Combining Gas Chromatography-Mass Spectrometry and Principal Component Analysis to Facilitate Complete Detection and Identification of Ignitable Liquids

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Abstract. This paper reports an approach that developed instrumental parameters with two different GC-MS instruments. Data from the two devices were combined with principal component analysis (PCA) to analyze genuinely and ignited ignitable liquid residues (ILR). We simulate the field samples by burning seasoned pinewood soaked with each ignitable liquid (IL). Enough unburnt components from an IL remained on the burnt wood. These components were enough to reveal the chromatographic fingerprint of an IL. Most importantly, the chromatographic profile from a pure IL and IL poured onto a wooden substrate and ignited was identical. The chromatographic profiles reported from each instrument for each IL were reproducible to within 3% RSD. The MS data from both GC-MS instruments showed similar m/z peaks from all ILs, indicating similar hydrocarbon(s) and or fragmentation cluster patterns in the ILs studied ingredients. The PCA data showed characteristic differences giving rise to the separation between incendiaries, albeit some were overshadowed by clustering. In some cases, ILs that showed similar components in their mass spectra profile grouped as a class on the PCA display. We demonstrate an approach using direct headspace injection to individualize ILs recovered from crime scenes. Direct headspace injection and GC-MS combined with PCA are shown as promising facile methods for the qualitative determination of specific ILs in real-world arson samples. Initially, our project started as an undergraduate instrumental analysis guided-inquiry (GI) project. Such labs have been reported to enhance student learning and improve students' critical and problem-solving abilities. We plan to incorporate this approach in both an undergraduate instrumental analysis class and a graduate-level analytical chemistry class.

Introduction

In the United States, municipal fire departments respond to an estimated 261,330 fires per year ignited by ignitable liquids (ILs). These fires cause more than 440 civilian deaths, 1,310 injuries, and $1 billion in direct damages [1]. When a fire occurs under a suspicious circumstance, forensic scientists examine the fire residues for the presence of ignitable liquid residues (ILR). The detection of ILR on fire debris collected from a crime scene typically indicates a fire was set deliberately. Detecting an ignitable liquid (IL) to some confidence level is crucial in arson investigations [2, 3]. A significant challenge for determining that an IL was present in fire debris is the presence of heat-generated breakdown products from the combustion of materials at the scene [4-12]. Decomposition products are often extracted together with ILR forming a complex mixture that requires a carefully designed method to detect, separate, and identify components in the mix. The American Society for Testing and Materials (ASTM) has described standard approaches using gas chromatography-mass spectrometry (GC-MS) for testing and identification of IL collected from fire debris in ASTM E1618-14 [13]. GC-MS is a hyphenated technique in which gas chromatography (GC) is interfaced with mass spectrometry (MS). The method is a versatile separation and identification method customarily used for chemical compounds' sensitive and selective investigation approach. The separation and detection process can be divided into four steps: sample introduction, compound separation, mass separation, and mass identification [14, 15]. Data from a GC-MS instrument has been invaluable in analyzing ILR and other decomposition products from arson scenes because they provide information on the chemical components present in the holistic residue extract. The ASTM E1618-14 approach documents three methods to data analysis for classifying ILRs. These are visual chromatographic pattern recognition, extracted ion chromatographic profiling, and target compound analysis [13].

Visual chromatographic pattern recognition is performed by visually comparing the crime scene's sample pattern to the reference material of known classification. Studies have reported the classification or identification of ILR or IL based on visual chromatographic pattern recognition [16] and total ion spectra [17-19]. In an extracted ion chromatography profiling, the analyst extracts chromatographic data from selected ions of known m/z. The extraction can involve a single ion or a group of ions to help visualize the IL classes' patterns. It is also possible to use this technique to eliminate unwanted ions from decomposition products that might

obscure the chromatographic profile of a particular type of IL [3, 20]. Methods have been developed for analyzing and identifying selected ions for specific chromatographic peaks found in IL [21-23]. A target compound identification approach enables the analyst to visualize low concentrations of ILR in high concentration levels of decomposition products [24-25]. Several other works have applied principal component analysis (PCA) to the association and discrimination of ILs and fire debris analysis [26-29].

Earlier investigations have reported different approaches to discriminate IL, and associate ILR extracted from the ignited substrate back to the corresponding IL. Sigman et al. used a covariance mapping method to demonstrate that unevaporated gasoline samples from the same geographic region could have come from different sources [30]. Covariance mapping approaches typically lead to Type II errors, which can be costly in forensic science. This same group introduced a summed ion spectrum, otherwise known as the total ion spectrum, as an alignment-free preprocessing step for raw GC-MS data from fire debris chromatograms [18]. Waddell et al. used temperature programming combined with Pearson product-moment correlation coefficients and principal component analysis to evaluate discrimination differences among diesel samples. They showed that the association and discrimination of diesel samples were primarily unaffected by the temperature program [31]. They note as GC ramp rates increases, resolution and analysis time increases; however, the total analysis time (reported as 113 minutes) was not feasible for fire debris analysis. Other studies have employed chemometric techniques for identifying IL in simulated [32-36] and casework [37-38] reviews. Recently, Harynuk et al. used a segmented total ion spectrum to compare the performance with the total ion spectrum for classifying fire debris gasoline samples in casework [39]. Among several other features of the technique, the study demonstrates that the segmented total ion spectrum reduces the number of misclassification when validating fire debris data. Solventless methods, such as solid-phase microextraction (SPME), have been used to analyze IL (gasoline, kerosene, and diesel) through headspace and direct-contact approaches [40].

The analysis of fire debris for the presence of ILR has been a routine aspect of arson investigations. In this aspect, investigators have employed several instrumental techniques for this purpose [41-43]. The most evolving of all instrumental methods used for fire debris analysis have been GC-FID and GC-MS [44-50], mainly because ILs are volatile fluids with mixed components. GC-MS and or GC-FID of these complex mixtures produce highly detailed chromatograms characteristic of a particular sample. Despite the extensive use of GC-MS to analyze fire debris evidence, there still may be opportunities to improve the collection and confidence in identifying ILs by cheaper non-contact direct headspace injection. The hypothesis is that the combination of direct headspace injection to GC-MS and principal component analysis (PCA) may provide a comprehensive approach to facilitate chromatographic pattern recognition from the total ion spectrum. We can then extend the approach to extracted ion chromatography profiling for the wide recognition and identification of ILR collected at crime scenes. Most investigations in the past have employed the passive headspace sampling approach to recover flammable and combustible liquid from fire debris. The passive headspace approach uses activated charcoal strips to adsorb liquid residues, followed by elution with carbon disulfide or other suitable solvents. Passive headspace requires the use of solvents and adsorbent material preparation. SPME, also a solventless method, is more expensive than just a direct headspace injection. In general, is it possible for us to analyze ILs with only direct headspace injection and GC-MS? Is it possible to group ILs showing similar components in their total ion mass spectra data on the principal component profile?

We employed a direct headspace injection combined with a Shimadzu GC-MS and an Agilent GC-MS to test our hypothesis. This paper seeks to develop instrumental experimental parameters on two different GC-MS instruments. We used two GC-MS devices because the Shimadzu instrument required service immediately after collecting genuine (pure) sample data. Despite the use of two instruments, the data, when subjected to PCA analysis, can together serve as an efficient novel holistic approach to recognize chromatographic patterns and profile extracted ions from ILR collected at crime scenes. This work has provided two senior-level undergraduate students training through guided-inquiry (GI) laboratory experiments or active learning hands-on-experience activity in a classroom environment. Incorporating critical thinking and problem-solving skills in a classroom environment for current and future students is an effective strategy for building a competitive global economy in today's national security environment [51-52]. We report on the chromatographic profile pattern of several of the ILs investigated.

Experimental Section

Materials and Reagent. Seasoned pinewood and eight ILs (lamp oil, fuel carburetor injector, kerosene, enzyme fuel oil, scotch guard, odorless lighter fluid, tiki torch fuel, and paint thinner) were purchased from Walmart (Winston-Salem, NC). The diesel, regular, and super petrol were obtained from a gas station in Winston Salem.

GC-MS Analysis - Pure Ignitable Liquids. The pure ILs were analyzed with Shimadzu GC-MS instruments. 0.5 mL of each IL was placed in a 10 mL headspace screwcap vial sealed with a rubber septum purchased from Sigma-Aldrich Chemical Company (St. Louis, MO). The vial was left to equilibrate on a hot plate obtained from Fisher Scientific (Hanover Park, IL) at 50 ºC. A heated gas-tight syringe purchased from Sigma-Aldrich was used to withdraw 0.2 mL of the headspace vapor. The sample was injected into a Shimadzu GC17A-MS QP5000 for analysis.

GC-MS Analysis - Field Samples. Field samples were prepared by setting fire to pinewood that had been cut into pieces (2 cm × 2 cm × 5 cm) and soaked with 10 mL of IL. The soaked wood was allowed to stand for 5 minutes before being ignited. After burning, the wood debris was allowed to cool. The charred sections of the wood surface were scraped off with a sharp knife. We used the same knife to shave off small thin pieces of the intact wood beneath. Fifty to sixty mg of these shavings were placed in a headspace vial and allowed to equilibrate at 50 ºC on a hot plate. A gas-tight syringe was used to withdraw 0.2 mL of the gas from the headspace and injected into the Agilent GC 7890-MS 5975.

PCA Analysis. Principal components analysis (PCA) was carried out using the prcomp function in R (version 3.1.1) integrated with an in-house script for data visualization. The data were centered and scaled using the prcomp function before PCA. The data collected from the GC-FID and the total

Table 1: Summary of the instrument conditions for the GC 2010-FID, GC 17A-MSQP5000, and GC 7890-MS 5975C.

Parameter	GC 2010-FID	GC 17A-MS QP5000	GC 7890-MS 5975C
Column dimensions	15 m × 0.25 mm × 0.25 µm	30 m × 0.25 mm × 0.25 µm	30 m × 0.25 mm × 0.25 µm
Injector	250 ºC	250 ºC	250 ºC
Detector	290 ºC	-	-
Interface temperature	-	300 ºC	250 ºC
Carrier gas	Helium	Helium	Helium
Linear velocity	26.1 cm/s	37.5 cm/s	37.8 cm/s
Column flow	0.91 mL min^{-1}	1.1 mL min^{-1}	1.1 mL min^{-1}
Total flow	1.1 mL min^{-1}	30 mL min^{-1}	4.3 mL min^{-1}
Purge flow	0.2 mL min^{-1}	-	3.0 mL min^{-1}
Split ratio	splitless	splitless	splitless
Pressure	40.4 kPa	64.5 kPa	51.8 kPa

GC 2010-FID program: 32 ºC hold for 1 min., 7 ºC/min. to 80 ºC (hold 0 min.), 30 ºC/min. to 250 ºC (hold 3 min.)
GC 17A-MS QP5000 program: 30 ºC hold for 0 min, 7 ºC/min. to 80 ºC (hold 0 min.), 30 ºC/min. to 250 ºC (hold 3 min.); MS: acquisition mode; full scan, m/z range; 40-400 Da, solvent delay; 0 min., scan speed; 1000, threshold; 1000, interval; 0.5 s.
GC 7890-MS 5975 program: 30 ºC hold for 0 min, 7 ºC/min. to 80 ºC (hold 0 min.), 30 ºC/min. to 250 ºC (hold 3 min.); MS: acquisition mode; full scan, m/z range; 40-400 Da, solvent delay; 0 min., EMV mode; relative, scan speed; normal, time window; 17.00 min.
Column stationary phase: GC 2010-FID; SH-Rxi™-5 MX
GC 17A-MS QP5000; Crossbond™ 5% diphenyl/95% dimethyl polysiloxane
GC 7890-MS 5975; Crossbond™ 5% diphenyl/95% dimethyl polysiloxane

ion chromatogram (TIC.) GC-MS data were exported as .csv. The data from the GC-FID were bucketed using R into 1651 bins, each representing approximately 0.01 minutes of the analysis and to match the size of the GC-MS data collected on the Agilent and Shimadzu instruments (2058 and 1983 data points, respectively). In all cases, PC1 and PC2 explained the most amount of variance; however, PC3 explained a large portion of variance as well. Subsequently, PC1 vs. PC2 and PC1 vs. PC3 were plotted for each method.

Instrumental Conditions. We analyze reference standards on a GC 17A-MS QP5000 (Shimadzu Scientific Instruments, Maryland, USA) and field sample on a GC 7890-MS 5975C (Agilent Scientific Instruments, Santa Clara, CA, USA). The sample introduction approach was a non-contact direct headspace introduction. Previous research reported direct headspace injection for analyzing ILR with several advantages, but the instrumental detection method was MS [53]. To our knowledge, a solventless direct headspace concentration approach that is not SPME is used for the first time with GC-MS and PCA to recover flammable and combustible liquids. Previous studies have used the passive headspace concentration approach. Table 1 summarizes all the experimental operating parameters developed on the GC 17A-MS QP5000 instrument and transferred to the GC 7890-MS 5975C unit used in this investigation.

Results and Discussions

Gas Chromatography 17A Mass Spectrometry QP5000 Analysis of Pure Ignitable Liquids. In addition to recognizing patterns in an ignitable liquid, GC-MS provides additional details, making the technique useful for analyzing samples recovered at an arson scene [20]. GC-MS's separation capability allows it to analyze flammable fluids recovered from two crime scene scenarios: (i). situations where a combination of flammable liquids may be present in an arson sample; and (ii). situations where a flammable liquid may have been mixed with heat-generated breakdown products from other materials burning at the arson scene. We investigated ten pure ignitable liquids on the Shimadzu GC-MS. Figure 1 illustrates the example spectra of the ten ignitable liquids. The chromatography fingerprint for each of the ten ignitable liquids was identical to those collected on a Shimadzu GC-FID instrument (data not shown). All MS data were collected using the full scan mode (40-400 Da). Additionally, we used a NIST library to identify major peaks from each ignitable liquid putatively. Table 2 summarizes the retention time and identity corresponding to major components that make up the ingredients of each ignitable liquid. With the exception of Figure 1 [d] and [e], each spectra displays a peak at 2.367 ± 0.010 minutes. The NIST library identified a match for the mass spectra of this peak as corresponding to argon. As an example of the NIST library used for peak identification, the gas chromatograph of lamp oil shows peaks at 10.675 ± 0.011, 11.035 ± 0.016, 11.446 ± 0.013, 11.519 ± 0.010, 11.819 ± 0.017, and 12.676 ± 0.014 minutes. The NIST library search identified hits for these peaks as 2-methyl octane (87% confidence), 4,6,8-trimethyl-1-nonene (81% confidence), 2,3,3-trimethylpentane (86% confidence), 2,4-dimethyl-3-hexanone (80% confidence), 2,6-dimethyl heptane (88% confidence), and 4-methyl tridecane (86% confidence), respectively. The tiki torch fuel shows peaks at 11.817 ± 0.016, 11.983 ± 0.012, 12.667 ± 0.014, and 12.775 ± 0.011 minutes. The NIST library search identified hits for these peaks as 2,6-dimethyl heptane (89% confidence), 2-isopropyl-3-vinyl oxirane (89% confidence), 4-methyl tridecane (85% confidence), and butyl ester pyruvic acid (88% confidence), respectively. The peaks similar between lamp oil and tiki torch fuel were 2,6-dimethyl heptane and 4-methyl tridecane. Several other ignitable liquid components show similaringredients in the mass spectra profile (see Table 2). For example, kerosene, fuel carburetor, and paint thinner showed peaks identified as 2-methyl octane, 2,5-dimethyl heptane, and 4-methyl tridecane, plus other components in the mass spectra. We investigate two gasoline samples (regular and super) in this study. The spectra are shown in Figure 1**,** [d], and [h] for

Table 2: Summary of GC 17A-MS QP5000 retention times, peak identity, and percentage of confidence identity for major peaks found in the ILs investigated.

Lamp Oil			
Ret. Time (min)	Ret. Time Identity	Mass (Da)	% confidence
10.675 ± 0.011	2-methyl octane	128.26	87
11.035 ± 0.016	4,6,8-trimethyl-1-nonene	168.32	81
11.446 ± 0.013	2,3,3-trimethyl pentane	114.23	86
11.519 ± 0.010	2,4-dimethyl-3-hexanone	128.21	80
11.819 ± 0.017	2,6-dimethyl heptane	128.20	88
12.676 ± 0.014	4-methyltridecane	198.39	86
Diesel			
6.535 ± 0.010	n-1-octene	112.24	78
6.983 ± 0.010	Heptyl hydroperoxide	90.12	84
9.128 ± 0.009	Octane	114.23	83
10.675 ± 0.012	No good match found	-	-
11.818 ± 0.017	2,5-dimethylhexane	128.26	85
Kerosene			
9.431 ± 0.014	Nonane	128.20	87
10.673 ± 0.011	2-methyloctane	128.66	84
10.958 ± 0.010	Butanoic acid, 2-propenyl ester	128.17	86
11.813 ± 0.011	2,5-dimethylhexane	128.26	84
12.674 ± 0.013	4-methyltridecane	198.39	86
Regular Gasoline			
2.492 ± 0.011	n-methylene ethane amide	59.11	86
2.667 ± 0.010	2,3-dimethylbutane	86.18	93
3.216 ± 0.011	1-chloro-2-methyl propane	92.57	89
4.689 ± 0.001	Toluene	92.14	89
6.285 ± 0.015	Bis(1,1-dimethyl ethyl) nitroxide	144.23	94
Super Gasoline			
2.425 ± 0.009	Trans-2-butene	56.11	86
2.660 ± 0.012	2-methyl-1-propene	56.10	82
3.216 ± 0.011	1-chloro-2-methyl propane	92.57	88
4.633 ± 0.001	Toluene	92.14	89
6.258 ± 0.007	2-methyl-1,5-hexadiene-3-yne	106.16	90
Fuel Carburetor			
9.138 ± 0.012	Octane	114.23	88
10.680 ± 0.012	2-methyloctane	128.26	80
11.817 ± 0.007	2,5-dimethyl hexane	114.23	89
12.677 ± 0.006	4-methyltridecane	198.39	84
Enzyme Fuel Oil			
12.653 ± 0.012	2-methyloctane	128.26	83
13.167 ± 0.011	n-decane	142.29	83
13.343 ± 0.013	2,6-dimethylheptane	198.39	85
Odorless Lighter Fluid			
8.434 ± 0.010	2,6-dimethyl heptane	128.26	88
9.416 ± 0.013	Nonane	128.20	89
9.036 ± 0.018	Heptane	100.21	88
10.161 ± 0.011	2-methyloctane	128.26	86
10.666 ± 0.014	4-methyltridecane	198.39	89
Paint Thinner			
9.403 ± 0.011	Nonane	128.22	88
9.683 ± 0.014	Heptylhydroperoxide	118.17	85
10.117 ± 0.012	2-methylundecane-2-thiol,	202.40	85
10.649 ± 0.005	2-methyl octane	128.26	87
10.842 ± 0.012	3-methylheptan-4-one	128.21	89
11.950 ± 0.015	4-methyl tridecane,	198.39	89
Scotch Guard			
9.133 ± 0.010	2,6-dimethylheptane	128.26	88
9.842 ± 0.017	2,4,6,8-tetramethyl-1-undecene	210.40	78
10.680 ± 0.016	2-methyloctane	128.26	89
11.808 ± 0.011	4-methyl tridecane	198.39	89
Tiki Torch Fuel			
11.817 ± 0.016	2,6-dimethylheptane	128.26	89
11.983 ± 0.012	2-isopropyl-3-vinyloxirane	112.17	89
12.667 ± 0.014	4-methyl tridecane	198.39	85
12.775 ± 0.011	Butyl ester pyruvic acid	144.17	88

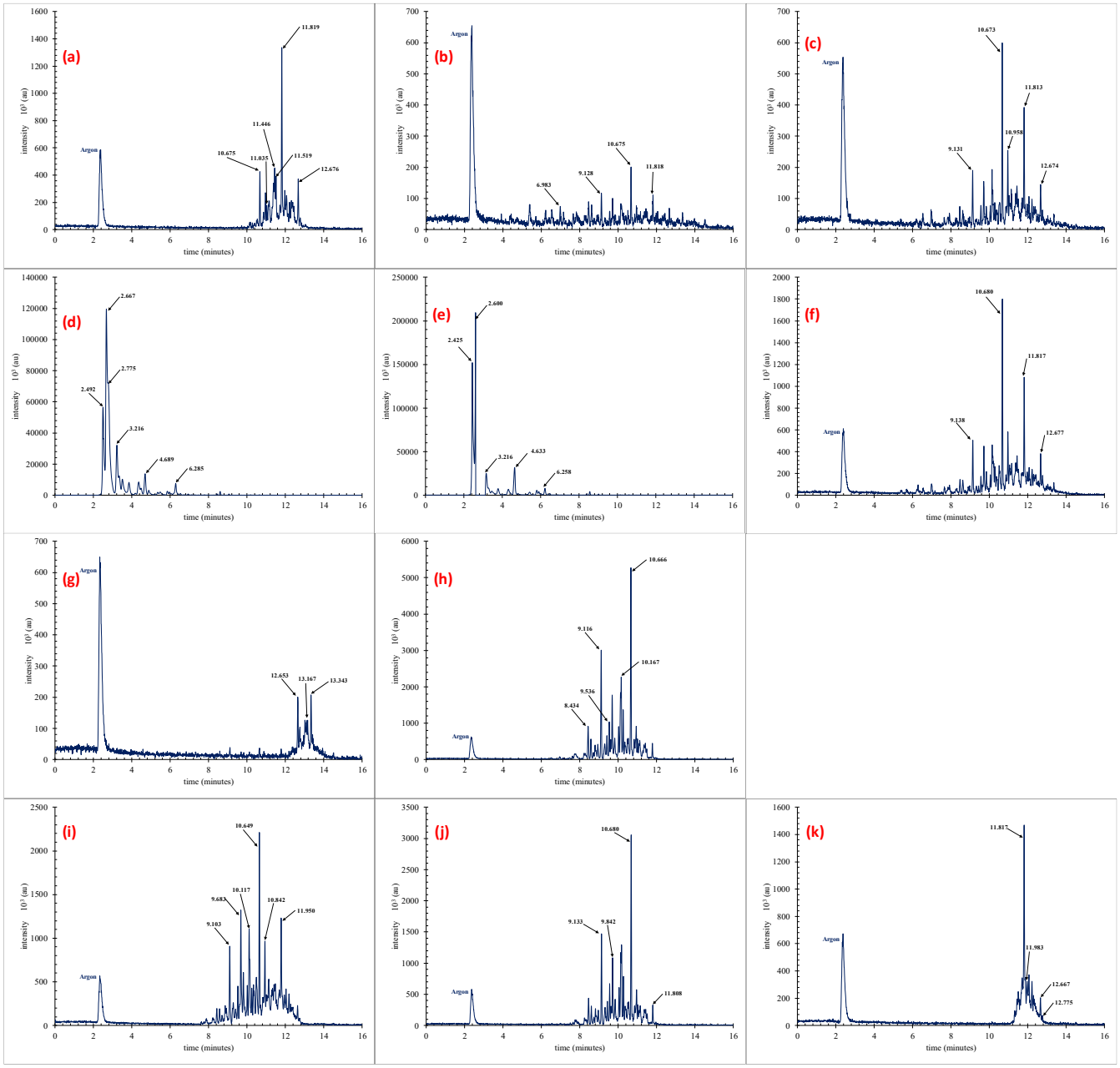

Figure 1: GC 17A spectra from genuine ignitable liquid samples for lamp oil (a), diesel (b), kerosene (c), regular gasoline (d), super gasoline (e), fuel carburetor (f), enzyme fuel oil (g), odorless lighter fuel (h), paint thinner (i), scotch guard (j), and tiki torch fuel (k). The retention times displayed on each plot indicate peaks identified by the MS QP5000. The identity of each peak and the confidence of identification are shown in Table 2.

Table 3: ASTM classification for the ten ignitable liquids studied.

Ignitable Liquid Name	Class	Light/Medium/Heavy
Lamp Oil	Petroleum distillate	Medium
Diesel	Petroleum distillate	Heavy
Kerosene	Petroleum distillate	Heavy
Gasoline	C_4-C_{12}	Medium
Fuel Carburetor Injection	Isoparaffinic	Heavy
Enzyme Fuel Oil	Isoparaffinic	Heavy
Odorless Lighter Fluid	Isoparaffinic	Medium
Paint Thinner	Petroleum distillate	Medium
Scotch Guard	Naphthenic paraffinic liquid	Medium
Tiki Torch Fuel	Oxygenated solvent	Light

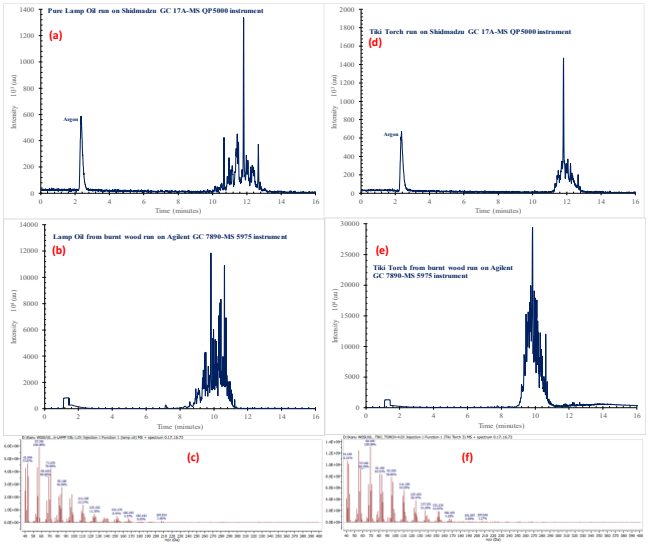

Figure 2: GC spectra for (a) chromatogram produced from pure lamp oil (Shimadzu GC 17A-MS QP5000), (b) chromatogram produced from a wood burnt with lamp oil (Agilent GC 7890-MS 5975), (c) mass spectra (0.17-16.73 minutes) created from a wood burnt with lamp oil (Agilent GC 7890-MS 5975), (d) chromatogram produced from genuine tiki torch fuel (Shimadzu GC 17A-MS QP5000), (e) chromatogram produced from wood burnt with tiki torch fuel (Agilent GC 7890-MS 5975), and (f) mass spectra (0.17-16.73 minutes) created from a wood burnt with tiki torch fuel (Agilent GC 7890-MS 5975). Note the argon peak in chromatograms (a) and (d).

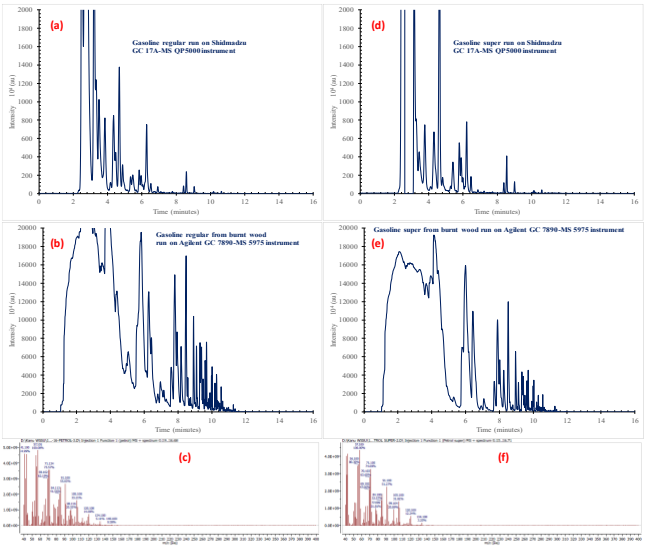

Figure 3: GC spectra for (a) chromatogram produced from pure regular gasoline (Shimadzu GC 17A-MS QP5000), (b) chromatogram produced from wood burnt with regular gasoline (Agilent GC 7890-MS 5975), (c) mass spectra (0.19-16.68 minutes) created from a wood burnt with regular gasoline (Agilent GC 7890-MS 5975), (d) chromatogram produced from pure super gasoline (Shimadzu GC 17A-MS QP5000), (e) chromatogram produced from wood burnt with super gasoline (Agilent GC 7890-MS 5975), and (f) mass spectra (0.15-16.71 minutes) created from a wood burnt with super gasoline (Agilent GC 7890-MS 5975). Note the argon peak in chromatograms (a) and (d).

the gasoline samples were identical. However, there were some differences in the ingredients identified. Figure 1 [d] is the spectra of regular gasoline. The peaks at 2.492 ± 0.012, 2.667 ± 0.010, 3.216 ± 0.011, 4.689 ± 0.001, and 6.285± 0.015 minutes corresponded to n-methylene ethane amine (89%confidence), 2,3-dimethyl butane (93% confidence), 1-chloro-2-methyl propane (89% confidence), toluene (89% confidence), and, bis(1,1-dimethyl ethyl) nitroxide (94% confidence), respectively. Figure 1 [e] is the spectra for super gasoline. We identify the same ingredients in regular gasoline and super gasoline, except for the peaks at 2.425 ± 0.009, 2.600 ± 0.012, and 6.258 ± 0.007 minutes, respectively. The NIST library identified these peaks in super gasoline as trans-2-butene (86% confidence), 2-methyl-1-propene (82% confidence), and 2-methyl-1,5-hexadiene-3-yne (90% confidence), respectively. The replicate spectra for each pure IL studied on the GC 2010-FID and the GC 17A-MS QP5000 were reproducible within 3% RSD. We determine this RSD by taking the average intensity response of each replicate. The mean, standard deviation, and RSD were determined using the three average responses.

Table 3 shows the ASTM 1618 classification scheme for the ten IL studied. Using the data from Table 2 and additional peaks identified from the MS spectrum for each IL, we deduce a classification scheme. We classify the lamp oil as a petroleum distillate liquid due to more n-alkanes in the spectra. The spectra range for diesel and kerosene contains the majority of hydrocarbons. Thus, we categorize diesel and kerosene fuels as petroleum distillate. The other classification schemes are shown in Table 3.

The detection of ILs residue recovered from the crime scene is difficult. However, our data demonstrate the additional dimensionality provided by GC-MS helps solve this problem. In some cases, when we use MS in selective ion mode operation, the MS can act as a filter allowing the analyst to see only peaks linked to the ions selected for a particular IL.

Gas Chromatography 7890 Mass Spectrometry 5975 Analysis of Burnt Ignitable Liquids. Figure 2 shows the GC-MS spectra for two ILs (lamp oil and tiki torch fuel) investigated. As mentioned previously, we conducted this investigation on two different GC-MS instruments due to the initial Shimadzu instrument requiring service immediately after the genuine (pure) sample data was collected. We gained access to an Agilent instrument as an option to complete the investigation for field samples ignited in wood, and undoubtedly there was a sensitivity difference between the two devices. The sensitivity differences lead to the visibility of extra peaks in the IL spectra from burnt wood. These additional peaks may have been due to decomposition products from the burnt wood. There were also retention times shifts because of the instrument change. However, the chromatographic fingerprint for each IL (pure and ignited) remain identical. Figure 2(a) and (b) show the chromatographic profile for lamp oil (pure and when ignited with wood), respectively. The two chromatographic profiles are identical. Note that the intensity of peaks in Figure 2(b) is much higher because the Agilent instrument has a higher sensitivity. Figure 2(c) is the mass spectra for the chromatographic profile in Figure 2(b). The full scan mass spectra for lamp oil show a range of masses, with the three most abundant being 57.100 (100%) Da, 43.099 (77.87%) Da, and 71.100 (70.90%) Da. Previous studies have identified a cluster of ions between 56-58 Da as the presence of isobutylene and ether groups [2]. Figure 2(d) and (e) shows an identical chromatographic profile for tiki torch fuel (pure and when ignited in wood), respectively. The full scan mass spectra for tiki torch fuel ignited in the wood are shown in

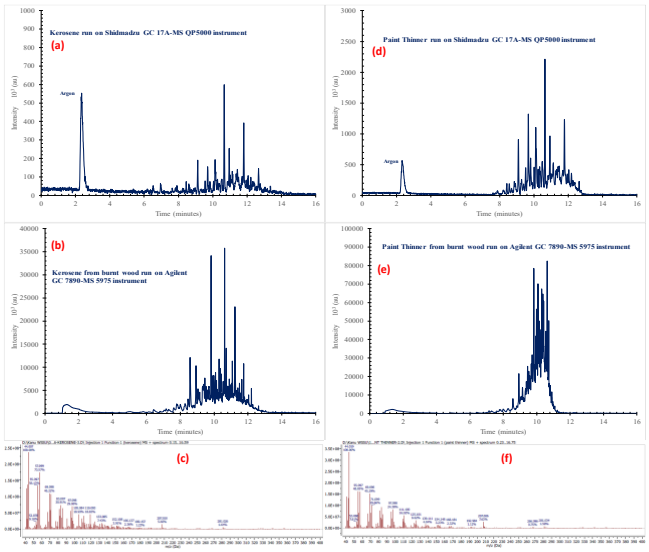

Figure 4: GC spectra for (a) chromatogram produced from pure kerosene (Shimadzu GC 17A-MS QP5000), (b) chromatogram produced from wood burnt with kerosene (Agilent GC 7890-MS 5975), (c) mass spectra (0.15-16.59 minutes) created from a wood burnt with kerosene (Agilent GC 7890-MS 5975), (d) chromatogram produced from genuine paint thinner (Shimadzu GC 17A-MS QP5000), (e) chromatogram produced from wood burnt with paint thinner (Agilent GC 7890-MS 5975), and (f) mass spectra (0.23-16.75 minutes) created from a wood burnt with paint thinner (Agilent GC 7890-MS 5975). Note the argon peak in chromatograms (a) and (d).

Figure 2(f). The three significant peaks from the spectra occurred at 79.100 (100%) Da, 41.100 (81.61%) Da, and 57.100 (69.78%) Da. It is important to note that even though the two instruments have different sensitivity, the chromatographic fingerprints of the IL remain unchanged.

Figure 3 shows the chromatographic profile for two types of gasoline (regular and super). Figure 3(a) and (b) show the chromatographic profile for regular gasoline (pure and when ignited in wood), respectively. Figure 3(c) is the mass spectra for the chromatographic profile of regular gasoline in Figure 3(b). Figures 3(d) and (e) show the chromatographic profile for super gasoline (pure and when ignited in wood). Figure 3(f) is the mass spectra for the chromatographic profile of super gasoline in Figure 3(e). With very few exceptions, the mass spectra for regular and super gasoline shows identical masses, with clusters of ions at comparable m/z values. As discussed earlier with the investigation from the Shimadzu instrument, the only difference we noted was that some of the ingredients in super gasoline corresponded to alkenes and alkynes, which may suggest fuel additives were the essential distinguishing components for these gasoline samples. When burnt in the wood, both chromatographic profiles for regular and super gasoline show a broad peak at the spectra's start. We attribute this broad peak to artifacts generated during the chromatographic run.

Figure 4(a) and (b) show the chromatographic profile for kerosene (pure and when ignited in wood), respectively. Figure 4(c) is the mass spectra for the chromatographic profile of kerosene in Figure 4(b). The full scan mass spectra for kerosene show a range of masses, with the three most abundant occurring at 44.002 (100%) Da, 57.099 (73.57%) Da, and 55.097 (56.13%) Da. The highest mass observed with abundance above 1% was 281.026 Da. Figures 4(d) and (e)

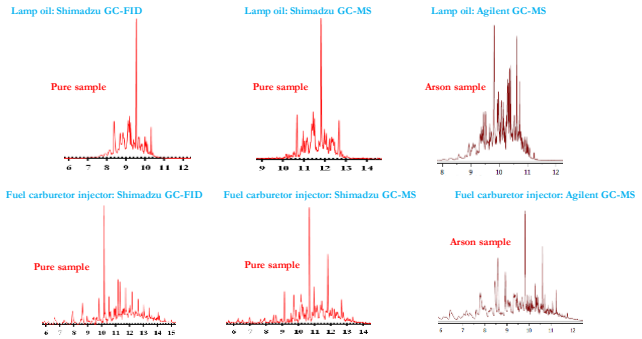

Figure 5: Illustrative GC spectra showing chromatographic pattern recognition for lamp oil and fuel carburetor injector from Shimadzu GC-FID, Shimadzu GC-MS, and Agilent GC-MS.

show the chromatographic profile for paint thinner (pure and when ignited in wood). Figure 4(f) is the mass spectra for the chromatographic profile of paint thinner in Figure 4(e). In the case of paint thinner, the full mass spectra show masses of the three most abundant peaks at 44.019 (100%) Da, 55.097 (48.05%) Da, and 69.098 (45.29%) Da. One unique behavior observed during this investigation is that the chromatographic fingerprint from all instruments (Shimadzu GC-MS and Agilent GC-MS) for all ILs investigated shows identical pattern recognition for both the pure IL and IL poured on a wooden substrate and ignited (see Figure 5 for an illustration with lamp oil and fuel carburetor injector).

It is worth noting that the two GC-MS used in this investigation have their strengths and weaknesses. As shown earlier, the Shimadzu GC-MS instrument can search for individual peaks in a chromatographic profile. Also, it can display mass spectra hits from a NIST library of possible compounds corresponding to the identity. However, it could not generate a complete MS for the chromatographic profile. On the other hand, the Agilent GC-MS instrument can generate a full MS for a chromatographic profile. Also, it could generate individual peak mass spectra. To confirm identity, however, a suitable mass spectra library not installed on the instrument must be used. We have also displayed the result from the arson samples to demonstrate the strength of the Agilent GC-MS instrument. Figure 6 shows the results from a lamp oil arson sample analysis, including the overall MS for the chromatographic profile and MS for some of the individual peaks found in ignited lamp oil. The same result is shown for fuel carburetor injector fluid in Figure 7. Even though pattern recognition on the chromatographic fingerprint for each IL was identical for the two different GC-MS instruments, the investigation observed other peaks in the chromatographic profile of IL samples ignited in the wood when compared to the pure samples. As noted earlier, this may be due to heat-generated products from the seasoned pinewood used to prepare the field samples. In future studies, we plan to investigate selective ion monitoring mass spectrometry to eliminate these peaks.

PCA Unsupervised Incendiaries. Principal component analysis (PCA) is a statistical procedure that rotates and transforms the original axes, each representing an original variable, into new axes called principal components (PCs) that are linear combinations of the actual variables and account for most of the variance in the data. The approach can reveal variables or a variety of variables that describe some inherent structure within a data set that we can interpret in chemical or

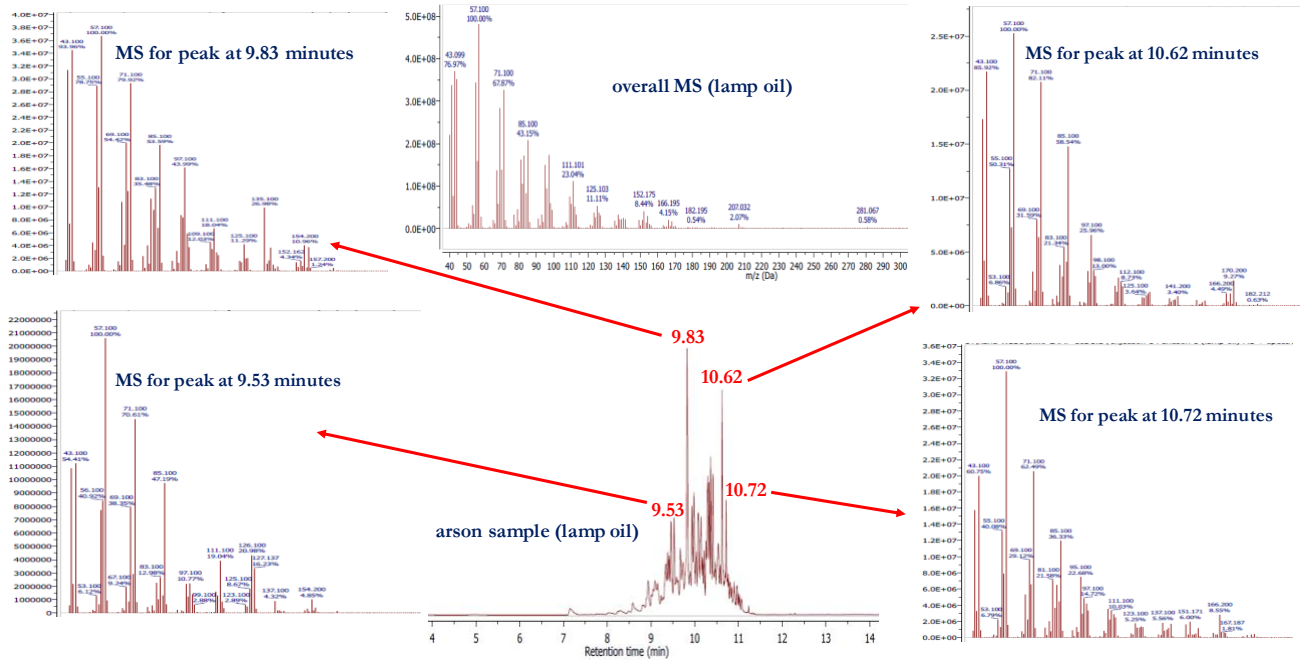

Figure 6: Graphs showing the chromatographic profile from an arson sample of lamp oil, the overall MS, and individual MS for chromatographic peaks at 9.53, 9.83, 10.62, and 10.72 minutes, respectively.

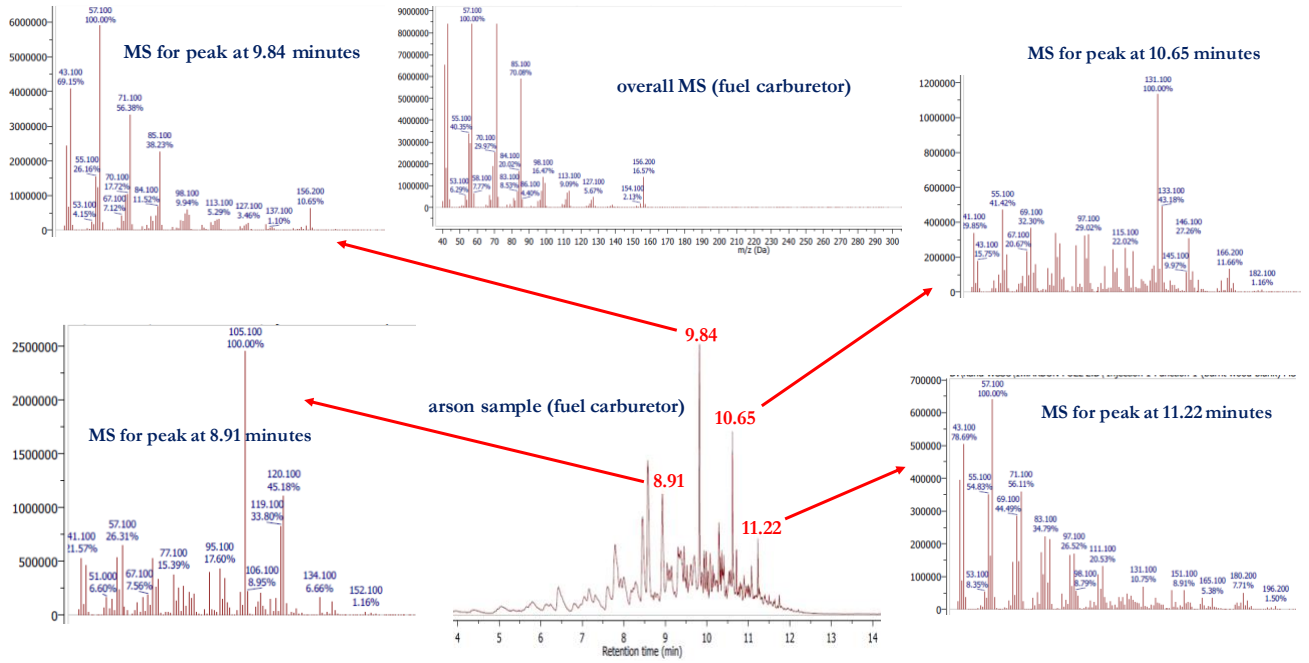

Figure 7: Graphs showing the chromatographic profile from an arson sample of fuel carburetor injector, the overall MS, and individual MS for chromatographic peaks at 8.91, 9.84, 10.65, and 11.22 minutes, respectively.

physicochemical terms [16, 54]. For all the instrument signal analysis (except for Agilent GC-MS), a total of ten total ion spectrum samples formed the investigation, with two replicates per sample for a total of 20 individual samples. Also, each data was blank subtracted before the PCA analysis. Figure 8(a) shows the score plot for the GC-FID signal analysis of several different incendiaries. Several PCs were plotted (PC1 to PC4), and the PCs that contributed to the most significant variance were PC1, PC2, and PC3. Subsequently, PC1 vs. PC2 and PC1 vs. PC3 were plotted. The PC1 and PC2 represent 33.6% and 29.2% of the variance for the GC-FID samples, respectively. The GC-FID sample classes self-categorized into three distinct groups. Group 1 contains gasoline (C_4-C_{12} class); group 2 contains kerosene (petroleum distillate class), diesel (petroleum distillate class), fuel carburetor injection (isoparaffinic class), and tiki torch fuel (oxygenated solvents class); group 3 contains odorless lighter fluid (isoparaffinic class), scotch guard (naphthenic paraffinic class), enzyme fuel oil (isoparaffinic class), paint thinner (petroleum distillate class) and lamp oil (petroleum distillate class). We see that the data for diesel spread along PC1. The score plots indicate this may be due to instrument intensity differences between the ILs. Further, the data shows that different IL classes are grouped in the PCs and made it necessary to investigate

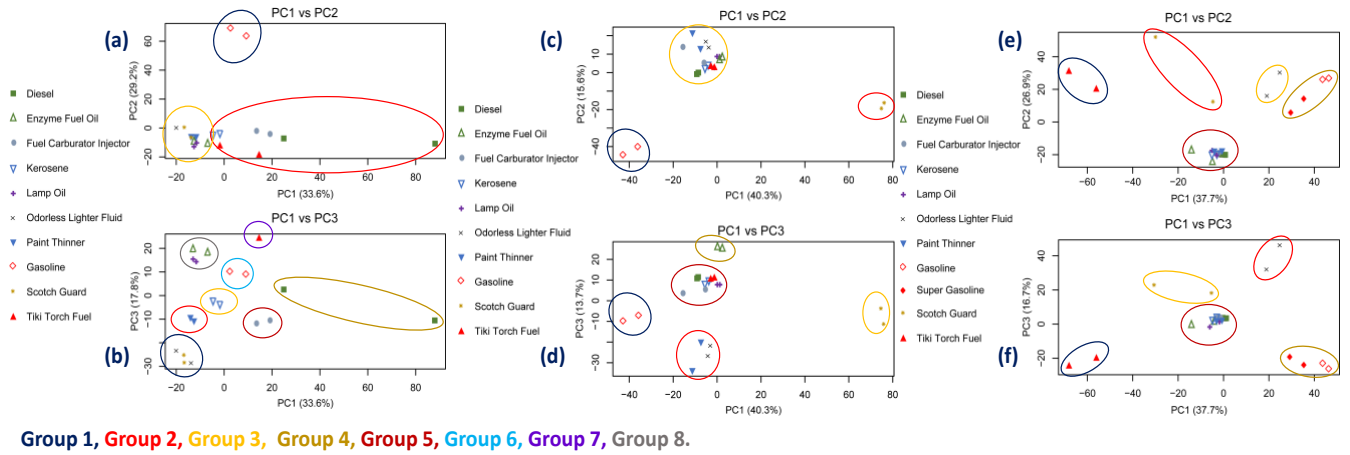

Figure 8: Principal Component Analysis unsupervised analysis of various incendiaries for (a) & (b) Shimadzu GC-FID, (c) & (d) Shimadzu GC-MS, and (e) & (f) Agilent GC-MS. The figure shows the score plot from the data collected by (a, b) GC-FID, (c, d) GC-MS (Shimadzu), and (e, f) GC-MS Agilent. We show the first, second, and third principal components as plots of PC1 vs. PC2 (a, c, e) and PC1, and PC3 (b, d, f) and the variance describing each score are in parenthesis.

additional PCs. Note that the variance for this component plot (PC1 vs. PC3) is lower for all signals, but it did show some further self-categorization. Figure 8(b) shows the PC 1 vs. PC3, representing 33.6%, and 17.8% of the variance reveals further differentiation that self-categorize into eight groups. Group 1 contains scotch guard (naphthenic paraffinic class), and odorless lighter fluid (isoparaffinic class); group 2 contains paint thinner (petroleum distillate class); group 3 contains kerosene (petroleum distillate class); group 4 contains diesel (petroleum distillate class); group 5 contains fuel carburetor injection (isoparaffinic class); group 6 contains gasoline (C_4-C_{12} class); group 7 contains tiki torch fuel (oxygenated solvents class); group 8 contains enzyme fuel oil (isoparaffinic class), and lamp oil (petroleum distillate class). It is noted that for this instrument signal, scotch guard and the odorless lighter fluid are grouped in the PC, even though they are classed differently. Table 2 shows these two ILs have similar ingredients (2,6-dimethyl heptane, 2-methyl octane, 4-methyl tridecane) in their mass spectra. The same was true for group 7 of the PC1 vs. PC3 plots. Closer inspection of group 7 ILs did show some separation between the groups, indicating some inherent differences between those incendiaries, even though the differences for the other groups are overshadowing them.

As with the GC-FID data, we plot several PCs for the GC-MS data. The plots that contributed the most significant variance to the GC-MS data (Shimadzu instrument) were the plots for PC1 vs. PC2 and PC1 vs. PC3. For the plot corresponding to PC1 vs. PC2, the total cumulative proportion of the variance was 55.9%. This cumulative variance corresponds to 40.3% and 15.6%, respectively, for PC1 and PC2. Figure 8(c) shows that the GC-MS sample classes are self-categorized into three distinct groups. Group 1 contains gasoline (C_4-C_{12} class); group 2 contains scotch guard (naphthenic paraffinic class); group 3 contains kerosene (petroleum distillate class), diesel (petroleum distillate class), enzyme fuel oil (isoparaffinic class), fuel carburetor injection (isoparaffinic class), lamp oil (petroleum distillate class), odorless lighter fluid (isoparaffinic class), paint thinner (petroleum distillate class), and tiki torch fuel (oxygenated solvents). As discussed previously, there is not much self-categorization in the PC1 and PC2 components, making it necessary to investigate other PCs. Again, the PCs with a lower variance that show appreciable self-categorization was the PC1 vs. PC3 plot. For the plot corresponding to PC1 vs. PC3, the total cumulative proportion of the variance was 54.0% (which was marginally lower than the cumulative variance for PC1 and PC2 at 55.9%). This cumulative variance corresponds to 40.3% and 13.7%, respectively, for PC1 and PC3 (Figure 8(d)). Group 1 contains gasoline (C_4-C_{12} class); group 2 contains odorless lighter fuel (isoparaffinic class) and paint thinner (petroleum distillate class); group 3 contains scotch guard (naphthenic paraffinic class); group 4 contains enzyme fuel (isoparaffinic class); and group 5 consists of kerosene (petroleum distillate class), diesel (petroleum distillate class), lamp oil (petroleum distillate), fuel carburetor injection (isoparaffinic class), and tiki torch fuel (oxygenated solvents). Even though odorless lighter fuel and paint thinner falls in different class categories, these two ILs have similar components in their mass spectra profile (e.g., nonane, 2-methyl octane, and 4-methyl tridecane) plus other ingredients, enabling them to fall in group 4. We noted a similar observation for kerosene, diesel, fuel carburetor, lamp oil, and tiki torch fuel. These four ILs contain two or more of octane, 2-methyl octane, 2,5-dimethyl hexane, and 4-methyl tridecane, plus other ingredients in their mass spectra profile. The PCA score plots reveal that the ILs possess characteristic differences giving rise to separations between incendiaries, albeit some overshadowed by clustering.

Figure 8(e) and (f) show the scores plot for the GC-MS data (a burnt IL) collected by the Agilent instrument. As discussed previously, we observed burnt substrate peaks in the IL profile for the instrument signal for the Agilent GC-MS data. However, it should be noted that these new peaks did not change the overall IL profile signature. For the plot corresponding to PC1 vs. PC2, the total cumulative proportion of the variance was 64.6%. This cumulative variance corresponds to 37.7% and 26.9%, respectively, for PC1 and PC2. There were eleven groups of different samples in the data set with two replicates per sample.

Interestingly, there were five distinct groupings in the Agilent GC-MS data compared with the data collected using other instruments. For the Agilent GC-MS data set, the groups were tiki torch (group 1), scotch guard (group 2), odorless lighter fluid (group 3), and regular gasoline and super gasoline (group 4). The fifth group included the remaining fuels tested

(kerosene, diesel, fuel carburetor injection, paint thinner, lamp oil, and enzyme fuel oil), (Figure 8(e)). Note that the data for tiki torch fuel, scotch guard, and odorless lighter fluid spread along PC1. As discussed previously, this may be due to instrument intensity differences between the ILs. For the plot corresponding to PC1 vs. PC3, the total cumulative proportion of the variance was 54.4%. This cumulative variance corresponds to 37.7% and 16.7%, respectively, for PC1 and PC3 (Figure 8(f)) - the data for this self-categorize into the same five groups we observed for the PC1 vs. PC2 plot. Also, the spreading along the PC1 was much lower for the scotch guard. The grouping we found in this investigation is very much dependent on the total ingredients present in the overall sample.

Conclusions

Developing a reliable, informative instrumental approach for the analysis of arson samples is particularly challenging, as the combustion of heat-generated products often conceals ignitable liquid residues. This investigation has developed a cheaper direct headspace injection combined with two different instruments. The chromatographic profile from the two devices showed unique and similar fingerprint patterns to a specific IL. All chromatographic profiles reported from each instrument for a particular IL were reproducible to within 3%. This work is not exhaustive, but it demonstrates a new potential for using direct headspace injection with GC-MS combined with PCA for arson investigations. The MS data from both GC-MS instruments showed some similar m/z peaks from all ILs. This indicates identical hydrocarbon(s) or fragmentation cluster patterns may be present, representing the ILs studied ingredients. The PCA data showed characteristic differences giving rise to the separation between incendiaries, albeit some were overshadowed by clustering. In some cases, ILs who showed similar components in their mass spectra profile grouped as classes on the PCA display. The sample introduction technique in this work is cheaper and requires no adsorbent preparation, uses no solvents, and could be applied to other support materials such as carpets, clothing, soils, etc. We would expect a slight change in the chromatographic fingerprint and even the mass spectra for additional support materials, especially for real-world arson samples. We have incorporated this GI laboratory project into an undergraduate-level instrumental analysis class. We also plan to integrate the PCA portion into a graduate-level analytical chemistry class. We expect students in these classes to investigate more ILs and develop loading plots to investigate grouping patterns of ILs further. Incorporating such projects into semester lab activities will improve students' critical thinking and problem-solving skills, strengthen our undergraduate chemistry program, and enhance and facilitate overall student learning.

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References and Notes

1. R. Campbell, National Fire Protection Association – Intentional Fires Report, July 2017. Available at https://www.nfpa.org/-/media/Files/News-and-Research/Fire-statistics-and-reports/US-Fire-Problem/Fire-causes/osintentional.ashx (accessed 06/11/2019).
2. I. Barnett, M. Zhang, Discrimination of brands of gasoline by using DART-MS and chemometrics. Forensic Chemistry 10 (2018) 58-56.
3. A. Akmeemana, M.R. Williams, M.E. Sigman, Major chemical compounds in the Ignitable Liquids Reference Collection and Substrate databases. Forensic Chemistry 5 (2017) 91-108.
4. R. Clodfelter, E. Hueske, A comparison of decomposition products from selected burned materials with common arson accelerants. J. Forensic Sci. 22(1) (1977) 116-118.
5. W. Bertsch, Volatiles from carpet: a source of frequent misinterpretation in arson analysis. J. Chromatogr. A 674(1-2) (1994) 329-333.
6. J.J. Lentini, Differentiation of asphalt and smoke condensates from liquid petroleum distillates using GC/MS. J. Forensic Sci. 43(1) (1998) 97-113.
7. J.J. Lentini, J.A. Dolan, C. Cherry, The petroleum laced background. J. Forensic Sci. 45(5) (2000) 968-989.
8. J.D. DeHann, K. Bonarius, Pyrolysis products of structure fires. J. Forensic Sci. Soc. 28(5-6) (1988) 299-309.
9. M. Fernandes, C.M. Lau, W.C. Wong, The effect of volatile residues in burnt household items on the detection of fire accelerants. Sci. & Justice 42(1) (2002) 7–15.
10. K. Cavanagh, E. Du Pasquier, C. Lennard, Background interference from car carpets - the evidential value of petrol residues in cases of suspected vehicle arson, Forensic Sci. Int. 125(1) (2000) 22-36.
11. E. Stauffer, Concept of pyrolysis for fire debris analysts. Sci. & Justice 2003;43(1):29-40.
12. S.B.Wells, The identification of isopar H in vinyl flooring. J. Forensic Sci. 50(4) (2005) 1-8.
13. ASTM E1618-14, Standard Test Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography-Mass Spectrometry, in: ASTM International (Ed.) West Conshohocken, PA, 2014.
14. AB Kanu, M. Pajski, M. Hartman, I. Kimaru, S. Marine, and L.J. Kaplan, Exploring Perspectives and Identifying Potential Challenges Encountered with Crime Scene Investigations when Developing Chemistry Curricula. J. Chem. Educ. 92(8) (2015) 1353-1358.
15. AB Kanu, L.J.Kaplan, The quest for confirmatory data in crime scene investigations. Chemical Educator 21 (2016) 231-239.
16. WNSM Desa, NN. Daeid, D. Ismail, K.Savage, Application of unsupervised chemometric analysis and self-organizing feature map (SOFM) for the classification of lighter fuels. Anal. Chem. 82(15) (2010) 6395-6400.
17. E.E. Waddell, J.L. Frisch-Daiello, M.R. Williams, M.E.Sigman, Hierarchical cluster analysis of ignitable liquids based on the total ion spectrum. J. Forensic Sci. 59(5) (2014) 1198-1204.
18. M.E. Sigman, .M.R Williams, J.A. Castelbuono, J.G. Colca, C.D. Clark, Ignitable liquid classification and identification using the summed-ion mass spectrum. Instrum. Sci. Technol. 36(4) (2008) 375-393.
19. E.E. Waddell, M.R. Williams, M.E. Sigman, Progress toward the determination of correct classification rates in fire debris analysis II: utilizing soft independent modeling of class analogy (SIMCA). J. Forensic Sci. 59(4) (2014) 927-935.
20. R.Saferstein, An Introduction to Forensic Science. Pearson Prentice Hall: New Jersey, 2011.
21. R.O. Keto, P.L. Wineman, Detection of petroleum-based accelerants in fire debris by target compound gas chromatography/mass spectrometry. Anal. Chem. 63(18) (1991) 1964-1971.

22. R.O.Keto, GC/MS data interpretation for petroleum distillate identification in contaminated arson debris. J. Forensic Sci. 40(3) (1995) 412-423.
23. J.L. Frisch-Daiello, M.R. Williams, E.E. Waddell, M.E.Sigman, Application of self-organizing feature maps to analyze the relationships between ignitable liquids and selected mass spectral ions. Forensic Sci. Int. 236 (2014) 84-89.
24. WY Lu, J.G. Rankin, A. Bondra, C. Trader, A. Heeren, P.D.Harrington, Ignitable liquid identification using gas chromatography/mass spectrometry data by projected difference resolution mapping and fuzzy rule-building expert system classification. Forensic Sci. Int. 220(1–3) (2012) 210-218.
25. Y. Lu, P. Chen, P.D. Harrington, Comparison of differential mobility spectrometry and mass spectrometry for gas chromatographic detection of ignitable liquids from fire debris using projected difference resolution. Anal. Bioanal. Chem. 394 (2009) 2061-2067.
26. L.J. Marshall, J.W. Mcllroy, V.L. McGuffin, W.R. Smith, Association and discrimination of diesel fuels using chemometric procedures. Anal. Bioanal. Chem. 394 (2009) 2049-2059.
27. K.R. Prather, S.E. Towner, V.L. McGuffin, W.R. Smith, Effect of Substrate Interferences from High-Density Polyethylene on Association of Simulated Ignitable Liquid Residues with the Corresponding Liquid. J. Forensic Sci. 59(1) (2014) 52-60.
28. D.A. Turner, J.V.Goodpaster, Comparing the Effects of Weathering and Microbial Degradation on Gasoline Using Principal Components Analysis. J. Forensic Sci. 57(1) (2012) 64-69.
29. D.A. Turner, J.V.Goodpaster, The effects of season and soil type on microbial degradation of gasoline residues from incendiary devices. Anal. Bioanal. Chem. 405 (2013) 1593-1599.
30. M.E. Sigman, M.R. Williams, R.E.Ivy, Individualization of gasoline samples by covariance mapping and Gas Chromatography/Mass Spectrometry. Anal. Chem. 9 (2007) 3462-3468.
31. J.M. Baerncopf, V.L. McGuffin, R. Waddell Smith, Effect of gas chromatography temperature program on the association and discrimination of diesel samples. J. Forensic Sci. 55(1) (2010) 185-192.
32. J.M. Baerncopf, V.L. McGuffin, R.W.Smith, Association of ignitable liquid residues to neat ignitable liquids in the presence of matrix interferences using chemometric procedures. J Forensic Sci 56(1) (2011) 70-81
33. E.E. Waddell, J.L. Frisch-Daiello, M.R. Williams, M.E.Sigman, Hierarchical cluster analysis of ignitable liquids based on the total ion spectrum. J Forensic Sci 59(5) (2014) 1198–204.
34. J.I. Cacho, N. Campillo, M. Aliste, P. Viñas, M. Hernández-Córdoba, Headspace sorptive extraction for the detection of combustion accelerants in fire debris. Forensic Sci Int 238 (2014) 26-32.
35. M. Ferreiro-González, J. Ayuso, J.A. Álvarez, M. Palma, C.G.Barroso, Application of an HS–MS for the detection of ignitable liquids from fire debris. Talanta 142 (2015) 150-6.
36. M. Lopatka, AA Sampat, S. Jonkers, L.A. Adutwum, H.G.J. Mol, G. van der Weg et al., Local ion signatures (LIS) for the examination of comprehensive two-dimensional gas chromatography applied to fire debris analysis. Forensic Chem. 3 (2017) 1-13.
37. NA. Sinkov, B.M. Johnston, P.M.L. Sandercock, J.J. Harynuk, Automated optimization and construction of chemometric models based on highly variable raw chromatographic data. Anal Chim Acta 697(1–2) (2011) 8-15.
38. NA. Sinkov, P.M.L. Sandercock, J.J. Harynuk, Chemometric classification of casework arson samples based on gasoline content. Forensic Sci. Int. 235 (2014) 24-31.
39. L.A. Adutwum, R.J. Abel, J.Harynuk, Total ion spectra vs. segmented ion spectra as processing tools for gas chromatography-mass spectrometry data. J. Forensic Sci. 63(4) (2018) 1059-1068.
40. H. Yoshida, T. Kaneko, S. Suzuki, A solid-phase microextraction method for the detection of ignitable liquids in fire debris. J. Forensic Sci. 53(3) (2008) 668-676.
41. L. Meal, Arson analysis by second derivative ultraviolet spectrometry. Anal. Chem. 58 (1986) 834-836.
42. K.L. Bryce, I.C. Stone, K.E. Daugherty, Analysis of fire debris by nuclear magnetic resonance spectroscopy. J. Forensic Sci. 26(4) (1981) 678-685.
43. J. Alexander, G. Mashak, N, Kapitan, J.A. Siegel, Fluorescence of petroleum products II: three-dimensional fluorescence plots of gasoline. J. Forensic Sci. 32(1) (1987) 72-86.
44. B. Tan, J.K. Hardy, R.E. Snavely, Accelerant classification by gas chromatography-mass spectrometry and multivariate pattern recognition. Anal. Chim. Acta 422(1) (2000) 37-46.
45. J.R.Wallace, GC/MS data from fire debris samples: interpretation and applications. J. Forensic Sci. 44(5) (1999) 996-1012.
46. B.J. DeVos, Gas chromatography coupled with ion trap mass spectrometry (GC-MS and GC-MS-MS) for arson debris analysis, in: Thesis for the degree of Master of Science in Chemistry, Department of Applied Chemistry, University of Pretoria, Pretoria, 2005.
47. R. Hirz, Gasoline brand identification and individualization of gasoline lots. J. Forensic Sci. Soc. 29(2) (1989;)91-101.
48. G. Zadora, R. Borusiewicz, J. Zieba-Palus, Differentiation between weathered kerosene and diesel fuel using automatic thermal desorption-GC–MS analysis and the likelihood ratio approach. J. Sep. Sci. 28(13) (2005) 1467-1475.
49. E. Stauffer, J.A. Dolan, R. Newman, Fire Debris Analysis, Academic Press, Burling-ton, MA, 2008.
50. J.E. Nichols, M.E. Harries, T.M. Lovestead, T.J. Bruno, Analysis of arson fire debris by low temper. J. Chromatogr. A 1334 (2014) 126-138.
51. President's Council of Advisors on Science and Technology (2012). Engage to Excel: Producing One Million Additional College Graduates with Degrees in Science, Technology, Engineering, and Mathematics. Available at https://obamawhitehouse.archives.gov/sites/default/files/microsites/ostp/pcast-engage-to-excel-final_2-25-12.pdf (accessed on December 1, 2020).
52. A. B. Kanu, K. E. Levine, L. G. Haines, M. Massey, T. Codio, Measurement of Mercury Levels in a Commercial Fish Oil Brand by Inductively Coupled Plasma Mass Spectrometry. Chem. Educator 20 (2015) 234-239.
53. M. Ferreiro-González, G.F. Barbero, M. Palma, J. Ayuso, J.A. Álvarez, C.G. Barosso, Determination of Ignitable Liquids in Fire Debris: Direct Analysis by Electronic Nose. Sensors 16(5) (2016) 695.
54. M.J. Adams, Feature Selection and Extraction. Chemometrics in Analytical Spectroscopy. 2nd Ed., Royal Society of Chemistry: Cambridge, UK, pp72-81, 2004.