Validation of an HS-MS method for direct determination and classification of ignitable liquids

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ABSTRACT

Fire debris analysis is a key step in fire investigation. Most of the analytical methods used for the analysis of ignitable liquid residues in fire debris require pre-concentration of the ignitable liquid residues prior to the chromatographic analysis. The standard method, ASTM E1412, involves a passive headspace concentration with activated charcoal strips to isolate the ignitable liquid residues from fire debris followed by a desorption procedure from the carbon strip with carbon disulfide.

In this study a non-separative analytical method based on HS-MS eNose (headspace mass spectrometry electronic nose) in combination with chemometric tools, including hierarchical cluster analysis and linear discriminant analysis, has been used to detect and classify ignitable liquid residues in fire debris into the classes defined by the ASTM E1618 standard method. This method allows a direct analysis of fire debris in 10 min and avoids the use of solvent and sorbents.

The method was validated by analyzing a set of burned samples by GC–MS according to the standard methods ASTM E1412 and ASTM E1618. The results obtained on using the method proposed in this study were comparable to those obtained with the reference method. The correct classification rates for assigning ignitable liquid residues into ASTM E1618 classes were in the range of 90% for both methods. In comparison to the standard methods HS-MS does have specific advantages. Apart from the speed of the analysis and the fact that the sample does not require sample pre-concentration, this technique is also safer and ecofriendly since it does not use any solvents or produce any residues.

1. Introduction

The American Society for Testing and Materials (ASTM) standard provides guidelines for the analysis, identification and classification of ignitable liquid residues (ILRs) from fire debris by using GC–MS [1]. ASTM E1618 includes eight classes of ignitable liquids (ILs): aromatic products (AR), gasoline (GAS), petroleum distillates (PD), iso-paraffinic products (ISO), naphthenic-paraffinic products (NP), normal alkane products (NA), oxygenated solvents (OXY) and a miscellaneous category (MISC). The National Center for Forensic Science includes a large online database of ignitable liquids analyzed in accordance with the ASTM E1618 standard test methods [2].

According to ASTM E1618 the identification of the presence of an ignitable liquid and the assignment of it into the correct ASTM class is based on the visual pattern recognition of the total ion chromatogram (TIC), extracted ion chromatograms (EIC), and target compound [1].

This method works well but there are several factors that can alter the chromatographic profile, thus complicating the classification, such as the volume of ignitable liquid, the type of substrate or the pyrolysis products amongst others [3]. Moreover, visual pattern recognition is highly dependent on the skill and experience of the analyst and it does not allow automation, thus making this procedure time consuming. On the other hand, fire debris analysis requires an automated database searching tool that minimizes laboratory-to-laboratory chromatographic variations, simplifies ignitable liquid assignment to ASTM categories, and allows product identification. The application of chemometric tools can potentially help the analyst to identify the presence of ignitable liquid residue and to discriminate between similar samples in a shorter time. As an alternative to TIC some authors have proposed the use of Total Ion Spectrum (TIS), which is calculated by summing the intensities of each nominal mass over all chromatographic times during a GC–MS analysis. In contrast to TIC, TIS is time independent and it therefore allows inter-laboratory comparisons and it has been demonstrated to contain sufficient information for the rapid identification of ignitable liquids in a database [2]. TIS has already been used for the identification

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and assignment of ignitable liquid residues to ASTM classes by discriminant analysis [4], soft independent modeling of class analogy [5], target factor analysis with soft Bayesian decision theory [6], and hierarchical clustering analysis (HCA) [7].

It is well known that the most widely used analytical technique for the analysis of ignitable liquids is GC–MS [8]. Although GC-MS has proven to be useful in this field it requires pre-concentration of the ignitable liquid residues prior to the chromatographic analysis. There are several ways to achieve this goal, including solid phase microextraction [9], static headspace adsorption with Tenax [10] or headspace sorptive extraction [11] amongst others [12]. In the USA, the procedure described in ASTM E1412 based on passive headspace concentration with activated charcoal strips (ACS) [13] is currently the most commonly used method to isolate ILRs from fire debris because of its sensitivity, ease of use, and its non-destructive nature [14,15]. The desorption of the carbon strips is carried out by using a solvent and the eluent is then ready for analysis by GC–MS. Carbon disulfide has proven to be the most efficient solvent but it is very toxic and has a very low autoignition temperature [16]. Furthermore, GC–MS requires long analysis times. Consequently, the development of non-separative methods to solve different analytical problems is of increasing interest. It has been observed that in some cases it is sufficient to obtain a signal profile or fingerprint of the sample formed by all of the components [17].

The HS-MS eNose (headspace mass spectrometry electronic nose) is a non-separative analytical technique used in both the agrifood industry and the environmental field [18]. However, it has previously been optimized and successfully applied for the discrimination of neat ignitable liquids including gasoline samples with different research octane numbers [19,20] and for the thermal desorption of ACSs containing ILRs [21]. In a previous study, the optimization of the parameters which affects the headspace generation (incubation temperature and incubation time) for fire debris in HS-MS system was carried by using wood as a substrate and gasoline or diesel as a ignitable liquids to burn [22]. Different incubation temperatures (ranging from 85 °C to 145 °C) and different incubation times (ranging from 5 min to 60 min) were tested. Based on this study, 10 min was selected as the optimal incubation time and 115 °C as the optimal incubation temperature.

According to this preliminary study, the applicability of the HS-MS eNose in the analysis of the studied ignitable liquid residues was demonstrated. In the work described here, a more robust method applicable to all type of fire debris samples, capable to detect the presence/absence of a ILR but also to classify them into the classes defined by the ASTM E1618 is presented. In order to propose a new method as an alternative to the reference standard method ASTM E1412, it is mandatory to validate the method by using the same sample set. HS-MS eNose combined with chemometric tools is proposed for the direct analysis and classification of ignitable liquids in fire debris. The mass spectra (MS) obtained by the HS-MS eNose are similar to the TIS and they were obtained in a very short time period since chromatographic separation is not required.

Hierarchical cluster analysis (HCA) and liner discriminant analysis (LDA) were applied to the MS data obtained by the HS-MS eNose (45–200 *m/z*) and to the TIS obtained by GC–MS (30–350 *m/z*) for the identification of a set of 92 fire debris samples according to the ASTM E1618 classification. The results obtained on using both techniques were then compared.

2. Materials and methods

2.1. Samples

In this study a total of ten ignitable liquids were used, one from each class, including light, medium, and heavy petroleum distillates (Table 1). All of the ILs are included in the ILRC database at the NCFS [2]. Ten different materials (paper, wood, plastic, cloth etc.) were used as substrates to be burned (see Table 1). Some of these substrates are

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

IL ASTM class	Code	Substrate	Code
Gasoline (SRN 166)	G	Flooring (MRN 097)	fl
Light Petroleum Distillate (SRN 8)	L	Pine wood	pw
Medium Petroleum Distillate (SRN 30)	M	Carpet (MRN 093)	ca
Heavy Petroleum Distillate (SRN 206)	H	Towel (90% cotton 10% polyester)	to
Aromatic (SRN 59)	A	Newspaper	ne
Isoparaffinic (SRN 81)	I	Plastic bottle (PETE)	pb
Normal-Alkanes Products (SRN 241)	F	Plastic bottle (HDPE)	pd
Naphthenic-Paraffinic Products (SRN 53)	P	Parquet	pa
Oxygenated Solvents (SRN 218)	O	Fine grain cork	co
Others-Miscellaneous (SRN 131)	S	Cotton socks	so
None	N		

included in the substrate database at NCFS (http://ilrc.ucf.edu/substrate/). All of the substrates were burned alone without any accelerant and then with each of the ten ignitable liquids.

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

2.2. Burned samples

To simulate post burn samples, laboratory fire debris samples were generated by following the Modified Destructive Distillation method for burning [13] but, in this case, in addition to the 5 cm × 5 cm piece of substrate a further 2 cm × 2 cm piece of the same material was added. The rest of the steps were the same. Once the can was cool, the ignitable liquid residue was extracted from the burned sample by two different methods: (i) by following the ASTM E 1412 standard for adsorption onto activated charcoal strips (ACS) [13] and (ii) the optimized method by HS-MS eNose.

The small pieces of burned substrate were added to an empty 10 mL sealed electronic nose vial (Agilent Crosslab) and analyzed by HS-MS electronic nose. The remaining ignitable liquid residues were extracted with ACS as follows: The headspace above the samples was collected on a 10 mm × 22 mm activated charcoal strip (USA Albrayco Technologies Inc., Cromwell, Connecticut, USA), which was suspended in the headspace of the can by a paperclip and unwaxed dental floss. The can was sealed and heated for 18 h at 66 °C in an oven. The activated charcoal strip was subsequently removed from the can and cut in half lengthwise. One half was desorbed with 1 mL of carbon disulfide and analyzed by GC–MS under the conditions described below. The other half was saved in case further analysis was required.

2.3. Acquisition of HS-MS spectra

Analysis of the samples was performed on an Alpha Moss (Toulouse, France) HS-MS system composed of an HS 100 static headspace autosampler and a Kronos quadrupole mass spectrometer (MS). The samples were placed in 10 mL sealed vials (Agilent Crosslab), which were placed in the autosampler oven to be heated and agitated in order to generate the headspace. Headspace was taken from the vial using a gas syringe and injected into the mass spectrometer. The gas syringe was heated above the sample temperature (+5 °C) to avoid condensation phenomena. Between each sample injection, the gas syringe was flushed with carrier gas (nitrogen) to avoid cross-contamination.

The optimized experimental conditions for the headspace sampler were as follows: incubation temperature 115 °C, incubation time 10 min, agitation speed 500 rpm, syringe type 5 mL, syringe temperature 150 °C, flushing time 120 s, fill speed 100 µL/s, injection volume