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Study of chemical modifications in acidified ignitable liquids analysed by GC–MS

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Abstract: In this work, mixtures of gasoline with sulphuric acid and diesel fuel with sulphuric acid were analysed by gas chromatography–mass spectrometry (GC–MS). The results showed considerable qualitative and semi-quantitative modifications in the chromatographic profiles of the ignitable liquids (ILs). In the case of acidified gasoline, the alteration of the abundances of aromatic compounds and the hydrolysis of an oxygenated compound such as methyl tert-butyl ether (MTBE), in addition to the immediate and unexpected appearance of tert-butylated compounds were observed. In the case of acidified diesel fuel, the alteration of aromatic compounds occurred. These sequential changes were then studied in detail in order to explain the chemical modifications taking place. These extensive chemical modifications may be considered as a new chromatographic profile distortion effect, the acidification of ILs. As such modifications are not generally taken into account in the criteria followed to assess the classification of an IL, we propose some recommendations helping to the identification of acidified ILs. This information can be especially useful to detect and identify non-burned ILs from seized or failed improvised incendiary devices made with mixtures of sulphuric acid–IL, or ILs altered intentionally with the aim to modify their composition.

Keywords: Acidified ignitable liquid; Diesel fuel; Fire investigation; Gasoline; Improvised incendiary device; Molotov cocktail.

1. Introduction

Among improvised incendiary devices (IIDs), classic Molotov cocktails may be used as a mean to commit arson, either as an act of vandalism, of revenge or for setting a fire motivated by the lure of profit. A more dangerous version of this device is the so-called chemical ignition Molotov cocktail (CIMC) [1], [2], which is based on self-ignition through rapid heat generated by an exothermic reaction between two chemical substances integrated in the device. The most frequently encountered recipe of CIMCs is based on a bottle of glass containing an ignitable liquid (IL), often gasoline, kerosene or diesel fuel, mixed with concentrated sulphuric acid. Besides, potassium chlorate (powder) is wrapped in an envelope or a folded sheet of paper that is taped to the bottle. As soon as the container breaks against a target, sulphuric acid and potassium chlorate get in contact and react very violently setting fire to the aerosol of IL mixed with air.

According to preliminary results obtained in casework, analyses performed either on the content of seized IIDs prepared with IL and sulphuric acid, or on samples grabbed on the ground where a CIMC was thrown, have sometimes lead to unexpected and weird results. In some of the analyses, generally performed by headspace extraction followed by gas chromatography and mass spectrometry analysis (HS-GC-MS), total ion current chromatograms (TICs) and extracted ion chromatograms (EICs) presented huge differences with reference data from neat ILs. Semi-quantitative and qualitative alterations of the chromatographic profile were observed, leading to great difficulties in detecting and/or assessing the presence and identification of an IL. Although in some cases similar profiles to ILs such as gasoline, kerosene or diesel fuel were detected, some of the obtained chromatograms clearly differed from known ILs. These findings suggested that the mixing of concentrated sulphuric acid may react with some ILs, leading to the alteration of their composition, and thus of the chromatographic profile obtained by HS-GC-MS analysis. As the detection, characterization and classification of ILs from casework evidence can be very meaningful and provide significant intelligence to a forensic investigation, it is of utmost importance to understand the effect of mixing sulphuric acid with ILs.

Several works have been focused on the analysis of neat ILs and ignitable liquid residues (ILRs) looking for identifiable distinctive profiles [3], [4], [5], [6], [7]. With such samples, the characterization and classification of the detected IL is straightforward: very distinctive chromatographic patterns allow to distinguish the different classes of IL [3], [8]. The outcomes of these analyses may be of importance as they may contribute to a

police or prosecution inquiry, leading to the production of evidence of the use an IL as accelerant, or may initiate a further process of comparison in a common source inference perspective. In some cases however, it is found that a modification of the chromatographic profile obtained after HS-GC–MS analysis occurred in comparison to a putative or known IL. The chromatographic profile after the analytical process presents important differences with the neat IL, complicating significantly the process of comparison and identification, and precluding the possibility of common source inference (if required). Such a situation may happen due to: 1) strong weathering, which is the natural process of evaporation that alters the composition of ILs; 2) matrix interactions or interferences that can ensue from the constitution of the matrix, its thermal degradation or from the thermal constraints encountered by the environment; 3) biodegradation resulting from bacterial activity; and 4) extraction strategy or parameters chosen for the extraction step. The effects of these different forms of changes in the chromatographic profile and the potential impact on the process of IL classification and identification have been extensively addressed by previous publications [5], [6], [7], [8], [9], [10]. However, to our knowledge, none of these studies considered the presumable action of mixing an IL with a strong acid, as sulphuric acid, as well as its impact on the use of the results in a forensic intelligence perspective or for the production of evidence.

Thus, this work was undertaken with the aims of analysing samples of acidified ILs by GC–MS and studying the chemical modifications induced in the ILs. Two types of gasoline and diesel fuel mixed with sulphuric acid were analysed by GC–MS to gather fundamental data and knowledge on the IL chemical modifications. The acquired knowledge was used to formulate some recommendations for the identification of acidified ILs.

2. Materials and methods

2.1. Samples and reagents

Gasoline 98 Research Octane Number (RON), gasoline 95 RON and diesel fuel were obtained from a local petrol station (SOCAR, Lausanne, Switzerland) and they were stored in glass jars at room temperature. Working samples from neat gasoline and diesel fuel were then prepared for GC–MS analysis by diluting at 1% (v/v) in dichloromethane purchased from Sigma Aldrich (Buchs, Switzerland). All other chemicals used in this

study were also purchased from Sigma Aldrich (Buchs, Switzerland): sulphuric acid (95–98%, m/v) and pure methyl tert-butyl ether (MTBE).

2.2. Sample preparation

Simulated solutions of CIMCs were prepared by pouring, first, sulphuric acid (2 mL or 1/3 v/v) and then, the IL (4 mL or 2/3 v/v) in 10 mL glass vials. These vials were immediately closed with screw silicone/polytetrafluoroethylene (PTFE) caps (Sigma Aldrich, Buchs, Switzerland) taking extreme care not to shake or mix the phases before analysis. At regular time intervals, 10 μ L aliquots of the organic fraction of the simulated solutions (gasoline or diesel fuel) were taken using a positive-displacement pipette Rainin® Pos-D™ purchased from Mettler-Toledo (Greifensee, Switzerland), avoiding to take sulphuric acid. These aliquots were diluted in dichloromethane at 1% (v/v) and analysed by GC–MS. The time intervals that were considered are the following: during the first hour, sampling of an IL aliquot was performed every 5 min. Then, every hour during the next 24 h, and every 24 h during the next 6 days. The last aliquot was thus sampled 7 days after the preparation of the simulated solution (mixture of sulphuric acid and IL). In total, 41 samples collected at different time intervals were considered for each simulated solution of CIMCs. Additional experiments were performed using an orbital shaker at 600 rpm shaking new simulated solutions during several time intervals: 5, 50, 100, 150 and 200 min. After each time interval, an aliquot from the organic fraction was taken, diluted in dichloromethane at 1% (v/v) and analysed.

With the aim to study the changes in the organic fraction when it is doped with MTBE, a simulated solution of CIMC (using gasoline 98 RON as IL) was prepared, and 100 μ L of pure MTBE was added immediately over the organic fraction. Then, an aliquot of 10 μ L of the organic fraction was sampled and analysed by GC–MS at each of the following time intervals: immediately after preparing the mixture, and after 5 min, 35 min, 24 h, 48 h and 96 h. After each sampling of the organic fraction, the simulated solution was doped anew with 100 μ L of pure MTBE. The extracted aliquots were diluted at 1% (v/v) in dichloromethane before analysis by GC–MS. Additionally, to check if the reaction stops when sulphuric acid is extracted from the organic fraction, another simulated solution of CIMC (using gasoline 98 RON as IL) was prepared. After 18 h, the organic fraction (upper part of the mixture) was extracted using a positive-displacement pipette. This fraction was poured in another vial and an aliquot of 10 μ L was sampled and analysed by GC–MS at several time intervals: immediately after separate the organic fraction from the original simulated solution of CIMC, and after 24, 48, 72 and 168 h.

2.3. GC–MS analysis

Gas chromatography hyphenated to mass spectrometry (GC–MS) analyses were carried out on an Agilent 7890A gas chromatograph connected to an Agilent 5975C inert XL mass spectrometer (Agilent Technologies, Santa Clara, CA, USA). Chromatographic separation was achieved with a 12 m HP5-MS capillary column (0.2 mm i.d., 0.33 μm thickness) from Agilent Technologies (Santa Clara, CA, USA).

Injection was performed at 250 °C in split mode (25:1), with an injection volume of 1 μL . Oven temperature programme started at 35 °C for 1.4 min, and was then ramped at 10 °C/min up to 250 °C (hold time of 9 min). Helium (99.999% purity) was used as carrier gas at a constant flow of 0.8 ml/min. The MS instrument was used in scan mode (10–400 m/z) with a 3.66 scan/s sampling rate.

2.4. Data analysis and image processing

Peak area information was extracted from integrated chromatograms using MSD ChemStation® software (Agilent Technologies). Data were loaded and calculation performed in Microsoft® Excel.

In order to study and illustrate physical changes occurring in simulated solution of CIMCs, pictures of these solutions were recorded at each time interval by means of a Canon 60D camera and with the constant illumination of a Digital Imaging Box (MEDALight, Hong Kong).

3. Results and discussion

3.1. Gasoline mixed with sulphuric acid

First, the modifications of neat gasoline when it is mixed with sulphuric acid were studied. This was first based on the visual examination of the simulated mixtures of gasoline–sulphuric acid at different times. Fig. 1 shows a photographic sequence of the first 48 h of a gasoline–sulphuric acid mixture. A reaction was taking place at the interface between the two liquids, and progressively the appearance and colours of both liquids

changed. Firstly, sulphuric acid became black from its interface with gasoline, and the latter started to darken, suggesting chemical changes.



Fig. 1. Pictures of a vial with gasoline 98 RON (upper part) and sulphuric acid (lower part) at 2/3 (v/v) and 1/3 (v/v), respectively. Pictures (from left to right) were taken at 0 h, 3 h, 7 h, 30 h and 48 h after mixing both liquids.

In a second step, the chemical composition of the organic phase was considered. Neat gasoline holds a characteristic GC–MS profile that allows its identification by considering the semi-quantitative combination of several compounds recognized through their retention times and mass spectra. Table 1 shows a list of the main gasoline compounds and their major ions fragments. Aromatic compounds (i.e., toluene or C2-alkylbenzenes), alkanes (C4–C12) and MTBE were detected by the analysis of neat unweathered gasoline 98 RON (Fig. 2a). At the beginning of the chromatogram, MTBE as well as normal and branched alkanes were detected. They were followed by toluene, C2, C3- and C4-alkylbenzenes. Indane and naphthalene were as well clearly identified.

Table 1. List of typical compounds and fragmentation ions found in neat and un-weathered gasoline.

Compound family	Compounds	Characteristic m/z ions
Aromatics	Toluene	91
	C ₂ -alkylbenzenes	91, 106
	C ₃ -alkylbenzenes	91, 105, 120
	C ₄ -alkylbenzenes	91, 119, 134
	Indanes	117, 132
	Naphthalenes	128, 142
Alkanes	n, Iso-alkanes	43, 57, 71, 85
	Cycloalkanes	41, 55, 69, 83
Oxygenates	Ethanol	31
	Methyl tert-butyl ether (MTBE)	57, 73
	Ethyl-tert-butyl ether (ETBE)	59, 87

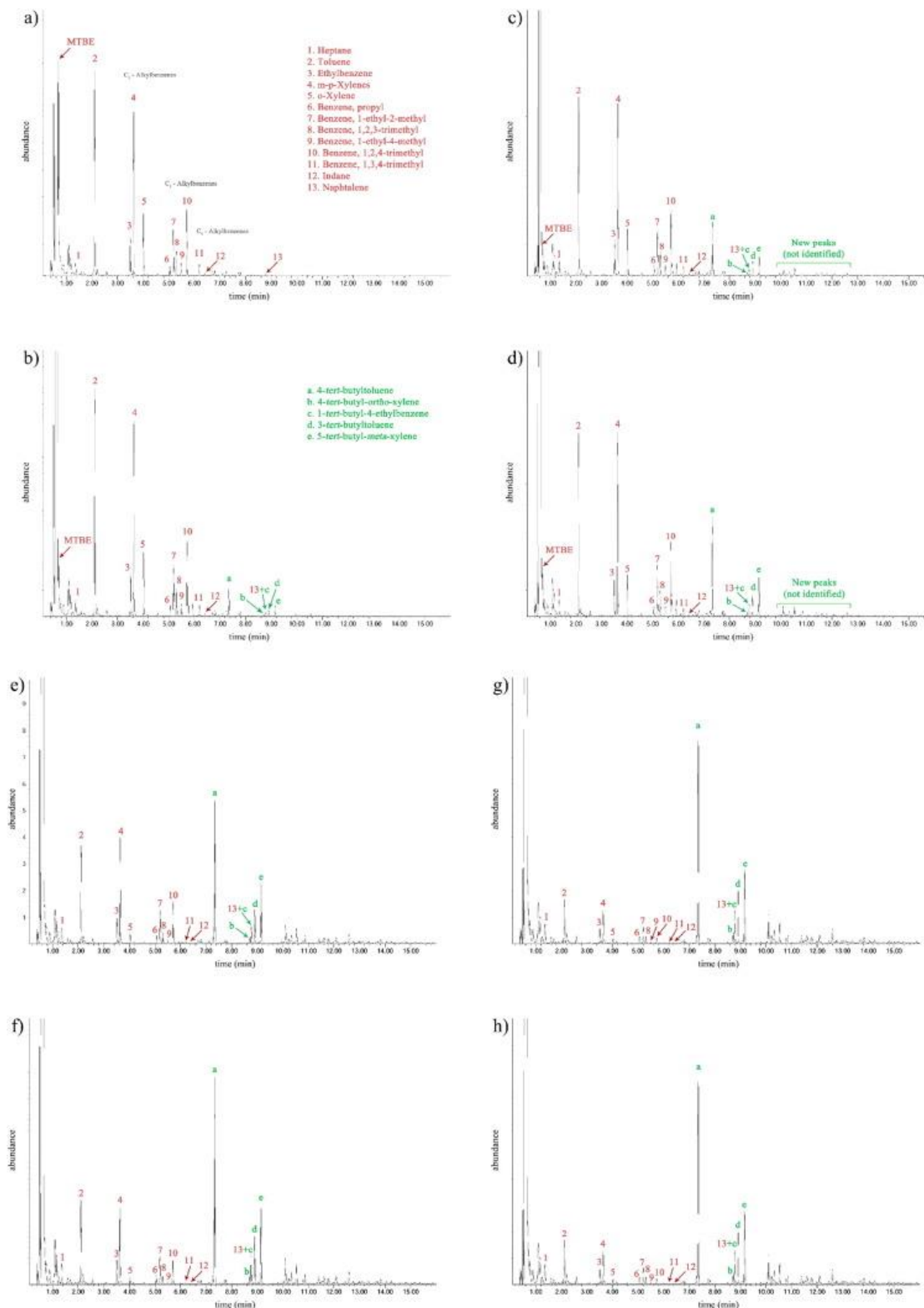


Fig. 2. TICs of a) neat gasoline 98 RON, and aliquots of the organic fraction from a mixture of gasoline 98 RON and sulphuric acid that were sampled after b) 5 min; c) 55 min; d) 2 h; e) 19 h; f) 48 h; g) 144 h (6 days); and h) 168 h (7 days). All samples were diluted at 1% (v/v) in dichloromethane. Abundance equivalent to $\times 10^6$. Number in red: original compounds in neat gasoline. Small letters in green: new compounds identified in the organic fraction of mixtures of gasoline with sulphuric acid. GC-MS conditions as shown in Section 2.3.

In order to study the modification of gasoline composition that was suggested by the visual examination of the simulated solutions, aliquots sampled at different time intervals (from 5 min to 7 days) from the organic fraction of these gasoline–sulphuric acid mixtures were analysed by GC–MS. Fig. 2b to h show the results obtained at different time intervals. As suggested by the visual examination, the chromatographic profiles of the gasoline samples changed over the reaction time with sulphuric acid in comparison to the neat gasoline profile. Some peaks corresponding to gasoline characteristic compounds, mainly aromatic hydrocarbons such as toluene or C2-alkylbenzenes, decreased over time (indicated with red numbers in Fig. 2). Specifically, Fig. 2e to h (after 19 h to 168 h–7 days — mixed) illustrate that the abundance of these compounds is substantially lowered. The decrease is less obvious at the naked eye for the C3-alkylbenzenes.

In order to better understand the extent of the modification occurring, the ratios of the peak area at the different time intervals were calculated in reference to the area at t_0 (neat gasoline). This was undertaken for the main aromatic compounds that seemed to be altered; these ratios are compiled in Fig. 3. First, for each time interval, the peak areas of the considered compounds were normalized to the area of heptane, as this compound was not altered by sulphuric acid under these conditions (see explanation below). Then, ratios were calculated by dividing the normalized peak areas at each time point by the normalized peak areas at t_0 .

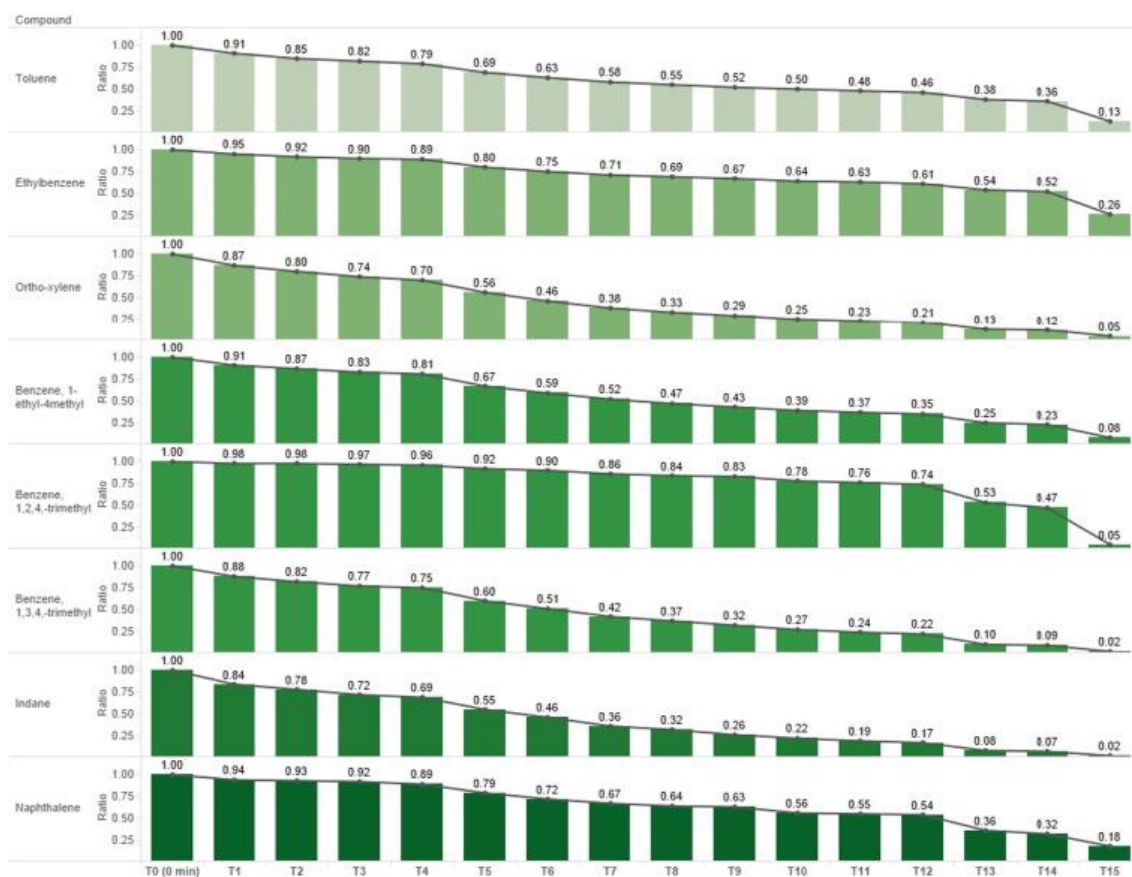


Fig. 3. Ratios of some typical aromatic compounds in gasoline 98 RON after some hours mixed with sulphuric acid. Several time intervals of analysis taken after mixing gasoline and sulphuric acid are considered. t_0 = neat gasoline; t_1 = 5 min; t_2 = 25 min; t_3 = 45 min; t_4 = 55 min; t_5 = 120 min; t_6 = 180 min; t_7 = 240 min; t_8 = 300 min; t_9 = 360 min; t_{10} = 420 min; t_{11} = 480 min; t_{12} = 540 min; t_{13} = 1140 min; t_{14} = 1440 min; t_{15} = 10,080 min. Area ratio regarding heptane peak area is expressed in percentage on base 1. Area quantifications were performed considering the major ion fragment for each compound.

After 5 min (t_1), all peak areas of the compounds indicated in Fig. 3 have already decreased. After 180 min (t_6), the areas of some of them such as ortho-xylene or indane decreased around 50%. After 7 days (t_{15}), some peaks have almost disappeared. It is important to remind that, in addition to the sole absence or presence of these compounds (pure qualitative approach), the identification of gasoline relies on a semi-quantitative approach based on the measurements of the relative abundances within and between groups of compounds. In our study, we clearly notice that over the reaction time with sulphuric acid, relative abundances of the major aromatics were affected. This is for example the case with the relative proportions of the C2-alkylbenzenes (see Fig. 2) that

changed over time. More surprisingly, we observed that MTBE disappeared also very quickly. Comparing chromatograms of gasoline obtained after 5 min in contact with sulphuric acid (Fig. 2b), and of neat gasoline (Fig. 2a), we observed that MTBE had almost completely disappeared, which was confirmed by studying EICs of its main ions fragments.

At the same time, new peaks (indicated in green small letters in Fig. 2) appeared in the gasoline chromatograms after some minutes of contact with sulphuric acid (Fig. 2b–h). All of them showed up in the time range between 6 and 15 min, among peaks already existing or in new groups of peaks. In Fig. 2b, we noticed the sudden appearance of a new compound, identified as 4-tert-butyltoluene (4-t-BTO) with its mass spectrum, in the acidified gasoline sample, already after 5 min of exposition to the acid. The abundance of this compound rapidly increased in the obtained chromatograms during the first 48 h (Fig. 2c–f) and remained rather constant after this. Meanwhile, a group of new peaks arose around the naphthalene peak (Fig. 2b). EICs revealed that naphthalene (retention time of approximately 8.7 min) decreased over time (reduction of its characteristic ions), but this was not noticeable in the TIC, suggesting that a new compound appeared at the same retention time. This compound was eventually identified as 1-tert-butyl-4-ethylbenzene on the basis of its mass spectrum. Physical and chemical properties of 4-t-BTO and four other new compounds eventually identified in the acidified gasoline samples are collected in Table 2, with relevant GC–MS data related to their identification.

Table 2. New compounds appearing in acidified gasoline. Chemical characteristics of interest for their separation by GC–MS are collected. Some divergence can be found between the different publications considered as their flash point or density values. *, no data.

Compound	IUPAC name	Retention time (min)	Formula	Quantification Ions (m/z)	Density (g/mL)	Molecular mass (g/mol)	Vapour pressure (mm/Hg) at 25 °C	Boiling point (°C)	Flash point (°C)	Reference
4- <i>tert</i> -Butyltoluene	Benzene, 1-(1,1-dimethylethyl)-4-methyl-	7.4	C ₁₁ H ₁₆	133; 105; 148	0.858 (at 25 °C)	148.24	0.65	191	54	[12], [13]
4- <i>tert</i> -Butyl- <i>ortho</i> -xylene	Benzene, 4-(1,1-dimethylethyl)-1,2-dimethyl-	8.70	C ₁₂ H ₁₈	147; 119; 162	0.86 (at 25 °C)	162.27	*	216.3	78.3	[14]
1- <i>tert</i> -Butyl-4-ethylbenzene	Benzene, 1-ethyl-4-(1,1-dimethylethyl)	8.77	C ₁₂ H ₁₈	147; 162	0.8568 (at 20 °C)	162.27	0.1 (at 20 °C)	216	75	[15], [16]
3- <i>tert</i> -Butyltoluene	Benzene, 1 (1,1-dimethylethyl)-3-methyl	8.9	C ₁₁ H ₁₆	133; 105; 148	0.87	148.24	0.811	188.8	60.5	[17], [18]
5- <i>tert</i> -Butyl- <i>meta</i> -xylene	Benzene, 1-(1,1-dimethylethyl)-3,5-dimethyl-	9.1	C ₁₂ H ₁₈	147; 119; 162	0.86	162.27	*	207–209	84	[19]

After several hours of storage with sulphuric acid, the gasoline 98 RON chromatographic profile significantly changed in comparison to the one of neat gasoline 98 RON: that is, the composition of the IL had undergone extensive modifications and could no longer be clearly attributed to gasoline (depending on the selected identification criteria). One of the fastest disappearing compounds was MTBE. Others major compounds of neat gasoline that experimented a high reduction with sulphuric acid were toluene, *ortho*-xylene, 1,2,3-trimethylbenzene and indane. In similar experiments using gasoline 95 RON instead of gasoline 98 RON, the results turned out to be very analogous (data not shown). It is important to bear in mind that these experiments were carried out at static and room temperature conditions. As chemical reaction is occurring, temperature and agitation may have an impact, accelerating the transformation. Additional experiments were performed undergoing the simulated solutions to movement using an orbital shaker at 600 rpm (see Section 2.2). Results obtained confirmed that the reaction was accelerated and the changes previously described occur faster.

On the basis of these results, and after a thorough review of the literature on some of the main identified new compounds, the origin of these new compounds was interpreted. They were attributed to the alkylation of the compounds present in neat gasoline such as toluene, ethylbenzene or xylenes, with tert-butylating agents (or alkylating agents), and sulphuric acid as catalyst [20], [21], [22]. The main substances able to act as such tert-butylating agents are isobutylene, diisobutylene, MTBE or tert-butyl alcohol (TBA) [22]. Yet, as previously mentioned, the samples of neat gasoline used in this work contained MTBE and this compound was quickly altered in presence of sulphuric acid. In fact, MTBE is sensitive to hydrolysis under strong acid conditions, which is favoured by the low water content of this kind of mixtures [23]. Therefore, in the interface between sulphuric acid and gasoline the following reactions were interpreted: 1) catalytic hydrolysis of MTBE in presence of sulphuric acid producing methanol and TBA, also known as 2-methyl-2-propanol or tert-butanol; 2) reaction of TBA in sulphuric media to form isobutene; 3) protonation of isobutene by the catalyst to form tert-butyl carbocation; and 4) alkylation of alkylbenzenes, catalysed by sulphuric acid, with tertiary carbocations producing tert-butylated compounds [22]. For example, tert-butyl carbocations react:

- with toluene, producing 4-t-BTO and 3-t-BTO (3-t-BTO being an isomerization product from 4-t-BTO) (Fig. 4a);

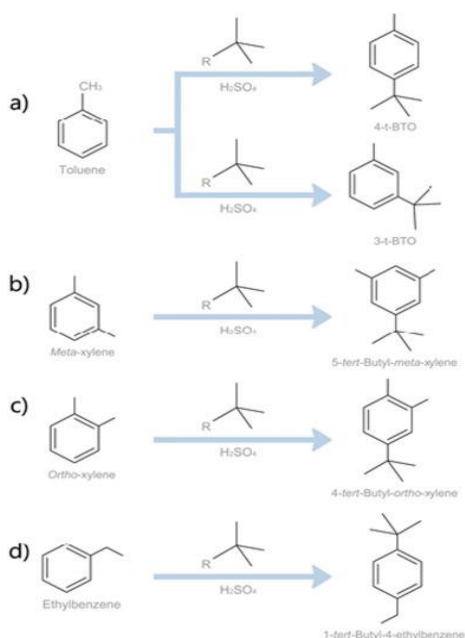


Fig. 4. Hypothetical reactions occurring in mixtures of gasoline and sulphuric acid. Molecular structure of the new compounds identified in these samples based on the information obtained from [20], [21], [22], [23], [24].

- with xylenes, producing 4-tert-butyl-meta-xylene or 5-tert-butyl-ortho-xylene (Fig. 4b–c);
- with ethylbenzene, producing 1-tert-butyl-4-ethylbenzene (Fig. 4d).

The higher amount of 4-t-BTO compared with the other new compounds ensues to our knowledge from the para-position which is favoured due to the influence of the steric hindrance of the methyl group on one side and the voluminous tert-butyl group on the other side [24]. Tert-butyl carbocations also react with para-xylenes, although it is the less favourable bond.

Thus, GC–MS results and reported information lead us to suggest a hypothetical explanation of the reactions taking place. Following a scientific approach based on a hypothetico-deductive reasoning, additional experiments were then carried out in order to test our hypothesis. Pure MTBE was added to a gasoline–sulphuric acid mixture that was analysed over time. After each analysis step of the organic fraction, the mixture was doped anew. It was observed that MTBE peak was not detected. However, some of the new peaks such as 4-t-BTO grew quickly, meanwhile alkylbenzene signals were declining proportionally. Additionally, control experiments were carried out in order to confirm that sulphuric acid has a key influence on these changes. The organic fraction from a gasoline–sulphuric acid mixture (mixed for 18 h) was extracted and introduced in another vial. An aliquot from this gasoline was sampled and immediately analysed by GC–MS, producing a similar profile to other aliquots analysed at the same time interval and under the same conditions. Further samples from this organic fraction were then analysed for several time intervals after the extraction of the gasoline from the gasoline–sulphuric acid mixture (at 24, 48, 72 and 168 h). All these GC–MS results displayed comparable chromatographic profiles, similar to the one obtained for the first sample. This indicated that the reaction stopped as soon as the gasoline was no more in contact with sulphuric acid, highlighting the crucial contribution of sulphuric acid in the alteration of the gasoline composition.

Besides all the modifications that the gasoline composition main undergo, some compounds that are important for identification of the presence of gasoline do not seem to be affected by sulphuric acid under the studied conditions. For example, benzene was not affected, nor alkanes such as n-hexane, n-heptane, n-octane or 2-methylpentane. This is related to the high aromatic stability of benzene or to the absence of double bonds of the normal and branched alkanes, rendering these substances less sensitive to strong acids [25].

In addition to all the changes described, several other peaks appeared over time in the acidified gasoline profile between 10 to 14 min (Fig. 2c–h). While these compounds could not be clearly identified on the basis of their mass spectrum, we presume that the series of reactions previously discussed can continue in presence of sulphuric acid, leading to the production the new alkylation products.

3.2. Diesel fuel mixed with sulphuric acid

In order to assess if neat diesel fuel would undergo similar composition modifications than those observed in gasoline–sulphuric acid mixtures, experiments testing diesel fuel–sulphuric acid mixtures were also carried out. Diesel fuel is mainly composed of alkanes (normal and branched). Its chromatographic profile is characterized by a series of n-alkane peaks, often depicted as a Gaussian-like distribution. Fig. 5a shows the results of analysis of neat diesel fuel. Normal alkanes are interspersed with branched alkanes, cycloalkanes and aromatic compounds, which are less abundant.

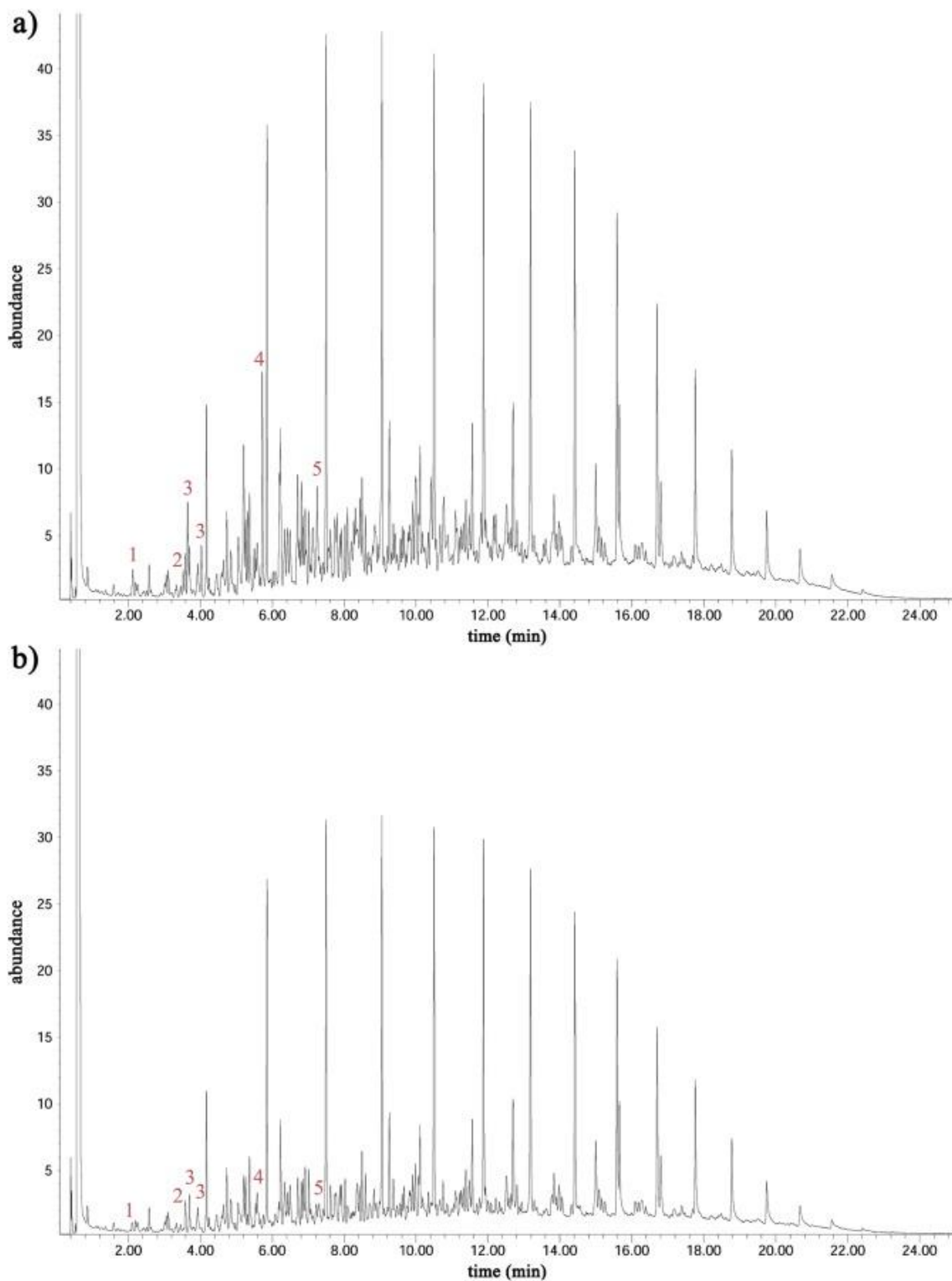


Fig. 5. TIC of a) a sample of neat diesel fuel and, b) a sample from mixture of diesel fuel with sulphuric acid after 19 h. Aromatic compounds: 1. toluene; 2. ethylbenzene; 3. xylenes; 4. benzene 1,2,3-trimethyl; and 5. benzene 1-ethyl-2,4-dimethyl. Samples were diluted at 1% (v/v) in dichloromethane. Abundance equivalent to $\times 10^6$. GC–MS conditions as shown in Section 2.3.

Assuming that the hypothesis previously exposed on the mechanism of gasoline compounds modification by sulphuric acid under the specified conditions was correct, we expected that the main compounds of diesel fuel (alkanes) would not undergo modifications, while an alteration of the aromatic compounds would occur. In order to assess this assumption, a simulated solution of CIMC with neat diesel fuel and sulphuric acid was prepared. Samples of the organic fraction were taken and analysed by GC–MS at different time intervals (from 5 min to 7 days). As example, Fig. 5b shows the TIC chromatogram of an aliquot of the organic fraction that was sampled 19 h after being mixed with sulphuric acid. It can be clearly observed that no major changes occurred in comparison with the neat diesel fuel TIC, except for aromatic compounds such as toluene, ethylbenzene, xylenes or C3-alkylbenzenes (Fig. 5), corroborating our hypothesis. The effect on the aromatic hydrocarbons appeared more clearly by considering selected EICs and comparing neat diesel fuel (black chromatogram, upside down in Fig. 6) with diesel fuel after being in contact with sulphuric acid for 19 h (blue chromatogram, upside up in Fig. 6). Fig. 6a, depicting the profiles that were measured for ion 91, shows how the relative abundances of C2- and C3-alkylbenzenes in acidified diesel fuel are altered. On Fig. 6c, considering ion 128, the decreasing abundance of naphthalene is obvious.

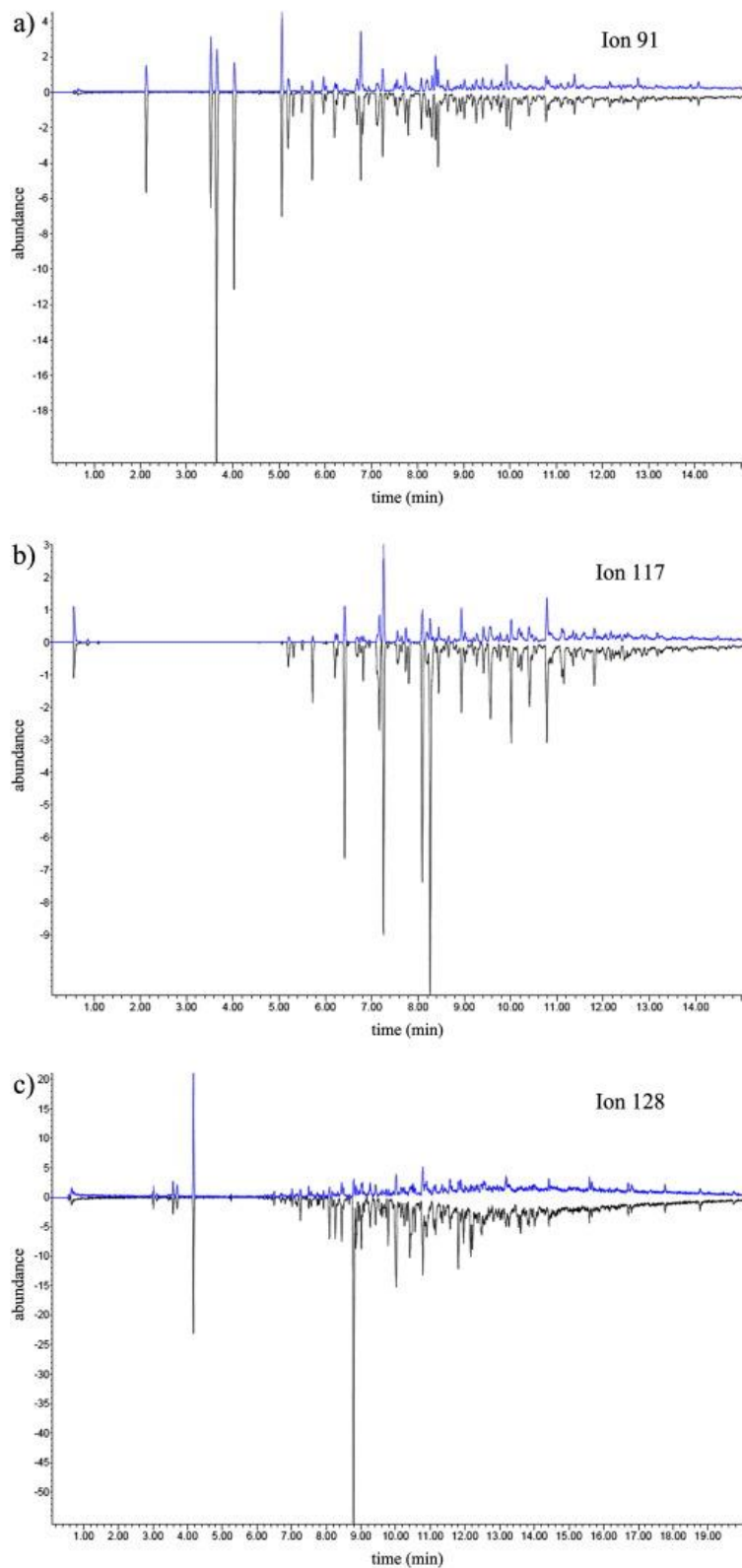


Fig. 6. EICs of neat diesel fuel (in black, in the web only, and upside down) and diesel fuel after 19 h mixed with sulphuric acid (in blue, and upside up). EICs of a) ion 91; b) ion 117 and c) ion 128.

It is important to point out that neat diesel fuel usually does not have MTBE [26] and the amount of other oxygenated compounds is low [27], [28], [29]. Therefore, there are not tert-butylation agents responsible of the alkylation of aromatic compounds. Accordingly, no products of alkylation were detected when diesel fuel and sulphuric acid were mixed (even after longer time intervals) although aromatic compounds decreased slightly.

It is known that some of the aromatic compounds, for example toluene, also react with sulphuric acid producing para-toluenesulfonic acid in the aromatic sulfonation reaction [30]. This compound is soluble in water; therefore it is not possible to find it in the organic fraction of these mixtures. Xylenes can also react with sulphuric acid and form, for example, para-xylene-2-sulfonic acid [31]. Sulfonic salts being soluble in water and insoluble in non-polar solvents, it is possible that sulfonation reactions are favoured in these mixtures in the absence of tertiary carbocations, and that the sulfonated compounds that are produced are extracted in the aqueous fraction of the mixture.

Finally, further simulated solutions with neat diesel fuel and sulphuric acid were prepared and shaken for 200 min before being analysed by GC–MS. In this case, no additional modifications, other than those described above, were noticed.

3.3. Recommendations for the identification of acidified gasoline and diesel fuel

As demonstrated by the different sets of experiments, the chromatographic profile of gasoline mixed with sulphuric acid displayed significant qualitative and semi-quantitative differences comparing to neat gasoline profiles, and those differences increased over the reaction time. Some of the most important compounds for the identification of gasoline (following the generally accepted ASTM E1618 standard [3]) are substantially altered in abundance, while new compounds not present in neat gasoline appeared. All these changes could cause great difficulties in the detection, classification and characterization of gasoline. To our knowledge, this chromatographic profile distortion effect has not been addressed to date and the 'traditional' identification/classification schemes do not take into account the contingency of mixing gasoline with sulphuric acid.

It is obvious that the identification of acidified gasoline following the usual criteria could be possible in some aspect, especially during earlier stages of the reaction. However, it is important to take into account that agitation or temperature can accelerate this reaction and, to consider that more often than not, GC–MS analysis are undertaken

several hours to several days after collection of samples. For these reasons, according to the obtained results, we propose a series of recommendations for the identification of acidified gasoline or diesel fuel. First of all, if there is suspicion of the presence of an IL mixed with a strong acid, we recommend carry out a first pH test to corroborate an acidic media. If a clearly acid pH is obtained, the GC–MS analysis should consider the knowledge gathered through the experiments we have reported in this work. While the ‘characteristic pattern’ of a known IL is not recognized, the following characteristics may orientate on the possibility of and acidified gasoline: 1) aromatic compound alteration: a significant decrease of some aromatic compounds can occur, leading to a change of their relative abundance in the chromatographic profile in comparison to their usual relative proportions in gasoline; 2) MTBE disappearance: MTBE is not present; 3) tert-butylated compound presence: a new group of tert-butylated compounds is detected in the chromatographic profile, and 4) alkane non-alteration; normal and branched alkanes are not altered in comparison to their usual relative proportions in gasoline.

A valuable fact to keep in mind is that tert-butylated compounds do not appear in neat gasoline and neither as consequences of other gasoline modification effects. Therefore, this group of compounds may be considered as diagnostic group to point to the potential identification of gasoline acidified by sulphuric acid.

In the case of acidified diesel fuel, the modifications of its composition are not deleterious for its identification following the traditional criterion, at least under the studied conditions. However, it is important to take into account that aromatic compounds contained in diesel fuel can be modified in their relative abundances or not be found in the analyses of the organic fraction.

4. Conclusions

In this work, mixtures of gasoline with sulphuric acid and diesel fuel with sulphuric acid were analysed by GC–MS and the analytical results were studied to understand the visual and chromatographic modifications occurring. In the case of gasoline with sulphuric acid, it has been shown that sulphuric acid affects the gasoline chemical composition, modifying some of its original compounds and changing its chromatographic profile. The performed experiments suggest that sulphuric acid catalyses several reactions, promoting the production of tertiary carbocations from the hydrolysis of MTBE and the alkylation of aromatic compounds with these tertiary carbocations. The series of reactions leads to a significant decrease or disappearance

of some aromatic compounds, affecting their relative abundances, the disappearance of MTBE, and the immediate appearance of a new group of compounds identified as tert-butylated compounds. Normal and branched alkanes are not altered at all.

In the case of diesel fuel with sulphuric acid, it has been observed that the sulphuric acid alter the diesel fuel in a much smaller extent. Aromatic compounds are affected, decreasing their abundance. It is supposed that sulphuric acid is favouring the sulfonation of these aromatic compounds and their probable elution in the aqueous fraction of the mixture. Normal and branched alkanes, the main compounds of diesel fuel as the main indicators for its identification, are not affected by the sulphuric acid action.

All these changes may complicate the process of detection, classification and characterization of these ILs, especially in the case of gasoline. As this chromatographic profile modification effect has not previously been described, we make some recommendations to help with the identification of these mixtures. While the findings of this work may already be of some operational use, further studies are necessary to better understand the ILs acidification effect, prior to the formulation of specific identification schemes for non-burn acidified ILs. Besides, further research is necessary to assess the consequences on the extraction process of acidified ILRs from fire debris.

Novelty statement

In this manuscript the chemical modifications of gasoline and diesel fuel when mixed with sulphuric acid are studied. The chromatographic profiles of the acidified ignitable liquids showed considerable changes, which leads us to propose the acidification of ignitable liquids as a novel modification effect of the chromatographic profiles. Besides, as this is not taken into account in the generally applied criteria, we propose some recommendations for the identification of acidified ignitable liquids. It allows us to identify non-burned samples from seized or failed improvised incendiary devices made with mixtures of sulphuric acid-ignitable liquid, or ignitable liquids altered intentionally with the aim to modify their composition.

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References

- [1] C. Martín-Alberca, J. Sáiz, J.L. Ferrando, C. García-Ruiz. Qualitative determination of inorganic anions in incendiary device residues by capillary electrophoresis. *Anal. Methods*, 4 (2012), pp. 2680-2686.
- [2] C. Martín-Alberca, J.L. Ferrando, C. García-Ruiz. Anionic markers for the forensic identification of Chemical Ignition Molotov Cocktail composition. *Sci. Justice*, 53 (2013), pp. 49-54.
- [3] ASTM Method E1618-14, Standard Test Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography–Mass Spectrometry. ASTM International, West Conshohocken, PA (2014).
- [4] Technical and Scientific Working Group for Fire and Explosions (T/SWGFEX), The Ignitable Liquids Database (ILDB) and Ignitable Liquids Reference Collection (ILRC).
- [5] E. Stauffer, J.A. Dolan, R. Newman. *Fire Debris Analysis*. Elsevier Academic Press, Burlington, Massachusetts, USA (2007).
- [6] P.M.L. Sandercock. Fire investigation and ignitable liquid residue analysis — a review: 2001–2007. *Forensic Sci. Int.*, 176 (2008), pp. 93-110.
- [7] J.R. Almirall, K.G. Furton. *Analysis and Interpretation of Fire Scene Evidence*. CRC Press, Boca Raton, FL, USA (2004).
- [8] A.D. Pert, M.G. Baron, J.W. Birkett. Review of analytical techniques for arson residues. *J. Forensic Sci.*, 51 (2006), pp. 1033-1049.
- [9] K.R. Prather, V.L. McGuffin, R. Waddell Smith. Effect of evaporation and matrix interferences on the association of simulated ignitable liquid residues to the corresponding liquid standard. *Forensic Sci. Int.*, 222 (2012), pp. 242-251.
- [10] D.A. Turner, J.V. Goodpaster. Comparing the effects of weathering and microbial degradation on gasoline using principal components analysis. *J. Forensic Sci.*, 57 (2012), pp. 64-69.

- [11] X. Archer, U. Hendriks, J. Hendrikse, F. Schäfer. Guideline for the identification of ignitable liquids in fire debris. ENFSI Fire & Explosion Investigation Working Group (2011).
- [12] National Institute of Standards and Technology (NIST): <http://www.sigmaaldrich.com/catalog/product/aldrich/b102628?lang=fr®ion=CHc>. (visited in May 2015).
- [13] Fisher website: <http://www.fishersci.ca/viewmsds.do?catNo=AC296320250> (visited in May 2015).
- [14] National Institute of Standards and Technology (NIST): <http://webbook.nist.gov/cgi/cbook.cgi?ID=C7397060&Mask=80> (visited in May 2015).
- [15] National Institute of Standards and Technology (NIST): <http://webbook.nist.gov/cgi/cbook.cgi?ID=C7364194&Mask=400> (visited in May 2015).
- [16] Website: <http://www.chemspider.com/Chemical-Structure.73840.html> (visited in May 2015).
- [17] National Institute of Standards and Technology (NIST): <http://webbook.nist.gov/cgi/cbook.cgi?ID=C1075383&Mask=4> (visited in May 2015).
- [18] Website: <http://www.guidechem.com/dictionary/en/1075-38-3.html> (visited in May 2015).
- [19] Website: <http://www.chemspider.com/Chemical-Structure.7100.html> (visited in May 2015).
- [20] G. Kostrab, D. Mravec. The transformations of 4-tert-butyltoluene over Ce-modified modernite zeolites. *Pet. Coal*, 46 (2004), pp. 28-33.
- [21] B.V. Ioffe, R. Lemann, B.V. Stolyarov. Isomerization and orientation in alkylation of toluene with butyl alcohols. *Neftekhimiya*, 9 (3) (1969), pp. 386-393.
- [22] M. Selvaraj, S.H. Jeon, J. Han, P.K. Sinha, T.G. Lee. A novel route to produce 4-tert-butyltoluene by t-butylation of toluene with t-butylalcohol over mesoporous Al-MCM-41 molecular sieves. *Appl. Catal. A Gen.*, 286 (2005), pp. 44-51.
- [23] K.T. O'Reilly, M.E. Moir, C.D. Taylor, C.A. Smith, M.R. Hyman. Hydrolysis of tert-Butyl Methyl Ether (MTBE) in dilute aqueous acid. *Environ. Sci. Technol.*, 35 (2001), pp. 3954-3961.

[24] D. Mravec, P. Zavadan, A. Kaszonyi, J. Joffre, P. Moreau. Tert-Butylation of toluene over zeolite catalysts. *Appl. Catal. A Gen.*, 257 (2004), pp. 49-55.

[25] William Reusch. Virtual Text of Organic Chemistry. Aromaticity: <http://www2.chemistry.msu.edu/faculty/reusch/virttxtjml/react3.htm> (1999). (Visited in May 2015).

[26] G.A. Robbins, B.J. Henebry, T.M. Cummins, C.R. Goad, E.J. Gilbert. Occurrence of MTBE in heating oil and diesel fuel in Connecticut. *Groundw. Monit. Remediat.*, 20 (2000), pp. 82-86.

[27] D.W. Naegeli, S. Moulton, E.C. Owens, E.A. Frame. Oxygenates for Advanced Petroleum-based Diesel Fuels, U.S. Army TARDEC Fuels and Lubricants Research Facility (SwRI). Southwest Research Institute, San Antonio, TX, USA (2001).

[28] F. Frusteri, F. Arena, G. Bonura, C. Cannilla, L. Spadaro, O. Di Blasi. Catalytic etherification of glycerol by tert-butyl alcohol to produce oxygenated additives for diesel fuel. *Appl. Catal. A Gen.*, 367 (2009), pp. 77-83.

[29] M.T. Lovestead, T.J. Bruno. Comparison of diesel fuel oxygenate additives to the composition-explicit distillation curve method. Part 3: t-Butyl glycerols. *Energy Fuels*, 25 (2011), pp. 2518-2525.

[30] Medelset, Organic Chemistry Practice Problems and Problem Sets, Properties of Hydrocarbons: http://www.mendelset.com/articles/689/properties_hydrocarbons (visited in May 2015).

[31] Website.
<http://chemicalland21.com/specialtychem/NH/XYLENESULFONIC%20ACID.htm>.
(visited in May 2015)