CHEMOMETRIC TOOLS USED IN THE PROCESS OF FIRE INVESTIGATION

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ABSTRACT

Fire debris analysis is one of the most challenging steps in fire investigation. Data analysis is subjected to human interpretation by comparing with a reference database. In recent years, chemometric tools have been successfully applied to data in order to avoid misunderstandings and make data interpretation less subjective. In the present study, two ignitable liquids (ILs) (diesel and ethanol) as well as two substrates (cork from *Quercus suber* bark and cotton sheet) were used. Fire debris samples were prepared following the modified procedure of Destructive Distillation Method for Burning. Sampling was performed in delayed times. In accordance with a progressive approach to data, multivariate statistical analyses, such as unsupervised hierarchical cluster analysis (HCA) and principal component analysis (PCA) as well as supervised linear discriminant analysis (LDA) were applied. The aim of the current research is to investigate whether HS-MS eNose is able to detect different ILs among fire debris samples containing different substrates after delayed times of sampling.

Key words: HS-MS eNose, Chemometrics, Fire Debris Analysis, Total Ion Spectrum.

INTRODUCTION

In many criminal activities, such as arsons, ignitable liquids (ILs) are usually used as accelerants. Gasoline and diesel are the most commonly identified accelerants reported by American forensic laboratories since they are easy to obtain (Mach 1977). Samples collected from fire scenes are further analyzed in a laboratory to determine the presence of ignitable liquid residues (ILRs) (STAUFFER *et al.* 2008). Interpretation of laboratory analysis of fire debris is considered as one of the most complicated analysis among forensic sciences (STAUFFER *et al.* 2003). Forensic chemists are tasked with target compounds analysis. The presence of particular target compounds characterizes ignitable liquid. The targets that remain are detectable even when IL is evaporated, diluted or contaminated (KETO and WINEMAN 1991; ALMIRALL and FURTON 2004). The determination of ILRs in fire debris might be the difference between fires that were deliberately or unintentionally set (BAERNCOPF *et al.* 2011).

The American Society for Testing and Materials (ASTM) published standard methods for fire debris analysis and created a classification system for ignitable liquids consisting of eight classes of products. Each class has a precise description (STAUFFER and LENTINI 2003). Currently, The ASTM E1618 (ASTM 2014) describes the standard method for identification of ILRs in extracts from fire debris by Gas Chromatography-Mass Spectrometry (GC-MS). This standard is the most widely used in the globe. According to BORUSIEVITZ (2004), this

methodology is subjected mainly to human interpretation as it is based on the evaluation of total ion chromatogram (TIC) or extracted ion chromatogram (EIC) of the major compounds by visual pattern comparison to a reference database (BORUSIEWICZ *et al.* 2004). Moreover, this methodology is time-consuming and the interpretation of results becomes more complicated as samples are not neat ILS but collected from fire debris.

Problems related to data interpretation are: weathering, microbiological activity and interfering compounds (BAERNCOPF *et al.* 2011). In recent years, several studies have alerted about acid alteration of ILs (MARTÍN-ALBERCA *et al.* 2016). MARTÍN-ALBERCA *et al.* (2016, 2015b, 2015a) verified acidification and acid modifications on ILs. The authors declared, that the interpretation of the compounds of interests are affected, when gasoline is mixed with concentrated sulphuric acid (STAUFFER *et al.* 2003). In addition, it is complicated to classify post-burn samples due to the presence of volatile compounds resulting from substrate backgrounds, combustion or pyrolysis products (ALMIRALL and FURTON 2004; FERNANDES *et al.* 2002).

However, during last years, some improvements on this methodology and new alternatives approaches have been reporting to overcome some of the drawbacks that this methodology presents and to face the new challenges that fire debris examiners have (MARTÍN-ALBERCA *et al.* 2016).

WADDELL *et al.* (2014) stated, that one of the strain of fire debris classification from different laboratories may be caused by comparison of chromatographic data, specifically TICs. Total ion spectrum (TIS) provides an alternative approach for data analysis (SIGMAN *et al.* 2008). The TIS is identical to an average mass spectrum (MS) covering the complete chromatographic range.

Nevertheless, the most of the forensic laboratories perform fire debris analysis by GC-MS, several authors have been working on alternative methodologies that can complement or may become an alternative to traditional methods because of advantages they provide. In this sense, FERREIRO-GONZÁLEZ *et al.* (2014) successfully optimized and validated an electronic nose based on mass spectrometry (HS-MS eNose). The HS-MS eNose was successfully applied for thermal desorption of ILR from carbon strips as an alternative to the use of CS_2 solvent (FERREIRO-GONZÁLEZ *et al.* 2015). The technique was applied to weathered samples (ALIAÑO-GONZÁLEZ *et al.* 2018) also optimized for analysis of fire debris samples without any pre-treatment (FERREIRO-GONZÁLEZ *et al.* 2016) and the results were validated by comparison to those obtained by the GC-MS reference method (FERREIRO-GONZÁLEZ *et al.* 2017).

The HS-MS eNose is an analytical technique that gives specific responses to an entire aroma in a way similar to humans without previous separation. For this reason, it performs an overall mass spectrum (MS) of an volatile profile characteristic of each sample (PÉREZ PAVÓN *et al.* 2006).
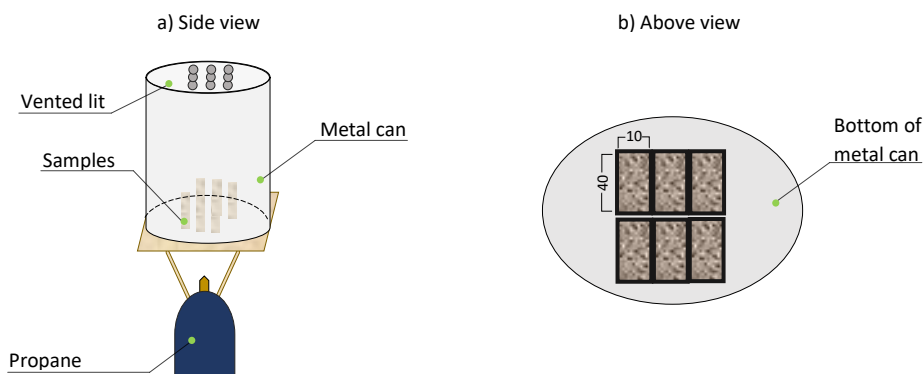
The aim of the present study is to investigate whether HS-MS eNose together with chemometric tools are able to clearly detect the presence /absence of different ILs from simulated fire debris samples. Two different materials were used as substrates and sampling was performed after delayed times. Total ion mass spectrum (TIS) from burned samples was analyzed by applying chemometric tools by using IBM SPSS Statistics 22 software.

MATERIAL AND METHODS

Fire debris samples
Two different substrates, cotton sheet and cork (a part of *Quercus suber* bark) and to different ignitable liquids (IL) were used for investigation in this study. Fire debris preparation

followed the modified procedure of Destructive Distillation Method for Burning (WILLIAMS *et al*. 2012). One piece of a substrate (5 × 5 cm) was replaced by six small pieces (1 × 4 cm) and placed on the bottom of a metal can (Fig. 1). 0. 5 mL of ignitable liquid were applied onto surfaces. Respectively, diesel and ethanol were used. Subsequently, the can with vented lit was placed above a propane torch. When a smoke appeared the samples were burned for approximately two additional minutes. The can was then removed from the flame and allowed to cool down. After a cooling time of approximately three minutes one of the two fire suppression agents was applied by spraying it onto the carpet surface and the sample was covered and re-lit. The sampling of prepared fire debris was performed in delayed times – 10 minutes, 1 and 6 hours. The samples were labelled by following codes: fire debris (FD), cotton sheet (CS), cork (CO) and delayed time (0h, 1h, 6h). All the combinations of variations were used for fire debris preparation. Burned samples were denoted by the substrate code followed by a liquid code: diesel (DIE) and ethanol (ETH). For instance: for burned cotton sheet substrate without IL when sampling was performed 1 hour after burning the code was FD – CS _1h, for burned cork with diesel when sampling was performed 6 hours after burning, the code was FD-CO+DIE_6h. The simulated fire debris were placed directly into vials and analyzed by HS – MS eNose.

Fig. 1 Schematics of side (a) and above (b) view of the experimental setup. All measurements are in mm.

HS-MS eNose spectra acquisition

Analysis of the samples was performed on an Alpha Moss (Toulouse, France) electronic nose based on mass detector system composed of an HS 100 static headspace autosampler and a Kronos quadrupole mass spectrometer. Nitrogen was used as a carried gas. Samples in 10 mL sealed vials (Agilent Crosslab, Santa Clara, CA, USA) were placed in the autosampler oven and heated. Headspace was taken from the vial by a gas syringe. To avoid condensation, the syringe was heated above the sample temperature (+5 °C) and consequently injected into the mass spectrometer. Between each sample injection, the gas syringe was flushed with nitrogen to avoid cross-contamination. The experimental conditions used for the headspace sampler were optimized in another study (FERREIRO-GONZÁLEZ *et al*. 2016) and consisted in the following conditions: incubation temperature 115 °C, incubation time 10 min, agitation speed 500 rpm, syringe type 5 mL, syringe temperature 125 °C, flushing time 120 s, fill speed 100 µL/s, injection volume 4.5 mL and injection speed 75 µL/s. The total time per sample was 15 min. The components in the headspace of the vials were passed directly to the mass detector without any chromatographic separation or sample pre-treatment. In this way, the resulting total ion mass spectrum (TIS) gives a fingerprint of the sample. The electron ionization spectra were recorded in the range of 45–200 mass-to-charge ratios (m/z). The instrument control was

achieved using Residual Gas Analysis software and Alpha Soft 7.01 software package (Alpha Moss, Toulouse, France).

Data analysis

Total ion mass spectrum (TIS) from burned samples was arrange in a data matrix named $D_{m \times n}$, where m is the number of m/z intensities in the range of 45–200 and n is the number of fire debris samples. The intensities of each m/z were taken as independent variables, standardized by feature scaling.

Multivariate statistical analyses represented by HCA, PCA and LDA were performed by using IBM SPSS Statistics 22 software (Armonk, NY, USA).

RESULTS AND DISCUSSION

First of all, the exploratory multivariate analysis technique HCA was applied with the aim to investigate natural clustering among fire debris samples. HCA was carried out by using all the m/z intensities as independent variables for forming clusters ($D_{36 \times 156}$). Ward's hierarchical agglomerative clustering method and squared Euclidean distances were employed for the HCA. The dendrogram resulting from the HCA is represented in Fig. 2.

As can be clearly seen form Fig. 2, fire debris samples are divided into two major clusters. The major cluster A contains 100 % of samples burned with ILs. This cluster is widely distributed into two subclusters A1 and A2 that fully discriminate according to the type of used IL. Based on the results, fire debris samples are clustered due to their chemical composition – alcohols and diesel. The alcohol subcluster (A1) consists of samples solely containing ethanol. The subcluster A2 is formed by fire debris samples with diesel. Based on the presence of any type of IL, ethanol and diesel are joint in the same cluster at shorter distance than the cluster B that includes burned samples without any IL. The second major cluster B consists of fire debris samples without ILs. The cluster further discriminates between substrates used in fire debris samples. While the subcluster B1 contains solely samples with cork, the subcluster B2 is formed by fire debris samples with cotton sheet. A tendency related to the sampling time was not observed.
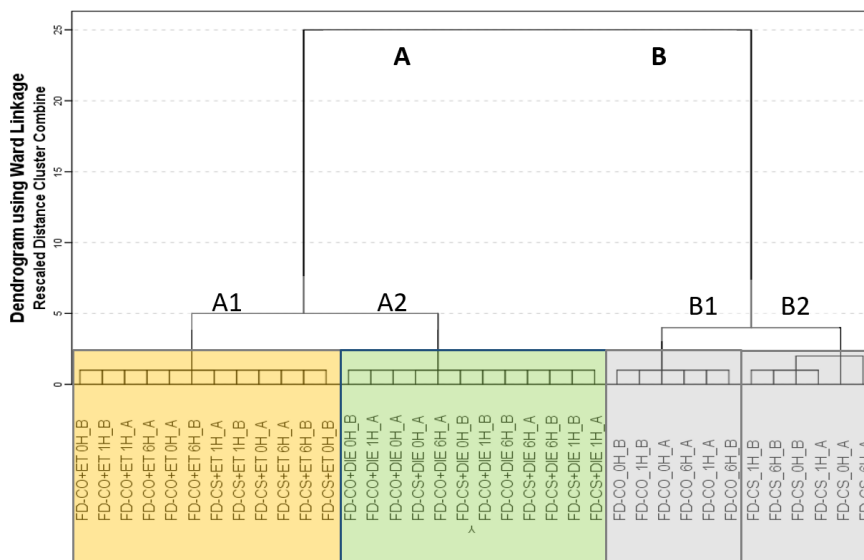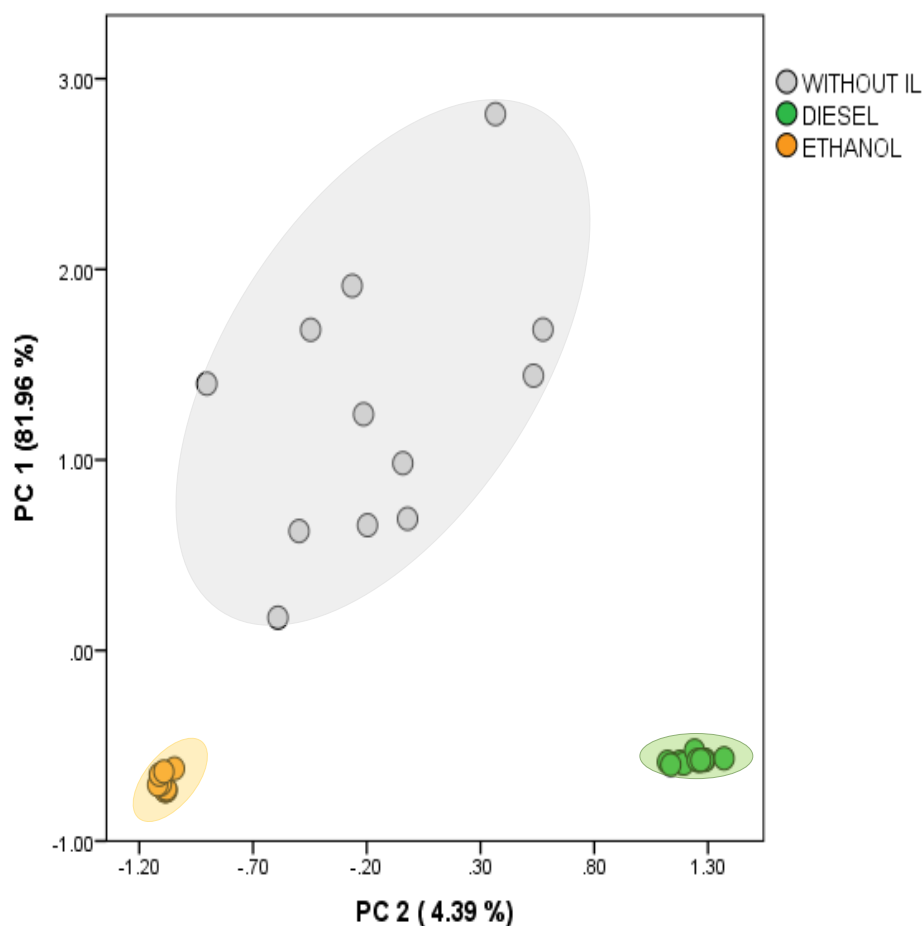

Fig. 2 Dendrogram obtained from the HCA for all the fire debris samples using the signal from the HS-MS eNose (45–200 m/z).

In order to further investigate the tendencies proposed by HCA - particular ILs and distinguishing them, further analyses were required. The unsupervised pattern recognition PCA method was employed to the whole data set $D_{36 \times 156}$ of fire debris samples. Nine principal components (PCs) were extracted with the eigenvalues greater than 1.0. The most of the variability in the data is explained by first four PCs (92.22 % of the accumulative variance). Thus, the data matrix has effectively been reduced to 2 dimensions, while still remaining 86.35 % of the information. Fig. 3 displays score scatter plot of first two PCs. The following general observations can be made from the visual inspection:
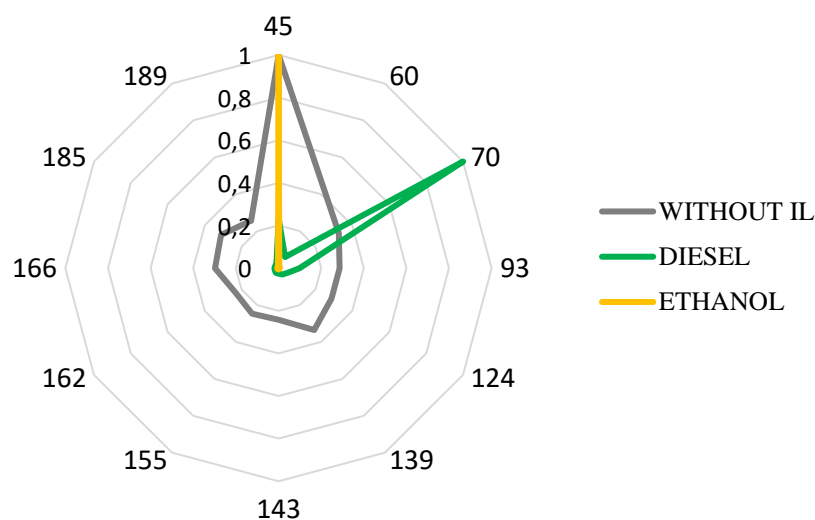

Fig. 3 Scores for the fire debris samples (n=36) in the two dimensional PC1-PC2 space.

Plotting PC1 versus PC2 allows seeing a grouping of samples due to the presence of any of the ILs. Whereas PC1 refers to the overall results and separate samples in accordance with the presence/absence of ILs, PC2 is related to the type of IL Almost all the m/z show high influence on the PC1 with positive values, except m/z 55 and m/z 57, that show loadings with low negative values, respectively -.080 and -.0.95.

PC2 allows the full discrimination regarding the ILs (diesel or ethanol). M/z with the highest influence in PC2 with positive values above .08 are the following: m/z 55, m/z 56, m/z 57, m/z 69 and m/z 71. The high negative value is represented by m/z 45 (-.88). These results suggest that the data from the HS-MS eNose are mainly related to those compounds responsible first for the discrimination of the fire debris due to the presence/absence of ILs and second to the type of used IL.

Based on the tendency showed in the unsupervised techniques, it was preceded with the application of a supervised technique named LDA to identify whether there are specific

m/z values in the TIS that are more significant than the others when discriminating samples according to the type of IL, a supervised chemometric technique LDA was applied to the data set $D_{36 \times 156}$. Three groups (samples without ILs, samples burned with ethanol and samples burned with diesel) were established a priori. Stepwise method was applied. Based on LDA results, two canonical functions were obtained that explain, sequentially, 83.90 % and 16.10 % of the variance. The full discrimination were obtained (100 % of cross-validated grouped cases were correctly classified). Groups of predicted variables will make predictions that are statistically significant (p= .00) in their accuracy. The m/z values selected for classification in the accordance of discriminant functions were: m/z 45, m/z 60, m/z 70, m/z 93, m/z 124, m/z 139, m/z 143, m/z 155, m/z 162, m/z 166, m/z 185 and m/z 189.

Fig. 4 Fingerprinting of the burned samples with and without the presence of ILs.

When only intensity values of the signals (m/z) selected by the LDA for developing the Fisher's linear discriminant functions are displayed, a different fingerprint for burned samples with and without ILs is obtained (Fig. 4). All the m/z values were normalized to the base peak at 100%.

As the Fig. 4 displays, a characteristic fingerprint for each type of IL was also obtained. Fire debris samples without any of IL do not represent any characteristic m/z. Samples burned with diesel present only one characteristic m/z of the highest intensity, which is found in samples with both substrates. M/z 70 that refers to alkanes that are abundantly presented in petroleum distillate products such as diesel. Samples burned with ethanol are related to only m/z 45 with the highest value that refers to alcohols.

CONCLUSION

The presented study focuses on identification ILs from simulated fire debris samples. A progressive approach to data analysis is represented by applying multivariate statistical analysis. Based on results, chemometric tools successfully discriminate samples regarding the presence of any ILs used. According to tendencies obtained from results from HCA, PCA as unsupervised pattern recognition was further applied. Based on the results, it is suggested that data obtained from HS-MS eNose are firstly related to compounds that discriminate fire debris samples due to the presence / absence of the ILs. In addition, results from supervised LDA clearly demonstrate different fingerprints among simulated fire debris samples that

might be used on purpose to preliminary determine the presence of the ILs. To sum up, the results obtained from this study support the idea of previous studies that HS-MS eNose is able to detect and identify particular ILs from fire debris samples and might be used as complementary analytical method to reference method broadly used in forensic laboratories. The useful results could be also obtained in the case of other natural substrates on the base of wood, not only for cork. Further research should be performed to deal with other aspects of HS-MS eNose to be considered as an alternative method to fire debris analysis.

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