Simulation of Fire Debris for the Training of Chemometric Models for the Identification of Ignitable Liquids

by

Xiao Qin Lee

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Department of Chemistry
University of Alberta

ABSTRACT

Arson is one of the most challenging crimes for forensic scientists to investigate. The variability in the composition of ignitable liquids, including changes in chemical composition during and after the fire, and the presence of pyrolysis products generated from burning substrates yields a very complex mixture of volatile compounds in samples of fire debris. Headspace extraction of debris samples followed by gas chromatography-mass spectrometry (GC-MS) is the most common approach for fire investigation. For many laboratories, data interpretation is the bottleneck in the workflow, consuming an inordinate amount of analyst time. It is also a process that is highly dependent on the experience and skill of analysts which gives rise to subjective results.

Chemometrics offers an alternative to manual data interpretation. However, for this work to be applicable in real-world fire investigations, the chemometric model must be able to classify all major classes of ignitable liquids that can be possibly found in a fire. Construction of a chemometric model requires abundant casework data. This is this not a problem for gasoline, which is the most commonly used ignitable liquid, but it is a challenge for other ILs. The lengthy time needed for the collection of casework debris containing other ILs for the model construction limits the practical use of this work. Therefore, it would be a great benefit if models applicable to casework samples could be generated based on simulated debris profiles.

An established debris simulation protocol has been shown to be effective in generating realistic debris for training human analysts. This thesis evaluates the applicability of this simulation protocol for generating debris that are chemometrically identical to casework debris. It was discovered that models trained on the simulated debris were not applicable to casework samples without a significant loss in the accuracy of the model. It was established that the reason for the inadequacy of the simulated debris was that it did not contain sufficient C_2-alkyl benzenes and non-aromatic hydrocarbons. Consequently these features which are not characteristic of gasoline were selected by the chemometric model and model quality degraded for real samples.

Thus research turned to a study of the effects of temperature on the pyrolysis of household materials, mainly flooring and roofing materials, at temperatures above 400 °C. I was particularly interested in finding conditions that will generate additional BTEX and aliphatic hydrocarbons, which were generally lacking in debris pyrolyzed at 400 °C with the established simulation method.

PREFACE

CHAPTER 2 has been submitted to *Analytical and Bioanalytical Chemistry* for publication. I was responsible for the generation of simulated debris, data collection and analysis of data, as well as the manuscript composition. P.M.L. Sandercock advised some of the project planning, and was in charge with the data acquisition for casework debris samples. He was and also involved editing the manuscript. L.A. Adutwum helped with building and fixing some of the MATLAB scripts used to process the data. J.J. Harynuk was the supervisory author and was involved with the concept formation and manuscript composition and edits.

CHAPTER 3 has been submitted to *Analytical and Bioanalytical Chemistry* for publication. I was responsible for the experimental design, pyrolysis of samples, data collection and analysis of data, as well as the manuscript composition. P.M.L. Sandercock was involved with concept formation and manuscript edits. J.J. Harynuk was the supervisory author and was also involved with the concept formation and manuscript composition and edits.

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List of Abbreviations

ANOVA - Analysis of variance

ASTM - American Society for Testing and Materials

BE - Backwards elimination

BE/FS - Hybrid backwards elimination / forward selection

BTEX - Benzene, toluene, ethylbenzene, xylenes

COW - Correlation optimised warping

CR - Cluster resolution

GC - Gas chromatography

GC-MS - Gas chromatography – mass spectrometry

EI - Electron impact ionization

EIC - Extracted ion chromatogram

f ratio - Fisher ratio

FS - Forward selection

ILs - Ignitable liquids

LDF - Ledium-density fibreboard

LV - Latent variable

MDF - Medium-density fibreboard

MS	-	Mass spectrometry
OSB	-	Oriented strand board
PAHs	-	Polycyclic aromatic hydrocarbons
PC	-	Principal component
PCA	-	Principal component analysis
PET	-	Poly(ethylene terephthalate)
PLS-DA	-	Partial least squares discriminant analysis
PVC	-	Poly(vinyl chloride)
PU	-	Polyurethane
Py-GC/MS	-	Flash pyrolysis/ gas chromatography – mass spectrometry
RCMP	-	Royal Canadian Mounted Police
RMSEVC	-	Root mean square error of cross-validation
SIMCA	-	Soft independent modelling by class analogy
SPME	-	Solid phase microextraction
SR	-	Selectivity ratio
TIC	-	Total ion chromatogram

List of Symbols

d_f - Film thickness

m/z - Mass-to-charge ratio

CHAPTER ONE: Introduction

1.1 Arson and fire

Arson is the deliberate use of fire to cause damage to property. Some of the suspected motives for an arson are curiosity, thrills, intimidation, crime concealment, domestic violence, insurance fraud, burglary, self-destructive behavior, or attention-seeking [1–3]. In 2013, approximately 1.2 million fires were handled by public fire departments in the United States. Home structure fires and highway vehicle fires made up 39% and 15% of these fires, respectively. Other fires, such as brush and wildland fires, accounted for the rest of the numbers. Among all the fires, 33,000 cases were confirmed as arson, including 22,500 structure fires and 10,500 vehicle fires. The annual cost due to arson-related property damage in the United States has been estimated at $663 million by the National Fire Protection Association. Beside the financial loss, these arson-related fires also led to 150 civilian deaths in 2013 [4]. From the standpoint of public safety and economic considerations it is important that fire investigation is completed accurately and objectively, without any prejudgment.

Fire investigation is one of the most difficult and challenging forensic tasks, due to the complex nature of the event and distortion of evidence by the fire. The primary purposes of a fire investigation are to establish the origin and the cause of the fire [3, 5]. The point of origin of the fire refers to the location where the fire first starts. In some instances, it can be determined based on the location of the smoke and fire alarm that was first triggered or the area with the worst burn damage. At the point of origin, fire investigators look for the characteristics or artefacts that are associated with ignition. They often collect different items of evidence such as fire debris or incendiary devices. Based on the results of scene examination, the analysis of physical evidence and all the background information provided by associated personnel, fire investigators aim to identify whether the cause of the fire was accidental, natural, or deliberate.

During the scene investigation, various types of physical evidence can be collected. Fire debris is one of the most common types of evidence as it can often retain ignitable liquids (ILs) which are commonly used by arsonists to accelerate a fire [6]. The use of ILs often leaves distinct burning patterns or trailing marks at the scene. In some cases where the duration of fire is short or an incredibly large amount of ILs was used, pools of ILs may be found, indicating the presence of ILs. In standard practice, chemical analysis is used to verify the presence of ILs in fire debris samples. The results may help fire investigators to determine the cause of the fire and support the inference of arson.

It is important to note that the fire investigation is not solely based on the results provided by fire debris analysts. In other words, a positive identification of ILs does not necessarily lead to the conclusion that a fire was set intentionally and a negative result does not preclude the possibility that ILs were present. Other considerations must be taken into account, for examples, ILs may be present for legitimate reasons or the trace amount of ILs used to start the fire were fully consumed. Despite this, the identification of ILs in debris samples collected from a fire scene provides a critical piece of evidence to support the fire investigation.

1.2 Forensic analysis of fire debris

1.2.1 Background

1.2.1.1 Ignitable liquids

Ignitable liquids (ILs) are broadly categorized as petroleum or nonpetroleum. Petroleum-based ILs are products derived from the refinement of crude oil and include gasoline, kerosene, and diesel fuel. These products are comprised of aliphatic and aromatic hydrocarbons that extend over a wide boiling range. Nonpetroleum-based ILs include those obtained through all other sources, such as oxygenated species (ethanol) and naturally derived products (turpentine). Their compositions, although varied, are usually much simpler.

The common classes of petroleum-based ILs are gasoline, petroleum distillates, isoparaffinic products, naphthenic paraffinic products, aromatic products and normal-alkanes products. American Society for Testing and Materials (ASTM) classifies ILs to each particular class based on the types of compounds present as listed on **Table 1-1**. The compounds of forensic interest are saturated aliphatics (including normal-alkanes, isoalkanes and cycloalkanes) and aromatics in the boiling ranges of C_4 to approximately C_{20}.

Among all these petroleum-based ILs, gasoline is the most commonly used fire accelerant because it is easily accessible to public, can be carried in large quantities without arousing suspicion, and is very effective [7–9] (**Figure 1-1**). Gasoline has a hydrocarbon range between C_4 and C_{12} and usually contains a large abundance of aromatic compounds in a mixture of alkanes and cycloalkanes. The aromatic compounds are typically benzene, toluene, C_2-, C_3-, and C_4-alkylbenzenes, as well as indanes, methylindanes, naphthalene and alkylnaphthalenes, with the exception that the last two compounds may be absent in some gasoline. Alkanes are always present in gasoline but this pattern may vary across different brands and grades [10].

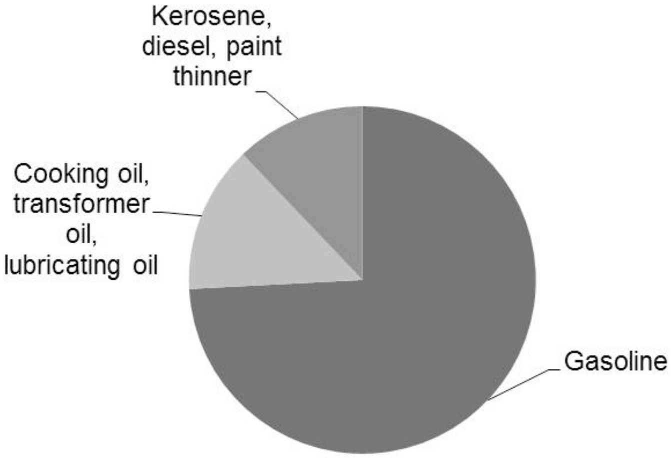


Figure 1-1. Identifiable types of ignitable liquids (ILs) used in intentional structure fires in the United States annually for the years 2007-2011 [7].

Table 1-1. Petroleum-based ASTM classes and their chemical composition [5, 11].

Class	Main characteristics	Alkanes	Cycloalkanes	Aromatics	Condensed ring aromatic (including indanes)
Gasoline	Abundant aromatics	Present, less abundant than aromatics, pattern vary by brand, grade and lot	Small amounts	Abundant	Present
Petroleum distillates	Gaussian distribution of *n*-alkanes	Abundant, predominant *n*-alkanes with isoparaffins present	Present, less abundant than alkanes	Present, less abundant than alkanes	May be present
Isoparaffinic products	Excusively branched chain aliphatics (isoparaffins)	Branched alkanes abundant, n-alkanes absent or insignificant	Absent or insignificant	Absent or insignificant	Absent
Naphthenic paraffinic products	Mainly isoparaffins and cyclic alkanes (napthenes)	Branched alkanes abundant, n-alkanes absent or insignificant	Abundant	Insignificant	Insignificant
Aromatic products	Exclusively aromatics or condensed ring aromatics or both	Insignificant	Insignificant	Abundant	May be present
Normal-alkanes products	Exclusively *n*-alkanes	*n*-Alkanes abundant, isoparaffin absent or insignificant	Insignificant	Insignificant	Insignificant

The compositions of ILs found at fire scenes often exhibit a slightly different pattern or relative intensities than that of the fresh liquid. Due to the fact that each petroleum-based ILs are comprised of compounds encompassing a range of boiling points, these compounds do not evaporate uniformly. The compounds with lower boiling points evaporate quicker than those with higher boiling point. This process is called weathering of ILs. ILs weather at different rates in each fire so the relative intensities of their compositions can vary significantly.

1.2.1.2 Pyrolysis of household materials

Combustion and pyrolysis reactions are the dominant processes that occur in a fire. Fire occurs due to two types of combustion: flaming combustion and smoldering combustion [3, 5]. Flaming combustion is the most common type of combustion with characteristic flames for which it is named. This process involves a reaction between oxygen and fuel in the gas phase. On the contrary, smoldering combustion is a flameless combustion in which atmospheric oxygen directly reacts with the surface of a solid combustible in an environment with limited ventilation [3, 5, 12]. Since flaming combustion is an entirely gas phase process, solid and liquid fuels must undergo a phase change or a chemical change to enter the gas phase. For some fuels this is achieved by simple evaporation; however, for the vast majority of substrates pyrolysis is required to support flaming combustion. Pyrolysis is the process whereby (typically large) organic compounds undergo thermal decomposition in the absence of oxygen (or other oxidants) [5, 13]. The products of this process are called pyrolysis products or pyrolysates. The process of pyrolysis commonly involves three mechanisms of degradation: random scission, side-group scission and monomer reversion. Random scission is a process where the large polymeric species is broken at random positions along the backbone. Polyethylene can undergo this process to produce alkanes, alkenes and alkadienes [13]. In side-group scission, the side chain of the polymer is cleaved prior to the breaking of the backbone. The side-group scission of polyvinyl chloride generates a series of aromatic compounds such as benzene, toluene, ethylbenzene, styrene, and naphthalene [13]. Monomer reversion, as its name implies, is a depolymerisation process that gives rise to monomers and other products. The actual pyrolysis pathways are usually variable and unpredictable during the fire, which increases the complexity of the pyrolysis products.

Much work has been devoted to understanding the combustion and pyrolysis behavior of flooring materials and the interference potential of pyrolysis products with the detection of ILs. Some of the first attempts were described by Ettling et al. [14]. Different types of wood (Douglas fir, lauan, white pine, oak, and pitch pine), sheets of fabric (cotton, polyester, wool, and vinyl) and sheets of paper (newspaper and brown wrapping paper) were pyrolyzed in a muffle furnace at 600 °C in their studies. They concluded that the concentration of extracted hydrocarbon volatiles is not a reliable indication of the presence of ILs. Smith [15] characterized the volatiles given off by control charred carpet which were obtained from fire scenes and observed styrene and BTEX (benzene, toluene, ethylbenzene and xylenes). Howard [16] demonstrated the pyrolysis of styrene-butadiene copolymer material in a test tube with a Bunsen burner to compare the volatile products generated from this polymer to those from the control charred carpets collected at fire scene. Later on, Dehaan et al. [17] demonstrated a full scale simulation of a structure fire for the identification of volatiles produced from pyrolysis of a few different types of flooring products, including nylon carpets, polyethylene/polypropylene carpets and polyurethane foam underlay. The goal was to investigate whether the volatile products from these materials could be distinguished from those found from common petroleum distillates or synthetic blends. Bertsch [18] pyrolyzed carpet and carpet underlay in one-gallon paint cans over a Bunsen burner. In his study, styrene, methylstyrene, ethylbenzene, naphthalene and methylnaphthalenes were identified as pyrolysis products. Chasteen et al. [19] burned building materials under four different sets of conditions and constructed a library of pyrolysis products based on the results. Fernandes et al. [20] burned three types (polypropylene, nylon and wool) of carpets with sponge rubber padding using a Bunsen burner. All three samples generated toluene and poplypropylene carpet also generated styrene and limonene.

Many studies have been performed to characterize pyrolysis products of various types of natural and synthetic polymers over the last few decades [21–29]. These results may be useful for deducing the fire behavior of household products as most incorporate polymers. Some of the examples include poly(ethylene terephthalate) (PET) and nylon carpets, polyurethane foam underlay and polyvinyl chloride (PVC) sheet floorings. Smith [24] established a library of pyrolysis products generated from different type of synthetic polymers including polystyrene, polyethylene and nylons. The characteristic pyrolysis products used to identify each polymer were also listed. Bednas et al. [30] studied the pyrolysis of PET fabrics at 700 °C and 900 °C setting using flash pyrolysis/gas chromatography-mass spectrometry (Py-GC/MS). Benzene, vinyl benzoate, benzoic acid and biphenyl were observed as the main constituents of its pyrolysis products. Dzięcioł et al. [31–33] conducted several studies about the influence of temperature and atmosphere on the pyrolysis of PET granulate. They pyrolyzed the samples at constant temperatures from 200 to 700 °C in constant nitrogen or air flow. Moltó et al. [34] also burned used polyester fabrics isothermally under these two atmospheres at temperatures of 650 to 1050 °C. McNeill et al. [23] identified 60 products from the pyrolysis of poly(vinyl chloride) (PVC) under helium atmosphere up to 1000 °C. The pyrolysis products of PVC were found to contain aromatics and polycyclic aromatic hydrocarbons (PAHs) such as BTEX, naphthalene, biphenyl and their substituted products [21–23]. Alajbeg characterized the pyrolysis products of PVC window blinds [22], rigid polyurethane foam [28] and commercial phenol-formaldehyde resin foam [35] in a flow reactor with mixture of oxygen and nitrogen atmosphere (1:1) under three different temperatures: 550 °C, 750 °C, and 950 °C. Nylon 6 and nylon 6,6 are two types of polyamide fibres widely utilized in the industry for producing nylon carpets. The former produces caprolactam as the major pyrolysis product [24, 25]. Nylon 6,6 pyrolysates exhibit a characteristic cyclopentanone peak [24, 25, 27]. Polyurethane is a polymer frequently used in the production of carpet underlay. Its pyrolysis was found to generate considerable amounts of benzene, toluene, styrene, aniline, benzonitrile, 1-propenyl-bezene and naphthalene [28, 29].

Wood is the primary structural material used in residential construction and is also found in flooring and furniture. Wood consists mainly of cellulose (approximately 50%), hemicellulose (approximately 25%) and lignin (approximately 25%) [3]. Pyrolysis of wood generally produces guaiacols and phenols which originate from lignin, as well as levoglucosan which originates from cellulose [36–40]. Asphalt shingles are another combustible material commonly found in household fires. These are one of the most common roofing materials in North America and are fabricated from the residual bottoms remaining after the vacuum distillation of crude oil. This petroleum-based product yields pyrolysates comprising primarily n-alkanes, alkenes, aromatics and PAHs [41, 42].

It is shown that many of the flooring materials, synthetic polymers and petroleum-based household products generated non-aromatic hydrocarbon, BTEX and naphthalene as pyrolysis products. These compounds could complicate the fire debris analysis due to their presence as components of petroleum ILs, especially gasoline.

1.2.2 Collection and laboratory analysis of fire debris

1.2.2.1 Sample collection

Fire investigation first begins with the collection of appropriate samples. Absorbent materials, such as carpet and wood, are the preferred materials for collection as they provide good protection for ILs. They can retain ILs easily in their inner layers, without exposing the ILs to the fire directly. Additionally, ILs tend to travel downward from the surface and seep through to deeper layers of porous materials via gravity. Thus, samples are mostly collected from lower levels of the structure or the location where it is suspected that an IL has been poured, preferably where some sort of pool pattern is shown.

After the samples are collected, it is important for them to be preserved during transport to the laboratory for analysis. Containers that are commonly used for sample packaging are metal paint cans and nylon bags [5]. Each of them has their own advantages and drawbacks. In Canada, the majority of samples submitted for analysis are packaged in paint cans lined with an epoxy coating which emits virtually zero volatiles and prevents wet debris from causing the metals to rust. They are rigid and offer a very good physical barrier against loss and contamination. Nylon bags, being advantageous due to their transparency and flexibility, are used for larger and odd shaped samples. They are often heat sealed or folded and taped.

1.2.2.2 Sample preparation techniques

Once debris samples have been collected and packaged at the fire scene, they are labeled and transferred to forensic laboratories. The goal of sample preparation is to extract volatiles from the samples for subsequent analysis. Historically, steam distillation and solvent extraction techniques were used [43–47]; however these have been largely replaced by headspace methods [48–53] since the ASTM revised their guidelines in 2009 [43].

The most frequently used extraction technique in arson analysis is passive headspace extraction with activated charcoal [19, 48, 54–62]. In standard practice, debris samples are laid at the bottom of a closed container. An activated charcoal strip is pierced by a safety pin and suspended from the inner surface of the container's lid using a rare earth magnet placed outside of the lid (**Figure 1-2**). Other materials such as Carbotrap 300® [63] and Tenax [20, 64] have also been used as adsorbents for headspace extraction. The containers are then placed in an oven at 50 °C to 80 °C for 8 - 24 hours. During this period, the debris are heated gently to promote vaporization of volatile components. The analyte vapors released into the headspace are then adsorbed to the activated charcoal strip. After the containers are removed from the oven and cooled to room temperature, the carbon strips are removed and placed into separate gas chromatography vials. Solvents are then added into each of the vials to extract the volatiles and the resulting solution is ready for analysis.

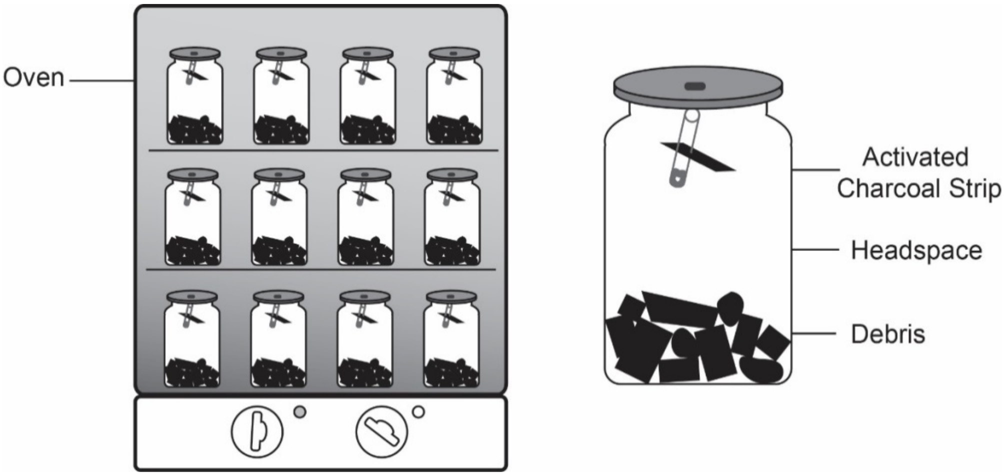


Figure 1-2. Set up for passive headspace extraction with activated charcoal strip.

The adsorption time of the charcoal strips is related to the adsorption temperature and nature of the substrates. Heavier compounds require longer time for vaporization and adsorption than lower molecular weight components. Most of the time, the adsorption is carried for 16 – 24 hours to match with analysts' work schedule [65, 66]. The solvent used in the desorption process is generally carbon disulfide, *n*-pentane, or diethyl ether [48], though other solvents such as dichloromethane, hexane and isopropanol [5, 62] have also been investigated. Among all the solvents, carbon disulfide is the best solvent overall for desorbing alkanes and PAHs in petroleum-based ILs and diethyl ether is the best choice for alcohols or oxygenated compounds.

A variant of passive headspace extraction with activated charcoal is called solid phase micro-extraction (SPME) [50, 67–71]. Instead of activated charcoal, a solid-phase sorbent-coated fibre is exposed to the heated headspace in closed container for a given period of time. Analytes adsorb to the fibre which is then withdrawn from the sample container. Analytes are released into the analytical system by thermal desorption. This is a simple, fast and solventless technique. However, it poses several disadvantages for application to arson investigations. These include displacement of lighter by heavier compounds on the fibres, lack of automation for sampling from large containers needed for fire debris and fragility of the fibres [6, 72, 73].

1.2.2.3 Gas chromatography – mass spectrometry

After volatile components from the debris are extracted, they are separated and identified, typically via gas chromatography – mass spectrometry (GC-MS) [11]. Gas chromatography (GC) is an analytical technique used for the separation of mixtures of volatile and semi-volatile organic compounds. The mass spectrometer (MS) is the current state-of-the-art detector used for fire debis analysis. It offers a main advantage of providing structural information of chemical compounds separated by the chromatographic column. This sophisticated instrumentation has demonstrated excellent separations and identification of complex mixtures containing ILs, heterogeneous matrices of pyrolysis products and substrates background. Thus, it has become an indispensable analytical tool for fire debris analysis [74].

The four major components of a gas chromatograph are the injector, column oven, column, and detector [75, 76] (**Figure 1-3**). The extract solution is introduced to the injector of the GC using a microsyringe. In the inlet, the volatile analytes and solvent are rapidly evaporated and mixed with carrier gas. All or small fractions of the mixture of vapors are then swept to the column, depending on the injection mode. The two most common injection modes for gas chromatography are split and splitless injection. Split injection is preferred when the sample concentration is high as only 0.2-2% of the sample will be delivered to column and analyzed. On the other hand, splitless injection is used when the sample concentration is at trace level so that all of the analytes can be transferred to column. The carrier gas is generally helium, hydrogen, or nitrogen. The type of carrier gases used, together with injection volume and flow rate can affect column efficiency and detector performance [75].

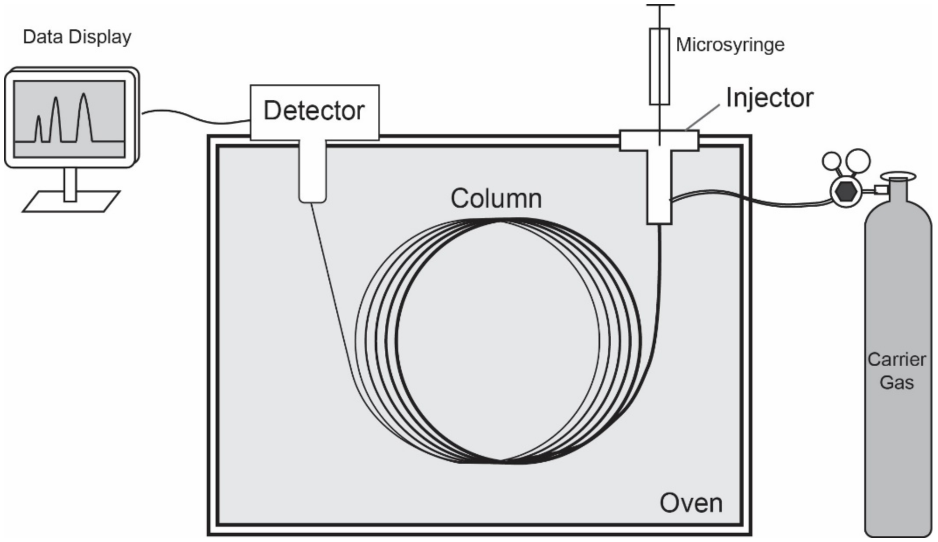


Figure 1-3. Schematic of a gas chromatography (GC) system.

The columns that are currently used for most GC analyses are capillary columns. A capillary column is a long narrow tube made from fused silica, with a thin layer of polymeric liquid (stationary phase) immobilized on the internal wall. These wall-coated open tubular (WCOT) columns are usually 10 – 30 m in length and 0.10 – 0.25 mm in internal diameter, while the film thickness of the stationary phase is 0.1 – 5.0 μm [76]. The column is held inside an oven, where the temperature is controlled in a precise manner during the separation. Temperature is the primary variable in a gas chromatographic separation. The oven can be heated isothermally or with temperature programming [75, 76], depending on the types of compounds to be separated, as well as the purpose of the experiments.

When the analytes travel through the column, each of them equilibrates between the stationary phase and mobile phase differently, depending on their chemical affinity for the stationary phase and their vapour pressure. Analytes that have a lower affinity for the stationary phase or a higher vapour pressure at the oven temperature will spend less time in the stationary phase than analytes with higher affinities for the stationary phase and/or lower vapour pressures and elute faster from the column, leading to their separation. Stationary phase is an important parameter to consider when selecting a column. Column is selected based on the chemical properties/ structure of analytes. It generally follows the principle of "like dissolves like". The separation of analytes is best achieved using column with stationary phase that has similar chemical properties [77, 78]. ILs and majority of the pyrolysis products from a fire are hydrocarbons. Thus non-polar columns such as (5%-phenyl)-dimethylpolysiloxane [66, 79], 100% dimethylpolysiloxane, are generally preferred for arson analysis [57, 61, 80, 81].

After the samples are separated and eluted from the column, they are analyzed by mass spectrometer. Neutral molecules entering the mass spectrometer are ionized, typically using electron impact ionization (EI) for arson investigations. This process yields an energetic radical cation which rapidly fragments in a reproducible manner. These ions typically have a +1 charge in EI. The ions are then introduced to a mass analyzer which sorts them based on their mass-to-charge ratio (m/z) [5, 75, 76].

Quadrupole [59, 80, 82–84] and ion trap [70, 85] mass spectrometers are are two typical mass analyzer used for fire debris analysis. Quadrupoles are the most popular due to their robustness. A quadrupole consists of four cylindrical rods in parallel [75]. Radiofrequency and direct-current voltages are applied to the rods to create a hyperbolic electric field. This electric field allows stable trajectory motion of ions with a specific *m/z* as they travel from the ionization chamber toward the detector. Ions with other *m/z* values would have unstable trajectories, causing them to collide with the rods and lost before reaching the detector. Increasing the applied voltages simultaneously enables ions with a range of *m/z* values to pass through analyzer and be detected [75, 76].

The signals from the mass resolved ions are converted into recordable currents in detector, which is usually electron multiplier for fire debris analysis. For detection with an electron multiplier, electrons induced by the collision of ions are multiplied by a series of metal plates through secondary emission. This amplifies the original signal and gives rise to a current that is measured by system [5, 76].

GC-MS data are represented in the form of a time series of mass spectra. They are generally viewed as a total ion chromatogram (TIC) or extracted ion chromatogram (EIC). A TIC displays chromatographic separation in a plot of response intensity versus time. The response intensity in the case of a TIC is the sum of the intensities of all ions in each spectrum plotted in sequence. Extracted ion chromatograms are plots of a single ion (or a few selected ions) as a function of time.

1.2.3 Data interpretation

1.2.3.1 Human Analysts

In standard practice, initial analysis of fire debris involves a visual comparison of the sample TIC and reference IL TICs obtained under similar conditions [11]. However, interfering compounds resulting from the fire debris due to the pyrolysis or partial combustion can sometimes preclude the identification of an IL. In this case, direct comparison of chromatograms based solely on the information obtained in the TIC is not very useful. Thus, examining extracted ion chromatograms (EICs) for specific m/z values characteristic of marker compounds is also performed to determine what, if any, IL is present [5, 11, 86]. Analysts often use a combination of these techniques to interpret the data. The typical ions extracted for each class of compounds of interest to fire debris analysis are listed in **Table 1-2**.

Table 1-2. Major ions present in mass spectra for each class of compounds in common ignitable liquids [11].

Compound type	Ions (*m/z*)
Alkanes	43, 57, 71, 85, 99
Cycloalkanes/alkenes	55, 69, 83
Aromatic-alkylbenzenes	91, 92, 105, 106, 119, 120, 134
Indanes	117, 118, 131, 132, 146
Alkylnaphthalenes	128, 141, 142, 155, 156, 170
Alkylstyrenes	104, 117, 118, 132, 146
Alkylanthracenes	178, 192, 206
Alkylbiphenyls/acenaphthenes	154, 168, 182, 196
Monoterpenes	93, 136
Ketones	43, 58, 72, 86
Alcohols	31, 45

While these ions are generated by compounds that are characteristic of common ILs, some of these compounds can also be produced from pyrolytic processes in a fire. Thus, the mere presence of peaks on EICs does not justify the identification of an IL. For this reason, fire debris analysts also focus on the distinct grouping pattern shown on EICs of debris samples when comparing them against the reference IL chromatograms. Each of these grouping patterns represents a group of isomers of compounds that commonly found in petroleum-based ILs. Some of the most common diagnostic peak groupings are C_2-, C_3-, C_4-alkylbenzenes and methylnaphthalenes (**Figure 1-4**) [5, 86]. These patterns are often hidden from interfering compounds in a TIC of debris samples but can be clearly shown on EICs if a petroleum-based IL is present. The key feature about these groupings is the relative ratio of the isomers within a group. These peak ratios are specific to petroleum-based products. Pyrolysis products containing the same compounds may not generate the same pattern unless they are petroleum-based. Thus, if these compounds belong to a petroleum-based IL, they should be present at approximately the same relative concentration as are observed in reference chromatograms [5, 11, 86].

The peak ratios of each group of isomer and the relative abundance of each group of compounds to another may vary by location, the refinery process, the grade and the state of weathering [10, 87]. So, each fire debris analytical laboratory has a large collection of reference chromatograms for different ILs collected from different parts of the country, capturing as many as possible type of ILs that are being sold to consumers. When comparing the chromatograms, instead of looking for an exact match, fire debris analysts only search for similar pattern and ratios exhibited by the reference chromatograms. TIC and EICs of gasoline are shown in **Figure 1-5** as an example of reference chromatogram. Since gasoline is easily accessible, it is the popular choice of IL for arsonists (as seen in **Figure 1-1**) [7–9]. Gasoline is dominantly comprised of aromatics and this gives gasoline a unique chromatographic pattern that may be used for identification. Fresh gasoline is rich in C_1-, C_2- and C_3-alkylbenzenes, while alkane, cycloalkane, aromatic, indanes and naphathelenes are also present [5, 11, 86]. EICs clearly show the diagnostic patterns of the major compounds present in gasoline and can be used to compare against the patterns from sample chromatograms.

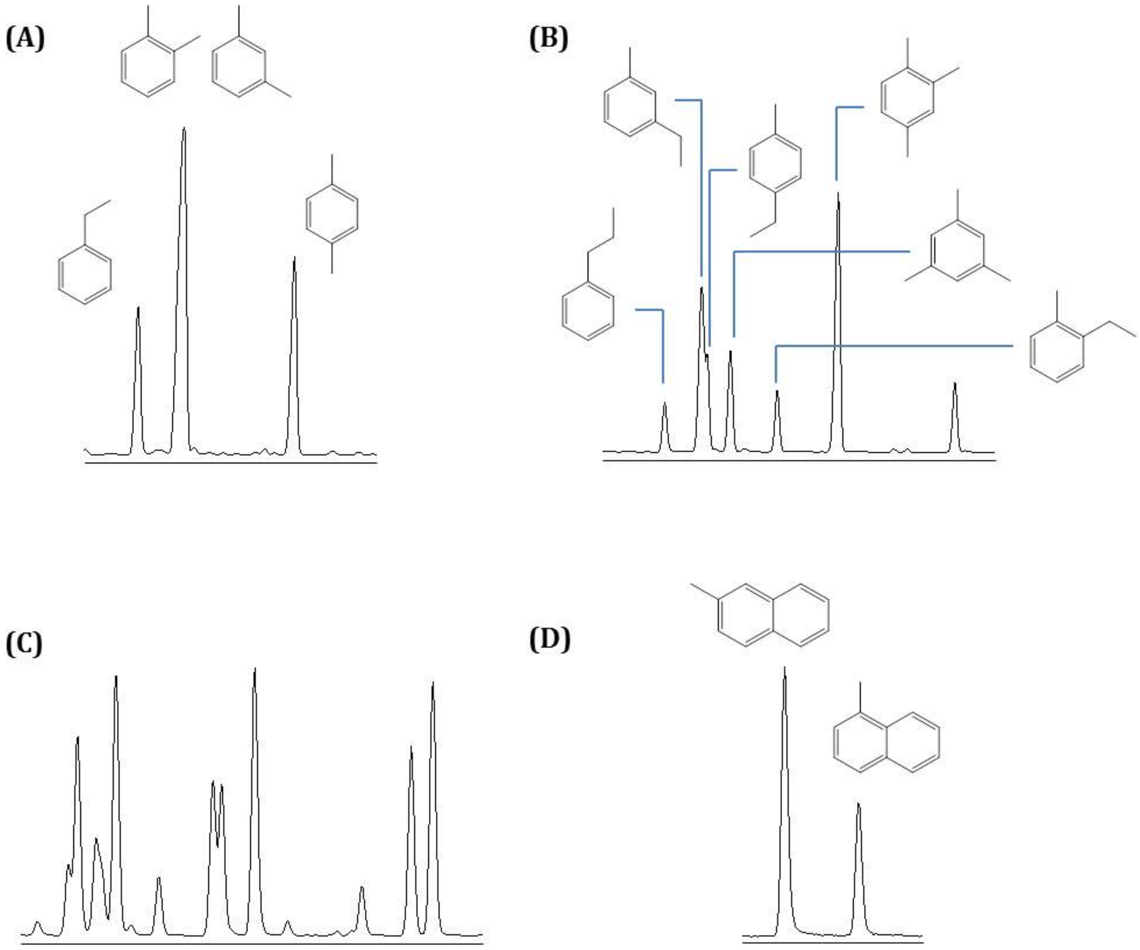


Figure 1-4. Some common diagnostic patterns of ILs: (A) C_2-akylbenzenes; (B) C_3-akylbenzenes; (C) C_4-akylbenzenes; and (D) methylnaphthalenes. The range shown in each figure includes all the isomers within the group. Some of the isomer peaks have not been identified.

Adapted from reference [5] using a chromatogram from a typical 91-octane gasoline sample analyzed over the course of this research.

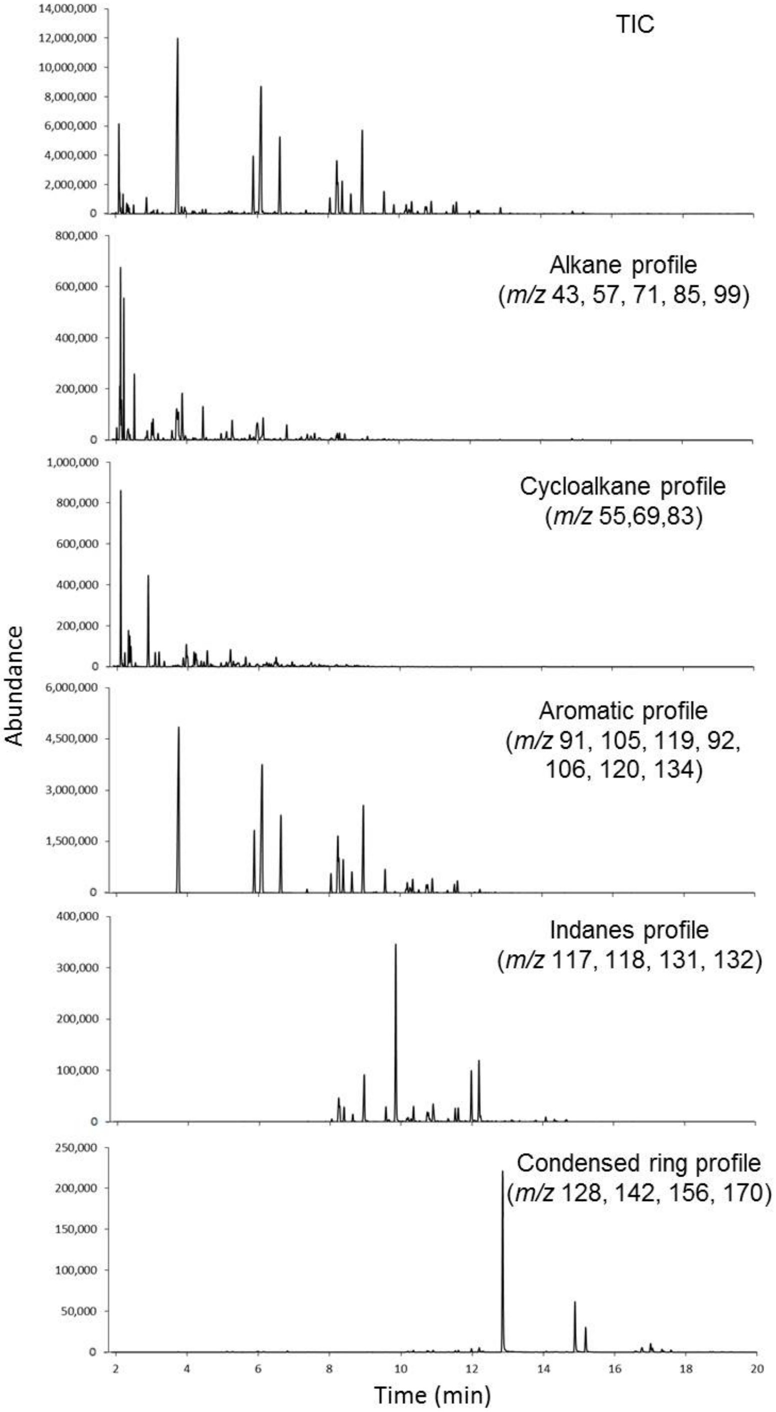


Figure 1-5. TIC and EICs of a neat gasoline, which show the different classes of compounds.

Adapted from reference [5] using a chromatogram from a typical 91-octane gasoline sample analyzed over the course of this research.

After the pattern recognition, major peaks on EICs from the debris samples are identified by searching their mass spectra against a reliable library. Finally, the results are concluded on the basis of the mass spectra and relative retention time of the compounds of interest by comparison to reference IL chromatograms that were obtained under similar conditions. It should be noted that this chromatogram comparison using pattern recognition is only applicable to petroleum-based ILs but not oxygenated solvents. This is because oxygenated solvents often consist of only a few peaks. The lack of peak information precludes any kind of pattern recognition. Thus, their identification is often achieved using GC retention time coupled with mass spectral identification [5, 11, 86].

Although this analysis workflow seems relatively easy to execute, it is much more complex in nature and several issues might complicate the analysis. The chromatographic pattern of ILs may be skewed toward high boiling compounds due to weathering in a fire. This can subsequently change the relative intensities between each class of compounds [5, 88]. Apart from this, ILs could be degraded by microbial activity [54, 89]. Bacteria may selectively metabolize one class of hydrocarbons or hydrocarbons with a specific structural feature. The specific process is unpredictable due to variability across different species of bacteria, moisture levels, temperatures, and so forth. While these factors can cause the IL pattern to change, they are generally not the main interference for data interpretation. Instead, the fire debris matrix is the main source of interfering compounds encountered in the analysis of fire debris. It is because most of the pyrolysis products (e.g. benzene, toluene, ethylbenzene, xylene – BTEX) derived from the matrix are also the components found in some common ILs [5, 18, 55, 67, 90]. These problems have the net result of lengthening the data interpretation time.

Data interpretation has become the bottleneck of the fire debris analysis workflow. Generally, two analysts are required to manually analyze the chromatograms independently. Each analyst could spend 20-60 min per sample, or more for very complex samples. Furthermore, in some cases where the comparison of chromatograms is needed, a control sample will have to be pyrolyzed and analyzed [16]. These extra efforts would then lengthen the analysis. Also, the data interpretation is somewhat subjective and relies heavily on the experience and skill of analysts.

1.2.3.2 Chemometric analysis

1.2.3.2.1 Chemometric modelling

Chemometrics is a discipline involving the application of multivariate statistical techniques to the analysis of chemical data. Chemometric methods can reveal the underlying chemical information and relationships between different groups of samples. It is a useful tool for data visualization/exploration; classification and identification through pattern recognition; and quantitative analyses via regression techniques [91].

A focus of arson-related research is the application of chemometrics for pattern recognition, in both unsupervised and supervised manners [66, 81, 83, 92–94]. Unsupervised pattern recognition is mainly applied to assess if any clustering or grouping in data set can be found without the knowledge of class membership about samples. One example of this approach is principal components analysis (PCA) [95, 96]. In the forensic context, PCA has been used for the grouping recognition of liquid fuels over recent years [79, 82, 83, 93, 97–99]. The application of supervised pattern recognition methods requires knowledge of class membership of the samples for the model training dataset [95, 96]. Supervised methods are mostly used for classification purposes. Two of the most common supervised methods are partial least squares discriminant analysis (PLS-DA) [66, 81, 100] and soft independent modelling by class analogy (SIMCA) [81, 91, 95]. Both of them have been recently applied by previous researchers in our group for the classification of simulated and casework debris based on gasoline content [66, 81].

Classification methods fall into two categories: hard and soft modelling. PLS-DA is an example of a hard classification technique, while SIMCA is a soft technique. Hard classification forces samples into a single modelled class (i.e. every sample must belong to one and only one class). On the other hand, soft classification methods do not force samples to be in any classes. Samples can be assigned to a single class, multiple classes, or even classified as not belonging to a modelled class [95]. In developing a classification model, a set of data with known class assignments is needed to construct the model that can then be applied to unknown samples. When constructing a classification model, sufficient samples are required to have a model training and cross-validation set. An additional external validation set is beneficial.

Chromatographic data can be presented on PLS-DA models several different ways. Two common ones are predicted Y-value and score plots [66, 81, 101]. Predicted Y-value plot shows the predictions for all samples to be in a class. Samples located above the discrimination line are predicted to be in the defined class and vice versa. Scores plots project all samples into a new coordinate system that reveals the grouping pattern of samples. The samples located close to each other implies that they behave similar. Examples of predicted Y-value and score plots are shown in **Figure 1-6** [66].

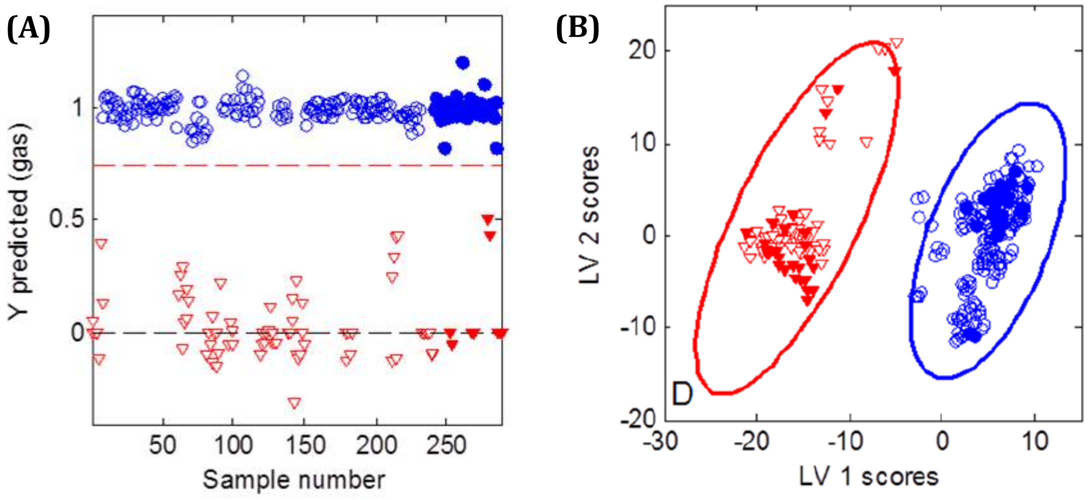


Figure 1-6. (A) Predicted Y-value and (B) score plots for PLS-DA models of debris data. Red and blue markers represent gasoline-containing and gasoline-free samples respectively.

Figures reprinted from reference [66] with permission.

A SIMCA model is a collection of PCA models, which each one representing one class in the data set [91, 95]. The samples are projected into each PCA model and their Hotelling T^2 and Q residuals scores for each model are calculated. Residual scores tell how well the sample fits into a class model. Lower residual scores represent higher likelihood that a sample belongs to the class. Q is a measure of the variation outside the model and Hotelling T^2 is a measure of the distance from the center of the model [101]. If one considers a calibration curve as a model, samples with linear response but falling outside the calibration range (as shown as red triangles in **Figure 1-7**) would have large Hotelling T^2. Samples that do not have linear response as other samples in the model and lie on some distance off the linear regression line (as shown as green square in **Figure 1-7**) would have large Q residual.

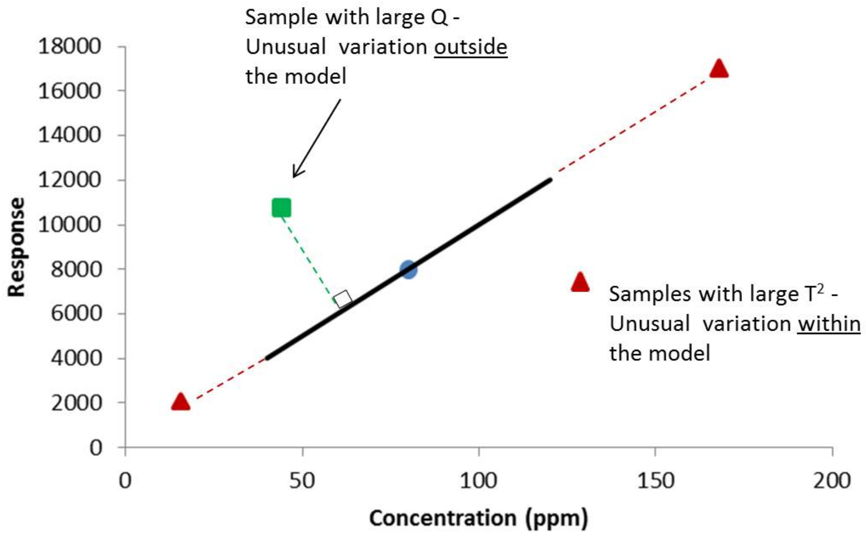


Figure 1-7. Simulation of calibration curve.

A plot of Q residuals versus Hotelling T^2 can be used to visually illustrate the SIMCA classification [66, 81, 101]. The classification boundaries are based on the defined confidence limit. **Figure 1-8** shows an example of SIMCA residuals plot for the classification of casework debris data based on gasoline content [81]. Gasoline-containing samples are located near to the origin of the plot and gasoline-free samples drift toward top right corner of the plot.

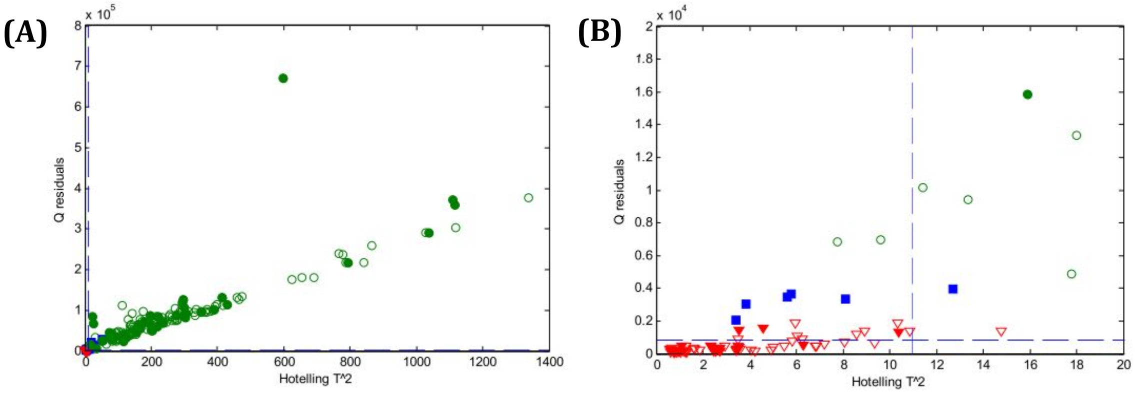


Figure 1-8. SIMCA residuals plot for arson data. Red, green and blue markers represent gasoline-containing, gasoline-free and ambiguous debris samples respectively. Dashed lines indicate 95% confidence levels.
Figures reprinted from reference [102] with permission.

1.2.3.2.2 Application of chemometrics to chromatographic data

1.2.3.2.2.1 Challenges with chromatographic data

Before the application of chemometrics to chromatographic data, some associated problems need to be understood. Variations in chromatographic data are based on chemical and non-chemical aspects of analysis. Chemical variations provide both relevant and irrelevant information. Irrelevant chemical variations include chemical “bleed” signals from stationary phases, and chemical peaks in the matrix that have no bearing on the given chemometric objective. The most notable example of non-chemical variation is the shifting of retention time between different analytical runs. This can be caused by degradation of stationary phase and changes in the chemistry of stationary phase by heavy matrix components. These irrelevant chemical and non-chemical variations often overwhelm the regions that contain relevant chemical variations. This is especially a problem when multivariate techniques are applied on raw chromatographic data. A 30-minute GC-MS chromatogram operated with an acquisition rate of 10 Hz over a 30 – 300 *m/z* mass range contains 4,878,000 data points. However, only a small percentage of them contain chemical profiles of interest while most of them consist of irrelevant information, background matrix or detector noise. The efficiency and predictive ability of chemometrics significantly relies on the variables that are included in the modelling [103]. If the model includes irrelevant data and noise, it must account for these variations and its performance will be detrimentally affected. Therefore, it is important to pre-process the chromatographic data before applying chemometrics to remove maximum number of non-chemical and irrelevant chemical variations while not sacrificing any the relevant chemical information [104–107, 102].

1.2.3.2.2.2 Pre-processing steps for chromatographic data

Initially efforts in dealing these problems was done by using an integrated peak table [79, 82, 93, 108]. Peak areas of all compounds or compounds of interest were integrated using commercial software and compiled into a peak table to be used for chemometric analysis. However, one main concern with this technique is the potential for integration errors of raw signals. It is not suitable for complex chromatographic data involved in debris analysis, which co-elution is frequently observed [107]. Therefore, applying chemometrics directly on raw chromatographic data is a better approach for fire debris analysis [66, 81]. For chemometric treatment of raw chromatographic data, retention time alignment and variable selection are two critical pre-processing steps.

1.2.3.2.2.2.1 Retention time alignment

Chemometric techniques are inherently sensitive to retention time precision. It is critically important for the peak for a given compound to be registered in the exact same position in the data matrix, allowing the algorithms to recognize the signals correctly. Several chromatographic alignment techniques are available to compensate minor drifts in retention time for preparing dataset for the application in chemometrics such as correlation optimised warping (COW) [109, 110] and piecewise peak-matching algorithm [111]. While these algorithms worked well for the chromatograms that have similar matrices (such as gasoline data [111]) or minor retention time shifting, it is not adequate for debris chromatograms that consist of extremely variable and dissimilar chemical profiles. Our group developed a chromatogram alignment technique based on perdeuterated alkane ladder to handle complex arson data matrices [66]. A perdeuterated alkane ladder generates unique mass spectral signals that serve as "anchor" for peak alignment (as shown as red trace in **Figure 1-9**). Peaks are warped in the region between two signals of deuterated alkanes in sample chromatograms. This deuterated alkane ladder technique has been demonstrated as a superior alignment approach in simulated and casework fire debris analysis [66, 81].

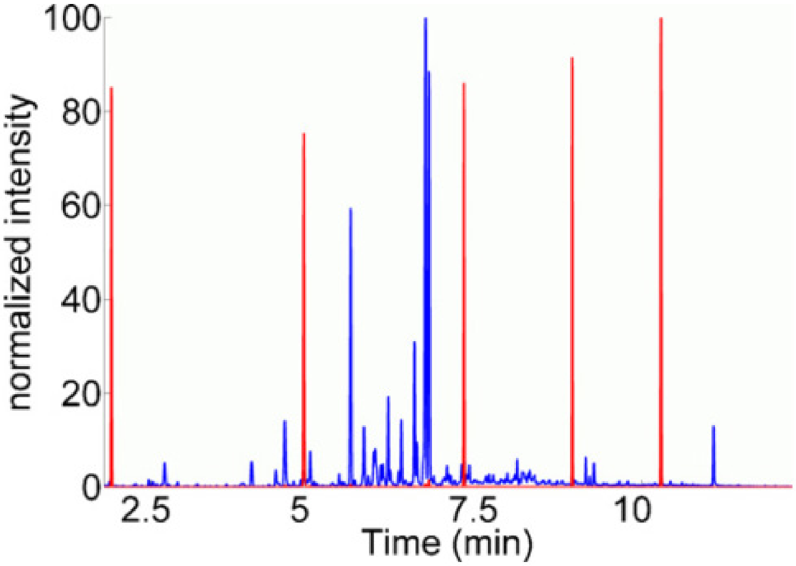


Figure 1-9. Deuterated alkane ladder signal for retention time alignment superimposed over a TIC of debris sample.
Figure reprinted from reference [66] with permission.

1.2.3.2.2.2.2 Feature selection

Feature selection is an important process in chemometrics to select relevant information from overloaded data and remove unnecessary variations. There are many algorithms and approaches to feature selection. The one used in this research was developed in our group and has been applied to debris data successfully. It is a fully automated and objective feature selection approach [66, 81]. It generally involves two steps: variable ranking and variable selection. In the first step, variables are ranked in terms of their perceived utility in distinguishing samples from different class assignments using statistics such as selectivity ratio (SR) [81, 100, 112] and analysis of variance (ANOVA) [66, 106]. The optimal set of variables to be included in the model is then selected based on quality of the model constructed using a hybrid backwards elimination / forward selection (BE/FS) approach. During optimization, model quality is assessed using Cluster Resolution, a model quality metric invented by our group [66, 81] (**Figure 1-10**).

The relevant features that are selected from the process can be related to chemical compounds using *m/z* information and library search. For an instance, Sinkov et al. [81] revealed C_3-, C_4-, and C_5-alkylbenzenes to be reliable markers for gasoline, as shown in **Figure 1-11**. These compounds were responsible for the classification of casework debris based on gasoline content.

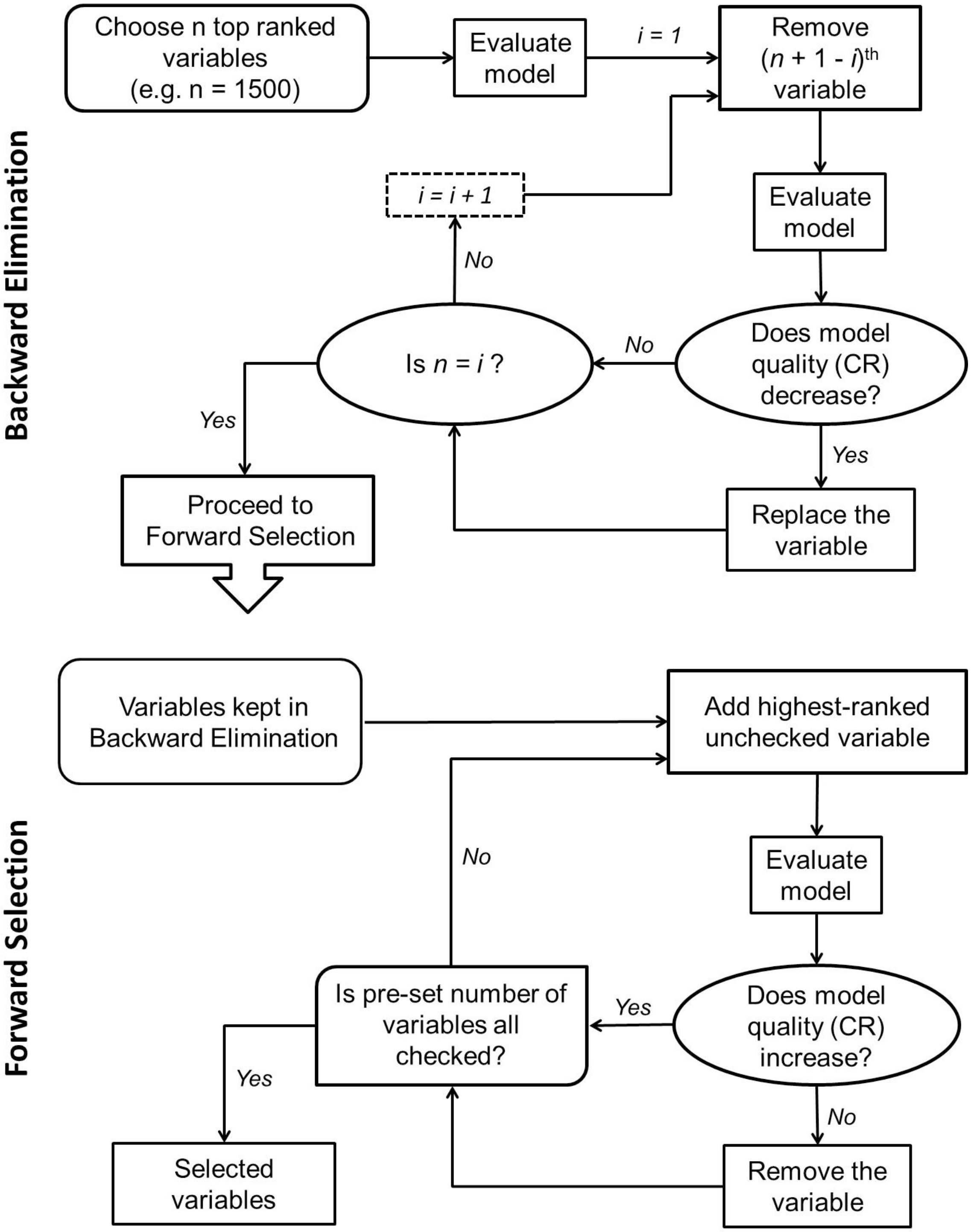


Figure 1-10. Hybrid backwards elimination / forward selection (BE/FS) guided by cluster resolution (CR).
Figure adapted from reference [81] with permission.

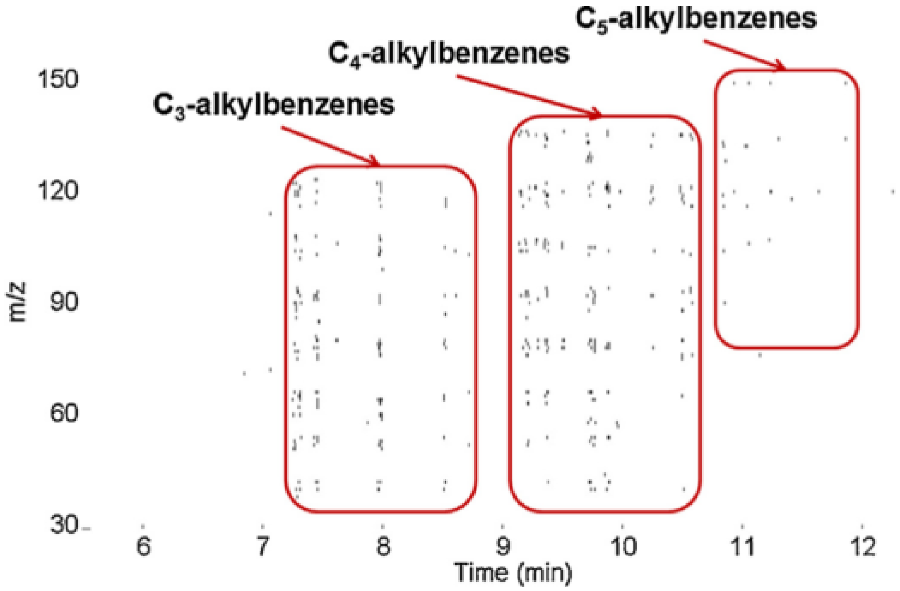


Figure 1-11. Variables included in chemometric model trained by casework debris for identification of gasoline in arson debris.
Figure reprinted from reference [81] with permission.

1.2.3.2.2.3 Validation of chemometric model

Upon the completion of all the pre-processing and basic modification (eg. normalization and autoscaling), chemometric models can be constructed using dataset from training and cross-validation set. These models are then tested against validation set. The presence of validation set can reaffirm that the pre-processing steps work properly so that these models can be used to classified unknown samples subsequently.

1.3 Motivation and scope

Current practices in fire debris analysis use manual interpretation of TICs and EICs to determine the presence and ASTM class of an IL. The analysis methodology relies on visual recognition to identify the presence of an IL in fire debris samples. Data interpretation of fire debris is currently the most labour-intensive and time-consuming step during the process of fire investigation. The process entirely relies on the analyst's skill and experience, and is subject to human error and bias.

Chemometric techniques offer a route to fast, objective data interpretation. It could also provide quantified probabilities of an identification. By speeding up the interpretation of results, its laboratory throughput would increase, permitting more debris samples to be collected and analyzed. As well, results would be returned to the investigators more quickly, which is a benefit for investigators trying to follow up leads quickly. Last but not least, by decreasing the analyst time demanded by arson investigations, the throughput and turnaround times for other analyses would be improved as the scientists' time that would otherwise have been spent reviewing fire debris data would be freed for other tasks.

Our group had previously demonstrated the first successful classification of casework fire debris based on the gasoline content. This endeavor represents a significant step towards automated analysis of fire debris. However, for this work to be applicable in real-world fire investigations, the chemometric model would ideally be able to classify all major classes of ILs that are possibly found in a fire. In order to construct a classification model applicable for other types of ILs, training data are required. However, the collection of casework debris samples that contain ILs other than gasoline represents a significant challenge. Due to the inherent variability in the debris and gasoline signatures, it required ~6 months to acquire sufficient casework samples for the gasoline study. Gasoline is the most commonly used IL. Other ILs being so much less common would require years to obtain sufficient casework data for training. Thus the approach of using casework data is impractical for ILs other than gasoline. To overcome this challenge, a simulated approach to rapidly obtain fire debris containing all types of ILs is required. A method of simulating fire debris that closely mimics the pyrolysis products found in casework samples could meet our goal.

This thesis presents studies into the simulation of fire debris for the training of chemometric models for the interpretation of fire debris. **CHAPTER 2** presents the construction and application of chemometric models trained by simulated debris for classifying casework debris based on gasoline content. The debris were simulated based on an established protocol [80]. This approach was not sufficient for our purposes, so **CHAPTER 3** presents a preliminary study into the effects of pyrolysis temperature on the pyrolysates of residential materials (wood, shingles, carpet, etc). Chemical analysis of the solvent extracts from pyrolyzed materials are are presented. The final chapter, **CHAPTER 4** describes new equipment that was designed and purchased to study debris simulation and pyrolysis in greater detail.

CHAPTER TWO: Comparison of Simulated and Casework Arson Debris for the Training of Chemometric Ignitable Liquid Detection Models

2.1 Introduction

Arson is one of the most challenging and time-consuming crimes for forensic scientists to investigate. Not only does the variable debris matrix result in a unique and complex volatile background for every sample, but there is a large number of possible ignitable liquids (ILs) that may be used to accelerate a fire. Gasoline is the most common accelerant found at arson scenes [8, 9, 113]. It has a unique chromatographic pattern that may be used for identification. However, the exact composition of gasoline will depend on a variety of factors, including the refinery in which it was produced [10, 87], when evaporation of sample takes place, and whether microbial degradation has occurred [54, 89]. In addition, the fire debris matrix is comprised of combustion and pyrolysis products from whatever materials happened to be burned at the fire scene. The matrix is usually the main source of interfering volatile compounds encountered in the analysis of fire debris because many pyrolysis products (e.g. benzene, toluene, ethylbenzene, xylene – BTEX) are also components found in some ignitable liquids (ILs) [5, 18, 55, 67, 90]. Each of these factors can cause the gasoline pattern to change which in turn makes data interpretation more challenging [5]. Data interpretation is presently the most labor intensive step in the analytical process. It generally involves having two experienced analysts manually examine multiple extracted ion profiles and diagnostic peak ratios in the chromatograms to determine if ILs are present. If this analysis could be fully automated, it would significantly reduce the amount of time required to interpret fire debris.

In order to automate the process of IL detection, one must rely on chemometric techniques. Several authors have reported the use of chemometrics to identify ILs [79, 82, 83, 93] and to interpret simulated fire debris [5]. Comparing the models previously constructed for simulated [66] and casework [81] debris by our group, different features were selected to predict the presence of gasoline. C_2-alkylbenzenes were selected in the models trained by simulated debris whilst models trained by casework debris selected C_3-, C_4-, and C_5-alkylbenzenes (or indanes) as the characteristics of gasoline. It became apparent that the features selected for the simulated debris were sufficiently different from those selected for the casework debris that the model used for simulated debris would fail for casework samples. Herein we test another debris simulation method which has been shown to generate realistic, challenging debris for training human analysts [80]. This chapter evaluates the efficacy of this method of debris generation for the development of a chemometric model that can be used to identify gasoline in casework arson samples. It is not practical to obtain from arson casework the required number of samples to train chemometric models for the less common ILs, and so a method of simulating fire debris that closely mimics the pyrolysis products found in casework samples is required in order to extend the capabilities of this approach beyond gasoline.

2.2 Experimental

2.2.1 Materials and Reagents

Fifteen different gasoline samples with a range of octane ratings (87, 89, and 91) were collected from five local gas stations. A variety of materials were used to generate simulated debris: polyethylene plastic bags, glossy magazine pages, asphalt shingles, polyvinyl chloride siding, polyvinyl chloride tubing, cotton, polypropylene, polyethylene terephthalate (PET) detergent bottle, polyethylene-coated paperboard (milk carton), cardboard, expanded polystyrene foam, oriented strand board (OBS) with an epoxy resin binder, spruce lumber, medium-density fibreboard (MDF), painted MDF, low-density fibreboard (LDF), and spruce plywood. A perdeuterated alkane ladder solution containing 20 µL L^{-1} each of *n*-heptane-d16, *n*-nonane-d20, *n*-undecane-d24, *n*-tridecane-d28, and *n*-pentadecane-d32 (CDN Isotopes, Pointe-Claire, QC) in CS_2 (Omnisolv; VWR, Mississauga, ON) was used to extract volatile analytes from 8 mm × 20 mm activated carbon strips (Albrayco Technologies, Cromwell, CT).

2.2.2 Preparation of Gasoline Samples

Aliquots of each gasoline sample were evaporated to approximately 50%, 75%, and 90% (by weight), under a stream of compressed air. To prevent contamination of the samples during the evaporation process, the compressed air was filtered through a Pasteur pipette fitted with a plug of glass wool and a 3 cm bed of granular activated carbon (6 – 14 mesh; Fisher Scientific, Nepean, ON). Including the unweathered gasoline samples, a total of 60 different gasoline samples were generated.

2.2.3 Preparation of Simulated Debris

Samples used to generate simulated fire debris were weighed (0.1 – 0.7 g), placed in Kimax culture tubes, and capped with black phenolic screw caps (13 × 100 mm borosilicate glass; Kimble Chase, Vineland, NJ). The tubes were individually inserted into a Carbolite MTF 10/15 mini-tube furnace fitted with a Eurotherm 818 electronic temperature controller (Carbolite, Hope Valley, U.K.) preheated to 400 °C. The tube was removed from the furnace after 30 min and quickly inserted into a room-temperature-water-jacketed copper tube for cooling [80]. A total of 256 pyrolyzed samples were generated.

2.2.4 Passive Headspace Extraction

Sixty-seven samples of simulated fire debris were prepared in separate 1 L canning jars: 31 samples consisted of up to three tubes of pyrolyzed debris samples together with 5 µL of gasoline spiked directly into one of the tubes, and 36 samples consisted of up to three tubes of pyrolyzed debris samples without the addition of gasoline. An activated carbon strip was pierced by a safety pin and suspended from the inner surface of the jar lid using a rare earth magnet placed on the outside of the jar lid; two carbon strips were placed in each canning jar. The jars were placed in an oven at 60 °C for 16 h to equilibrate. The jars were removed from the oven and cooled to room temperature before removing the carbon strips and placing them in to separate 1.8 mL GC vials (Chromatographic Specialties, Brockville, ON). Volatiles were extracted from each strip by the addition of 0.5 mL of the perdeuterated alkane ladder in CS_2 solution.

2.2.5 GC-MS Analysis

2.2.5.1 Simulated Debris Samples

The extracts of one carbon strip from each canning jar were analyzed in-house at the University of Alberta, and the extracts of second carbon strip from the each canning jar were analyzed at the Royal Canadian Mounted Police (RCMP) forensic laboratory in Edmonton, Alberta.

Sample analysis at the RCMP laboratory was performed using an Agilent Technologies 6890 GC with a 5973 quadrupole mass spectrometer (MS) fitted with a 7683 auto sampler (Agilent Technologies, Mississauga, ON) an a 30 m × 250 µm; 0.25 µm d_f HP-1MS column (100% dimethyl polysiloxane, Agilent). Data acquisition and automation were performed using MS ChemStation (Agilent). The oven was programmed from 40 °C (held for 3 min) to 250 °C at a rate of 8 °C min^{-1}. Samples were injected in split mode to an injector held at 250 °C. The injection volume was 1 μL, with a split ratio of 20:1. The transfer line and source temperature were 300 °C and 230 °C respectively. Hydrogen carrier gas was used with flow rate of 1.1 mL min^{-1}.

Analysis of duplicate samples were performed in the Department of Chemistry Mass Spectral Services Laboratory at the University of Alberta using an Agilent Technologies 7890A gas chromatograph (GC) with a 5975 quadrupole mass spectrometer (MS) fitted with a 7683 auto sampler (Agilent Technologies, Mississauga, ON) and a 30 m × 250 μm; 0.25 μm d_f Rxi-1MS column (crossbond 100% dimethyl polysiloxane, Restek). All other instrument parameters were the same as those used at the RCMP laboratory except that helium carrier gas was used (flow rate 1 mL min^{-1}) and the transfer line temperature was 200 °C.

2.2.5.2 Casework Debris Samples

Casework debris samples were analyzed at the RCMP laboratory using standard protocols (see conditions listed above). These samples are described in detail in a previous work [81].

2.2.6 Data Handling

Chromatograms for 31 gasoline-containing samples and 36 gasoline-free samples were exported from Chemstation as CSV files and then imported into

MATLAB (version 8.1.0; The Mathworks, Natick, MA). They were then aligned using an in-house MATLAB algorithm based on the piecewise alignment of the perdeuterated alkane ladder [66]. The chemometric model was optimized with a lab-built backward-elimination/forward selection (BE/FS) hybrid approach [107] relying on two-dimensional cluster resolution as the model quality metric for optimization [66, 105]. The optimized model was then applied to the data with MATLAB routines written in-house using some analysis function from the PLS Toolbox 5.2 (Eigenvector Research Inc, Wenatchee, WA). Mass spectral searching to identify selected features was performed against the NIST08 (NIST, Gaithersburg, MD) and W8N08 libraries (John Wiley and Sons, Inc., New York, NY).

2.3 Results and Discussion

In this work we set out to evaluate a fire debris simulation protocol [80] to determine its suitability for generating debris that could be used for automated optimization and training of chemometric models for the detection of gasoline in casework arson samples. The set of casework data was collected from fire scenes across Canada over a period of several months; a process that is not only time consuming, but also requires each sample to be analyzed and then evaluated by a forensic analyst for the presence of ignitable liquid before it can be used to train a chemometric model. Previously, we demonstrated that gasoline could be detected in casework samples when casework data were used for the construction of the chemometric model [81]. It was during this prior research that we also observed that for the simulation method used in early work towards automated model construction [66], the features used to identify gasoline included C_2-alkylbenzenes which are known to be of little diagnostic value because they are common pyrolytic products found in fire debris. It was also observed that the model based on simulated debris could not classify casework samples successfully. This pointed to the need for an improved debris simulation protocol in order to generate simulated fire debris for the training of chemometric models which can be applied to casework samples.

For any chemometric treatment of raw chromatographic data, retention time alignment is critical. There are a variety of alignment methods that have been applied to raw chromatographic data. For arson investigations, alignment is more difficult than for many other situations due to the presence of numerous peaks from the burned matrix with highly similar spectra that are present in uncontrolled patterns. Relying on the peaks that occur natively in the samples typically results in mismatched peaks and poor alignment. Consequently, we developed a strategy relying on a series of perdeuterated alkanes spiked into the solvent that serve as a retention alignment ladder [66]. This was the approach used in this work.

In the handling of raw GC-MS data, variable selection is also critical. A raw GC-MS chromatogram can easily contain over 1 million data points for a 30-minute separation; however, the majority of the data points contain little useful information. Inclusion of all of the variables results in the inclusion of excessive noise which degrades the final model to the point where it is often ineffective. The variable selection method that we used in this research was a hybrid backwards elimination / forward selection approach detailed elsewhere [107] which relies on pre-ranking of variables by selectivity ratio [100, 112] and uses cluster resolution [105] as the model quality metric to be optimized. Prior to model construction, all chromatograms were normalized to a total signal area of 1 followed by autoscaling.

One variable that we investigated was the influence of carrier gas on the models to determine if data collected using helium as a carrier gas could be used to construct a model that would work to predict the presence/absence of gasoline when the same samples were analyzed on a system using hydrogen carrier gas. To this end, simulated debris samples with and without gasoline were analyzed on the University of Alberta (UA) system (helium carrier) and on the RCMP system (hydrogen carrier). The RCMP data were then split into a training, optimization, and validation set to build a preliminary partial least squares discriminant analysis (PLS-DA) classification model for the identification of gasoline in debris. The model was then applied to the UA data from the same samples. The number of latent variables (LVs) was chosen based on the root mean square error of cross-validation (RMSECV) estimated from venetian blinds cross-validation with 10 data splits. One LV was used in this model construction. These results (**Figure 2-1**) show that the data with hydrogen carrier could be used to predict the results for helium carrier.

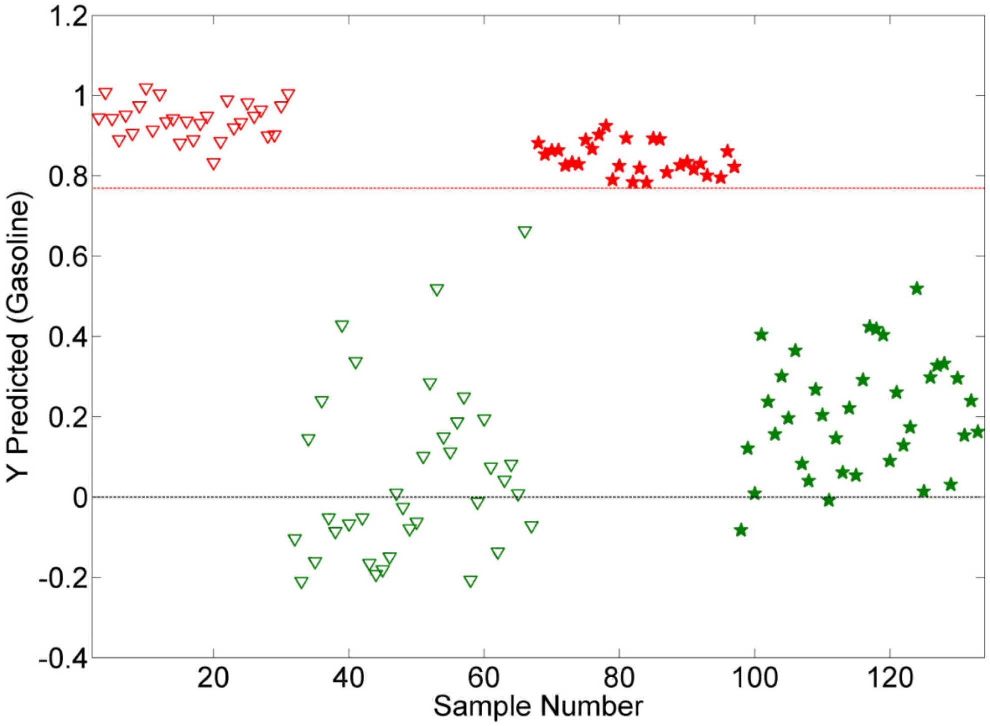


Figure 2-1. PLS-DA plot for arson data. Triangles represent RCMP data of simulated debris (hydrogen carrier gas) and stars represent UA data of simulated debris (helium carrier gas). Red and green markers represent gasoline-containing and green markers represent gasoline-free sample, respectively. Hollow markers indicate training and optimization set data. Filled markers indicate validation set data. Red dashed line indicates classification boundary.

Subsequently, we tested a PLS-DA model constructed with simulated debris analyzed on the RCMP system (**Figure 2-2**) for the classification of casework samples. One LV was chosen in the model construction of PLS-DA as it provided the lowest misclassification rate. In this PLS-DA model, the sensitivity, specificity, and accuracy were 0.9677, 0.9872, and 0.9786, respectively. This performance is poorer than the performance for a model trained on casework data, which had perfect specificity, sensitivity, and accuracy [81].

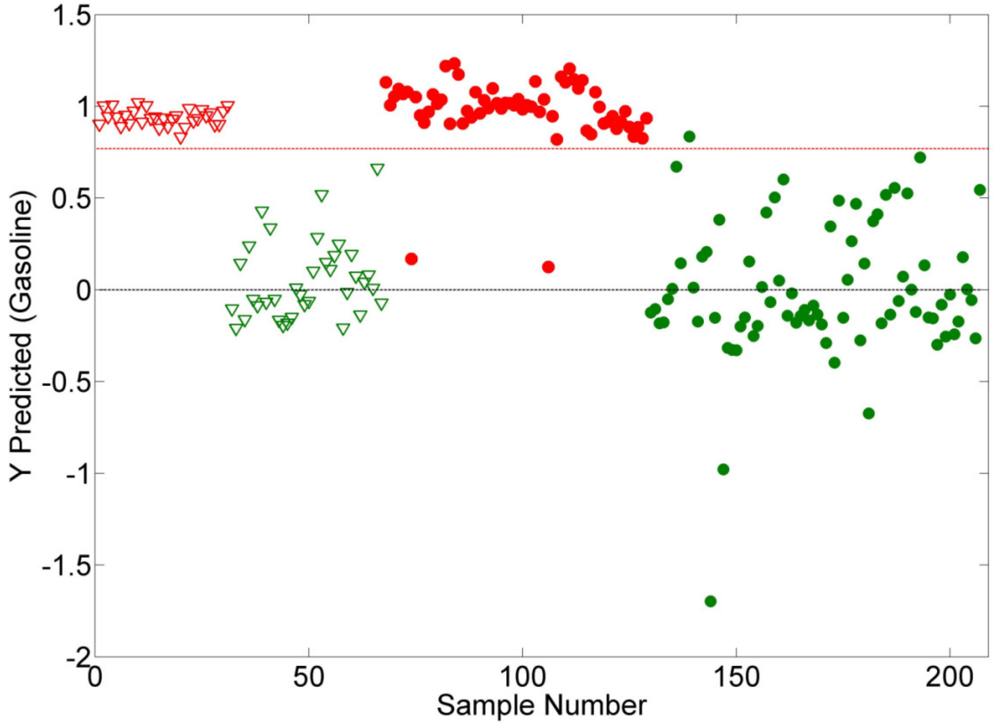


Figure 2-2. PLS-DA plot for arson data. Triangles represent RCMP data of simulated debris and circles represent casework debris data. Red and green markers represent gasoline-containing and green markers represent gasoline-free sample, respectively. Hollow markers indicate training and optimization set data. Filled markers indicate validation set data. Red dashed line indicates classification boundary.

We then tested a PLS-DA classification model trained with simulated debris analyzed at UA to classify casework debris chromatograms which were collected previously by the RCMP. Two LVs were used in this model construction. In the PLS-DA classification model (**Figure 2-3**), the sensitivity, specificity, and accuracy were

0.9032, 0.9615, and 0.9357, respectively. The relatively poorer performance as compared to the previous model based on simulated debris data collected at the RCMP is most likely due to subtle differences between column chemistries and slight shifts in retention times for some analytes as the carrier gas is changed.

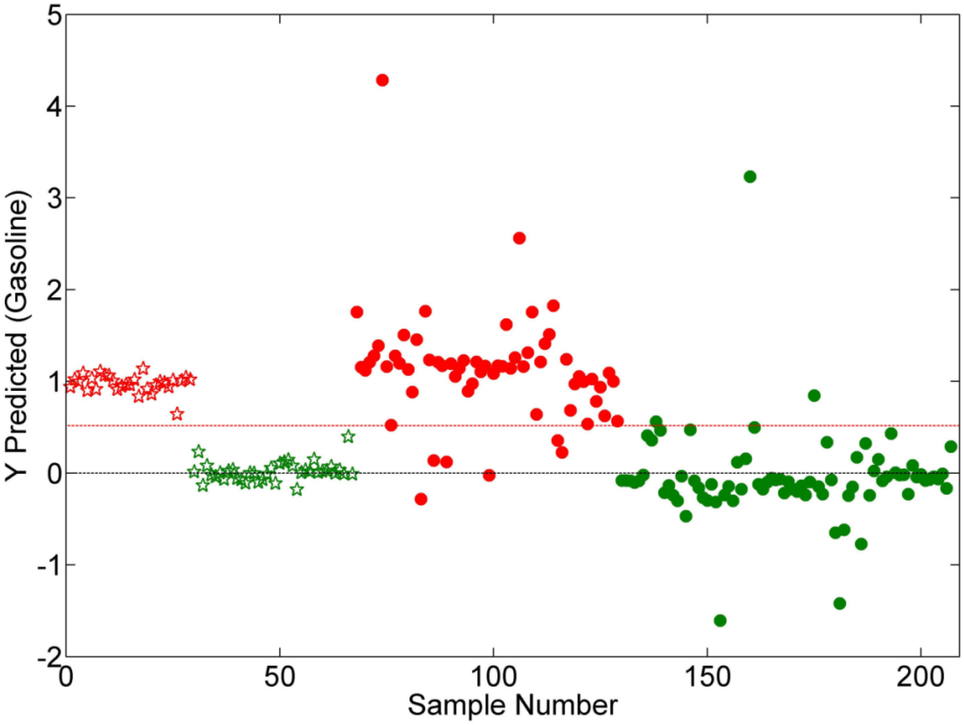
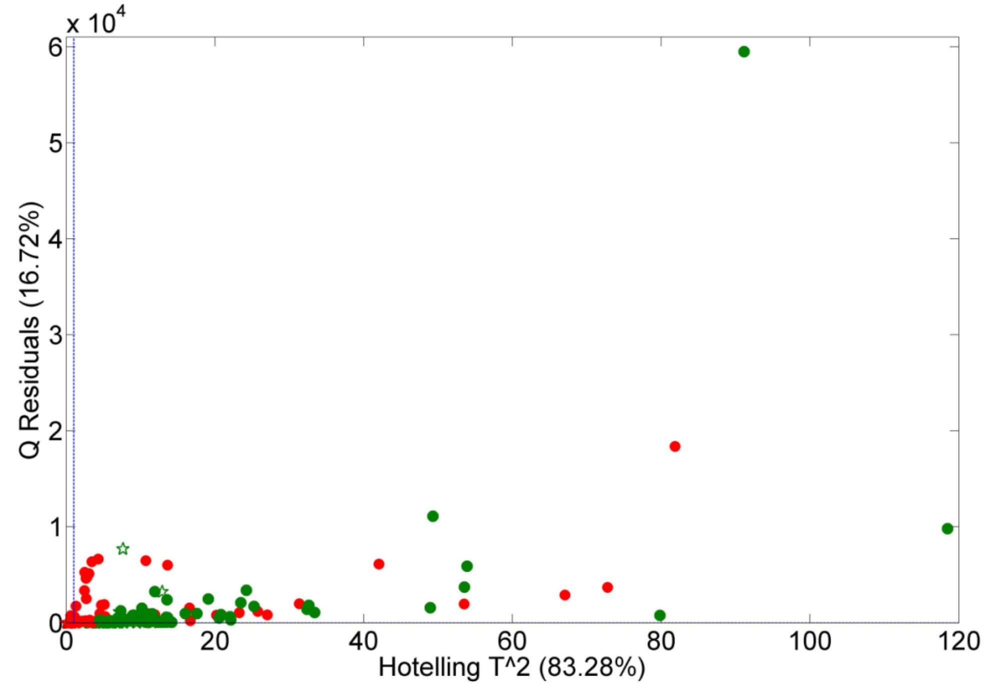
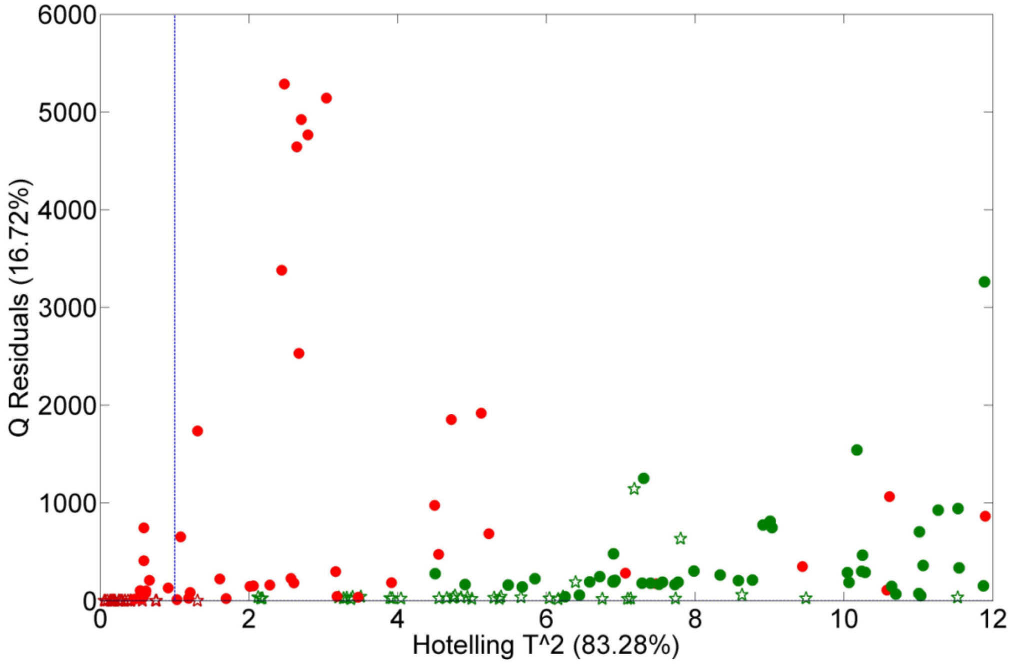


Figure 2-3. PLS-DA plot for arson data. Stars represent UA data of simulated debris and circles represent casework debris data. Red and green markers represent gasoline-containing and green markers represent gasoline-free sample, respectively. Hollow markers indicate training and optimization set data. Filled markers indicate validation set data. Red dashed line indicates classification boundary.

In the case of fire debris analysis, PLS-DA is likely not the most appropriate tool to use since it is a hard classification model that forces samples to be in one and only one class. In the case of analyzing real fire debris where one or more ignitable liquids may or may not be present, and the non-IL containing class (background matrix) does not have a uniform composition or profile (i.e. the negative samples are not necessarily similar and will not necessarily project into the same region in model scores space), an approach such as soft independent modelling by class analogy (SIMCA) may be more appropriate. With this approach the data are tested to see how similar they are to known classes, and samples can belong to no class, one class, or multiple classes. **Figure 2-4** and **2-5** show the residuals plots for SIMCA models of gasoline-containing class trained by data from simulated debris collected at UA and RCMP respectively. The number of principal components (PCs) is chosen based on the root mean square error of cross-validation (RMSECV) by venetian blinds with 10 data splits. Six LVs were used in both model constructions. The results show that only the gasoline-containing simulated data fall within the 95% confidence intervals of the model (as indicated by the dashed lines in the figures). In both plots, gasoline-containing casework debris scatter over a wide range of Q residuals, but with relatively low T^2 for the most part, indicating that the casework samples do not conform well to the model. Gasoline-free debris, regardless its origin, have high residuals and would not be classified as containing gasoline.


x 10^4
Q Residuals (16.72%)
Hotelling T^2 (83.28%)
0
1
2
3
4
5
6
0
20
40
60
80
100
120


Q Residuals (16.72%)
Hotelling T^2 (83.28%)
0
1000
2000
3000
4000
5000
6000
0
2
4
6
8
10
12

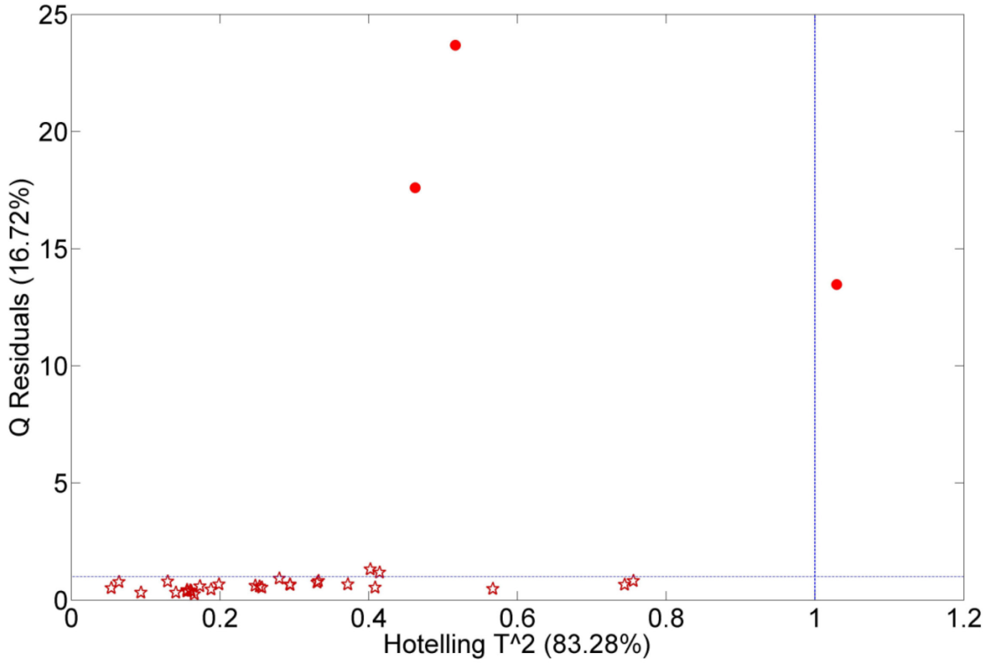
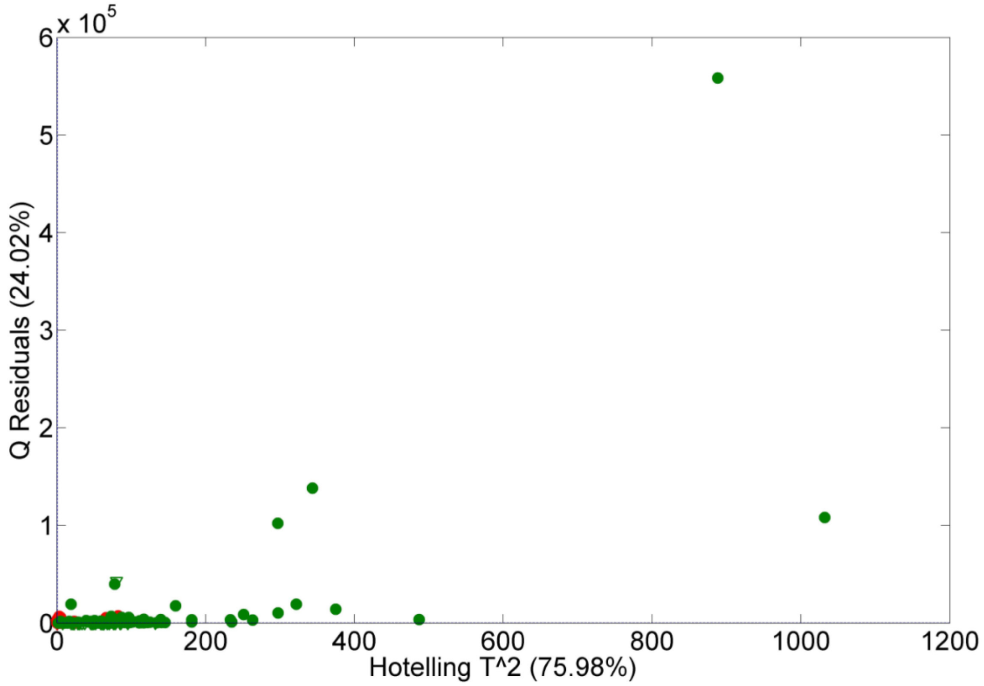
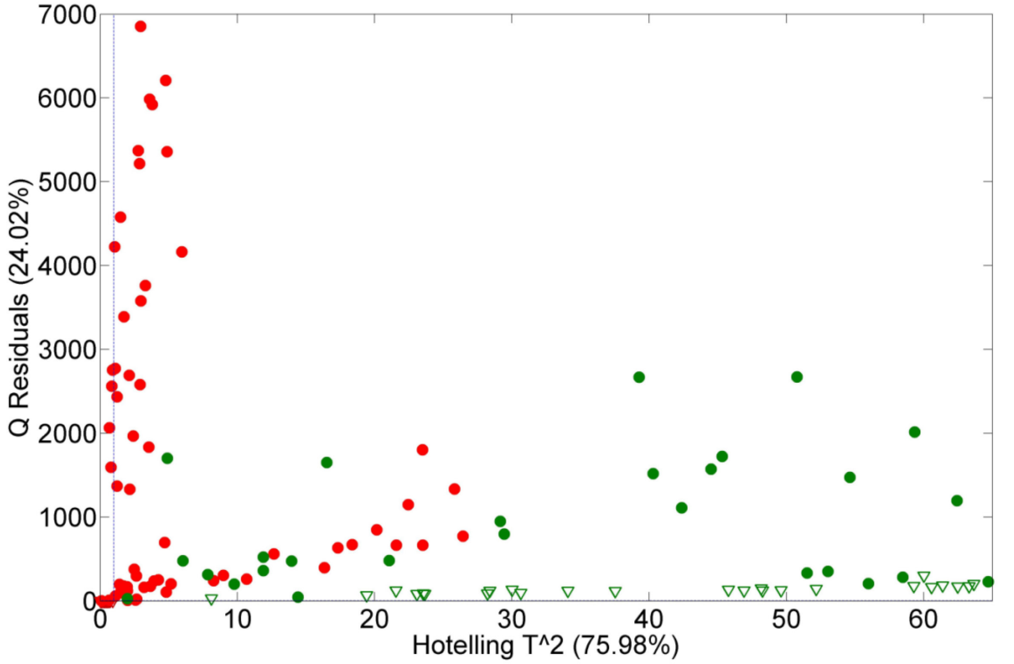


Figure 2-4. SIMCA plots with different zooms for arson data. Stars represent UA data of simulated debris and circles represent casework debris data. Red and green markers represent gasoline-containing and green markers represent gasoline-free sample, respectively. Hollow markers indicate training and optimization set data. Filled markers indicate validation set data. Blue dashed lines indicate 95% confidence limit for Hotelling T^2 and Q residuals.


x 10^5
6
5
4
3
2
1
0
Q Residuals (24.02%)
0
200
400
600
800
1000
1200
Hotelling T^2 (75.98%)


7000
6000
5000
4000
3000
2000
1000
0
Q Residuals (24.02%)
0
10
20
30
40
50
60
Hotelling T^2 (75.98%)

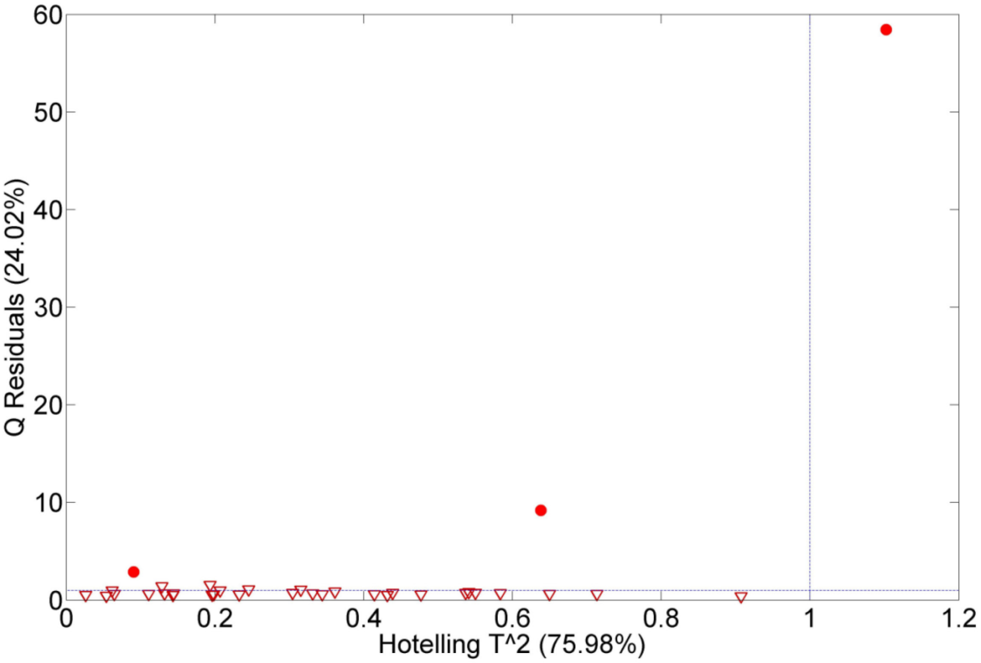


Figure 2-5. SIMCA plots with different zooms for arson data. Triangles represent RCMP data of simulated debris and circles represent casework debris data. Red and green markers represent gasoline-containing and green markers represent gasoline-free sample, respectively. Hollow markers indicate training and optimization set data. Filled markers indicate validation set data. Blue dashed lines indicate 95% confidence limit for Hotelling T^2 and Q residuals.

The features in the data that were selected to predict the presence of gasoline are shown in **Figure 2-6**. It is apparent that there are significant contributions from C_2-, C_3-, and C_4-alkylbenzenes as well as non-aromatic hydrocarbons. This is different from the features selected when training the models with casework debris. In a previous study, the important signals were due to C_3-, C_4-, and C_5-alkylbenzenes (or indanes) [81] which was encouraging because these are some of the same markers identified by ASTM E1618 as being characteristic of gasoline [11]. In the present research, the poor classification is likely due to the fact that the optimization algorithm relies on significant contributions from C_2-alkylbenzenes and generic non-aromatic hydrocarbons. While these compounds are certainly major components of gasoline, they are not characteristic of gasoline because they are also produced in abundance during pyrolytic processes that occur in a fire. This points to a deficiency in the debris simulation protocol, at least from the point of view of automated chemometric model construction. C_2-alkylbenzenes and non-aromatic hydrocarbons are not generated abundantly from the simulation process, so they are misunderstood by the model as being characteristic of gasoline. Thus, gasoline-free casework debris containing these compounds at high concentration were misclassified.

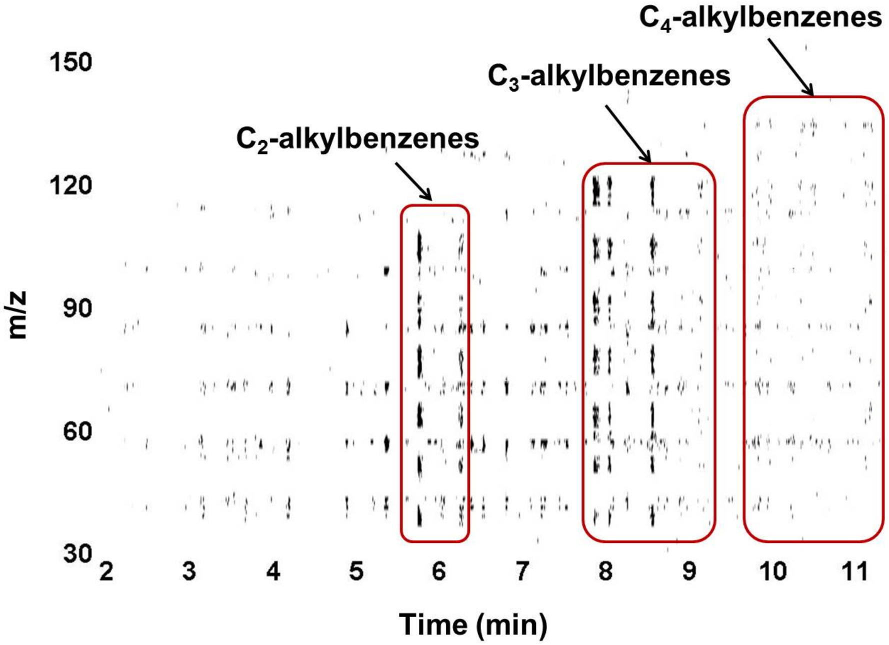


Figure 2-6. Variables selected from GC-MS chromatograms included in chemometric model for identification of gasoline in debris sample. The framed dots are C_2-, C_3- or C_4-alkylbenzenes as specified and the unframed dots are non-aromatic hydrocarbons.

This simulation protocol has been previously demonstrated to generate fire debris that contains pyrolysis products similar to those commonly found at fire scenes [80]. However, this finding is due to the fact that human analysts focus on extracted ion chromatograms (EICs) and profiles of specific marker compounds and extensive *a priori* knowledge of the data. Gasoline has unique extracted ion profiles that can be differentiated from other pyrolysis products by human analysts. This differs from our model construction algorithm which is seeking to automatically discover those molecules which can be used reliably for class discrimination and depends very heavily on having realistic input data. Refinement of the debris generation approach is thus required.

2.4 Conclusions

In this research, an automated chemometric model construction and optimization approach has been applied to simulated debris which were generated based on an established simulation protocol [80]. Both PLS-DA and SIMCA models have been constructed to demonstrate their performance on identification of gasoline. The simulation protocol had been previously shown to be able to generate suitable data for training human analysts to identify gasoline in casework debris. However, the chemometric models have demonstrated that this simulation approach does not produce a sufficient C_2-alkylbenzene and non-aromatic hydrocarbons background (as would often be found in fire debris). Thus, models constructed automatically based on fire debris simulated using this protocol are inadequate for the task of constructing a reliable model for the classification of casework debris samples. Further research is required for the development of a simulation approach that generates debris which are chemometrically equivalent to casework debris and can be used to establish models for the detection ignitable liquids other than gasoline in casework debris.

CHAPTER THREE: The Influence of Temperature on the Pyrolysis of Household Products

3.1 Introduction

Pyrolysis is the process whereby (typically large) organic compounds undergo thermal decomposition in the absence of oxygen (or other oxidants) [5, 13]. Common pyrolysis products of common materials found in a household fire include benzene, toluene, ethylbenzene and xylenes (BTEX), alkanes, and PAHs [13]. These compounds are also components of petroleum-based ignitable liquids (ILs). This clearly indicates the potential for pyrolysis to interfere with the detection of petroleum-based ILs. These interfering compounds can confound the results when looking for diagnostic features of ILs and make the data interpretation more challenging.

In an effort of applying chemometrics to the detection of gasoline in casework arson debris, the chemometric models trained by simulated debris were not able to classify casework debris based on gasoline content without introducing an unacceptable number of false positives and false negatives [114]. It was shown that the debris simulation approach that was used [80] did not produce a sufficient abundance of C_2-alkylbenzenes and non-aromatic hydrocarbons (as often found in casework fire debris) to cause the model optimization algorithm to ignore these features when identifying which peaks to retain for the chemometric model. Consequently, C_2-alkylbenzenes and non-aromatic hydrocarbons were chosen by the model to be reliable marker compounds for indicating the presence of gasoline. This, in turn, resulted in a model which would frequently misclassify casework debris samples. Thus a refinement of the simulation protocol is required to generate debris that is adequate for the automated construction of a chemometric model for classifying casework debris samples.

Many factors such as pyrolysis temperature and atmospheric conditions can affect the chemical profiles of the resultant pyrolysates of household materials. Although several studies have been conducted to investigate the influence of temperature on pyrolysis products, there has been no research about pyrolysis conducted with ramped-temperature profiles that mimic temperature profiles in a real fire to our knowledge. Additionally, there has been no comprehensive study across a broad range of building materials under identical conditions and with identical apparatus to our knowledge. In this research, we evaluate the influence of temperature and heating profile on the pyrolysis products of eight types of household materials, which are frequently submitted for arson analysis, as a step toward developing a lab-scale fire debris simulation protocol that results in more realistic debris samples suitable for chemometric modelling.

3.2 Experimental

3.2.1 Materials and Reagents

Eight different types of household materials were obtained locally and used in this study: spruce plywood (0.1 g/sample), vinyl sheet flooring (0.1 g/sample), polyethylene terephthalate (PET) carpet (0.2 g/sample), Nylon 6 carpet (0.2 g/sample), polyurethane (PU) foam carpet underlay (0.1 g/sample), asphalt shingle (0.8 g/sample), medium-density fireboard (MDF) shelving (0.2 g/sample) and spruce timber (0.3 g/sample). Chemical reference standards used for peak identification were obtained from the University of Alberta Recycled Chemicals Stores. The identities of compounds were verified by GC-MS. A full list of reference standards is given in **Table 3-1**.

Table 3-1. List of positively identified compounds.

Peak Label	Compounds	Experimental Retention Indices	MS Matching Factor
A	Benzene	675	965
B	Heptane	700	807
C	Toluene	769	967
D	Octane	800	877
E	Furfural	837	861
F	Ethylbenzene	865	961
G	*m*-Xylene	874	953
H	*p*-Xylene	875	929
I	*o*-Xylene	893	958
J	Nonane	900	885
K	Benzonitrile	988	912
L	Decane	1000	909

Peak Label	**Compounds**	**Experimental Retention Indices**	**MS Matching Factor**
M	*p*-Toluidine	1079	914
N	Guaiacol (2-Methoxyphenol)	1089	948
O	Undecane	1100	875
P	Naphthalene	1197	975
Q	Dodecane	1200	873
R	Thianaphthene	1208	888
S	2,4,6-Trimethylphenol	1209	865
T	p-Methylbenzoic acid	1282	914
U	Tridecane	1300	823
V	1-Methylnaphthalene	1328	931
W	Biphenyl	1395	974
X	Tetradecane	1400	865
Y	2,6-Dimethylnaphthalene	1426	841
Z	2,3-Dimethylnaphthalene	1464	792
AA	1,5-Dimethylnaphthalene	1469	778
BB	Acenaphthylene	1473	932
CC	Pentadecane	1500	789
DD	Acenaphthene	1507	941
EE	4-Methylbiphenyl	1516	903
FF	Fluorene	1610	881
GG	9H-fluoren-9-one	1778	872
HH	Phenanthrene	1818	955
II	Anthracene	1829	902
JJ	1-Phenylnaphthalene	1885	843
KK	2-Methylphenanthrene	1945	766
LL	1-Methyphenanthrene	1972	798
MM	2-Phenylnaphthalene	2007	936
NN	Fluoranthene	2118	936
OO	Pyrene	2168	919
PP	Triphenyl phosphate	2438	811
QQ	Triphenylene	2505	764

3.2.2 Pyrolysis of Materials

Substrates were weighed to an accuracy of ± 0.0005 g and loaded into pyrolysis tubes. Two types of tubes with similar dimensions were used in this research to accommodate different target temperatures: glass culture tubes (13 × 100 mm borosilicate glass; Kimble Chase, Vineland, NJ) and quartz tubes (12 x 110 mm fused quartz) manufactured in-house. To prevent over-pressurization and possible explosion, the caps were modified for some samples by drilling 0.25" and 0.358" diameter holes through the centres of the caps for the glass and quartz tubes, respectively, into which a polytetrafluoethylene septum was placed. A fused silica capillary (1 m × 100 μm; Agilent Technologies) was inserted through the septum in the cap, protruding approximately 0.5 cm into the tube. The outlet of the capillary was passed through the septum of the cap of a 2 mL GC vial (Chromatographic Specialties, Brockville, ON) containing 1 mL of CS_2 (ACS reagent grade; Fisher Chemical, Edmonton, AB) and submerged in the solvent (CS_2 volatiles trap). A needle also pierced the septum of the GC vial to allow venting as needed.

Pyrolysis was performed in a Carbolite MTF 10/15 mini-tube furnace fitted with a Eurotherm 818 electronic temperature controller (Carbolite, Hope Valley, U.K.). With the sample at the bottom of the pyrolysis tube, the tube was inserted into the preheated tube furnace such that the sample was located in the centre of the furnace to ensure the consistency of heating. Each sample was pyrolysed for a specific period of time and with a specific temperature-time profile (see below). Once the desired pyrolysis time was reached, the capillary vent tube was removed (if present) and the tube was removed from the furnace and inserted into a room-temperature water-jacketed copper tube to cool to room temperature [80]. After cooling, the cap on the tube was unscrewed, 0.5 mL CS_2 was quickly added, the tube recapped and shaken for 30 s. The extracted solution in the tube was removed by Pasteur pipette and filtered through a glass wool plug in another glass pipette. Another 0.5 mL of CS_2 was then used to rinse the glass wool into the final extract. Volatiles trapped in the CS_2 volatiles trap were also retained for analysis.

3.2.3 Temperature Profiles

The temperature profiles were based on temperature profiles observed in experiments involving fires in full-scale wood-frame structural fires [115]. Fifteen different heating profiles were explored in our work, including both isothermal and ramped temperatures. The three target temperatures were 400, 700, and 900 °C. For the isothermal heating profiles, each sample was inserted into a preheated furnace for 30 or 60 min at each target temperature. For the ramped temperature profiles, the initial temperature was 50 °C. This temperature was chosen because it was the lowest stable temperature that the furnace could reach within a reasonable cooling period. Samples were heated to the target temperature in 30 minutes and held at the final temperatures for 10, 30, or 60 min. The ramping profiles used for each experiment are described in **Figure 3-1**.

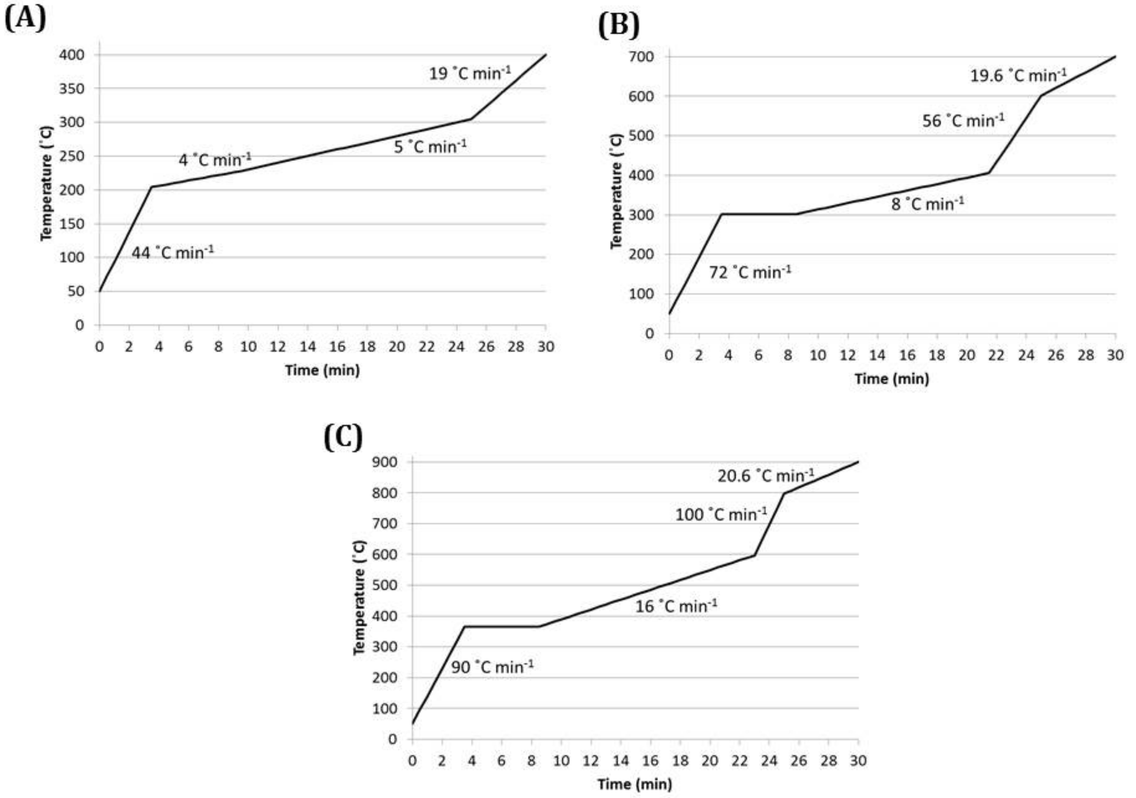


Figure 3-1. Pyrolysis ramped-temperature profiles for (A) 400 °C, (B) 700 °C and (C) 900 °C.

3.2.4 GC-MS Analysis

Extracts and CS_2 volatiles traps (if present) were analysed using an Agilent 7890A GC with 5975C quadrupole mass spectrometer and 7683 auto sampler (Agilent Technologies, Mississauga, ON). The column was a 28 m × 250 μm; 0.25 μm d_f ZB-5MS column (5%-phenyl-arylene/95%-dimethylpolysiloxane; Phenomenex, Torrence, CA). Helium (5.0 grade) carrier gas at a flow rate of 1 mL min^{-1} was used. Data acquisition and automation were performed by MassHunter Workstation (Agilent). The oven temperature program was set at 40 °C (3 min hold) to 320 °C (3 min hold) at 20 °C min^{-1}. Samples were injected in split mode (50:1) with the injector held at 280 °C and transfer line temperature was 200 °C.

3.2.5 Peak Identification

Compounds listed in **Table 3-1** were positively identified by mass spectral matching with the NIST 08 library (NIST, Gaithersburg, MD) using NIST MS Search Program (v. 2.0; NIST, Gaithersburg, MD) and retention index matching with the reference standard analysed using the same experimental conditions. Compounds listed in **Table 3-2** were tentatively identified by comparison to NIST 08 library mass spectra (NIST, Gaithersburg, MD) and by retention index matching with the library hit. Experimental retention indices were calculated from the retention time of known *n*-alkane standard solution (*n*-C_7 to *n*-C_{40}; Sigma-Aldrich, Edmonton, AB) [116]. Compounds were identified if the mass spectral match factors were above 750 and retention indices were within ±40 units.

Table 3-2. List of tentatively identified compounds.

Peak Label	Compounds	Experimental Retention Indices	Library Retention Indices	Differences in Retention Indices	MS Matching Factor
1	2,5-Dimethylfuran	704	696	8	860
2	C_8-Alkene	710			> 806
3	1-Methylpyrrole	735	722	13	880
4	Pyrrole	751	733	18	820
5	2-Methylheptane	768	767	1	841
6	Pentanenitrile	782	764	18	753
7	2-Ethyl-4-methyl-1,3-dioxolane	786	773	13	924
8	Cyclopentanone	795	766	29	863
9	1-Octene	798	785	13	844

Peak Label	Compounds	Experimental Retention Indices	Library Retention Indices	Differences in Retention Indices	MS Matching Factor
10	1-Isopropoxy-2-propanol	803	814	11	893
11	Methyl-2-cyclopenten-1-one	838			>898
12	C_9-Alkene	843			> 776
13	Trimethylcyclohexane	845			> 750
14	C_9-Alkene	849			> 791
15	Furanmethanol	859	826	33	915
16	1-(Acetyloxy)-2-propanone	871	839	32	820
17	Hexanenitrile	882	851	31	899
18	Styrene	893	914	21	900
19	Methyl-2-cyclopenten-1-one	900			> 791
20	Dimethylpyrazine	914			> 750
21	2-Hydroxy-2-cyclopenten-1-one	921	919	2	862
22	Propenylbenzene	950	950	0	911
23	Propylbenzene	958	944	14	915
24	5-Methyl-2-furancarboxaldehyde	963	924	39	852
25	Benzaldehyde	965	928	37	945
26	C_3-Alkylbenzene	966			> 780
27	C_3-Alkylbenzene	973			> 750
28	Aniline	981	946	35	957
29	α-Methylstyrene	983	980	3	880
30	C_3-Alkylbenzene	987			> 767
31	Phenol	989	960	29	944
32	1-Decene	992	987	5	901
33	C_3-Alkylbenzene	998			> 810
34	3-Methyl-1,2-cyclopentanedione	1025	1043	18	918
35	C_3-Alkylbenzene	1029			> 832
36	Indane	1045	1030	15	880
37	3-Butenylbenzene	1049	1039	10	
38	Indene	1050	1037	13	936
39	Methylphenol	1054			> 861
40	Chloro-C_2-alkylbenzene	1070			> 800
41	Acetophenone	1073	1052	21	966
42	Methylphenol	1075			> 877
43	1-Undecene	1092	1088	4	821
44	n-Pentyl isothiocyanate	1102	1112	10	909
45	Dimethylphenol	1110			> 823

Peak Label	Compounds	Experimental Retention Indices	Library Retention Indices	Differences in Retention Indices	MS Matching Factor
46	Dimethylphenol	1113			> 767
47	3-Ethyl-2-hydroxy-2-cyclopenten-1-one	1117	1100	17	882
48	Vinyl benzoate	1143	1150	7	938
49	C_2-Alkylphenol	1149			> 812
50	C_2-Alkylphenol	1151			> 827
51	3-Methylindene	1163	1155	8	818
52	Benzoic acid	1177	1170	7	903
53	Creosol	1193	1165	28	961
54	1-Dodecene	1192	1187	5	856
55	Phenyl isothiocyante	1203	1163	40	870
56	C_3-Alkylphenol	1238			>750
57	4-Ethylguaiacol	1278	1250	28	920
58	Cyclohexyl isothiocyanate	1248	1260	12	811
59	Caprolactam	1291	1260	31	931
60	2-Methylnapthalene	1312	1298	14	919
61	4-Vinylguaiacol	1315	1293	22	908
62	Tolyl isothiocyanate	1340			> 798
63	Benzenebutanenitrile	1348	1337	11	915
64	Eugenol	1358	1337	21	922
65	4-Propylguaiacol	1369	1345	24	903
66	C_2-Alkylbenzoic acid	1376			> 765
67	1-Tetradecene	1392	1385	7	787
68	Toluenediamine	1398			> 841
69	Toluenediamine	1401			> 785
70	Vanillin	1403	1403	0	901
71	*cis*-Isoeugenol	1409	1410	1	909
72	2-Chloroethyl benzoate	1413	1373	40	958
73	C_2-Alkylnaphthalene	1443			> 750
74	Methylbiphenyl OR Diphenylmethane	1452			> 840
75	*trans*-Isoeugenol	1455	1429	26	948
76	*p*-Diacetylbenzene	1467	1470	3	845
77	Apocynin	1490	1503	13	849
78	1-Pentadecene	1492	1486	6	743
79	Methylbiphenyl	1507			> 814
80	1-Isopropenylnaphthalene	1516	1500	16	825
81	Guaiacylacetone	1532	1538	6	861

Peak Label	Compounds	Experimental Retention Indices	Library Retention Indices	Differences in Retention Indices	MS Matching Factor
82	2,2,4-Trimethyl-1,3-pentanediol diisobutyrate	1592	1591	1	835
83	1,3-Diphenylpropane	1677	1665	12	901
84	C_7-Alkylbenzoate	1717			> 775
85	2-Propenal, 3-(4-hydroxy-3-methoxyphenyl)- OR Coniferaldehyde	1743	1741	2	844
86	Diaminodiphenylmethane	2102			> 891
87	1,3-Propanediol dibenzoate	2173	2199	26	840
88	Terphenyl	2237			> 825
89	Dioctyl terephthalate	2752	2730	22	973

3.3 Results and Discussion

3.3.1 Reproducibility of the Simulation Method

Reproducibility of the pyrolysis experiment was evaluated using asphalt shingles and MDF shelving material. For these materials, each experiment was repeated three times. Visual comparison of the normalized chromatograms showed good reproducibility in terms of the product identities, intensities, and peak ratios. Replicate chromatograms from the pyrolysis of MDF shelving are shown in **Figure 3-2** as an example.

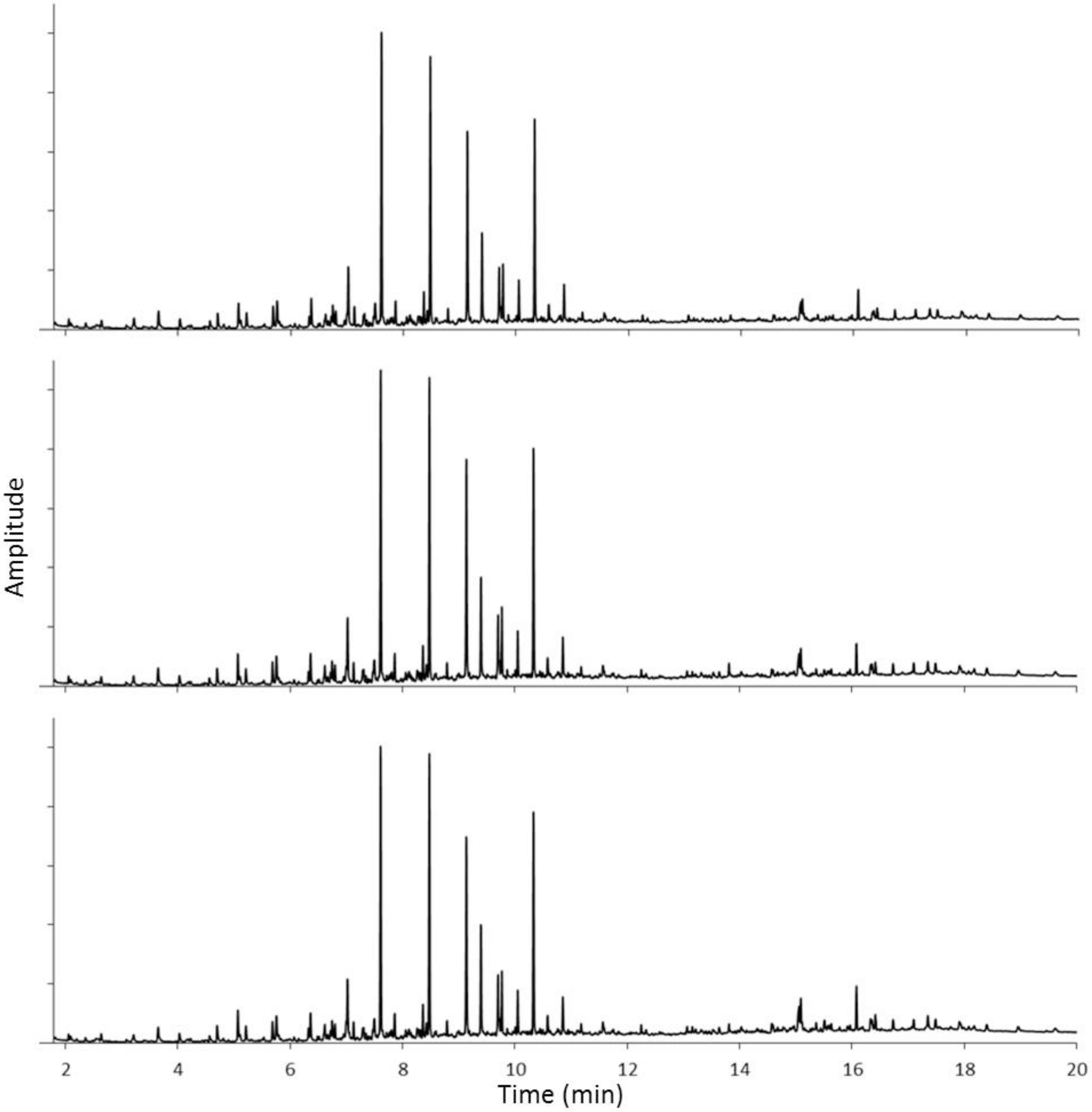


Figure 3-2. Plot of total ion chromatographic data from three replicate samples of MDF shelving each pyrolyzed at 400 °C for 30 min.

3.3.2 Comparison of Isothermal and Temperature-Programmed Pyrolysis at Each Target Temperature

For the isothermal pyrolysis experiments, each material was heated for 30 min and 60 min, at each target temperature. The general pattern in each chromatogram for a given substrate at different heating periods is similar in terms of the peak identities and their relative intensities, that is, the heating period does not significantly affect the pyrolysis products generated. The only exception was the 900 °C isothermal pyrolysis of Nylon 6 carpet in which the dominant compound (the tallest peak in the TIC) was different for the two times tested.

Comparison of the pyrolysates produced isothermally and with temperature ramping to temperatures of 400 °C showed very few differences in the compounds produced and their relative peak ratios. The temperature ramping and different heating times had no influence on the results for any of the substrates at 400 °C. This lack of change with heating rates/times did not always hold true for the pyrolysis reactions at 700 and 900 °C. When heating to 700 or 900 °C, some compounds generated by isothermal pyrolysis were not observed during the temperature-programmed pyrolysis, or vice versa. Additionally, the temperature-programmed pyrolysis with a 10 minute hold did not produce the same chemical profile as pyrolysis with longer hold times.

3.3.3 Comparison of Pyrolysate Profiles of Substrate under Different Conditions

3.3.3.1 Asphalt Roofing Materials

Asphalt shingles are manufactured from the residue derived from the vacuum distillation of crude oil, and are composed of saturated hydrocarbons, polycyclic aromatics, polar aromatics and heterocyclic compounds. The chromatograms of pyrolysates generated from asphalt shingle at three different temperatures are shown in **Figure 3-3**. Asphalt shingle is the only material we studied that generated an extensive series of alkanes and alkenes in significant abundance. Its pyrolysis at 400 °C generated mainly alkenes and alkanes (both straight chain and branched). *n*-Alkenes and *n*-alkanes appeared as couplets for C_7 to C_{30} although for C_{16} to C_{30} they were not identifiable based on our criteria for MS and RI matching. Some isomers including 2-methylheptane and C_9-alkene were also tentatively identified from the 400 °C pyrolysis experiments. These isomers presumably originated from the combination of radicals produced during the thermal degradation of hydrocarbons present in the petroleum-based materials [42]. BTEX were not produced from any of the 400 °C pyrolysis experiments on asphalt shingles but appeared as major products at 700 °C. Ethylbenzene and xylenes were most noticeably in asphalt shingle among all materials investigated. Except for BTEX, the pyrolysates of asphalt shingles at 700 °C also contained of alkanes, alkenes and several aromatic compounds (naphthalene, methylnaphthalenes and biphenyl). C_3-alkylbenzenes were also generated when asphalt shingle was pyrolyzed at 700 °C and had similar relative ratios as those in petroleum-based ILs. When pyrolysis was conducted at 900 °C, BTEX were also observed but the quantity of ethylbenzene and xylenes generated was insignificant (< 5% of tallest peak). The pyrolysis products mainly consisted of polyclyclic aromatic compounds (PAHs) such as acenapthylene, acenaphthene, 9H-fluorene, phenanthrene, anthracene, phenylnaphthalenes, fluoranthene and pyrene although pyrene was only observed from the temperature-programmed 900 °C pyrolysis with a hold time of 60 min. Acenaphthylene, acenaphthene and 9H-fluorene were newly discovered in our study from the pyrolysis of asphalt shingle while others are known to originate from hot asphalt roofing tar [117].

The pyrolysis of asphalt shingle reliably generated long chain n-alkane/ n-alkene couplets and naphthalene as reported in the literature [42, 57]. The pyrolysis of asphalt shingles at 400 and 700 °C reproducibly generated pyrolysates with an abundance of compounds (alkanes and BTEX) that could mask the signature of gasoline and other petroleum-based ILs. This suggests that a mixture of asphalt shingles pyrolyzed at both 400 and 700 °C is an important component for simulated debris that mimics casework debris for training a chemometric classification model. **Table 3-3** lists the pyrolysis products that are important to chemometric analysis, and also lists new compounds that have not been previously reported in the pyrolysis.

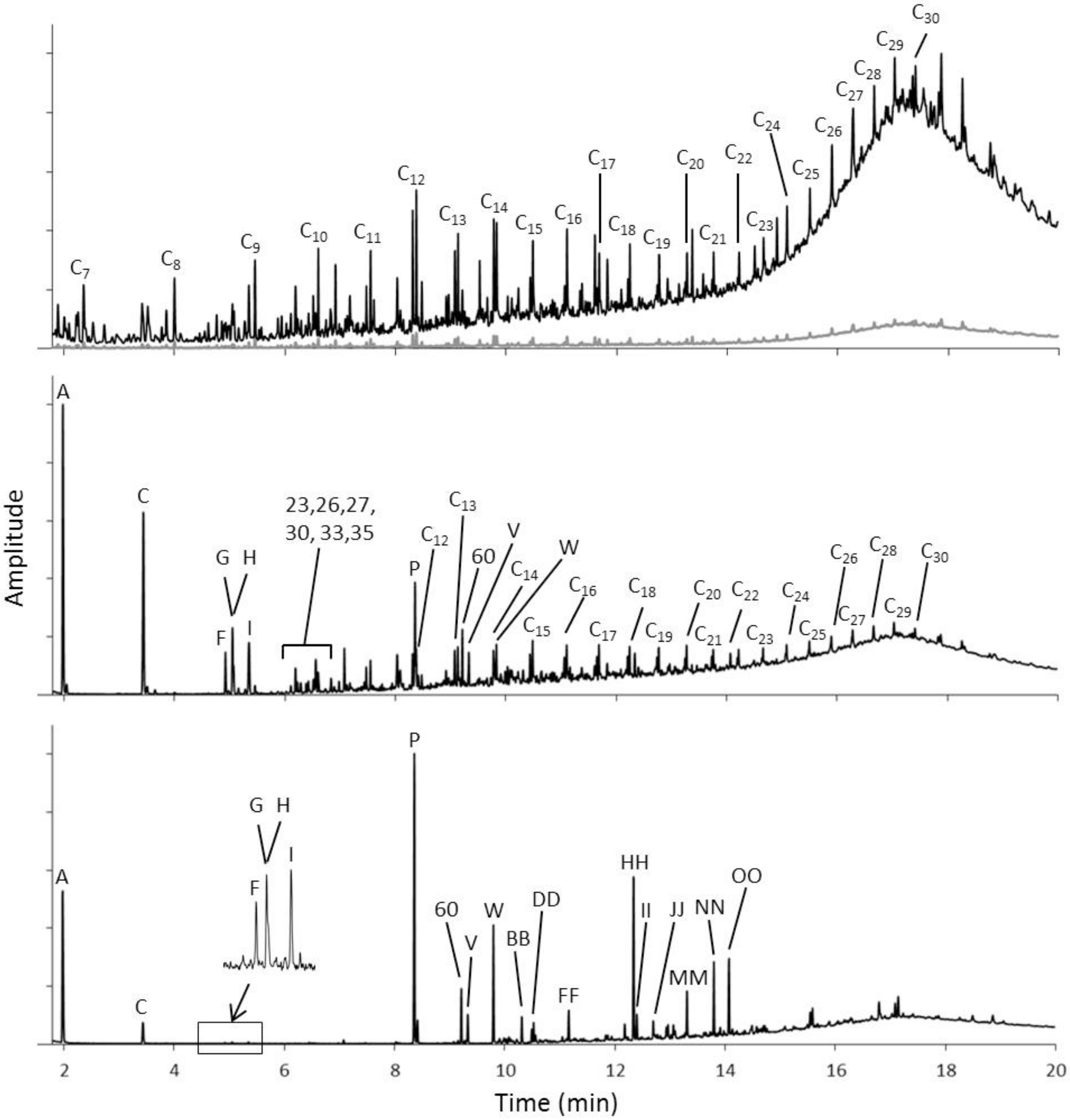


Figure 3-3. Comparison of chromatographic profiles obtained from isothermally pyrolyzed asphalt shingle at 400 °C (top), 700 °C (middle) and 900 °C (bottom). Note that peak heights are normalized to 100% for the tallest peak in each chromatogram. The top chromatogram is drawn in grey at the same scale as the middle and bottom chromatograms.

Peak assignments may be found in Tables 3-1 and 3-2, where letters indicate positively identified compounds (Table 3-1), and numbers indicate tentatively identified compounds (Table 3-2).

Table 3-3. Pyrolysis products of interest of each material at different groups of temperature. IT and TP represent isothermal and temperature-programmed pyrolysis respectively. The number after IT and TP represents the target temperature and the second part of number for temperature-programmed pyrolysis indicates the hold time. "X" indicates the presence of compound of interest.

Asphalt Shingle

Compounds of Interest	**IT 400 TP 400**	**IT 700**	**TP 700-10**	**TP 700-30 TP 700-60**	**IT 900**	**TP 900-10**	**TP 900-30 TP 900-60**
Benzene		X	X	X	X	X	X
Toluene		X	X	X	X	X	X
Ethylbenzene		X	X	X	X	X	X
Xylenes		X	X	X	X	X	X
C_3-Alkylbenzene		X	X	X			
Alkanes (C_7-C_{11})	X						
Alkanes (C_{11}-C_{30})	X	X	X	X			
Alkenes	X	X					
Acenaphthylene					X	X	X
Acenaphthene					X	X	X
Fluorene					X	X	X

PET Carpet

Compounds of Interest	**IT 400 TP 400**	**IT 700**	**TP 700-10**	**TP 700-30 TP 700-60**	**IT 900**	**TP 900-10**	**TP 900-30 TP 900-60**
Benzene		X	X	X	X	X	X
Toluene	X	X	X	X	X	X	X
Ethylbenzene	X	X	X	X	X	X	X
Xylenes		X	X	X	X	X	X
C_3-Alkylbenzenes	X	X	X	X			
Alkanes (C_7-C_{11})	C7						
Alkanes (C_{11}-C_{30})							
Alkenes	C9						

Nylon 6 Carpet

Compounds of Interest	**IT 400 TP 400**	**IT 700**	**TP 700-10**	**TP 700-30 TP 700-60**	**IT 900**	**TP 900-10**	**TP 900-30 TP 900-60**
Benzene		X	X	X	X	X	X
Toluene	X	X	X	X	X	X	X
Ethylbenzene	X	X	X	X	X	X	X
Xylenes		X	X	X	X	X	X
C_3-Alkylbenzenes	X	X	X	X	30 min	X	
Alkanes (C_7-C_{11})							
Alkanes (C_{11}-C_{30})							
Alkenes	C9	C9	C9	C9	C9	C9	C9
Pentanenitrile	X	X	X	X	X	X	X
Hexanenitrile	X	X	X	X	X	X	X
n-Pentyl isothiocyanate	X	X	X	X			
Cyclohexyl isothiocyanate		X	X	X			
Benzonitrile					X	X	X

PU Carpet Underlay

Compounds of Interest	**IT 400 TP 400**	**IT 700**	**TP 700-10**	**TP 700-30 TP 700-60**	**IT 900**	**TP 900-10**	**TP 900-30 TP 900-60**
Benzene		X	X	X	X	X	X
Toluene	X	X	X	X	X	X	X
Ethylbenzene	X	X	X	X	X	X	X
Xylenes		X	X	X	X	X	X
C_3-Alkylbenzenes	X	X	X	X			
Alkanes (C_7-C_{11})							
Alkanes (C_{11}-C_{30})							
Alkenes							
Phenyl isothiocyanate	X	X	X	X	X	X	X
Benzenebutanenitrile	X	X	X	X	X	X	X
Toluediamine	X	X	X	X			
1,3-Diphenylpropane	X					X	X
Diaminodiphenylmethane	X						
Toly isothiocyanate	X	X	X	X	X	X	X
Triphenyl phosphate	X	X	X	X	X	X	X
Thianaphthene							X

PVC Sheet Flooring

Compounds of Interest	IT 400 TP 400	IT 700	TP 700-10	TP 700-30 TP 700-60	IT 900	TP 900-10	TP 900-30 TP 900-60
Benzene	X	X	X	X	X	X	X
Toluene	X	X	X	X	X	X	X
Ethylbenzene	X	X	X	X	X	X	X
Xylenes	X	X	X	X	X	X	X
C_3-Alkylbenzenes		X	X	X	X	X	X
Alkanes (C_7-C_{11})							
Alkanes (C_{11}-C_{30})							
Alkenes							
Chloro-C_2-alkylbenzene		X	X	X	X		
2-Chloroethyl benzoate	X	X	X	X	X	X	X

Spruce Lumber

Compounds of Interest	IT 400 TP 400	IT 700	TP 700-10	TP 700-30 TP 700-60	IT 900	TP 900-10	TP 900-30 TP 900-60
Benzene		X	X	X	X	X	X
Toluene		X	X	X	X	X	X
Ethylbenzene		X	X	X	X	X	X
Xylenes							
Alkanes (C_7-C_{11})							
Alkanes (C_{11}-C_{30})							
Alkenes							

Spruce Plywood

Compounds of Interest	IT 400 TP 400	IT 700	TP 700-10	TP 700-30 TP 700-60	IT 900	TP 900-10	TP 900-30 TP 900-60
Benzene		X	X	X	X	X	X
Toluene		X	X	X	X	X	X
Ethylbenzene					X	X	X
Xylenes							
Alkanes (C_7-C_{11})							
Alkanes (C_{11}-C_{30})							
Alkenes							

MDF Shelving

Compounds of Interest	IT 400 TP 400	IT 700	TP 700-10	TP 700-30 TP 700-60	IT 900	TP 900-10	TP 900-30 TP 900-60
Benzene		X	X	X	X	X	X
Toluene	X	X	X	X			
Ethylbenzene	X	X	X	X			
Xylenes	X	X	X	X			
Alkanes (C_7-C_{11})							
Alkanes (C_{11}-C_{30})							
Alkenes							

3.3.3.2 Carpets

Nylon and PET are two materials commonly used in carpet production. **Figure 3-4** shows the peak heights of BTEX and C_3-alkylbenzenes relative to the dominant peak in the chromatograms for each material pyrolyzed at different temperatures. When the carpets were pyrolyzed at 400 °C, benzene and xylenes were not observed. They generated BTEX only when pyrolyzed at either 700 or 900 °C, but the relative intensity of ethylbenzene and xylenes were much lower at 900 °C. It was also observed that larger amounts of ethylbenzene are produced compared with the xylenes. This result is consistent with results reported in the literature [18], and the pattern differs from the usual pattern observed for the C_2-alkylbenzenes in gasoline [5]. Two and one C3-alkylbenzenes were identified from the pyrolysis of PET, and one identified from pyrolysis of and Nylon 6 carpet, respectively but neither in insignificant amounts. These results show that including PET and Nylon 6 carpets pyrolyzed at 700 °C would add substantial C_2-alkylbenzenes content to the matrix. High abundances of BTEX were also observed in the chromatograms of carpets pyrolyzed 700 °C isothermally, as shown in **Figure 3-5**. The presence of these compounds in the matrix may be helpful in the training of more reliable chemometric models.

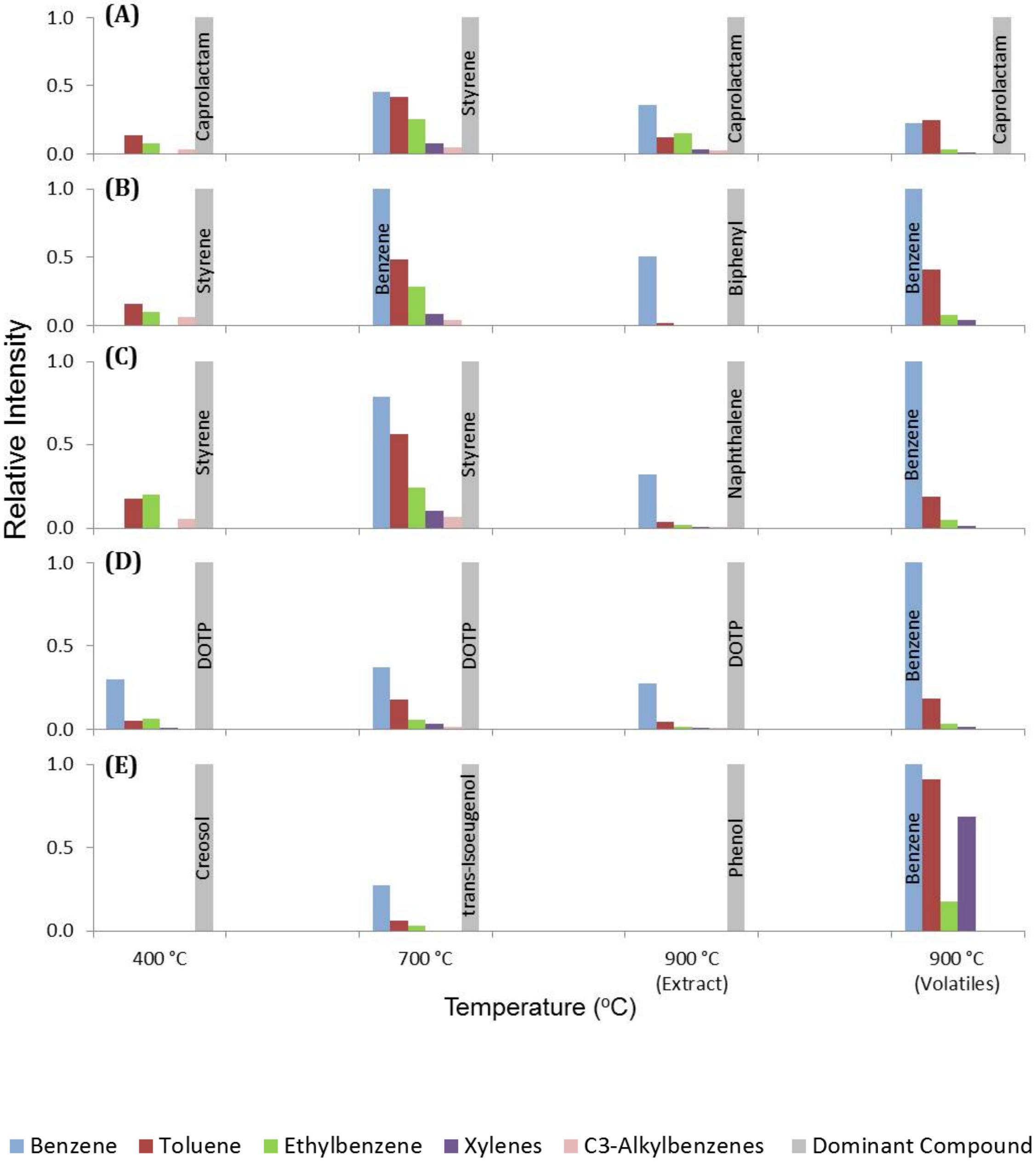


Figure 3-4. Bar charts for peak heights of BTEX and C_3-alkylbenzenes relative to dominant peak of chromatogram of (A) PET carpet, (B) Nylon 6 carpet, (C) carpet underlay, (D) vinyl flooring, and (E) spruce plywood at different pyrolysis temperatures.

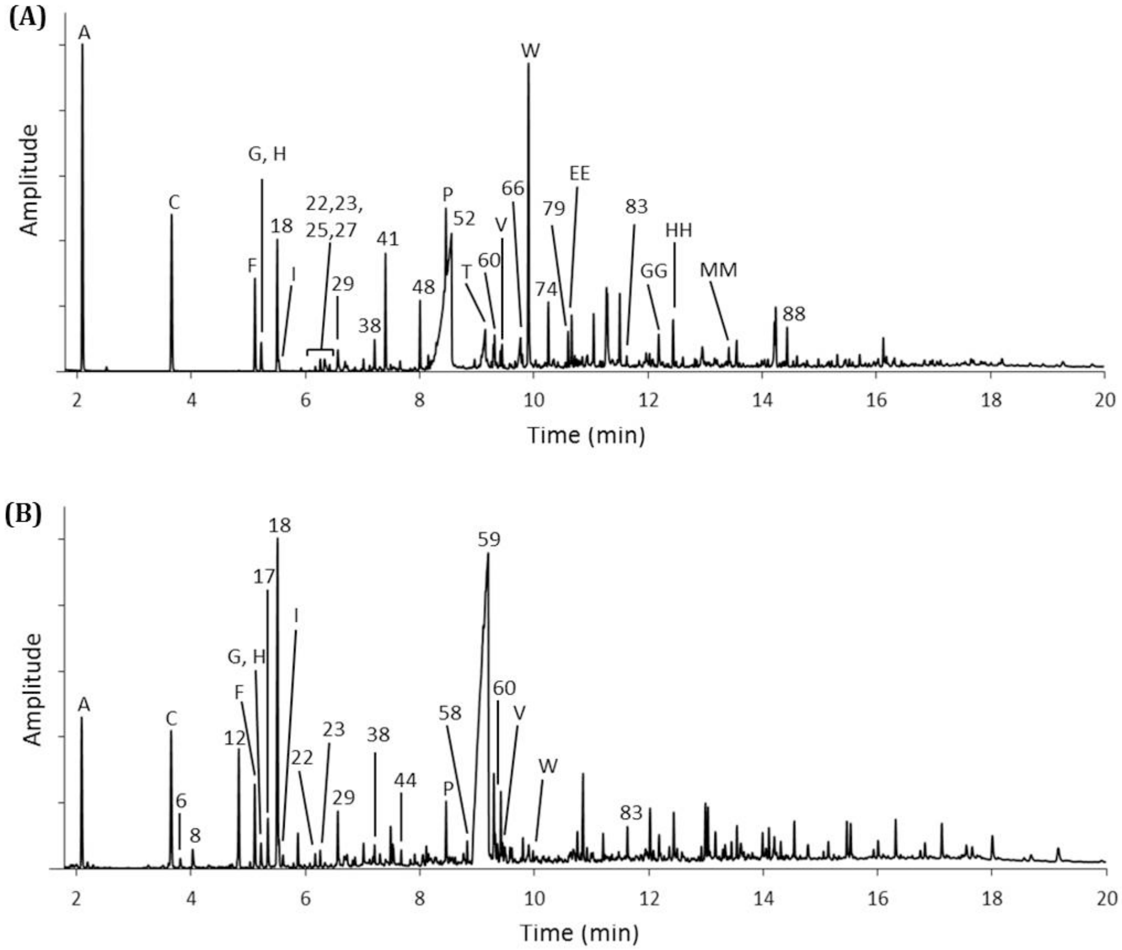


Figure 3-5. Total ion chromatographic data of (A) PET and (B) nylon carpet pyrolyzed at 700 °C for 30 min. Note that peak heights are normalized to 100% for the tallest peak in each chromatogram.
Peak assignments may be found in Tables 3-1 and 3-2, where letters indicate positively identified compounds (Table 3-1), and numbers indicate tentatively identified compounds (Table 3-2).

The characteristic pyrolysis product of PET, benzoic acid, was observed at all temperatures [30]. While pyrolysis of PET fibres is known to produce many benzoates [30], only vinyl benzoate was identified from the pyrolysates in our study. In addition, the chromatographic profile of temperature-programmed 700 °C pyrolysis generated two C_9-alkene isomer peaks which were not formed during at any of the other experiments at 700 °C. These two isomers were also observed in all experiments at 400 °C. Significant quantities of caprolactam monomer [118], formed by ring-opening polymerization, were observed during the pyrolysis of Nylon 6. Interestingly, two isothiocyanates and three nitriles were tentatively identified in the pyrolysates of Nylon 6 carpet. *n*-Pentyl isothiocyanates were detected at both 400 and 700 °C while cyclohexyl isothiocyanates were only observed at 700 °C. Nylon has been previously reported to produce acetonitrile at 770 °C [119], however this was not observed in our study. Instead, pentanenitrile, hexanenitrile and benzonitrile were generated from the pyrolysis of Nylon 6 carpet. Benzonitrile was observed only when Nylon 6 was pyrolyzed at 900 °C, while pentanenitrile was observed across all temperatures. Although hexanenitrile has been previously shown to be produced from Nylon 8 when it was pyrolyzed at temperatures up to 700 °C and not generated from Nylon 6 [119], in our study it was observed in all pyrolysis experiments of Nylon 6.

Both types of carpets also produced naphthalene and both methylnaphthalene isomers when they were heated to 700 and 900 °C. The intensity of naphthalene increased, while the relative intensities of the methylnaphthalene isomers fluctuated, with an increase in the pyrolysis temperature. Styrene was a major pyrolysis product from both types of carpet, a result that was consistent with the literature [15, 16, 118]. The production of α-methylstyrene during the pyrolysis of carpet has also been reported in literature [18, 118]; it was observed in all pyrolysis experiments involving Nylon 6 carpet, but was only generated at 400 °C and 700 °C from PET carpet.

Except for *n*-heptane that was observed from 400 °C pyrolysis of PET carpet, no other alkanes or alkenes were identified from any other carpet pyrolysates. However, several polycyclic aromatic and non-aromatic hydrocarbons were formed during the pyrolysis of PET and Nylon 6 carpets at 700 and 900 °C. Indene was generated from the pyrolysis of both types of carpets at both temperatures, while acenaphthylene, 9H-fluorene, and anthracene were present in all 900 °C pyrolysis experiments. Phenanthrene was generated from the pyrolysis of PET carpets at temperatures of 700 and 900 °C but only observed from the 900 °C pyrolysis experiments of Nylon 6 carpet. A few other PAHs were tentatively identified from the pyrolysis of PET carpets, such as 9H-fluoren-9-one, triphenylmethane and terphenyl. These were generated when PET carpet was heated to temperatures of 700 and 900 °C. Phenylnaphthalenes and fluoranthene are two other PAH products observed in the thermal degradation of PET carpets at 900 °C.

3.3.3.3 Carpet Underlay

The pyrolysis behaviour of carpet underlay is similar to carpets. Although it only generated benzene and xylenes when pyrolyzed at temperature above 700 °C, toluene and ethylbenzene were formed at all three temperatures. Overall, BTEX had a higher relative intensity at 700 °C (**Figure 3-6**) compared with other temperatures, although the relative intensity of ethylbenzene was similar at both

400 and 700 °C. Traces of propylbenzene and another C_3-alkylbenzene isomer were also identified at 400 and 700 °C but only in small amounts.

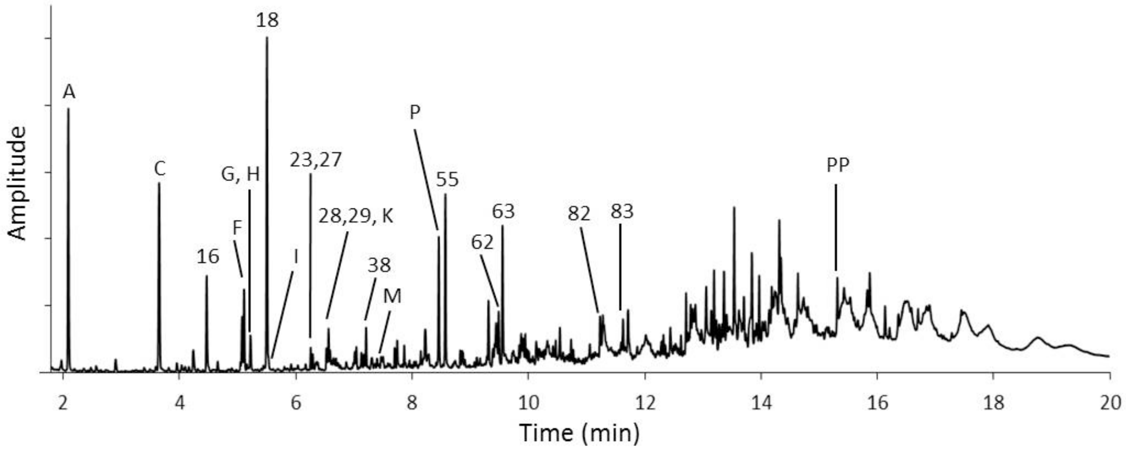


Figure 3-6. Total ion chromatographic data of carpet underlay pyrolyzed at 700 °C isothermally for 30 min. Note that peak heights are normalized to 100% for the tallest peak in each chromatogram.
Peak assignments may be found in Tables 3-1 and 3-2, where letters indicate positively identified compounds (Table 3-1), and numbers indicate tentatively identified compounds (Table 3-2).

The isothermal pyrolysis of PU carpet underlay generated slightly different chromatographic patterns compared to the temperature-programmed pyrolysis at 700 and 900 °C. At 700 °C, the isothermal pyrolysis generated styrene as the tallest peak whilst the dominant peak from temperature-programmed pyrolysis was phenyl isothiocyanate. The relative intensity of ethylbenzene was similar in both isothermal and temperature-programmed pyrolysis, but the relative intensity of benzene, toluene and xylenes were much higher in the isothermal pyrolysis. At 900 °C, although naphthalene and benzenebutanenitrile were, respectively, the tallest peaks in isothermal and temperature-programmed pyrolysis, the relative intensity of BTEX remained similar. Although the volatiles trap solution collected at 900 °C had high relative intensity of BTEX, the relative intensity of toluene, ethylbenzene and xylenes were lower than that at 700 °C. Therefore, isothermal pyrolysis of carpet underlay at 700 °C could potentially be used to generate realistic debris that would be useful in training a chemometric model for the classification casework samples.

Some other compounds that were tentatively identified from pyrolysis of carpet underlay include cyclopentanone, benzenebutanitrile, toluenediamine, 1,3-diphenylpropane, and diaminodiphenylmethane. Adipic acid is a monomer used for the production of polyurethane, which contributes to the generation of cyclopentanone [29, 120]. While cyclopentanone is a common pyrolysis product of PU, benzenebutanitrile, toluenediamine, 1,3-diphenylpropane and diaminodiphenylmethane have not been reported before. The toluenediamines, formed at 400 °C, may have been generated because they are precursors of toluene diisocyanate, which is used to make polyurethane [121]. Fused-ring compounds such as indene, phenanthrene, anthracene, acenaphthylene, fluoranthene, and pyrene were also found after the carpet underlay was pyrolysed at 900 °C, which is in agreement with previous studies [28, 29]. Triphenyl phosphate was also identified from the pyrolysis of PU carpet underlay at all temperatures; however, it has not been previously reported in the literature as a pyrolysis product of PU. This compound may have originated from a flame retardant added to the carpet padding

[122–124]. Apart from this, we also discovered three sulphur-containing compounds from the pyrolysis of PU carpet underlay: phenyl isothiocynate, tolyl isothiocyanate, and thianaphthene. These compounds have not been previously reported in the pyrolysates of PU, whereas pyrolysis of PU typically generates isocyanates because they are the precursors in the manufacture of polyurethanes [28, 29, 120, 121].

Similar to carpets, carpet underlay pyrolyzed at 700 °C also generated C_2-alkylbenzenes, and so this material would be useful for simulating debris with which to train a chemometric model for casework samples.

3.3.3.4 Vinyl Flooring

Among all the materials investigated, PVC flooring is the only one that generated BTEX in all pyrolysis experiments, and this was the only material tested that generated benzene at 400 °C. When heated above 200 °C, PVC polymers undergo stepwise dehydrochlorination and produce conjugated unsaturated chains, which then lead to cyclization and the formation of benzene and other hydrocarbon compounds with conjugated unsaturation [125, 126]. Similar to carpets, the intensities of ethylbenzene and xylenes relative to dioctyl terephthalate (DOTP) (the tallest peak), were highest at 700 °C (**Figure 3-7**). BTEX were also observed from the volatiles trap solution collected at 900 °C, with slightly lower relative intensities as compared to 700 °C. Three C_3-alkylbenzene isomers were observed in insignificant amounts from vinyl flooring pyrolyzed at 700 and 900 °C. Although pyrolysis of vinyl flooring generated BTEX with comparable intensities at both 700 and 900 °C, 700 °C would be a more practical pyrolysis temperature because the other materials investigated generated substantial amounts of BTEX when they were pyrolyzed at this temperature compared with pyrolysis at 900 °C.

Plasticizers are incorporated into PVC during manufacture to improve flexibility. DOTP, diethylene glycol dibenzoate [127], 2,2,4-trimethylpentane-1,3-diol diisobutyrate [128] and 1,3-propanediol dibenzoate [129] are examples of plasticizers used in the manufacture of stain-resistant flooring. These compounds, except for diethylene glycol dibenzoate, were tentatively identified in all pyrolysis experiments of PVC flooring. Diethylene glycol dibenzoate could not be identified based on our criteria for RI matching although it has high MS match factor (845). Among all the pyrolysis experiments, DOTP was generated as the dominant product, followed by 2,2,4-trimethylpentane-1,3-diol diisobutyrate and 1,3-propanediol dibenzoate. Benzoic acid and C_7-alkylbenzoate were generated in low abundance at 400 °C and may have originated from dibenzoate plasticizers.

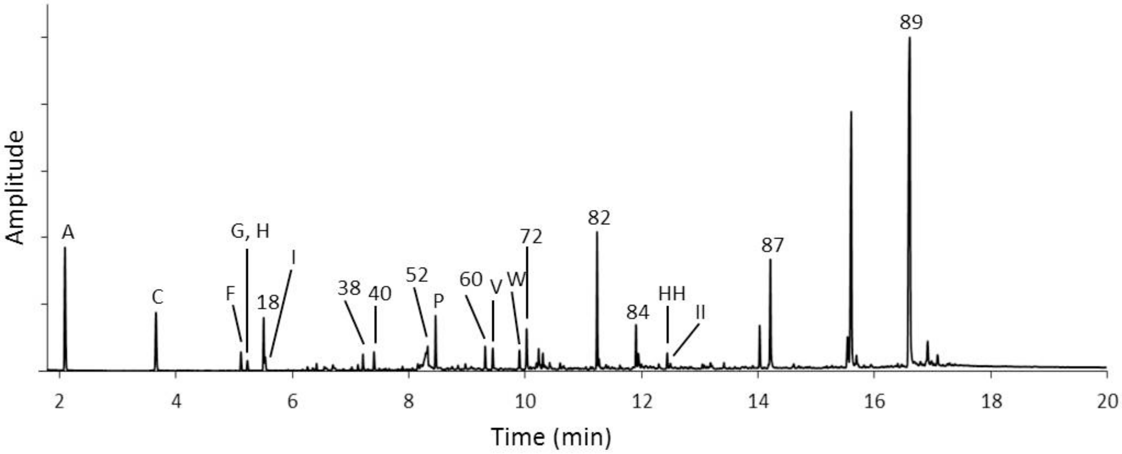


Figure 3-7. Total ion chromatographic data of vinyl sheet flooring pyrolyzed at 700 °C isothermally for 30 min. Note that peak heights are normalized to 100% for the tallest peak in each chromatogram.
Peak assignments may be found in Tables 3-1 and 3-2, where letters indicate positively identified compounds (Table 3-1), and numbers indicate tentatively identified compounds (Table 3-2).

Naphthalene and styrene were positively identified in all pyrolysis experiments of PVC flooring. The relative intensity of naphthalene generally increased with pyrolysis temperature; however, its relative intensity from temperature-programmed pyrolysis at 900 °C with 10 min hold time was as low as that from pyrolysis at 400 °C. Styrene appeared in low relative intensity at all 400 °C and temperature-programmed 900 °C pyrolysis experiments with 30 min and 60 min hold time.

Chloro-C_2-alkylbenzene and 2-chloroethyl benzoate were also tentatively identified from the 400 °C pyrolysis of PVC. These have not been previously reported in pyrolysates of PVC but their presence is likely due to secondary reactions of HCl with non-chlorinated chemical species (impurities) in the PVC. Contrary to the literature [22, 125], vinyl chloride and chlorobenzene, two common products generated from PVC pyrolysis, were not observed in our study. Pyrolysis at 700 °C produced indene, methylnaphthalenes, biphenyl, phenanthrene, and anthracene. They were formed via intramolecular cyclization or intermolecular mechanisms from the dehydrochlorinated polymer. Their abundance increased when pyrolysed at 900 °C. Apart from these, a large number of fused-ring or PAHs with aliphatic moieties were also identified, including C_3-alkylbenzenes, indane, C_2-alkylnaphthalenes, 3-methylindene, acenaphthylene, methylbiphenyl, fluorene, phenylnaphthalenes, and fluoranthene. These aromatic compounds were found in low abundance at both 700 °C and 900 °C. Pyrene and triphenylene were positively identified only at 900 °C. It is worth-mentioning that 3-methylindene, phenanthrene, and anthracene were not present when the pyrolysis was temperature-programmed to 700 and 900 °C with a hold time of 10 min. Also fluoranthene and 1-phenylnaphthalene were generated from the isothermal 700 and 900 °C pyrolysis but not the temperature-programmed pyrolysis reaching the same final temperatures. The pyrolysis of PVC is known to produce many PAHs including all of those mentioned above [21–23]; however, here we report for the first time the production of C_2-alkylnaphthalenes, and triphenylene from PVC pyrolysis at 900 °C.

3.3.3.5 Cellulose Materials

Wood is composed of lignin, cellulose and hemicellulose. Lignin accounts for approximately 25%-35% of the organic matter in spruce, and contributes to the majority of the pyrolysis products observed [130–132]. Lignin is formed from three main monomers: coumaryl-, coniferyl- and sinapyl alcohol [130, 131]. When treated at high temperature, lignin breaks down to smaller molecules via primary and secondary pyrolysis reactions [133] to form phenol, guaiacol, syringol and their poly-substituted products [130, 134]. Guaiacol, and its substituted products 4-ethylguaiacol, 4-vinylguaiacol, eugenol, 4-propylguiacol, *cis*- and *trans*-isoeugenol, apocynin, and guaiacylacetone, were observed as pyrolysis products for all three types of cellulose material tested at all temperatures and they appeared as major products during pyrolysis at 400 °C and 700 °C. Vanillin is another related pyrolysis product generated by both spruce lumber and plywood; however, it was not found in any pyrolysis experiments of MDF shelving. Phenols, including methylphenols and dimethylphenols, the products of reactions between radicals produced from the thermal degradation of guaiacol [135], were also observed. Spruce plywood generated phenols at all temperatures while spruce lumber and MDF only generated phenols at 700 and 900 °C. In addition, furfural, 2-furanmethanol and 5-methyl-2-furancarboxaldehyde, which are the products due to the pyrolysis of cellulose component [36], were also characteristically observed. Spruce lumber and plywood generated furfural, furanmethanol and 5-methyl-2-furancarboxaldehyde, while MDF generated only 2-furanmethanol.

Each of the cellulosic materials investigated generated BTEX in a slightly different manner. Benzene, toluene, and ethylbenzene were generated from spruce lumber pyrolyzed at 700 °C and 900 °C but xylenes were never observed. The pyrolysis of spruce plywood generated benzene, toluene and ethylbenzenes at 700 °C and 900 °C, but xylenes only observed at 900 °C. BTEX were collected in the volatiles trap solution obtained at 900 °C. The intensities of *m*- and *p*-xylene are three times greater than those of ethylbenzene and *o*-xylene. Their relative intensities were high in the volatiles trap solution but the intensities of these compounds relative to other pyrolysis products (partially collected in the extract solution) could not be accurately calculated. Nevertheless, the presence of BTEX could be potentially useful for generating simulated debris to train a chemometric model. In contrast to the pyrolysis of spruce wood, MDF generated BTEX when it was pyrolyzed at 700 °C, while benzene and C_2-alkylbenzenes were absent from the pyrolysis products at 400 and 900 °C, respectively. The relative intensities of BTEX are low as compared to that obtained from other materials pyrolyzed at 700 °C. In terms of creating simulated debris for a chemometric model , spruce lumber and MDF were found to be inferior to plywood and the other materials that were investigated.

Similar to other materials, several PAHs were generated from the pyrolysis of cellulosic materials. For the pyrolysis of spruce plywood, acenaphthylene, fluorene, phenanthrene, and anthracene were all generated at 900 °C except for the temperature-programmed 900 °C pyrolysis with 10 min hold time. Pyrolysis of spruce lumber produced fluorene, phenanthrene, anthracene, fluoranthene, and pyrene at all 900 °C experiments but pyrolysis of MDF shelving only produced phenanthrene and pyrene at the same temperature. While biphenyl was identified from the pyrolysates of most of the other materials (asphalt shingle, carpets and vinyl sheets flooring) at 700 and 900 °C, it was also generated from the pyrolysis of spruce lumber and MDF at 900 °C. It is interesting to note that biphenyl was generated during the pyrolysis of wood in our study because it was used as internal standard for quantification in other studies of wood pyrolysis [40, 133].

3.4 Conclusions

In this research each of the eight investigated household materials were pyrolyzed using 15 temperature profiles. The heating periods and ramped temperatures did not generally affect the pyrolysis results when the target temperature was 400 °C. At 700 and 900 °C, however, the pyrolysis behaviours of the materials differed, depending on the temperature program used. Temperature-programmed pyrolysis with longer hold times behaved similarly to isothermal pyrolysis with the same target temperature, while those with short (30 min or less) hold times were observed to be missing some compounds that were found in other pyrolysis experiments at the same target temperature with longer hold times. The relative peak ratios of different compounds also differed between isothermal and temperature-programmed pyrolysis at the higher temperatures.

For the majority of the materials investigated, benzene and toluene were observed. The relative intensities of ethylbenzene and the xylenes are generally not as high as benzene and toluene and were especially low for cellulosic materials.

Overall, pyrolysis of carpets, carpet underlay, and vinyl flooring at 700 °C and spruce plywood at 900 °C generated a reasonable amount of BTEX. Pyrolysis of asphalt at 400 and 700 °C also generated significant amounts of both BTEX and non-aromatic hydrocarbons. These pyrolysis conditions may be suitable for generating more realistic simulated debris samples for chemometric modelling.

Several new compounds were also identified in our study, which, to our knowledge, have not been reported in literature. These include: acenaphthylene, acenaphene, and fluorene from asphalt shingle; pentanenitrile, hexanitrile, *n*-pentyl isothicyanate, cyclohexyl isothiocyanate, and benzenitrile from nylon carpet; phenyl isothiocyanate, benzenbutanitrile, toluenediamine, 1,3-diphenylpropane, diaminodiphenylmethane, toly isothiocyanate, triphenylphosphate, and thianaphthene from polyurethane foam carpet underlay; and, chloro-C_2-alkylbenzene and 2-chloroethyl benzoate from vinyl flooring. The identification of these compounds enhances our knowledge about the pyrolysis products generated by the burning of household materials.

The presence of BTEX and non-aromatic hydrocarbons in simulated fire debris will improve the construction of a chemometric classification model. These compounds are commonly found in gasoline and fire debris and so are not reliable markers for gasoline. Their presence in simulated debris, as in real casework debris, may allow the chemometric model to ignore them and select only the features that are characteristic to gasoline (C_3- to C_5-alkylbenzenes). Although C_3-alkylbenzenes were also generated from the pyrolysis of some of the materials investigated, usually only one to three of the more than six isomers in gasoline were present in very low relative abundance. In addition, C_4- and C_5-alkylbenzenes were not found in any of the experiments indicating that C_3-, C_4- and C_5-alkylbenzenes are reliable markers for the identification of gasoline.

These results increase our understanding how temperature will affect the pyrolysis of household materials and will contribute to the development of a method to simulate fire debris that is chemically equivalent to casework debris so that it may be used for training chemometric models for the identification of ILs in casework samples. Further research is required to investigate other factors, including atmospheric composition and the interaction of different substrates by the simultaneous pyrolysis of more than one material at a time, which may also influence the pyrolysis products generated.

CHAPTER FOUR: Conclusions and Future Work

4.1 Conclusions

Arson investigation is one of the most complex challenges encountered by forensic chemists. Fire weathers ignitable liquids (ILs) and pyrolyzes substrates, greatly increasing the variability and complexity of the already uncontrolled and complex mixture of matrix and IL. Fire debris are important physical evidence for fire investigators. The common approach to analyse debris samples is headspace extraction followed by gas chromatography-mass spectrometry (GC-MS). The most labour-intensive step for the analysts is data interpretation. In order to develop a chemometric model that can identify multiple ignitable liquids in fire debris, a route to realistic simulated debris is required.

In **CHAPTER 2**, I evaluated an existing simulation protocol [80] to determine if it could generate debris that was suitable for training a chemometric model. Although the simulation protocol has been previously shown to generate realistic data for training human analysts, it was found to be inadequate for generating debris that is suitable for training chemometric models for classifying casework debris. This was due to a lack of generated C_2-alkylbenzenes and non-aromatic hydrocarbons in the pyrolyzed materials. The model optimization step thus identified these compounds as being characteristic of gasoline. This poses a problem for casework samples where an abundance of these compounds may be present due to the pyrolysis products in the matrix.

Consequently, I began to explore the effect of pyrolysis temperature and heating profile on the pyrolysis products of household materials. This was presented in **CHAPTER 3**. Household materials, mainly floor coverings, were pyrolyzed at temperatures and heating profiles that are similar to a fire. It was demonstrated that the influence of temperature ramping is more significant at temperatures higher than 700 °C. In addition, 700 °C is the most favoured pyrolysis temperature to generate BTEX and non-aromatic hydrocarbons; molecules that are required in the debris in order to obtain realistic debris profiles.

4.2 Future Work

Our goal is to develop a chemometric approach for detecting ILs from fire debris. The challenge lies in the rapid generation of training data for the construction of classification models for less common ILs. It is critical to develop a simulation approach that creates chemometrically-realistic arson debris. To achieve an ideal simulation approach, several factors need to be taken into consideration. I explored pyrolysis temperature and profiles and how these affected the composition of the debris. Other factors, such as co-pyrolysis of mixtures of debris materials and atmospheric conditions are worth exploring.

In this study, I was limited by the physical size of the mini tube furnace available for pyrolyzing samples. Thus I could not explore mixtures of debris materials. While pyrolysis of single substrates provides useful information about the pyrolysates produced by the individual component, the results might not be realistic. A fire generally involves more than one type of substrate. These substrates are thermally degraded at elevated temperatures as a mixture. Many small molecules and free radicals are generated, and pyrolysis products from multiple substrates could interact and generate other compounds that are not observed when only one substrate is pyrolyzed [23]. The free radical reactions between different substrates could also produce higher or lower concentrations of some pyrolysis products as compared to pyrolysis of individual substrates [136].

Apart from the temperature, atmospheric conditions could be another major factor affecting the generation of pyrolysis products. Air comprises 79% nitrogen (N_2) and 21% oxygen (O_2) [5]. Oxygen in the air reacts with combustibles in a combustion reaction. Carbon dioxide (CO_2) is the major combustion product when O_2 is not a limiting reagent. In the circumstances where ventilation is restricted, oxygen deficiency leads to incomplete combustion and results in the production of carbon monoxide (CO) as the major product. Studying the pyrolysis of individual and mixtures of substrates under different atmospheric conditions and temperatures would improve our abilities to understand the processes occurring in structural fires as well as our ability to generate more realistic simulated fire debris.

Recently, we obtained funding to begin setting up new equipment to study pyrolysis processes. The new set up includes a new tube furnace which is both longer and wider in diameter than the previous furnace. There is also a dedicated gas delivery system that we are developing which will permit control of the flow rate and mixing ratio of N_2, O_2, CO_2, and CO in the atmosphere that passes through the pyrolysis tube, which is being re-designed as a flow-through tube (**Figure 4-1**). The outlet of the pyrolysis tube will lead to a physical trap for semi-volatile species (glass wool plug) and an activated carbon trap for volatiles, or perhaps a tube containing chilled solvent.

A commercial prototype of our ignitable liquid detection software is being developed as well.

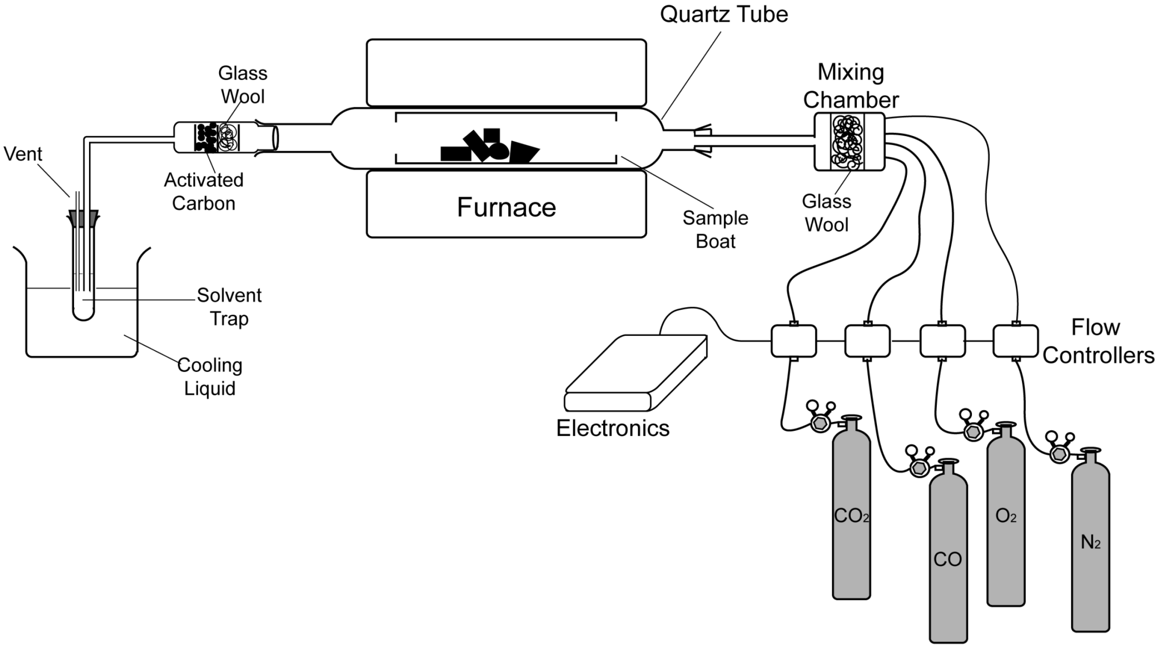


Figure 4-1. Schematic of new pyrolysis experimental setting.

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APPENDIX A: Self-validation PLS-DA Models Trained by Simulated Debris in **CHAPTER 2**

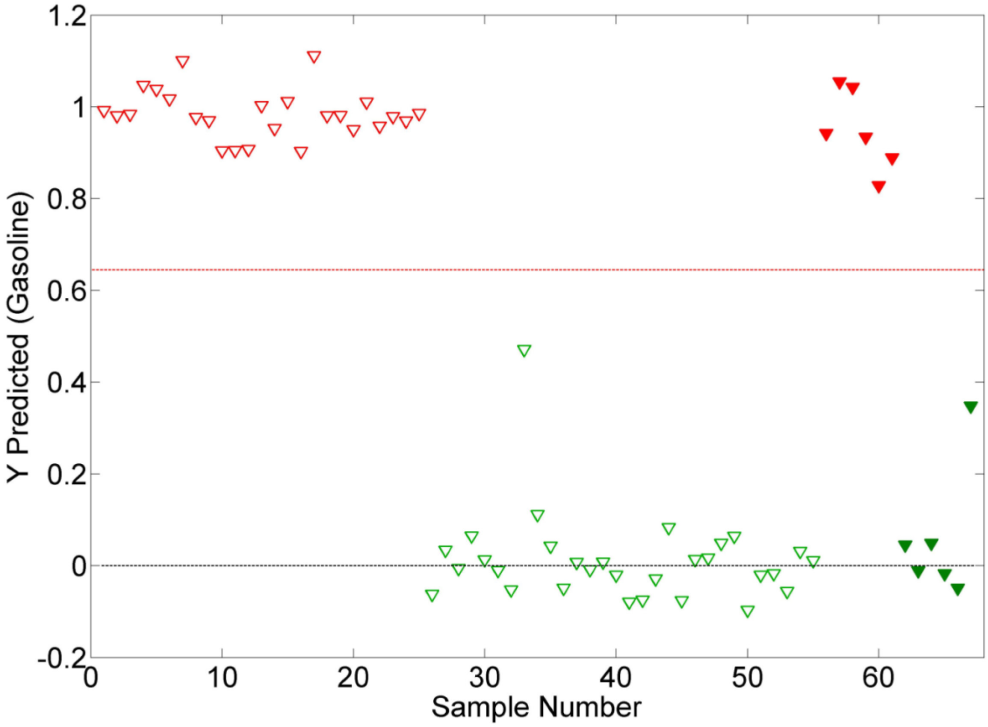

Figure A-1. Self-validation PLS-DA model trained by RCMP data of simulated debris.

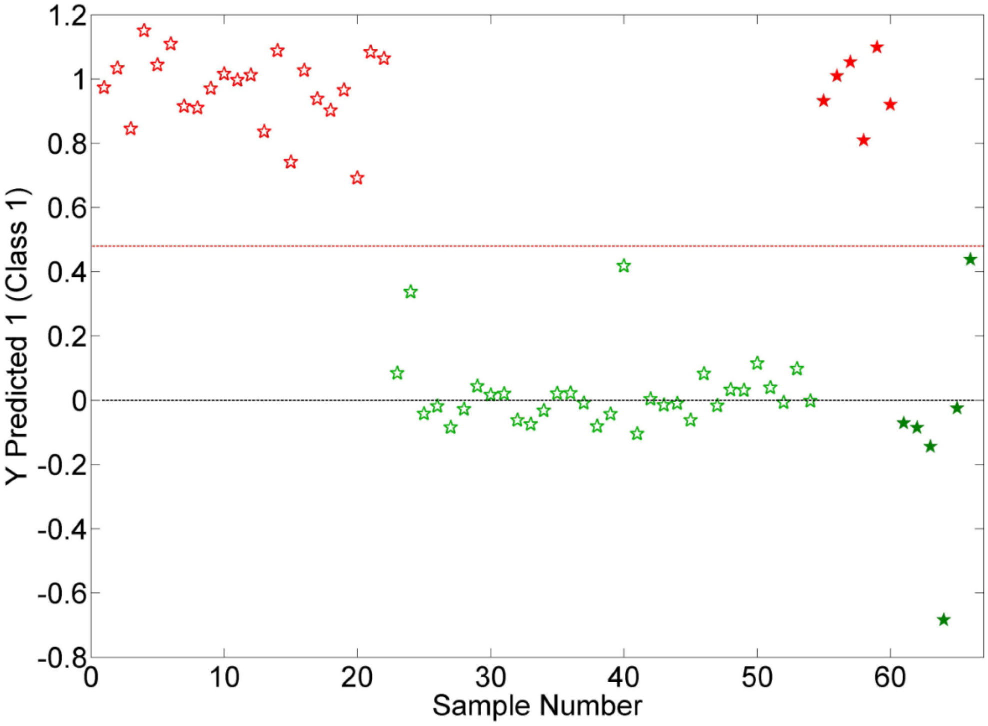

Figure A-2. Self-validation PLS-DA model trained by UA data of simulated debris.

APPENDIX B: List of Positively and Tentatively Identified Compounds for Each Materials Pyrolyzed in **CHAPTER 3**

Material	Target Temperature	Temperature Profiles	Positively and tentatively identified compounds
Asphalt Shingle	**400**	IT 400-30	B, 2, 5, 9, D, 13, 14, J, 32, L, 43, O, 54, Q, U, 67, X, 78, CC
		IT 400-60	B, 2, 5, 9, D, 13, 14, J, 32, L, 43, O, 54, Q, U, 67, X, 78, CC
		TP 400-10	B, 2, 5, 9, D, 13, 14, J, 32, L, 43, O, 54, Q, U, 67, X, 78, CC
		TP 400-30	B, 2, 5, 9, D, 13, 14, J, 32, L, 43, O, 54, Q, U, 67, X, 78, CC
		TP 400-60	B, 2, 5, 9, D, 13, 14, J, 32, L, 43, O, 54, Q, U, 67, X, 78, CC
	700	IT 700-30	A, C, F-I, 23, 26, 27, 30, 33, 35, P, 54, Q, U, 67, X, 78, CC, 60, V, W, CC
		IT 700-60	A, C, F-I, 23, 26, 27, 30, 33, 35, P, 54, Q, U, 67, X, 78, CC, 60, V, W, CC
		TP 700-10	A, C, F-I, 23, 26, 27, 30, 33, 35, P, 54, Q, U, 67, X, 78, CC, 60, V, W, CC
		TP 700-30	A, C, F-I, 23, 26, 27, 30, 33, 35, P, 54, Q, U, 67, X, 78, CC, 60, V, W, CC
		TP 700-60	A, C, F-I, 23, 26, 27, 30, 33, 35, P, 54, Q, U, 67, X, 78, CC, 60, V, W, CC
	900	IT 900-30	A, C, F-I, P, 60, V, W, BB, DD, FF, HH, II, JJ, MM, NN, OO
		IT 900-60	A, C, F-I, P, 60, V, W, BB, DD, FF, HH, II, JJ, MM, NN, OO
		TP 900-10	A, C, F-I, P, 60, V, W, BB, DD, FF, HH, II, JJ
		TP 900-30	A, C, F-I, P, 60, V, W, BB, DD, FF, HH, II, JJ, MM, NN, OO
		TP 900-60	A, C, F-I, P, 60, V, W, BB, DD, FF, HH, II, JJ, MM, NN, OO
PET Carpet	**400**	IT 400-30	B, C, 12, 14, F, 18, 22, 23, 25, 29, 37, 41, 48, 52, T, 66, W, 83
		IT 400-60	B, C, 12, 14, F, 18, 22, 23, 25, 29, 37, 41, 48, 52, T, 66, W, 83
		TP 400-10	B, C, 12, 14, F, 18, 22, 23, 25, 29, 37, 41, 48, 52, T, 66, W, 83
		TP 400-30	B, C, 12, 14, F, 18, 22, 23, 25, 29, 37, 41, 48, 52, T, 66, W, 83
		TP 400-60	B, C, 12, 14, F, 18, 22, 23, 25, 29, 37, 41, 48, 52, T, 66, W, 83
	700	IT 700-30	A, C, F-H, 18, I, 22, 23, 25, 27, 29, 38, 41, 48, 52, P, T, 60, V, 66, W, 74, 79, EE, 83, GG, HH, MM, 88
		IT 700-60	A, C, F-H, 18, I, 22, 23, 25, 27, 29, 38, 41, 48, 52, P, T, 60, V, 66, W, 74, 79, EE, 83, GG, HH, MM, 88
		TP 700-10	A, C, 14, F-H, 18, I, 22, 23, 25, 27, 29, 38, 41, 48, 52, P, T, 60, V, 66, W, 74, 79, EE, 83, HH, GG, MM, 88
		TP 700-30	A, C, F-H, 18, I, 22, 23, 25, 27, 29, 38, 41, 48, 52, P, T, 60, V, 66, W, 74, 79, EE, 83, GG, HH, MM, 88
		TP 700-60	A, C, F-H, 18, I, 22, 23, 25, 27, 29, 38, 41, 48, 52, P, T, 60, V, 66, W, 74, 79, EE, 83, GG, HH, MM, 88
	900	IT 900-30	A, C, F-H, 18, I, 28, 38, 41, 48, 52, P, T, 60, V, 66, W, 74, 76, BB, 79, EE, FF, 83, GG, HH, JJ, MM, NN, 88
		IT 900-60	A, C, F-H, 18, I, 28, 38, 41, 48, 52, P, T, 60, V, 66, W, 74, 76, BB, 79, EE, FF, 83, GG, HH, JJ, MM, NN, 88
		TP 900-10	A, C, F-H, 18, I, 28, 38, 41, 48, 52, P, T, 60, V, 66, W, 74, 79, EE, FF, 83, GG, HH, JJ, MM, NN, 88
		TP 900-30	A, C, F-H, 18, I, 28, 38, 41, 48, 52, P, T, 60, V, 66, W, 74, 79, EE, FF, 83, GG, HH, JJ, MM, NN, 88
		TP 900-60	A, C, F-H, 18, I, 28, 38, 41, 48, 52, P, T, 60, V, 66, W, 74, 79, EE, FF, 83, GG, HH, JJ, MM, NN, 88

Material	Target Temperature	Temperature Profiles	Positively and tentatively identified compounds
Nylon 6 Carpet	**400**	IT 400-30	C, 6, 8, 12, F, 17, 18, 22, 23, 29, 44, 58, 59, 83
		IT 400-60	C, 6, 8, 12, F, 17, 18, 22, 23, 29, 44, 58, 59, 83
		TP 400-10	C, 6, 8, 12, F, 17, 18, 22, 23, 29, 44, 58, 59, 83
		TP 400-30	C, 6, 8, 12, F, 17, 18, 22, 23, 29, 44, 58, 59, 83
		TP 400-60	C, 6, 8, 12, F, 17, 18, 22, 23, 29, 44, 58, 59, 83
	700	IT 700-30	A, C, 6, 8, 12, F-H, 17, 18, I, 22, 23, 29, 38, 44, P, 58, 59, 60, V, W, 83
		IT 700-60	A, C, 6, 8, 12, F-H, 17, 18, I, 22, 23, 29, 38, 44, P, 58, 59, 60, V, W, 83
		TP 700-10	A, C, 6, 8, 12, F-H, 17, 18, I, 22, 23, 29, 38, 44, P, 58, 59, 60, V, W, 83
		TP 700-30	A, C, 6, 8, 12, F-H, 17, 18, I, 22, 23, 29, 38, 44, P, 58, 59, 60, V, W, 83
		TP 700-60	A, C, 6, 8, 12, F-H, 17, 18, I, 22, 23, 29, 38, 44, P, 58, 59, 60, V, W, 83
	900	IT 900-30	A, C, 6, 8, 12, F-H, 17, 18, I, 22, 23, 29, K, 38, P, 58, 59, 60, V, W, BB, 79, FF, HH, II
		IT 900-60	A, C, 6, 8, 12, F-H, 17, 18, I, 22, 29, K, 35, P, 59, 60, V, W, BB, 79, FF, HH, II
		TP 900-10	A, C, 6, 8, 12, F-H, 17, 18, I, 22, 23, 29, K, 38, P, 58, 59, 60, V, W, BB, FF, HH, II
		TP 900-30	A, C, 6, 8, 12, F-H, 17, 18, I, 22, 29, K, 38, P, 59, 60, V, W, BB, FF, HH, II
		TP 900-60	A, C, 6, 8, 12, F-H, 17, 18, I, 22, 29, K, 38, P, 59, 60, V, W, BB, FF, HH, II
PVC Sheet Flooring	**400**	IT 400-30	A, C, F-H, 18, I, 23, 52, P, 82, 84, 87, 89
		IT 400-60	A, C, F-H, 18, I, 23, 52, P, 82, 84, 87, 89
		TP 400-10	A, C, F-H, 18, I, 23, 52, P, 82, 84, 87, 89
		TP 400-30	A, C, F-H, 18, I, 23, 52, P, 82, 84, 87, 89
		TP 400-60	A, C, F-H, 18, I, 23, 52, P, 82, 84, 87, 89
	700	IT 700-30	A, C, F-H, 18, I, 23, 26, 27, 30, 36, 38, 40, 51, 52, P, 60, V, W, Y, 73, 74, Z, AA, BB, EE, 80, FF, 82, 84, HH, II, JJ, KK, LL, MM, NN, 87, 89
		IT 700-60	A, C, F-H, 18, I, 23, 26, 27, 30, 36, 38, 40, 51, 52, P, 60, V, W, Y, 73, 74, Z, AA, BB, EE, 80, FF, 82, 84, HH, II, JJ, KK, LL, MM, NN, 87, 89
		TP 700-10	A, C, F-H, 18, I, 23, 26, 27, 30, 36, 38, 40, 52, P, 60, V, W, Y, 73, Z, AA, BB, EE, 80, FF, 82, 84, KK, LL, MM, 87, 89
		TP 700-30	A, C, F-H, 18, I, 23, 26, 27, 30, 36, 38, 40, 51, 52, P, 60, V, W, Y, 73, Z, AA, BB, EE, 80, FF, 82, 84, HH, II, KK, LL, MM, 87, 89
		TP 700-60	A, C, F-H, 18, I, 23, 26, 27, 30, 36, 38, 40, 51, 52, P, 60, V, W, Y, 73, Z, AA, BB, EE, 80, FF, 82, 84, HH, II, KK, LL, MM, 87, 89
	900	IT 900-30	A, C, F-H, 18, I, 23, 26, 27, 30, 36, 38, 40, 51, 52, P, 60, V, W, Y, 73, 74, Z, AA, BB, EE, 80, FF, 82, 84, HH, II, JJ, KK, LL, MM, NN, OO, 87, QQ, 89
		IT 900-60	A, C, F-H, 18, I, 23, 26, 27, 30, 36, 38, 40, 51, 52, P, 60, V, W, Y, 73, 74, Z, AA, BB, EE, 80, FF, 82, 84, HH, II, JJ, KK, LL, MM, NN, OO, 87, QQ, 89
		TP 900-10	A, C, F-H, 18, I, 23, 26, 27, 30, 36, 38, 40, 42, P, 60, V, Y, 73, Z, AA, BB, EE, 80, FF, 82, 83, 84, KK, LL, MM, OO, 87, QQ, 89
		TP 900-30	A, C, F-H, 18, I, 23, 26, 27, 30, 36, 38, 40, 51, 52, P, 60, V, W, Y, 73, Z, AA, BB, EE, 80, FF, 82, 83, 84, HH, II, KK, LL, MM, OO, 87, QQ, 89
		TP 900-60	A, C, F-H, 18, I, 23, 26, 27, 30, 36, 38, 40, 51, 52, P, 60, V, W, Y, 73, Z, AA, BB, EE, 80, FF, 82, 83, 84, HH, II, KK, LL, MM, OO, 87, QQ, 89

Material	Target Temperature	Temperature Profiles	Positively and tentatively identified compounds
PU Carpet Underlay	**400**	IT 400-30	C, 8, F, 18, 23, 27-29, 38, M, 55, 62, 63, 68, 69, 82, 83, 85, PP
		IT 400-60	C, 8, F, 18, 23, 27-29, 38, M, 55, 62, 63, 68, 69, 82, 83, 85, PP
		TP 400-10	C, 8, F, 18, 23, 27-29, 38, M, 55, 62, 63, 68, 69, 82, 83, 85, PP
		TP 400-30	C, 8, F, 18, 23, 27-29, 38, M, 55, 62, 63, 68, 69, 82, 83, 85, PP
		TP 400-60	C, 8, F, 18, 23, 27-29, 38, M, 55, 62, 63, 68, 69, 82, 83, 85, PP
	700	IT 700-30	A, C, F-H, 18, I, 23, 27-29, K, 38, M, P, 55, 62, 63, 82, 83, PP
		IT 700-60	A, C, F-H, 18, I, 23, 27-29, K, 38, M, P, 55, 62, 63, 82, 83, PP
		TP 700-10	A, C, F-H, 18, I, 23, 27-29, K, 38, M, P, 55, 62, 63, 82, 83, PP
		TP 700-30	A, C, F-H, 18, I, 23, 27-29, K, 38, M, P, 55, 62, 63, 82, 83, PP
		TP 700-60	A, C, F-H, 18, I, 23, 27-29, K, 38, M, P, 55, 62, 63, 82, 83, PP
	900	IT 900-30	A, C, F-H, 18, I, 28, 29, K, 38, M, P, 55, 62, 63, W, BB, HH, 82, 83, NN, OO, PP
		IT 900-60	A, C, F-H, 18, I, 28, 29, K, 38, M, P, 55, 62, 63, W, BB, HH, 82, 83, NN, OO, PP
		TP 900-10	A, C, F-H, 18, I, 28, 29, 38, M, P, 55, 62, 63, HH, 82, 83, OO, PP
		TP 900-30	A, C, F-H, 18, I, 28, 29, K, 38, M, R, P, 55, 62, 63, HH, 82, 83, NN, OO, PP
		TP 900-60	A, C, F-H, 18, I, 28, 29, K, 38, M, R, P, 55, 62, 63, BB, HH, 82, 83, NN, OO, PP
Spruce Lumber	**400**	IT 400-30	E, 15, 24, 34, N, 53, 64, 65, 71, 75, 77, 81, 85
		IT 400-60	E, 15, 24, 34, N, 53, 64, 65, 71, 75, 77, 81, 85
		TP 400-10	E, 15, 24, 34, N, 53, 64, 65, 71, 75, 77, 81, 85
		TP 400-30	E, 15, 24, 34, N, 53, 64, 65, 71, 75, 77, 81, 85
		TP 400-60	E, 15, 24, 34, N, 53, 64, 65, 71, 75, 77, 81, 85
	700	IT 700-30	A, C, E, F, 15, 24, 31, 34, 39, 42, N, 49, 50, 53, P, 56, 57, 61, 64, 65, 70, 71, 75, 77, 81, 85
		IT 700-60	A, C, E, F, 15, 24, 31, 34, 39, 42, N, 49, 50, 53, P, 56, 57, 61, 64, 65, 70, 71, 75, 77, 81, 85
		TP 700-10	A, C, E, F, 15, 24, 31, 34, 39, 42, N, 49, 50, 53, P, 56, 57, 61, 64, 65, 70, 71, 75, 77, 81, 85
		TP 700-30	A, C, E, F, 15, 24, 31, 34, 39, 42, N, 49, 50, 53, P, 56, 57, 61, 64, 65, 70, 71, 75, 77, 81, 85
		TP 700-60	A, C, E, F, 15, 24, 31, 34, 39, 42, N, 49, 50, 53, P, 56, 57, 61, 64, 65, 70, 71, 75, 77, 81, 85
	900	IT 900-30	A, C, E, F, 24, 31, 34, 39, 42, N, 49, 50, 53, P, 56, 57, 60, 61, V, 64, 65, W, 70, 71, 75, BB, 77, 81, FF, 85, HH, II, NN, OO
		IT 900-60	A, C, E, F, 24, 31, 34, 39, 42, N, 49, 50, 53, P, 56, 57, 60, 61, V, 64, 65, W, 70, 71, 75, BB, 77, 81, FF, 85, HH, II, NN, OO
		TP 900-10	A, C, E, F, 24, 31, 34, 39, 42, N, 49, 50, 53, P, 57, 60, 61, V, 64, 65, W, 70, 71, 75, BB, 77, 81, FF, 85, HH, II, NN, OO
		TP 900-30	A, C, E, F, 24, 31, 34, 39, 42, N, 49, 50, 53, P, 57, 60, 61, V, 64, 65, W, 70, 71, 75, BB, 77, 81, FF, 85, HH, II, NN, OO
		TP 900-60	A, C, E, F, 24, 31, 34, 39, 42, N, 49, 50, 53, P, 57, 60, 61, V, 64, 65, W, 70, 71, 75, BB, 77, 81, FF, 85, HH, II, NN, OO

Material	**Target Temperature**	**Temperature Profiles**	**Positively and tentatively identified compounds**
Spruce Plywood	**400**	IT 400-30	E, 15, 19, 24, 31, 34, 39, 42, N, 45, 47, 49, 53, S, 57, 61, 64, 65, 70, 71, 75, 77, 81, 85
		IT 400-60	E, 15, 19, 24, 31, 34, 39, 42, N, 45, 47, 49, 53, S, 57, 61, 64, 65, 70, 71, 75, 77, 81, 85
		TP 400-10	E, 15, 19, 24, 31, 34, 39, 42, N, 45, 47, 49, 53, S, 57, 61, 64, 65, 70, 71, 75, 77, 81, 85
		TP 400-30	E, 15, 19, 24, 31, 34, 39, 42, N, 45, 47, 49, 53, S, 57, 61, 64, 65, 70, 71, 75, 77, 81, 85
		TP 400-60	E, 15, 19, 24, 31, 34, 39, 42, N, 45, 47, 49, 53, S, 57, 61, 64, 65, 70, 71, 75, 77, 81, 85
	700	IT 700-30	A, B, C, E, 18, 15, 19, 24, 26, 31, 34, 39, 42, N, 45- 47, 49, 53, P, S, 57, 61, 64, 65, 70, 71, 75, 77, 81, 85
		IT 700-60	A, B, C, E, 18, 15, 19, 24, 26, 31, 34, 39, 42, N, 45- 47, 49, 53, P, S, 57, 61, 64, 65, 70, 71, 75, 77, 81, 85
		TP 700-10	A, C, E, 15, 19, 24, 31, 34, 39, 42, N, 45- 47, 49, 53, P, S, 57, 61, 64, 65, 70, 71, 75, 77, 81, 85
		TP 700-30	A, C, E, 15, 19, 24, 31, 34, 39, 42, N, 45- 47, 49, 53, P, S, 57, 61, 64, 65, 70, 71, 75, 77, 81, 85
		TP 700-60	A, C, E, 15, 19, 24, 31, 34, 39, 42, N, 45- 47, 49, 53, P, S, 57, 61, 64, 65, 70, 71, 75, 77, 81, 85
	900	IT 900-30	A, B, C, E, F, G, H, 18, I, 19, 24, 27, 31, 34, 39, 42, N, 45-47, 49, 53, P, S, 57, 61, 64, 65, 70, 71, 75, BB, 77, 81, FF, 85, HH, II
		IT 900-60	A, B, C, E, F, G, H, 18, I, 19, 24, 27, 31, 34, 39, 42, N, 45-47, 49, 53, P, S, 57, 61, 64, 65, 70, 71, 75, BB, 77, 81, FF, 85, HH, II
		TP 900-10	A, B, C, E, 15, F, G, H, 18, I, 19, 24, 27, 31, 34, 39, 42, N, 45-47, 49, 53, P, S, 57, 61, 64, 65, 70, 71, 75, 77, 81, 85
		TP 900-30	A, B, C, E, 15, F, G, H, 18, I, 19, 24, 27, 31, 34, 39, 42, N, 45-47, 49, 53, P, S, 57, 61, 64, 65, 70, 71, 75, BB, 77, 81, FF, 85, HH, II
		TP 900-60	A, B, C, E, 15, F, G, H, 18, I, 19, 24, 27, 31, 34, 39, 42, N, 45-47, 49, 53, P, S, 57, 61, 64, 65, 70, 71, 75, BB, 77, 81, FF, 85, HH, II
MDF Shelving	**400**	IT 400-30	1, 3, 4, C, 8, 15, G-I, 19, 20, 34, 39, 42, N, 53, 57, 61, 64, 65, 71, 75, 78, 81
		IT 400-60	1, 3, 4, C, 8, 15, G-I, 19, 20, 34, 39, 42, N, 53, 57, 61, 64, 65, 71, 75, 78, 81
		TP 400-10	1, 3, 4, C, 8, 15, G-I, 19, 20, 34, 39, 42, N, 53, 57, 61, 64, 65, 71, 75, 78, 81
		TP 400-30	1, 3, 4, C, 8, 15, G-I, 19, 20, 34, 39, 42, N, 53, 57, 61, 64, 65, 71, 75, 78, 81
		TP 400-60	1, 3, 4, C, 8, 15, G-I, 19, 20, 34, 39, 42, N, 53, 57, 61, 64, 65, 71, 75, 78, 81
	700	IT 700-30	A, C, 15, G-I, 19, 20, 31, 34, 39, 42, N, 49, 50, 53, P, 57, 61, 64, 65, 71, 75, 77, 81
		IT 700-60	A, C, 15, G-I, 19, 20, 31, 34, 39, 42, N, 49, 50, 53, P, 57, 61, 64, 65, 71, 75, 77, 81
		TP 700-10	A, C, 15, G-I, 19, 20, 31, 34, 39, 42, N, 49, 50, 53, P, 57, 61, 64, 65, 71, 75, 77, 81
		TP 700-30	A, C, 15, G-I, 19, 20, 31, 34, 39, 42, N, 49, 50, 53, P, 57, 61, 64, 65, 71, 75, 77, 81
		TP 700-60	A, C, 15, G-I, 19, 20, 31, 34, 39, 42, N, 49, 50, 53, P, 57, 61, 64, 65, 71, 75, 77, 81
	900	IT 900-30	A, C, 31, 39, 42, N, 49, 50, 53, P, 57, W, 71, 75, HH, OO
		IT 900-60	A, C, 31, 39, 42, N, 49, 50, 53, P, 57, W, 71, 75, HH, OO
		TP 900-10	A, C, 15, 31, 34, 39, 42, N, 49, 50, 53, P, 57, 61, 64, 65, W, 71, 75, 77, 81, HH, OO
		TP 900-30	A, C, 15, 31, 34, 39, 42, N, 49, 50, 53, P, 57, 61, 64, 65, W, 71, 75, 77, 81, HH, OO
		TP 900-60	A, C, 31, 34, 39, 42, N, 49, 50, 53, P, 57, 61, 64, 65, W, 71, 75, 77, 81, HH, OO

APPENDIX C: List of Filenames of Samples Pyrolyzed in **CHAPTER 3**

Samples	**Temperature**	**Temperature Profiles**	**Filenames**
Asphalt Shingle	400	IT 400-30	D6
		IT 400-60	D7
		TP 400-10	D8
		TP 400-30	D9
		TP 400-60	D10
	700	IT 700-30	D11
		IT 700-60	D12
		TP 700-10	D25
		TP 700-30	D28
		TP 700-60	D29
	900	IT 900-30	D19
		IT 900-60	D24
		TP 900-10	D31
		TP 900-30	D38
		TP 900-60	D40
PET Carpet	400	IT 400-30	PE2
		IT 400-60	PE3
		TP 400-10	PE5
		TP 400-30	PE6
		TP 400-60	PE4
	700	IT 700-30	PE1
		IT 700-60	PE7
		TP 700-10	PE9
		TP 700-30	PE10
		TP 700-60	PE8
	900	IT 900-30	PE11H
		IT 900-60	PE15H
		TP 900-10	PE12H
		TP 900-30	PE13H
		TP 900-60	PE14H

Samples	**Temperature**	**Temperature Profiles**	**Filenames**
Nylon 6 Carpet	400	IT 400-30	NY2
		IT 400-60	NY3
		TP 400-10	NY5
		TP 400-30	NY6
		TP 400-60	NY7
	700	IT 700-30	NY1
		IT 700-60	NY4
		TP 700-10	NY8
		TP 700-30	NY9
		TP 700-60	NY10
	900	IT 900-30	NY11H
		IT 900-60	NY13H
		TP 900-10	NY12H
		TP 900-30	NY14H
		TP 900-60	NY15H
PU Carpet Underlay	400	IT 400-30	FU3
		IT 400-60	FU4
		TP 400-10	FU5
		TP 400-30	FU6
		TP 400-60	FU7
	700	IT 700-30	FU1
		IT 700-60	FU2
		TP 700-10	FU8
		TP 700-30	FU9
		TP 700-60	FU10
	900	IT 900-30	FU14H
		IT 900-60	FU11H
		TP 900-10	FU15H
		TP 900-30	FU13H
		TP 900-60	FU12H

Samples	Temperature	Temperature Profiles	Filenames
PVC Sheet Flooring	400	IT 400-30 IT 400-60 TP 400-10 TP 400-30 TP 400-60	VS3 VS4 VS5 VS6 VS7
	700	IT 700-30 IT 700-60 TP 700-10 TP 700-30 TP 700-60	VS1 VS2 VS8 VS9 VS10
	900	IT 900-30 IT 900-60 TP 900-10 TP 900-30 TP 900-60	VS17 VS16 VS15 VS19 VS18
Spruce Lumber	400	IT 400-30 IT 400-60 TP 400-10 TP 400-30 TP 400-60	SP1 SP2 SP7 SP8 SP9
	700	IT 700-30 IT 700-60 TP 700-10 TP 700-30 TP 700-60	SP3 SP4 SP10 SP11 SP12
	900	IT 900-30 IT 900-60 TP 900-10 TP 900-30 TP 900-60	SP5 SP6 SP13 SP14 SP15

Samples	**Temperature**	**Temperature Profiles**	**Filenames**
Spruce Plywood	400	IT 400-30	PW6
		IT 400-60	PW7
		TP 400-10	PW8
		TP 400-30	PW9
		TP 400-60	PW10
	700	IT 700-30	PW5
		IT 700-60	PW4
		TP 700-10	PW3
		TP 700-30	PW2
		TP 700-60	PW1
	900	IT 900-30	PW15H
		IT 900-60	PW19H
		TP 900-10	PW16H
		TP 900-30	PW17H
		TP 900-60	PW18H
MDF Shelving	400	IT 400-30	D23
		IT 400-60	D34
		TP 400-10	D35
		TP 400-30	D36
		TP 400-60	D37
	700	IT 700-30	D30
		IT 700-60	D42
		TP 700-10	D44
		TP 700-30	D45
		TP 700-60	D46
	900	IT 900-30	D22
		IT 900-60	D43
		TP 900-10	D47
		TP 900-30	D48
		TP 900-60	D49