Towards chemical profiling of ignitable liquids with comprehensive two-dimensional gas chromatography: Exploring forensic application to neat white spirits

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ABSTRACT

The application of GC × GC–FID and GC × GC–MS for the chemical analysis and profiling of neat white spirit is explored and the benefit of the enhanced peak capacity offered by comprehensive two-dimensional gas chromatography is demonstrated. An extensive sampling exercise was conducted throughout The Netherlands and the production and logistics in terms of bottling and distribution of white spirits were studied. An exploratory approach based on target-peak tables and principal component analysis was employed to study the brand-to-brand differences and production variations over time. Despite the complex chemical composition of white spirit samples this study shows that chemical variation during productions is actually quite limited. Hence care has to be taken with the chemical comparison for forensic purposes. Although some clustering was noticed on brand level, the large scale production process leads to a very consistent composition across stores and brands. However, because of the broad specifications of this commodity product, substantial chemical variation was found over time. This temporal discrimination could be of forensic value when considering white spirits supplies in individual households.

1. Introduction

Domestic and industrial fires annually result in substantial damage, financial loss, injury and loss of life. In 2013 over 36,000 fires were reported in The Netherlands, of which 15,000 were indoor fires and 19,000 outdoor fires [1]. The majority of these fires were accidental in nature, resulting from unfortunate circumstances, human error and/or technical failure. However, fires can also be deliberately started out of criminal motives. Arson is committed for a number of reasons, including (i) mental disorder (e.g. pyromania), (ii) vandalism, iii) revenge, (iv) crime concealment (to destroy physical and biological evidence) and (v) insurance fraud [2]. As arson often leads to considerable damage to society and the victims involved, most forensic institutes maintain fire-investigation expertise and dedicated facilities for analysing fire debris and ignitable liquids.

To this day, the most frequent used analytical methodology for the analysis of fire-debris samples and ignitable liquids (IL) is capillary gas chromatography with mass-spectrometric detection (GC–MS). Most institutes and research centres do use analytical methods that are in line with ASTM (American Society for Testing and Materials) protocols that are generally acknowledged as global benchmarks [3,4]. On the other hand research facilities keep

working on improving standard methodologies and sampling techniques in order to answer forensic questions.

In most cases forensic experts have to deal with fire-debris samples, but in a significant fraction of cases intact ignitable liquid is available for analysis. Without the complications of an actual fire and the highly variable interfering matrix, a much-more-detailed chemical analysis can be undertaken. This allows for classification and even within-class differentiation of ignitable liquids. Establishing the type of product through chemical analysis can provide a valuable lead in a criminal investigation. Furthermore, when evidence found at the crime scene can be compared with intact liquid related to a suspect, the degree of chemical similarity can be investigated. A nearly identical chemical composition supports the hypothesis that the liquids have a common source, thereby indicating a potential link of the suspect to the crime scene. However, the degree of support is determined by the rarity of the composition within a relevant reference population. It is the task of the forensic expert to assess this by studying the manufacturing processes and the variation in chemical composition as function of brand, type and time. A lot of interesting studies are performed based on evaluating the forensic potential of differentiating between- and within-classes of neat ignitable liquids. Dolan and Stauffer [5] conducted a comprehensive screening of middle distillates (cleaners, paint thinners, lighting fluids, mineral spirits) using GC–MS with extracted-ion chromatogram (EIC), in which a broad range of products and chemical compositions was covered. Although the classification was consequently challenging, the authors were able to demonstrate the potential for forensic comparison [5]. In another study of Doble et al. [6] principal component analysis (PCA) and artificial neural networks (ANNs) were applied for the differentiation of premium and regular gasolines based on GC–MS data. Application of linear discriminant analysis (LDA) on the first four PCA scores resulted in a correct classification rate of 93%. By using properly trained ANNs, 97% of the samples could be correctly assigned to their winter/summer sub-class. In 2003–2004 Sandercock and Du Pasquier published the results of a comprehensive study into the chemical fingerprinting of gasoline [7–9]. Substituted naphthalenes were found to be excellent discriminators for gasoline samples. Substituted-naphthalene profiles were obtained by GC–MS analysis in SIM (selected-ion monitoring) mode. These profiles were analysed with PCA followed by LDA based on the first three PC scores. With this approach 14 samples obtained on the same day from gas stations in the metropolitan area of Sydney (Australia) could all be distinguished. It was also demonstrated that the naphthalene profiles could be used for weathered gasoline samples up to 90% evaporation. This robustness with respect to evaporation is important for forensic application since partial evaporation of the IL at the crime scene is likely to occur [8]. The final publication in this series [9] illustrated that the forensic expert also requires knowledge on regional petrochemical production and supply-chain conditions to apply the method and correctly interpret the data in a given forensic context.

Monfreda and Gregori describe a solid-phase micro-extraction (SPME) method in combination with GC–MS for differentiation of gasoline brands [10]. This study involved 50 Italian gasoline samples from five suppliers. A total of 34 target peaks were selected. Best results were obtained by applying PCA followed by LDA for the first three principal components to a dataset limited to 16 aromatic compounds. Lu et al. [11] used two-way GC–MS profiles and target-compound ratios from GC–MS data for the characterization and classification of US gasoline and kerosene samples. By using several chemometric tools accuracies in the range of 91–97% were reported. Unsupervised pattern recognition techniques (PCA, hierarchical cluster analysis (HCA) and self-

organizing feature map (SOFM)) were also applied by Mat-Desa et al. [12]. A total of 56 medium petroleum distillates (white spirit, paint brush cleaner and lamp oil) were purchased at local stores and analysed with GC–MS. With the use of SOFM it was possible to classify these products based on type and brand. They also succeeded in linking weathered samples to the original neat samples.

Haraczaj et al. [13] demonstrated the forensic use of a commercial software package, named Carburane, for analysing and comparing premium gasoline samples. This software automatically identifies compounds from GC–FID (flame ionization detection) data on the basis of retention indices. Relative amounts were calculated based on peak areas for up to 450 individual hydrocarbons and these were grouped in seven classes. In recent work of Schwartz et al. [14] the potential of compound-specific $^{13}C/^{12}C$ isotope ratios was explored for the analysis of ignitable liquids and fire debris. The authors succeeded in distinguishing two lubricant and turpentine samples on the basis of $\delta^{13}C$ values of sample constituents.

Given the complex composition of oil-based ignitable liquids, the use of comprehensive two-dimensional gas chromatography (GC × GC) can be of added value in forensic fire investigations. Since its introduction in 1991 [15] GC × GC has matured into a robust and versatile analytical technique and has been successfully used in many application areas [16,17]. Surprisingly, the use of GC × GC in forensic science and in forensic-fire investigations has been rather limited so far [18]. The forensic potential of GC × GC for the analysis of ignitable-liquid residues in fire debris was demonstrated by Frysinger and Gaines [19] by analysing first neat samples of potential accelerants, such as camp fuel, paint thinner, lacquer thinner, and turpentine with GC × GC. Significant overlap between various classes of compounds was observed, with the exception of turpentine. Differences could be spotted by rapid switching between GC × GC chromatograms on the computer screen, which was referred to by the authors as the "blink method". Taylor et al. used GC × GC coupled to a quadrupole mass spectrometer for the detailed analysis of complex ignitable liquid residue samples [20]. Neat gasoline, kerosene and diesel samples were diluted in dichloromethane (DCM) and analysed as such. Real fire-debris samples were obtained from a local fire department. Ignitable liquid residues (ILRs) were successfully detected after direct extraction of fire debris with DCM, through a combination of GC × GC and selected-ion monitoring for alkanes, alkyl benzenes, and alkyl naphthalenes. Recently published environmental studies of fire debris convincingly demonstrated how the combination of GC × GC with high-resolution time-of-flight (TOF) MS provides highly detailed chemical analysis [21,22]. The forensic potential of GC × GC was further demonstrated by Frysinger and Gaines [23], who used the technique for the analysis of crude-oil biomarkers in oil spills and by Pedroso et al. [24], who used GC × GC–FID to detect gasoline adulteration.

In the present study we report on the analysis of neat white spirits which are regularly detected in arson cases in the Netherlands. An extensive sampling exercise was undertaken throughout The Netherlands and the operations of a major bottling site serving the Dutch market was studied to establish the potential of the comprehensive chemical analysis for forensic comparison. Chemical analysis was performed through compound identification with GC × GC–MS and GC × GC–FID to establish the semi-quantitative composition. A straightforward procedure based on PCA of a selection of robust GC × GC peaks allowed for a study into the brand-to-brand and temporal variations of Dutch neat white spirits. From this procedure several compounds could be identified that are potentially valuable in the differentiation of neat white spirits.