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## Acid alteration of several ignitable liquids of potential use in arsons

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### ABSTRACT

Ignitable liquids such as fuels, alcohols and thinners can be used in criminal activities, for instance arsons. Forensic experts require to know their chemical compositions, as well as to understand how different modification effects could impact them, in order to detect, classify and identify them properly in fire debris. The acid alteration/acidification of ignitable liquids is a modification effect that sharply alters the chemical composition, for example, of gasoline and diesel fuel, interfering in the forensic analysis and result interpretation. However, to date there is little information about the consequences of this effect over other accelerants of interests. In this research paper, the alteration by sulfuric acid of several commercial thinners and other accelerants of potential use in arsons is studied in-depth. For that purpose, spectral (by ATR-FTIR) and chromatographic (by GC-MS) data were obtained from neat and acidified samples. Then, the spectral and chromatographic modifications of each studied ignitable liquid were discussed, proposing several chemical mechanisms that explain the new by-products produced and the gradual disappearance of the initial compounds. Hydrolysis, Fischer esterification and alkylation reactions are involved in the modification of esters, alcohols, ketones and aromatic compounds of the studied ignitable liquids. This information could be crucial for correctly identifying these accelerants. Additionally, an exploratory analysis revealed that some of the most altered ignitable liquid samples might be very similar with each other, which could have impact on casework.

### 1. Introduction

Ignitable liquids (ILs) such as fuels, alcohols and thinners are frequently used in different daily-life situations. They can be also employed in criminal actions, for example arsons or to make some kind of improvised incendiary devices (IIDs) [1]. In cases where there are suspicions of illicit use of ILs, characterization of samples collected at fire scenes is of primary importance since they may produce significant intelligence to an investigation. In order to aid forensic analysts in the accurate characterization of samples, numerous researchers have deeply studied the composition of neat ILs and their fire residues [2–6]. However, analysts sometimes find samples difficult to classify and identify. This happens due to ILs, and/or their well-known chromatographic profiles, can suffer changes that hinder the identification process. These modifications could be produced before the use of ILs, during fire events and suppression efforts, or even during sample storage. These chemical and/or chromatographic changes are known as

matrix effect, evaporation/weathering effect, microbial degradation, and acid alteration/acidification [7–9].

Of these above mentioned modification effects, the acid alteration or acidification of ILs was recently described. Consequently there is little information available about its relevance in a forensic investigation. To date, gasoline 95 and 98 research octane number (RON), and diesel fuel was studied in the presence of concentrate sulfuric acid [9–13]. When gasoline is mixed with sulfuric acid, oxygenated compounds are hydrolysed and aromatic compounds are alkylated (i.e., *tert*-butylated), while alkanes, apparently, are not affected by sulfuric acid action [9,10,13]. In the case of diesel fuel, some aromatic compounds are sulfonated [9,10,12,13]. These chemical modifications jeopardize the forensic identification process of these ILs or their residues. To date, some recommendations were published in these works in order to facilitate the characterization of gasoline and diesel fuel altered by acid and their acidified fire debris residues. However, it would be necessary to formulate specific classification schemes. Furthermore, it is still

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unknown whether the chemical composition of other different ILs is also modified when they are mixed with sulfuric acid, and hence its consequences in a forensic context. Therefore, further study of the chemical characteristics of other acidified ILs is urgently required.

Acidified gasoline and diesel fuel liquid samples were analysed using different techniques: gas chromatography coupled to mass spectrometry (GC–MS) [9], comprehensive two-dimensional gas chromatography coupled with time-of-flight mass spectrometry (GC × GC–TOFMS) [12], portable Raman [11] and attenuated total reflection Fourier transform infrared (ATR–FTIR) spectroscopy [10]. In addition, acidified gasoline and diesel fuel fire debris residues were analysed by a solid phase microextraction (SPME)–GC–MS methodology [13]. On the one hand, these above mentioned separation methodologies allow better characterization and have higher sensitivity than the proposed spectroscopic techniques. However, it is important to consider that this type of samples could damage columns and SPME fibres due to their low pH value, increasing instrument deterioration and costs [9,13]. On the other hand, the proposed spectroscopic techniques have some interesting features for this type of analysis. They do not require sample treatment or consumption, and allow fast and cheap analyses without damaging the instruments [10,11]. In addition, the portability of some of these instruments allows their in-situ use, helping in the decision-making process. All these methodologies can be combined with chemometric tools in order to obtain a more objective and easier interpretation of data and classification of samples [10,12].

The aim of this research work is to study the effect of alteration by acid in several commercial thinners and other ILs of potential use in arsons (liquid form), other than those studied before [9–13]. For that, first, 10 ILs of interest were preselected and analysed (neat samples and samples obtained after mixing with sulfuric acid) by ATR–FTIR. The results were studied in order to decide which ILs would be further studied (priority list). 4 of them, 3 different commercial thinners and bitumen of Judea, showed clear modifications in their IR absorption spectra, and consequently they were selected for an in-depth study. Then, GC–MS analyses of these neat and acidified samples were carried out, and their chemical, chromatographic and spectral characteristics were discussed in detail. Lastly, a PCA analysis using the spectral data was carried out for an objective interpretation of all data.

## 2. Material and methods

### 2.1. Samples, materials, reagents and instruments

Several ILs of several brands were purchased. From “OK” brand: epoxy thinner, ref: 16133691; acrylic rubber solvent, ref: 1613312; universal thinner, ref: 16133705; synthetic solvent, ref: 16133733; white spirit, ref: 16133614 and turpentine, ref: 16133530. From “Xylazel” brand: enamel paint, ref: 11246270 also called oxirite thinner. From “Velas Lumar S.L” brand: liquid paraffin. From “Productos Promade” brand: bitumen of Judea, ref: 10102932. And from “Productos Económicos Auchan” brand: barbecue burning fuel, also called kerosene. All above-mentioned ILs were acquired in Leroy Merlin (Alcalá de Henares, Madrid, Spain) except for kerosene, which was bought in Alcampo (Alcalá de Henares, Madrid, Spain). They were transferred to 500 mL glass containers with screw cap purchased from Labbox (Mataró, Barcelona, Spain) and kept at room temperature (21–22 °C). Pure sulfuric acid (98% p/v) was purchased from Labkem (Mataró, Barcelona, Spain) while potassium carbonate and dichloromethane were purchased from Merck KGaA (Darmstadt, Germany). Glass vials (26 mL) with screw caps use for making mixtures of ILs with sulfuric acid were bought from Labbox (Mataró, Barcelona, Spain).

A FTIR spectrometer with ATR sampling accessory (Nicolet iS10 version) from Thermo-Fisher scientific (Waltham, MA, USA) was used for analyse neat and acidified samples. GC–MS analyses of neat and acidified samples were performed in an Agilent 6890 series gas

chromatograph equipped with a PAL COMBI-xt sample injector and 5973-N MS detector (Agilent Technologies, Palo Alto, CA, USA). The GC separation column used was a 30 m × 0.25 mm × 0.25 μm DB-1MS. Injection was performed in split mode (25:1), with an injection volume of 1 μL. The injector and detector temperature was set at 250 °C. Oven temperature was programmed with an initial temperature of 45 °C for 1 min, followed by an increase at a rate of 4 °C/min to 130 °C, finally, oven temperature was increased at a rate of 15 °C/min up to 270 °C. Helium was used as the carrier gas (99.999%) at 7.5 psi constant pressure (1.0 mL/min flow rate). Data were acquired in SCAN mode. An event was created from retention time 1.75 to 2.00 min to avoid the appearance of the signal corresponding to dichloromethane.

### 2.2. Sample preparation and analysis

According to the changes seen in the IR spectrum of each IL after 23 h of reaction with sulfuric acid (which are discussed in Section 3.1), four of these ILs were chosen to further study: epoxy thinner, oxirite thinner, universal thinner and bitumen of Judea. From each reagent, 4 mL were poured into 26 mL glass vials with screw caps. Next, 2 mL of concentrate sulfuric acid were added, having a final IL/acid ratio of 2:1 (v/v). Those vials were stored at room (steady) temperature and kept still during the experiments. Aliquots of 20 μL and 10 μL from the organic part, located at the top of the solution, were taken and poured directly on the diamond crystal surface of the ATR sampling accessory or diluted in dichloromethane at 1% (v/v) and analysed by GC–MS. In the case of the FTIR measurements, the ATR sampling accessory was cleaned after each measurement with a clean paper tissue soaked with 2-propanol. In the case of GC–MS measurements, all the aliquots were passed through a disposable syringe containing approximately 100 mg of potassium carbonate in order to neutralize the acidic solutions.

Three aliquots of each mixture were taken every hour over 24 h. In order to cover the 24 h experiment, four independent set of samples were required. First of them was analysed between the 1st h and the 7th h. Another set of mixtures were analysed from 8th h to 12th h. Third experiment collected from 13th h to 17th h, and the last one covered from 18th h to 24th h. Moreover, another set of mixtures was prepared and analysed after 1, 2, 3, 4, 29 and 44 days of reaction (throughout these days). In each experiment, three independent mixtures of each IL were prepared.

### 2.3. Data acquisition

IR absorption spectra were recorded from 4000 to 600 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup> and taken averages of 16 scans. A higher number of scans was not possible due to the quick evaporation of some of the neat and acidified ILs. All data were imported from Omnic Scientific software (Waltham, MA, USA) to The Unscrambler X 10.1 software (CAMO, Norway) for data treatment and chemometric analysis.

In GC–MS measurements, peak area information was extracted from integrated chromatograms using MSD ChemStation® software (E.02.02.1431 version, Agilent Technologies).

### 2.4. Data analysis

In order to compare neat and acidified IR absorption spectra of the four in-depth studied ILs, an exploratory technique (PCA) was applied. First of all, as absorption bands were only present in the regions from 3620 cm<sup>-1</sup> to 2700 cm<sup>-1</sup> and from 1900 cm<sup>-1</sup> to 650 cm<sup>-1</sup>, those regions were chosen to study. The remainder data were cut down. Once the interest regions had been imported to The Unscrambler X 10.1, the following treatment was applied to all the data. Baseline correction, baseline offset with a minimum value of 0, SNV normalization and Savitzky-Golay smoothing with a 2nd degree polynomial was consecutively applied to the data matrix.

After this treatment, PCA analyses were made. Every data point

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