ABSTRACT

SHINDE, ADHIRAJ DHANANJAY. Analysis of Fireground Contamination of Firefighting Turnouts using Headspace Sampling-Gas Chromatography-Mass Spectrometry (HS-GC-MS) (Under the direction of Dr. R. Bryan Ormond).

Firefighters are at a 1.5- 2 times greater risk of contracting cancer as compared to the general population. These first responders undergo tremendous physiological heat stress as well as psychological stress. Recently, it was observed that one of the major causes of death among firefighters is due to the exposure to toxic smoke and chemicals. After preliminary studies, it was evident that contaminated turnout gear and ensemble elements could be linked to heightened cancer rates amongst firefighters. Compounds such as polycyclic aromatic hydrocarbons (PAHs), perfluorinated compounds (PFOA's), phenols, phthalates, brominated flame retardants, dioxins, volatile organic compounds (VOC's) and many others are present in the contaminated gear. Many of these compounds are known or suspected carcinogens. The chemical exposure to firefighters includes a complex mixture of volatile and semi-volatile gases, respirable particulate matter, toxic chemicals and toxic gases such as carbon monoxide, nitrogen oxide, carbon dioxide, etc. According to an on-field study by the Office of State Marshal, Oregon it was found that severely toxic chemicals such as acrolein, arsenic, benzene, formaldehyde, hydrogen cyanide, hydrogen chloride and particulate matter were above the OSHA Permissible Limit Time Weighted Average (PEL-TWA). Interaction with these chemicals through inhalation, dermal exposure and hand-to-mouth ingestion are known to cause severe health issues such as bronchitis, asthma, cardiovascular diseases, etc. The efficiency of decontamination procedures currently being used for cleaning contaminated gear is estimated at approximately 40%, which is not enough to mitigate the risk of cancer and other diseases.

Certain fireground contaminant chemicals were chosen for analysis based on the likelihood of them being present in the smoke and on their chemical properties, toxicity and carcinogenicity. For this research, fabrics used in firefighter turnout gear were contaminated using a controlled reference mix of known toxic fireground contaminants. An extraction procedure was developed to extract maximum chemicals from the spiked fabric samples using a pressurized solvent extractor. The extractor is efficient at removal of contaminants by selected solvents accompanied by application of a high pressure combined with a high temperature. Techniques such as gas chromatography-mass spectrometry (GC-MS) were used to separate and identify individual components in the toxic sample mixture.

When used turnout gear is transported in the trunk of a car or stored in fire stations, off-gassing of volatile and semi-volatile compounds can occur for a prolonged period, due to the exposure of heat. In addition, as the contaminated gear is repeatedly used in fighting fires, the toxic chemicals adsorbed on the garment gets released in the air. Both the conditions increase the risk to firefighters and could lead them to contracting severe health issues. The GC/MS instrument coupled with a headspace sampler was used to identify and quantify the toxic compounds released by heating the samples for a set equilibration time, followed by directly injecting the vapor components into the GC column.

After developing validated methods to analyze the laboratory contaminated samples, actual field-contaminated samples of turnout jackets were obtained from live-burn conducted around the Raleigh area. The gear was then evaluated according to the methods that were developed for the specimens contaminated in the laboratory.

The off-gassing experimentation provided an understanding of the effect of time and temperature on the amount of contaminant that off-gasses from a fabric sample. Having precise

data of the chemical contamination, analytical methods for extraction and off-gassing would be crucial in the removal of toxic contaminants from field-contaminated firefighter turnout gear.

Having the ability to remove most of the chemicals off the firefighting gear has the potential to substantially reduce secondary exposures of firefighter exposures to toxicants, which may be an important step in reduction of cancer rates among firefighters across the world.

Analysis of Fireground Contamination of Firefighting Turnout Jackets and Pants using Headspace Sampling-Gas Chromatography-Mass Spectrometry (HS-GC-MS)

by
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BIOGRAPHY

Adhiraj Dhananjay Shinde was born to Dhananjay and Ashwini Shinde on December 31, 1995 in Nashik, Maharashtra, India. He spent most of his childhood in the city of Nashik and graduated from Fravashi International Academy with a Cambridge A Levels certificate. After graduation, Adhiraj moved to Mumbai to pursue an undergraduate degree at the prestigious 'Institute of Chemical Technology'. Adhiraj was an active member of the various cultural and sporting events that took place during his undergraduate years. He also was part of the public relations core team for the annual sports festival of the college. Adhiraj pursued two internships in the knits processing and carbon fiber manufacturing domain during the course of his Bachelor's degree. He actively collaborated on research projects, two of which were published as research articles in reputed scientific journals.

Adhiraj graduated with a Bachelor's degree in Fibers and Textile Processing Technology in May 2017. He then sent out applications to various universities across the United States that provided a textiles/materials degree. He was fortunate to be accepted to the North Carolina State University for a MS degree in Textile Engineering. In the course of the two years of the Master's degree, Adhiraj attended various conferences and had the opportunity to present his research at an international conference in London.

Adhiraj further plans to pursue a career closely related to R&D of materials and textiles.

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TABLE OF CONTENTS

LIST OF TABLES xii

LIST OF FIGURES xiv

LIST OF EQUATIONS xix

ABBREVIATIONS xx

Chapter 1: Purpose and Objectives of Research 1

1.1 Purpose of Research 1

1.2 Research objectives 3

1.2.1 Development of a gas-chromatography-mass-spectrometry (GC-MS) method for analysis of select fireground contaminants 3

1.2.2 Development of a liquid extraction method for the extraction of fireground contaminants from outer shell fabrics using pressurized solvent extractor 3

1.2.3 Development of a thermal extraction method for the extraction of fireground contaminants from outer shell fabrics using headspace-GC-MS 5

1.2.3.1 Evaluation of the headspace sampler to be used as a screening method to measure off-gassing 5

1.2.3.2 Assessment of off-gassing of compounds as a hazard to the firefighters at ambient temperatures 6

1.2.4 Comparison of liquid extraction versus thermal extraction for the extraction of fireground contaminants from outer shell fabrics 7

1.2.5 Quantitation of compounds off-gassing from the field-contaminated turnout Jacket using headspace GC 8

1.3 Flowchart of the sequence of steps followed for this research study 9

Chapter 2: Introduction to Firefighting 10

2.1 Fire statistics around the world 10

2.2 Types of exposures in firefighting 11

2.2.1 Thermal exposures 12

2.2.2 Chemical exposures 13

2.3 Occupational exposure limits in firefighting 15

2.4 Actual on-field contaminant levels 18

2.5 Current protection used by firefighters 19
2.6 Care and maintenance of firefighter turnout gear 21
2.7 Storage of firefighter gear and ensemble elements 23
2.8 Health concerns due to toxic chemicals 24
2.8.1 Cancer studies among firefighters 25
Chapter 3: Fireground Contaminants 27
3.1 Introduction 27
3.2 Phenols 27
3.2.1 What are phenols? 27
3.2.2 Physical and chemical properties 27
3.2.2.1 Selected properties that affect analytical analysis 28
3.2.3 Applications of Phenols 29
3.2.4 Toxicity and Occupational Exposure Limits of Phenols 29
3.2.5 Previous studies on analysis of phenols using GC 31
3.3 Phthalates 33
3.3.1 What are phthalates? 33
3.3.2 Physical and chemical properties 34
3.3.2.1 Selected properties that affect analytical analysis 35
3.3.3 Applications of Phthalates 35
3.3.4 Toxicity and Occupational Exposure Limits of Phthalates 35
3.3.5 Previous studies on analysis of phthalates using GC 37
3.4 Polycyclic aromatic hydrocarbons (PAHs) 39
Chapter 4: Gas-chromatography (GC) 40
4.1 Introduction to Gas-chromatography (GC) 40
4.1.1 Primary components of a GC system 41
4.2 Working of a GC system 41
4.3 Detectors used in conjunction with a GC system 42
4.4 Chromatographic columns used in a GC 43
4.4.1 Parameters for column selection 44
4.5 The chromatogram 46
4.6 Precautionary features of a GC system 47

4.7 Limitations of GC 48
Chapter 5: Mass Spectrometry (MS) 49
5.1 Introduction to mass spectrometry 49
5.1.1 Main components of a mass spectrometer 49
5.2 Working principle of a MS 50
5.3 Ionization of the analytes 50
5.3.1 Electron Ionization (EI) 51
5.4 Mass analyzers used in MS 51
5.4.1 Single quadrupole 52
Chapter 6: Controlled contamination and extraction 54
6.1 Contamination of fabric samples in the laboratory 54
6.2 Previous studied for extraction of contaminants from fabric samples in the laboratory 55
Chapter 7: Headspace sampling (HS) 62
7.1 Introduction to headspace sampling 62
7.2 Working of the headspace GC system *63*
7.3 Salient features of the headspace GC system *63*
7.4 Previous analysis using the headspace GC system (HSGC) 64
7.5 Fundamentals and theory of headspace GC 67
7.5.1 Partition co-efficient (K) 67
7.5.2 Effect of temperature 68
7.5.3 Effect of pressure 69
7.5.4 Effect of equilibration time 69
7.6 Quantitation of headspace GC 70
Chapter 8: Off-gassing of contaminants 73
8.1 What is off-gassing? 73
8.1.1 Case 1: Storage of firefighter gear 73
8.1.2 Case 2: Use of firefighter gear in structural fires *74*
8.2 Conditions for off-gassing in car trunks 74
8.3 Conditions for off-gassing in fire stations 79
8.4 Previous studies on off-gassing of toxic contaminants 81

8.5 Other studies and methods for air sampling of heated liquids and gases 92
Chapter 9: Development of a GC-MS method for the analysis of select fireground contaminants 98
9.1 Introduction 98
9.1.1 Relevance of the GC-MS method for analysis of firefighter turnout gear 99
9.2 Materials 100
9.3 Selection of compounds 101
9.4 Compounds properties 102
9.5 Methods 102
9.5.1 Preparation of test solutions for selection of solvent 102
9.5.2 Preparation of calibration solutions 103
9.5.3 Chromatographic method development 103
9.5.4 Sample trials of phenols, phthalates and PAHs using n-hexane and Methylene chloride in the GC-MS system 104
9.6 Results and Discussion 105
9.6.1 Solvent selection for GC-MS system 105
9.6.1.1 Master mix in methanol and acetonitrile at 10 ng/µL 105
9.6.1.2 Master mix in methylene chloride at 10 ng/µL 108
9.6.1.3 Master mix in n-hexane at 10 ng/µL 108
9.6.2 Preferred solvent for liquid extraction 109
9.6.3 GC-MS trials using n-hexane as the solvent 110
9.6.3.1 Calibration curve for phenols 110
9.6.3.2 Calibration curve for phthalates 111
9.6.3.3 Calibration curve for PAHs 112
9.6.3.4 Variability in replicate GC-MS runs for phenol 114
9.6.3.5 Variability in replicate GC-MS runs for 2,4,6-Trichlorophenol 115
9.6.3.6 Variability in replicate GC-MS runs for pentachlorophenol 115
9.6.3.7 Variability in replicate GC-MS runs for di-butyl phthalate 116
9.6.3.8 Variability in replicate GC-MS runs for benzyl butyl phthalate 116
9.6.3.9 Variability in replicate GC-MS runs for di-ethylhexyl phthalate 117
9.6.3.10 Variability in replicate GC-MS runs for naphthalene 117

9.6.3.11 Variability in replicate GC-MS runs for phenanthrene 118
9.6.3.12 Variability in replicate GC-MS runs for pyrene 118
9.6.3.13 Variability in replicate GC-MS runs for benzo[a] pyrene 119
9.7 Conclusion 119
Chapter 10: Development of a liquid extraction method using the Buchi pressurized solvent extractor 121
10.1 Introduction 121
10.1.1 Relevance of the liquid extraction method for analysis of firefighter turnout gear 122
10.2 Materials 123
10.3 Methods 124
10.3.1 GC-MS calibration method 124
10.3.2 Controlled contamination and extraction using n-hexane 124
10.3.3 Pressurized solvent extraction method 125
10.3.4 Calculation of the extraction efficiencies 127
10.3.5 Calculation of error bars for all the graphs plotted 128
10.4 Results and Discussion 129
10.4.1 Extraction efficiency data for all the compounds in the master mix 129
10.4.1.1 Extraction efficiencies for phenolic compounds in the master mix 130
10.4.1.2 Extraction efficiencies for phthalates in the master mix 134
10.4.1.3 Extraction efficiencies for PAHs in the master mix 136
10.5 Conclusion 138
Chapter 11: Development of a thermal extraction method using the headspace GC ... 139
11.1 Introduction 139
11.2 Materials 141
11.2.1 Compound properties 141
11.3 Methods 141
11.3.1 Calibration method development on the headspace sampler GC 141
11.3.1.1 Calibration solution preparation for HS 141
11.3.1.2 The GC-MS analysis method 142
11.3.2 Thermal extraction method development on the headspace GC 142

11.3.3 Calculation of the extraction efficiencies 145
11.3.4 Calculation of error bars for all the graphs plotted 147
11.4 Results and Discussion 147
11.4.1 Effect of equilibration time on off-gassing 147
11.4.1.1 Extraction efficiencies for phenols 148
11.4.1.2 Extraction efficiencies for phthalates 149
11.4.1.3 Extraction efficiencies for PAHs 150
11.4.1.4 Best suited equilibration time for off-gassing 152
11.4.2 Effect of equilibration temperature on extraction efficiency 152
11.4.2.1 Extraction efficiencies for phenols 155
11.4.2.2 Extraction efficiencies for phthalates 157
11.4.2.3 Extraction efficiencies for PAHs 158
11.4.2.4 Best suited method for thermal extraction using headspace GC 160
11.5 Conclusion 162
Chapter 12: Comparison of liquid extraction and thermal extraction methods for analyzing outer shell materials 165
12.1 Introduction 165
12.2 Materials 167
12.3 Methods 167
12.3.1 The GC-MS analysis method for liquid extraction 167
12.3.2 Extraction using n-hexane in the pressurized solvent extractor 167
12.3.3 Calculation of extraction efficiencies for the liquid extraction 168
12.3.4 The GC-MS analysis method for thermal extraction 168
12.3.5 Calibration of the headspace GC system 168
12.3.6 Thermal extraction using the headspace sampler 169
12.3.7 Calculation of the extraction efficiencies for thermal extraction 169
12.3.8 Compound properties 169
12.4 Results and Discussion 169
12.4.1 Calculation of error bars for all the graphs plotted 169
12.4.2 Calibration of headspace sampler at 200°C, 30 minutes 169
12.4.3 Comparison of extraction efficiencies using liquid extraction v/s thermal

extraction 170
12.4.3.1 Extraction efficiencies for phenols 171
12.4.3.1 Extraction efficiencies for phthalates 172
12.4.3.1 Extraction efficiencies for PAHs 174
12.5 Conclusion 175
Chapter 13: Quantitation of compounds from firefighter gear materials using headspace GC 177
13.1 Introduction 177
13.2 Materials 178
13.3 Methods 179
13.3.1 Calibration method development on the headspace sampler GC 179
13.3.1.1 GC-MS chromatographic method 179
13.3.1.2 Calibration solution trials for HS liquid and HS fabric at 100°C, 30 minutes 179
13.3.1.3 Calibration solution trials for HS liquid injection at 200°C, 30 minutes 179
13.3.3 Sample collection from the live training burn and analysis using headspace GC 179
13.3.4 Thermal extraction using headspace GC at 100°C for 30 minutes 180
13.3.5 Properties of the reference compounds in the master mix 180
13.3.6 Calculation of error bars for all the graphs plotted 180
13.4 Results and Discussion 181
13.4.1 HS liquid and HS fabric calibration for headspace GC 181
13.4.2 Thermal extraction of the retired field-contaminated gear using headspace-GC-MS at 100°C for 30 minutes 181
13.4.3 Quantitation of naphthalene off-gassing from field contaminated jackets at 100°C for 30 minutes 183
13.4.4 Thermal extraction of the retired field-contaminated gear using headspace-GC-MS at 200°C for 30 minutes 184
13.4.4.1 Analysis of the retired turnout jacket 185
13.4.4.2 Analysis of the unused turnout jacket 189
13.4.5 Quantitation of field-contaminated gear samples at 200°C, 30 minutes 192

13.4.5.1 Concentrations of DEHP off-gassing from the retired field-contaminated gear at various times of air exposure 193
13.4.5.2 Concentrations of DEHP off-gassing from the unused field-contaminated gear at various times of air exposure 194
13.6 Conclusion 195
Chapter 14: Research conclusions, Recommendations and Proposed Future Research 196
14.1 Summary of Research and Overall Conclusions 196
14.2 Research Conclusions 196
14.2.1 Conclusion pertaining to the development of liquid extraction using the pressurized solvent extractor 196
14.2.2 Conclusion pertaining to the development of thermal extraction using headspace GC 197
14.3 Proposed Future Research 199
14.3.1 Future Research on liquid extraction of firefighter turnout gear fabrics 199
14.3.2 Future Research on thermal extraction of firefighter turnout gear fabrics 200
References 201

LIST OF TABLES

Table 2.1 Occupational Exposure limits for toxic compounds as per NIOSH [18, 20-22] 17

Table 2.2 Exposure limits for chemicals according to NIOSH and OSHA [23] 18

Table 3.1 Substituted phenols with selected properties [64] 30

Table 3.2 Retention times of phenols with detection limits [50] 31

Table 3.3 Parameters for gas chromatography method 32

Table 3.4 Selected properties of substituted phthalates [64] 36

Table 3.5 Retention times for phthalates using EPA 8270D method on GC-MS [66] 38

Table 3.6 Selected properties of PAHs [64] 39

Table 4.1 Polarity of columns [71] 44

Table 4.2 Column efficiency parameters [71] 44

Table 4.3 Benefits and limitations of altering film thickness [71] 45

Table 8.1 Difference in study between NIOSH and QFES [118] 82

Table 9.1 Master mix compounds and their properties 101

Table 9.2 LOD and LOQ values for the compounds in the master mix using n-hexane and methylene chloride 109

Table 9.3 Retention time and limits of detection for GC-MS analysis using n-hexane 112

Table 10.1 Reference table with the concentration and peak area values 126

Table 10.2 Reference table depicting the calculation of extraction efficiencies 127

Table 10.3 Concentration of compounds extracted using pressurizes solvent extractor 129

Table 10.4 Calculation of extraction efficiencies for phenol 131

Table 11.1 Conditions used for headspace GC method development runs 142

Table 11.2 Reference data of mass-in vial and peak areas used in HS liquid calibration 145

Table 11.3 Calculation of percent extraction efficiencies for spiked fabric samples 145

Table 11.4 Masses of compounds detected using headspace GC at 100°C for 30, 60 and 120 minutes 147

Table 11.5 Masses of compounds off-gassing at various temperatures..... 152

Table 12.1 Extracted concentrations and masses using liquid extraction and thermal extraction..... 170

Table 13.1 Replicate data for HS liquid calibration and HS fabric calibration samples 182

LIST OF FIGURES

Figure 1.1 Flowchart of the steps followed for the research 9

Figure 2.1 The fire triangle [3] 10

Figure 2.2 Wildland firefighting gear [22] 21

Figure 2.3 Structural firefighting gear [23] 21

Figure 2.4 HAZMAT protective suit [24] 21

Figure 2.5 Storage of firefighting gear in fire stations 24

Figure 3.1 Structure of a phenol [45] 27

Figure 3.2 Structure of 2,4,6-trichlorophenol 30

Figure 3.3 Structure of pentachlorophenol 30

Figure 3.4 Structure of a phthalate ester [54] 34

Figure 3.5 Structure of DEHP 37

Figure 3.6 Structure of naphthalene 39

Figure 3.7 Structure of benzo[a] pyrene 39

Figure 4.1 Setup of gas-chromatography [69] 41

Figure 4.2 Chromatogram output from GC [72] 46

Figure 5.1 Components of a mass spectrometer [76] 49

Figure 5.2 Diagram of an electron ionization source [77] 50

Figure 5.3 Working of a single quadrupole [73] 51

Figure 5.4 Single ion monitoring (SIM) [73] 51

Figure 5.5 Scan mode [73] 51

Figure 6.1 Automated solvent extraction schematic [82] 57

Figure 6.2 UAE for sold samples [84] 60

Figure 7.1 Setup of a headspace sampler connected to GC_MS 61

Figure 7.2 Schematic of the headspace internal system [85] 62

Figure 8.1 Average rise in car interior temperature v/s time [101] 73

Figure 8.2 Inside and outside car temperature [101] 74

Figure 8.3 Vehicle parked in the sun on a 100F day for 60 mins [103] 75

Figure 8.4 Vehicle parked in shade on a 100F day for 60 mins [103] 75

Figure 8.5 How hot does your car get [104] 76

Figure 8.6 Vehicle interior air temperature v/s time [155] 77

Figure 8.7 Off-gassing setup at TPACC, NCSU [120] 84

Figure 8.8 Test apparatus of cup furnace [121] 86

Figure 8.9 Schematic of testing method [122] 87

Figure 8.10 PAH levels in fire engines and fire stations [126] 91

Figure 9.1 Chromatogram of the master mix in methanol using GC-MS liquid injection 105

Figure 9.2 Poor peak shapes using methanol as the solvent for analysis 105

Figure 9.3 Chromatogram of the master mix in acetonitrile using GC-MS liquid injection 106

Figure 9.4 Poor peak shapes using acetonitrile as the solvent for analysis 106

Figure 9.5 Chromatogram of the master mix in methylene chloride using GC-MS liquid injection 107

Figure 9.6 Chromatogram of the master mix in n-hexane using GC-MS liquid injection 108

Figure 9.7 Calibration curve for phenols in n-hexane 110

Figure 9.8 Calibration curve for phthalates in n-hexane 111

Figure 9.9 Calibration curve for PAHs in n-hexane 112

Figure 9.10 Variability in replicate GC-MS runs for phenol 113

Figure 9.11 Variability in replicate GC-MS runs for 2,4,6-trichlorophenol 114

Figure 9.12 Variability in replicate GC-MS runs for pentachlorophenol 114

Figure 9.13 Variability in replicate GC-MS runs for di-butyl phthalate 115

Figure 9.14 Variability in replicate GC-MS runs for benzyl butyl phthalate 115

Figure 9.15 Variability in replicate GC-MS runs for di-ethylhexyl phthalate 116

Figure 9.16 Variability in replicate GC-MS runs for naphthalene 116

Figure 9.17 Variability in replicate GC-MS runs for phenanthrene 117

Figure 9.18 Variability in replicate GC-MS runs for pyrene 117

Figure 9.19 Variability in replicate GC-MS runs for benzo[a] pyrene 118

Figure 10.1 Schematic of the control contamination, liquid extraction and analysis 125

Figure 10.2 Buchi E-916 speed extractor 125

Figure 10.3 Chromatogram depicting the efficiency of extraction of the compounds on the master mix spiked at a concentration of 10 ng/µL 128

Figure 10.4 Interference of the siloxane peak with the phenol compound peak 132

Figure 10.5 Extraction efficiencies for phenols using pressurized solvent extraction with n-hexane 133

Figure 10.6 Extraction efficiencies for phthalates using pressurized solvent extraction with n-hexane 134

Figure 10.7 Concentrations of phthalates extracted in each cycle of the liquid extraction process 135

Figure 10.8 Extraction efficiencies for PAHs using pressurized solvent extraction

with n-hexane 136

Figure 11.1 Extraction efficiencies for phenols using headspace GC at 100°C for 30 minutes 148

Figure 11.2 Extraction efficiencies for phthalates using headspace GC at 100°C for 30 minutes 149

Figure 11.3 Extraction efficiencies for PAHs using headspace GC at 100°C for 30 minutes 150

Figure 11.4 Effect of temperature on extraction of compounds from outer shell fabrics 153

Figure 11.5 Magnified chromatogram showing peak areas at various temperatures 154

Figure 11.6 Extraction efficiencies for phenols using headspace GC at 36°C, 50°C, 100°C and 200°C for 30 minutes 156

Figure 11.7 Extraction efficiencies for phthalates using headspace GC at 36°C, 50°C, 100°C and 200°C for 30 minutes 157

Figure 11.8 Extraction efficiencies for PAHs using headspace GC at 36°C, 50°C, 100°C and 200°C for 30 minutes 159

Figure 11.9 Overlaid chromatograms of the liquid compounds and extracted compound using headspace GC injection at 200°C for 30 minutes 160

Figure 12.1 Adjusted calibration curves to show linearity versus saturation 169

Figure 12.2 Comparison of liquid extraction and HS extraction for phenols 171

Figure 12.3 Comparison of liquid extraction and HS extraction for phthalates 172

Figure 12.4 Comparison of liquid extraction and HS extraction for PAHs 174

Figure 13.1 Area v/s mass-on fabric curve for naphthalene on the headspace GC at 100°C for 30 minutes 180

Figure 13.2 Chromatogram of retired field-contaminated sample analyzed using HS at 100°C for 30 minutes 181

Figure 13.3 Concentrations of naphthalene off-gassing from retired field-contaminated samples analyzed using HS at 100°C for 30 minutes 183

Figure 13.4 '0-hour' air exposure sample chromatogram for compounds off-gassing from retired turnout jacket analyzed using headspace-GC-MS at 200°C, 30 minutes. 185

Figure 13.5 Amount of off-gassing of compounds from retired turnout jacket 187

Figure 13.6 '0-hour' air exposure sample chromatogram for compounds off-gassing from unused turnout jacket analyzed using headspace-GC-MS at 200°C, 30 minutes 188

Figure 13.7 Amount of off-gassing of compounds from unused turnout jacket 190

Figure 13.8 Calibration curve for DEHP using HS liquid at 200°C, 30 minutes 191

Figure 13.9 Concentrations of DEHP off-gassing from retired turnout gear at various times of air exposure, extracted using headspace GC at 200°C, 30 minutes 192

Figure 13.10 Concentrations of DEHP off-gassing from unused turnout gear at various times of air exposure, extracted using headspace GC at 200°C, 30 minutes 193

LIST OF EQUATIONS

Equation 7.1 Partition co-efficient (K) 66

Equation 9.1 Limit of detection (LOD) 103

Equation 9.2 Limit of quantitation (LOQ) 103

Equation 10.1 Straight line 126

Equation 10.2 Calculation of slope for a straight line 126

Equation 10.3 Calculation of the y-intercept for a straight line 126

Equation 10.4 Calculation of standard error 127

Equation 10.5 Calculation of confidence interval 128

Equation 10.6 Reference equation of a straight line 130

Equation 11.1 Calculation of mass-in vial 144

Equation 11.2 Straight line for HS 145

Equation 11.3 Calculation of slope for a straight line for HS 145

Equation 11.4 Calculation of the y-intercept for a straight line for HS 145

Equation 11.5 Calculation of standard error for HS 146

Equation 11.6 Calculation of confidence interval for HS 146

Equation 13.1 HS liquid calibration equation for naphthalene, 100°C, 30 minutes 181

Equation 13.2 HS fabric calibration equation for naphthalene, 100°C, 30 minutes 181

Equation 13.3 HS liquid calibration equation for DEHP, 200°C, 30 minutes 191

LIST OF ABBREVIATIONS

2,4,6-TCP	2,4,6-Trichlorophenol
BBP	Benzyl butyl phthalate
DBP	Di-butyl phthalate
DEHP	Di-ethylhexyl phthalate
HS	Headspace sampler
GC	Gas chromatography
LOD	Limit of detection
LOQ	Limit of quantitation
MS	Mass spectrometry
NFPA	National Fire Protection Association
OSHA	Occupational Safety and Health Administration
PAH	Polycyclic aromatic hydrocarbons
PCP	Pentachlorophenol
PPE	Personal protective equipment
TPACC	Textile Protection and Comfort Center
VOC	Volatile organic compounds

CHAPTER 1: Purpose and Objectives of Research

1.1 Purpose of Research

Firefighting is classified as a '2B'- Probable carcinogenic profession by the IARC (International Agency for Research on Cancer) based on the cancer occurrence among firefighters over the years [64]. The obvious reason for the same is the tremendous exposure of the firefighters to toxic gases and particles. Every structure burns differently because of the varied products present inside and the construction materials used. With increasing use of synthetic products, the amount of chemicals used to manufacture these products is also increasing. When a house burns, a complex mix of compounds is released, including volatiles, semi-volatiles, particulates, gases, etc. Even though a firefighter has the required protective gear and respiratory protection while encountering a fire, the compounds get deposited onto the ensemble elements. According to a study by Fent et al, it was noted that the volatile compounds off-gassed for about 30 minutes after the overhaul state of firefighting [1]. Currently, there are no studies that focus on the semi-volatile compounds that have high boiling points and could possibly be off-gassing for a much longer time. Many of the semi-volatile compounds such as polycyclic aromatic hydrocarbon (PAHs) are known carcinogens and pose a grave risk to the health of firefighters. It is essential to effectively wash and decontaminate the turnout gear for the health and safety of the personnel wearing them. To analyze the contaminants, present on the gear and assess the washing efficiency, the contaminants must be extracted from the fabrics. To remove the contaminants, a liquid extraction or a thermal extraction could be utilized. The values of peak area obtained from the extraction methods must be compared against standard values of known concentration. Hence, to quantify the amount of chemicals and calculate the concentration, an analytical method must be developed and validated. GC-MS is an analytical technique that can be used to identify and analyze

compounds in a mixture. The liquid extracts from the extraction runs can be injected into the GC for analysis. Additionally, to measure the vaporization of chemicals from outer shell fabrics, also known as off-gassing; a headspace sampler could be used. The headspace sampler is an instrument that can simulate off-gassing and when connected to a GC-MS system can identify the contaminants and quantify the amounts as well.

Off-gassing is prevalent in the field of firefighting and occurs at several instances. One such instance is after a fire scenario; the turnout gear gets transported back to the fire stations in car trunk or fire trucks enclosed inside plastic bags. When the temperature outside is high, the interior of a vehicle can get quite hot. The exposure of the recently contaminated gear to elevated temperatures could lead to off-gassing of compounds. These vapors entrapped inside the plastic bags could be hazardous to the firefighters handling the gear at the fire stations, often not wearing respiratory protection. Further, the gear stored in the engine bay of the fire stations can be exposed to relatively high ambient temperatures. This could also be a source for potential off-gassing of compounds and in turn, affect the health of the firefighters in the fire station.

The contaminated turnout gear must be washed according to the NFPA 1851 washing procedures. Studies show that the procedures are only about 40% effective in removing the toxic contaminants from the gear [2]. The conditions set are sufficiently high and elevating the wash conditions including temperature, agitation and pH could damage the fabric materials. If the contaminated gear could be kept in enclosed heated cabinets inside the fire stations, volatile compounds having a low boiling point could be vaporized. This could be used as a novel decontamination technique to extract the volatile compounds off the gear before it undergoes conventional washing.

1.2 Research objectives

1.2.1 Development of a Gas-chromatography-mass spectrometry (GC-MS) method for the analysis of select fireground contaminants

The aim was to develop and validate an analytical method to be able to detect and analyze fireground contaminants. A standard reference mix (master mix) of pure liquid chemicals (fireground contaminants) was put together that consisted of 3 phenols, 3 phthalates and 4 polycyclic aromatic hydrocarbons (PAHs). These compounds are commonly found in structural fires and most of them have some level of carcinogenicity. The compounds were suitable for gas chromatography-mass spectrometry (GC-MS) analysis, since the boiling points were significantly different. To analyze for the same set of contaminants, a calibration solution was prepared using two solvents- n-hexane and methylene chloride. After multiple iterations of the GC-MS parameters, a suitable method using n-hexane as the solvent was developed. The calibration solution set was analyzed using the developed method, the retention times were known, and all the compounds were detected with acceptable response values. The LOD (limit of detection) and LOQ (limit of quantitation) values were calculated to understand the sensitivity of the instrument. Finally, the validated method would be useful in analyzing chemicals extracted from field-contaminated turnout gear.

1.2.2 Development of a liquid extraction method for the extraction of fireground contaminants from outer shell fabrics using pressurized solvent extractor

When a qualitative and quantitative assessment of contamination from a contaminated turnout gear is to be done, the contaminants must be extracted from the fabric sample into a liquid solution for analytical analysis. The previously developed GC-MS method was used to analyze

the extracts obtained from the extraction runs. To analyze field-contaminated samples, a controlled contamination and extraction method was developed in the laboratory. The method was tested multiple times and validated to eliminate variability.

One of the challenging tasks was to contaminate the fabric samples realistically while maintaining repeatability. A method using a repeater pipette was found, to contaminate the fabrics with a known concentration of pure liquid chemicals. It is difficult to simulate the complex mix of compounds generated in an actual fire, hence compounds commonly occurring in a structural fire were chosen- phenols, phthalates and PAHs. These compounds were formed as a reference master mix and chosen based on their carcinogenicity profiles and toxicity to humans.

After a suitable method for control contamination was developed, a method to extract the chemicals from the fabric using the pressurized solvent extractor was developed. The pressurized solvent extractor was used to extract the known contaminants from spiked fabric samples to evaluate efficiency of extraction. Specific conditions of temperature, pressure and other parameters were optimized to achieve maximum removal of compounds from the fabrics. The extraction method that is developed using the reference master mix and reference outer shell fabrics could be then used for analysis of field-contaminated samples.

1.2.3 Development of a thermal extraction method for the extraction of fireground contaminants from outer shell fabrics using headspace-GC-MS

1.2.3.1 Evaluation of the headspace sampler to be used as a screening method to measure off-gassing

The aim is to evaluate headspace sampler to be used as a screening method to measure the levels of contaminants off-gassing from firefighter's gear at elevated temperatures. When materials are heated, vaporization of certain compounds take place and they are released as vapors. This phenomenon is known as 'off-gassing' and occurs commonly in most materials. Similarly, when a contaminated firefighter turnout gear is heated, the compounds present in the gear would off-gas. The headspace sampler was used as a thermal extractor to heat the fabrics and analyze the compounds off-gassing from the fabrics at different temperatures. The headspace sampler is a sophisticated instrument that has the capability to heat a solid/liquid matrix in a crimp-top glass vial. The salient feature is that the gas evolving from the substrates can be injected in the GC directly and analyzed using regular GC-MS methods. For this study, the headspace sampler was run at elevated temperatures of 100°C and 200°C. The study is aimed at exploring the capabilities of the instrument for the extraction of compounds from pure liquid chemicals and outer shell materials.

First, pure liquid chemicals was analyzed to understand their properties when heated. A calibration curve was obtained to test the response of selected compounds on heating. Further, the liquid compounds were spiked on reference outer shell fabrics and analyzed on the headspace-GC to obtain extraction efficiency values. The controlled spiking of liquid compounds onto fabric samples provided an idea of the interaction of the compound with the fabric. The extraction data

from control contaminated fabric samples was used to calculate the concentration of contaminants from field samples.

1.2.3.2 Assessment of off-gassing of compounds as a hazard to the firefighters at ambient temperatures.

Two major questions are to be answered for this research. First, whether off-gassing poses a hazard to the firefighters at ambient temperatures, such as the storage of gear in car trunks/fire trucks and fire stations? Second, whether heating the gear to elevated temperatures in a closed environment be used as a novel thermal decontamination method?

Often, as seen in fire stations, the turnout gear and ensemble elements are hung on open racks in the engine bay. The engine bay is often not air conditioned and sunlight falls onto the gear through the windows in the engine bay. These conditions contribute to the gear being exposed to higher temperatures. There is a probable chance of off-gassing of some compounds in the fire station, where the firefighters are not wearing respiratory protection. This can be a respiratory hazard for the first responders in the fire station environment.

After a fire incident, the contaminated gear gets stored in plastic bags. The plastic bags are transported to the fire stations either in the trunk of cars or in fire trucks. A firefighter on an average, takes about 30 minutes to transport the used gear back to the station. During this time, the gear gets exposed to hot conditions inside the trunk, which could lead to off-gassing of certain compounds. Also, after the gear is removed out from the plastic bag at the fire station, the entrapped vapors pose a respiratory hazard to the personnel, often without respiratory protection. Off-gassing is detrimental as a phenomenon, but what if it is used as a decontamination method. The contaminated gear, if kept inside heated cabinets for a specific time would probably off-gas

some of the volatile compounds. The exhaust gases could be scrubbed off and piped away from the fire station. If a suitable practically achievable temperature is found through research; the same could be implemented as a novel decontamination method. The gear could be off-gassed before it undergoes conventional washing to remove the low-boiling volatiles.

To test the conditions mentioned above, we selected a test temperature of 36°C was tested to mimic ambient conditions in the fire station on a hot day. Also, a temperature of 50°C was tested to simulate elevated temperatures in heated car trunks/ heated cabinets. Pure liquid chemicals and control contaminated samples were analyzed to understand the levels of off-gassing and to develop calibration curves. The validated methods were utilized to test the off-gassing from field-contaminated turnout gear samples.

1.2.4 Comparison of liquid extraction versus thermal extraction for the extraction of fireground contaminants from outer shell fabrics.

Both, liquid extraction and thermal extraction are known methods for extracting chemicals from fabric samples. To analyze the levels of contamination, properties such as volatility, polarity, solubility, etc. must be known to choose the appropriate extraction method-liquid extraction or thermal extraction. The best scenario would be to have a single method targeted at extracting all the required compounds. However, that might not always be possible, since different compounds might not be compatible with the solvent used for liquid extraction or off-gas at a temperature in the headspace sampler. Either a combination of methods or methods targeted at certain specific compounds would work best for achieving maximum extraction efficiencies of compounds from fabrics. Several experiments were carried out with the

pressurized solvent extractor and the headspace sampler to completely understand the applicability of a method towards a compound.

1.2.5 Quantitation of compounds off-gassing from the field-contaminated turnout jacket using headspace GC

After developing a method to simulate the off-gassing of compounds from control spiked fabric samples, the next step is to be able to analyze field contaminated fabric samples. Calibration curves were setup to understand the linearity that the compounds follow at various concentrations. Two types of calibration curves were prepared- using pure liquid chemicals (HS liquid) or spiking the liquid compounds on outer shell fabric samples (HS fabric). After a suitable calibration curve was chosen, the concentration of compounds off-gassing from field-contaminated samples were quantitated. The temperature used for extraction of compounds from the fabric samples was chosen as 200°C. The quantitation method was used to calculate the levels of off-gassing from field-contaminated firefighter gear samples.

1.3 Flowchart of the sequence of steps followed for this research study

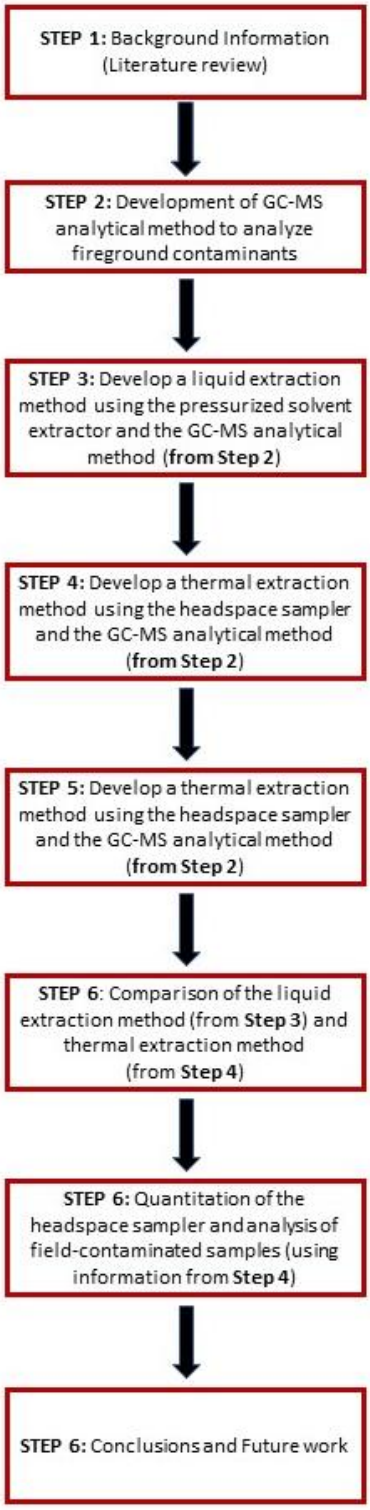


Figure 1.1. Flowchart of the steps followed for the research

CHAPTER 2: Introduction to Firefighting

2.1 Fire Statistics around the world

Firefighting is a noble profession, helping thousands of families from fire hazards. Firefighting could be either in the urban zone- structural firefighting- or in the wilderness- wildland firefighting. There are set protocols that the firefighters must follow to contain fires of different classes. Risks for firefighters occur due to several reasons. Firefighters must contain the fire and prevent further spread of the fire in the surroundings. For structural fires, there are both internal and external exposures such as carpets, furniture, other buildings, cars that are in close proximity to the actual fire and may eventually start burning if the fire is not contained [2]. Generally, wildland fires are extremely widespread and difficult to contain

For a fire to initiate and propagate, there are three essential elements, depicted in Figure 2.1.

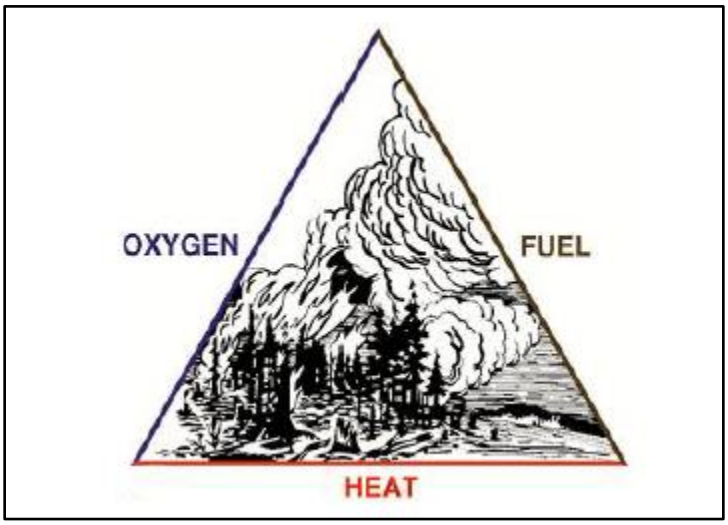


Figure 2.1. The fire triangle [3]

Some interesting fire statistics in the United States from 2017:

- Public fire departments across the United States responded to a total of 1,319,500 fires in 2017 alone [4]
- Every 24 seconds, a fire department in the United States responds to a fire across the nation [5]
- 77% percent of all fire deaths occurred in homes
- Home fires were responsible for 10,600 civilian injuries which was a startling 72% of all civilian injuries
- An estimated $23 billion in property damage occurred as a result of several fires [6]
- One structure fire was reported every 63 seconds
- One civilian fire death occurred every 2 hours and 34 minutes
- One highway vehicle fire was reported every 3 minutes 8 seconds [6]

It is surprising to know that about 90% of the wildland fires in the United States are caused due to human activities, according to the U.S. Department of Interior. The remaining 10% are due to lightning or lava. Some human activities that cause fires are campfires left unattended, the burning of debris, negligently discarded cigarettes, and intentional acts of arson [7].

2.2 Types of exposure in firefighting

Firefighting is a complex activity, which encompasses several stresses that the firefighters must undergo. There is inevitably the thermal discomfort and extreme temperatures

that the responders must face while fighting fires, but there are tremendous toxic chemical exposures as well. In lieu of the excruciating circumstances to work, firefighters are often prone to health hazards, both physically and mentally. The toxic gases and particles cause various deadly diseases such as bronchitis, skin cancer, asthma, etc. Firefighters usually have 10 to 24-hour work shifts depending on the geographical location, staffing and types of call. Wildland firefighters at times spend about ten days at a stretch trying to contain the fires on hills and remote locations.

2.2.1 Thermal Exposures

A fire has several temperature zones which depend on the material undergoing combustion. There are three forms of heat transfer that occur in a fire scenario – conduction, convection and radiation. Conduction refers to heating of solids such as metals, ceramics, glass, convection refers to the rising hot gases and vapors that travel across the room, and radiation refers to the electromagnetic waves that directly arise out of the flame. The development of fires is a combination of several factors such as type of fuel, quantity of fuel, location of fire, enclosed area and ambient conditions. Firefighters must be prepared for the worst-case scenarios being flash fires. Flashover is the development of a fire in which the surfaces are exposed to thermal radiation from gases rising out of the fire that exceed temperatures of 600°C and reach the ignition temperature from where it spreads rapidly causing mass damage. The temperature of the gases starts to exceed well above 400°C at the start of the flashover. On continuous burning inside a room, the temperatures could reach above 1000°C which are known as flashover conditions [8]. Firefighters have two physiological systems that are affected because of the extreme conditions – cardiovascular system and body core temperature. The heat stress caused on duty puts an additional load on the cardiovascular system of the body, thus leading to higher

heart rates in hot conditions. Having the protective suit on during hot conditions and strenuous work, adds physiological and psychological stress to the firefighter. On exposure to extreme heat, there is a high chance of dehydration which can lead to lowered stroke volume and in turn an increase in the heart rate. At temperatures above 100°F (37.7°C), there is a chance of heatstroke caused due to hyperthermia which could lead to organ damage and central nervous system slowdown [9,10,11].

2.2.2 Chemical Exposures

The smoke from fires contains a plethora of gases, vapors, suspended liquids and solid particulate matter. The chemical composition of the smoke completely depends on the fuel that is burning, which means that structural and wildland firefighting has different chemical exposures. Complete combustion gives out carbon dioxide and water as the products, but it is the incomplete combustion and pyrolysis that leads to the generation of free radicals and toxic compounds.

In structural fires, plastics and polymers are major polluting elements. Thermal degradation of polymers gives out methane, benzene, toluene, acrylonitrile, styrene, phenols, phthalates, polycyclic aromatic hydrocarbons (PAHs), perfluorooctanoic acid (PFOA), brominated flame retardants, urea, dioxins, volatile organic compounds (VOC's) and many other compounds. Burning of plastic specifically releases compounds such as hydrochloric acid, acrolein, hydrogen cyanide and soot. The concern is that many of these chemicals are known to be potential carcinogens, thus severely affecting the health of the responders working closely. Another serious issue is the generation of particulate matter on incomplete combustion of the fuel. The particulate matter is basically an aerosol containing condensed phased components of combustion products and un-burnt suspended carbon particles. The particulates are microscopic

in size but condense and hence are visible. They pose a danger since they act as adsorbents and help carry other toxic compounds along. Other combustion gases that have short-term acute effects are carbon dioxide, carbon monoxide, nitrogen oxides, sulfur oxides and hydrogen cyanide which have very high levels for short periods of time [12].

There are several factors that increases the risk of cancer among firefighters along with other health issues such as cardiac arrest, bronchitis, etc. Using contaminated gear is one major issue, since it may not be frequently cleaned and chemicals may off-gas to a large extent during storage. Vehicles exhaust has carbon compounds that can get directly inhaled by the firefighters during work. Also, the responder is subjected to on-field exposure to smoke and chemicals, especially in the absence of using personal protective equipment [13].

There are some additional places where there is a significant potential for exposure, but these areas are often ignored. Gear and station uniforms stored in racks in the fire stations get contaminated frequently due to the smoke emission from the fire trucks. Toxic gases and soot get deposited on the pre-contaminated gear that goes unnoticed. On wearing contaminated gear while driving, there might be a transfer of contaminants onto the seat material and that could be a possible source of further contamination to cleaned gear. Repeated dirty hand-to-mouth contact could give way to oral exposure of benzo(a)pyrene and dioxins that could cause cancer. Skin exposure to hydrocyanic acid and benzo(a)pyrene is dangerous and can be potentially carcinogenic. Exposure to phenols and formaldehyde can aggravate this effect [14].

In wildland fires, burning of wood and other vegetation gives rise to certain different toxic compounds as compared to the structural fires. The compounds commonly found in wildland fire smoke are carbon dioxide, carbon monoxide, particulate matter of various sizes, formaldehyde, acrolein, benzene, aerosols, VOC’s, PAHs, ozone, sulphur dioxide and

crystalline silica. The emission factor depends on the geographical locations which helps in considering the vegetation type and the atmospheric conditions [15-17]. According to a research study, there were 15 compounds named as chemicals of potential concern (COPC). Most of which belong to the class of PAHs (polycyclic aromatic hydrocarbons). The EPA set a regional removal management level (RML) range of 10^{-4} to 10^{-6} as the acceptable long-term risk range for the carcinogenic compounds. The chemicals are as follows: acrolein, benzene, anthracene, benzo(a)pyrene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, carbon monoxide, chrysene, fluoranthene, formaldehyde, pyrene, phenanthrene, respirable particulate matter ($PM_{2.5}$) and indeno (1,2,3-cd)pyrene [18].

2.3 Occupational Exposure Limits in Firefighting

Firefighting is a unique profession, in the sense that the conditions are almost never the same between fires. This is because the fuel burning varies along with the changing atmospheric conditions. It is of utmost importance that there are fixed personal exposure limits for certain toxic chemicals and gases that are harmful to firefighter's lives. Agencies such as the EPA, NFPA, OSHA and ACGIH mandate prescribed limits for both wildland and structural firefighting. This is in line with the personal protective equipment that must be used to protect against specific chemicals/conditions. The most commonly used exposure limits are TLV (Threshold Limiting Value), STEL (Short-Term Exposure Limit), Immediately Dangerous to Life and Health (IDLH), Ceiling Limit and the most prominent, TWA (Time-Weighted Average). These limits are described below.

- Threshold Limiting Value/ Permissible Exposure Value - It is the allowable concentration of a chemical in which a person can safely work.

- Ceiling Limit- Maximum allowable human exposure limit for gaseous chemicals which is not to be exceeded even momentarily.
- Time Weighted Average- It is the exposure that measures for work shifts during which the ceiling limit is not exceeded. The TWA for firefighters is 8 hours/day and 40 hours/week [19].
- Short-Term Exposure Limit- It is the TWA exposure for a 15-minute period.
- Immediately Dangerous to Life and Health (IDLH)- The exposure which can instantaneously be dangerous to human health.

The exposure values for only the most concerning chemicals are available and occupational limits are set accordingly. Statutory bodies like OSHA, NIOSH and ACGIH define the exposure limits for harmful compounds such as carbon monoxide, sulphur dioxide, total particulate matter, respirable particulate matter, formaldehyde, acrolein, etc. There is a constant revision of the limits by various these governing agencies. The TWA limits are modified and amended as per the required conditions.

Table 1 provides the most recent edition of the occupational exposure limits for selected toxic compounds set by NIOSH. Most importance is given to carbon monoxide, since it has severe implications on human health. Also, formaldehyde, benzene and $PM_{2.5}$ (respirable particulate matter having a diameter of less than 2.5 micron) are the secondary toxic chemicals. The levels of carbon monoxide found on the field are drastically high as compared to the laboratory readings.

Table 2.1. Occupational Exposure Limits for toxic compounds as per NIOSH [18,20-22]

Chemicals	Permissible Exposure Limit (PEL)		Short-Term Exposure Limit (STEL)
	TWA (ppm)	Ceiling (ppm)	(ppm)
Acrolein	0.1	-	-
Benzene	1	-	5
CO	25	200	-
CO_2	5000	-	30000
Formaldehyde	0.75	-	2
Silica Dust	6 mg/m^3	-	-
VOC	0.2 mg/m^3	-	-
Phenols	20 mg/m^3	60 mg/m^3	60 mg/m^3
Phthalates	5 mg/m^3	-	-
PAHs	0.1 mg/m^3	-	-

2.4 *Actual on-field contaminant levels*

Even though there are set exposure limits for chemicals, there are few studies performed on the actual levels found on-site for firefighters. This is because of complexity in measuring a lot of chemicals and without a proper portable device. According to a study by Oregon State Fire Marshal Department, the levels of several toxic compounds were detected, shown in Table 2.2 [23]:

Table 2.2. Exposure limits for chemicals according to NIOSH and OSHA [23]

Exposures	OSHA TWA PEL (ppm)	NIOSH REL ST (ppm)	IDLH (ppm)	# fire analyzed	# fires found	#>PEL	#>STEL
Acrolein	0.1	0.3	2	11	4	4	4
Aldehydes (total aliphatic)	N.D	N.D	N.D	29	19	N.A	N.A
Ammonia	50	35	300	29	8	0	0
Arsenic	0.05	N.D	3	8	2	2	N.A
Benzene	1	5	500	29	10	3	0
Benzyl chloride	1	1	10	12	3	0	0
Carbon disulphide	20	10	500	3	3	0	0
Carbon monoxide	50	200	1200	38	30	3	1
Formaldehyde	0.75	2	20	29	4	0	0
Furfural	5	N.D	100	3	3	*N.A	*N.A
Glutaraldehyde	N.D	0.2	N.D	12	12	N.A	*5
Hydrogen chloride	5	5	50	37	8	5	1
Mercury vapor	0.012	N.D	0.24	29	5	3	N.A
Naphthalene	10	15	250	37	7	0	0
Nitrogen dioxide	5	1	20	37	28	13	22
Nitrogen monoxide	25	N.D	100	39	28	0	0
Ozone	0.1	N.D	5	39	21	17	N.A
Phenol	5	5	250	39	9	0	0
PID	N.D	N.D	N.D	19	19	N.A	N.A
Sulphur dioxide	5	5	100	29	2	0	0
Styrene	100	100	700	29	25	0	0
Toluene	200	150	500	29	27	0	0
Particulates (<10 µm)	5	N.D	N.D	21	21	14	0

The actual levels on-field were found to be lower than the occupational exposure limits for most of the compounds, but for some compounds it was significantly higher.

According to studies by various researchers, it was found that there was an exposure to PAHs despite the use of personal protective equipment [24]. Heavy hydrocarbons such as phenols, phthalates and PAHs were found along with metals such as barium, lead, zinc, chromium, cadmium and nickel. The concentrations of some of the chemicals were alarmingly high: for dioctyl phthalate - 4000 mg/mL and surface concentration of pyrene - 75 mg/cm^2.

A study conducted in Buffalo, New York stated that firefighters are regularly exposed to hazardous compounds such as benzene, carbon dioxide, sulphur dioxide, hydrogen cyanide, aldehydes, hydrogen chlorides and dichlorofluoromethanes [23, 25, 26]. Benzene is a by-product of common combustion products and is classified as carcinogenic by the International Agency on Cancer Research (IARC). Benzene is also linked to increase in the risk of contracting Non-Hodgkin's lymphoma [23, 25, 26].

2.5 Current protection used by firefighters

The profession of firefighting is so complex in nature that it requires multiple types of protection to the responder. There are thermal, chemical, biological and particulate hazards that firefighters are faced with. The challenges of developing a sufficient protective ensemble are complex material response, synergies among materials, fabric-to-garment transitions and effect of ancillary equipment and accessories. It is important to strike a balance between protective performance and clothing comfort, so that the gear does not cause hinderance in performing duties. The protection factor must also be compared to durability of the gear because they are expensive to manufacture. The objectives of thermal protective clothing are to reduce thermal exposure from an external heat source, minimize the burn injury, provide time for the wearer to escape and provide a comfortable and economical gear to use. Firefighters must face thermal exposure of various forms such conduction, convection and radiation; all at once.

The most common personal protective equipment (PPE) elements include turnout jackets, trousers, hoods, helmets, gloves, boots and respirator-type devices [27]. National Fire Protection Agency (NFPA) is the governing agency in the United States that all fire departments must comply with. The NFPA sets guidelines for the usage of appropriate gear and equipment. The NFPA has several clear classifications of gear to be used according to the severity of the

hazard. According to the NFPA 1971 standard, all turnout gear have three layers: outer shell, moisture barrier and thermal barrier. The outer shell is to protect against direct flame exposure with providing abrasion and tear resistance. The outer shell can be manufactured by using a variety of fiber blends and different weights and weaves to optimize the strength, abrasion resistance and durability. The moisture barrier functions to protect the firefighter against water and NFPA-prescribed common liquids such as gasoline, battery acids, chlorine, etc. This layer is an engineered membrane that is laminated onto a woven or a non-woven base substrate. The layer functions to provide breathability and to ease perspiration for the wearer. The thermal liner is made of woven material quilted to multiple layers of non-woven material. The function is to provide thermal protection by means of ambient heat entrapping. The inner thermal liner is made up of a variety of spun or filament fibers and is soft and comfortable to wear [28]. A combination of these three layers is the best suited defense against the conditions of firefighting. Some of the common materials used in the gear are flame-resistant (FR) cotton, FR rayon, Nomex®, Kevlar®, FR wool, polybenzimidazole (PBI), and aluminized fabrics.

The gear used varies for structural firefighters (Figure 2.2), wildland firefighters (Figure 2.3) and station uniforms. There are additional components such as respirator devices, HAZMAT suits (Figure 2.4**)**, personal alarm devices, etc. that are designed for a specific issue.

Figure 2.2. Wildland Firefighting gear [29]

Figure 2.3. Structural firefighting gear [30]

Figure 2.4. HAZMAT Protective Suit [31]

2.6 Care and Maintenance of firefighter turnout gear

The NFPA has set rules for cleaning of firefighter gear [36]. Fire stations use washer-extractor devices to clean their turnout gear after exposure. Typically, a 40-pound machine is used in fire stations that is to be loaded up to 80% capacity. The gear is routinely washed after it

gets contaminated and a second set of gear is usually ready for use. The washed gear is air dried or hung on racks inside the fire station to dry naturally. The cleaning not only depends on the technical availability and capability, but also on factors such as firefighters' culture, structural influences and occupational practice. These factors can contribute to risk of further carcinogenic contamination of dirty and contaminated gear [32].

NFPA has various classifications that govern the decontamination procedures for gear depending on the type of exposure. For hazardous materials, there are several levels such as A-light hazards, B-medium hazards, C-extreme hazards, D-dry contamination for water-reactive substances, E-etiologic agents and R-radioactive materials. The decontamination could have to be done at the incident site and/or at the stations depending on the severity [33]. Although general cleaning procedures are set by NFPA 1851, Standard on Selection, Care, and Maintenance of Protective Ensembles for Structural Fire Fighting and Proximity Fire Fighting they fail to efficiently remove contaminants after washing. The current processes manage to obtain only about 40% decontamination efficiency [34]. Previous studies have identified the fireground contaminants, but there is no validated method for complete removal [35].

At the fire incident, donning should be carried out having gloves on to prevent further contamination to the skin. The contaminated gear should be stored in plastic/sealed bags to make sure that no off-gassing of compounds occurs during transport [14].

There are three types of cleaning defined by NFPA 1851 (2014): routine, advanced and specialized. Routine cleaning includes removing debris off the gear, rinsing with water by hand and application of spot cleaner to the necessary areas. Advanced cleaning required the soiled gear to be washed in washing machines every year or after a specified number of samples are soiled. Specialized cleaning is to be done through professional cleaners when the gear is contaminated

with hazardous materials [36]. Laundering of firefighter turnout gear is a mandatory requirement by the manufacturer and NFPA. Careful attention must be given to the specifications of the procedure, since harsh conditions could break down garment materials and reduce their performance. Drying of the garments must be done by hanging the garments in the open but not in contact with direct sunlight, as it might degrade textile properties. Cross-contamination is commonly observed when cleaning multiple sets of contaminated turnout gear at once [37]. The washing efficiency is better when fewer garments are run as compared to multiple garments in a cycle. Currently, even though most of the contamination is prevalent upto the middle layer of clothing, contamination occurs through all layers when washed at once.

2.7 Storage of firefighter gear and ensemble elements

After attending a fire incident, the turnout gear is transported either in the fire trucks for professional firefighters or in the case of volunteer firefighters, in the boot of personal cars. In the fire stations, the gear is usually hung onto racks or kept inside lockers. The helmets are kept on top shelves of the racks and pants are kept at the bottom of the racks as shown in Figure 2.2.

Figure 2.5. Storage of firefighting gear in fire stations

2.8 Health concerns due to toxic chemicals

The extreme heat conditions take a huge toll on the health of firefighters. But it is the exposure to chemicals that causes short-term and severe long-term diseases such as heart diseases, which can be exacerbated due to inhalation of carbon monoxide that reduces oxygen absorbing capacity. The exposure to carcinogenic compounds could result in contracting several types of cancers such as colon, brain, bladder, kidney and Hodgkin's lymphoma. Additionally, inhalation of toxic gases and particulate matter in the fire smoke can paralyze alveoli and cause severe lung issues such as bronchitis and other chronic respiratory diseases such as asthma [38].

Exposure to toxic gases such as carbon monoxide could cause confusion, dizziness and neurological impairment.

2.8.1 Cancer studies among firefighters

There have been several studies conducted to understand the risk of cancer associated with the field of firefighting. In a study conducted at New Zealand in 1996, they identified and surveyed for major causes of death among firefighters such as malignant tumors, circulatory diseases, respiratory diseases, etc. On statistical analysis, they confirmed that firefighters had an increased risk of testicular cancer, although the reason for the same was unknown [39]. A set of German researchers conducted a population-based case-control study with 296 testicular cases and 797 controls to find relation between firefighting and testicular cancer. They found a strong association between the occurrence of testicular cancer and occupational exposures in firefighting [40]. A comprehensive study was conducted on over 3000 firefighters in California from 1988 to 2003. The study confirmed the previous hypothesis that firefighting increases the risk to testicular cancer, melanoma, brain cancer, esophageal cancer and prostate cancer [41]. Another study was conducted to review and perform a meta-analysis of 32 previous studies on cancer occurrences in firefighting. The study categorized the 21 types of cancers into probable, possible and unlikely risk types. The findings were that multiple myeloma was an elevated risk among firefighters. Also, there is a probable association with non-Hodgkin lymphoma, prostate and testicular cancer [42]. This particular study is the largest research study by far counting the number of participants involved in it. A total of 30,000 firefighters were chosen and studied as subjects by the National Institute of Occupational Safety and Health (NIOSH) from 1950 to 2009. They observed that the rates of several types of cancers were higher for three largest cities as compared to the entire US population. They reported a two-fold risk of malignant mesothelioma among firefighters; that

had not been found earlier. They also found that cancers of the respiratory system, digestive system and the urinary systems accounted for higher rates of cancer [43].

CHAPTER 3: Fireground Contaminants

3.1 Introduction

The synthetic products burning in a structural fire released a variety of volatile and semi-volatile compounds. These include compounds such as phenols, phthalates, PAHs, volatile organic compounds (VOCs), particulates and soot. Some of these chemicals are carcinogenic in nature, while others have varying toxicities [12]. A firefighter could be exposed to these chemicals by various means such inhalation and dermal absorption.

3.2 Phenols

3.2.1 What are Phenols?

Phenols are cyclic compounds containing the aromatic ring with the phenyl hydroxide or its substituted radicals. The hydroxyl (-OH) group is directly attached to the aromatic ring or phenyl ring, shown in Figure 3.1. Phenol is also known as carbolic acid and its derivatives are found in nature in essential oils and plant tissues [44].

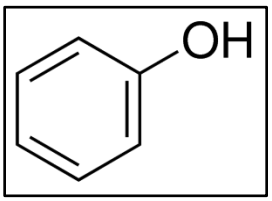


Figure 3.1 Structure of a phenol [45]

3.2.2 Physical and Chemical Properties

Phenols are generally colorless or white crystalline solids at room temperature. They have a distinctly aromatic- sweet and acrid odor with a sharp burning taste. Some phenols are volatiles

while some are semi-volatile in nature. Phenol on its own has a boiling point of 181.1°C and a molecular weight of 94.113 g/mol. The compound is soluble in water with a solubility of 1 gm/15 mL of water. One of the important properties for analysis using the High-performance liquid chromatography (HPLC) is the octanol-water partition coefficient (K_{ow}), which gives reference of solubility in octanol versus the solubility in water. The K_{ow} value for phenol is 1.46, which is a low number and states that the compound is more soluble in water as compared to its solubility in octanol [46].

3.2.2.1 Selected properties that affect analytical analysis

Phenol is known to be slightly acidic and is more acidic than regular alcohols with an -OH group. On adding phenol to water, the hydrogen ion can break away from the hydroxyl group thus forming phenoxide ion. The phenoxide ion is stable to a certain extent, since the negative charge on the oxygen gets delocalized around the ring. The pH of phenol dissolved in water is typically 5-6 which shows that the compound is slightly acidic [47]. The log P value gives the hydrophobicity of a compound. The higher the value of log P, the greater is the hydrophobicity. The value of log P for phenol is 1.46 which shows that it is fairly soluble in water. Phenols are soluble in water since the hydrogen atom in the hydroxyl group can form a weak bond with the lone pair of oxygen in water molecule. Nevertheless, the larger part of phenol is a phenyl group that is non-polar and hence makes the compound have limited soluble. Having multiple substitutions on the phenyl ring in phenol, draws the lone pair of oxygen in the ring and deactivates the system, thus reducing the possibility of hydrogen bond formation.

3.2.3 Applications of Phenols

Phenols find applications in a number of household, industrial and commercial applications. One such application is the use in curing of bonding resin in plywood manufacturing, insulation materials and bonded abrasions. Phenolic compounds are used in industrial coating formulations in drum and can linings, water tanks and air-conditioning. They are also used in the synthesis of thermosetting phenolic resins and for synthesis of caprolactam used to make nylon-6 fibers and plastics. Additionally, they are used in manufacturing of agricultural chemicals, intermediates, rubbers and synthesis of preservatives for dyes, perfumes and fungicides. In homes, phenols are found in disinfectant in mouthwashes, nose drops and throat lozenges [48,49].

3.2.4 Toxicity and Occupational Exposure Limits of Phenols

Phenols are highly toxic compounds that can cause protein degradation and tissue erosion. The OSHA set TWA for phenols is 5 ppm on skin for an 8-hour work shift and the odor recognition is 0.05 ppm. NIOSH suggests a PEL of 20 mg/m^3 averaged over a 10-hour work shift/day for 40 hours/week and a ceiling limit of 60 mg/m^3 over a 15-minute period. The IDLH limit by NIOSH is 960 mg/m^3. The compound on exposure to skin causes the skin to whiten and burn with a blister. Having a large amount of phenol exposure can lead to death due to paralysis of the central nervous system [48]. Some of the substituted phenols are known carcinogens and should be cautiously dealt with. Phenols are released during structural and wildland fires, since they are present in man-made and natural sources. There are several mono and multi-substituted phenols that have distinct properties. The exposure levels of phenols in firefighting are generally found to be much lower than the occupational exposure limit of 5 ppm. Yet, the exposure through

various routes such as inhalation of the off-gassed compound and dermal absorption could be life-threatening. There are several health hazards of phenols to human health such as anorexia, diarrhea, vertigo, dark coloration of urine, liver issues, etc. Chronic inhalation exposure to phenols may cause cardiovascular, respiratory, kidney, liver and central nervous system disorders. Even though, phenol is classified as Group D (non-carcinogenic) by EPA, its substituted compounds are known to be carcinogenic.

Table 3.1. Substituted Phenols with selected properties

Compounds	Boiling Point (°C)	Volatility	Vapor Pressure at 25°C (mmHg)	IARC[a] Classification
Phenol	182	Volatile	3.50E-01	Group 3
2,4,6-Trichlorophenol (2,4,6-TCP)	246	Volatile	8.00E-03	Group 2B
Pentachlorophenol (PCP)	310	Semi-volatile	1.1E-04	Group 2B

[a] The International Agency for Research on Cancer (IARC) classifies substances to show whether they are suspected to cause cancer or not. It places the substances into 4 categories depending on the strength of evidence for their carcinogenicity. The categories are as follows: Group 1-Carcinogenic to humans, Group 2A-Probably carcinogenic to humans, Group 2B- Possibly carcinogenic to humans and Group 3- Not classifiable as to its carcinogenicity to humans [64].

The following compounds of the mix are known carcinogens:

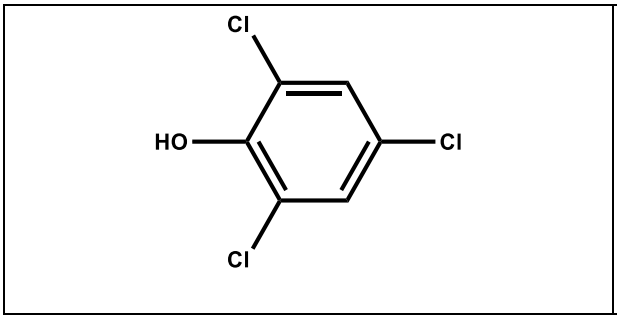


Figure 3.2. Structure of 2,4,6-trichlorophenol

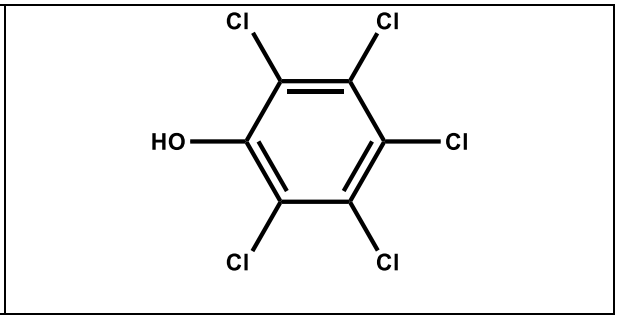


Figure 3.3. Structure of pentachlorophenol

3.2.5 Previous studies on analysis of phenols using GC

Substituted phenols comprise of both volatile and semi-volatile compounds, making it suitable for analysis using the GC instrument. In a study to identify phenols, a measured volume of sample, approximately 1 L, was acidified and extracted with methylene chloride using a separatory funnel. The methylene chloride extract was dried and exchanged to 2-propanol during concentration to a volume of 10 mL or less. The extract was run through the gas chromatograph column and was analyzed using the FID detector. The GC column used for the analysis was a 1.8 m long x 2 mm ID glass, packed with 1% SP- 1240DA on Supelcoport (80/100 mesh) or equivalent. The retention times for the phenols are depicted in Table 3.2 [50].

Table 3.2: Retention times of phenols with detection limits

Parameter	Retention time (min)	Method detection limit (µg/L)
2-Chlorophenol	1.70	0.31
2-Nitrophenol	2.00	0.45
Phenol	3.01	0.14
2,4-Dimethylphenol	4.03	0.32
2,4-Dichlorophenol	4.30	0.39
2,4,6-Trichlorophenol	6.05	0.64
4-Chloro-3-methylphnenol	7.50	0.36
2,4-Dinitrophenol	10.00	13.0
2-Methyl-4,6-dinitrophenol	10.24	16.0
Pentachlorophenol	12.42	7.4
4-Nitrophenol	24.25	2.8

According to literature, the selectivity and sensitivity of GC and HPLC with a MS are not enough for direct determination of phenols and phthalates at very low concentrations [51]. A sample pre-treatment step prior to GC or HPLC is necessary. For liquid samples, liquid-liquid extraction with organic solvents such as hexane or dichloromethane is used since the compounds

are highly polar. Extraction adsorbent such as C8, C18, silica, etc. may be used. Stock solutions of each chemical or mixture of chemicals were made by dissolving approximately 5-10 μg of the neat chemicals in liquid, solid or in solution into 10 mL of hexane. The standard solutions used in these experiments were made from appropriate dilutions of these stock solutions. Calibration solutions for preparing GC-MS calibration curves were made by diluting 1-200 μL of the standard solutions in hexane (final volume 200 μL). The parameters used in the GC-MS are shown in Table 4 [51]

Table 3.3. Parameters for gas chromatography method

GC-MS	**Alkylphenol parameters**
Column	GP-5ms (30m* 0.25mm* 0.25μm)
Injection	1 μL
Injection temperature program	280°C, pulsed splitless, 20 psi for 2 mins
Carrier gas	Helium, 1 mL/min
Oven Gradient	80°C (1 min) to 130°C (3 min) @ 30°C/min to 240°C @ 10°C/min to 300°C (5 min)

Often a direct analysis of pure compounds is difficult due to various factors such as volatility, polarity mis-match and incompatibility with the column stationary phase [52]. In such cases a process known as derivatization must be performed before the compounds are injected into the gas chromatograph column. To analyze phenolic compounds, derivatized was carried out and the dried eluent was reconstituted with 50μL acetonitrile and N-methyl-N-(tert-butyldimethylsilyl) trifluoroacetamide (MTBSTFA) of the derivatizing reagent was added and the mixture was vortex mix for 90 seconds. This was derivatized at 90°C for 20 min in GC oven

according to Olujimi et al. (2010). The sample was cooled down to room temperature and 1µL was injected into GC-MS for analysis [52].

An Agilent 6890N gas chromatograph/5975 mass selective detector system operating at 70 eV with ion source temperature set at 230°C was used for this study [53]. The gas chromatograph was equipped with a DB-5MS fused silica column (phenyl methyl siloxane) (30 m x 0.25 mm i.d.; 0.25 um film thickness. The injector temperature and GC–MS interface temperature were maintained at 260°C and 280°C, respectively. The sample was introduced into the gas chromatograph in splitless mode and the helium carrier gas flow rate was set at 1.0 mL/min. The oven temperature of the GC was set at 80°C for 1 min, then increased to 280°C at 25C/min and held for 7 min. The post run temperature was set at 300°C for 2 min to clean up the column before the next injection. External calibration was used to quantify extracts. Calibration was by plotting peaks area versus amount injected. Linearity of the system was measured at 4-5 points. Calibration ranged from 2.5 to 1000µgL-1 [53].

3.3 Phthalates

3.3.1 What are Phthalates?

Phthalates, also known as phthalate esters, are esters of phthalic acid, structure shown in Figure 3.4 They are vastly used as plasticizers in a number of applications to increase flexibility, transparency and durability. They are also used in softening polyvinyl chloride (PVC).

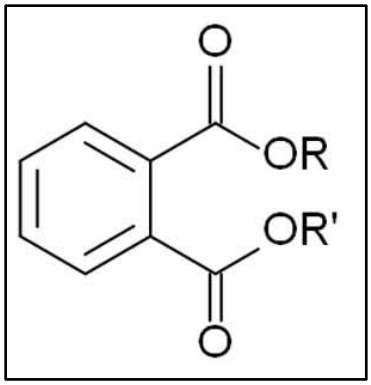


Figure 3.4: Structure of Phthalate ester [54]

Phthalates are categorized into high and low molecular weight compounds and accordingly used in suitable applications:

High Phthalates- These have 9-13 carbon atoms in their backbone that provides them with increased permanency and durability. These find use in PVC products such as flooring, roofing, synthetic leather, self-adhesive films, etc. The common high phthalates are diisodecyl phthalate (DIDP), diisononyl phthalate (DINP) and dipropylheptyl phthalate (DPHP).

Low Phthalates- These have 3- 8 carbon atoms in their chemical backbone. These find use in inks, cosmetics, medical devices, etc. The common low phthalates are di(2-ethylhexyl) phthalate (DEHP) and dibutyl phthalate (DBP) [55].

3.3.2 Physical and Chemical Properties

Phthalates exist as white crystals or as white fine powder at room temperature. They have a flash point of around 168°C and easily decompose. The phthalate class of compounds have a very low solubility of 1 mg/mL in water. These compounds have high octanol-water coefficients, stating that they have greater affinity for organic liquids [56].

3.3.2.1 Selected properties that affect analytical analysis:

Phthalates are made by destructive bond dissociation of phthalic anhydride. Phthalates are therefore diesters of orthophthalic acid. The esters are made up of acid that contains an aromatic ring or two alcohols. The hydrocarbon chains of the alcohol could be made up of ring-shaped hydrocarbons or aromatic rings. Hence, the chemical and physical properties depend on the substituted hydrocarbon chain. Higher the hydrocarbon chain length, hydrophobicity increases. The phthalate compound is sparingly soluble since it has no functional groups that can form bonds with water or other hydroxyl groups. The log P or the octanol-water co-efficient is therefore very high for these class of compounds. A high log P value signifies that the compounds are highly hydrophobic, therefore will have higher affinity to the non-polar stationary phase in the reverse-phase HPLC and GC columns. These compounds will elute out at higher retention times since they would have higher interaction with the stationary phase [57].

3.3.3 Applications of Phthalates

Phthalates are commonly found in commercial, industrial and household products. The most common application is the use as a plasticizer in the manufacturing of PVC plastics. It is also found as a component of floorings, roofing and cables, paints and adhesives. Phthalates are used in articles such as shoes, artificial leather and some functional fabrics.

3.3.4 Toxicity and Occupational Exposure Limits of Phthalates

Phthalates are known to adversely affect reproductive system by causing reduction in anogenital distance in boys, reduced sex and thyroid hormones and shortened pregnancy [58]. The biomonitoring data from amniotic fluid and urine have showed significant exposure to phthalates in uterus, infants, puberty and adulthood. Phthalates are extremely dangerous and

affect testosterone levels, male and female reproductivity [59]. The compounds having between 4-6 carbon atoms are the most potent at causing phthalate syndrome effects. The Consumer Products Safety Commission banned the use of DBP, BBP and DEHP permanently while placed an interim ban on DIDP, DINP and DnOP in child articles at concentrations greater than 0.1% under the Consumer Product Safety Information Act 2008. The Safe Drinking Water Act permits the maximum concentration of phthalates to be 0.006 mg/L. DEHP and DBP are listed as hazardous air pollutants under the Clean Air Act [60]. The NIOSH REL for DEP is 5 mg/m^3 and the TLV is 5 mg/m^3 [61]. The OSHA PEL, NIOSH PEL and TWA for DBP is 5 mg/m^3 and the NIOSH IDLH is 4000 mg/m^3 [62]. DEHP is known to be a possible carcinogen; The 8-hour OHSA TWA limit is 5 mg/m^3, 15-minute TLV-STEL is 10 mg/m^3 [63].

Phthalates are commonly released in structural fires due to their near ubiquitous presence in a variety of products such as pipes, child articles and many more. Firefighters must wear appropriate respiratory protection to avoid inhalation of the toxic phthalates.

Table 3.4: Selected properties of substituted phthalates

Compounds	Boiling Point (°C)	Volatility	Vapor Pressure at 25°C (mmHg)	IARC[a] Classification
Di-butyl phthalate (DBP)	340	Semi-volatile	2.00E-05	Group 3
Benzyl butyl phthalate (BBP)	370	Semi-volatile	8.25E-06	Group 3
Di-ethylhexyl phthalate (DEHP)	384	Semi-volatile	1.42E-07	Group 2B

[a] The International Agency for Research on Cancer (IARC) classifies substances to show whether they are suspected to cause cancer or not. It places the substances into 4 categories depending on the strength of evidence for their carcinogenicity. The categories are as follows: Group 1-Carcinogenic to humans, Group 2A-Probably carcinogenic to humans, Group 2B- Possibly carcinogenic to humans and Group 3- Not classifiable as to its carcinogenicity to humans [64].

The properties of the compounds such as carcinogenicity, volatility, octanol-water partition co-efficient and preferred absorption wavelength were studied. The log P values for all the compounds ranged from around 1.6- 8.8, which means that the compounds would elute out of the HPLC column at significantly different times. The entire principle of HPLC is dependent on the affinity towards the stationary and mobile phase, hence such vast difference in hydrophobicity will give rise to separated elution. As observed, all the compounds are semi-volatile in nature having a boiling point greater than 260°C. This makes it difficult for GC analysis, where the volatility and difference in boiling points is the key factor for separation of compounds. A column capable of attaining high temperatures would be needed. The structure of a possible carcinogen is shown in Figure 3.5:

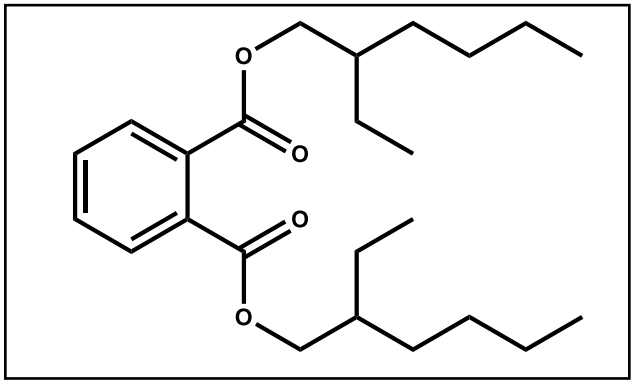


Figure 3.5. Structure of DEHP

3.3.5 Previous studies on analysis of phthalates using GC

There are several studies undertaken to identify and analyze phthalate esters from various sources such as water, plastics and other synthetic products. A study done by the EPA found that firefighters attending to residential fires often have their gloves and hoods contaminated with a lot of organic and inorganic contaminants such as phthalates, PAHs and plasticizers.

Polyhalogenated hydrocarbons and phthalate diesters are expected to be absorbed into the skin at higher temperatures in firefighting scenarios. The samples were extracted using methylene chloride and analyzed using EPA 8270D method. All the layers of firefighter suits were tested for levels of these chemicals. The study concluded that the chemicals are found in even the innermost layer, probably due to the fabric-to-hand contact [65].

An Agilent 6890N gas chromatograph/5975 mass selective detector system operating at 70 eV with ion source temperature set at 230°C was used was used to analyze phthalates [53]. The gas chromatograph was equipped with a DB-5MS fused silica column (phenyl methyl siloxane) (30 m x 0.25 mm i.d.;0.25 um film thickness. The injector temperature and GC–MS interface temperature were maintained at 260°C and 280°C, respectively. The sample was introduced into the gas chromatograph in splitless mode and the helium carrier gas flow rate was set at 1.0 mL/min. The oven temperature of the GC was set at 80°C for 1 min, then increased to 280°C at 25°C/min and held for 7 min. The post run temperature was set at 300°C for 2 min to clean up the column before the next injection. Further a SPE and derivatization procedure was used to clean up the wastewater obtained from the river [53].

EPA 8270D is a direct method for the analysis of a variety of semi-volatile organic compounds using GC. For analysis, the column used was 30-m x 0.25-mm ID (or 0.32-mm ID) 1-μm film thickness silicone-coated fused-silica capillary column (J&W Scientific DB-5 or equivalent). Standard stock solutions of 1000 mg/L were used for the analysis. The retention times for the compounds is shown in Table 3.5 [66].

Table 3.5. Retention times for phthalates using EPA 8270D method on GC-MS

Compound	DMP	DEP	DBP	BBP	DEHP	DnOP
Retention time (min)	14.48	16.70	21.78	26.43	28.47	30.48

3.4 Polycyclic aromatic hydrocarbons (PAHs)

PAHs are semi-volatile compounds containing one or more benzene rings in its chemical structure. They range from volatile, semi-volatile to non-volatile compounds. PAHs are commonly found in structural fires, of which many are known carcinogens. Compounds such as naphthalene, acenaphthylene, benzo[a] pyrene, benzo[a]fluoranthene and others have been found to be released from the materials burning in a structural fire [112,123]. PAHs are extremely toxic and heightens the risk to contracting certain types of cancers. These compounds have been found on human skin as well as ensemble elements that firefighters wear [126].

The mix of the reference fireground contaminants contained four PAHs. Table 3.6 shows some of the important properties that would be required for the analysis of these compounds from contaminated firefighter gear.

Table 3.6. Selected properties of PAHs

Compounds	Boiling Point (°C)	Volatility	Vapor Pressure at 25°C (mmHg)	IARC[a] Classification
Naphthalene (NA)	218	Volatile	08.5E-02	Group 2B
Phenanthrene (PA)	340	Semi-volatile	1.21E-04	Group 3
Pyrene (PY)	404	Semi-volatile	4.5E-06	Group 3
Benzo[a] pyrene (BaP)	495	Semi-volatile	5.49E-09	Group 1

The structures of possible carcinogens are shown in Figure 3.6 and Figure 3.7:

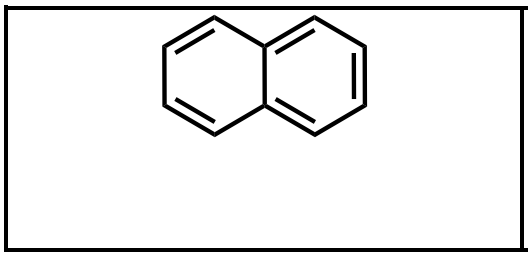


Figure 3.6. Structure of naphthalene

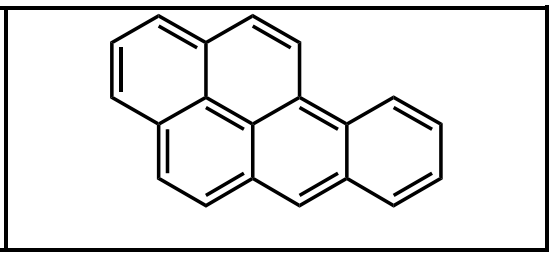


Figure 3.7. Structure of benzo[a] pyrene

CHAPTER 4: Gas-chromatography

4.1 Introduction to Gas-chromatography (GC)

Gas Chromatography (GC) is one of the modern analytical chemistry techniques that is used to separate organic compounds in a mixture for quality control and research. The GC uses a gaseous mobile phase to transport the sample analytes through packed or hollow columns containing a polymeric liquid stationary phase [67]. The GC can analyze solids, liquids and gases that are in the molecular weight range of 2 to 800 molecular atomic units. Gas tight syringes or gas sampling valves are used to inject gases. Extracted chemicals from solids, either in the form of liquids or gases can be injected too. The concentration of the compounds can be detected as low as parts per trillion (ppt) depending on the selected detector. The technique uses the difference in volatility, that is different boiling points between compounds and the interaction of the analyte with the stationary and mobile phases, to separate very complex mixtures. It is a destructive form of testing, where the compounds injected are broken down and cannot be recovered at the end. The instrument gives fingerprint-type results, meaning if the same compound will give the exact same reading on multiple injections through the GC. The GC is an expensive, sophisticated instrument that needs to be maintained with the proper air inlets and working conditions. Gas chromatography is used in a variety of applications such as cosmetics, pharmaceuticals, petrochemical, environmental toxins, forensics, and the agricultural industry among many others. The fundamental limitation of GC is that the samples must be volatilized within the temperature limits of the instrument, before they can be injected and further analyzed. The autosampler attached to the GC ensures that precise amount of liquid sample is injected into the injector port each time. The instrument can be seen in Figure 4.1.

4.1.1 Primary components of a gas-chromatography system:

- Carrier gas from a pressurized cylinder or a generator. Typical gases are He, H, N, Ar with purity greater than 99.9995%. The carrier gas is filtered through a gas filter.
- Sample introduction- 0.2 to 3 microlitres of liquid is injected using a syringe
- Column- contains a very viscous stationary phase liquid and is temperature controlled
- Detector- amount of sample content from the original mixture measured
- Computer integrator- measures the amount of sample components as they pass through the detector and to identify components based on retention times. The chromatograms give us peak heights, peak areas and retention times [68].

Figure 4.1. Setup of Gas-Chromatography [69]

4.2 Working of a GC system

Inert carrier gas such as helium or nitrogen is supplied to the GC by means of gas cylinders. The pressure of the gas in controlled either manually of by pneumatic pressure controls. The controlled gas is supplied to the inlet of the column and flows through the column and to the detector. The sample is injected into the heated injection port, where it gets volatilized and gets transported through the column by the carrier gas. The column is usually made up of silica and

has a small internal diameter in the range of 0.1 to 0.7 mm. The sample gets separated inside the column due to the differential partition of the analytes between the stationary and mobile phases based on relative vapor pressure and solubility in the liquid stationary phase. On elution from the column, the analytes and carrier gas pass into the detector, where the detector responds due to some physicochemical property of the analyte and generates an electronic signal that measures the amount of analyte present. The signal is amplified and sent to the data system which then produces an integrated chromatogram. Different compounds produce peaks on chromatogram that have unique retention times. If a sample with unknown concentration is to be measured, then a standard sample with a known concentration is first injected. The standard sample peak retention time is compared to the test sample to calculate concentration [70]. The GC uses ovens that can be tuned to the required temperature. The typical operation range is 10°C to 400°C [67].

4.3 Detectors used in conjunction with a GC system

Some of the commonly used detectors are flame ionization detector (FID), electron capture detector (ECD), photoionization detector (PID), thermal conductivity detector (TCD), mass spectrometer (MS), flame photometric detector (FPD) and nitrogen phosphorous detector (NPD).

GC detectors detect isolated components and helps in identification and quantification of the sample. The detectors respond to a physicochemical property of the analyte, amplify the response and an electronic signal gets generated for the data system to generate a chromatogram. The most commonly used detector is the FID in which the components are ionized by subjecting them to flame in the chamber. As ions are formed, they are drawn towards either anode or cathode based

on the charge. As they impinge on the electrodes, current is passed which gets recorded. The strength and intensity of the current depends on the sample [68].

4.4 Chromatographic columns used in a GC

The columns in GC can range from 1 m up to 100 m. The column is in a coiled form to fit inside the thermal chamber. The column is generally made up of glass or steel. Column selection is done based on the internal diameter of the column and the film thickness of the stationary phase. The larger the diameter and the film thickness, the higher is the surface area available for the injected components to interact with. Typically, a column length of 30 m is suitable for most separations. The longer the column, the higher the number of theoretical plates and the better the separation of compounds. There are two types of columns typically used in a GC system. The column type depends on the analyte to be tested. Various factors such as polarity, packing type and film thickness must be considered while choosing the right column.

Of the two column types used, the packed column is packed with a substance holding the stationary phase and is about 2 meters long. In contrast, the capillary column has the inner surface coated with stationary phase and is about 30-60 meters long. The column is made up of fused silica glass and is coated on the outside by polyimide- a high temperature polymer that allows the column to be bent without breaking. The stationary phase is typically a high viscous material such as methyl silicone and is coated in the diameter range of 0.3 to 3 micron. Examples of commonly used columns are wax columns which have different stationary phases such as polyethylene glycol, polydimethylsiloxane and other cross-bonded siloxanes. The columns are engineered to sustain a fixed maximum temperature that could range between -60°C to 400°C.

4.4.1 Parameters for column selection [71]

- Polarity of the stationary phase: non-polar, mid-polar and highly polar (Table 4.1)

Table 4.1. Polarity of columns [71]

Compound polarity	Compound examples
Non-Polar	Alkanes
Polar	Alcohols, amines, esters, ketones, diols
Polarizable	Alkenes, alkynes and aromatic hydrocarbons

- The column efficiency (number of theoretical plates) and sample capacity (amount of sample that can be run on the column without overloading) are decided by the inner diameter, as shown in Table 4.2.

Table 4.2. Column efficiency parameters [71]

Inner diameter (mm)	Total plates (N)	Sample analyte capacity (ng)
0.53	39000	1000-2000
0.32	69000	400-500
0.25	87750	50-100
0.20	109500	<50
0.18	121500	<50
0.10	219000	<10

- Column Length- The typical column length is about 15 m to 60 m. It is observed that a 30 m column generally provides the best resolution, analysis time and column head pressure. Increasing the column length provides better resolution since there is an increase in the theoretical number of plates but increase back pressure.

- Film thickness- Increasing or decreasing the film thickness in the column affects the interaction between the analyte and the stationary phase. The film thickness decides the actual surface area available for the analyte to interact with. Low film thickness is suitable for analytes with high boiling points (greater than 300°C) such as phthalates, PAHs and other semi-volatile compounds. High film thickness is desirable for analytes with low boiling points such as VOC's and gases. The implications of altering the film thickness is shown in Table 4.3.

Table 4.3. Benefits and Limitations of altering film thickness [71]

Alterations	Benefits	Limitations
Increasing film thickness	• Increased sample capacity • Increased elution temperature* • Increased analyte retention*	• Increased peak width • Increased column bleed • Reduced maximum operating temperature for column.
Decreasing film thickness	• Sharper peaks • Reduced column bleed • Increased maximum operating temperature for column • Shorter retention times* • Retention at lower temperatures*	• Increased analyte retention with tubing wall

Phase ratio (β)- Effects of film thickness are co-related with column I.D by the equation β= column radius/ 2* film thickness. The range of β have a significance such as $\beta < 100$ for highly volatile, low molecular weight compounds, $100 < \beta < 400$ for wide range of compounds and $\beta > 400$ for high molecular weight compounds for trace analysis. Phase ratios are important while changing columns, since the columns with same phase ratios will give similar retention times and elution orders under same analytical conditions.

4.5 The chromatogram

The chromatogram is the graphical representation of the sample elution and response. Each peak has a unique retention time when it elutes from the column and passes through detector. Detector response is characterized by selectivity and sensitivity. Selectivity determines the types of compounds that the detector will detect. Sensitivity defines the concentration of the compounds that the detector will detect. Minimum Detectable Limit (MDL) is the lowest concentration level the detector will detect. The dynamic range is the concentration range in which the detector will detect. There are selective and non-selective types of detectors that can be used. The FID detector will detect anything organic (non-selective detector). A peak is considered when the height of the peak is 2-3 times that of the noise level. Retention times are a qualitative analysis to identify the sample component. Peak area or peak heights are quantitative analysis to measure the amount of the sample component. A reference chromatogram showing the abundance v/s retention times can been seen in Figure 17.

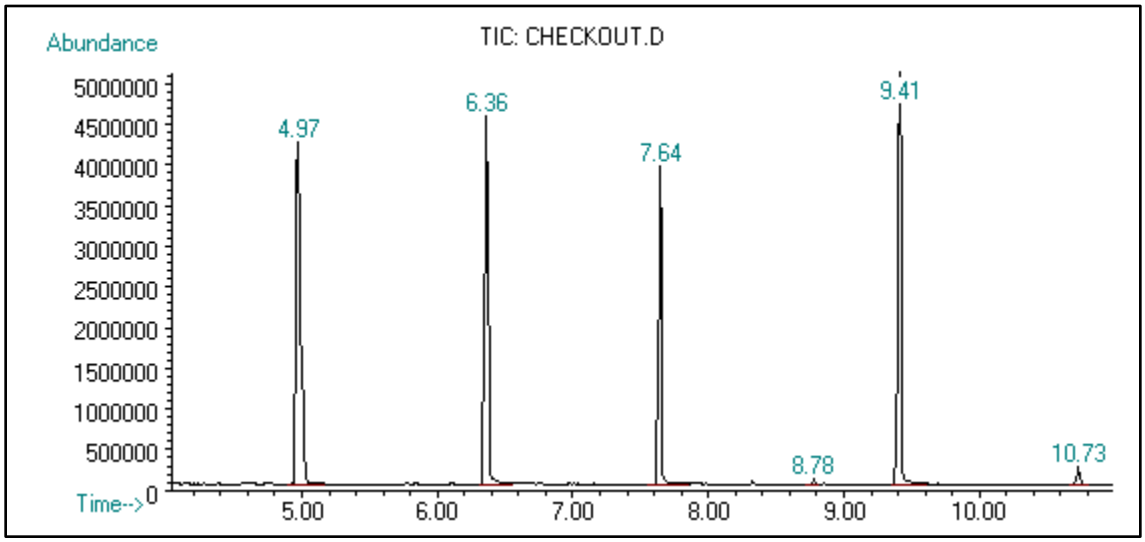


Figure 4.2. Chromatogram output from GC [72]

4.6 Precautionary features of a GC system

These help to ensure that the entire sample is transferred into the inlet and vaporized properly.

- Temperature controlled injection ports
- Septum used to seal the injection ports and to make sure that the GC system does not get in contact with the outside atmosphere.
- Liners used to control the volume of the injection port.

4.7 Limitations of GC

The GC, despite being a sophisticated instrument, has some limitations. One such shortcoming is that the samples to be analyzed using GC must be volatile; i.e.- have a significant vapor pressure below 250° C. For some compounds, derivatization could be done to increase their volatility but is complex and time-consuming. Highly polar analytes may be less volatile than expected when dissolved in a polar solvent due to presence of intermolecular forces such as hydrogen bonding [67]. GC methods are not conducive for analysis of large molecular compounds such as proteins and polymers, since they are not volatile. The analysis using GC is a destructive form of testing, thus the analyte injected cannot be recovered after the process is completed.

CHAPTER 5: Mass Spectrometry

5.1 Introduction to mass spectrometry (MS)

Mass Spectrometry, popularly known as MS is an analytical chemistry technique that can be connected to a chromatographic system to identify the amount and type of chemicals present in the analyte. It does so by measuring the mass-to-charge ratio (m/z) and abundance of gas-phase ions. MS works by ionizing chemical compounds to generate charged molecule fragments and thereafter measuring their mass-to-charge ratios. The mass spectrometer can be used as a combination in HPLC-MS and GC-MS. The output is produced as a mass spectrum, which is a plot of ion signal as a function of mass-to-charge ratio [73].

Simply put, the MS works by identifying compounds based on the atomic sample composition of the molecules and their charged state. Analysis of completely unknown samples is possible since MS does not require detailed information about the sample composition. There are several applications of mass spectrometry such as trace gas analysis, isotope dating, forensics, clinical applications and many more [74].

5.1.1 Main components of a mass spectrometer, shown in Figure 5.1:

There are 3 main parts [75]:

- Ion source- Produces gaseous ions from the analyte being studied
- Mass analyzer- To resolve the ions into their characteristic mass components as per their mass-to-charge ratio
- Detector- To detect the ions and record the relative abundance of each ionic resolved species

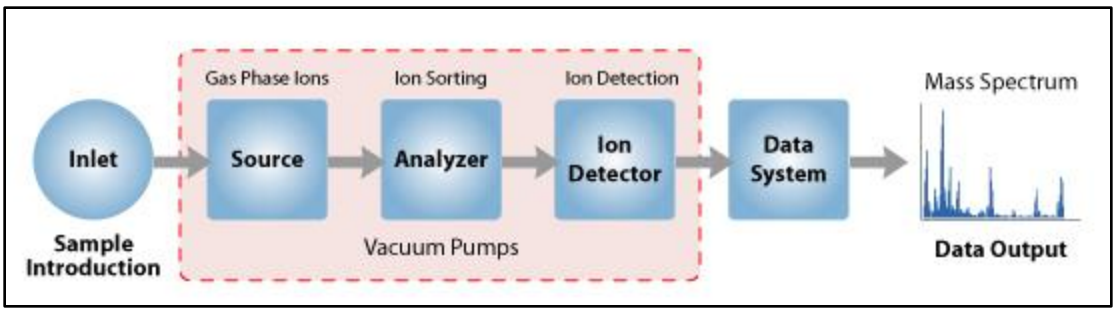


Figure 5.1. Components of a Mass Spectrometer [76]

5.2 Working principle of a MS

The analyte is converted to gas phase ions by electron ionization. These molecular ions undergo fragmentation and further fragmentation into smaller ions. The ions are transported to the mass analyzer by means of magnetic or electrical fields. The ions get separated according to their mass to charge ratio (m/z) in the mass analyzer. Selected ions are fragmented, and the fragments are analyzed in a second analyzer. The detector records the charge induced or the current produced when the ions from the last analyzer passes by or hit the surface of the detector. The abundance of the ions with the detector is measured and the detector converts the ions into electrical signals. A plot of ion abundance v/s m/z is produced on the screen. Identification is done by correlating known masses to the identified masses [75,76].

5.3 Ionization of the analytes [73,77]

The polarity of the analytes determines the type of ionization source to be used. For gaseous samples, either electron ionization (EI) or chemical ionization (CI) can be used. For liquid samples, several ionization techniques can be used such as electrospray ionization (ESI), atmospheric pressure chemical ionization (APCI), atmospheric pressure photo ionization (APPI),

multimode ionization (MMI), matrix assisted laser desorption ionization (MALDI) and inductively coupled plasma (ICP).

5.3.1 Electron Ionization (EI)

A heated filament gives off electrons in this system. The electron beam is accelerated towards an anode and collides with the incoming molecules from the gas chromatograph. This removes an electron from the molecule resulting in a charged ion. Hence, single charged molecular ions and fragment ions are produced. The schematic can be seen in Figure 5.2.

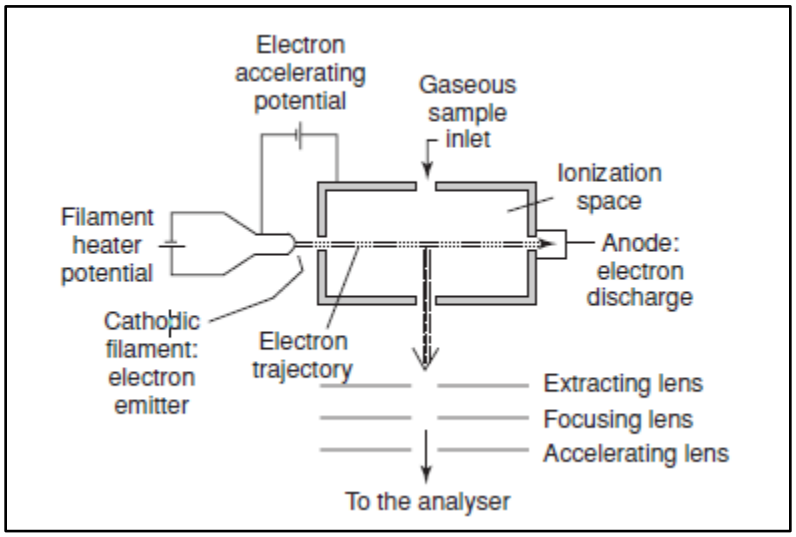


Figure 5.2. Diagram of an electron ionization source [77]

5.4 Mass analyzers in MS

After the analyte molecules have been ionized and the ions are transported into the mass analyzer. The mass spectrometer then measures the ion signals that produces a mass spectrum. The mass spectrum provides information about the molecular weight, structure, identity and quantity of a compound.

5.4.1 Single quadrupole

The quadrupole mass analyser, shown in Figure 5.3 and Figure 5.4 is scanned sequentially such that only a single ion m/z may be passed at once. All the other ions are lost in the process. The information received is the mass spectrum of the specific compound.

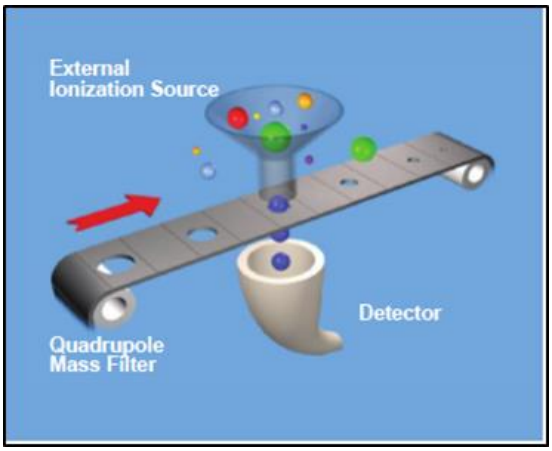


Figure 5.3. Working of single quadrupole [73]

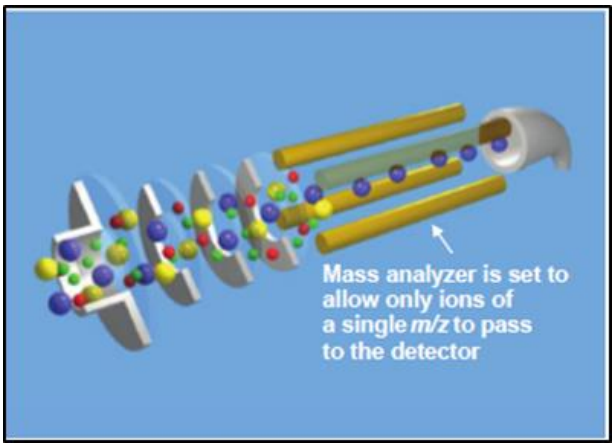


Figure 5.4. Single ion monitoring (SIM) [73]

The target ion with a specific m/z is monitored. The single-ion monitoring (SIM), allows ions having a specific m/z to pass through to the detector. When SIM is used with a single quadrupole, it allows the best sensitivity for quantitation but lacks specificity.

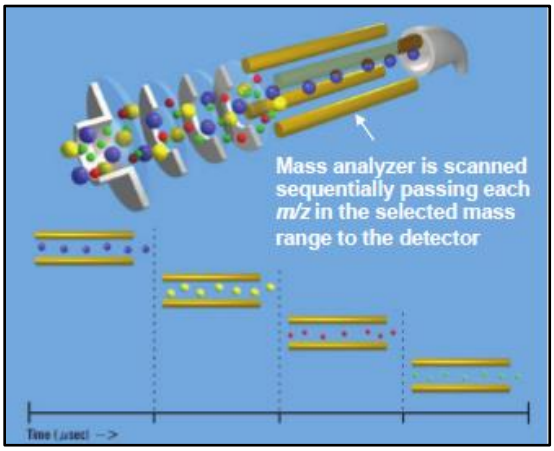


Figure 5.5. Scan Mode [73]

In the Scan mode, shown in Figure 5.5 in mass spectrometry, the single quadrupole mass analyzer is scanned sequentially allowing only 1 m/z at a time to pass to the detector and the accumulated information allows for precise identification of the analyte.

CHAPTER 6: Controlled contamination and extraction

6.1 Contamination of fabric samples in the laboratory

To imitate the contaminated turnout gear, fabric samples need to be treated with chemicals in a manner that they penetrate the fabric completely and not just remain on the surface. To be able to achieve that:

1) Dip-nip roller system could be a viable option wherein the fabrics are squeezed through the pressure between two rollers and the trough contains the selected contaminant liquid solution. This method would ensure that the solution gets completely into the fabric and the % exhaustion could be tuned as well. The only drawback with this method is that using toxic compounds such as phenols, phthalates and PAHs, there could be evaporation during the experiment which is a health hazard.
2) Another method that is convenient and equally effective is using a multi-channel pipette to evenly distribute the chemicals on the fabric samples. A 12-tip multi-channel pipette could be adjusted to draw the required solution and evenly displace it onto the fabric sample strip of the designated dimension.
3) There have been studies to carry out controlled contamination of fabrics such as Kevlar®, Nomex® and PBI. The fabric samples were dipped in a vial containing the required concentration of a chemical. The fabric was allowed to stay in for 5 minutes after which it was removed.

6.2 Previous studies for extraction of contaminants from fabric samples in the laboratory

Solvent extraction is the most commonly used method to remove contaminants from fabrics for analysis. After choosing a suitable solvent, an appropriate equipment such as an extractor or a sonicator must be used. There are other methods such as dry cleaning and forced air circulation, but these methods would not be suitable for the removal of toxic contaminants. A possible method would be to contaminate the fabrics using the multi-channel pipette. The fabrics can then by placed in a vial containing a suitable solvent. The vial be then placed in a sonicator for a stipulated amount of time to extract maximum chemicals. As per a study, to extract the contaminants from the gear, the contaminated samples were placed in a round-bottom flask containing 40 mL of hexane. The vial was shaken for 30 minutes and left to soak for 12 hours. The solvent was evaporated using a Buchler evaporator. The extracted samples were kept in glass vials and 2 mL of petroleum ether was added to the round-bottom to rinse [78]. Firefighter clothing is exposed to a variety of chemicals and undergoes rough usage in the field. Laundering is an important aspect to clean the contaminated gear. Yet, it is often seen that laundering affects the materials in the clothing. To test the effect, two washing machines were used to compare the differences between the physical properties of the fabrics pre and post washing. The target was to effectively remove soil and chemical from the fabrics. The method of contamination used for the study was that the specimen samples were dipped in a solvent containing known concentrations of ethyl benzene, anthracene and dioctyl phthalate. Diethyl ether was the solvent used to extract the chemicals from the fabrics. The contaminant formulation was prepared using the following chemicals- 1 gram of anthracene (5000 ppm), 2.05 mL of dioctyl phthalate (10,000 ppm), 2.3 mL ethyl benzene (10,000 ppm), 280 mL dichloromethane. Sets of washed and unwashed gear were immersed in the contaminant solution for 5 minutes, suspended and allowed

to dry in the fume hood. Prior to analysis, 200 μL of dichloromethane and 2 μL of decane (used as an internal standard) were added to each specimen in a glass container with the container and specimen agitated for 30 seconds. The extract specimens were analyzed using GC-FID. Control solutions consisting of a synthetic mixture containing 0.011 g of anthracene, 20 μL of ethyl benzene, 20 μL of octyl phthalate and 20 μL of decane (as internal standard) were prepared in 2 mL of dichloromethane. Samples (1 μL) of the mixture were injected into the gas chromatograph. These concentrations were chosen to be close to the concentration of the contaminants in the solution in which the fabric specimens were immersed. The retention times were found to be 3.75 minutes for ethyl benzene, 4.77 minutes for decane (internal standard), 8.97 minutes for anthracene and 19.71 minutes for dioctyl phthalate. The experimental samples were also analyzed by injecting 1 μL into the gas chromatograph. The peaks were integrated electronically and normalized using the internal standard. The concentration of the identified contaminant present in the sample was calculated from the values from the synthetic mixture and the volumes of solvent used to dissolve the samples. The decontamination efficiency was calculated using the equation: Decontamination efficiency = {[(CBb B- CBcB) - (CBtB - CBcB)]/ (CBb B- CBcB)} x 100, where CBcB = Average contaminant concentration in control specimens, CBbB = Average contaminant concentration in baseline specimens and CBtB = Average contaminant concentration in test specimens. The GC method used included a DB wax column, 30 m length, internal diameter 0.53 mm with a helium carrier gas flowrate of 5mL/minute. The oven gradient was 60°C (hold 2 mins) to 250°C (hold 13 mins) @ 30°C/min. A flame ionization detector was used to detect the compounds and set at 280°C. The injection temperature was 260°C [79].

It is hypothesized that the contamination present in the ambient air affects the readings taken in a laboratory. To evaluate that, concentrations of DnBP, DiBP and DEHP in laboratory air were

calculated and were reported between 0.37 and 3.0 μg/m^3, which could cause contamination of glassware and solvents. To be sure that no contamination occurs during sampling, it is advisable to avoid the usage of personal use of hand creams, perfumes, deodorants, and any cosmetic products that contain phthalates. All the materials used during sampling should be made of glass, Teflon®, aluminum or stainless steel. Other precautions such as prewashing the laboratory material and equipment with an appropriate organic solvent such as cyclohexane, n-hexane, isooctane, methanol is necessary. An acidic solution such as hydrochloric acid or mixture of ammonium persulfate and sulfuric acid can also be used. The glassware should be heated at 450-550°C overnight to remove organic materials. The use of plastic materials throughout the procedure is absolutely prohibited. Possible sources of contamination can also be derived from SPE cartridges, filters, vial caps, syringes and septa. It is also noteworthy that deionized water from purification systems (such as Milli-Q RG, Millipore) can contain phthalates. The study found that the common background contamination was about 0.02, 0.15, 0.005 and 0.49 μg/L for DEP, DnBP, BBzP and DEHP, respectively. Methods such as LLE, SPE and SPME can be used to extract the phthalates from the liquid medium [80].

Phthalate compound analysis:

A study was carried to study extraction of phthalates from solid and liquid matrices

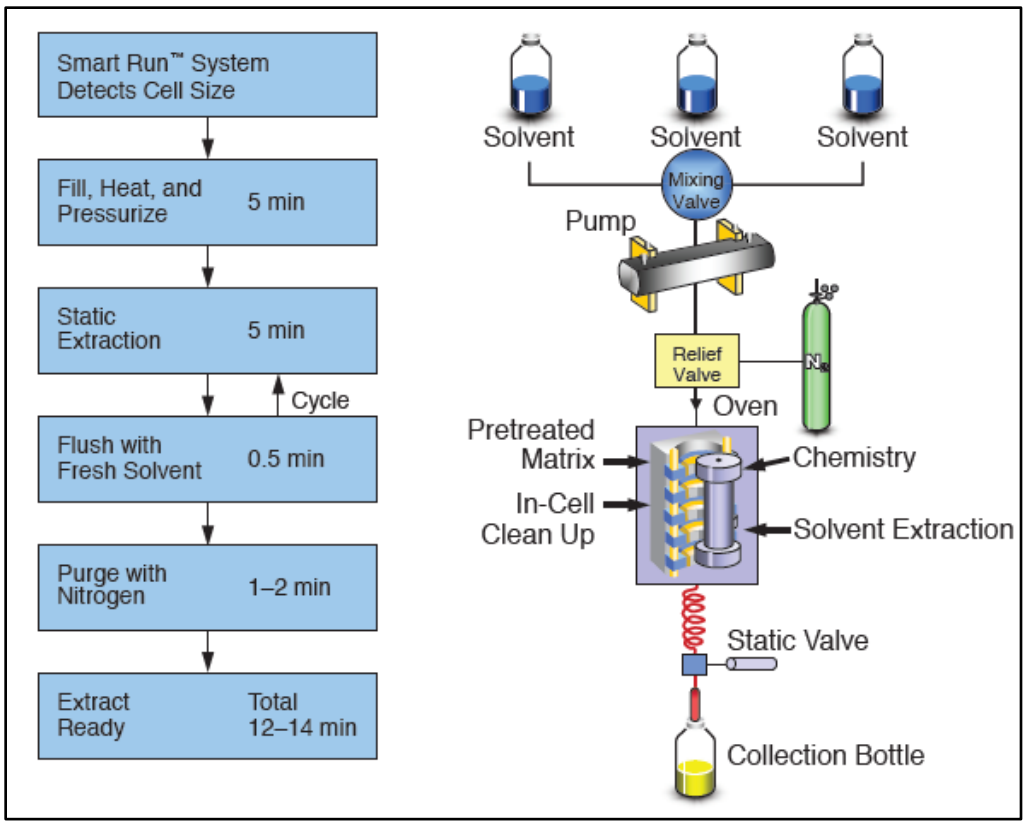


Figure 6.1: Automated solvent extraction schematic [82]

The samples were shoes that were cut into pieces and put into 10 mL cells. The extraction parameters included a pressure of 1500 psi, oven temp of 120°C, heating time of 5 mins, static time of 2*5 min cycles, flush volume as 60% of total cell volume, purge time of 60 secs and the solvent used was hexane. The EPA Method 625 was used in conjunction with the Dionex Autotrace 280 Solid-Phase Extraction Instrument (schematic shown in Figure 6.1). Sample pre-treatment was performed by adding 2.5 mL methanol and 2 mL of concentrated sulfuric acid to 500 mL of sample. The condition, rinse and load program was to rinse the cartridge with 2 mL methanol, rinse cartridge with 5 mL ethyl acetate and dichloromethane. Condition cartridge with 10 mL methanol and water. Load 550 mL of sample onto cartridge. Dry the cartridge with gas for 10 mins. The sample elute program was to collect 5 mL fraction using ethyl acetate, collect 2 mL fraction using dichloromethane. The solid-phase extraction (SPE) method used water,

methanol, ethyl acetate and methylene chloride as the solvents. The flow rates used were; Load flow- 3 mL/min, rinse flow- 40 mL/min, elute flow- 20 mL/min, rinse- air pus 20 mL/min. The sample was then injection in GC-MS system for analysis [82].

Phenolic compound analysis:

Ultrasound-assisted extraction of phenolic compounds from wheat bran was carried out in an ultrasonic cleaning bath. The volume of the bath was 10 L with a working frequency of 40 kHz. Samples were placed in 100 mL volumetric flasks with the appropriate solvent and sonicated at the required temperature for different sonication times. After the extraction, the flask was cooled to room temperature using cooling water. The wheat bran extracts were filtered through filter paper under vacuum. The solution collected in the volumetric flask was used for determination of total phenolic content. Selection of extraction solvent- Five grams of wheat bran were extracted with 100 mL of 70% methanol, 70% ethanol and 70% acetone in a volumetric flask (100 mL) and kept for sonication at 50°C. After 20 min, the supernatant and the sediment were separated by vacuum filtration. The extracts were used for the determination of the total phenolic content. The procedure of ultrasonic extraction of material was repeated twice under the same conditions. Effect of ethanol concentration on extraction of total phenolic compounds- Ethanol–water mixtures were used as extraction solvents. Phenolic compounds were extracted from wheat bran using different ethanol concentrations ranging from 20% to 95%. The wheat bran was macerated with the extracting solvents and sonicated for 20 min at 50°C. The extract was filtered under vacuum and the filtrates were used for the determination of the total phenolic content. Effect of extraction temperature on extraction of total phenolic compounds- Five grams of wheat bran were macerated with 70% ethanol, and sonicated for 20 min at different

temperatures ranging from 25°C to 75°C. The extract was filtered under vacuum and the filtrates were used for the determination of the total phenolic content [81].

This study compared conventional extraction to ultrasound assisted extraction for extraction of polyphenols from plant cells. Conventional extraction-Water bath is an indirect heating method. The plant material is heated slowly for maximum removal of chemicals. With the rise in temperature, the inner material of the plant cells starts to leach out into the aqueous medium. Longer the extraction time, better is the result. The typical temperature range for extraction of polyphenols is 20 to 50°C, since above 70°C the polyphenols start to degrade.

Ultrasound assisted extraction (UAE) is the extraction that is carried out by using ultrasound waves that creates destructive waves. This method is specifically useful to intensify mass transfer and to enhance penetration and capillary effects. Higher temperatures increases the solubility, diffusivity and pressure, which help the waves to penetrate the tissue. The contents get transported in a variety of organic and inorganic solvents. The cavitational effects of the ultrasonic waves facilitate the release of extractable compounds. Increase in the extraction of tanning material under ultrasonic vibration at a frequency of 8000 KHz for 15 min is compared with stirring at 1400 rpm for 8 h. The influence of ultrasound frequency, time and intensity on the extraction of tannins using different solvents is observed in this study [83]. Another study focussed on the use of ultrasound to aid in the extraction of contaminants from environmental samples (seen in Figure 6.2) [84]. A process known as dispersive liquid-liquid microextraction (DLLME) was used, which consists of extraction with a water-immiscible solvent and a disperser that are rapidly injected into the aqueous solution containing the analytes. This results in the formation of a cloudy solution that is separated afterwards by centrifugation. The DLLME method is simple and required short extraction times. The use of sonication in this technique

provides an increase rate of mass transfer of the analytes from the aqueous phase to the fine droplets. The recovery of the analytes depends on factors such as extraction and dispersing solvents used, the volume of the solvents, amount of sample and pH. Chlorinated hydrocarbons were used as extraction solvents and methanol, acetone was used as disperser solvents. Thus, a variety of methods can be used to carry out extraction of contaminants from fabric samples. The right method must be chosen based on the physical and chemical properties of the compounds of interest.

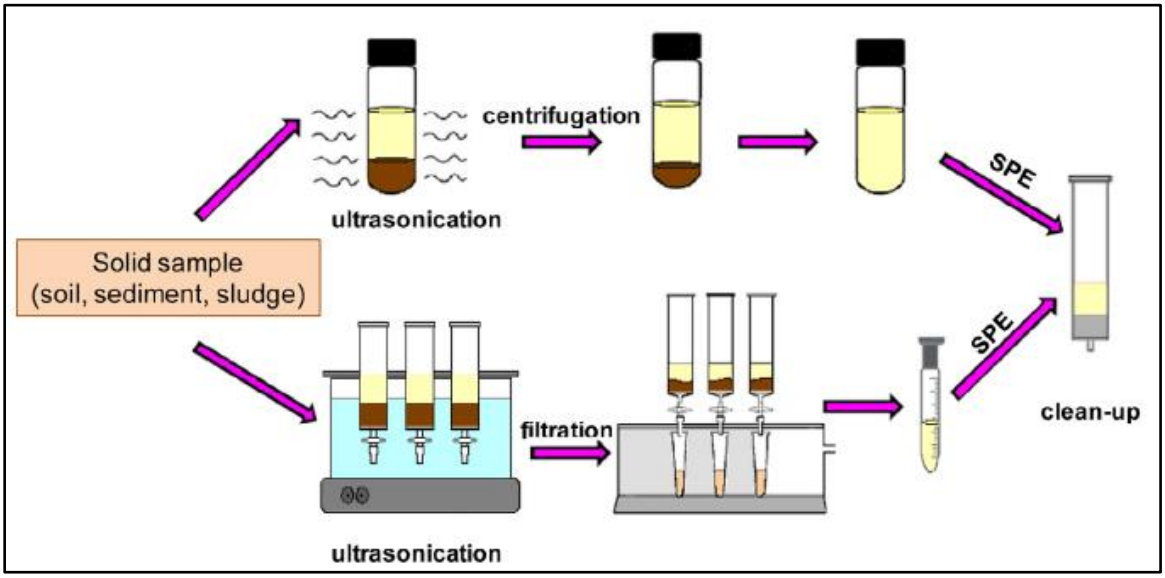


Figure 6.2: UAE for solid samples [84]

CHAPTER 7: Headspace sampling (HS)

7.1 Introduction to headspace sampling

A headspace sampler is an add-on sample introduction component that can be installed in conjunction to the GC system. The headspace GC system is used to identify and analyze volatile compounds that are released on heating in the headspace area above the sample in the vial. Some of the types of samples that can be analyzed on the headspace GC are volatiles, semi-volatiles, solvents used in packaging, blood samples, industrial oils, etc. [85]. The special feature of the headspace technique is that any solid or liquid sample can be analyzed, which otherwise is not always possible in liquid injection on the GC directly. The analytes in the headspace vial are heated at a fixed temperature and allowed to equilibrate for a fixed amount of time. The gases evolved in the headspace are then sampled using a needle [86]. The setup of the HS-GC-MS can be seen in Figure 7.1**.**

Figure 7.1. Setup of a headspace sampler connected to GC-MS

7.2 Working of the headspace GC system

The analysis of the samples begins with placing the solid/liquid sample of interest in a glass crimp top vial. A specific temperature is set for the vial to heat at for a set amount of time. The vial could also be shaken inside the oven. All the three zones in the HS instrument (oven, loop and transfer line) need to be maintained at specific temperatures. The schematic is shown in Figure 7.2. The technique follows a four-step process:

- Standby- The sample inside the vial gets heated at the set conditions in the oven present inside the headspace sampler.
- Pressurization- Inert gas is forced in the vial using a needle to increase the vapor pressure.
- Loop vent- The headspace gas is made to pass through a gas sampling loop to vent.
- Injection- The carrier gas is allowed to flow through the loop and carry the analyte gas to the GC inlet through an inert heated transfer line [85].

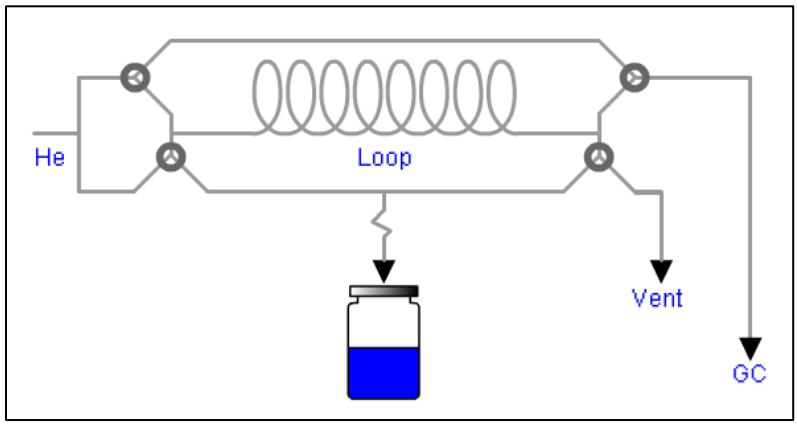


Figure 7.2. Schematic of the headspace internal system [85]

7.3 Salient features of the headspace GC system

The headspace GC system is a unique setup that allows analysis like no other instrument. The technique requires almost no sample preparation before it can be analyzed. For both, solid

and liquid analytes, the samples must be simply placed in the vial and crimped top for analysis. This helps in eliminating the signal typically lost in adsorbing and then extracting using a solvent before analysis. The headspace sampler is also a very precise at maintaining a temperature and shaking the vials inside the oven at a set rate. The oven in the HS can maintain temperatures at a very wide range of temperatures- practically 35°C to 260°C. The transfer line is inert and completely transfers all the gas directly into the split/splitless injection of the GC inlet. There are several types of modes in the headspace sampler with an option to perform multiple extractions from the same vial. The software also has a method development tool that allows to ramp up one parameter at a time to create a profile of either temperature or time with the analyte concentration.

7.4 Previous analysis using the headspace GC (HSGC) system

Even though, headspace GC is a newer generation instrument, a lot of research has been performed using this technique, owing to its unique analysis type and minimal solvent preparation. In one study the headspace sampler connected to a GC-MS system was used to analyze propolis (bee glue). The sample was allowed to equilibrate in the vial at 50°C for 10 mins after which the headspace vapor was injected into the GC inlet. The headspace method proved successful since the analyte was volatile and any sample preparative methods would lose most of the signal in the further analysis [87]. Cow's milk was analyzed for presence of volatile compounds by using the headspace GC system. Milk samples from 12 farms were collected and analyzed on the headspace GC-MS system using a heat trap set at 240°C. The results showed 41 different types of volatile compounds including aldehydes, ketones, sulfur compounds and alcohols. This method of analysis was particularly helpful to measure the low-molecular weight compounds that are difficult to measure using other techniques [88]. Acetaldehyde levels

generated from ethanol on oxidation were measured by headspace sampling. The aim was to assess whether acetaldehyde compound is responsible for increased alcohol consumption. A GC-MS single quad connected to a headspace sampler was used to heat ethanol at 60°C for 5 minutes without agitation. The GC inlet temperature was maintained at 200°C and the headspace transfer line was kept at 230°C. This method proved to be sensitive enough for detection of low levels of ethanol and acetaldehyde [89].

A study was carried out to understand the stable isotopes in nature by relating to the halogenated volatile organic compounds (HVOC's) in industrial groundwater. Dilute aqueous solutions of several chemicals such as benzene, chloroform, toluene, chlorobenzene, bromobenzene, etc were prepared in methanol as the solvent. 1-mL of these solutions was placed in the 20-mL crimp top vial and heated in the headspace oven at 37°C for 30 secs. The procedure was effective at measuring low-molecular weight VOC/HVOC's in a rapid manner [90].

Headspace GC was used to analyze the total acid number in biodiesel by a chemical reaction. In the headspace vial, a 300-mg of biodiesel sample was placed along with 5-mL isopropanol, 0.5-mL sodium chloride solution and 0.5-mL of sodium bicarbonate solution. The headspace vial was heated to 75°C for 25 mins after which the headspace gas was injection into the GC inlet. The carbon dioxide formed by the reaction of sodium bicarbonate with the acidic compounds in the biodiesel was detected by the GC [91].

Eight types of mushrooms were tested for volatile compounds that are present in the mushroom aroma. Pieces of mushroom were cut and placed in headspace vials with sodium sulphate. The vial was heated at 60°C for 20 mins and transferred to the GC inlet using a transfer line heated at 120°C. The triple axis MSD detector was used to identify 31 volatile compounds in the aroma [92].

Headspace GC-FID was used to analyze methyl bromide from Itraconazol API drug. Headspace GC was a suitable method since determination of the API at trace levels requires a highly sensitive technique where least amount of signal is lost. The drug was placed in the vial and was heated to 90°C for 30 minutes. The transfer line was heated at 110°C and a split ratio of 10:1 was used in the GC inlet injection. The HS-GC method was successful in determining Itraconazole rapidly and reliably with the LOD and LOQ detection limits [93].

Headspace GC connected to a flame ionization detector (FID) was used as a novel technique to determine VOC's from printed paper packaging materials. Printed samples were cut and placed in the headspace vial and heated at 90°C for 15 mins. The study concluded that the type of ink used for printing on the papers affected the VOC's that were detected. Headspace GC was a useful method to understand the pattern of migration of VOC's from packaging materials [94]. The volatile organosulfur compounds released from fresh and black garlic cloves were distinguished using headspace GC system. Cloves of garlic were placed inside crimp top HS vials and heated at 103°C for a fixed time. The headspace gases were injected in the GC inlet heated at 180°C. After thorough analysis, a total of 51 volatile compounds were analyzed from the garlic samples. HSGC was the right method to study the flavor volatile profiles for both the garlic types [95].

The residual solvent in Omeprazole API was measured using the HSGC system coupled to a FID detector. A standard solution of the drug was prepared in N,N-dimethylacetamide as the solvent. 1-mL of the solution was transferred into a crimp top vial and heated at 80°C for 45 mins. The headspace gas was transferred to the GC inlet set at split 10:1 mode and heated to 170°C. The analysis was successful in calculating the %recovery, LOD and LOQ limits [96].

7.5 Fundamentals and theory of headspace GC

Headspace sampling is an extraction technique that allows the volatile analytes to be separated from the heavier analytes and directly injected into the gas chromatograph for analysis. Volatile compounds can be separated from the non-volatile compounds and isolated in the vapor portion of the sample vial. The matrix to be analyzed is either in the solid/liquid phase and forms an equilibrium with the vapor molecules that are formed. A solid-vapor or liquid-vapor equilibrium is governed by the partition co-efficient (K).

7.5.1 Partition co-efficient (K)

When a sample matrix is heated, the migration of compounds into the headspace phase is also affected by the affinity to the original phase, apart from the volatility of the compounds. If the matrix is kept inside the vial for a sufficiently long time, the relative concentrations between the solid/liquid phase and the headspace phase will attain equilibrium. Each compound has a thermodynamic energy that differs when the compound is in the headspace phase v/s the solid/liquid phase. The thermodynamic energy decides the migration of the compounds between the two phases.

The partition co-efficient (K) is proportional to the ratio of the concentration of the molecules between the two phases when at equilibrium. The formula is as follows:

$$K = \frac{\mathrm{Cs}}{Cg} \qquad \text{Eq 7.1}$$

where K= partition co-efficient, Cs= concentration of the compound in the (solid/liquid) sample phase and Gg= concentration of the compounds in the headspace phase

The samples having a high K value will have a higher affinity for the sample phase as compared to the headspace phase. Ideally, the compounds to be analyzed using the headspace GC must have a lower K value than the unwanted compounds in the sample mixture. The value of K will largely depend on the compounds of interest, sample matrix and temperature used. The best results will be obtained only when a sample-headspace phase equilibrium phase is reached. This stage is also referred to as 'static headspace sampling'. If the analysis is carried out when the system is not in an equilibrium stage, the analytical results will not be accurate and there might be uncertainties in the limits of detection that are calculated.

7.5.2 Effect of temperature

Temperature is known to have an effect on the amount of analyte that gets converted to the headspace phase from the sample matrix phase. The partition co-efficient of a compound is inversely proportional to the vapor pressure. Vapor pressure increases with temperature and hence the value of K will decrease, thus transferring more compound into the headspace phase. An exception to that is water, where the vapor pressure increases with an increase in the temperature. It is generally observed that most sample matrices contain water as one of the compounds. In such a case, the temperature that is used for sampling must be carefully reviewed. Increasing the temperature significantly can increase the vapor pressure inside the vial because of the presence of water and cause over-pressurization of the vial above its rated capacity. Over-pressurization can cause a premature injection and cause double-peaks in the chromatogram.

7.5.3 Effect of Pressure

The concentration of the compound in the headspace phase is proportional to its partial pressure in the headspace phase. The pressure in the vial would increase either if the temperature is increased or a carrier gas is used to pressurize the sample vial to elevate the pressure prior to sampling. The change in pressure due to temperature is often unavoidable, since the temperature used is an important consideration for carrying out headspace GC. The elevation of pressure due to the carrier gas though, reduces the effective concentration of the sample when expressed in mole fraction. After the headspace vapor is extracted by the injector needle, the pressure would reduce as it passes through the transfer line. This may cause a dilution and ultimately affect the amount that gets injected into the GC column. This effect is only significant with higher vial pressures in use.

7.5.4 Effect of equilibration time

The time that the sample matrix is present inside the vial affects the portioning of the compound. Partitioning is when the molecules need to move between the sample phase and the headspace phase across the phase boundary. After a stipulated time, they reach equilibrium. It is difficult to understand and precisely calculate the kinetic energy of the molecules that would provide us with an optimum equilibrium time. Often multiple experiments must be performed using the same amount of analyte and analytical parameters, with different equilibration times. The peak response from the chromatogram with varied equilibration times would give an idea of the effect of equilibration time on the formation of partition co-efficient. A partition co-efficient is the ratio of the concentration of the analyte in the sample phase to the concentration in the gas

phase (as shown in Eq. 7.1). When an analyte-vapor equilibrium is reached, a maximum transfer of the analytes into the headspace phase occurs [97].

7.6 Quantitation of headspace GC

Having a headspace sampler along with the typical GC-MS has the ability to provide information about the off-gassing of compounds. With that, the instrument must be tuned separately, depending on the characteristics of the compounds to be analyzed. Factors such as vapor pressure, boiling point, equilibration time and temperature of headspace oven must be considered to achieve proper analysis. With the regular GC liquid injection, it is certain that all the analytes would be deposited onto the chromatographic column. But, when using a headspace sampler, it is almost never possible to transfer a 100% of the analytes onto the chromatographic column. This could be due to various factors such as insufficient equilibration time, lower temperature exposure and inadequate pressurization of the headspace vial. Since the amount (in mL) entering the chromatographic column is unknown, it becomes difficult to calibrate the instrument to create a method for a particular application. The quantitation is further complicated while analyzing off-gassing from a solid sample matrix, such as analyzing off-gassing of contaminants from a firefighter gear. In such cases, the compounds from the solid/liquid are usually unknown. Hence, after a qualitative identification of the compounds is done, a pure liquid reference chemical sample must be placed directly in the headspace vial and analyzed using the same instrument parameters as the solid/liquid matrix.

In one instance, headspace GC was used to measure levels of alcohol components in the blood. The target compounds were ethanol, acetaldehyde, methanol, isopropanol and acetone. For the analysis, n-propanol was used as an internal standard to measure relative amounts of the

target compounds. Simulated blood alcohol samples were prepared and analyzed by having calibration solutions of ethanol ranging from 0.01% to 0.5% in concentration. The instrument parameters encompassed an oven temperature of 40°C isothermally, GC injection temperature of 200°C, carrier gas as helium, sample equilibration temperature of 70°C, sample equilibration time of 15 minutes, vial pressure of 30 psi, transfer line temperature as 200°C and a split flow of 20 mL/min. °C [98].

Headspace GC finds numerous applications in the analysis of pharmaceutical samples, especially for trace analysis. A static headspace GC method was developed to quantitatively determine the residual solvents in a drug substance. A water-DMSO mixture was used as the base solution for the preparation of standard solutions. Additionally, n-propanol was used as the internal standard and added to all the standard solutions. The aim of the experiment was to quantitate the amounts of ethanol, THF and toluene. Reference solutions were prepared by adding 0.2 gm of the sample into individual HS vials. Then 5-mL of water-DMF solution and 1-mL of the standard solution was added. A blank solution was prepared by adding 5-mL of the water-DMF solution and 1-mL of the standard solution. The vials were then sonicated for 5 mins. The instrument parameters included a split mode injection with a split flow of 25 mL/min, injection temperature of 140°C, HS oven temperature of 80°C, HS equilibration time of 60 min, transfer line and loop temperatures at 85°C and a vial pressure of 18 psi. The quantitation of ethanol, THF and toluene was performed by using the standard addition technique. The relative areas of the compounds were plotted versus the standard added amounts. The calibration curve was calculated using the least squares method. The absolute x-value when the y-axis equals zero is the residual solvent amount in the sample added to the HS vial. Further runs were performed to validate the method and determine the limits of detection and quantitation [99].

Headspace GC coupled with a SPME setup was used to qualitatively and quantitatively analyze the volatile compounds in raw and roasted Georgia pecans. Deuterium labelled compounds including hexanal, octanal, methylpyrazine, hexanoic-6,6,6 acid and n-nonane were used as internal standards. After the chromatographic analysis, the aroma compounds were identified using their individual retention times. For quantitation, the TIC values were obtained from the mass spectrum scan. Then extracted ion peak areas of the volatile compounds and the internal standards were used to obtain relative quantitation [100].

CHAPTER 8: Off-gassing of contaminants

8.1 What is off-gassing?

8.1.1 Case 1- Storage of firefighter gear

After turnout gear is used in active firefighting, a volunteer firefighter usually carries the gear in the trunk of a sedan/SUV car or in a pickup truck, whereas a professional firefighter would carry it in a fire truck. In cars and fire trucks, there is convective heating of the gear that takes place. In pickup trucks, both sunlight (radiant) and convective heat act on the gear. There is a possibility that on heating, the gear could off-gas certain chemicals adsorbed onto the surface of the materials. The semi-volatile compounds would be of most interest, since they would keep off-gassing for longer periods of time as compared to volatiles, that immediately evaporate within 30 minutes of exposure [1]. The gear then gets stored at fire stations, either in lockers or hung on the walls. The turnout jackets are along the wall at chest level with helmets placed above them. The boots and pants are kept at head level on a platform. Even though some of the modern fire stations may be air-conditioned, most of them are still considerably hot inside. They have transparent windows that allows direct sunlight to penetrate the building. The gear that is hung on the wall experiences convective heat regularly. But it also faces radiant heat due to the direct exposure of sun rays onto it. The typical temperatures that are found in fire stations can range from 70°F to 150°F. There are other forms of contamination that are not looked in detail such as contact transfer of contaminants to the boot lining/seats in the cars. Diesel emission from trucks is a major source of toxic chemical pollution that occurs on the turnout gears. To ensure that trucks do no emit gases inside the stations, exhaust hose devices are developed.

8.1.2 Case 2: Use of firefighter gear in structural fires

When a turnout garment is used repeatedly in fire scenarios, the volatile and semi-volatile chemicals are adsorbed onto the garment. When the same gear is used in another fire scene, the embedded chemicals could be emitted from the garment. This poses to be a respiratory threat to the first responder handling the gear unprotected. The off-gassed chemicals could also penetrate through the skin at the portions under protected such as neck and the wrist. These chemicals are in addition to the fresh compounds that get released because of the burning mass.

8.2 Conditions for off-gassing in car trunks

There were several studies done to assess the heating of the inside of the car when exposed to high external temperatures. One such article depicts how hot the interior of a car can get and how quickly can it get there, shown in Figure 8.1. The plots are studies conducted at the San Francisco State University. According to this study, the maximum temperature that the interior of a car can reach is about 43°C shown in Figure 8.2 [101].

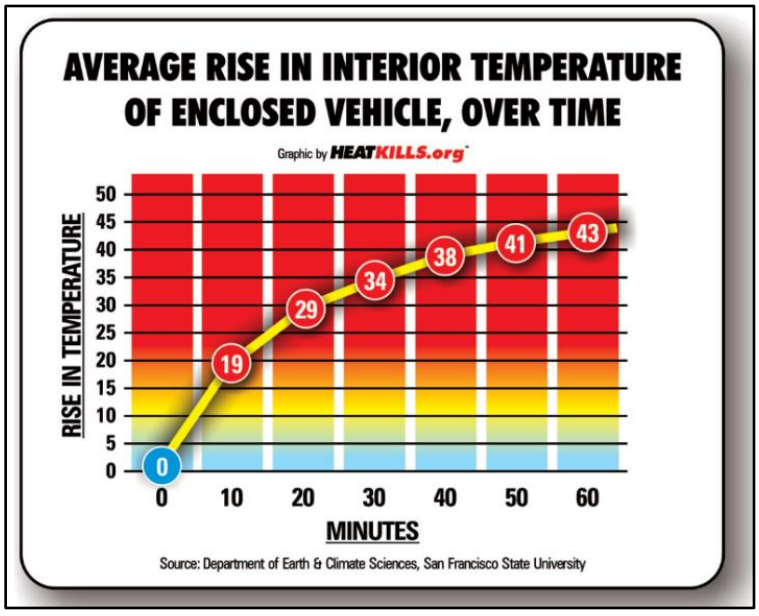


Figure 8.1. Average rise in car interior temperature v/s time [101]

Figure 8.2 Inside and outside car temperatures [101]

An interesting study by ABC news highlights the dreadful effects of high temperature inside the car. When temperatures outside range from 80°F to 100°F, the temperature inside a car parked in direct sunlight can quickly climb to between 130°F to 172°F. The temperature inside a closed car rises most quickly during the first 15 minutes that it is left in the sun [102]. Research conducted at Arizona State University and UC San Diego titled, 'How long does it take a parked car to reach deadly hot temperatures?', explains the rise in the temperature at different zones in a car that is parked out in the sun, depicted in Figure 8.3 and Figure 8.4 [103].

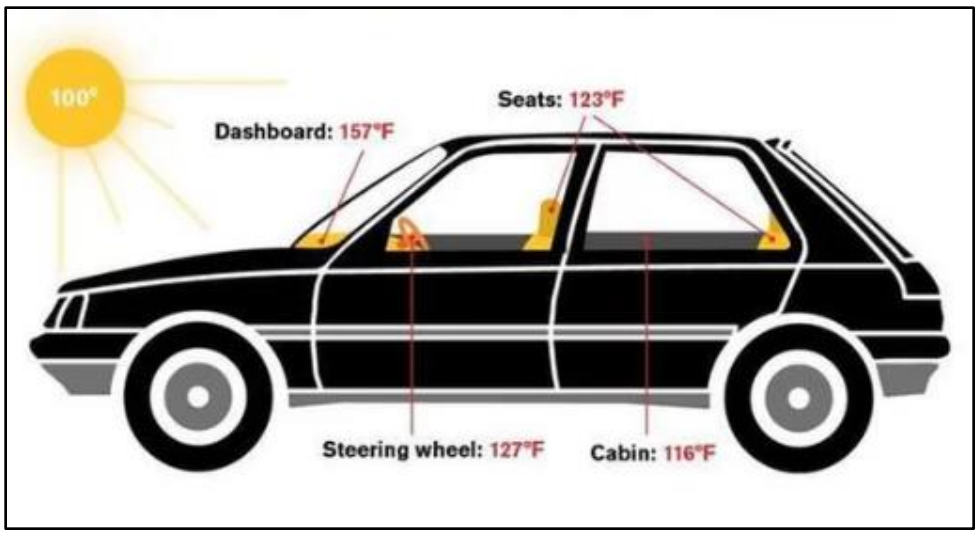


Figure 8.3. Vehicle parked in the sun on a 100°F day for 60 mins [103]

The findings were that within 1 hour, the temperature inside of a car parked in the sun on a day that reached 95°F (35°C) or hotter, hit an average of 116°F (47°C). The cars' dashboards got even hotter, reaching 157°F (69°C), on average; the steering wheels climbed to a temperature of 127°F (53°C), on average; and the temperature of the seats hit 123°F (51°C), on average.

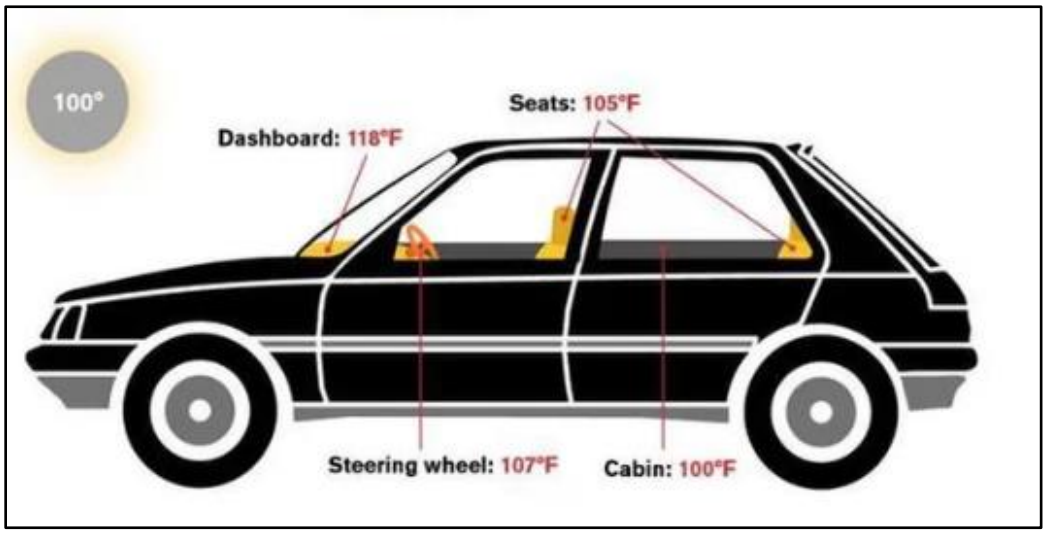


Figure 8.4. Vehicle parked in the shade on a 100°F for 60 mins [103]

Cars parked in the shade on a hot day had lower temperatures, shown in Figure 8.3. After 1 hour, the interior temperature of these cars reached an average of 100°F (38°C). The dashboards of these cars averaged 118°F (48°C); the steering wheel averaged 107°F (42°C); and the seats averaged 105°F (41°C). Another article titled, 'How hot does your car get?' shows the relative temperatures to the heating of a car at different conditions, shown in Figure 8.5.

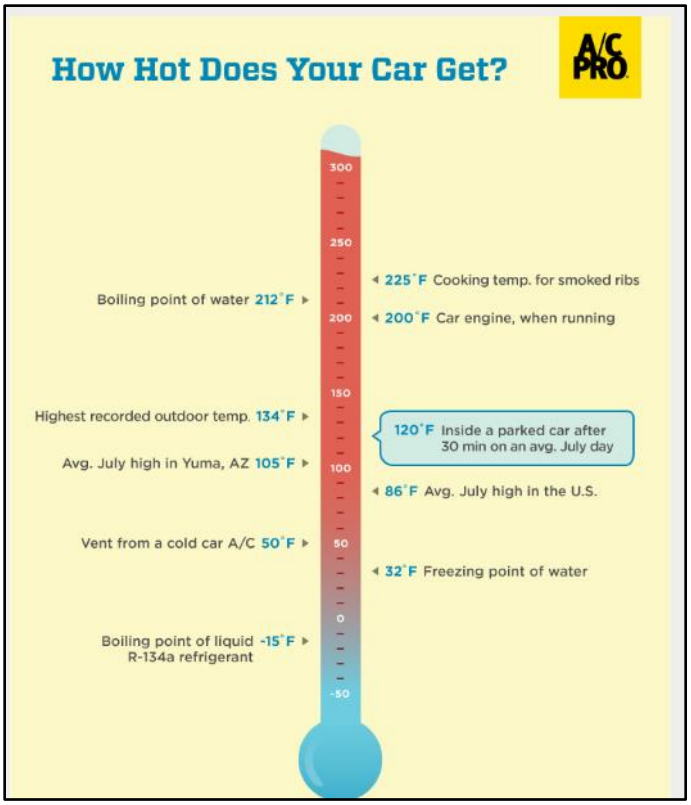


Figure 8.5. How hot does your car get [104]

A study was undertaken to study the heatstroke deaths of children in vehicles. The study gives a clear idea of the heating with time, shown in Figure 8.6.

Estimated Vehicle Interior Air Temperature v. Elapsed Time

Source: Heatstroke Deaths of Children in Vehicles (http://noheatstroke.org)

Elapsed Time	Outside Air Temperature (F)								
	70	75	80	85	90	95	100*	105*	110*
0 minutes	70	75	80	85	90	95	100	105	110
10 minutes	89	94	99	104	109	114	119	124	129
20 minutes	99	104	109	114	119	124	129	134	139
30 minutes	104	109	114	119	124	129	134	139	144
40 minutes	108	113	118	123	128	133	138	143	148
50 minutes	111	116	121	126	131	136	141	146	151
60 minutes	113	118	123	128	133	138	143	148	153
> 1 hour	115	120	125	130	135	140	145	150	155

* Unpublished, anecdotal data.

Figure 8.6. Vehicle interior air temperature v/s time [105]

Researchers at the Stanford University Medicine Department found that cars can get extremely hot even on cooler days. The temperature rise inside a parked car on sunny days with highs ranging from 72 to 96°F. This study published in the journal Pediatrics, showed that a car's interior can heat up by an average of 40°F within an hour, regardless of ambient temperature. Eighty percent of the temperature rise occurred within the first half-hour [106]. This research focuses on the interior car temperatures parked out in the sun and in the shade. The paper is titled 'Evaluating the impact of solar radiation on pediatric heat balance within enclosed, hot vehicles'. The Interior temperatures averaged 39.5°C and 47.6°C in the shade and sun, respectively, at steady-state. The study also compared the heating of midsize-sedan, minivan and economy car at the dashboard, wheel and seat areas [107]. This paper measured the heat stress that is caused due to enclosed vehicles. The study related the ambient temperature to the rise in temperature in enclosed vehicles. The basis of the study was to analyze the temperature rise in cars that leads to deaths among children. The internal

temperature of a car can reach 117°F within 60 mins, 80% of which is in the first 30 minutes, with the ambient temp being 72°F. Generally, after 60 mins, the internal temp can increase by 40F when the outside temp is between 72°F to 96°F. Even opening the windows did not lead to a huge decrease in internal car temperatures [108].

Volunteer firefighters carry the contaminated gear back to the fire station in the trunk of their cars and professional firefighters usually carry the gear in the fire trucks. However, in both the cases the interior of the vehicles gets hot. As seen in multiple studies, the temperature inside a car can get sufficiently hot, as high as 172°F [102]. In such a case, the contaminants present on the used firefighter gear could possibly off-gas compounds that have a boiling point around that range of temperature. Generally, the gear placed in the vehicle gets taken out after about an hour. During this time, if chemicals off-gas, the firefighters are at a grave risk of inhaling the chemicals. Some of the chemicals that off-gas could be toxic and would pose a health hazard to the firefighters, who are not protected by respiratory protection in the vehicle.

8.3 Conditions for off-gassing in fire stations

The contaminated gear stored in the fire stations could possibly be off-gassing because of the elevated temperatures inside the engine bays and the facility where the gear is stored. The Department of Defense mandates rules and regulations about the maintenance and architecture of a fire station. These details are a part of the ‘Unified Facilities Criteria’ document which contains every aspect of the infrastructure, storage, cleaning and the auxiliary requirements of fire stations and other emergency responder stations. The PPE provides storage for the firefighters’ protective gear. A well-ventilated locker is assigned to each member of the firefighting crew. Sufficient floor area in front of each locker is required for easy access during

operation. The area is kept under constant negative pressure to evacuate gaseous emissions from stored gear. The minimum ceiling height is 2.4 m (8 ft). The temperature is to be maintained between 20°C (68 F) and 26°C (78 F). This room has to be negatively pressurized with a dedicated exhaust vent to the outside [109]. The research identified the immediate thermal environment of firefighters in live-fire training scenarios. The pre-flashover conditions have temperatures between 100°C and 300°C with a radiant flux between 5 kW/m^2 and 12 kW/m^2 [110].

This study was focused on the equipment contamination in fire stations. It is advisable to store and transport turnout ensembles outside personal vehicle cabins during the ride back to the station, if possible. It has been demonstrated that most off-gassing of VOCs occurs initially. This is the most vital period during which to avoid riding in a closed cab with used turnout gear. Try to place gear in a protective case or bag to prevent cross contamination, when it must be transported prior to cleaning and/or decontamination [111]. The risks associated with PPE and other equipment are- The gear being in contact with non-volatile contaminants such as polyaromatic hydrocarbons (PAHs) and diesel exhaust particles. Permeation and penetration of some contaminants through turnout gear and PPE. Inconsistent use of protective gloves and other PPE to prevent contact during overhaul activities. Wearing the wrong gloves which do not provide the required protection. Failure to properly decontaminate turnout gear, hoses and other equipment, some of which are made of fabric materials and porous in nature.

8.4 Previous studies on off-gassing of toxic contaminants

The paper by Fent et al, presents the study on contamination of firefighter personal protective equipment and skin and the effectiveness of decontamination procedure [112].

Chemicals arising as by-products of combustion can penetrate through the skin. Also, cross transfer of contaminants can occur from the PPE to the skin. For the study, PAHs and VOC's were used as markers for volatile and non-volatile substances respectively to investigate the contamination on the firefighter's turnout gear and skin. Several samples were taken during the experiment- wipe sample from the exterior of the turnout gear, pre and post fire, VOC off-gassing from the gear was measured pre, post fire and post decontamination, wipe samples were taken from neck and finger pre and post fire. PAH particulates were looked at for skin and surface testing, while VOC, HCN gas and vapors were used to look at off-gassing. Suits were hung in closets and the air was sampled after every 15 min to test for off-gassed products. For the sampling of off-gassing, before and after the firefighting scenario, the gear was hung on a 1.8 m high bars inside enclosures measuring 7.1 cubic meters. The enclosed cabinets were used to imitate the volume of a 6-seat cabin. The cabinets were lined with Tyvek® material, kept outside in an open bay away from the sun. Ambient temperature was maintained for the study that ranged from 18°C to 22°C. The experiment on sampling for VOC's and HCN was carried out for 15 minutes, which was a representative time of the firefighting crew returning to their fire stations [112].

The Firefighter Cancer Support Network published some startling figures about the prominence of cancer in the firefighting profession. Firefighters are 2.2 times more prone to have cancer than the general population. Some of the more specific rates are as follows- Testicular cancer: 2.02 times higher than normal, Multiple myeloma: 1.53 times higher, Non-Hodgkin's lymphoma: 1.51 times, Skin cancer: 1.39 times, Prostate cancer: 1.28 times, Malignant melanoma: 1.31 times, Brain cancer: 1.31 times, Colon cancer: 1.21 times, Leukemia: 1.14 times.

Currently, the turnout gear is cleaned using detergents/soaps with water. ROutibe and advanced cleaning of structural suits include specific requirements of pH, etc. for the chemicals to be used as per NFPA [113].

Air sampling was carried out to analyze the off-gassing of toxic chemicals from shipping products. For the same, the ambient air from the containers and storage houses was sampled to be able to detect any fumigants or chemicals that possibly off-gas from products that are shipped globally. TD-GC-MS (Thermal desorption-GC-MS) was used to detect the recommended exposure limit (REL) for methyl bromide, sulfuryl fluoride (sulfuryl difluoride), methyl iodide (iodomethane), propylene dichloride (1,2-dichloropropane), ethylene dichloride (1,2-dichloroethane), chloropicrin (trichloronitromethane), and the toxic industrial solvents benzene, toluene and carbon disulphide. The method for experimental off-gassing was to investigate the desorption behavior of fumigants from consumer products in a specified time course, wrapping paper (80 g/m 100% cellulose) and nylon socks (85% polyamide and 15% elastane) were fumigated with 100 ppm phosphine, methyl bromide or 1,2-dichloroethane, for 72 h in a fumigation chamber of 4 L volume. 3 independent replicates of the same setup were taken. Then, the fumigation samples were transferred to a desorption chamber having a 52-liter capacity. At consecutive days, air samples were collected repeatedly from the side of the chamber using a gas jumbo syringe having a 1-liter volume. After each sampling, the chamber had been ventilated completely with fresh air to simulate natural conditions at a storage room or a consumer home. This procedure was repeated till the concentration of fumigants in the air samples reached the detection limit. Air samples that were transferred from the gas jumbo syringe into tedlar bags were analyzed by TD-2D-GC-MS/FPD. Toys were found to off-gas way higher than the occupational exposure limits even after 21 days [114,115,116,117].

A study by Firedex explained the fireground threats, risks and issues with personal protective equipment that firefighters use. Combustion by-products on the turnout suits include non-volatile, semi-volatile and volatile compounds that are in the form of condensed liquid/solid and gas phase. Non-volatiles include flame retardants, semi-volatiles include PAHs and benzene/toluene are VOC's. The non-volatile compounds on the PPE may be dermally absorbed into the skin or hand-to-mouth ingestion and cause problems. Volatiles and semi-volatiles could be inhaled since the PPE acts as a temporary adsorptive material for the airborne contaminants that may be released in the air [118]

The differences between the NIOSH and QFES studies are shown in Table 8.1 [118]

Table 8.1: Differences in study between NIOSH and QFES [118]

	NIOSH study	QFES study
PPE tested for off-gassing	Turnout coat, trousers, hood, boots, helmet and gloves	Turnout coat and trousers
Pre-fire condition of PPE	Laundered turnout coat and trousers, new hood; and other items were used and not cleaned	New turnout coat and trousers
Analytes	VOC's	VOC's, hydrogen cyanide (HCN), carbonyl compounds (ketones and aldehydes), low molecular weight PAHs
Fuel package for fires	Typical family room furnishings (overstuffed chair, bookshelf, computer, table, carpet and padding)	Particle board
Number of scenarios	PPE tested for off-gassing after use in one scenario	PPE tested for off-gassing after use in four consecutive scenarios
Duration of each scenario	18-20 min	10- 18 min
Timing of off-gas sampling	Began measurements 25 min after completing firefighting and sampled over 15 min	Began measurements immediately after completing firefighting and sampled over 24 hours
Enclosure for off-gas sampling	Polycarbonate case, 6.4ft^3	Polyethylene bag, 3.2 ft^3
Number of off-gas tests	6 pre-fire and 6 post-fire	3 pre-fire, 3 post-fire and 3 post-laundering
Other tests	Measured firefighters' exhaled breath immediately after each scenario and analyzed for VOC's	Measured PAH deposition on turnout gear after each scenario

Other compounds such as benzene, toluene, ethyl benzene, xylene, styrene, aldehydes and HCN. VOC's generally evaporate from the surface quickly whereas the semi-volatile compounds evaporate a long period of time. Also, PAHs and other carbonaceous substances that contaminate PPE acts as activated carbon and adsorbs VOC's that may be released in the atmosphere later [118].

The accumulation of off-gassing products such as PAHs, VOC's and carbonyl compounds was assessed in another investigation. Phenols, phthalates and PAHs were found to be present in the gear on destructive testing. Controlled fires were set up with firefighters wearing proper PPE and multi-layered turnout suit. To test PAH deposition, 4 wipes were attached to the outer part of the suit to collect contaminants; each was taken off after one part of the experiment. They were stored at -4°C and tested using EPA Compendium Method TO-13A. For analyzing off-gassing, samples were kept in polyethylene bags for 24 hours, air was continuously drawn through the bag to sample the air. PAHs were sampled at flow rates of 2000 mL/min using glass sorbent tubes filled with 76 mm of polyurethane foam and incorporating a glass fiber pre-filter. Samples were solvent-extracted and analyzed by using the principles of the EPA Compendium Method TO-13A. Volatile organic compounds were sampled at flow rates of 75 mL/min using stainless steel tubes supplied by Queensland Health Forensic and Scientific Services, containing 150 mg of Tenax followed by 100 mg of Carboxen 569. Carbonyl compounds (aldehydes and ketones) were sampled using glass sorbent tubes packed with 2,4-dinitrophenylhydrazinecoated silica gel and incorporating an ozone scrubber (SKC model 226-120), at flow rates of 500 mL/min [119].

A research experiment conducted at the Textile Protection and Comfort Center (TPACC), measure the off-gassing products from protective fabrics exposed to simulated flash fire conditions [121]. There could be chemical skin burns due to the acid off-gassing from flame

retardant (FR) materials used in clothes for the firefighters. Flash fire conditions are extremely intense conditions that comprise of conductive, convective and radiant heat and flame exposures for a short period of about 3-5 secs. The gases evolved in such conditions is different from the regular fire scenarios. Materials such as FR cotton, Aramid and many others were tested to see what gets released. The flame retardants possibly evaporate from the garment on exposure to heat which is dangerous to the wearer. The typical TPP method, shown in Figure 8.7 was modified as following- A test specimen of a fixed dimension was placed on the TPP tester. A 6.5 mm spacer and a copper slug calorimeter were mounted on a horizontal source that provided convective and radiant heat with an exposure of 84 kW/m^2. As the thermal energy passed through the fabric sample there was a change in the temperature. This was measured in combination with the time of the calorimeter to achieve a cumulative thermal energy. The cumulative thermal energy was plotted against an empirical performance curve from Stoll criteria. The HTP value was then found as per the ASTM F2700-8 Standard Test Method for Unsteady-State Heat Transfer Evaluation of Flame Resistant Materials for Clothing and Continuous Heating.

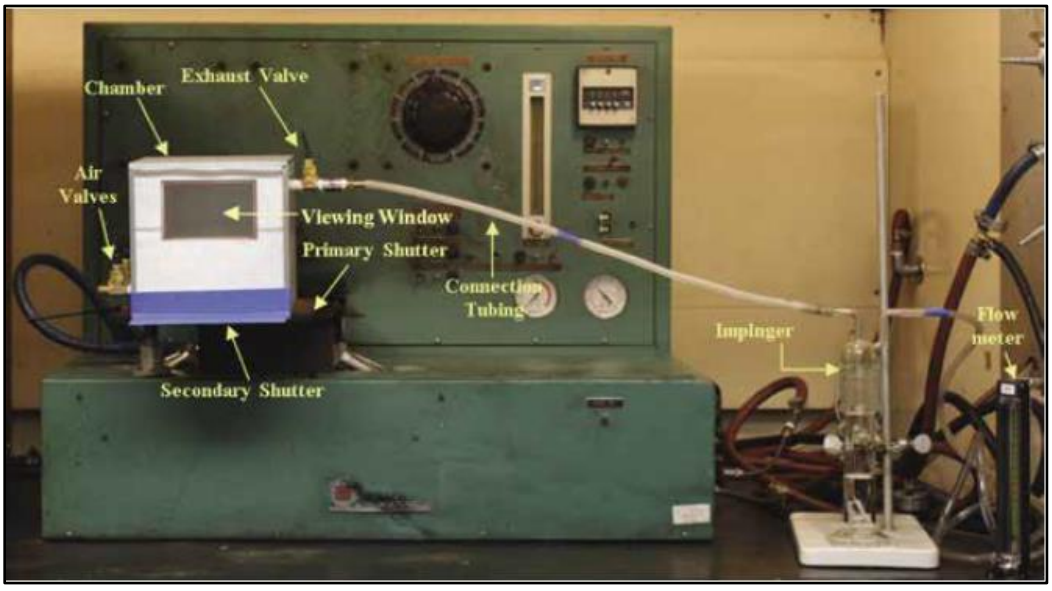


Figure 8.7. Off-Gassing setup at TPACC, NCSU [120]

The study looked at chlorides (HCL off-gas), cyanides (HCN off-gas), volatiles organic compounds. The off-gassed air from the chamber was passed into an impinge containing 0.1 N NaOH solution. Different analytical methods were used for chloride analysis, cyanide analysis and organic chemical analysis. Reagent free Ion-chromatography was used for cyanide and chloride analysis, whereas GC-MS was used for volatile organics. The GC parameters were, Rxi-624 Sil MS column (20m, 0.18mm ID, 1.0µmdf) with a split ratio of 50:1, Inlet temp- 250°C, Injection vol- 1µL. The results showed that toxic chemicals such as HCN gas, HCl gas, Volatile organic gases were released from flame-resistant treated fabrics [120]. A cup furnace apparatus was used to observe the thermal decomposition of selected flame-resistant clothing materials. The sample material was placed inside a temperature controlled- heated quartz crucible and a 42-litre glass collection vessel were attached to collect the decomposed materials (seen in Figure 8.8). For sampling of acid gases, an impinger filled with dilute sodium hydroxide was used. Gases such as oxygen, carbon-monoxide and carbon-dioxide were measured too. A special Tedlar bag was used to collect the decomposed materials at the midpoint of the test to test for organic materials.

Figure 8.8. Test apparatus of cup furnace [121]

Four FR materials that were used in study were aramid, FR-treated cotton, modacrylic/aramid blend and modacrylic/cotton blend. The sample was weighed to 2 gm and placed in the crucible in a rolled form. Temperature ranges used were 275-475°C. The samples were placed in the heated crucible for 10 mins and further heated. The impinger was passed with atmosphere from the collection chamber at a flow rate of 1 mL/min. At the mid-point (5 min) into the test, a 1-litre atmosphere sample was drawn from the collection chamber for gas-phase composition analysis. Sometimes, the impinger solution became dark colored and viscous. The 10 min exposure was chosen according to the US Forest Service 5100-615 test method. The initial volume of NaOH was 20 mL, which was increased to 25 mL by adding distilled water for rinsing. The results proved that all materials off-gassed HCN and HCL gases after exposure. Individual materials released a host of other toxic chemicals depending on the chemical structure and the finishing agent used [121].

The toxicity of the fire effluents released from textiles and upholstery materials was tested after exposure to higher temperatures. 11 different textile and 6 upholstery materials were

exposed to a range of temperatures to analyze the airborne contaminants released. The toxicities were further examined on rats as experimental animals. The textile materials used were cotton, viscose, cotton-viscose blend, wool, polyester, modacrylic, polyvinyl alcohol- polyvinylchloride. All the materials were treated with different flame retardants and other chemicals. The method (seen in Figure 8.9) used was: The samples were placed inside a quartz tube within a moving ring oven with airflow as per DIN 53436 test method. The temperature inside the tube was adjusted to 500°C or 700°C. The dimensions of test samples were 40 cm long and 1.5 cm wide. The weight of the samples was adjusted to 0.12 gm/cm. Air was passed through the tube at 100 l/hr. The fire gases and smoke were carried by the air flowing into the mixing chamber, where additional 300 l/hr of air was passed to dilute and cool the mixture. The test was run for a total of 30 minutes.

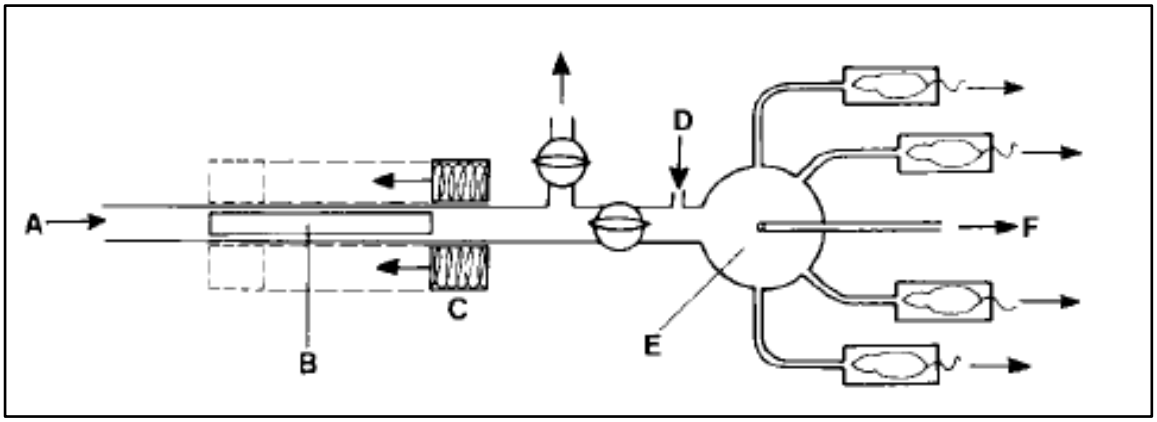


Figure 8.9. Schematic of testing method [122]

where, A- combustion air, B- sample placed in a cuvette, C-moving furnace, D-dilution air, E-distribution chamber, F- gas sampling. HCN and HCL were measured using setups for air bubbling and ion-selective electrode testing. VOC's were measured by absorbing them onto Tenax packed within a steel tube through which the gas was passed at a speed of 0.5 to 1 l/min. The ID of the tube was 0.5 cm and the amount of Tenax was 0.35 gm. The VOC's were analyzed on a GC-MS using a Porapak Q/1 steel column. Different materials were compared at different

temperatures for the gases that evolved out. Toxicity tests were conducted in rats to evaluate the effect of various toxic gases [122].

Volatile organic compounds off-gassing from firefighters' personal protective equipment ensembles after use were analyzed [123]. 15 firefighters were exposed to actual simulation of a structural fire. They wore the exact gear used in regular fires with the complete equipment. 2 of the firefighter ensembles were chosen to be tested for off-gassing of VOC. The air inside the burning structure was collected using 6-litre canisters every 15 minutes and a 1-hour sample for background samples. After the fire, the used gear was kept for 25 minutes, since that is the time that the firefighters require to pack their equipment after a structural fire. Then the gear elements were placed inside a closed case. Canisters were connected to the case to be able to collect the air from inside. The temperature range used for the used gear was 28 to 30°C. A blank run using new turn-out coat and trousers was performed at a temperature range of 23 to 28°C. After analyzing the air, it was found that 14 main compounds off-gassed from the gear. The concentrations were compared with brand new gear and with background samples. The short-term OEL was calculated for all the compounds. The areas of the body that were susceptible to dermal absorption were studied. The possibility of inhalation of these compounds was assessed. Benzene and syrene were found to be off-gassing, which were conclusively marked as group 1 (carcinogenic to humans) and group 2B (possibly carcinogenic to humans), by the International Agency for Research on Cancer. Results suggest that the concentrations of VOC's post 25-min of exposure was well below the short-term OEL. The compounds could be inhaled by the first responders in absence of a respirator such as after doffing of PPE, wearing part of the PPE, packing their equipment or storing their PPE in the vehicles driving back to the fire station [1]. The systemic exposure to PAHs and benzene in firefighters suppressing controlled structure fires

was tested. Controlled burns were carried out with firefighters wearing laundered gear. Several parameters such as PAH and benzene concentrations, urine analysis, skin wipe sampling, exhaled breath air sampling and air sampling of the room was carried out. The respirable matter was sampled using aluminum cyclone and PTFE filters. Gases and vapors were sampled using SKC XAD-2 adsorbent tube. The flowrate was 2.5 l/min that provided a 4 µm aerodynamic diameter cut point for the cyclone. The analysis of the samples were carried out using NIOSH Method 5506 which used HPLC with photodiode array detector. The conclusions of the study were that even firefighters with full protective ensembles are prone to PAHs entering their skin. This is especially through the neck area and through the hoods, that provide insufficient dermal protection [123].

Rreal-time monitoring and assessment of thermal and toxicological risk associated with fire retardant textiles was conducted in a full-size simulation of an engulfment flash fire. A flash fire condition was replicated using ASTM F1930 and ISO 13506. A manikin was subjected to a 84 kW/m2 heat exposure using propane torches for 3-4 secs. 9 different types of fabrics were tested, some of which were FR materials. Air was sampled from the chamber in two ways: 1) was passed through a heated line into the in-line FTIR 2) passed to the cyclone separator. Calorimeters were placed at various parts of the manikin to measure the heat flux received. Concentrations of hydrogen chloride, hydrogen cyanide, nitrogen oxides and sulphur dioxide were recorded.

IDLH values for different gases with their health effects were hydrogen chloride- 50 ppm or 57.8 mg over a 90-sec period (causes localized inflammation and necrosis; forms HCl on reacting with water).Hydrogen Cyanide- 20.1 mg for a period of 20 sec (could cause progressive neurological impairment, unconsciousness). Nitrogen Oxides- 29.2 mg for a period of 90 secs (produces nitric

acid when mixes with the water in the mucosal lining of the respiratory tract).Sulphur Dioxide-203 mg for a period of 90 secs (respiratory irritant, produces sulphuric acid on mixing with the water in the lining of the respiratory tract). Antimony Trioxide (particulate matter)- 193 mg over a period of 90 secs (chronic respiratory diseases) [124].

The occurrence of fumigants and hazardous off-gassing chemicals in shipping containers arriving in Sweden was researched. A qualitatively and quantitatively assessment of the gaseous fumigants and volatile compounds off-gassing from shipping containers was performed. For most of the samples, a FTIR and PID were used to analyzed the compounds. GC-MS was used to analyze a small number of adsorbent samples. The air inside the container was measured using a specialized tool: 40-cm stainless steel tube (outer diameter 20 mm) with a flat nozzle (outer dimensions 20 × 3 × 0.5 cm) and two 9-mm entry holes near the tip. The handheld PID was calibrated to toluene, for which the Swedish OEL is 50 ppm. The collected container was put into Tedlar sample bags and pumped through adsorbent tubes (Anasorb 747) with a flow rate of 200 mL/min. Each bag held about 6 l of air. The adsorbent tubes were extracted with dichloromethane and analyzed using a GC-MS. The column used on the GC column was a phenyl-dimethylpolysiloxane. The VOC's were assessed in the 80-300°C boiling point range. The method was also used to determine aromatics, aliphatics, terpenes, aldehydes, ketones, alcohols, glycol ethers and chlorinated compounds qualitatively. A lot of compounds were found in the sampled air. Prominently acetaldehyde, acetone, benzene, formaldehyde, methane, phosphine, toluene, trichloroethylene and xylene. The readings from PID, FTIR and GC-MS were compared and shortcomings of the methods was discussed [125].

The occupational exposure to polycyclic aromatic hydrocarbons and elevated cancer incidence in firefighters was studied. A controlled burn was carried out and various types of

samples were collected to measure the amount of PAHs (seen in Figure 8.10). PAHs are known carcinogens and adversely affect the human health. Wipe samples were taken from skin and PPE, XAD adsorption tubes were used to collect airborne PAHs from the general room and storage areas [126].

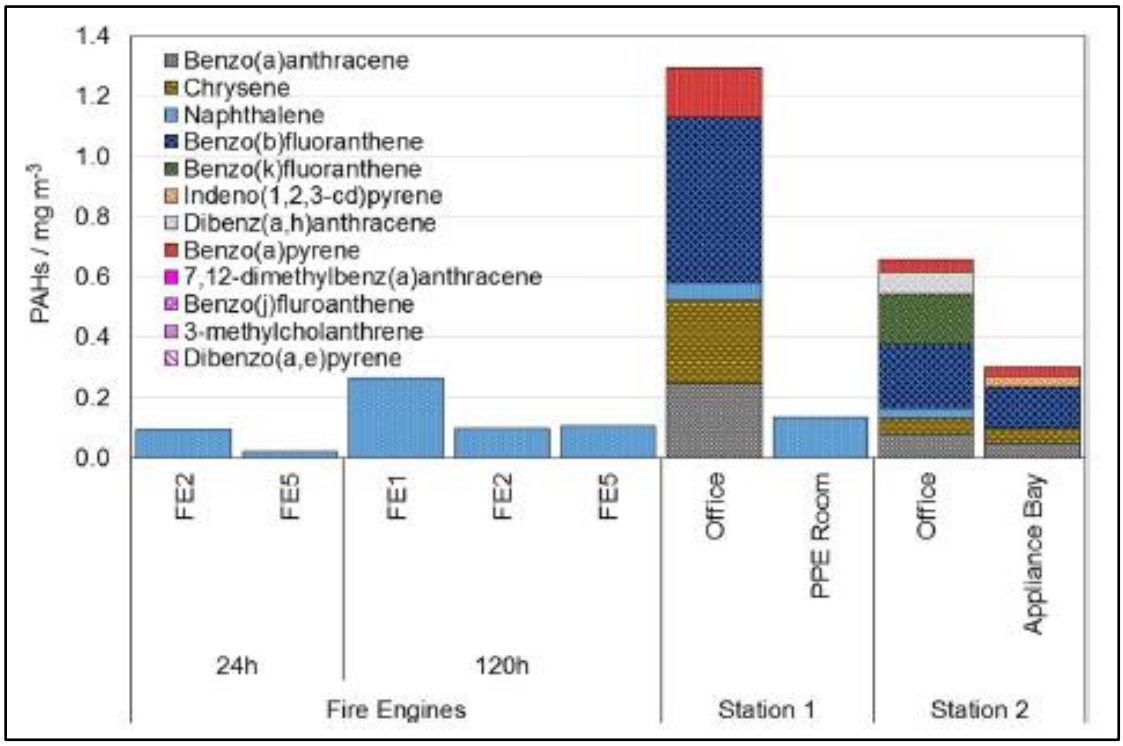


Figure 8.10. PAH levels in fire engines and fire stations [126]

8.5 Other Studies and methods for air sampling of heated liquids and gases

There are various methods for sampling the gases/vapors released from materials, when exposed to heat. Some of them include solid-phase microextraction (SPME), headspace sampling and active air sampling using a pump. Fire debris analysis is a crucial aspect in understanding the details of the occurrence and the propagation of the fire. To review the assessment, various methods and configurations were discussed. This included a variety of methods, including the headspace vapor sampling. This technique follows principles of ASTM E1388-00 method which

requires a closed lid container with a tiny opening, temperature measuring device inserted in the container, a 0.5-5 mL syringe to collect gas and a heating oven. The container is heated for about 20 to 60 minutes until it reaches a temperature of 90°C. After taking the container out of the oven, the syringe is plunged in and is flushed three times with the gases. Another method is the dynamic headspace concentration which follows principles of ASTM E1413-00 method. This requires a positive/negative pressure apparatus, adsorption tube, heating assembly and a temperature measurement device. Simultaneous off-gassed vapors are drawn into the adsorbent tube as the container system is heated. The adsorbent material used is activated carbon. After the sample is collected in the tube, the tube is cooled and then an elution solvent is passed for further analysis.

The dynamic headspace method is a destructive form of testing. Additionally, passive headspace concentration with activated carbon can be used to carry out fire debris analysis. This technique follows principle of ASTM E1412-00 method that requires a heating assembly, temperature measurement device and activated charcoal. The rectangular activated charcoal strip is perforated and suspended inside the container. The assembly is then heated for several hours in the oven. After cooling, the activated carbon strip is taken out and elution solvent such as carbon disulphide or diethyl ether is run to desorb the contaminants.

Another method is the headspace concentration with solid phase microextraction. This technique follows principles of ASTM E2144-01 method that requires a heating assembly, temperature measurement device, a SPME fiber with holder, punch and a septum. The SPME fiber is coated with a polymeric stationary phase which is held within a needle contained inside a holder. A SPME fiber with a 100 μm thickness of polydimethylsiloxane (PDMS) is recommended for ignitable liquids in the C10 – C25 range and a fiber with an 85 μm thickness of polyacrylate or a fiber with a 75 μm thickness of Carboxen/PDMS is recommended for

ignitable liquids in the C1 – C10 range. After the container lid is punctured, a septum is inserted into the hole. The container is placed within an oven at a temperature between 60°C to 80°C for approximately 30 minutes to volatilize the ignitable liquid residues into the headspace. Immediately after removal from the oven the septum in the container lid is punctured with the SPME needle. The SPME fiber is inserted into the headspace allowing the ignitable liquid residues to adsorb onto the fiber. After one exposure of 5-15 minutes, the SPME fiber is retracted into the needle and the SPME assembly is removed from the septum. Upon removal from the heated headspace, the SPME fiber is inserted in the heated injection port of a GC [127].

A study was performed to study the rapid, one-pot derivatization and distillation of chlorophenols from solid samples with their on-line enrichment. An open vessel microwave-assisted steam distillation system has been employed for extractive distillation of chlorophenols, mainly for pentachlorophenol which a carcinogenic compound. Stock solution used was 1000 mg/l of a mixture of chlorophenols that was calibrated on GC using 0.01-1 ug/mL n-hexane. Microwave waves were bombarded on the samples, which off-gassed the VOC's that passed through the SPE extraction phase [128].

A comparative study to analyze VOC gases was performed. The test ASTM D 2369 method used was compared to the standardized existing methods such as SCAQMD Method 313 (M313), ASTM Standard Test Method E 1868-10 (E1868), and U.S. EPA Reference Method 24 (M24). ASTM Method D 2369 is used to determine the VOC content in coatings. The specimens are heated to 110°C for 20 mins in forced draft oven. Experimental methods used for testing included an ambient evaporation of compounds weighing 1 gm, placed in 9-mm petri dishes. The temperature was kept between 20°C and 30°C until the coatings evaporated. Another method used was the ASTM Standard Test Method E 1868-10. For the same, the experiments were

carried out on a STA 449 F1-Jupiter equipped with a silicon carbide furnace with a type S thermocouple and a thermogravimetric (TG) sample carrier with a radiation shield, a 10-mm aluminum oxide slip-on plate, a Q5000 100-mL platinum pan and a type S thermocouple. Pure compounds were analyzed and volatilization was reported as weight percent nonvolatile. The E1868 method calculates volatility by converting weight percent loss at the end of 110 min at 81°C in a TGA into VOC content. A volatile compound is defined as a compound that evaporates more than 95% by weight within 6 months under ambient evaporation testing conditions. A semi-volatile compound is defined here as a compound that evaporates between 5% and 95% by weight during the 6 months under ambient evaporation testing conditions. A nonvolatile compound is defined as a compound that evaporates less than 5% by weight in 6 months under ambient evaporation testing conditions [129].

Different compounds present after a fire scene were tested using a variety of test methods. To test the presence of PAHs, the OSHA 58 test method was used. This method required cassettes containing glass fiber filters, air tubing, and an air pump set at 2 liters per minute. An Aircheck 52 pump to was connected to a 3/8 inch Tygon air tubing that was outfitted with a plastic luer lock adapter and an air flow regulator. The air flow rate was checked by attaching an air flow rotameter. The testing cassette was inserted onto the tubing and the pump was started for a minimum of 10 minutes. When the appropriate time had elapsed, the pump was turned off, and the cassette was removed from the tubing. The glass fiber filter was removed from the cassette and placed in a glass vial, which was sealed with a cap containing a PTFE liner. The sample was then refrigerated, kept out of sunlight, and shipped to the laboratory cold within 24 hours of collection. The presence of aldehyde was carried out using the NIOSH 2016 method. The aldehyde profile included testing for Benzaldehyde, Valeraldehyde, Propionaldehyde,

Butyraldehyde, Crotonaldehyde, Formaldehyde, Isovaleraldehyde, and Acetaldehyde. The method utilizes a sorbent tube containing silica gel, air tubing, and an air pump set at 0.4 liters per minute. An Aircheck® 52 pump was connected to a 1/4 inch Tygon air tubing which is fitted with a plastic luer lock adapter and air flow regulator. The air flow rate was checked by attaching an air flow rotameter. The pump was attached and tubing was fitted onto the tripod to prepare for the insertion of the testing ampule. The testing ampule ends are broken and the sorbent tube is inserted onto the tubing. The pump is then started for a minimum of 10 minutes. After a stipulated time, the pump is turned off and the sorbent tube is removed from the tubing. The sorbent tube ends are capped and the tube is refrigerated, kept out of sunlight, and shipped to the laboratory cold within 24 hours of collection. The presence of acids was studies using the NIOSH 7903 test method. The acid profile included testing for Sulfuric Acid, Phosphoric Acid, Hydrogen Bromide, Hydrochloric Acid, Hydrofluoric Acid, and Nitric Acid. The test method utilizes sorbent tubes, air tubing, and an air pump set at 0.5 liters per minute. The entire procedure is the same as for aldehydes except that the acid sorbent tubes need not be refrigerated. HCN- The NIOSH 6010 testing method is used which requires sorbent tubes, air tubing, and an air pump set at 0.2 liters per minute (lpm). The entire procedure is the same as for aldehydes except that the acid sorbent tubes need not be refrigerated. The presence of VOC profile was tested for the 63 most prevalent compounds found in the sample using the OSHA TO15 testing method. The actual device collected air samples is an evacuated air cylinder. The air cylinder holds 400cc of air and is outfitted with a quick grab regulator, which regulates the flow of air to a constant rate from vacuum pressure. Sampling in the field is accomplished by a) positioning the sampler and the evacuated air cylinder in the atmosphere to be sampled; b) attaching the quick grab regulator to the evacuated air cylinder; c) allowing the evacuated air cylinder to draw air for 10 minutes d)

removing the quick grab regulator. The sample is contained within the evacuated air cylinder and shipped to the laboratory within 24 hours [130].

A targeted standardized method must be used to analyze specific compounds. The physical and chemical properties of the compounds of interest must be considered carefully while using a test method to detect and analyze samples.

Chapter 9: Development of a GC-MS method for the analysis of select fireground contaminants

9.1 Introduction

Gas chromatography (GC) coupled with a suitable detector is an analytical technique that is commonly used to detect, identify and analyze various chemicals. The gas chromatograph separates the compounds based on the difference in their boiling points. The instrument has several parameters that must be tuned to obtain the required chromatographic separation and analysis. Some of the important considerations are the inlet temperature, column flow rate, injection mode (split/splitless) and the oven gradient. A lot of variability could be seen if any of these parameters are changed. A method is developed and validated when a combination of all the parameters is set and tested multiple times yielding consistent results.

Even though, a pure chemical or a mixture of pure chemicals can be purchased from a manufacturer, a specific method might not always be available. To analyze a set of certain compounds on an instrument, many iterations of the different parameters are necessary to develop a suitable method. Once the method is developed, the chromatogram obtained should have sharp peaks and maintain linearity across the calibration range.

The gas chromatograph by itself can simply separate the compounds that are injected. In order to further analyze the amounts and detect the type of compounds, a detector must be attached to the GC. Some of the common detectors that are used in conjunction with the GC are the flame ionization detector (FID), electron capture detector (ECD) and the mass spectrometer (MS) [131]. MS is the only detector that has the ability to identify the peaks.. With a mass spectrometer, it is also possible to quantitate the peak areas. With electron ionization, the MS bombards the compound and repeatably splits it into fragments that have unique masses. Each

compound has a unique combination of fragmenting and a mass spectrum. A mass spectral library from the National Institute of Standards and Technology (NIST) is available, which has a compound database with individual mass spectrum information. The MS with a NIST library add-on provides the ability to confidently identify many compounds from the chromatogram.

Once the GC-MS method is developed and the retention times of the specific compounds of interest are known, it is relatively convenient to analyze samples from the field. Yet, the challenge with field samples is that the concentration range of compounds is typically unknown. To tackle this issue, a calibration range starting from a low concentration to a high concentration must be prepared. Analytical analysis is especially useful in trace analysis of compounds, hence a calibration range with significantly low concentrations is necessary. The calibration solutions are prepared by diluting pure chemicals in a suitable solvent. The solvent must be in line with the polarity of the analytes and they should have a good solubility in the solvent. Use of unsuitable solvents could lead to several issues such as column backflush, peak splitting, poor peak shapes, etc. [132].

9.1.1 Relevance of the GC-MS method for analysis of firefighter turnout gear

Firefighter gear is exposed to a host of toxic chemicals and gases, often termed as fireground contaminants. Some of the fireground contaminants present on the gear are known carcinogens and pose a serious health hazard to the firefighters wearing the gear. The toxic chemicals present in structural fires is a complex mixture of gases, particles and soot. Some of the most commonly occurring fireground contaminants are phenols, phthalates and polycyclic aromatic hydrocarbons (PAHs). Some of these chemicals are carcinogens and their identification from a contaminated gear is important in devising an effective decontamination strategy. To

identify, both qualitatively and quantitatively, a GC-MS system is one of the best suited methods. This is because the chosen compounds have a wide range of boiling points and are suitable for a GC separation. The aim of the GC-MS method is to confidently separate and understand the calibration process for known concentration of pure liquid chemicals. After successive trial runs, methods of detection are found which are crucial in knowing the boundaries of the instrument capabilities. Once a method is validated using pure chemicals, the same method can be used while analyzing extracts from other unknown/ field-contaminated samples containing the fireground contaminants. After the fireground contaminants from field-contaminated firefighter gear is extracted, the calibration curve prepared using the pure liquid chemicals can be used to measure the concentration of compounds. The knowledge of the concentration is important in assessing the risk that the chemicals pose while being present in the gear. The GC-MS method is also crucial when analyzing aliquots to evaluate pre-washed and post-washed firefighter gear samples.

9.2 Materials

A custom calibration standard of phenols, phthalates and polycylic aromatic hydrocarbons prepared in methylene chloride was purchased from Agilent Technologies. The mix had each of the compounds at a concentration of approximately 2,000 ng/µL and was packaged in 2-ml amber coloured vials and stored at room temperature. Analytical grade solvents- n-hexane (gas chromatography grade, 99,9+%, ACROS chemicals), methanol (Optima LC/MS grade, 99.9%, Fisher Scientific), acetonitrile (Optima LC/MS grade, 99.9%, Fisher Scientific) and methylene chloride (gas chromatography grade, 99.9%, Fisher Scientific) were ordered. Pipette tips ranging from 1 to 1,000 µL were purchased from Eppendorf. Several borosilicate glassware beakers, measuring cylinders and 10-mL volumetric flasks were obtained.

9.3 Selection of compounds

The reference ‘master mix’ had a total of 10 compounds present in it. The base stock solution of 2,000 ng/µL of each component would be referred as ‘master mix’ throughout the study. The compounds were chosen based on their toxicity levels and relevance as fireground contaminants. Some of the compounds are volatile in nature having a boiling point below 250°C, while others are semi-volatile compounds having higher boiling points. Initially, it was decided to only analyze phenols and phthalates for this study, but PAHs were taken into consideration as well due to their toxicity and relevance in the fireground [133]. The full list of selected compounds is as follows:

phenol, 2,4,6-trichlorophenol, pentachlorophenol, dibutyl phthalate, butyl benzyl phthalate, di-ethylhexyl phthalate, naphthalene, phenanthrene, pyrene and benzo[a] pyrene.

9.4 Compound properties

Table 7.1 lists the compounds present in the master mix with the properties that are relevant for GC-MS and further analysis. The compounds having boiling points of 250°C or lower are considered as volatile, whereas the higher boiling compounds are semi-volatile compounds [135].

Table 9.1. Master mix compounds and their properties

Compound	Boiling Point (°C)	Volatile or Semi-volatile	Vapor Pressure at 25°C (mmHg)	IARC Classification[a]
Phenol	182	Volatile	0.35	Group 3
2,4,6-Trichlorophenol (2,4,6-TCP)	246	Volatile	0.008	Group 2B
Pentachlorophenol (PCP)	310	Semi-volatile	0.00011	Group 2B
Di-butyl phthalate (DBP)	340	Semi-volatile	0.00002	Group 3
Benzyl butyl phthalate (BBP)	370	Semi-volatile	0.00000825	Group 3
Di-ethylhexyl phthalate (DEHP)	384	Semi-volatile	0.000000142	Group 2B
Naphthalene	218	Volatile	0.085	Group 2B
Phenanthrene	340	Semi-volatile	0.000121	Group 3
Pyrene	404	Semi-volatile	0.0000045	Group 3
Benzo[a] pyrene	495	Semi-volatile	0.00000000549	Group 1

Note: The International Agency for Research on Cancer classifies substances to show whether they are suspected to cause cancer or not. It places the substances into 4 categories depending on the strength of evidence for their carcinogenicity. The categories are as follows: Group 1- Carcinogenic to humans, Group 2A- Probably carcinogenic to humans, Group 2B- Possibly carcinogenic to humans and Group 3- Not classifiable as to its carcinogenicity to humans [64].

9.5 Methods

9.5.1 Preparation of test solutions for selection of solvent

A 50-µL aliquot of the master mix solution was diluted into a 10-mL volumetric flask to obtain a concentration of 10 ng/µL using four different solvents – methanol, acetonitrile, n-hexane and methylene chloride. The solvents were chosen based on their range of polarities and compatibilities with the compounds of interest. The chromatograms were looked at for various factors such as response and peak shapes to select the best suited solvent.

9.5.2 Preparation of calibration solutions

The reference master mix containing three phenols, three phthalates and four PAHs were obtained from Agilent Technologies at a concentration of 2,000 ng/µL for each compound. A calibration range was prepared from 0.2 ng/µL to 10 ng/µL. Appropriate amounts were diluted into 10-mL standard volumetric flasks using n-hexane and methylene chloride, separately. The calibration solutions were then transferred to 2-mL amber coloured GC vials, capped tightly and stored in the refrigerator at approximately 4°C.

9.5.3 Chromatographic method development

The analysis of phenols, phthalates and PAHs was carried out using Agilent 7890B gas chromatographic system coupled to an Agilent 5977B mass spectrometer equipped with electron ionization (EI). Chromatographic analysis was conducted in the splitless mode with a purge flow of 100 mL/min at 1 min. The column used in the GC was an Agilent DB-UI 8270D, fused silica capillary column (30 m × 0.25 mm × 0.25 µm). An Agilent 5190-3136 UI splitless single taper with glass wool liner was used in the inlet for injection. The injection volume was 1 µL and the injection temperature was kept at 250°C and a helium flow rate of 1.2 mL/min. The oven gradient was set to begin at 40°C, increased to 280°C for 1 min at a rate of 10°C/min, further increased to 300°C at 5°C/min for 1 min. The total run time was 30 minutes. The MS transfer line was kept at 280°C throughout the run. The MS quadrupole temperature was maintained at 230°C and the ion source temperature was kept at 150°C. The gain factor used was 1.00. The analysis was conducted in scan mode (35-550 amu) using EI with an energy of 70eV.

9.5.4 Sample trials of phenols, phthalates and PAHs using n-hexane and methylene chloride in the GC-MS system

A total of five calibration solutions were prepared- 0.2 ng/µL, 0.6 ng/µL, 2 ng/µL, 5 ng/µL and 10 ng/µL by pipetting 1 µL, 3 µL, 10 µL, 25 µL and 50 µL of the 2,000 ng/µL master mix stock solution and diluting them in 10-mL standard volumetric flasks using n-hexane and methylene chloride separately. The calibration solution set was run three times and the average values were considered in order to minimize error. The lowest detectable concentration of every compound in the solution was then run ten times each to aid in the calculation of limits of detection. Selected compounds were viewed as total ion chromatograms (TIC) and identified on the Mass Hunter Qualitative software using their mass-to-charge (m/z) ratios and comparing with the NIST 17 Mass spectral standard library. All the compounds had a purity (or % assurity) of 95% and above. The peak areas were noted, and values of area versus concentration were plotted. A calibration curve was established with a minimum R-square co-efficient of 0.98 for all the compounds.

The limit of detection (LOD) was calculated using the formula [136].

$$LOD = (\frac{3\sigma}{m}) \quad \textbf{Eq. 9.1}$$

where σ is standard deviation of ten successive runs and m is the slope of the calibration curve. The LOD gives an idea of the minimum value at which the compound can be confidently differentiated from instrument noise.

The limit of quantitation (LOQ) was calculated using the formula [136].

$$LOQ = (\frac{10\sigma}{m}) \quad \textbf{Eq. 9.2}$$

where σ is standard deviation of ten successive runs and m is the slope of the calibration curve. The LOQ gives the minimum value at which the compound could be confidently quantitated to achieve the peak area and the resulting concentration.

9.6 Results and Discussion

9.6.1 Solvent selection for GC-MS method

9.6.1.1 Master mix in methanol and acetonitrile at 10 ng/µL

Methanol and acetonitrile were chosen as a probable solvents for analysis because of their wide use in analysis of semi-volatile compounds using GC-MS [137,138,139]. After reviewing the chromatograms(seen in Figure 9.1 and Figure 9.2 for methanol and Figure 9.3 and Figure 9.4 for acetonitrile), it was decided that methanol and acetonitrile were not suitable solvents for several reasons. One of the reasons could be that they are polar in nature and the phthalates and PAHs in the master mix are non-polar. Thus, this possess a solvent-solute polarity mis-match for analysis.. The peaks as pointed near 10 minutes and 17 minutes are split peaks and have poor peak shapes. The irregular peak shapes could also be because of overloading of the column with analytes. When analysis is performed in the splitless mode, maximum amount of analyte is injected into the column. The odd-shaped peak between 20 minutes and 21 minutes is detected as Benzo[g,h,i] perylene and is prominently seen in both the chromatograms for methanol and acetonitrile.

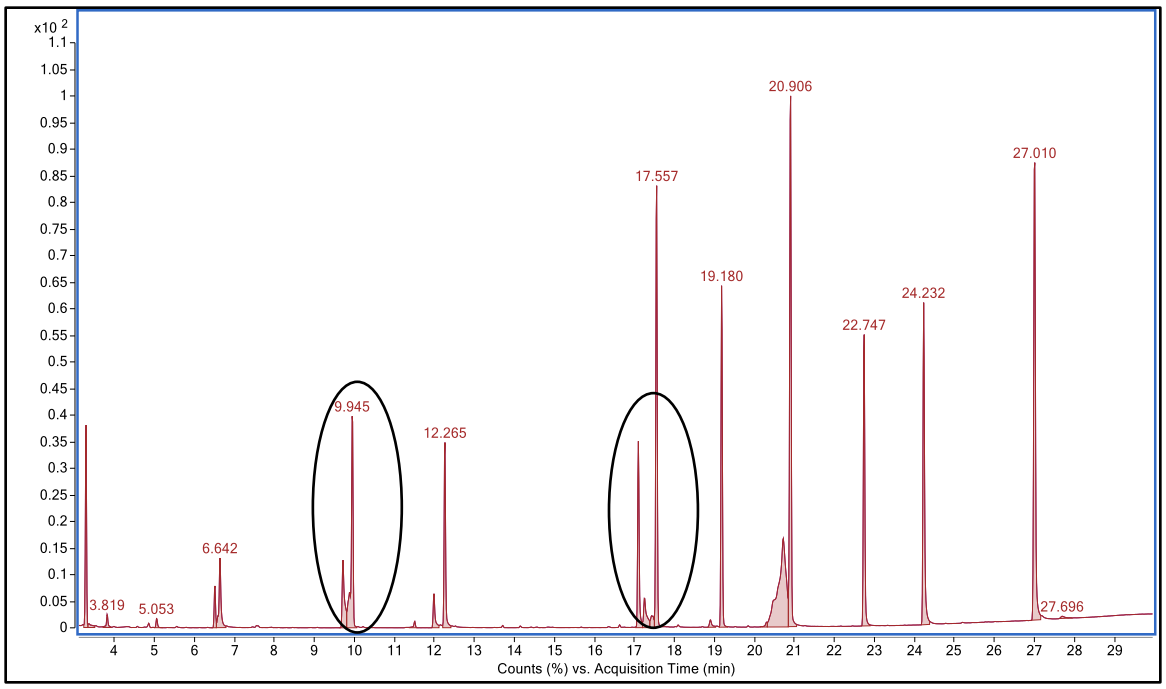


Figure 9.1. Chromatogram of the master mix in methanol using GC-MS liquid injection

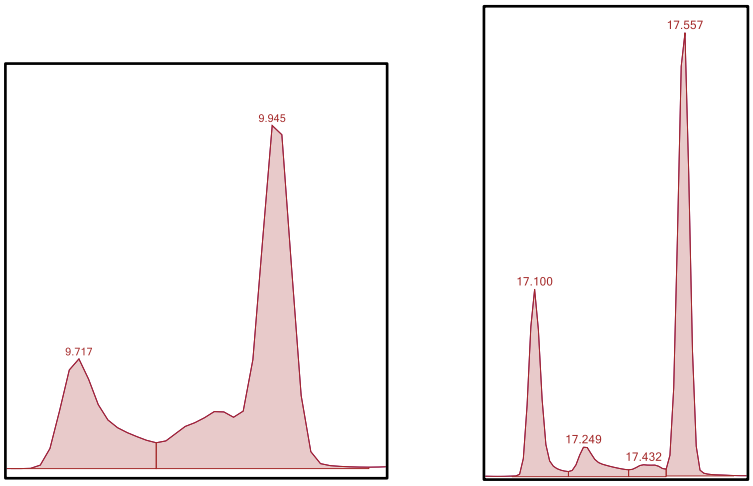


Figure 9.2. Poor peak shapes using methanol as the solvent for analysis

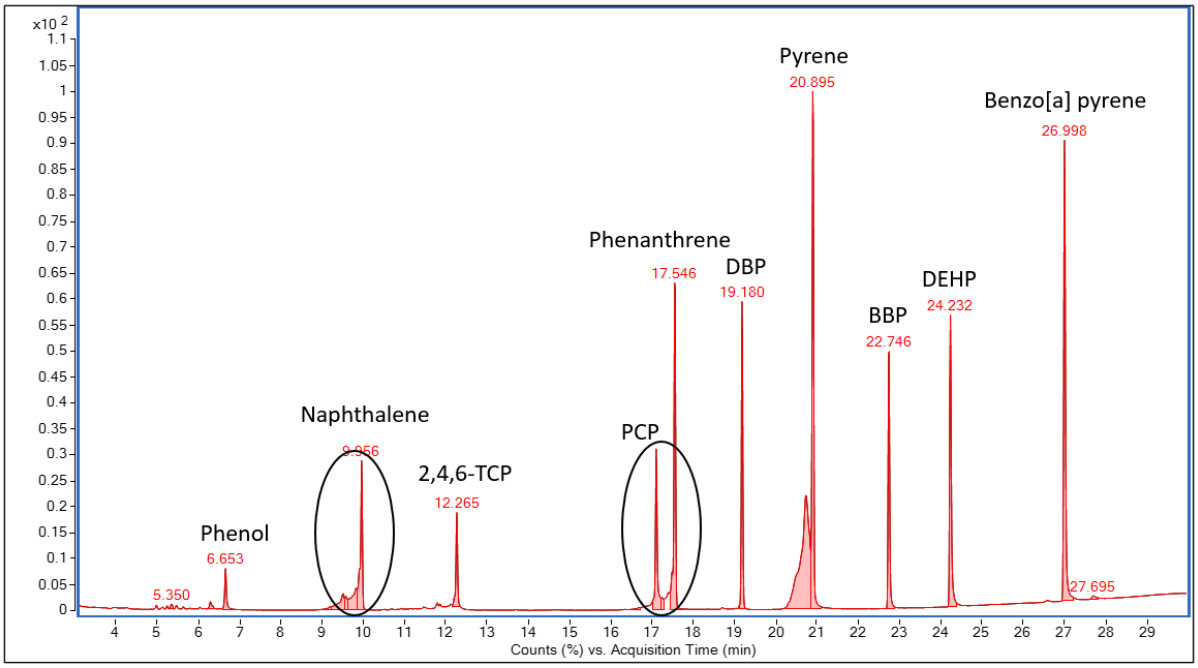


Figure 9.3. Chromatogram of the master mix in acetonitrile using GC-MS liquid injection

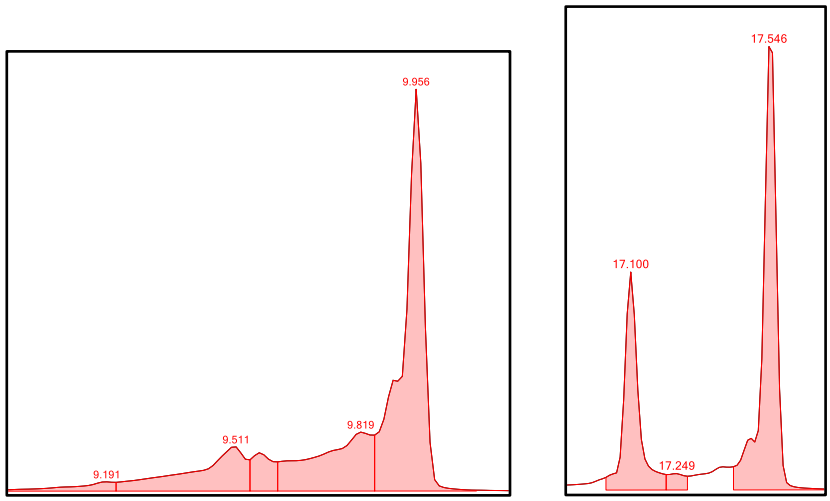


Figure 9.4. Poor peak shapes using acetonitrile as the solvent for analysis

9.6.1.2 Master mix in methylene chloride at 10 ng/µL

Methylene chloride was a probable suitable solvent. Even though it is polar in nature, Figure 9.5 shows good peak shapes and good separation. A possible explanation for this could be that the master mix was manufactured with methylene chloride as the solvent, therefore the uniformity was maintained.

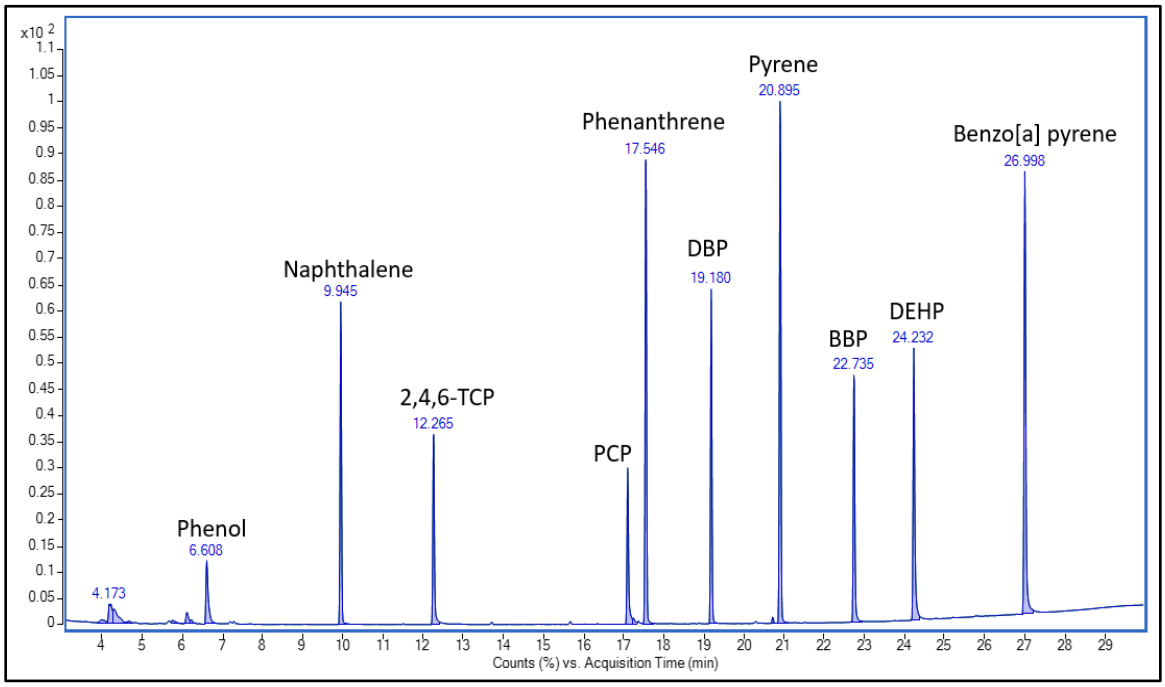


Figure 9.5. Chromatogram of the compounds in the master mix in methylene chloride using GC-MS liquid injection

9.6.1.3 Master mix in n-hexane at 10 ng/µL

n-hexane was the best suited solvent because of its non-polar nature. Phthalates and PAHs are non-polar and thus the solvent was a perfect fit for the dissolution of the compounds. As seen in Figure 9.6, the compounds had proper peak shapes and good separation. There are other factors

such as the compatibility of n-hexane with the pressurized solvent extractor, that would be used to guide its selection for extraction of these compounds from fabric samples.

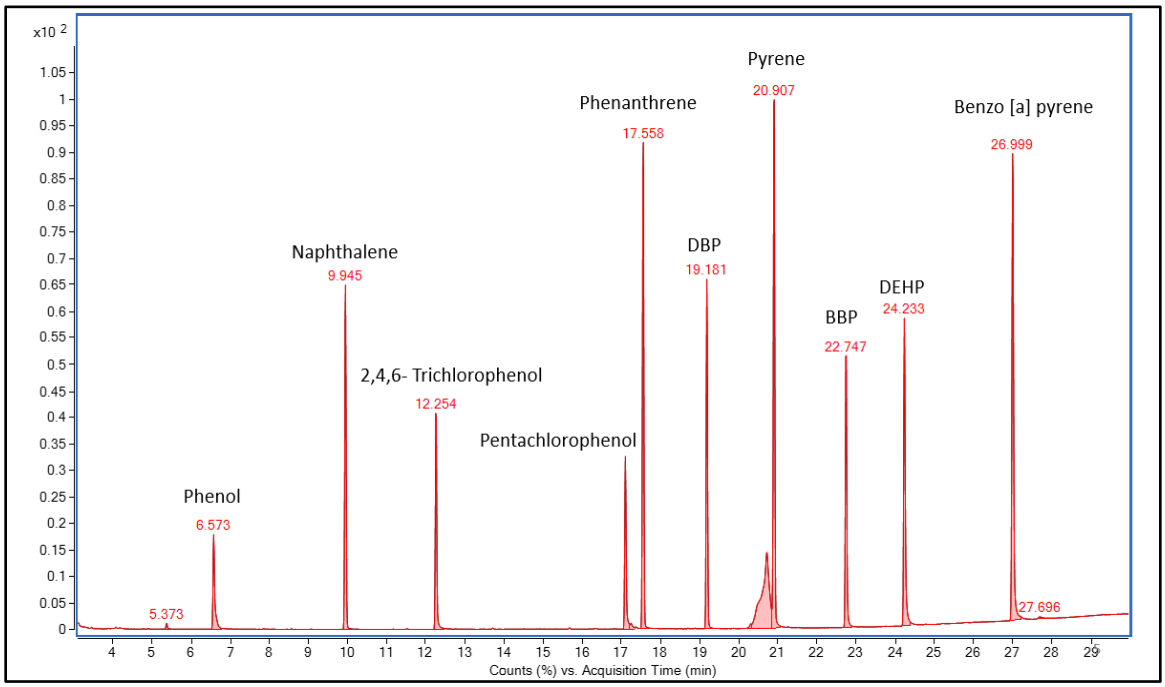


Figure 9.6. Chromatogram of the compounds in the master mix in n-hexane using GC-MS liquid injection

9.6.2 Preferred solvent for liquid extraction

All the LOD and LOQ values are seen in Table 9.2 below. The LOQ value indicates the lowest concentration at which a particular compound can be quantified. The lower the LOQ value, the better is the sensitivity, and the compound can be quantified at a lower concentration, which is ideal. For the compounds in the master mix, n-hexane had a lower LOQ value for 6 out of 10 compounds: phenol, 2,4,6-TCP, pentachlorophenol, naphthalene, pyrene and benzo[a] pyrene. While for di-butyl phthalate and phenanthrene, the LOQ values were almost comparable for both

solvents. Consequently, n-hexane was chosen as the best solvent for analysis of phenols, phthalate and PAHs in the master mix.

Table 9.2. LOD and LOQ values for the compounds in the master mix using n-hexane and methylene chloride

	LOD		LOQ	
Compound	**n-Hexane**	**Methylene Chloride**	**n-Hexane**	**Methylene Chloride**
Phenol	0.023	0.109	0.078	0.363
2,4,6-Trichlorophenol	0.030	0.045	0.100	0.150
Pentachlorophenol	0.022	0.090	0.073	0.302
Di-butyl phthalate	0.026	0.023	0.087	0.079
Benzyl butyl phthalate	0.065	0.024	0.216	0.082
Di-ethylhexyl phthalate	0.110	0.034	0.346	0.114
Naphthalene	0.016	0.029	0.056	0.096
Phenanthrene	0.017	0.015	0.059	0.051
Pyrene	0.026	0.156	0.098	0.522
Benzo[a] pyrene	0.058	0.070	0.195	0.233

9.*6.3 GC-MS trials using n-hexane as the solvent*

The chromatogram showing the individual compound peaks can be seen in Figure 9.6. The following graphs depict the calibration curves for all the compounds in the master mix analyzed using a liquid injection on the GC-MS.

9.6.3.1 Calibration curve for phenols

Figure 9.7 shows the linear equations for phenol, 2,4,6-TCP and PCP analyzed using GC-MS liquid injection.

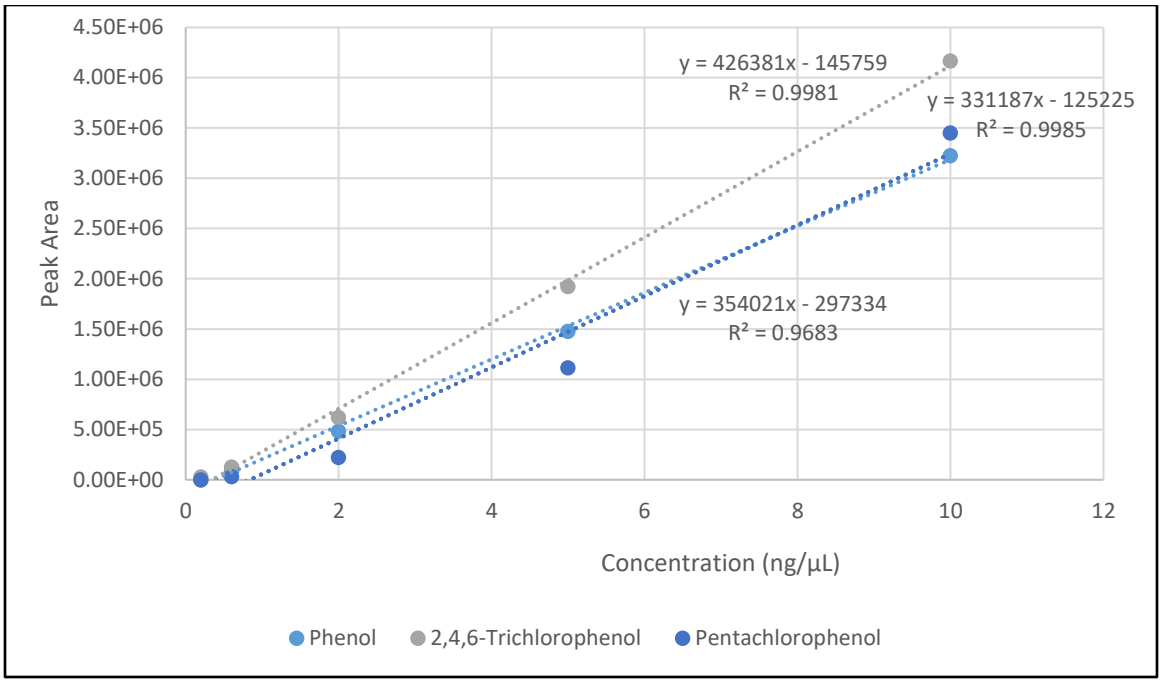


Figure 9.7. Calibration curve for phenols in n-hexane

9.6.3.2 Calibration curve for phthalates

Figure 9.8 shows the linear equations for DBP, BBP and DEHP analyzed using GC-MS liquid injection. All the compounds have a R^2 (co-efficient of linearity) value of over 0.99, which is desirable.

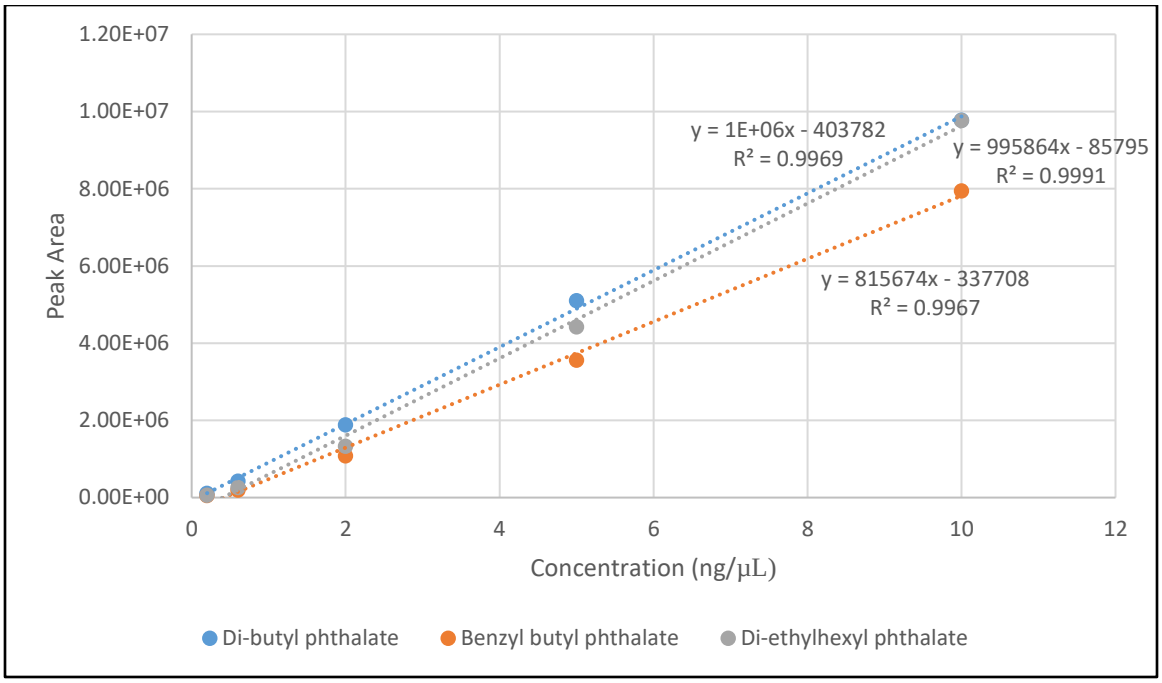


Figure 9.8. Calibration curve for phthalates in n-hexane

9.6.3.3 Calibration curve for PAHs

Figure 9.9 shows the linear equations for PAHs. All the four compounds display R^2 values of over 0.99, which is ideal.

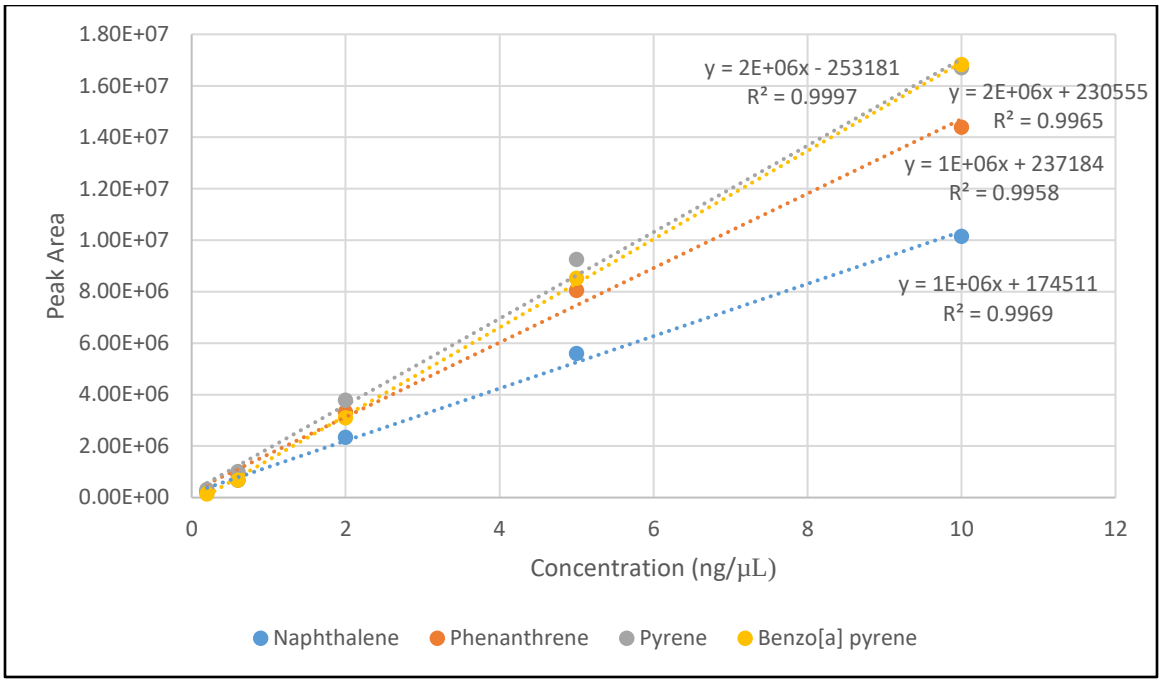


Figure 9.9. Calibration curve for PAHs in n-hexane

All ten compounds with their retention times, limit of detection (LOD) and limit of quantitation (LOQ) are shown in Table 9.3:

Table 9.3. Retention time and limits of detection for GC-MS analysis using n-hexane

Compound	Retention time (min)	Limit of detection (ng/µL)	Limit of quantitation (ng/µL)	R^2 coefficient
Phenol	6.608	0.023	0.076	0.9988
Naphthalene	9.989	0.016	0.056	0.9973
2,4,6-trichlorophenol	12.259	0.030	0.100	0.9995
Pentachlorophenol	17.100	0.022	0.073	0.9830
Phenanthrene	17.551	0.017	0.059	0.9966
Dibutyl phthalate	19.186	0.026	0.087	0.9994
Pyrene	20.900	0.029	0.098	0.9972
Butyl benzyl phthalate	23.741	0.065	0.216	0.9991
Di-ethyl hexyl phthalate	24.226	0.110	0.346	0.9990
Benzo[a] pyrene	26.993	0.058	0.195	0.9999

The following graphs show the variability in the replicate samples with n-hexane solvent, analyzed using GC-MS

Each graph has three calibration lines, representing the three individual calibration solution replicate runs. The deviation between the lines represents the variability among three successive calibration trials. Ideally, closer the lines to each, higher precision is obtained for that compound using the GC-MS method. As seen in Figure 9.10, the calibration lines for phenol are consistent and that translates that phenol was suitable for a GC-MS analysis, producing satisfactory results.

9.6.3.4 Variability in replicate GC-MS runs for phenol

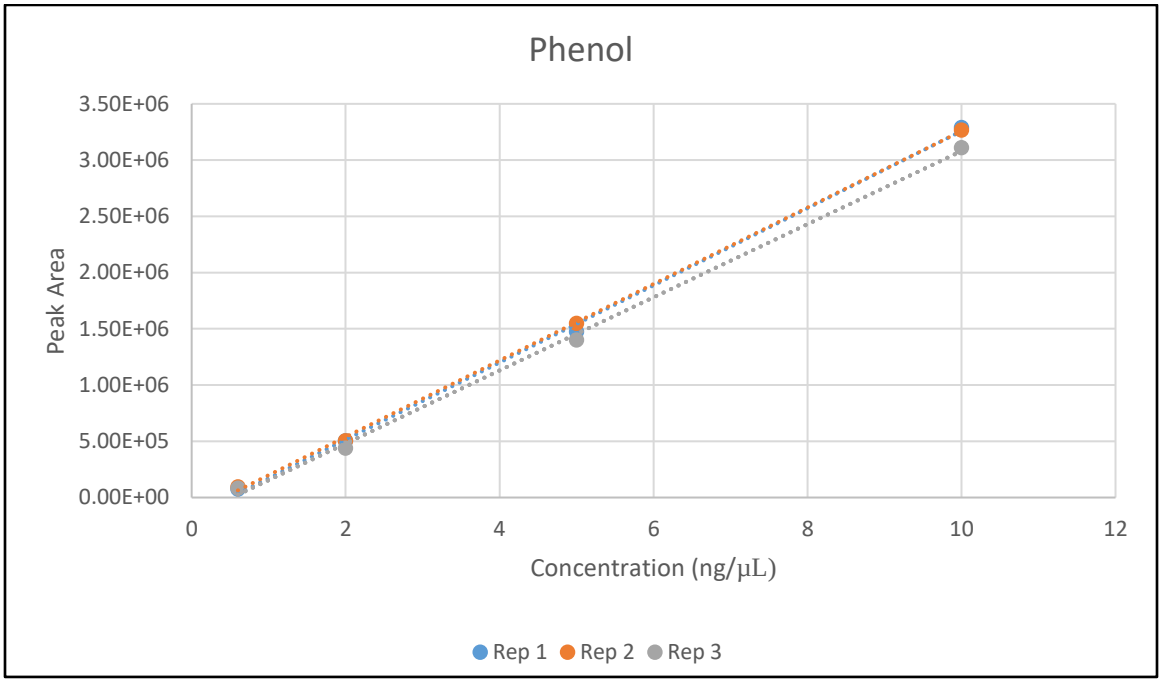


Figure 9.10. Variability in replicate GC-MS runs for phenol

9.6.3.5 Variability in replicate GC-MS runs for 2,4,6-Trichlorophenol

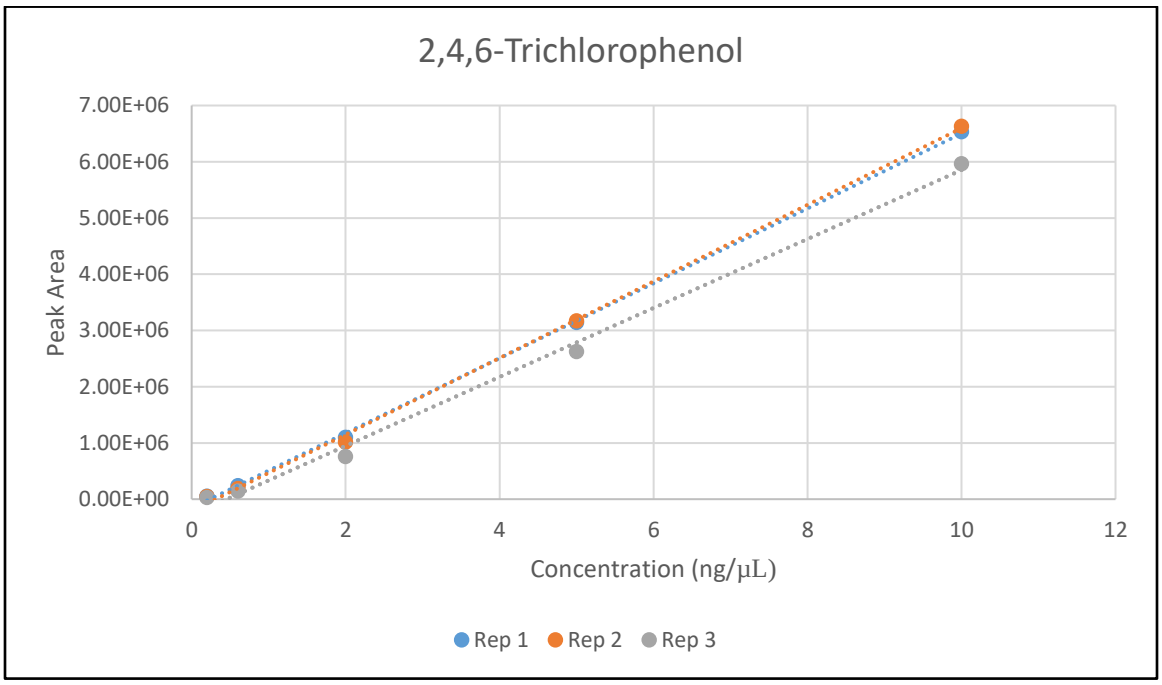


Figure 9.11. Variability in replicate GC-MS runs for 2,4,6-Trichlorophenol

9.6.3.6 Variability in replicate GC-MS runs for pentachlorophenol

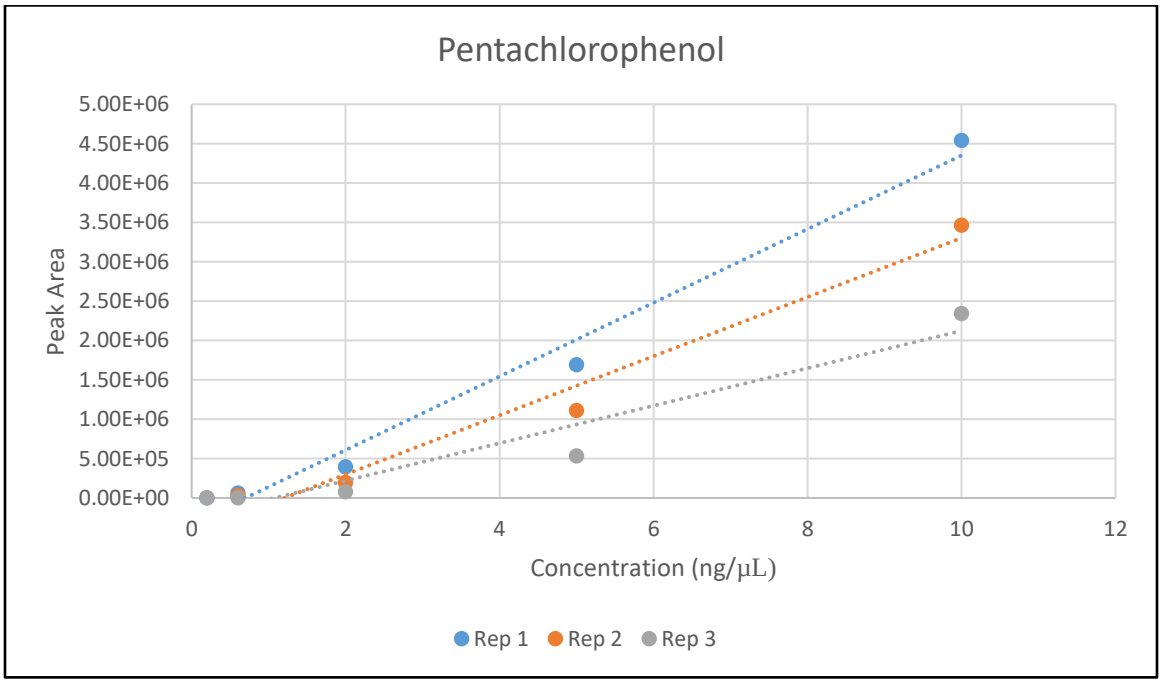


Figure 9.12. Variability in replicate GC-MS runs for pentachlorophenol

9.6.37 Variability in replicate GC-MS runs for di-butyl phthalate

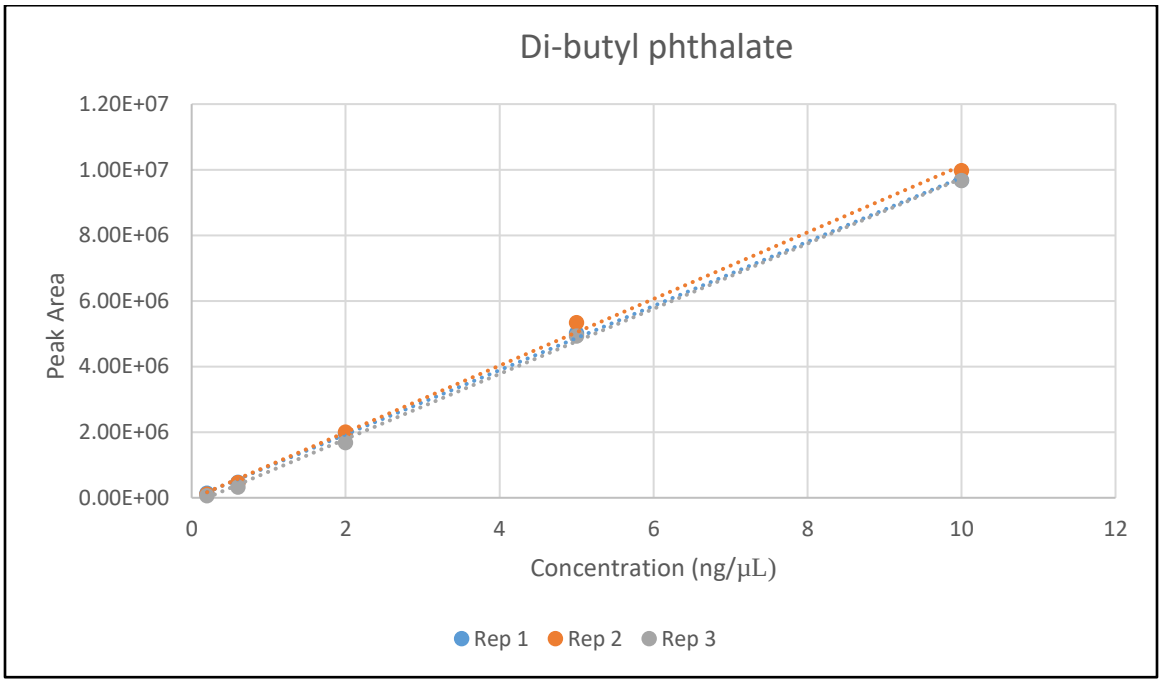


Figure 9.13. Variability in replicate GC-MS runs for di-butyl phthalate

9.6.3.8 Variability in replicate GC-MS runs for benzyl butyl phthalate

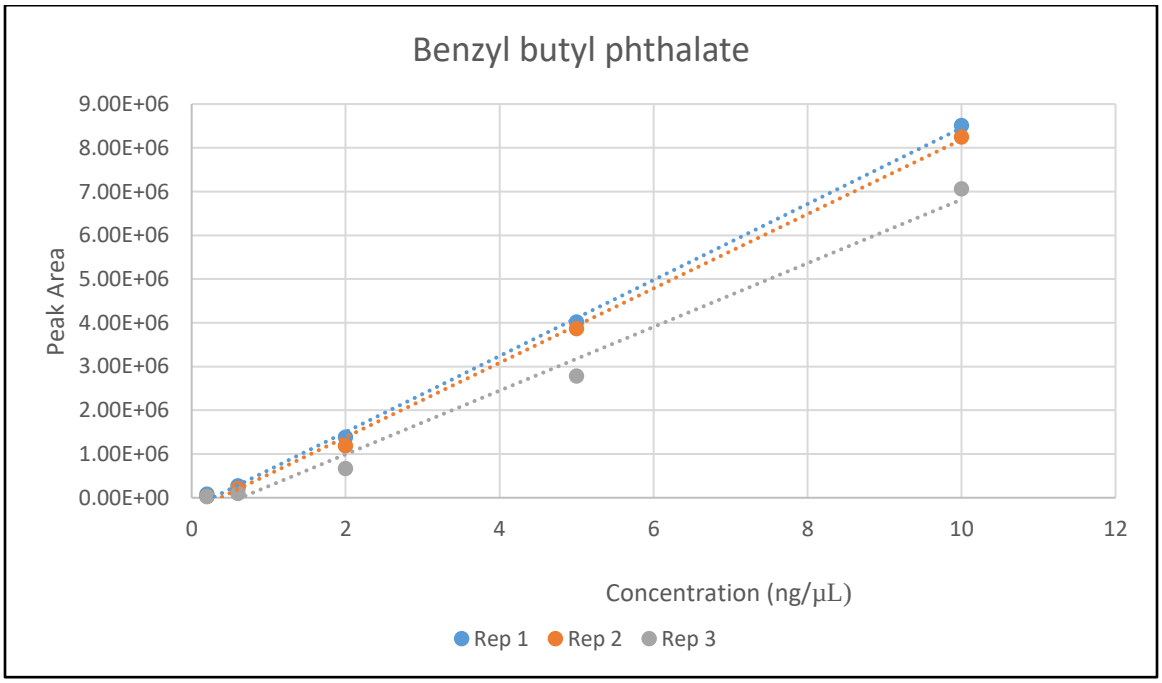


Figure 9.14. Variability in replicate GC-MS runs for benzyl butyl phthalate

9.6.3.9 Variability in replicate GC-MS runs for di-ethylhexyl phthalate

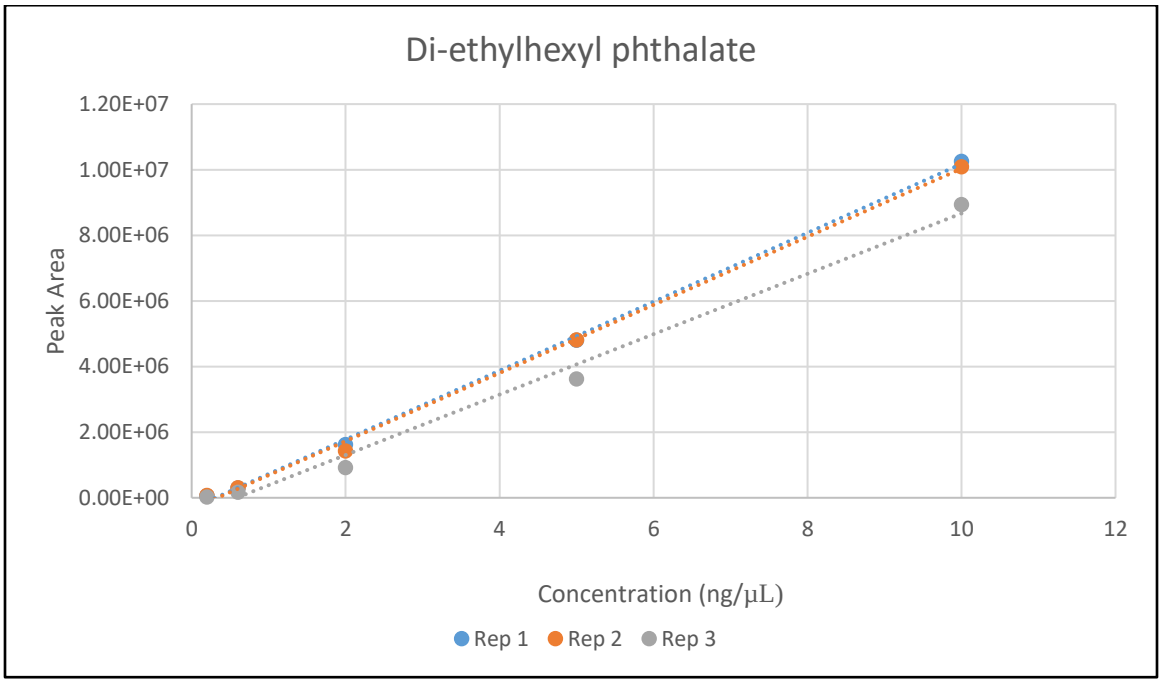


Figure 9.15. Variability in replicate GC-MS runs for di-ethylhexyl phthalate

9.6.3.10 Variability in replicate GC-MS runs for naphthalene

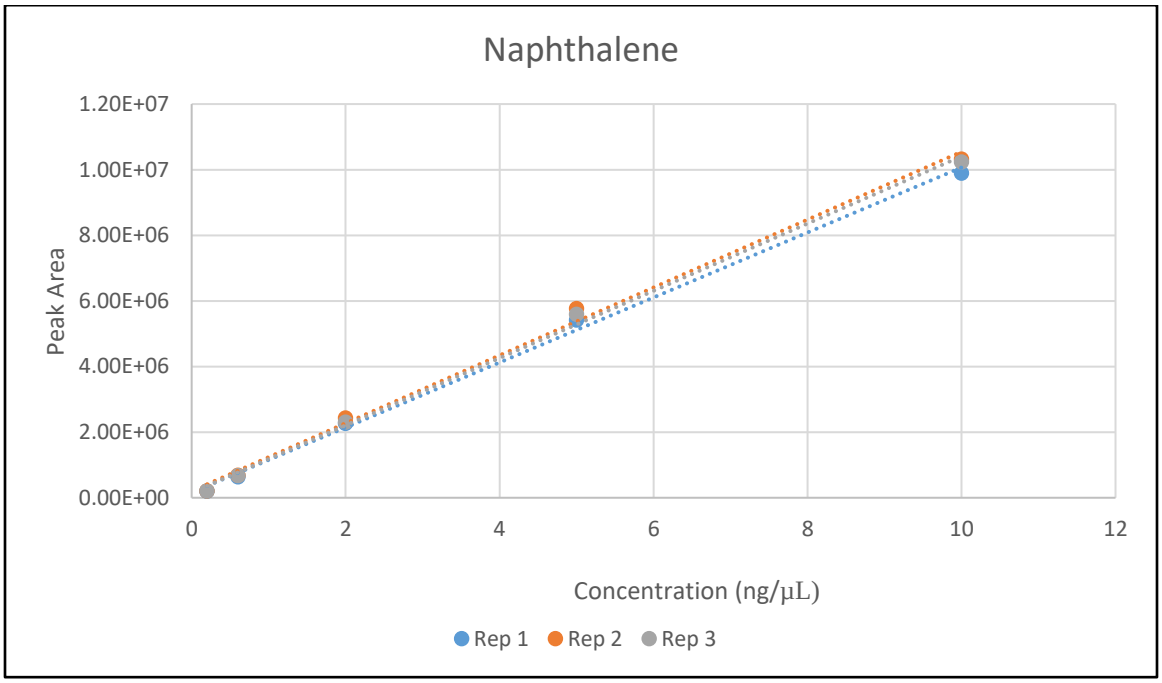


Figure 9.16. Variability in replicate GC-MS runs for naphthalene

9.6.3.11 Variability in replicate GC-MS runs for phenanthrene

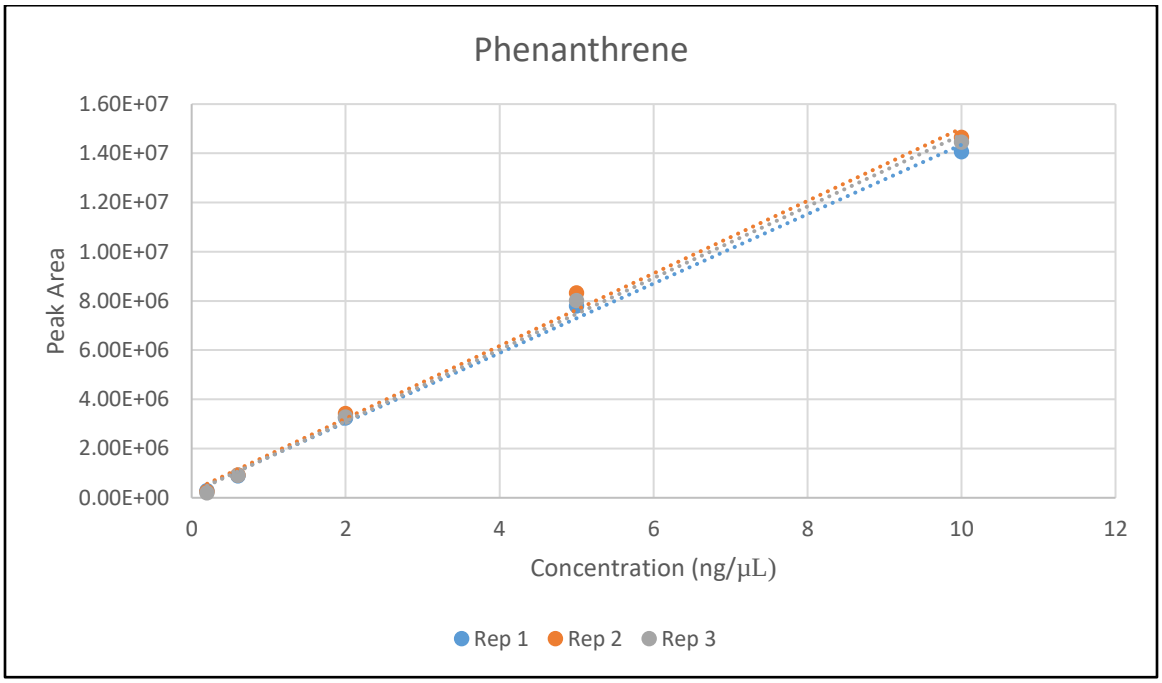


Figure 9.17. Variability in replicate GC-MS runs for phenanthrene

9.6.3.12 Variability in replicate GC-MS runs for pyrene

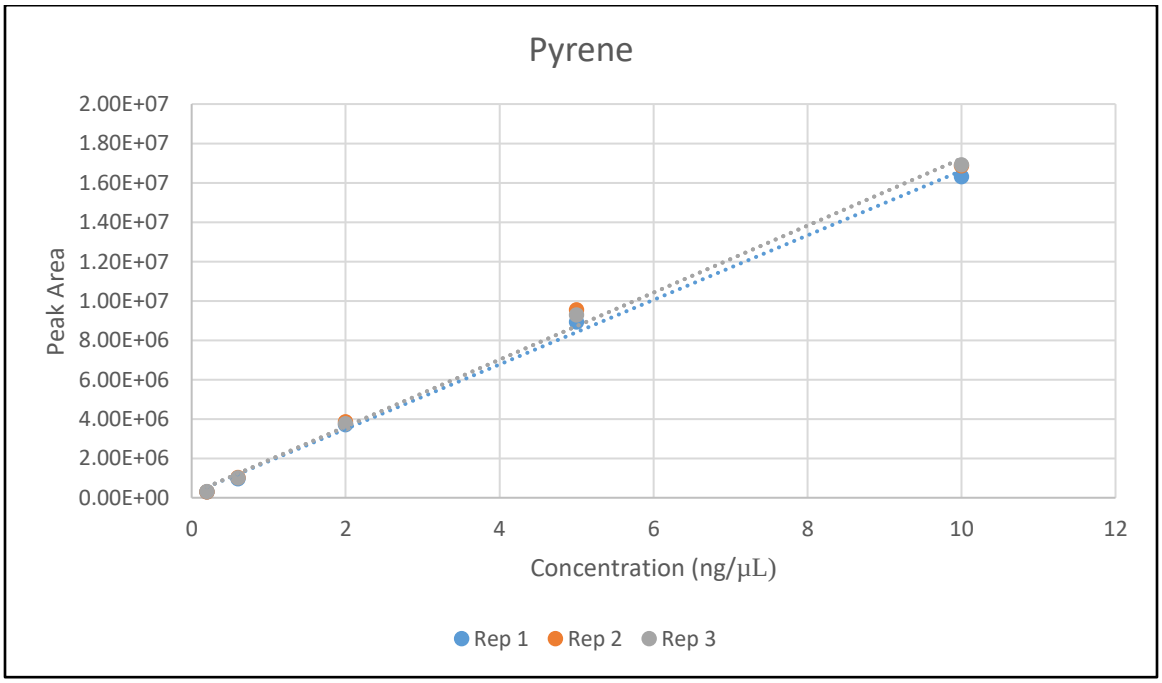


Figure 9.18. Variability in replicate GC-MS runs for pyrene

9.6.3.13 Variability in replicate GC-MS runs for benzo[a] pyrene

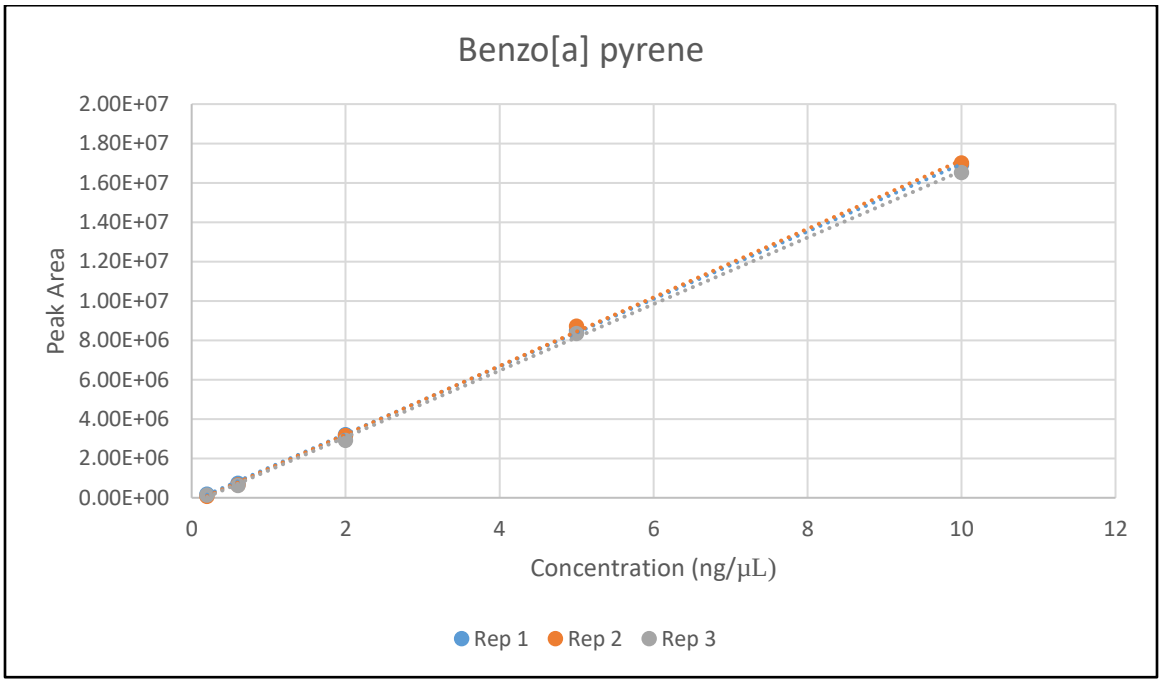


Figure 9.19 Variability in replicate GC-MS runs for benzo[a] pyrene

9.7 Conclusion

The calibration solutions using n-hexane and methylene chloride as the solvents were analyzed on the developed GC-MS liquid injection method. All the compounds could be identified and quantitated with precision. The method was validated by averaging three consecutive runs of the calibration solution set. Further on, the LOD and LOQ detection values were found. These methods are crucial for further analysis, where the compounds of interest would have to be analyzed from fabric samples. The method is novel since it analyzes phenols, phthalates and PAHs which would probably be found in contaminated fabric samples from firefighter turnout gear, together within a single challenge mixture.

The solvent chosen as the best suited for the analysis of the compounds in the master mix was found to be n-hexane. This is due to the lower LOD and LOQ values for the compounds in n-hexane.

The GC-MS liquid injection method needs to be tested while analyzing actual fabric samples from the field to test the applicability of the concentrations in the calibration curve set. The method uses a broad range of 0.2 ng/µL to 10 ng/µL, yet the concentration present in contaminated fabric samples could be below or above the calibration range. In such a case, a suitable calibration range must be prepared using the same GC-MS liquid injection method to encompass the samples to be analyzed.

Chapter 10: Development of a liquid extraction method using the Buchi pressurized solvent extractor

10.1 Introduction

The GC-MS analytical method using n-hexane, developed in the previous chapter (Section 9.5.3) is used for analysis of compounds in the current chapter. The current chapter aims at developing a method to perform liquid extraction of reference fireground contaminants spiked onto firefighter gear material. Extraction is an important step in recovering the analytes of interest from solid/liquid matrices. The extraction method is necessary in recovering useful products such as metals, pharmaceutical samples, etc. The method is also useful in screening fabric samples for potential contamination. An example would be if washing efficiency were to be assessed; the residual contaminant on the washed fabric must be extracted by using a liquid solvent.

After an analytical method is developed to analyze pure chemicals, a suitable extraction method must be developed to effectively remove chemicals from solid substrates. The GC-MS instrument setup allows a liquid injection of the analyte into the column. To be able to extract the contaminants from a solid substrate, a suitable solvent must be used. The solvent must be compatible with the polarity of the compounds to be extracted. When performing an extraction run at atmospheric conditions, the boiling point of the compounds must be considered as well. If the solvent evaporates, the concentration of the contaminants would be affected, and the extraction efficiencies would not be accurate. Various other methods to extract the contaminants from the solid matrices can be used such as sonication, liquid-liquid extraction, and centrifugation [140]. For extracting analytes from fabrics, it is generally known that exposing the fabric to a higher temperature, pressure and agitation conditions, improves the efficiency of contaminant removal. A pressurized solvent extractor is effective at removing chemicals from solid substrates.

The instrument is faster as compared to the traditional Soxhlet extractor. While in the extractor, the fabric samples are exposed to elevated temperatures and pressures, while a solvent is forced through the samples. Having a high pressure helps in maintaining the solvent in a liquid state, since the temperatures are typically above the boiling points of most solvents. Also, the combination of high temperature and pressure results in an improved mass transfer because of higher analyte solubility and enhanced penetration into the solid matrix. The advantage of the extractor is that multiple samples can be loaded simultaneously into metal cells, having separate inlet and outlet valves. This configuration prevents any cross-contamination and keeps the liquid pipelines free of any clogging. The extractor has a functionality to set the number of cycles and other conditions to develop the most efficient method for a particular application. The extractor is convenient, easy to use and automated in the function. The extraction technique can be used for a variety of purposes such as extraction of polymer additives, dyes, residues and contaminants. The process also finds use in extraction of crude oil/fats and environmental analysis of volatile organic compounds [141].

10.1.1 Relevance of the liquid extraction method for analysis of firefighter turnout gear

The firefighter gear is known to be contaminated with a variety of toxic compounds, arising from the synthetic materials burning in a fire. Potentially carcinogenic compounds such as benzene, PAHs, phenols, phthalates and other VOC's are known to be adsorbed onto the turnout gear that firefighters wear [119,126,142]. The firefighter gear is made up of three layers- outer shell, moisture barrier and thermal liner. The outer shell is a woven Kevlar®/PBI material, being the outermost layer, is the most exposed layer. The firefighters' gear must be washed in accordance to the NFPA-certified washing procedures. Currently, the effectiveness of the

washing procedure is only about 40% [34]. In order to evaluate the washing efficiency, the residual contamination must be extracted from the fabric into a suitable solvent. Liquid extraction using the Buchi pressurized solvent extractor is an efficient method of extracting a wide range of compounds present on the contaminated firefighter gear samples. Using a suitable solvent that it compatible with the compounds to be extracted, would assist in the removal of the compounds and transferring it into the solvent. The solvent containing the compounds can then be injected into the GC and analyzed using the method developed in Chapter 9.

10.2 Materials

A custom calibration standard (referred to as the 'master mix') of phenols, phthalates and polycylic aromatic hydrocarbons (PAHs) prepared in methylene chloride was purchased from Agilent Technologies. The master mix comprised of phenol, 2,4,6-Trichlorophenol (2,4,6-TCP), pentachlorophenol (PCP), di-butyl phthalate (DBP), benzyl butyl phthalate (BBP), di-ethylhexyl phthalate (DEHP), naphthalene, phenanthrene, pyrene and benzo[a] pyrene. All the compounds were at an approximate concentration of 2,000 ng/µL and was packaged in 2-mL amber coloured vials and stored at room temperature. Analytical grade solvents- n-hexane (Gas chromatography grade, 99,9+%, ACROS chemicals), methanol (Optima LC/MS grade, 99.9%, Fisher Scientific), acetonitrile (Optima LC/MS grade, 99.9%, Fisher Scientific) and methylene chloride (Gas chromatography grade, 99.9%, Fisher Scientific) were ordered. Repeater pipette (Eppendorf) and pipette tips ranging from 1 µL to 1000 µL were purchased from Eppendorf. Borosilicate glassware beakers, measuring cylinders, 20-mL glass vials, 60-mL glass vials were purchased from Thermo Scientific. Top and bottom cellulose filters were purchased from Buchi for use with

the Buchi Speed Extractor E-916, and 0.2-µm PTFE filters were purchased from Advanced Microdevices Pvt Ltd.

10.3 Methods

10.3.1 GC-MS calibration method

The GC-MS analysis method developed in Section 9.5.3 was used in this study.

10.3.2 Controlled contamination and extraction using n-hexane

Controlled contamination: Three separate experiments were run by spiking 30 µL, 40 µL and 50 µL of the 2,000 ng/µL master mix stock solution to achieve a mass of 60,000 ng, 80,000 ng and 100,000 ng respectively on the 5 cm x 5 cm outer shell fabric samples. The fabric samples were allowed to air dry for an hour in order to make sure that all the spiked liquid was absorbed completely.

Extraction: Each experiment was comprised of three fabric replicates, a negative control (only fabric) and a positive control (direct spiking in the extractor cell). The samples were run through three cycles of solvent passing through the 10-mL metal cell. Each cycle collected an unknown volume of elute in the 60-mL glass vial placed below the 10-mL metal cells. The eluents were diluted to 10 mL in a standard volumetric flask using n-hexane. The 10-mL solution was then filtered into the 2-mL amber colored GC vials through 0.2 µm PTFE filters to remove any particles or other suspended solids prior to analysis. The resulting theoretical concentrations in the GC vials at 100% extraction efficiencies were 6 ng/µL, 8 ng/µL and 10 ng/µL, respectively for the 60,000 ng, 80,000 ng and 100,000 mass spiked samples. After analyzing the solutions using the GC-MS liquid injection and obtaining the peak areas, the peak areas were used to calculate the resulting concentration. The concentration obtained from the positive control sample

was considered the maximum achievable through the extractor and noted as 100% efficiency. The concentrations of the fabric samples were based on the positive control to provide the relative extraction efficiency.

10.3.3 Pressurized solvent extraction method

The Buchi Speed Extractor E-916 (seen in Figure 10.2) was used for extraction of the contaminated compounds from the fabrics. The solvent used for extraction was n-hexane, being non-polar and best suited to the master mix. The temperature of the cells was maintained at 100°C and a pressure of 100 bar was used. Nitrogen was the carrier gas used to create pressure and create an inert condition inside the extractor cells. Outer shell fabric samples (5 cm x 5 cm) were spiked with a pre-set concentration of the master mix solution, allowed to dry for 1 hour and then rolled and placed into the 10-mL metal cells. Glass beads were sonicated in n-hexane to remove any contamination. Five grams of glass beads were filled inside each metal cells to fill the void volume so that the analysis could be done with a lower amount of solvent. Cellulose filters were placed at the top and the bottom of the cells to filter out potential particles arising from the fabrics. The extraction method had a total of three cycles and a flush run at the end. Each cycle was composed of one-minute heat-up, a five-minute hold and a two-minute discharge. After each cycle, the extractant was collected in 60-mL glass vials at the bottom of each metal cell. The 60-mL glass vials were replaced after each cycle. A flush cycle was added at the end of the three cycles to flush out any residual contamination for any further runs. The total run time including the three run cycles and the flush cycle was about 50 minutes. The complete schematic of the process is shown in Figure 10.1

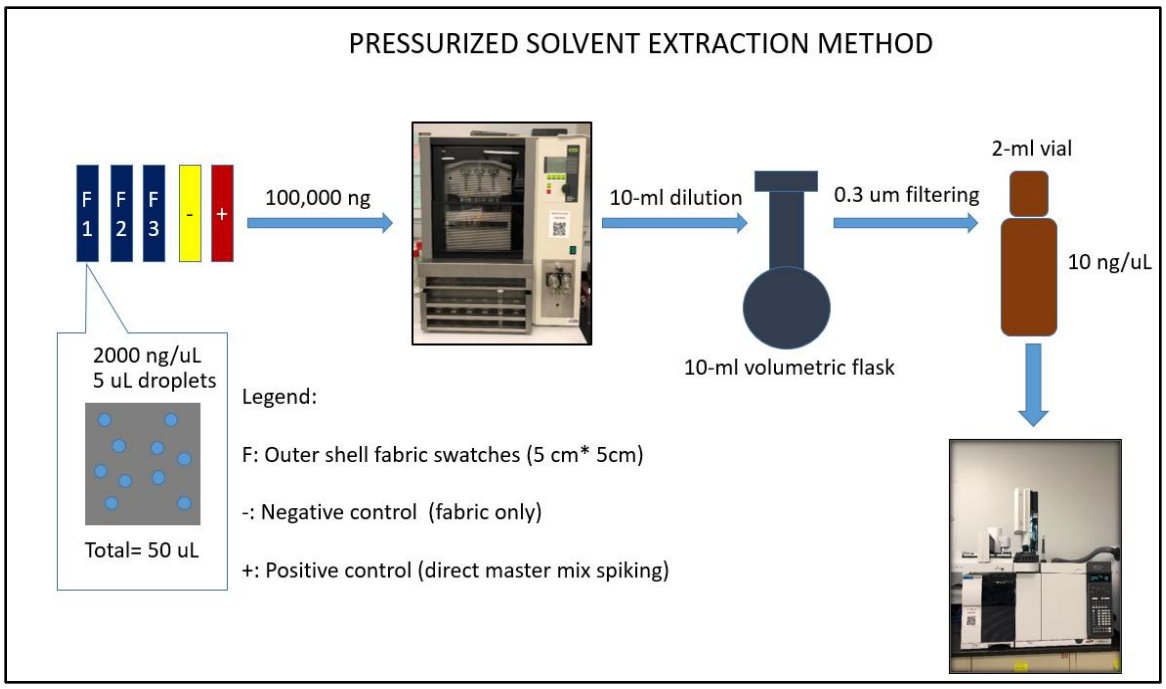


Figure 10.1. Schematic of the control contamination, liquid extraction and analysis

Figure 10.2. Buchi E-916 speed extractor

10.3.4 Calculation of the extraction efficiencies

The peak areas for the compounds were obtained from the chromatograms of each cycle. The areas for individual cycles (c1, c2, c3) were added to get a $Total\ run\ area = c1 + c2 + c3$. The area from the negative control (fabric only) was subtracted from the total run area. The total run area (y) was entered into the equation 10.1 (calibration curve equation) to get the resulting concentration. The same was repeated for the all the fabric samples. The concentration of individual fabric samples was divided by the concentration of the positive control sample to obtain the percent extraction efficiency. The process is depicted in Table 10.1.

Table 10.1. Reference table with the concentration and peak area values

Concentration (ng/µL)	Peak Area
0.2	Y1
0.6	Y2
2	Y3
5	Y4
10	Y5

Considering Table A as the calibration run details, the equation of the line would be:

$$y = mx + c \qquad \textbf{\textit{Eq. 10.1}}$$

The slope can be calculated using the formula:

$$Slope(m) = (y - c)/x \qquad \textbf{Eq. 10.2}$$

The y-intercept can be calculated by using the formula:

$$Intercept(c) = \frac{(Y5 - Y1)}{(10 - 0.2)} \qquad \textbf{Eq. 10.3}$$

For noting the extraction values, consider the following Table 10.2:

Table 10.2. Reference table depicting the calculation of extraction efficiencies

	Peak Area			Total Area	Effective concentration (ng/µL)	Original concentration (ng/µL)	Relative % extraction efficiency
Samples	Cycle 1 (C1)	Cycle 2 (C2)	Cycle 3 (C3)	(C1+C2+C3)	(substitute in calibration curve equation)	(the concentration after dilution at 100% efficiency)	(relative to the positive control)
Fabric 1	F_1C_1	F_1C_2	F_1C_3	$F1_a$	$[F1_a - c]/m = F1_c$	10	$(F1_c/T_c)$ *100
Fabric 2	F_2C_1	F_2C_2	F_2C_3	$F2_a$	$[F2_a - c]/m = F2_c$	10	$(F2_c/T_c)$ *100
Fabric 3	F_3C_1	F_3C_2	F_3C_3	$F3_a$	$[F3_a - c]/m = F3_c$	10	$(F3_c/T_c)$ *100
Negative control	J	K	L	S	$[S-c]/m = S_c$	0	(S_c/T_c) *100
Positive control	M	N	O	T	$[T-c]/m = T_c$	10	100

Some of the compounds were present in blank outer shell fabrics or certain compounds eluting at the same retention times as of the compounds in the master mix. Their peak areas were subtracted from the spiked sample areas (J, K, L) and the net total peak areas ($F1_a$, $F2_a$, $F3_a$) was calculated respectively.

10.3.5 Calculation of error bars for all the graphs plotted

Error bars were plotted as standard error with 95% confidence interval, which is calculated using the formula:

$$Standard\ error = 1.96 * \frac{\sigma}{\sqrt{n}} \qquad \textbf{Eq. 10.4}$$

where 1.96 = z-score value for 95% CI, σ = standard deviation of n samples and n = number of samples in consideration

The standard error when added and subtracted from the sample mean would give the upper bound and lower bound for the 95% confidence interval:

$$Confidence\ interval = Mean\ \pm 1.96 * \frac{\sigma}{\sqrt{n}} \qquad \textbf{Eq. 10.5}$$

10.4 Results and Discussion

10.4.1 Extraction efficiency data for all the compounds in the master mix

The compounds in master mix were run using a GC-MS liquid injection at 10 ng/µL concentration. The compounds showed a good response and displayed sharp peaks with the desired separation, as seen in Figure 10.3. All the 10 compounds spiked onto the fabric samples were detected by the GC-MS after undergoing solvent extraction. The overlaying of the chromatograms gives an idea of the recovery of the compounds from the spiked fabrics, when compared to pure liquid compounds directly injected into the GC-MS system.

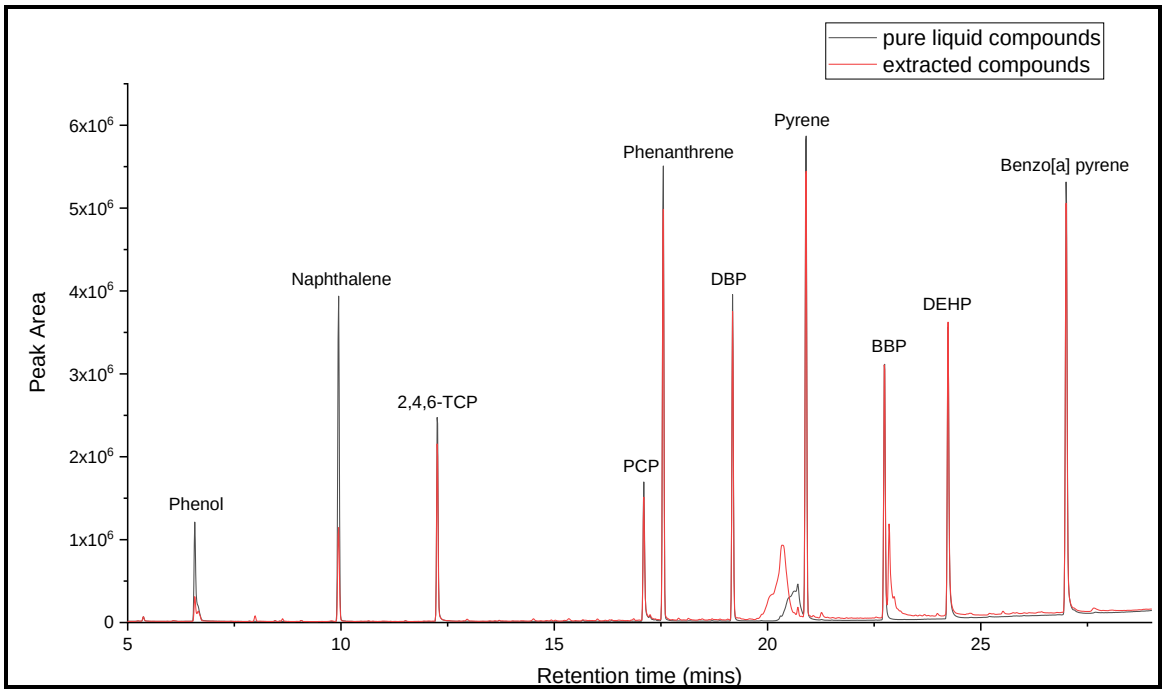


Figure 10.3. Chromatogram depicting the efficiency of extraction of the compounds in the master mix spiked at a concentration of 10 ng/µL

Since the extraction efficiencies were calculated based on positive control samples as reference, it is important to know the actual concentrations (ng/µL) of the compounds extracted from the outer shell materials. Table 10.3 shows the concentration of compounds extracted from outer shell materials. The original spiking amounts in Experiments 1,2 and 3 were 10 ng/µL, 8 ng/µL and 6 ng/µL.

Table 10.3. Concentration of compounds extracted using pressurized solvent extractor

Compounds	Experiment 1 Concentrations (ng/µL)	Experiment 2 Concentrations (ng/µL)	Experiment 3 Concentrations (ng/µL)
Phenol	3.12	2.18	0.76
2,4,6-Trichlorophenol (2,4,6-TCP)	14.81	10.43	6.91
Pentachlorophenol (PCP)	13.02	1.71	1.13
Di-butyl phthalate (DBP)	10.23	8.61	6.64
Benzyl butyl phthalate (BBP)	11.91	8.18	6.21
Di-ethylhexyl phthalate (DEHP)	12.28	8.83	6.98
Naphthalene	2.47	1.7	0.23
Phenanthrene	9.87	8.66	6.48
Pyrene	10.59	8.90	6.89
Benzo[a] pyrene	10.2	8.03	6.03

10.4.1.1 Extraction efficiencies for phenolic compounds in the master mix

The data represented in Figure 10.5, shows the efficiency of extraction for the phenolic compounds. The compounds were a part of the master mix, that was spiked onto outer shell fabrics and extracted using the Buchi pressurized solvent extractor. Table 10.2 shows the amount of phenol present in each cycle, including the positive and negative control samples. The same format of the table is used for all the other compounds in the master mix as well.

The reference equation of the straight line is :

$$Peak\ Area\ (y) = slope\ of\ the\ line\ (m) \times concentration\ (x) + y - intercept\ (b) \quad \textbf{Eq. 10.6}$$

The equation of line for phenol (y= 331187 x- 125225) was used to calculate the effective concentration by substituting the total area of the samples in the equation to obtain the resulting concentration. The negative control (reference unused fabric), yielded no peak area, stating that phenol was not present in the unused reference outer shell fabrics. The positive control sample (direct spiking in the extractor cell) yielded an effective concentration of 5.64 ng/µL after 3 cycles. This translates to a 56.4% extraction efficiency, which is the maximum achievable concentration while using the solvent extractor. Since, the positive control is yielding a fairly low concentration, it is the extraction-analysis process that is not efficient for phenol particularly. Therefore, introducing the added factor of spiking the chemical on a fabric would further reduce the extraction efficiency. This is because it can be assumed that fabric construction allows for the liquid chemical to seep in and be absorbed. Thus, while comparing concentrations obtained from the positive control to the spiked fabric, ideally the positive control would be much higher as compared to the spiked fabric samples. For phenol, the concentrations from the spiked fabric samples ranges between 2.7-3.5 ng/µL, whereas the concentration of the positive control sample is 5.64 ng/µL.

Table 10.4. Calculation of extraction efficiencies for phenol

Samples	Cycle 1 Area	Cycle 2 Area	Cycle 3 Area	Total Area	Effective concentration (ng/µL)	Original spiking concentration (ng/µL)	% Extraction efficiency
1	837133	83084	0	920217	3.15	10	55.9
2	903289	121481	0	1024770	3.47	10	61.5
3	657689	133095	0	790784	2.76	10	49.0
Negative control	0	0	0	0	0	0	0
Positive control	1677782	65633	0	1743415	5.64	10	100

Each colored bar in the graph (Figure 10.5) represents an average of three fabric sample replicates used in an experiment. The extraction efficiency values for phenol are varying (17-55%) between each experiment because of an octamethyl-cyclotetrasiloxane compound peak interfering with the phenol compound peak, as seen in Figure 10.4. The pure phenol peak at 6.573 minutes is being overlapped by the siloxane peak at 6.653. It is possible that the unwanted siloxane peak is arising because of leaching of the stationary phase of the chromatographic column. It could also be septum material/top-rubber part of the vial (made up of silicone), contaminating the injection needle and injecting the silicone particles in the column. Ways to correct this issue could be frequently replacing the inert-high temperature septum (used for current analysis) and avoiding multiple injections from the same vial. This could reduce the amount of silicone being picked up by the needle. Baking the column at a higher temperature (around 200°C) could possibly tackle the issue of leaching of the silicone from the stationary phase of the column.

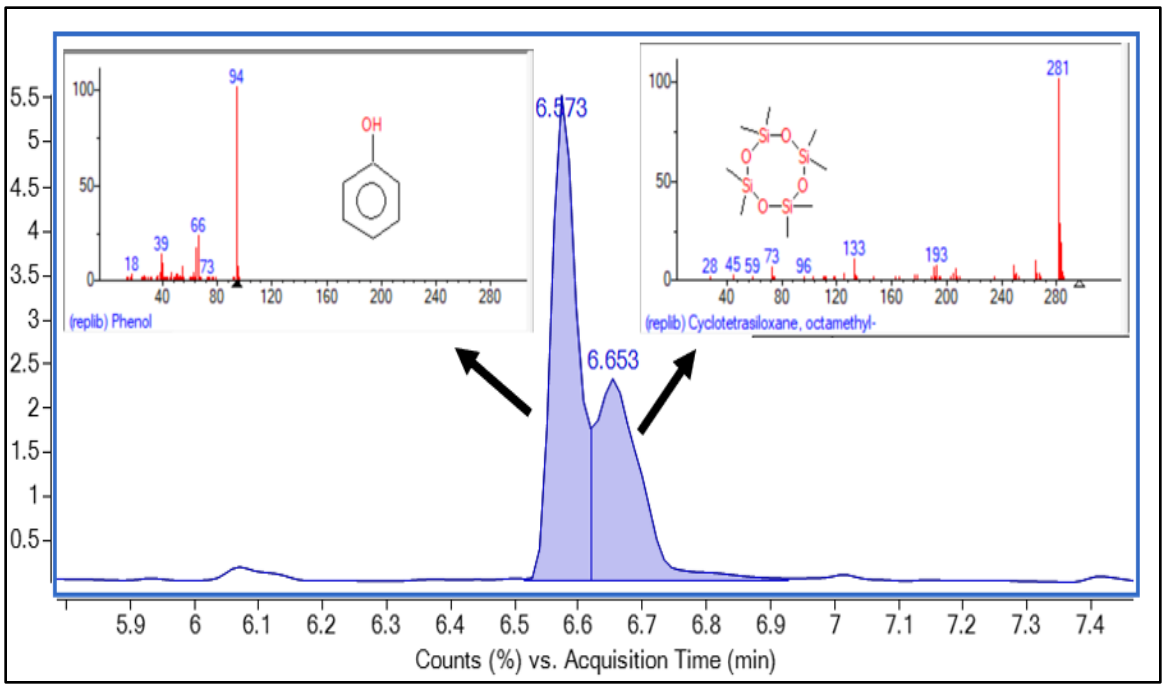
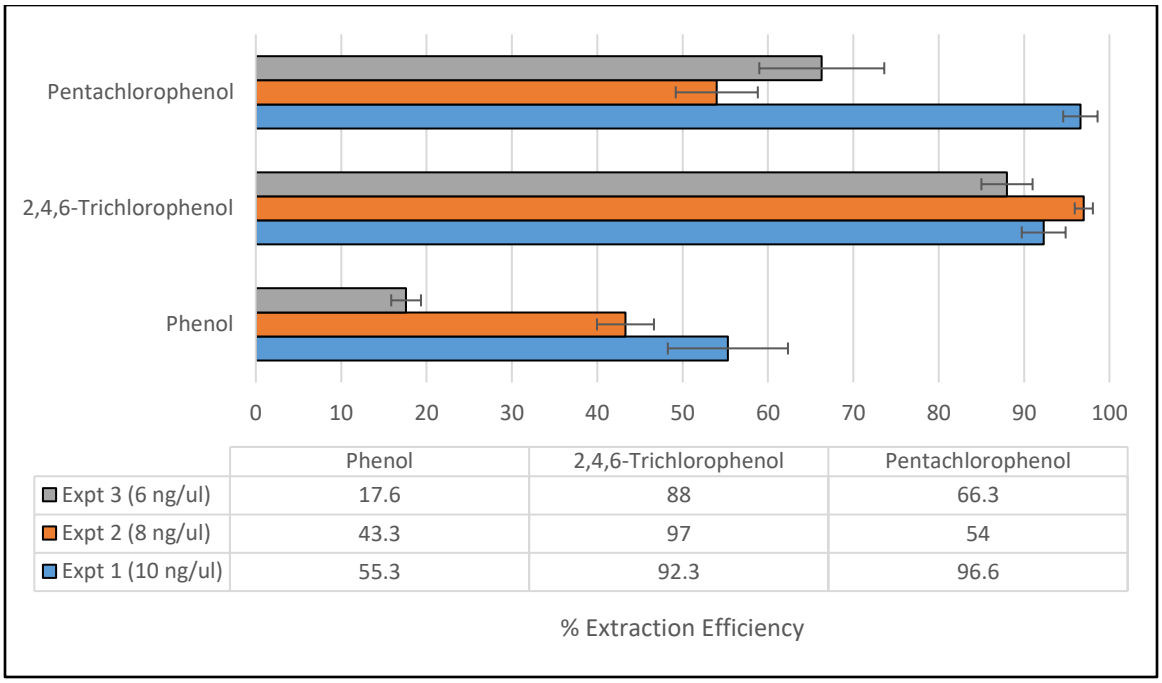


Figure 10.4. Interference of the siloxane peak with the phenol compound peak

2,4,6-TCP showed a consistent extraction efficiencies across the experiments. The PCP compound had a large variability in the extraction efficiencies across the experiments. One of the probable reasons could be that PCP does not respond equally well as compared to the other compounds in the master mix. This is also evident from the R^2 value being 0.9683, being lower than most compounds, seen in Figure 9.7. Comparing the phenolic compounds and the phthalate esters, the phthalate esters show a higher consistency in the extraction efficiencies across the three replicate runs. This could be related to the difference in the boiling points, as all phthalates have a high boiling point (>350°C) and hence they are more stable as compared to the phenols, which have lower boiling points.

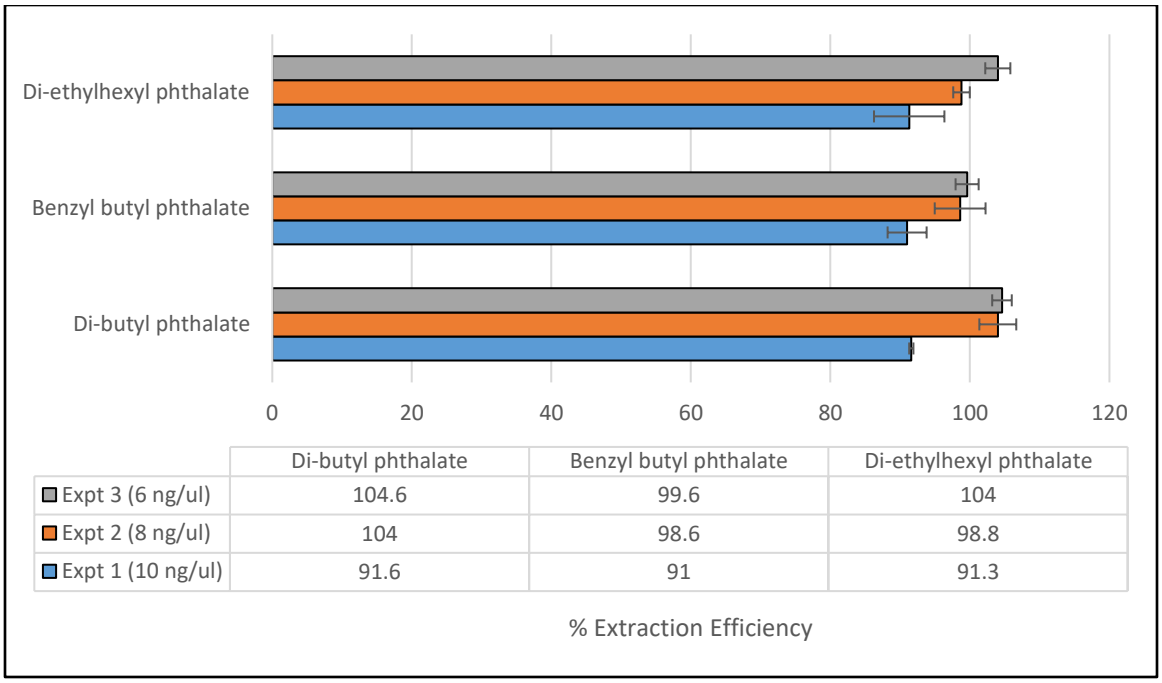


	Phenol	2,4,6-Trichlorophenol	Pentachlorophenol
Expt 3 (6 ng/ul)	17.6	88	66.3
Expt 2 (8 ng/ul)	43.3	97	54
Expt 1 (10 ng/ul)	55.3	92.3	96.6

Figure 10.5. Extraction efficiencies for phenols using pressurized solvent extraction with n-hexane

10.4.1.2 Extraction efficiencies for phthalates in the master mix

A general trend for phthalates as seen in Figure 10.6 is that the extraction efficiency increases with lesser mass of the compounds spiked onto the fabric. A possible explanation for the same could be that when lesser particles are present on the fabric samples, they are being effectively removed by the solvent in a given area of the sample, as seen in Figure 10.6. As seen, only DBP has a detection of 0.09 ng/µL in the third cycle, whereas all the other compounds are absent in the third cycle. The liquid extraction method using n-hexane as the solvent is suitable for the extraction of phthalates as seen in Figure 10.6. All the three phthalates have extraction efficiencies between 90-100%. The strong non-polar nature of n-hexane is compatible with the non-polar properties of phthalates and facilitates better removal of the contaminants from the fabric samples.



	Di-butyl phthalate	Benzyl butyl phthalate	Di-ethylhexyl phthalate
Expt 3 (6 ng/ul)	104.6	99.6	104
Expt 2 (8 ng/ul)	104	98.6	98.8
Expt 1 (10 ng/ul)	91.6	91	91.3

Figure 10.6. Extraction efficiencies for phthalates using pressurized solvent extraction with n-hexane

The concentrations of phthalates obtained in individual cycles of the extraction process is shown in Figure 10.7. For all the compounds, the concentrations obtained in the first cycle is high and having a second cycle ensures that almost all of the compounds spiked on the fabric is recovered.

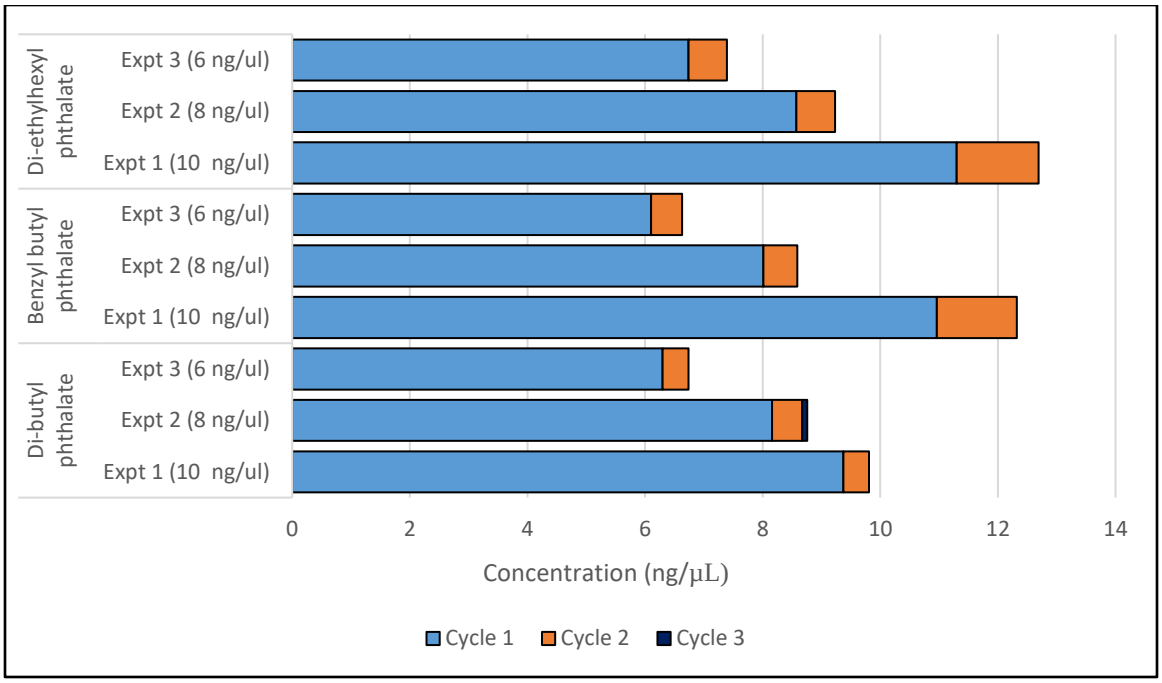
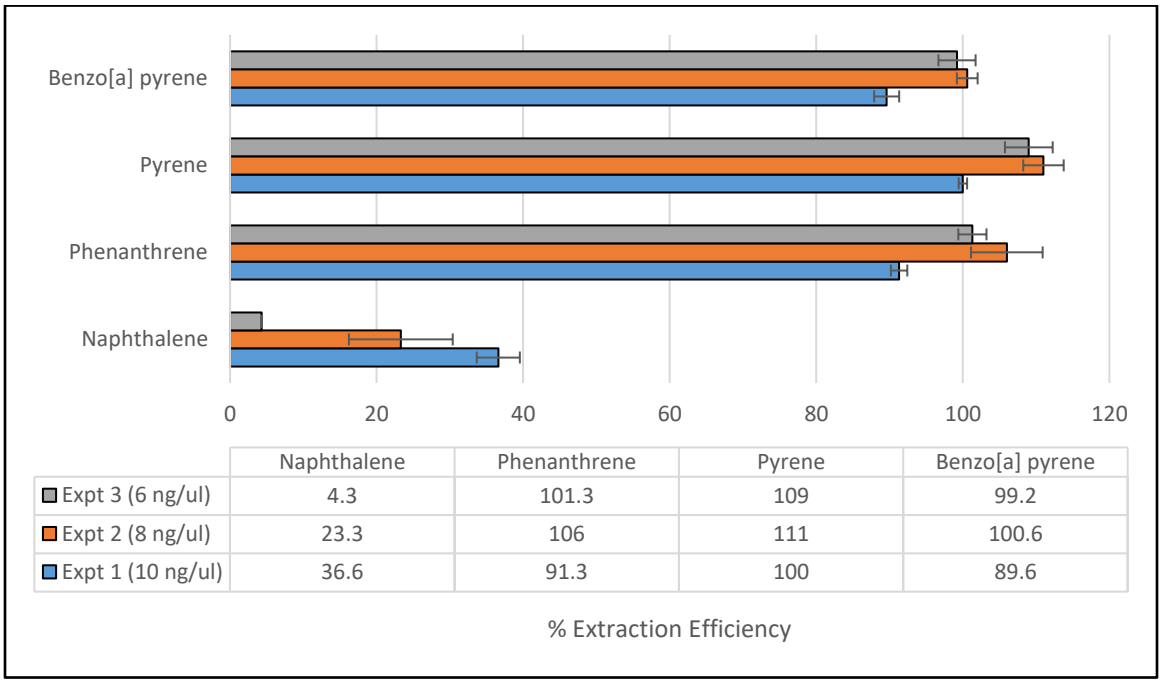


Figure 10.7. Concentrations of phthalates extracted in each cycle of the liquid extraction process

10.4.1.3 Extraction efficiencies for PAHs in the master mix

Benzo[a] pyrene, pyrene and phenanthrene have extraction efficiencies between 89-111%, as seen in Figure 10.8, which is considered to be very efficient. Since, all the three compounds have a high boiling point (>340°C), as seen in Table 10.8, the compounds are stable to the high temperature and pressure conditions and thus produce consistent results. Since PAHs are also non-polar in nature and having n-hexane as a highly non-polar solvent, the compounds were effectively extracted from the fabric samples. For naphthalene though, a very low extraction efficiency, between 4-36% was obtained. The reason could be that naphthalene is a relatively volatile compound compared to the other PAHs, having a high vapor pressure even at room temperature. The compound sublimes and turns into a gaseous phase directly from solid state even at room temperature, if kept for a long duration [143]. The naphthalene could be

evaporating when the spiked fabric samples were allowed to air-dry for 1-hour. Also, the liquid extractor uses a temperature of 100°C for extraction and hence the extract arising into the 60-mL is comparatively warm. There might be a possibility that the naphthalene compound could be evaporating during the further processes of diluting, filtering and transferring to a GC vial. The concentrations obtained from the positive control samples for the three replicates were 6.69 ng/µL, 6.74 ng/µL and 5.76 ng/µL respectively for the 10 ng/µL, 8 ng/µL and 7 ng/µL spiking amounts on outer shell fabrics. This data shows that the positive control, where the fabric was not present, had a variability in the amounts detected. The recovery of the positive control for the three experiments varied between 67% and 96%. Consequently, the relative extraction efficiencies for the fabric samples based on the positive control samples shows a large variability, as seen in Figure 10.8.



	Naphthalene	Phenanthrene	Pyrene	Benzo[a] pyrene
Expt 3 (6 ng/ul)	4.3	101.3	109	99.2
Expt 2 (8 ng/ul)	23.3	106	111	100.6
Expt 1 (10 ng/ul)	36.6	91.3	100	89.6

Figure 10.8. Extraction efficiencies for PAHs using pressurized solvent extraction with n-hexane

10.5 Conclusion

The liquid extraction method was tested for the extraction of a wide range of fireground contaminants such as phenols, phthalates and PAHs. A liquid extraction method using the speed extractor was developed and validated by carrying out three separate experiments. Each experiment had different amounts spiked onto the fabric samples to test the extraction capability of the instrument. For the outer shell fabric material, the conditions set on the extractor were optimized such that all the compounds could be extracted at their maximum efficiencies. For 7 of the 10 compounds, the efficiency of extraction was between 85-100%, which is a significant amount considering the extraction cycles were a total of only 50 minutes. The method is also unique wherein a combination of 3 types of compounds can be extracted in a single experiment using n-hexane. The method is suitable for compounds with a high boiling point, which are stable to the high temperature and pressure used during the extraction. The only drawback of the method is that compounds that are volatile in nature might evaporate and could skew the extraction results. Naphthalene was an example, possible evaporated through the process, being highly volatile, and hence did not yield consistent extraction efficiencies. The liquid extraction method using the pressurized solvent extractor was validated by comparing the data from three individual experiments performed on three separate days.

Chapter 11: Development of a thermal extraction method using headspace GC

11.1 Introduction

It was mentioned in chapter 2, that liquid extraction is an efficient method of removing contaminants from fabric samples. Liquid extraction is also the most widely used method to remove contaminants because there is extensive data available and a solvent typically is compatible with a wide range of compounds. But there are other methods of extraction that can be used to extract the contaminants from solid/liquid matrices. One such method is thermal extraction, which utilizes heat to remove analytes from a substrate. Thermal extraction, also known as off-gassing, translates to evolution of chemicals from a solid/liquid matrix in a vapor phase. The solid sample on heating reaches a solid-vapor equilibrium after a certain time, which is the maximum amount that would be released.

Thermal extraction is particularly useful in removing compounds that have lower boiling points from fabrics. A headspace sampler (HS) is an instrument that has the capability to simulate off-gassing in solid or liquid matrices. The samples are placed in HS crimp-top glass vials and heated at a set temperature for a fixed amount of time. The instrument is built so that the vial can be equilibrated and shaken in the oven precisely with a 0.1°C accuracy. The best feature of this add-on is that it can be directly attached the gas chromatograph (GC) inlet via a heated transfer line. After a sample is heated, the gases evolving from the sample are collected in the headspace area between the sample and the vial cap. A needle precisely pierces through the sealed cap and transfers the gas to the transfer line through a heated loop. The heated transfer line then carries the gas into the GC inlet without any loss. One of the major advantages with using the headspace sampler is that there is very little sample preparation required. Any solid or liquid sample can be placed inside the glass vial and can be heated in the oven for analysis. In contrast to the off-

gassing, measuring the off-gassed air through any other method such as polymer sorption/liquid extraction or active/passive air sampling requires an elaborate set-up and complex sample preparation.

With previous studies of off-gassing of firefighter gear it is known that the level of off-gassing of chemicals is largely dependent on the time after exposure/contamination that the fabric is sampled and the temperature that the fabric was exposed to. In respect to firefighting, the turnout jacket and pants are exposed to numerous toxic chemicals in the fire scenario. Thereafter, the off-gassing depends on the condition in which it is stored, transported and re-used for another fire incident. The headspace sampler can be used for a variety of applications depending on the temperature and time that is used. For example, if an outer shell material is exposed to a temperature of 200°C, it would simulate the temperature in an actual fire [147]. A temperature of 200°C could also be justified as a temperature used for the extraction of contaminants from the firefighter gear; causing deliberate off-gassing to remove the toxic unwanted contaminants. Having the outer shell materials exposed to 36°C would be in the ambient range of temperatures and closest to the skin temperature. An exposure of 50°C would simulate a heated car trunk or the inside of a fire truck on a hot sunny day [145].

At all the above-mentioned temperatures, the time that the sample is allowed to equilibrate in the headspace oven could be a factor deciding the amount released from the materials. This is because there is a solid-gas equilibrium that gets formed inside the heated vial. When the equilibrium is reached, no more of the contaminants will be released from the fabric. Several temperature and time conditions must be tested to obtain the best suited method targeted at removing phenols, phthalates and polycyclic aromatic hydrocarbons (PAHs) from outer shell materials.

11.2 Materials

Chemicals and glassware used are provided in Section 9.2. Additionally, headspace crimp-top caps, glass vials, crimp-top crimper and de-crimper were ordered from Agilent. Outer shell fabric (PBI Max), made of twill weave Kevlar®/PBI blend were used as unused reference firefighter gear materials. The yarns used in the fabrics are 70% spun and 30% filament. The materials are tested to withstand a temperature of 1175°C and has excellent tear strength, being light-weight [144].

11.2.1 Compound properties

The compounds and their properties relevant to the headspace GC analysis are provided in Table 9.1

11.3 Methods

11.3.1 Calibration method development on the headspace sampler GC

11.3.1.1 Calibration solution preparation for HS

A 50 ng/µL stock solution was prepared by pipetting 250 µL of the 2,000 ng/µL master mix stock solution into a 10-mL volumetric flask and diluting with n-hexane. Further, a total of nine calibration solutions ranging from 50 ng to 10,000 ng (as per mass of compound-in vial) were prepared using two solutions: 50 ng/µL stock solution was used to prepare the 50 ng, 100 ng, 200 ng, 500 ng, 1000 ng samples by pipetting 1 µL, 2 µL, 4 µL, 10 µL and 20 µL, respectively into HS crimp-top vials. The 2,000 ng/µL stock solution was used to prepare the 2,000 ng, 4,000 ng, 8,000 ng and 10,000 ng samples by pipetting 1 µL, 2 µL, 4 µL and 10 µL, respectively into HS crimp-top vials. Every liquid calibration solution was spiked in a 20-mL crimp-top glass vial.

11.3.1.2 The GC-MS analysis method

The analysis of phenols, phthalates and PAHs was carried out using Agilent 7890B gas chromatographic system coupled to an Agilent 5977B mass spectrometer equipped with electron ionization (EI). Chromatographic analysis was conducted in the split mode with a split ratio of 10:1. The column used in the GC was an Agilent DB-UI 8270D, fused silica capillary column (30 m × 0.25 mm × 0.25 μm). An Agilent 5190-3136 UI splitless single taper with glass wool liner was used in the inlet for injection. The injection volume was 1 μL and the injection temperature was kept at 250°C and a helium flow rate of 1.2 mL/min. The oven gradient was set to begin at 40°C, increased to 280°C for 1 min at a rate of 10°C/min, further increased to 300°C at 5°C/min for 1 min. The total run time was 30 minutes. The MS transfer line was kept at 280°C throughout the run. The MS quadrupole temperature was maintained at 230°C and the ion source temperature was kept at 150°C. The gain factor used was 1.00. The analysis was conducted in scan mode (35-550 amu) using EI with an energy of 70eV. A calibration curve of peak area versus mass-in vial (ng) was plotted for all the compounds.

11.3.2 Thermal extraction method development on the headspace GC

The 7697A Agilent headspace sampler connected to a 7890B GC and 5977B MS was used to thermally extract the contaminants from the fabric samples. Three replicates of 1 cm x 1 cm outer shell fabric materials were spiked with 10,000 ng (mass-on fabric) of the master mix by evenly spreading 5 drops of 1μL having a concentration of 2,000 ng/μL. An unused reference outer shell fabric was chosen as the negative control to obtain the baseline signal. A positive control was used, for which 5 μL of the master mix was directly spiked into the headspace vial. The positive control is crucial in understanding the maximum concentration that could be

extracted through the HS. Even though 10,000 ng of a pure liquid chemical is directly spiked in a HS vial and analyzed, it is mostly found that the instrument detects either a lower or higher mass. To account for this variability in calculating the extraction efficiencies of spiked fabric samples, the value of the positive control sample is considered as the maximum mass the instrument can detect. The positive control sample is also important in calculating the percent extraction efficiencies for all the compounds.

All the extraction efficiencies calculated in this chapter are relative extraction efficiencies based on the mass of the positive control sample. The value of the percent extraction efficiency cannot be directly compared to the mass originally added on the fabric, without knowing the mass of the positive control detected. The spiked fabrics and both the control samples were placed in 20-mL crimp-top glass vials. The GC-MS method mentioned in Section 11.3.1.2 was used for the headspace GC analysis. A set of different temperatures and times was used to understand the temperature and time profiles. Table 11.1 shows the various conditions that were tested.

Table 11.1. Conditions used for headspace GC method development runs

Temperature (°C)	Time (mins)
36°C	30 minutes
50°C	30 minutes
100°C	30 minutes, 60 minutes, 120 minutes
200°C	30 minutes

The 36°C temperature condition was chosen since it is closest to the skin temperature, when the firefighter is regularly wearing a turnout jacket. It is also the temperature that is

prevalent in fire stations, where the gear is stored [145]. Having the data to understand what off-gases at ambient temperature is important since it is a direct hazard to the first responders in the fire stations without respiratory protection. An equilibration time of 30 minutes was chosen since it was also used for the other temperature conditions and was better for comparison.

The 50°C temperature condition was used since it represents elevated storage temperatures. When a turnout gear is transported in car boots or fire trucks, often the interior gets hot and could reach temperatures of around 50°C [101,103]. Having the ability to analyze what off-gases at that condition is important to the health and safety of the firefighter. A 30-minute equilibration time was chosen since it is reasonable to assume that firefighters take about 30-minutes to 1-hour to carry the contaminated gear to the fire stations from the scene of exposure. The time was chosen to provide a realistic understanding of the off-gassing from the outer shell materials, if stored in a heated car/fire truck. A temperature of around 50°C could also be used as thermal decontamination technique for cleaning firefighting gear. If contaminated turnout gear is kept in an enclosed cabinet for a certain time, the compounds off-gassing from the gear can be vented out and the technique can function as a decontamination method to clean the gear.

The 100°C temperature condition was selected since it a temperature commonly seen in most house fires and would be relevant in understand the risks associated with chemicals off-gassing from the gear [147]. 100°C was also used as a temperature to assess the thermal extraction of compounds from the outer shell materials. Equilibration times of 30 minutes, 60 minutes and 120 minutes were chosen to understand the effect of equilibration time on the off-gassing amounts of the fireground contaminants. One of the most important factors in the vaporization of the compounds from the solid fabric matrix is the formation of solid-vapor equilibrium. To achieve that, sufficient equilibration time is the most crucial aspect, as described in Section 7.5.

The 200°C temperature condition was chosen based on the representative data for temperatures present in structural fires [147] and also represents the extreme training temperatures that firefighters undergo in their field training. 200°C is also near the physical upper limit of the headspace sampler oven without any physical constraints. Thus, the off-gassing at 200°C for an equilibration time of 30 minutes would provide an idea of thermal extraction at an elevated temperature. The same could be compared with the thermal extraction at 100°C condition.

The physical limit of the headspace sampler oven is 260°C . Initial trials at 260°C showed that the crimp-top caps were separated from the vial, possibly because of excessive pressure being built up in the vial. Hence, the maximum temperature used for all headspace analysis was limited to 200°C for the smooth functioning of the instrument.

11.3.3 Calculation of the extraction efficiencies

The peak areas for the compounds were obtained from the chromatograms, as seen in Table 11.2. This area was entered in Eq. 11.2 (calibration curve equation) to get the resulting concentration. The same was repeated for the fabric and control samples. The concentration of individual fabric samples was divided by the concentration of the positive control sample to obtain the % extraction efficiency.

$$Mass\ of\ compound\ in\ vial\ (ng) = Concentration\ of\ solution\ (ng/\mu L)\ *\ Volume\ spiked\ (\mu L) \quad \textbf{Eq. 11.1}$$

Table 11.2. Reference data of mass-in vial and peak areas used in HS liquid calibration

Mass-in vial (ng)	Peak Area
2,000	Y1
4,000	Y2
8,000	Y3
10,000	Y4

Considering Table 11.2 as the calibration run, the equation of the line would be:

$$y = mx + c \qquad \textbf{Eq. 11.2}$$

The slope of the line can be calculated using the formula:

$$Slope(m) = \frac{y - c}{x} \qquad \textbf{Eq. 11.3}$$

The y-intercept can be calculated by using the formula:

$$Intercept(c) = \frac{(Y4 - Y1)}{(10000 - 2000)} \qquad \textbf{Eq. 11.4}$$

For noting the extraction values, consider the following Table 11.3.

Table 11.3. Calculation of percent extraction efficiency for spiked fabric samples

	Peak area	Effective concentration	Original concentration	Relative % extraction efficiency
Samples		(substitute in calibration curve equation)	(the mass of master mix used in spiking)	(relative to the positive control)
Fabric 1	$F1_a$	$[F1_a - c]/m = F1_c$	10,000	$(F1_c/K_c) * 100$
Fabric 2	$F2_a$	$[F2_a - c]/m = F2_c$	10,000	$(F2_c/K_c) * 100$
Fabric 3	$F3_a$	$[F3_a - c]/m = F3_c$	10,000	$(F3_c/K_c) * 100$
Negative control	O	$[O - c]/m = O_c$	0	$(O_c/K_c) * 100$
Positive control	K	$[K - c]/m = K_c$	10,000	100

Some of the compounds were present in blank outer shell fabrics or certain compounds eluting at the same retention times as of the compounds was noted (O). That was subtracted from the sample areas ($F1_a$, $F2_a$, $F3_a$) and the effective concentrations ($F1_c$, $F2_c$, $F3_c$) were calculated, as seen in Table 11.3. The concentrations obtained from the fabric samples were divided by the concentration of the positive control sample to obtain percent extraction efficiencies. These relative extraction efficiencies are based of positive control samples and cannot be directly compared to the original mass (10000 ng) that was spiked on the fabric.

11.3.4 Calculation of error bars for all the graphs plotted

Error bars were plotted as standard error with 95% confidence, which is calculated using the formula:

$$Standard\ error = 1.96 * \frac{\sigma}{\sqrt{n}} \quad \textbf{Eq. 11.5}$$

where 1.96 = z-score for 95% CI, σ= standard deviation of n samples and n=number of samples in consideration

The standard error when added and subtracted from the sample mean would give the upper bound and lower bound for the confidence interval:

$$Confidence\ interval = Mean\ \pm 1.96 * \frac{\sigma}{\sqrt{n}} \quad \textbf{Eq .11.6}$$

11.4 Results and Discussion

11.4.1 Effect of equilibration time on off-gassing

Equilibration time is an important factor that governs the amount of a compound volatilizing into the vapor phase. The solid/liquid matrix in the headspace vial must be allowed to equilibrate for sufficient time so that a complete sample-vapor equilibrium can be reached. Effective transfer into the vapor phase is possible, only when an equilibrium is reached inside the

vial. Even though, the temperature of exposure might be lower than the boiling point of the compound to be extracted, if the compound is left inside the vial for enough time, thermal extraction is possible. An optimum equilibration time must be calculated based on the extraction efficiencies obtained for the compounds. There might be a possibility that having an equilibration time much greater than the optimum time could actually lead to re-deposition of the vapor phase into the fabric sample/surfaces inside the vial. The current section assesses the effect of equilibration time on the off-gassing of phenols, phthalates and PAHs spiked onto outer shell fabrics. Table 11.4 shows the actual masses of compounds detected using the headspace GC at 100°C for 30, 60 and 120 minutes.

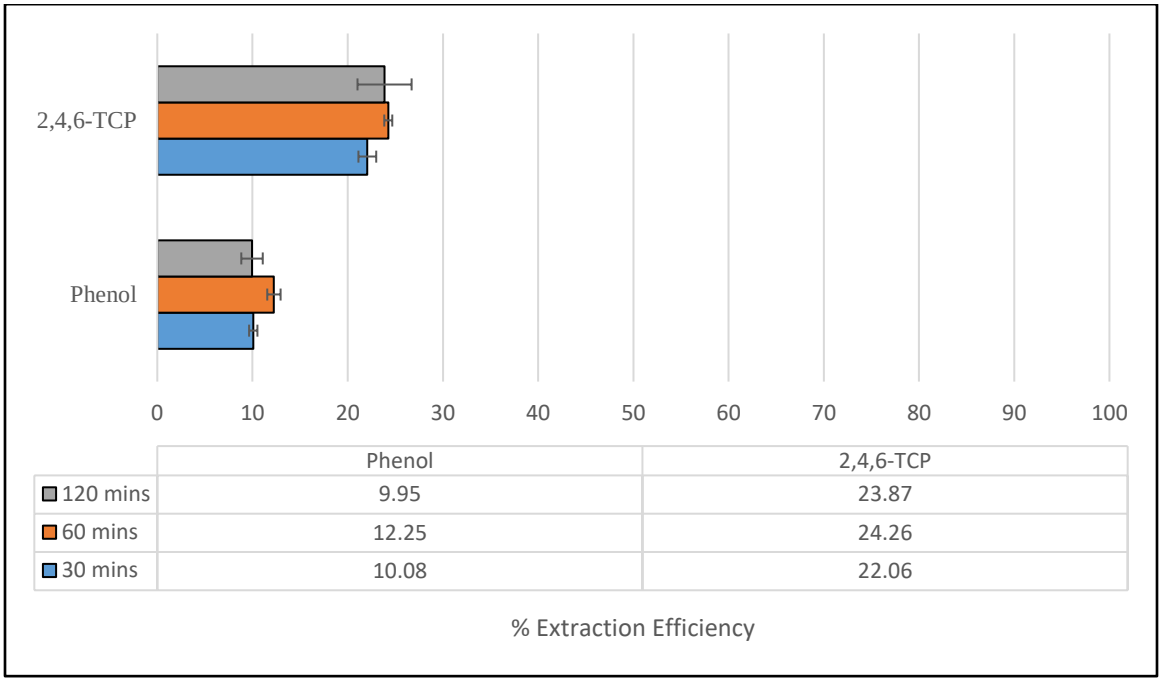
Table 11.4. Masses of compounds detected using headspace GC at 100°C for 30, 60 and 120 minutes

Compounds	30 minutes	60 minutes	120 minutes
Phenol	979 ng	1,350 ng	1,093 ng
2,4,6-Trichorophenol (2,4,6-TCP)	2,150 ng	2,333 ng	2,371 ng
Di-butyl phthalate (DBP)	118 ng	313 ng	240 ng
Naphthalene	7,506 ng	7,817 ng	7,658 ng
Phenanthrene	1,358 ng	1,568 ng	1,773 ng
Pyrene	360 ng	236 ng	317 ng

11.4.1.1 Extraction efficiencies for phenols

Firstly, of the three phenolic compounds present in the master mix that was spiked onto the outer shell fabrics, only two compounds were detected, as seen in Figure 11.1. The fabric exposure temperature was below the boiling point for all the compounds. Phenol had a lower extraction efficiency of about 10%, because of the octamethyl-cyclotetrasiloxane peak interfering with the compound peak, as seen in Figure 10.4. 2,4,6-TCP was detected but had a low efficiency

of around 24%, since it has a boiling point of 246°C, which is significantly above the temperature of exposure (100°C). The 30-minute equilibration time caused about 2,160 ng of 2,4,6-TCP compound to off-gas, from the 10,000 ng that was spiked onto the fabric. PCP was absent since it has a boiling point of 310°C and an exposure of 100°C was probably not enough for the transfer of the compound into the vapor phase. This shows that the solid-gas equilibrium of phenol takes place at most in the first 30 minutes of heating and any further equilibration time would be insignificant.



	Phenol	2,4,6-TCP
120 mins	9.95	23.87
60 mins	12.25	24.26
30 mins	10.08	22.06

Figure 11.1 Extraction efficiencies for phenols using headspace-GC at 100°C for 30 minutes, 60 minutes and 120 minutes

11.4.1.2 Extraction efficiencies for phthalates

Of the three phthalates present in the master mix spiked onto the outer shell fabrics, only DBP was detected, as seen in Figure 11.2. The boiling point of all the compounds is above 300°C and hence the exposure of the fabrics to 100°C was not sufficient for the extraction of the compounds significantly. DBP was detected at a very low efficiency of 1% (about 383 ng) with

a large standard error of almost 1%, which states that the compound could be absent in one of the three fabric replicates that were run. Even though, the extraction efficiencies for DBP were low, increasing the equilibration time from 30 minutes to 60 minutes produced a near 3-fold increase in the extraction efficiency. But, when the equilibration time was increased further from 60 minutes to 120 minutes, the extraction efficiency reduced from 3.36% to 2.53%. The masses detected at these times followed the same trend as that of the extraction efficiency.

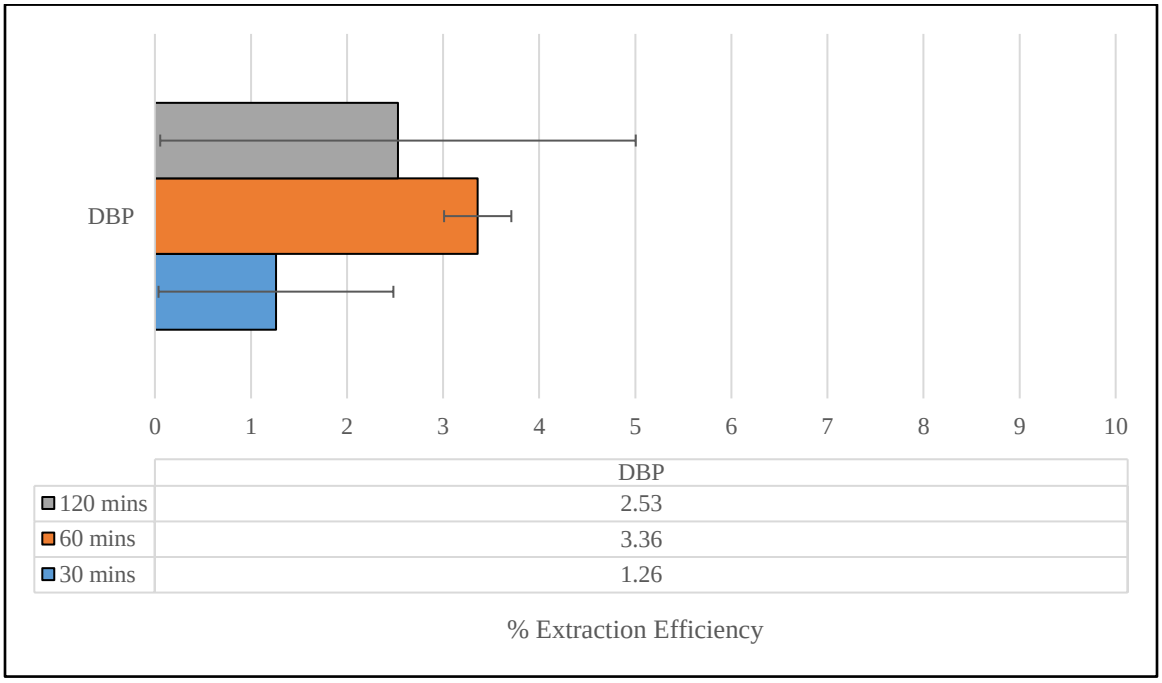
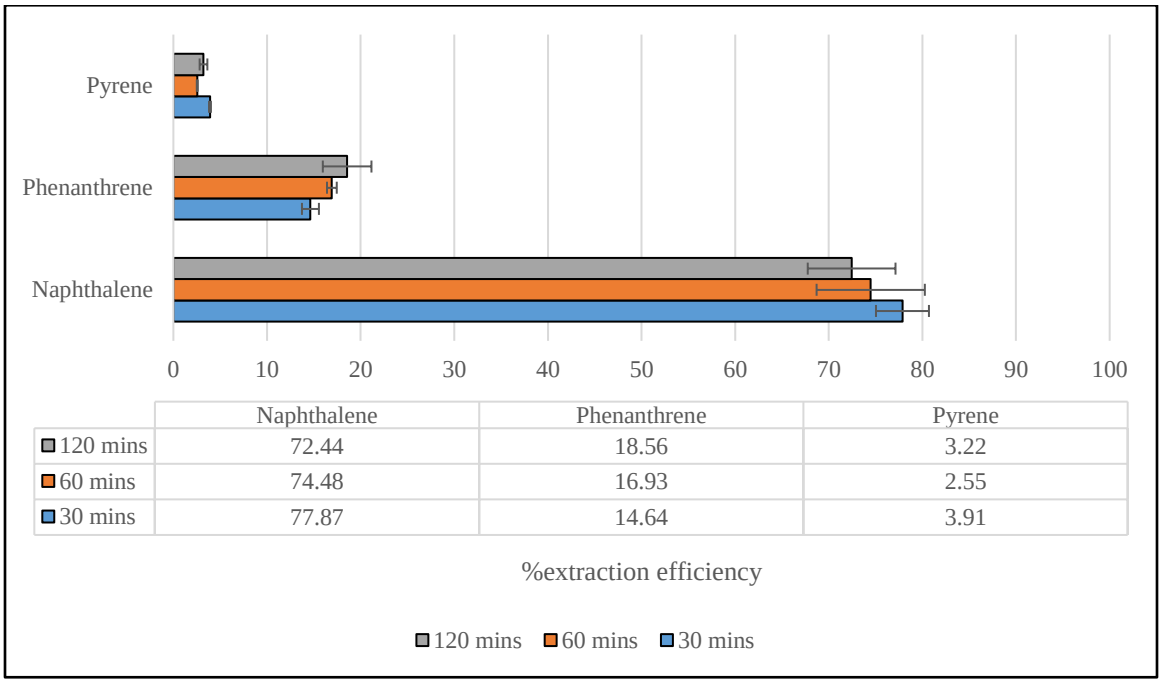


Figure 11.2. Extraction efficiencies for phthalates using headspace-GC at 100°C for 30, 60 and 120 minutes

11.4.1.3 Extraction efficiencies for PAHs

Three out of the four PAHs present in the master mix that was spiked on the outer shell material were detected, as seen in Figure 11.3. Pyrene, phenanthrene and benzo[a] pyrene are semi-volatile compounds having boiling points over 300°C. Hence, even an exposure to 100°C at the highest equilibration time of 120 minutes was not enough to extract significant amounts from the fabrics. For pyrene and phenanthrene, the relative extraction efficiencies were between

2-4% and 14-19% respectively. But naphthalene had a significantly higher extraction efficiency between 72-78%. This was interesting to note, since the temperature of 100°C used for analysis was below its boiling point of 182°C. This is because naphthalene is highly volatile and is known to sublime at as low as 50°C [143]. Hence, at a temperature of 100°C, the vapor pressure of naphthalene was sufficient to extract more than 7,500 ng of the compound with respect to the 10,000-ng spiked originally on the fabric. An interesting trend for naphthalene is that the extraction efficiency reduces with increase in the equilibration time. This could be justified by the fact that 30 minutes is a sufficient time to achieve the solid-gas equilibrium and any exposure further could possibly lead to absorption of the gaseous compound back into the fabric or other surfaces inside the vial. Overall, it was seen from Figure 11.3 that an equilibration time of 30 minutes was sufficient to cause maximum off-gassing at the 100°C temperature condition.



	Naphthalene	Phenanthrene	Pyrene
120 mins	72.44	18.56	3.22
60 mins	74.48	16.93	2.55
30 mins	77.87	14.64	3.91

Figure 11.3 Extraction efficiencies for PAHs using headspace-GC at 100°C for 30, 60 and 120 minutes

11.4.1.4 Best suited equilibration time for off-gassing

It was established in the earlier sections that 30 minutes was an optimum time for the off-gassing of the fireground contaminants from outer shell fabrics. The headspace sampler equilibration time combined with the GC-MS analysis run time, equates to a 1-hour method for analyzing a single sample. Compared to other methods of analyzing off-gassing, the method developed in this chapter is much faster. The samples to be used for headspace GC analysis do not need sample preparation as well, therefore the analysis can be done in relatively less time and with multiple samples being analyzed continuously, when added to a sequence on the instrument.

11.4.2 Effect of equilibration temperature on extraction efficiency

It is known that the vapor pressure of most compounds, except water, reduces as the temperature is increased. Lower the vapor pressure, easier it is for a compound to volatilize into its vapor phase. The data shown in this section outlies the effect of the temperature on the amount of off-gassing of fireground contaminants from spiked outer shell materials. Section 11.3.3 explains the relevance of the temperatures used for this study. For a firefighter gear application, it is important to understand the types and amounts of compounds off-gassing at various exposures of heat. To test the effect of temperature, a mass of 10,000 ng of the master mix was spiked onto the outer shell materials for headspace GC analysis. Table 11.5 shows the masses of compounds off-gassing at the various temperatures.

Table 11.5. Masses of compounds off-gassing at various temperatures

Compounds	36°C	50°C	100°C	200°C
Phenol	114 ng	186 ng	979 ng	6,126 ng
2,4,6-Trichlorophenol (2,4,6-TCP)	0	416 ng	2,160 ng	10,553 ng
Pentachlorophenol (PCP)	0	0	0	9,228 ng
Di-butyl phthalate (DBP)	0	0	118	8,782 ng
Benzyl butyl phthalate (BBP)	0	0	0	7,052 ng
Di-ethylhexyl phthalate (DEHP)	0	0	0	6,688 ng
Naphthalene	1,446 ng	3,336 ng	7,506 ng	9,719 ng
Phenanthrene	0	0	1,358 ng	8,190 ng
Pyrene	0	0	383 ng	6,234 ng
Benzo[a] pyrene	0	0	0	2,453 ng

The chromatogram shown in Figure 11.4 shows an overlay of individual chromatograms of compounds extracted from outer shell fabrics at various temperatures. The height of the peak represents the masses of compounds off-gassing from the outer shell fabrics at respective temperatures. The compounds seen are the compounds that are detected at the temperatures they were tested at. The chromatogram (Figure 11.4) can be matched to the Table 11.5 to provide understanding of the values of masses that were detected. While all compounds were detected at 200°C, only six were detected at 100°C, three were detected at 50°C and two at 36°C.

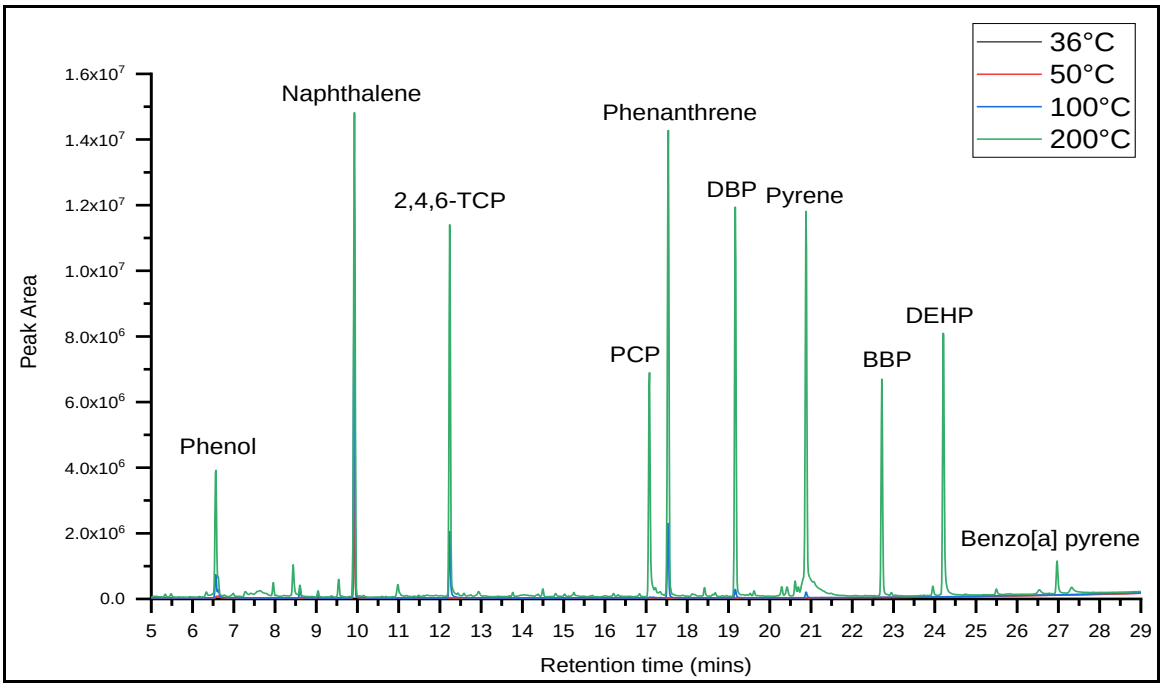


Figure 11.4. Effect of temperature on extraction of compounds from outer shell fabrics

A proper comparison of the amounts at various temperatures is not clearly visible in Figure 11.4. Hence, Figure 11.5 shows the representative comparison for naphthalene in a magnified version. It can be seen from the peak heights that higher amounts of naphthalene are detected at higher temperatures.

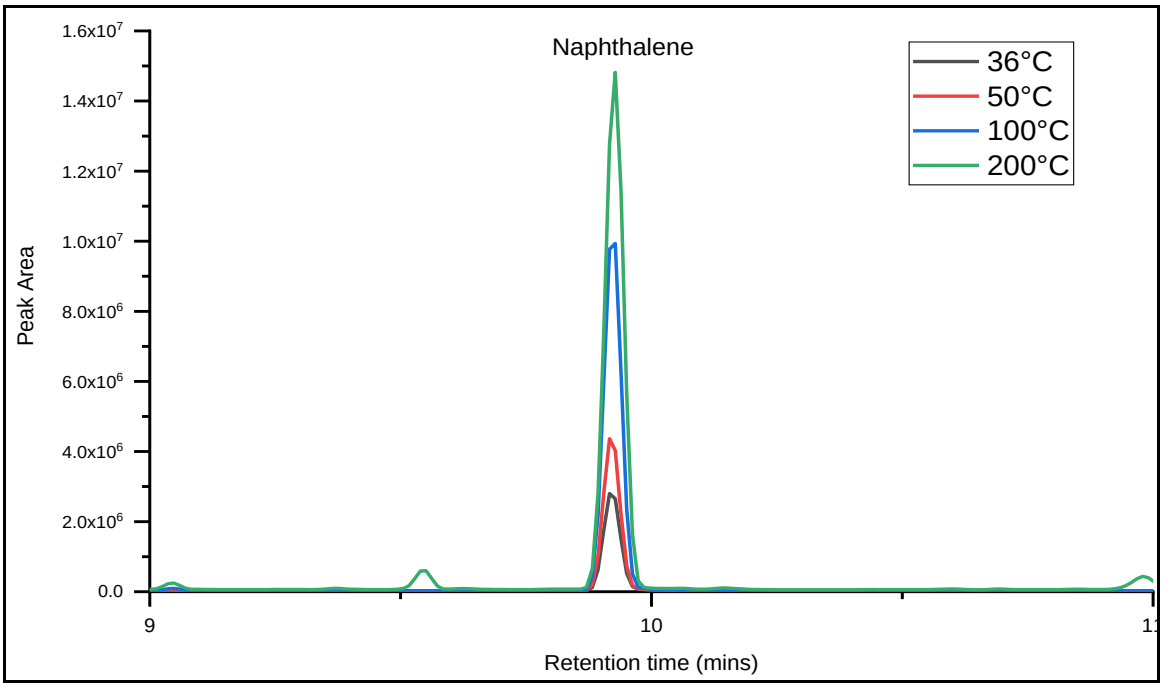
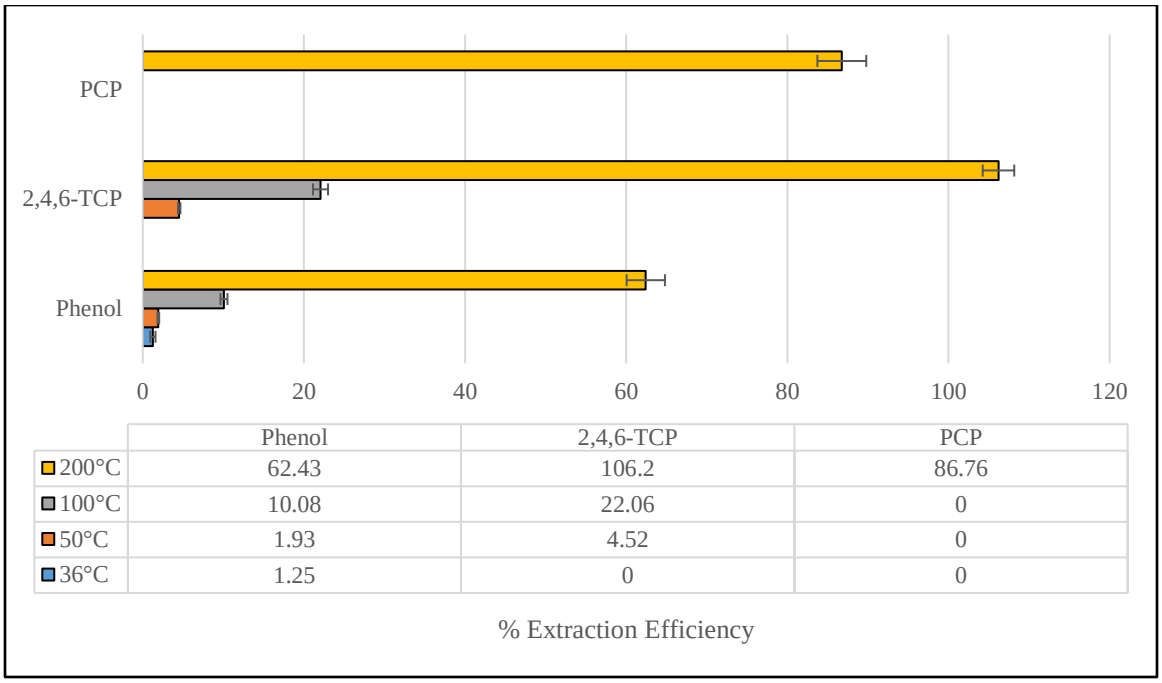


Figure 11.5. Magnified chromatogram showing the peak areas at various temperatures

11.4.2.1 Extraction efficiencies for phenols

It can be seen in Figure 11.6, that all the three phenolic compounds were detected at 200°C, while two were detected at 100°C, two were detected at 50°C and only one was detected at 36°C. The extraction efficiencies for phenols were in the range of 60-100%. Ideally, phenol should have had a significantly high extraction efficiency since its boiling point of 182°C was lower than the 200°C temperature of exposure. But, the efficiency for phenol was lower, probably due to the octamethyl-cyclotetrasiloxane peak interfering with the compound peak and skewing the calculation of the extraction efficiency, as seen in Figure 10.4. PCP is a semi-volatile compound having a boiling point of 310°C, thus it was detected only at an exposure of 200°C for the 30-minute equilibration time, presumably because the equilibration time caused 9228 ng of the 10000 ng spiked compound to volatilize from the fabric samples. Phenol and 2,4,6-TCP had increasing extraction efficiencies when they were exposed to higher temperatures. For phenol, the extraction went up by almost 52% when comparing the

efficiency at 100°C and 200°C, which was more than a 6-fold increase in the mass detected, seen in Table 11.5. For 2,4,6-TCP, the extraction went up by almost 84% when comparing the efficiency at 100°C and 200°C, translating to an almost 5-fold increase in the mass detected. This significant increase is because the vapor pressure of the compounds increases with an increase in the temperature. At a higher vapor pressure, the volatility of the compounds is higher, and higher mass of compound gets converted to vapor phase (described in Section 7.5). Of the 3 phenols that were spiked onto the fabric, only 2 of them were detected when the spiked fabric samples were exposed to 50°C for 30 minutes. 2,4,6-TCP was detected but had a low removal since it has a boiling point of 246°C which is significantly above the temperature of exposure and allowing the fabric to equilibrate for 30 minutes did not allow for the solid-vapor equilibrium to be formed. At the 36°C exposure, only phenol was detected. Phenol, had a lower extraction efficiency of only 1.25% (mass of 114 ng), because the temperature of exposure was well below its boiling point of 182°C. The risks associated with the off-gassing of phenolic compounds does not seem to be significant since only about 100-450 ng of the compound off-gassed at the 36°C and 50°C conditions. At these conditions, the firefighter is not wearing respiratory protection and there is a chance of direct inhalation of these compounds. It can be established that the 200°C exposure conditions works the best at thermally extracting the phenols spiked onto the fabrics, causing between 6,000- 10,500 ng of compound to off-gas.



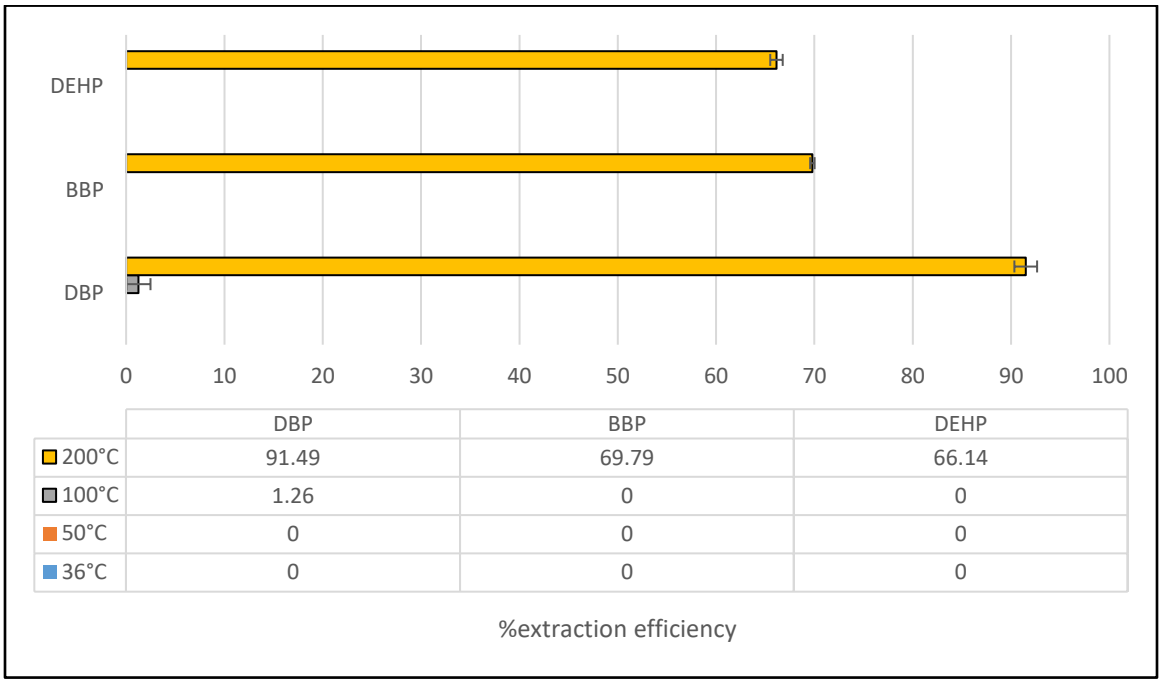
	Phenol	2,4,6-TCP	PCP
200°C	62.43	106.2	86.76
100°C	10.08	22.06	0
50°C	1.93	4.52	0
36°C	1.25	0	0

Figure 11.6. Extraction efficiencies for phenols using headspace GC at 36°C, 50°C, 100°C and 200°C for 30 minutes

11.4.2.2 Extraction efficiencies for phthalates

It can be seen in Figure 11.7, that all the three phthalates were detected at 200°C, while only one was detected at 100°C. None of the phthalates were detected at 50°C and 36°C. All the compounds are semi-volatile compounds having boiling points over 300°C, hence the vaporization at temperatures below 300°C exposure was not significant. Yet, at 200°C DEHP had a relative extraction efficiency of about 92%, translating to a mass of 6688 ng. BBP had a relative extraction efficiency of about 70% (7,052 ng) and DBP had a relative extraction efficiency of about 66% (8,782 ng). This could be because a 30-minute equilibration time was enough to form a partial solid-vapor equilibrium. These amounts are because the fabrics were exposed for 30 minutes, which was presumably enough to obtain a solid-gas equilibrium and extract some amount of compound from the outer shell fabrics. The extraction efficiencies do not directly co-relate to the amounts added onto the outer shell fabrics. The extraction efficiencies

have been calculated based on the mass of the positive control sample detected. DBP had an almost 75-fold increase in the masses evolved when the fabrics were exposed to 200°C as compared to 100°C. This could be due to the 2-fold rise in temperature being used to thermally extract the compound. None of the compound masses were detected at 36°C and 50°C.



	DBP	BBP	DEHP
200°C	91.49	69.79	66.14
100°C	1.26	0	0
50°C	0	0	0
36°C	0	0	0

Figure 11.7. Extraction efficiencies for phthalates using headspace-GC at 36°C, 50°C, 100°C and 200°C for 30 minutes

11.4.2.3 Extraction efficiencies for PAHs

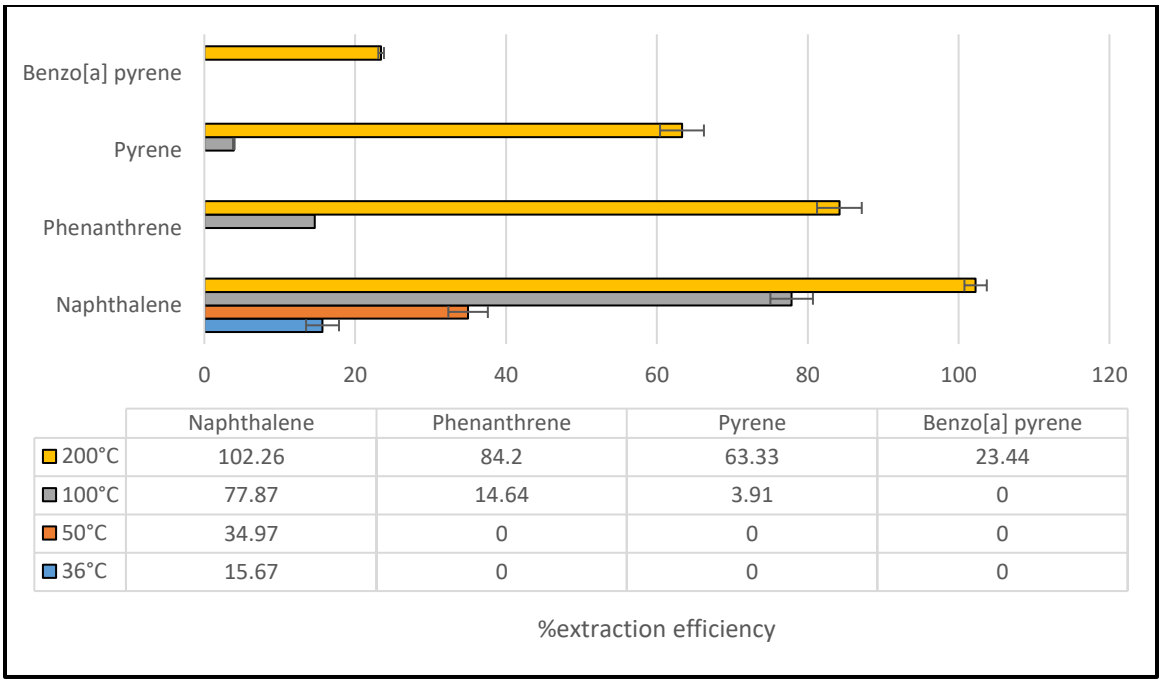
It can be seen in Figure 11.8, that all the four PAHs were detected at 200°C, three were detected at 100°C, while only one compound was detected at 50°C and 36°C. Benzo[a] pyrene is a semi-volatile compound having a boiling point of 495°C, thus it was detected only at an exposure of 200°C for 30 minutes. This is presumably because a 200°C exposure was enough only for a mass of 2,453 ng to off-gas from the 10,000-ng spiked outer shell fabric (extraction efficiency of about 24%). Naphthalene, phenanthrene and pyrene had increasing extraction

efficiencies when they were exposed to higher temperatures. When comparing the efficiency at 200°C versus at 100°C, phenanthrene had a 6-fold increase in the mass extracted, pyrene had a 16-fold increase and naphthalene has just over 1.5-fold increase fold. This significant increase is because the vapor pressure of the compounds increases with an increase in the temperature. At a higher vapor pressure, the volatility of the compounds is higher, and more could be vaporized. Of all the compounds, only naphthalene was detected at all the temperatures tested. The extraction efficiency and masses extracted for naphthalene almost doubled when increasing the temperature from 36°C to 50°C and from 50°C to 100°C. Naphthalene is a highly volatile compound with a high vapor pressure at room temperature. It is known to sublime even at room temperature, if kept for a long time [143]. Hence, when exposed to elevated temperatures, the vapor pressure is even higher and higher vaporization of the compound occurs.

At an exposure of 36°C, only naphthalene was detected. This was evident as the boiling points of phenanthrene, pyrene and benzo[a] pyrene are over 300°C and an exposure of 36°C was extremely low to form a solid-vapor equilibrium and extract them from the fabric samples. About 1,500 ng of naphthalene off-gassed at 36°C and 3,300 ng off-gassed at 50°C. These are significant amounts considering the mass spiked onto the fabric. This finding proves that if a contaminated firefighter gear is either stored in a car trunk or in a fire station, naphthalene and other volatile compounds with similar volatility/ vapor pressure values could off-gas. The off-gassing of naphthalene at those conditions could prove hazardous to the firefighters. The inhalation of naphthalene could cause serious health risks, since the compound is classified as a 2B- possible carcinogen, refer Table 9.1.

Overall, the 200°C exposure was best suited among all the temperatures tested for the thermal extraction of PAHs. Yet, thermal extraction using headspace GC might not be the best

method to extract the semi-volatile PAHs. Except naphthalene, all compounds are high-boiling semi-volatile compounds and using the 200°C temperature for an equilibration time of 30 minutes allows for a partial solid-vapor equilibrium formation. For benzo[a] pyrene though, even the highest exposure temperature of 200°C yielded only a 24% extraction, since it has a very high boiling point of 495°C.



	Naphthalene	Phenanthrene	Pyrene	Benzo[a] pyrene
200°C	102.26	84.2	63.33	23.44
100°C	77.87	14.64	3.91	0
50°C	34.97	0	0	0
36°C	15.67	0	0	0

Figure 11.8. Extraction efficiencies for PAHs using headspace-GC at 36°C, 50°C, 100°C and 200°C for 30 minutes

11.4.2.4 Best suited method for thermal extraction using headspace GC

After headspace GC analysis of spiked outer shell materials at 36°C, 50°C, 100°C and 200°C, it can be concluded that 200°C with an equilibration time of 30 minutes is the best suited method for the extraction of fireground contaminants. Phenols had an extraction efficiency between 62-106% (masses between 6,000- 10,600 ng), phthalates had an extraction efficiency between 66-92% (masses between 6,600-8,800 ng) and PAHs had an extraction efficiency

between 23-102% (masses between 24,00-9,800 ng). The method worked the best for 2,4,6-TCP, PCP, DBP, phenanthrene and naphthalene.

The chromatogram (seen in Figure 11.9), shows the compound peaks for pure liquid chemicals overlaid with compounds extracted from outer shell materials. The analysis was conducted using headspace GC at 200°C, 30 minutes. As seen in Figure 11.9, the peak heights for the pure liquid compounds is higher than the extracted compounds. This is because when the fabrics are spiked onto fabrics, factors such as fabric construction and absorption affect the ability to off-gas. It is observed that the masses of the compounds detected from spiked fabric samples were always lesser than pure liquid samples. Most fabrics have higher binding capabilities for compounds, hence analysis of pure liquid chemicals results in higher responses. The chromatogram, shown in Figure 11.9 displays a good resolution with sharp peak shapes, which is required for effective analysis.

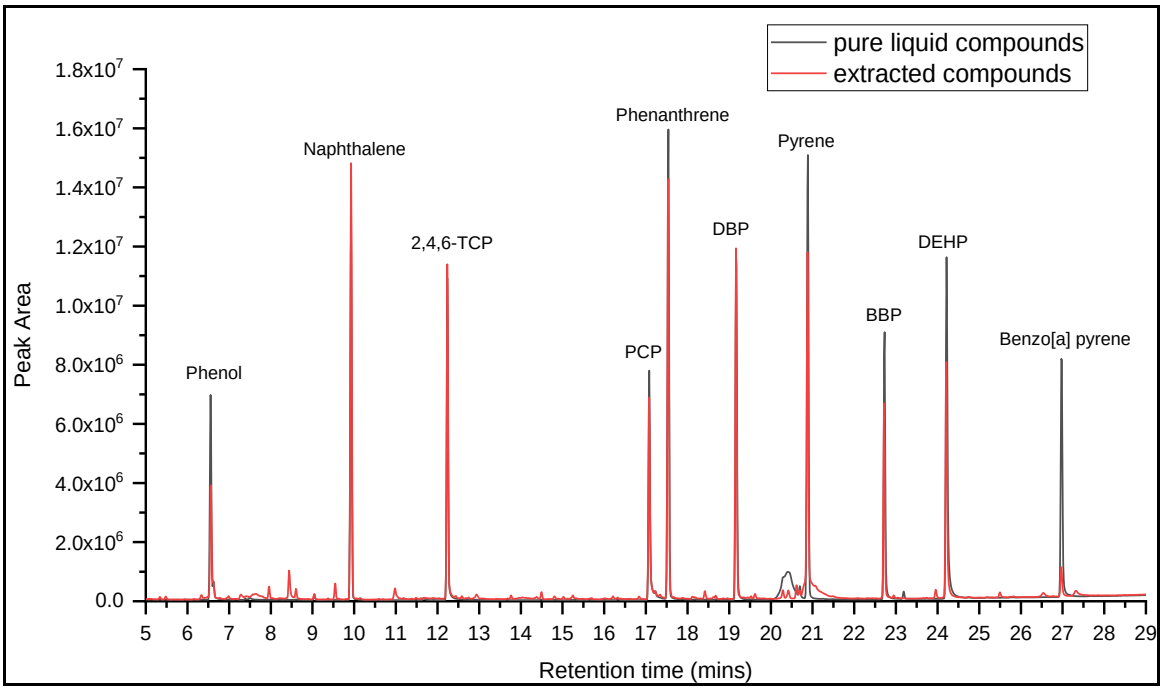


Figure 11.9. Overlaid chromatogram of the liquid compounds and extracted compounds using headspace GC injection at 200°C for 30 minutes

11.5 Conclusion

From the various temperatures tested, it can be concluded that 200°C was the most suited temperature to extract the maximum amounts of phenols, phthalates and PAHs from the outer shell material used in firefighter turnout gear. This data paves a method for using the headspace sampler as a 'thermal extraction' technique. The compounds tested included volatile and semi-volatile compounds, many of which are found in actual field-contaminated samples. The headspace GC is a novel method to analyze fireground contaminants from firefighter gear samples. A field-contaminated firefighter gear sample is known to have a plethora of chemicals present in it. The headspace sampler connected to a GC-MS system has the ability to identify all the compound off-gassing from the sample and possibly quantify the compounds (if suitable calibration curves are developed). The headspace GC at 200°C for 30 minutes is especially useful for the extraction of naphthalene, phenanthrene, DBP, 2,4,6-TCP and PCP; with significant extraction efficiencies of 102.26%, 84.2%, 91.49%, 106.2% and 86.76% respectively. This study proves that the method is between 80-100% effective at extracting certain types of phenols, phthalates and PAHs. The method is especially useful for extracting highly volatile compounds such as naphthalene. This is because naphthalene evaporates in other methods of extraction such as the pressurized solvent extraction, resulting in poor extraction efficiencies (refer Figure 10.4). Volatile compounds such as benzene, acetic acid, acetone and other compounds are known fireground contaminants and can be extracted using the headspace GC thermal extraction technique. The headspace GC technique is not suitable for the extraction of high boiling compounds, such as PAHs with multiple aromatic rings. Since the physical temperature constraint of the headspace sampler is 200°C, compounds having a significantly higher boiling points might be difficult to extract, even though they are allowed to equilibrate for a sufficient

time. Such compounds would have to be extracted using traditional methods such as the liquid extraction method developed in 10.3.3.

It was observed for all the compounds that increasing the temperature of exposure, lead to the evolution of higher amounts. Some compounds such as phenol and naphthalene that are volatile in nature off-gassed at lower temperatures of 36°C and 50°C as well, while the other higher boiling compounds such as phenanthrene and pyrene off-gassed only at higher temperatures of 100°C and 200°C. This study also shows that the equilibration time does not affect the amount of extraction of the compounds from the outer shell material significantly. An equilibration time of 30 minutes was found to be optimum for most of the compounds that were analyzed. This is an important finding and can be decided as the standard condition while performing further thermal extraction analysis.

The trials at 50°C detected only volatile compounds such as phenol, 2,4,6-TCP and naphthalene If a contaminated firefighter turnout gear is heated in an enclosed space at 50°C for 30 minutes, some amounts of naphthalene and minimal amounts of phenol would off-gas, based on the study conducted. An actual firefighter gear is contaminated with a variety of chemicals that includes a lot of other volatile chemicals as well. Compounds such as acetic acid, acetone, benzene and others have been found on contaminated gear (refer Section 2.4). These compounds have a fairly low boiling point and volatilities similar to phenol (<100deg). They would possibly off-gas when exposed to a temperature of around 50°C, while being transported in a heated car trunk/ fire truck [101,103]. The off-gassing of these volatile and possibly toxic chemicals could pose a health hazard to the firefighters present in the vicinity of the gear. Particularly, firefighters are not wearing respiratory protection while travelling in their vehicles and there is a direct chance of inhalation of these toxic chemicals that could off-gas from the contaminated gear. Since, it is

seen that certain volatile compounds do off-gas at temperatures around 50°C , the same could be used as a thermal decontamination technique to clean firefighter gear. As a contaminated gear is brought to the fire station from the scene of exposure, the gear could be isolated in a heated cabinet. The temperature inside the heated cabinet could be maintained around 50 °C , thus promoting off-gassing of certain compounds. The off-gassed compounds could then be removed and could be established as a thermal decontamination technique.

The trials at 36°C showed that only the most volatile compounds such as naphthalene and phenol were detected. If a contaminated firefighter turnout gear is stored in the engine bay of the fire station or is at ambient temperatures, volatile compounds such as phenol and naphthalene would off-gas. Other compounds with similar volatilities would off-gas as well and is a potential danger to the firefighters, typically in the absence of respiratory protection, while in the fire stations. Even though, the amounts of off-gassing detected were low, the contamination from freshly exposed gear could be very high depending on the type of exposure. Also, multiple sets of gear are stored together and the combined exposure from all the gear could be significant.

CHAPTER 12: Comparison of liquid extraction and thermal extraction methods for analyzing outer shell materials

12.1 Introduction

As described in chapter 2 and 3, both, liquid extraction and thermal extraction could be used to extract compounds from a firefighter gear material. Yet, the most suited method of extraction is crucial in targeting the removal of specific set of analytes from fabric samples. While certain compounds respond better to a physical interaction of liquid solvent, some types of compounds prefer exposure to heat. The pressurized solvent extractor uses a solvent that is forced through the solid sample of interest. Elevated temperature and pressure are typically used, since the rate of removal of compounds increases with an increase in the temperature. The relevance of a higher pressure is to maintain the solvent in the liquid state, since the temperature used might be above the boiling point of the solvent and may volatilize it. The combination of a higher temperature and pressure is that there is an improved mass transfer because of higher analyte solubility and enhanced penetration. Some compounds having a higher boiling point such as long chain hydrocarbons and polycyclic aromatic hydrocarbons might be better extracted using the pressurized solvent extractor as compared to the headspace sampler. This is because a very high temperature would be needed in the thermal extraction to get the same amount of contaminant as with the solvent extraction at a much lower temperature. The Buchi E-916 speed extractor is a type of pressurized solvent extractor. The instrument has six cells with a 10-mL solvent capacity. The operational temperature range is 30°C to 200°C and the pressure range is 50 bar to 150 bar. A variety of solvents could be passed through the samples of interest such as methanol, acetonitrile, n-hexane, and methylene chloride among others. The extractor has the feature to use a maximum of two solvent combinations at once. The method can be set as per the requirement

of the contaminants that encompasses heating time, holding time, discharge time, number of cycles, and flush cycles.

The solvent extractor is relevant in the extraction of toxic contaminants from firefighter turnout gear. The gear is typically made up of thermally resistant fibers such as Nomex®, Kevlar®, and PBI, and it is finished with a variety of specialty finishes such as flame retardants and water repellants. This outer shell material typically gets heavily contaminated after being used in a fire incident. A plethora of compounds are absorbed onto the material. Some of the compounds are high boiling compounds such as phthalates and PAHs which are non-polar in nature as well. In such cases, the solvent extractor is a suitable instrument to remove these contaminants from the outer shell fabric materials. The extraction technique is an essential step in the analysis of assessing washing efficiency or simply understanding the level of contamination in a fabric sample.

Alternatively, thermal extraction could be performed by heating the fabric samples in an enclosed oven. Thermal extraction uses the principle of boiling point to extract the compounds of interest from solid or liquid samples. The headspace sampler connected to the GC-MS could be used as a thermal extraction tool, since it has the functionality to expose the solid/liquid matrices to an elevated temperature. The most salient feature of the headspace-GC is that the extracted vapors can be directly injected into the GC inlet without any loss. The other advantage is that the sample preparation is limited to placing the appropriately sized solid or liquid sample inside the crimp top glass vial and crimping the vial. This greatly reduces both the time required for the analysis and the likelihood of sample loss. The headspace-GC setup can be used to facilitate and analyze the removal of compounds from contaminated firefighter turnout gear materials. The evolution of compounds from solids on heating is commonly referred to as ‘off-

gassing'. Volatile compounds found in contaminated firefighter gear would be relatively easy to extract since they have lower boiling points and high vapor pressures, even at room temperatures

The type of extraction to be used would really depend on a couple of factors: the boiling point of the analyte of interest, the polarity of the compounds to be extracted and the affinity of the compound to the solvent used for pressurized solvent extraction. Headspace sampling is also the most suited method if the concentrations of compounds were to be assessed with respect to exposure times. For example, to measure levels of off-gassing of volatiles at certain time ranges after a gear has been worn in a fire incident. The solvent extractor would be more suitable for a full extraction of the contaminants present in a turnout gear that has undergone washing procedures.

12.2 Materials

The materials used for this study are mentioned in Section 9.2.

12.3 Methods

12.3.1 GC-MS Analysis method for liquid extraction

The GC-MS chromatographic method for liquid extraction is mentioned in Section 9.5.3.

12.3.2 Extraction using n-hexane in the pressurized solvent extractor

The details of the experiment trials are mentioned in Section 10.3.3. Only the 100,000 ng spiking experiment was considered for this study.

12.3.3 Calculation of extraction efficiencies for the liquid extraction

The extraction efficiencies for liquid extraction are calculated as mentioned in Section 10.3.4.

12.3.4 GC-MS method for thermal extraction

The GC-MS chromatographic method for thermal extraction is mentioned in Section 11.3.2.

12.3.5 Calibration of the headspace GC system

Even though, calibration using the headspace GC was previously done in Section 11.3.1.2, but the mass ranges used for this study were different. Separate calibration ranges (ranging from 2,000 ng to 100,000 ng) were prepared for this study and a suitable range was selected for each compound in which the linearity was maintained. The calibration ranges had to be adjusted to maintain linearity because the MS detector was possibly getting saturated at the 50,000 ng and 100,000 ng masses. The calibration range used for this study is ranging from 2,000 ng to 100,000 ng. A total of 7 calibration solutions (as per mass-in vial) were prepared using the 2000 ng/µL stock solution for the 2,000 ng, 4,000 ng, 8,000 ng, 10,000 ng, 20,000 ng, 50,000 ng and 100,000 ng by pipetting out 1 µL, 2 µL, 4 µL, 5 µL, 10 µL, 25 µL and 50 µL into individual vials. The samples were equilibrated in the HS oven at 200°C for 30 minutes. 200°C temperature with an equilibration time of 30 minutes was chosen based on the findings in Section 11.4.2. A similar study with a spiking of 10000 mass-on fabric was previous performed, as shown in Section 11.3.1.

12.3.6 Thermal extraction using the headspace sampler

The extraction procedure is a modified version of the procedure mentioned in Section 11.3.1. The spiking amounts used are 100,000 ng, which was achieved by evenly spreading 10 drops of 5 µL having a concentration of 2,000 ng/µL. The temperature of exposure was 200°C for an equilibration time of 30 minutes. The other parameters are consistent with the procedure mentioned in Section 11.3.2.

12.3.7 Calculation of the extraction efficiencies for thermal extraction

The computation of the extraction efficiencies for thermal extraction were carried out as per the calculations mentioned in Section 11.3.1. The only variation was that a mass of 100,000 ng was spiked onto the outer shell materials for this study.

12.3.8 Compound properties

The compounds properties relevant for analysis are mentioned in Table 9.1

12.4 Results and Discussion

12.4.1 Calculation of error bars for all the graphs plotted

The error bars were calculated as described in Section 11.4.

12.4.2 Calibration of headspace sampler at 200°C , 30 minutes

The calibration curves for all the compounds were plotted as peak area v/s mass-on fabric. Since, a very wide range of 2,000 ng to 100,000 ng was chosen, it was found that the calibration curve did not maintain linearity at the higher mass values, as seen in line 1 of Figure 12.1. This

is because of saturation in the headspace vial at very high masses of compounds used. Ideally, calibration standards should be incorporated between the higher mass standards and the range of linearity must be tested. However, due to a lack of time, the following was not undertaken for the current study. To maintain linearity for the current range of values though, a suitable lower range was chosen, such that the points on the calibration formed a straight line, as seen in line 2 of Figure 12.1.

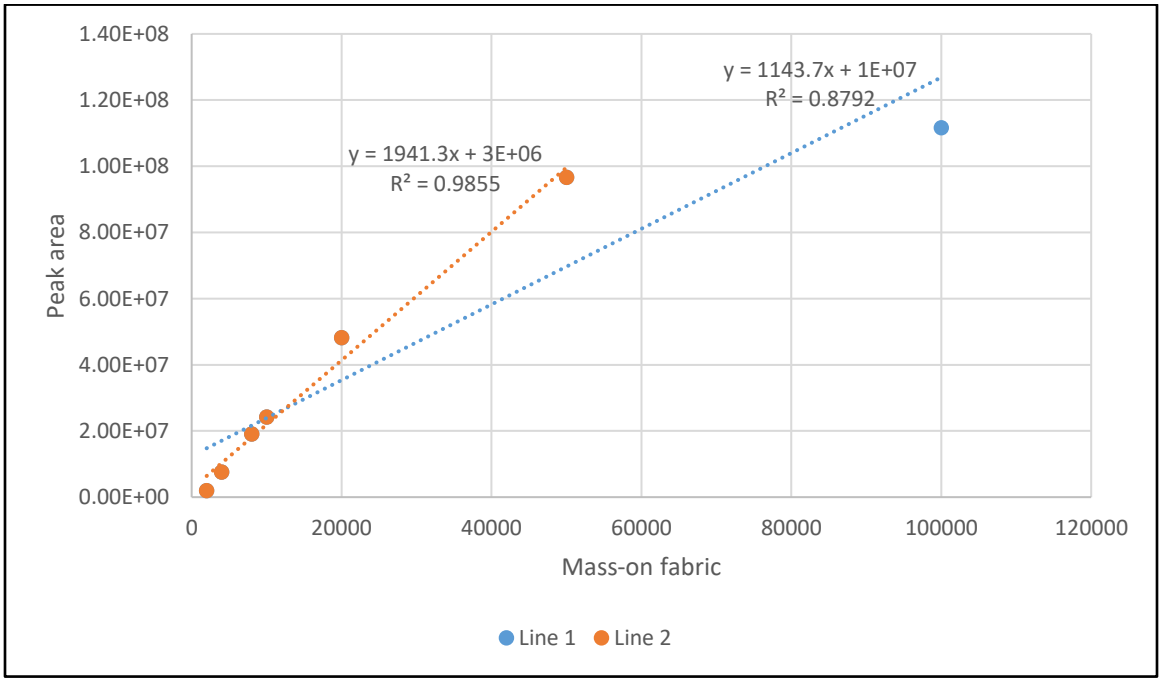


Figure 12.1. Adjusted calibration curves to show linearity versus saturation

12.4.3 Comparison of extraction efficiencies using liquid extraction v/s thermal extraction

The Buchi pressurized solvent extractor was used to perform the liquid extraction of compounds in the master mix spiked onto outer shell materials. 100,000 ng of the master mix was spiked onto unused reference outer shell materials and diluted with 10,000 µL of n-hexane solvent. This translates to an effective concentration of 10 ng/µL in the solution that was analyzed on the GC-MS. The headspace GC-MS setup was used to perform thermal extraction of compounds in the master mix spiked onto outer shell materials. 100,000 ng of the master mix

was spiked onto unused reference outer shell materials and analysis was conducted at 200°C for 30 minutes.

Table 12.1 shows the actual concentrations and masses of the compounds recovered via liquid extraction and thermal extraction respectively. The values are averages of the three replicates used in each extraction method.

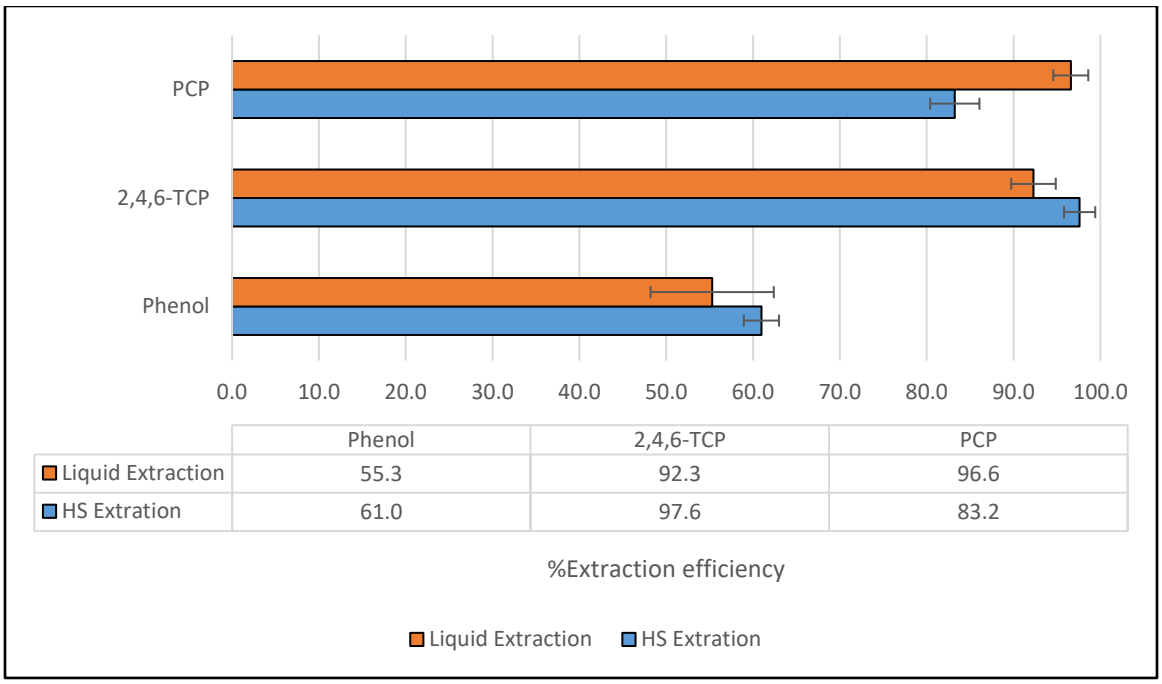
Table 12.1. Extracted concentrations and masses using liquid extraction and thermal extraction

Compounds	Liquid Extraction Masses (ng)	Thermal Extraction Masses (ng)
Phenol	31,200	47,161
2,4,6-Trichlorophenol (2,4,6-TCP)	148,100	94,294
Pentachlorophenol (PCP)	130,200	58,168
Di-butyl phthalate (DBP)	102,300	63,766
Benzyl butyl phthalate (BBP)	119,100	38,362
Di-ethylhexyl phthalate (DEHP)	122,800	27,739
Naphthalene	24,700	75,098
Phenanthrene	98,700	67,723
Pyrene	105,900	44,648
Benzo[a] pyrene	102,000	10,566

12.4.3.1 Extraction efficiencies for phenols

All the three phenolic compounds present in the master mix were extracted and detected using both, liquid and thermal extraction, as seen in Figure 12.2. Phenol and 2,4,6-TCP showed similar extraction efficiencies while comparing liquid and thermal methods. Phenol had a low recovery using the liquid extraction with only 3,120 ng being detected. The compound also has a wide error bar because of an octamethyl-cyclotetrasiloxane peak interfering with the compound peak, as seen in Figure 10.4. 2,4,6-TCP detected a mass of 148,100 ng, with an extraction efficiency of 92.3% using the liquid extraction because the positive control sample for that

experiment detected a concentration higher than that of 2,4,6-TCP. Phenol and 2,4,6-TCP are volatile compounds, hence were better suited to the thermal extraction and showed higher extraction values (equivalent to a mass of 47,161 ng and 94,294 ng respectively) using thermal extraction as compared to liquid extraction. Both the compounds have boiling points around 200°C, which is also the temperature of exposure used in the thermal extraction method. This provides a good medium for formation of a solid-vapor equilibrium. For PCP, the liquid extraction had a significantly higher efficiency as compared to thermal extraction. This is because the boiling point of PCP is 310°C and the thermal extraction was carried out at 200°C. As observed in Section 11.4.2.4, using a temperature lower than the boiling point does not completely volatilize the compound.



	Phenol	2,4,6-TCP	PCP
Liquid Extraction	55.3	92.3	96.6
HS Extration	61.0	97.6	83.2

Figure 12.2. Comparison of liquid extraction and HS extraction for phenols

12.4.3.2 Extraction efficiencies for phthalates

Both, liquid extraction and thermal extraction were successful at extracting all the phthalates present in the master mix. As seen in Figure 12.3, it is evident that the liquid extraction

method is a better suited method, having higher extraction efficiencies for all the phthalates as compared to the thermal extraction values. All the three phthalates had a resulting mass of greater than the 100,000 ng, that was originally spiked onto the outer shell materials. This is because the positive control sample had higher concentrations than the compounds that were detected. BBP and DEHP had nearly 25% and 15% higher extraction efficiencies respectively using liquid extraction as compared to thermal extraction. It can be seen in Table 12.1 that only 38,362 ng and 27,739 ng of BBP and DEHP were detected using the thermal extraction method, when 100,000 ng was spiked onto outer shell fabrics. Phthalates are semi-volatile compounds with boiling points of 340°C, 370°C and 384°C for DBP, BBP and DEHP respectively. The thermal extraction was carried out at 200°C for an equilibration time of 30 minutes. It can be pointed out that the temperature of exposure was not enough for effective removal of phthalates. Phthalates are non-polar in nature and n-hexane being used as the solvent provides a compatible environment for solubility and efficient removal of the compounds from fabric samples.

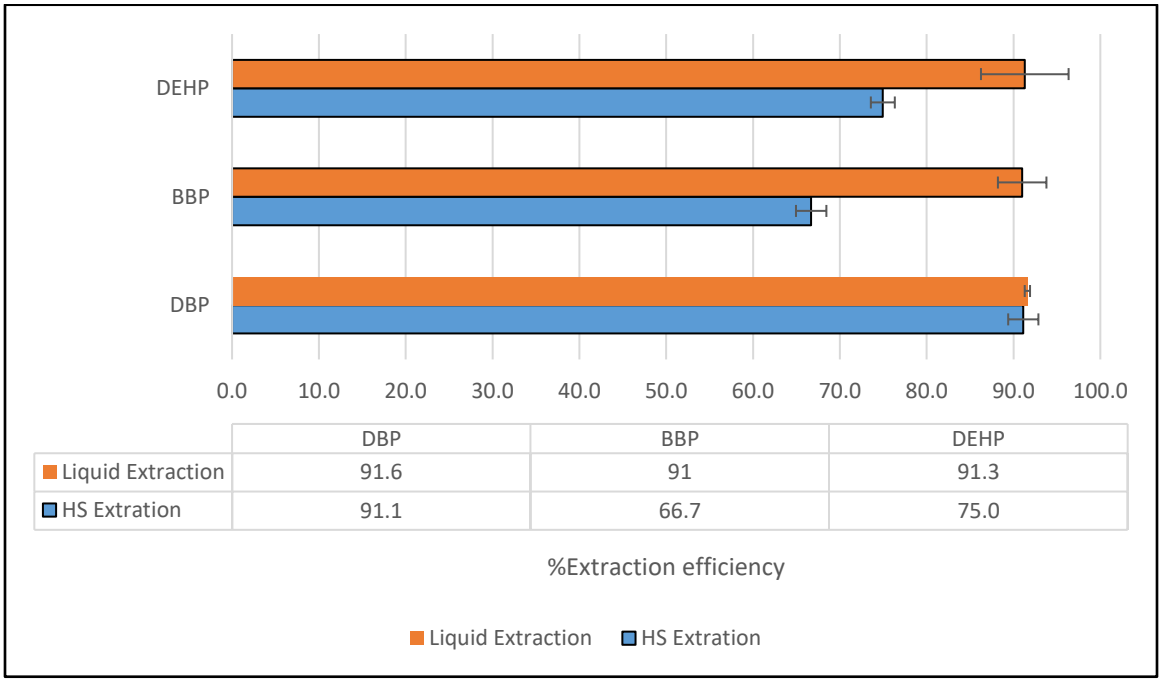


Figure 12.3. Comparison of liquid extraction and HS extraction for phenols

12.4.3.3 Extraction efficiencies for PAHs

Figure 12.4 shows that liquid extraction was better suited for the removal of pyrene and benzo[a] pyrene and thermal extraction was better for naphthalene. This is because PAHs being highly non-polar are compatible with n-hexane and makes it easier to pull off the compounds from fabric samples using liquid extraction method. Both the methods showed similar extraction efficiencies for phenanthrene. Pyrene and benzo[a] pyrene had significantly higher extraction efficiencies (100% and 89.6% respectively) using the liquid extraction as compared to the thermal extraction (67.4% and 45% respectively). Very low mass values of 44,646 ng and 10,566 ng were detected for pyrene and benzo[a] pyrene using the thermal extraction. All the compounds except naphthalene are semi-volatile having a boiling point over 300°C. Thus, an exposure of 200°C in the headspace sampler was probably not enough for the volatilization of the compound and formation of a solid-vapor equilibrium. Naphthalene is an exception, that has an extraction efficiency of only 36.6% using liquid extraction whereas 95.8% using the thermal extraction (mass detection of 75,098 ng). This is because naphthalene is a highly volatile compound, which sublimes even at room temperature if kept for a sufficiently long time [143]. A temperature of 100°C is used in the process of liquid extraction. The extract collected in the vials must undergo dilution and filtration to be finally transferred into 2-ml GC vials. During this time period, the compounds could possibly be vaporizing, thus leading to lower extraction efficiency values.

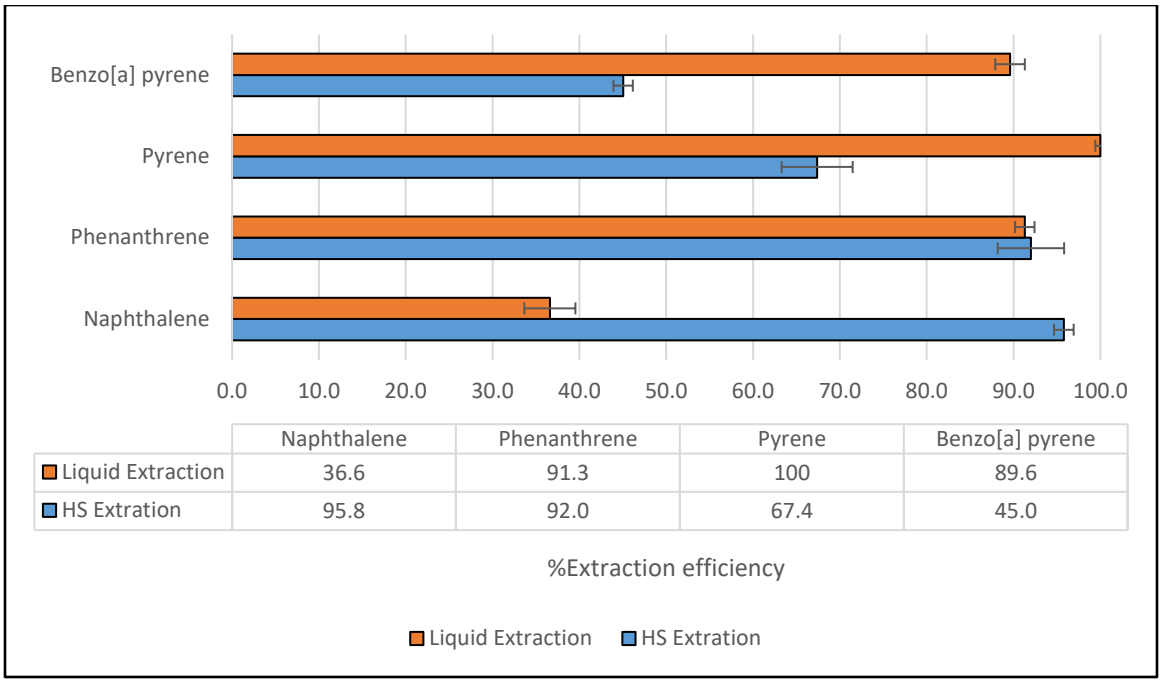


Figure 12.4. Comparison of liquid extraction and HS extraction for PAHs

12.5 Conclusion

The study concludes that a single method of extraction might not be suitable for a mixture of compounds with different polarities and boiling points. A targeted method must be used depending on the physical and chemical properties of the compounds of interest. Volatile compounds, having a lower boiling point (<200°C) such as phenol and naphthalene are better suited to extraction using the headspace sampler. This is because a temperature of 200°C is optimally used to thermally extract the compounds. The compounds having a lower boiling point can easily form a solid-vapor equilibrium in the vial, while the compounds having a higher boiling point can only form a partial solid-vapor equilibrium. Once the equilibrium is formed, efficient transfer of the compounds can occur from the liquid phase in the outer shell fabric to the vapor phase. Volatile compounds have a higher vapor pressure and are easier to volatilize, which is the property essential for thermal extraction using headspace GC. However, the thermal extraction

of the compounds is unable to remove toxic and potentially carcinogenic compounds such as benzo[a] pyrene and other PAHs significantly. These compounds are toxic and are commonly found as fireground contaminants in field-contaminated firefighter gear [112,123]. Even though, headspace GC analysis is a simple and fast method, it has limitations on the compounds that it can analyze. Compounds such as PAHs and others with higher boiling points can be removed efficiently using traditional methods such as liquid extraction. The liquid extraction is a better method for the extraction of compounds with a higher boiling point (typically >200°C). Yet, it was observed that some compounds having boiling points over 200°C (such as 2,4,6-TCP) responded well to thermal extraction. This is only because the compounds were allowed to equilibrate for 30 minutes inside the headspace vial. Compounds having very high boiling points are not suitable with the thermal extraction process and requires a physical solvent for extraction. n-hexane used in the pressurized solvent extractor with a temperature of 100°C and pressure of 100 bar, works better to extract the higher boiling compounds from the outer shell materials. However, highly volatile compounds such as naphthalene and phenol are not compatible with the pressurized solvent extractor. The compounds that volatilize at lower temperatures would provide low extraction efficiencies using liquid extraction, since there is a possibility of loss of the compounds through evaporation. Therefore, to completely analyze the contamination in a field-contaminated gear, a combination of liquid and thermal methods must be used.

CHAPTER 13: Quantitation of compounds from firefighter gear materials using headspace GC

13.1 Introduction

Headspace sampling (HS) as an air sampling technique has gained an impetus owing to its ease of operation and simple sample preparation. The technique can practically be used to analyze the off-gassing of chemicals from any solid or liquid matrix. The headspace sampler is an instrument that is used to heat solid/liquid samples in a glass crimp-top vial. The practical operational temperature range of the instrument is 35°C to 260°C. The vial can be then placed in the oven and equilibrated for a specific time. The vapors generating from the samples get collected in the headspace between the sample and the vial cap. A needle is inserted into the vial and transfers the vapors to the heated HS transfer line via a heated loop system. The vapors are then directly injected into the Gas chromatograph (GC) inlet through the heated transfer line. This process ensures that there is no loss of compound and that no condensation of vapor occurs inside the machine parts.

Materials cut from contaminated firefighter turnout gear would be tested to analyze the compounds off-gassing at a set temperature and equilibration time. With the mass-spectrometer connected to the GC, it is possible to qualitatively analyze the compounds Yet, to quantitate the amounts, the headspace sampler must be calibrated separately in conjunction to GC-MS. The signals obtained from the contaminated samples need to be compared to a reference known calibration standard. To do so, 2 types of calibration could be prepared. First, spiking pure liquid compounds (HS liquid calibration) part of the reference master mix into the HS vials at a certain mass-in vial and creating a calibration for a range of mass-in vial values. Second, spiking the liquid compounds from the reference master mix onto outer shell fabrics (HS fabric calibration)

at a certain mass-on fabric. These fabrics can then be placed inside the HS vials and analyzed to create a calibration curve. The two calibration sets yield different results because of the difference in vaporization of pure liquid chemicals by itself and vaporization of chemicals from outer shell fabrics. Generally, the amount of compound off-gassing when spiked onto a fabric is lesser than the compound directly spiked in the vial. The construction, weave and other properties of the fabric affects the volatilization of the spiked chemicals. The signal generated from analyzing field-contaminated samples must be compared with both, HS liquid calibration and HS fabric calibration. The calibration curve that provides the most realistic values must be used for all further quantitation.

The difference when calculating concentrations using GC liquid injection and HS liquid injection is that in the GC liquid injection, a fixed amount of liquid is injected into the column (usually 1 µL). But in the HS liquid injection, the vapors evolving from the solid/liquid samples are directly injected into the column. The amount vaporizing and entering inside the GC column is unknown when using the HS injection. A mass-in vial or a mass-on fabric calibration must be used to calibrate the HS instrument instead of a traditional concentration (ng/µL) used for GC liquid injection. The dimensions of the control fabric sample and field-contaminated samples would be kept constant at 1 cm* 1cm. This would ensure that the chemicals off-gassing would always be (per cm^2) of fabric sample. The concentrations obtained from fabric samples would therefore bear the units of ng/cm^2.

13.2 Materials

Materials used for this study are as mentioned in Section 11.2. Additionally, field-contaminated outer shell materials were procured from Raleigh training facility.

13.3 Methods

13.3.1 Calibration method development on the headspace sampler GC

13.3.1.1 GC-MS chromatographic method

The chromatographic method used for analysis is as described in Section 11.3.1.2. A calibration curve of peak area v/s mass-in vial (ng) was plotted for the HS liquid calibration and a curve of peak area v/s mass-on fabric (ng/cm^2) was plotted for the HS fabric calibration.

13.3.1.2 Calibration solution trials for HS liquid and HS fabric trial at 100°C, 30 minutes

The calibration solutions for HS liquid and fabric trials were prepared as mentioned in Section 11.3.1.1.

13.3.1.3 Calibration solution trials for HS liquid injection at 200°C, 30 minutes

The calibration solutions for the HS liquid and fabric trials were prepared as mentioned in Section 11.3.1.1.

13.3.3 Sample collection from the live training burn and analysis using headspace GC

One retired turnout jacket and one unused turnout jacket was used for the study. A to-be demolished building was set on fire by firefighters as a training protocol. The contents inside the building such as couch, magazines, electronics and plastics were not removed to achieve a realistic fire exposure. In the room that was burnt, a retired jacket and an unused jacket was hung on the ceiling. The jackets were allowed to hang in the room until the room was completely burnt down and the fire was dozed off by spraying pressurized water. As the jackets were taken out, one large piece of fabric, each measuring about 30 cm*30 cm was cut out from the retired and

the unused jacket respectively. Subsequently, 3 replicate fabric samples measuring 5 cm by 5 cm were cut from each jacket and placed in 20-ml crimp-top glass vials at 0-hour, 0.5-hour, 1-hour 4-hour and 48-hour after the jacket was taken out of the burning building. The vials were crimp-top to avoid any gases from escaping to the atmosphere. The vials were run on the headspace sampler at 200°C for an equilibration time of 30 minutes. The 7697A Agilent headspace sampler connected to a 7890B GC and 5977B MS was used to analyze the contaminants.

13.3.4 Thermal extraction using headspace GC 100°C for 30 minutes

9 samples measuring 1 cm*1 cm were taken from the retired field-contaminated turnout jacket, about 48 hours after the exposure. The fabric samples were placed in 20-ml glass crimp-top vials and analyzed using the headspace sampler at 100°C for 30 minutes. The 7697A Agilent headspace sampler connected to a 7890B GC and 5977B MS was used to analyze the contaminants.

13.3.5 Properties of the reference compounds in the master mix

The properties of the compounds relevant for analysis have been mentioned in Table 9.1.

13.3.6 Calculation of error bars for all the graphs plotted

The error bars were calculated as described in Section 11.4.

5.4 Results and Discussion

13.4.1 HS liquid and fabric calibration for headspace GC

The HS liquid calibration of the compounds in the master mix was performed as mentioned in Section 11.3.1.1. A different calibration range was chosen for this study to suit the analysis of field-contaminated gear. Referring Figure 13.1, the only compound found in the field-contaminated gear, relevant for analysis, was naphthalene. The graph below shows the area v/s mass-on fabric calibration curve (HS fabric calibration) and area v/s mass-in vial calibration curve (HS liquid calibration) for naphthalene using headspace GC at 100°C, 30 minutes.

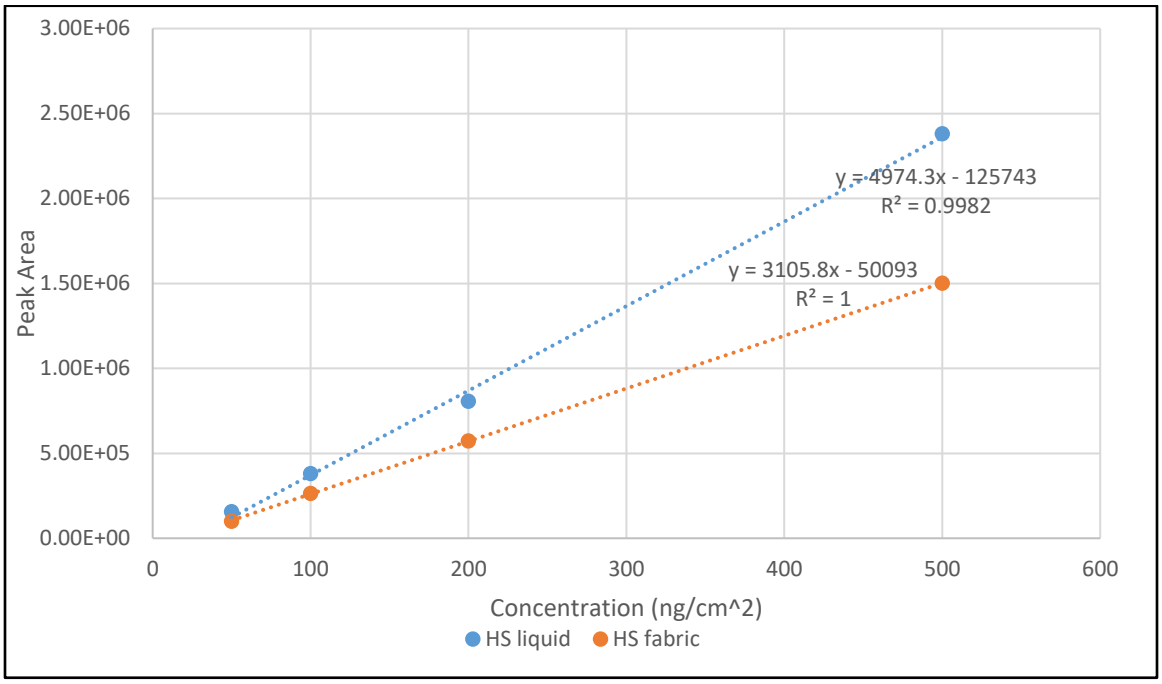


Figure 13.1. Area v/s Mass-on fabric curve for naphthalene on the headspace-GC at 100°C at 30 minutes

13.4.2 Thermal extraction of the retired field-contaminated gear using headspace-GC-MS at 100°C, 30 minutes

3 fabric samples measuring 1 cm* 1cm were cut from retired field contaminated gear and placed inside 20-ml HS crimp-top vials. The samples were then analyzed using the headspace-

GC method at 100°C for 30 minutes. The chromatogram (as seen in Figure 13.2) represented a variety of compounds, but naphthalene was the only compound that was relevant for analysis. The peak areas from the retired field-contaminated samples were substituted in both the HS calibration curve equations. Naphthalene was the only compound that was relevant for analysis, since it was one of the reference fireground contaminant present in field-contaminated sample. Figure 13.2 shows the chromatogram for the retired field-contaminated sample analyzed using headspace GC at 100°C for 30 minutes. The number of peaks represent the variety of compounds off-gassing from the turnout jacket.

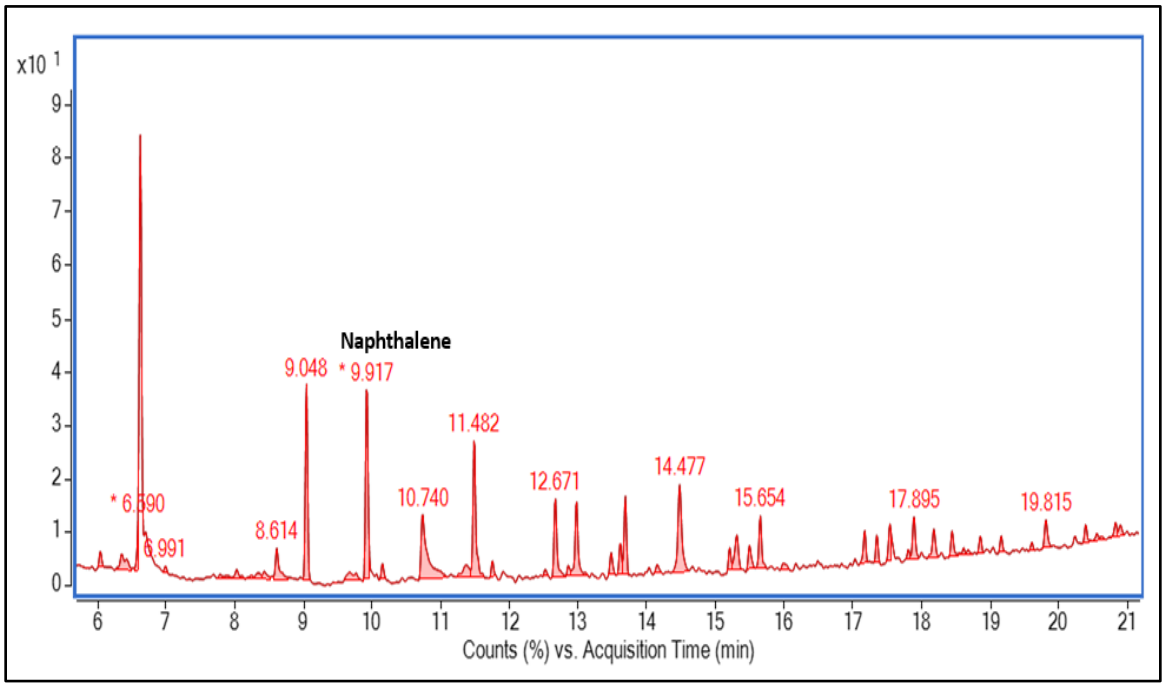


Figure 13.2. Chromatogram of retired field-contaminated sample analyzed using HS at 100°C, 30 minutes

Calculation of concentrations from the naphthalene calibration curve, see Figure 13.1

HS liquid calibration	$y = 4974.3x - 125743$	**Eq. 13.1**
HS fabric calibration	$y = 3105.78x - 50093$	**Eq. 13.2**

where y is the peak area and x is the concentration (ng) for HS liquid calibration and x is the concentration (ng/cm^2) for HS fabric calibration.

13.4.3 Quantitation of naphthalene off-gassing from retired field-contaminated jackets, calibrated using HS liquid calibration and HS fabric calibration at 100°C, 30 minutes

The peak areas from the HS liquid and HS fabric calibrations for naphthalene were noted and substituted in both the HS calibration equations (equation 13.1 and equation 13.2). Table 13.1 shows the replicate data for the HS liquid calibration and HS fabric calibration. The data was used to further prepare Figure 13.3.

Table 13.1. Replicate data for HS liquid calibration and HS fabric calibration samples

Calibration method	Rep 1	Rep 2	Rep 3
HS liquid calibration	56.7 ng	42.8 ng	43.6 ng
HS fabric calibration	66.5 ng/cm^2	44.2 ng/cm^2	45.5 ng/cm^2

As is evident from Figure 13.3, both the calibration methods produced similar concentrations. The HS fabric calibration had a larger error bar as compared to the HS liquid calibration. This could be because of factors such as fabric construction and absorption of the chemical in the fabric, that impact the volatilization of the compounds. Considering the average of three replicate samples, the HS liquid calibration provided a concentration of 47.79 ng/cm^2, whereas the HS fabric calibration provided a concentration of 52.12 ng/cm^2. Both the calibration methods produced similar concentrations. It was decided that HS liquid calibration be used for further analysis, since it also produces lower variability in the results among replicates.

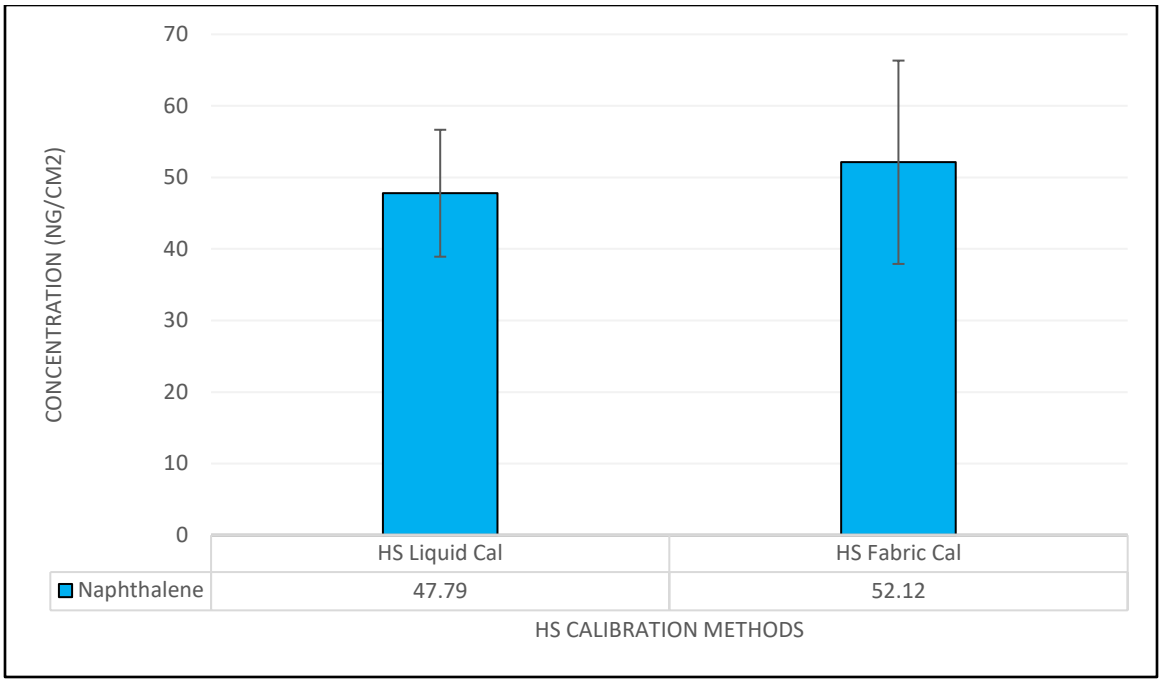


Figure 13.3. Concentrations of naphthalene off-gassing from retired field-contaminated samples analyzed using HS at 100°C, 30 minutes compared with the HS liquid and HS fabric calibration

13.4.4 Thermal extraction of the field contaminated jackets using headspace GC at 200°C, 30 minutes

The aim was to understand the type of compounds that off-gas from a retired gear after a live-burn. The objective was also to understand the effect of air exposure to the amounts of compounds off-gassing from the outer shell material. As mentioned in Section 11.4.2.4, a temperature of 200°C with an equilibration time of 30 minutes was concluded as the best suited condition for thermal extraction of outer shell materials. Figure 13.4 and Figure 13.6 shows the chromatogram of headspace GC analysis of field-contaminated firefighter fabric samples conducted at 200°C for 30 minutes. The samples are termed as a '0-hour' air exposure, meaning that the sample was immediately placed inside the HS vial, after the contaminated jacket was taken out of the burning building.

As seen in Figure 13.4 and Figure 13.6, several peaks are generated in the chromatogram. On analyzing each peak using the NIST 17 Mass Spectral library, the peaks having a minimum percent match of 50% and above were chosen. Also, the peaks having a peak height significantly above the baseline were considered. Figure 13.4 shows the amounts of off-gassing of compounds from retired field-contaminated firefighting gear. The values of the compounds off-gassing are average amounts (peak areas) taken from the three replicate fabric samples analyzed.

13.4.4.1 Analysis of the retired turnout jacket

The fabric samples taken from the retired turnout jackets were analyzed for off-gassing of compounds using the headspace GC at a temperature of 200°C for an equilibration of 30 minutes. The chromatogram shown in Figure 13.4 shows a number of peaks, each of which represents a different compound. The chromatogram is of the ‘0-hour’ exposure sample, that was taken immediately after the jacket was taken out of the burning building. It can be inferred from the chromatogram that the retired turnout jacket had a huge contamination after being exposed to contaminants in the burning building.

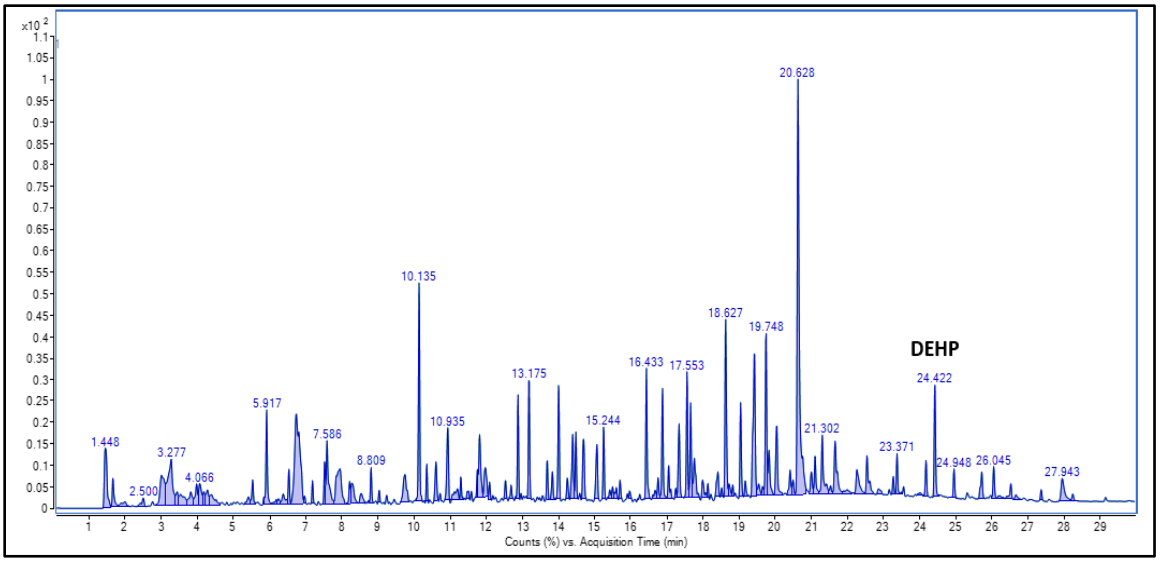
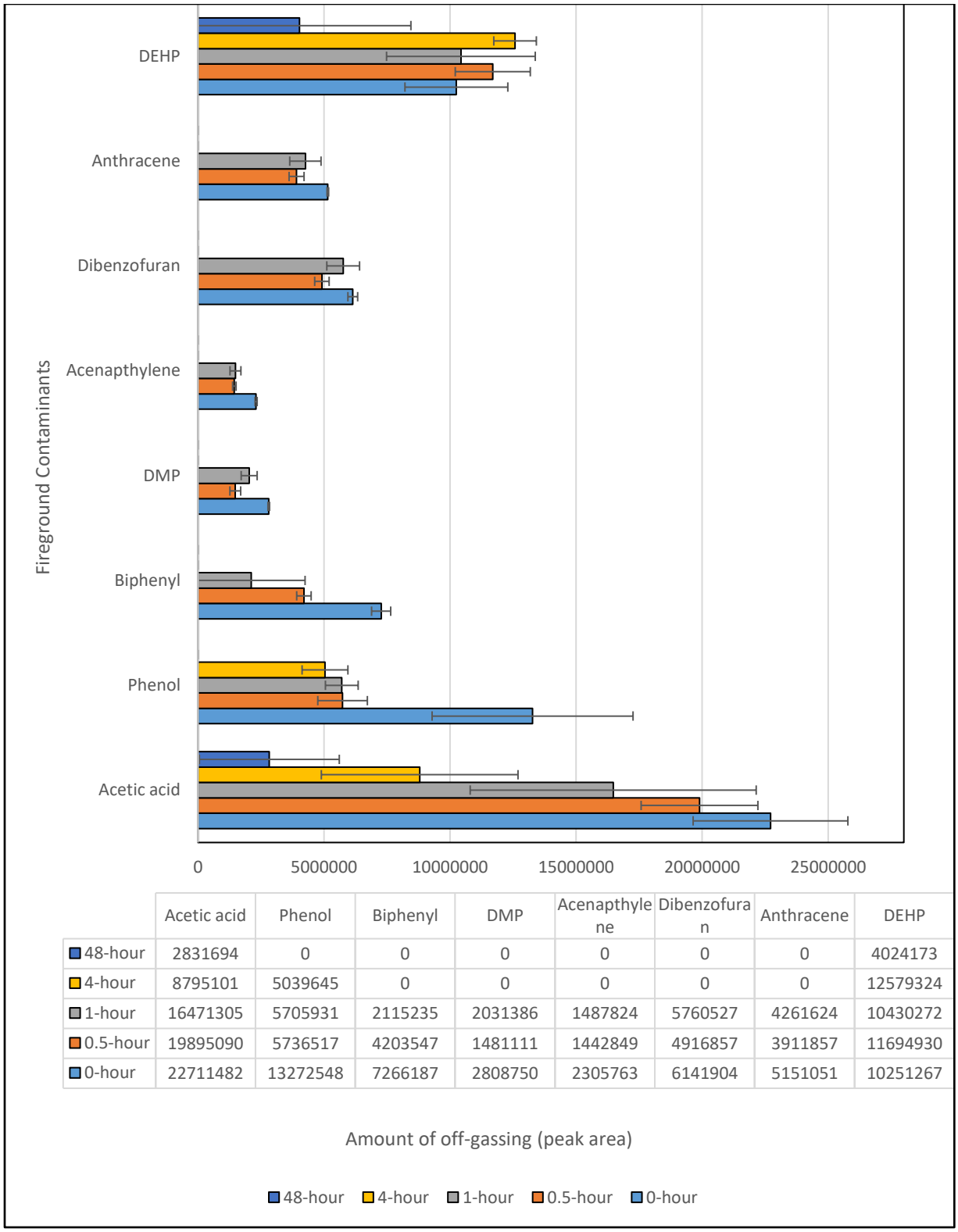


Figure 13.4. '0-hour' air exposure sample chromatogram for compounds off-gassing from retired turnout jacket using headspace-GC-MS at 200°C, 30 minutes

The times of exposures used for comparison are 0-hour, 0.5-hour, 1-hour, 4-hour and 48-hour. It can be derived from Figure 13.5 that the amount of acetic acid evolved reduces with increasing time of air exposure. This is because acetic acid is a highly volatile compound and hence, with an increase in the time of air exposure, the amount of off-gassing would reduce. For phenol, the amount of off-gassing reduced drastically for the first 30 minutes, then remained almost constant for the next 30 minutes. Thereafter, it showed a slight decrease at 4-hour and was absent at 48-hour. Phenol, being a volatile compound, probably off-gassed from the outer shell fabrics as it was exposed to air and hence showed a decrease in the off-gassing amounts with time. Biphenyl had a decrease in the amount off-gassing from 0-hour to 1-hour and was absent at 4-hour and 48-hour. The error bars at 1-hour are wide and spans across the entire compound bar. This denotes that the compound might have been absent in one or more replicates. A peculiar trend was observed for acenaphthylene, dibenzofuran and anthracene, wherein the amount off-gassing reduced slightly from 0-hour to 0.5-hour. It then went up at 1-hour and was absent for 4-

hour and 48-hour. For di-ethylhexyl phthalate (DEHP), the off-gassing trend was randomly distributed with time of air exposure. DEHP, being a semi-volatile compound, with a boiling point of 384°C, was present at the 48-hour time exposure. But the error bar is wide and covers the entire bar of the compounds, stating that DEHP could be absent in one or more replicates. Dimethyl phthalate (DMP) was detected from 0-hour until 1-hour and was absent after 1-hour air exposure.



	Acetic acid	Phenol	Biphenyl	DMP	Acenapthylene	Dibenzofuran	Anthracene	DEHP
48-hour	2831694	0	0	0	0	0	0	4024173
4-hour	8795101	5039645	0	0	0	0	0	12579324
1-hour	16471305	5705931	2115235	2031386	1487824	5760527	4261624	10430272
0.5-hour	19895090	5736517	4203547	1481111	1442849	4916857	3911857	11694930
0-hour	22711482	13272548	7266187	2808750	2305763	6141904	5151051	10251267

where DMP is dimethyl phthalate and DEHP is di-ethylhexyl phthalate

Figure 13.5. Amount of off-gassing of compounds from retired turnout jacket

13.4.4.2 Analysis of unused turnout jacket

The fabric samples taken from the unused turnout jackets were analyzed for off-gassing of compounds using the headspace GC at a temperature of 200°C for an equilibration of 30 minutes. The chromatogram shown in Figure 13.6 shows a number of peaks, each of which represents a different compound. It can be inferred from the chromatogram that the unused turnout jacket was exposed to a lot of contaminants, which off-gassed during analysis. Comparing Figure 13.4 with Figure 13.6, the retired jacket shows a much higher contamination (higher number of peaks) as compared to the unused turnout jacket. It seems reasonable that the retired turnout jacket had a higher contamination, since it was possibly exposed to contaminants at multiple instances through its service life.

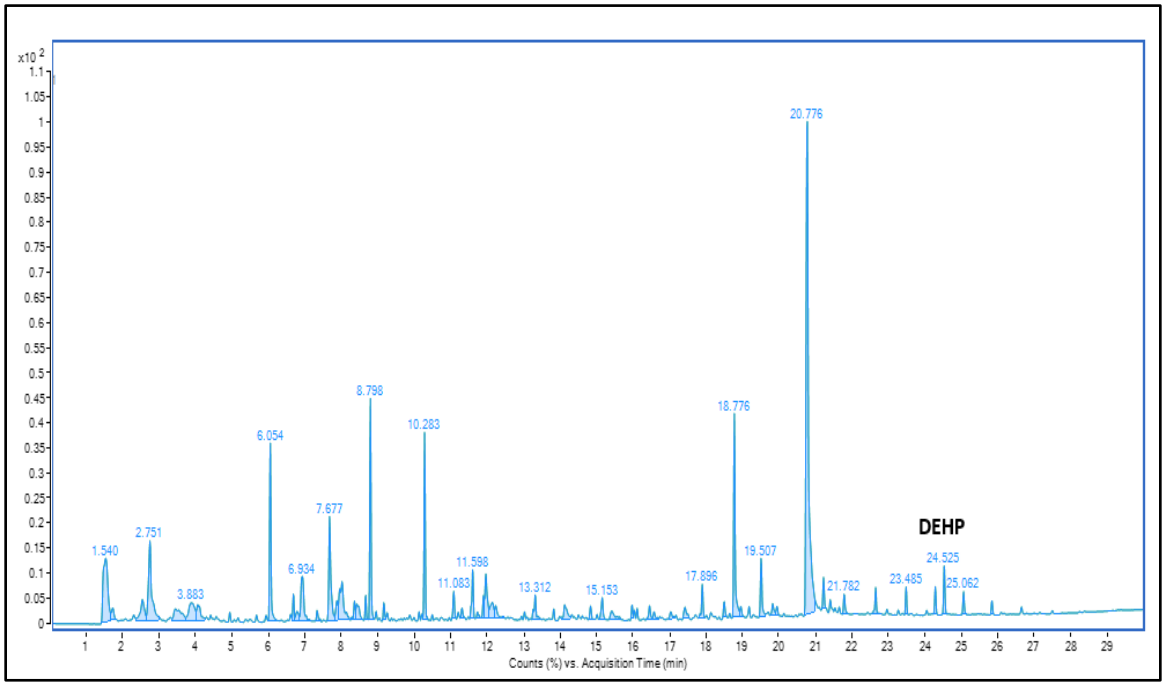
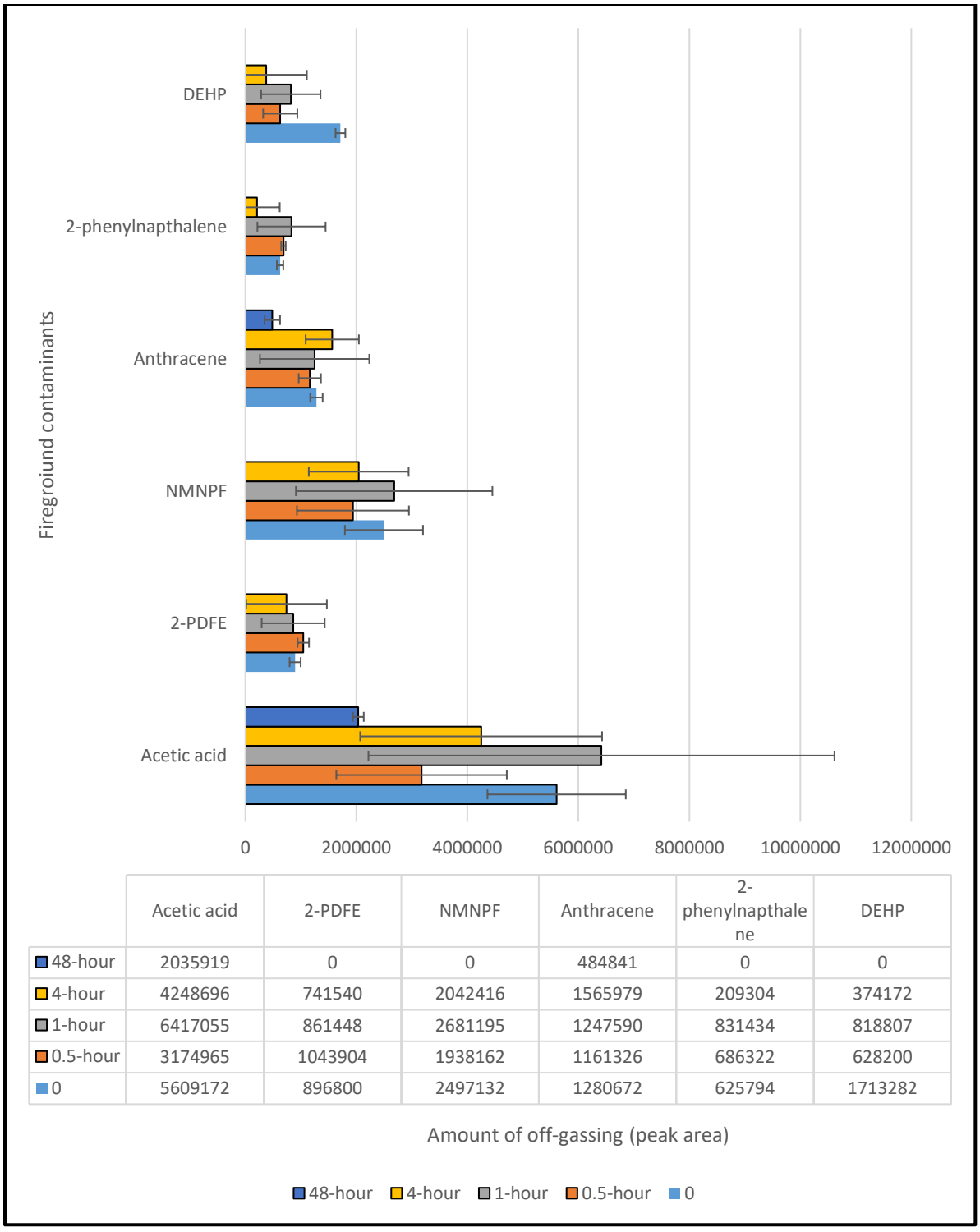


Figure 13.6. '0-hour' air exposure chromatogram for compounds off-gassing from unused turnout jacket using headspace-GC-MS at 200°C, 30 minutes

Figure 13.7 shows the amounts of off-gassing of compounds from retired field-contaminated firefighting gear. The times of exposures used for comparison are 0-hour, 0.5-hour,

1-hour, 4-hour and 48-hour. The amount of acetic acid off-gassing decreased from 0-hour to 0.5-hour but increased from 0.5-hour to 1-hour. This increase is unexpected, since acetic acid is a volatile compound and the amount off-gassing should ideally reduce with time of air exposure. The error bar for 1-hour sample is wide and shows a great variability in the amount across all replicates. The amount then reduces for both the 4-hour and 48-hour samples. 2-Propenoic acid-heptadecafluorodecyl ester showed almost similar amount of off-gassing with time from 0-hour to 4-hour, while it was absent at 48-hour. A random trend was observed for N-methyl-N-phenyl-formamide, Anthracene and 2-phenylnaphthalene wherein the amount off-gassing did not correlate to either an increase or decrease with time. The amounts kept varying in a random fashion but were in the similar range overall. For DEHP, the amount decreased from 0-hour to 0.5-hour, whereas it increased slightly from 0.5-hour to 1-hour. It further reduced at 4-hour and was absent at 48-hour.



	Acetic acid	2-PDFE	NMNPF	Anthracene	2-phenylnapthalene	DEHP
48-hour	2035919	0	0	484841	0	0
4-hour	4248696	741540	2042416	1565979	209304	374172
1-hour	6417055	861448	2681195	1247590	831434	818807
0.5-hour	3174965	1043904	1938162	1161326	686322	628200
0	5609172	896800	2497132	1280672	625794	1713282

where DEHP is di-ethylhexyl phthalate, NMNPF is N-methyl-N-phenyl-formamide and 2-PDFE is 2- propenoic acid heptadecafluorodecyl ester

Figure 13.7. Amount of off-gassing of compounds from unused turnout jacket

13.4.5 Quantitation of field-contaminated gear samples at 200°C for 30 minutes

After the unused and retired turnout jackets were analyzed using the headspace-GC-MS, a list of compounds was obtained with their respective peak areas. DEHP was the only compound (from the compounds in the master mix) that was detected in the field-contaminated turnout jacket samples. As mentioned in Section 13.4.4, it was decided to use the HS liquid calibration for calculating concentrations from field-contaminated samples. Figure 13.8 shows the calibration curve for DEHP using HS liquid calibration.

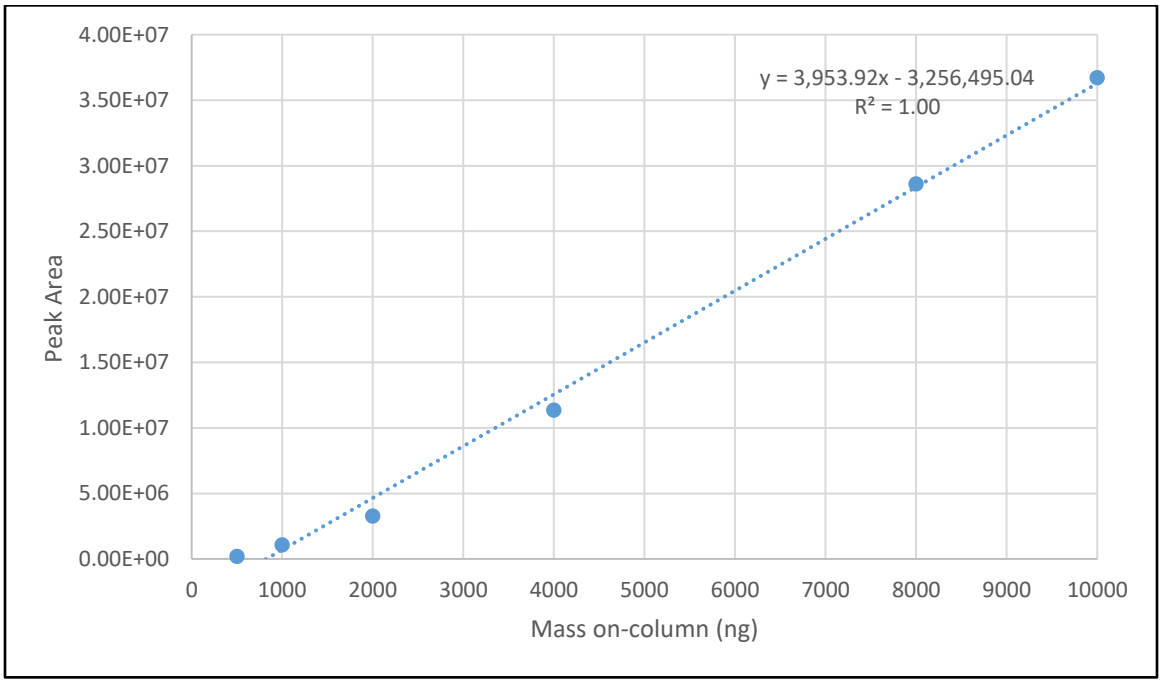


Figure 13.8. Calibration curve for DEHP using HS liquid at 200°C, 30 minutes

Calibration equation for DEHP using HS liquid calibration (Figure 13.8) at 200°C, 30 minutes:

$$y = 3{,}953.92x - 3{,}256{,}495.04 \qquad \textbf{Eq. 13.3}$$

where y is the peak area and x is the concentration (ng)

The peak areas (y) from the retired and unused field-contaminated turnout fabric samples were then substituted in Eq 13.3 to obtain the concentration (x) values.

13.4.5.1 Concentrations of DEHP off-gassing from the retired field-contaminated gear at various times of air exposure

As seen in Figure 13.9, the concentration of DEHP remained consistent in the range of 927-951 ng/cm^2 upto 6-hour of air exposure. The concentration then dropped to 864 ng/cm^2 while the measurement was taken at 48-hour. DEHP is a semi-volatile compound having a high boiling point of 384°C and does not easily off-gas from the fabric at room temperature. However, it was observed that the concentration dropped by almost 10% when the fabric was allowed an air exposure for 48 hours. This throws light on the fact that semi-volatile compounds remain trapped inside contaminated firefighter gear fabrics even after 48 hours of exposure. The concentrations across all times of air exposure for the retired jacket (Figure 13.9) were higher as compared to the unused jacket (seen in Figure 13.10).

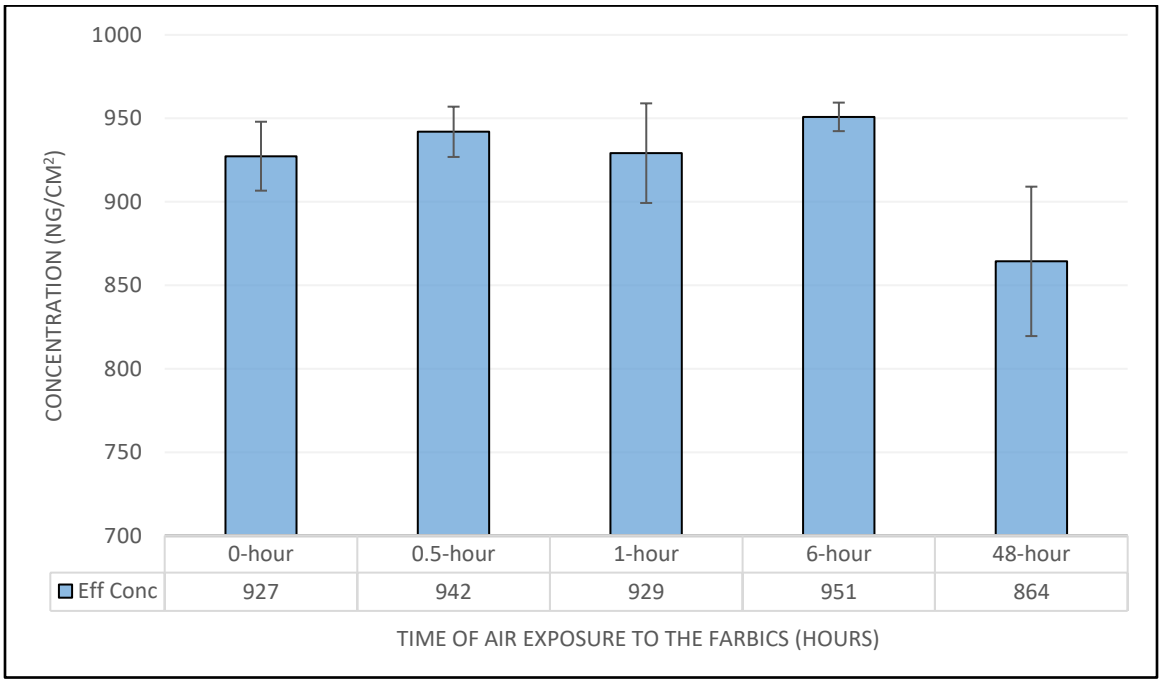


Figure 13.9. Concentrations of DEHP off-gassing from the retired turnout gear at various times of air exposure, extracted using headspace GC at 200°C, 30 minutes

13.4.5.2 Concentrations of DEHP off-gassing from the retired field-contaminated gear at various times of air exposure

The concentration of DEHP is decreasing with longer time of air exposure, as seen in Figure 13.10. A sharp decrease can be seen in the first 30 minutes of the air exposure. This is representative of the fact that the gear off-gassed the immediate available compound attracted to the gear while it was still hot as it was taken out of the fire. The concentration values for 0.5-hour and 1-hour are similar possibly because of the short duration between the samples. The concentration further decreased while the sampling was performed at 4-hour. The compound was absent completely at 48-hour sampling time.

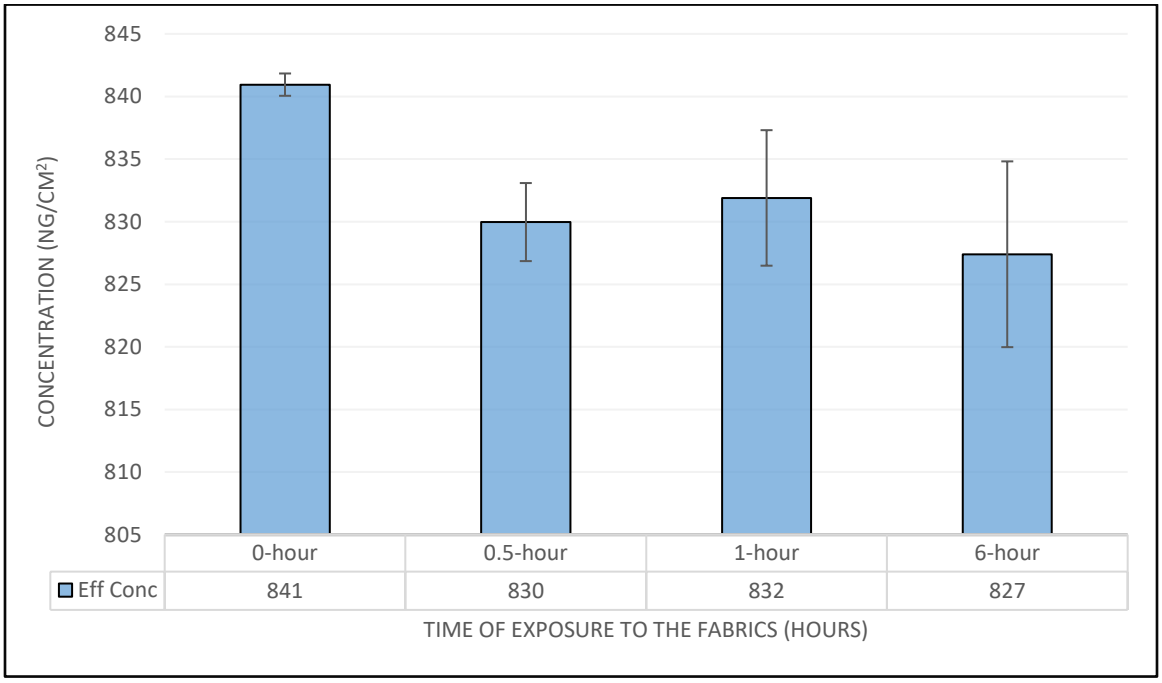


Figure 13.10. Concentrations of DEHP off-gassing from the unused field-contaminated gear at various times of air exposure, extracted using headspace GC at 200°C, 30 minutes

13.5 Conclusion

The headspace sampler-GC-MS setup was tested and validated to analyze the off-gassing from field-contaminated firefighter gear. Based on the data analysis of the HS liquid and HS fabric calibration methods, it was concluded that HS liquid calibration is the better suited method for quantitation of compounds off-gassing from field-contaminated firefighter jacket samples. Yet, on comparing the responses using both HS liquid and HS fabric calibration curves, it was seen that both the calibration curves yielded similar results. The analysis points out that either of the calibration methods could be used to quantitate the compounds off-gassing from field-contaminated samples. A larger data set must be studied to understand the applicability of either of the calibration methods for other compounds, especially semi-volatile compounds that higher boiling points. The analysis of the field-contaminated gear using the HS-GC-MS at 200°C, 30 minutes at various times of air exposure showed that certain compounds do off-gas at a higher rate as compared to others. The 48-hour samples showed a decrease in off-gassing levels for most compounds, that had a higher level of off-gassing at the 0-hour sample. This indicates that if a gear is stored after exposure, certain compounds would still be present in the gear even after 48-hours. The contaminated gear when stored in the engine bay of the fire station could possibly off-gas certain compounds and create a toxic environment for the firefighters. After analysis, volatile compounds, having lower boiling points, such as acetic acid were observed to off-gas significantly even after the contaminated gear was tested at 48-hours. This would pose a health hazard to the firefighters present in the fire station in the absence of respiratory protection.

CHAPTER 14: Research conclusions, Recommendations and Proposed Future Research

14.1 Summary of Research and Overall Conclusions

The studies that were conducted as a part of this research project were focused on developing methods to analyze the fireground contaminants from contaminated firefighter turnout gear. Gas chromatography-mass spectrometry, combined with two methods, namely liquid extraction and thermal extraction were developed to analyze the efficacy of removal of contaminants from outer shell materials. The methods were tested with control fabric samples and validated by applying the methods on field-contaminated outer shell fabrics. The aim was to be able to evaluate the contamination profile and quantitate the compounds present in a field-contaminated firefighter gear and understand the realistic implication for the firefighters.

14.2 Research Conclusions

14.2.1 Conclusion pertaining to the development liquid extraction using pressurized solvent extractor

The major objective of this research was to develop a suitable method to facilitate the extraction of fireground contaminants from outer shell fabrics. Several iterations of the parameters such as temperature, pressure and number of cycles were performed on the Buchi pressurized solvent extractor to obtain the best method for maximum removal of the contaminants. The method was specifically developed for the extraction of contaminants from outer shell materials, present as the outermost layer in firefighter turnout gear. The second objective was to develop an analytical method using GC-MS for identification and analysis of

the selected fireground contaminants (phenols, phthalates and PAHs), extracted from the outer shell fabrics. In-depth literature review of the analytical instrument, the fireground contaminants and previous studies undertaken is provided in Chapters 3-6.

Even though this study was performed using reference unused firefighter gear materials, the extraction and analysis method can be used to analyze field-contaminated gear as well. The results from the research point out that the liquid extraction method is better suited for the extraction of semi-volatile compounds such as DEHP and benzo[a] pyrene, having higher boiling points. Volatile compounds such as naphthalene yielded very low extraction efficiencies, possibly because of evaporation of the compound during the extraction procedure. A drawback of the solvent extractor is the inability to effectively extract volatile compounds, without loss of analytes.

The method that was developed in this study was validated by conducting multiple experiments and comparing the results across the experiments. Apart from analyzing the contamination from contaminated outer shell fabrics, the solvent extraction-GC-MS procedure could also be used to evaluate the washing efficiency of firefighter turnout gear. Overall, the liquid extraction is a robust method for the extraction of compounds from outer shell materials.

14.2.2 Conclusions pertaining to the development of thermal extraction using headspace GC

The main objective of this research was to evaluate the headspace sampler instrument as a screening method to analyze the off-gassing of contaminants from firefighter turnout gear. Two important parameters, equilibration time and temperature were extensively studied, which is mentioned in Section 7.5. Multiple iterations were performed to understand the effect of temperature and equilibration time on the levels of off-gassing of compounds. Results indicate

that the amount of off-gassing increases drastically with an increase in the temperature of exposure. While, with the various equilibration times tested, 30 minutes was found as the optimum time for obtaining maximum off-gassing. The headspace GC was successfully used as a tool to carry out the thermal extraction of contaminants from outer shell fabrics. A temperature of 200°C with an equilibration time of 30 minutes was found to be the best method for removal of compounds. The analysis at lower temperatures, such as 36°C and 50°C , showed that only volatile compounds such as phenol and naphthalene off-gassed. Even though the level of off-gassing was lower at these temperatures, studies have shown that volatile compounds such as benzene, acetic acid and acetone are present in field-contaminated firefighter gear. The off-gassing of compounds at 36°C , a condition found in fire stations, would prove to be a health hazard for the firefighters who are typically present without respiratory protection. The inhalation of some of these chemicals could lead the firefighters to several types of diseases. While the off-gassing at 50°C , a condition found in heated car trunks/ fire trucks, would pose a risk of inhalation as well for the firefighters. While off-gassing is generally seen as a harmful concept, it could be put to an advantage. The 50°C temperature could be used as a thermal decontamination technique for firefighter gear, by placing the contaminated gear in a heated cabinet.

The off-gassing of control samples using the headspace sampler point out that the method works the best for volatile compounds such as naphthalene and phenol. This is because the operational temperature of the headspace GC method is 200°C and most of the semi-volatile compounds have higher boiling points. The method lacks the ability to effectively volatilize the compounds with high boiling points and hence only a part of the compound gets vaporized and

detected. A traditional method such as the pressurized solvent extraction must be used to effectively extract the high boiling compounds.

The analysis of field-contaminated gear material produced a chromatogram with a number of compounds that were seen. That included compounds such as phenol, DEHP, acenaphthylene and acetic acid. Appropriate calibration curves were used to quantitate the amounts of certain compounds that off-gassed from the gear. An important aspect that was achieved was the ability to quantitate the off-gassing levels using the headspace sampler. Another important aspect was understand the effect of air exposure on the off-gassing levels from contaminated fabrics. The analysis showed that volatile compounds such as acetic acid showed a steady decrease for over 48-hours after the fabrics were exposed, whereas semi-volatile compounds such as DEHP showed an almost consistent trend. These findings not only gather information about the types of compound off-gassing from field-contaminated gear, but also that the contaminants kept off-gassing for as long as 48 hours.

With the knowledge gained from all the off-gassing experiments conducted, it can be said that headspace sampler is a useful tool to thermally extract compounds from a contaminated firefighter gear. Also, that compounds off-gassing from the turnout gear at realistic temperatures poses a threat to the firefighters in the vicinity of the gear.

14.3 Proposed Future Research

14.3.1 Future Research on liquid extraction of firefighter turnout gear fabrics

The experiments conducted for the current research used control contaminated outer shell materials. Liquid fireground contaminants were pipetted onto unused outer shell materials, which

although was a repeatable procedure, did not represent a realistic exposure. In reality, the contamination on an actual firefighter gear is comprised of particles, soot and volatile/semi-volatile compounds. To test the viability of the solvent extractor for carrying out liquid extraction, actual field-contaminated fabric samples taken from firefighter gear must be analyzed. Additionally, the extractor could also be used to extract efficacy of contaminated wipe samples and other layers of the firefighter turnout gear. In reality, the contamination present on the surface of the outer shell material is not necessarily harmful until the bio-availability of the chemicals is known. To assess that, experiments such as contact transfer must be carried out, to know how much of the contaminant from the fabric samples passes through the skin.

14.3.2 Future Research on thermal extraction of firefighter turnout gear fabrics

The results of the thermal extraction conducted at 200°C proved that both, volatile and semi-volatile compounds off-gas from contaminated firefighter gear. However, the data set for the quantitation of off-gassing was limited and requires the analysis of a larger set of field-contaminated outer shell materials for the validation of the method. The studies at 36°C and 50°C using control samples proved that certain compounds off-gas, but the same must be tested with actual field-contaminated outer shell materials at those conditions. The experiments were conducted only for the outer shell layer of the firefighter turnout jacket. The same could be extrapolated to the other layers of the jacket, trousers and ensemble elements as well. There are several questions that needs to be answered. One of them is, whether off-gassing at realistic conditions is a threat to the firefighters? Second, how does the off-gassing of compounds from the turnout gear relate to the bio-availability of the compounds in the body?

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