Olor a Fresa	Betres Loofah Exfoliant
Added Fragrance (Yes/No)	N	N	Y	Y	Y	Y	Y	Y	Y
Human Compounds									
.alpha.-Pinene				X	X	X			
.beta.-Pinene					X	X		X	
1,6-Octadien-3-ol, 3,7-dimethyl-				X	X	X			
1-Hexanol								X	
1-Octene			X						
5-Hepten-2-one, 6-methyl-				X	X	X			
Acetophenone								X	
Benzaldehyde				X	X	X			
Benzyl Alcohol							X		
Camphene				X	X	X			
Caryophyllene				X	X	X			
D-Limonene								X	
Octane			X						
p-Xylene			X						
Toluene			X						

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