
Electronic Theses and Dissertations, 2004-2019

2008

The Identification Of Ignitable Liquids In The Presence Of Pyrolysis Products: Generation Of A Pyrolysis Product Database

Joseph Castelbuono
University of Central Florida

 Part of the [Chemistry Commons](#), and the [Forensic Science and Technology Commons](#)

Find similar works at: <https://stars.library.ucf.edu/etd>

University of Central Florida Libraries <http://library.ucf.edu>

This Masters Thesis (Open Access) is brought to you for free and open access by STARS. It has been accepted for inclusion in Electronic Theses and Dissertations, 2004-2019 by an authorized administrator of STARS. For more information, please contact STARS@ucf.edu.

STARS Citation

Castelbuono, Joseph, "The Identification Of Ignitable Liquids In The Presence Of Pyrolysis Products: Generation Of A Pyrolysis Product Database" (2008). *Electronic Theses and Dissertations, 2004-2019*. 3626.

<https://stars.library.ucf.edu/etd/3626>



THE IDENTIFICATION OF IGNITABLE LIQUIDS IN THE PRESENCE OF
PYROLYSIS PRODUCTS: GENERATION OF A PYROLYSIS PRODUCT
DATABASE

by

JOSEPH CASTELBUONO
B.S. University of Central Florida, 2008

A thesis submitted in partial fulfillment of the requirements
for the degree of Master of Science
in the Department of Chemistry
in the College of Sciences
at the University of Central Florida
Orlando, Florida

Fall Term
2008

© 2008 Joseph Castelbuono

ABSTRACT

The fire debris analyst is often faced with the complex problem of identifying ignitable liquid residues in the presence of products produced from pyrolysis and incomplete combustion of common building and furnishing materials[1]. The purpose of this research is to investigate a modified destructive distillation methodology provided by the Florida Bureau of Forensic Fire and Explosive Analysis to produce interfering product chromatographic patterns similar to those observed in fire debris case work. The volatile products generated during heating of substrate materials are extracted from the fire debris by passive headspace adsorption and subsequently analyzed by GC-MS. Low density polyethylene (LDPE) is utilized to optimize the modified destructive distillation method to produce the interfering products commonly seen in fire debris. The substrates examined in this research include flooring and construction materials along with a variety of materials commonly analyzed by fire debris analysts. These substrates are also burned in the presence of a variety of ignitable liquids. Comparisons of ignitable liquids, pyrolysis products, and products from pyrolysis in the presence of an ignitable liquid are performed by comparing the summed ion spectra from the GC-MS data. Pearson correlation was used to determine if substrates could be discriminated from one another. A pyrolysis products database and GC-MS database software based on comparison of summed ion spectra are shown to be useful tools for the evaluation of fire debris.

This thesis is dedicated to my mom and dad. If not for their guidance and dedication I would never have been able accomplish all that I have done.

ACKNOWLEDGEMENTS

Members of the committee:

Dr. Michael Sigman

Dr. Barry Fookes

Dr. Andres Campiglia

Colleagues and friends:

Mary Williams

Carl Chasteen

Douglass Clark

Candice Bridge

Katie Steele

Jessica Frisch

Erin McIntee

Jeniffer Molina

Christopher Moody

Kimberly Painter

Joseph Colca

Ashley Walker

Neil Christiana Jr.

Angela Fischer

Kelly McHugh

TABLE OF CONTENTS

LIST OF FIGURES	ix
LIST OF TABLES	xv
CHAPTER ONE: INTRODUCTION.....	1
Purpose of the Research	1
Brief Synopsis	1
Arson	2
CHAPTER TWO: BACKGROUND.....	4
Ignitable Liquids.....	4
Classification System	4
Mass Spectral Analysis of Ignitable Liquids.....	6
Criteria for Identification.....	6
Weathering	8
Concepts of Combustion and Pyrolysis.....	14
CHAPTER THREE: COLLECTION AND PREPARATION OF FIRE DEBRIS	16
Sample Collection	16
Sample Preparation Methods.....	17
Distillation	18
Solvent Extraction	18
Direct Headspace.....	19
Solid-Phase Microextraction	19
Dynamic Headspace (purge and trap)	19
Passive Headspace.....	20
CHAPTER FOUR: METHODOLOGY	21
Research Method.....	21

Instrumental Parameters	23
Covariance Mapping and Summed Ion Method.....	23
Statistical Comparison Method	27
CHAPTER FIVE: VARIABILITY TESTING.....	30
Method Variability Testing	30
Applied Heat.....	30
Distance of Flame.....	32
Size and Mass of Substrate.....	32
Heating Time.....	34
Volume of Ignitable Liquid.....	36
Summary	38
CHAPTER SIX: PYROLYSIS OF SUBSTRATES.....	40
Substrate Comparisons	40
Introduction	40
Carpets, Carpet blends, and Padding.....	41
Hardwoods and Softwoods.....	44
Vinyl and Linoleum Flooring	48
Laminate Hardwood Flooring	50
Miscellaneous Substrates.....	53
Substrates in the Presence of Ignitable Liquids.....	57
CHAPTER SEVEN: CONCLUSION.....	62
Conclusion.....	62
Future Direction	63
APPENDIX: SUBSTRATE TOTAL ION CHROMATOGRAMS AND TABLES OF	
PRODUCTS.....	65

REFERENCES 118

LIST OF FIGURES

Figure 1: TIC of Phillips 66 Unleaded Regular Gasoline (unweathered)	9
Figure 2: TIC of Phillips 66 Unleaded Regular Gasoline (top 25%, middle 50%, and bottom 75% weathered)	10
Figure 3: TIC of Klean Strip Odorless Mineral Spirits (unweathered)	12
Figure 4: TIC of Klean Strip Odorless Mineral Spirits (top 25%, middle 50%, and bottom 75% weathered)	13
Figure 5: Apparatus setup.....	22
Figure 6: Post burn setup inside can.....	22
Figure 7: Graph summarizing the constant temperature applied to the can. Shown are the thermocouple temperature readings above flame position (T1) and directly on the flame (T2).....	31
Figure 8: TIC of a 1 g sample of LDPE burned.	33
Figure 9: TIC of a 4 g sample of LDPE burned.	33
Figure 10: TIC of a 10 g sample of LDPE burned.	34
Figure 11: Ten grams of LDPE burned for two minutes.....	35
Figure 12: Ten grams of LDPE burned for five minutes.....	35
Figure 13: Headspace temperature of Nylon Carpet and Pad with various volumes of gasoline..	38
Figure 14: Plot discriminating nylon carpet from olefin carpet using Z-transform and Pearson correlation +/- standard deviation error bars.	43
Figure 15: Plot discriminating nylon carpet from olefin/nylon blend carpet using Z-transform and Pearson correlation +/- standard deviation error bars.....	44
Figure 16: TIC and summed ion (inset) comparison of White Pine (top) and Douglass Fir (bottom)	48

Figure 17: Graph showing increase in similarity with standard deviation error bars of an isoparaffinic liquid (top) and a low petroleum distillate (bottom) after alder wood was incorporated in the database search.....	59
Figure 18: Graph showing increase in similarity with standard deviation error bars of a gasoline (top), oxygenated (middle), and naphthenic (bottom) ignitable liquid after cedar wood was incorporated in the database search.....	60
Figure 19: TIC of Polyester Carpet Unburned	66
Figure 20: TIC of Polyester Carpet Burned	66
Figure 21: TIC of PET Polyester Carpet Unburned	67
Figure 22: TIC of PET Polyester Carpet Burned	67
Figure 23: TIC of Nylon Carpet Unburned	68
Figure 24: TIC of Nylon Carpet Burned	68
Figure 25: TIC of Polyester/Nylon Blend Carpet Unburned.....	69
Figure 26: TIC of Polyester/Nylon Blend Carpet Burned.....	69
Figure 27: TIC of Olefin Carpet Unburned.....	70
Figure 28: TIC of Olefin Carpet Burned	70
Figure 29: TIC of UV Olefin Carpet Unburned	71
Figure 30: TIC of UV Olefin Carpet Burned	71
Figure 31: TIC of Olefin Nylon Blend Carpet Unburned	72
Figure 32: TIC of Olefin Nylon Blend Carpet Burned.....	72
Figure 33: TIC of Cedar Wood Unburned	73
Figure 34: TIC of Cedar Wood Burned.....	73
Figure 35: TIC of Cherry Wood Unburned.....	74
Figure 36: TIC of Cherry Wood Burned	74
Figure 37: TIC of Hickory Wood Unburned.....	75
Figure 38: TIC of Hickory Wood Burned	75

Figure 39: TIC of Douglass Fir Wood Unburned.....	76
Figure 40: TIC of Douglass Fir Wood Burned.....	76
Figure 41: TIC of Oak Wood Unburned	77
Figure 42: TIC of Oak Wood Burned.....	77
Figure 43: TIC of Yellow Pine Wood Unburned	78
Figure 44: TIC of Yellow Pine Wood Burned	78
Figure 45: TIC of White Pine Wood Unburned	79
Figure 46: TIC of White Pine Wood Burned	79
Figure 47: TIC of Maple Wood Unburned.....	80
Figure 48: TIC of Maple Wood Burned.....	80
Figure 49: TIC of Aspen Wood Unburned.....	81
Figure 50: TIC of Aspen Wood Burned.....	81
Figure 51: TIC of Poplar Wood Unburned.....	82
Figure 52: TIC of Poplar Wood Burned.....	82
Figure 53: TIC of Alder Wood Unburned.....	83
Figure 54: TIC of Alder Wood Burned	83
Figure 55: TIC of Trex Composite Wood Unburned	84
Figure 56: TIC of Trex Composite Wood Burned	84
Figure 57: TIC of Vinyl Unburned.....	85
Figure 58: TIC of Vinyl Burned.....	85
Figure 59: TIC of Industrial Vinyl Unburned	86
Figure 60: TIC of Industrial Vinyl Burned.....	86
Figure 61: TIC of Vinyl/Linoleum Unburned	87
Figure 62: TIC of Vinyl/Linoleum Burned	87
Figure 63: TIC of Bamboo Hardwood Unburned	88
Figure 64: TIC of Bamboo Hardwood Burned.....	88

Figure 65: TIC of Hickory Laminate Hardwood Unburned.....	89
Figure 66: TIC of Hickory Laminate Hardwood Burned.....	89
Figure 67: TIC of Cherry Laminate Hardwood Unburned.....	90
Figure 68: TIC of Cherry Laminate Hardwood Burned.....	90
Figure 69: TIC of Troya Laminate Hardwood Unburned.....	91
Figure 70: TIC of Troya Laminate Hardwood Burned.....	91
Figure 71: TIC of Teak Laminate Hardwood Unburned.....	92
Figure 72: TIC of Teak Laminate Hardwood Burned.....	92
Figure 73: TIC of Clear Hard Maple Laminate Flooring Unburned.....	93
Figure 74: TIC of Clear Hard Maple Laminate Flooring Burned.....	93
Figure 75: TIC of Character Walnut Laminate Flooring Unburned.....	94
Figure 76: TIC of Character Walnut Laminate Flooring Burned.....	94
Figure 77: TIC of Clear Hickory Laminate Hardwood Flooring Unburned.....	95
Figure 78: TIC of Clear Hickory Laminate Hardwood Flooring Burned.....	95
Figure 79: TIC of Clear Red Oak Hardwood Flooring Unburned.....	96
Figure 80: TIC of Clear Red Oak Hardwood Flooring Burned.....	96
Figure 81: TIC of Clear White Oak Laminate Flooring Burned.....	97
Figure 82: TIC of Cinderblock Unburned.....	98
Figure 83: TIC of Cinderblock Burned.....	98
Figure 84: TIC of Asphalt Roofing Shingles Unburned.....	99
Figure 85: TIC of Asphalt Roofing Shingles Burned.....	99
Figure 86: TIC of Roofing Tiles Unburned.....	100
Figure 87: TIC of Roofing Tiles Burned.....	100
Figure 88: TIC of Foil Insulation Unburned.....	101
Figure 89: TIC of Foil Insulation Burned.....	101
Figure 90: TIC of Fiberglass Insulation Unburned.....	102

Figure 91: TIC of Fiberglass Insulation Burned.....	102
Figure 92: TIC of Black Leather Unburned	103
Figure 93: TIC of Black Leather Burned	103
Figure 94: TIC of 100% Cotton Pajama Pants Unburned	104
Figure 95: TIC of 100% Cotton Pajama Pants Burned	104
Figure 96: TIC of 100% Polyester Quilt Batting Unburned.....	105
Figure 97: TIC of 100% Polyester Quilt Batting Burned.....	105
Figure 98: TIC of 100% Polyurethane Foam Mattress Pad Unburned.....	106
Figure 99: TIC of 100% Polyurethane Foam Mattress Pad Burned.....	106
Figure 100: TIC of Thermal Paper Unburned	107
Figure 101: TIC of Thermal Paper Burned	107
Figure 102: TIC of Cardboard Box Unburned	108
Figure 103: TIC of Cardboard Box Burned.....	108
Figure 104: TIC of Finegrain Cork Tiles Unburned.....	109
Figure 105: TIC of Finegrain Cork Tiles Burned.....	109
Figure 106: TIC of Magazine Unburned	110
Figure 107: TIC of Magazine Burned	110
Figure 108: TIC of Diamond Braid Polyester Rope Unburned.....	111
Figure 109: TIC of Diamond Braid Polyester Rope Burned	111
Figure 110: TIC of Twisted Nylon Rope Unburned.....	112
Figure 111: TIC of Twisted Nylon Rope Burned.....	112
Figure 112: TIC of White Casual Shoe Unburned	113
Figure 113: TIC of White Casual Shoe Burned	113
Figure 114: TIC of Flip Flops Unburned	114
Figure 115: TIC of Flip Flops Burned.....	114
Figure 116: TIC of Rain Boot Shoe Covering Unburned.....	115

Figure 117: TIC of Rain Boot Shoe Covering Burned.....	115
Figure 118: TIC of Brown Casual Shoe Unburned.....	116
Figure 119: TIC of Brown Casual Shoe Burned.....	116
Figure 120: TIC of Street Smart Boots Unburned.....	117
Figure 121: TIC of Street Smart Boots Burned.....	117

LIST OF TABLES

Table 1: Ignitable Liquid Classification Scheme 5

Table 2: Major Ions for Common Compound Types found in EIP..... 6

Table 3: Pattern Type for each class..... 7

Table 4: Percent composition of fire debris (matrix) from a burned sample of nylon carpet with pad and gasoline and the similarity of summed ion spectra to that percent weathered gasoline..... 37

Table 5: Z-transform/Pearson correlation figures (bottom) and standard deviation (top) for same sample (ss) comparisons of carpet..... 42

Table 6: Z-transform/Pearson correlation figures (bottom) and standard deviation (top) for different sample (ds) comparisons of carpet..... 42

Table 7: Discrimination of different carpet types..... 42

Table 8: Z-transform/Pearson correlation figures (bottom) and standard deviation (top) for same sample (ss) comparisons of wood..... 45

Table 9: Z-transform/Pearson correlation figures (bottom) and standard deviation (top) for different sample (ds) comparisons of wood 46

Table 10: Discrimination of different wood types..... 46

Table 11: Z-transform/Pearson correlation figures (bottom) and standard deviation (top) for same sample (ss) comparisons of vinyl flooring 49

Table 12: Z-transform/Pearson correlation figures (bottom) and standard deviation (top) for different sample (ds) comparisons of vinyl flooring 49

Table 13: Discrimination of vinyl flooring 49

Table 14: Z-transform/Pearson correlation figures (bottom) and standard deviation (top) for same sample (ss) comparisons of laminate hardwood flooring 50

Table 15: Z-transform/Pearson correlation figures (bottom) and standard deviation (top) for different sample (ds) comparisons of laminate hardwood flooring..... 51

Table 16: Discrimination of different laminate flooring types	51
Table 17: Miscellaneous substrate I.D. table.....	53
Table 18: Z-transform/Pearson correlation figures (bottom) and standard deviation (top) for same sample (ss) comparisons of miscellaneous substrates	54
Table 19: Z-transform/Pearson correlation figures (bottom) and standard deviation (top) for different sample (ds) comparisons of miscellaneous substrates	54
Table 20: Discrimination of Miscellaneous Substrates	55
Table 21: Same substrate comparison of Shoes	56
Table 22: Comparison of the average similarity (bottom) and standard deviation (top) of different shoes.	56
Table 23: Discrimination of different shoes	56
Table 24: Retention Times and Products of Unburned Polyester Carpet.....	66
Table 25: Retention Times and Products of Burned Polyester Carpet	66
Table 26: Retention Times and Products of Unburned PET Polyester Carpet.....	67
Table 27: Retention Times and Products of Burned PET Polyester Carpet	67
Table 28: Retention Times and Products of Unburned Nylon Carpet.....	68
Table 29: Retention Times and Products of Burned Nylon Carpet	68
Table 30: Retention Times and Products of Unburned Polyester/Nylon Blend Carpet	69
Table 31: Retention Times and Products of Burned Polyester/Nylon Blend Carpet.....	69
Table 32: Retention Times and Products of Unburned Olefin Carpet.....	70
Table 33: Retention Times and Products of Burned Olefin Carpet.....	70
Table 34: Retention Times and Products of Unburned UV Olefin Carpet.....	71
Table 35: Retention Times and Products of Burned UV Olefin Carpet	71
Table 36: Retention Times and Products of Unburned Olefin Nylon Blend Carpet	72
Table 37: Retention Times and Products of Burned Olefin Nylon Blend Carpet	72
Table 38: Retention Times and Products of Unburned Cedar Wood	73

Table 39: Retention Times and Products of Burned Cedar Wood	73
Table 40: Retention Times and Products of Unburned Cherry Wood.....	74
Table 41: Retention Times and Products of Burned Cherry Wood.....	74
Table 42: Retention Times and Products of Unburned Hickory Wood.....	75
Table 43: Retention Times and Products of Burned Hickory Wood.....	75
Table 44: Retention Times and Products of Unburned Douglass Fir Wood	76
Table 45: Retention Times and Products of Burned Douglass Fir Wood	76
Table 46: Retention Times and Products of Unburned Oak Wood.....	77
Table 47: Retention Times and Products of Burned Oak Wood	77
Table 48: Retention Times and Products of Unburned Yellow Pine Wood.....	78
Table 49: Retention Times and Products of Burned Yellow Pine Wood.....	78
Table 50: Retention Times and Products of Unburned White Pine Wood.....	79
Table 51: Retention Times and Products of Burned White Pine Wood.....	79
Table 52: Retention Times and Products of Unburned Maple Wood	80
Table 53: Retention Times and Products of Burned Maple Wood.....	80
Table 54: Retention Times and Products of Unburned Aspen Wood	81
Table 55: Retention Times and Products of Burned Aspen Wood.....	81
Table 56: Retention Times and Products of Unburned Poplar Wood	82
Table 57: Retention Times and Products of Burned Poplar Wood	82
Table 58: Retention Times and Products of Unburned Alder Wood.....	83
Table 59: Retention Times and Products of Burned Alder Wood.....	83
Table 60: Retention Times and Products of Unburned Trex Composite Wood.....	84
Table 61: Retention Times and Products of Burned Trex Composite Wood	84
Table 62: Retention Times and Products of Unburned Vinyl	85
Table 63: Retention Times and Products of Burned Vinyl	85
Table 64: Retention Times and Products of Unburned Industrial Vinyl.....	86

Table 65: Retention Times and Products of Burned Industrial Vinyl	86
Table 66: Retention Times and Products of Unburned Vinyl/Linoleum.....	87
Table 67: Retention Times and Products of Burned Vinyl/Linoleum.....	87
Table 68: Retention Times and Products of Unburned Bamboo Hardwood	88
Table 69: Retention Times and Products of Burned Bamboo Hardwood	88
Table 70: Retention Times and Products of Unburned Hickory Laminate Hardwood	89
Table 71: Retention Times and Products of Burned Hickory Laminate Hardwood.....	89
Table 72: Retention Times and Products of Unburned Cherry Laminate Hardwood	90
Table 73: Retention Times and Products of Burned Cherry Laminate Hardwood.....	90
Table 74: Retention Times and Products of Unburned Troya Laminate Hardwood.....	91
Table 75: Retention Times and Products of Burned Troya Laminate Hardwood	91
Table 76: Retention Times and Products of Unburned Teak Laminate Hardwood.....	92
Table 77: Retention Times and Products of Burned Teak Laminate Hardwood.....	92
Table 78: Retention Times and Products of Unburned Clear Hard Maple Laminate Flooring.....	93
Table 79: Retention Times and Products of Burned Clear Hard Maple Laminate Flooring	93
Table 80: Retention Times and Products of Unburned Character Walnut Laminate Flooring	94
Table 81: Retention Times and Products of Burned Character Walnut Laminate Flooring.....	94
Table 82: Retention Times and Products of Unburned Clear Hickory Laminate Hardwood Flooring	95
Table 83: Retention Times and Products of Burned Clear Hickory Laminate Hardwood Flooring	95
Table 84: Retention Times and Products of Unburned Clear Red Oak Hardwood Flooring	96
Table 85: Retention Times and Products of Burned Clear Red Oak Hardwood Flooring	96
Table 86: Retention Times and Products of Burned Clear White Oak Laminate Flooring.....	97
Table 87: Retention Times and Products of Unburned Cinderblock.....	98
Table 88: Retention Times and Products of Burned Cinderblock.....	98

Table 89: Retention Times and Products of Unburned Asphalt Roofing Shingles	99
Table 90: Retention Times and Products of Burned Asphalt Roofing Shingles	99
Table 91: Retention Times and Products of Unburned Roofing Tiles	100
Table 92: Retention Times and Products of Burned Roofing Tiles.....	100
Table 93: Retention Times and Products of Unburned Foil Insulation	101
Table 94: Retention Times and Products of Burned Foil Insulation	101
Table 95: Retention Times and Products of Unburned Fiberglass Insulation	102
Table 96: Retention Times and Products of Burned Fiberglass Insulation	102
Table 97: Retention Times and Products of Unburned Black Leather	103
Table 98: Retention Times and Products of Burned Black Leather	103
Table 99: Retention Times and Products of Unburned 100% Cotton Pajama Pants.....	104
Table 100: Retention Times and Products of Burned 100% Cotton Pajama Pants.....	104
Table 101: Retention Times and Products of Unburned 100% Polyester Quilt Batting	105
Table 102: Retention Times and Products of Burned 100% Polyester Quilt Batting.....	105
Table 103: Retention Times and Products of Unburned 100% Polyurethane Foam Mattress Pad	106
Table 104: Retention Times and Products of Burned 100% Polyurethane Foam Mattress Pad .	106
Table 105: Retention Times and Products of Unburned Thermal Paper.....	107
Table 106: Retention Times and Products of Burned Thermal Paper	107
Table 107: Retention Times and Products of Unburned Cardboard Box.....	108
Table 108: Retention Times and Products of Burned Cardboard Box	108
Table 109: Retention Times and Products of Unburned Finegrain Cork Tiles	109
Table 110: Retention Times and Products of Burned Finegrain Cork Tiles	109
Table 111: Retention Times and Products of Unburned Magazine.....	110
Table 112: Retention Times and Products of Burned Magazine.....	110
Table 113: Retention Times and Products of Unburned Diamond Braid Polyester Rope	111

Table 114: Retention Times and Products of Burned Diamond Braid Polyester Rope.....	111
Table 115: Retention Times and Products of Unburned Twisted Nylon Rope	112
Table 116: Retention Times and Products of Burned Twisted Nylon Rope	112
Table 117: Retention Times and Products of Unburned White Casual Shoe	113
Table 118: Retention Times and Products of Burned White Casual Shoe	113
Table 119: Retention Times and Products of Unburned Flip Flops	114
Table 120: Retention Times and Products of Burned Flip Flops	114
Table 121: Retention Times and Products of Unburned Rain Boot Shoe Covering	115
Table 122: Retention Times and Products of Burned Rain Boot Shoe Covering.....	115
Table 123: Retention Times and Products of Unburned Brown Casual Shoe.....	116
Table 124: Retention Times and Products of Burned Brown Casual Shoe	116
Table 125: Retention Times and Products of Unburned Street Smart Boots	117
Table 126: Retention Times and Products of Burned Street Smart Boots	117

CHAPTER ONE: INTRODUCTION

Purpose of the Research

The purpose of this research was to develop a modified destructive distillation methodology to produce interfering product chromatographic patterns similar to those observed in fire debris case work and to establish the initial data set for an internet accessible GC-MS database tool for fire debris analysts to use in the evaluation of casework data. Chromatographic patterns observed in fire debris must often be scrutinized carefully because some chromatographic interpretation depends on the analyst viewing it. It can be difficult to identify peaks in the chromatogram as arising from either an ignitable liquid or from the pyrolysis of a substrate. Not only does this research aid in creating a database of chromatograms and products specific to the pyrolysis of common building materials, but it also introduces a new technique for analyzing fire debris called the summed ion method. A summed ion profile is created by summing the intensity of each m/z ratio across the entire chromatographic range and normalizing the resulting spectrum. This method enables an analyst using comparison software to interpret results faster than when analyzing a chromatogram peak by peak or by identifying patterns by hand.

Brief Synopsis

In order for a fire to be classified as arson an accelerant or ignitable liquid is usually involved. All ignitable liquids worldwide can be characterized under the same classification system designed by the American Society for Testing and Materials

(ASTM) Committee E30 on Forensic Science. An ignitable liquid falls under one of eight classes. They are gasoline, distillate, aromatic, isoparaffinic, naphthenic/paraffinic, normal alkane, oxygenates, and miscellaneous. Each sample is analyzed with a gas chromatograph-mass spectrometer and a data system capable of storing and manipulating chromatographic and mass spectral data.

Pyrolysis is the chemical decomposition of a material brought on by heat in the absence of oxygen. Through the application of heat, pyrolysis will lyse or break down a material into simpler compounds. Pyrolysis products can be found in the chromatographic patterns similar to those observed in fire debris casework. It is important to be able to identify the products produced by substrates during pyrolysis and incomplete combustion because they may interfere in the identification of ignitable liquids residues. This study intends to show that carefully analyzing the interfering products produced from substrates found in fire debris can be discriminated using the summed ion method coupled with a variety of statistical techniques, but can also aid in the identification of trace ignitable liquid residues.

Arson

According to the United States Fire Administration, in 2006, there were 31,000 intentionally set structure fires in the U.S. which led to 305 civilian deaths and 755 million dollars and property damage. This was down from 10 years before when there were 78,500 arson related fires resulting in 455 deaths and over a billion dollars in property damage[2]. Arson is defined as the deliberate and malicious intent of starting a fire to a building or some property belonging to oneself or another[3]. The majority of

arson cases are monetarily driven. Arson often involves filing fraudulent insurance claims after setting a fire and claiming it accidental. However, there are many other motives to commit arson. Arson for the sake of vandalism often occurs when juveniles are desperate for attention and do not understand the severity and consequences of their actions. Another motive is starting a fire for the sheer excitement of it which often leads to photographing or video taping the fire in progress, these people are considered pyromaniacs[3]. Revenge is a common arson motive as is concealing a crime. Fires have been started to destroy evidence at a crime scene or to cover up the death of another human being that wasn't caused by the fire. Therefore, the purpose of the fire analyst is to determine the origin of the fire, and the cause of the fire, or if the fire was accidental, or brought about by natural causes.

CHAPTER TWO: BACKGROUND

Ignitable Liquids

Accidental fires can occur in a number of ways ranging from a gas leak, to an electrical short, to carelessness involving a cigarette or candle[3]. However, when fires are intentionally set generally an ignitable liquid is used. The term accelerant has been used interchangeably with an ignitable liquid. An accelerant is exactly what its name suggests; an accelerant is any type of ignitable liquid that speeds up the development of a fire. This means that the fire will burn at an accelerated rate, at a higher temperature, and it would spread rapidly. An ignitable liquid is also exactly what its name suggests, a liquid that is flammable, that can ignite a fire. An ignitable liquid is considered an accelerant if it is proven to be used in order to accelerate a fire[1].

Classification System

All ignitable liquids worldwide can be characterized under the same classification system designed by the American Society for Testing and Materials (ASTM) Committee E30 on Forensic Science. The classification system is the direct responsibility of Subcommittee E30.01 on Criminalistics. Standard ASTM E 1618 recommends that each fire debris analysis laboratory maintain its own library of common ignitable liquids which can help each lab account for any shifts in chromatographic peak retention times[4-8]. Each sample is analyzed with a gas chromatograph-mass spectrometer and a data system capable of storing and manipulating chromatographic and mass spectral data. Data analysis generates extracted ion profiles characteristic of the chemical compounds

commonly found in ignitable liquids[9]. Most can be identified based on their chromatographic retention times from the total ion chromatogram (TIC) and mass spectral data. The mass spectral data is based on the extracted ion profile (EIP) for the alkane, alkene, alcohol, aromatic, cycloalkanes, ester, ketone, and polynuclear aromatic compound types. The most recent ignitable liquid classification scheme can be seen in table 1 below[9].

Table 1: Ignitable Liquid Classification Scheme

Class	Light, Carbon Range (C ₄ -C ₉)	Medium, Carbon Range (C ₈ -C ₁₃)	Heavy, Carbon Range (C ₈ -C ₂₀₊)
Gasoline Gasohol	Found in light and medium. (C ₄ -C ₁₂)	Found in light and medium. (C ₄ -C ₁₂)	
Petroleum Distillates	Petroleum Ether Lighter Fluids* Camping fuels*	Charcoal Starters* Paint Thinners* Dry Cleaning Solvents*	Kerosene Diesel Fuel Jet fuels* Charcoal Starters*
Isoparaffinic Products	Jet Fuel Specialty Solvents*	Charcoal Starters* Paint Thinners* Copier Toners*	Commercial Specialty* Solvents
Aromatic Products	Paint and Varnish* Removers Automotive Parts Cleaners* Xylene, Toluene-based products	Automotive Parts Cleaners* Specialty Cleaning Solvents Insecticide Vehicles* Lamp Oils*	Insecticide Vehicles* Lamp Oils* Industrial Solvents
Napthenic – Paraffinic Products	Cyclohexane based solvents/products	Charcoal Starters* Insecticide Vehicles* Lamp Oils*	Insecticide Vehicles* Lamp oils* Industrial Solvents
Normal Alkane Products	Solvents Pentane Hexane Heptane	Candle Oils* Copier Toners*	Candle Oils* Carbonless forms Copier Toners*
Oxygenated Solvents	Alcohols Ketones Lacquer Thinners* Fuel Additives Preparation solvents*	Lacquer thinners* Industrial Solvents* Metal Cleaners/Gloss Removers	
Other/Miscellaneous	Single Component Products Blended Products* Enamel Reducers	Turpentine Products Blended Products* Specialty Products*	Blended Products* Specialty Products*

* Refers to “some” of each description

Following ASTM protocols, an investigator can test the ignitable liquid residues (ILR) of any of the liquids mentioned above. An ILR is a residue left from an ignitable liquid that has been absorbed by a burned substrate i.e. a carpet or piece of furniture.

ASTM makes it a point to note that the identification of an ignitable liquid residue in a fire scene does not necessarily conclude that a fire was an act of arson. Also, due to the high volatility of these liquids the absence of residues does not necessarily mean that an ignitable liquid was not present. It is important to note that materials normally found in a building, upon exposure to extreme temperatures, will form pyrolysis and combustion products. The extracted ion profile can or may facilitate the identification of an ignitable liquid in the extract by reducing interferences generated from pyrolysis products[9]. The purpose of this research is to document and create a database of the interfering products produced by these burned substrates.

Mass Spectral Analysis of Ignitable Liquids

The extracted ion profile (EIP) is vital to classifying an ignitable liquid. The more common major ions present for each compound type are listed in table 2 [9]. It is also important to compare all major chromatographic peaks to known standards such as a library or online database.

Table 2: Major Ions for Common Compound Types found in EIP

Compound Type	m/z
Alkanes	43, 57, 71, 85, 99
Cycloalkanes and alkenes	55, 69
Aromatic	91, 105, 119; 92, 106, 120
Indanes	117, 118; 131, 132
Ketones	43, 58, 72, 86
Alcohols	31, 45

Criteria for Identification

In order for an extract to be characterized as containing a particular class of ignitable liquid, the following minimum criteria must be met according to ASTM[9]:

Table 3: Pattern Type for each class

Class	TIC	Alkane	Cycloalkane	Aromatic	Condensed Ring Aromatic
Gasoline	Abundant Aromatics	Present, but pattern will vary	Absent or small	High presence of alkylbenzenes	Present but may be absent in some gasolines
Distillates	Gaussian Dist. of alkanes and aromatics	High abundance	Present, but in less abundance	Present but in less abundance than alkanes	May be present in small amounts
Isoparaffinic	Exclusively branched chain aliphatic compounds	High abundance	Absent or small	Absent or small	Not present
Aromatic	Exclusively aromatic or condensed ring aromatic	Absent or small	Absent or small	High Abundance	Present
Naphthenic/Paraffinic	Comprised of branched chain (Isoparaffinic) and cyclic (naphthenic) alkanes	High abundance	High abundance	Absent or small	Not present
Normal Alkane	Exclusively n-alkanes	High with small to no presence of isoparaffins	Absent or small	Absent or small	Absent or small
Oxygenated	Contains major oxygenated components.	Depends on formulation	Depends on formulation	Depends on formulation	Not significant

It is important to note that the mere presence of alkylbenzenes does not confirm gasoline. They must be present at approximately the same relative concentrations as are observed in known samples of gasoline. Also, oxygenated solvents such as alcohols do not indicate a foreign ignitable liquid is present, alcohols must be in large excess and an order of magnitude above the peaks produced by the substrate the liquid was found in (matrix peaks)[9]. The miscellaneous class is comprised of ignitable liquids that do not fall under any of the circumstances listed in the table above or liquids that fall into multiple categories and are usually considered synthetic mixtures. The previous three tables should give an arson investigator the means to identify the presence of an ignitable

liquid in a residue by GC-MS and allow them to properly characterize and identify the class to which the suspect ignitable liquid belongs.

Weathering

When an analyst views a TIC of an ignitable liquid, such as gasoline, one factor that they must keep in mind is complications due to weathering or biological degradation[10]. When an ignitable liquid is weathered through evaporation the smaller, more volatile hydrocarbons are lost creating greater relative peak intensities for the less volatile hydrocarbons as compared to the smaller compounds. This effect is illustrated by the following data for gasoline evaporation. A vial was filled with 8mL of Phillips 66 Unleaded Regular Gasoline (HC range C6-C13); markings were placed at the 2mL (75% weathered), 4mL (50% weathered), and 6mL (25% weathered) positions. The vial was placed in a well filled with sand and a gentle, dry heat bath was applied to speed up the weathering process in the face of a fume hood. One microliter was extracted at each of the three positions and analyzed using GC-MS. The chromatograms below show the effects of weathering as it is commonly seen in fire debris casework.

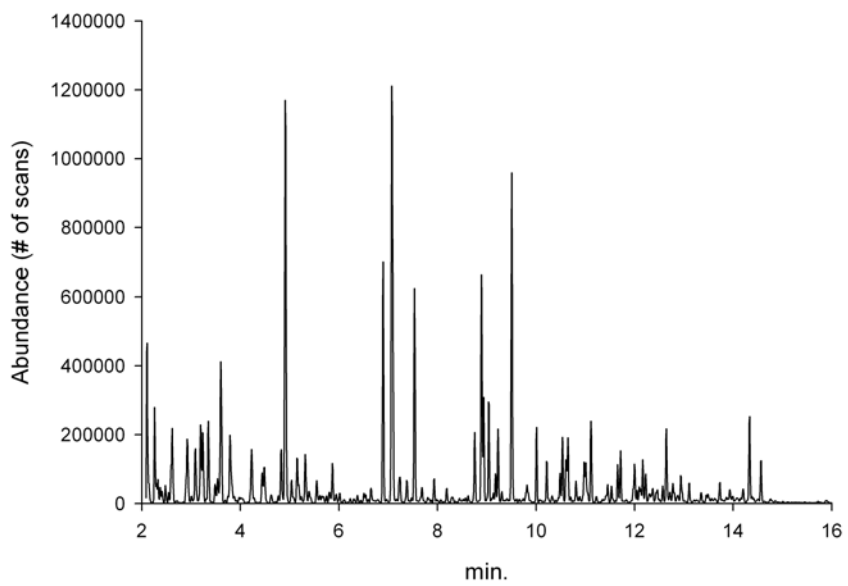


Figure 1: TIC of Phillips 66 Unleaded Regular Gasoline (unweathered)

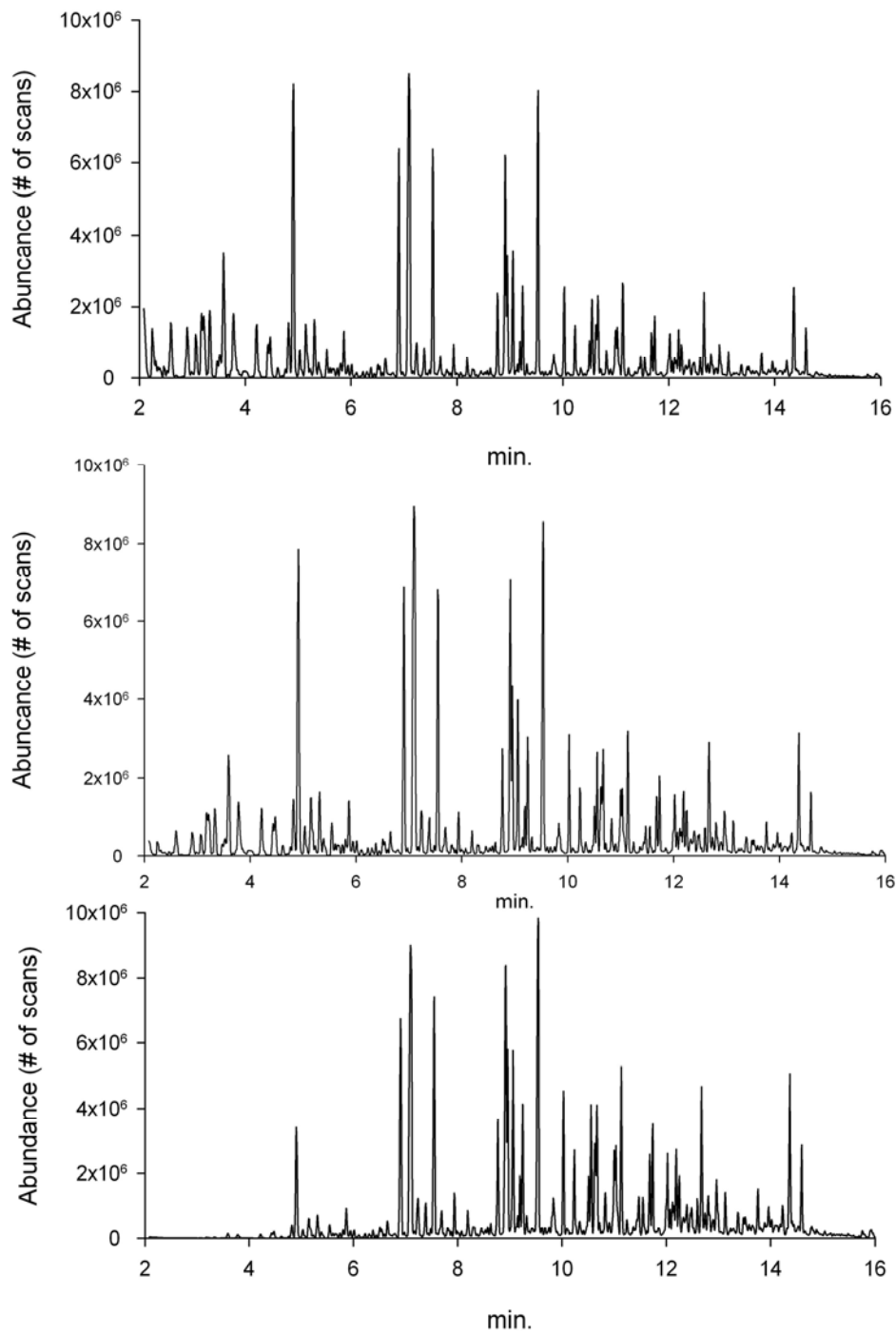


Figure 2: TIC of Phillips 66 Unleaded Regular Gasoline (top 25%, middle 50%, and bottom 75% weathered)

Examination of Figure 2 reveals that the 25% weathered sample still contains the more volatile hydrocarbons, but as the sample continues to weather to 50% and 75% the more volatile hydrocarbons dissipate and the less volatile hydrocarbon peak at 14.5min. becomes more prominent as the sample weathers. Another peak of interest is the toluene peak at 4.91min. As the sample continues to weather to 95% and 99%, the toluene peak may become so low in abundance that a peak will no longer be prominent and this could be troublesome to an analyst trying to identify this chromatogram as gasoline and searching for a toluene peak for confirmation, although alkylbenzenes are still present.

The same weathering analysis was performed on all classes of ignitable liquids. Some classes proved to be more troublesome than others, such as the medium petroleum distillates (MPD) which were slow to evaporate. The MPD required not only a dry heat sand bath, but also required N₂ gas to blow the sample down and speed up evaporation. Klean Strip Odorless Mineral Spirits (HC range C8-C12) was used as a representative medium petroleum distillate (MPD). The figures below summarize the results.

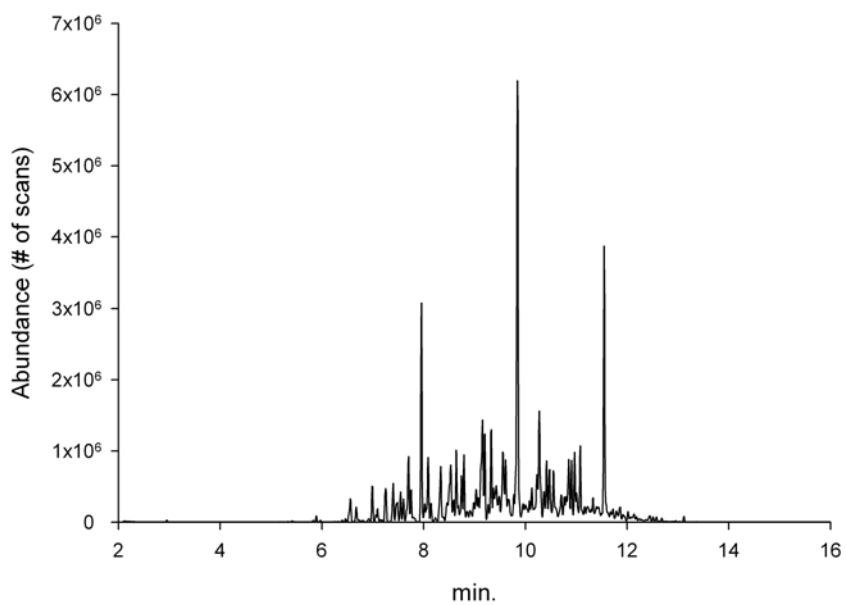


Figure 3: TIC of Klean Strip Odorless Mineral Spirits (unweathered)

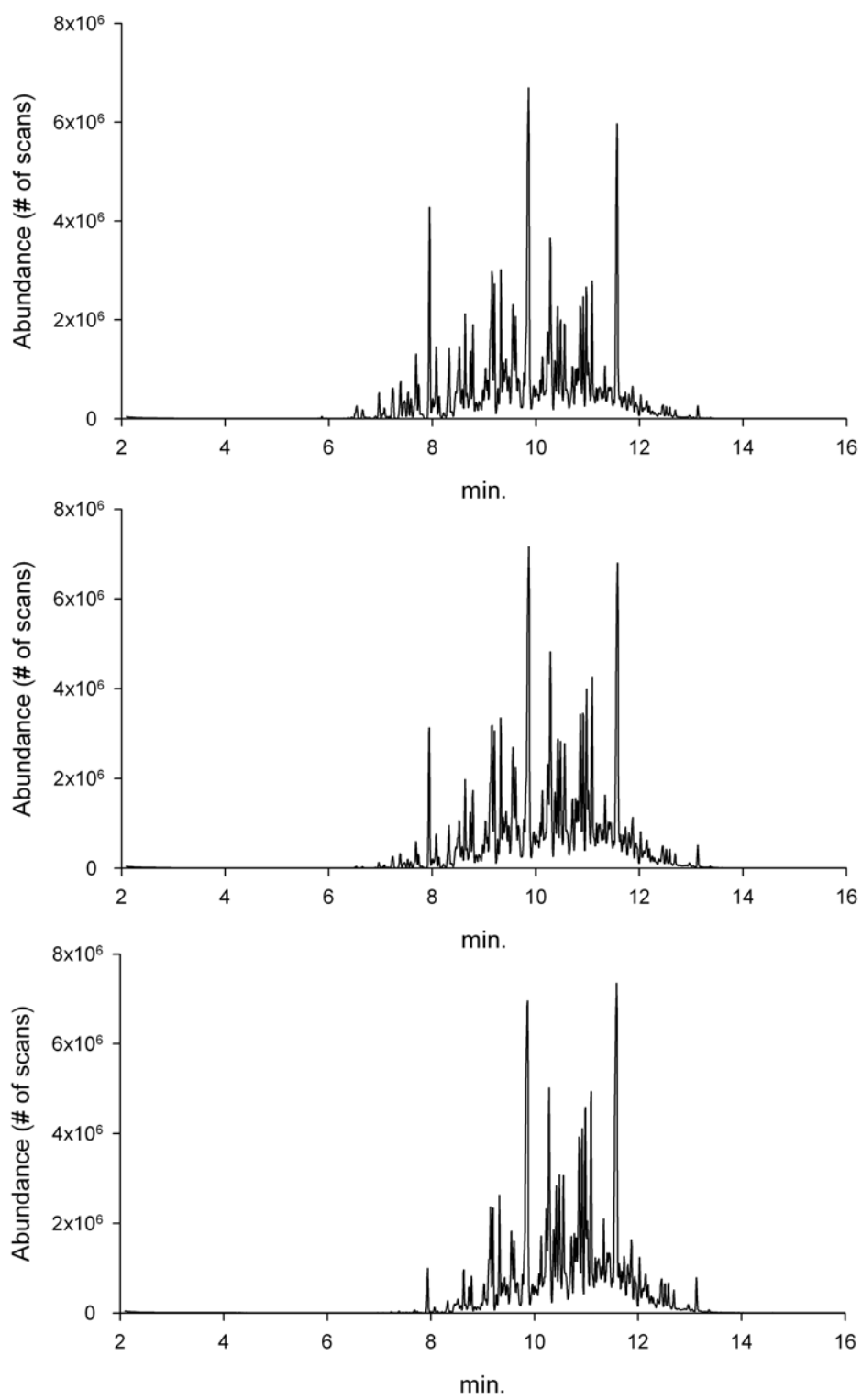


Figure 4: TIC of Klean Strip Odorless Mineral Spirits (top 25%, middle 50%, and bottom 75% weathered)

The data in Figure 4 displays results analogous to those of the gasoline. The n-nonane peak at 8.00 min. becomes less prominent as the sample weathers and all earlier peaks decrease in abundance. For some classes including the heavy petroleum distillates, weathering could not be achieved with a dry heat bath and blowing down with N₂ gas; a rotary evaporator would be needed. A related study has shown that there are chemical markers that are present in weathered gasoline[11]. GC/MS analyses of weathered gasoline and fire debris residues containing gasoline have allowed for the detection of chemical markers identified as diphenyl disulfide and its homologues. These disulfides are absent in other petroleum products analyzed such as diesel fuel[11].

Concepts of Combustion and Pyrolysis

Combustion is an exothermic oxidation reaction that proceeds at such a rapid rate that it generates detectable heat and light[3]. There are two types of combustion: flaming combustion, when both the fuel and oxidizer are gases and glowing combustion, where the surface of a solid fuel reacts with an oxidizer (usually air). In order for combustion to occur a combustible fuel must be present, an oxidizer (oxygen) must be available in sufficient quantities, energy as a means of ignition (heat) must be applied, and the fuel and oxidizer must interact in a self-sustaining chain reaction[3]. The action of pyrolysis is analogous to combustion. As has been previously defined, pyrolysis is the chemical decomposition of a material brought on by heat in the absence of oxygen whereas combustion requires oxygen. Through the application of heat, pyrolysis will lyse or break down a material into simpler compounds. The more heat that is provided, the faster the pyrolysis occurs and if an oxidizer is present a flame will form. Pyrolysis

products can be found in the chromatographic patterns similar to those observed in fire debris casework. These products interfere with the identification process of an ignitable liquid in a suspected arson case. That is why it is important to take control samples from the fire scene to ensure correct interpretation[12]. In one study[13, 14] charred vinyl floor was submitted and revealed the presence of an accelerant. The vinyl alone was burned and the accelerant that was misidentified was actually a natural product produced during burning. The pyrolysis products released from carpet and carpet padding has been studied extensively as well[15-18] and all of which support control sample collecting. The importance of collecting control samples at a fire scene was stressed in another article by Lentini[19]. The authors studied the volatile components emitted in common household products and paper products. The article concluded that during post-burn analysis newspapers emit medium and heavy petroleum distillates, magazines produce patterns typical of kerosene, and cardboard emits a series of homologous aldehydes similar to some cotton products. Lentini also mentions that the only common ignitable liquid not resembled by one of the various substrates burned was gasoline. Reliance on only one or two families of compounds can lead to misidentification[19].

CHAPTER THREE: COLLECTION AND PREPARATION OF FIRE DEBRIS

Sample Collection

The proper collection of evidence is the first crucial step in the analysis of fire debris. The main purpose is to preserve the evidence so that it can be properly analyzed in a laboratory and to avoid the hazard of contamination or cross contamination between two samples. Multiple studies have been performed to identify any potential risk of contamination caused by the analyst at a crime scene. One study showed that exhaust from motor vehicles at a fire scene was not enough to contaminate any samples collected from the fire scene[20]. Also, footwear worn by a fire scene investigator will not track ignitable liquid residues from one location to another within the fire scene[21].

Preservation also prevents ignitable liquids that may be present in the evidence from evaporating. For fire debris analysis two major concerns are the evaporation of volatile liquids and a high chance for contamination.

The most common types of evidence packaging materials are mason jars, unlined paint cans, and sealable plastic bags. Mason jars are transparent and allow for easy visual examination, but can be easily broken if mishandled. Unlined paint cans are the most popular evidence collection because they are considered airtight, unbreakable, and the top can be easily punctured for headspace sampling, but over time the metal paint cans will rust[22]. Extensive research into plastic Kapak® bags and plastic containers has been performed[22-24]. Plastic containers are advised against in certain cases because they can be easily punctured and the sample risks being contaminated. It is important for an analyst to understand which sampling containers, such as the plastic containers, will react

with the ignitable liquids. Gasoline and other volatile hydrocarbons can dissolve certain containers. Polypropylene jars have been considered permissible with gasoline, but not polystyrene which is soluble in gasoline. Polyethylene plastic bags are permeable to some hydrocarbons and allow them to escape[3]. There are some drawbacks to the glass mason jars. In one study[25], over several days at 66°C, a glass mason jar was shown to allow hydrocarbons to escape from the container. The hydrocarbons subsequently were able to enter a nearby jar, leading to cross contamination. The study showed that properly heat-sealed copolymer bags retained all of the hydrocarbons. The one drawback to the copolymer bag is that it can be easily punctured, leading to contamination and loss of sample. According to the study, the paint cans and mason jars leaked losing the hydrocarbons in different proportions due to their individual closing mechanisms thus changing the hydrocarbon composition and chromatographic profile. Over time, leaking jars containing hydrocarbons can cross-contaminate one another if stored in close proximity and hydrocarbons from the immediate environment can penetrate the jar[25].

Sample Preparation Methods

Once a sample has been collected the next step is determining a suitable sample preparation method for chemical analyses is to identify the presence of an ignitable liquid residue. Ignitable liquids have an array of physical and chemical properties, and there is no single optimal sample preparation method for their recovery from fire debris.

Traditional methods of analyte isolation, based on procedures such as distillation and solvent extraction have, to a large extent, been replaced by headspace analysis

methods[26]. The following are brief descriptions of common sample preparation methods and some advantages and disadvantages for each[27]:

Distillation

Steam distillation is one of the oldest techniques used for the recovery of ignitable liquid residues[28]. A sample may be distilled in an apparatus similar to those seen with steam and vacuum distillation, allowing the volatile products to be collected. Samples can be split into aliquots and characterized by various spectroscopic methods. However, distillation is cumbersome and time consuming. This method is destructive and discriminates compounds based on volatility and solubility[29]. It also holds the potential for sample contamination. It is not as sensitive as charcoal absorption methods, but can provide a neat liquid sample without introduction of extraneous solvents[3].

Solvent Extraction

A sample is extracted with a solvent that is not miscible with water and extract analyzed most commonly with gas chromatography-mass spectrometry. This method provides good recovery for most heavy petroleum products, but is not suitable for isolating light petroleum distillates due to their volatility[28]. Solvent extraction is considered destructive, has low method sensitivity and the potential for sample contamination exists[30].

Direct Headspace

In this method the headspace aliquot is withdrawn from the heated debris with a syringe and is analyzed by gas chromatography-mass spectrometry[31]. Direct headspace analysis is fast, simple, non destructive, and does not pose a risk for contamination. However, direct headspace has low method sensitivity and a low recovery rate[27].

Solid-Phase Microextraction

The Solid-phase microextraction (SPME) procedure is similar to direct headspace except instead of a syringe in the headspace a fiber coated with an adsorbent is placed in the headspace of a heated sample[32]. GC-MS is then used to detect the ignitable liquid. Sample is collected by the SPME fibers penetrating the bag that contains the sample. This technique yields a high recovery of low-volatile components and is a non-destructive, simple, and rapid screening method for detecting ignitable liquids in fire debris[33].

Dynamic Headspace (purge and trap)

Gas or air is drawn over a heated sample and the ignitable liquid vapors are adsorbed onto an adsorbent and recovered by a solvent or thermal desorption[27]. A vacuum pump is used to withdraw the headspace. This technique is fast, non-destructive, and is very useful because of its high sensitivity and applicability to all classes of ignitable residues including alcohols and ketones[3]. However, this cumbersome technique poses a slight risk for contamination.

Passive Headspace

Passive headspace sampling is a technique where a fire debris sample is placed in an appropriate container and heated in an oven. Volatile liquids present in the sample will evaporate and adsorb onto an activated charcoal strip suspended in the headspace of the can[31]. The sample is then recovered by a solvent, typically carbon disulfide, and then analyzed using gas chromatography mass spectrometry. Advantages of this technique include a limited chance for contamination because of the sample being confined to a closed container, simple sample preparation, and this method is non-destructive. However, a small disadvantage to this method is the difficulty encountered in identifying light petroleum distillates (LPDs) because of preferential adsorption of heavy hydrocarbons. The extent of displacement of adsorbed hydrocarbons is controlled by the strength of the interaction of each hydrocarbon with the surface upon physical adsorption. This distortion of the TIC pattern, from the charcoal strip, is the result of heavy petroleum distillates (HPDs), with a high abundance of aromatics that bind well to the strip, displacing LPDs that contain straight chain alkanes[34]. Also, molecules can be displaced from the activated carbon strip by other molecules based on the square of their polarizability. This occurs when there are not enough adsorption sites on the carbon strip.

CHAPTER FOUR: METHODOLOGY

Research Method

The method developed under this research for producing interfering products commonly encountered in fire debris analysis was based on a modified destructive distillation methodology was provided by the Florida Bureau of Forensic Fire and Explosive Analysis. This method was developed in the Fire Marshall laboratory to produce interfering product chromatographic patterns similar to those observed in fire debris case work. The method involved placing a known mass of material in one-quart paint can (unlined), placing a lid containing nine 1 mm diameter holes loosely on top of the can, and applying heat to the bottom of the can with a propane torch. Temperatures at the bottom of the can and in the headspace were monitored and recorded during the burn. Once burning was complete the lid was replaced with a lid without holes to allow the vapors to condense at room temperature.

For this research, passive headspace adsorption was applied to sample the post burn debris. An activated carbon strip (1cm x 3cm) was attached to a paper clip and tied to a piece of unwaxed dental floss which was suspended in the headspace of the can. The can was then sealed and heated for 16-18 hours at 66°C to allow the vapors of any volatile compounds formed in the burn to be sampled for analysis.

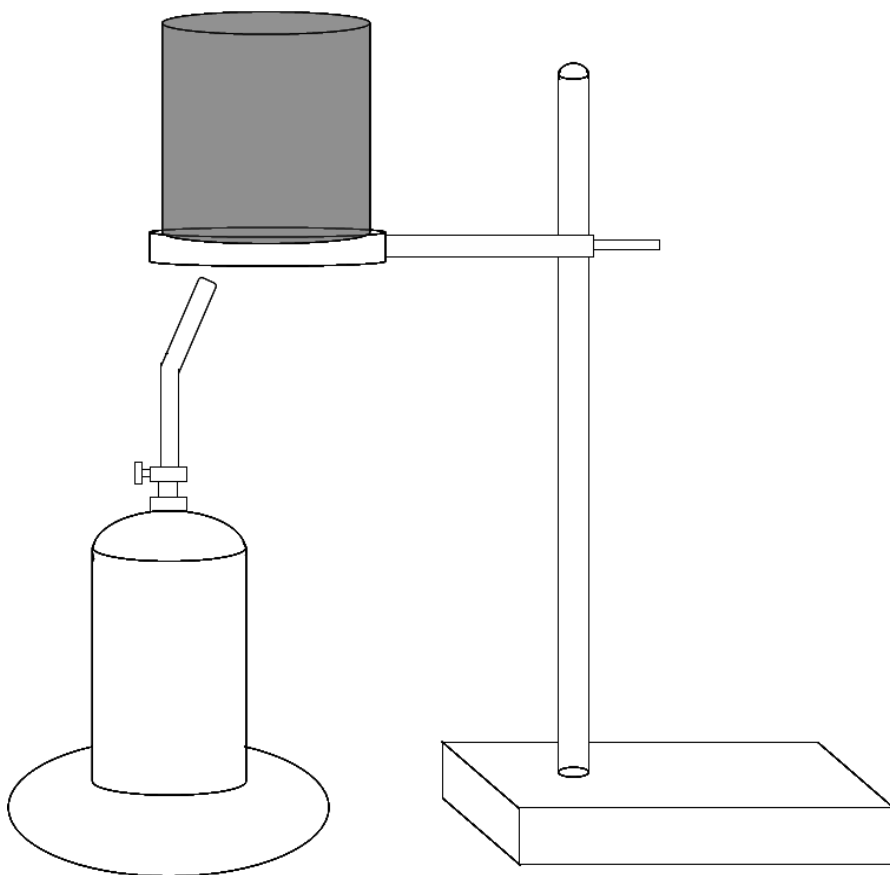


Figure 5: Apparatus setup

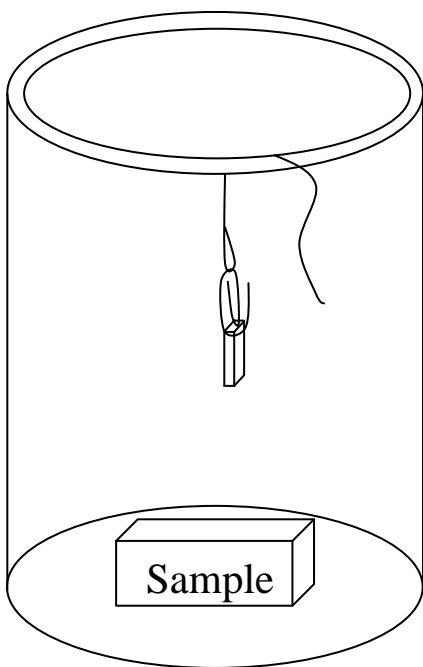


Figure 6: Post burn setup inside can.

The carbon strip was then removed and half was archived while the other half was placed in 1mL of CS₂ for GC-MS analysis. Parameters that were varied for method optimization included the size/mass of the substrate, the heating time, and the distance from the flame to the bottom of the can. The volume of ignitable liquid placed on the sample was varied and the percent matrix composition of the burnt sample was identified. The optimum parameters will be discussed in the next chapter.

Instrumental Parameters

All samples were analyzed on an Agilent 6890 gas chromatograph with a 7683 series autosampler and interfaced to a 5973 mass spectrometer. The sample was introduced through a split/splitless injector, and 1 µl of sample was split 50:1 at a temperature of 250°C. The chromatographic column was a HP-1 (methyl siloxane) column of 0.2 mm i.d., 25 m length, and 0.5 µm film thickness. Helium carrier gas was maintained at a constant flow of 34 cm/min on the column. The initial oven temperature was held at 50°C for 3 min., then ramped at a rate of 10°C/min. to a final temperature of 280°C and held for 4 min. for a total run time of 30 min. The mass analyzer was scanned from 30 to 350 *m/z* with a scan rate: 2-3 scans/sec; equivalent to 6-10 scans per peak; following a 2 min. solvent delay. The mass spectrometer transfer line was maintained at 280°C with a source temperature at 230°C.

Covariance Mapping and Summed Ion Method

The slight variations in experimental conditions when analysts are utilizing different instrumentation can lead to variations in chromatographic results, even though

the same sample is being tested. In GC-MS analysis, lab-to-lab variations in the TIC profile are common, thereby complicating the use of a common database. A few techniques have been applied to enhance automated database searching in an attempt to overcome these difficulties. Covariance mapping has been applied to time-of-flight mass spectrometry to resolve discrepancies[35-39]. Covariance mapping with the implementation of simple distance and similarity metrics has been applied to the analysis of complex GC-MS data from commercial ignitable liquids[40]. The covariance mapping method allowed the grouping of ignitable liquids having the same ASTM classification while retaining some of the chromatography information which is encoded in the covariance of the different ions. However, computing the data with the covariance mapping method is quantitatively tedious and time consuming when it is implemented with database searching software. The covariance method encodes the difference in spectral intensities and the pairwise variances in each ion intensity profile during chromatographic separation[35]. The covariance method removes the time profile through multiplication of the data matrix by its transpose, and normalizes the product by setting the sum of all the matrix values equal to one. Covariance maps are compared based on simple distance (D) and similarity (S) metrics as given by:

$$D = \frac{\sum_i \sum_j |Z_{ij} - Z'_{ij}|}{2}$$

$$S = 1 - D$$

where Z_{ij} and Z'_{ij} are the normalized covariance matrix elements for the two samples being compared. The closer to zero the distance (D) is, the more similar two samples are.

However, as useful as the covariance mapping is, this extensive quantitation of comparing one sample against a large database is time consuming.

One bit encoding is obtaining a spectrum, over a specific mass range, where only the presence or absence of a peak is denoted. Therefore, peak height is denoted by one bit. A “0” indicates no peak greater than the threshold intensity and a “1” is denoted as a peak being present at an intensity greater than a threshold value. The maximum information being stored in a spectrum is limited to the mass range that was selected for that spectrum. The information content has been calculated for the mass spectra of a large number of pure compounds[41]. In theory, a mass spectrum of only 200 amu or 200 bits contains enough information to provide for a distinct identification of all known compounds[42]. One bit encoding for data storage would not only take up less data storage space, but it would also be easy to transmit and an analyst is still getting enough information to perform database searches. However, there are drawbacks to one-bit encoding. Intensity errors resulting from the measurement, the recording, and the coding of the spectra are not incorporated[43]. There are multiple ways to improve the retrieval and use of this by applying more than two encoding levels which in turn would increase the number of samples that could be uniquely encoded, and by including more or less pre-search criterion in the retrieval. Both of these methods would increase the amount of information content that is stored in each spectra. The idea of using more than 106 m/z values or reducing the error probabilities has been proposed[43]. However, the former would lead to encoding noise and the latter, although proven to be useful, would require protocols for intense coding standardization of every compound. It is important to understand when a database consist of a large amount of data, for example a unique

spectrum for a large number of compounds, binary encoding would decrease the amount of data being stored by that database, thereby decreasing the probability of a unique compound identification. However, binary encoding would accelerate online database searches.

The summed ion method is an alternative to the covariance mapping method. A summed ion profile is created by summing the intensity of each ion across the entire chromatographic range and normalizing the resulting spectrum such that the intensity of all ions sum to a value of one. Unlike the covariance mapping method, the summed-ion spectrum does not encode the chromatographic (time profile) information. The benefit of the summed ion spectrum is that it removes the highly analysis-dependent chromatographic profile. Summed ion spectra can be compared by simple distance (D) and similarity (S) metrics are used for comparing two summed ion spectra[35].

$$D = \frac{\sum_i |Z_i - Z'_i|}{2}$$

$$S = 1 - D$$

Where Z_i and Z'_i are the intensities of the normalized spectra at each m/z ratio.

Calculations of spectral similarity were performed utilizing software written in-house.

The usefulness of the summed ion method and one bit encoding was shown in one study[35]. The summed ion spectra for 440 commercially available ignitable liquids were calculated from their corresponding GC-MS data sets by summing the intensity in each m/z channel. The summed ion m/z channels with intensities less than 1% of the most intense peak were encoded as “0” and those with intensities greater than or equal to 1% of the base peak intensity were encoded as “1”. The one bit encoded spectra were

compared and it was determined that spectra differed in five channels, which is very similar to the previously reported differences between pure compounds. It was also shown that the summed ion spectral comparisons for the set of 440 ignitable liquids, without binary encoding, are sufficiently different to allow for the classification of the spectra into the 25 ASTM categories based on simple distance and similarity metrics[35]. These results demonstrated the feasibility of searchable databases based on the same metrics. It is important to note that ASTM protocol requires that a reference liquid and the case sample be analyzed on the same instrument and the data sets directly compared in forensic analyses. It encourages the use of databases for the preliminary identification of ignitable liquids[35].

Statistical Comparison Method

For a more rigorous statistical comparison of summed ion spectra the Pearson correlation was used to identify the correlation between two samples. The Pearson correlation coefficient is obtained by the equation:

$$\sum (a_i - \bar{a})(b_i - \bar{b}) / \sqrt{\sum (a_i - \bar{a})^2 \sum (b_i - \bar{b})^2},$$

where $\bar{a} = \sum a_i / n$ and $\bar{b} = \sum b_i / n$.

The fisher transformation (Z) of Pearson correlation is used to determine if the two samples can be correlated[44] where r is the Pearson correlation, a_i and b_i are the summed ion specific m/z values for two samples a & b, and

$$Z = \frac{1}{2} \log[(1 + r) / (1 - r)].$$

The larger the z-value is between two samples the more correlated they are.

A t-test was performed to determine if the correlation between multiple burns of one sample were sufficiently different from correlations between two samples as to allow different substrates to be discriminated from one another. The data compared were the Z values, obtained from the summed ion method. First correlations and standard deviations were calculated between the same sample summed ion spectra of repeat burns in order to determine the confidence interval of the average Z(r) of each same sample subset. For example: Sample 1 was burned three times denoted as a, b, and c. Therefore, average correlations was calculated by the following equation:

$$\bar{Z}_{ss} = \frac{(Z_{ab} + Z_{ac} + Z_{bc})}{3}$$

Then once the standard deviation was calculated, the interval was identified for same samples (ss):

$$\bar{Z}_{ss} (r) \pm SD_{ss}$$

The same calculations were performed on a second sample.

In order to discriminate between two separate samples the correlations and standard deviation was calculated between the summed ion spectrum for the two sample burns. For example: Sample 1a was compared to Sample 2a, 2b, 2c and then Sample 1b to 2a, 2b, 2c, etc., eventually obtaining an average Z of different samples (ds). When comparing t_{calc} to t_{tab} , t_{calc} was determined by the following equation:

$$t_{calc} = \frac{|\bar{D}_{ds} - \bar{D}_{ss}|}{S_{x_1-x_2}}$$

where

$$S_{x_1-x_2} = \sqrt{\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}}$$

In this case the sample sizes and the variance are unequal. The D.F. was calculated using the Welch-Satterthwaite equation[45].

$$D.F. = \frac{\left(\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2} \right)^2}{\frac{\left(\frac{s_1^2}{n_1} \right)^2}{(n_1 - 1)} + \frac{\left(\frac{s_2^2}{n_2} \right)^2}{(n_2 - 1)}}$$

If $t_{\text{calc}} > t_{\text{tab}}$ then the different samples can be discriminated from one another with a prescribed statistical significance.

CHAPTER FIVE: VARIABILITY TESTING

Method Variability Testing

In order to optimize the method provided by the Florida Bureau of Forensic Fire and Explosive Analysis, the experimental parameters were tested and adjusted accordingly in order to yield reproducible results. The parameters that were varied for method optimization included the applied heat, size/mass of the substrate, the heating time, and the distance from the flame to the bottom of the can. Also, the volume of ignitable liquid placed on the sample was varied and the percent matrix composition for post burn samples was determined.

Low density polyethylene (LDPE) was chosen as the standard to test all variables because of the simplicity of its pyrolysis products. The products obtained from the pyrolysis of LDPE are a series of dienes, alkenes, and alkanes (see figure below). Therefore, any extraneous peaks and products can be detected visually and the variable leading to the production of that peak can be adjusted accordingly.

Applied Heat

The initial variable tested was to determine if the heat applied by the torch produced a temperature that reached a maximum value and remained relatively constant throughout the burning process. One thermocouple was placed in the bottom of the can on the inside, directly above the central location of the flame (T1). A second thermocouple was attached to the bottom of the can, on the outside, one inch from the tip of the burner (T2). This analysis was performed in triplicate inside a fume hood.

Temperature readings were recorded every two seconds. The graph below summarizes the results for three runs (R1-R3), and shows data plotted on a 4 second interval.

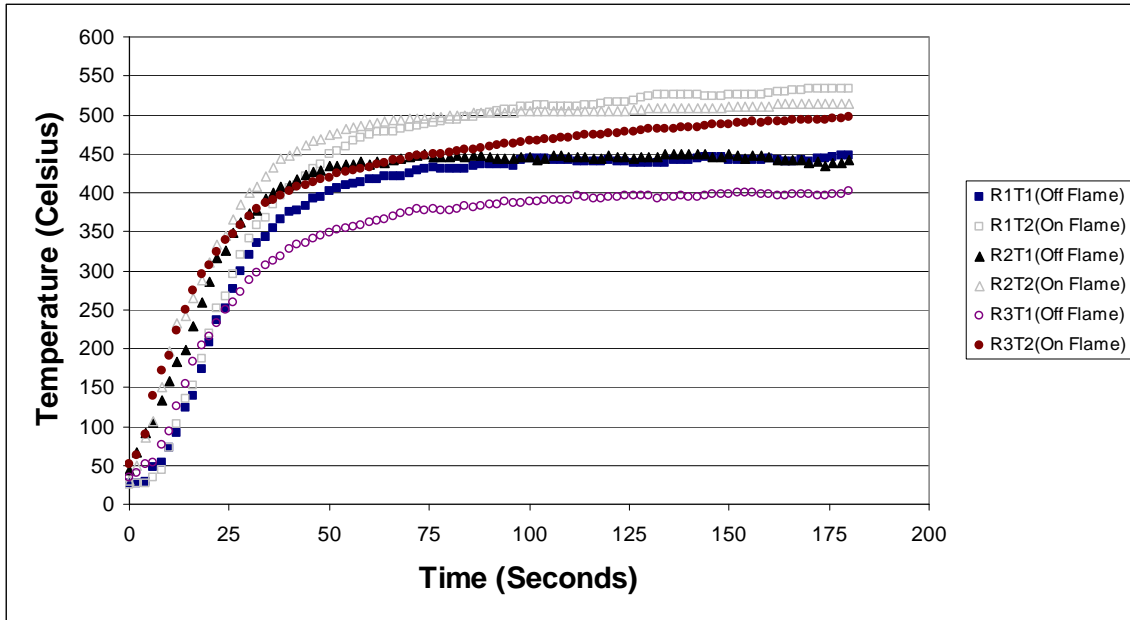


Figure 7: Graph summarizing the constant temperature applied to the can. Shown are the thermocouple temperature readings above flame position (T1) and directly on the flame (T2).

The graph indicates that the temperature inside the can (on flame), where the substrate would be placed, was heated with the same trend, approaching a limiting value for all three analyses. The same can be said for the temperature on the outside of the can (off flame). The top three lines are representative of the outside thermocouples (T2) and ranged from 495°C to 535°C. The thermocouples on the inside (T1), the bottom three lines, ranged from 400°C to 450°C. The reason for this experiment was to determine if the sample was being heated at a similar temperature inside the can as it would by direct contact with the torch.

Distance of Flame

Thermocouples were used to record the temperature of the matrix during a two minute heating at different distances between the flame and the can. The tip of the burner, with the flame off, was placed 2 cm, 3 cm, 4 cm, and 4.5 cm away from the bottom of the can. The matrix temperatures at all four intervals showed little variation in temperature ranging from 685°C to 795°C. . Therefore, the distance between the can and the flame, over this small distance change, has some measurable effect (14%) on the heat applied to the can. For this research, 4 cm was chosen for the distance of the flame to the bottom of the can.

Size and Mass of Substrate

Approximately 1, 4, and 10 gram samples of LDPE were tested. Each sample was burned for two minutes after smoke initially appeared. The TIC for each sample (Figures below) was compared to the previously reported TIC and the products produced from the pyrolysis of LDPE[46].

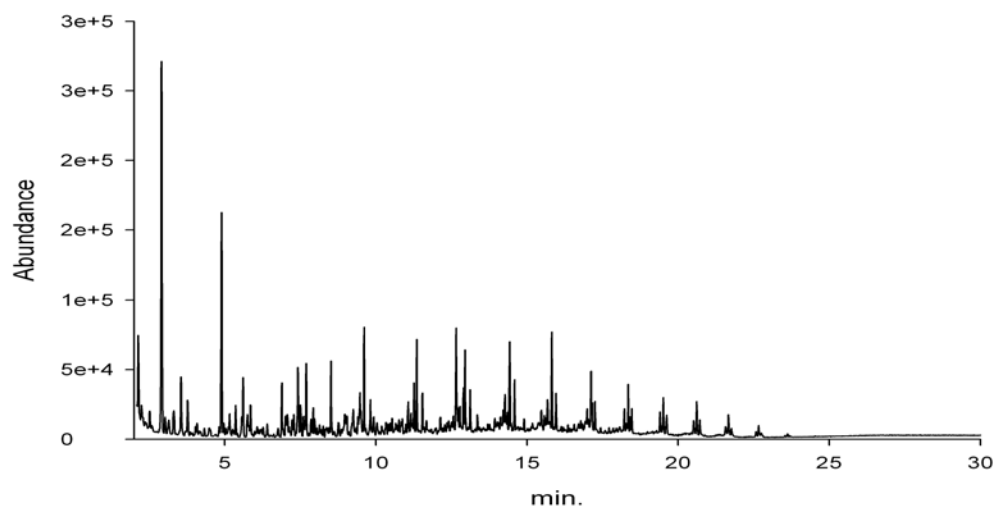


Figure 8: TIC of a 1 g sample of LDPE burned.

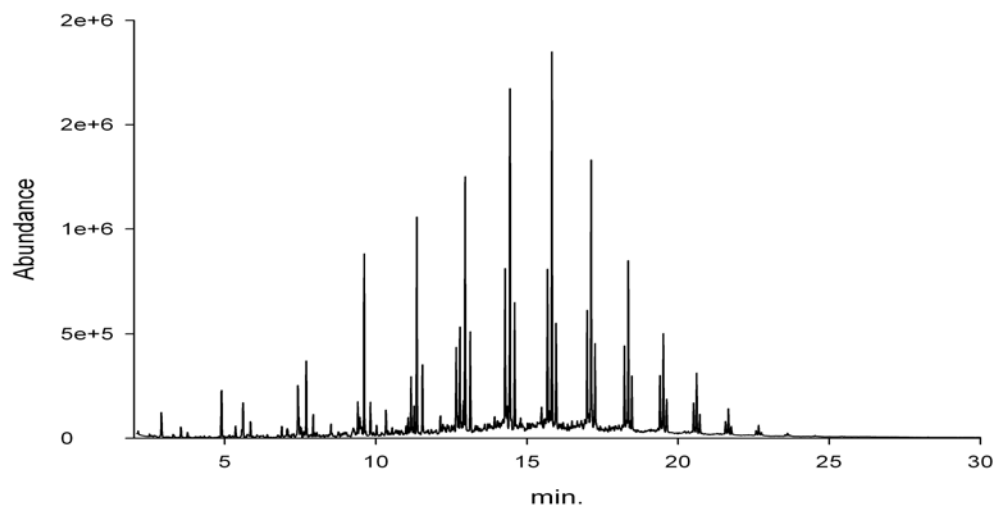


Figure 9: TIC of a 4 g sample of LDPE burned.

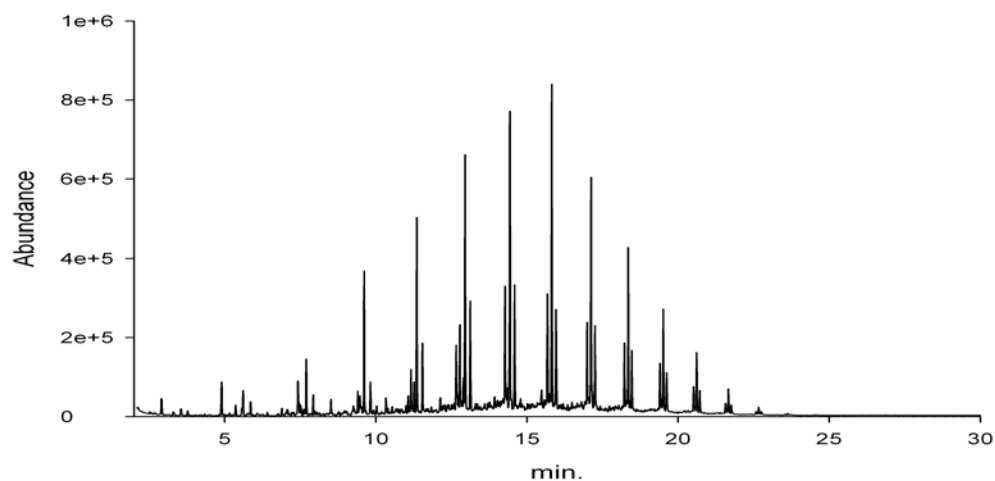


Figure 10: TIC of a 10 g sample of LDPE burned.

The 1 g sample had a very low abundance of the non-oxygenated products normally seen in pyrolyzed LDPE. The two most abundant peaks observed for the 1 g sample were benzene and toluene and the presence of LDPE products (alkanes, alkenes, and dienes) were limited. Therefore, a 1g sample would be too small for a representative analysis of substrates because the standard products would be burnt off. The 4g and 10g samples of LDPE produced very similar chromatograms and products. The most abundant products for the 4g and 10g samples of LDPE are alkenes and both weights generate a Gaussian distribution of pyrolysis products. They both have a clean baseline with sets of triplicate peaks of dienes, alkenes, and alkanes unlike the 1g sample. Therefore, a sample between 4g and 10g was used for a representative analysis of substrates because of the limited amount of oxygenated products.

Heating Time

The duration of time that a sample should be heated was also investigated. Samples of LDPE were used for this experiment and burned in duplicate. Two 10g

samples were each heated for two and five minutes after smoke initially appeared. The chromatograms below show the TIC for two minute and five minute burns respectively.

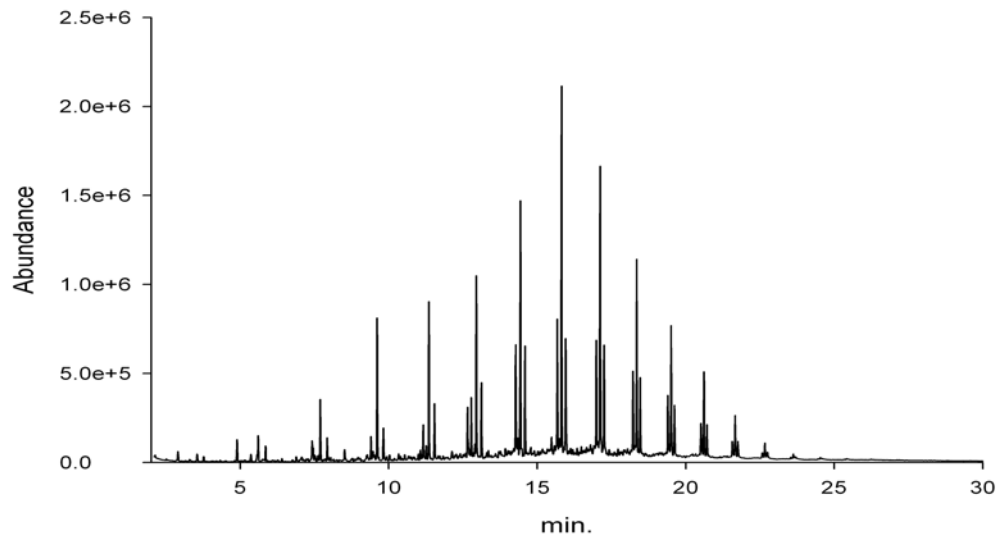


Figure 11: Ten grams of LDPE burned for two minutes.

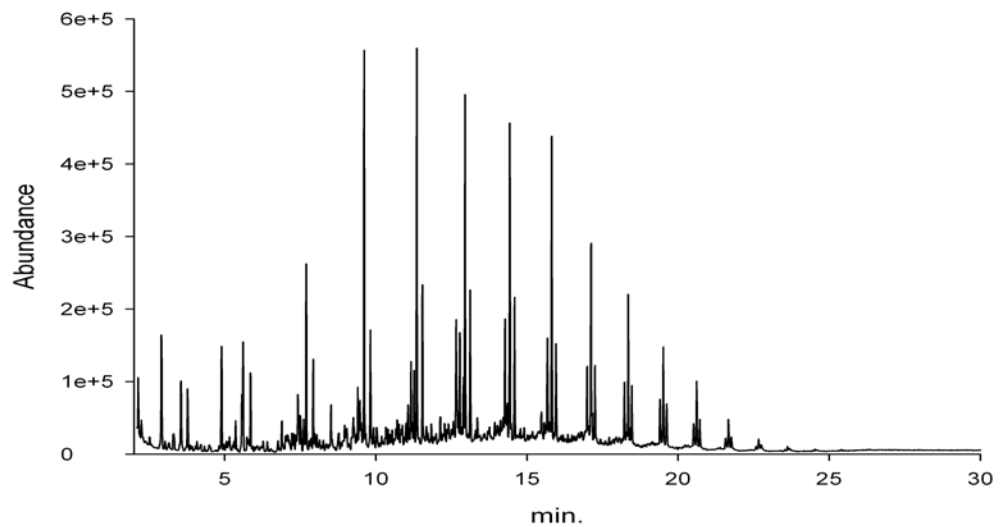


Figure 12: Ten grams of LDPE burned for five minutes.

Both two minute burns (only one shown above) displayed Gaussian distributions with baseline resolved clusters of alkenes, dienes, and alkanes. Oxygenates were not

observed in the pyrolysis products. Therefore, heating for two minutes can be considered ideal for all substrates. To the contrary, heating for five minutes is considered too long for this process due to the observed raised baseline and the presence of oxygenates. Here alcohols 1-decanol and dodecanol replace the alkene equivalent location which is the large center peak in the three peak cluster. The presence of oxygenated products is an indication of combustion in air, rather than pyrolysis.

Volume of Ignitable Liquid

Various volumes of gasoline were deposited onto nylon carpet with padding then subsequently burned to determine which volume of ignitable liquid provided representative fire debris samples. A relative composition of ignitable liquid and interfering products from the fire debris of nylon carpet with padding (substrate) and gasoline (ignitable liquid) was determined by calculating the similarity of the summed ion spectra of the fire debris sample to various composites of weathered ignitable liquid and burned substrate summed ion spectra. Ideally, a 50% composition of substrate and ignitable liquid is desired in order to have equal contributions from both the liquid and the substrate in the matrix. The substrate to be burned was a 100% nylon carpet and a common carpet padding, both of which can be easily obtained at a local hardware store. Both samples were cut to 6 cm x 6 cm in order to fit into a 1 quart paint can. The ignitable liquid applied was unweathered Hess regular unleaded gasoline. The liquid was allowed to soak for 30 seconds before the burning commenced. The carpet and pad was placed upside down with the carpet in contact with the bottom of the can and the pad on top. This was done to simulate an actual fire scene where the heat is normally applied

from the top with the carpet as compared to this research with the heat applied at the bottom. The table below summarizes the different volumes of gasoline and the percent gasoline and matrix composition attributed post burn. The percentage beside each volume of gasoline refers to the amount the gasoline was weathered. The summed ion spectrum of a fire debris sample originally containing 2 mL of ignitable was composed of approximately 60% ignitable liquid summed ion data and 40% interfering products summed ion data. The highest similarity of 0.816 indicated the 2 mL volume of gasoline weathered (evaporated) by 75% during the modified destructive distillation.

Table 4: Percent composition of fire debris (matrix) from a burned sample of nylon carpet with pad and gasoline and the similarity of summed ion spectra to that percent weathered gasoline.

0.5mL (weathered %)	0%	25%	50%	75%
Percent Gas	6	6	6	8
Percent Matrix	94	94	94	92
Similarity	0.887	0.893	0.894	0.895
1mL (weathered %)	0%	25%	50%	75%
Percent Gas	25	24	25	27
Percent Matrix	75	76	75	73
Similarity	0.743	0.767	0.787	0.814
2mL (weathered %)	0%	25%	50%	75%
Percent Gas	62	62	61	61
Percent Matrix	38	38	39	39
Similarity	0.655	0.729	0.791	0.816
4mL (weathered %)	0%	25%	50%	75%
Percent Gas	73	84	76	73
Percent Matrix	27	16	24	27
Similarity	0.532	0.624	0.703	0.725
6mL (weathered %)	0%	25%	50%	75%
Percent Gas	76	79	74	77
Percent Matrix	24	21	26	23
Similarity	0.525	0.611	0.677	0.687

During this process, in order to ensure that the substrates were being heated at the same temperatures and that the temperatures measure at the same rates, a thermocouple was inserted into the headspace of the can. The chart below summarizes the results.

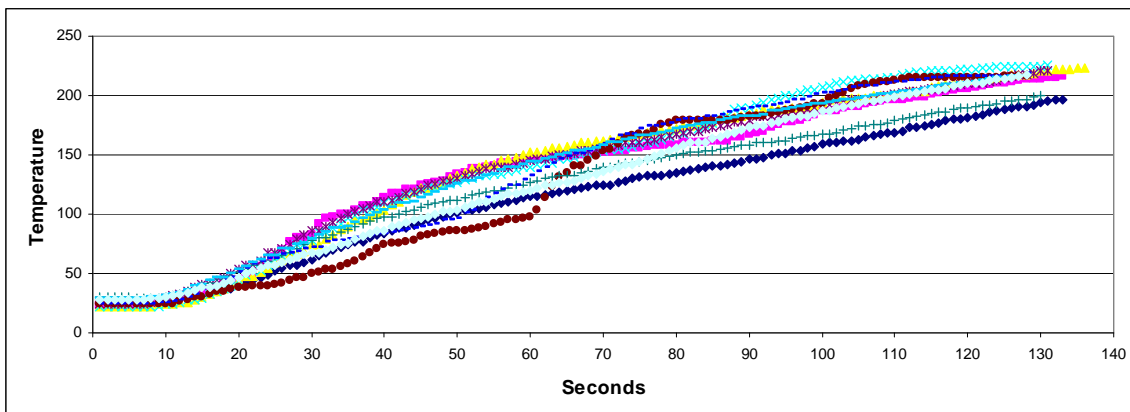


Figure 13: Headspace temperature of Nylon Carpet and Pad with various volumes of gasoline.

The headspace temperature increased consistently throughout all six burns.

Summary

Low density polyethylene (LDPE) was utilized to optimize method parameters of modified destructive distillation method to a 4-10g mass of substrate heated for two minutes after smoke appears with a torch distance of 4 cm from the can. These parameters produced both pyrolysis and combustion interfering products within the carbon range of most ignitable liquids. Headspace temperatures recorded during burning of polyester carpet and pad with 2mL volumes of various ignitable liquids, utilizing the optimized modified destructive distillation method, do not vary significantly. Finally, 2mL of ignitable liquid added to a 4g sample of substrate was ideal for a relatively equal contribution of liquid and matrix composition to a post-burn sample. It is important to note that optimized parameters allow for the recovery of pyrolysis products commonly observed in fire debris casework while at the same time limiting the amount of oxygenates produced, as suggested by members of the Ignitable Liquids Reference Committee of the technical working group on fire and explosives. Oxygenates can not be

completely limited because that would not be representative of what is seen in a fire debris sample. Some oxygenates can in fact come from the substrates themselves.

CHAPTER SIX: PYROLYSIS OF SUBSTRATES

Substrate Comparisons

Introduction

Once the optimum parameters for the modified destructive distillation method were established, the next step was to determine how similar the substrates burn to each other and the difference in the overall product distribution from each substrate. Although two chromatograms (see appendix) may appear similar with the same three major peaks, the summed ion spectra of the interfering products of two substrates were compared statistically to determine if they could be distinguished from one another.

In chapter 5 a simple similarity comparison was sufficient to determine the mixture of ignitable liquid and pyrolysis products that best matched a fire debris sample. However, in this chapter a statistical comparison is required to determine if two pyrolysis samples can be discriminated. A reliable statistical comparison is achieved through a t-test on the Fisher-transformed Pearson correlation $Z(r)$ between samples, as described in chapter 4.

A large set of substrates was obtained from local hardware supply stores, fabric stores, and home and office retail stores; all of which can be found in any major city. The substrates consist of carpets and carpet blends along with a common carpet padding made of recycled materials. They include hardwoods and softwoods, vinyl and linoleum flooring, laminate hardwoods from multiple manufacturers, and a variety of miscellaneous materials that are used in home or building construction. The major

products produced from pyrolysis of each substrate and their retention times can be found in Appendix A. Each substrate was burned and analyzed a minimum of three times.

Carpets, Carpet blends, and Padding

The following carpet types were obtained: nylon, polyester, Polyethylene terephthalate (P.E.T.) polyester, polyester nylon blend, 100% olefin, UV olefin, olefin/nylon blend. The goal was to determine how different the products produced from heating the carpets are from one another and the reproducibility of obtaining those same products. Comparisons were drawn to determine the post burn spectra correlation. Data was also obtained to determine the similarity between same fiber types, i.e. polyester and P.E.T. polyester.

Initially a simple similarity test was performed on nylon carpet to test if the modified destructive distillation method would yield reproducible results. A 6 cm x 6 cm sample of nylon carpet was burned with pad on eight occasions within two weeks of each other. The set of eight samples had an average similarity of 0.90. The high average similarity showed that using the modified destructive distillation method, the samples can be burned reproducibly. Comparisons were drawn to see if the pad involved had any effect on the average similarity of the nylon carpet. The average similarity of the burned nylon carpet only, was 0.805; therefore the pad increased the average similarity between burns. It is appropriate to use combined carpet and padding comparisons because carpet in a home is not found generally without some type of padding.

Next, each same sample carpet type was compared and their z-values and standard deviations are listed in tables 5. The table compares the triplicate distances for

each same sample carpet and then averages them. For example the comparison z-value of nylon and olefin (2.374) was obtained by the average of the three nylon distances and calculating its z-transform value (2.33) by the three for olefin (2.418). These values were then compared with the different sample comparisons in table 6. Ultimately, the values in table 5 will be compared to the values in table 6 to determine if the different carpet types can be discriminated. This statistical method was performed on all substrates.

Table 5: Z-transform/Pearson correlation figures (bottom) and standard deviation (top) for same sample (ss) comparisons of carpet

	Nylon	Olefin	ON blend	PET Poly.	Polyester	PN Blend	UV Olefin
Nylon		0.254	0.910	0.238	0.606	0.426	0.576
Olefin	2.374		0.932	0.148	0.621	0.434	0.579
ON blend	1.71	1.754		0.956	0.693	0.680	0.803
PET Poly.	2.41	2.454	1.79		0.643	0.455	0.593
Polyester	1.91	1.954	1.29	1.99		0.385	0.565
PN Blend	2.023	2.066	1.402	2.102	1.602		0.460
UV Olefin	2.044	2.088	1.424	2.124	1.624	1.736	

Table 6: Z-transform/Pearson correlation figures (bottom) and standard deviation (top) for different sample (ds) comparisons of carpet

	Nylon	Olefin	ON blend	PET Polyester	Polyester	PN Blend	UV Olefin
Nylon		0.111	0.449	0.041	0.184	0.097	0.156
Olefin	1.156		0.735	0.061	0.143	0.113	0.453
ON blend	1.098	1.59		0.038	0.293	0.234	0.301
PET Polyester	0.743	0.698	0.621		0.140	0.074	0.097
Polyester	1.113	0.985	0.889	1.25		0.205	0.133
PN Blend	1.054	0.743	0.655	1.155	1.27		0.118
UV Olefin	0.748	1.459	1.012	0.799	0.763	0.556	

Table 7: Discrimination of different carpet types

	Nylon	Olefin	ON blend	PET Polyester	Polyester	PN Blend	UV Olefin
Nylon	0						
Olefin	1	0					
ON blend	0	0	0				
PET Poly	1	1	1	0			
Polyester	1	1	0	1	0		
PN Blend	1	1	1	1	0	0	
UV Olefin	1	0	0	1	1	1	0

The values in the plots below (figure 14) were obtained by comparing the same sample (ss) values in table 5 for nylon and olefin (2.374) and its standard deviation with the different sample value (ds) in table 6 (1.156) and its standard deviation. The same values were plotted for discriminating nylon carpet from the olefin nylon blend carpet (figure 15). If the error bars on the plot do not overlap then the sample can be discriminated.

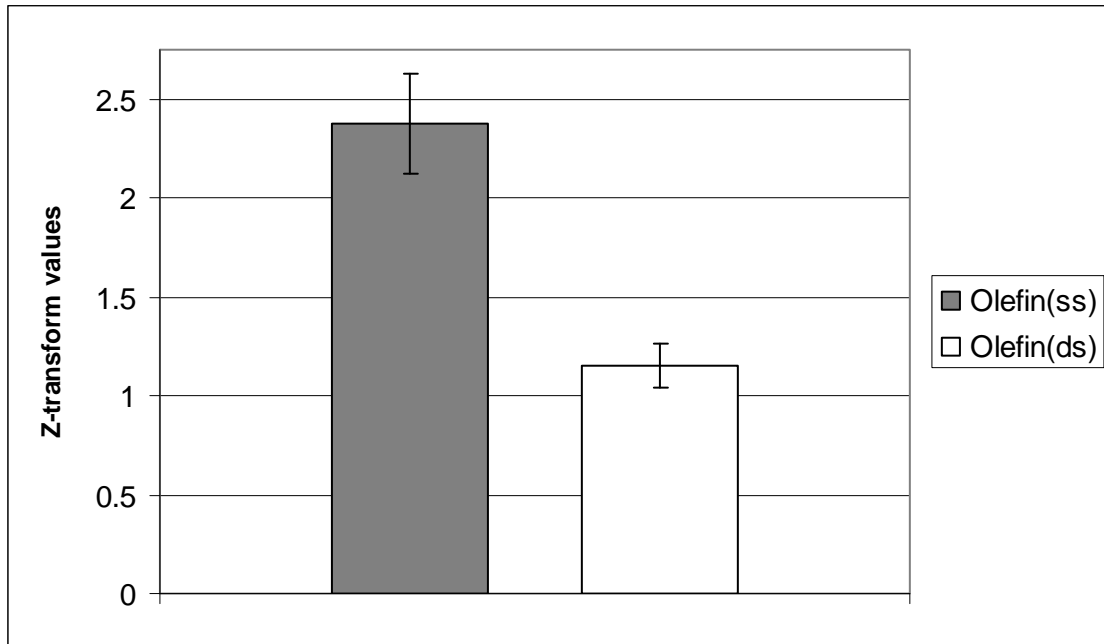


Figure 14: Plot discriminating nylon carpet from olefin carpet using Z-transform and Pearson correlation +/- standard deviation error bars.

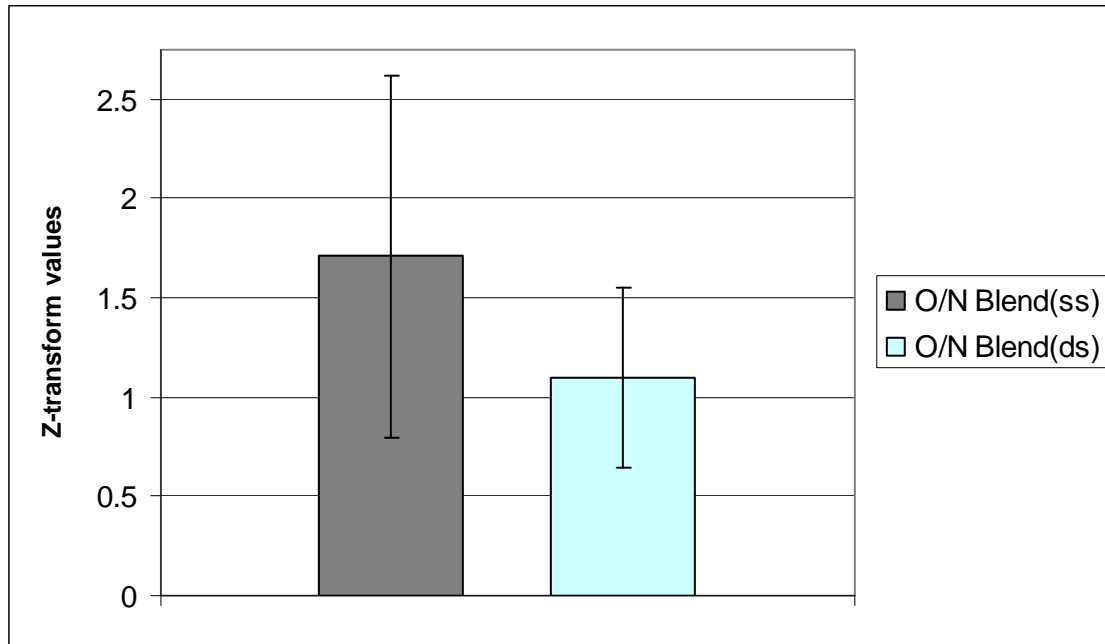


Figure 15: Plot discriminating nylon carpet from olefin/nylon blend carpet using Z-transform and Pearson correlation +/- standard deviation error bars.

A student's t-test was performed to determine if the different carpet types could be discriminated from one another. Table 7 summarizes the results with a "0" for no discrimination and a "1" for yes they can be discriminated. At an alpha .05 a total of 71.4% total discrimination was achieved for different carpet types. The olefin carpets could not be discriminated from one another, but the P.E.T. polyester carpet and normal polyester carpet can be discriminated. The olefin/nylon blend carpet could not be discriminated from the majority of the carpets because it contained a high same sample variance.

Hardwoods and Softwoods

The following hardwoods and softwoods were analyzed: maple, yellow pine, white pine, oak, Douglass fir, cedar, poplar, aspen, alder, cherry, hickory, and Trex

composite. Trex composite is not a naturally occurring wood, but it is made up of recycled woods and plastics. It contains synthetic materials used to prevent weathering and it is commonly used as an outdoor decking material. The analyses performed on the woods were analogous to those on the carpet. An average similarity of same samples was obtained for all burnt woods to ensure that all the woods were reproducibly pyrolyzed. Also, all woods were compared to every other wood to determine any similarities and differences between two types of woods. All wood samples were approximately 6 cm x 2 cm x 8cm. The same z-transform and Pearson correlation statistical testing that was performed on the carpet was also calculated for the woods.

Table 8: Z-transform/Pearson correlation figures (bottom) and standard deviation (top) for same sample (ss) comparisons of wood.

	Alder	Aspen	Cedar	Cherry	Dougllass Fir	Hickory	Maple	Oak	Poplar	Trex	White Pine	Yellow Pine
Alder		0.495	0.545	0.490	0.490	0.473	0.393	0.433	0.394	0.449	0.438	0.566
Aspen	1.986		0.687	0.374	0.459	0.511	0.412	0.388	0.417	0.523	0.346	0.620
Cedar	2.507	2.272		0.666	0.597	0.510	0.466	0.561	0.463	0.441	0.601	0.569
Cherry	2.019	1.785	2.305		0.460	0.502	0.405	0.391	0.410	0.510	0.356	0.610
Dougllass Fir	2.146	1.912	2.433	1.945		0.489	0.404	0.424	0.407	0.478	0.416	0.587
Hickory	2.263	2.028	2.549	2.061	2.189		0.382	0.435	0.383	0.427	0.446	0.551
Maple	2.224	1.99	2.511	2.023	2.15	2.267		0.334	0.279	0.351	0.340	0.492
Oak	2.131	1.896	2.417	1.929	2.057	2.173	2.135		0.337	0.424	0.340	0.544
Poplar	2.23	1.996	2.516	2.028	2.156	2.272	2.234	2.14		0.350	0.345	0.492
Trex	2.326	2.091	2.612	2.124	2.252	2.368	2.33	2.236	2.335		0.447	0.517
White Pine	2.069	1.835	2.356	1.868	1.995	2.112	2.073	1.98	2.079	2.175		0.560
Yellow Pine	2.311	2.076	2.597	2.109	2.237	2.353	2.315	2.221	2.32	2.416	2.16	

Table 9: Z-transform/Pearson correlation figures (bottom) and standard deviation (top) for different sample (ds) comparisons of wood

	Alder	Aspen	Cedar	Cherry	Douglass Fir	Hickory	Maple	Oak	Poplar	Trex	White Pine	Yellow Pine
Alder		.225	0.061	0.169	0.118	0.293	0.239	0.130	0.128	0.078	0.095	0.026
Aspen	1.019		0.102	0.329	0.075	0.332	0.300	0.191	0.230	0.164	0.259	0.032
Cedar	1.243	0.795		0.167	0.240	0.179	0.131	0.066	0.133	0.051	0.340	0.045
Cherry	1.128	1.396	1.06		0.088	0.169	0.205	0.176	0.112	0.087	0.151	0.051
Douglass Fir	0.914	0.589	1.369	0.728		0.103	0.095	0.111	0.097	0.032	0.227	0.150
Hickory	1.471	1.656	1.211	1.605	0.832		0.177	0.231	0.160	0.102	0.194	0.054
Maple	1.504	1.465	1.265	1.555	0.890	1.884		0.358	0.245	0.099	0.146	0.039
Oak	1.68	0.990	1.416	1.257	0.971	1.426	1.745		0.145	0.056	0.138	0.033
Poplar	1.48	1.108	1.416	1.254	0.97	1.590	1.812	1.735		0.095	0.193	0.053
Trex	0.756	0.618	0.601	0.531	0.53	0.715	0.701	0.685	0.823		0.091	0.013
White Pine	1.21	1.159	1.623	1.218	1.311	1.504	1.522	1.354	1.522	0.668		0.085
Yellow Pine	0.396	0.21	0.694	0.290	1.269	0.356	0.376	0.425	0.454	0.279	0.701	

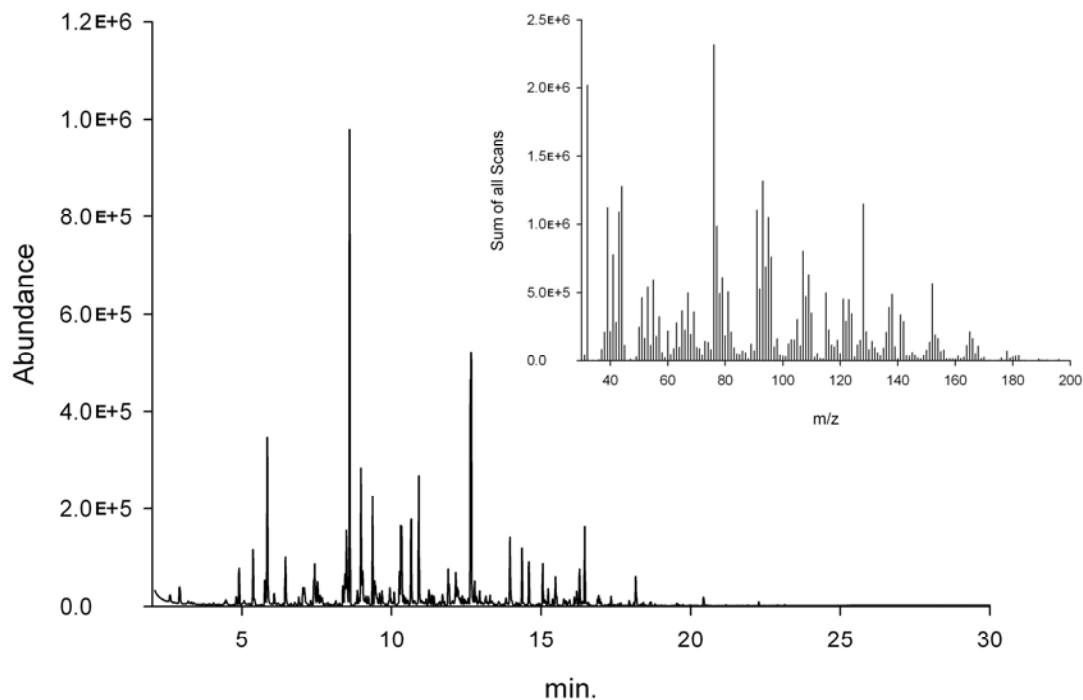
Table 10: Discrimination of different wood types

	Alder	Aspen	Cedar	Cherry	Douglass Fir	Hickory	Maple	Oak	Poplar	Trex	White Pine	Yellow Pine
Alder	0											
Aspen	1											
Cedar	1	1										
Cherry	1	0	1									
Douglass Fir	1	1	1	1								
Hickory	1	0	1	0	1							
Maple	1	1	1	1	1	0						
Oak	1	1	1	1	1	1	0					
Poplar	1	1	1	1	1	1	1	1				
Trex	1	1	1	1	1	1	1	1	1			
White Pine	1	1	1	1	1	1	1	1	1	1		
Yellow Pine	1	1	1	1	1	1	1	1	1	1	1	

Each wood was compared against every other wood in order to identify any noticeable differences in pyrolysis patterns. A student's t-test was also performed to

determine if the different wood types could be discriminated from one another. Table 10 summarizes the results with a “0” for no discrimination and a “1” for discriminated samples. At an alpha of .05 a total of 92.4% total discrimination was achieved for different wood types. White pine and yellow pine are two similar species of woods and two out of the three major products (alpha-pinene and limonene) are the same. However, it was the less prevalent pyrolysis products which make these two woods very different and based on the student’s t-test they can be discriminated from one another.

The majority of the major products from each wood include alpha-pinene, limonene, and 2-furaldehyde, among others, but different product distributions lead to high discrimination. A prime example is shown in the figure below. White pine and Douglass fir have very similar TIC’s, but based on the summed ion plots and the student’s t-test white pine and Douglass fir can be discriminated from one another.



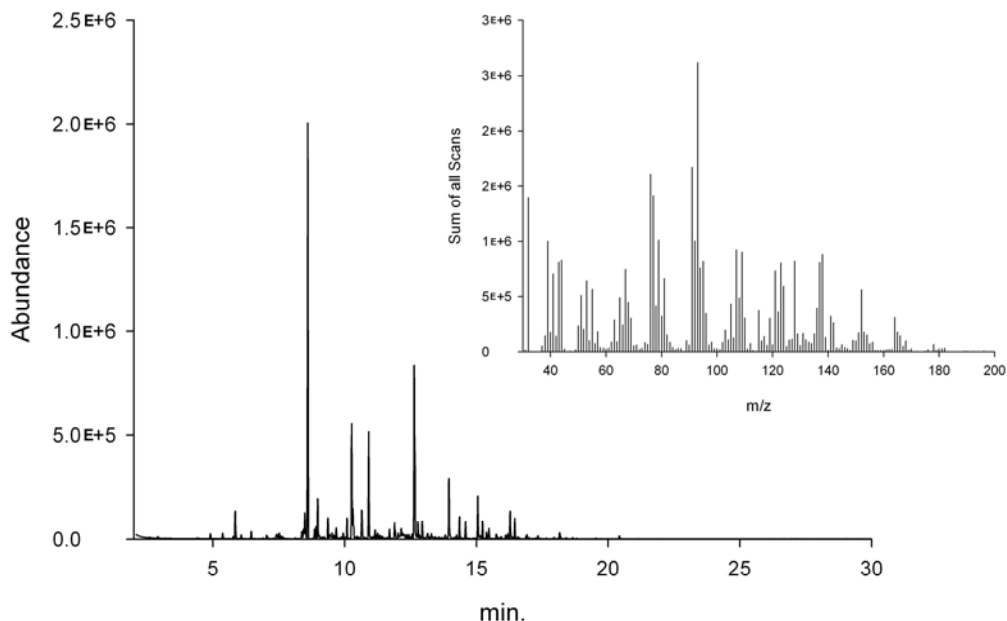


Figure 16: TIC and summed ion (inset) comparison of White Pine (top) and Douglass Fir (bottom)

These factors and tables 8-10 emphasized the sensitivity of the summed ion method and the use of statistical methods to help distinguish between burn samples which could look similar if an analyst were to casually observe the peaks in the TIC, without giving specific attention to the relative peak intensities.

Vinyl and Linoleum Flooring

A small number of vinyl/linoleum samples were analyzed because many of the major retailers continue to use these terms interchangeably, therefore it is difficult to differentiate the two. Linoleum has been used as the generic term to refer to both kinds of flooring, and can be considered problematic for classification purposes. According to many manufacturers' literature, the main difference between the two is that linoleum is derived from natural materials, including linseed oil from flax, while vinyl is a synthetic

product. They both release volatile organic compounds such as alkanals, alkenals and fatty acids[47]. The vinyl and vinyl/linoleum samples obtained have the same physical appearances and are being classified as such based on their respective packaging. They both are thin, flexible, and have a glossy outer coating. The industrial vinyl is thicker, more brittle and has no glossy outer coating. The sample size was similar to carpet (6 cm x 6 cm). The table below lists the average similarity between like substrates.

Table 11: Z-transform/Pearson correlation figures (bottom) and standard deviation (top) for same sample (ss) comparisons of vinyl flooring

	Industrial Vinyl	Vinyl	Vinyl/Linoleum
Industrial Vinyl		0.432	0.456
Vinyl	1.381		0.395
Vinyl/Linoleum	1.409	1.571	

Table 12: Z-transform/Pearson correlation figures (bottom) and standard deviation (top) for different sample (ds) comparisons of vinyl flooring

	Industrial Vinyl	Vinyl	Vinyl/Linoleum
Industrial Vinyl		0.276	0.165
Vinyl	0.799		0.247
Vinyl/Linoleum	0.941	0.896	

Table 13: Discrimination of vinyl flooring

	Industrial Vinyl	Vinyl	Vinyl/Linoleum
Industrial Vinyl			
Vinyl	1		
Vinyl/Linoleum	0	1	

A student's t-test was performed to determine if the different vinyl flooring types could be discriminated from one another. Table 13 summarizes the results with a "0" for no discrimination and a "1" for discriminated samples. At an alpha of .05 a total of 66.66% total discrimination was achieved for different vinyl types. Vinyl can be discriminated from its vinyl counterparts. Interestingly, industrial vinyl could be

discriminated from vinyl, but could not be discriminated from vinyl/linoleum even though their physical characteristics are so different. Vinyl/linoleum is glossy, thin, and malleable whereas industrial vinyl is thick, dull, and brittle.

Laminate Hardwood Flooring

Laminate hardwood flooring from two different manufacturers, K-Swiss USA (KS) and Sheoga (SG), were compared to determine the variability in pyrolysis products. The only exception was the bamboo flooring which was obtained from Home Depot. The data was analyzed in the same statistical manner as the previous substrates. The data also allows for a statistical comparison of substrates from two different manufacturers.

Table 14: Z-transform/Pearson correlation figures (bottom) and standard deviation (top) for same sample (ss) comparisons of laminate hardwood flooring

	Bamboo	KS Cherry	KS Hickory	KS Teak	KS Troya	SG Char. Walnut	SG Hard Maple	SG Hickory	SG Red Oak	SG White Oak
Bamboo		0.294	0.381	0.281	0.383	0.180	0.316	0.700	0.371	0.425
KS Cherry	1.959		0.469	0.332	0.391	0.273	0.405	0.782	0.407	0.432
KS Hickory	1.702	1.758		0.497	0.640	0.404	0.384	0.573	0.565	0.666
KS Teak KS	2.032	2.087	1.83		0.299	0.241	0.422	0.836	0.363	0.350
Troya SG Char.	2.226	2.281	2.024	2.353		0.321	0.550	1.012	0.357	0.200
Walnut SG Hard	1.954	2.009	1.752	2.081	2.275		0.329	0.741	0.338	0.370
Maple SG	1.782	1.837	1.58	1.909	2.103	1.831		0.623	0.495	0.581
Hickory SG Red	1.351	1.406	1.149	1.479	1.673	1.401	1.229		0.891	1.03
Oak SG	2.058	2.113	1.856	2.185	2.38	2.107	1.935	1.505		0.401
White Oak	2.227	2.282	2.025	2.354	2.549	2.276	2.104	1.674	2.381	

Table 15: Z-transform/Pearson correlation figures (bottom) and standard deviation (top) for different sample (ds) comparisons of laminate hardwood flooring

	Bamboo	KS Cherry	KS Hickory	KS Teak	KS Troya	SG Char. Walnut	SG Hard Maple	SG Hickory	SG Red Oak	SG White Oak
Bamboo		0.12	0.255	0.113	0.066	0.194	0.221	0.424	0.171	0.210
KS Cherry	1.458		0.342	0.197	0.144	0.145	0.225	0.404	0.146	0.122
KS Hickory	0.812	1.076		0.526	0.548	0.157	0.170	0.365	0.224	0.102
KS Teak KS	1.166	1.544	1.608		0.312	0.098	0.223	0.377	0.096	0.079
Troya SG Char.	1.124	1.484	1.600	2.323		0.089	0.222	0.350	0.069	0.068
Walnut SG Hard	1.114	1.224	1.113	1.242	1.219		0.331	0.684	0.203	0.143
Maple SG	0.487	0.539	0.559	0.583	0.572	0.925		0.283	0.286	0.250
Hickory SG Red	0.718	0.812	1.019	0.906	0.888	1.297	0.621		0.624	0.683
Oak SG	1.176	1.357	1.226	1.419	1.433	1.909	0.727	1.253		0.191
White Oak	1.016	1.036	1.045	1.091	1.086	1.693	0.716	1.325	1.701	

Table 16: Discrimination of different laminate flooring types

	Bamboo	KS Cherry	KS Hickory	KS Teak	KS Troya	SG Char. Walnut	SG Hard Maple	SG Hickory	SG Red Oak	SG White Oak
Bamboo										
KS Cherry	1									
KS Hickory	1	1								
KS Teak	1	1	0							
KS Troya	1	1	0	0						
SG Char. Walnut	1	1	1	1	1					
SG Hard Maple	1	1	1	1	1	1				
SG Hickory	0	0	0	0	0	0	0			
SG Red Oak	1	1	1	1	1	0	1	0		
SG White Oak	1	1	1	1	1	1	1	0	1	

The purpose of this experiment was to determine if a similar flooring type would pyrolyze differently based on whether the samples came from different manufacturers. A

student's t-test was performed to determine if the different K-Swiss laminate hardwood flooring types could be discriminated from one another and from the different Sheoga laminate hardwood flooring and the bamboo. Table 16 summarizes the results with a "0" for no discrimination and a "1" for discriminated samples. At an alpha of .05 a total of 71% discrimination was achieved for all types of laminate hardwood flooring. Most laminate hardwood flooring, including the two manufacturers used in this study, have a thin outer layer which was the actual wood itself and are composed of relatively similar materials underneath. This may explain why some samples could not be discriminated from one another. However, the majority of laminate hardwood flooring could be discriminated within the same manufacturer with the exception of the Sheoga hickory sample. Although the two hickory floorings had similar major pyrolysis products the reason for the lack of discrimination was that the Sheoga hickory sample had a low z-value which would make it less correlated and that coupled with a relatively high standard deviation would cause the sample to be less discriminated from all other laminate hardwood flooring types. Similar flooring samples can be differentiated from one manufacturer to another based on the pyrolysis product summed ion spectrum because of the supplemental materials they use in their flooring. Also, different types of flooring from the same manufacturer can be differentiated because either the outer wood layer plays enough of a role in the products obtained post-burn or the material they are composed of is different enough.

Miscellaneous Substrates

The following material selections were based on suggestions made from fire debris analysts who have at some point been asked to analyze some of these materials for casework. The materials included in this research are: Airtex® foam mattress pad, 100% cotton pajama pants (Target®), Orlando Visitor’s Guide magazine, cardboard box, black leather swatch, 100% polyester quilt batting, finegrain corktiles, thermal paper rolls, asphalt shingles, nylon rope, polyester rope, fiberglass insulation, foil insulation, cinderblock, and roofing tiles.

Along with the household and building materials mentioned, a variety of shoes were also examined. A separate database of shoes alone would be large, therefore for the purposes of this research a style of each footwear type was chosen. They include a Skechers’ walking shoe, Street Smart boots, Old Navy sandals, Wal-Mart rain boots, and Steve Madden casual shoes. All samples were burned and analyzed in triplicate and all statistical testing was conducted in the same fashion as the previous substrates. The table below lists the I.D. number for each substrate.

Table 17: Miscellaneous substrate I.D. table

Sample	Key ID #
Black Leather	1
Carboard Box	2
Cinderblock	3
Fiberglass Insulation	4
Finegrain Corktiles	5
Foam Mattress Pad	6
Foil Insulation	7
Magazines	8
Nylon Rope	9
Pajama Pants	10
Polyester Rope	11
Quilt Batting	12
Roofing Shingles	13
Roofing Tiles	14

Table 18: Z-transform/Pearson correlation figures (bottom) and standard deviation (top) for same sample (ss) comparisons of miscellaneous substrates

Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1		0.43	1.34	0.83	0.59	0.45	0.45	0.35	0.77	0.31	0.92	0.56	0.51	0.48	0.41
2	2.20		1.15	0.68	0.59	0.36	0.50	0.30	0.60	0.36	0.77	0.45	0.39	0.39	0.53
3	3.21	3.41		0.71	1.26	0.99	1.31	1.08	0.64	1.25	0.70	0.94	0.93	1.00	1.47
4	2.67	2.86	3.87		0.82	0.53	0.83	0.59	0.38	0.74	0.55	0.53	0.49	0.55	0.95
5	2.17	2.37	3.37	2.83		0.57	0.65	0.53	0.76	0.55	0.90	0.64	0.59	0.59	0.67
6	2.33	2.52	3.53	2.98	2.49		0.51	0.21	0.44	0.36	0.64	0.34	0.25	0.28	0.58
7	2.07	2.26	3.27	2.72	2.23	2.39		0.43	0.77	0.42	0.92	0.59	0.54	0.53	0.52
8	2.24	2.43	3.44	2.89	2.40	2.56	2.30		0.50	0.26	0.69	0.34	0.25	0.26	0.49
9	2.67	2.86	3.87	3.32	2.83	2.98	2.72	2.89		0.68	0.46	0.43	0.38	0.45	0.90
10	2.09	2.28	3.29	2.74	2.25	2.41	2.15	2.32	2.74		0.84	0.47	0.41	0.39	0.41
11	2.73	2.92	3.93	3.38	2.89	3.04	2.79	2.95	3.38	2.81		0.62	0.59	0.64	1.04
12	2.40	2.59	3.60	3.06	2.56	2.72	2.46	2.63	3.06	2.48	3.12		0.32	0.36	0.68
13	2.39	2.58	3.59	3.04	2.55	2.71	2.45	2.62	3.04	2.47	3.10	2.78		0.29	0.64
14	2.34	2.53	3.54	2.99	2.50	2.65	2.40	2.56	2.99	2.42	3.05	2.73	2.71		0.61
15	1.91	2.10	3.11	2.56	2.07	2.23	1.97	2.14	2.56	1.99	2.62	2.30	2.29	2.23	

Table 19: Z-transform/Pearson correlation figures (bottom) and standard deviation (top) for different sample (ds) comparisons of miscellaneous substrates

Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1		0.226	0.23	0.12	0.21	0.08	0.21	0.13	0.24	0.14	0.08	0.03	0.15	0.13	0.15
2	1.62		0.31	0.14	0.13	0.09	0.22	0.07	0.30	0.28	0.08	0.01	0.09	0.15	0.10
3	1.38	1.63		0.11	0.09	0.04	0.18	0.02	0.20	0.15	0.03	0.01	0.06	0.16	0.08
4	1.00	1.19	1.80		0.07	0.04	0.16	0.02	0.13	0.13	0.03	0.01	0.05	0.11	0.07
5	0.75	0.61	0.36	0.32		0.04	0.06	0.09	0.09	0.11	0.02	0.03	0.03	0.07	0.10
6	0.55	0.55	0.32	0.29	0.71		0.06	0.05	0.05	0.08	0.04	0.01	0.03	0.05	0.05
7	0.82	0.78	0.48	0.43	0.88	0.83		0.08	0.18	0.13	0.18	0.03	0.14	0.12	0.05
8	0.55	0.46	0.26	0.24	0.85	0.55	0.64		0.02	0.07	0.07	0.02	0.10	0.02	0.18
9	1.47	1.70	2.74	1.69	0.42	0.37	0.55	0.29		0.15	0.04	0.01	0.06	0.17	0.08
10	1.07	1.40	0.83	0.71	0.76	0.69	0.98	0.63	0.89		0.09	0.04	0.08	0.12	0.06
11	0.41	0.41	0.15	0.14	0.62	0.69	1.25	0.49	0.20	0.63		0.01	0.03	0.03	0.02
12	0.29	0.25	0.22	0.23	0.40	0.14	0.15	0.42	0.23	0.24	0.06		0.03	0.01	0.03
13	0.54	0.42	0.18	0.17	1.10	0.72	1.16	0.83	0.24	0.63	1.02	0.34		0.05	0.03
14	0.94	1.08	1.30	1.07	0.31	0.30	0.36	0.22	1.31	0.70	0.15	0.19	0.17		0.07
15	0.71	0.64	0.42	0.38	0.84	0.49	0.59	1.23	0.46	0.80	0.39	0.47	0.71	0.36	

Table 20: Discrimination of Miscellaneous Substrates

Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	1														
2	1	1													
3	1	1	1												
4	1	1	1	1											
5	1	1	1	1	1										
6	1	1	1	1	1	1									
7	1	1	1	1	1	1	1								
8	1	1	1	1	1	1	1	1							
9	1	1	1	1	1	1	1	1	1						
10	1	1	1	1	1	1	1	1	1	1					
11	1	1	1	1	1	1	1	1	1	1	1				
12	1	1	1	1	1	1	1	1	1	1	1	1			
13	1	1	1	1	1	1	1	1	1	1	1	1	1		
14	1	1	1	1	1	1	1	1	1	1	1	1	1	1	
15	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1

Every miscellaneous substrate appeared different based on the TIC's, but a student's t-test was performed to determine if any of the miscellaneous substrates could not be discriminated from one another. Table 20 summarizes the results with a "0" for no discrimination and a "1" for discriminated samples. At an alpha of .05 a total of 100% discrimination was achieved for all types of substrates. Many of the substrates in this category, including cinderblock and roofing tiles, produced no visible products with a relatively high abundance because of the lack of volatiles. All same sample z-values were relatively high which means that they all can be correlated.

Shoes are another miscellaneous substrate being investigated based on the suggestions of fire debris analyst throughout the country. All shoes obtained were previously worn and were sawed into pieces for triplicate analysis. Most portions of the footwear were obtained from the front of the shoe. The same statistical analysis as previous was performed and the following tables summarize the results.

Table 21: Same substrate comparison of Shoes

	Rain boots	Old Navy Sandals	Skechers Walking Shoe	S. Madden Casual Shoe	S.S. Boots
Rain boots		0.981	0.520	0.617	1.303
Old Navy Sandals	2.524		0.688	0.494	0.469
Skechers Walking Shoes	3.032	2.186		0.409	0.974
S. Madden Casual Shoes	2.865	2.019	2.526		0.768
S.S. Boots	2.204	1.359	1.866	1.699	

Table 22: Comparison of the average similarity (bottom) and standard deviation (top) of different shoes.

	Rain boots	Old Navy Sandals	Skechers Walking Shoe	S. Madden Casual Shoe	S.S. Boots
Rain boots		0.422	0.019	0.043	0.398
Old Navy Sandals	1.555		0.124	0.143	0.399
Skechers Walking Shoes	0.348	0.499		0.116	0.197
S. Madden Casual Shoes	0.334	0.494	0.116		0.208
S.S. Boots	0.970	1.114	0.197	0.208	

Table 23: Discrimination of different shoes

	Rain boots	Old Navy Sandals	Skechers Walking Shoe	S. Madden Casual Shoe	S.S. Boots
Rain boots					
Old Navy Sandals	0				
Skechers Walking Shoes	1	1			
S. Madden Casual Shoes	1	1	1		
S.S. Boots	0	0	1	1	

A student's t-test was performed to determine if shoe types could be discriminated from one another. Table 26 summarizes the results with a "0" for no discrimination and a "1" for discriminated samples. At an alpha of 0.05 a total of 70% total discrimination was achieved. The Street Smart Boots could not be discriminated from the rain boots or the sandals. Initially, after the triplicate burns of the street smart boots, the sample

chromatograms were different. Analyst error was thought to be the reason; therefore two more burns were conducted and compared to each other and the originals. The two new burns were incorporated instead, but the sample could still not be discriminated. The many layers which compose the heavy duty utility boots could be the source of the error leading to a greater variation in the products post-burn. Other than the street smart boots all shoes could be discriminated from one another. This is encouraging for any researcher looking to create a large database solely on the products given off from shoes post-burn.

Substrates in the Presence of Ignitable Liquids

With all the substrates individually analyzed, the next step was to determine the importance of the substrate in identifying the presence of an ignitable liquid in a matrix. Combinations of 2mL of ignitable liquid was added to different wood samples and burned for two minutes. Triplicate analyses were performed on each combination. Before the data can be interpreted it must first be analyzed by software written in-house.

First, a sample file is loaded which is a 3-D CSV excel file which was exported from the original data set. The sample file contains data from the combined burn of an ignitable liquid and for these testing purposes a 6 cm x 6 cm piece of wood as the substrate. A search of the summed ion spectra from the ILRC database was performed and an ordered list was generated from highest to lowest similarity of ignitable liquid. In fire debris analysis when the liquid is not known the analyst can determine the likelihood of what liquid may have been involved in the burn based on its rank and relative distance as compared to the other ignitable liquids in the database. Based on the results, if the

known liquid did not reside near the top of the list during a database search, usually a liquid of a similar class was ranked near the top or a weathered counterpart of the liquid when applicable.

Performing a database search without loading a matrix may yield large distances (low similarities). Therefore, it may be necessary to incorporate a matrix file (i.e. the burned substrate in combination with the ignitable liquid data and comparison to the burned sample file. For example, a “sample” file of a burned substrate (i.e. nylon) with an unknown ignitable liquid was compared to combinations of an ILRC data file and a “matrix” files comprising a burned sample of nylon with no liquid. In all cases tested, the distances decreased and the rank of the known liquid used in the burn increased to the top or near the top of the list when the matrix data was included in the search. A few examples of the effectiveness of incorporating a matrix when identifying the presence of an ignitable liquid in a burned sample can be seen in the following figures. For each pair of bar graphs the bar on the left reflects the similarity of the sample to the ignitable liquid used in the burn, as determined by a database search without incorporating a matrix file. The bar on the right reflects the search results after the matrix was incorporated in the search. Note the significant increase in similarity when the matrix was added.

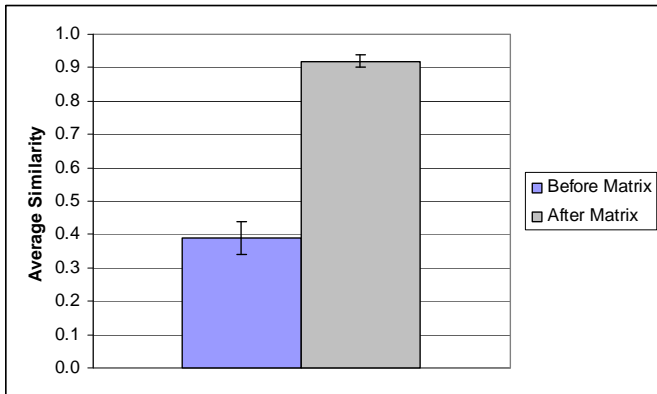
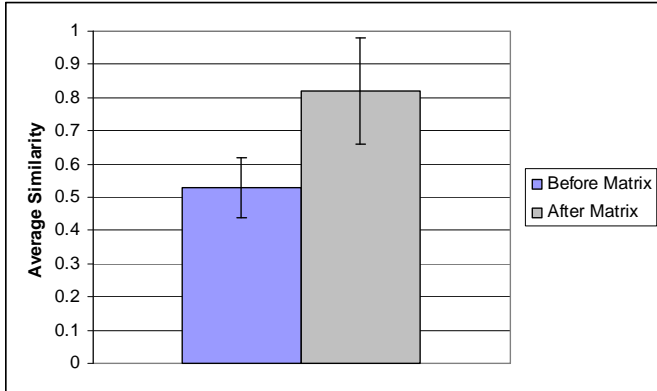


Figure 17: Graph showing increase in similarity with standard deviation error bars of an isoparaffinic liquid (top) and a low petroleum distillate (bottom) after alder wood was incorporated in the database search.

The average similarity increase in the isoparaffinic set of samples was 0.296 and 0.528 for the light petroleum distillates. Once the matrix was added and the distances were calculated the respective liquids and their three weathered counterparts (25%, 50%, and 75%) all were in the top four results. These results stress the importance of incorporating a substrate file to identify an ignitable liquid in a burn sample for a database search. The average similarity increase was not always as large as can be seen in the following group of samples with different classes of liquids burned with cedar wood.

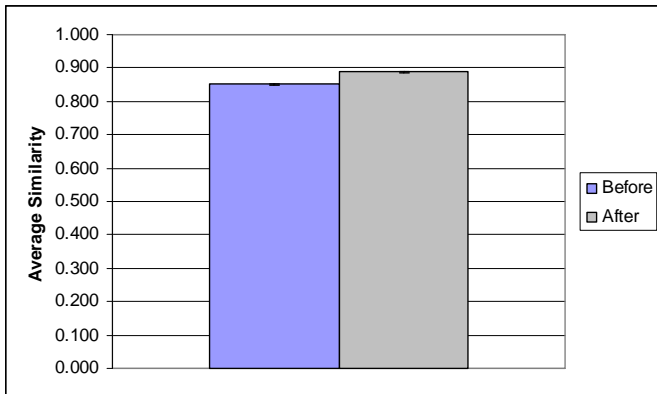
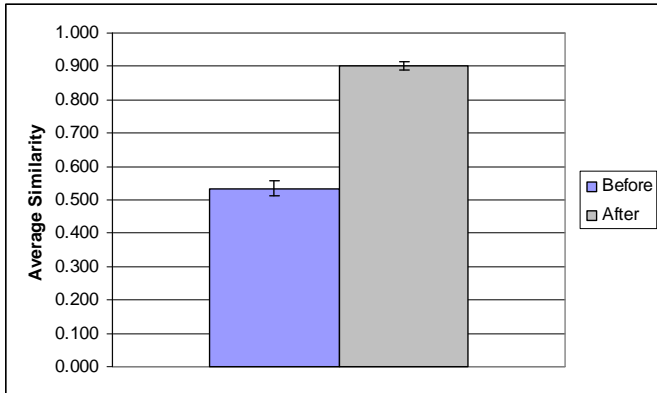
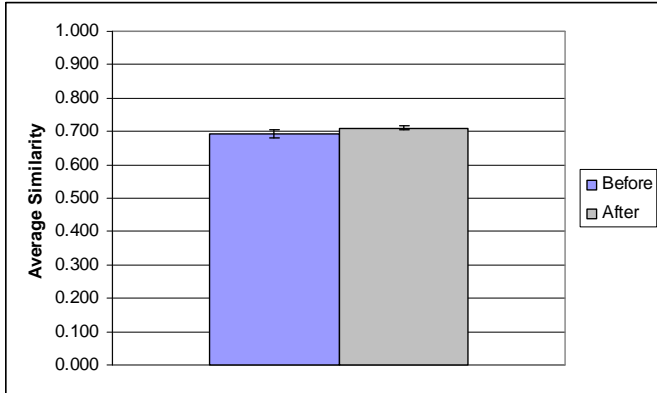


Figure 18: Graph showing increase in similarity with standard deviation error bars of a gasoline (top), oxygenated (middle), and naphthenic (bottom) ignitable liquid after cedar wood was incorporated in the database search.

The average similarity increase for two of the samples (gasoline and naphthenic/paraffinic) with cedar wood was much lower than any of the cases with alder wood mentioned previously. The average similarity increase of the gasoline sample with

cedar wood was 0.017. However, in the case of gasoline, after the database search, all three samples ranked the gasoline sample and its weathered counterparts in the top ten with the highest match being second on the list. The top match was still one of the gasoline samples found in the database. The cedar wood sample burned with the oxygenated ignitable liquid yielded typical results with an average similarity increase of 0.367. All three samples ranked in the top eight with the highest being in the top spot. Finally, although the naphthenic liquid only had an average similarity increase of 0.037, before the matrix was added, the results were still positive with a high similarity in the 0.8 to 0.9 range. The naphthenic liquid was ranked in the top ten of all the liquids with its highest ranking at third, but the other two liquids on the list ranked above it were both from the naphthenic class.

The data stresses the importance of incorporating a substrate when analyzing fire debris samples suspected of containing an ignitable liquid. A TIC chromatogram of fire debris may contain pyrolysis of the substrates incorporated in fire debris. If certain products can be ruled out from a fire debris sample because they are known to be found in a particular substrate that was at a fire scene, this could aid in determining if the remainder of the products was the result of an ignitable liquid being present. The substrate in fire debris should not be overlooked.

CHAPTER SEVEN: CONCLUSION

Conclusion

Over the past three years arson has been responsible for hundreds of deaths and hundreds of millions of dollars in property damage. The majority of arson cases are monetarily driven, [3]. The goal of the fire debris analyst is to determine the origin of the fire, and the cause of the fire. The fire debris analyst is often faced with the complex problem of identifying ignitable liquid residues in the presence of interfering products from pyrolysis and incomplete combustion of common building and furnishing materials[1]. This thesis has addressed that challenge

Fire debris is collected at the scene and returned to a laboratory where there are arrays of different extraction methods for extracting ignitable liquid residues. One factor that makes fire debris analysis so difficult are the outside variables that can distort the overall fire debris sample during analysis. The weather plays an important role along with how the fire was extinguished (fire extinguisher or excessive water). Also, the interfering products produced from the substrate itself and the pyrolysis products formed from the incomplete combustion of the sample play an important role in fire debris analysis.

The purpose of this research was to investigate a modified destructive distillation methodology. The volatile products generated during heating of substrate materials are extracted from the fire debris by passive headspace adsorption and subsequently analyzed by GC-MS. The substrates examined in this research include flooring and construction materials along with a variety of materials commonly analyzed by fire debris analysts.

The pyrolysis products produced from these samples were identified and recorded into a database. The effects of weathering on ignitable liquids were analyzed. These substrates were also burned in the presence of an array of ignitable liquids. Comparisons of ignitable liquids, interfering products, and ignitable liquids with interfering products are performed by comparing the summed ion spectra from the GC-MS data. The summed ion method was tested and able to rapidly identify the liquid present in the burnt substrate from a database of over 440 ignitable liquids or in some cases narrow down the liquid to its class. An interfering products database and GC-MS database software based on comparison of summed ion spectra was created and will be a useful tool for the evaluation of fire debris.

In conclusion, there are varieties of extraction techniques available to a fire debris analyst in order to extract an ignitable liquid residue from a fire debris sample. However, if the products produced from the pyrolysis of common building materials are similar to the composition of an ignitable liquid and prevents the positive identification of an ignitable liquid, then the door is open for reasonable doubt in the courtroom. Therefore, it is imperative to understand the significance of the interfering products produced from these common materials and the significance of their analysis.

Future Direction

In laboratory analysis, for the extraction of ignitable liquid residues, solid phase microextraction has received a lot of attention, but has yet to be a common technique in many forensic laboratories[48]. SPME has a high recovery rate for low volatile compounds which could be more efficient than activated charcoal strips for their

recovery. Activated charcoal strips create distortion because the low volatility compounds will displace the highly volatile compounds on the activated charcoal strip. Further research comparing both techniques on the same burned sample would be useful to see which technique would yield a better recovery of low volatility compounds. Hopefully, future pyrolysis studies should delve into whether the products produced from substrates differ between a manual burn in a fume hood or from a pyrolyzer. Also, further research into determining the limits of detection and limits of quantitation for each class of ignitable liquid in all types of burnt substrates could provide considerable information in trace fire debris analysis.

Currently, extensive studies with in-house developed software have been used to identify ignitable liquids when the substrate is known. Further studies into performing best-match identification while using the summed ion method to identify the most likely combination of an ignitable liquid and a substrate would be useful. These multiples comparisons of a best match of all substrates against all liquids could only expedite the analysis further. This used in conjunction with Digital Weathering, (currently under investigation at UCF) has not received much attention. The method which involves determining an algorithm for digitally weathering ignitable liquids without manual laboratory work could be considered a useful complimentary tool for fire debris analysis.

Finally, all research was performed on a small scale, in a controlled environment. The next step would be to do large scale burns in a controlled environment and perform target analysis and principal component analysis (PCA) to identify liquids and liquid dispersion from the point of origin. However, the semantics for large scale burns would be more challenging as compared to a laboratory setting.

**APPENDIX: SUBSTRATE TOTAL ION CHROMATOGRAMS AND TABLES OF
PRODUCTS**

Sample: Polyester Carpet Unburned

Source: Home Depot

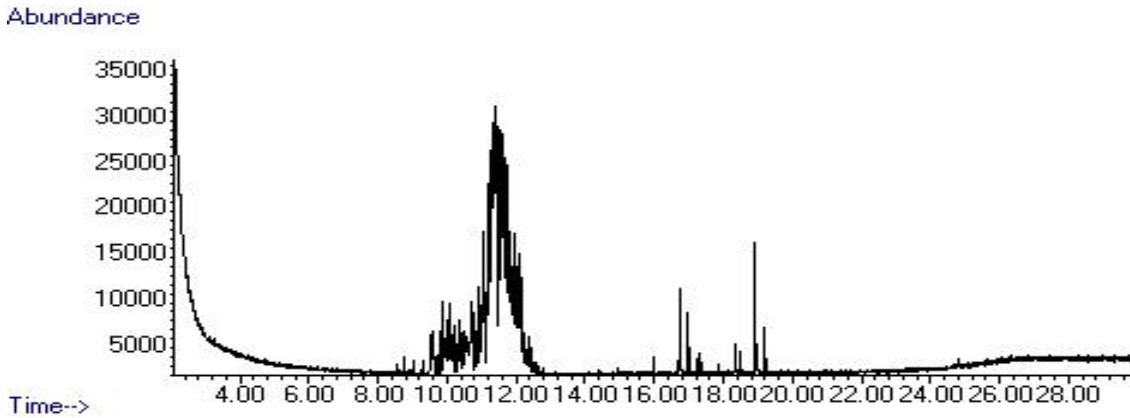


Figure 19: TIC of Polyester Carpet Unburned

Table 24: Retention Times and Products of Unburned Polyester Carpet

Retention time (min.)	Product
N/A	N/A

Sample: Polyester Carpet Burned

Source: Home Depot

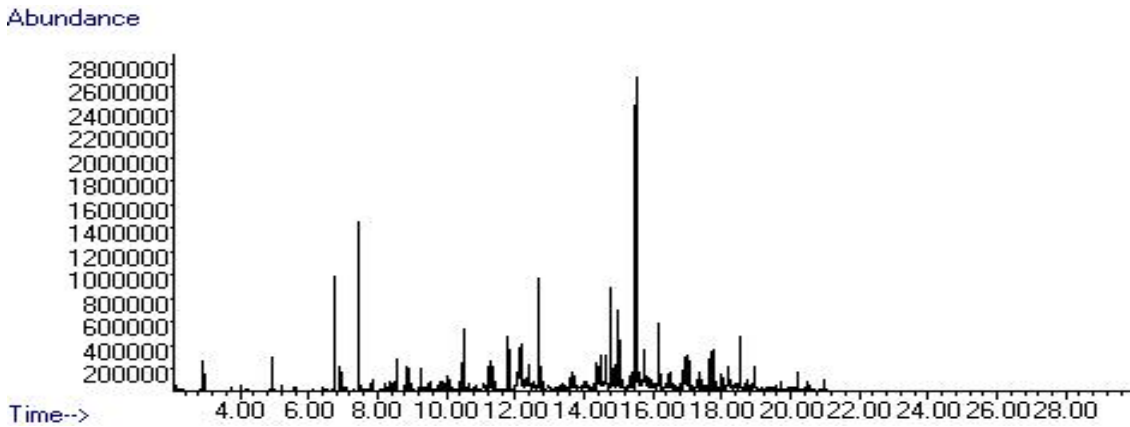


Figure 20: TIC of Polyester Carpet Burned

Table 25: Retention Times and Products of Burned Polyester Carpet

Retention time (min.)	Product
7.457	Styrene
12.692	Naphthalene
15.508	Biphenyl

Sample: PET Polyester Carpet Unburned

Source: Home Depot

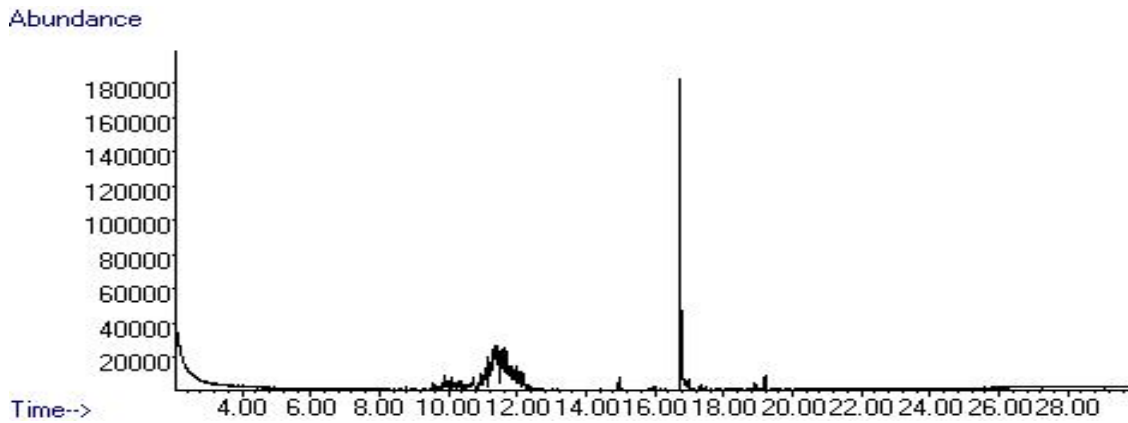


Figure 21: TIC of PET Polyester Carpet Unburned

Table 26: Retention Times and Products of Unburned PET Polyester Carpet

Retention time (min.)	Product
16.739	1-decene

Sample: PET Polyester Carpet Burned

Source: Home Depot

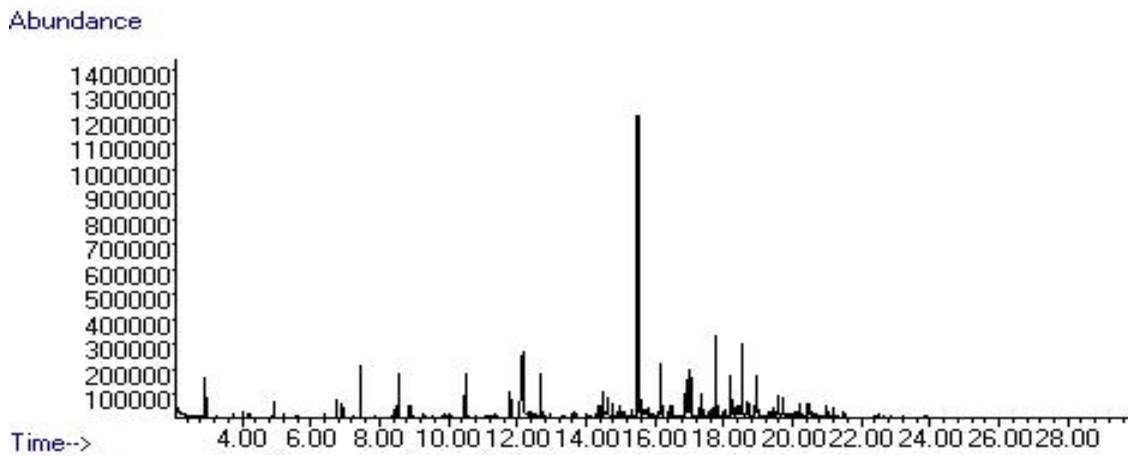


Figure 22: TIC of PET Polyester Carpet Burned

Table 27: Retention Times and Products of Burned PET Polyester Carpet

Retention time (min.)	Product
12.161	Benzoic Acid
15.504	2-ethenyl-naphthalene

Sample: Nylon Carpet Unburned

Source: Home Depot

Abundance

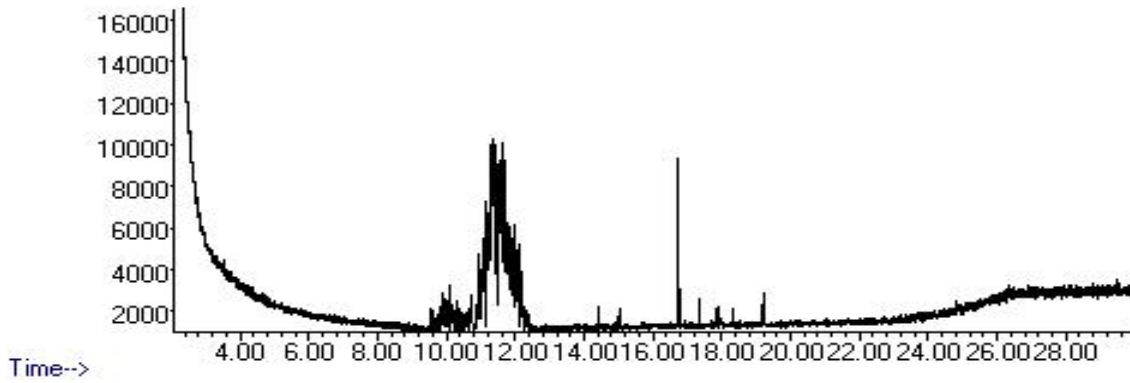


Figure 23: TIC of Nylon Carpet Unburned

Table 28: Retention Times and Products of Unburned Nylon Carpet

Retention time (min.)	Product
N/A	N/A

Sample: Nylon Carpet Burned

Source: Home Depot

Abundance

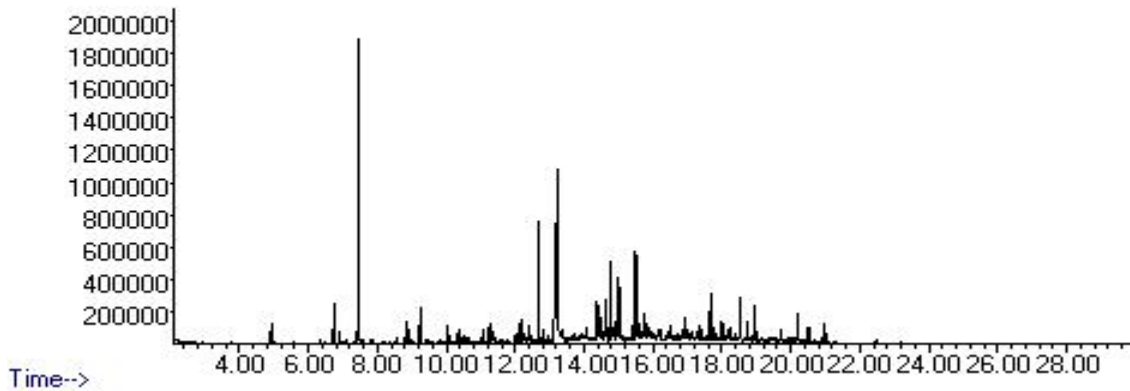


Figure 24: TIC of Nylon Carpet Burned

Table 29: Retention Times and Products of Burned Nylon Carpet

Retention time (min.)	Product
7.457	Styrene
12.692	Naphthalene
15.508	Biphenyl

Sample: Polyester/Nylon Blend Carpet Unburned

Source: Home Depot

Abundance

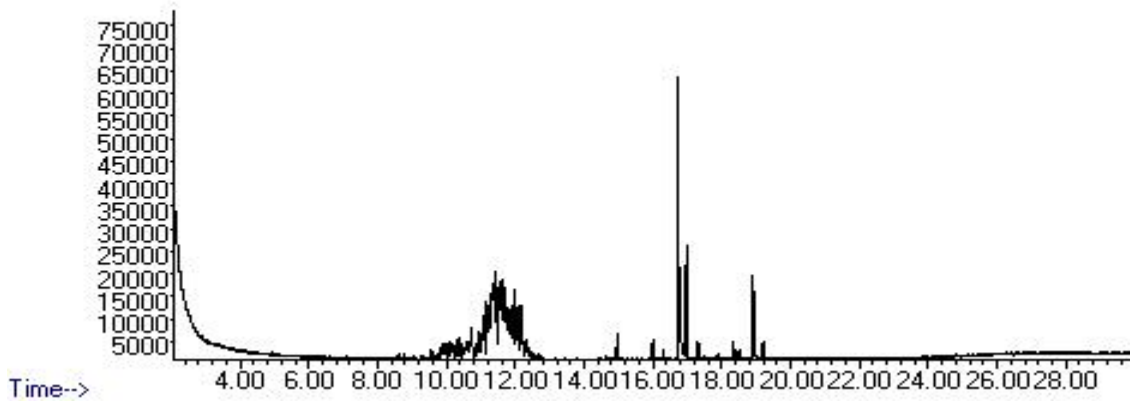


Figure 25: TIC of Polyester/Nylon Blend Carpet Unburned

Table 30: Retention Times and Products of Unburned Polyester/Nylon Blend Carpet

Retention time (min.)	Product
16.739	1-Decene

Sample: Polyester/Nylon Blend Carpet Burned

Source: Home Depot

Abundance

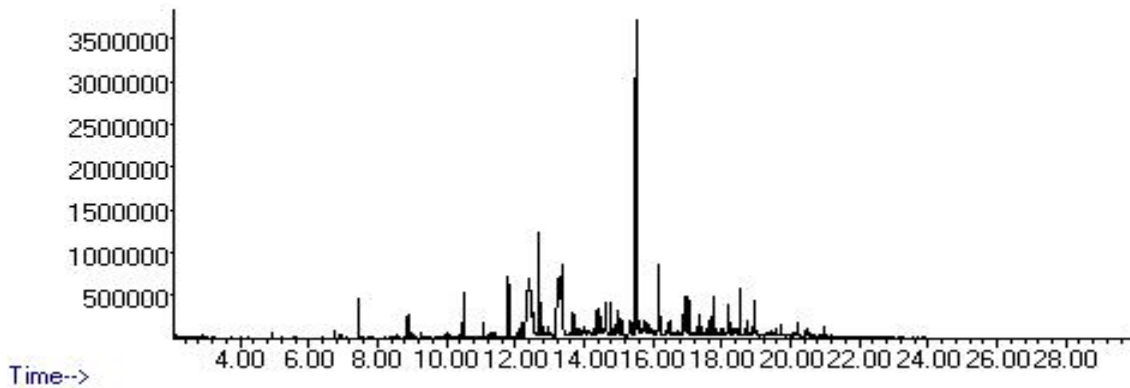


Figure 26: TIC of Polyester/Nylon Blend Carpet Burned

Table 31: Retention Times and Products of Burned Polyester/Nylon Blend Carpet

Retention time (min.)	Product
11.807	Isopropyl phenyl ketone
12.695	Azulene
15.512	Biphenyl

Sample: Olefin Carpet Unburned

Source: Home Depot

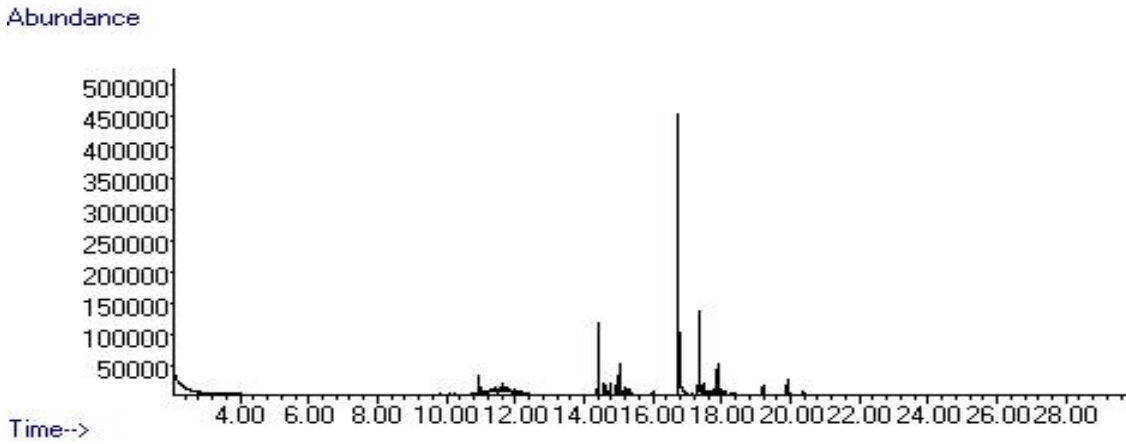


Figure 27: TIC of Olefin Carpet Unburned

Table 32: Retention Times and Products of Unburned Olefin Carpet

Retention time (min.)	Product
16.739	1-decene
17.346	n-tetracosane

Sample: Olefin Carpet Burned

Source: Home Depot

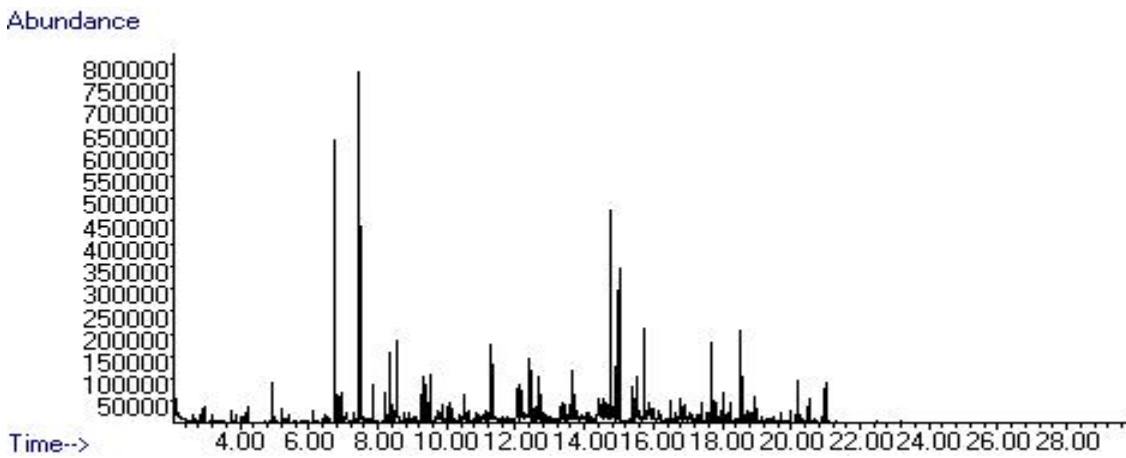


Figure 28: TIC of Olefin Carpet Burned

Table 33: Retention Times and Products of Burned Olefin Carpet

Retention time (min.)	Product
6.75	2,4-dimethyl-1-heptene
7.46	Styrene

Sample: UV Olefin Carpet Unburned

Source: Home Depot

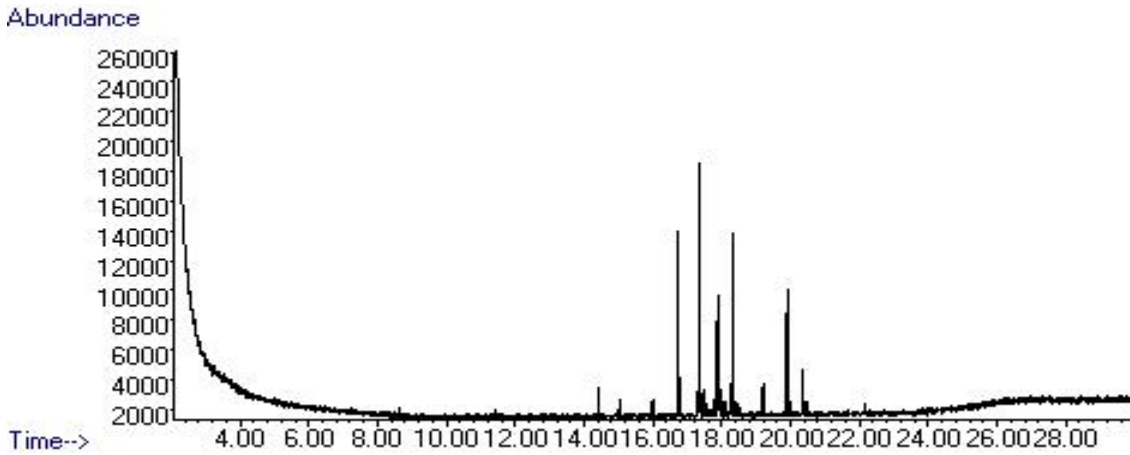


Figure 29: TIC of UV Olefin Carpet Unburned

Table 34: Retention Times and Products of Unburned UV Olefin Carpet

Retention time (min.)	Product
17.348	n-tetracosane

Sample: UV Olefin Carpet Burned

Source: Home Depot

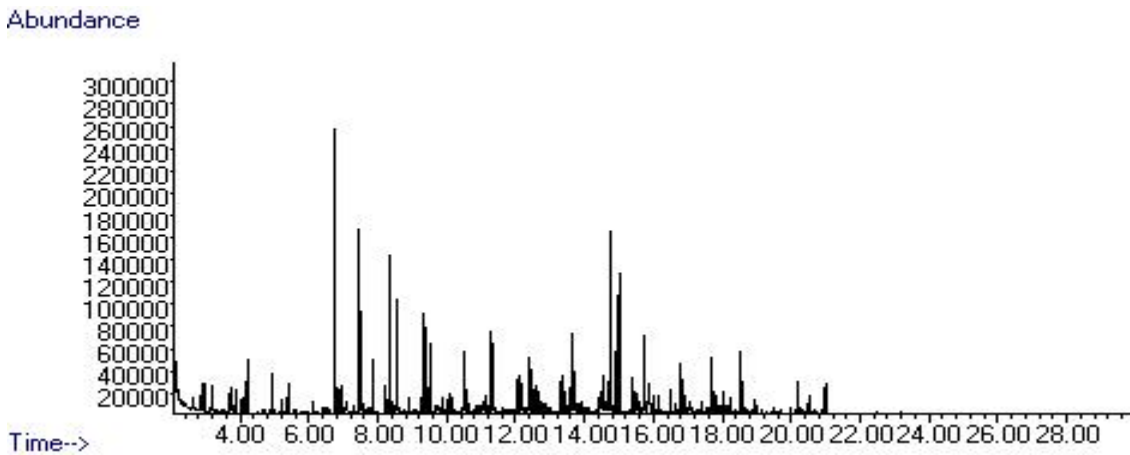


Figure 30: TIC of UV Olefin Carpet Burned

Table 35: Retention Times and Products of Burned UV Olefin Carpet

Retention time (min.)	Product
6.751	2,4-dimethyl-1-heptene
7.46	Styrene
8.335	4-methyl-2-heptanone

Sample: Olefin Nylon Blend Carpet Unburned

Source: Home Depot

Abundance

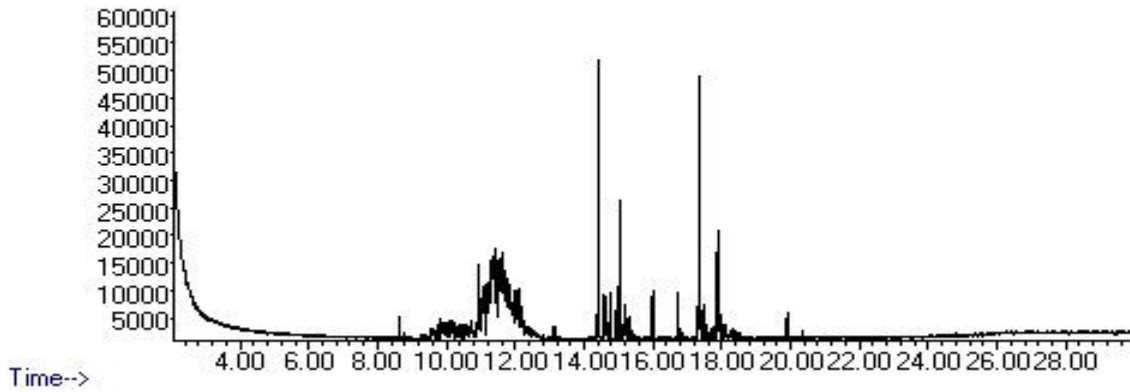


Figure 31: TIC of Olefin Nylon Blend Carpet Unburned

Table 36: Retention Times and Products of Unburned Olefin Nylon Blend Carpet

Retention time (min.)	Product
17.347	n-tetracosane
17.886	Docosane

Sample: Olefin Nylon Blend Carpet Burned

Source: Home Depot

Abundance

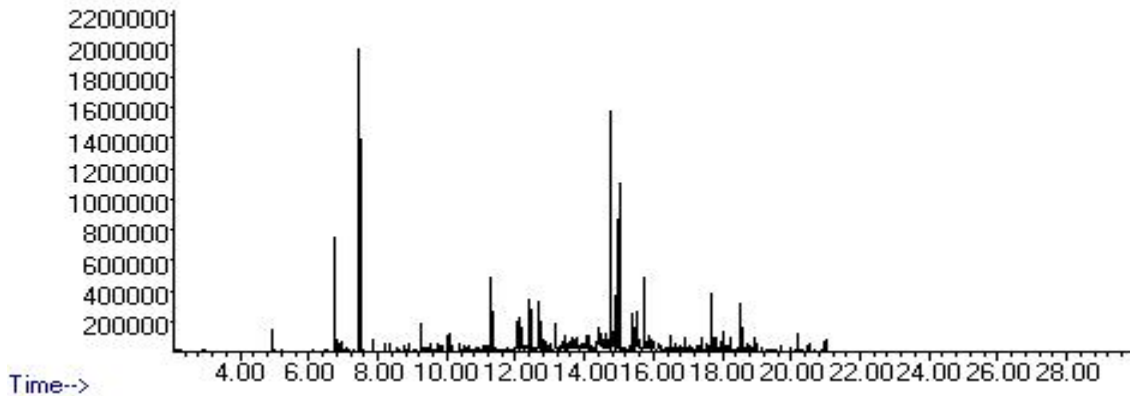


Figure 32: TIC of Olefin Nylon Blend Carpet Burned

Table 37: Retention Times and Products of Burned Olefin Nylon Blend Carpet

Retention time (min.)	Product
6.751	2,4-dimethyl-1-heptene
7.462	Styrene

Sample: Cedar Wood Unburned

Source: Home Depot

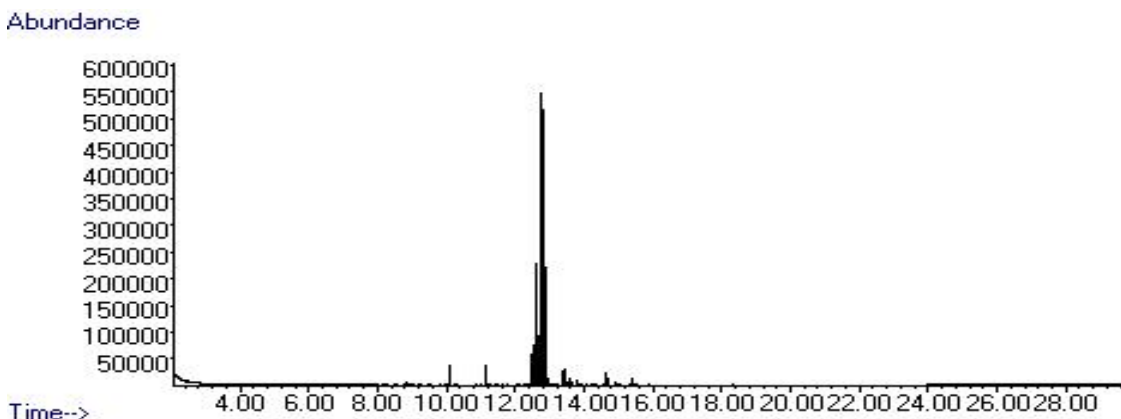


Figure 33: TIC of Cedar Wood Unburned

Table 38: Retention Times and Products of Unburned Cedar Wood

Retention time (min.)	Product
12.631	4-methyl-1-(1-methylethyl)3-cyclohexen-1-ol
12.781	trans-5-methyl-3-(1-methylethenyl)-cyclohexene
12.891	6,6-dimethyl-bicyclo(3.1.1)hept-2-ene-2-methanol

Sample: Cedar Wood Burned

Source: Home Depot

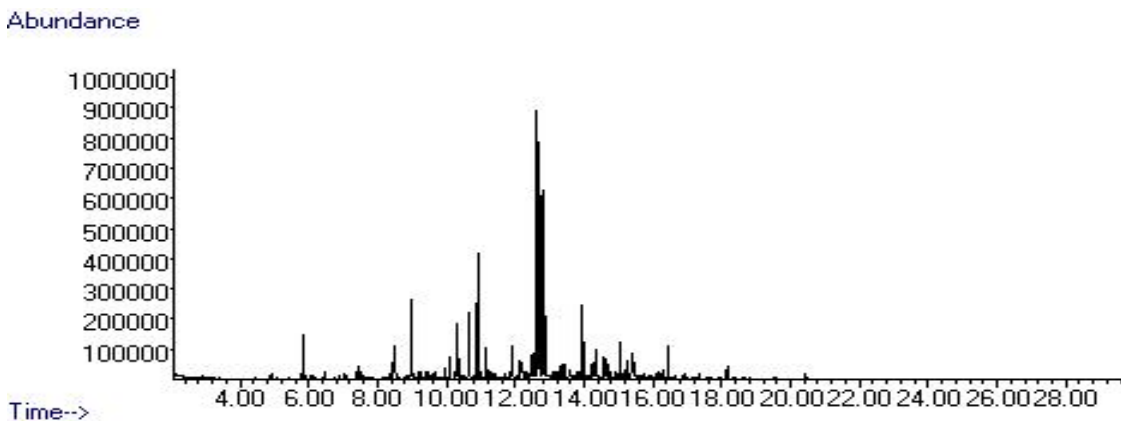


Figure 34: TIC of Cedar Wood Burned

Table 39: Retention Times and Products of Burned Cedar Wood

Retention time (min.)	Product
10.914	2-methoxyphenol
12.64	2-methoxy-4-methylphenol
12.784	1-methyl-3-(1-methylethenyl)-cyclohexene

Sample: Cherry Wood Unburned

Source: BBQ Woods

Abundance

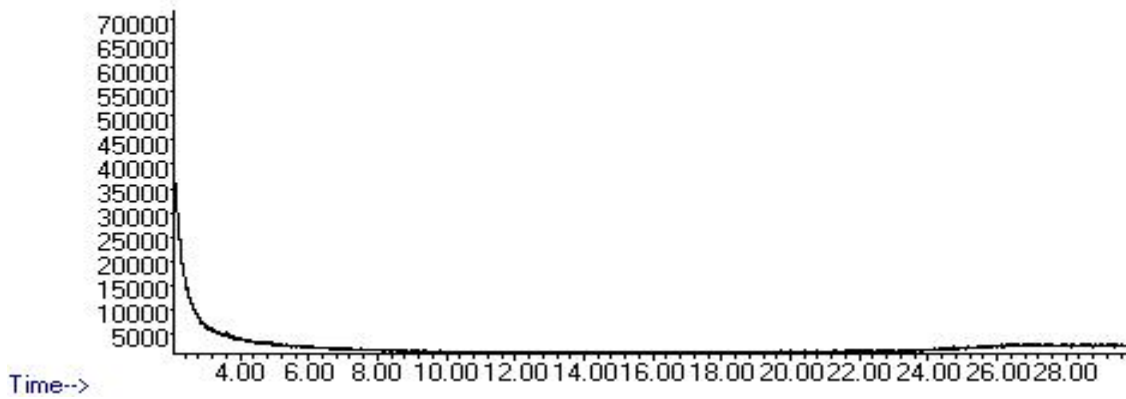


Figure 35: TIC of Cherry Wood Unburned

Table 40: Retention Times and Products of Unburned Cherry Wood

Retention time (min.)	Product
N/A	N/A

Sample: Cherry Wood Burned

Source: BBQ Woods

Abundance

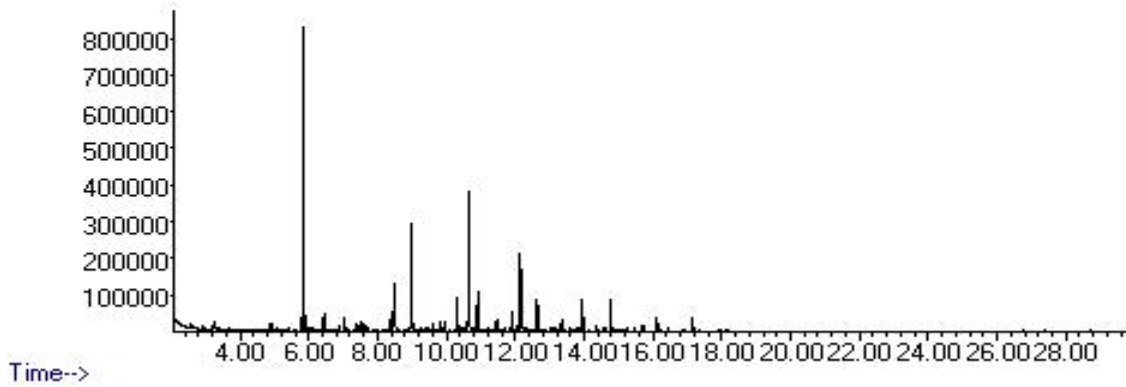


Figure 36: TIC of Cherry Wood Burned

Table 41: Retention Times and Products of Burned Cherry Wood

Retention time (min.)	Product
5.847	2-furaldehyde
8.978	Phenol
10.645	p-cresol

Sample: Hickory Wood Unburned

Source: BBQ Woods

Abundance

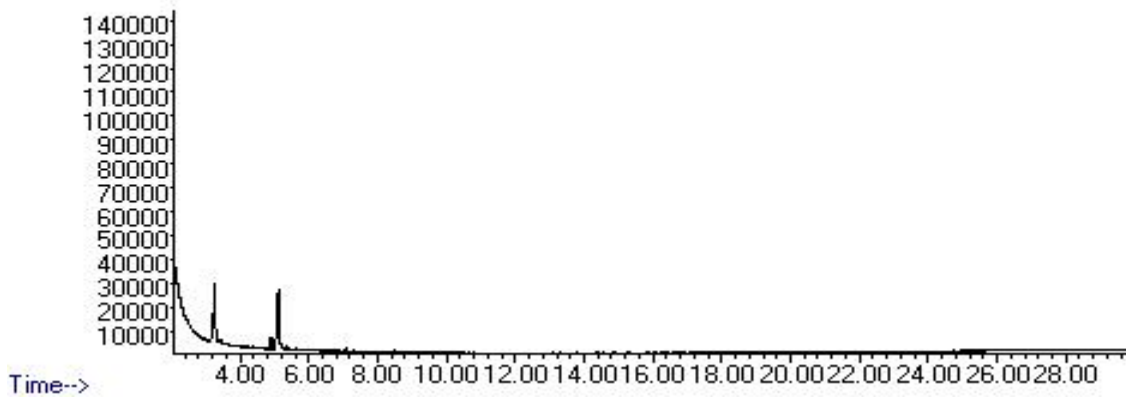


Figure 37: TIC of Hickory Wood Unburned

Table 42: Retention Times and Products of Unburned Hickory Wood

Retention time (min.)	Product
N/A	N/A

Sample: Hickory Wood Burned

Source: BBQ Woods

Abundance

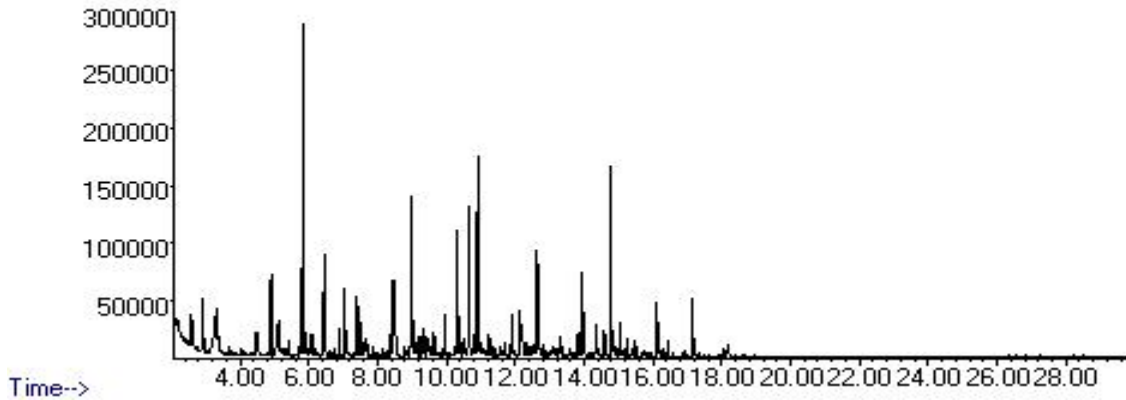


Figure 38: TIC of Hickory Wood Burned

Table 43: Retention Times and Products of Burned Hickory Wood

Retention time (min.)	Product
5.846	2-furaldehyde
10.912	2-methoxyphenol
14.781	2,6-dimethoxyphenol

Sample: Douglass Fir Wood Unburned

Source: Home Depot

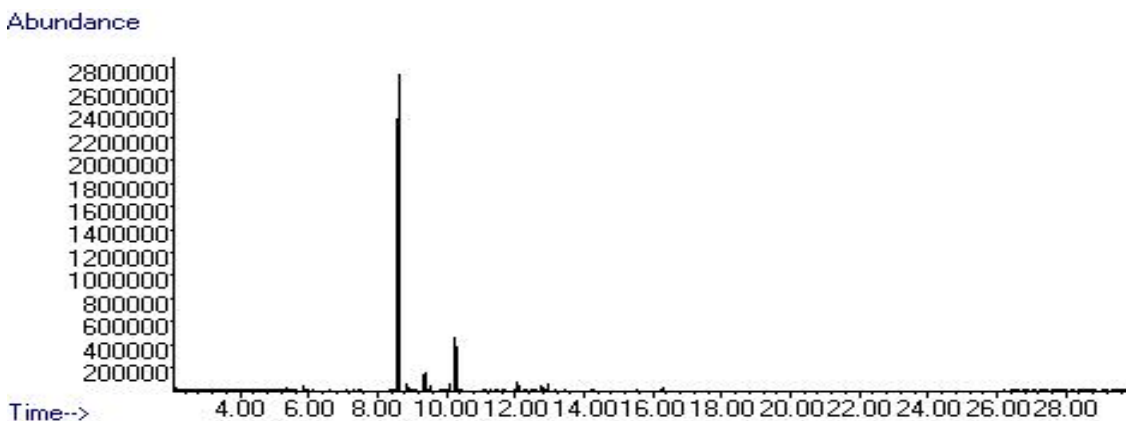


Figure 39: TIC of Douglass Fir Wood Unburned

Table 44: Retention Times and Products of Unburned Douglass Fir Wood

Retention time (min.)	Product
8.603	alpha-pinene
9.367	beta-pinene
10.267	limonene

Sample: Douglass Fir Wood Burned

Source: Home Depot

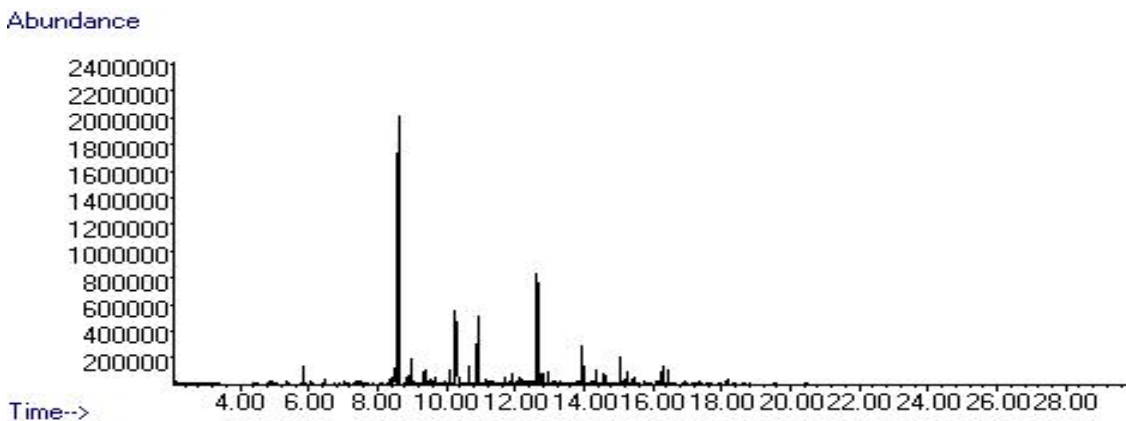


Figure 40: TIC of Douglass Fir Wood Burned

Table 45: Retention Times and Products of Burned Douglass Fir Wood

Retention time (min.)	Product
8.602	alpha-pinene
10.268	limonene
12.643	2-methoxy-4-methylphenol

Sample: Oak Wood Unburned

Source: Home Depot

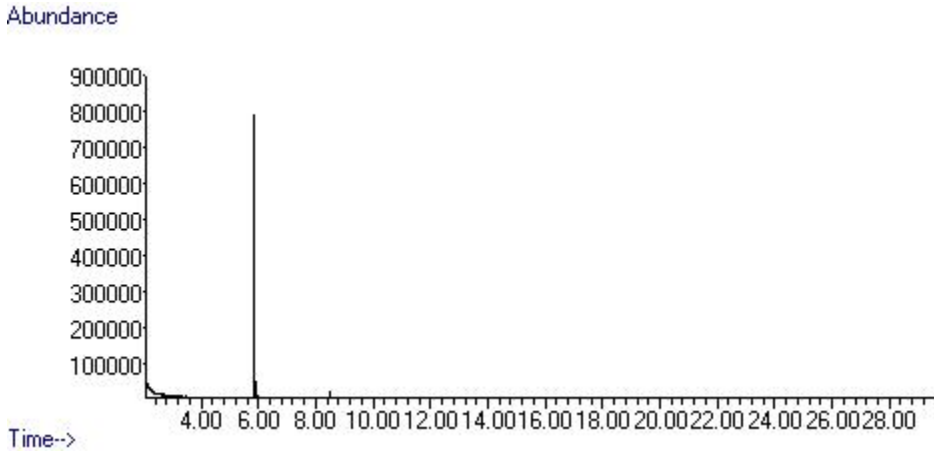


Figure 41: TIC of Oak Wood Unburned

Table 46: Retention Times and Products of Unburned Oak Wood

Retention time (min.)	Product
5.848	2-furaldehyde

Sample: Oak Wood Burned

Source: Home Depot

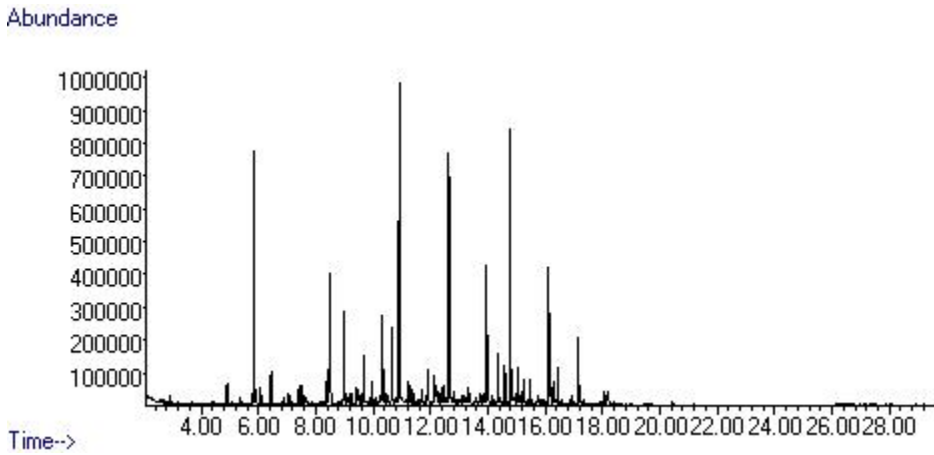


Figure 42: TIC of Oak Wood Burned

Table 47: Retention Times and Products of Burned Oak Wood

Retention time (min.)	Product
5.847	2-furaldehyde
10.915	2-methoxyphenol
14.785	2,6-dimethoxyphenol

Sample: Yellow Pine Wood Unburned

Source: Home Depot

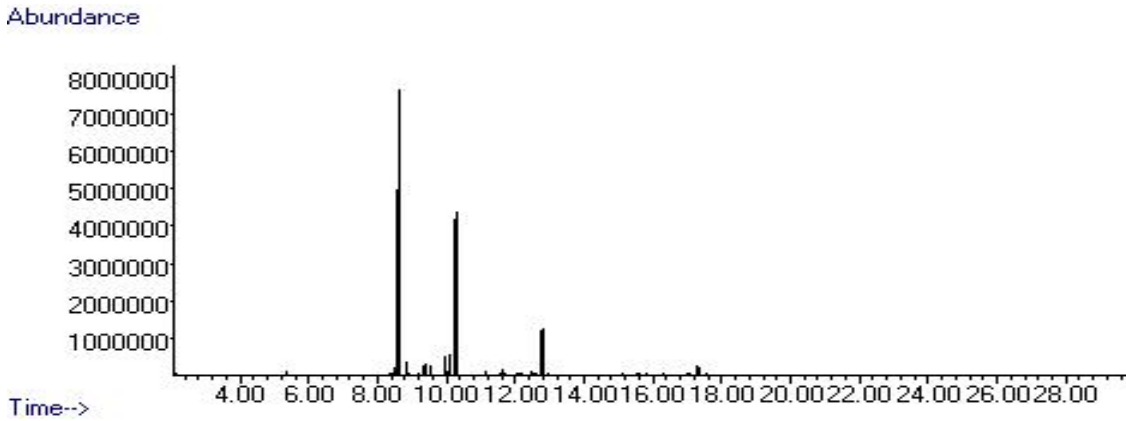


Figure 43: TIC of Yellow Pine Wood Unburned

Table 48: Retention Times and Products of Unburned Yellow Pine Wood

Retention time (min.)	Product
8.621	alpha-pinene
10.274	limonene
12.874	alpha, alpha. 4-trimethyl-3-cyclohexen-1-methanol

Sample: Yellow Pine Wood Burned

Source: Home Depot

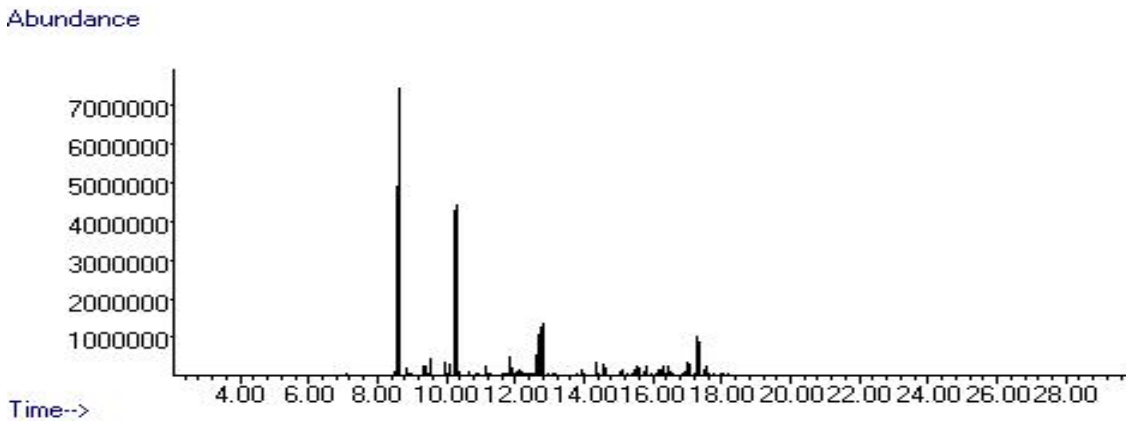


Figure 44: TIC of Yellow Pine Wood Burned

Table 49: Retention Times and Products of Burned Yellow Pine Wood

Retention time (min.)	Product
8.615	alpha-pinene
10.273	limonene
12.785	alpha, alpha. 4-trimethyl-3-cyclohexen-1-methanol

Sample: White Pine Wood Unburned

Source: Home Depot

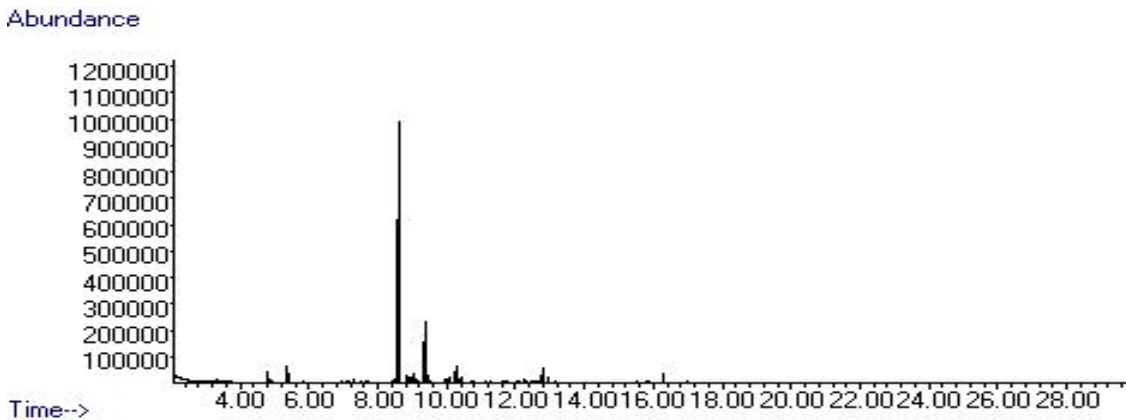


Figure 45: TIC of White Pine Wood Unburned

Table 50: Retention Times and Products of Unburned White Pine Wood

Retention time (min.)	Product
8.559	alpha-pinene
9.368	beta-pinene
10.267	limonene

Sample: White Pine Wood Burned

Source: Home Depot

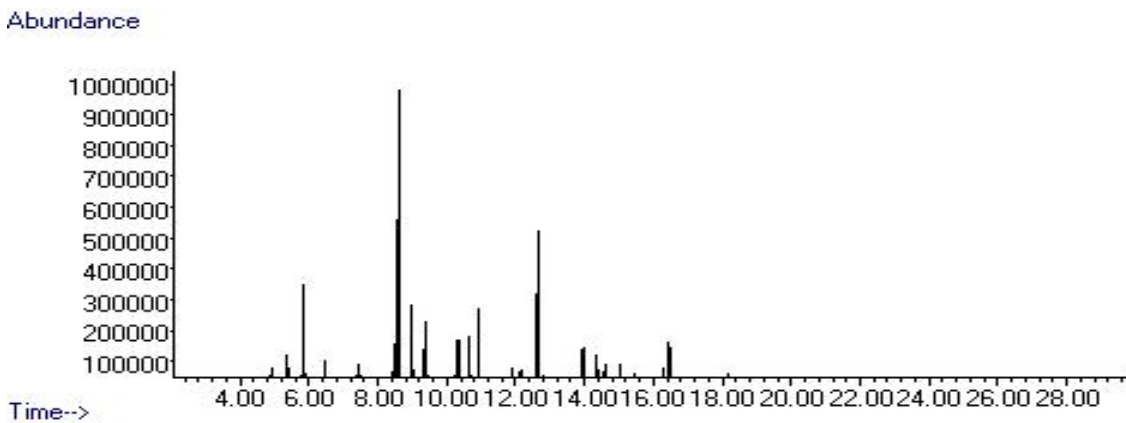


Figure 46: TIC of White Pine Wood Burned

Table 51: Retention Times and Products of Burned White Pine Wood

Retention time (min.)	Product
8.599	alpha-pinene
12.641	2-methoxy-4-methylphenol
12.665	naphthalene

Sample: Maple Wood Unburned

Source: Home Depot

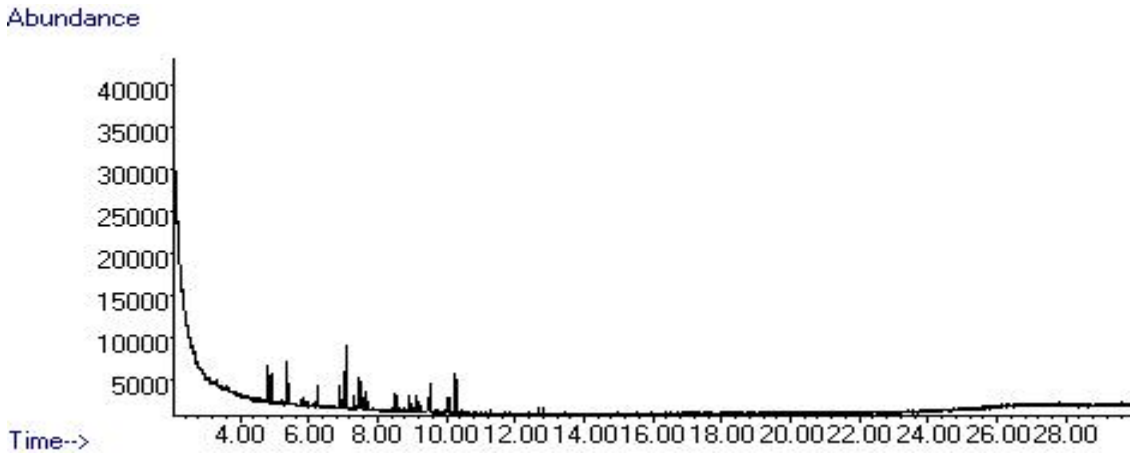


Figure 47: TIC of Maple Wood Unburned

Table 52: Retention Times and Products of Unburned Maple Wood

Retention time (min.)	Product
N/A	N/A

Sample: Maple Wood Burned

Source: Home Depot

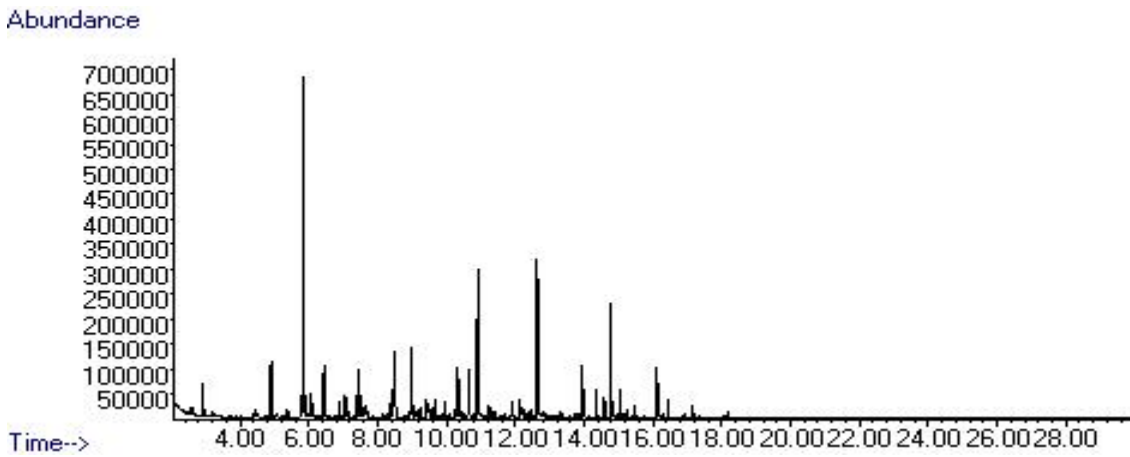


Figure 48: TIC of Maple Wood Burned

Table 53: Retention Times and Products of Burned Maple Wood

Retention time (min.)	Product
5.847	2-furaldehyde
10.913	2-methoxyphenol
12.64	2-methoxy-4-methylphenol

Sample: Aspen Wood Unburned

Source: Home Depot

Abundance

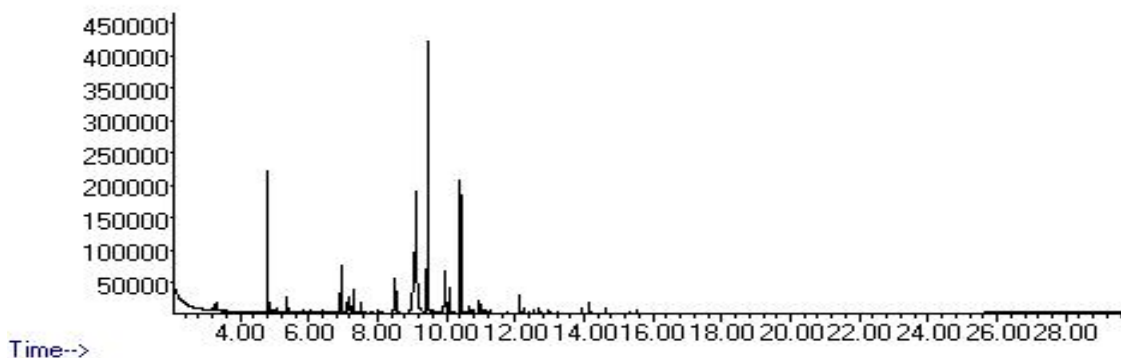


Figure 49: TIC of Aspen Wood Unburned

Table 54: Retention Times and Products of Unburned Aspen Wood

Retention time (min.)	Product
4.796	1-pentanol
9.547	2-pentylfuran
10.407	(E)-2-octenal

Sample: Aspen Wood Burned

Source: Home Depot

Abundance

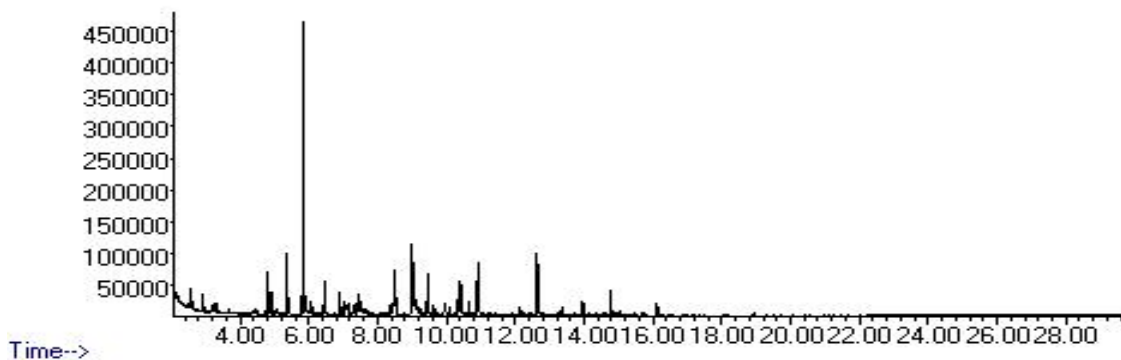


Figure 50: TIC of Aspen Wood Burned

Table 55: Retention Times and Products of Burned Aspen Wood

Retention time (min.)	Product
5.844	2-furaldehyde
8.978	Phenol
9.06	Hexanoic acid

Sample: Poplar Wood Unburned

Source: Home Depot

Abundance

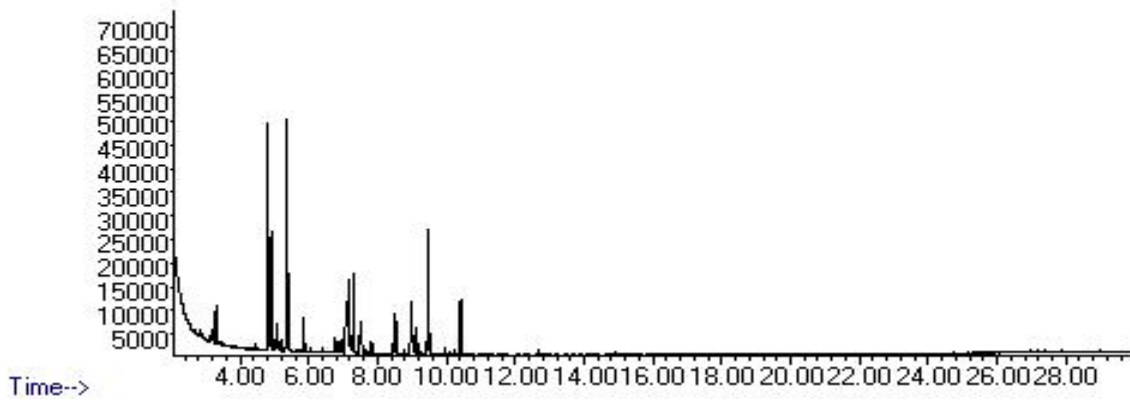


Figure 51: TIC of Poplar Wood Unburned

Table 56: Retention Times and Products of Unburned Poplar Wood

Retention time (min.)	Product
N/A	N/A

Sample: Poplar Wood Burned

Source: Home Depot

Abundance

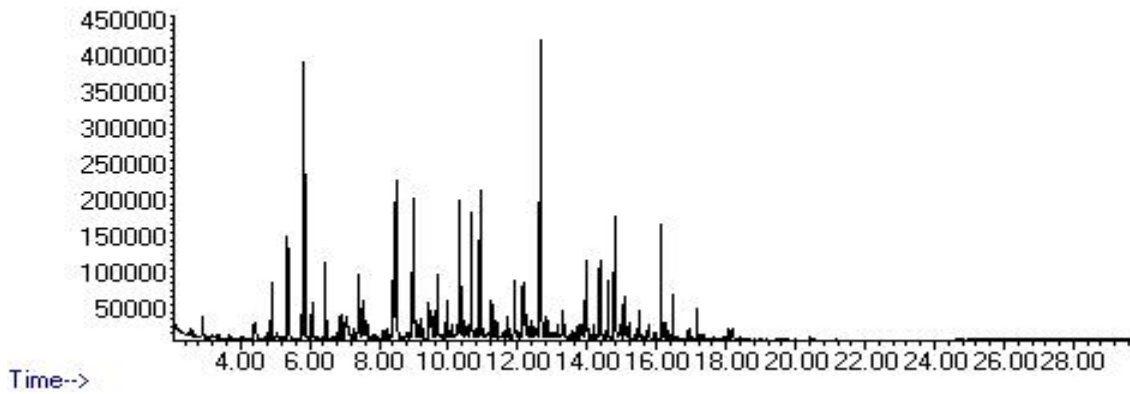


Figure 52: TIC of Poplar Wood Burned

Table 57: Retention Times and Products of Burned Poplar Wood

Retention time (min.)	Product
5.848	2-furaldehyde
8.493	5-methylfurfural
12.665	naphthalene

Sample: Alder Wood Unburned

Source: BBQ Woods

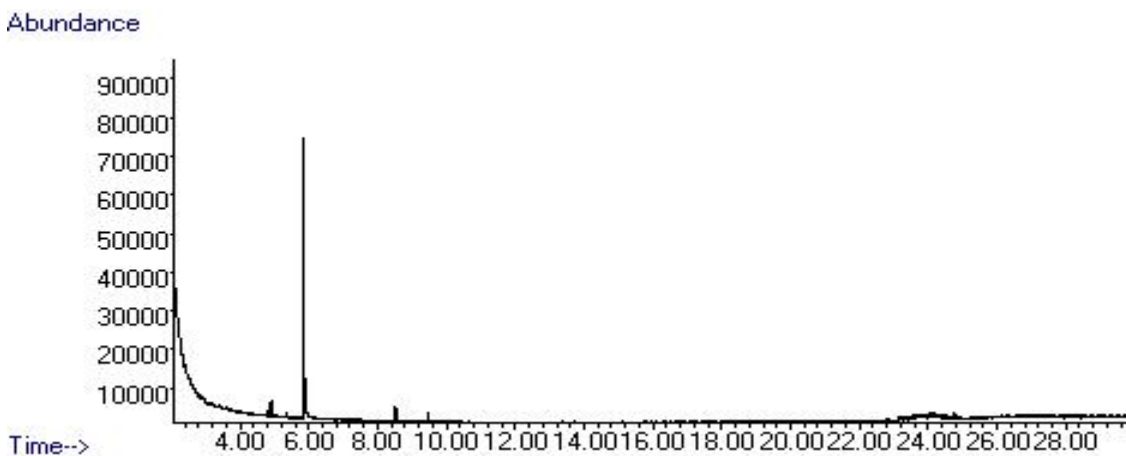


Figure 53: TIC of Alder Wood Unburned

Table 58: Retention Times and Products of Unburned Alder Wood

Retention time (min.)	Product
N/A	N/A

Sample: Alder Wood Burned

Source: BBQ Woods

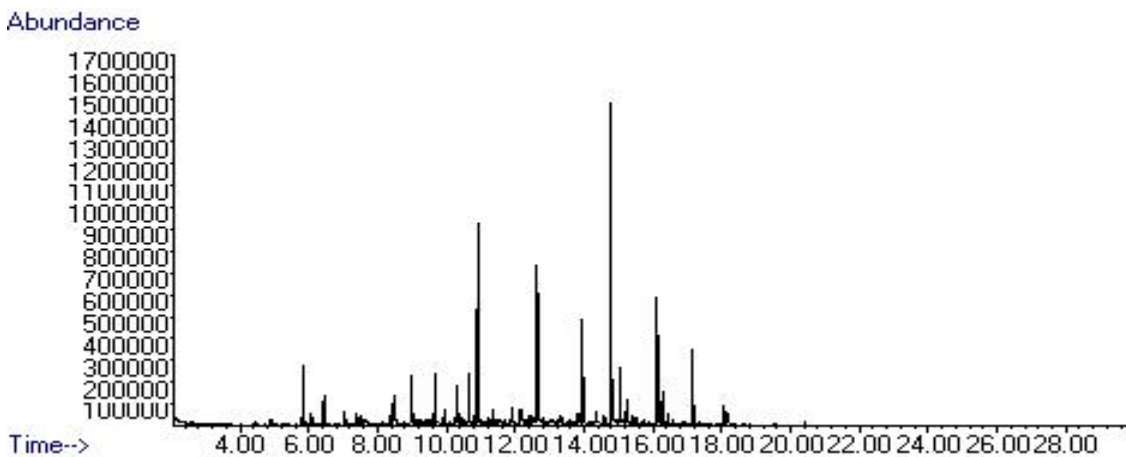


Figure 54: TIC of Alder Wood Burned

Table 59: Retention Times and Products of Burned Alder Wood

Retention time (min.)	Product
10.914	2-methoxyphenol
12.64	2-methoxy-4-methylphenol
14.787	2,6-dimethoxyphenol

Sample: Trex Composite Wood Unburned

Source: Home Depot

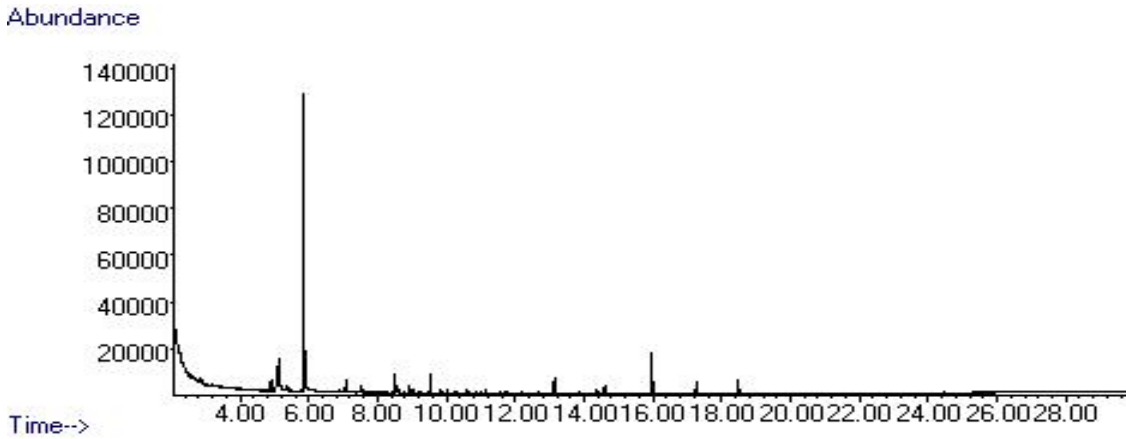


Figure 55: TIC of Trex Composite Wood Unburned

Table 60: Retention Times and Products of Unburned Trex Composite Wood

Retention time (min.)	Product
5.85	2-furaldehyde

Sample: Trex Composite Wood Burned

Source: Home Depot

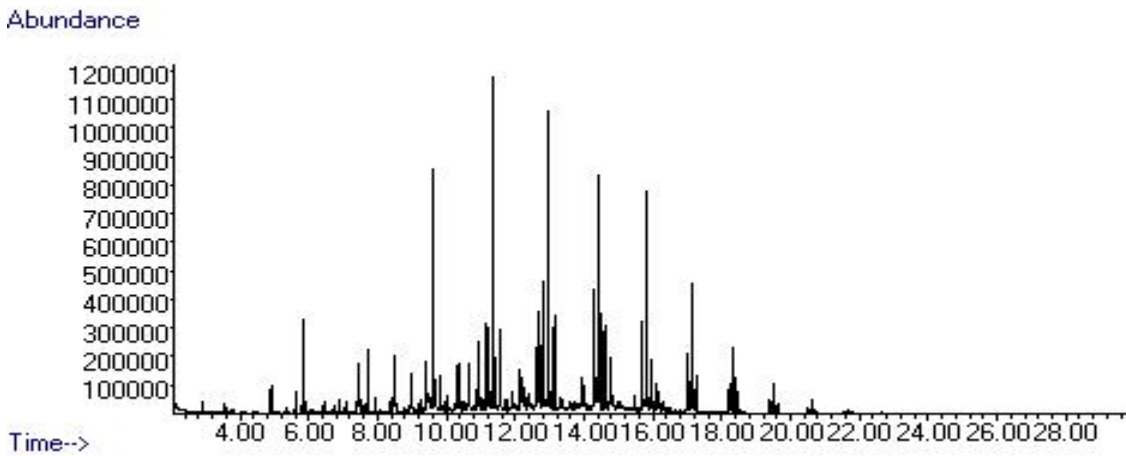


Figure 56: TIC of Trex Composite Wood Burned

Table 61: Retention Times and Products of Burned Trex Composite Wood

Retention time (min.)	Product
11.371	1-decanol
12.967	1-dodecene
14.445	1-tridecene

Sample: Vinyl Unburned

Source: Home Depot

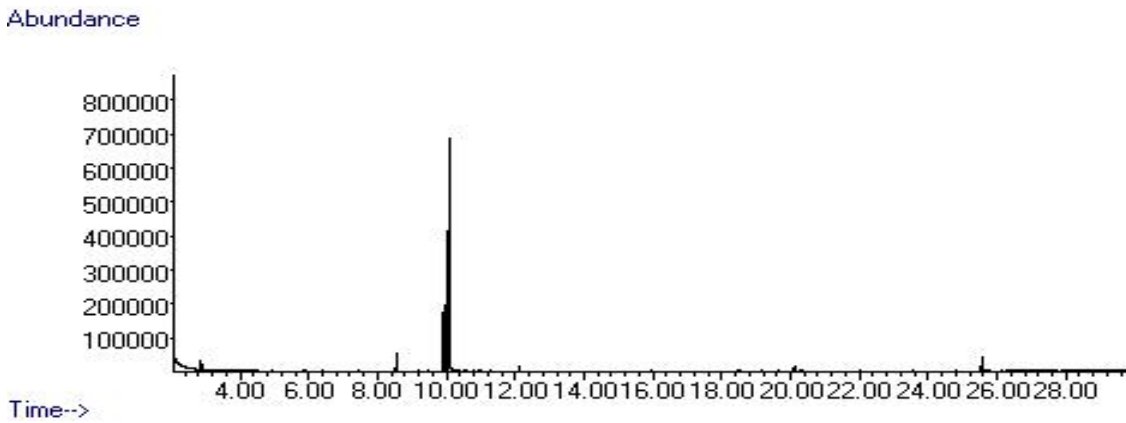


Figure 57: TIC of Vinyl Unburned

Table 62: Retention Times and Products of Unburned Vinyl

Retention time (min.)	Product
8.549	Benzaldehyde
9.927	Benzyl alcohol
10.072	2-ethyl-1-hexanol

Sample: Vinyl Burned

Source: Home Depot

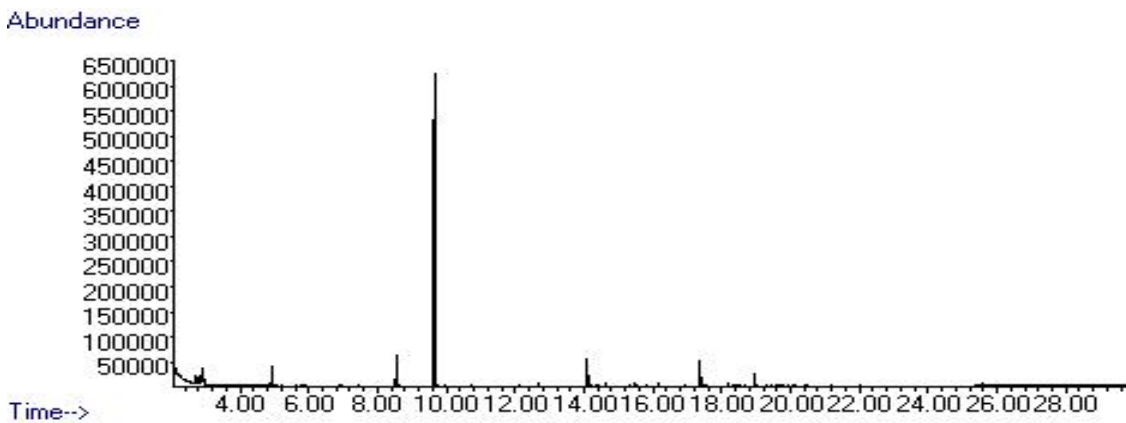


Figure 58: TIC of Vinyl Burned

Table 63: Retention Times and Products of Burned Vinyl

Retention time (min.)	Product
8.548	Benzaldehyde
9.653	Benzyl chloride
14.096	Phthalic anhydride

Sample: Industrial Vinyl Unburned

Source: Home Depot

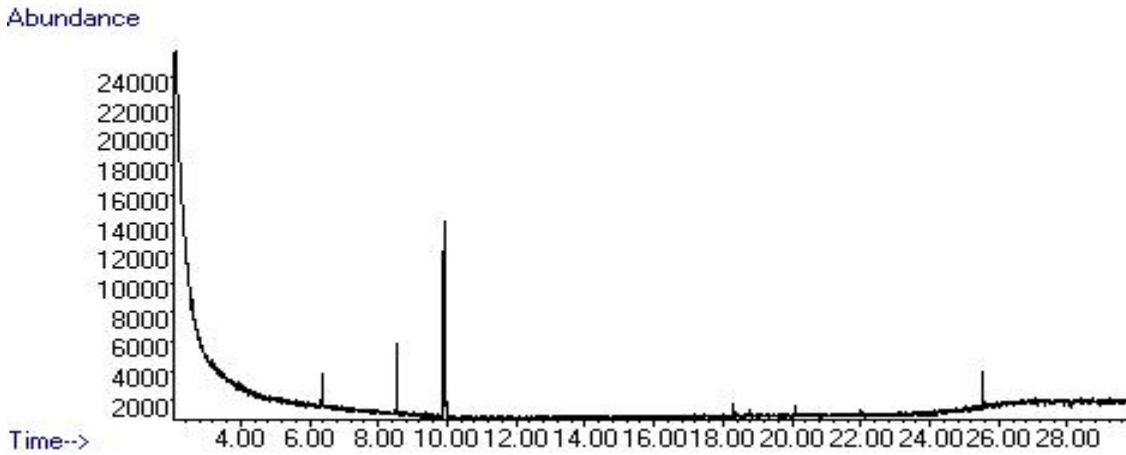


Figure 59: TIC of Industrial Vinyl Unburned

Table 64: Retention Times and Products of Unburned Industrial Vinyl

Retention time (min.)	Product
9.908	Benzyl Alcohol

Sample: Industrial Vinyl Burned

Source: Home Depot

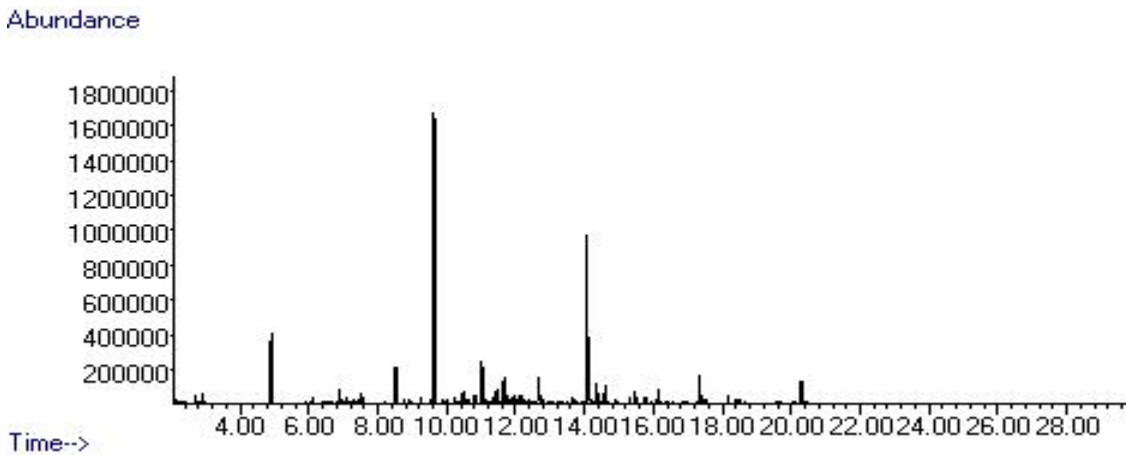


Figure 60: TIC of Industrial Vinyl Burned

Table 65: Retention Times and Products of Burned Industrial Vinyl

Retention time (min.)	Product
4.90	Toluene
9.633	Benzyl chloride
14.082	Phthalic anhydride 99%

Sample: Vinyl/Linoleum Unburned

Source: Home Depot

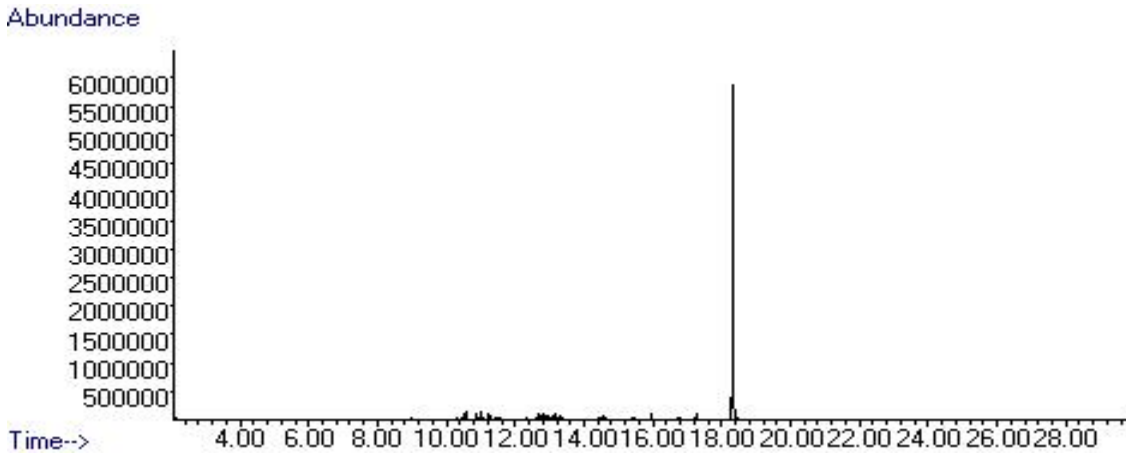


Figure 61: TIC of Vinyl/Linoleum Unburned

Table 66: Retention Times and Products of Unburned Vinyl/Linoleum

Retention time (min.)	Product
N/A	N/A

Sample: Vinyl/Linoleum Burned

Source: Home Depot

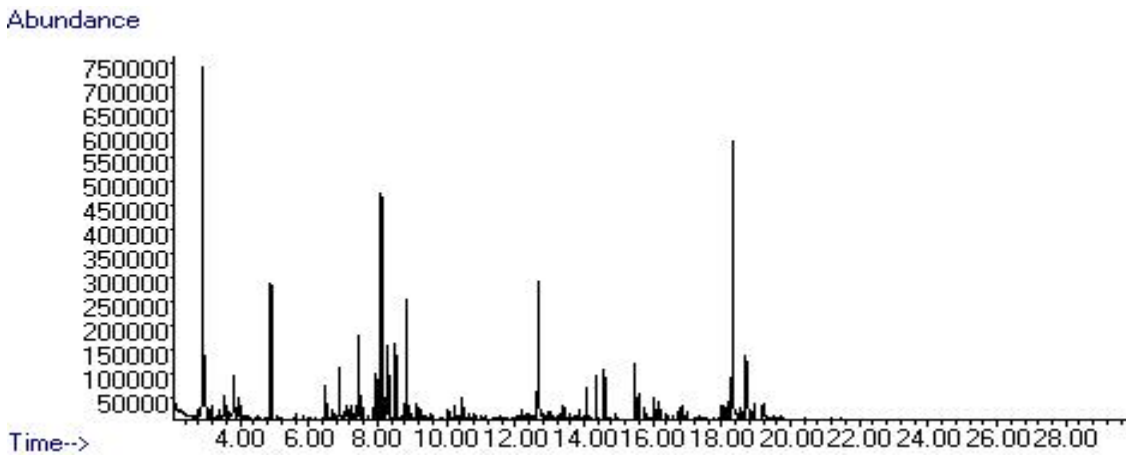


Figure 62: TIC of Vinyl/Linoleum Burned

Table 67: Retention Times and Products of Burned Vinyl/Linoleum

Retention time (min.)	Product
2.907	Benzene
4.902	Toluene
12.665	Naphthalene

Sample: Bamboo Hardwood Unburned

Source: Home Depot

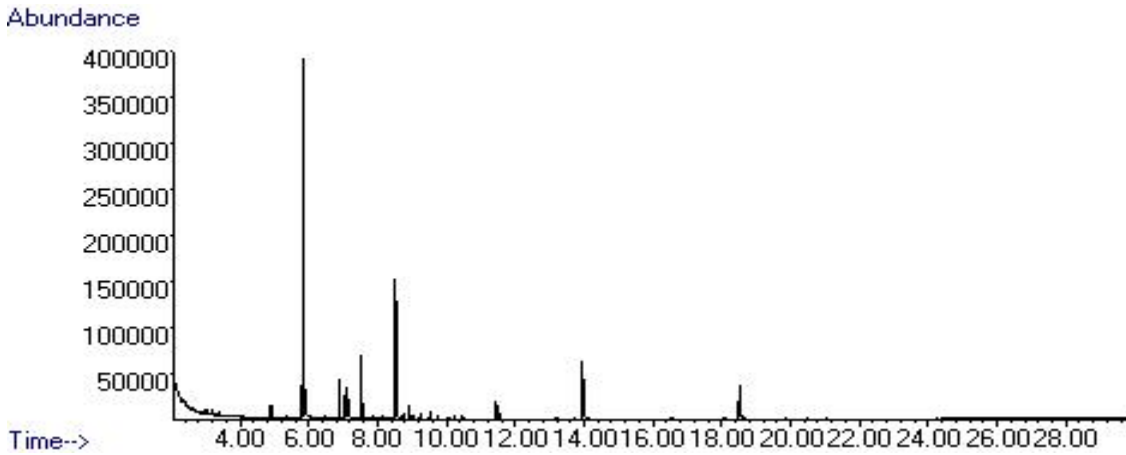


Figure 63: TIC of Bamboo Hardwood Unburned

Table 68: Retention Times and Products of Unburned Bamboo Hardwood

Retention time (min.)	Product
N/A	N/A

Sample: Bamboo Hardwood Burned

Source: Home Depot

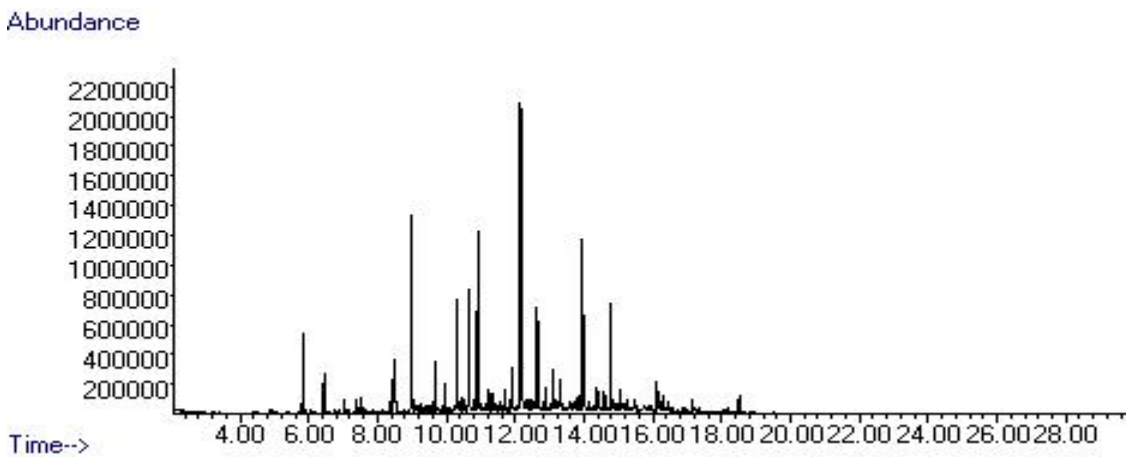


Figure 64: TIC of Bamboo Hardwood Burned

Table 69: Retention Times and Products of Burned Bamboo Hardwood

Retention time (min.)	Product
8.983	Phenol
10.915	2-methoxyphenol
12.518	4-ethylphenol

Sample: Hickory Laminate Hardwood Unburned

Source: Buildirect (K-Swiss USA)

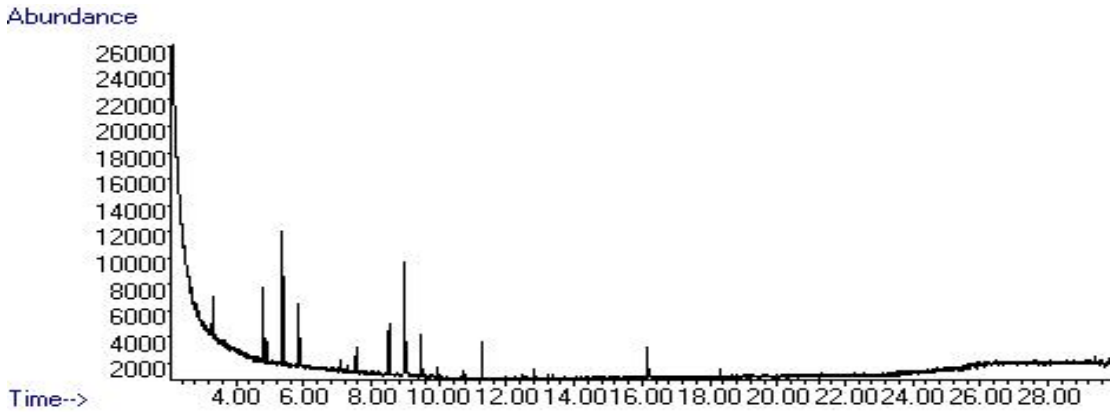


Figure 65: TIC of Hickory Laminate Hardwood Unburned

Table 70: Retention Times and Products of Unburned Hickory Laminate Hardwood

Retention time (min.)	Product
5.371	Hexanal
8.989	Hexanoic acid

Sample: Hickory Laminate Hardwood Burned

Source: Buildirect (K-Swiss USA)

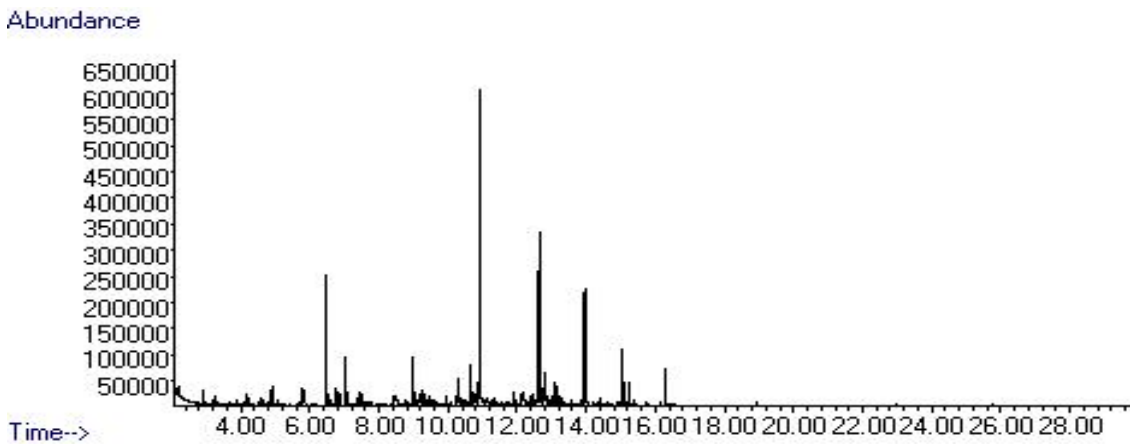


Figure 66: TIC of Hickory Laminate Hardwood Burned

Table 71: Retention Times and Products of Burned Hickory Laminate Hardwood

Retention time (min.)	Product
10.913	2-methoxyphenol
12.638	2-methoxy-4-methylphenol
13.96	4-ethyl-2-methoxyphenol

Sample: Cherry Laminate Hardwood Unburned

Source: Buildirect (K-Swiss USA)

Abundance

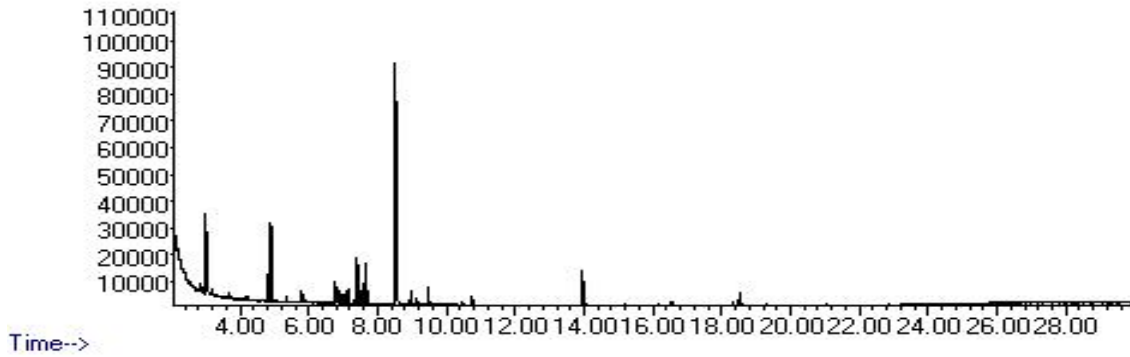


Figure 67: TIC of Cherry Laminate Hardwood Unburned

Table 72: Retention Times and Products of Unburned Cherry Laminate Hardwood

Retention time (min.)	Product
4.901	Toluene
8.525	Benzaldehyde

Sample: Cherry Laminate Hardwood Burned

Source: Buildirect (K-Swiss USA)

Abundance

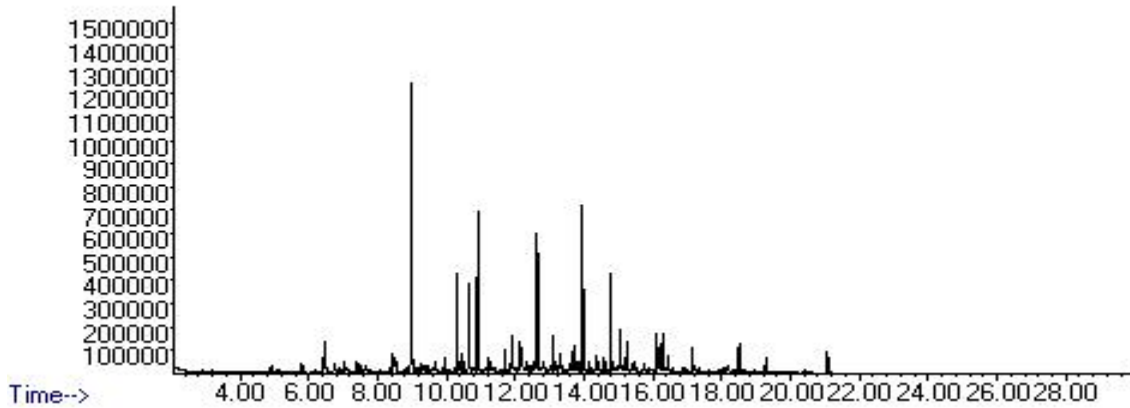


Figure 68: TIC of Cherry Laminate Hardwood Burned

Table 73: Retention Times and Products of Burned Cherry Laminate Hardwood

Retention time (min.)	Product
8.985	Phenol
10.914	2-methoxyphenol
13.961	4-ethyl-2-methoxyphenol

Sample: Troya Laminate Hardwood Unburned

Source: Buildirect (K-Swiss USA)

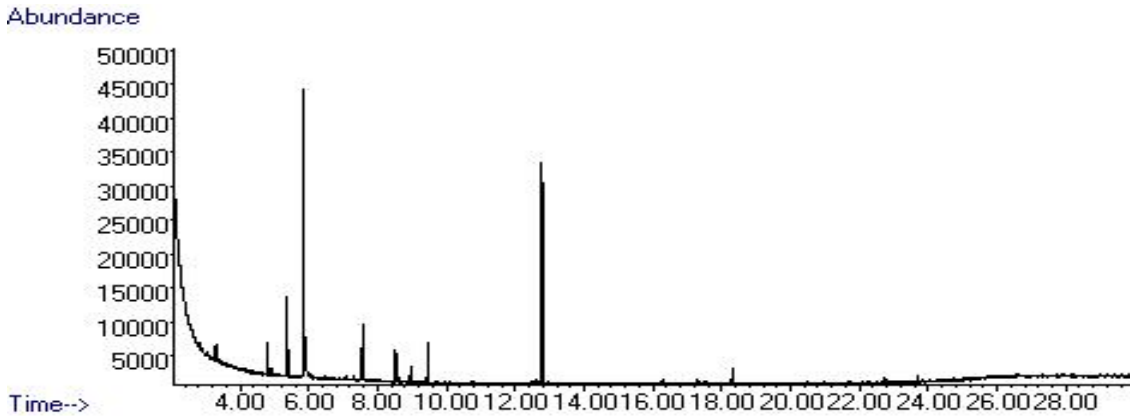


Figure 69: TIC of Troya Laminate Hardwood Unburned

Table 74: Retention Times and Products of Unburned Troya Laminate Hardwood

Retention time (min.)	Product
5.848	Furaldehyde
12.781	alpha, alpha, 4-trimethyl-3-cyclohexene-1-methanol

Sample: Troya Laminate Hardwood Burned

Source: Buildirect (K-Swiss USA)

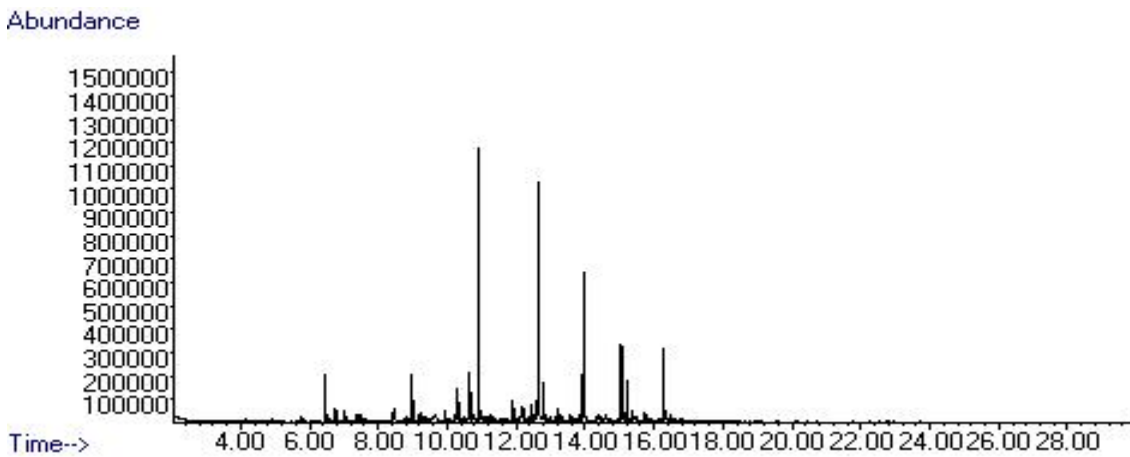


Figure 70: TIC of Troya Laminate Hardwood Burned

Table 75: Retention Times and Products of Burned Troya Laminate Hardwood

Retention time (min.)	Product
10.916	2-methoxyphenol
12.641	2-methoxy-4-methylphenol
13.961	4-ethyl-2-methoxyphenol

Sample: Teak Laminate Hardwood Unburned

Source: Buildirect (K-Swiss USA)

Abundance

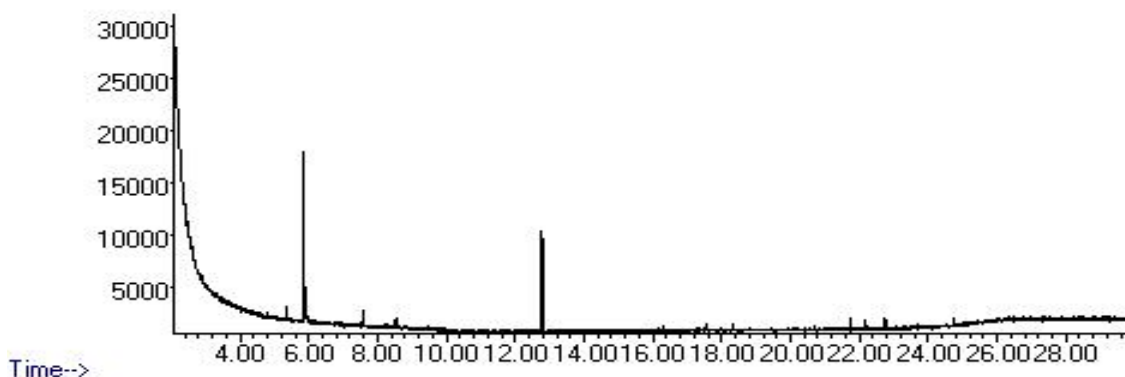


Figure 71: TIC of Teak Laminate Hardwood Unburned

Table 76: Retention Times and Products of Unburned Teak Laminate Hardwood

Retention time (min.)	Product
5.852	2-furaldehyde

Sample: Teak Laminate Hardwood Burned

Source: Buildirect (K-Swiss USA)

Abundance

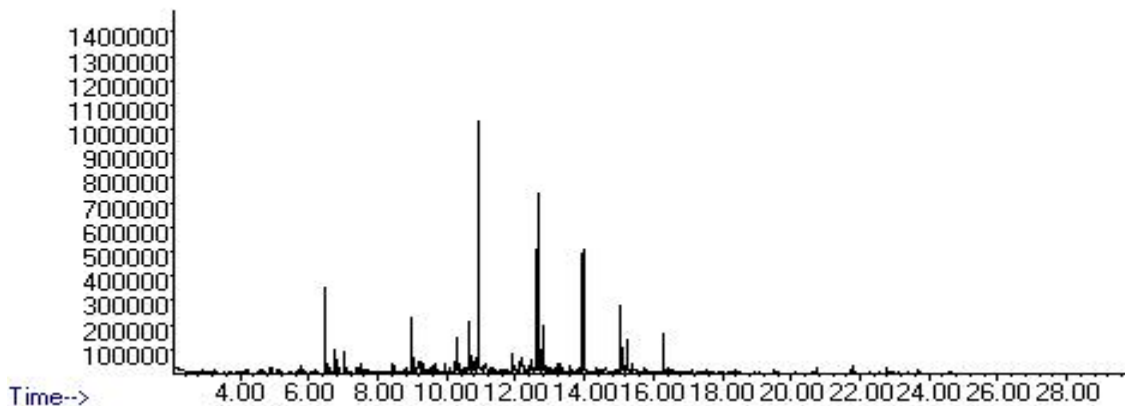


Figure 72: TIC of Teak Laminate Hardwood Burned

Table 77: Retention Times and Products of Burned Teak Laminate Hardwood

Retention time (min.)	Product
10.915	2-methoxyphenol
12.64	2-methoxy-4-methylphenol
13.96	4-ethyl-2-methoxyphenol

Sample: Clear Hard Maple Laminate Flooring Unburned

Source: Sheoga Flooring

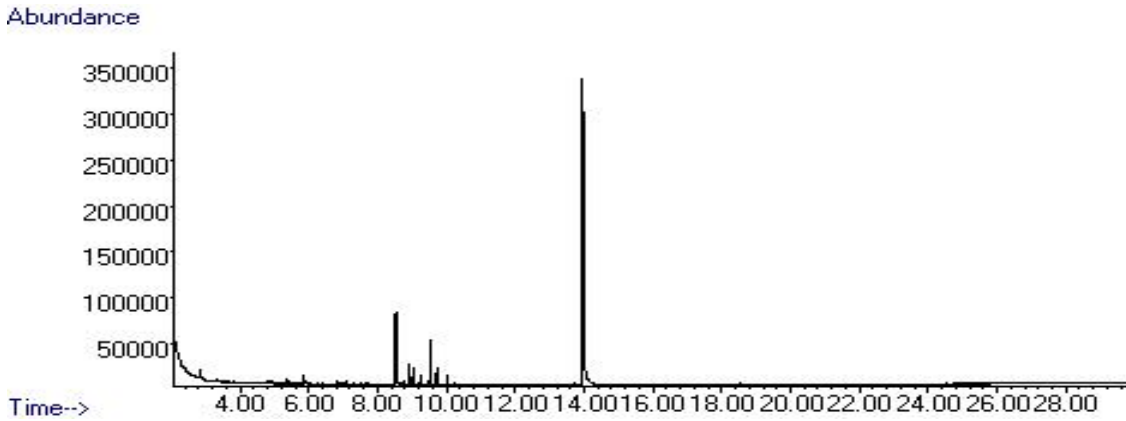


Figure 73: TIC of Clear Hard Maple Laminate Flooring Unburned

Table 78: Retention Times and Products of Unburned Clear Hard Maple Laminate Flooring

Retention time (min.)	Product
8.532	Benzaldehyde
9.524	1,2,3-trimethylbenzene

Sample: Clear Hard Maple Laminate Flooring Burned

Source: Sheoga Flooring

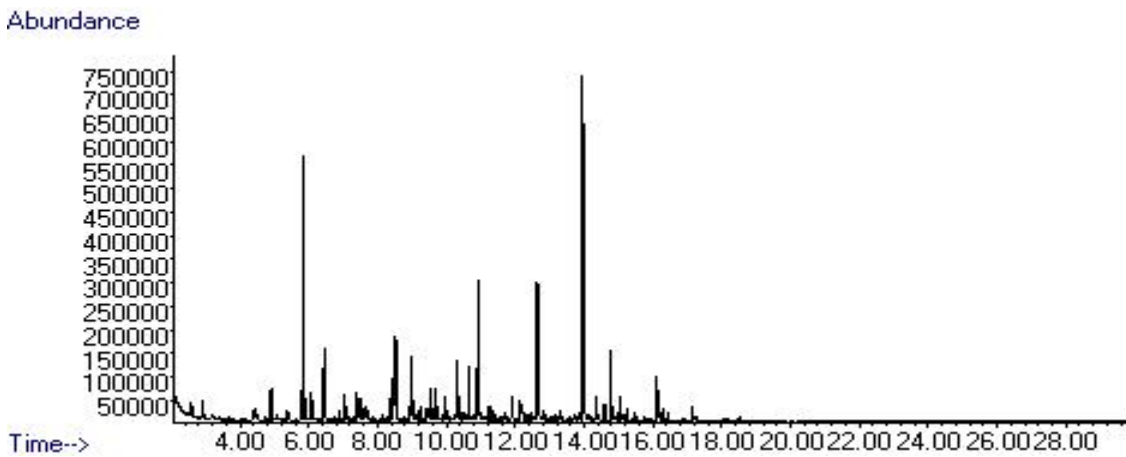


Figure 74: TIC of Clear Hard Maple Laminate Flooring Burned

Table 79: Retention Times and Products of Burned Clear Hard Maple Laminate Flooring

Retention time (min.)	Product
5.849	2-furaldehyde
10.919	2-methoxyphenol
12.645	2-methoxy-4-methylphenol

Sample: Character Walnut Laminate Flooring Unburned

Source: Sheoga Flooring

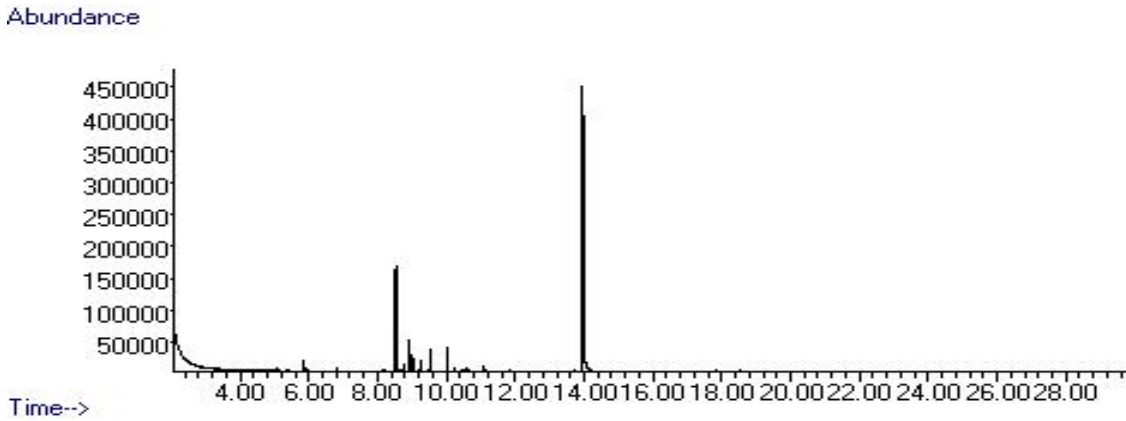


Figure 75: TIC of Character Walnut Laminate Flooring Unburned

Table 80: Retention Times and Products of Unburned Character Walnut Laminate Flooring

Retention time (min.)	Product
8.532	Benzaldehyde
9.525	1,3,5-trimethylbenzene

Sample: Character Walnut Laminate Flooring Burned

Source: Sheoga Flooring

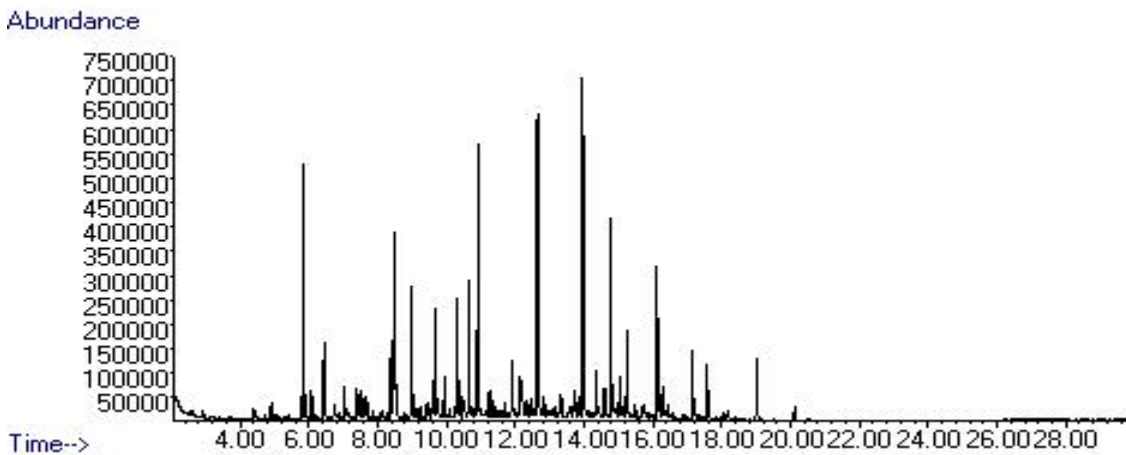


Figure 76: TIC of Character Walnut Laminate Flooring Burned

Table 81: Retention Times and Products of Burned Character Walnut Laminate Flooring

Retention time (min.)	Product
10.92	2-methoxyphenol
12.646	2-methoxy-4-methylphenol
13.967	4-ethyl-2-methoxyphenol

Sample: Clear Hickory Laminate Hardwood Flooring Unburned Source: Sheoga Flooring

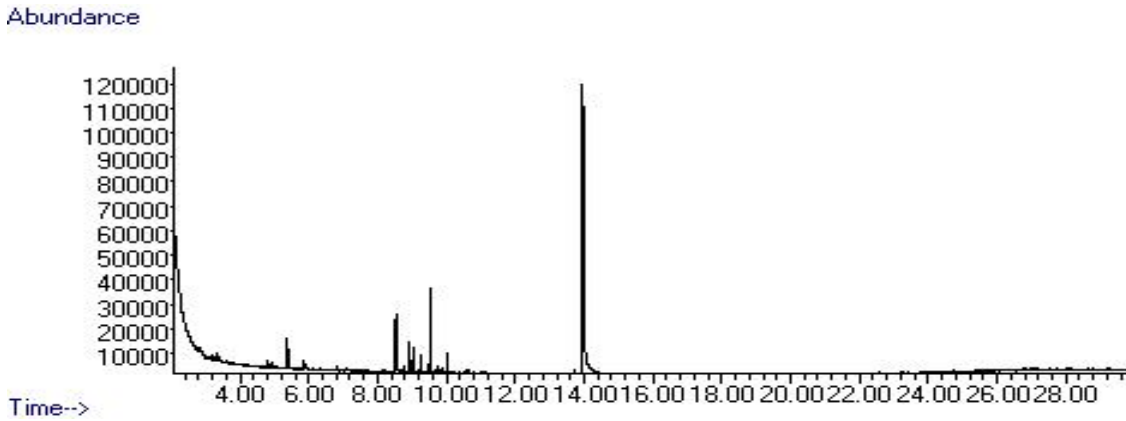


Figure 77: TIC of Clear Hickory Laminate Hardwood Flooring Unburned

Table 82: Retention Times and Products of Unburned Clear Hickory Laminate Hardwood Flooring

Retention time (min.)	Product
8.532	Benzaldehyde
9.525	1,3,5-trimethylbenzene

Sample: Clear Hickory Laminate Hardwood Flooring Burned Source: Sheoga Flooring

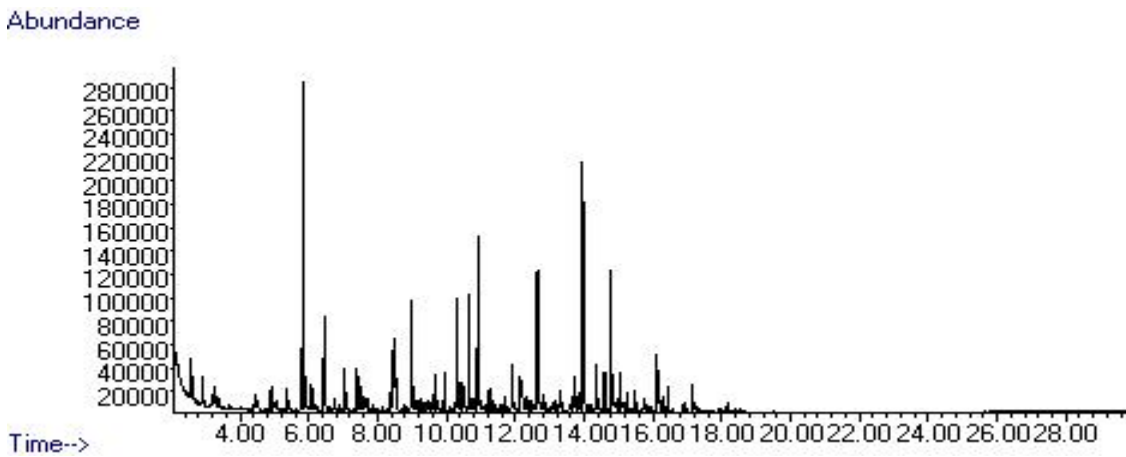


Figure 78: TIC of Clear Hickory Laminate Hardwood Flooring Burned

Table 83: Retention Times and Products of Burned Clear Hickory Laminate Hardwood Flooring

Retention time (min.)	Product
5.85	2-furaldehyde
10.92	2-methoxyphenol
12.646	2-methoxy-4-methylphenol

Sample: Clear Red Oak Hardwood Flooring Unburned

Source: Sheoga Flooring

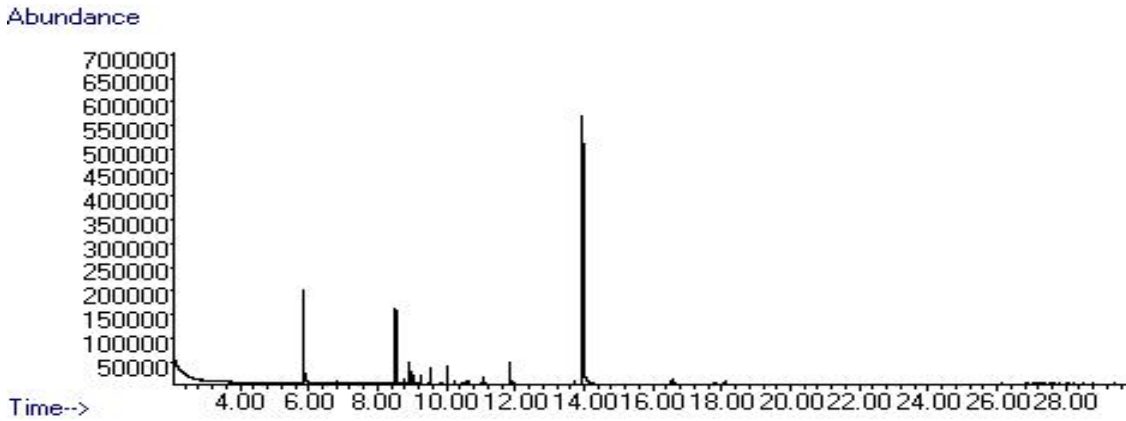


Figure 79: TIC of Clear Red Oak Hardwood Flooring Unburned

Table 84: Retention Times and Products of Unburned Clear Red Oak Hardwood Flooring

Retention time (min.)	Product
5.85	2-furaldehyde
8.532	Benzaldehyde
9.525	1,3,5-trimethylbenzene

Sample: Clear Red Oak Hardwood Flooring Burned

Source: Sheoga Flooring

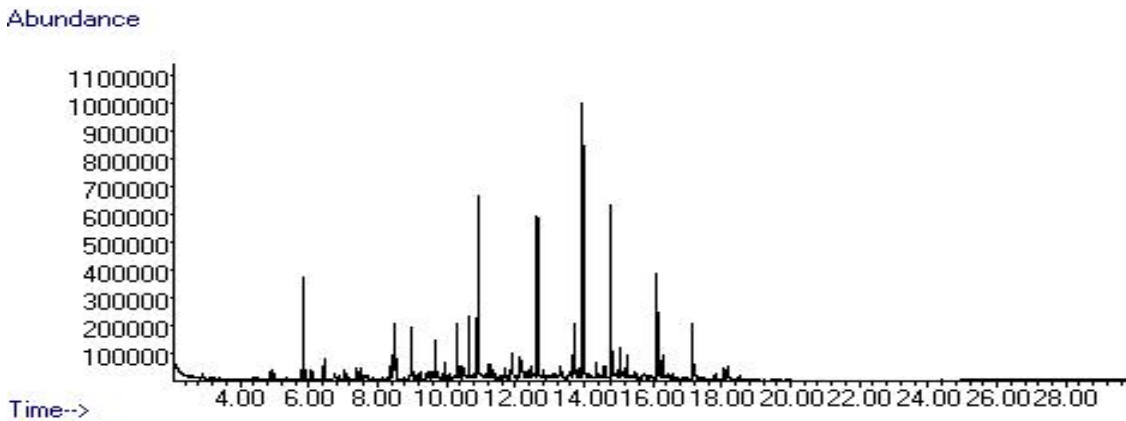


Figure 80: TIC of Clear Red Oak Hardwood Flooring Burned

Table 85: Retention Times and Products of Burned Clear Red Oak Hardwood Flooring

Retention time (min.)	Product
10.92	2-methoxyphenol
12.645	2-methoxy-4-methylphenol
14.786	2,6-dimethoxyphenol

Sample: Clear White Oak Laminate Flooring Unburned

Source: Sheoga Flooring

Unburned analysis not available due to lack of sample

Sample: Clear White Oak Laminate Flooring Burned

Source: Sheoga Flooring

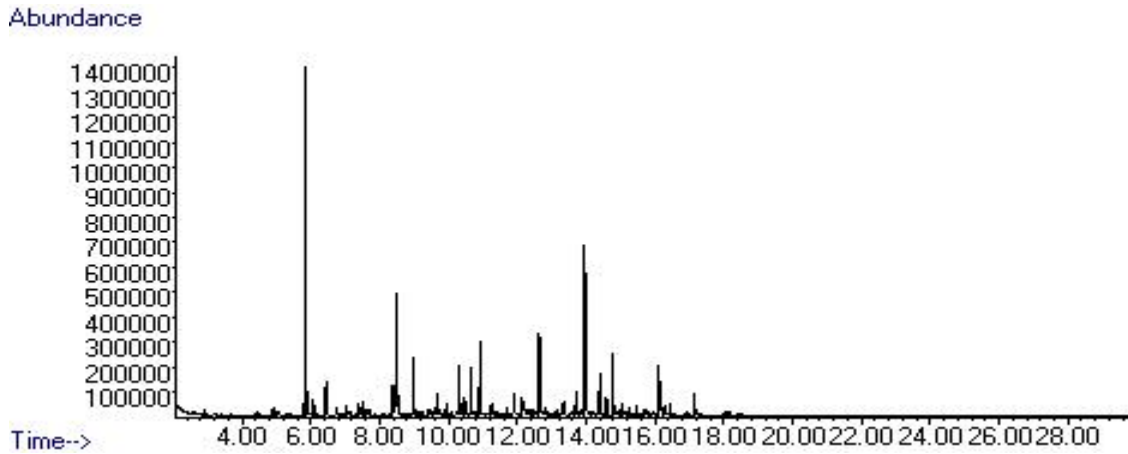


Figure 81: TIC of Clear White Oak Laminate Flooring Burned

Table 86: Retention Times and Products of Burned Clear White Oak Laminate Flooring

Retention time (min.)	Product
5.853	2-furaldehyde
8.499	5-methylfurfural
12.645	2-methoxy-4-methylphenol

Sample: Cinderblock Unburned

Source: Lowes

Abundance

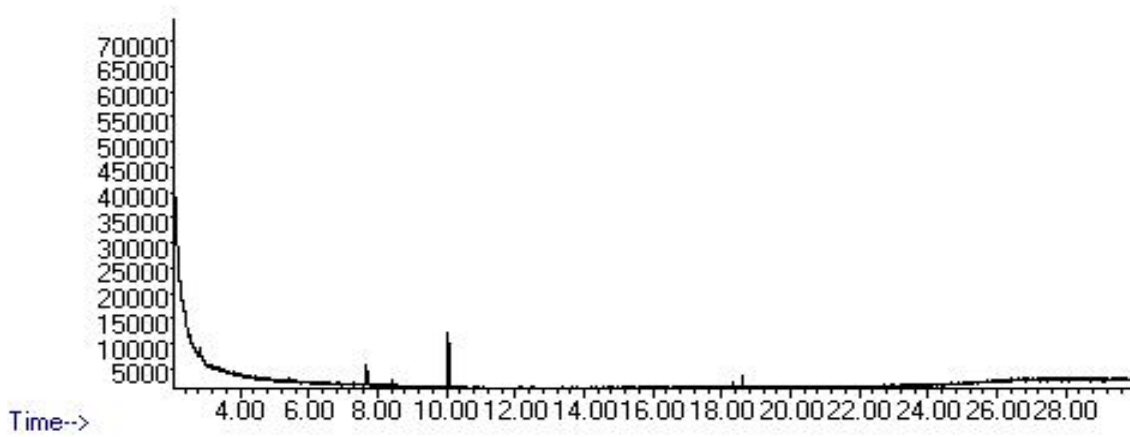


Figure 82: TIC of Cinderblock Unburned

Table 87: Retention Times and Products of Unburned Cinderblock

Retention time (min.)	Product
N/A	N/A

Sample: Cinderblock Burned

Source: Lowes

Abundance

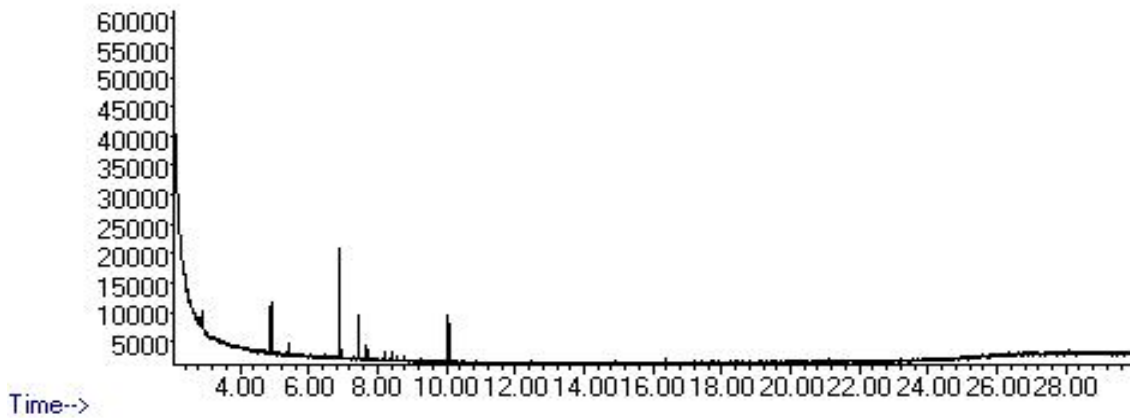


Figure 83: TIC of Cinderblock Burned

Table 88: Retention Times and Products of Burned Cinderblock

Retention time (min.)	Product
6.902	Ethylbenzene

Sample: Asphalt Roofing Shingles Unburned

Source: Lowes

Abundance

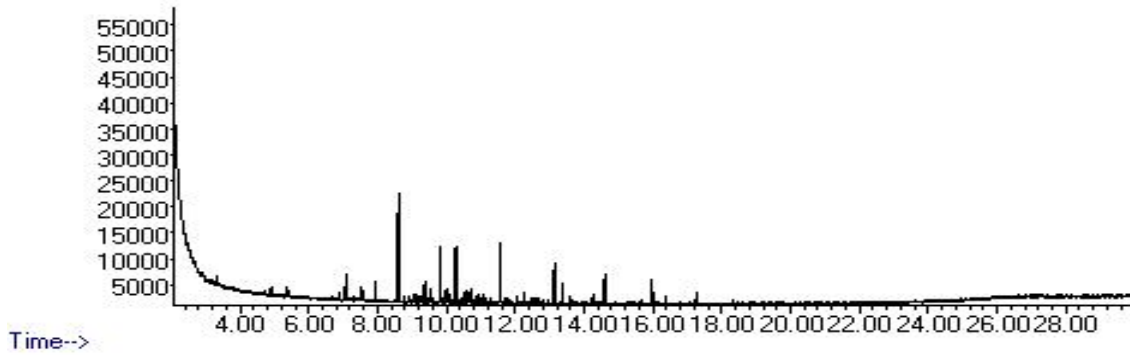


Figure 84: TIC of Asphalt Roofing Shingles Unburned

Table 89: Retention Times and Products of Unburned Asphalt Roofing Shingles

Retention time (min.)	Product
8.603	alpha-pinene
9.836	n-decane
11.556	n-undecane

Sample: Asphalt Roofing Shingles Burned

Source: Lowes

Abundance

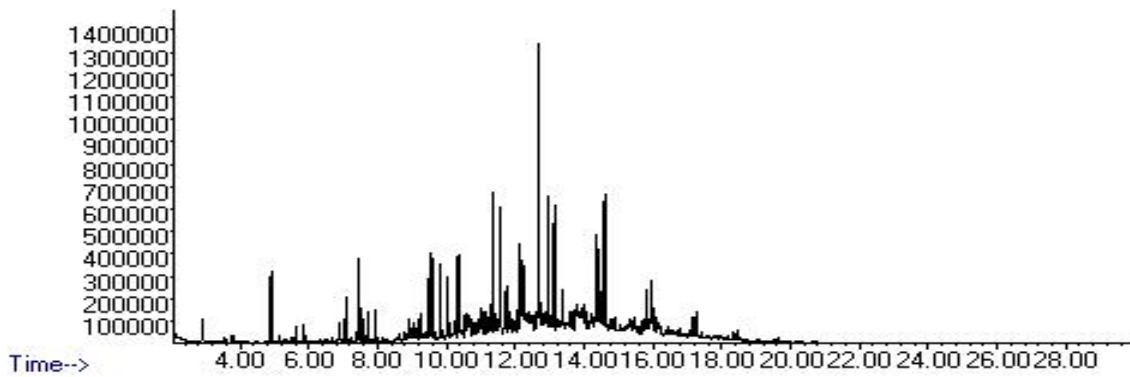


Figure 85: TIC of Asphalt Roofing Shingles Burned

Table 90: Retention Times and Products of Burned Asphalt Roofing Shingles

Retention time (min.)	Product
11.369	1-decanol
12.674	Naphthalene
14.599	n-tridecane

Sample: Roofing Tiles Unburned

Source: Hacienda Florida (Hanson)

Abundance

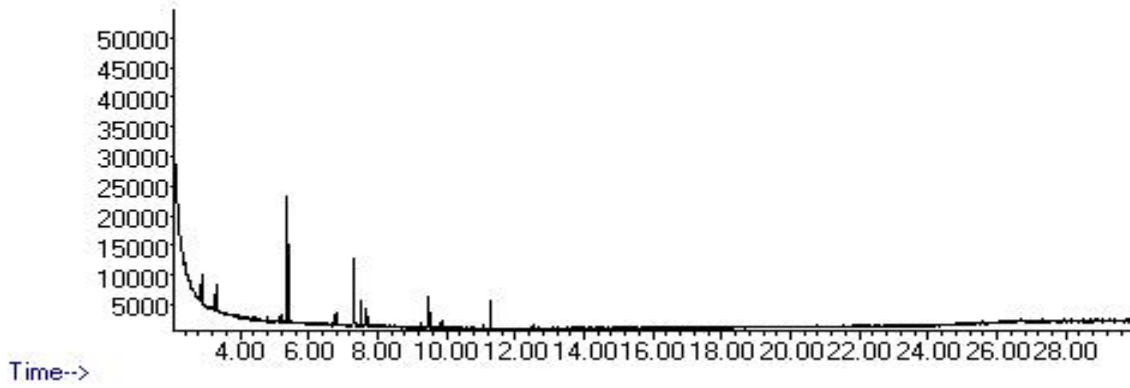


Figure 86: TIC of Roofing Tiles Unburned

Table 91: Retention Times and Products of Unburned Roofing Tiles

Retention time (min.)	Product
N/A	N/A

Sample: Roofing Tiles Burned

Source: Hacienda Florida (Hanson)

Abundance

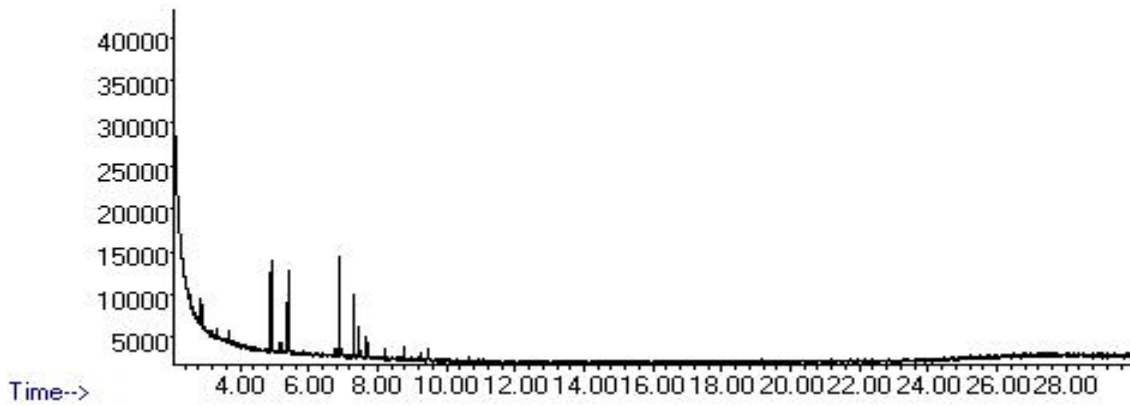


Figure 87: TIC of Roofing Tiles Burned

Table 92: Retention Times and Products of Burned Roofing Tiles

Retention time (min.)	Product
N/A	N/A

Sample: Foil Insulation Unburned

Source: Lowes (Reflectrix)

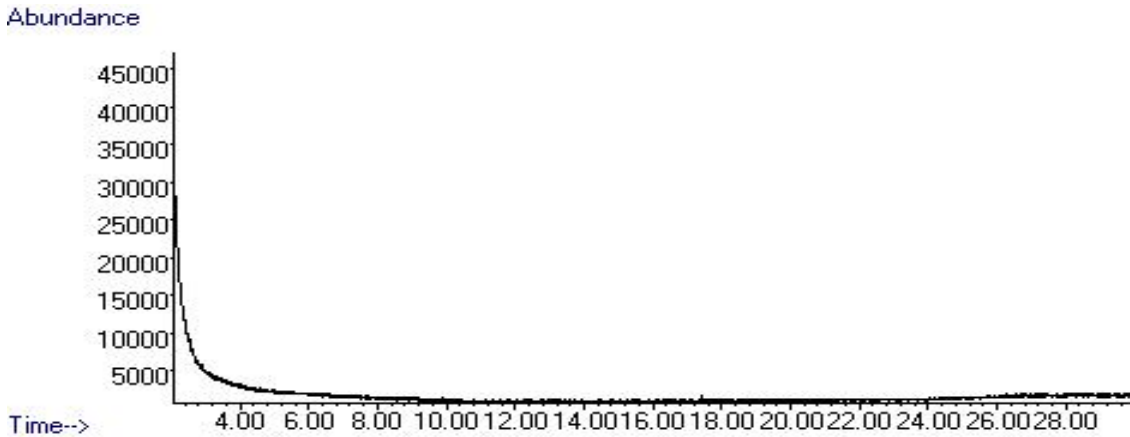


Figure 88: TIC of Foil Insulation Unburned

Table 93: Retention Times and Products of Unburned Foil Insulation

Retention time (min.)	Product
N/A	N/A

Sample: Foil Insulation Burned

Source: Lowes (Reflectrix)

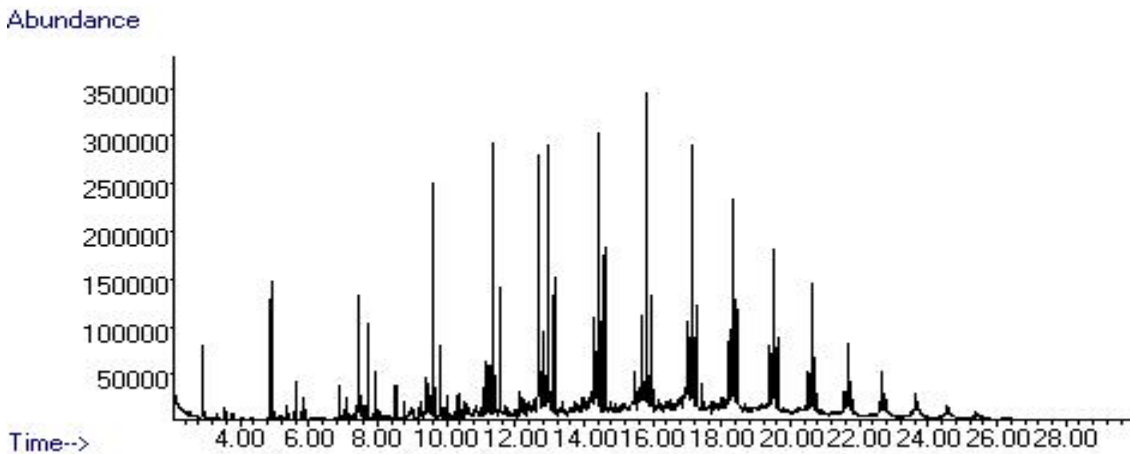


Figure 89: TIC of Foil Insulation Burned

Table 94: Retention Times and Products of Burned Foil Insulation

Retention time (min.)	Product
14.443	1-tridecene
15.826	1-tetradecene
17.125	1-pentadecene

Sample: Fiberglass Insulation Unburned

Source: Lowes (Frost King)

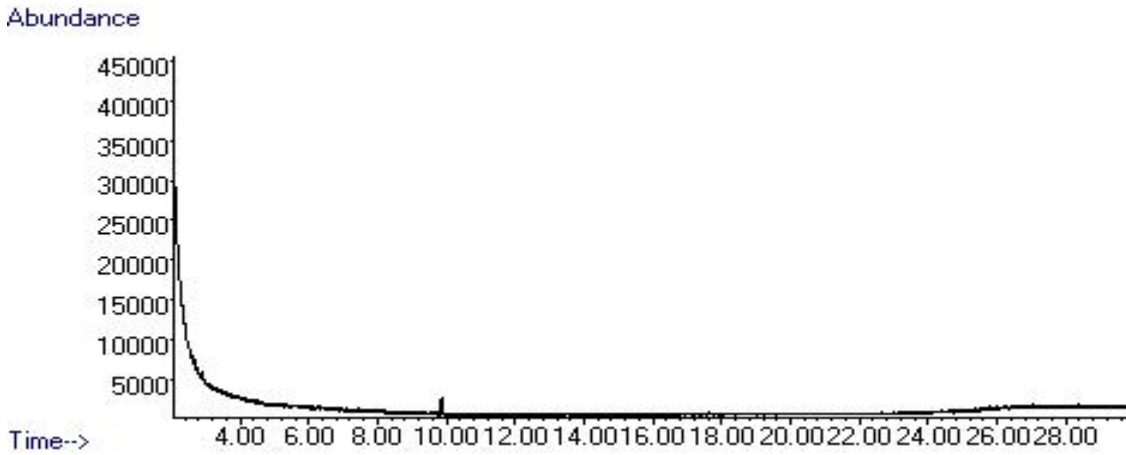


Figure 90: TIC of Fiberglass Insulation Unburned

Table 95: Retention Times and Products of Unburned Fiberglass Insulation

Retention time (min.)	Product
N/A	N/A

Sample: Fiberglass Insulation Burned

Source: Lowes (Frost King)

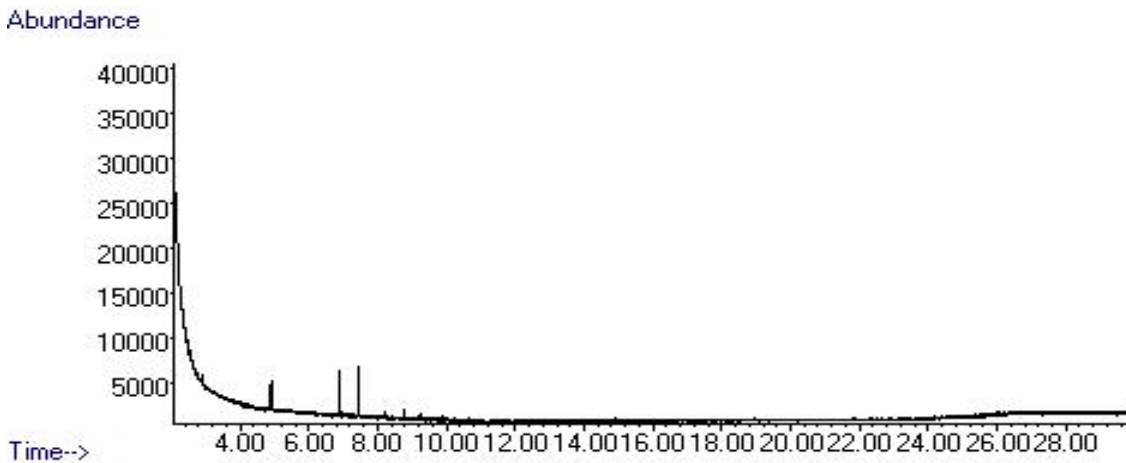


Figure 91: TIC of Fiberglass Insulation Burned

Table 96: Retention Times and Products of Burned Fiberglass Insulation

Retention time (min.)	Product
N/A	N/A

Sample: Black Leather Unburned

Source: Jo-Ann Fabric

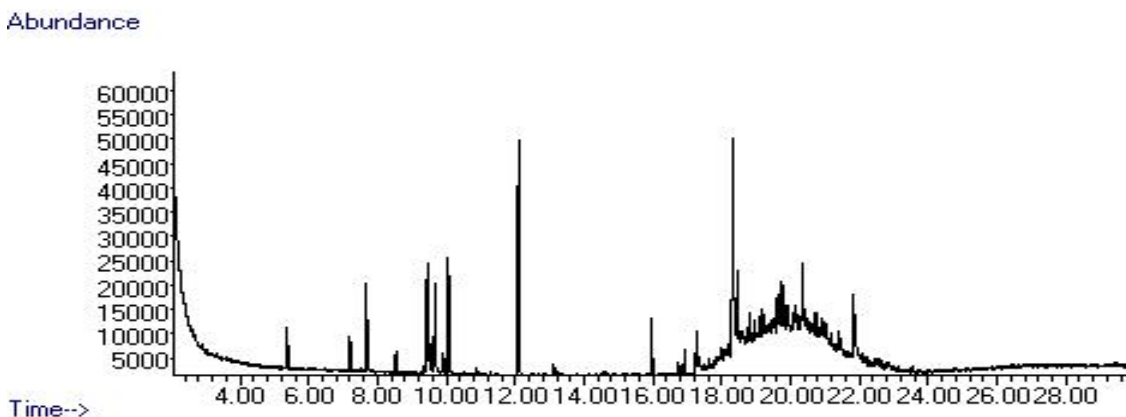


Figure 92: TIC of Black Leather Unburned

Table 97: Retention Times and Products of Unburned Black Leather

Retention time (min.)	Product
10.057	2-ethyl-1-hexanol
12.092	2-ethylhexyl ester acetic acid
18.317	2,2,4-trimethyl-3-carboxyisopropyl isobutyl ester pentanoic acid

Sample: Black Leather Burned

Source: Jo-Ann Fabric

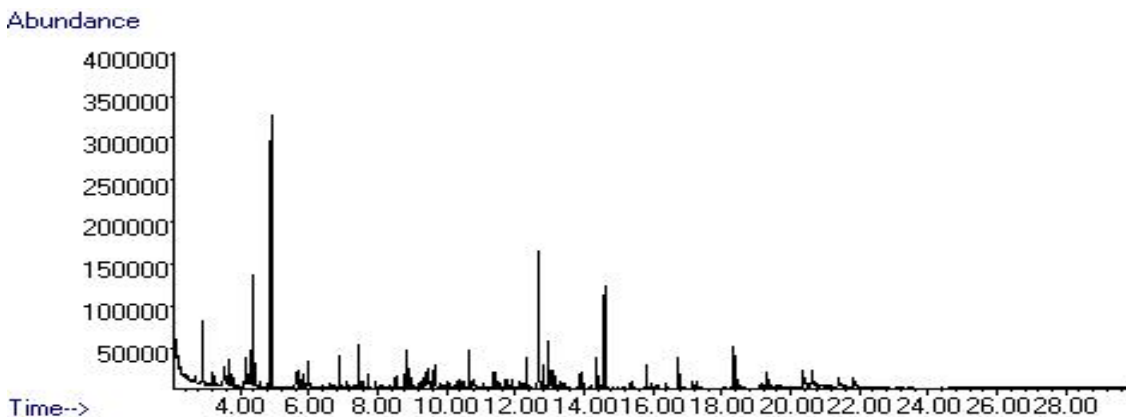


Figure 93: TIC of Black Leather Burned

Table 98: Retention Times and Products of Burned Black Leather

Retention time (min.)	Product
4.906	Toluene
12.673	Naphthalene
14.599	1-methylnaphthalene

Sample: 100% Cotton Pajama Pants Unburned

Source: Target

Abundance

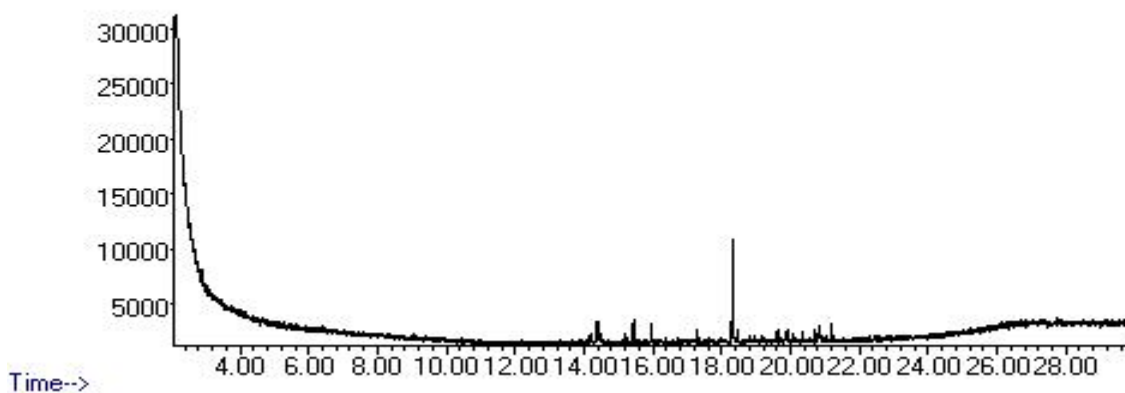


Figure 94: TIC of 100% Cotton Pajama Pants Unburned

Table 99: Retention Times and Products of Unburned 100% Cotton Pajama Pants

Retention time (min.)	Product
N/A	N/A

Sample: 100% Cotton Pajama Pants Burned

Source: Target

Abundance

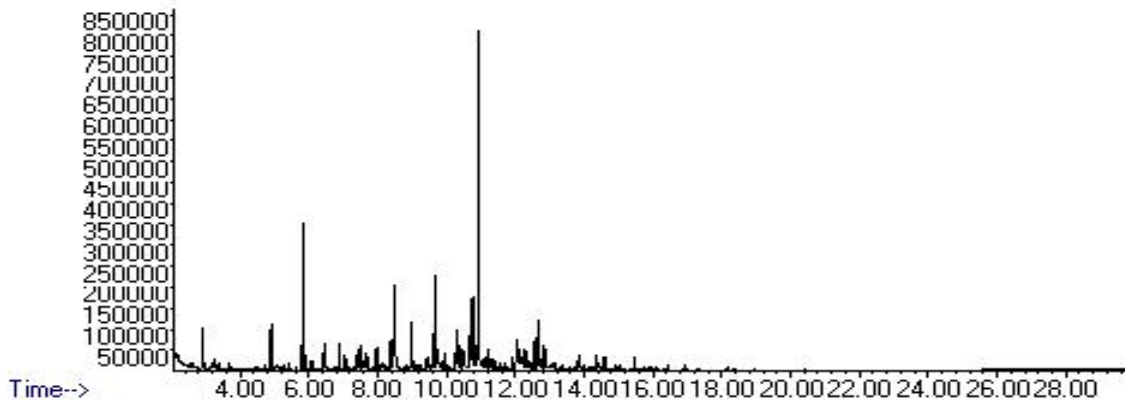


Figure 95: TIC of 100% Cotton Pajama Pants Burned

Table 100: Retention Times and Products of Burned 100% Cotton Pajama Pants

Retention time (min.)	Product
5.849	2-furaldehyde
8.498	5-methylfurfural
9.692	2-hydroxy-3-methyl-2-cyclopenten-1-one

Sample: 100% Polyester Quilt Batting Unburned

Source: Jo-Ann Fabric

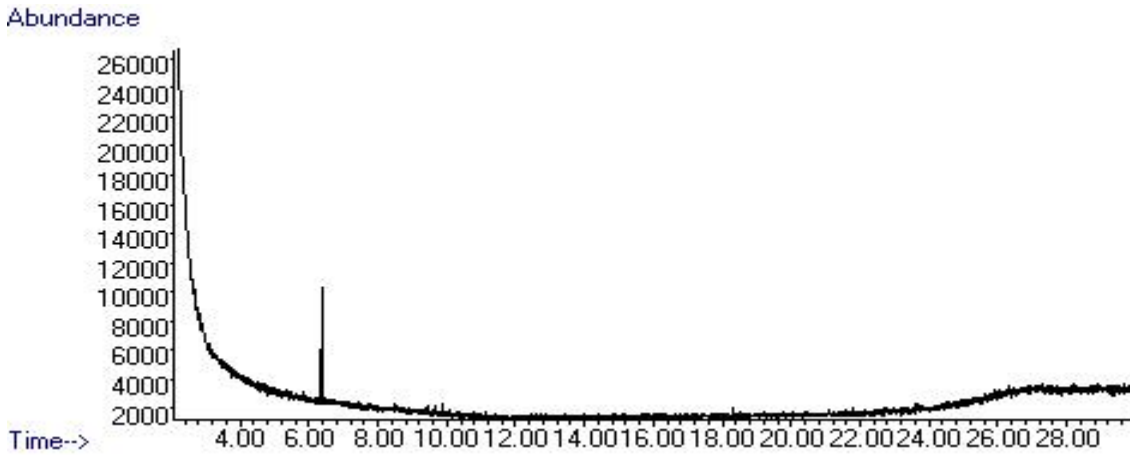


Figure 96: TIC of 100% Polyester Quilt Batting Unburned

Table 101: Retention Times and Products of Unburned 100% Polyester Quilt Batting

Retention time (min.)	Product
N/A	N/A

Sample: 100% Polyester Quilt Batting Burned

Source: Jo-Ann Fabric

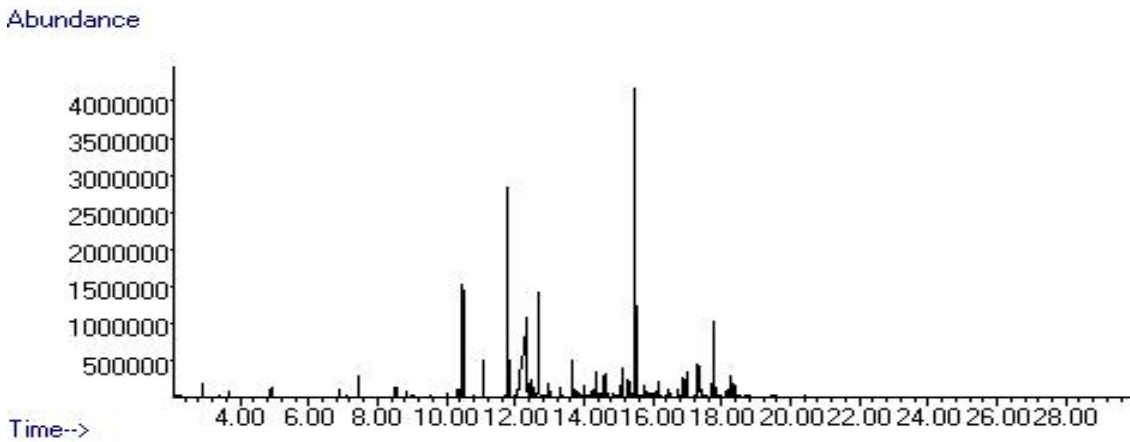


Figure 97: TIC of 100% Polyester Quilt Batting Burned

Table 102: Retention Times and Products of Burned 100% Polyester Quilt Batting

Retention time (min.)	Product
11.793	1-phenyl-1,2-propanedione
12.677	Naphthalene
15.488	Biphenyl

Sample: 100% Polyurethane Foam Mattress Pad Unburned

Source: Jo-Ann Fabric

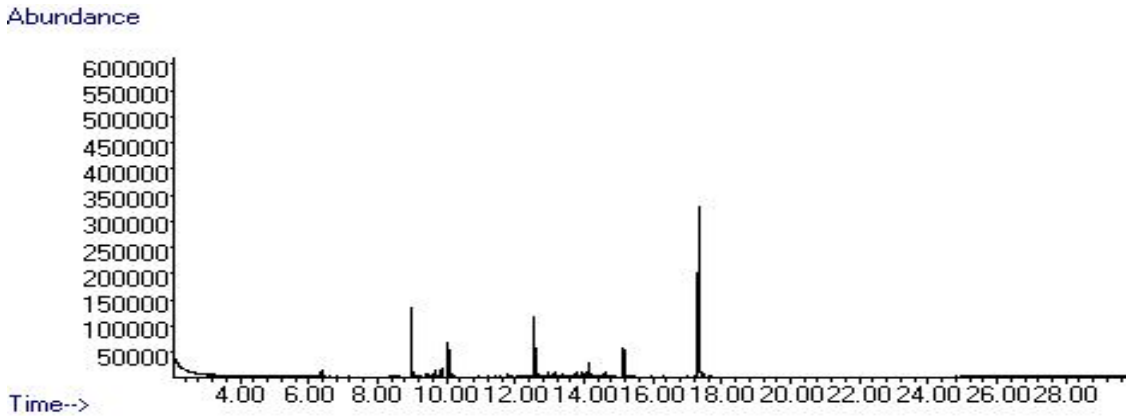


Figure 98: TIC of 100% Polyurethane Foam Mattress Pad Unburned

Table 103: Retention Times and Products of Unburned 100% Polyurethane Foam Mattress Pad

Retention time (min.)	Product
8.984	Phenol
10.056	2-ethyl-1-hexanol
17.329	5,6-dipropyldecane

Sample: 100% Polyurethane Foam Mattress Pad Burned

Source: Jo-Ann Fabric

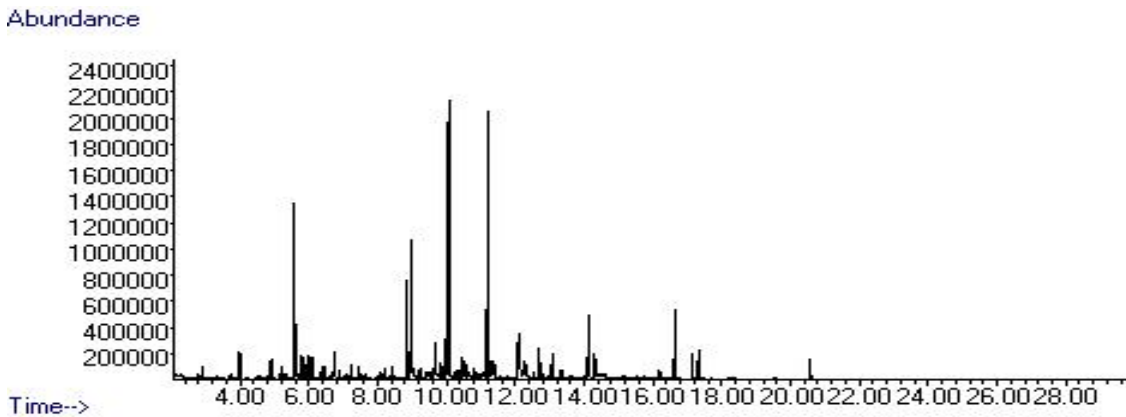


Figure 99: TIC of 100% Polyurethane Foam Mattress Pad Burned

Table 104: Retention Times and Products of Burned 100% Polyurethane Foam Mattress Pad

Retention time (min.)	Product
5.581	2-methyl-4-methylenehexane
8.99	Phenol
11.20	3-(bromomethyl)heptane

Sample: Thermal Paper Unburned

Source: Office Max



Figure 100: TIC of Thermal Paper Unburned

Table 105: Retention Times and Products of Unburned Thermal Paper

Retention time (min.)	Product
4.905	Toluene
20.412	1,1-(1,2-ethanediylbis(oxy))bis-benzene

Sample: Thermal Paper Burned

Source: Office Max

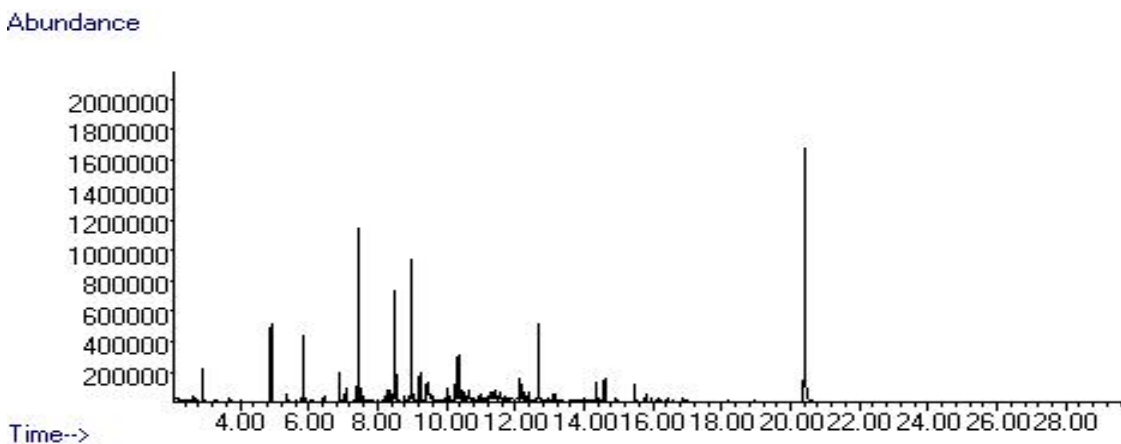


Figure 101: TIC of Thermal Paper Burned

Table 106: Retention Times and Products of Burned Thermal Paper

Retention time (min.)	Product
5.854	2-furaldehyde
7.44	Styrene
8.51	5-methylfurfural

Sample: Cardboard Box Unburned

Source: Dasani

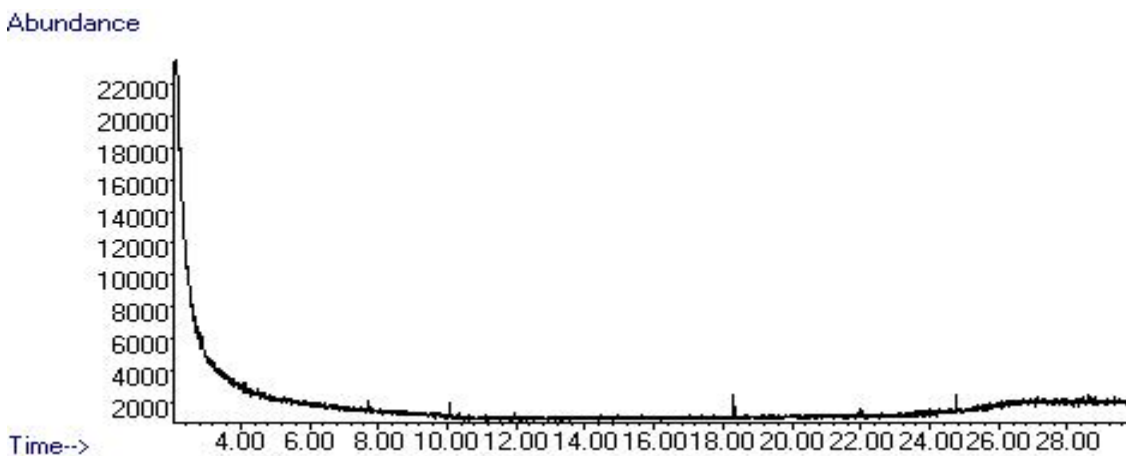


Figure 102: TIC of Cardboard Box Unburned

Table 107: Retention Times and Products of Unburned Cardboard Box

Retention time (min.)	Product
N/A	N/A

Sample: Cardboard Box Burned

Source: Dasani

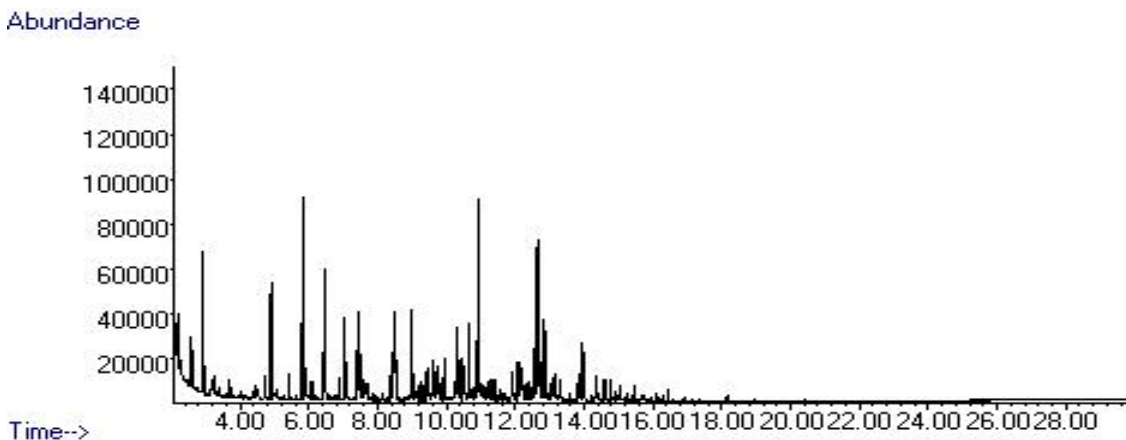


Figure 103: TIC of Cardboard Box Burned

Table 108: Retention Times and Products of Burned Cardboard Box

Retention time (min.)	Product
5.85	2-furaldehyde
10.921	2-methoxyphenol
12.646	2-methoxy-4-methylphenol

Sample: Finegrain Cork Tiles Unburned

Source: Office Max

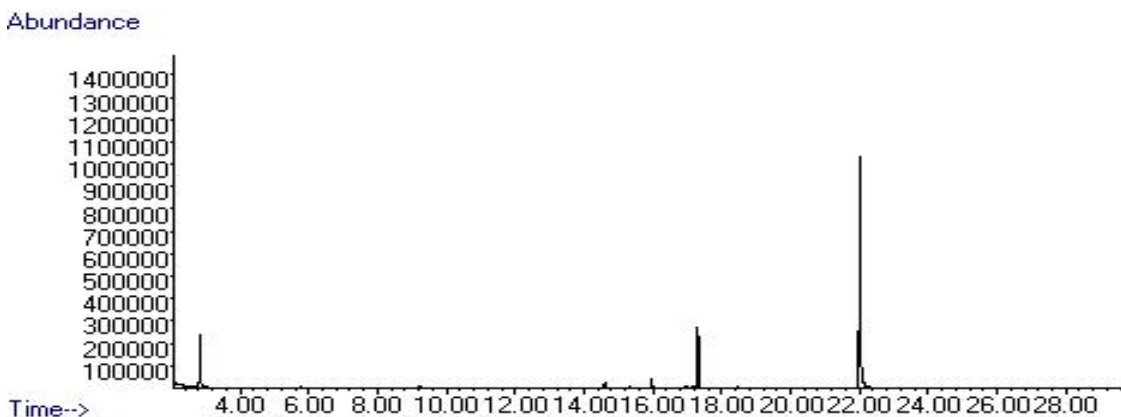


Figure 104: TIC of Finegrain Cork Tiles Unburned

Table 109: Retention Times and Products of Unburned Finegrain Cork Tiles

Retention time (min.)	Product
15.972	n-tetradecane
17.314	1,2,4a,5,6,8a-hexahydro-4-7-dimethyl-1-(1-methylethyl)naphthalene
22.01	Dibutyl phthalate

Sample: Finegrain Cork Tiles Burned

Source: Office Max

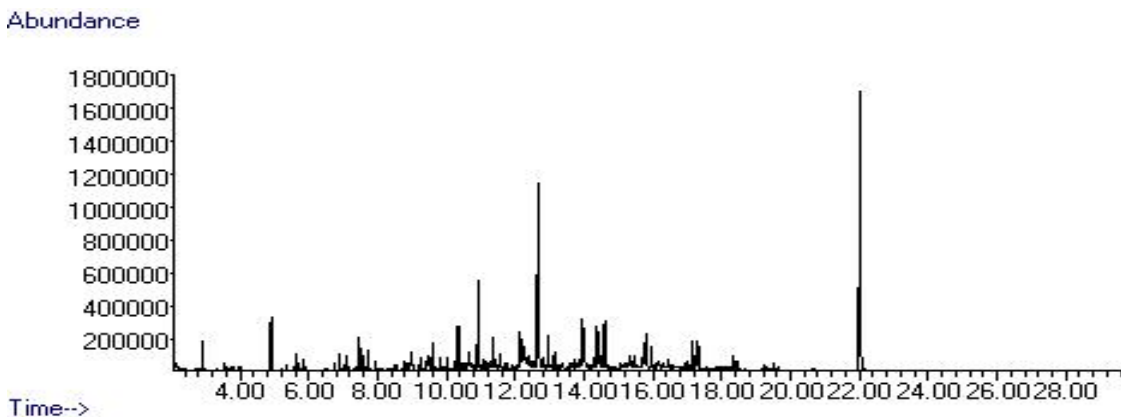


Figure 105: TIC of Finegrain Cork Tiles Burned

Table 110: Retention Times and Products of Burned Finegrain Cork Tiles

Retention time (min.)	Product
10.921	2-methoxyphenol
12.674	Naphthalene
22.009	Dibutyl phthalate

Sample: Magazine Unburned

Source: Orlando Visitor Guide

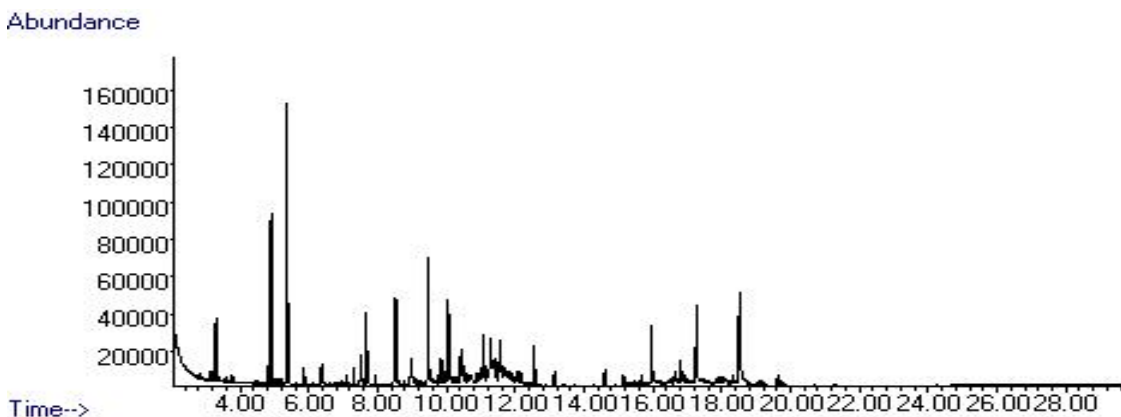


Figure 106: TIC of Magazine Unburned

Table 111: Retention Times and Products of Unburned Magazine

Retention time (min.)	Product
4.904	Toluene
5.369	Hexanal
9.464	2-pentylfuran

Sample: Magazine Burned

Source: Orlando Visitor Guide

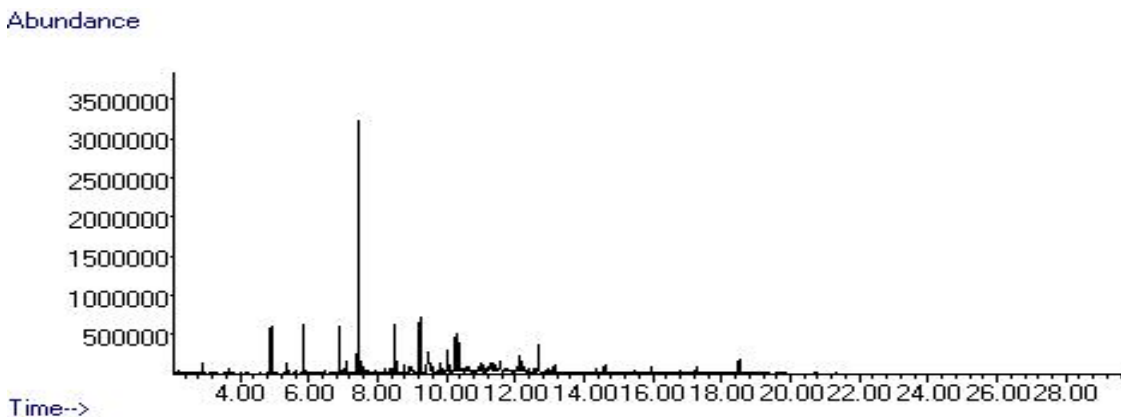


Figure 107: TIC of Magazine Burned

Table 112: Retention Times and Products of Burned Magazine

Retention time (min.)	Product
6.901	Ethylbenzene
7.442	Styrene
8.50	5-methylfurfural

Sample: Diamond Braid Polyester Rope Unburned

Source: Lowes

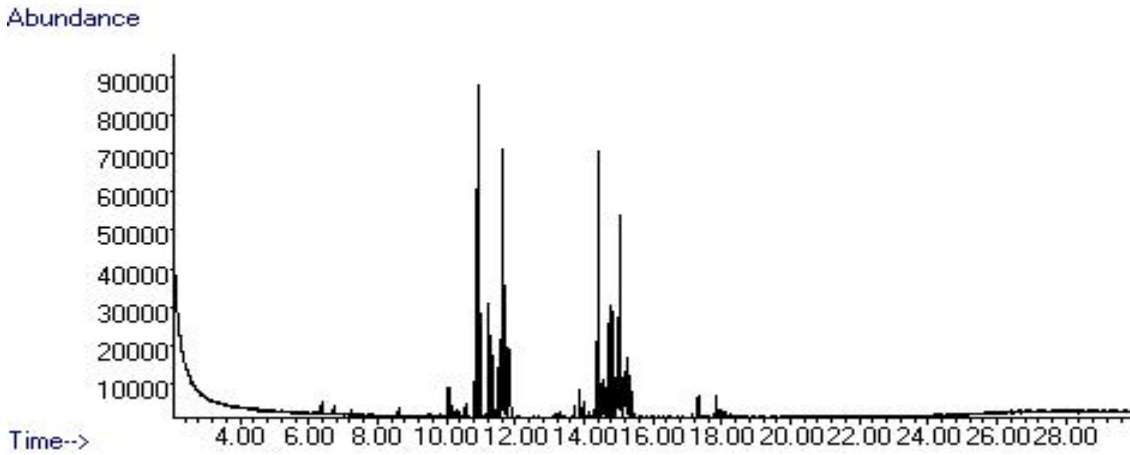


Figure 108: TIC of Diamond Braid Polyester Rope Unburned

Table 113: Retention Times and Products of Unburned Diamond Braid Polyester Rope

Retention time (min.)	Product
N/A	N/A

Sample: Diamond Braid Polyester Rope Burned

Source: Lowes

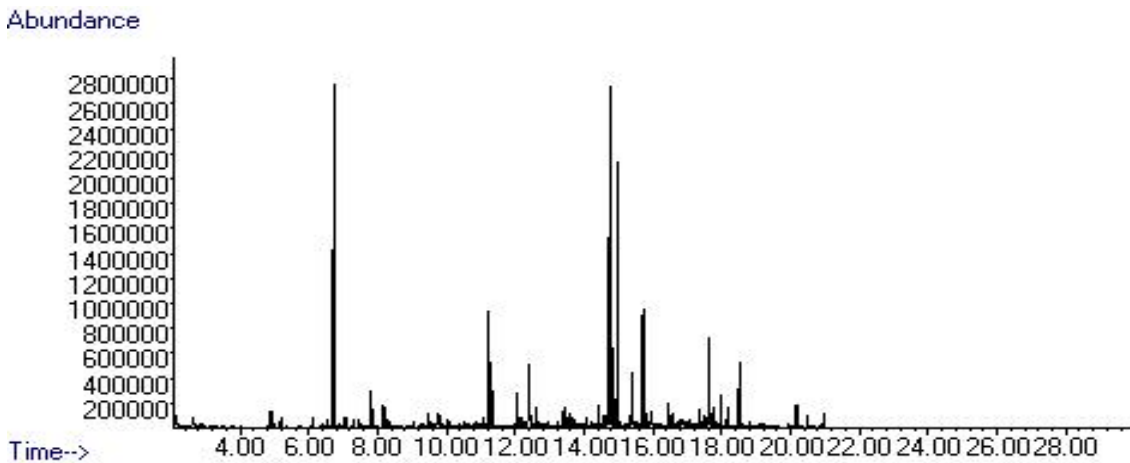


Figure 109: TIC of Diamond Braid Polyester Rope Burned

Table 114: Retention Times and Products of Burned Diamond Braid Polyester Rope

Retention time (min.)	Product
N/A	N/A

Sample: Twisted Nylon Rope Unburned

Source: Lowes

Abundance

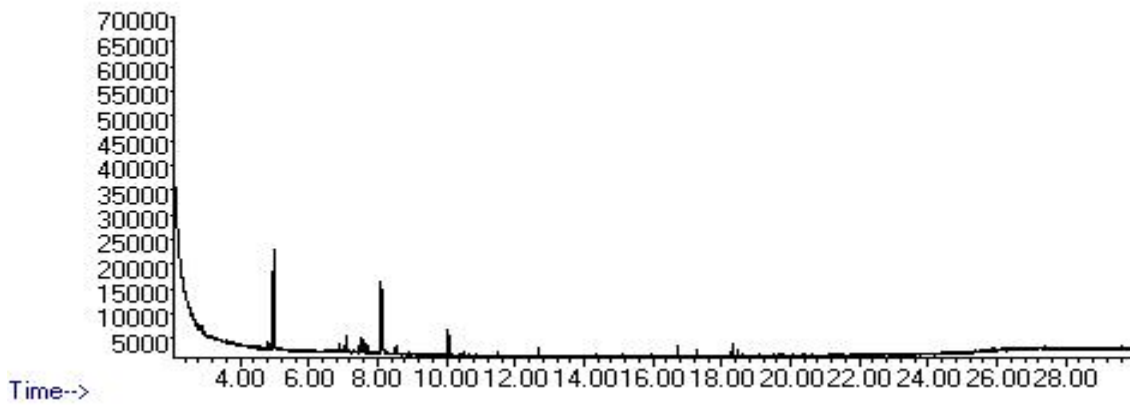


Figure 110: TIC of Twisted Nylon Rope Unburned

Table 115: Retention Times and Products of Unburned Twisted Nylon Rope

Retention time (min.)	Product
N/A	N/A

Sample: Twisted Nylon Rope Burned

Source: Lowes

Abundance

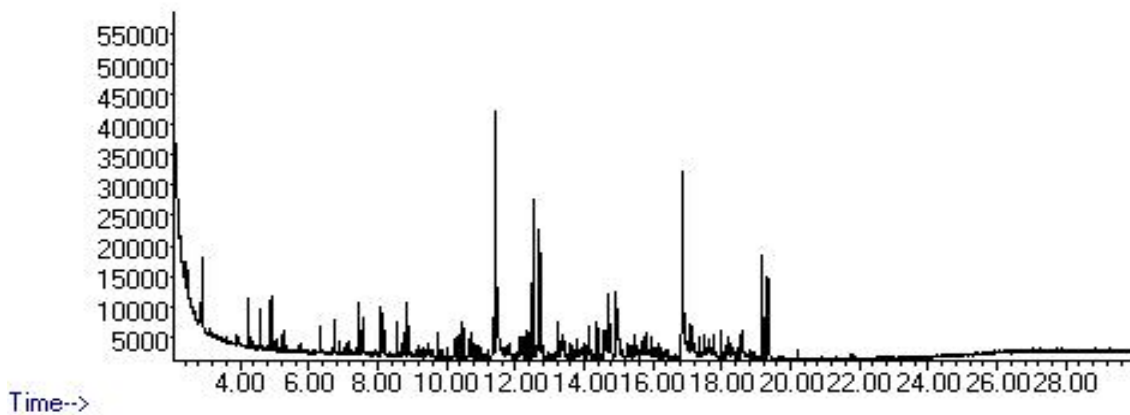


Figure 111: TIC of Twisted Nylon Rope Burned

Table 116: Retention Times and Products of Burned Twisted Nylon Rope

Retention time (min.)	Product
11.432	Hexanedinitrile

Sample: White Casual Shoe Unburned

Source: Skechers

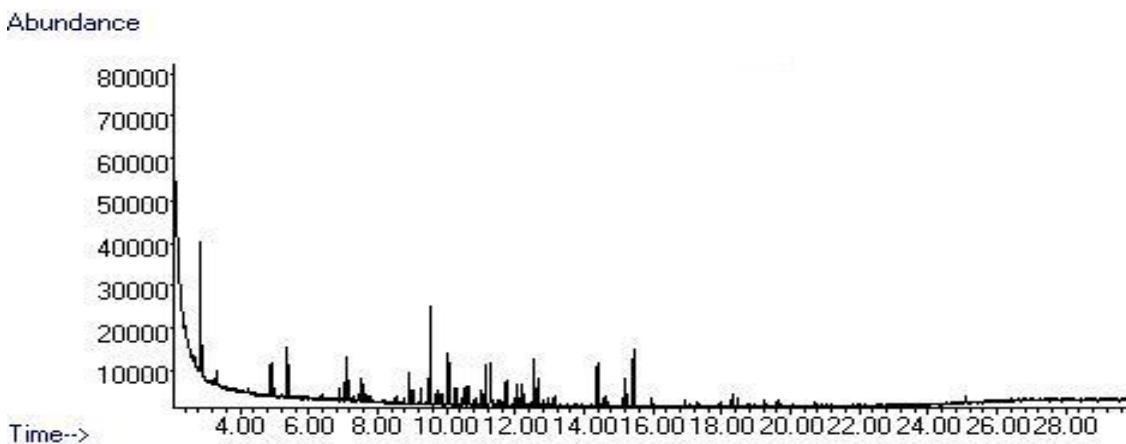


Figure 112: TIC of White Casual Shoe Unburned

Table 117: Retention Times and Products of Unburned White Casual Shoe

Retention time (min.)	Product
9.524	1,2,4-trimethylbenzene

Sample: White Casual Shoe Burned

Source: Skechers

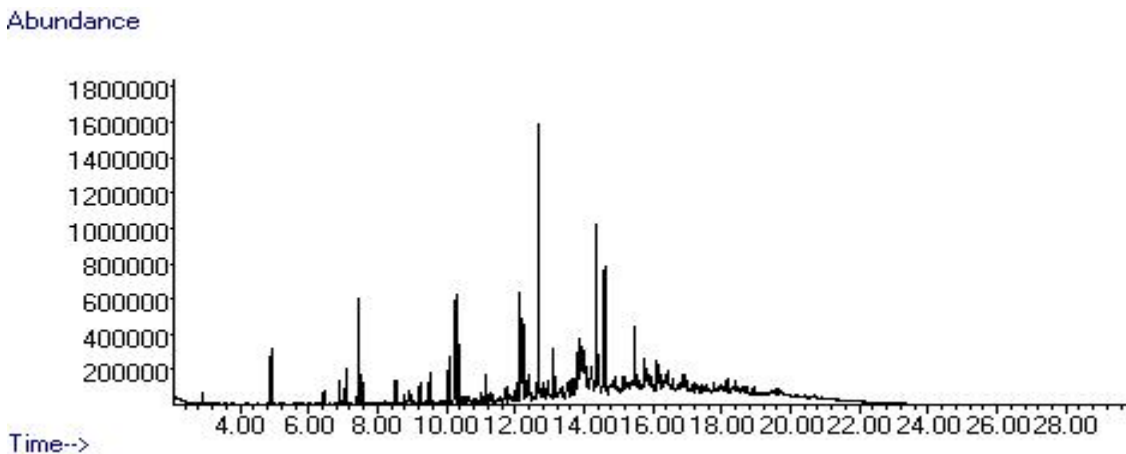


Figure 113: TIC of White Casual Shoe Burned

Table 118: Retention Times and Products of Burned White Casual Shoe

Retention time (min.)	Product
12.151	2-methylindene
12.674	Naphthalene
14.367	1-methylnaphthalene

Sample: Flip Flops Unburned

Source: Old Navy

Abundance

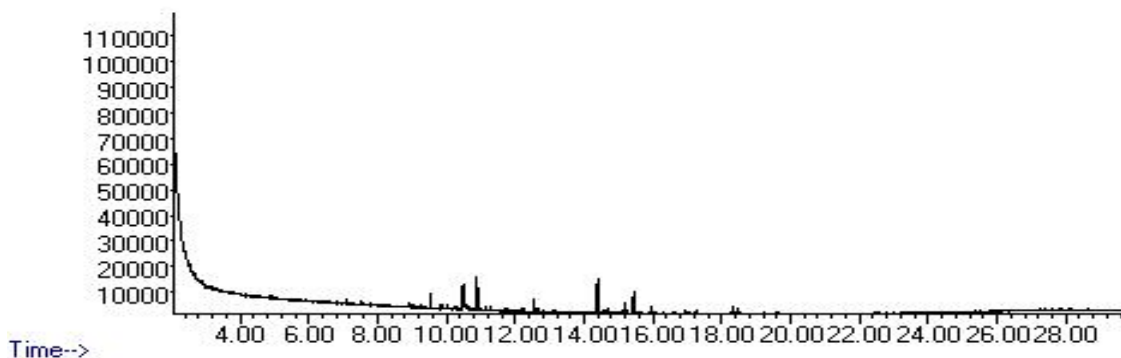


Figure 114: TIC of Flip Flops Unburned

Table 119: Retention Times and Products of Unburned Flip Flops

Retention time (min.)	Product
N/A	N/a

Sample: Flip Flops Burned

Source: Old Navy

Abundance

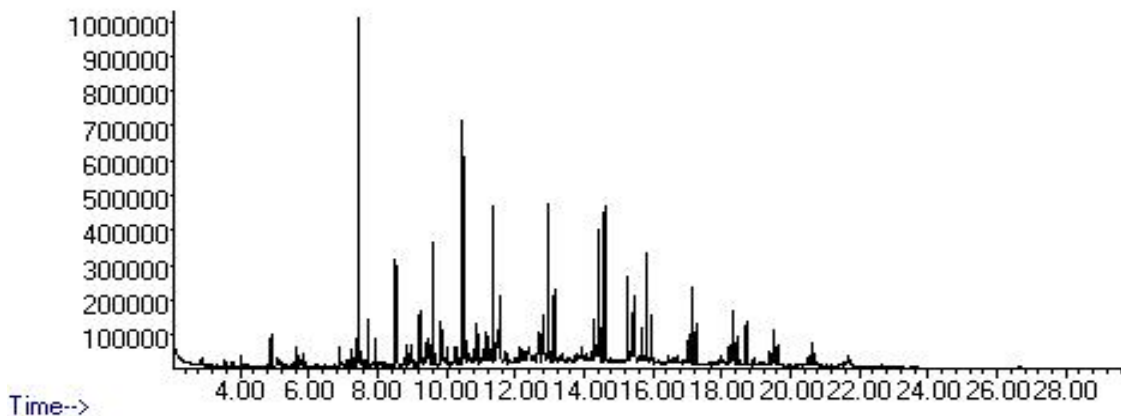


Figure 115: TIC of Flip Flops Burned

Table 120: Retention Times and Products of Burned Flip Flops

Retention time (min.)	Product
7.438	Styrene
10.478	Acetophenone
12.963	1-dodecene

Sample: Rain Boot Shoe Covering Unburned

Source: Walmart

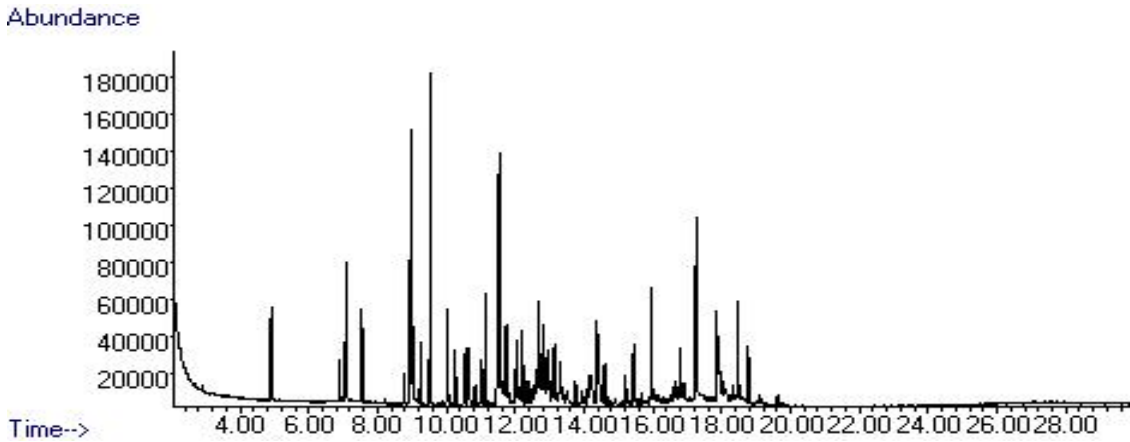


Figure 116: TIC of Rain Boot Shoe Covering Unburned

Table 121: Retention Times and Products of Unburned Rain Boot Shoe Covering

Retention time (min.)	Product
8.982	Phenol
9.524	1,2,4-trimethylbenzene
11.533	2-ethylhexanoic acid

Sample: Rain Boot Shoe Covering Burned

Source: Walmart

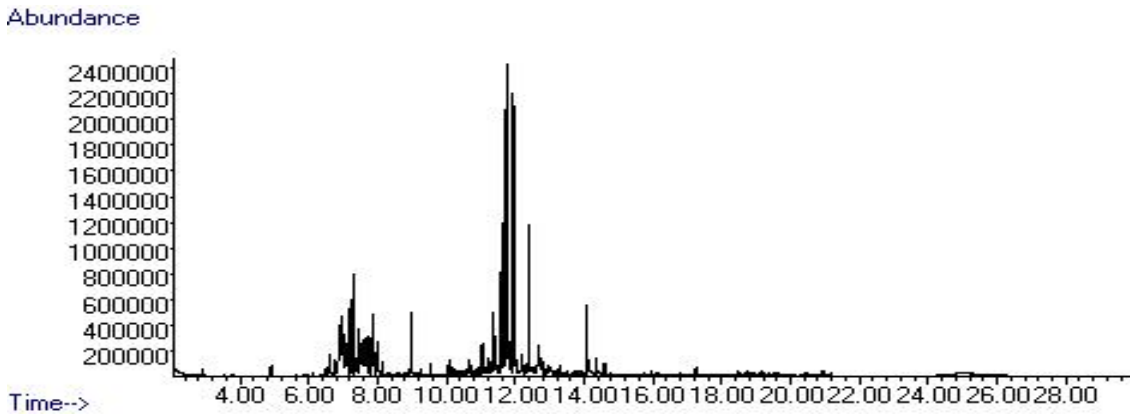


Figure 117: TIC of Rain Boot Shoe Covering Burned

Table 122: Retention Times and Products of Burned Rain Boot Shoe Covering

Retention time (min.)	Product
8.982	Phenol
14.082	Phthalic anhydride

Sample: Brown Casual Shoe Unburned

Source: Steve Madden

Abundance

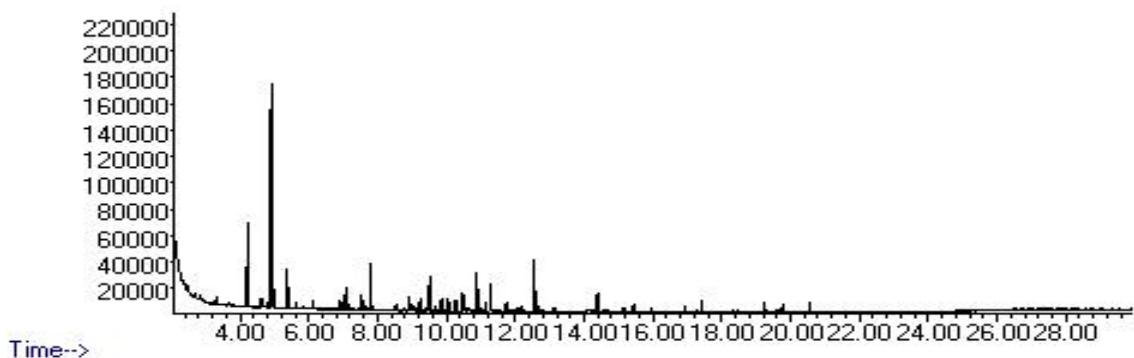


Figure 118: TIC of Brown Casual Shoe Unburned

Table 123: Retention Times and Products of Unburned Brown Casual Shoe

Retention time (min.)	Product
4.222	Mehtylcyclohexane
4.907	Toluene
5.375	Hexanal

Sample: Brown Casual Shoe Burned

Source: Steve Madden

Abundance

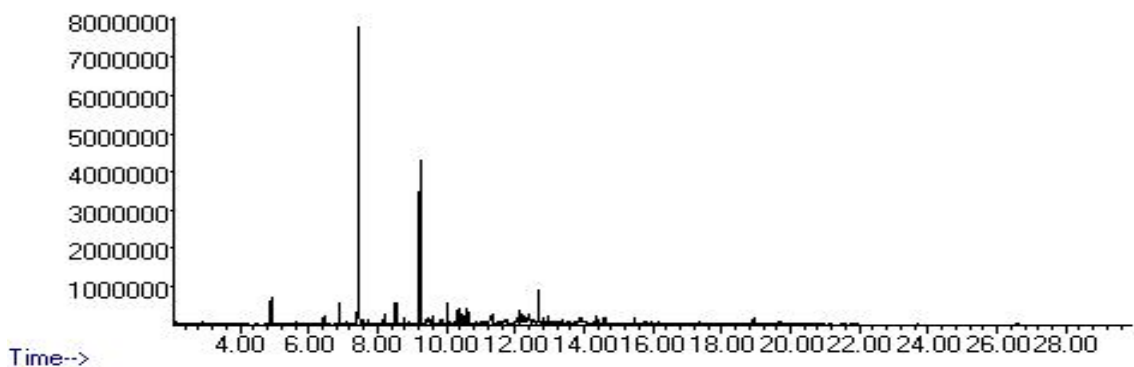


Figure 119: TIC of Brown Casual Shoe Burned

Table 124: Retention Times and Products of Burned Brown Casual Shoe

Retention time (min.)	Product
7.457	Styrene
9.235	alpha-methylstyrene
12.672	Naphthalene

Sample: Street Smart Boots Unburned

Source: Payless Shoe Store

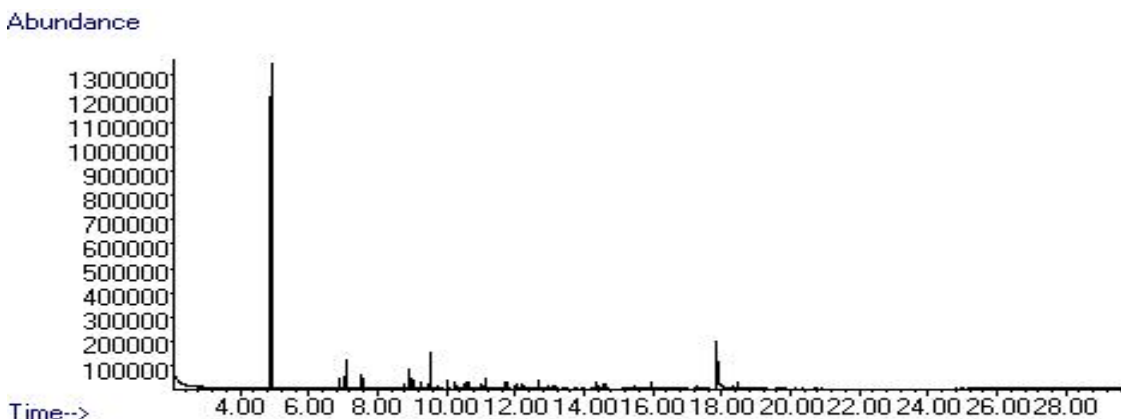


Figure 120: TIC of Street Smart Boots Unburned

Table 125: Retention Times and Products of Unburned Street Smart Boots

Retention time (min.)	Product
4.907	Toluene
9.524	1,2,4-trimethylbenzene
17.684	Diethyltoluamide

Sample: Street Smart Boots Burned

Source: Payless Shoe Store

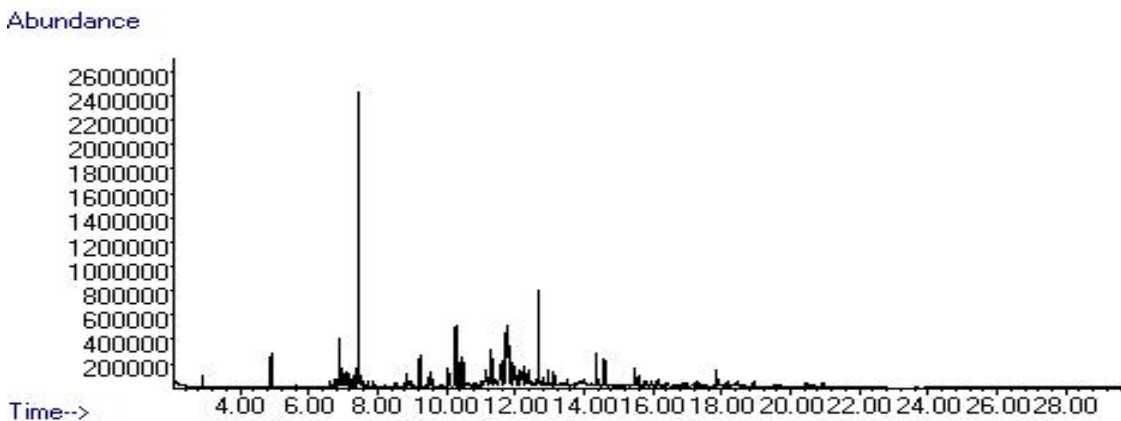


Figure 121: TIC of Street Smart Boots Burned

Table 126: Retention Times and Products of Burned Street Smart Boots

Retention time (min.)	Product
7.44	Styrene
10.274	Limonene
12.672	Naphthalene

REFERENCES

1. Stauffer, E., *Concepts of Pyrolysis for Fire Debris Analysts*. Science and Justice, 2003. **43**(1): p. 29-40.
2. Administration, U.S.F., *Arson in the United States*, in *Topical Fire Research Series*. January 2001.
3. DeHaan, J.D., *Kirk's Fire Investigation*. 4 ed. 1997, Upper Saddle River, NJ: Prentice Hall, Inc.
4. Fraga, C.G.P., B.J.; Synovec, R.E., *Comprehensive two-dimensional gas chromatography and chemometrics for the high-speed quantitative analysis of aromatic isomers in a jet fuel using the standard addition method and an objective retention time alignment algorithm*. Analytical Chemistry, 2000. **72**: p. 4154-4162.
5. Bruckner, C.A.P., B.J.; Synovec, R.E., *Comprehensive two-dimensional high speed gas chromatography with chemometric analysis*. Analytical Chemistry, 1998. **70**: p. 2796-2804.
6. Pierce, K.M.H., J.L.; Johnson, K.J.; Wright, B.W.; Synovec, R.E., *Classification of gasoline data obtained by gas chromatography using a piecewise alignment algorithm combined with feature selection and principal component analysis*. Journal of Chromotography, 2005. **1096**: p. 101-110.
7. Pierce, K.M.W., B.W., *Unsupevised parameter optimization for automated retention time alignment of severly shifted gas chromatographic data using the piecewise alignment algorithm*. Journal of Chromotography, 2007. **1141**: p. 106-116.
8. Watson, N.E.V., M.M.; Pierce, K.M.; Wright, B.W.; Synovec. R., *Classification of high-speed gas chromatography-mass spectrometry day by day principal component analysis coupled with piecewise alignment and feature selection*. Journal of Chromotography, 2006. **1129**: p. 111-118.

9. *Standard Test method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography-Mass Spectrometry.* ASTM International; E1618-06.
10. Mann, D.C.G., W.R., *Microbial degradation of gasoline in soil.* Journal of Forensic Science, 1990. **35**: p. 913-923.
11. Coulombe, R., *Chemical Markers in Weathered Gasoline.* Journal of Forensic Science, 1995. **40**(5): p. 867-872.
12. Thomas, C., *Arson Debris and Control Samples.* Fire and Arson Investigator, 1978. **28**: p. 23-25.
13. J. Nowicki, C.S., *Comparison of Fire Debris Analysis Techniques,* in *Arson Analysis Newsletter.* 1983. p. 98-108.
14. Stone, I.C.L., J.N., *False positive in analysis of fire debris.* The Fire and Arson Investigator, 1984. **34**: p. 36-40.
15. Bertsch, W., *Volatiles from carpet: a source of frequent misinterpretation in arson analysis.* Journal of Chromotography, 1994. **674**: p. 329-333.
16. Dehaan, J.D.K.B., *Pyrolysis products of structure fires.* Journal of the Forensic Science Society, 1988. **28**: p. 299-309.
17. Howard, J.M., A.B. , *A fire investigation involving combustion of carpet material.* Journal of Forensic Science, 1984. **29**: p. 919-922.
18. Smith, R.M., *Arson analysis by mass chromatography.* Analytical Chemistry, 1982. **54**: p. 1399A-1409A.
19. John J. Lentini, J.A.D., Cheryl Cherry, *The Petroleum-Laced Background.* Journal of Forensic Science, 2000. **45**(5): p. 968-989.
20. Koussiafes, M.P., *Evaluation of fire scene contamination by using positive-pressure ventilation fans.* Forensic Science Community, 2002. **4**(4).
21. A. Armstrong, V.B., D.L. Holmes, C. Martin, R. Powell, S. Riggs, L.D. Young, *The evaluation of the extent of transporting or "tracking" an identifiable ignitable liquid*

- (gasoline) throughout fire scenes during the investigative process. *Journal of Forensic Science*, 2004/2005. **49**(4).
22. W. R. Dietz, D.C.M., *Evidence Contaminated by Polyester Bags*. *Scientific Sleuthing Newsletter*, 1988(12): p. 5-6.
 23. Dehaan, J.D., *Evaluation of kapak plastic pouches*. *Arson Analysis Newsletter*, 1981(5): p. 6-11.
 24. J.F. Demers-Kohls, a., *An evaluation of different evidence bags used for sampling and storage of fire debris* *Canadian Society for Forensic Science Journal*, 1994(27).
 25. Mary R. Williams, M.S., *Performance Testing of Commercial Containers for Collection and Storage of Fire Debris Evidence*. *Journal of Forensic Science*, 2007. **52**(3).
 26. R. Borusiewicz, G.Z., J. Zieba-Palus, *Application of Head-Space Analysis with Passive Adsorption for Forensic Purposes in the Automated Thermal Desorption-Gas Chromatography-Mass Spectrometry System*. *Chromatographia*, 2004(60): p. s133-s142.
 27. Jose R. Almirall, K.G.F., *Analysis and Interpretation of Fire Scene Evidence*. 2004, Boca Raton: CRC Press.
 28. J.D. DeHaan, K.B., *Pyrolysis products of structure fires*. *Journal of the Forensic Science Society*, 1988. **28**: p. 299-309.
 29. M. Frenkel, S.T., *Field sampling of arson areas by the adsorption tube method*. *Arson Analysis Newsletter*, 1986(9).
 30. W. Bertsch, G.H., *Analysis of accelerants in fire debris by gas chromatography / mass spectrometry in forensic applications of mass spectrometry*, ed. J. Yinon. 1995, Boca Raton: CRC Press.
 31. *American Society for Testing and Materials "ASTM E1387-95 Standard Practice for Sampling of Headspace Vapors from Fire Debris Samples*. *Annual book of ASTM Standards*, 1995.

32. K.G. Furton, J.B., J.R. Almirall, *A Simple, inexpensive, rapid, sensitive and solventless technique for the analysis of accelerants in fire debris based on SPME*. Journal of High Resolution Chromatography, 1995(18).
33. Hiroaki Yoshida, T.K., Shinichi Suzuki, *A Solid-phase microextraction method for the detection of ignitable liquids in fire debris*. Journal of Forensic Science, 2008. **53**(3).
34. Mary R. Williams, D.F., Candice Bridge, Derek Dorrien, Stefanie Elliot, Michael Sigman, *Adsorption saturation and chromatographic distortion effects on passive headspace sampling with activated charcoal in fire debris analysis*. Journal of Forensic Science, 2005. **50**(2).
35. Michael E. Sigman, M.R.W., Joseph A. Castelbuono, Joseph G. Colca, C. Douglas Clark, *Ignitable Liquid Classification and Identification Using the Summed-Ion Mass Spectrum*. Instrument Science and Technology, 2008.
36. Frasiniski, L., Codling, J.K., Hatherly, P.A., *Covariance mapping: A correlation method applied to multiphoton multiple ionization*. Science, 1989. **246**: p. 1029-1031.
37. Jukes, P.B.A.J., A.B.; Stace, A., *Covariance images of the primary response from rare gas cluster ions to photoexcitation*. J. Chem. Phys., 1997. **106**: p. 1367-1372.
38. Foltin, M.S., G.J.; Bernstein, E.R., *Dynamics of neutral cluster growth and cluster ion fragmentation for toluene/water, aniline/argon, and 4-fluorostyrene / argon clusters: Covariance mapping of the mass spectral data*. J. Chem. Phys., 1998. **109**: p. 4342-4360.
39. Feldman, A.B.A., M.; Lin, J.S.; Demirev, P.A., *Covariance mapping in matrix-assisted laser desorption/ionization time-of-flight mass spectrometry*. Rapid Commun. Mass Spectrom., 2003. **17**: p. 991-995.
40. Michael E. Sigman, M.R.W., Rebecca G. Ivy, *Individualization of Gasoline Samples by Covariance Mapping and Gas Chromatography/Mass Spectrometry*. Analytical Chemistry, 2007. **79**(9).

41. van Marlen, G.D., A., *Information theory applied to selection of peaks for retrieval of mass spectra*. Analytical Chemistry, 1976. **48**(3): p. 595-598.
42. Grotch, S.L., *Matching of mass spectra when peak height is encoded to one bit*. Analytical Chemistry, September 1970. **42**(11).
43. Geert van Marlen, A.D., Henk A. van't Klooster, *Influence of errors and matching criteria upon the retrieval of binary coded low resolution mass spectra*. Analytical Chemistry, March 1979. **51**(3).
44. Ni, L., *Data Analysis Summary of Laser Spectra*. 2008: Department of Statistics and Actuarial Sciences, University of Central Florida.
45. Sachs, L., *Applied Statistics: A Handbook of Techniques*. Second ed, ed. S.S.i. Statistics. 1982, New York: Springer-Verlag.
46. Moldoveanu, S.C., *Analytical Pyrolysis of Synthetic Organic Polymers*. 2005, Winston-Salem, NC: Elsevier.
47. Jensen, B.W., P.; Wilkins, C.K.; Clausen, P.A., *Characterization of linoleum. Part 1: Measurement of volatile organic compounds by use of the field and laboratory emission cell, "FLEC"*. Indoor Air, 1995. **5**(1): p. 38-43.
48. P. Mark, L.S., *Fire investigation and ignitable liquid residue analysis - A review: 2001-2007*. Forensic Science International, 2008(176): p. 93-110.