



Application of an HS–MS for the detection of ignitable liquids from fire debris



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ABSTRACT

In arson attacks, accelerants such as ignitable liquids are commonly used to initiate or accelerate a fire. The detection of ignitable liquid residues at fire scenes is therefore a key step in fire investigations. The most widely used analytical technique for the analysis of accelerants is GC–MS. However, pre-concentration of the ignitable liquid residues is required prior to the chromatographic analysis. The standard method, ASTM E1412, involves passive headspace concentration with activated charcoal strips as a method to isolate the ignitable liquid residues from fire debris and these residues are subsequently desorbed from the carbon strip with solvents such as carbon disulfide.

In the work described here, an alternative analytical technique based on an HS–MS (headspace mass spectrometry) has been developed for the thermal desorption of the carbon strips and analysis of different ignitable liquid residues in fire debris. The working conditions for the HS–MS analytical procedure were optimized using different types of fire debris (pine wood burned with gasoline and diesel). The optimized variables were desorption temperature and desorption time. The optimal conditions were 145 °C and 15 min.

The optimized method was applied to a set of fire debris samples. In order to simulate post burn samples several accelerants (gasoline, diesel, citronella, kerosene, paraffin, and alcohol) were used to ignite different substrates (wood, cotton, cork, paper, and paperboard). Chemometric methods (cluster analysis and discriminant analysis) were applied to the total ion spectrum obtained from the MS (45–200 m/z) to discriminate between the burned samples according to the accelerant used. The method was validated by analyzing all samples by GC–MS according to the standard methods ASTM E1412 and ASTM E1618. The results obtained on using the method developed in this study were comparable to those obtained with the reference method. However, the newly developed HS–MS method is faster, safer, and more environmental friendly than the standard method.

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1. Introduction

The phenomenon of arson, especially forest fires, is becoming one of the major problems facing our society. In Spain during 2013, fire destroyed over 173,000 acres of forest, the majority of which were in protected areas. In most cases human activity was responsible for these fires [1]. It is estimated that more than 90% of the forest fires in the world is caused by humans (intentionally or accidentally) [2]. Fires also cost the lives of people and animals and the financial burden, in terms of damages, compensation for victims, private insurance, costs for fire protection, and governmental

services, amongst others, is huge. However, the destructive nature of fire makes its investigation difficult since most evidence is damaged and altered by the fire itself and by firefighting efforts. This is one of the main reasons why crimes involving arson do not have a significant clear-up rate.

In arson attacks accelerants, such as ignitable liquids, are commonly used to initiate or accelerate a fire. The detection of ignitable liquid residues (ILRs) at fire scenes can be a useful step in the investigation. The most commonly used ignitable liquids are petroleum-based products like gasoline, diesel or kerosene as they are readily available and ignite easily [3]. In some cases, traces of accelerant may remain at the fire scene and these could be matched to samples that are associated with a suspect [4]. Hence, the development of analytical techniques for the analysis of fire debris in

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order to identify qualitatively the presence or absence of an accelerant is of great interest. Identification of the type of accelerant is very useful for investigators when there is a suspected arsonist [5].

Numerous analytical techniques have been applied in the analysis of fire debris, including Raman [6], vapor-phase ultraviolet spectroscopy, thin-layer chromatography (TLC), and high-performance thin-layer chromatography (HPTLC) [7]. However, gas chromatography coupled with an FID or MS detector is the most widely used analytical technique for the analysis of ILR in fire debris [8,9]. Indeed, the American Society for Testing and Materials (ASTM) standard E1618-11 provides guidelines for the identification and classification of ILRs from fire debris samples by GC–MS [10]. Prior to chromatographic analysis a pre-concentration of the ILR from fire debris samples is required. There are several ways to achieve this goal, including solid phase microextraction [11], static headspace adsorption with Tenax [12] or headspace sorptive extraction [5] to name but a few. However, passive headspace concentration with activated charcoal strips (ACSs) is currently the most commonly used method to isolate ILRs from fire debris because of its sensitivity, ease of use, and its non-destructive nature [13,14]. Besides, activated charcoal is an excellent nonpolar adsorbent for the collection and retention of C6–C20 hydrocarbons so it is an ideal material for petroleum-based products [15]. The ACS is suspended in the headspace of a container, i.e., a metal can that is then heated in an oven to facilitate the absorption of the volatilized compounds onto the carbon strip. After several hours, depending on the chosen temperature, the strip is removed from the metal can and eluted with a solvent (carbon disulfide, pentane or diethyl ether) to remove the adsorbed species from the strip. This eluent is then ready for analysis by gas chromatography. Carbon disulfide has proven to be the most efficient solvent, although it is very toxic and has a very low autoignition temperature, around 100 °C, thus making it dangerous even around the boiling point of water [16].

Regardless of the isolation method, the analysis of accelerants is carried out by gas chromatography. The methodology outline in ASTM E1618 relies on visual pattern recognition of the total ion chromatogram (TIC), extracted ion chromatograms (EIC), and target compound analysis in order to identify the presence of an ignitable liquid residue in fire debris samples [10]. Although this method works well, there are several factors that can alter the chromatographic profile, thus complicating the classification, and these include the volume of ignitable liquid, the type of substrate, the pyrolysis products, and the temperature reached in the fire [17]. Furthermore, this method is time consuming, the interpretation of the results is highly dependent on the experience of the analyst, and it does not allow automation. Therefore, the use of chemometric tools is almost mandatory to help the analyst to identify and classify accelerants easily in a shorter time. However, fire debris analysis requires an automated database searching tool that minimizes laboratory-to-laboratory chromatographic variations, facilitates ignitable liquid assignment to ASTM categories, and allows product identification. For this reason, some authors have proposed alternative methods to TIC. Sigman et al. developed a covariance mapping method to group ignitable liquids belonging to the same ASTM classification while retaining some of the chromatographic information, which is encoded in covariance of the different ions [14,18]. This method allowed the grouping similar ignitable liquids but it was computationally demanding when implemented as a database search application. Therefore, the same authors subsequently proposed another approach, namely the total ion spectrum (TIS), in which the mass spectra are calculated by summing the intensities of each nominal mass over all chromatographic times during a GC–MS analysis. The TIS is time-independent, which allows inter-laboratory comparisons, and it contains sufficient information to allow rapid identification of ignitable liquids. TIS has proven to be a potential method for the rapid identification of ignitable liquids in a database [19]. TIS has also been applied as a method to discriminate and

classify fire debris samples as well as to predict classification error rates [20–24].

Although GC–MS has proven to be useful in this field, it requires long analysis times and it cannot be applied as a screening technique or for rapid quantitative analysis. Consequently, the development of non-separative methods for the resolution of different analytical problems is of increasing interest. In some cases, it is sufficient to obtain a signal profile or fingerprint of the sample formed by all the components [25].

In the work described here, an alternative analytical technique based on HS–MS (headspace mass spectrometry) is proposed for the analysis of ignitable liquids in fire debris. The HS–MS allows the spectrum to be obtained in a very short time period since chromatographic separation is not required. This technique has previously been applied in other fields but not for fire debris analysis. Pavon et al. performed a comparative study to analyze methyl tert-butyl ether in gasoline samples using three different methods with detection by mass spectrometry: namely, fast gas chromatography and two non-separative methods, such as HS–MS or direct injection into MS [26]. All of the proposed methods were successfully applied in the rapid detection and quantification of methyl tert-butyl ether, although on using the non-separative methods the analysis times were significantly reduced. Feldhoff et al. compared the performance of chemical and mass spectrometry for the discrimination of diesels and they concluded that mass spectroscopic data were easier to obtain and were more reproducible [27].

Most of the applications of HS–MS to date have been related to food and beverage analyses for quality control [28–31] and for characterization and discrimination studies [28,29,31–34]. Usually for food analysis, authors refer to the HS–MS systems as HS–MS electronic noses or simply HS–MS eNose. Pavón et al. reviewed the main applications of the HS–MS electronic noses with special reference to applications in the environmental field [35]. The same authors presented a study on the determination of biomarkers in saliva samples using HS–MS [25] and a mass spectrometry-based electronic nose with a programmed vaporization temperature [36].

Regardless of the technique used, the resulting total ion spectrum is characteristic of the sample being analyzed. Suitable chemometric treatment of the signal is essential in order to extract the information contained in the signal profile, as is the case for most non-separative methods [35]. TIS has already been used for the identification and assignment of ignitable liquid residues to ASTM classes by discriminant analysis [22], soft independent modeling of class analogy [23], target factor analysis with soft Bayesian decision theory [24], and hierarchical clustering analysis (HCA) [21]. The HS–MS has previously been optimized and successfully applied in our group for the identification of gasoline samples with different research octane numbers by using HCA and discriminant analysis [37].

Similar systems, i.e. electronic noses based on sensors have previously been used for the initial evaluation of a fire scene [38,39]. However, the use of an array of sensors over MS detectors has several disadvantages, such as poisoning, profile masking by some major constituents of the sample, the strong influence of moisture, and the non-linearity of signals [35]. All of these drawbacks can be overcome by using an MS detector.

The work described here concerns the optimization of HS–MS for desorbing, analyzing, and classifying ILRs absorbed on activated charcoal strips. In this system, the carbon strip containing the ILRs is placed in a vial inside the static headspace autosampler oven to be heated and agitated in order to generate the headspace. The headspace is subsequently removed from the vial using a gas syringe and injected into the mass spectrometer without any chromatographic separation. The pattern response obtained by HS–MS is the total ion spectrum, which is different for each sample.

In comparison to the standard method there are advantages associated with this HS–MS technique: (i) a shorter analysis time is required because there is no chromatographic separation and (ii) the absence of solvent because the analytes are desorbed from the strip by applying temperature, which is both safe and does not contaminate the environment. Furthermore, the method has a high sensitivity, good accuracy, low cost, and is easy to use for routine analysis.

2. Material and methods

2.1. Materials

Six substrate samples (pine wood, cork, paper, newspaper, cardboard, and cotton sheet) were burned alone without any accelerant and then with each of six ignitable liquids (gasoline, diesel, kerosene, citronella, paraffin, and ethanol). Substrates and ignitable liquids were purchased in local Spanish stores.

Burned samples were denoted as the liquid code followed by the substrate code, for instance, *Npw* for pine wood burned alone, *Gpa* for paper burned with gasoline and so on (Table 1).

2.2. Burned samples

To simulate post burn samples, laboratory fire debris samples were generated by adding 500 μL of different ignitable liquids to different materials. The material samples were placed upside down in an unlined one-quart paint can and covered with a vented lid with nine 1 mm diameter holes. Heat was applied to the bottom of the can by a flame from a propane torch held at a distance 4 cm from the bottom. Once smoke appeared the contents of the container were allowed to burn for two additional minutes and the can was allowed to cool to room temperature. The perforated lid was replaced with an intact lid to avoid losing the volatile compounds from the headspace. Once the can was cool, the ignitable liquid residue was extracted from the burned sample by passive headspace analysis by following the ASTM E1412 standard for adsorption onto activated charcoal strips [40]. The headspace above the samples was collected on a 10 mm \times 22 mm activated charcoal strip (USA Albrayco Technologies Inc., Cromwell, Connecticut, USA), which was suspended in the headspace of the can by a paperclip and unwaxed dental floss. The can was sealed and heated for 18 h at 66 $^{\circ}\text{C}$ in an oven. The activated charcoal strip was subsequently removed from the can and cut in half lengthwise. One half was desorbed with 1 mL of carbon disulfide and analyzed by GC–MS under the conditions described below. The other half was deposited in an empty 10 mL sealed vial (Agilent Crosslab) and analyzed by the HS–MS system.

2.3. GC–MS analysis acquisition

A total of 42 samples were analyzed by GCMS according to the ASTM E1618 method. A Waters Quattro microTM GC interface and a

Table 1
Ignitable liquids and substrates used for burned samples preparation.

Ignitable liquid	Code IL	Substrate	Code substrate
None	N	Pine wood	pw
Gasoline	G	Cork	co
Diesel	D	Paper	pa
Ethanol	E	Newspaper	np
Citronella	C	Cardboard	ca
Kerosene	K	Sheet	sh
Paraffin	P		

quadrupole mass spectrometer were used. All the ACS containing the ILRS were placed in 1 mL of carbon disulfide for GCMS analysis. Samples of 1 μL were introduced by an autosampler with a 50:1 split in a split/splitless injector maintained at 250 $^{\circ}\text{C}$. The mass spectrometer transfer line was maintained at 280 $^{\circ}\text{C}$ and the source temperature was 230 $^{\circ}\text{C}$. Mass spectra were repetitively scanned from m/z 30 to 350.

Samples were chromatographed on a BP 5 capillary column (0.25 mm i.d. and 30 m length) (SGE Analytical Sciences) with a 0.25 μm film thickness. Helium carrier gas was maintained at a constant flow of 0.8 mL/min on the column. The initial oven temperature of 50 $^{\circ}\text{C}$ was held for 3 min, followed by a temperature ramp of 5 $^{\circ}\text{C}/\text{min}$ to a final temperature of 110 $^{\circ}\text{C}$, which was held for 0 min, followed by a temperature ramp of 20 $^{\circ}\text{C}/\text{min}$ to a final temperature of 280 $^{\circ}\text{C}$, which was held for 4 min. The total run time was 27.5 min.

2.4. HS–MS spectra acquisition

Analysis of the samples was performed on an Alpha Moss (Toulouse, France) HS–MS eNose system composed of an HS 100 static headspace autosampler and a Kronos quadrupole mass spectrometer (MS). The samples were contained in 10 mL sealed vials (Agilent Crosslab), which were placed in the autosampler oven to be heated and agitated in order to generate the headspace. Headspace was taken from the vial using a gas syringe and injected into the mass spectrometer. The gas syringe was heated above the sample temperature (+5 $^{\circ}\text{C}$) to avoid condensation phenomena. Between each sample injection, the gas syringe was flushed with carrier gas (nitrogen) to avoid cross-contamination. Five samples produced no signals in the spectra, then they were removed from the study, specifically: *Dnp*, *KnP*, *Cpa*, *Kpa* and *Pco*, therefore 37 samples were used. All samples were analyzed in duplicate.

The optimized experimental conditions for the headspace sampler were as follows: incubation temperature 145 $^{\circ}\text{C}$, incubation time 15 min, agitation speed 500 rpm, syringe type 5 mL, syringe temperature 150 $^{\circ}\text{C}$, flushing time 120 s, fill speed 100 $\mu\text{L}/\text{s}$, injection volume 4.5 mL and injection speed 75 $\mu\text{L}/\text{s}$. The carrier gas was nitrogen. The total time per sample was approximately 15 min.

The components in the headspace of the vials were passed directly to the mass detector without any chromatographic separation or sample pre-treatment. In this way, for any given measurement, the resulting mass spectrum gives a fingerprint of the sample. Electron ionization spectra were recorded in the range m/z 45–200. Instrument control was achieved using RGA (Residual Gas Analysis software package) and Alpha Soft 7.01 software.

2.5. Data analysis and software

All the spectra were normalized by assigning one unit to the maximum intensity in both techniques. Multivariate analysis of the data, which included hierarchical cluster analysis (HCA) and quadratic discriminant analysis (QDA), was performed using the statistical computer package SPSS 17.0 (SPSS Inc., Chicago, IL, USA) and Unscrambler X (Camo Software AS, Oslo, Norway). A Principal Components Analysis was run previously to the QDA.

3. Results and discussion

3.1. Fire debris samples

It was necessary to prepare burned samples before optimizing the experimental conditions for the HS–MS for thermally desorbing the ACSs. Different laboratory fire debris samples were created in

order to include different and possible real fire debris to which the developed method could be applied.

In the optimization process similar burned samples were created so that the resulting signal depended only on the desorption process to be optimized rather than on the sample itself. Therefore, only one type of substrate was used for the optimization process, namely pine wood sticks, which were burned using gasoline (Gpw) and diesel (Dpw) separately as accelerants. Two different accelerants were used in the optimization process to ensure that the resulting optimized method is applicable to different types of ignitable liquids. Gasoline and diesel are chemically different and they are the ignitable liquids most commonly used by arsonists. The separation of the ILRs from the fire debris was achieved by passive headspace concentration with ACS, as described in standard ASTM E1412. With the aim of ensuring that all of the ACSs contained the same ILRs, 5 ACSs were suspended in the headspace of each metal can. All of the ACS were cut in half lengthwise. As a consequence, at least 10 halves of the ACS from each metal can were equivalent. All combustion experiments were carried out in duplicate and a total of 22 half-ACSs containing ILRs from Gpw and 22 from Dpw were obtained.

3.2. Headspace generation. Desorption optimization

Once the ILRs had been adsorbed onto the ACSs, the thermal desorption of the ACS was studied rather than solvent desorption with CS₂ and the ILRs were then analyzed. An HS-MS system was used and this allowed headspace generation for both solid and liquid samples, in this case the activated charcoal strips, by applying temperature. The experimental conditions that affect the desorption process were studied and those that can be controlled are incubation temperature and incubation time. The reference method takes around 30 min to complete and the possibility of reducing the analysis time was studied first. All analyses were carried out in duplicate and the average spectra values are presented.

The results obtained under the different experimental conditions were compared by considering the signals (m/z) from the MS that had at least 10% of the intensity of the maximum abundance from the spectra. In the case of the ACSs that contained Gpw ILRs, only m/z values of 45 and 60 were selected. Signals below 10% of the maximum were not considered because they would produce noise rather than information of interest.

The abundances obtained when the Gpw ACS samples were heated for different times (from 5 min to 60 min) at a constant temperature of 145 °C are shown in Fig. 1. This temperature was used on the basis of results obtained in previous experiments on the same system [37], although the temperature would require optimization at a later stage. It can be observed that the maximum signal was obtained when the ACSs were heated for 15 min at 145 °C (abundance=27.5). This result indicates that the desorption process produces more intense signals under these conditions. For incubation times of less than 15 min the signal decreased by 40% on using an incubation time of 5 min. In the same way, an increase in the incubation time led to a decrease in the signal and this was particularly apparent in the low abundance obtained for a time of 60 min (74% lower abundance). This trend could be due to degradation or reactions between the desorbed compounds, although it is also possible that losses could occur in the system due to overpressure generated within the vial.

An optimal incubation time of 15 min was selected on the basis of the results discussed above. The incubation temperature was then optimized by fixing the incubation time at 15 min and comparing the results obtained on applying different incubation temperatures (range from 105 °C to 145 °C). The results obtained in the temperature optimization in the case of ACS for Gpw samples are represented in Fig. 2. It can be seen that a higher

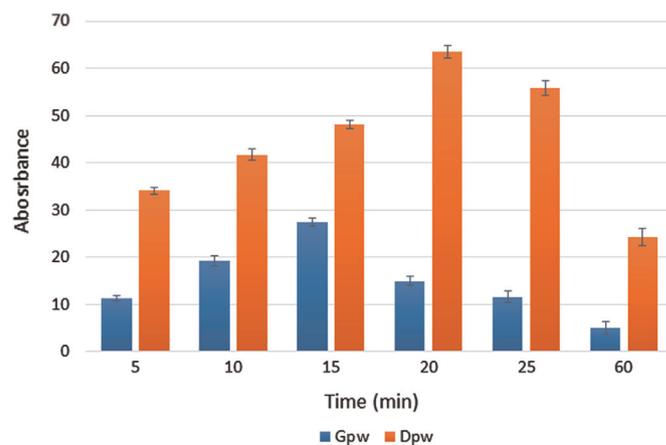


Fig. 1. Abundance values obtained by thermal desorption of ACS for Gpw and Dpw samples using different incubation times ($T=145^{\circ}\text{C}$).

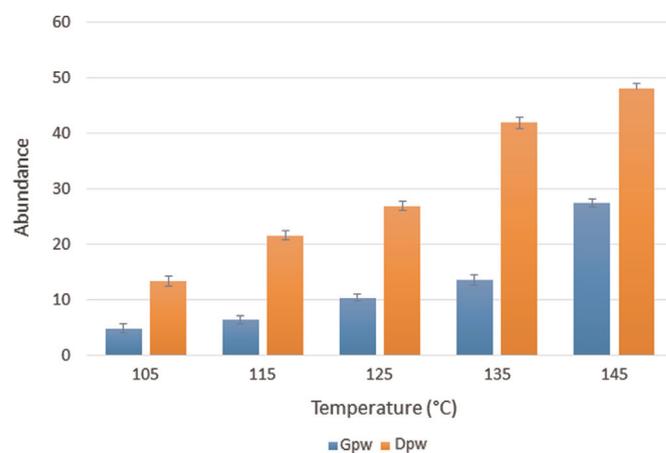


Fig. 2. Abundance signals obtained from the ACS thermal desorption using different incubation temperatures for the Gpw and Dpw samples (time = 15 min).

incubation temperature leads to a higher amount of ILR being desorbed from the ACS. On decreasing the temperature from 145 °C to 135 °C the abundance decreased by half. As a consequence 145 °C was chosen as the optimal temperature.

The same optimization procedure was then performed for the Dpw samples. The m/z values selected for the comparison were again those whose abundances were at least 10% of the maximum one. In the case of Dpw samples the m/z values selected were 55, 56, 57, 67, 69, 70, 71, 81, 83, and 85. As far as the Dpw samples are concerned, the incubation temperature was fixed at 145 °C and the results obtained for different incubation times were evaluated. The results are shown in Fig. 1. In this case the maximum abundance was reached at 20 min. This result is due to the fact that diesel contains more heavy compounds and it can therefore persist for longer times at high temperatures. However, once again it was observed that the abundance decreased markedly when the ACS was heated for 60 min. The increase observed in the signal when the incubation time was increased from 15 min to 20 min was around 25%. However, for Gpw samples an increase in the incubation time to 20 min led to a loss of signal of around 50%. Besides, the signal for Dpw at 15 min is strong enough (abundance=50) and, therefore, even though the maximum signal for Dpw samples was obtained at 20 min, a time of 15 min was selected as the optimal incubation time. Different incubation temperatures were subsequently assessed for the desorption of the ACS. As in the previous case, the use of a higher temperature led to an increase in

the abundance (Fig. 2). The optimum temperature was defined as 145 °C because the system used in this work could not be operated at higher temperatures.

3.3. Repeatability and reproducibility

The repeatability and intermediate precision were determined by analyzing 20 ACSs containing ILRs from burning paper with diesel, *Dpa*, and using the optimized method. The samples were analyzed on three different days: 12 analyses on the first day and four on the two following days. It should be noted that the 12 samples analyzed on the same day came from different tins although the same substrate and ignitable liquid were used since only 4 ACSs were used in each can.

All the spectra were normalized at the maximum abundance (m/z of 57). RSD values were calculated for all m/z signals producing abundances above 10% of the abundance obtained at m/z 57. Intra-day and inter-day relative standard deviations (RSD) were calculated (Table 2). It can be seen that all of the RSD values obtained were below 10%. This means that the optimized method has high repeatability and reproducibility, since the error is low, despite the fact that all of the burned samples could not be identical since they came from different sets.

3.4. Applicability for the discrimination of different types of fire debris

A range of different burned samples was created in order to assess the applicability of the optimized method in the discrimination of different ILRs from fire debris according to the ignitable liquids used as accelerants. Different substrates (pine wood, cork, paper, newspaper, paperboard, and cotton sheet) and ignitable liquids (gasoline, diesel, kerosene, citronella, paraffin, and ethanol) were used. The samples were denoted as shown in Table 1. The concentrations of ILRs were determined using ACSs according to the method described in the experimental section. All samples were analyzed in duplicate.

Table 2
Intra day and Inter day relative standard deviations.

RSD% intra day (12)	7.7
RSD% inter day (4, 4, 4)	6.9

Firstly, in order to assess the tendency of the different burned samples to cluster, an exploratory chemometric technique was initially applied. HCA was applied by using all the m/z (45–200 m/z) values obtained from HS–MS as a variable to form groups. All spectra were normalized by assigning one unit to the maximum intensity.

The results of the HCA are represented in the dendrogram in Fig. 3, in which all of the samples are listed, and the level of similarity (dissimilarity) at which any of the two clusters were joined is indicated. The Ward method was used for cluster preparation and square Euclidean distance was used to measure distances between clusters. Other methods for cluster selection were also evaluated, including the between-groups linkage method and the within-groups linkage method. All of these methods produced similar results.

A classification of the samples according to the ignitable liquid used as an accelerant was not found on applying HCA. It can be observed that there are two large clusters, namely Clusters 1 and 2. Cluster 1 is divided into 2 sub-groups; Cluster 1.1, which includes four of the six samples burned with ethanol, 2 samples burned without using an IL, one sampled burned with gasoline, and another one with citronella. Cluster 1.2 includes all of the samples burned with paraffin, kerosene, citronella, and diesel. Cluster 2 is divided into four different clusters, namely 2.1, 2.2, 2.3, and 2.4. Cluster 2.1 includes three of the six samples burned with gasoline and one burned with ethanol. Cluster 2.2 contains two samples burned without IL, one burned with gasoline, and one burned with ethanol. Cluster 2.3 contains two samples burned without IL and the remaining cluster contains only one sample burned with gasoline.

Although the samples could not be classified according to the IL used, there is a tendency for the heavy ignitable liquids to be grouped together (Cluster 1.2). In contrast, the substrates burned with lighter accelerants tend to be clustered apart from the heavy IL group, although they are mixed with this latter group and also mixed with the substrates burned without IL.

After reviewing the results from the cluster analysis shown in Fig. 3, a supervised technique was applied, specifically a QDA (Quadratic Discriminant Analysis) was performed using the cross validation technique. A PCA was run before QDA, then principal components were used as variables for the discriminant analysis. A total of 10 factors were needed to build the discriminant functions. A full discrimination between the seven groups was obtained for

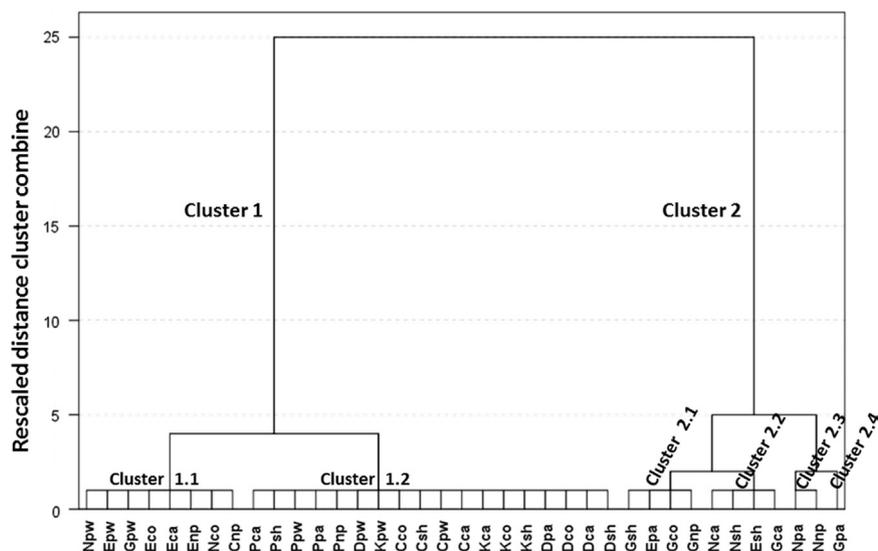


Fig. 3. Dendrogram obtained from the hierarchical cluster analysis using the Ward method.

samples in the study. After analyzing the loadings for the resulting factors, only factor number two showed a clear contribution from specific m/z signals (Fig. 4). Specifically, m/z values of 45, 55, 57, 68, 69 and 71 showed the highest scores. Loadings for the highest m/z values were much lower than those for the m/z signals in the range $m/z=45$ –85.

3.5. Validation study

In order to validate the method, the results obtained by the approach developed here with the HS–MS were compared with those obtained by the reference method, which involves desorption of the ILRs from the ACS with CS₂ (ASTM E1412) and analysis of the eluent by GC–MS. In the case of the GC–MS, TIS was also applied as a method to discriminate fire debris samples as described in the literature [20–24]. In this case TIS was calculated by summing the intensity of each ion across the entire chromatographic range, which was wider than in the HS–MS (30–349 m/z), and normalizing the resulting spectrum.

Once again a QDA was used to build the model and this allowed discrimination between samples. Cross validation was also employed in an effort to improve the discrimination results. A full discrimination for samples in the study was also obtained. The resulting loadings for the 8 factors calculated in the QDA were markedly different than those in the analysis carried out using the HS–MS system. The loading for factor 1 in the QDA is represented in Fig. 5. It can be seen that the most important region in the spectrum is directly related to the m/z values above 105. However, the final results were

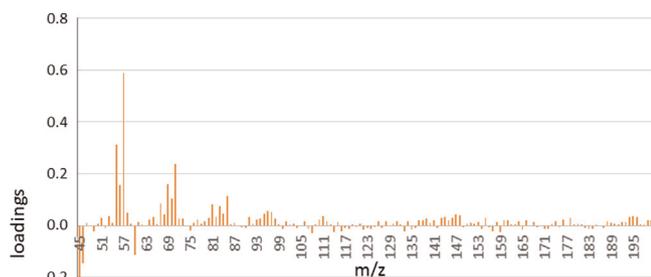


Fig. 4. Loadings in the QDA analysis for factor 2.

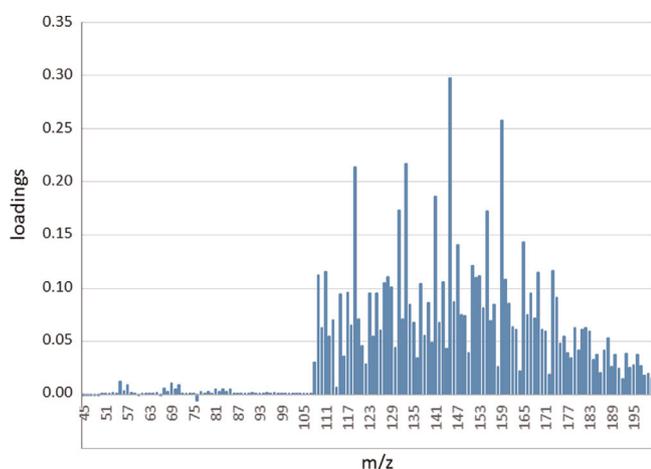


Fig. 5. Loadings obtained in the QDA analysis for factor 1.

comparable for both methods, i.e., a full discrimination between the six groups of samples. These results demonstrate that the new method has the same discrimination power as the reference method.

4. Conclusions

A new HS–MS method developed for activated charcoal strips desorption allows the full discrimination between fire debris samples obtained using different ILRs. In the new HS–MS technique a different mass spectroscopic region is used than for the reference method, probably due to the different desorption procedure used to remove compounds from the activated charcoal strip. However, both methods gave the same discrimination results, thus showing that it is possible to discriminate between this kind of sample by considering different areas in the mass spectroscopic region.

The new HS–MS based method was validated against the reference method and it proved to be useful in the analysis of fire debris, producing clearly different spectroscopic results but with the same discrimination power. In comparison to the standard method, the new HS–MS method is faster, safer, and more environmental friendly.

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