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# Analytical tools for the analysis of fire debris. A review: 2008–2015

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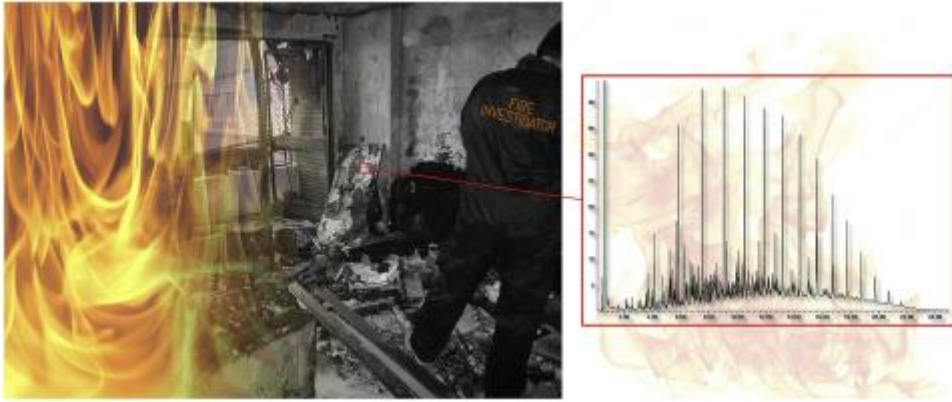
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**Abstract:** The analysis of fire debris evidence might offer crucial information to a forensic investigation, when for instance, there is suspicion of the intentional use of ignitable liquids to initiate a fire. Although the evidence analysis in the laboratory is mainly conducted by a handful of well-established methodologies, during the last eight years several authors proposed noteworthy improvements on these methodologies, suggesting new interesting approaches. This review critically outlines the most up-to-date and suitable tools for the analysis and interpretation of fire debris evidence. The survey about analytical tools covers works published in the 2008–2015 period. It includes sources of consensus-classified reference samples, current standard procedures, new proposals for sample extraction and analysis, and the most novel statistical tools. In addition, this review provides relevant knowledge on the distortion effects of the ignitable liquid chemical fingerprints, which have to be considered during interpretation of results.

**Keywords:** Arson; Chemometrics; Fire debris; Fire investigation; Gasoline; Ignitable liquid residues.

**Abbreviations:** IID, improvised incendiary devices; IL, ignitable liquids; ILR, ignitable liquid residues; CIMC, chemical ignition Molotov cocktail; ADC, advanced distillation curve; HS, headspace; HSSE, headspace sorptive extraction; PLOT, porous layer open tubular; TIC, total ion current chromatogram; EIS, extracted ion spectra; TIS, total ion spectrum; EIP, extraction ion profile; ACS, Activated carbon strips; DVB, Divinylbenzene; CAR, Carboxen; HAS, high-surface area; PHRED, passive headspace residue extraction device; EI, electron impact; FA, fatty acid; FAME, fatty acid methyl ester; RON, research octane number; SPME, solid-phase microextraction; PDMS, Polydimethylsiloxane; FID, flame ionization detector.

**Graphical abstract:**

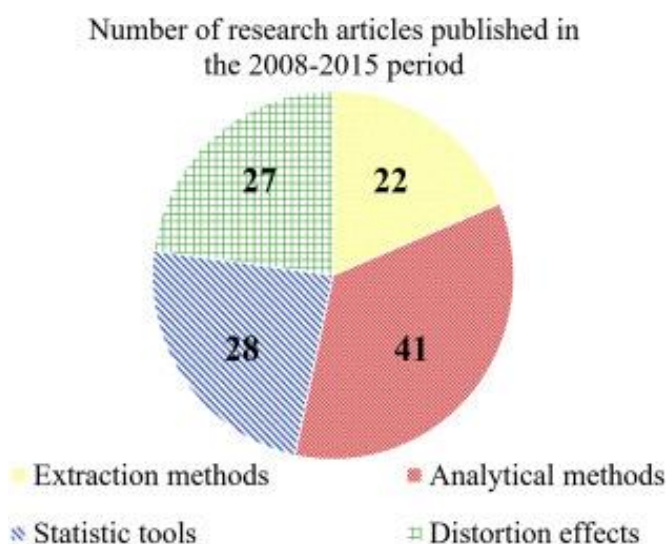


## 1. Introduction

One way to start or accelerate a fire is using ignitable liquids (ILs). Detecting and identifying unexplained neat ILs in a fire scene, or recovering ignitable liquid residues (ILRs) from fire debris, may provide valuable forensic intelligence. However, in some cases, the detection and characterization of those samples might be a challenge. Evidence might suffer modifications of its chemical composition, for example, resulting in distortions and/or changes to their chromatographic profiles compared to the well-known reference profiles [1]. This could happen, for instance, as a consequence of the destructive nature of fire or firefighting efforts, which might produce interferences from background matrices or from fire suppression foams or powders [1], [2]. Besides, pyrolysis, weathering/evaporation or microbial degradation of IL compounds might also lead to additional difficulties [1], [2]. Therefore, in order to carry out reliable evidentiary analyses and arrive at a correct interpretation, forensic practitioners require knowledge in a wide variety of areas. Especially important are: (i) the knowledge on the fire nature and combustion mechanisms, (ii) the understanding of ILs or substrates diversity and characteristics, and (iii) the effects modifying their chemical fingerprints. In addition, it is crucial that forensic practitioners are well-informed of the most suitable analytical tools and the new fire scene investigation techniques.

To date, the sample pre-treatment of these evidence is mainly conducted in forensic laboratories using a handful of extraction techniques which are usually based on solvent or headspace (HS) extraction. Then, the analysis of fire debris samples is largely dominated by one analytical technique; Gas Chromatography (GC) coupled to a mass spectrometry (MS) detector. This is explained by the ILs nature as complex mixtures of volatile compounds, and the technique's selectivity, specificity, and identification capability. This well-established analytical technique, as well as alternative approaches and crucial knowledge on fire investigations, were depicted in previous literature. A good background is given in two relevant books [1], [3] and review articles such as the one published in 2006 by Pert et al. on analytical techniques for the analysis of arson samples [4], and Sandercock's wide review about fire investigation and the analysis of fire debris covering the 2001–2007 period [5]. However, since then, no other comprehensive review has been published collecting the novelties and improvements on extraction techniques and the novelties developed for the analysis of fire debris samples. As can be seen in Fig. 1, during the last eight years (2008–2015), a high number of

research works focused on the improvement or development of methodologies for sample extraction and analysis of fire evidence. Apart from the application of appropriate analytical techniques, it is crucial to carry out a correct interpretation of the results. Thus, an interesting topic that has received increased attention during the last years is the demand of more statistical evaluation of data (Fig. 1). Statistical techniques provide an objective decision-making tool that may aid during the data interpretation and analysis for finding available associations of questioned versus reference samples. Furthermore, several researches aimed at increasing the understanding of the distortion effects of ILs and ILR samples (Fig. 1). The information reported in these topics greatly assist the forensic scientists during the interpretation of the analytical results.



**Fig. 1.** Number of research articles considered in this work, published in the 2008–2015 period. They have been classified according to the different sections of this review article.

This review aims to give an overview of the most recent and suitable analytical tools for the analysis of fire debris evidence. It collects sources of reference samples and current standard procedures, discussing critically the new methodologies proposed up to 2015 for the extraction and analysis of neat ILs and fire debris samples. It also considers new approaches for the statistical evaluation of data, and presents new relevant knowledge on the distortion effects of the IL chemical fingerprints.

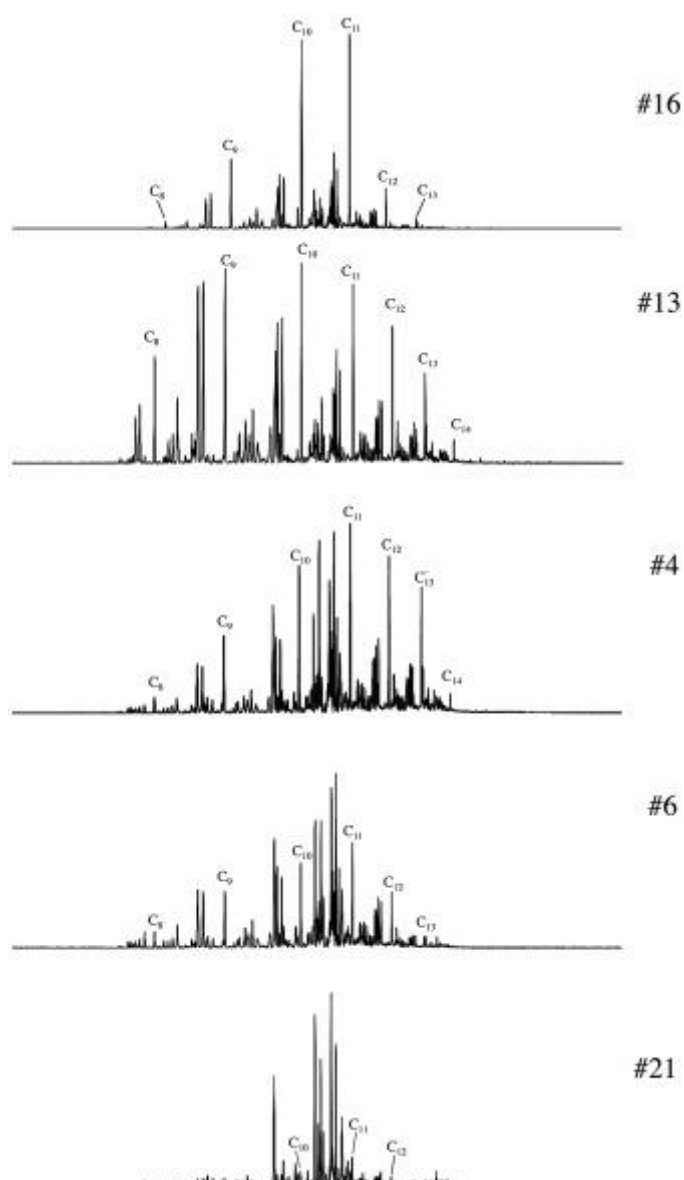
## 2. Analytical tools

In this section, the most recent publications on analytical tools for the forensic analysis of fire debris are reviewed. First, the standard analytical procedures and some sources of consensus-classified reference samples are provided. Second, the existing extraction methodologies and innovations on this topic are critically explained and compared. Then, the developments published from 2008 up to 2015 for the analysis of IL, ILRs and other fire debris samples are discussed. Finally, this section includes the most novel statistical tools used in this field.

### 2.1. Standard procedures and reference samples

The accreditation of laboratories and the use of standardized procedures lead to high quality work and analytical results. Likewise, the certification of the forensic experts ensures that the analysts have sufficient knowledge to perform quality analysis [6], [7], [8], [9]. These three elements assist the court in assessing whether or not to accept the presented analytical results. Regarding to the use of standardized procedures, the National Institute of Standards and Technology (NIST) [10] and the American Society for Testing and Materials (ASTM International) [11] are some of the institutions who provide detailed (technical) information and develop quality consensus guidelines. Examples of these are the guides covering the extraction of ILRs, the analysis of fire debris, and the classification of IL and ILR samples. The current ASTM standard practices for the extraction of ILRs are described in Refs. [12], [13], [14], [15] and the standard test method for the interpretation of ILRs extracted from fire debris samples is showed in Ref. [16]. This last ASTM standard also recommends that each lab should have its own database of IL references and extracts from common substrate materials containing no additional ILs. However, not all forensic laboratories can obtain and maintain a large collection of reference samples. For that reason, the National Center for Forensic Science (NCFS) at the University of Central Florida (UCF) keeps updating the Ignitable Liquids Reference Collection (ILRC) [17]. This is a comprehensive library of representative samples of ILs and characterization data, gathered according to the ASTM guidelines, and developed jointly with the Technical/Scientific Working Group for Fire and Explosives (T/SWGFEX) [18]. Besides, the NCFS and other institutions from the E.U., for instance The Netherlands Forensic Institute (NFI) have created an international database of substrates [19]. These information-rich databases are very useful to obtain additional data and reference samples of usual and unusual ILs [1], for trying to determine directly or indirectly the IL source, or for direct comparison of datasets and inter-laboratory data.

They are also important since some samples of interest, such as gasoline, have an inherent variability within some compound classes, which depends on a broad range of factors such as the geographical location (e.g., country or state), season, refinery, or brand. As is well said by Baerncopf and Hutches, it is essential to bear in mind that this variability might affect the examiner's perception of what is contemplated to be within the normal range of a given class [20]. In this regard, Sandercock published data on 73 gasolines sold in diverse Canadian service stations, and representing different refiners operating in winter 2010 [21]. The author highlighted some of the unusual features patterns of these samples. It is important to note that some of the Canadian-refined gasoline is exported into the domestic market of other countries (e.g., USA), so they might be detected in casework from some regions of those countries. In another survey, in this case, dealing with gasoline collected from the US market during 2008 [22], Hetzel tried to determine the real variability of their chemical compositions. An example is depicted in Fig. 2, where the extracted ion profiles (EIPs) of several gasoline samples displayed wide variety in their alkane content. Branched alkane dominated the chromatogram at the bottom of Fig. 2, and n-alkanes dominated the chromatogram at the top of the figure.



**Fig. 2.** Alkane extracted ion profiles (EIPs) of several gasoline samples at the 90% evaporated stated collected from different sources. The n-alkanes are indicated in the profiles as C<sub>n</sub>, where n indicates the number of carbons present in the n-alkane. The number on the right is the sample number studied in Ref. [22]. Reprinted from Ref. [22] with permission from Wiley.

Bruno et al. applied the advanced distillation curve (ADC) method to study ILs [23], [24]. This tool might provide forensic laboratories with IL reference data which can predict the ILs evaporation patterns. It can also be useful for results validation or providing more information in certain cases (e.g., unusual ILs [20]) where evaporation or weathering hampers the identification process. Besides, it is mainly useful where evaporation of a neat IL is not possible due to the small amounts of liquid, and for training analysts. Nonetheless, for the time being, it does not replace the use of experimental weathering at the laboratory with subsequent GC–MS analysis, since this methodology



cannot reproduce other important parameters in the weathering process such as ventilation, HS above the liquid or liquid volume. Additionally, Sandercock proposed a very useful methodology to create libraries of pyrolysis reference samples generated from common materials [25]. It consists of a temperature programmable steady-state mini-tube furnace which has shown very reproducible data.

## 2.2. Extraction methodologies

Kabir et al. reviewed the innovations and trends reported up to 2011 regarding the preparation techniques for several forensic applications, like ILR samples from fire debris [26]. Nonetheless, such good review did not consider some articles published in the 2008–2011 period, which will be discussed henceforth after a brief comparison of the current standardized practices covered by ASTM. In addition, the most recent innovations and methodologies in laboratory sampling techniques for fire debris samples in the 2011–2015 period will also be examined.

### 2.2.1. Comparison of extraction methodologies

The laboratory sample preparation step should be minimized in forensic applications. When sample preparation cannot be avoided, it is important to prevent any sample loss and concentrate the analytes to achieve as low detection limits as possible. The current standardized extraction and concentration practices covered by ASTM International include solvent extraction, and passive and dynamic HS concentration [12], [13], [14], [15]. Among these extraction methodologies, solvent extraction is the oldest, although it is still widely accepted as a valid technique when appropriate due to its high efficiency for extracting ILs. It is useful for extracting samples with nonporous matrices, and for heavier and non-volatile molecules (e.g., compounds above C18 or triglyceride molecules from vegetable oil) [1], [27]. Amid its drawbacks, this methodology requires toxic organic solvents for extracting the analytes, its potential for damaging the matrix and the instrument due to the plasticizers extracted from the matrix, the possible production of by-products and extensive matrix interferences [1], [27]. In addition, the selected solvent might be incompatible with the solubility of certain ILRs, such as polar compounds, and it may cause losses in the higher volatile fraction when evaporating the sample solvent. HS/adsorption techniques are easy to operate, allowing enough sensitivity while keeping the samples integrity whilst offering the possibility of multiple extraction from the same sample, automation, and portability [1]. Activated carbon strips

(ACS), which are composed of a homogeneous mixture of activated carbon and embedded polytetrafluoroethylene (PTFE), are used to extract ILRs from fire debris. This methodology has high adsorbing capacity for a wide range of compounds. However, it might involve long extraction times, followed by a required solvent desorption of the analytes prior the actual sample injection [27]. Some of these solvents, such as carbon disulfide, are toxic and harmful to the environment [4]. In this regard, a study proposed alternative solvents for the extraction of 57 volatile organic compounds [28], although they should be tested with real ILR samples. Another drawback is that some compounds might be preferentially adsorbed because ACS has low efficiency recovering oxygenated and low molecular weight compounds, leading to skewing of the chromatograms [27]. Compared to ACS, solid-phase microextraction (SPME) benefits from several types of sorbents [4], [27], it involves relatively shorter extraction times, and allows the ILRs direct extraction from aqueous matrices [29]. Moreover, the analytes desorption is achieved by high temperature in the analytical instrument's port, therefore the procedure is rather solvent-less [1]. The downside of SPME is that it shows significant skewing of the chromatograms because the number of adsorption sites in the SPME fibres is very limited compared to ACS [27]. Depending on the fibre type, some compounds may be preferentially adsorbed (e.g., heavier components over lighter ones) [27]. In addition, SPME fibres are fragile, have limited lifetime, and need to be cleaned between analysis to avoid contamination [1], [27]. There are also some limitations with the SPME autosamplers, for which small and representative samples have to be selected, which may not be feasible in certain cases. This technique has, so far, been recommended for screening tests by ASTM International [13]. Dynamic HS extraction (purge and trap) can be run in positive or negative pressure modes (using inert gas or vacuum), therefore it might require more complex instruments: evidence containers fitted with an input and an exit tube, a gas or vacuum line and heaters [1]. The vapours will pass through an adsorbent (ACS or Tenax®). In the case of use ACS, after the extraction and concentration step, it is necessary to remove the analytes from the adsorbent, washing it with a solvent, or by thermal desorption [27]. It offers very fast extractions and high (or the highest) sensitivity. However, it may be destructive when using ACS as adsorbent because any ILR present in the sample could have been completely removed. Nonetheless, it is possible to preserve part of the extract [1], [27]. When using Tenax®, the desorption step is deemed destructive since the thermal desorption does not turn out in any sample surplus, but the methodology is still considered non-destructive since the volume of HS sampled is very small [27]. Table 1 summarizes and compares important features of these extraction techniques such as sensitivity, time of extraction or destructiveness.

**Table 1.** Comparison of some features of the most used extraction techniques in fire debris analysis. Adapted from Ref. [27].

Technique	Required volume of IL ( $\mu\text{L}$ ) <sup>a</sup>	Extraction time (h)	Contamination	Destructive technique?
Solvent extraction	1–10	1–2	Moderate	Yes
ACS	0.1	1–16	Little to none	No
SPME	0.1	2	Moderate	No
Dynamic HS	>0.1	1.5	Moderate	Yes/no

<sup>a</sup>It may depend on the nature of the sample, the size of the container, the amount of ILRs, and the extraction parameters.

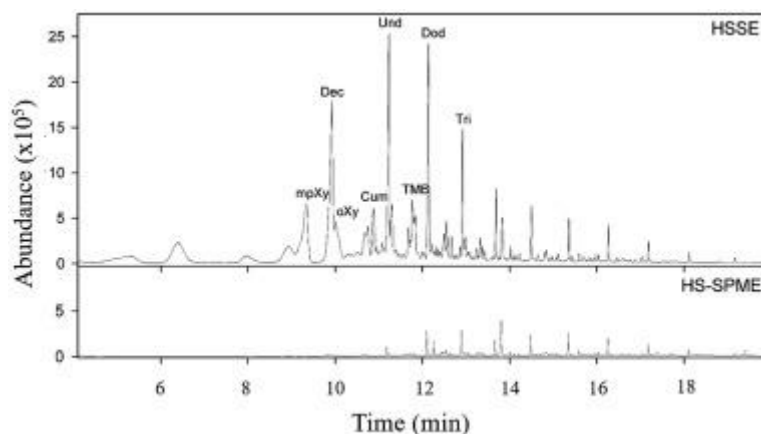
### 2.2.2. Novelties in passive HS concentration

During the last years, some novelties have been published about passive HS concentration. In 2008, Ahmad et al. [30], and in 2011, Amini et al. [31] proposed new materials for modifying the SPME fibres as an alternative to the commercially available SPME fibres. They also looked for better qualities for ILR extraction from fire debris. In the first work [30], a home-made SPME fibre coating prepared by sol–gel technology was proposed. It showed a good selectivity towards gasoline, diesel fuel and kerosene compounds, and slightly higher extraction capability by comparing it with the conventional Polydimethylsiloxane/Divinylbenzene (PDMS/DVB) fibres. However, the authors did not provide information about their thermal stability or durability. In the second study [31], the new proposed material was an ionic liquid bonded to the fused-silica fibre. It was reported to give the appropriate thermal stability and durability. The authors successfully tested the chemically modified fibres during the methyl tert-butyl ether (MTBE) extraction from gasoline samples. However, other important gasoline

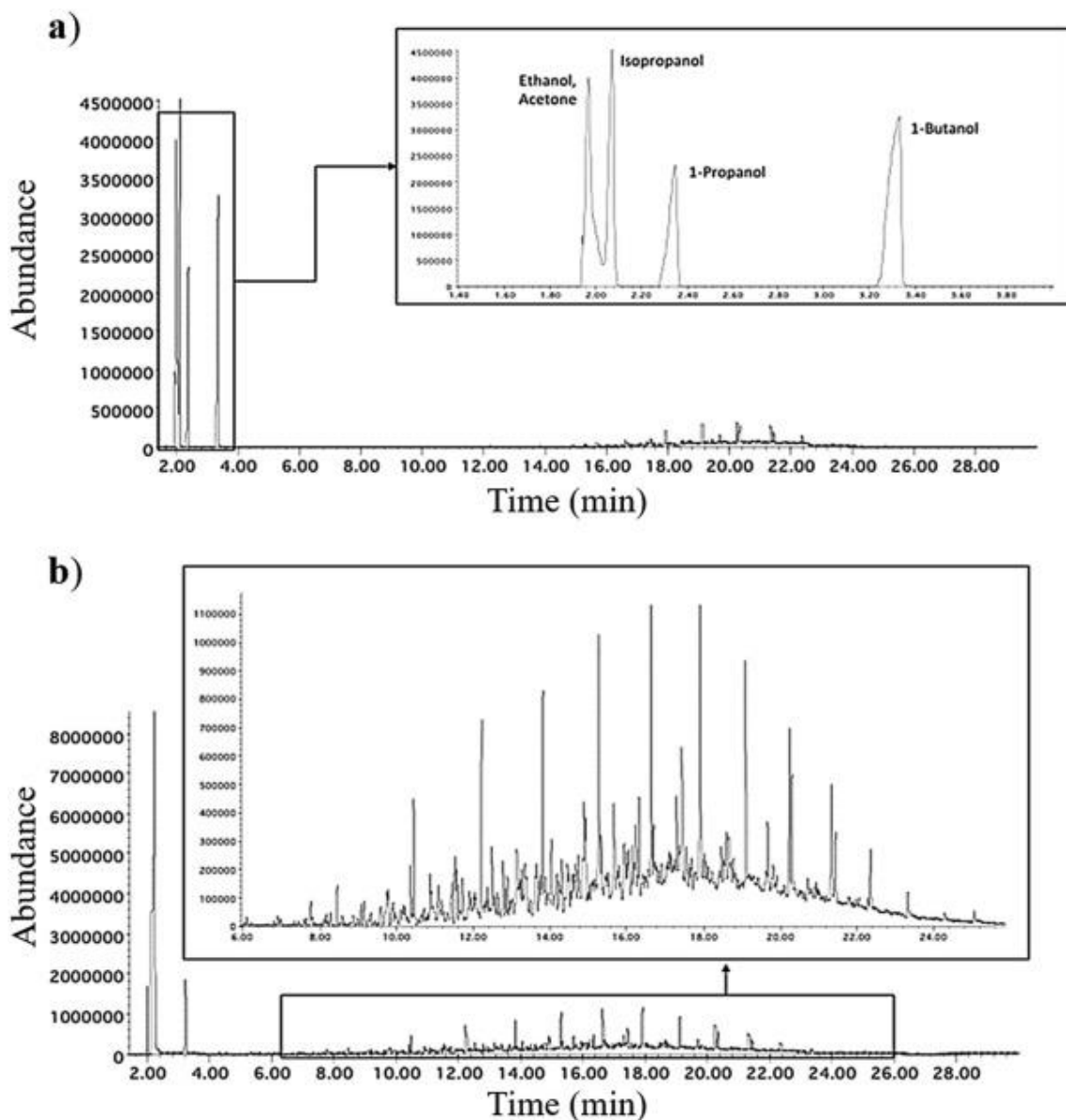
compounds were not evaluated. Two new SPME methodologies were recently proposed. One of these works was focused on the determination of ILs in aqueous samples using a PDMS fibre [29]. The complete procedure by SPME–GC coupled to a flame ionization detector (FID) was validated and applied to water contaminated by gasoline and water used to extinguish a simulated fire. In the second study, Fettig et al. proposed HS–SPME for the analysis of ILRs from fire debris [32]. The selected fibre was a mixed polymeric stationary phase (Divinylbenzene/Carboxen/Polydimethylsiloxane, DVB/CAR/PDMS) able to adsorb analytes of different polarities. This type of versatile fibre is interesting because of the previous unknown nature of the ILRs, which hinder the selection of the most suitable technique. They applied this methodology for extracting mixtures of gasoline and diesel fuel from burnt carpets and particleboard. They achieved the recovery of the selected compounds from both ILs types, however they did not address the recovery of oxygenated compounds. Then, the same research group went further by applying that methodology to the analysis of swipe soot samples obtained from walls of real fire scenarios where gasoline was used to start the fire [33]. They were able to detect the presence of ILRs in some of them.

As an alternative to the SPME methodologies, Cacho et al. proposed in 2014 a novel procedure for the ILRs pre-concentration [34]. They used HS sorptive extraction (HSSE) with PDMS stir bars, followed by a GC–MS analysis. This was the first application of this technique in this field. They analysed spiked samples of 5 different ILs types (gasoline, diesel fuel, kerosene, industrial solvent, and turpentine), and simulated fire debris made with a sawdust–soil mixture. Then, they compared their results using HSSE with those from a HS–SPME–GC–MS methodology. Fig. 3 shows a comparison of both methodologies while analysing a soil spiked sample comprising a gasoline and diesel fuel mixture. The HSSE approach reached higher sensitivity and better effective extraction than the SPME method because of the higher PDMS extraction phase volume of the HSSE stir bar. HSSE does not need organic solvents because the stir bars are directly desorbed thermally. Some disadvantages of the HSSE extraction technique are: a strong matrix effect, the requirement of an exhaustive control of the extraction temperature, the PDMS stir bars are assembled into a specific and expensive GC injection port, and the bars must be properly cleaned and conditioned before the next use. This is because some high boiling point compounds such as polycyclic aromatic hydrocarbons (PAHs) may not have been properly removed after the desorption step. Besides, the system cannot store samples for later analysis, the sampling cannot be automated, and it has a limited variety of analyte polarities for the available stationary phases [35]. Therefore, further investigation is necessary to develop new adsorption

materials with a more efficient thermal desorption, and thus, a wider applicability on a broader analytes range, including polar compounds. Adam B. Hall and his research group published two studies in 2014 regarding a new heated passive HS extraction methodology based on zeolites [36], [37]. Their new procedure was motivated by ACS's low efficiency when recovering oxygenated and low molecular weight compounds. The first study focused on the recovery of oxygenated ILs (acetone, ethanol, propanol, butanol and isopropanol) from fire debris [36]. Zeolites showed higher affinity for polar compounds than other adsorption materials, improving their recovery from the tested fire debris and also from mixtures with water. This is important when considering fire brigades' intervention, which may use water to extinguish the fire. In the second paper, zeolites were presented as complementary technique to ACS since they may be useful to analyse unknown ILs mixtures [37]. When using the dual-mode adsorption method with both ACSs and zeolites, carbon strips were able to recover gasoline/diesel fuel compounds while zeolites recovered oxygenated compounds. In other words, this combined method presents the benefits of both separate techniques. Fig. 4 shows a competitive extraction of oxygenated ILs and diesel fuel. In spite of those good results, zeolites still need solvents for the analyte desorption as ACS do. Moreover, even though the extraction procedure is carried out in a single step, both extraction aliquots have to be analysed separately by GC–MS.



**Fig. 3.** Comparison of the elution profiles of a gasoline and diesel fuel mixture from a sawdust–soil sample obtained using HSSE and HS-SPME procedures. Analytical conditions in Ref. [34]. Adapted from Ref. [34], Copyright (2014), with permission from Elsevier.



**Fig. 4.** Chromatographic data produced by competitive recovery of oxygenated compounds and diesel fuel by: a) zeolite 13x desorbed in methanol, and b) carbon strip desorbed in carbon disulfide. Merged figures (Fig. 7, Fig. 8) from Ref. [37]. Adapted from Ref. [37], Copyright (2014), with permission from Elsevier.

Passive HS concentration has also been used for sampling at fire scene. Thus, a recent research article by Smale et al. focused on the search of suitable techniques for extracting ILRs from concrete at fire scene [38]. Before, some adsorbents such as flour, diatomaceous earth or coffee grounds were used for this aim. In this case, they compared four techniques, three adsorbent materials (adsorbent matting, cotton pads, and cat litter), and a new device called passive headspace residue extraction device (PHRED). The first two adsorbent materials produced negative results extracting

gasoline residues from concrete. It should be noted that this research work seems to dismiss the use of cotton pads for this purpose, which have been used in casework. Between cat litter and PHRED, the latter was the most effective in recovering ILRs. This device might be a suitable way to obtain ILRs directly at the fire scene, however it did not show identifiable IL compounds in all tests. Another interesting issue of the fire investigation and the analysis of its related evidence is the collection of ILs from suspects' hands. Two research groups, one of them from the University of Lausanne (Switzerland) and the other from the Israeli Police, proposed simple methodologies by passive HS techniques for the in-the-field sampling of these traces. The first one proposed placing polyvinyl chloride (PVC) gloves on the suspects' hands for 20 min, and then extracting the ILs by ACS [39], [40]. The second research group suggested the use of nylon bags and ACS devices which are placed on the suspects' palms [41], [42]. The methodology proposed by the research group from the Israeli Police reached better level of sensitivity, detecting little amounts of ILs (around 10–50  $\mu\text{L}$ ).

Although vegetable oils are less common samples in casework, they might be also found in fire debris. They might be used to start fires due to their propensity for self-heating (e.g., when used as delaying ignition systems in improvised incendiary devices, IIDs), and their capacity to increase the fuel load of a fire initiated by other means. These ILs contain fatty acids (FAs), which are not volatile, therefore the solvent extraction is usually followed by a derivatization into fatty acid methyl esters (FAMES), and GC–MS analysis [43]. Nonetheless, as it will be discussed, HS concentration has also been explored for the analysis of samples related to vegetable oils. Mikuma and Kaneko suggested a methodology for the analysis of neat vegetable oils with SPME–GC–MS [44]. It comprises the immersion of the fibre in the sample for 30 min, and then the fibre is directly injected into the GC injection port. However, this method is only suitable for the analysis of the unsaponifiable components of vegetable oils such as sterols. After the thermal desorption of these constituents, the fibre is exposed to solvents to recover the FAs which are analysed on GC as FAMES after their base-catalysed transesterification. Schwenk and Reardon, investigated some factors related to the degradation of vegetable oils and their composition modification [45]. They concluded that the exposure to the heating during passive HS concentration does not modify the FAMES composition of the studied vegetable oils. Other fuels of interest in fire debris analysis are biodiesel and ethanol blend fuel. GC–MS together with the extraction methodologies above discussed, SPME and solvent extraction, were proposed for the analysis of these neat ILs and ILRs obtained from fire debris [46]. However, SPME showed lower efficiency extracting FAME components from biodiesel. Other authors also

developed methods based on solid phase extraction–GC–MS for the characterization of biodiesel composition [47], [48].

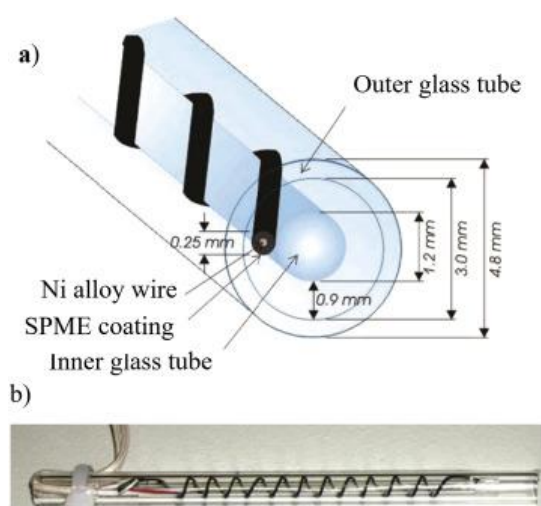
Recently, a real approximation to evaluate the chance of finding traces of gasoline on clothing and shoes of a person after performing common activities such as refuelling a vehicle with gasoline or using a lawn mower has been studied using ACS for sampling [49]. This study might assist in the evaluation of defence arguments in court, claiming the legitimate source of gasoline residues. None of the 29 subjects studied produced positive results in the analysis of traces amounts of gasoline after refuelling their cars. In the case of the subjects who used a lawn mower, only 3 of 17 participants produced positive results, although the chemical components found in the sample were insufficient to confirm the presence of gasoline. HS–GC–MS was also used in order to find gasoline residues in lung tissue and heart blood samples from fire victims. This may help to determine if a victim was alive at the time of a fire [50].

### 2.2.3. Novelties in dynamic HS concentration

In 2009, a high-surface area SPME (HSA-SPME) sampler device for dynamic sampling at high air velocities was proposed by Ramsey et al. [51]. It consists of an oxidation-resistant metallic wire coated with a helical CAR/PDMS film which is in direct contact with the sample air flow. Fig. 5 depicts the configuration of this device. After the extraction, the analytes are thermally desorbed applying an electric current to the metallic wire. Then, it is necessary to reconcentrate the sample on a microtrap for its subsequent analysis. The HSA-SPME method was compared against both passive HS and dynamic flow SPME conditions. This method showed high sensitivity and quick sampling capabilities (around 10 s) for benzene, toluene, ethylbenzene, and xylenes compounds. Although this extraction technique allows to enhance the efficiency of conventional straight SPME fibres due to its 10 times greater total area of extracting phase, it still needs to be tested in the context of fire debris analysis. In 2010, Ueta et al. proposed a methodology using a polymer particle-packed extraction needle [52]. The extraction medium selected was a polymer of DVB, which was packed into the needles. The needles were attached to a vacuum device to manually obtain gaseous samples from a height of 10 cm above the burnt surface. The sampling step was refined to gather only for about 5 min. Then, the extraction needles were attached to an injection syringe containing N<sub>2</sub> gas to consequently inject the sample into the GC injection port. This methodology resulted simple and useful at the scene, not requiring further heating the debris. However, its extraction selectivity and efficiency was not studied in depth.



Besides, for the time being, this methodology has been optimized only for the more volatile aromatic compounds of gasoline (e.g., C1- and C2-alkylbenzenes) and some alkanes (C8 to C14). Recently and for the first time, Nichols et al. applied a methodology called PLOT-cryoadsorption (PLOT-cryo) for the analysis of ILs obtained from fire debris. This is based on the dynamic adsorption of HS vapours on porous layer open tubular (PLOT) columns maintained at low temperature [53]. The system was coupled to GC–MS. They analysed eleven neat ILs in soil samples, and ILRs obtained from three non-burnt and burnt substrates. The authors stated that PLOT-cryo had higher efficiency collecting HS vapours of neat ILs, and that it was faster than conventional dynamic HS or ACS methods. However, the amount of IL (the more volatile components) recovered by the ACS method was greater than that of PLOT-cryo. This was true in spite that the collection time performed for the ACS method was not sufficient enough to fully heat the sample, and that they used acetone as the desorption solvent, which is known to perform very poorly for ACS. This methodology allowed quick ILRs sampling (even under 3 min) from small and large burnt substrates samples. This technique can handle thermally desorbed analytes, although a solvent had to be used for eluting from capillaries. Some additional attractive advantages of this technique include the relative low cost and robustness of these capillaries, the wide variety of sorbent phases available, and the potential portability of this technique. The latter is also an interesting issue regarding fire scene investigations, which still needs further research.



**Fig. 5.** HSA-SPME sampler design of: a) Cross section, depicting the helical SPME phase limited to the region between two tubes of glass. The sampled air is restricted to the space surrounding the HSA-SPME element; b) HSA-SPME device (78.5 mm in length) showing the power connection to the left. Adapted with permission from Ref. [51]. Copyright [2009] American Chemical Society.

## 2.3. Analytical methodologies

This section will discuss the novel methodologies published between 2008 and 2015 for the analysis of samples from fire debris.

### 2.3.1. Novelties in GC analysis

GC–MS is the most used technique to analyse neat ILs and ILRs from fire debris. On this matter, ASTM International proposed a standardized methodology that is generally applied in forensic laboratories [16]. However, during the last years several research groups have proposed some new improvements to that ASTM standard. In 2012, Salgueiro et al. proposed a procedure for quality control of ILRs analysis using internal standards [54], based on the ASTM standards [15], [16]. This procedure checks the sample conservation during storage, the analytes extraction (from fire debris and from ACS), and is also appropriate to check the GC–MS repeatability. Therefore, unlike the methodology proposed by Locke et al. where eight internal standards were evaluated for monitoring only the extraction efficiency [55], this proposed quality control method checks the pre-analytical and analytical steps. Its use could help to identify an inadequate conservation of the samples or wrong extractions, which might give false negative results. In other words, these type of procedures could be useful to confirm true negative results while avoiding false negative ones. Although it could be easily implemented, it would involve extra work such as internal standards addition, weighing or calculation operations. Additionally, from a forensic point of view, it is always better to avoid adding anything to the evidence. In fact, special attention has to be paid while using this methodology with evidence obtained from improvised devices made with gasoline-pool chlorinator mixtures [56]. C<sub>2</sub>, C<sub>3</sub> and C<sub>4</sub>-alkylbenzenes present in gasoline convert to chlorinated alkylbenzenes when gasoline is mixed with pool chlorinators. These chlorinated compounds are similar to the internal standards proposed by Ref. [54]. In 2011, Choodum and Daeid published two articles [57], [58] also focused on improving the ASTM GC–MS methodology E1618-06 (which was already updated [16]). In the first study, they systematically modified several parameters, obtaining enhanced sensitivity and shorter separations times [57]. In the second work, they evaluated the performance of three commercially available GC columns for the analysis of ILs [58]. These GC columns were compared, looking for the best separation efficiency. Baerncopf et al. studied the effect of GC temperature program on the

discrimination of five diesel fuel samples obtained from four different gas stations in the U.S [59]. They tested six different temperatures programs with the ramp rate varying in each program, concluding that this parameter does not affect the association of sample replicates or the discrimination among different samples.

Recently, in 2015, a portable GC–MS instrument was proposed for the analysis of ILRs from fire debris at the fire scene [60]. In this work, a sampling methodology was developed using SPME fibres which took only 3 min for the sampling, and 2 min for the samples analysis. The authors used simulated and real fire debris samples considering four different ILs (gasoline, kerosene, diesel fuel, and mineral turpentine), and seven substrates. The results showed a high percentage of ILRs identified, with a low rate of false negative results. This was true despite that some compounds may be preferentially adsorbed by the SPME fibre, and although there are some downsides in the method's resolution and sensitivity. This instrument showed very valuable features for the presumptive on-site analysis, and as a tool to provide forensic intelligence to fire investigators while they are still at the scene. However, there are some limitations in the analytes extraction and concentration since only specific SPME fibres can be used. Besides, there are also some limitations while configuring some instrumental parameters such as the injection port temperature or the SPME desorption time. Another downside is that the number of analysis and work hours might be delimited by the battery power and the available carrier gas. This instrument should be deployed by the forensic chemists since a prior training is necessary for the use of the instrument and also for the interpretation of the results.

GC–MS shows some limitations separating and identifying structural isomers and heavy hydrocarbons from complex mixtures. To address this concern, some authors proposed new alternatives for the analysis of ILs with potential interest for the field of fire debris analysis. In 2008, Fialkov et al. developed a methodology for the characterization and identification of diesel fuel, kerosene and oils by GC–MS with supersonic molecular beams (Supersonic-GC–MS) [61]. This method allows to characterize heavy hydrocarbons of several ILs, although it was not tested analysing real fire debris. In 2012, Isaacman et al. used GC–MS with vacuum-ultraviolet (VUV) ionization instead of GC–MS with electron impact (EI) ionization [62]. This methodology was able to resolve certain compounds and structural isomers from complex mixtures, such as diesel fuel. This was possible because its ionization system uses less energy than the conventional EI ionization. In addition, comprehensive two-dimensional gas chromatography (GCxGC) coupled to FID [63] or quadrupole MS detector [64] were used for the analysis of fire debris. Likewise, GCxGC-FID was also applied for the analysis of FAMES in biodiesel

fuels [65]. GCxGC is a powerful separation technique, suitable for the analysis of complex samples, with great selectivity and peak capacity, reducing the analyte coelution. However, some of the technique's drawbacks hindering its acceptance for routine analysis in forensic laboratories include the difficulty for interpreting the chromatograms, the lack of data compatibility among laboratories, or its cost [66]. The GC-Fourier transform ion cyclotron resonance MS technique (GC-FT-ICR-MS) showed similar drawbacks while analysing neat gasoline [67]. Nevertheless, it is a powerful instrument for sample characterization and identification of unknown species in low-concentration complex mixtures.

### 2.3.2. Alternative approaches

Other alternatives to GC analysis were also explored between 2008 and 2015 in this topic. They include isotope ratio mass spectrometry (IRMS), artificial nose systems, Laser-induced thermal desorption coupled with Fourier transform mass spectrometry (LITD-FTMS), capillary electrophoresis (CE) and vibrational spectroscopic techniques.

IRMS has shown potential applicability to investigate forensic issues related to the analysis of neat ILs [68]. This tool has interesting features for differentiating ILs sources. In 2011, Gentile et al. proposed a rather theoretical methodological framework using IRMS for several forensic fields consisting of a six-step approach [69]. They discussed many factors that must be considered when using this technology for source identification. The authors suggested the proposal might be applied to both bulk and compound-specific isotope analysis (CSIA), in order to obtain comparable information and quality results. Shortly after, two research groups applied this technology to discriminate neat ILs. Heo et al. used IRMS to study different neat gasoline samples from four different South Korean suppliers [70]. They differentiated among suppliers using multivariate statistical analysis on the obtained data. Harvey et al. studied four different diesel fuel samples from various sources (several geographic locations and time periods), looking for specific components useful for sample correlations and source inference [71]. In this case, because diesel fuel has thousands of compounds, they had to isolate the n-alkane from the diesel fuel samples before the GC separation. They confirmed that IRMS needed pure chromatographic peaks for the isotopic determination of individual components. Therefore, the before mentioned methodological framework [69] might be not useful as-is for all bulk analyses of some type of samples. The obtained data was used to perform multivariate analysis, leading to a good discrimination among the samples. In 2013, Schwartz et al. used GC-IRMS for the analysis of neat ILs (lighter

fluid, lubricant or turpentine) and ILRs from burnt pieces of carpet [72]. They were able to discriminate the different neat ILs by their compound-specific  $\delta^{13}\text{C}$  values. However, they could not obtain similar results analysing post-burnt samples because, after the combustion, there were some changes in several compound-specific  $\delta^{13}\text{C}$  values. Besides, as was mentioned above, the peak purity requirement might not be compatible with interfering compounds from the pyrolysis or matrices. Although, to date, some efforts have been already made by several research groups regarding the effects of weathering on the compounds present in gasoline [73], [74], it would be necessary to fully understand the isotopic fractionation of the analytes of interest, for instance, in the adsorption, dilution, dissolution, volatilisation, biodegradation or matrix interaction [69]. In addition, this technology has been applied to other samples obtained from fire scenes, specifically to burnt matches [75]. The authors analysed the central unburnt wood of burnt matches, which were burnt using ILs and also exposed to extinguishing chemicals. The isotope profile of the unburnt wood was unaffected even after the presence of both type of chemicals. Therefore, this tool can be used to study the origin of the matchstick material (e.g., a box of unburnt matches or the geographical origin of the wood).

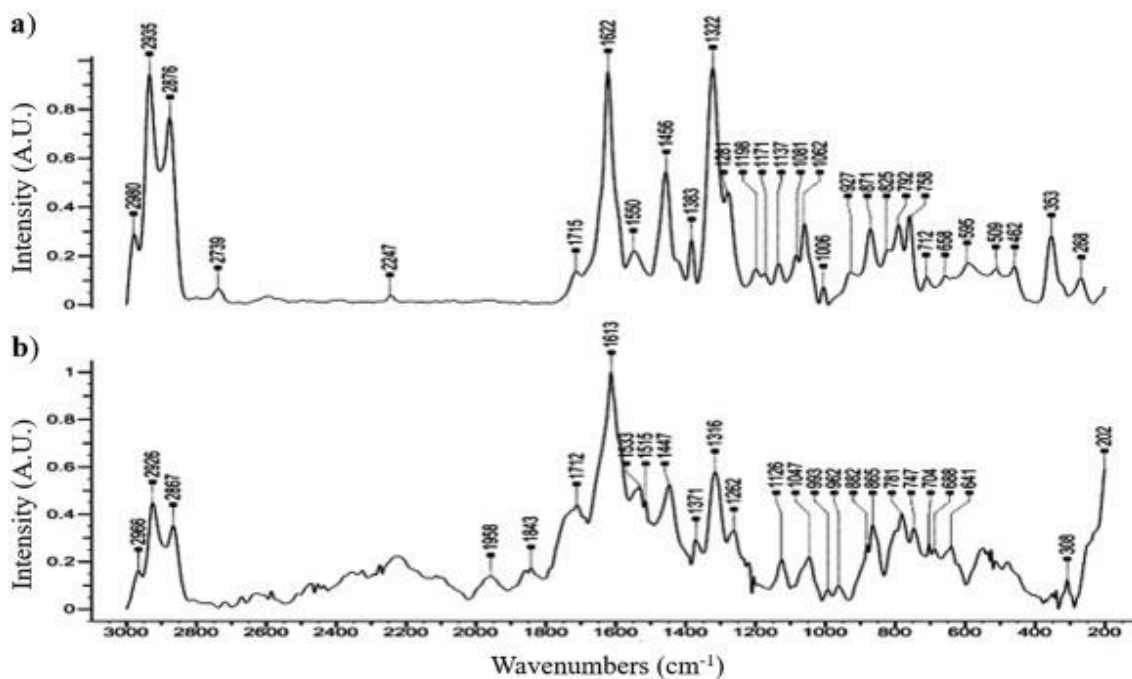
A fluorescence-based artificial nose system for the detection of three neat ILs (gasoline, diesel fuel, and an odourless charcoal starter) and their ILRs obtained from simulated fire debris samples, was employed by Aernecke and Walt [76]. The response of this system was processed using a support vector machine (SVM) pattern recognition algorithm. They obtained high classification accuracy (greater than 97%) for the presence and classification of ILRs in the samples. This methodology might be useful for the rapid identification of ILs or ILRs at the scene. However, its usefulness determining trace amounts of ILRs was not studied. In 2014, Ferreiro-González et al. studied neat gasoline with a HS–MS methodology complemented by multivariate analyses (principal component analysis, PCA; hierarchical cluster analysis, HCA; and linear discriminant analysis, LDA) [77]. The HS was collected with a gas syringe and directly injected into the MS. The method was less expensive, easier and faster (less than 15 min) because it did not require a chromatographic separation. The authors discriminated thirty gasoline samples with two different octane ratings, obtaining a 100% classification of their octane rating. However, because there is no pre-concentration of the samples, the sensitivity of this methodology may be insufficient for certain cases. Some critical parameters such as sample temperature, and samples vials size should be studied more in-depth. Other downsides to mention are its inability to archive samples for later analysis and automatization inability. In 2015, this research group used again HS–MS, in addition to near infrared (NIR) spectroscopy, combined with chemometrics (HCA and LDA) to

discriminate, in this case, 60 gasoline samples by their octane rating [78]. The complete discrimination of two types of gasoline was obtained using LDA. Also in 2015, this research group used the HS-MS to analyse fire debris and other neat ILs [79]. Six substrate samples (pine wood, cork, paper, newspaper, cardboard, and cotton sheet) were burnt with and without any accelerant (gasoline, diesel fuel, kerosene, citronella, paraffin, and ethanol). However, in this case, carbon strips were used to adsorb and pre-concentrate the analytes, avoiding any possible lack of sensitivity. Although this additional pre-concentration step was relatively time consuming, the entire methodology was fast, and did not need solvents for desorbing the carbon strips since thermal desorption was performed. Nonetheless, this procedure would need the optimization of several parameters such as equilibration time, sample temperature, and extraction time. Moreover, in order to avoid signal drifts when monitoring the mass detector state, some kind of normalization procedure is required.

LITD-FTMS was applied by Hutches et al. to study layered soot samples in an attempt to identify gasoline residues [80]. This technique is not common in forensic laboratories, and not especially for this kind of samples because there are other instruments useful for their analysis. Nonetheless, they used this technique after determining the appropriate laser power density for the analysis of soot samples of gasoline on glass surfaces. They also attempted to determine the characteristics of the potential mass spectral profile. They encounter an important shortcoming; that only strong adsorbed compounds of the soot could be analysed. Besides, other pyrolysis and/or background compounds in fire scenes might be strongly adsorb on these samples.

Capillary electrophoresis (CE), with a diode array detector (DAD), is another separation technique that has recently been used for the analysis of fire debris, although this technique has been little used in this field, and it is not as selective and identifying as others. In this case, CE was used for the analysis of a specific type of IID, the chemical ignition Molotov cocktail (CIMC) [81], [82]. The authors proposed a methodology to analyse CIMCs residues in order to obtain the ionic information from their inorganic composition. Additionally, some anionic markers were proposed to identify the ignition system of these IIDs, although some of them may be found in the environment in elevated amounts. A complementary analysis is required to determine any ILs present in the sample. Besides, this procedure requires the alteration of the sample, or even its complete destruction.

Vibrational spectroscopic techniques (e.g., Raman or Infrared) are commonly used in the identification of materials such as PVC or polystyrene obtained from fire debris. González-Rodríguez et al. used Raman spectroscopy for the analysis of household plastic materials (CD and DVD cases, foam packaging, nylon stockings, and carpet) after burning them with several common ILs (gasoline, kerosene, ethanol, and diesel fuel) or with no added IL [83]. They used a complementary PCA classification method on the Raman data of each IL, obtaining in some cases discrimination among materials even after the burning process, and in spite of the abundance of pyrolysis products. However, when the samples were burnt without ILs, the authors were only able to discriminate between samples in the case of nylon and polystyrene from the CD case. In 2013, Kerr et al. published two papers where micro-Raman and FTIR with an attenuated total reflectance (ATR) accessory were used to study household polymeric materials in fire debris [84], [85]. They increased the number of spectra of burnt household materials available in the literature. In both studies, the materials were burnt using newspaper instead of ILs. The Raman spectra of unburnt and burnt polyurethane depict several differences because of the breakdown of some of its compounds, the density and mass loss due to oxidative pyrolysis during burning (Fig. 6). They achieved the material identification combining both techniques and PCA on the generated data. These spectroscopic techniques might also be used for the analysis of other type of evidence found in fire scenes, for instance, residues of pyrotechnic devices like road flares, which are known devices used to ignite fires, or even used as part of IIDs [86]. The potential of these techniques for analysing pre- and post-blast residues of pyrotechnic items has recently been assessed [87], [88]. Furthermore, the analysis of neat ILs (e.g., gasoline) has been performed by several spectroscopic techniques such as nuclear magnetic resonance (NMR) [89], IR spectroscopy [90], [91], NIR spectroscopy [78], [92], [93], [94] and Raman spectroscopy [95]. In addition, a recent work reported the use of a portable ATR-FTIR system for analysing ILs chemically altered by reaction with concentrated sulphuric acid [96]. The acidification or acid alteration process leads to the IL composition change, and therefore, to the modification of their spectral characteristics. Moreover, a portable-Raman system was also used on the non-invasive analysis of ILs inside bottles of Molotov cocktails and for analysing acid altered ILs [97]. Section 3.4 shows more information about this alteration process and its effects. Although these two studies are useful to analyse non-evaporated acidified ILs, for instance used to make IIDs such as CIMCs, further research is necessary regarding the use of these techniques for the analysis of ILRs from fire debris.



**Fig. 6.** Raman spectra of polyurethane: a) unburnt; and b) burnt. Adapted from Ref. [84].

## 2.4. Statistical tools

Multivariate analysis can facilitate and simplify the processing and understanding of the vast quantities of experimental data gathered with analytical techniques (e.g., GC-MS, IR or Raman). During last years, there has been a call for the development of chemometric tools to assist the researchers during the data interpretation, easing it and making it more objective. Although the review proposed by Sandercock reported only few works using chemometric tools [5], its use for the fire debris analysis has increased considerably during recent years. Nonetheless, the Bayesian statistics are still widely accepted and used in the forensic field, and so are being applied for the analysis of fire debris. Hence, this section will discuss the works published from 2008 up to 2015 dealing the statistical analysis of data related to neat ILs and fire debris samples. It has been outlined discussing, in a first place, those works using chemometric approaches, and then those studies applying Bayesian statistics.

### 2.4.1. Chemometric tools

In some of the above mentioned works, PCA only [83], [84], [85], [96], and PCA, HCA and LDA [77] were used to either simplify the data or as complementary tools to corroborate the results. Hereafter other publications use several chemometric tools for



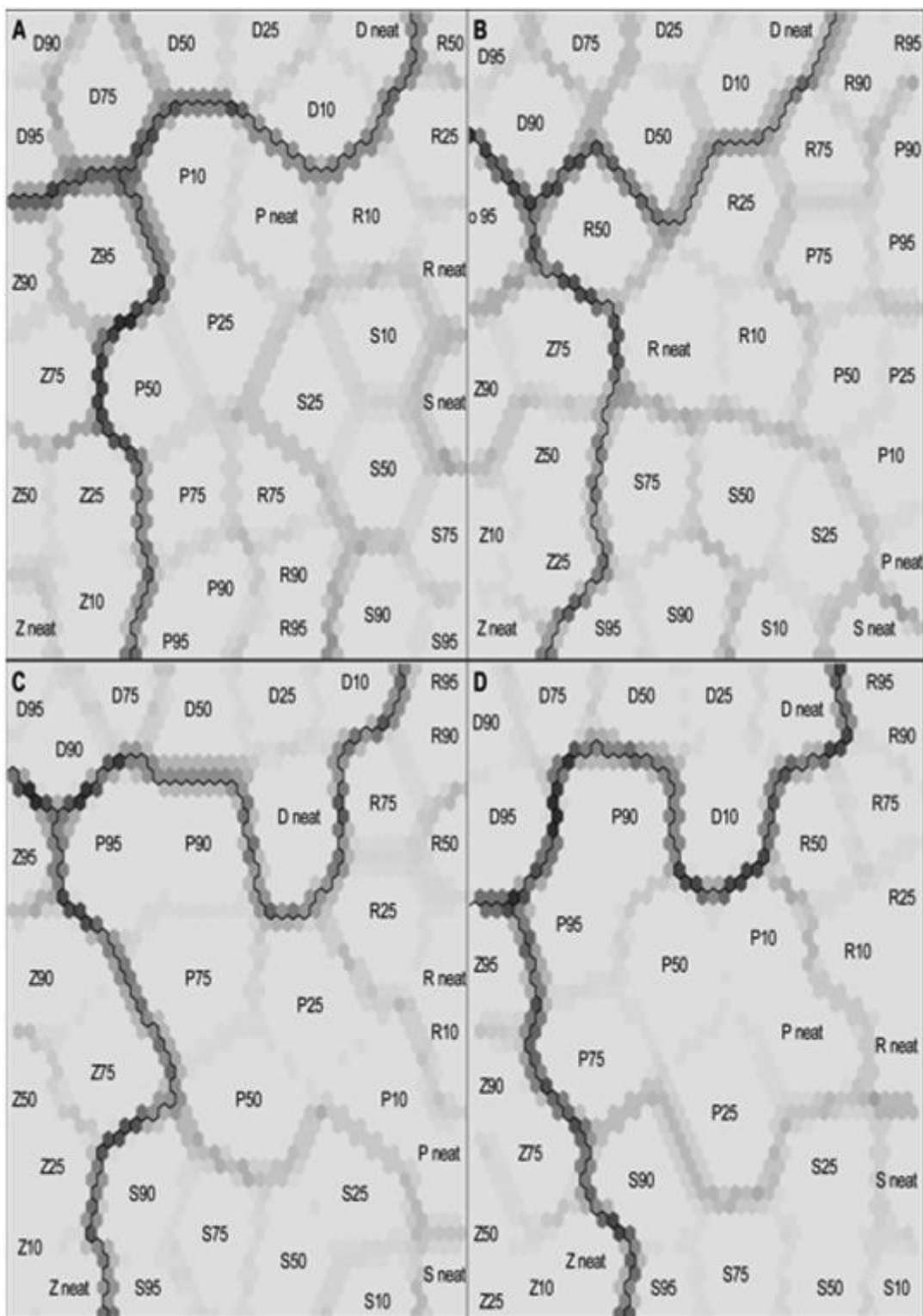
comparing results, differentiating and clustering very similar samples into brand or ASTM classes, or for linking neat IL to ILRs samples. The reviewed studies generally applied the chemometric procedures on a wide range of ILs, always contrasted with well-known ILs classification schemes like ASTM. The most common targeted GC–MS features are TICs, total ion spectrum (TIS, which is an average mass spectrum across the chromatographic profile), extracted ion chromatograms (EICs), EIPs and summed-ion mass spectra (SIMS).

In 2011, Zorzetti et al. used GC–MS, partial least squares-discriminant analysis (PLS-DA), nonlinear PLS (PolyPLS), and locally weighted regression (LWR or LOESS) for the analysis GC–MS data in order to predict the time for which the light petroleum mixture had been exposed to evaporative weathering [63], [98]. All samples were weathered under controlled conditions. In the first work [98], they prepared a 9-compounds mixture representing the characteristic gasoline components. In the second work [63], they used two-dimensional GC×GC–MS and extended their work to gasoline samples with varying octane ratings and from several vendors. In both studies, the hierarchical application of multivariate tools predicted the time for which the samples had been exposed to evaporative weathering. An initial PLS-DA classification model could predict two individual classes: relatively fresh (<12 h exposure time) or highly weathered (>20 h exposure time) samples. The root mean square error of prediction (RMSEP) was used to evaluate the accuracy of the subsequent regression models for these two classes. Remarkably, using a subsequent LWR regression method, the fresh samples of the synthetic gasoline could be predicted to within 40 min of exposure, while the fresh gasoline samples were predicted to within 30 min of exposure. Likewise, the highly weathered synthetic samples were predicted to within 5.6 h of exposure, whereas the highly weathered gasoline samples were predicted to within 5 h of exposure. Although these studies were carried out under ideal controlled conditions, they suggested that this chemometric approach may also allow to date more complicated light petroleum mixtures, with varying weathering conditions or substrates for the weathering. However, it was only tested the direct injection of the samples (as liquid samples). Therefore, it was not studied the use of ACS or other extraction methodologies, which might result in overloading effects, and hence make samples appear more weathered. In 2009 and 2012, Harrington's research group used data pre-processing and projected difference resolution (PDR), PLS-DA, optimal-PSL-DA (o-PLS-DA), and Fuzzy rule-building expert systems (FuRES) to compare and group the experimental data obtained with several methods [99], [100]. In their first work [99], they used SPME–GC–MS and SPME–GC coupled to differential mobility spectrometry (DMS) for studying seven neat ILs and ILRs

from fire debris. Then, they used PDR to compare the gathered GC–MS and GC–DMS data, i.e., one-way TICs and two-way (integrated spectral) data. The results evinced a common experimental practise: the experimental design should include a reasonably large number of samples, and a basic pre-processing of the raw data (baseline correction, dimensionality reduction, normalization, spectral binning, smoothing, etc.) would generally improve the data analysis and its understanding. After calculating the minimum resolution values from the GC–MS and GC–DMS data, they found that the one-way mass data had higher resolution than DMS mass spectra, although the DMS chromatograms resulted more informative for differentiating ILs than the MS chromatograms. They also showed that the two-way data had higher resolution values for both methodologies than the one-way data, while GC–MS always exhibited better analytical performance than GC–DMS. In their second work [100], they used GC–MS to study several neat gasoline and kerosene samples from different gas stations. They also used PDR mapping to compare target component ratios and two-way profiles (chromatographic and spectral information). This approach allowed them to measure quantitative differences among neat IL profiles. In both studies, the FuRES classification was used to check the consistency of the PDR results, proving to be a robust classifier companion for either two-way or component ratio data structures. Likewise, the principal component transformation (PCT) used in both works help the authors to compare the data while keeping both the chromatographic and mass spectrometric information.

In 2011, Monfreda et al. used SPME–GC–MS and chemometrics to differentiate 50 neat gasoline samples of 5 different brands [101]. Their PCA and discriminant analysis (DA) sequence led to a 100% prediction ability in the sample clustering by brand. The study showed that it is possible to differentiate gasoline brands using neat samples. It also provides a data matrix useful to link known to questioned samples. However, because the gasoline composition varies greatly depending on many reasons, it is necessary to update the data matrix in order to apply it to real cases. Around the same time, Mat-Desa et al. published two excellent works using PCA, HCA, and self-organizing feature maps (SOFM) on chromatographic data [102], [103]. In the first one [102] they compared partially evaporated samples of 15 neat lighter fuels from 5 different brands. SOFM allowed them to relate by brand the degraded ILs samples to their non-evaporated ILs. Fig. 7 shows the SOFM topographic maps of neat and partially evaporated samples (U-Matrix visualization method). The degree of similarity/dissimilarity among groups is shown by the differences in the boundary lines, where darker boundary lines mean a higher degree of dissimilarity. The analysed samples were correctly classified (clustered) using normalized fourth root data (Fig. 7D).

In the second paper [103] they studied neat and evaporated medium petroleum distillates (white spirits, paint brush cleaner, and lamp oil). Again, using PCA, HCA, and especially SOFM, they could relate the brands of both neat and partially evaporated samples. This was particularly true with datasets containing hydrocarbon compounds showing higher boiling points.



**Fig. 7.** SOFM topographic maps of neat and partially evaporated samples of lighter fuels. A, B, C, and D represent the maps of raw data, normalized, normalized square root and normalized fourth root transformation data set, respectively. The different samples are represented inside the maps by letters and numbers: brands of lighter fuel are represented with a letter (D, P, R, S, and Z) and the degree of evaporation with a number. Reprinted with permission from Ref. [102]. Copyright [2010] American Chemical Society.

In 2011, Sinkov et al. performed PLS-DA on raw (non-integrated) chromatographic data of different samples aligned using a ladder of perdeuterated alkanes, which improves the quality of the data alignment [104]. Most other approaches were reported to face a challenge while aligning the chromatographic data when the background matrix of the samples varies greatly. This method involving the perdeuterated alkanes successfully discriminated on whether or not gasoline residues were present in some fire debris. In 2014 his research group applied, for the first time, chemometric tools to real casework arson data [105]. They used the same alignment procedure using a ladder of perdeuterated alkanes and then, the PLS-DA and soft independent modelling of class analogies (SIMCA) methodology. The samples used came from real caseworks, thus there was no control over the ILs amount, type of matrix, sample weathering state, or ILs origin. Furthermore, the samples were prepared by different analysts and analysed on different systems. Both well-trained classification models allowed them to classify the casework samples (with 100% accuracy) as being either gasoline-containing or gasoline-free samples.

In 2011, Cramer et al. studied tiny chemical changes produced during microbiological growth in four different inoculated diesel fuels [106]. They used interval-oriented one-factor parallel factor analysis (PARAFAC) spectral interpretation augmented with an ANOVA-based result-filtering step. This alternative GC-MS peak selection strategy was developed in order to increase the capability for detecting miniscule, chemically relevant compositional differences. They found that such strategy outpaces the deconvolution-based peak selection and two control strategies. Besides, because the methodology does not rely only on assessing the fuel analytes, other complex hydrocarbon mixtures and GC-MS data could also be analysed the same way. Moreover, it could be adequate for an automated analysis methodology ready for non-expert fuel analysts.

In 2012, Li and Dai applied several chemometric tools on Raman spectra from 128 gasoline samples belonging to three different brands from three dissimilar refineries [95]. They acknowledged that PCA alone could not result in a proper classification of gasoline samples when they are partly overlapped in the principal component space. Instead, they compared LDA based on PCA, least squares support vector machine (LSSVM), local LSSVM, and local correlation coefficient weighted LSSVM (R-LSSVM) classification algorithms. The Euclidean distance and R were used to select neighbouring samples. They reported that the best classification results were obtained when using the R-weighted LSSVM algorithm.

The research group led by Waddell Smith and McGuffin has made a great effort proposing new chemometric approaches. In 2008, they combined PCA and Pearson product moment correlation (PPMC) for studying the GC–MS data from 25 diesel fuel samples representing 13 different brands [107]. The mass-to-charge ratios were identified to represent aliphatic ( $m/z$  57) and aromatic ( $m/z$  91 and 141) compounds. PCA and PPMC evaluated the TIC and EICs of the chosen ions. The higher PPMC coefficients corresponded to the diesel fuel samples from the same brand, whereas those from different brands got lower values. In general, EICs showed a wider range of correlation coefficients than the TIC. PCA grouped the diesel fuel samples into four distinct clusters for the TIC. Given the relative amount of aliphatic versus aromatic components, both PPMC and PCA suggested that the aromatic components (specifically, those with  $m/z$  91) give the greatest discrimination among diesel fuel samples. In 2009, they used again this methodology to investigate the association and discrimination among five neat diesel fuel samples, and the association of a diesel fuel residue to its neat counterpart [108]. They used the TICs and EICs of the generated alkane and aromatic compound classes. They found that PPMC coefficients for pair-wise comparisons of the neat diesel fuel samples were usually greater than 0.80. Their approach could distinguish more pairs of diesel fuel samples based on TICs and aromatic EIPs than those based on alkane EIP. Thus, they concluded that the aromatic content was more variable among the diesel fuel samples, and probably more useful than the alkane EIP to distinguish the samples. Although the PCA studies on diesel fuel or diesel fuel residues showed some apparent clustering, they were generally not very successful. They acknowledged some limitations in the data set size, the retention time alignment algorithm, and the subsequent effect on the association and discrimination of those samples. Shortly after, this research group, performed two investigations combining again PCA and PPMC coefficients in order to study diesel fuel samples [59] and to compare ILRs from a burnt matrix to their corresponding neat ILs [109]. In the first work [59], they employed GC–MS on five diesel fuel samples to investigate how the association and discrimination of the samples may depend on the effect of the oven temperature program. For each temperature program, PPMC coefficients and PCA were applied on the TIC and EIPs to evaluate differences in discrimination among the diesel fuel samples. Based on the scores plots, the association of diesel fuel replicates and discrimination among samples were similar for all temperature programs. However, due to the similar alkane content of the diesel fuel samples, once again, the alkane EIP was not useful in discriminating samples. They concluded that the temperature programs including one- or two-step temperature ramps

did not affect the association and discrimination of diesel fuel samples. In the second work [109], they used a matrix consisting of a nylon carpet burnt with six different ILs like gasoline and diesel fuel. This way, weathering and matrix interferences were taken into account when trying to associate evaporated samples with neat ILs. They used the TICs obtained from the HS–GC–MS analyses. The combination of both chemometric tools permitted to link each ILR to its corresponding neat IL even in presence of matrix interferences. However, the use of TICs implies having the references analysed with the same methodology and instruments as the samples, which can be rather complicated. In addition, the IL volume used to burn the matrix was relatively high. For this reason, in 2014, they tried to show the importance of the matrix effect, using lower sample volumes while studying three different levels of evaporated gasoline, kerosene and lighter fluid burnt over a high-density polyethylene (HDPE) matrix [110]. The combination of these chemometric tools allowed them to associate the ILRs with their corresponding ILs. However, the effect of the matrix interferences did not permit to associate the specific evaporation level of the samples.

In 2013, the research group lead by M. Sigman used several chemometric tools to develop a classification procedure for detecting ILRs in fire debris samples [111]. PCA, LDA and quadratic discriminant analysis (QDA) were used on TIS data of neat ILs from the ILRC database [17], and fire debris from building and household materials. TIS data allow to compare inter-laboratory results because they are not influenced by the retention times as conventional TICs are. The optimal model (QDA based on 0% substrate contribution) achieved about 70.9% of true-positives and 8.9% of false-positives rates for fire debris samples. The rate of false-positives increased up when increasing the percent of substrate contribution. In another work from 2014, they performed SIMCA classification on TIS of ILRs samples from fire debris [112]. Although they obtained good classification rates when assigning ILRs into the ASTM classes, the method failed with gasoline and aromatic solvents possibly as a result of the weathering effect. This is due to the relatively low ratio of alkanes to aromatics in evaporated gasoline samples compared to neat gasoline. They also published another work in 2014 [113] using TIS data from the ILRC database [17]. This data comprised mainly un-weathered, burnt, and non-burnt samples from usual materials found in fire scenes. They applied HCA to classify ILs based on their TIS similarities or dissimilarities, achieving a proper clustering with regard to their ASTM classes. However, they excluded the oxygenated compounds and miscellaneous ASTM groups. In another work from 2014, they used SOFM [114] on ILs' extracted ion spectra (EIS) from the ILRC database [17]. EIS are defined as the time-averaged mass spectrum across the chromatographic profile for select ions (hence, a

specific subset of data from within the TIS). These ions are a specific ion subgroup selected from Table 2 of the ASTM standard [16]. They could cluster the EIS of neat and partially evaporated gasoline samples with their corresponding ASTM classes. SOFM enhanced the representation of the class relationships while using just fewer ions, and performing comparably when contrasted to HCA, which requires the TIS. EIS permitted the comparison of inter-laboratory data whilst avoiding retention time shifts. Although it is a promising methodology, more research needs to be done on other ILs and matrices before it is actually used in real caseworks.

In 2008, Petraco et al. studied the variability of gasoline components in 20 retained liquid gasoline samples from fire investigations by means of multivariate pattern recognition methods on GC–MS data [115]. They used PCA, canonical variate analysis (CVA), orthogonal canonical variate analysis (OCVA), and LDA. Considering the variability in the sample population, and knowing a priori the proper group assignments for the gasolines, PCA was able to differentiate all samples in the population using 10 dimensions of data, while CVA and OCVA required only three and four dimensions, respectively. Preliminary studies on weathered gasoline samples indicated that group predictions by CVA and OCVA could be applied to about 75–80% weathered by volume. Therefore, these multivariate procedures were suggested for future more formal and detailed studies. Although it is a constantly-changing field, it is clear that the great variety of chemometric tools are indeed helping in the analysis, classification and identification of ILs, and their by-products found in fire debris.

#### 2.4.2. Bayesian statistics

Regarding to Bayesian statistics, the research group lead by M. Sigman used Bayesian soft classification (BSC) and target factor analysis (TFA) to study household materials burnt with ILs (from laboratory and large-scale tests) [116]. In spite of the matrix interferences, a high percentage of sample classification (75–80%) was achieved. In this case, the chemometric sequence was performed on the TIS data of more than 500 GC–MS analyses of commercial ILs. Although this methodology may favour the assignment of complicated samples into groups, it might be difficult to implement it in real cases because it would require the analysis of multiple samples taken from a single fire scene. In 2014, Vergeer et al. compared the residues of evaporated gasolines (up to 75% weight loss under laboratory conditions), and highlighted the higher relevance of the likelihood ratio (LR) in forensic analysis with compared to the discrimination of gasolines used in classification studies [117]. They developed two LR methods built on distance functions



(based on selected ratios, and trends on vapour pressure, respectively), and one multivariate. The three methods were evaluated by the rates of misleading evidence, an analysis of the calibration, and an information theoretical analysis. In terms of discrimination and rates of misleading evidence, the first distance function performed better than the second one, and much better than the multivariate method. The concept of obtaining numerical values for the strength of evidence for the inference of identity of source in gasoline comparisons, is rather different and challenging. This is especially significant because it would need to be extended to other samples in order to be widely accepted and applied. In 2015, Haraczaj et al., used the commercial software Carburane and GC–FID for analysing about 350 French premium gasoline samples from three types (SP95, SP95-E10 and SP98) [118]. They contrasted the results with unburnt premium gasoline samples found at a crime scene, and at a burnt residential house. They focused on the characterisation of different hydrocarbon families by recognising the linear temperature-programmed retention indexes (ITP), which for an n-alkane corresponds to its carbon atom number multiplied by 100. The software also calculates the relative mass abundances for the identified chromatographic peaks, and the RON and motor octane number (MON) values of the samples. All this data is collected in a large database. For the comparison of the real forensic samples, the software implements the Bienaymé-Tchebychev and the Jarque-Bera statistical tests. The first is an inequality test that assessed the a priori belonging of a sample to one of the three premium gasoline groups. The second test checked the normality and coherence of the results based on the selected reference sample population of the chosen brand and type. All the data from the questioned sample were compared to the results from the normal laws explaining the various gasoline-type brand. Given some limitations of the first test, the second one is rather compulsory. This software combination is said to provide accurate characterisation and comparison of the samples, although the results rely on the analyst accepting the normality test's assessment given by the Gaussian law for each brand within each a priori type.

### **3. New knowledge on the distortion effects**

Some effects could change the IL or ILRs chromatographic patterns or modify their chemical compositions, making their study much more difficult. The presence of background pyrolysis products, the microbial activity on the samples, or the sample evaporation/weathering due to, for instance, the fire heat are the most common distortion effects. Information published before 2008 can be obtained from these references [1],

[3], [4], [5]. In this section, the most recent studies, from 2008 up to 2015, regarding this issue have been grouped according to the phenomena: microbial degradation, matrix effect, weathering/evaporation, and finally the acidification or acid alteration of ILs which has been recently reported.

### 3.1. Microbial degradation

Some bacteria genera can grow on complex mixtures of hydrocarbons, degrading some specific ILs compounds and therefore, the IL patterns might be skewed, hindering the identification process. This degradation might occur quickly in or on porous substrates, such as soil, wood, and other organic substrates. Bacteria can also start growing and damaging the original composition of samples awaiting analysis during storage (long time periods at room temperature in airtight containers). In addition, some fire suppression foams have bacteria deliberately added to assist in fire scene decontamination/soil remediation [119]. Turner et al. have made enormous efforts to shed light on this issue. In 2009 [120], they studied in a similar way to previous references [121], [122] the biodegradation of neat ILs in soil. They achieved similar conclusions on the modification of the composition of several ILs such as gasoline or diesel fuel, and additionally provided semi-quantitative data to elucidate degradation trends. The chemical modifications observed in gasoline samples included the degradation of n-alkanes and some aromatic compounds such as mono-substituted benzenes. Besides, they also observed that n-alkanes were the most affected compounds in petroleum distillates (e.g., lighter fluid, charcoal starter fluid, kerosene, and diesel fuel). In some of these petroleum distillates, the potential risk of IL misclassification is higher because they suffer a large reduction or loss of the most affected n-alkane. Later, they extended the study to other less common ILs like a naphthenic-paraffinic product, a miscellaneous liquid, and a de-aromatized petroleum distillate [123]. They found that the mainly affected compounds were C9–C16 n-alkanes and monocyclic aromatic. Although real fire debris samples were not considered in those studies, in a recent work, they evaluated the effect of microbial degradation in realistic samples over time (on a Molotov cocktail made with gasoline) [124]. This work studied simultaneously both the fire weathering effect and the microbial degradation. They found differences in the loss of diverse compounds depending on the substrate (glass or soil), the device size, and the season, being more extensive in winter than in summer. In this regard, this research group continued studying the effect of the soil and the season [125], [126]. Regarding the soil effect [125], they found differences in the alteration of the chemical composition of gasoline between three

soils obtained from different localization. Concerning the season effect [126], samples obtained during the summer were less affected by biodegradation, probably due to the dry and hot conditions during that period. In addition, the authors proposed benzaldehyde as marker for measuring the extent biodegradation. Furthermore, it is important to study common samples found in real fire cases. In 2013, K. Hutches studied the microbial degradation of gasoline in unused building materials (wood and gypsum wallboard) instead of soil [127]. The results showed the effects of gasoline microbial degradation, although in these cases the microbial colonies were not uniform throughout the substrate. All these results should be taken into account when determining the order of processing or setting the storage conditions for these type of samples. Finally, in 2014, Turner et al. explored different methodologies to avoid microbial degradation and to preserve ILR samples [128]. They proposed an anti-microbial compound to sterilize the soil samples, preserving the gasoline residues on their soil matrices. As consequence, it seems useful to study additional anti-microbial compounds to preserve other ILs on several types of matrices.

### 3.2. Matrix effect

An extra difficulty analysing ILR samples is the matrix, which can hamper their classification and identification. This is due to some type of matrices might release residual products in the boiling point range of common ILs because of its thermal decomposition or pyrolysis. This is the case of polystyrene or PVC, which release pyrolysis products such as aromatic compounds. For this reason, the ASTM standard states that laboratories should keep a library of common backgrounds [16]. As was mentioned in a previous section, the NCFS offers a substrates database [19]. Complementarily, a simple tool has been proposed for the characterization of pyrolysates produced from materials [25]. As an interesting contribution, Contreras et al. warned of a potential source of interferences [129]. While trying to put out fires, the firefighters may mix dishwashing liquids with water in order to create fire-extinguishing agents. Some of these dishwashing liquids contain high abundance of alkylbenzene sulfonates, which in turn could produce linear alkylbenzenes by thermal degradation. When pyrolysed, these linear alkylbenzenes could breakdown into toluene, ethylbenzene, xylenes, propylbenzene, indane or naphthalenes, which are compounds of gasoline. Nevertheless, any erroneous gasoline identification due to the use of dishwashing liquids would probably not be likely because the detected and relative abundances will be very inconsistent. However, the analyst should be aware of the surfactants as potential source

of interferences, and try to clearly identify them. Jhaumeer-Laulloo et al. used GC–MS to characterize 11 household materials (non-burnt and combustion products) because their volatile organic compounds may interfere with the analysis of gasoline residues [130]. Although some typical gasoline hydrocarbons such as toluene or alkanes were detected in several of the non-burnt and burnt samples, they were detected at low-concentration. In another work, a carpet was burnt under controlled conditions, with and without gasoline [131]. When the carpet was burnt without gasoline, the analysis detected the naphthalene produced during the combustion process, which is one of the most observed pyrolysis products. In 2014, Prather et al. analysed HDPE samples burnt without IL and with gasoline, kerosene and lighter fluid evaporated at three different levels [110]. The authors found toluene, alkadienes, alkanes and alkenes in HDPE debris burnt without ILs. HDPE produced Gaussian curves of n-alkanes and alkenes, which are similar to the curves of heavy petroleum distillates, but they could be discriminated from kerosene and also from the other ILs studied in this work.

### 3.3. Weathering/evaporation

Weathering normally results in a change of the ILs composition and the exhibition of slightly different chromatographic profiles. This is due to the evaporation and/or partial burning of the samples. Such events usually result in the loss of the most volatile compounds, shifting the chromatographic pattern to the later eluting fractions. Specific libraries of weathered samples [17] were published in order to help during the identification process. Likewise, some works provided prediction models and knowledge on the evaporation process of gasoline and other mixtures of ILs, and explained how this process affects ILs' properties like evaporation rates, flash points or vapour pressures [132], [133], [134], [135]. In addition, another work studied the sunlight exposure effects on FAMES, sterols and hydrocarbons of diesel fuel, biodiesel, biodiesel/diesel fuel mixtures [136].

In 2011, Zorzetti et al. tried to estimate the age of weathered IL samples. They published two works applying chemometric tools (explained above) to the GC–MS profiles of a homemade mixture similar to gasoline [98] and to the GCxGC–FID profiles of different gasoline samples [63]. These samples were evaporated under controlled conditions and their composition were monitored over time. This methodology could predict with a reasonable accuracy if a sample was relatively fresh or highly weathered, and its age. This model should be tested under other variables such as different substrates or weathering conditions. Furthermore, some new information about the

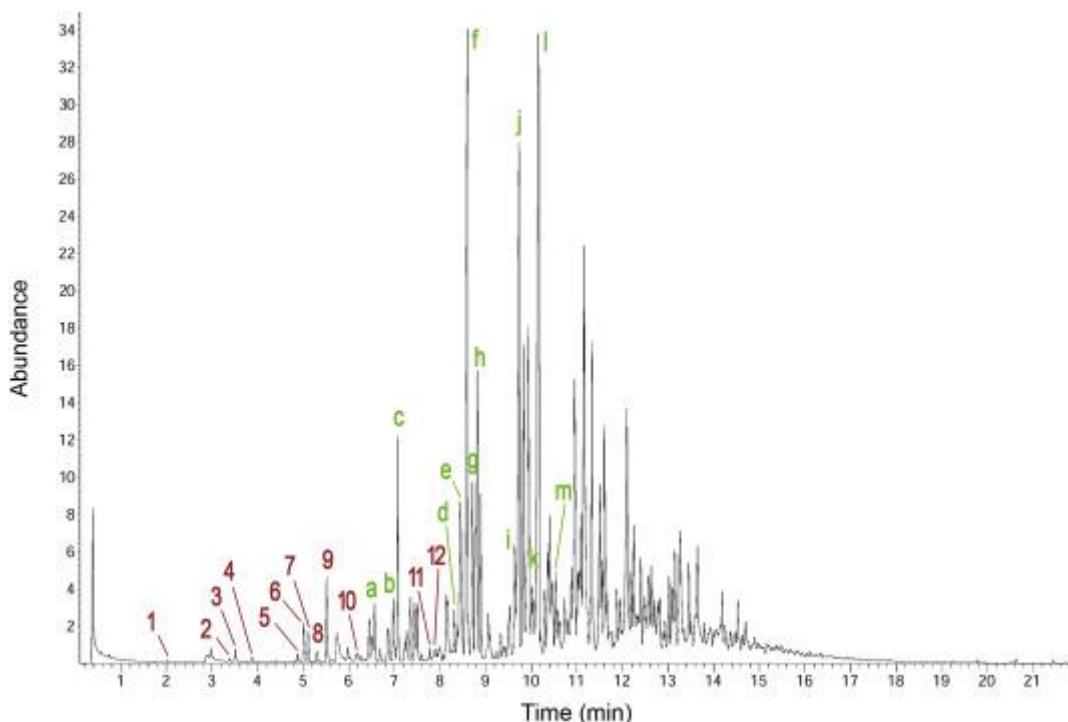
combination of weathering/evaporation, matrix interferences and microbial degradation effects has been recently reported. Prather et al. evaluated the evaporation effect of gasoline and kerosene together with matrix interferences [137]. The partial evaporated ILs were spiked onto a nylon carpet. Then the carpet was burnt, and the ILRs were extracted from the fire debris. The results were compared with neat samples by means of PPMC, HCA, and PCA. They were generally able to get an association of the ILRs with their neat ILs. However, they could not associate the samples with any evaporation degree. Turner et al. published a comparison of some distortion effects combined with multivariate methods [138]. Neat gasoline samples were intentionally weathered or exposed to microbial degradation, and their chromatographic data was studied by means of PCA. This analysis showed that weathering affected mainly the lighter components of gasoline, while microbial degradation mattered to certain compounds such as some mono-substituted aromatics and n-alkanes. Two specific gasoline compounds (1,3,5-trimethylbenzene and 2-ethyltoluene) were less vulnerable to both effects, as was indicated in a previous reference [121]. Henceforth, it would be very useful to study other ILs under both effects, and try to detect if there are other resistant compounds.

### 3.4. Acidification or acid alteration of ILs

In the last years, several works have alerted about the use of some IL-acid mixtures for various criminal purposes. In 2008, Kaneko et al. showed the preparation of illegal diesel fuel (taxed IL in Japan) from fuel oil-A (non-taxed IL) using concentrated sulphuric acid [139]. They mentioned how this practice eliminates the chemical compound added as a non-taxed marker to the fuel oil-A. In this occasion, no more chemical modifications were commented.

In 2015, Martín-Alberca et al. verified this IL modification effect [96], [140], [141]. They showed that gasoline is strongly affected when mixed with concentrated sulphuric acid [96], [140]. This form of mixtures are typical in a type of IID, the CIMC. They found that gasoline loses its aromatic and oxygenated compounds over the reaction time. In turn, new compounds appeared as reaction products, making the gasoline identification not possible using the common criteria [16]. The new compounds were identified as tert-butylated compounds. They were proposed as a powerful tool to identify acidified gasoline. Additionally, the acid alteration effect over diesel fuel was described [96], [140]. This IL was barely affected because its main compounds group, the n-alkane, was not modified by sulphuric acid. However, the modification of aromatic compounds in diesel fuel was indeed confirmed. Furthermore, acid altered gasoline residues from real CIMCs

weathered fire debris were extracted and analysed by SPME–GC–MS [141]. Fig. 8 shows a chromatogram for the acidified gasoline residues obtained from the fire debris of a CIMC. This pattern indicates extensive combustion, in addition to the presence of high amount of tert-butylated compounds. Therefore, the modifications previously observed in non-burnt acidified samples were confirmed in these strongly weathered samples.



**Fig. 8.** TIC for the acid altered gasoline 95 RON residues recovered from the fire debris of a CIMC made 24 h before it was thrown. The identified compounds were 1: toluene, 2: ethylbenzene, 3: 1,3-/1,4-xylene, 4: 1,2-xylene, 5: propylbenzene, 6: 1-ethyl-2-methylbenzene, 7: 1,2,3-trimethylbenzene, 8: 1-ethyl-4-methylbenzene, 9: 1,2,4-trimethylbenzene, 10: 1,3,4-trimethylbenzene, 11: 1,2,4,5-tetramethylbenzene, 12: 1,2,3,5-tetramethylbenzene, a: 2-ethyl-1,4-dimethylbenzene, b: 1-methyl-2-(2-methyl-2-propanyl)benzene, c: 1-methyl-4-(2-methyl-2-propanyl)benzene, d: 1,2-dimethyl-4-(2-methyl-2-propanyl)benzene, e: 1-ethyl-4-(2-methyl-2-propanyl)benzene, f: 1-methyl-4-(2-methyl-2-propanyl)benzene, g: 1-methyl-2-(1-ethylpropyl)benzene, h: 1,2-dimethyl-4-(2-methyl-2-propanyl)benzene, i: 1-isopropyl-3-(2-methyl-2-propanyl)benzene, j: 1,3-dimethyl-5-(2-methyl-2-propanyl)benzene, k: 1,2-dimethyl-4-(2-methyl-2-propanyl)benzene, l: 1-methyl-2-(2-methyl-2-propanyl)benzene, m: 1,2,3-trimethyl-5-(2-methyl-2-propanyl)benzene. SPME–GC–MS conditions as indicated in Table 2 of reference [141]. Abundance equivalent to  $\times 10^6$ . Adapted from Ref. [141] with permission from Wiley.

Finally, as a summary, Table 2 shows the main gasoline compounds affected by the different modification effects explained in this section.

**Table 2.** Main gasoline chemical compounds, and criteria to identify neat and weathered gasoline. Main compounds affected by microbial degradation and acidification of gasoline are also shown.

Compound(s)	Neat gasoline criterion	Weathered gasoline ASTM E1618-14 criterion [16]	Microbial degradation of gasoline	Acid altered gasoline
Toluene	Present in significant amount	Can be present; pattern comparable to reference	Degradation	Degradation to almost disappearance
C <sub>2</sub> -alkylbenzenes	Specific pattern, comparable to reference	Can be present; pattern comparable to reference	Ethylbenzene is quickly degraded	Possible pattern alteration
C <sub>3</sub> -alkylbenzenes	Specific pattern, comparable to reference	m,p,o-Ethyltoluene and 1,2,4-trimethylbenzene shall be present; pattern comparable to reference	Propylbenzene is quickly degraded	Pattern alteration
Naphthalenes	Could be present	May be present	<sup>a</sup>	Quick degradation
Indanes	Usually present	Usually present	<sup>a</sup>	Quick degradation
n, iso-alkanes	Present	Present	Quick degradation, particularly C <sub>9</sub> –C <sub>16</sub> n-alkanes	Present (no alteration)
Cycloalkanes	Present in not significant amount	Not present in significant amount	More resistant to degradation	No alteration
Ethanol	May be present	May be present	<sup>a</sup>	Quick degradation
Methyl tert-butyl ether (MTBE)	May be present	May be present	<sup>a</sup>	Quick degradation
Ethyl tert-butyl ether (ETBE)	May be present	May be present	<sup>a</sup>	Quick degradation
<i>Tert</i> -butylated compounds	Not present	Not present	<sup>a</sup>	Present in significant amount

<sup>a</sup>No information.

## 4. Conclusions and future trends

This review article collected more than 60 research articles, published in the last eight years, where several researchers proposed alternatives and improvements for the extraction and analytical procedures. It also added almost other 60 papers which contributed with very valuable new approaches for the interpretation of data.

The application of current consensus standard practices has been highlighted. Also, the significance of having reliable reference samples, which should lead to high quality analytical results, has been remarked. The international database of IL and substrates references is continually improving and growing, and is presented as a useful tool for fire debris investigations. In addition, several authors have contributed with surveys addressing the inherent variability in gasoline composition. Furthermore, the ADC method offer reference data of IL evaporation patterns to forensic laboratories. Additionally, a steady-state mini-tube furnace can be used generating pyrolysis reference samples of materials.

This review also has compared the features of the current extraction and concentration practices covered by ASTM International. The new proposals in passive HS concentration using new materials for SPME fibres and SPME methodologies have shown to improve the extraction step of several ILs compounds. HSSE and HS extraction based on zeolites have revealed several strengths for the extraction of IL compounds, although further research would be necessary before their routine implementation. New promising ideas for dynamic sampling as HSA-SPME and PLOT-cryo methodologies have demonstrated high sensitivity and quick sampling capabilities for several IL compounds.

GC-MS is well-established for the analysis of fire debris evidence. However, during last years some suggestions were made for improving its performance. For instance, a quality control phase in order to check the pre-analytical and analytical steps, new GC columns or setting different instrumental parameters. Moreover, in order to resolve some limitations of the conventional GC-MS methodology, some authors have used alternative techniques, as portable GC-MS, Supersonic-GC-MS, UVU-GC-MS, GCxGC-MS, GCxGC-FID, and GC-FT-ICR-MS, which have shown to be a good choice to analyse certain fire debris evidence. Regarding the use of IRMS for the analysis of ILs and fire debris, its implementation as a routine technique seems not to be possible



for the time being. HS–MS and spectroscopic techniques combined with chemometric tools are proving to be a promising tool for the discrimination of neat ILs or substrates.

During last years, there was a call for more statistical evaluation of the results. The various proposed methodologies allowed to compare results of similar samples with, for instance, slight variation in their composition. They helped to differentiate and cluster the samples (e.g., by weathering grade, brand, or ASTM class), to associate ILRs with their corresponding ILs, or even to compare data gathered from different laboratories or methodologies. The use of EIS/TIS data in chemometric sequences seemed to be more suitable than the use of other data types because it circumvented the retention time shifts produced by different instruments. The use of deuterated alkanes in order to align the data was also advantageous to compare samples from different sources and characteristics.

Four different distortion effects on neat ILs or ILRs have been reported in this review. The microbial action affects mainly n-alkanes and mono-substituted benzenes of neat gasoline samples. In petroleum distillates, it affects n-alkanes, while in de-aromatized petroleum distillate ILs, it influenced C9–C16 n-alkanes. The matrix effect can be especially important when dealing with synthetic materials related to petroleum products. Some works focused on the discrimination of evaporated samples in order to predict whether those samples were fresh or highly weathered. Regarding the ILs acidification effect, which have been recently reported, it has been demonstrated that is especially notable in gasoline. However, this modification effect on the ILs still needs further research, for instance, studying other acidified ILRs obtained from fire debris.

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