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Evaluation of field sampling and analysis methods for fire investigation including electronic noses and adsorption sampling/gas chromatography mass spectrometry

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FLORIDA INTERNATIONAL UNIVERSITY

Miami, Florida

EVALUATION OF FIELD SAMPLING AND ANALYSIS METHODS FOR FIRE INVESTIGATION INCLUDING ELECTRONIC NOSES AND ADSORPTION SAMPLING/GAS CHROMATOGRAPHY MASS SPECTROMETRY

A thesis submitted in partial fulfillment of the

requirements for the degree of

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in

FORENSIC SCIENCE

by

Laura Conner

2005

To: Interim Dean Mark Szuchman
College of Arts and Sciences

This thesis, written by Laura Conner, and entitled Evaluation of Field Sampling and Analysis Methods for Fire Investigation including Electronic Noses and Adsorption Sampling/Gas Chromatography Mass Spectrometry, having been approved in respect to style and intellectual content, is referred to you for judgment.

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

Yong Cai

Piero Gardinali

Kenneth Furton, Major Professor

Date of Defense: November 9, 2005

The thesis of Laura Conner is approved.

Interim Dean Mark Szuchman
College of Arts and Sciences

Dean Douglas Wartzok
University Graduate School

Florida International University, 2005

DEDICATION

For AJ, Uncle Mike and Pap

And Bruce and Sharon Conner

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ABSTRACT OF THE THESIS

EVALUATION OF FIELD SAMPLING AND ANALYSIS METHODS FOR FIRE INVESTIGATION INCLUDING ELECTRONIC NOSES AND ADSORPTION SAMPLING/GAS CHROMATOGRAPHY MASS SPECTROMETRY

by

Laura Conner

Florida International University, 2005

Miami, Florida

Professor Kenneth Furton, Major Professor

This study evaluates the use of commercially available instruments for locating and collecting accelerants in the field. Electronic noses can be used to scan a fire scene for the possible presence of an accelerant. The TLV Sniffer® was found to be able to detect accelerants at low levels but did alert to some burned matrix alone. When subjected to a proficiency test designed for canines, the TLV Sniffer® was able to locate accelerants in two of the three tests. The tpi®Pocket was found not to be sensitive or selective enough to be useful in locating accelerants. Once the location of possible accelerants has been determined, they can be collected by dynamic headspace sampling in the field with the Portable Arson Sampler (PAS). The PAS was found to be able to collect a broad range of compounds from ignitable liquids and had comparable efficiency to a conventional method.

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1. INTRODUCTION

1.1 Arson

Arson is a serious crime affecting the United States. According to the National Fire Protection agency, 305 people were killed and $692 million dollars in property damage was caused by arson structure fires in 2003[1]. Over half of these fires were set by juveniles. However, only one in six arson cases result in an arrest or are resolved by "exceptional means[1]." The number of intentionally set fires has been decreasing over the past few years. With continued research into new technologies, hopefully arrest and conviction rates will rise and the number of injuries and deaths will continue to fall.

Arson has been defined as, "the willful and malicious burning of property, sometimes with the intent of defrauding insurance companies[2]." Three goals of fire investigation have been determined:

> "1. Locate the origin of the fire
>
> 2. Determine the cause of the fire
>
> 3. Locate, document and preserve evidence that relates to the cause of the fire or associated criminal acts.[3]"

This study will evaluate new methods of accomplishing the third goal in the field. Commercially available electronic noses will be tested for their ability to locate evidence and a dynamic headspace sampler will be studied for its efficiency of in-field collection and preservation of evidence.

1.2 Ignitable Liquid Extraction

The cause of an intentionally set fire can be difficult to find. Many fires are started by the use of an accelerant. An accelerant can be a flammable liquid, usually made of petroleum based or similar components[4]. Accelerants have been classified based on the volatility range of their components as light, medium and heavy ignitable liquids by ASTM (American Society for Testing and Materials). Further classification is based on their general type of components such as petroleum distillates and aromatic products[5,6] (see Table 1). Residues of these accelerants (ignitable liquid residues or ILRs) can be extracted from the debris, but the process is very difficult and sometimes inefficient.

In addition to ignitable liquid residues, fire debris contains background, pyrolysis and combustion products from the matrix material. Background compounds come from the debris' composition itself and from any residual compounds from its manufacture other exposure to chemicals[7,8]. Pyrolysis and combustion compounds are formed during the fire process. Pyrolysis of materials occurs as the matrix breaks down due to heat in the absence oxygen[9]. The combustion process requires the presence of oxygen. The resulting compounds are found in all real fire debris and some of these compounds are the same type of compounds that make up the ignitable liquid residues (alkanes and aromatics for example)[7,8]. No currently used method for the extraction of ignitable liquids is selective for the collection of these residues without also collecting the background pyrolysis and combustion products. This is a crucial fact that must be considered in fire debris analysis. Because the compounds have similar composition, they may lead to false positives for the presence of accelerant, or false negatives because accelerant compounds were falsely

Table 1: Ignitable Liquid Classification Scheme defined in ASTM guidelines[5,6]

Class	Light (C_4-C_9)	Medium (C_8-C_{13})	Heavy (C_9- C_{20+})
Gasoline – all brands including gasohol	Fresh gasoline is typically in the range of C_4-C_{12}		
Petroleum Distillates	Petroleum Ether Some cigarette lighter fluids Some camping fuels	Some charcoal starters Some paint thinners Some dry cleaning solvents	Kerosene Diesel Fuel Some jet fuels Some charcoal starters
Isoparaffinic products	Aviation Gas Specialty solvents	Some charcoal starters Some paint thinners Some copier toners	Commercial Specialty solvents
Aromatic products	Some paint and varnish removers Some automotive parts cleaners Xylenes, Toluene-based products	Some automotive parts cleaners Specialty cleaning solvents Some insecticide vehicles Fuel additives	Some insecticide vehicles Industrial cleaning solvents
Naphthenic products	Cyclohexane based solvents/products	Some charcoal starters Some insecticide vehicles Some lamp oils	Some insecticide vehicles Some lamp oils Industrial solvents
Normal Alkanes products	Solvents Pentane, hexane, heptane	Some candle oils Copier toners	Some candle oils Carbonless forms Copier toners
De-Aromatized distillates	Some camping fuels	Some charcoal starters Some paint thinners	Some charcoal starters Odorless kerosenes
Oxygenated solvents	Alcohols Ketones Some lacquer thinners Fuels additives Surface preparation solvents	Some lacquer thinners Some industrial solvents Metal cleaners/Gloss removers	
Others-Miscellaneous	Single components products Some blended enamels Some enamel reducers	Turpentine products Some blended products Various specialty products	Some blended products Various specialty products

identified as coming from the matrix. For example, approximately two thirds of fire debris samples submitted to laboratories contain carpeting. In one study, approximately 10% of laboratories mis-identified the presence of an ignitable liquid on burned carpet that contained none[8]. Some of these difficulties can be overcome with mass spectrometry techniques.

Some of the methods used for extraction of ignitable liquid residues include solvent extraction, passive headspace extraction using activated charcoal strips (ACS), solid phase microextraction (SPME), and dynamic headspace sampling.[10,11,12,13,14] Dynamic headspace sampling takes advantage of the volatility of accelerant residues. A gas is passed over the sample to move volatiles from the headspace to be deposited onto a media. Passive headspace extraction with activated charcoal strips is performed by suspending the strip in the container with the debris, which is then heated, typically for 8 to 16 hours[3]. The adsorbed volatile compounds are extracted with a solvent wash for further analysis. Activated charcoal is an effective adsorbent for accelerants because they are comprised mostly of nonpolar compounds. However, the type of compound can affect its recovery. Aromatics are preferentially adsorbed over aliphatic hydrocarbons[3]. Also, displacement can occur based on the amount of time the strip is exposed to the debris and the temperature[3]. At higher temperatures or longer exposure times, higher boiling point compounds may displace the lower ones. The advantages and limitations of any method of ignitable liquid extraction must be considered before it is used for fire debris analysis.

1.3 Electronic Noses

Electronic noses are used for the initial evaluation for the presence of ILR's at a scene. Accelerant Detecting Canines can also be used for the same purpose, but they are limited in operating time and ability to work in hazardous conditions[3]. Also, false negatives may occur due to improper training or the handler not recognizing an alert the canines give to an accelerant containing sample[15]. As research and proper training techniques are developed, the performance of canines may improve. An advantage of using canines is that they may be able to determine a scent's to its point of origin by following the scent cone[3]. An electronic nose can be scanned over an area to find the highest response but would lack the canines' innate ability to track a scent. Canines are very sensitive and can distinguish between background from burned materials and actual ignitable liquid residues. In one study, canines were found to alert to as little as 0.005μL of gasoline spiked on a cotton ball[16]. Electronic noses are sensitive in that they can detect very low levels of compounds, but they are not selective in the types of compounds they detect. The low selectivity means they cannot discriminate between accelerants and background and pyrolysis products from the matrix[3]. This results in a high occurrence of false positives. However, because these types of instruments are used as an indicator of the possible presence of accelerants, the high occurrence of false positives may not be a significant problem. It may lead to more samples being collected than necessary and be more time consuming for the analyst in the laboratory, but this situation is preferable to not alerting when an accelerant is present. The results from an electronic nose are not used as proof in court; they are simply used to aid the investigator.

There are several types of electronic noses that have been developed. Though most have not been evaluated for detection of accelerants, they could be used for this purpose. The sensors used include carbon black-polymer composite sensors[16] and conducting polymers[17], which function by changes in conductivity when exposed to an analyte. Other sensors measure change in wavelength when a dye impregnated polymer reacts with the substance[18], or the swell in the surface coating of a piezoelectric crystal[18,19].

1.4 The TLV Sniffer®

The TLV Sniffer® is not complex in design (see Figure 1). A small pump pulls samples of air into the instrument. Here the samples reach a catalyst coated resistance element. As volatiles are oxidized by the catalyst, they produce heat, which changes the resistance of the element proportionally to the concentration of volatile compounds in the sample[20]. This change is measured and expressed on the meter in parts per million of hexane. A calibration curve published in the manual relates parts per million (ppm) of hexane to other compounds such as toluene and benzene[20]. The TLV Sniffer® was designed for measurement of hazards in an industrial environment, location of gas leaks[20], and for the possible presence of accelerants at a fire scene.

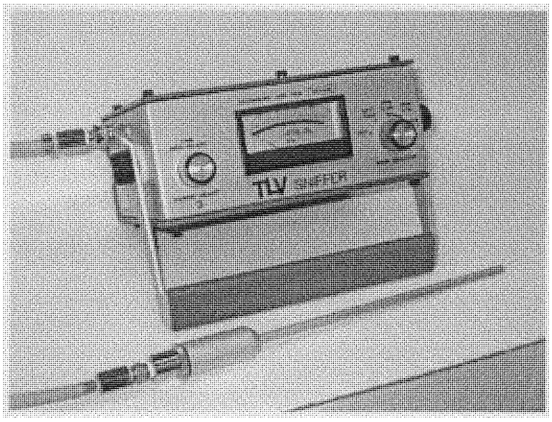


Figure 1: The TLV Sniffer®

Due to its abilities to detect low levels of volatile hydrocarbons, the TLV Sniffer® may be able to locate the presence of possible accelerants in fire debris. This instrument may work well in conjunction with the Portable Arson Sampler. First, the investigator will visually inspect the scene for possible burn patterns. These areas can then be tested with the TLV Sniffer® for the possible presence of accelerants. Finally, samples of the debris are collected with the Portable Arson Sampler and sent to the laboratory for analysis.

1.5 The tpi®Pocket Combustible Gas Leak Detector

The tpi®Pocket Combustible Gas Leak Detector is a handheld battery operated device that could potentially be used to detect accelerants in the field (see Figure 2). This detector gives an audible alarm and four lights indicating the level of alert. The device is designed to detect natural gas leaks and leaks from fuel lines or tanks[21]. The manual claims to be able to detect methane, butane, propane, diesel and kerosene. The manual also says that level 1 corresponds to more than 1000ppm methane, level 2 is greater than 2000ppm methane, level 3 is above 4000ppm of methane, and level 4 is above 5000ppm methane. It requires only two 1.5 volt batteries and can last up to three hours of continuous operating time[21].

The tpi®Pocket functions with the use of a metal oxide semiconductor sensor. Oxygen adsorbs to the metal oxide. When a gas interacts with the negatively charged oxygen, it decreases the charge, therefore decreasing the resistance of the sensor. The change in resistance is related to the concentration of the volatiles by the equation

$$Rs = A[C]^{-\alpha}$$

where Rs is the electrical resistance of the sensor, A is a constant, [C] is the concentration of the gas, and α is the slope of the resistance calibration curve generated for various concentrations of gases. Humidity can affect the sensor response because water will adsorb to the metal oxide[22]. Dramatic differences in temperature and humidity between uses could affect response and should be considered.

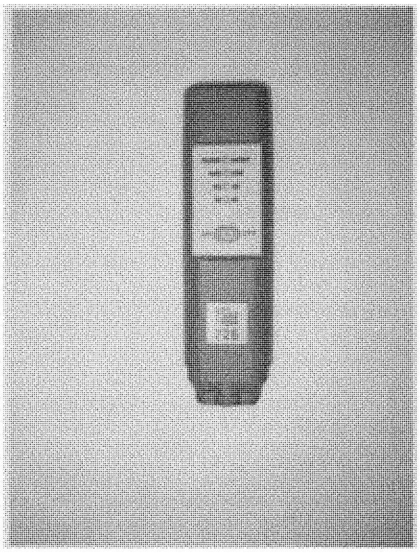


Figure 2: The tpi®Pocket Combustible Gas Leak Detector

1.6 Dynamic Headspace Sampling with the Portable Arson Sampler

The Portable Arson Sampler (PAS) is a dynamic headspace sampling instrument that has been designed to be field portable (see Figure 3). It consists of a heated Teflon™ lined sampling chamber (to prevent carryover), a vacuum system, and a sampling tube. A piece of suspected accelerant containing debris is placed in the heated chamber and sealed. The vacuum pulls volatile components from the headspace of the chamber into the sampling tube, which is filled with an adsorbent material (see Figure 4). The tube can then be capped and taken to the laboratory for analysis. This eliminates the need to transport and store many samples of debris. Several sampling tubes can be carried in a shirt pocket[23,24].

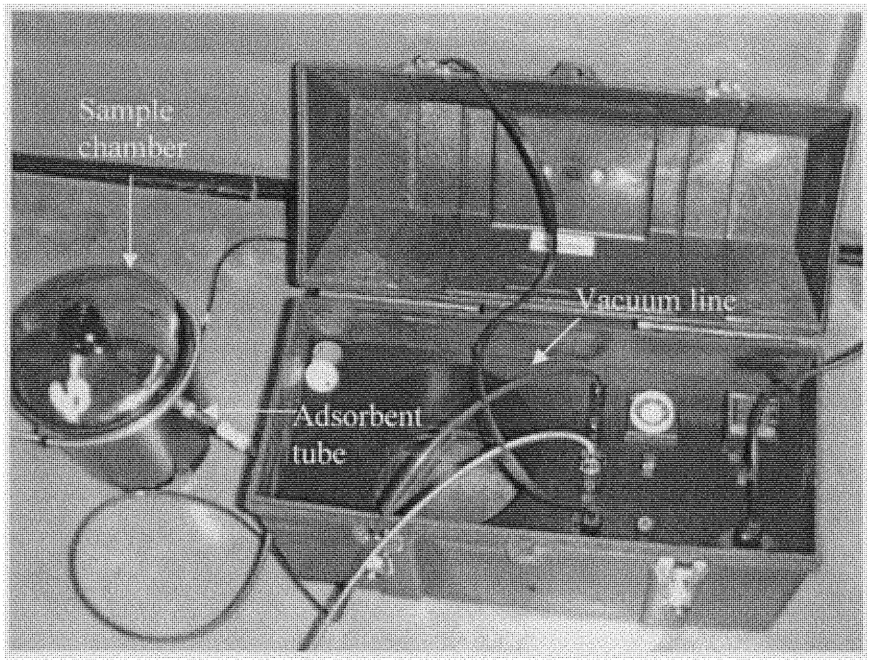


Figure 3: The Portable Arson Sampler

The Portable Arson Sampler (PAS) method of sampling has it advantages and disadvantages. It is non-destructive of the debris and the remaining adsorbent can be saved for re-testing, if necessary. It can also be used to sample large areas, such as concrete, that would be difficult to break up and transport back to the laboratory[23]. It is not a direct method of analysis; the sample must be extracted from the adsorbent. Inefficient extraction will lead to loss of sample. Also, solvents have similar properties to accelerants, so they may obscure data. Care must be taken in the development of the gas chromatography method to decrease the possible interference of the solvent.

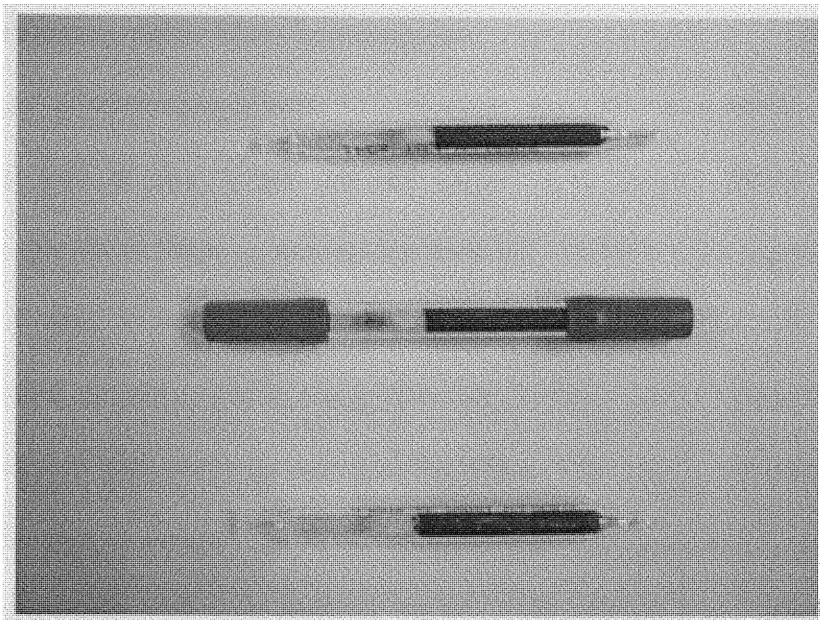


Figure 4: Adsorption tubes for the Portable Arson Sampler Top: sealed polymer tube, center: capped polymer tube, bottom: charcoal tube

One of the problems with many sampling methods is inefficient collection of the sample. Using activated charcoal strips and SPME, the sampling time effects the collection of the sample. For short collection times, the more volatile components are predominately collected. As the sampling time is increased, it has been shown that the less volatile components displace the more volatile ones[25]. When an accelerant is weathered (has been allowed to evaporate), the more volatile components evaporate more than the less volatile ones[26]. Dynamic headspace sampling has been said to cover the entire boiling point range of ignitable liquid residues[27]. Because the process is dynamic, the sampling tube is not competing with the air in the chamber for adsorption of the sample[23,24]. Compounds that are trapped in the airspace of the sample tube may reach equilibrium of exchange during storage and be able to be extracted.

1.7 Gas Chromatography/ Mass Spectrometry

A gas chromatograph/mass spectrometer (GCMS) is a useful and widely implemented tool in fire debris analysis (see Figure 5). A complex mixture of compounds, like those found in extractions from fire debris, can be separated based on the effect of their individual characteristics on their retention time in the column. Compounds that are more volatile and have a very different polarity than the solid phase of the column will elute more quickly than the others. The type of column used must be specific to the type of compounds to be separated. Since ignitable liquids contain mostly nonpolar compounds, and their analysis usually studies these types of components, a relatively nonpolar column is used. The temperature program, gas flow rate, and injection parameters can be adjusted to optimize separation. The resulting chromatogram shows the separated peaks in a pattern that can be compared to standards for the identification of possible ignitable liquids.

Mass spectrometry separates compounds based on their mass to charge ratio. The gas phase ions created are fragmented and show a characteristic pattern for the parent molecule. The fragmentation pattern can be electronically compared to standard libraries for identification of specific compounds. Fire debris samples can be very complex with many peaks eluting in the same range of retention times. The use of mass spectrometry in conjunction with gas chromatography results in more efficient analysis and better characterization of the components of a sample.

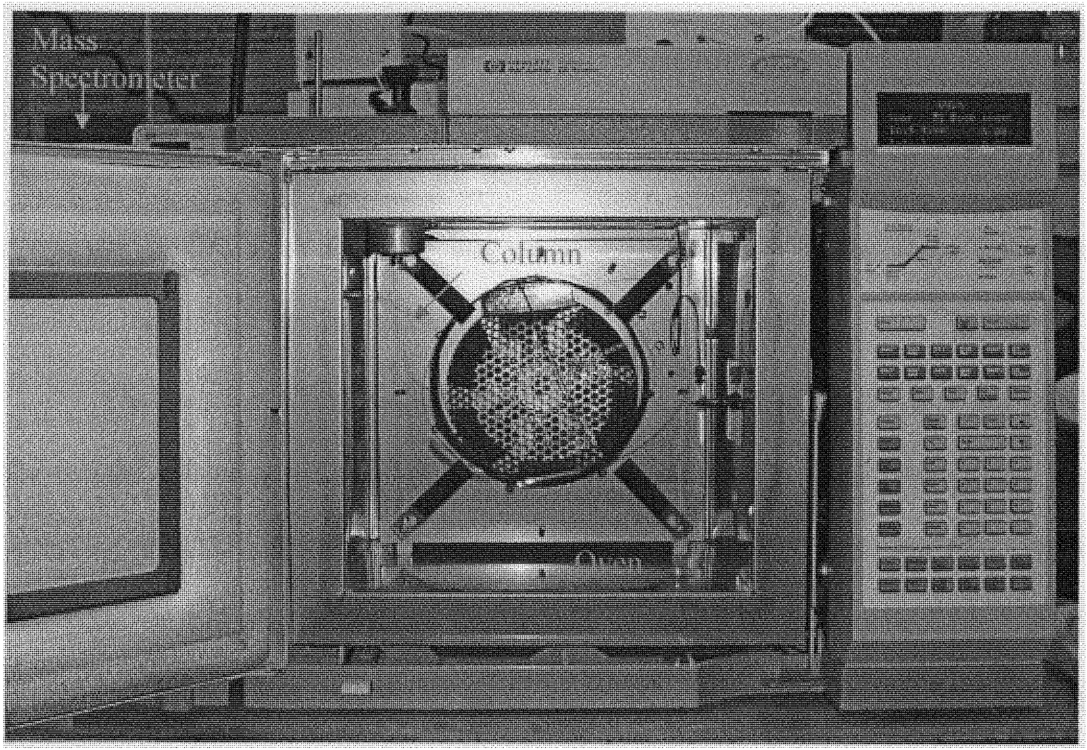


Figure 5: Mass Spectrometer/Gas Chromatograph showing interior of oven (Photo by Allison Curran, used with permission)

1.8 Project Objectives

Overall, the three commercially available devices in this study have been evaluated for their performance for infield sampling and collection of suspected arson debris. The TLV Sniffer® was studied for its response to accelerants alone, burned, and not burned. Different types of burned matrix materials were also examined for the levels they exhibit with the device. Comparison of these results to accelerants was used to determine if the Sniffer would falsely alert to burned materials alone. Reproducibility of the readings was also examined to study the reliability of the Sniffer. To compare the device to another commonly used method for infield accelerant detection, it was subjected to a proficiency test designed for accelerant detecting canines. If the occurrence of false positives is small or able to be cautioned to investigators, and the device is able to pass the proficiency test, the TLV Sniffer® could be an appropriate field portable tool to be used as a presumptive test for accelerant containing fire debris. The tpi®Pocket Combustible Gas Leak Detector was examined with some of the same parameters to evaluate its possible use in field detection of accelerants as well.

The Portable Arson Sampler was also evaluated for its practicality and efficiency for infield collection of suspected accelerant containing samples. Parameters such as sampling time, temperature, adsorbent type, and desorbtion solvent were first explored to determine an efficient procedure that would be useful in field collection. Samples of accelerants burned and not burned alone were collected to determine the sensitivity and efficiency of collection of the entire range of accelerants from light to heavy. Samples of burned materials were collected to determine the selectivity of the technique in collecting background, pyrolysis, and combustion products from the material alone. Then, the PAS was used to collect samples from burned materials that contained accelerants to further study the efficiency, sensitivity and selectivity of the device. The storage of samples in the adsorbent tubes was compared to storage in cans over time to determine if this type of storage, while being more spatially efficient, would better preserve the samples. In addition to field portability and space saving, another possible advantage of the PAS is the collection from large surfaces in the field. The PAS was used to collect directly from concrete and asphalt surfaces to study this advantage.

1.9 Novelty of Project

Detecting the location of possible accelerants is accomplished in a few different ways. Experienced fire investigators can visually determine suspicious areas by characteristic burn patterns possibly caused by accelerants. Flammable liquids can sometimes be located by human olfaction if enough is present for detection. Canines can detect these materials at lower levels than humans, but they can be limited in their operation time and must have extensive training and experienced handlers. The TLV Sniffer® and the tpi®Pocket Combustible Gas Leak Detector do not require experienced handlers and are limited in operating time only by their battery life. They may also be used in hazardous scenes where canines would not be able to go. In this study, they are evaluated for the first time for their ability to detect low levels of compounds from common accelerants and their ability to distinguish between background and pyrolysis products from burned debris and accelerants themselves. If they prove to be efficient, they could replace or supplement the traditional methods of accelerant detection in the field.

In most research conducted in this field, samples of materials are spiked with neat accelerant after the matrix has been burned. This study examines the performance of the devices using neat accelerants with no matrix not burned and burned, and accelerants burned with the matrix material. In actual fires, some or all of the accelerant would itself be burned along with the matrix. Some of the accelerant may remain unburned after a fire because it has been absorbed into matrix materials. The use of the mixed matrix containing absorbent materials like carpet padding and cotton was used to simulate this effect in actual fire scenes. By using not burned and burned accelerants, instead of the spike after the burn method used in other studies, actual fire conditions are better replicated.

Traditionally, suspected arson fire debris samples are collected, usually in metal paint cans, and taken to the laboratory for analysis. Some materials, like concrete slabs, prove difficult in removing a sample from the scene. The Portable Arson Sampler has been evaluated in this study for its ability to sample directly from these types of surfaces in the field.

Extended storage time in cans can result in loss of valuable evidence due to the evaporation of volatile accelerants. In this study, a fast simple field collection method is studied to determine if it would be more effective than the traditional method. If the volatile compounds are collected and stored in the adsorbent filled tubes, they may have a longer shelf-life than the debris stored in cans. If immediate laboratory analysis is not available, this method may be preferable to storage in cans.

2. EXPERIMENTAL

2.1 Materials and Instruments

Portable Arson Sampler (Portable Arson Samplers, Tooele, UT), TLV Sniffer® (Bacharach, Inc., Pittsburgh, PA), tpi®Pocket Combustible Gas Leak Detector (Professional Equipment, Inc. Hauppauge, NY), Hewlett Packard 6890 Gas Chromatograph and HP 5973 Mass Selective detector (Wilmington, DE), Isotemp® Oven Model 655G (Fisher Scientific, Pittsburgh, PA), Benzomatic® Trigger Start Torch (Newll Rubbermaid, Medina, NY), ORBO™ tube cutter (Supelco, Bellefonte, PA), Beige plush carpet 2x5 rug, (Home Depot, Mall of Americas, Miami, FL), bulk blue carpet padding, (Home Depot, Mall of Americas, Miami, FL), Millwork quality shims (Nelson Wood Shims, Cohasset, MN), 1x2 pine board, (Home Depot, Mall of Americas, Miami, FL), Plastic milk carton, (Publix, SW107th Ave and SW 16th St, Miami, FL), cotton balls, (Publix, SW107th Ave and SW 16th St, Miami, FL), Kimwipes® (Kimberly-Clark Professional, Roswell, GA), White Styrofoam peanuts (unknown manufacturer), Newspaper (*Tiempos del Mundo*, Miami, FL), Diesel Fuel (Texaco, SW 112the Ave and SW 40th St, Miami, FL), Charcoal Lighter, Odorless Fluid (Publix, SW107th Ave and SW 16th St, Miami, FL), Zippo® Premium Lighter Fluid, (Zippo Manufacturing Company, Bradford, PA), Diethyl Ether, GC grade (Aldrich, Milwauke, WI), Dicholormethane, reagent grade, (Phramco, Brookfield, CT), DFLEX® Diffusive Flammable Liquid Extraction [Activated Charcoal Strips], (DFLEX®, Cromwell, CT) ORBO™ 90 Adsorbent Tubes, (Supelco, Bellefonte, PA), ORBO™ 32 Standard Charcoal Tubes, (Supelco, Bellefonte, PA), Clear ABC vial with PTFE/Silicone Lined cap, 2mL, 4mL, 10mL, (Supelco, Bellefonte, PA), 1 quart paint cans with lids (All American

Container Corporation, Miami, FL), Lunch bags, standard size (Target Corporation, Minneapolis, MN), Disposable Pasteur Pipets, 9” soda lime glass, (Fisher Scientific, Pittsburgh, PA)

2.2 Sample Preparation

For samples of not burned accelerants, the flammable liquid was spiked onto three folded Kimwipes® tissues. For analysis with the TLV Sniffer®, the tissues were placed in a can, the lid was placed on, and the can was allowed to sit at room temperature for 24 hours to equilibrate. Blank samples containing only three clean tissues were also prepared. For sampling with the Portable Arson Sampler (PAS), the tissues were placed in the chamber in the removed bottom portion of a paper lunch bag. Matrix samples were prepared by weighing the matrix materials and placing them in a can (see Table 2 and Table 3). Care was taken that the cans were no more than half full. Carpet, padding, and plastic cartons were cut in approximately one inch square pieces. The newspaper was shredded into approximately one inch square pieces. The wood shims were cut in two or three pieces to allow them to fit in the cans. Flammable liquids were spiked onto the matrix materials before the burn, except for the simulated canine proficiency test where they were spiked after the burn to follow the procedure of the test.

Table 2: Matrix materials and amounts used in examination of burned and not burned materials

Matrix Material	Amount
Laboratory Tissues Kimwipes® (Kimberly-Clark Professional, Roswell, GA)	5 tissues for blank 3 for spike sample
Cotton Balls	5g
Styrofoam peanuts	20 (approx 1.4g)
Plastic Milk Carton High Density Polyethylene (HDPE)	15g
Wood shims Home Depot, Miami, FL	3 shims cut in half approx. 40g
Carpet and Padding Home Depot, Miami, FL	10g each
Newspaper *Tiempos del Mundo*, Miami, FL	20g

Table 3: Approximate amounts of material added for mixed matrix samples

Matrix Material	Amount in each can
Styrofoam	0.35-0.40g
plastic	5g
wood	9-10g
carpet and padding	5g each
cotton	2g
newspaper	5g

2.3 Burn Conditions

The prepared samples were burned in the one quart cans. The lid was removed immediately prior to the burn. A lit propane torch was then introduced to the can only long enough for the sample to catch fire on its own. Samples were then allowed to burn until partially charred (see Figure 6).

Figure 6: Mixed matrix sample burning in a paint can

The blank and spiked tissue samples were allowed to burn until they turned black and began to curl into a rose-like shape. The lids were replaced when the samples reached this state but were still on fire. The burned samples were allowed to cool before further analysis.

2.4 TLV Sniffer® and tpi®Pocket Combustible Gas Leak Detector Sampling

The TLV Sniffer® was placed outdoors in clean air and turned on at the lowest sensitivity setting for ten minutes to warm up. The instrument was then zeroed at the lowest sensitivity setting, and then the middle and higher sensitivities. The lid was loosened from the can and the Sniffer sample probe was introduced. The probe was not allowed to touch the sample but held approximately one inch from the debris. The lid was left to loosely cover the rest of the can. The probe was held in position until the meter reached its highest reading and began to decrease again. This peak level was recorded and the lid was replaced. Then the Sniffer level was allowed to decrease back to zero before the procedure was repeated two more times. After the third TLV® Sniffer reading was recorded, the tpi®Pocket Combustible Gas Leak Detector was introduced to the can. The sampling end was held first just above the debris but not in contact with the sample, and the level or lack of alert was recorded. The device was then removed from the can until the alarm stopped, and then reintroduced for the next reading. Three readings were taken this way. The device was then held in contact with the debris and three readings were taken. Finally, the tpi®Pocket was held approximately one and one half inches away from the debris and three readings were taken. The lid was then replaced and the sample was saved for collection with the Portable Arson Sampler.

2.5 Simulated Canine Proficiency Test with TLV Sniffer®

Materials were prepared as described in section 2.2 for the three part proficiency test designed by the Canine Accelerant Detection Association[28] (CADA, Note: multiple accelerants were used in this study, the CADA test uses only one). The CADA guidelines require 5μL 50% weathered gasoline (pure gasoline that has been allowed to evaporate to

50% of its original volume). In these tests, three accelerants (Zippo®, charcoal lighter and diesel fuel) were used and were not weathered. Burns were conducted in the same manner as before by burning approximately one half pint of debris until partially charred as required in the CADA testing.

Test 1: Basic Scent discrimination

Four aluminum cans were filled halfway with one of the following materials: wood, HDPE, Styrofoam, and carpet and padding (see Table 2) and contents were burned. A hole large enough for the sample probe to be interested was punched in the lid. Then, to facilitate a blind test, one student spiked 5µL of diesel fuel onto a cotton ball in a fifth can. The cans were labeled A through E. A different student, the "handler," sampled the can with the TLV Sniffer® and recorded the levels. This student noted which can was believed to contain the accelerant and was only then told whether this determination was correct.

Test 2: Mixed Matrix Scent Discrimination

Seven cans were filled with a mixture of the four materials used in Test 1 (see Table 4, CADA test uses five samples, but seven were prepared in this test to allow for the use of three accelerants). The materials were burned in the same manner and hole punched lids were placed on. One student labeled these cans F through L and spiked 5µL of Zippo®, charcoal lighter or diesel fuel into three of the cans without the knowledge of the handler. The handler sampled the cans with the TLV Sniffer® and noted which cans were believed to contain accelerant and was then given the results by the first student.

Table 4: Materials and amounts used in Test 2

Matrix Material	Amount in each can
Styrofoam	5 peanuts, 0.35g
HDPE	5g
Wood	12g
Carpet and padding	5g each

Test 3: Sample Location

Ten two foot long 1"x4" pine boards were divided into sections and labeled 1 through 30 with a pencil. The first student spiked 5μL of one of the accelerants at various locations on these boards. The handler then held the sample probe to the center of each of the 30 sections and recorded to level obtained. These results were then compared to the locations of the actual spiked accelerant.

2.6 Portable Arson Sampler Dynamic Headspace Sampling

The Portable Arson Sampler is first allowed to warm to its preset temperature (50°C is the standard set point). The debris in the paper bag or the open can and lid is placed in the chamber and the lid is placed on for 10 minutes. The ends of the adsorbent tube are broken off and the glass wool end is placed in the fitting on the side of the container. The vacuum line is attached to the other end of the tube, and the pump is turned on for 10 minutes. Immediately after the vacuum turns off the tube is removed, capped, and placed under refrigeration for at least 20 minutes. The tube is then broken open at both ends and the tube puller is used to push the glass wool end until the adsorbent is expelled from the tube. The tubes used in this study were packed with either activated coconut charcoal (ORBO 32) or beads of Carboxen™ polymer molecular sieves (ORBO 90). One milliliter of diethyl ether or dichloromethane is added to the sorbent and the samples are placed under refrigeration overnight. The solvent is then drawn off from the sorbent and transferred to a new auto sampler vial using a disposable pipette. For direct spike samples, the accelerant is added directly to the sorbent in the tube. The same desorbtion procedure is then followed. The samples can then be analyzed by GCMS. For sampling from concrete and asphalt, a 4 inch by 3 inch piece of asphalt or a two inch by three inch piece of concrete were placed on the floor as matrix. The accelerant was spiked onto the matrix and allowed to sit in open air for three minutes. The heated PAS chamber was then inverted and placed over the sample for ten minutes. The pump was then turned on for ten minutes. The samples were desorbed by the same method as the other samples.

2.7 Passive Headspace Extraction with Activated Charcoal Strips

The activated charcoal strips (ACS) used were enclosed in a metal package with netting holding the actual strip. The mixed matrix debris (see Table 3) was burned with no accelerant, 5μL of 1:1 diesel and Zippo, or 50μL diesel and Zippo®. The package was placed in the can with the debris and the lid was replaced. The cans were placed in an oven at 60°C for 16 hours. Then, the package was removed from the can and the netting is cut away from the strip. The strip was then removed with forceps and placed in a vial. One milliliter of solvent was added to the strip and allowed to sit for 20 minutes. The solvent was then transferred to a new vial with a disposable pipette. The samples were then analyzed by GCMS.

2.8 Gas Chromatography Conditions

External standards were prepared by diluting pure accelerants in solvent. For example, a 10,000ppm solution was prepared by adding a calculated amount of the pure liquid and mixing it with 100 times that volume of solvent minus the volume of the pure liquid. A

500ppm solution was then prepared by removing a calculated amount of the 10000ppm solution and diluting it 20 fold. The solutions were then examined with gas chromatography/mass spectrometry. A Hewlett Packard 6890 Gas Chromatograph and HP 5973 Mass Selective detector were used for analysis of the samples. The instrument has a DB-5MS, 29.7m x 250μm x 0.25μm column. The helium gas flow rate is constant at 1mL/min. The front inlet temperature is 250°C. One microliter of sample is injected splitless with a Hewlett Packard 7683 series injector for autosampling. The temperature program is a two minute hold in the injection port, an initial eight minute hold at 40°C, a 15°C/min ramp to 300°C and a final three minute hold.

2.9 Data Analysis

Chromatograms and mass spectra were viewed with the Hewlett Packard Chemstation software. For spectra peak identification, the NIST 98 (National Institute of Standards and Technology) library was used. Extracted ion profiles were constructed by selecting common fragments from different types of compounds (see Table 5). Only the chromatographic peaks that contain these ions are displayed in each profile.

Table 5: Ions selected for extracted ion profiles

Compound type	Ions chosen
alkane	57, 71, 85, 99
aromatic	91, 105, 119
cycloalkane	55, 69, 83

3. RESULTS

3.1 Simulated Canine Proficiency Test using the TLV Sniffer®

3.1.1 Test 1: Basic Scent Discrimination

An accelerant detecting canine must be able to detect the difference between burned materials and actual accelerants. The CADA proficiency test is designed to determine if an accelerant detecting canine and its handler can identify small amount of accelerant even in the presence of a complex background of matrix materials. With the aim of using a device such as the TLV Sniffer® for the same purpose, it must be determined the device can make this distinction as well. The basic scent discrimination test uses four cans filled with burned debris, and one can containing only a cotton ball spiked with 5μL of diesel fuel (not burned). Diesel fuel was chosen for this test because its low volatility would be similar to the weathered gasoline used in the original test. The test was performed blind so that the handler (the student operating the TLV Sniffer®) cannot be influenced by prior knowledge of the contents of the samples. The handler recorded TLV Sniffer® levels for the five cans in this test (see Table 10). Only one, can D, showed any reading. For this reason, the handler alerted that only can D contained accelerant. When the test preparer revealed the results, it was found that the handler's alert was correct, can D contained 5μL of diesel fuel. A level of 6 is low; however, low readings are expected for diesel fuel due to its low volatility. Despite the other samples containing burned materials that may have pyrolysis and combustion products that could have led to a false positive, the TLV Sniffer® did not alert. The basic scent discrimination test showed that the TLV Sniffer® could successfully discriminate between an accelerant and debris alone. It also demonstrated that 5µL of diesel fuel is above the limit of detection for the TLV Sniffer® for this type of situation.

3.1.2 Test 2: Mixed Matrix Scent Discrimination

In actual fire scenes, debris can consist of many different types of materials together, all of which may contribute background levels of volatile compounds and lead to false alerts with canines as well as devices such as the TLV Sniffer®. Test 2 was designed to examine the ability of the handler and the canine or device to alert only to debris that also contained an accelerant. All seven samples contained the same amount of burned wood, plastic, Styrofoam, carpet and padding (see Table 4). Each accelerant was spiked into one of the cans. The handler found readings for only four of the cans. The three highest of these readings were the cans that were determined to contain accelerant (see Table 11). The test preparer revealed that these three alerts were correct. The highest of all the readings, can I, had been spiked with the Zippo® fluid, the most volatile of the accelerants. The second highest, can L, contained charcoal lighter fluid, a medium volatility accelerant, and the lowest reading was found with the can containing diesel fuel. As higher readings are expected for higher volatility compounds, the TLV Sniffer® was able to demonstrate the differences between the three accelerants in this case. The results of this test have shown the ability of the TLV Sniffer® to alert to accelerants even in the presence of a complex matrix and to not falsely alert to matrix alone.

3.1.3 Test 3: Sample Location

Each of the three accelerants was spiked at three various positions among the thirty possible locations on the boards. The sample probe was introduced to every location but no level higher than 1 was reached and most locations showed no reading at all (see Table 12). In this situation, the TLV Sniffer® was not able to alert to any of the accelerants. The boards were not in an enclosed space like the cans in Test 1 and 2 (see Figure 7). The lids on the cans likely trapped volatile compounds, allowing detectable levels to be found. As seen in part 1, accelerants being left open to the environment greatly decreases the TLV Sniffer® levels detected. The accelerants spiked on the boards were able to evaporate more completely which may have lead to the inability of the handler and the device to alert in this test, despite its success in the previous two tests.

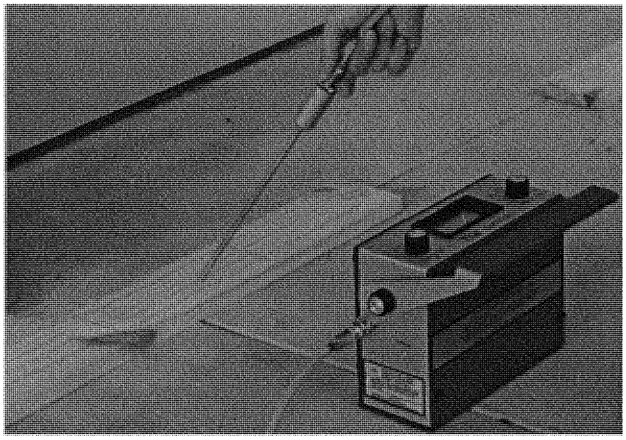


Figure 7: TLV Sniffer® performing CADA Test 3: Sample Location

In this situation, 5μL was below the detection limit of the TLV Sniffer®. To better determine the limit of detection, increasing amounts of diesel fuel were spiked onto another board and tested. A level of 1 was initially detected at 20μL and increased to level 4 at 50μL (see Table 13). Using these amounts, the TLV Sniffer® may have been able to successfully alert to the location of the spiked accelerants.

3.2 Standard Accelerant Chromatograms

Standard solutions of the accelerants were prepared and analyzed using gas chromatography/mass spectrometry. The Zippo® cigarette lighter fluid was found to be a light petroleum distillate with the major peaks occurring between five and eleven minutes on the chromatograms. Major peaks include octane, ethylcyclohexane, and nonane (See Figure 8). The charcoal lighter fluid was in the medium range with the peaks occurring between nine and sixteen minutes. Major peaks include nonane, decane, undecane, and dodecane (See Figure 9). The pattern of gasoline was seen between nine and seventeen minutes. Major peaks include ethylbenzene, m,p, and o-xylenes, trimethylbenzenes, and napthanlene (See Figure 10). Diesel fuel was a heavier petroleum distillate with a Gaussian shaped pattern occurring between thirteen and twenty two minutes. Major peaks include alkanes from undecane to heneicosane (See Figure 11). For certain analyses a mixture of the cigarette lighter fluid and diesel fuel was used. Because their patterns had little overlap and covered the range of light to heavy ignitable liquids, this mixture was used to examine the efficiency of a particular application over the entire range of accelerants (see Figure 12).

3.3 Polymer vs. Charcoal Adsorbent Tubes

Blanks of the polymer and charcoal tubes were desorbed with solvent and analyzed by GCMS (see Figures 13 and 14). An unidentified peak was found in most of the polymer tube samples (see Figure 15). This peak, occurring at 19.2 minutes, could not be confidently matched to any spectra in the library. The peak did not occur in any solvent blanks, standards, or charcoal tube samples. It is believed to come from the polymer tube adsorbent. The diesel fuel and Zippo® mixture was spiked directly onto the polymer and charcoal tubes to compare the efficiency between them. The abundance was much higher and the range was longer on the polymer tubes (see Figures 16 and 17). However, directly spiking the accelerant may not be the best way to compare the tubes. The accelerant may have been adhered to the glass or trapped in the spaces between the pieces of adsorbent and not actually adsorbed. Therefore, the accelerants were then spiked onto tissues and sampled with the PAS with both tubes to better examine the efficiency differences between the two types of tubes.

The efficiency of the polymer tubes was compared to the charcoal packed tubes for the Portable Arson Sampler. Both tubes showed the same pattern for sampling of 500μL of 10:1 ratio solution of diesel fuel and cigarette lighter fluid (see Figures 18 and 19). The pattern of the cigarette lighter fluid is seen but little of the diesel fuel is seen. However, the diesel is seen in other similar samples. (See Figures 24 to 27). Roughly the same abundance is seen using the charcoal tubes and the polymer tubes. The polymer tube showed slightly more of the range of diesel fuel than the charcoal did. Therefore, little difference in efficiency was found between the two types of tubes. For the remaining experiments, the polymer tubes were used because they collected the slightly longer range and were easier to handle. With some agitation, or even with normal storage, some of the charcoal would break down during the solvent desorbtion step, forming a suspension. Centrifugation might have allowed the clean solvent to be removed for injection in the GC. However, the polymer adsorbent was in the form of small beads and this problem did not occur, so these tubes were chosen for ease of use.

3.4 Diethyl Ether vs. Dichloromethane Solvent

Dichloromethane and diethyl ether were chosen as possible solvents for the desorbtion of the adsorbent tubes. Both solvents are relatively nonpolar, so they would lend themselves well for extraction of the nonpolar accelerants and injection into a GC system. They also have low boiling points that will elute in the solvent delay in the GC temperature program and not interfere with analysis. Carbon disulfide is a commonly used solvent for fire debris analysis[6] but it is toxic and has a strong odor, so it was not used in these studies. Samples with 100μL of charcoal lighter fluid spiked on tissues were collected with Portable Arson Sampler using the standard procedure. The tubes extracted with diethyl ether showed roughly the same pattern as those extracted with dichloromethane, but the abundance was higher for the ether (see Figures 20 and 21). Therefore, either solvent was determined to be efficient for these studies. Diethyl ether was chosen because the abundance in these samples was higher. Care must be taken that samples are analyzed quickly or they will evaporate due to the low boiling point (35-36°C) of diethyl ether.

3.5 Sampling Time in the Portable Arson Sampler

Samples of 500μL of 10:1 diesel and cigarette lighter fluid spiked on tissues were collected with the PAS pump turned on for one minute, five minutes, 10 minutes, 30 minutes and 60 minutes. No pattern of the accelerants is seen in the one minute and five minute samples (See Figures 22 and 23). At ten minutes (the standard time used in other experiments), the pattern is present and identifiable visually as cigarette lighter and diesel fuel (See Figures 24 and 25). However, the higher end of the pattern for diesel fuel is not seen. The pattern in the PAS samples ends around 18 minutes, instead of 22 minutes in the standard (see Figure 12). The dynamic headspace sampling is not, therefore, efficiently collecting the entire range of the diesel fuel, but it does collect enough to see the Gaussian pattern. At 30 minutes, the pattern is still clear and the abundance has increased (See Figure 26). The abundance further increases for the 60 minute sample (See 27 see Table 6). Thirty minutes would be a more optimal time for sampling than ten minutes. The 10 minute samples do show the desired pattern and are identifiable as accelerants, so this would be sufficient to collect a sample, particularly in the interest of using the Portable Arson Sampler as a fast method for in-field sample collection. The abundances obtained at 60 minutes were higher than would be necessary for analysis and no further range of the diesel fuel was collected despite the longer sampling time. Also, extracting each sample for 60 minutes would be an inefficient use of time in the field. Therefore, 10 minutes would be effective for sample collection, but samples may be collected for thirty minutes if time allows or there is some reason to believe low levels of accelerants are present. For the remaining samples in this study, 10 minutes was used as specified in the manual[23].

Table 6: Portable Arson Sampler sampling time abundance values

Sampling Time	Abundance
1 minute	0
5 minutes	0
10 minutes	500000
30 minutes	1400000
60 minutes	3500000

3.6 Sampling Temperature in the Portable Arson Sampler

Samples of 500µL 10:1 diesel and Zippo® spiked on tissues were extracted with the Portable Arson Sampler at 20°C, 40°C, 50°C, and 70°C. Extractions were also attempted at 80°C and 90°C, but steam emerged when the lid of the sample chamber was removed. These samples were not analyzed by GCMS due to the possibility of water being present. The sample extracted at 20°C shows some peaks in the Zippo® range (see Figure 28). The sample extracted at 40°C shows the full Zippo® and diesel pattern expected with PAS sampling (see Figure 29). Sampling at 50°C, again shows the full expected pattern at a higher abundance (see Figure 30). Extraction at 70°C showed the same pattern at slightly higher abundance (see Figure 31). The pattern at the later range of diesel fuel is more distinct at 70°C than at 50°C, but no significant increase in the range collected is seen, with both patterns ending around 18 minutes. (Note: The 50°C sample was extracted and analyzed on a different day than the other temperature samples and a different 10:1 diesel Zippo® solution was used). A sampling temperature of 50°C was chosen for all other experiments because this is the temperature suggested in the manual[23], and it showed a sufficiently high abundance and pattern for further analysis. Any increase in temperature could lead to the collection of water and may thermally degrade some of the background or accelerant compounds. Therefore, for collection efficiency, sample component preservation, and column integrity concerns, 50°C was chosen as the most efficient sampling temperature.

3.7 Comparison of Burned and Unburned Accelerants

3.7.1 TLV Sniffer® and tpi®Pocket Levels

A range of accelerant amounts from 10μL to 1000μL were examined burned, and not burned (all spiked on tissues) to determine the effect of pyrolysis and combustion products on the TLV Sniffer® readings. Zippo® fluid, charcoal lighter fluid, gasoline and diesel fuel were chosen as the accelerants because they cover the entire volatility range of common accelerants as classified by ASTM[5,6]. Zippo®, the most volatile is classified as a light petroleum distillate or product, gasoline is a reformulated petroleum product in the light to medium range, charcoal lighter fluid is a medium petroleum distillate or product, and diesel fuel, the least volatile, is a heavy petroleum distillate. By using these accelerants, the efficiency of the range of volatility collected by the PAS can be studied.

Triplicate samples were prepared for each of each amount of accelerant. It was discovered that reproducibility between these readings of the same type of samples was poor. One possible factor was the difficulty of controlling fire conditions. The samples were all burned to visually approximately the same degree of charring. The lids were placed on before the fire burned out or smoldering ceased. A certain amount of smoke would have been trapped in each can, but some cans could have contained more smoke than others. Other samples were allowed to burn until all fire and smoke ceased before the lids were placed on, but in these cases some samples did not completely burn and the same lack of reproducibility was observed. In the mixed matrix samples, some differences in results from the same samples could occur due to the absorbency of the materials. If more of the accelerant was spiked on the padding, it might have been absorbed and better retained after the fire, resulting in higher recorded levels. If the accelerants were spiked more on the plastic, they would have been able to burn more completely or evaporate due to exposure to the heat of the fire. Samples with spiked accelerant that were not burned were also tested. Differences in burn conditions were not a factor in these experiments, but reproducibility was still poor. Ten samples of 100μL 10:1 diesel and Zippo® spiked on tissues, not burned, were tested with the Sniffer. Levels were recorded three times in each sample and listed as trial 1, 2 and 3 (see Table 14). The mean level of the first trial was 625 with a standard deviation of 164.3. Based on this data, the first measurement of a tissue spiked with the diesel Zippo® mixture could occur anywhere from to 461 to 789 (see Figure 32). Therefore, the reproducibility of the Sniffer measurements was found to be poor. This experiment was performed without matrix that would further complicate the data and possibly lead to more poor reproducibility. Low reproducibility may be a problem with the TLV Sniffer®.

In general, charcoal lighter and Zippo® fluid gave higher readings not burned than burned. Zippo® fluid had the largest difference between burned and not burned samples (see Figures 33 and 37 and Tables 15 and 16). Gasoline had similarly high levels and a large difference between burned and unburned samples (see Figure 35 and Tables 19 and 20). Charcoal had less of a difference, but not burned still resulted in higher levels (see Figures 34 and 37 and Tables 17 and 18). However, diesel generally gave higher readings burned than not burned (see Figures 36 and 37 and Tables 21 and 22). A possible explanation for these findings is the volatility differences of the three accelerants. When Zippo® fuel is burned, the large amount of high volatility compounds may have burned and escaped more than the other two accelerants. Also, diesel fuel may produce more high volatility pyrolysis and combustion products as the long chain alkanes break down, increasing the TLV Sniffer® levels.

The levels of the not burned accelerants were also compared to each other (see Figure 37). Zippo® fluid showed higher levels for all spike amounts than the other two substances. Diesel showed the lowest levels. Such evidence is expected due to Zippo® fluid being the most volatile of all of the accelerants used.

The tpi®Pocket Combustible Gas Leak detector did alert to all four accelerants examined in this study. It alerted at lower levels for the volatile, not burned, charcoal lighter fluid. It did not alert consistently to the other not burned accelerants until 500μL was used (see Figure 38). It also alerted to cotton, newspaper and carpet burned without accelerant in some cases, which would result in false positive alerts. Due to its low sensitivity and selectivity, the device would not be a reliable tool in the location of accelerants in fire debris.

3.7.2 Chromatographic Analysis

Samples of accelerants spiked onto tissues and not burned were extracted with the Portable Arson Sampler. Using 5μL of the diesel Zippo® mixture, the characteristic pattern of diesel and Zippo® can be seen (see Figure 39). The pattern is more distinct in the 10μL and 50μL spike samples (see Figures 40 and 41). Therefore, in this case, the PAS is able to collect as low as 5μL not burned accelerant. No samples with smaller amounts than 5μL were prepared so the actual collection limit cannot be determined.

3.8 Burned Matrix Materials

3.8.1 TLV Sniffer® Levels

Burned matrix with no accelerant was studied to evaluate whether matrix alone could give readings as high as the accelerant samples (see Figure 42 and Table 23). Cotton, wood, newspaper, and carpet and padding all exhibited similar levels to accelerant spiked samples. These materials could lead to false positive alerts for accelerants which would need to be considered by investigators using such a device.

One milliliter of each accelerant was spiked on the mixed matrix samples and then burned. Over 10,000 was recorded for Zippo®, 8500 for charcoal lighter, 7000 for diesel fuel, and 4200 for gasoline (see Table 24). Gasoline recorded higher levels without matrix than diesel fuel. The low levels recorded for gasoline in these experiments could be due to absorption by the matrix, lack of reproducibility from the Sniffer or breakdown of the diesel into smaller, more volatile components. The CADA proficiency test was used to further study the ability of the TLV Sniffer® to discriminate between matrix alone and samples containing accelerants (see 3.1 Simulated Canine Proficiency Test).

3.8.2 Chromatographic Analysis

Each of the matrix materials was burned alone and sampled with the Portable Arson Sampler to determine if background, pyrolysis and combustion products from the materials could be collected by this method. Burned cotton (See Figure 43), plastic milk carton (see Figure 44), Styrofoam (See Figure 45), carpet and padding (See Figure 46), newspaper (See Figure 47) and wood (See Figure 48) all showed little to no peaks except for the unidentified peak attributed to the adsorbent material (see 3.3 Polymer vs. Charcoal Adsorbent tubes). The burned wood did show some small peaks in the range of

12 to 16 minutes but none were identified in the library. The inability of the PAS to collect these types of compounds would be an advantage to this method. Any accelerant profiles collected would not be affected by interferences from the background and lead to a lower occurrence of false positives. However, the ability of the method to collect accelerants effectively, and at low levels, must be weighed against the benefits of not collecting background, pyrolysis and combustion products before the method can be deemed useful.

Samples of accelerant burned on tissues were also examined. Zippo® and gasoline showed no peaks even with 1mL of accelerant spiked (see Figure 49 and 51). This may be because of the high volatility of these liquids. Charcoal lighter and diesel did show part of their characteristic patterns when burned (see Figures 50 and 52). These accelerants were also spiked onto the mixed matrix and burned. In this case, all accelerants showed their major peaks (see Figures 53 to 56). The gasoline and Zippo® were collected in this situation because some of the matrix materials were able to absorb the liquid (such as cotton and padding). This preserved more of the volatile compounds until after the fire, when sampling occurred. The tissues had small volume and were not very absorbent, resulting in loss of these compounds.

3.9 Sampling of Concrete and Asphalt

Large matrix materials such as flooring, concrete and asphalt may be difficult to sample. They could be sampled by solvent extraction (washing of the area with solvent and collecting the eluent for GCMS analysis)[10], but this method has limitations. If it is desired to bring the samples to a laboratory, pieces must be broken up in the field, which can be difficult, time consuming, require heavy equipment, and result in loss of sample.

The Portable Arson Sampler was inverted and placed over the sample to collect volatile compounds spiked onto asphalt and concrete. The diesel and Zippo® patterns were found on the spiked concrete and asphalt samples (see Figures 58 and 60). The materials sampled without accelerant showed no major peaks despite asphalt containing petroleum products (see Figures 57 and 59). More efficient collection occurred with the concrete as it is a more porous surface than asphalt. Both concrete and asphalt were able to be sampled with the chamber inverted, showing that sampling of large materials can be conducted in the field without having to break up and remove the material.

3.10 Passive Headspace Adsorption by Activated Charcoal Strips

Passive headspace extraction with activated charcoal strips (ACS) is another common method for concentration of accelerants from fire debris[12]. It has been shown to collect small amounts of accelerants in amounts as little as 0.1μL[29,30]. ACS strips were used to collect burned samples of the mixed matrix blank or spiked with 5μL and 50μL of diesel and cigarette lighter fluid and burned. The blank sample chromatogram did show peaks from the background, pyrolysis, and combustion products of the burned materials (See Figure 61). Major peaks include hexanal, nonanal, dodecane, tridecane and tetradecane. The pattern is inconsistent with any of the accelerants used, so it would not be confused with a positive for diesel fuel, charcoal lighter fluid, gasoline or cigarette lighter fluid. The samples spiked with 5μL accelerants show some broad peaks in the range of the cigarette lighter fluid of 5 to 11 minutes. Not enough of the pattern is visible to determine whether these peaks are from the accelerant (see Figure 62). The later part of the pattern from the blank burned matrix (16 to 20 minutes) is no longer seen in these samples. This may be due to displacement, because the strip was now adsorbing accelerant, so it was not collecting the matrix peaks as efficiently. The samples spiked with 50μL accelerant again show some broad peaks in the cigarette lighter fluid range and loss of peaks in the later range of matrix peaks (See Figures 63 to 65). The only peaks identified by the mass spectrometer library were styrene and α-pinene, which were not in the accelerants, but probably came from the matrix. No major peaks from background and pyrolysis were seen in the PAS samples of burned matrix alone (see Figures 43 to 48) or mixed matrix samples (see Figures 90 to 92). The Portable Arson Sampler may not be able to collect these products either because the adsorbents cannot pick up these types of compounds, or more likely, they are at levels to low for the PAS to collect.

For comparison of the collection efficiencies of the ACS method and the Portable Arson Sampler, extracted ion chromatograms were constructed. Characteristic ions from alkane, aromatic and cycloalkanes were used to visualize individual profiles for the different types of compounds. This technique is particularly useful when the total chromatogram also contains many peaks from the matrix, as in the ACS samples. The characteristic patterns of the accelerants can be more easily located when compared to the profiles of the standards.

The profiles for the diesel Zippo® standard show high alkanes and cycloalkanes and the Gaussian pattern of alkanes from the diesel fuel is easily seen (see Figures 75 to 77). The profiles from the mixed matrix blank extracted with ACS also show high alkanes, but not in the same pattern as the standard, so these background, pyrolysis, and combustion compounds would not be confused with diesel or Zippo® fluid (see Figures 66 to 68). With 5μL of accelerant burned on mixed matrix, the ACS profiles show some peaks in the Zippo® range that were not seen in the blank sample (see Figures 69 to 71). However, not enough of the pattern is present to say that the accelerants are present. In the 50µL sample, these Zippo® peaks are easily seen (see Figures 72 to 74). For PAS sampled burned matrix with 5µL diesel Zippo®, some peaks are seen in the Zippo® range, but again, not enough of the pattern is present to say the accelerant is present (see Figures 78, 81 to 83). In the 50µL PAS sample, the Zippo® peaks are more easily seen, particularly in the cycloalkane profile (see Figures 79 and 84 to 86). However, due to the presence of the unidentified peak from the polymer adsorbent rescaling the chromatogram, the pattern is not as easily seen as the corresponding ACS sample. The 500µL PAS profiles show the peaks from the Zippo® and diesel at higher abundance (see Figures 80 and 87 to 89).

With the aid of extracted ion profiling, the profiles of the burned spiked accelerants on mixed matrix were identified. Some peaks were visible in the range of Zippo® for 5µL samples in both the ACS and PAS extracted samples. However, it was determined that not enough of the pattern was present for identification. In both the ACS and PAS samples of 50µL spiked diesel and Zippo®, the patterns of the accelerant were clear enough to say accelerant is present. Therefore, the two methods in this study had comparable extraction efficiency.

3.11 Storage Time in Cans

3.11.1 TLV Sniffer® Levels

Table 7: Cans used for storage time in cans study

Can	Contents	Use
Ba	Burned Mixed Matrix	Week 0
Bb	Burned Mixed Matrix	Week 0
Bc	Burned Mixed Matrix	Week 0
0a	100µL Zippo® burned with mixed matrix	Week 0
0b	100µL Zippo® burned with mixed matrix	Week 0
0c	100µL Zippo® burned with mixed matrix	Week 0
1a	100µL Zippo® burned with mixed matrix	Week 1
1b	100µL Zippo® burned with mixed matrix	Week 1
1c	100µL Zippo® burned with mixed matrix	Week 1
2a	100µL Zippo® burned with mixed matrix	Week 2
2b	100µL Zippo® burned with mixed matrix	Week 2
2c	100µL Zippo® burned with mixed matrix	Week 2
3a	100µL Zippo® burned with mixed matrix	Week 3
3b	100µL Zippo® burned with mixed matrix	Week 3
3c	100µL Zippo® burned with mixed matrix	Week 3
4a	100µL Zippo® burned with mixed matrix	Week 4
4b	100µL Zippo® burned with mixed matrix	Week 4
4c	100µL Zippo® burned with mixed matrix	Week 4

Each week of the Storage study, the cans were sampled and TLV Sniffer® levels were recorded (see Table 7). Every can contained the same amount of matrix materials and all of the numbered samples contained the same amount of accelerant (100μL of Zippo® fluid). Despite this, the Sniffer levels of each sample with the same contents recorded in week zero were not the same (see Table 25). The levels ranged from 280 to 8400ppm hexane with an average of 4300. The blank samples (those containing matrix with no accelerant) ranged from 1600 to 2300 with an average of 3400. The average of the blanks was less than that containing the accelerants, but the range contained the average of the non-blank samples. Therefore, in this instance, the TLV Sniffer® would not have been able to discriminate accurately between a blank sample of burned matrix and one containing accelerant. With a larger amount of accelerant, this might have been possible.

Three samples that had been stored and not sampled the initial week, cans 1a, 1b, and 1c (the can had not been opened since the burn), were tested in week one (Note: due to unforeseen circumstances, week one measurements and chromatographic data were taken two weeks after the burn). These samples had Sniffer levels significantly lower than the initial week's measurements (a range from 32 to 54, see Table 26). Storage over time allowed volatile compounds to escape and decreased the measured levels. The samples stored for two and three weeks had levels higher in week two than in week one, and higher in week three than week two (see Tables 27 and 28). Over time, the concentration of the volatile samples may have increased as the accelerant and pyrolysis and combustion products were released into the headspace. In week four, these levels had begun to decrease (110 to 200 in week three and 12 to 120 in week four, see Table 29).

At this point, the evaporation of these compounds is not as significant as the loss of sample through escape from the can. Overall, the decrease in recorded levels is most significant over the first two weeks. The cans were able to maintain detectable levels over four weeks, but had decreased significantly over time.

3.11.2 Chromatographic Analysis

The samples were collected each week of the study with the Portable Arson Sampler. In the initial week, week 0, the blank samples (cans Ba, Bb, and Bc) showed some small peaks near the baseline but no consistent distinguishable pattern for any background, pyrolysis, or combustion products from the matrix burned alone (see Figures 90 to 92). The accelerant spike samples, (cans 0), did show the pattern seen with the cigarette lighter fluid (see Figures 93 to 95). In week 1, the new accelerant spiked samples (cans 1a, 1b and 1c) showed a small pattern that is consistent with the cigarette lighter fluid, but at lower levels than cans 0 in week one, which had the same contents (see Figures 96 to 98). By week two, this pattern in the new cans is no longer visible (see Figures 99 to 101). In week three, the small pattern consistent with the cigarette lighter fluid is again seen in the samples 3 (see Figures 102 to 104). In week four, the new samples again show no major peaks (see Figures 105 to 107). This is consistent with the TLV Sniffer® levels recorded for these weeks. The levels went up in week 3 for new cans and back down again in week 4. Over time, the samples stored in cans allowed the volatile compounds to escape and were no longer detectable by week 4. If a larger amount of accelerant or a less volatile accelerant been used to been the samples, the effect of time may have been easier to determine over a longer period.

3.11.3 Resampling of Cans

Table 8: Samples used in resampling study

Can	Contents	Use
Ba	burned mixed matrix	Initial Week and Resampling
Bb	burned mixed matrix	Initial Week and Resampling
Bc	burned mixed matrix	Initial Week and Resampling
0a	100μL Zippo® burned with mixed matrix	Initial Week and Resampling
0b	100μL Zippo® burned with mixed matrix	Initial Week and Resampling
0c	100μL Zippo® burned with mixed matrix	Initial Week and Resampling

The original blank matrix and spike matrix cans from week zero (cans B and 0) were resampled with the TLV Sniffer® and the Portable Arson Sampler each week to determine the effect on sample loss of repeated resampling (see Table 8). In week one, the resampled cans had significantly lower TLV Sniffer® levels (see Table 25 and 26). The blanks ranged from 0 to 14 and the accelerant samples ranged from 2 to 9. Once again, the Sniffer would not have been able to discriminate between accelerant containing and blank samples. The new stored cans (cans 1) had higher levels than these resampled cans (a range from 32 to 54), indicating that resampling of the cans does decrease the amount of volatile compounds in the sample. The blank samples' chromatograms still showed some small peaks (see Figures 117, 119, 121) and the resampled cans 0 showed a smaller pattern that was consistent with cigarette lighter fluid (see Figures 118, 120, 122). In weeks two and three, the blank samples maintained about the same Sniffer levels as week one (between 0 and 13 for week 2 and 3 to 20 for week three). However, the accelerant samples continued to decrease to nearly undetectable levels (1 to 2 for week two and 0 to 1 for week 3, see Tables 27 and 28 and Figures 123 to 134). At this point, much of the volatile compounds from the accelerants have escaped or been drawn off by the dynamic headspace sampling, but these samples still contained the burned matrix. Despite this, the levels were lower than the blank samples. This could be due to lack of reproducibility of TLV Sniffer® levels as seen in the differences between the levels measured in week one for samples of the same composition. Also, after subsequent re-samples, the lids of the cans became more bent and loose so they did not seal as well as the first week. The samples stored for two and three weeks that had never been sampled showed much higher levels than the re-sampled cans, but the lids were still sealed tightly. By week four, all of the resample cans had reached nearly undetectable levels (see Table 29 and Figures 135 to 140). The not previously sampled cans were able to maintain detectable levels over four weeks time, but the re-sampled cans were approaching, or had reached, undetectable levels. In weeks two through four, the chromatograms no longer showed the small peaks in the blanks or the pattern of Zippo® initially seen in weeks zero and one. Re-sampling of cans would, therefore, not be advisable because the repeated opening and closing damages the lids and allows volatile compounds to escape. However, the purpose of the TLV Sniffer® is for the initial evaluation of debris so repeated re-sampling would not be necessary.

3.12 Storage Time in Tubes

Table 9: Samples used in storage time in tubes study

Tube	Contents	Use
1d	100μL Zippo® burned with mixed matrix	Week 1
1e	100μL Zippo® burned with mixed matrix	Week 1
1f	100μL Zippo® burned with mixed matrix	Week 1
2d	100μL Zippo® burned with mixed matrix	Week 2
2e	100μL Zippo® burned with mixed matrix	Week 2
2f	100μL Zippo® burned with mixed matrix	Week 2
4d	100μL Zippo® burned with mixed matrix	Week 4
4e	100μL Zippo® burned with mixed matrix	Week 4
4f	100μL Zippo® burned with mixed matrix	Week 4

To study the effect of time on samples stored in tubes or vials, samples for weeks 1, 2 and 4 were collected with the PAS during the initial week (week 0) and the tubes were stored until needed (see Table 9). They were desorbed during the week they were used. The tubes from week 1 showed peaks consistent with the Zippo® pattern, but at lower abundance than some of the samples from week 0 (see Figures 108 to 110). In week 2, one of the tubes, 2e, did show a higher pattern of the cigarette lighter fluid than in week 1 (see Figures 111 to 113). The tubes from week four did show the small pattern like the cigarette lighter fluid (see Figures 114 to 116). By week 4 in the storage time in cans study, the pattern from the accelerant was not seen. By this study, the tubes were more effective in preserving the volatile compounds over time than leaving the debris unsampled in cans. However, more accelerant could have been used to burn the initial samples to more confidently study this loss of compounds over time. A less volatile accelerant could also have been used because it would probably have less significant loss over the period of four weeks. In real fire debris samples, though, highly volatile accelerants like Zippo® lighter fluid can be found, and the effect of their storage over time would be an important fact to consider in analysis.

Re-sampling was also conducted for adsorbed samples. The adsorbent from samples Ba, Bb, Bc and 0a, 0b, and 0c in week 0 was desorbed that week for analysis and then stored on a 2mL vial for resampling in subsequent weeks. To resample, another 1mL of solvent was added to the adsorbent in the vials during the week required. The next day, this solvent was drawn off for analysis and the adsorbent was again left in the vials for the process to be repeated the next week. In week one, the resampled adsorbent from samples B showed no major peaks (see Figures 141, 143 and 145). The resampled adsorbent from samples 0 did show some small peaks consistent with the cigarette lighter fluid (see Figures 142, 144 and 146). By week 2, the samples B and 0 showed no major peaks (see Figures 147 to 152). Again, no major peaks were seen in week 4 (see Figures 153 to 158). Resampling of the adsorbent would not be advisable, so multiple samples from debris should initially be taken if the need for resampling is expected. As seen, the storage of these samples in tubes is an effective way to preserve evidence over time.

Table 10: Results of simulated CADA Proficiency Test 1

Can	Matrix	Accelerant	Amount	TLV Sniffer® Level	Handler Alert
A	Wood	none	0	0	No
B	Styrofoam	none	0	0	No
C	Carpet and Padding	none	0	0	No
D	Cotton Ball	Diesel fuel	5μL	6	Yes
E	HDPE Plastic	none	0	0	No

Table 11: Results of simulated CADA Proficiency Test 2

Can	Matrix	Accelerant	Amount	TLV Sniffer® Level	Handler Alert
F	Mixed	none	0	0	No
G	Mixed	Diesel fuel	5μL	5	Yes
H	Mixed	none	0	0	No
I	Mixed	Zippo® fluid	5μL	68	Yes
J	Mixed	none	0	3	No
K	Mixed	none	0	0	No
L	Mixed	Charcoal lighter	5μL	16	Yes

Table 12: Results of simulated CADA Proficiency Test 3

Location	Accelerant	Amount	TLV Level	Handler Alert
1	none	0	0	No
2	Charcoal lighter	5μL	0	No
3	none	0	0	No
4	Charcoal lighter	5μL	1	No
5	none	0	0	No
6	none	0	0	No
7	Charcoal lighter	5μL	0	No
8	none	0	0	No
9	none	0	0	No
10	none	0	0	No
11	none	0	0	No
12	Diesel fuel	5μL	0	No
13	none	0	0	No
14	Diesel fuel	5μL	0	No
15	none	0	0	No
16	Diesel fuel	5μL	0	No
17	none	0	0	No
18	none	0	0	No
19	none	0	0	No
20	none	0	1	No
21	none	0	0	No
22	none	0	0	No
23	Zippo® fluid	5μL	0	No
24	none	0	0	No
25	Zippo® fluid	5μL	0	No
26	none	0	0	No
27	none	0	0	No
28	none	0	0	No
29	none	0	0	No
30	Zippo® fluid	5μL	0	No

Table 13: TLV Sniffer® levels for different amounts of diesel fuel spiked on a pine board

Accelerant	Amount	TLV Level
Diesel Fuel	0µL	0
Diesel Fuel	5µL	0
Diesel Fuel	10µL	0
Diesel Fuel	15µL	0
Diesel Fuel	20µL	1
Diesel Fuel	25µL	1
Diesel Fuel	50µL	4

Figure 8: 500ppm Zippo® cigarette lighter standard

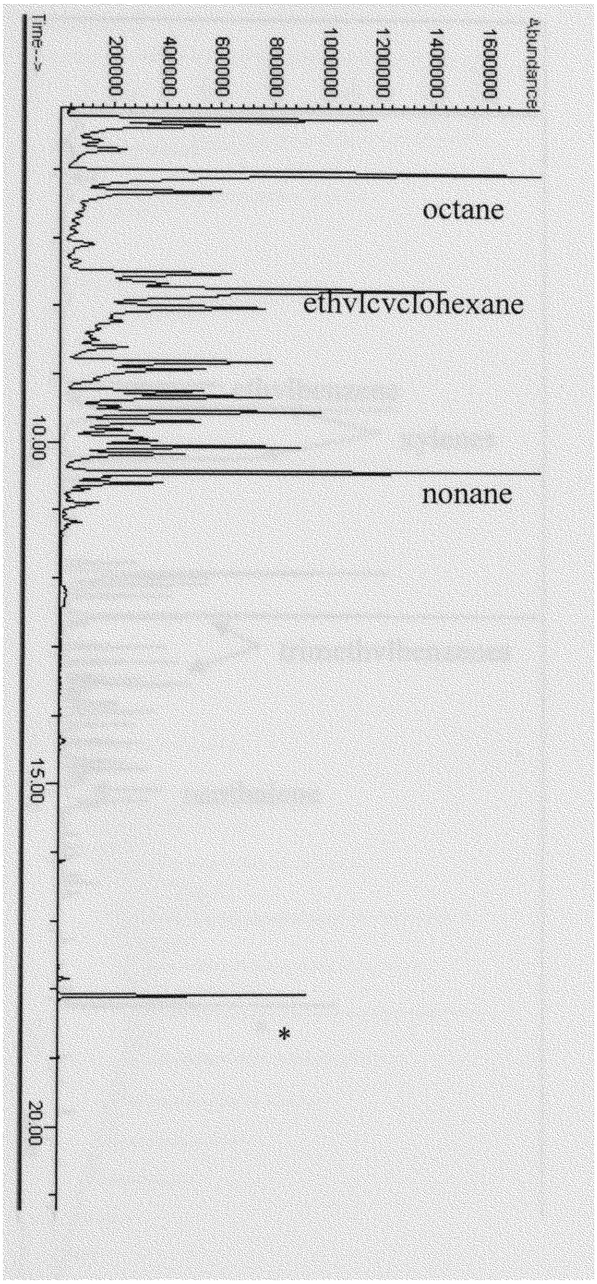


Figure 9: 500ppm charcoal lighter fluid standard

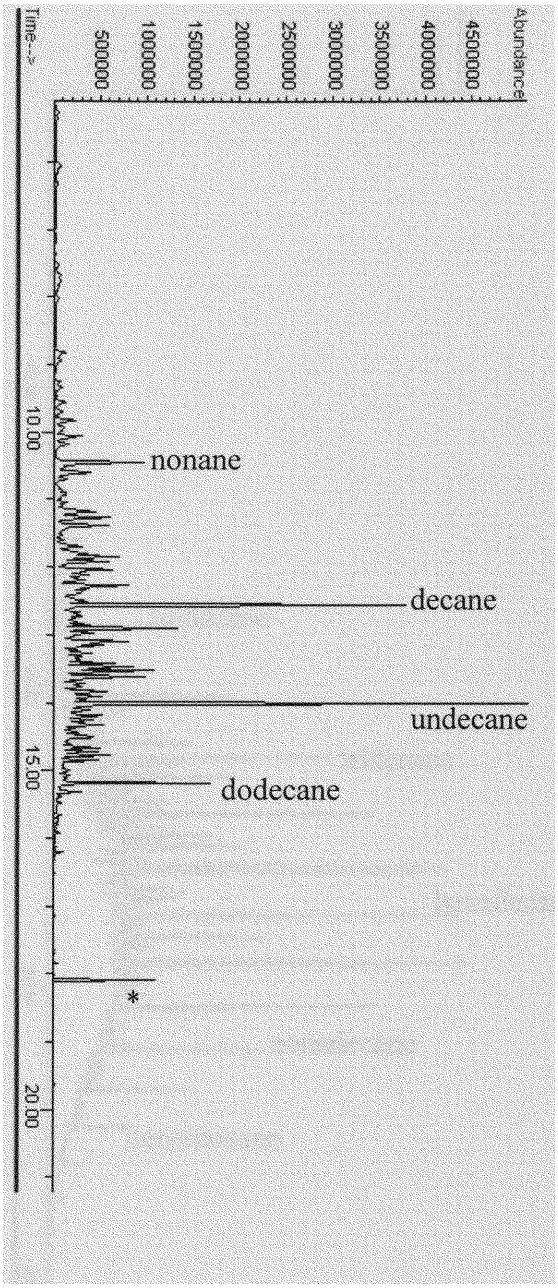


Figure 10: 500ppm gasoline standard

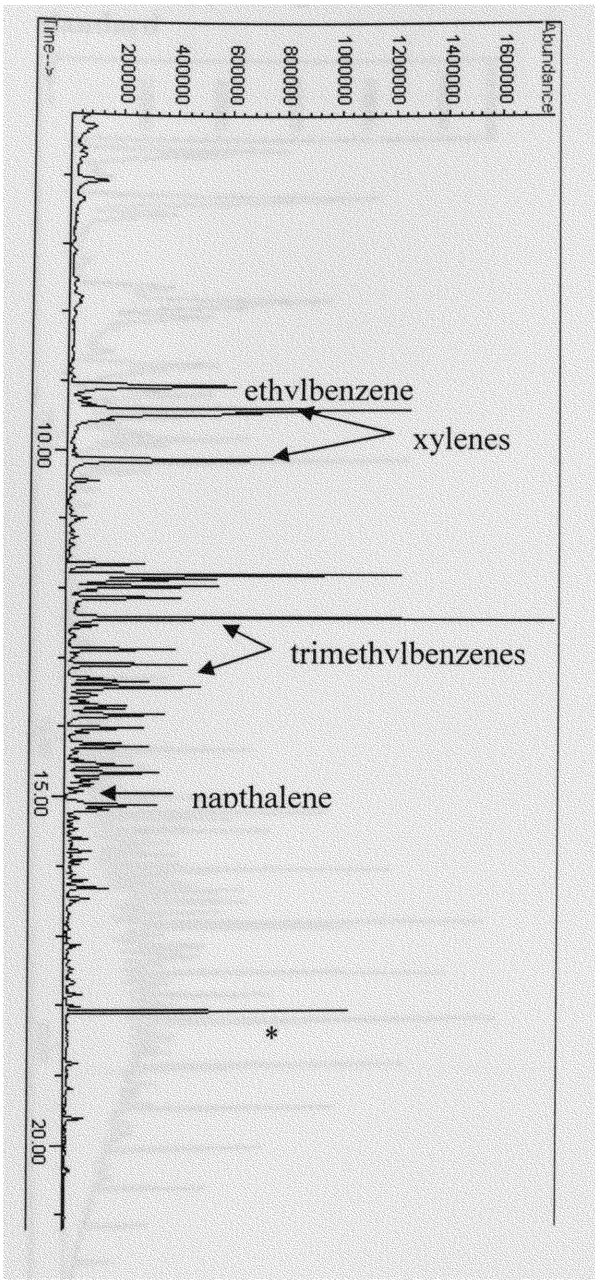


Figure 11: 500ppm diesel fuel standard

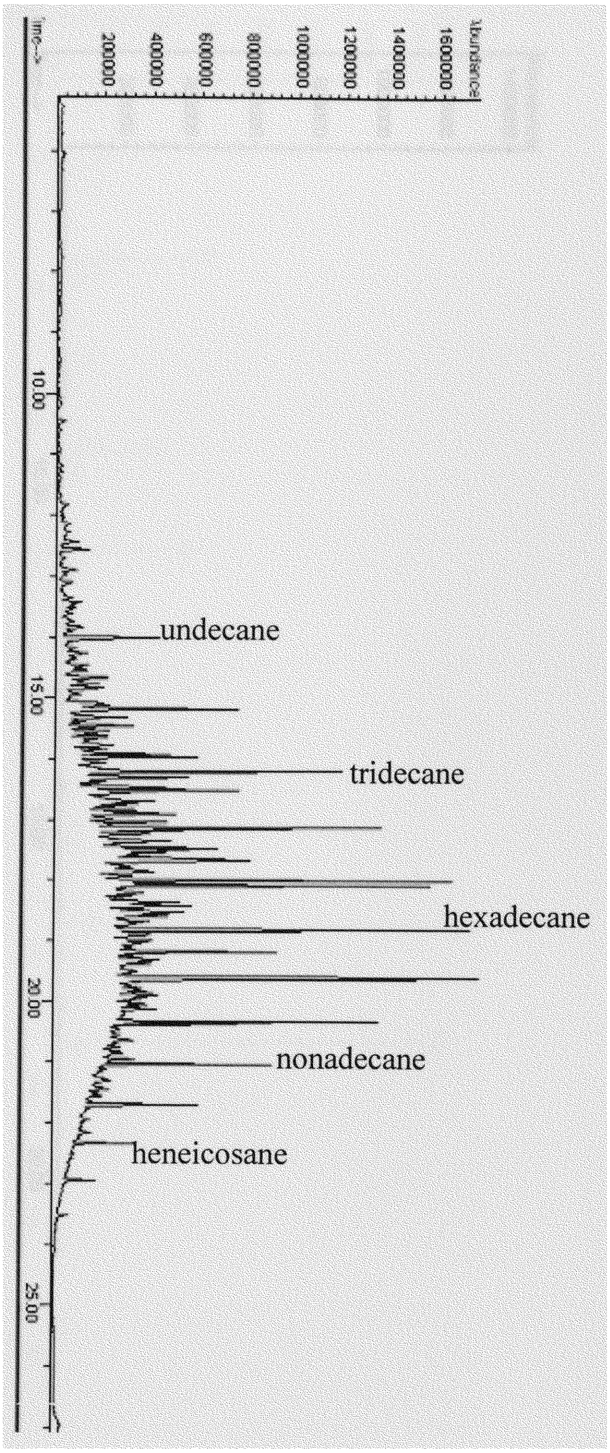


Figure 12: 500ppm 10:1 ratio diesel fuel and Zippo® cigarette lighter standard

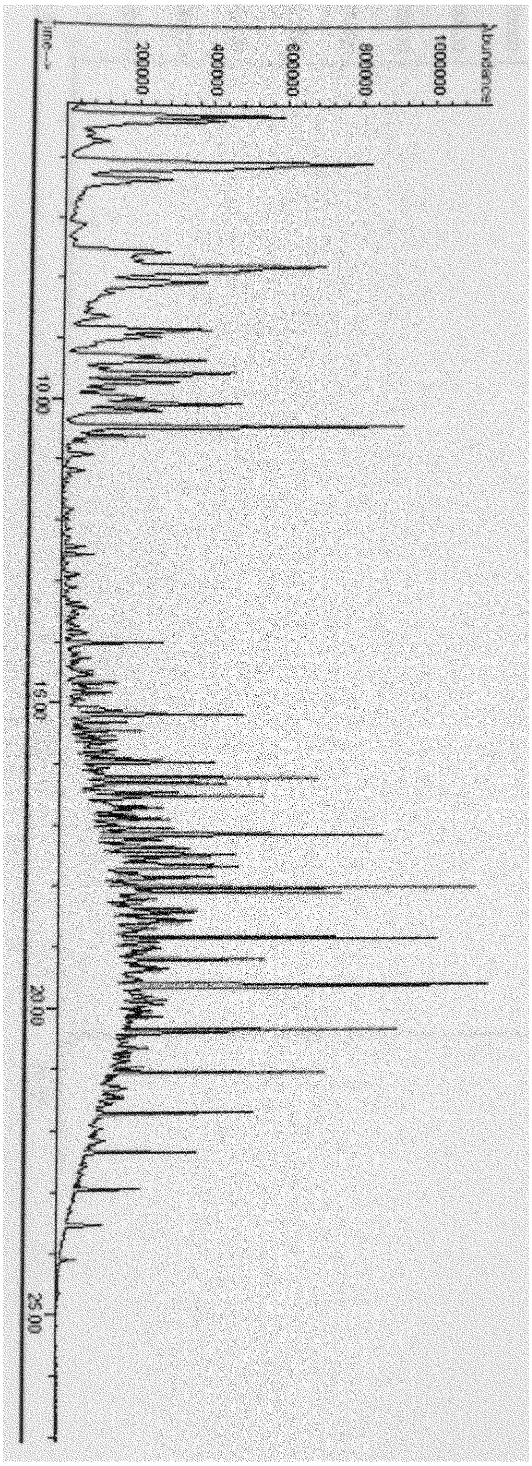


Figure 13: Blank charcoal tube run with Portable Arson Sampler

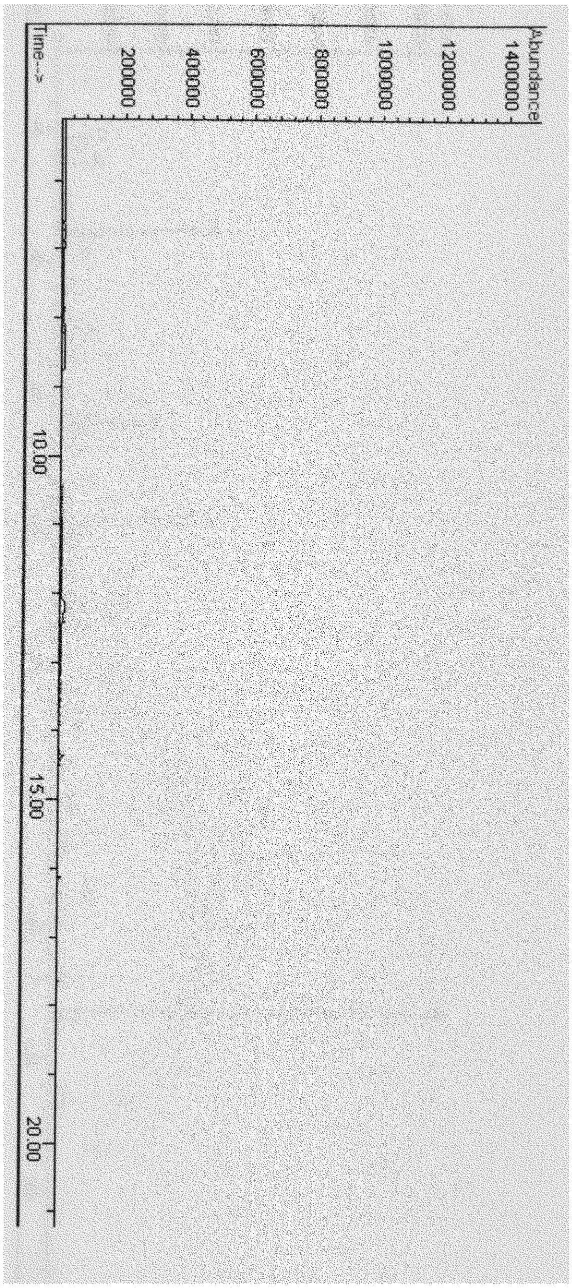


Figure 14: Blank polymer tube run with Portable Arson Sampler

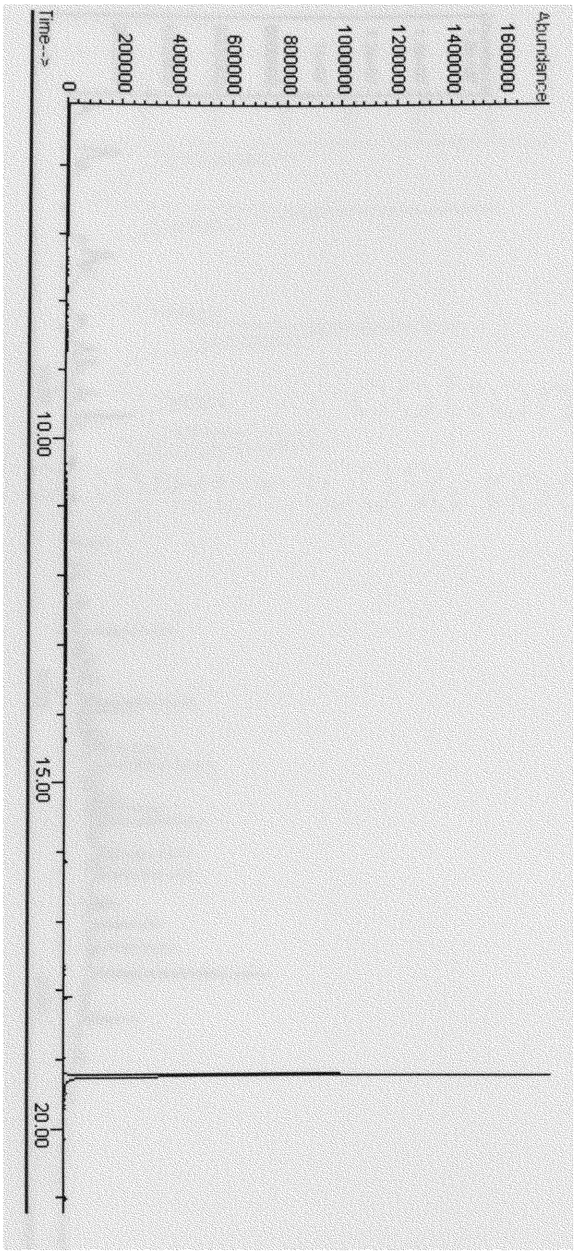


Figure 15: Blank polymer tube unidentified peak mass spectrum

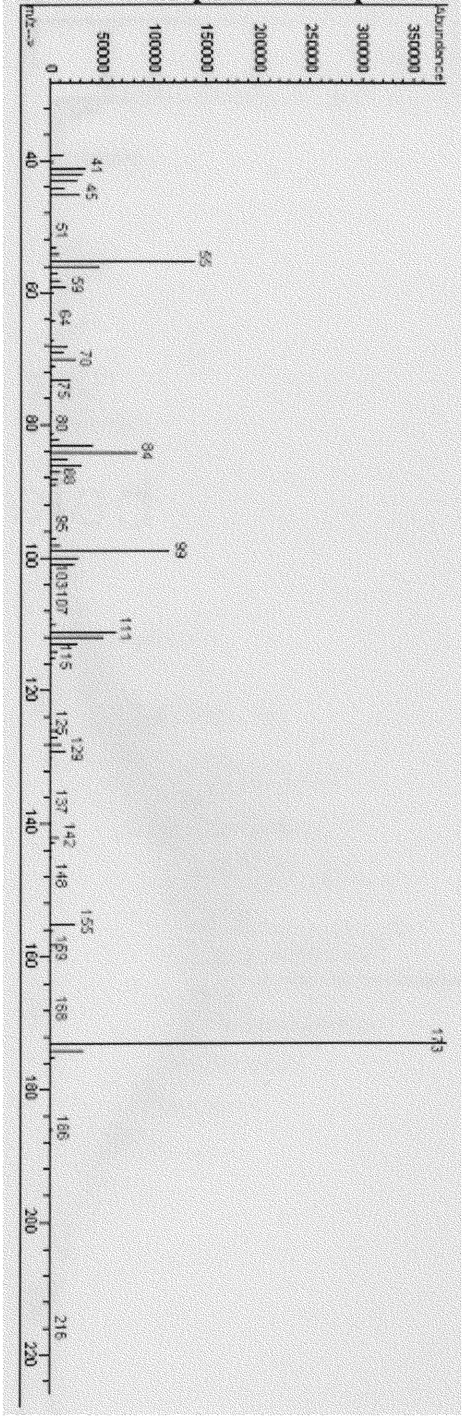


Figure 16: 10µL 10:1 diesel Zippo® spiked directly into charcoal tube

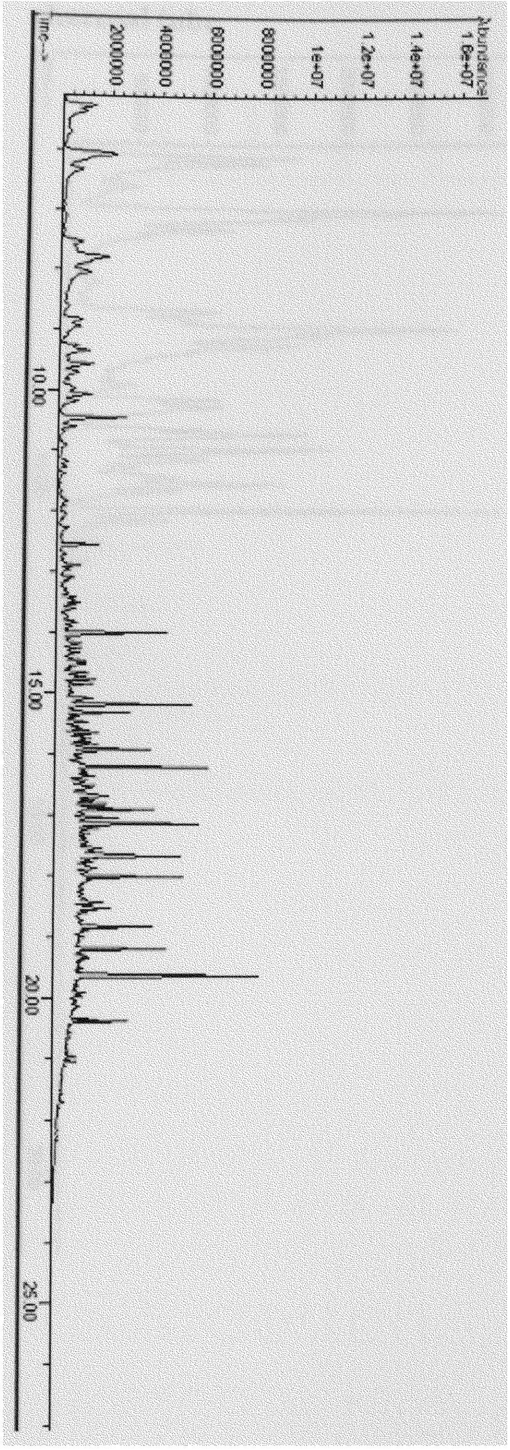


Figure 17: 10µL 10:1 diesel Zippo® spiked directly into polymer tube

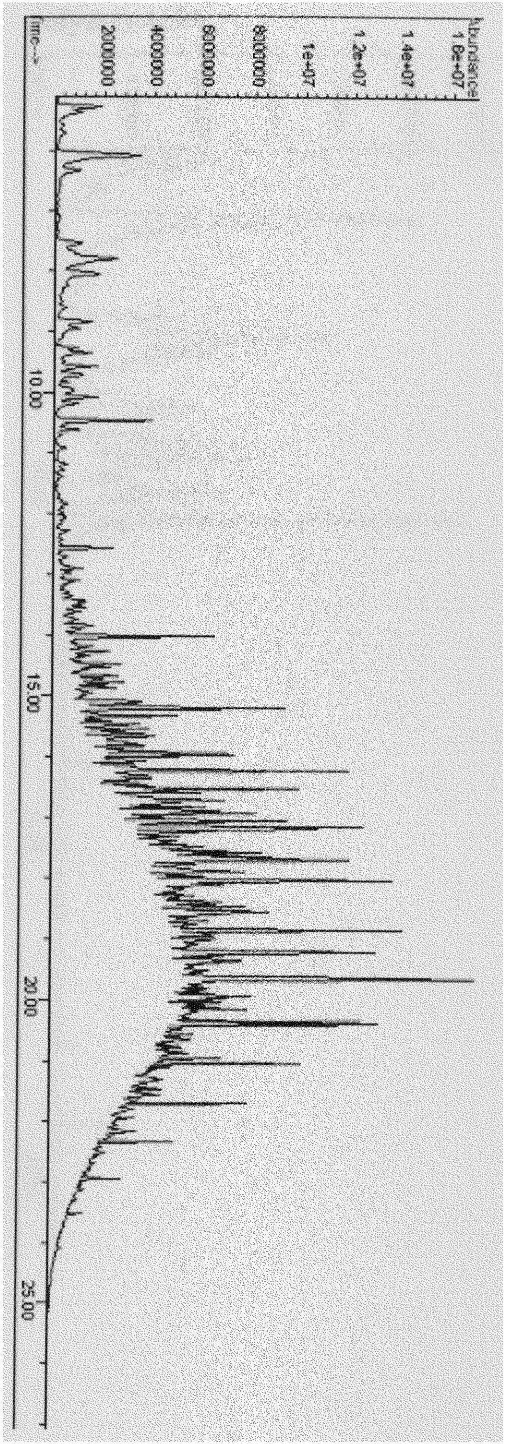


Figure 18: 500µL diesel Zippo® spike on tissues, extracted with PAS using charcoal tube

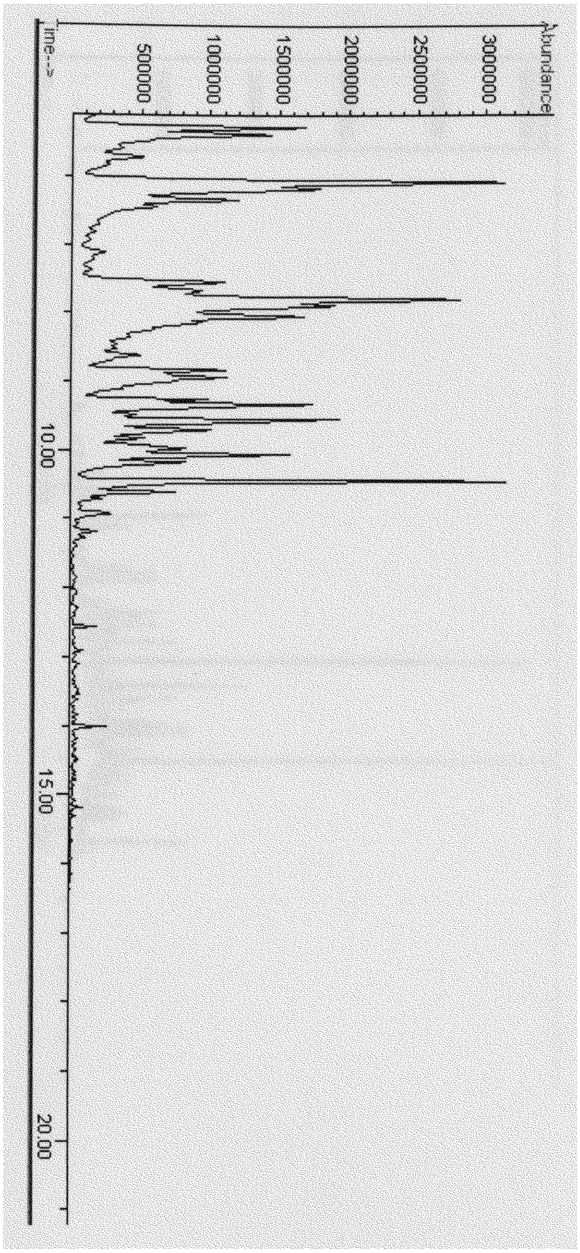


Figure 19: 500µL diesel Zippo® spike on tissues, extracted with PAS using polymer tube

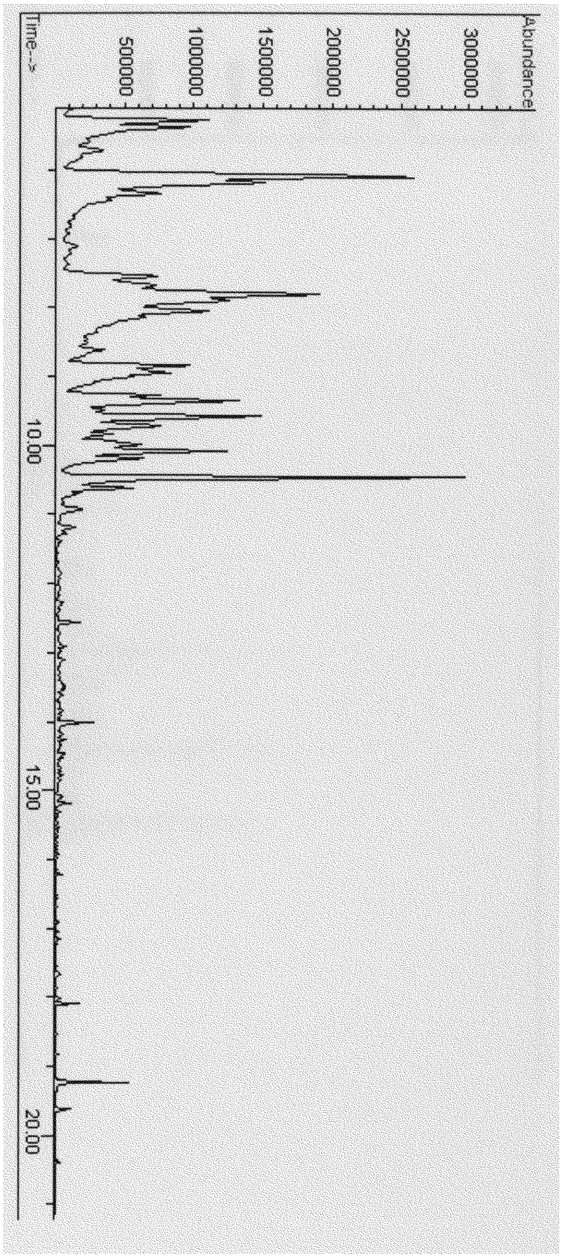


Figure 20: 100µL charcoal lighter spiked on tissues, PAS, desorbed with diethyl ether

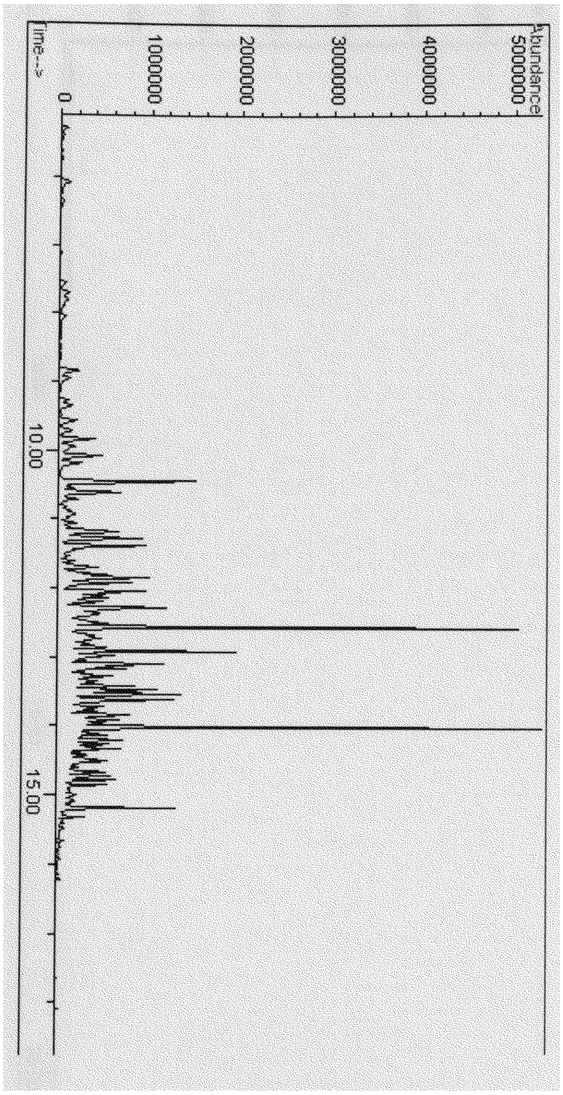


Figure 21: 100µL charcoal lighter spiked on tissues, PAS, desorbed with dichloromethane

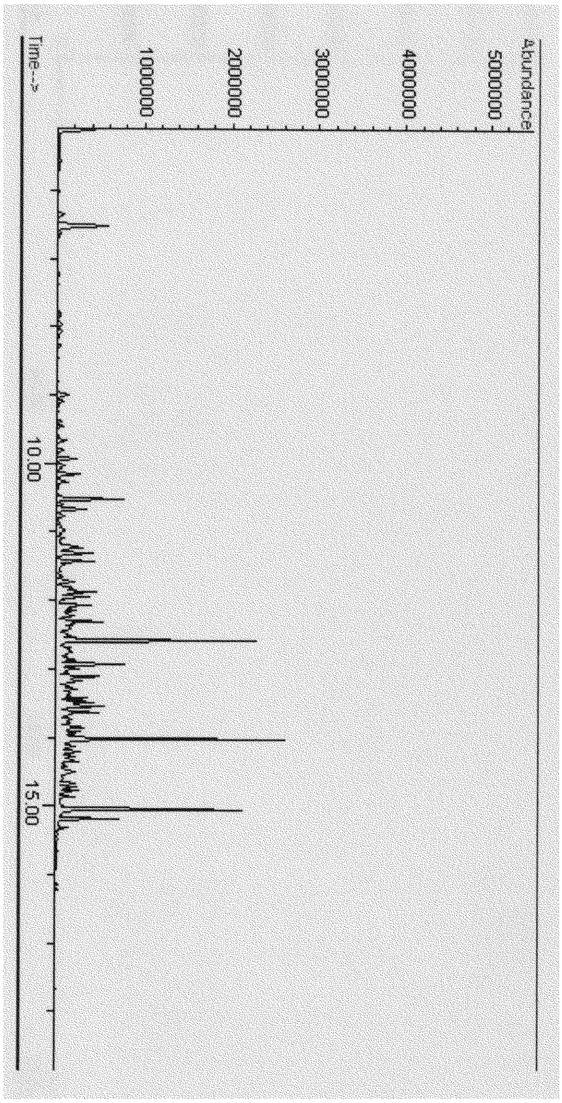


Figure 22: 500µL 10:1 diesel Zippo®, extracted with PAS for 1 minute

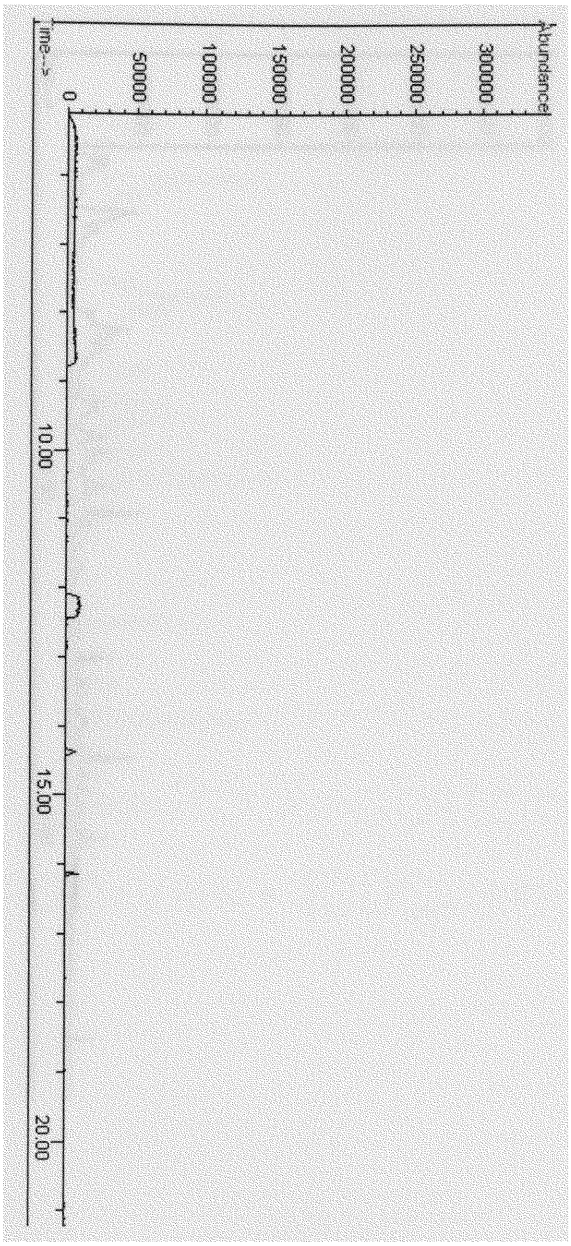


Figure 23: 500µL 10:1 diesel Zippo®, extracted with PAS for 5 minutes

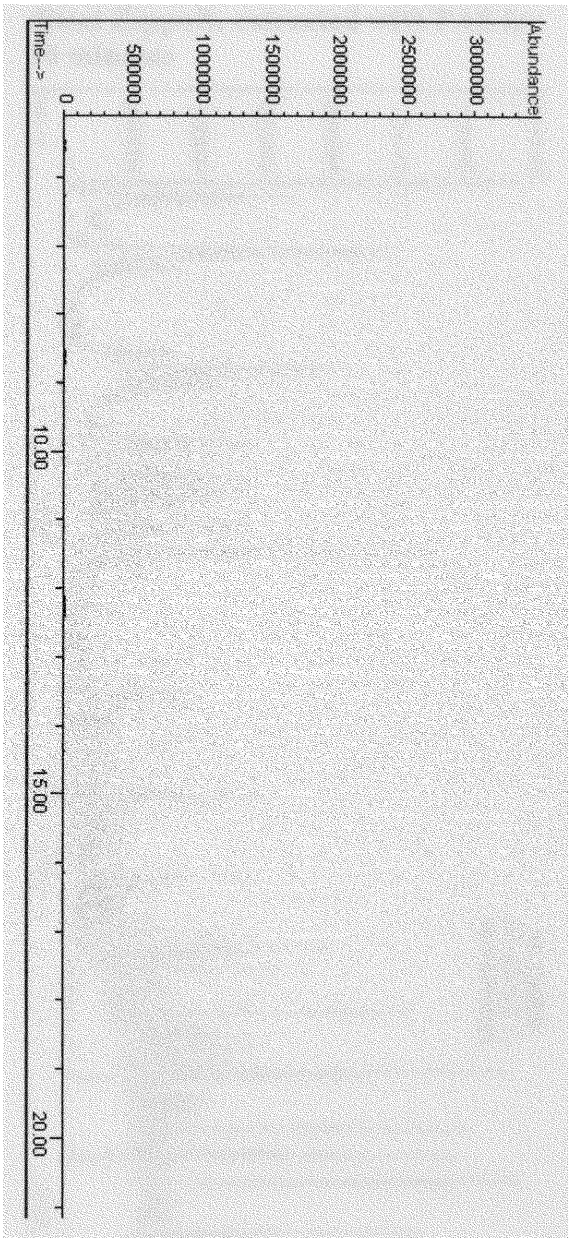


Figure 24: 500µL 10:1 diesel Zippo®, extracted with PAS for 10 minutes

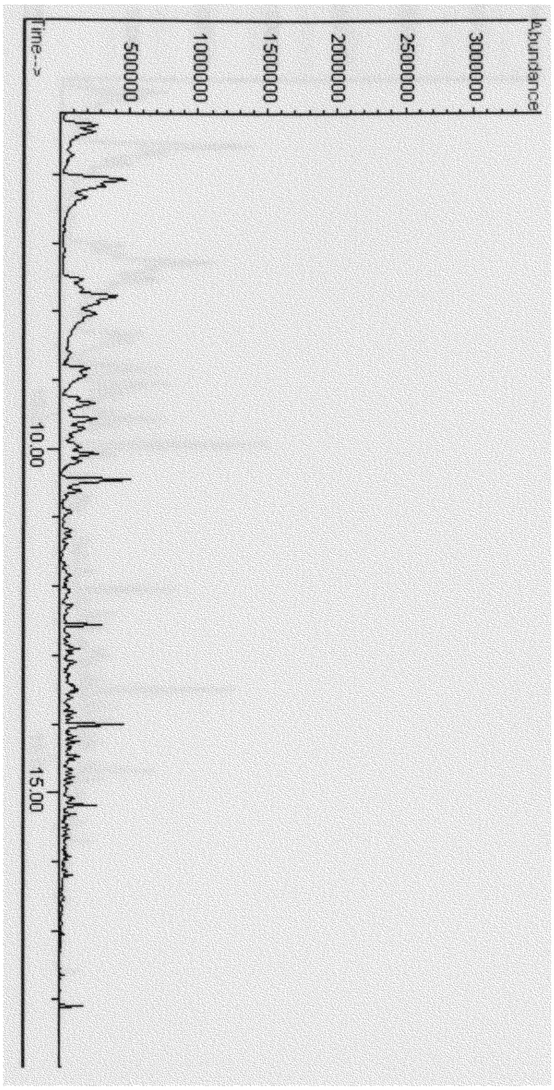


Figure 25: 500ppm diesel Zippo® standard overlayed with 500µL 10:1 diesel Zippo®, extracted with PAS for 10 minutes

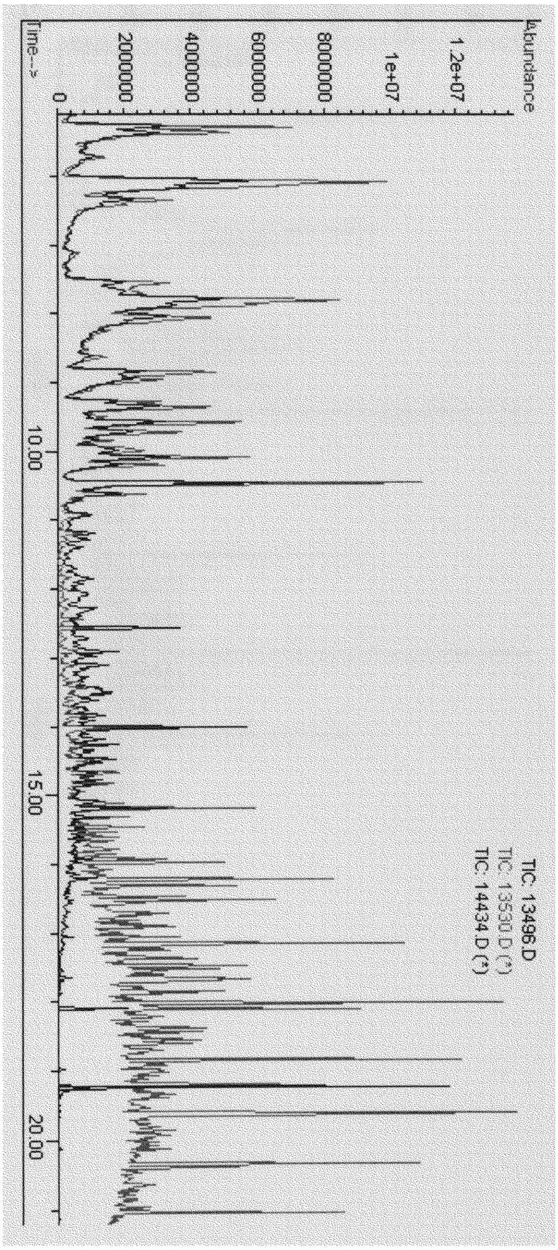


Figure 26: 500µL 10:1 diesel Zippo®, extracted with PAS for 30 minutes

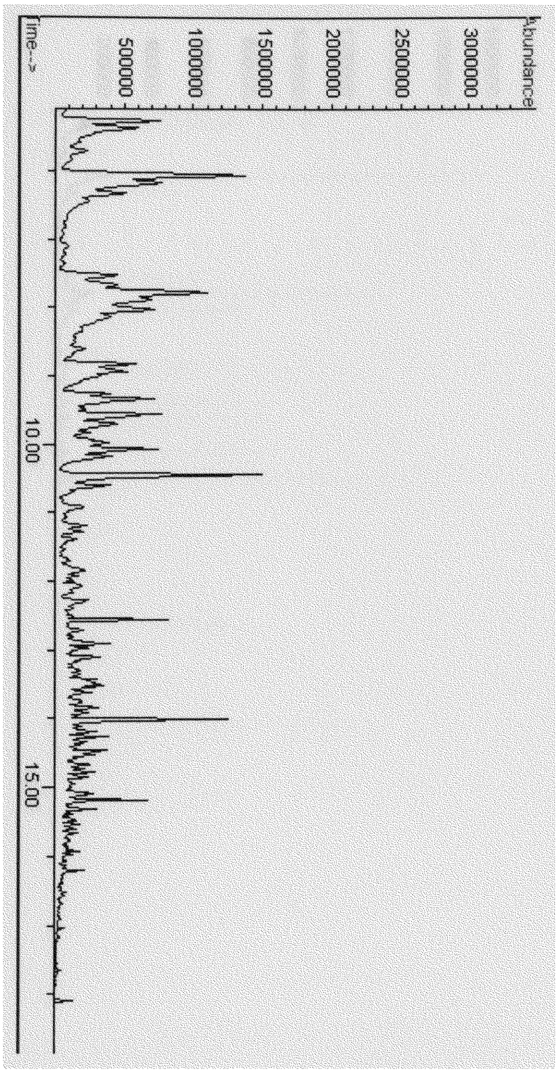


Figure 27: 500µL 10:1 diesel Zippo®, extracted with PAS for 60 minutes

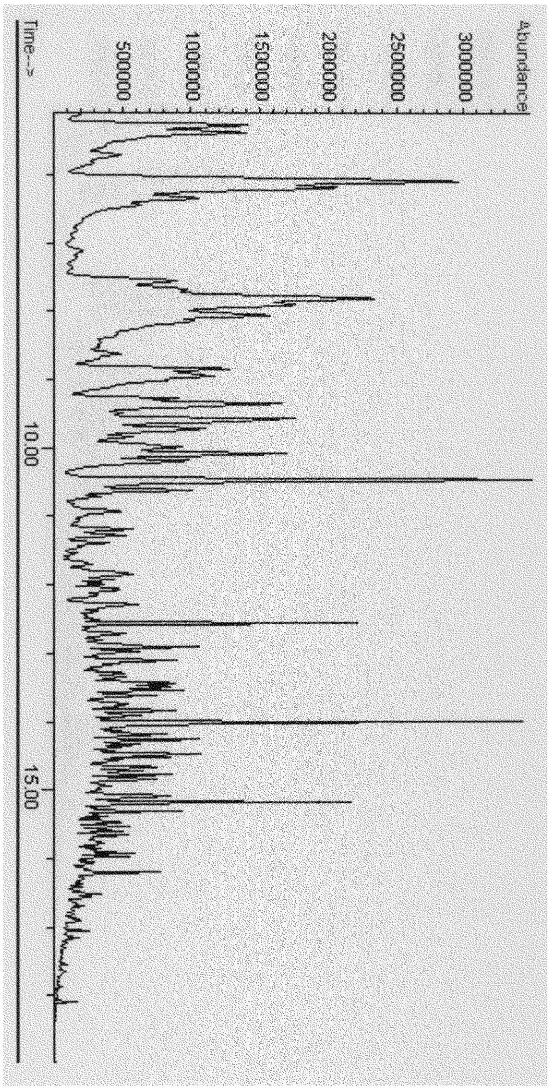


Figure 28: 500µL 10:1 diesel Zippo®, extracted with PAS at 20°C

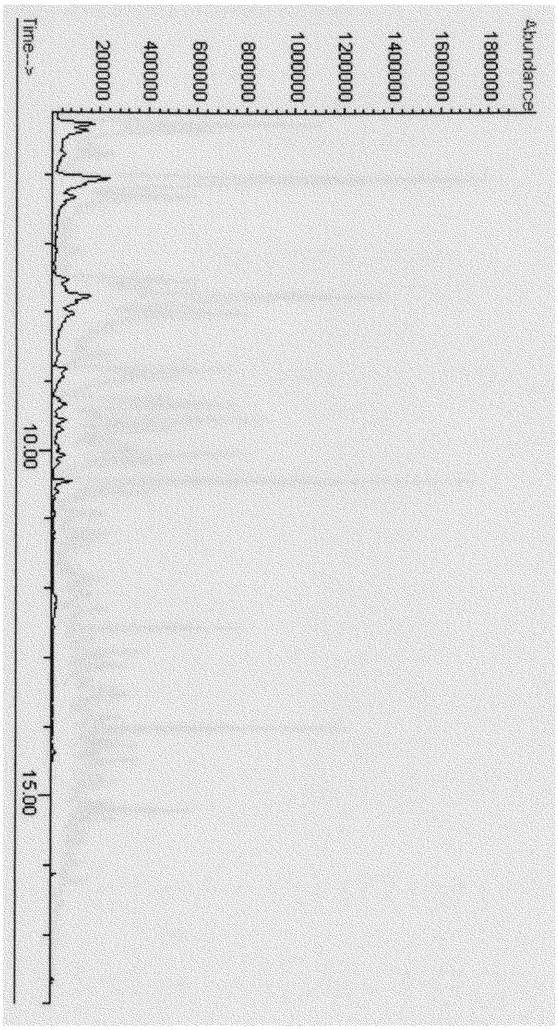


Figure 29: 500µL 10:1 diesel Zippo®, extracted with PAS at 40°C

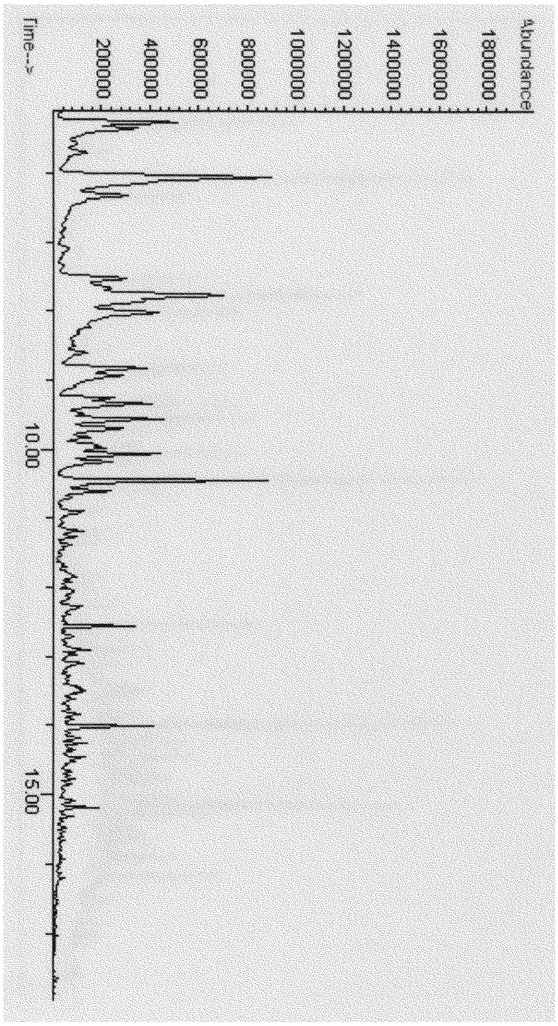


Figure 30: 500µL 10:1 diesel Zippo®, extracted with PAS at 50°C

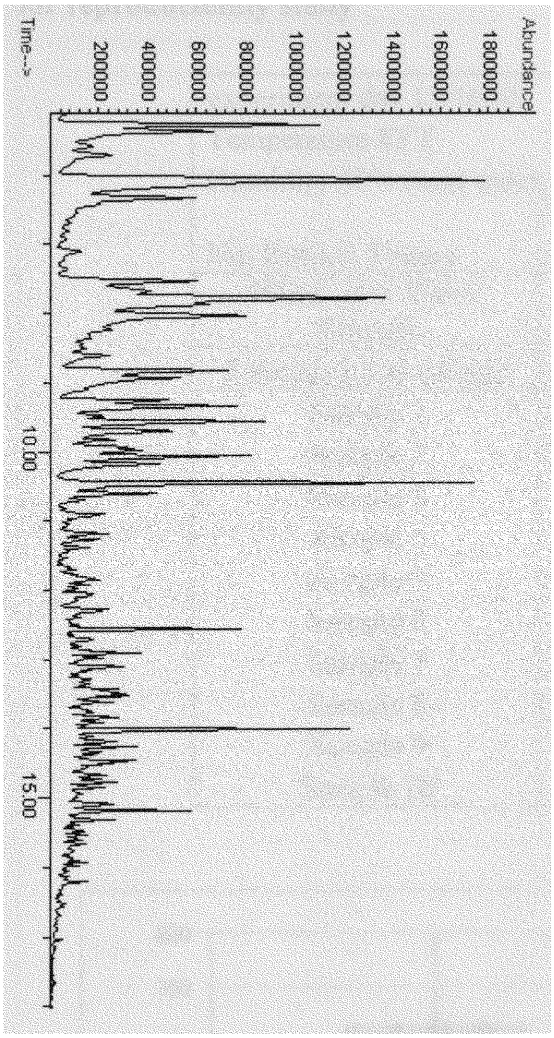


Figure 31: 500µL 10:1 diesel Zippo®, extracted with PAS at 70°C

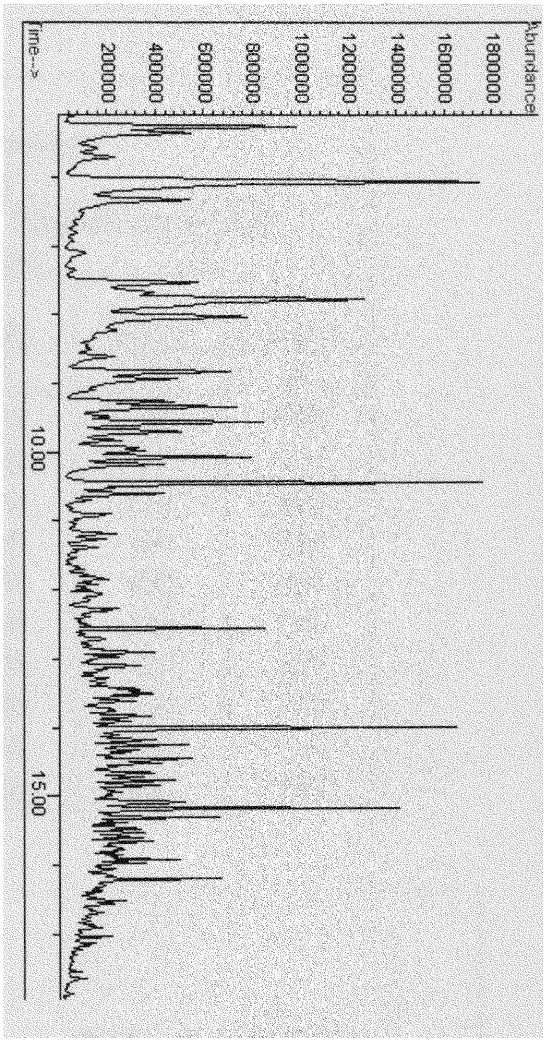


Table 14: TLV Sniffer® levels for not burned 10:1 diesel Zippo® spiked on tissues for reproducibility study

experiment day 11/16/05 Temperature 83˚F Dewpoint 64˚F Humidity 53% (heat index 84˚F)			
Not Burned Tissues	TLV Sniffer® Level (ppm hexane)		
100µL 10:1 Diesel Zippo®	trial 1	trial 2	trial 3
3 tissues no accelerant	0	0	0
Sample 1	570	360	190
Sample 2	640	430	310
Sample 3	740	640	400
Sample 4	360	160	130
Sample 5	670	430	350
Sample 6	510	220	150
Sample 7	570	170	100
Sample 8	680	310	120
Sample 9	530	290	210
Sample 10	980	430	200

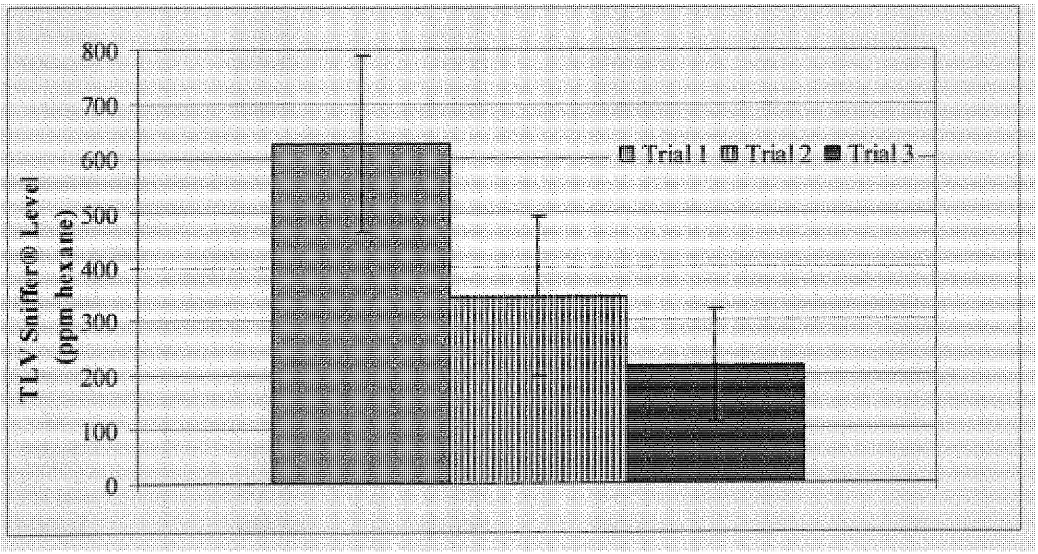


Figure 32: Mean TLV Sniffer® levels for reproducibility study showing standard deviation error bars

Table 15: TLV Sniffer® levels for not burned tissues spiked with Zippo® fluid with recorded weather conditions[31]

experiment day 6/08/05
Temperature 88°F Dewpoint 76°F
Humidity 68% (heat index 99°F)

Not burned	TLV Sniffer® Level (ppm hexane)			tpi®Pocket alert	
Zippo®	trial 1	trial 2	trial 3	in contact	not contact
0	0	0	0	0	0
10μL	580	160	68	0	0
50 μL	4800	1500	540	0	0
100μL	5400	2600	320	0	0
500μL	10000	8100	4000	4	4
1mL	10000	8100	10000	4	4

experiment day 6/12/05

Temperature 86°F Dewpoint 74°F
Humidity 67% (heat index 94°F)

Not burned	TLV Sniffer® Level (ppm hexane)			tpi®Pocket alert	
Zippo®	trial 1	trial 2	trial 3	in contact	not contact
0	0	0	0	0	0
10μL	430	230	130	0	0
50 μL	4500	1000	600	0	0
100μL	4900	1000	150	0	0
500μL	8700	7000	2200	4	4
1mL	8600	8800	5900	4	4

experiment day 6/12/05
Temperature 86°F Dewpoint 74°F
Humidity 67% (heat index 94°F)

Not burned	TLV Sniffer® Level (ppm hexane)			tpi®Pocket alert	
Zippo®	trial 1	trial 2	trial 3	in contact	not contact
0	0	0	0	0	0
10μL	820	310	160	0	0
50 μL	4700	2500	540	0	0
100μL	6900	1700	450	0	0
500μL	10000	10000	10000	4	4
1mL	10000	10000	9400	4	4

Table 16: TLV Sniffer® levels for burned tissues spiked with Zippo® fluid

experiment day 6/15/05
Temperature 85°F Dewpoint 73°F
Humidity 68% (heat index 92°F)

Burned	TLV Sniffer® Level (ppm hexane)			tpi®Pocket alert	
Zippo®	trial 1	trial 2	trial 3	in contact	not contact
0	0	0	0	0	0
10µL	430	110	22	0	0
50 µL	1000	230	140	0	0
100µL	320	140	46	0	0
500µL	330	50	10	0	0
1mL	1000	190	99	0	0

experiment day 7/1/05

Temperature 89°F Dewpoint 74°F
Humidity 61% (heat index 98°F)

Burned	TLV Sniffer® Level (ppm hexane)			tpi®Pocket alert	
Zippo®	trial 1	trial 2	trial 3	in contact	not contact
0	0	0	0	0	0
10µL	1200	380	110	0	0
50 µL	450	220	140	0	0
100µL	1300	490	200	0	0
500µL	78	45	28	0	0
1mL	1500	760	410	0	0

experiment day 7/1/05
Temperature 89°F Dewpoint 74°F
Humidity 61% (heat index 98°F)

Burned	TLV Sniffer® Level (ppm hexane)			tpi®Pocket alert	
Zippo®	trial 1	trial 2	trial 3	in contact	not contact
0	0	0	0	0	0
10µL	270	120	95	0	0
50 µL	450	200	100	0	0
100µL	640	280	160	0	0
500µL	500	270	100	0	0
1mL	1000	450	220	0	0

Table 17: TLV Sniffer® levels for not burned tissues spiked with charcoal lighter fluid

experiment day 5/24/05
Temperature 89°F Dewpoint 72°F
Humidity 57% (heat index 96°F)

Not burned	TLV Sniffer® Level (ppm hexane)			tpi®Pocket alert	
Charcoal lighter	trial 1	trial 2	trial 3	in contact	not contact
0	2	2	2	0	0
10μL	180	40	27	0	0
50 μL	1500	1100	600	1	0
100μL	2100	1500	1000	3	1
500μL	2800	2200	2200	4	4
1mL	3200	2900	2900	4	4

experiment day 6/1/05
Temperature 78°F Dewpoint 74°F
Humidity 87% (heat index 80°F)

Not burned	TLV Sniffer® Level (ppm hexane)			tpi®Pocket alert	
Charcoal lighter	trial 1	trial 2	trial 3	in contact	not contact
0	0	0	0	0	0
10μL	500	270	160	0	0
50 μL	1500	740	600	3	1
100μL	1600	1000	900	4	1
500μL	2300	2200	2100	4	4
1mL	2900	2500	2400	4	4

experiment day 6/08/05
Temperature 88°F Dewpoint 76°F
Humidity 68% (heat index 99°F)

Not burned	TLV Sniffer® Level (ppm hexane)			tpi®Pocket alert	
Charcoal lighter	trial 1	trial 2	trial 3	in contact	not contact
0	0	0	0	0	0
10μL	390	170	48	0	0
50 μL	1700	360	230	1	0
100μL	1200	560	630	4	0
500μL	1400	1200	1100	4	3
1mL	2800	2400	1200	4	3

Table 18: TLV Sniffer® levels for burned tissues spiked with charcoal lighter fluid

experiment day 6/15/05
Temperature 85°F Dewpoint 73°F
Humidity 68% (heat index 92°F)

Burned	TLV Sniffer® Level (ppm hexane)			tpi®Pocket alert	
Charcoal Lighter	trial 1	trial 2	trial 3	in contact	not contact
0	0	0	0	0	0
10μL	920	160	79	0	0
50 μL	1000	160	42	0	0
100μL	260	100	39	0	0
500μL	180	22	5	0	0
1mL	520	180	70	0	0

experiment day 7/1/05
Temperature 89°F Dewpoint 74°F
Humidity 61% (heat index 98°F)

Burned	TLV Sniffer® Level (ppm hexane)			tpi®Pocket alert	
Charcoal Lighter	trial 1	trial 2	trial 3	in contact	not contact
0	0	0	0	0	0
10μL	150	100	37	0	0
50 μL	200	100	35	0	0
100μL	440	190	120	0	0
500μL	390	160	99	0	0
1mL	3100	1900	1100	4	1

experiment day 7/1/05
Temperature 89°F Dewpoint 74°F
Humidity 61% (heat index 98°F)

Burned	TLV Sniffer® Level (ppm hexane)			tpi®Pocket alert	
Charcoal Lighter	trial 1	trial 2	trial 3	in contact	not contact
0	0	0	0	0	0
10μL	160	94	48	0	0
50 μL	240	120	77	0	0
100μL	220	73	32	0	0
500μL	360	210	100	0	0
1mL	1100	560	410	3	0

Table 19:TLV Sniffer® levels for not burned tissues spiked with gasoline

experiment day 8/4/05 Temperature 83˚F Dewpoint 76˚F Humidity 79% (heat index 91˚F)					
Not burned	TLV Sniffer® Level(ppm hexane)			tpi®Pocket alert	
Gasoline	trial 1	trial 2	trial 3	in contact	not contact
0	0	0	0	0	0
10µL	430	180	140	0	0
50 µL	380	230	120	0	0
100µL	3200	1800	1100	1	0
500µL	10000	6200	2900	4	1
1mL	10000	10000	10000	4	4

experiment day 8/4/05 Temperature 83˚F Dewpoint 76˚F Humidity 79% (heat index 91˚F)					
Not burned	TLV Sniffer® Level(ppm hexane)			tpi®Pocket alert	
Gasoline	trial 1	trial 2	trial 3	in contact	not contact
0	0	0	0	0	0
10µL	120	70	34	0	0
50 µL	480	220	140	0	0
100µL	4100	2300	1300	1	0
500µL	7900	3700	2300	4	1
1mL	10000	10000	10000	4	4

experiment day 8/4/05 Temperature 83˚F Dewpoint 76˚F Humidity 79% (heat index 91˚F)					
Not burned	TLV Sniffer® Level(ppm hexane)			tpi®Pocket alert	
Gasoline	trial 1	trial 2	trial 3	in contact	not contact
0	0	0	0	0	0
10µL	380	200	100	0	0
50 µL	890	440	360	0	0
100µL	4200	2500	1500	1	0
500µL	8700	3400	3400	4	1
1mL	10000	10000	10000	4	4

Table 20: TLV Sniffer® levels for burned tissues spiked with gasoline

experiment day 8/24/05 Temperature 90°F Dewpoint 74°F Humidity 59% (heat index 99°F)					
Burned	TLV Sniffer® Level(ppm hexane)			tpi®Pocket alert	
Gasoline	trial 1	trial 2	trial 3	in contact	not contact
0	0	0	0	0	0
10μL	540	270	180	0	0
50 μL	520	370	180	0	0
100μL	1400	950	390	0	0
500μL	690	320	300	0	0
1mL	820	520	310	0	0

experiment day 8/24/05 Temperature 90°F Dewpoint 74°F Humidity 59% (heat index 99°F)					
Burned	TLV Sniffer® Level(ppm hexane)			tpi®Pocket alert	
Gasoline	trial 1	trial 2	trial 3	in contact	not contact
0	0	0	0	0	0
10μL	590	340	220	0	0
50 μL	1100	750	320	0	0
100μL	460	210	110	0	0
500μL	510	310	210	0	0
1mL	600	270	120	0	0

experiment day 8/24/05 Temperature 90°F Dewpoint 74°F Humidity 59% (heat index 99°F)					
Burned	TLV Sniffer® Level(ppm hexane)			tpi®Pocket alert	
Gasoline	trial 1	trial 2	trial 3	in contact	not contact
0	0	0	0	0	0
10μL	570	320	190	0	0
50 μL	370	190	50	0	0
100μL	1200	640	350	0	0
500μL	1900	950	440	0	0
1mL	2200	1100	520	0	0

Table 21: TLV Sniffer® levels for not burned tissues spiked with diesel fuel

experiment day 6/1/05 Temperature 78°F Dewpoint 74°F Humidity 87% (heat index 80°F)					
Not burned	TLV Sniffer® Level(ppm hexane)			tpi®Pocket alert	
Diesel Fuel	trial 1	trial 2	trial 3	in contact	not contact
0	0	0	0	0	0
10μL	60	20	14	0	0
50 μL	150	100	88	0	0
100μL	190	120	120	0	0
500μL	260	240	190	not done	not done
1mL	370	270	240	not done	not done

experiment day 6/12/05 Temperature 86°F Dewpoint 74°F Humidity 67% (heat index 94°F)					
Not burned	TLV Sniffer® Level(ppm hexane)			tpi®Pocket alert	
Diesel Fuel	trial 1	trial 2	trial 3	in contact	not contact
0	0	0	0	0	0
10μL	28	20	14	0	0
50 μL	110	100	68	0	0
100μL	170	120	100	0	0
500μL	270	220	210	1	0
1mL	410	320	250	1	0

experiment day 6/12/05 Temperature 86°F Dewpoint 74°F Humidity 67% (heat index 94°F)					
Not burned	TLV Sniffer® Level(ppm hexane)			tpi®Pocket alert	
Diesel Fuel	trial 1	trial 2	trial 3	in contact	not contact
0	0	0	0	0	0
10μL	31	27	11	0	0
50 μL	100	72	40	0	0
100μL	160	99	98	0	0
500μL	250	220	180	1	0
1mL	290	170	150	1	0

Table 22: TLV Sniffer® levels for burned tissues spiked with diesel fuel

experiment day 6/15/05 Temperature 85°F Dewpoint 73°F Humidity 68% (heat index 92°F)					
Burned	TLV Sniffer® Level (ppm hexane)			tpi®Pocket alert	
Diesel Fuel	trial 1	trial 2	trial 3	in contact	not contact
0	0	0	0	0	0
10μL	690	200	110	0	0
50 μL	120	26	6	0	0
100μL	1400	500	280	0	0
500μL	290	69	32	0	0
1mL	290	90	43	0	0

experiment day 7/1/05 Temperature 89°F Dewpoint 74°F Humidity 61% (heat index 98°F)					
Burned	TLV Sniffer® Level (ppm hexane)			tpi®Pocket alert	
Diesel Fuel	trial 1	trial 2	trial 3	in contact	not contact
0	0	0	0	0	0
10μL	89	47	27	0	0
50 μL	1100	590	310	0	0
100μL	200	110	76	0	0
500μL	350	130	74	0	0
1mL	400	210	100	0	0

experiment day 7/1/05 Temperature 89°F Dewpoint 74°F Humidity 61% (heat index 98°F)					
Burned	TLV Sniffer® Level (ppm hexane)			tpi®Pocket alert	
Diesel Fuel	trial 1	trial 2	trial 3	in contact	not contact
0	0	0	0	0	0
10μL	490	220	150	0	0
50 μL	710	370	170	0	0
100μL	680	240	160	0	0
500μL	350	270	110	0	0
1mL	55	21	18	0	0

Table 23: TLV Sniffer® levels for burned matrix with no accelerant

experiment day 6/15/05
Temperature 85°F Dewpoint 73°F
Humidity 68% (heat index 92°F)

Burned	TLV Sniffer® Level (ppm hexane)			tpi®Pocket alert	
Matirx	trial 1	trial 2	trial 3	in contact	not contact
5 tissues	0	0	0	0	0
cotton	1400	160	92	0	0
HDPE	24	6	2	0	0
wood	320	200	110	0	0
carpet&pad	0	0	0	0	0
styrofoam	0	2	2	0	0

experiment day 7/1/05
Temperature 89°F Dewpoint 74°F
Humidity 61% (heat index 98°F)

Burned	TLV Sniffer® Level (ppm hexane)			tpi®Pocket alert	
Matrix	trial 1	trial 2	trial 3	in contact	not contact
cotton	1700	790	320	0	0
HDPE	9	8	8	0	0
wood	25	0	0	0	0
carpet&pad	1400	790	450	0	0
styrofoam	0	0	0	0	0
newspaper	1800	1000	660	0	0

experiment day 7/1/05
Temperature 89°F Dewpoint 74°F
Humidity 61% (heat index 98°F)

Burned	TLV Sniffer® Level (ppm hexane)			tpi®Pocket alert	
Matrix	trial 1	trial 2	trial 3	in contact	not contact
cotton	1500	320	86	0	0
HDPE	100	86	44	0	0
wood	20	11	4	0	0
carpet&pad	0	0	0	0	0
styrofoam	0	0	0	0	0
newspaper 2	560	210	120	0	0
newspaper 3	400	230	120	0	0

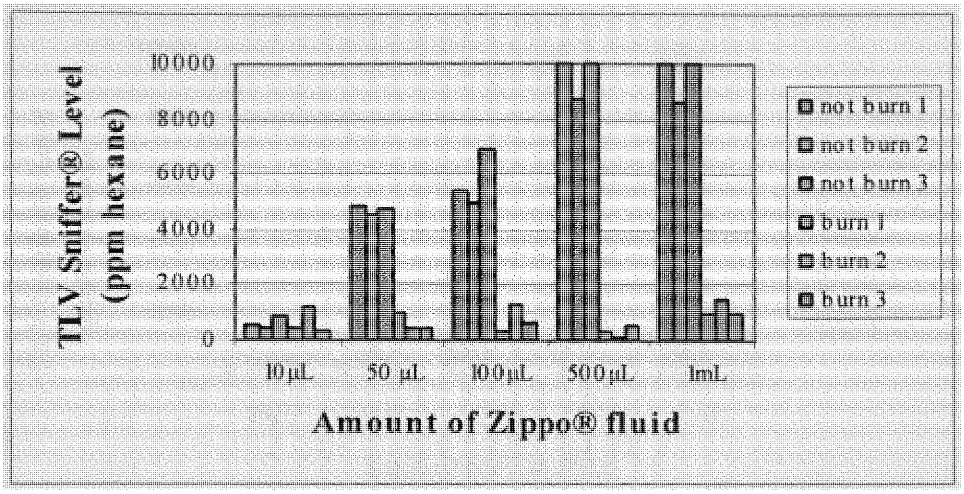


Figure 33: TLV Sniffer® levels for burned and not burned Zippo® fluid spiked on tissues

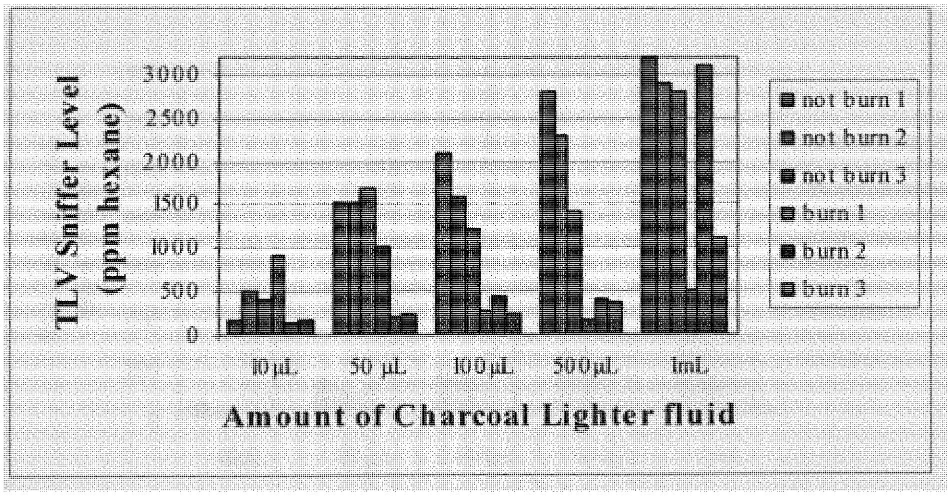


Figure 34: TLV Sniffer® levels for burned and not burned charcoal lighter fluid spiked on tissues

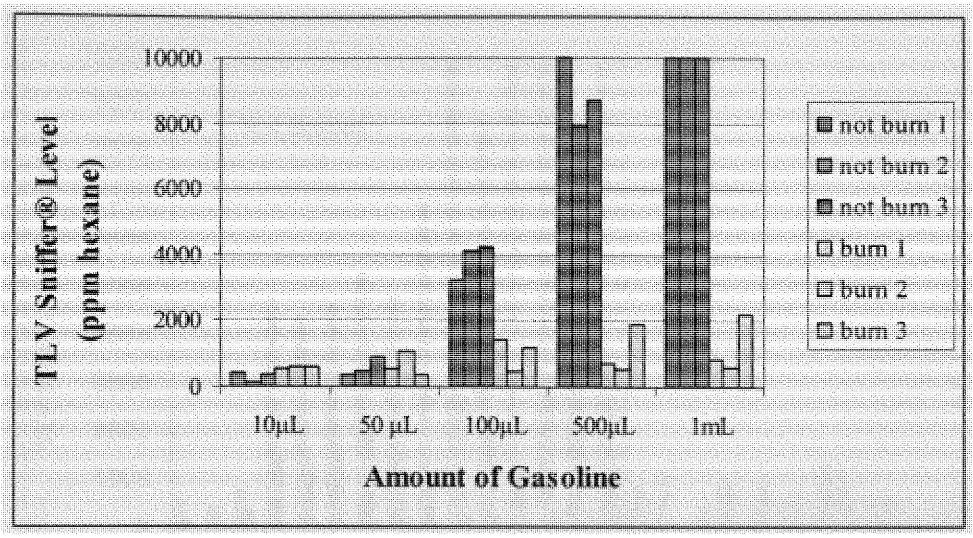


Figure 35: TLV Sniffer® levels for burned and not burned gasoline spiked on tissues

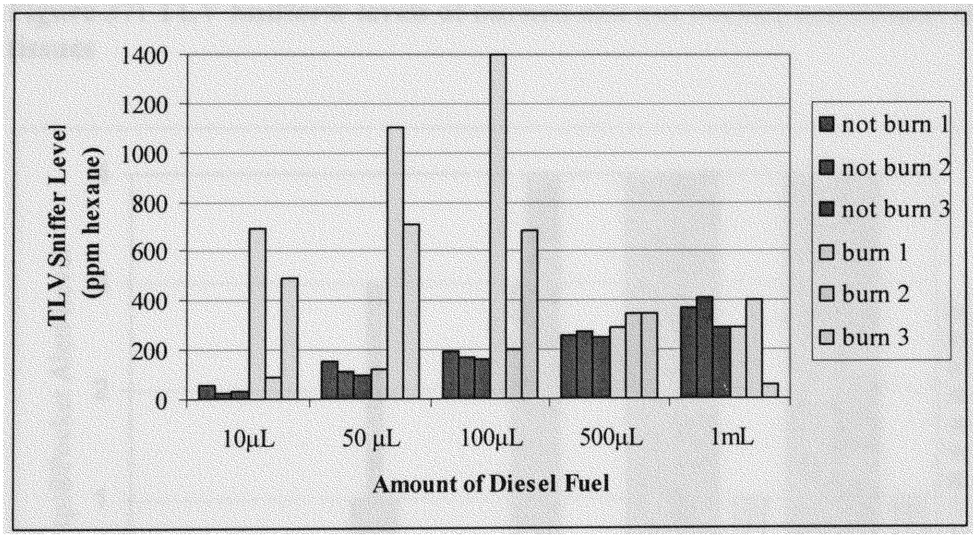


Figure 36: TLV Sniffer® levels for burned and not burned charcoal lighter fluid spiked on tissues

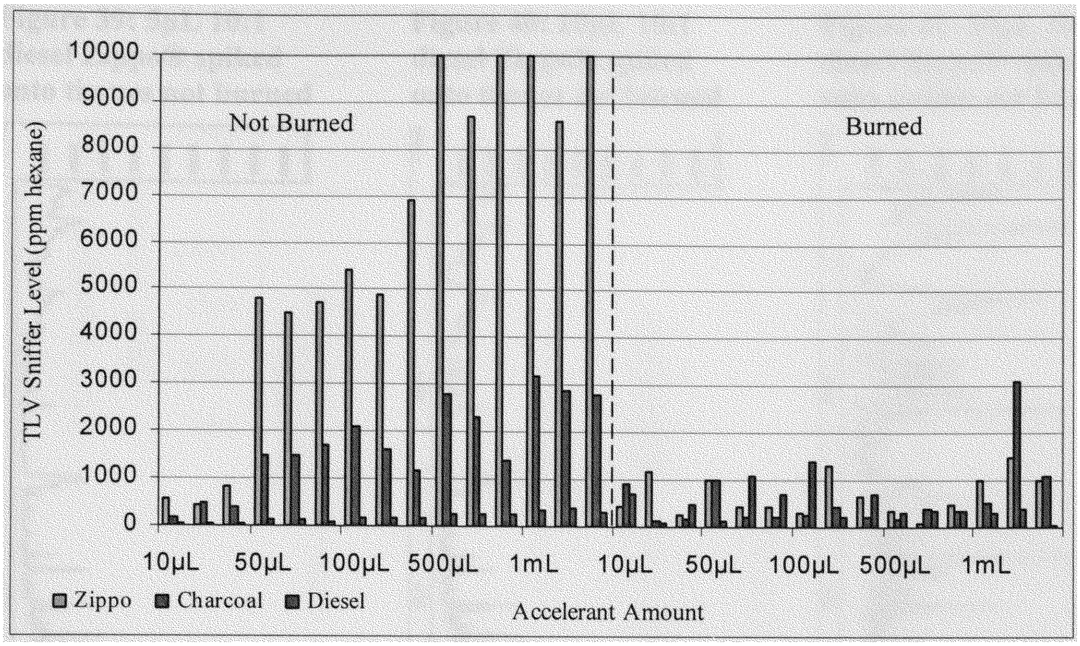


Figure 37: TLV Sniffer® levels of burned and not burned accelerants spiked on tissues

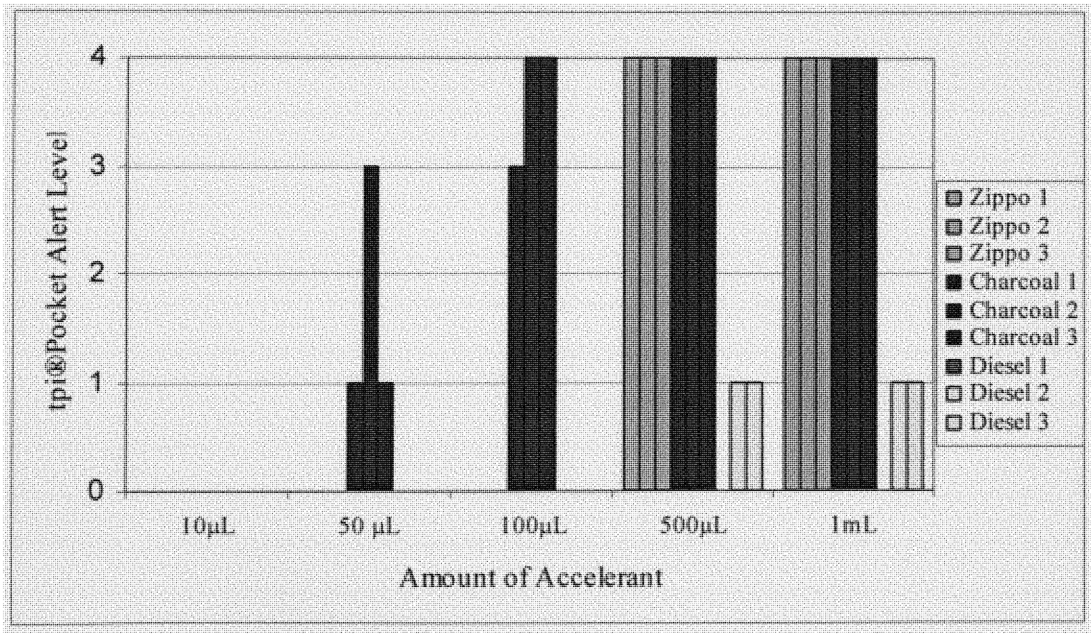


Figure 38: tpi®Pocket alerts for accelerants spiked on tissues not burned

Figure 39: 5µL 10:1 diesel Zippo® spiked onto tissues not burned

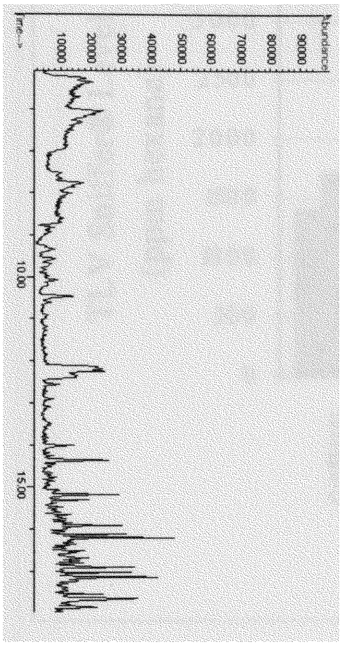


Figure 40: 10µL 10:1 diesel Zippo® spiked onto tissues not burned

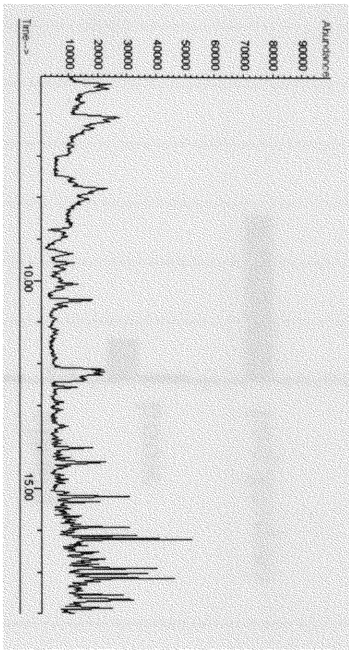
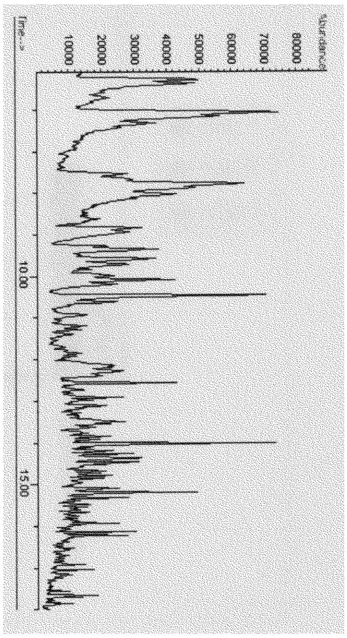


Figure 41: 50µL 10:1 diesel Zippo® spiked onto tissues not burned



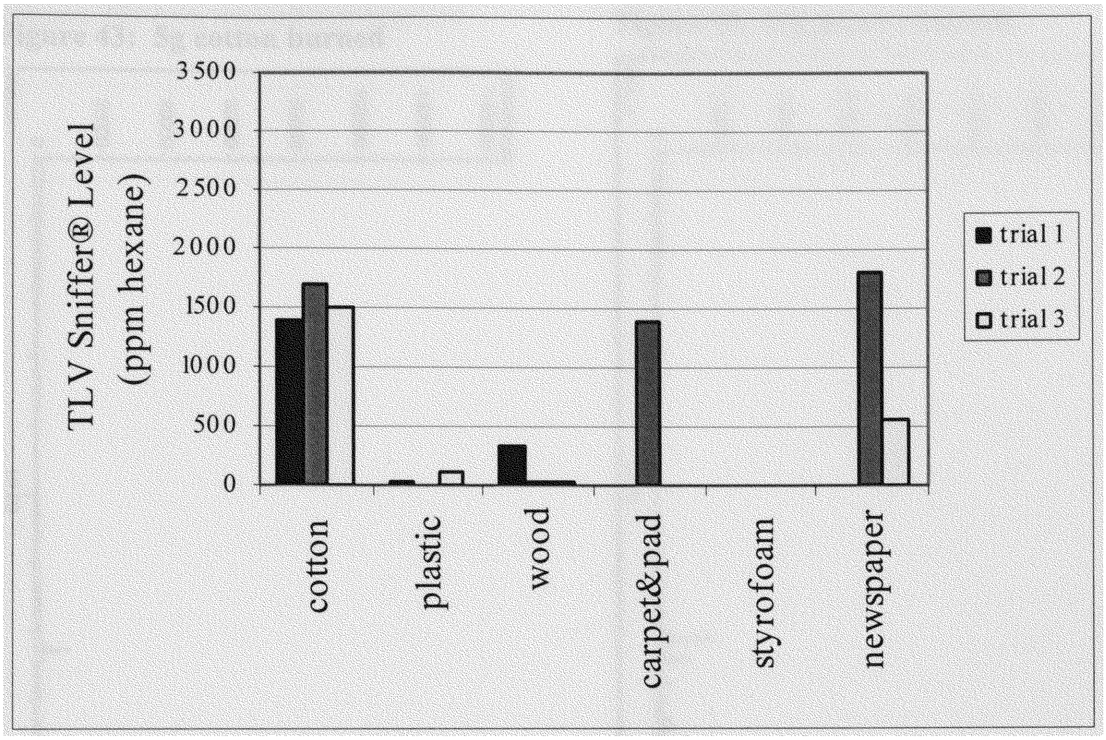


Figure 42: TLV Sniffer® levels of burned matrix with no accelerant

Figure 43: 5g cotton burned

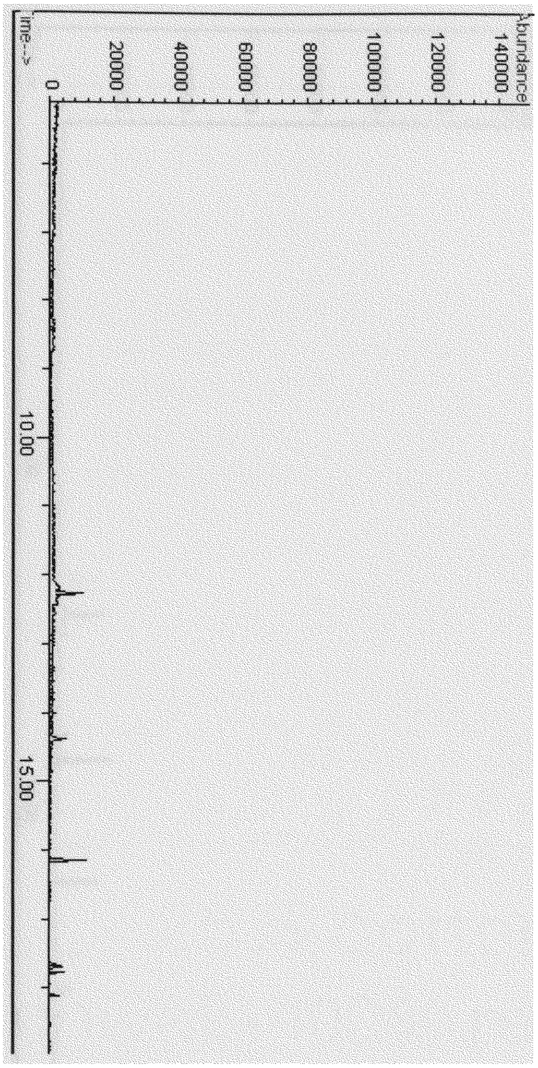


Figure 44: 15g plastic burned

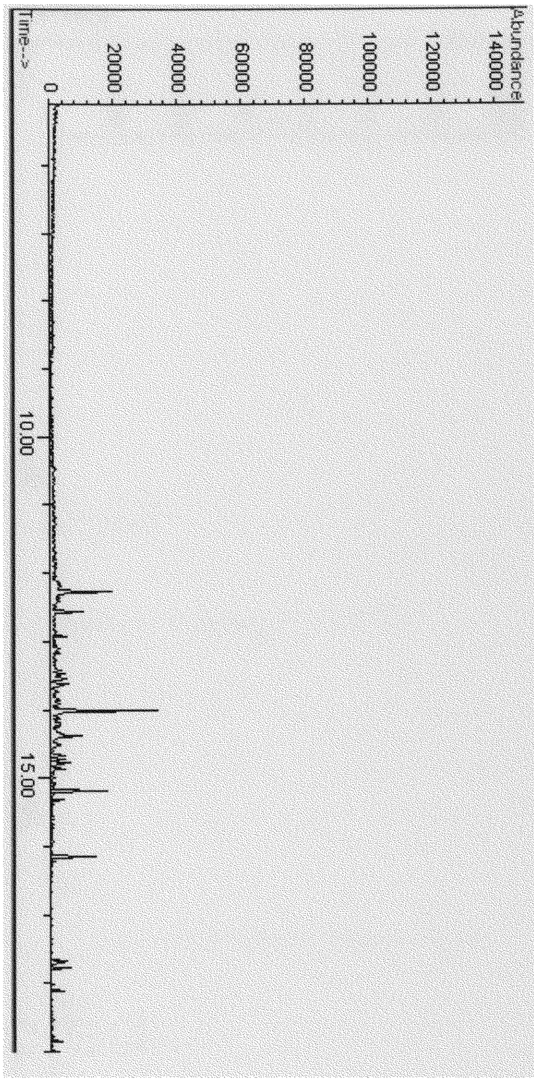


Figure 45: 1.4g Styrofoam burned

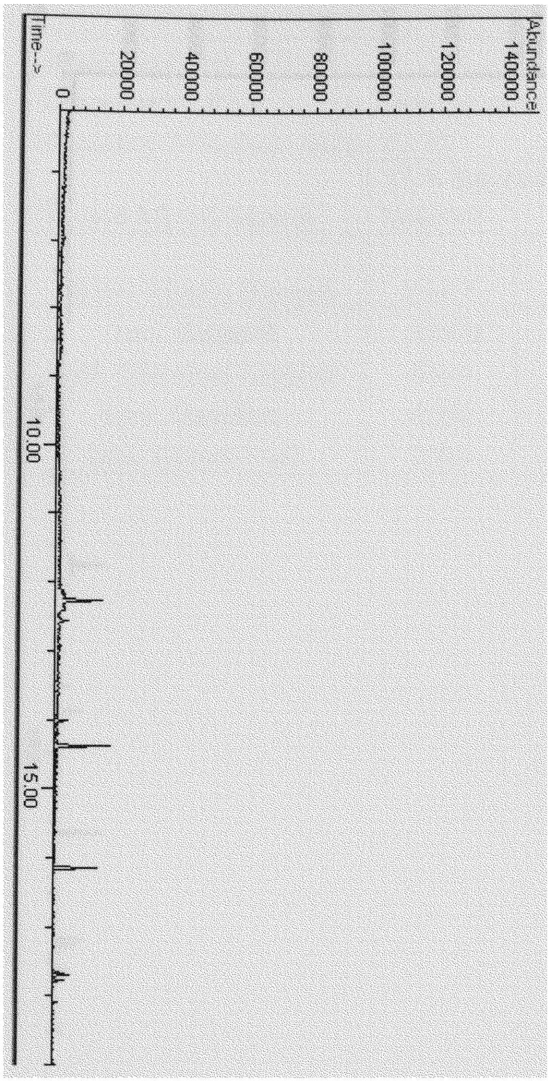


Figure 46: 10g carpet and padding burned

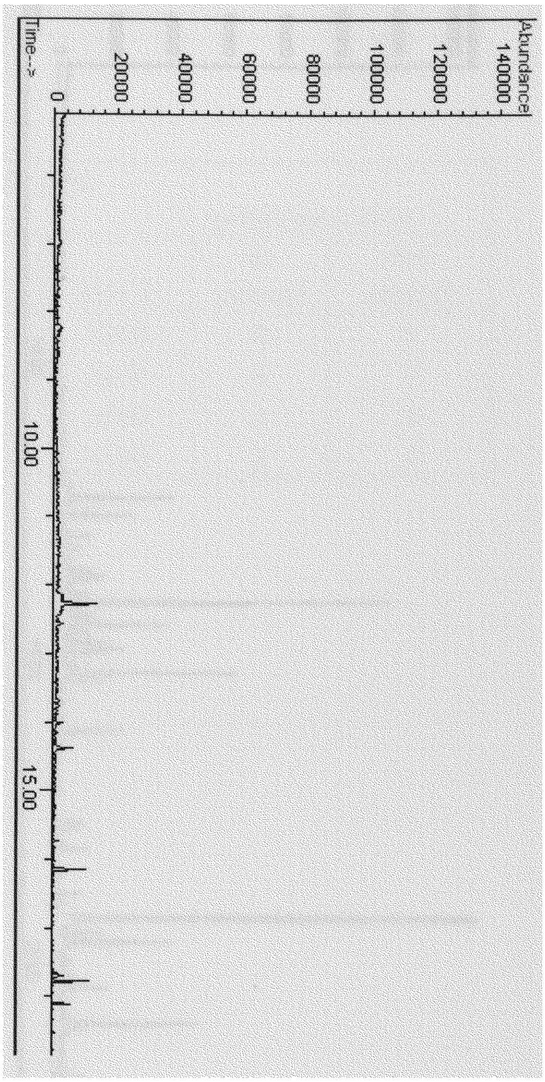


Figure 47: 20g newspaper burned

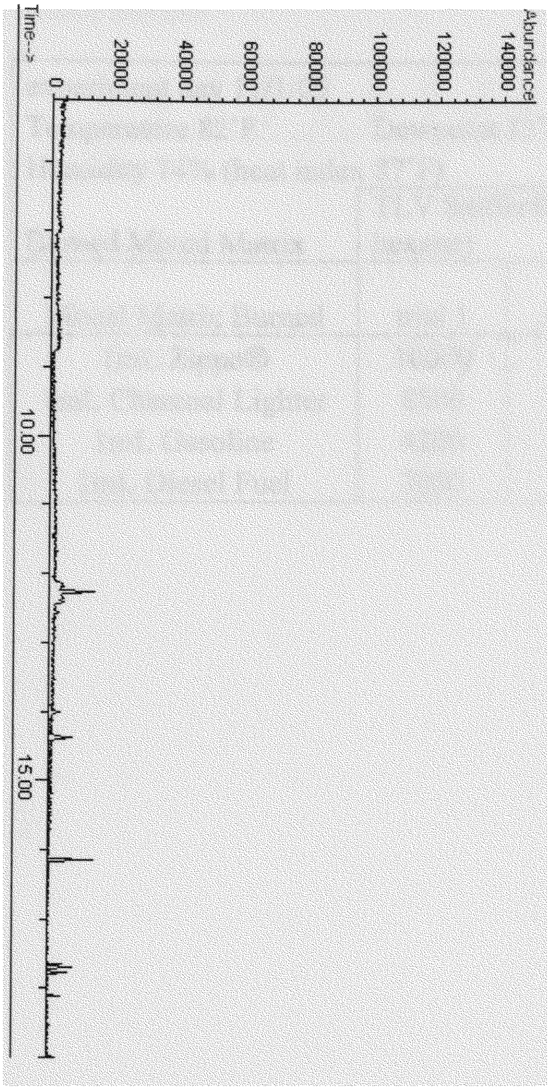


Figure 48: 52.3g wood burned

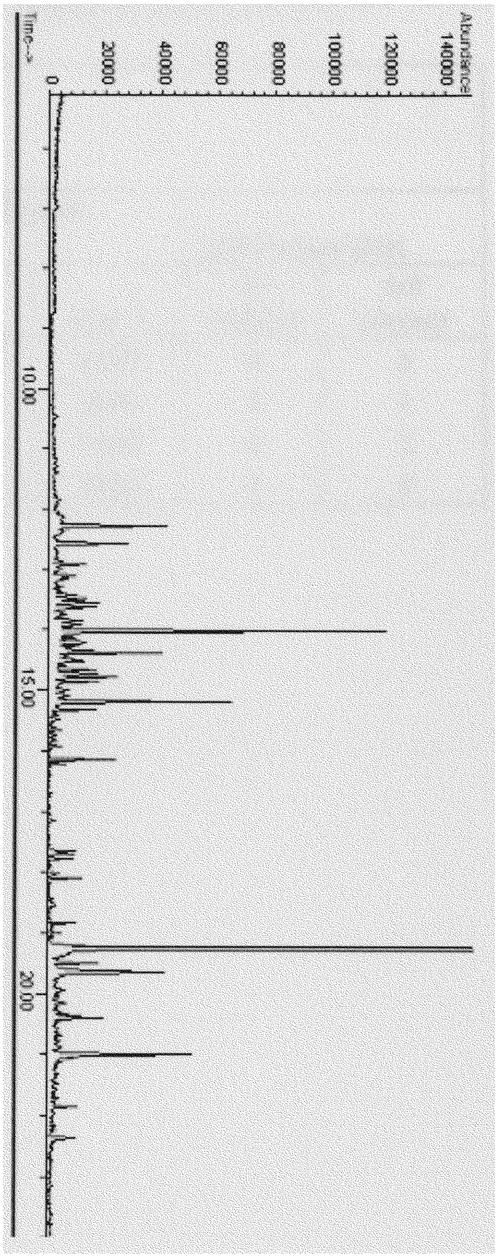


Table 24: TLV Sniffer® levels for accelerants spiked on mixed matrix and burned

experiment day 11/1/05 Temperature 82°F Dewpoint 73°F Humidity 74% (heat index 87°F)					
Burned Mixed Matrix	TLV Sniffer® Level (ppm hexane)			tpi®Pocket alert	
Mixed Matrix Burned	trial 1	trial 2	trial 3	in contact	not contact
1mL Zippo®	10000	7400	4300	4	4
1mL Charcoal Lighter	8500	3700	2600	4	3
1mL Gasoline	4200	2200	1400	4	2
1mL Diesel Fuel	7000	2900	2100	4	4

Figure 49: 1mL Zippo® spiked on tissues burned

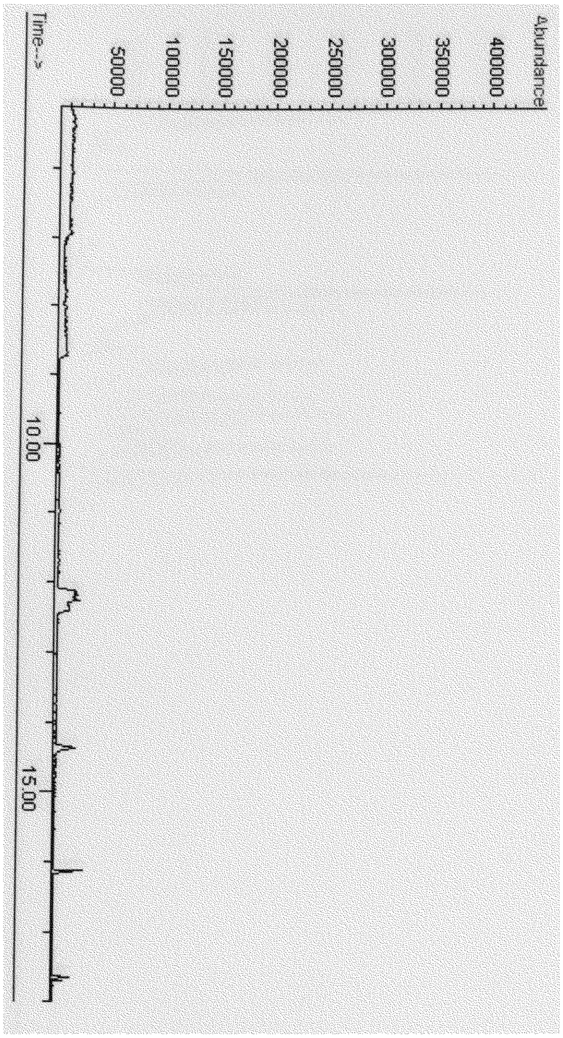


Figure 50: 1mL charcoal lighter spiked on tissues burned

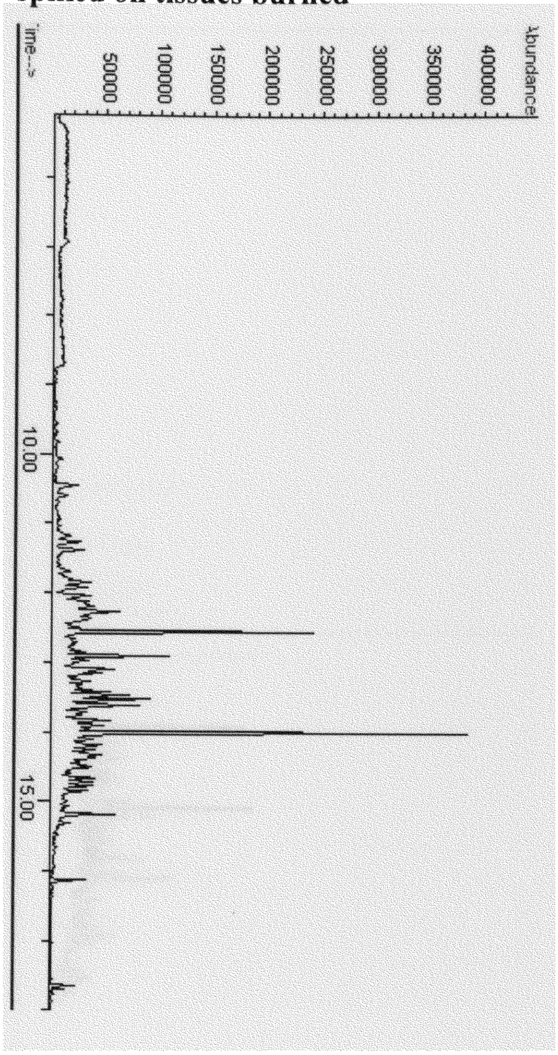


Figure 51: 1mL gasoline spiked on tissues burned

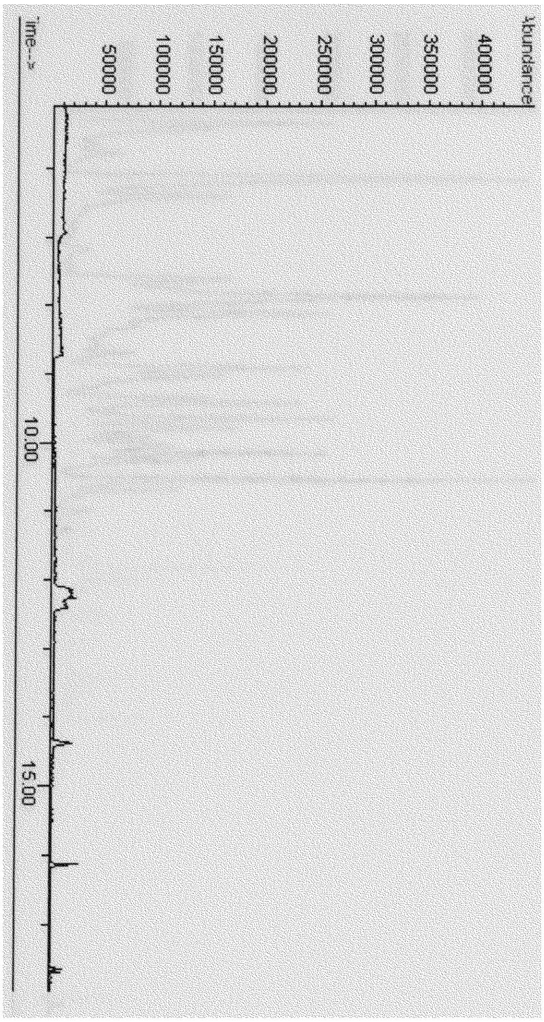


Figure 52: 1mL diesel fuel spiked on tissues burned

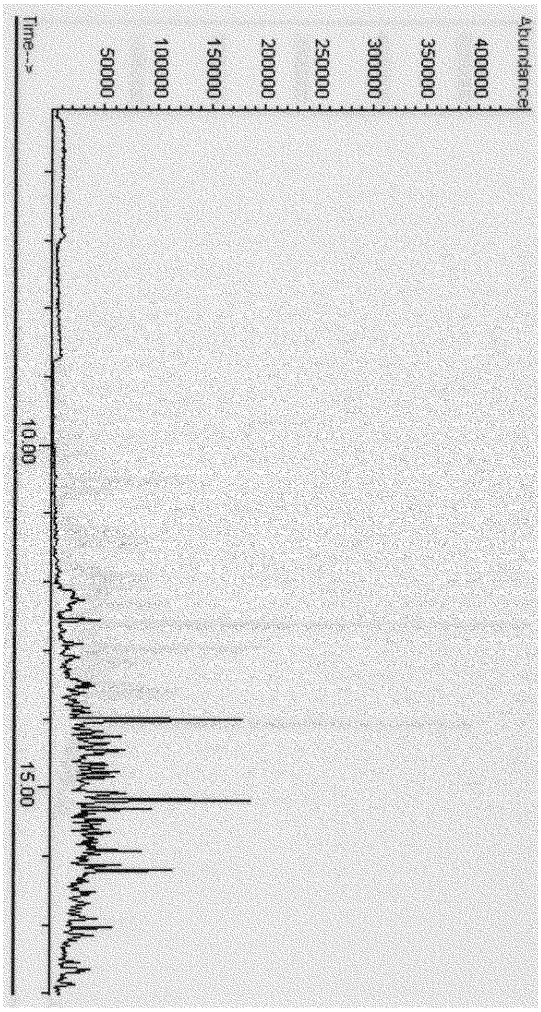


Figure 53: 1mL Zippo® spiked on mixed matrix burned

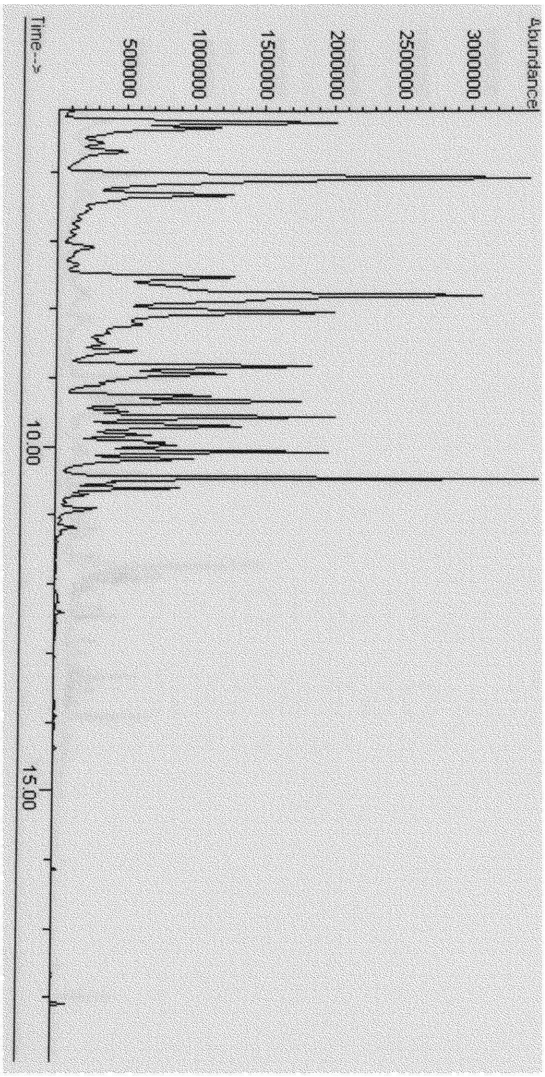


Figure 54: 1mL charcoal lighter spiked on mixed matrix burned

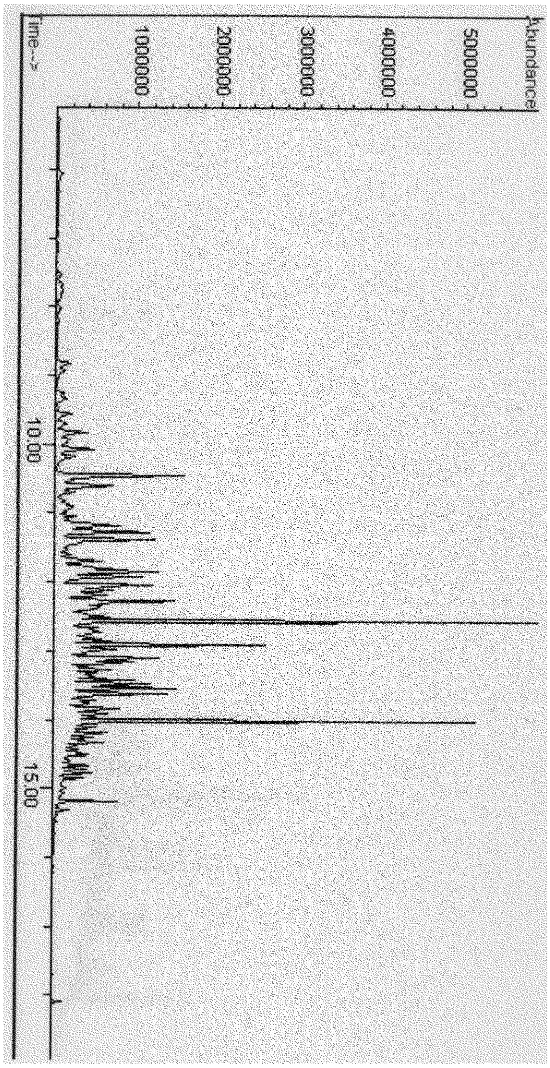


Figure 55: 1mL gasoline spiked on mixed matrix burned

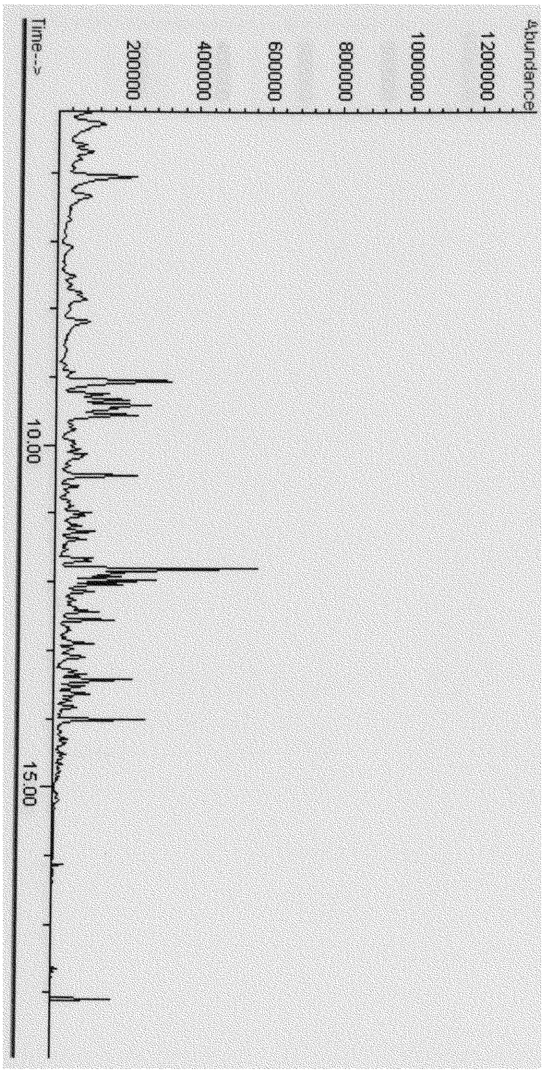


Figure 56: 1mL diesel fuel spiked on mixed matrix burned

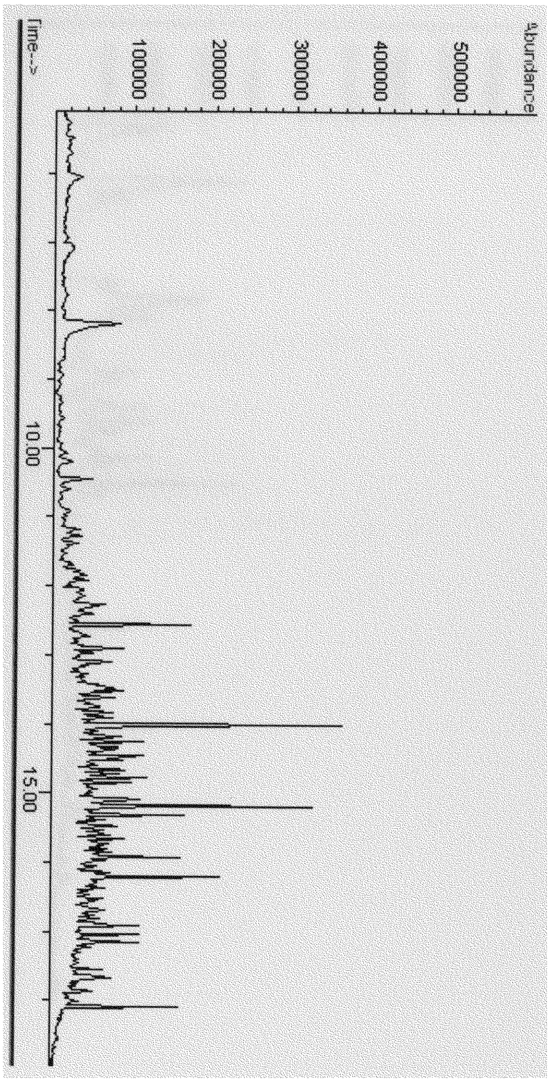


Figure 57: Asphalt with no accelerant extracted with PAS

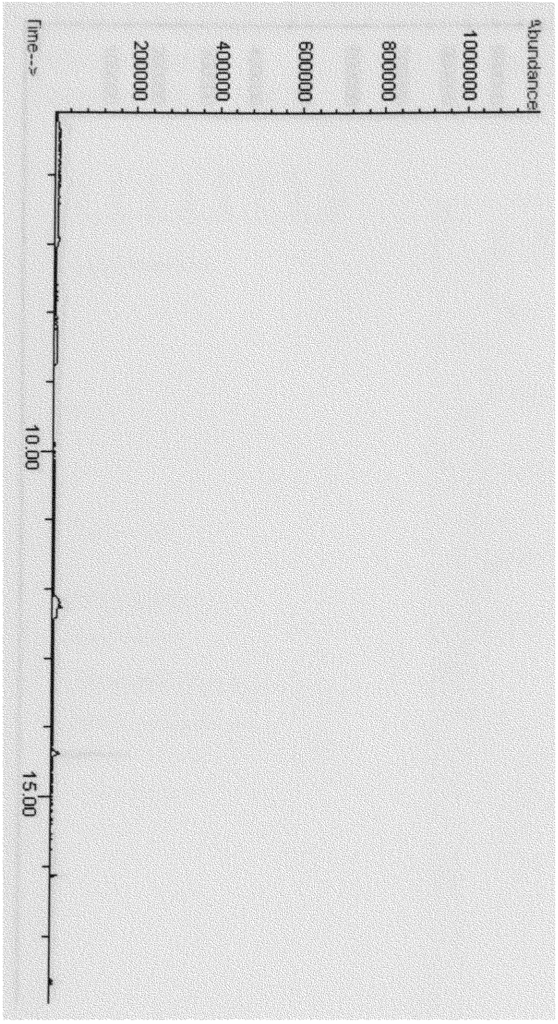


Figure 58: 1mL 10:1 diesel Zippo® spiked on asphalt not burned, PAS

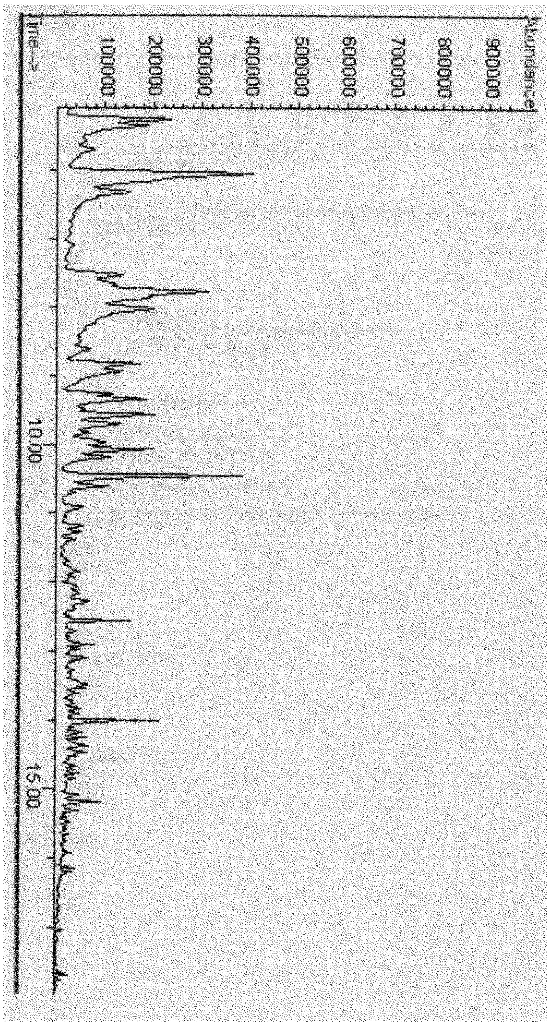


Figure 59: Concrete with no accelerant extracted with PAS

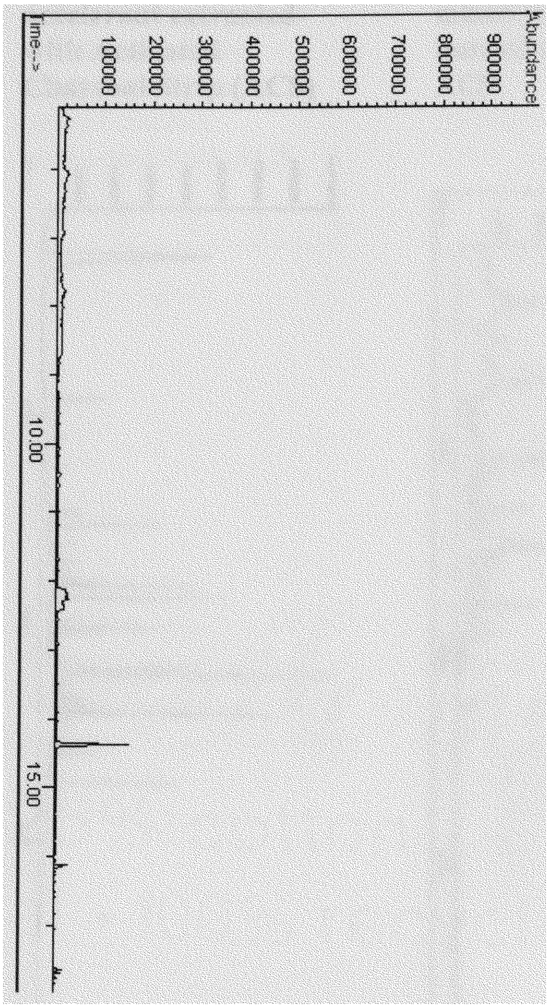
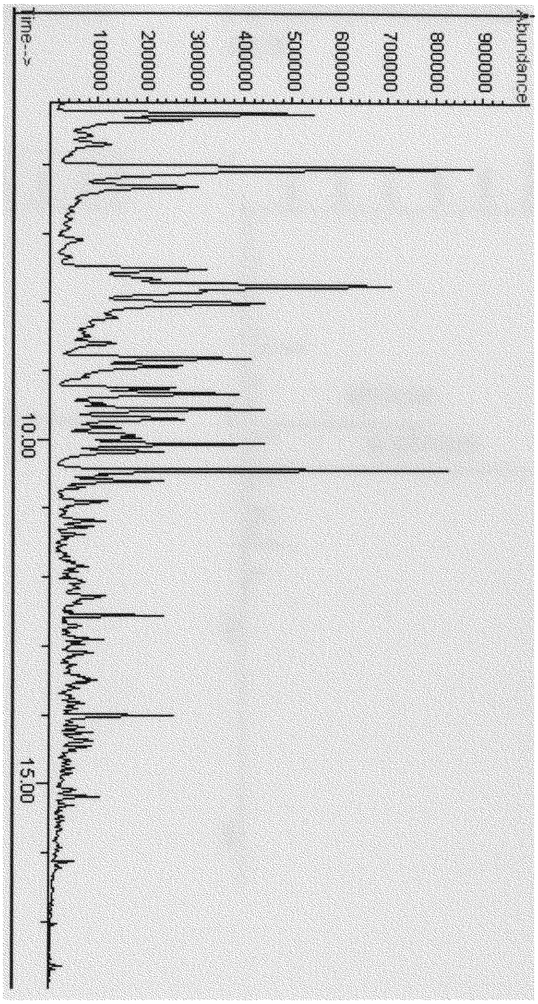


Figure 60: 1mL 10:1 diesel Zippo® spiked on concrete not burned, PAS



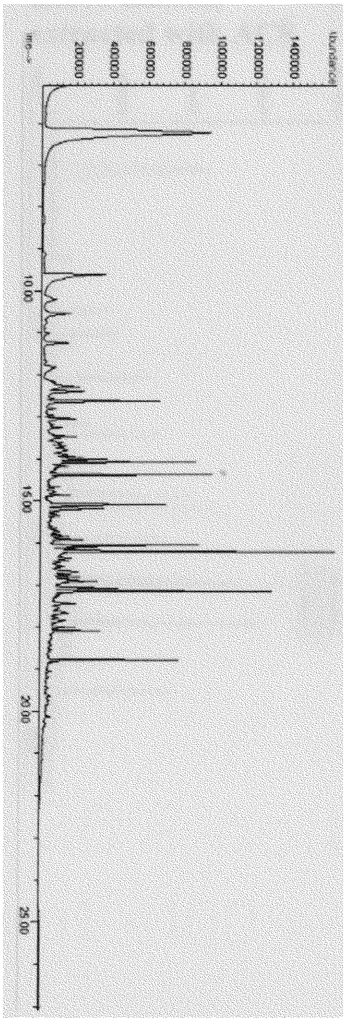


Figure 61: Mixed Matrix burned with no accelerant extracted with Activated Charcoal Strip (ACS)

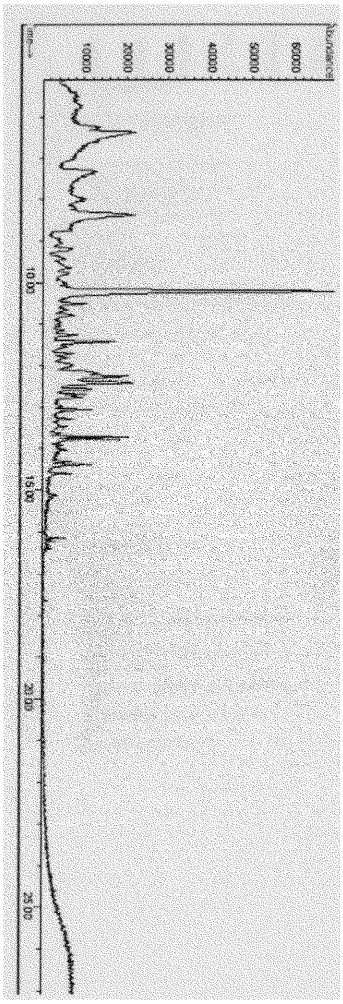


Figure 62: 5µL diesel Zippo® spiked on mixed matrix and burned extracted with ACS

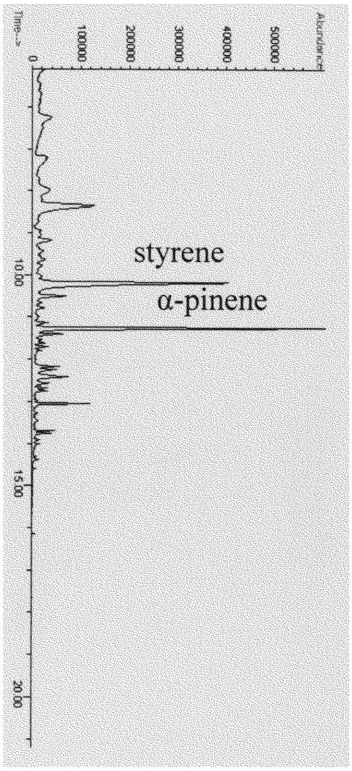


Figure 63: 50µL diesel Zippo® spiked on mixed matrix and burned extracted with ACS

Figure 64: Mixed matrix with no accelerant overlayed with 50µL diesel Zippo® spiked on mixed matrix, extracted with ACS

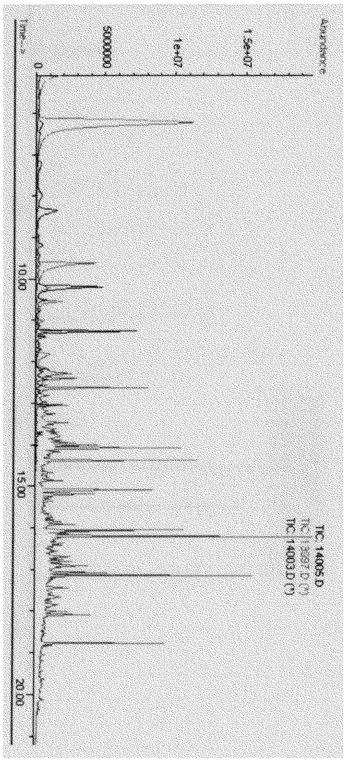


Figure 65: 500ppm 10:1 diesel Zippo® standard overlayed with 50µL diesel Zippo® spiked on mixed matrix extracted with ACS

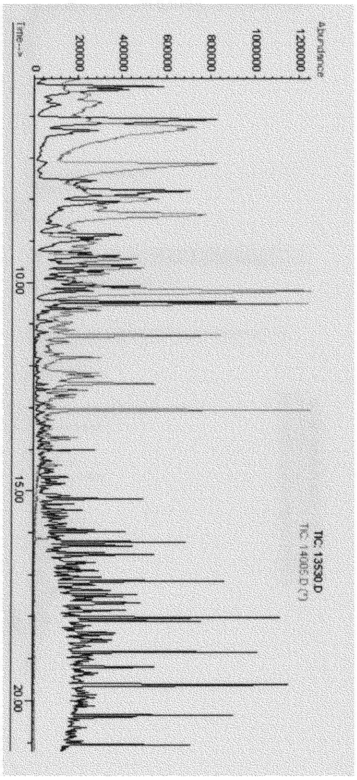


Figure 66: Mixed matrix with no accelerant extracted with ACS extracted ion alkane profile

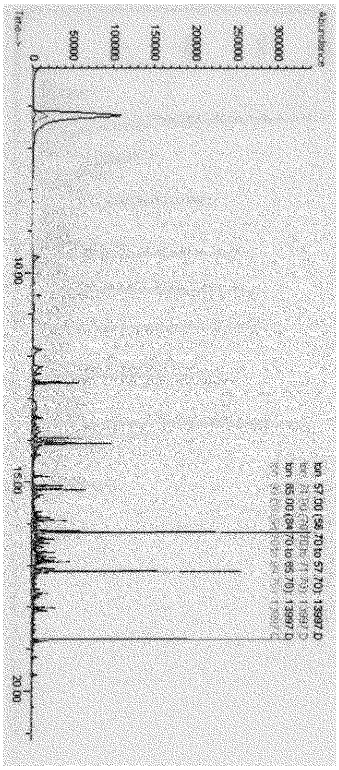


Figure 67: Mixed matrix with no accelerant extracted with ACS extracted ion aromatic profile

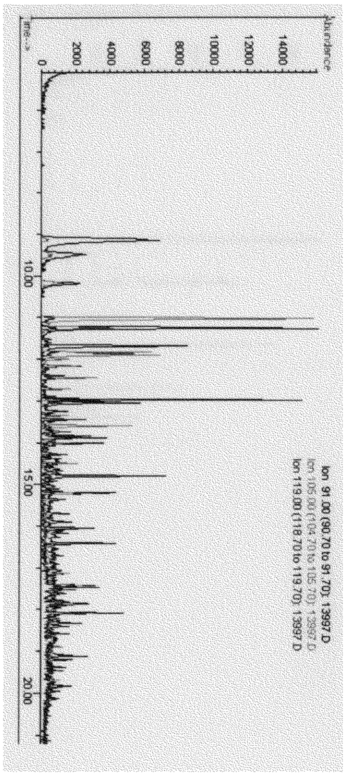


Figure 68: Mixed matrix with no accelerant extracted with ACS extracted ion cycloalkane profile

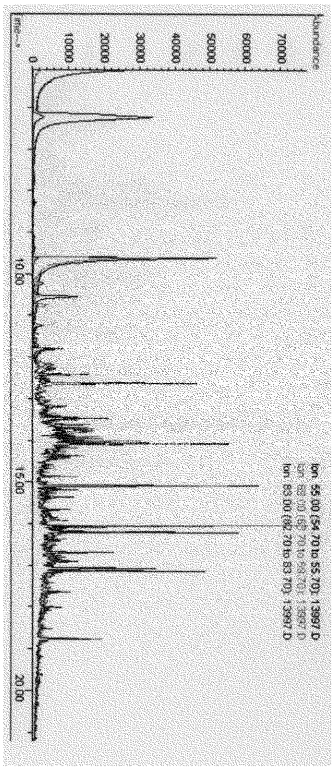


Figure 69: Mixed matrix with 5µL diesel Zippo® extracted with ACS extracted ion alkane profile

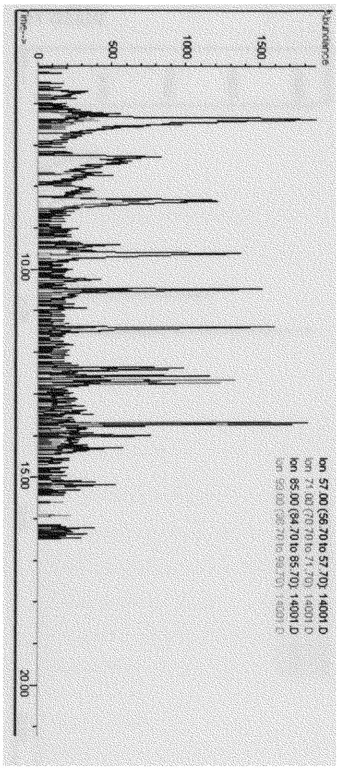


Figure 70: Mixed matrix with 5µL diesel Zippo® extracted with ACS extracted ion aromatic profile

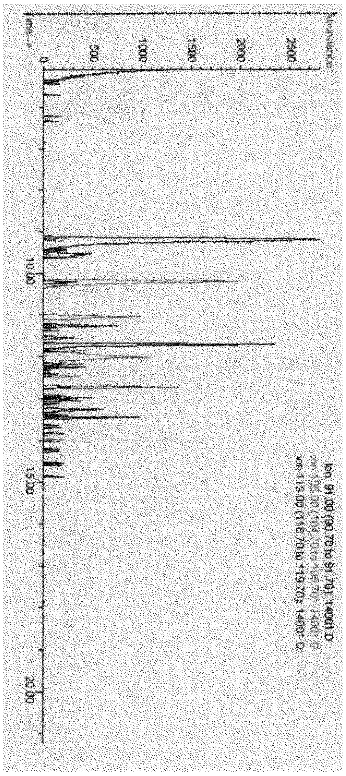


Figure 71: Mixed matrix with 5µL diesel Zippo® extracted with ACS extracted ion cycloalkane profile

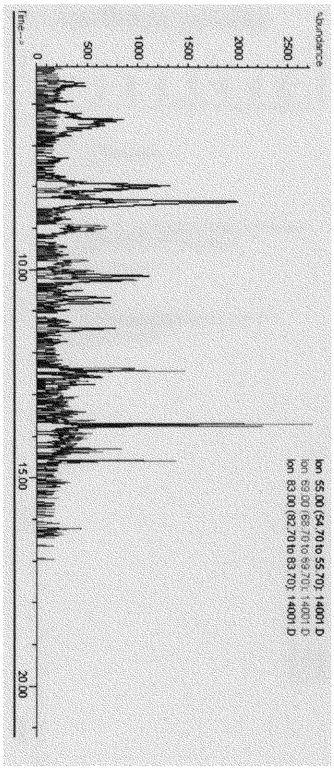


Figure 72: Mixed matrix with 50µL diesel Zippo® extracted with ACS extracted ion alkane profile

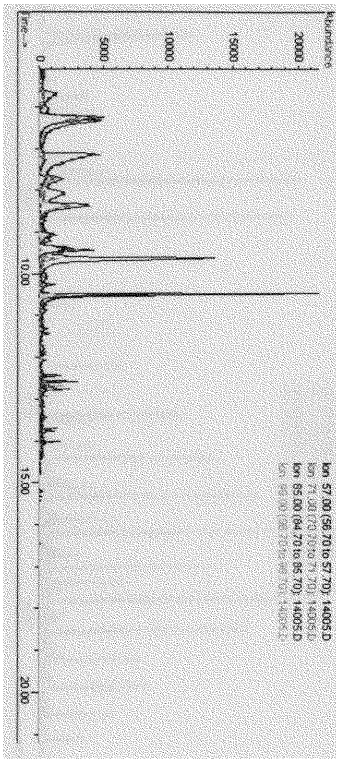


Figure 73: Mixed matrix with 50µL diesel Zippo® extracted with ACS extracted ion aromatic profile

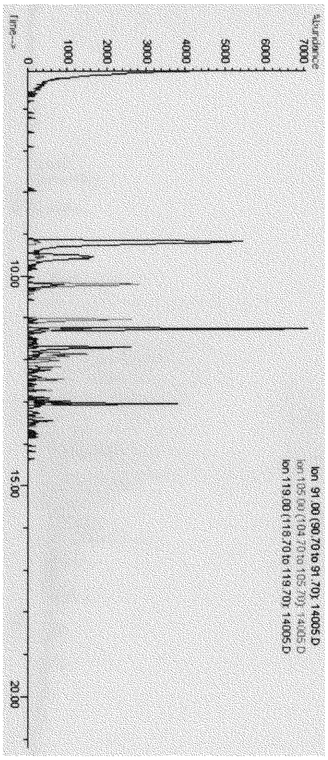


Figure 74: Mixed matrix with 50µL diesel Zippo® extracted with ACS extracted ion cycloalkane profile

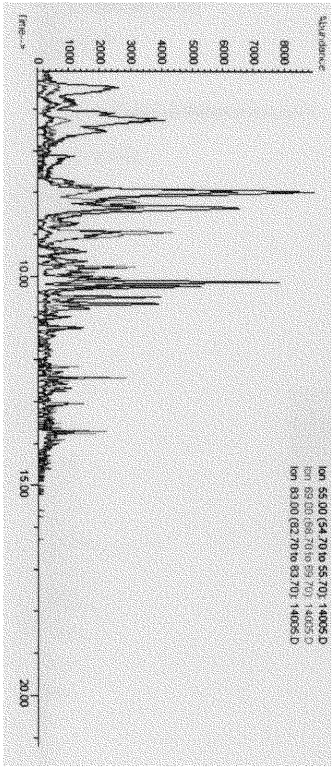


Figure 75: Diesel Zippo® standard extracted ion alkane profile

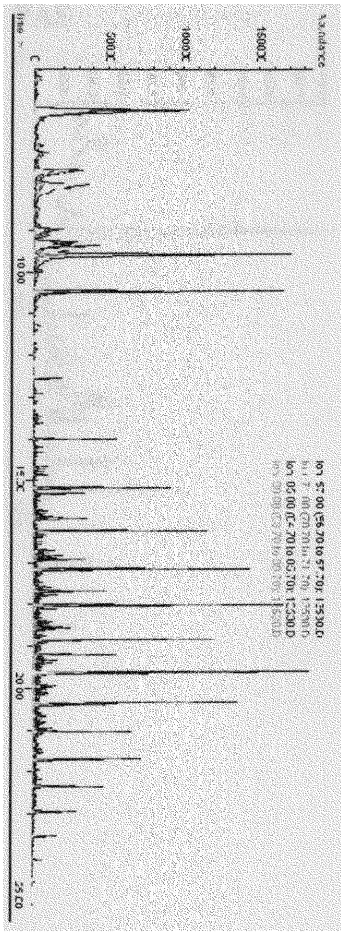


Figure 76: Diesel Zippo® standard extracted ion aromatic profile

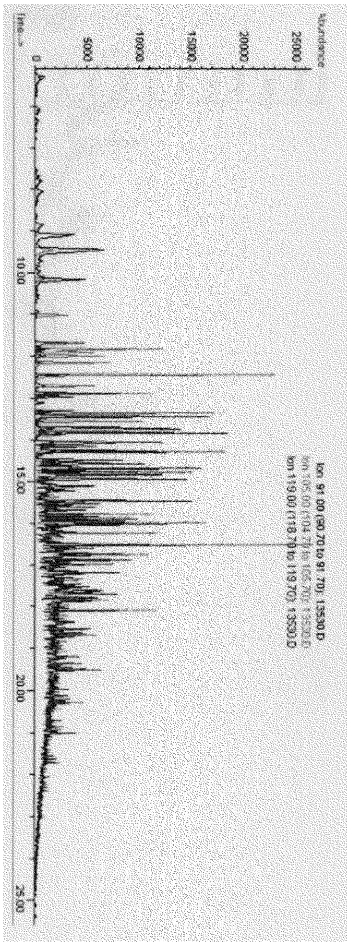


Figure 77: Diesel Zippo® standard extracted ion cycloalkane profile

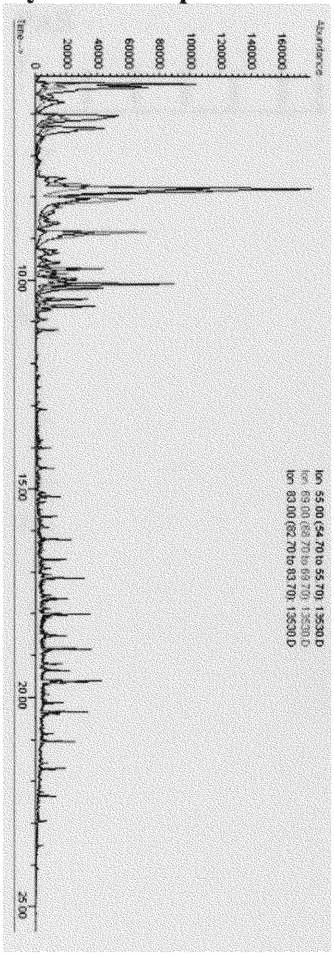


Figure 78: 5µL 10:1 diesel Zippo® spiked on mixed matrix burned extracted with PAS

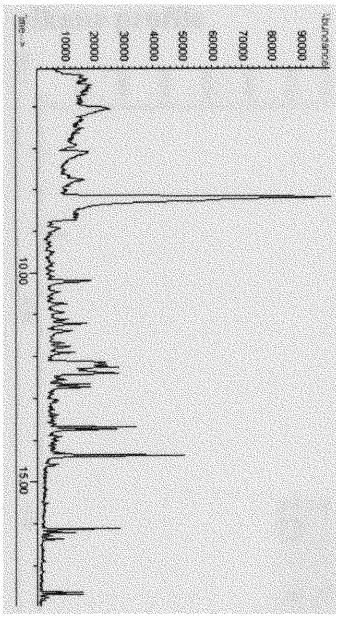


Figure 79: 50µL 10:1 diesel Zippo® spiked on mixed matrix burned extracted with PAS

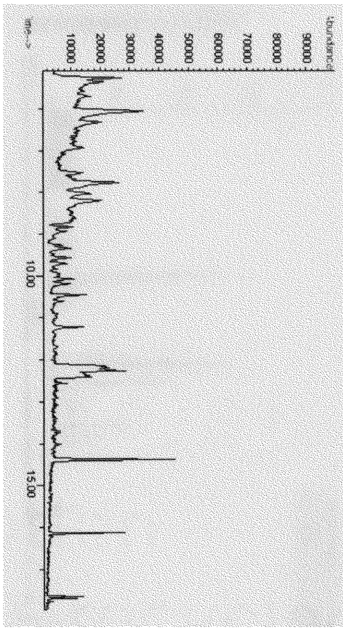


Figure 80: 50µL 10:1 diesel Zippo® spiked on mixed matrix burned extracted with PAS

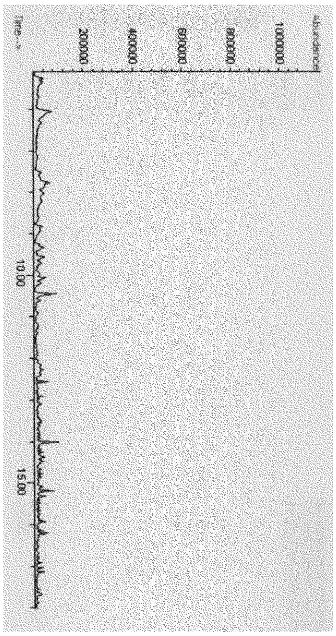


Figure 81: 5µL 10:1 diesel Zippo® spiked on mixed matrix burned extracted with PAS extracted ion alkane profile

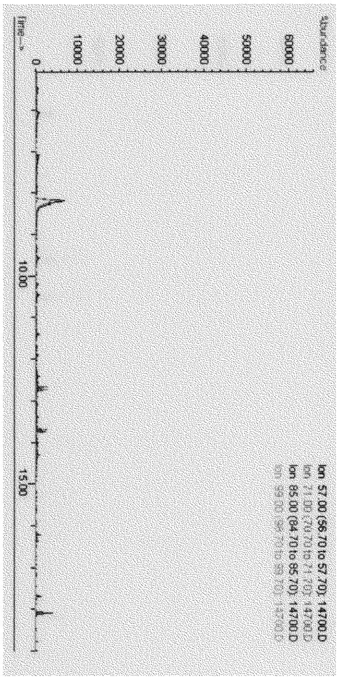


Figure 82: 5µL 10:1 diesel Zippo® spiked on mixed matrix burned extracted with PAS extracted ion aromatic profile

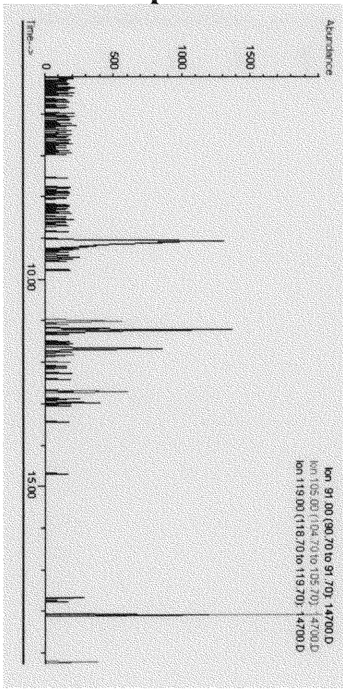


Figure 83: 5µL 10:1 diesel Zippo® spiked on mixed matrix burned extracted with PAS extracted ion cycloalkane profile

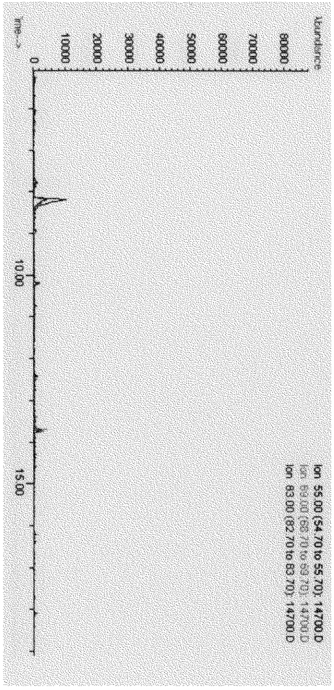


Figure 84: 50μL 10:1 diesel Zippo® spiked on mixed matrix burned extracted with PAS extracted ion alkane profile

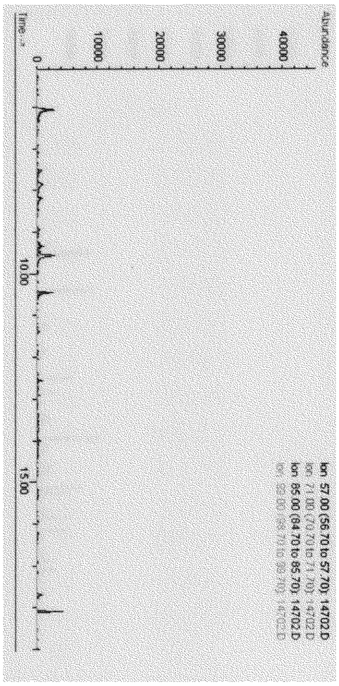


Figure 85: 50μL 10:1 diesel Zippo® spiked on mixed matrix burned extracted with PAS extracted ion aromatic profile

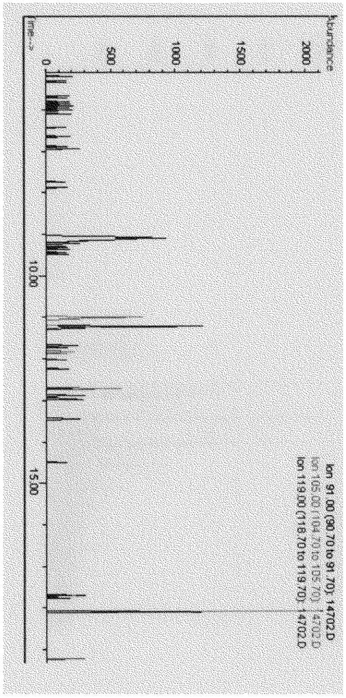


Figure 86: 50μL 10:1 diesel Zippo® spiked on mixed matrix burned extracted with PAS extracted ion cycloalkane profile

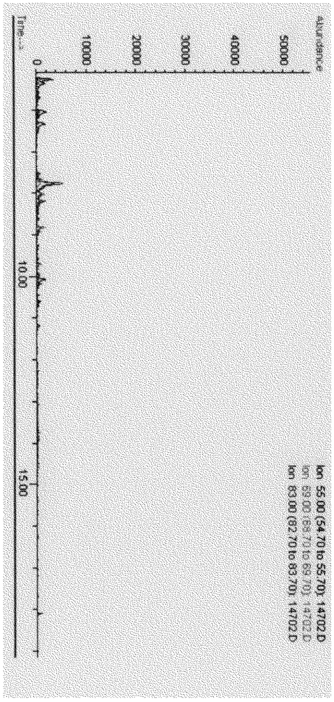


Figure 87: 500µL 10:1 diesel Zippo® spiked on mixed matrix burned extracted with PAS extracted ion alkane profile

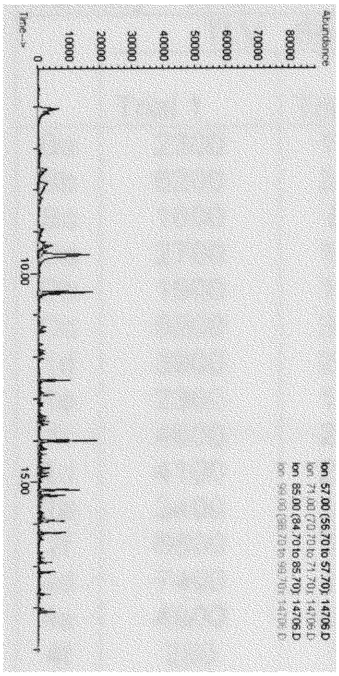


Figure 88: 500µL 10:1 diesel Zippo® spiked on mixed matrix burned extracted with PAS extracted ion aromatic profile

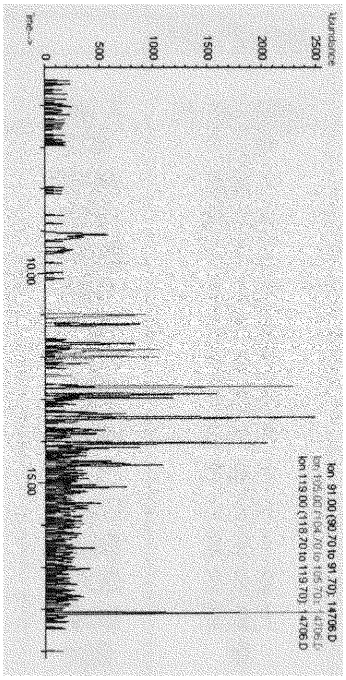


Figure 89: 500µL 10:1 diesel Zippo® spiked on mixed matrix burned extracted with PAS extracted ion cycloalkane profile

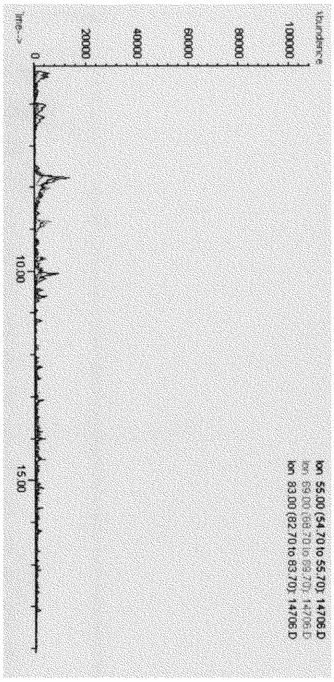


Table 25: TLV Sniffer® levels and tpi®Pocket levels for samples stored in cans over time: Week 0

Week Zero Burned 9/6/05 T= 87°F humidity = 78%					
	TLV Sniffer			Tpi Pocket	
	Trial 1	Trial 2	Trial 3	in contact	not in contact
Ba	2300	1500	670	1,1,0	na
Bb	6200	3500	2000	3,2,1	1,0,0
Bc	1600	860	570	0,1,0	0
Oa	2700	1600	1000	1,1,1	0
Ob	1900	1000	590	1,1,0	0
Oc	5200	3200	1800	1,1,1	0
1d	3900	2300	1300	1,1,1	0
1e	2300	1200	890	1,0,0	0
1f	4600	2500	2000	1,1,1	0
2d	4100	2900	1400	1,0,1	0
2e	3400	1900	1100	1,1,1	0
2f	6600	3900	2600	2,2,1	0
4d	7400	4700	2700	3,3,2	1,1,1
4e	4900	2600	2000	2,2,1	0
4f	280	150	100	0	0
6d	6500	3300	2200	2,1,1	0
6e	8400	4700	3400	3,3,1	0
6f	3700	2300	1200	1,1,1	0
8d	2100	1300	750	1,0,0	0
8e	2400	1200	600	1,0,0	0
8f	6300	4100	2100	3,1,1	0

Table 26: TLV Sniffer® levels for samples stored in cans over time: week 1

Week One Date 9/21/05 Temperature = 87°F index=103°F humidity = 80% dewpoint = 80°F			
	TLV		
	Trial 1	Trial 2	Trial 3
Ba	0	0	0
Bb	14	4	4
Bc	4	2	0
Oa	2	0	0
Ob	2	0	1
Oc	9	4	3

Table 27: TLV Sniffer® levels for samples stored in cans over time: week 2

Week Two Date 9/27/05 temp = 87°F index= 96°F humidity = 67% dewpoint = 75°F			
	TLV		
	Trial 1	Trial 2	Trial 3
Ba	0	0	0
Bb	13	9	4
Bc	3	1	0
Oa	1	0	0
Ob	1	0	0
Oc	2	0	1
2a	42	32	22
2b	82	43	24
2c	100	73	55

Table 28: TLV Sniffer® levels for samples stored in cans over time: week 3

Week Three date 10/4/05 temp = 83°F index=95°F humidity = 91% dewpoint = 80°F			
	TLV		
	Trial 1	Trial 2	Trial 3
Ba	20	12	0
Bb	8	7	4
Bc	3	2	2
Oa	1	2	1
Ob	0	2	1
Oc	1	3	2
3a	170	100	62
3b	110	53	33
3c	200	94	34

Table 29: TLV Sniffer® levels for samples stored in cans over time: week 4

Week Four date 10/11/05 temp = 83°F index=95°F humidity = 91% dewpoint = 80°F			
	TLV		
	Trial 1	Trial 2	Trial 3
Ba	1	0	0
Bb	0	1	1
Bc	1	1	1
Oa	0	0	1
Ob	0	0	0
Oc	1	1	1
4a	12	8	2
4b	120	89	65
4c	18	12	6

Figure 90: Storage time in cans, week 0, sample Ba

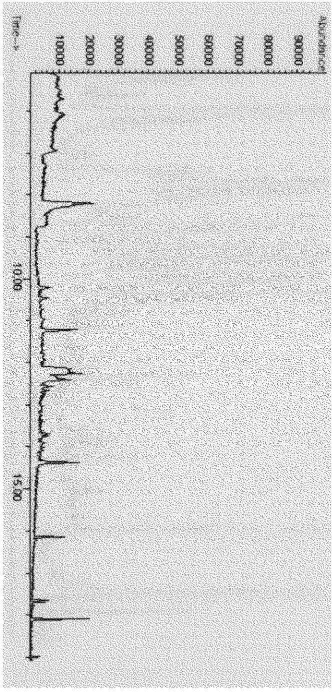


Figure 91: Storage time in cans, week 0, sample Bb

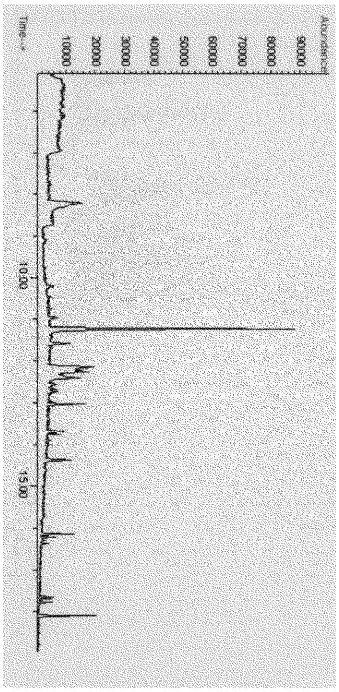


Figure 92: Storage time in cans, week 0, sample Bc

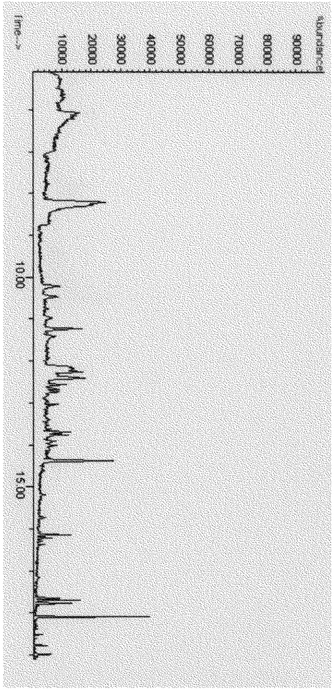


Figure 93: Storage time in cans, week 0, sample 0a

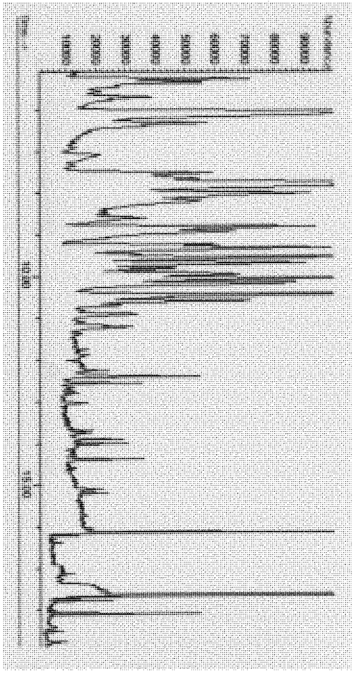


Figure 94: Storage time in cans, week 1, sample 1a

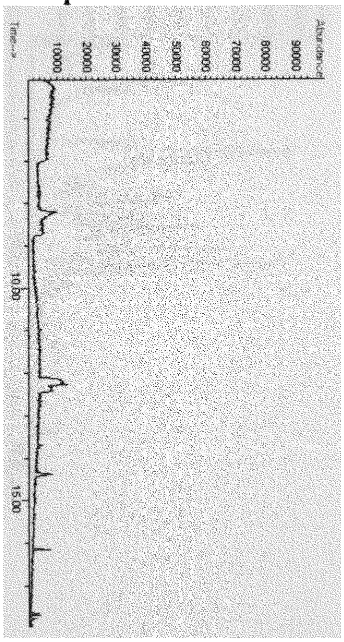


Figure 95: Storage time in cans, week 0, sample 0b

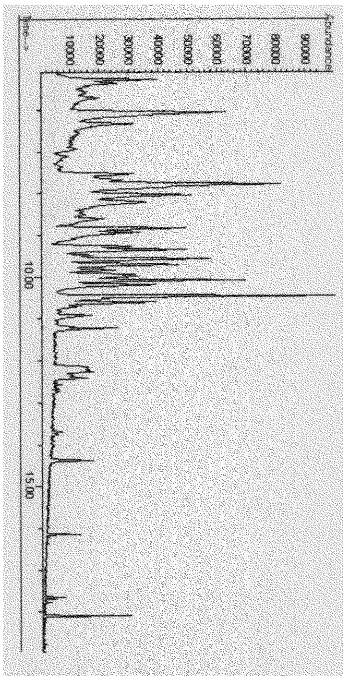


Figure 96: Storage time in cans, week 1, sample 1b

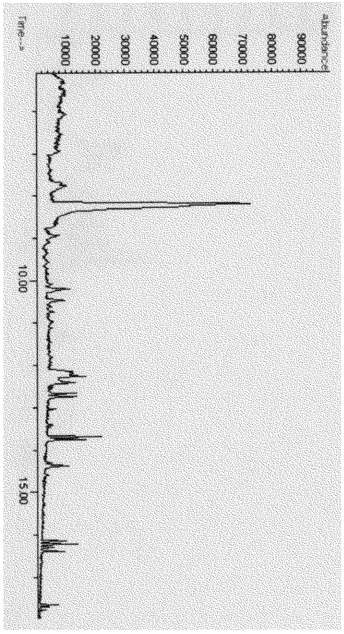


Figure 97: Storage time in cans, week 0, sample 0c

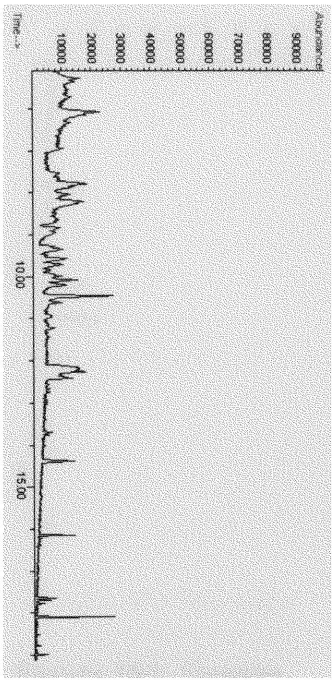


Figure 98: Storage time in cans, week 1, sample 1c

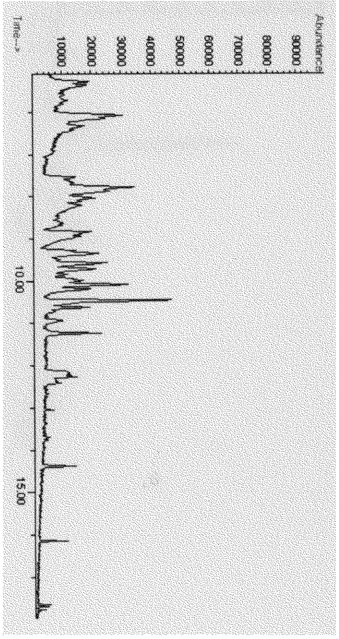


Figure 99: Storage time in cans, week 2, sample 2a

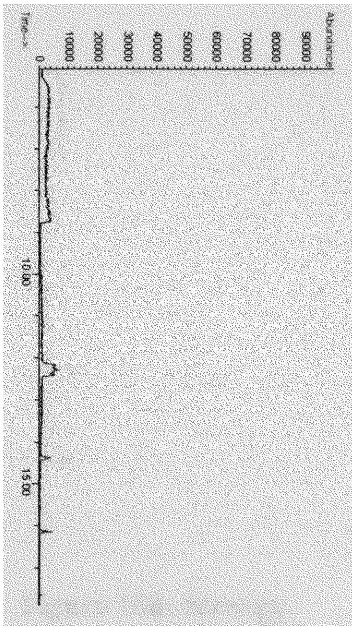


Figure 100: Storage time in cans, week 3, sample 3a

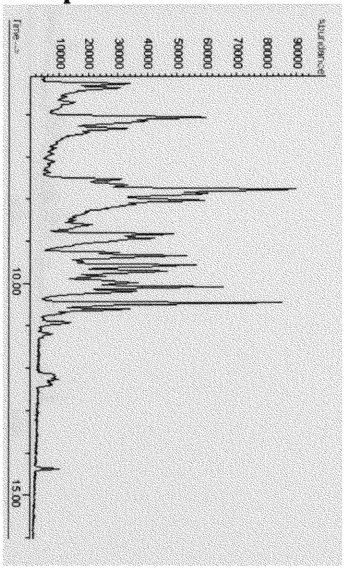


Figure 101: Storage time in cans, week 2, sample 2b

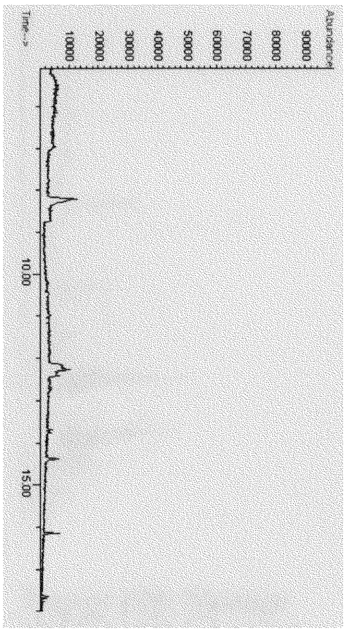


Figure 102: Storage time in cans, week 3, sample 3b

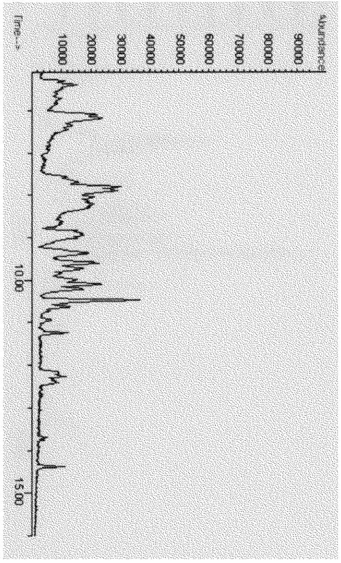


Figure 103: Storage time in cans, week 2, sample 2c

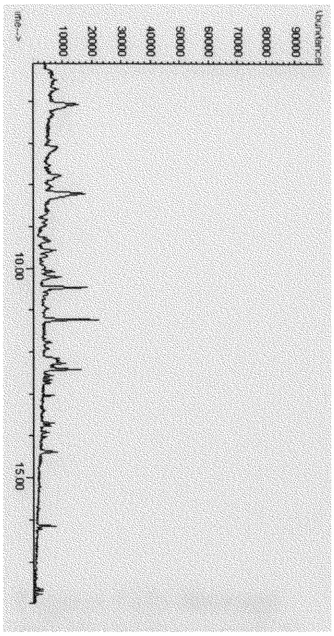


Figure 104: Storage time in cans, week 3, sample 3c

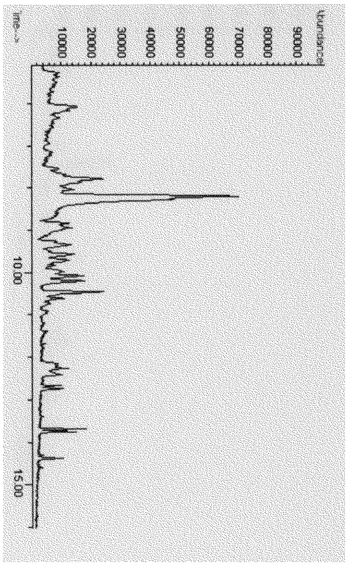


Figure 105: Storage time in cans, week 4, sample 4a

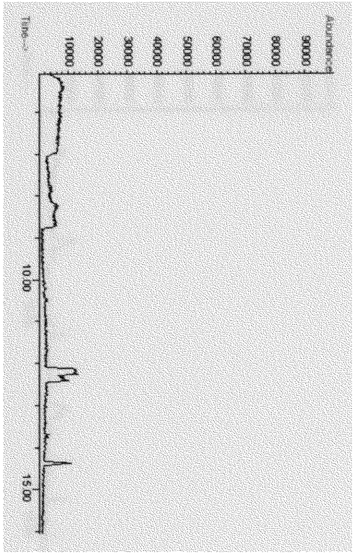


Figure 106: Storage time in tubes, week 1, sample 1d

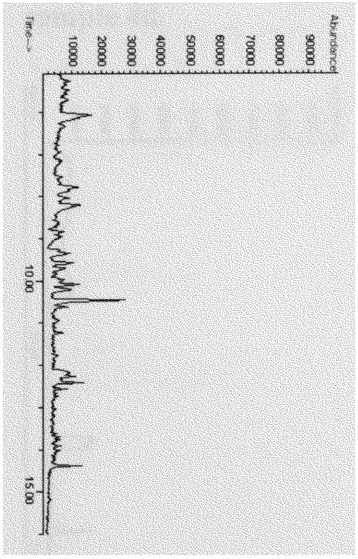


Figure 107: Storage time in cans, week 4, sample 4b

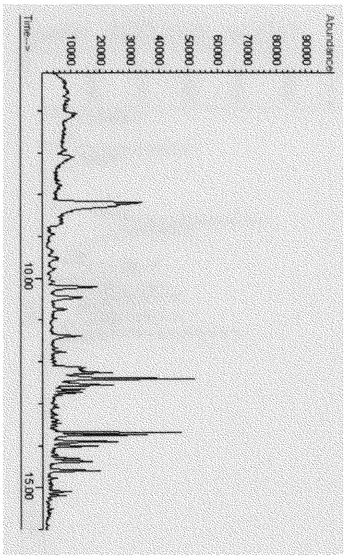


Figure 108: Storage time in tubes, week 1, sample 1e

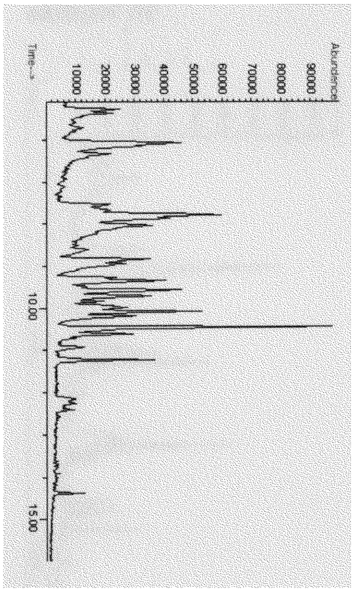


Figure 109: Storage time in cans, week 4, sample 4c

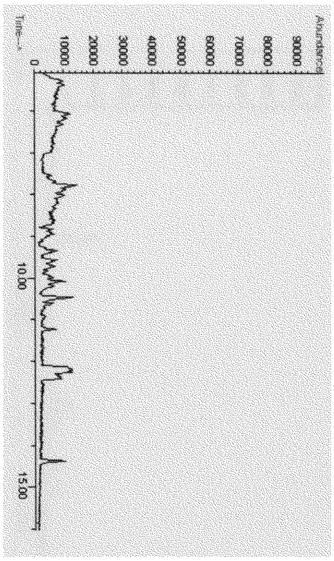


Figure 110: Storage time in tubes, week 1, sample 1f

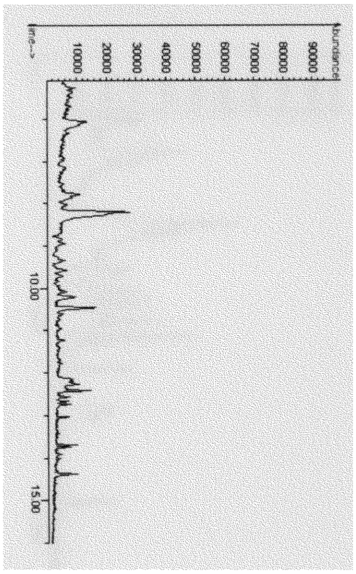


Figure 111: Storage time in tubes, week 2, sample 2d

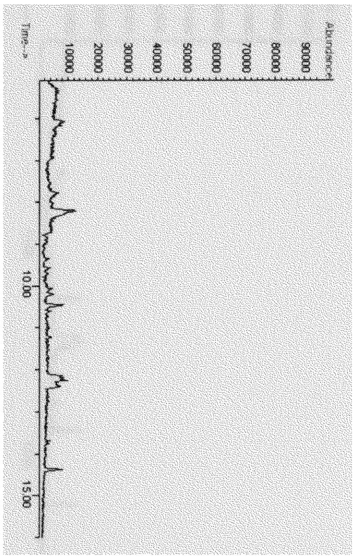


Figure 112: Storage time in tubes, week 4, sample 4d

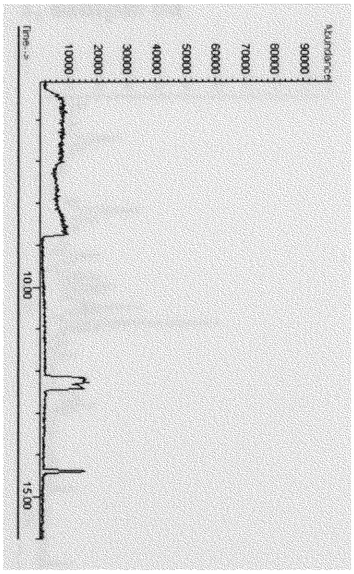


Figure 113: Storage time in tubes, week 2, sample 2e

(note: different scale)

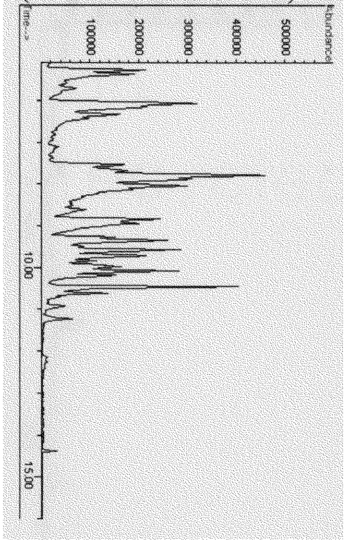


Figure 114: Storage time in tubes, week 4, sample 4e

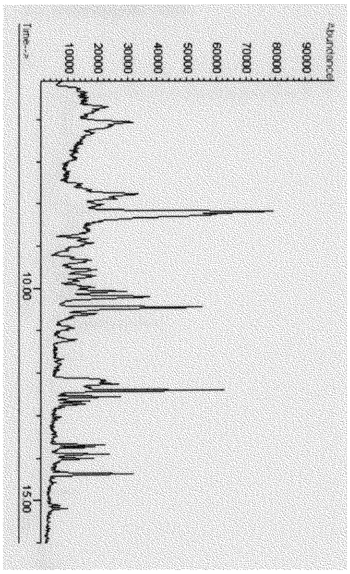


Figure 115: Storage time in tubes, week 2, sample 2f

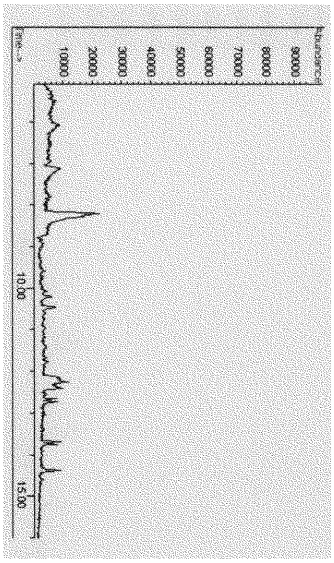


Figure 116: Storage time in tubes, week 4, sample 4f

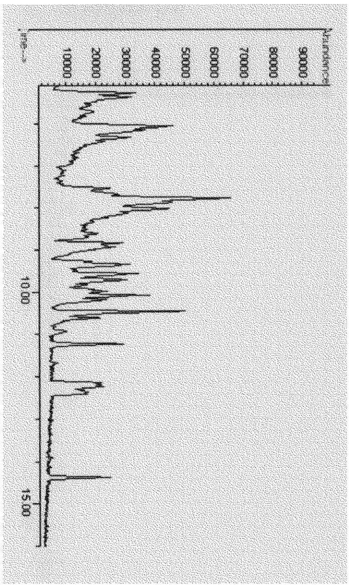


Figure 117:
Resampled cans, week 1, sample Ba

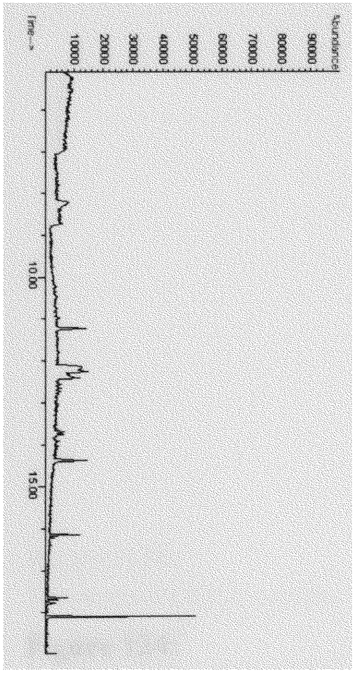


Figure 118:
Resampled cans, week 1, sample 0a

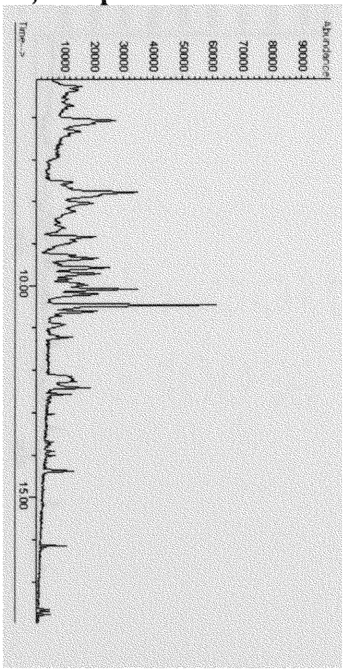


Figure 119:
Resampled cans, week 1, sample Bb

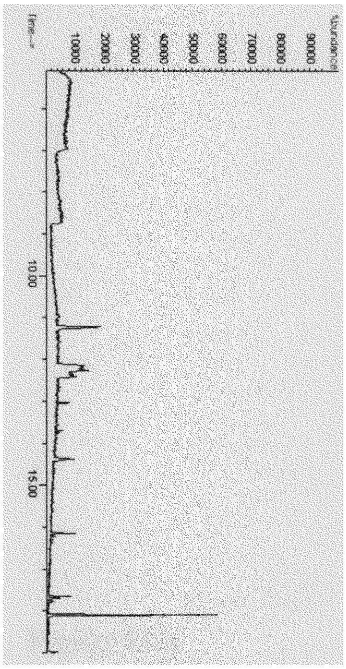


Figure 120:
Resampled cans, week 1, sample 0b

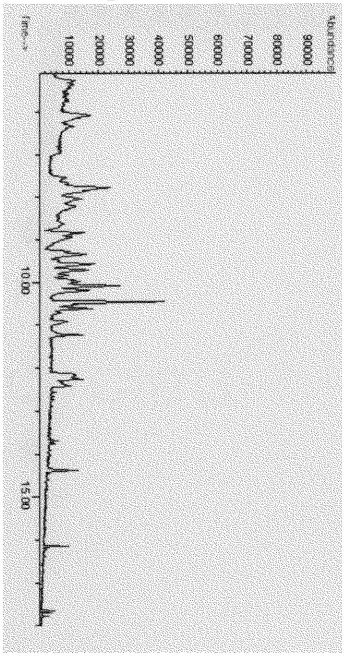


Figure 121:
Resampled cans, week 1, sample Bc

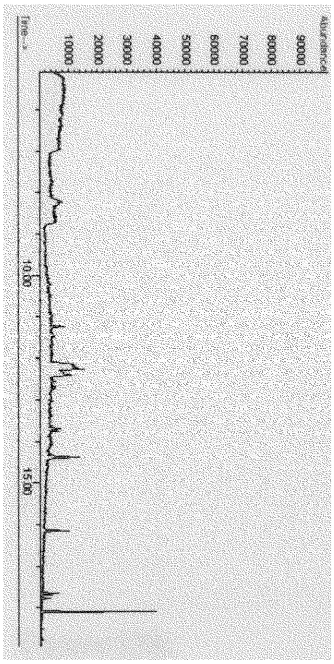


Figure 122:
Resampled cans, week 1, sample 0c

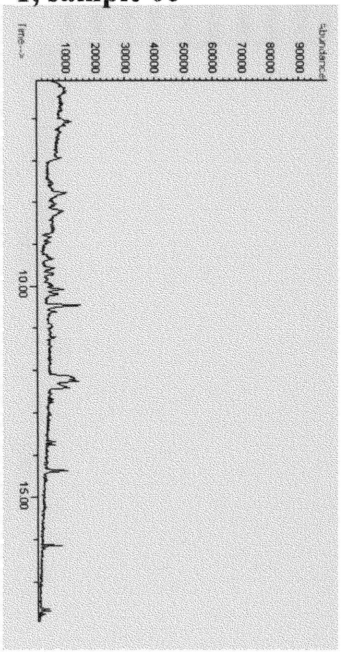


Figure 123: Resampled cans, week 2, sample Ba

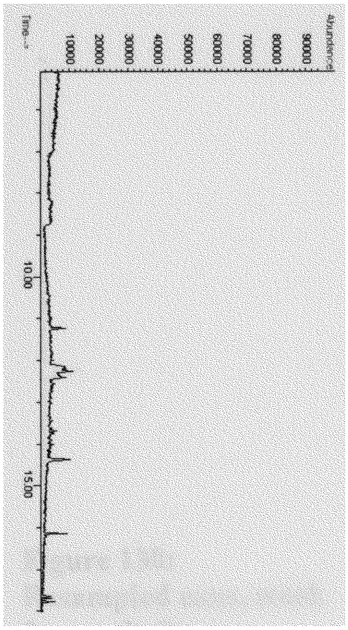


Figure 124: Resampled cans, week 2, sample 0a

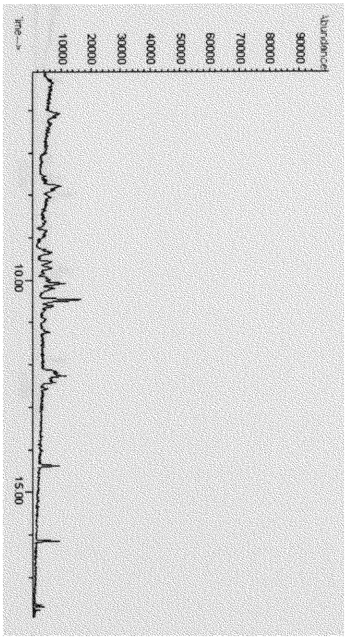


Figure 125: Resampled cans, week 2, sample Bb

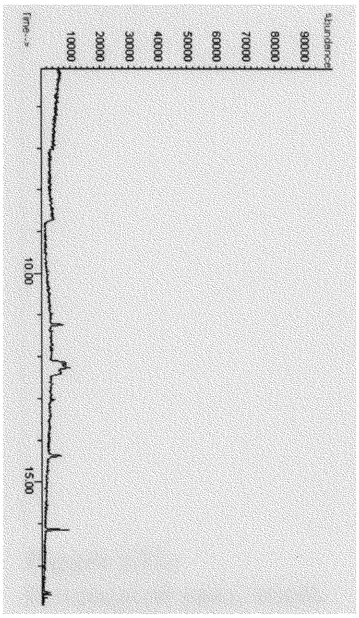


Figure 126: Resampled cans, week 2, sample 0b

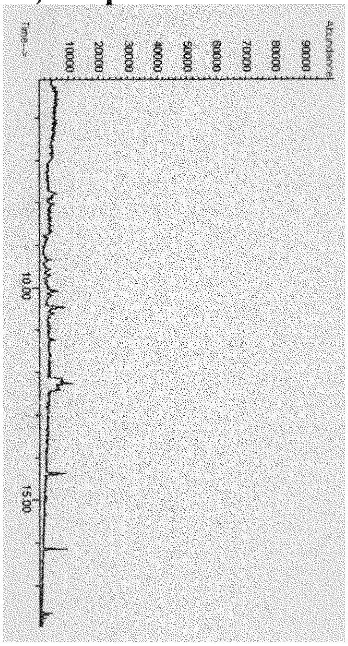


Figure 127: Resampled cans, week 2, sample Bc

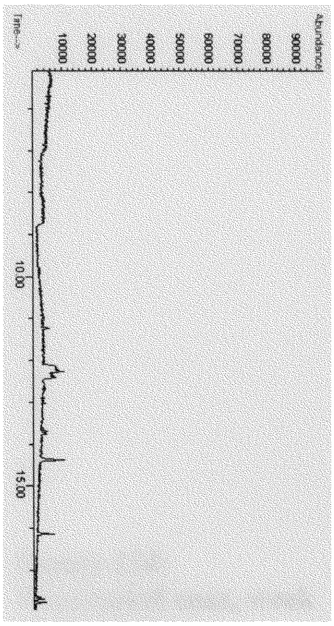


Figure 128: Resampled cans, week 2, sample 0c

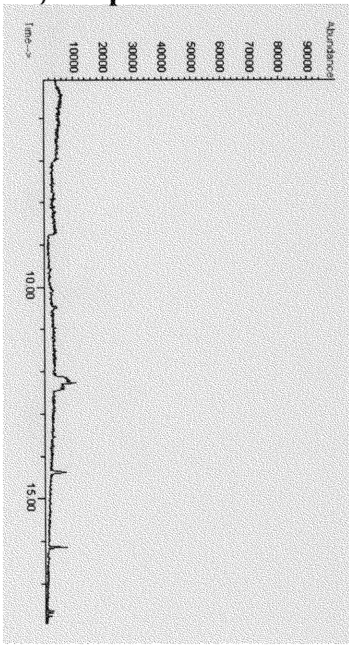


Figure 129:
Resampled cans, week 3, sample Ba

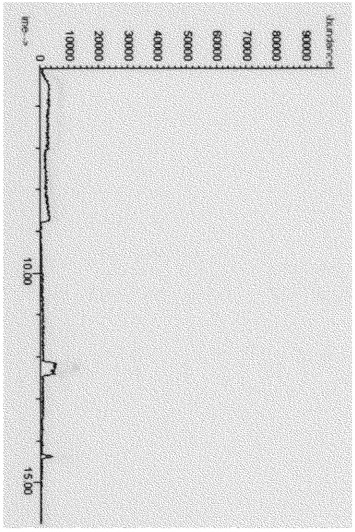


Figure 130:
Resampled cans, week 3, sample 0a

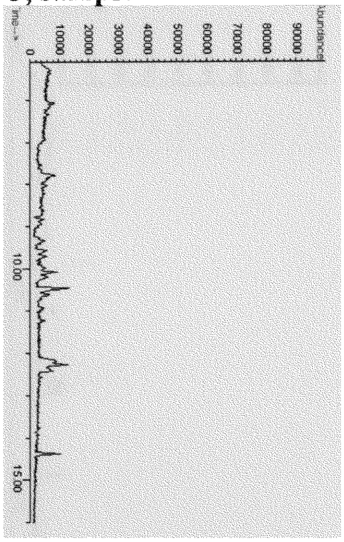


Figure 131:
Resampled cans, week 3, sample Bb

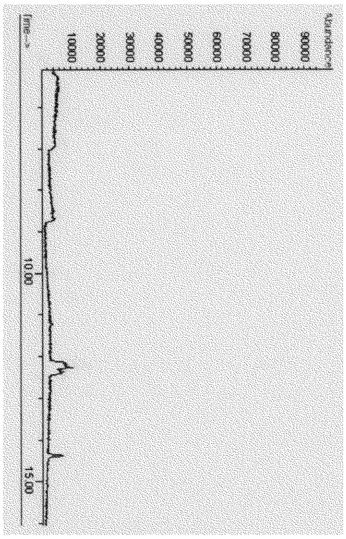


Figure 132:
Resampled cans, week 3, sample 0b

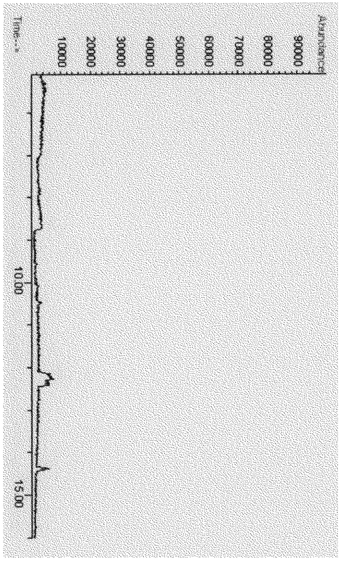


Figure 133:
Resampled cans, week 3, sample Bc

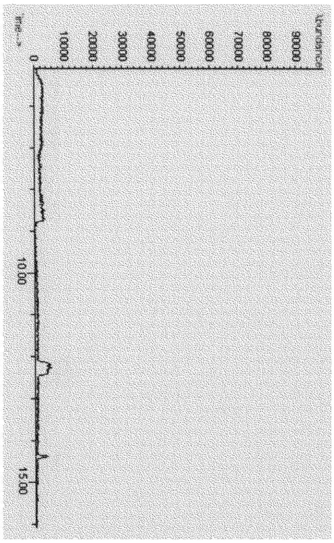


Figure 134:
Resampled cans, week 3, sample 0c

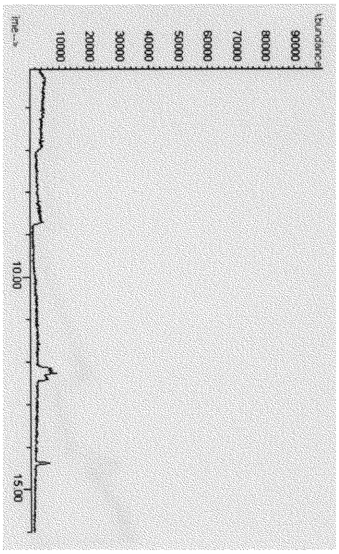


Figure 135:
Resampled cans, week 4, sample Ba

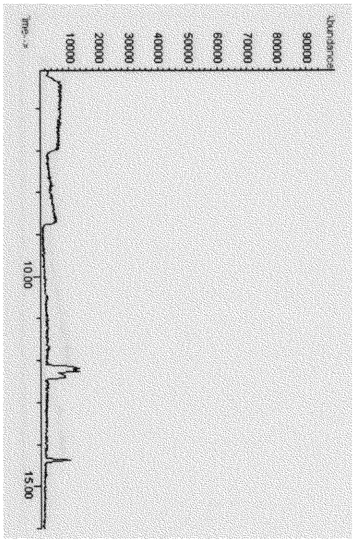


Figure 137:
Resampled cans, week 4, sample Bb

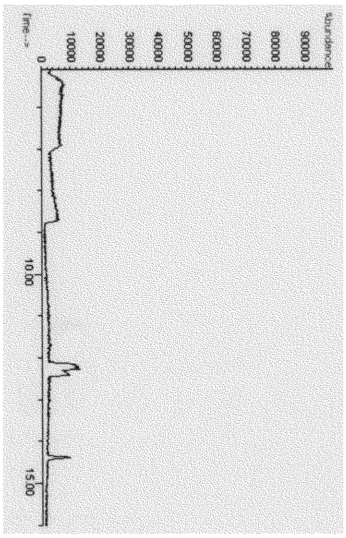


Figure 139:
Resampled cans, week 4, sample Bc

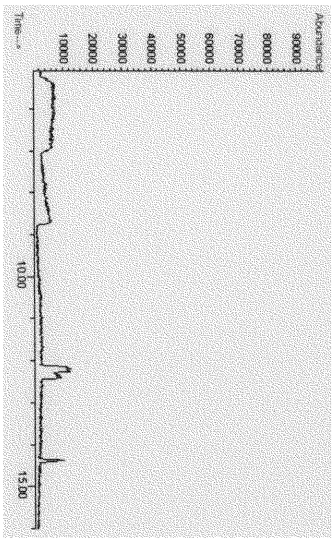


Figure 136:
Resampled cans, week 4, sample 0a

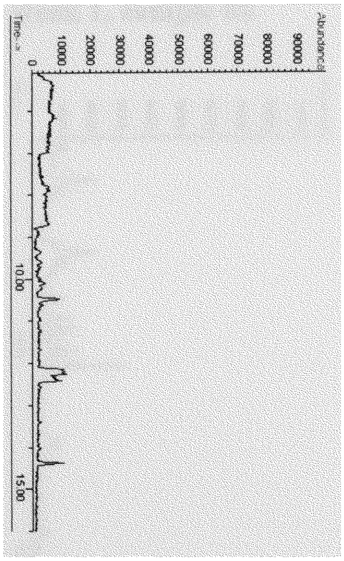


Figure 138:
Resampled cans, week 4, sample 0b

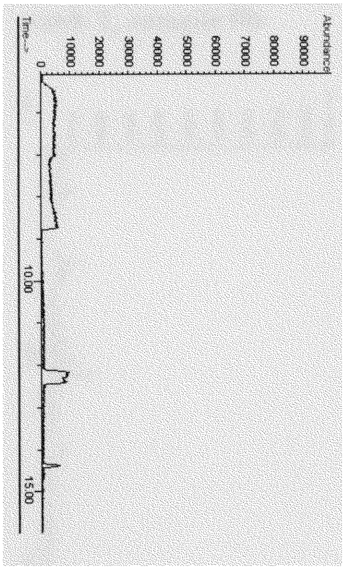


Figure 140:
Resampled cans, week4, sample 0c

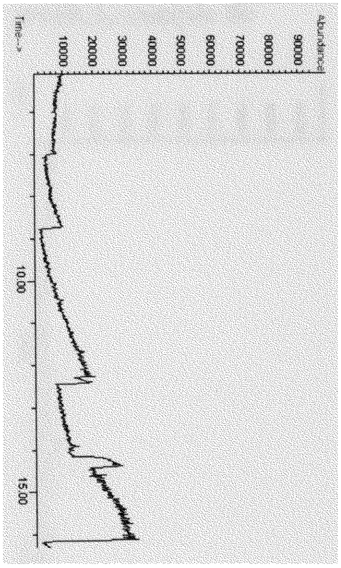


Figure 141: Resampled adsorbent, week 1, sample Ba

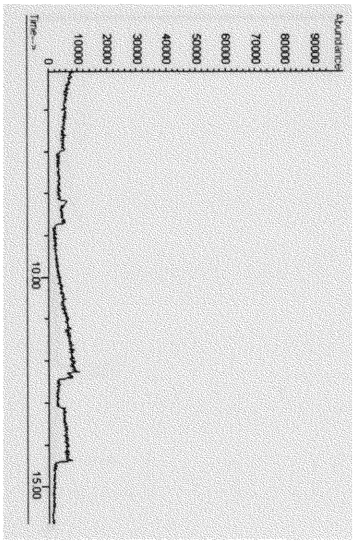


Figure 142: Resampled adsorbent, week 1, sample 0a

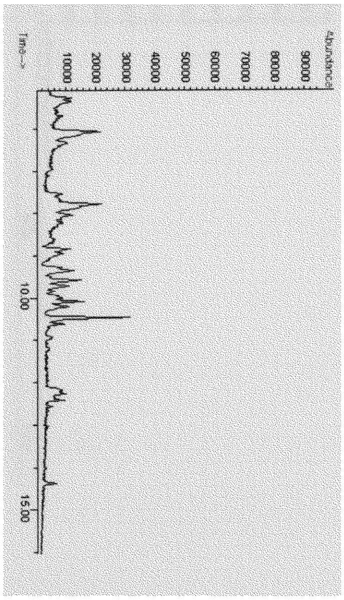


Figure 143: Resampled adsorbent, week 1, sample Bb

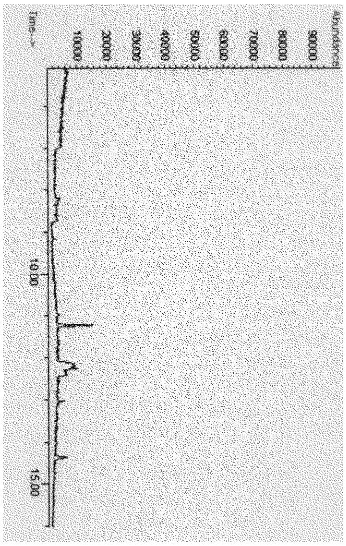


Figure 144: Resampled adsorbent, week 1, sample 0b

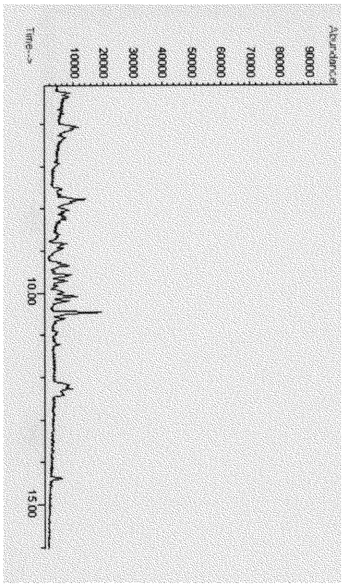


Figure 145: Resampled adsorbent, week 1, sample Bc

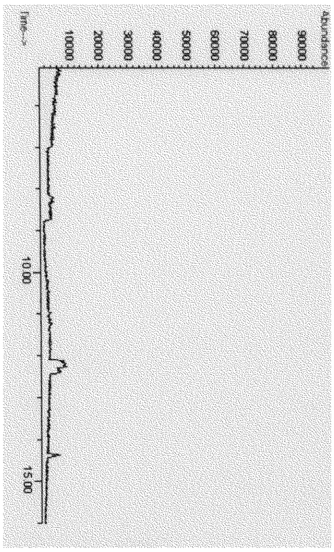


Figure 146: Resampled adsorbent, week 1, sample 0c

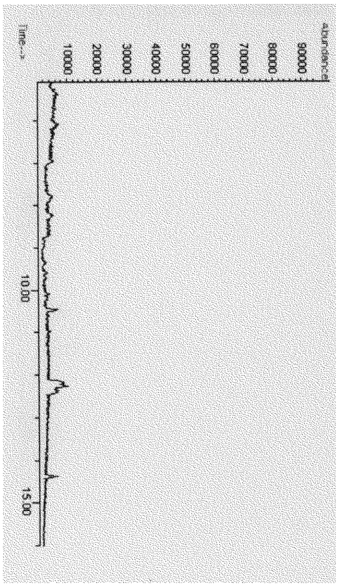


Figure 147:
Resampled adsorbent, week 2, sample Ba

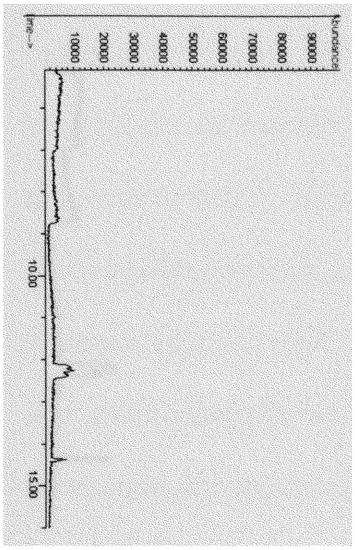


Figure 148:
Resampled adsorbent, week 2, sample 0a

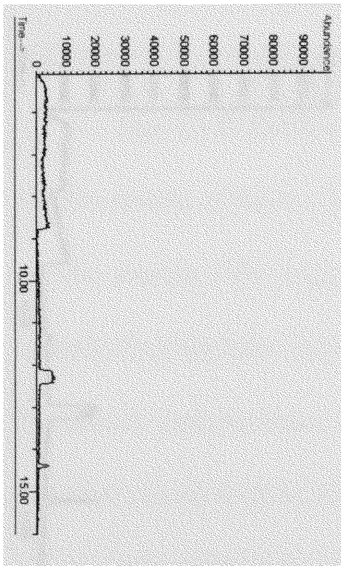


Figure 149:
Resampled adsorbent, week 2, sample Bb

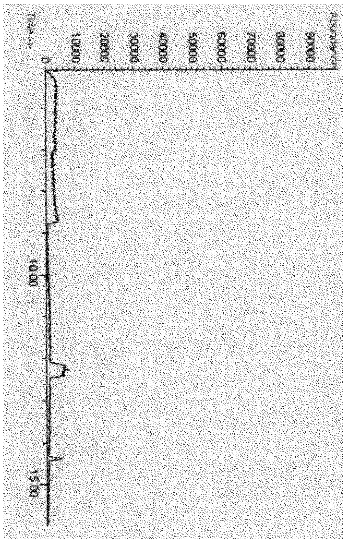


Figure 150:
Resampled adsorbent, week 2, sample 0b

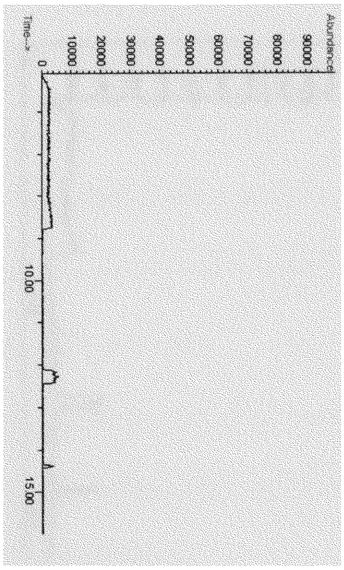


Figure 151:
Resampled adsorbent, week 2, sample Bc

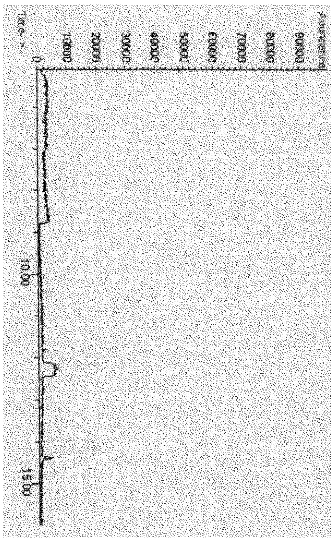


Figure 152:
Resampled adsorbent, week 2, sample 0c

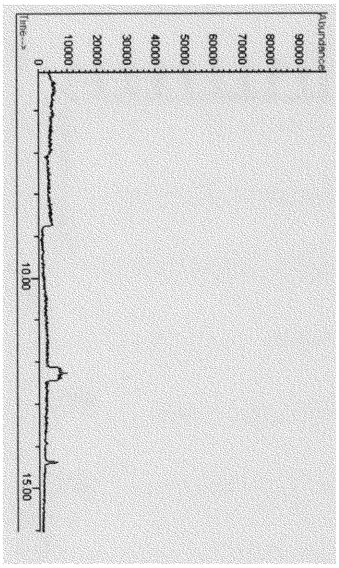


Figure 153:
Resampled adsorbent, week 4, sample Ba

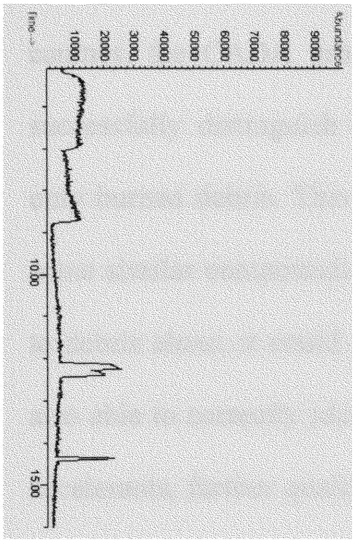


Figure 154:
Resampled adsorbent, week 4, sample 0a

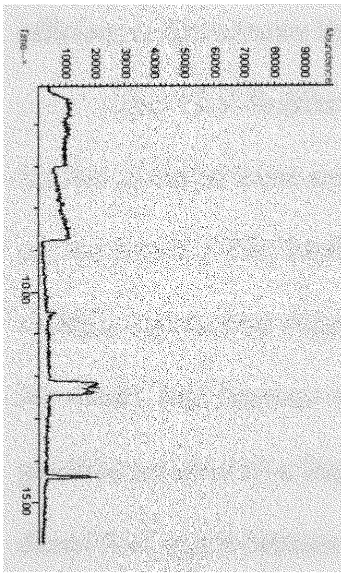


Figure 155:
Resampled adsorbent, week 4, sample Bb

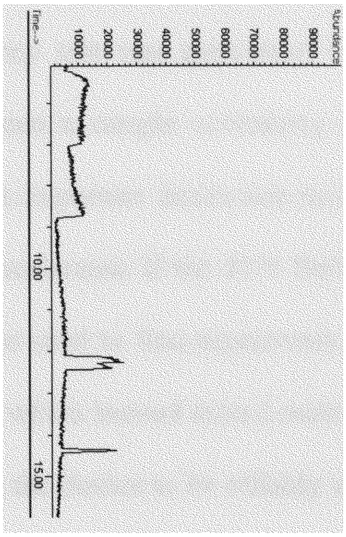


Figure 156:
Resampled adsorbent, week 4, sample 0b

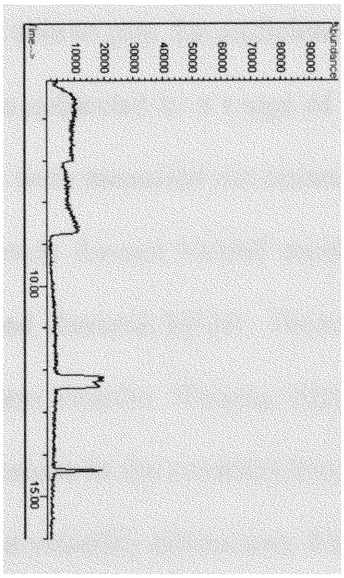


Figure 157:
Resampled adsorbent, week 4, sample Bc

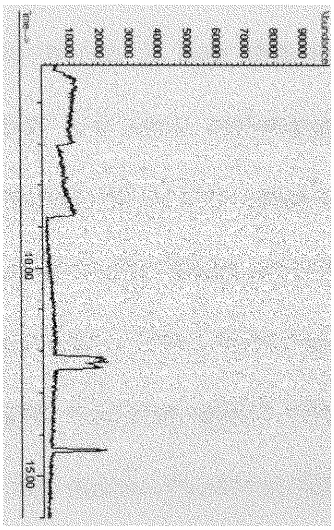
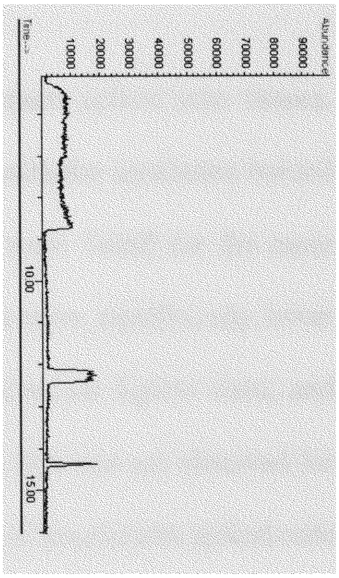


Figure 158:
Resampled adsorbent, week 4, sample 0c



4. DISCUSSION

To determine if the TLV Sniffer® would perform as well as accelerant detecting canines, the CADA proficiency test was performed with the device. It was able to successfully distinguish between a sample containing accelerant and those containing only burned debris. This is an important distinction because burned debris may contain some similar compounds to accelerants. If the TLV Sniffer® consistently falsely alerted to debris alone, it could not be used to find accelerants at a fire scene. The Sniffer was also able to correctly identify which burned mixed matrix samples had been spiked with accelerants, further qualifying the device to be reliably used at fire scenes. However, the Sniffer was not able to alert to a small amount of accelerant spiked onto a pine board. It was able to alert to higher amounts in this situation. In this case, the Sniffer is not as efficient as the canines that are able to pass the proficiency test.

The TLV Sniffer® was subjected to a range of accelerants spiked onto tissues. Sniffer levels of these samples were measured not burned and with the accelerant burned on the tissues. The highest levels for not burned accelerant were found for the more volatile liquids like Zippo® and charcoal lighter. These levels were significantly lower for diesel fuel because it is less volatile. Burning Zippo®, charcoal lighter fluid, and gasoline resulted in a large decrease in the recorded levels, but this was not observed for diesel fuel, again because of the volatility differences. Samples of accelerants spiked onto a mixed matrix and then burned were also examined. These samples still exhibited high levels for the accelerants with Zippo® and charcoal lighter having the highest. Some retention of not burned accelerant may have occurred because of absorbent materials in the matrix. This would allow the levels to remain high despite being burned. Many studies that evaluate fire debris analysis spike the accelerants onto burned matrix after it has been burned. This study burned the accelerant with the matrix to better replicate actual fire conditions.

Some of the burned matrix materials with no accelerants did have measurable levels with the TLV Sniffer®. Cotton, wood, newspaper, and carpet and padding all exhibited similar levels to accelerant spiked samples. These materials could lead to false positive alerts for accelerants, which, along with its low reproducibility, would need to be considered by investigators using such a device. However, due the Sniffer's performance in the CADA test, the device has shown that it may be useful in locating possible accelerants at a fire scene.

The tpi®Pocket Combustible Gas Leak Detector was also examined with unburned accelerants, burned matrix alone, and burned accelerants on matrix. It did not consistently alert to all accelerants below 500μL. It did alert to burned cotton, newspaper, and carpet and padding with no accelerant in some instances. This could lead to false positives and negatives in locating possible accelerants in the presence of matrix. Due to its low sensitivity and selectivity, the device would not be reliable in accelerant detection.

The conditions of the Portable Arson Sampler were examined to find the most efficient method of collecting accelerants from fire debris. The polymer adsorbent tubes were found to collect a slightly longer range and higher abundance that the charcoal tubes. Diethyl ether was found to be a more efficient solvent than dichloromethane. With the sampling chamber turned on for 30 or 60 minutes, more efficient sampling occurred. However, the accelerants were able to be collected in 10 minutes. Ten minutes was chosen because the shorter time would be more applicable to field sampling. The PAS was also found not to collect the entire range of the diesel fuel when compared to the standard, but the pattern seen is sufficient for identification. The PAS may not be the best method for sampling of heavy ignitable liquids.

Matrix materials and accelerants spiked on tissues were studied burned and not burned. The PAS was not able to collect the more volatile liquids, Zippo® and gasoline, spiked on tissues and burned even using one milliliter of accelerant. Charcoal lighter and diesel fuel were collected at these levels. However, when the same amount of accelerant was spiked onto a mixed matrix of cotton, wood, newspaper, plastic, and carpet and padding, the accelerants were able to be collected. This was attributed to the liquid being absorbed into some of the matrix materials. When sampling the burned matrix materials alone, no major peaks were seen and no peaks were identified. Therefore, the Portable Arson Sampler was not able to significantly collect background, pyrolysis, and combustion products from burned debris. This could be an advantage to the device, because these compounds can complicate analysis and lead to false negatives or positives for accelerants. But, the lack of collection of thee compounds may be due the device being unable to collect at low levels, a limitation for the Portable Arson Sampler.

For comparison, some samples were also extracted using passive headspace sampling with activated charcoal strips. The strips were able to collect background, pyrolysis, and combustion products from debris burned alone and burned with accelerant. Extracted ion profiling was conducted for the ACS and PAS samples to better visualize the accelerant peaks. In samples spiked with 5μL, peaks were seen in the range of one of the accelerants in the alkane and cycloalkane profiles of both the ACS and PAS methods, but not enough of the pattern was seen to say accelerant was present. For both methods, identification of the presence of accelerant was made in the 50μL samples that had been spiked with accelerant and then burned samples. Therefore, under the conditions of this study, the Portable Arson Sampler had comparable efficiency to the activated charcoal strip method commonly used for extraction of ignitable liquids from fire debris.

One of the advantages of using the Portable Arson Sampler may be that the adsorption tubes, as well as taking up less space, could retain samples for a longer period of time than storage of debris in paint cans. Over four weeks, samples were examined stored in cans and in tubes. Overall, the tubes were able to retain the compounds better than the cans. Repeated resampling of both the cans and the adsorbent resulted in complete loss of sample by week four. Therefore, storage in tubes may be a good method for long term preservation of compounds but multiple tubes should be saved if significant resampling is anticipated.

Finally, the Portable Arson Sampler was used to sample from asphalt and concrete. Large surfaces such as these would be difficult to break up and transport to the laboratory for sampling. The PAS was inverted over the surface and accelerants were efficiently collected from both surfaces. Sampling of these types of surfaces would be very difficult or inefficient with some other methods, making this a major advantage of the PAS.

5. CONCLUSION

The current results have shown that sampling and collection of fire debris in the field can be improved by utilizing an inexpensive electronic nose to help pinpoint the collection site, in combination with a field operational dynamic headspace method to collect and store accelerant residues. This method is particularly advantageous for collection from large surfaces.

The TLV Sniffer® was able to detect low levels of accelerant and discriminate between debris and accelerant containing debris in some situations. However, it was not as selective as well trained accelerant detecting canines and suffered from low reproducibility. Therefore, due to its limited abilities, it may be best utilized to confirm canine alerts to fire debris. It could also be used if canines are not available, or in hazardous situations where canines would not be able to enter a scene. The tpi®Pocket only alerted to large amounts of unburned accelerants and its high occurrence of false negatives makes it unsuitable for in-field detection of accelerants.

Sample collection in a method such as the use of the Portable Arson Sampler may not always be necessary but it has its applications. The PAS was shown to be able to efficiently collect accelerant residues from burned debris with comparable sensitivity to the established ACS method. Sampling from large surfaces was easily achieved. In addition, the sorbent trapping method utilized was shown to be superior to paint can storage by minimizing storage size and maximizing storage time. For its specific applications, the Portable Arson Sampler has shown to be useful and could supplement or replace currently used methods in some cases.

5.1 FUTURE WORK

Several parameters could be studied to further to evaluate the TLV Sniffer® and Portable Arson Sampler. A mass flow meter could be used to evaluate the consistency of the pumping systems in both devices. Calibration of the TLV Sniffer® with hexane in air would also optimize the measurements, and possibly reduce inconsistencies in results. Also, the effect of humidity could be studied with the Sniffer. The device could also be examined for its detection of different classes of compounds (such as alkanes versus aromatics) to determine if the type of compound may have an effect on response. This would be an important factor to consider due to the differences in the types of compounds that make up accelerants. Other types of sensors, such as polymer sensor arrays, that have been developed for the detection of hydrocarbons could be tested for their use with fire debris. The Portable Arson Sampler could use different adsorbent materials or a multi-stage process to improve sensitivity and collection efficiency. These adsorbents could be introduced to the GC with thermal desorbtion to possibly further increase sensitivity by eliminating loss and selectivity during the solvent desorbtion step. Both devices should be subjected to actual fire scenes to ensure they are effective in real world fire situations. Finally, if the devices prove worthwhile in field fire debris sampling and collection, ASTM guidelines could be developed for standard operating procedures and proper use.

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