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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.

**Keywords:** Acidification; Acid alteration; Arson; Ignitable liquid; Modification effect; Thinner.

## 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], [3], [4], [5], [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], [8], [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], [10], [11], [12], [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 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], [10], [11], [12], [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  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$  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  $\text{cm}^{-1}$  to 2700  $\text{cm}^{-1}$  and from 1900  $\text{cm}^{-1}$  to 650  $\text{cm}^{-1}$ , 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 (wavenumbers) of the spectral region selected was taken as variables (columns). They were named with their specific wavenumbers ( $\text{cm}^{-1}$ ). The sample classes (rows) were the neat and acidified samples. This was a total of 1116 IR absorption spectra, corresponding to two different experiments. The first one consisted of monitoring the four reactions for 24 h: 4 different mixtures of IL with sulfuric acid  $\times$  3 replicas of each mixture  $\times$  3 aliquots sampled every hour during 24 h + 1 extra sampling time (time zero = neat IL). This is a total of 900 IR absorption spectra. The second one consisted of monitoring the four reactions from the 24th h to the 44th day of reaction: 4 different mixtures of IL with sulfuric acid  $\times$  3 replicas of each mixture  $\times$  6 measuring points  $\times$  3 aliquots taken in each measuring point. This is a total of 216 IR absorption spectra. They were grouped in four different row groups, one for each IL studied, with their specific time of mixing with sulfuric acid and their experiment/repetition name (e.g., 71 h of mixing with sulfuric acid, experiment C of a total of three repetitions "71h\_C"). The proportional variance explained by every PC is also given.

### **3. Results and discussion**

#### **3.1. Selection of ILs for further study**

Several ILs of forensic interest and some other commercially available ILs were preselected in order to quickly explore which ILs undergo more chemical and spectral changes when they are mixed with sulfuric acid. Those preselected ILs showing clear modifications in their IR absorption spectra would be selected for an in-depth study. Table 1 shows the list of these 10 preselected ILs and their declared compositions. As it is already known, some aromatic and oxygenated compounds are modified by sulfuric acid [9], [10], [11], [12], [13]. A priori, almost all preselected ILs contain aromatic compounds (except for white spirit, paraffin and kerosene), and some of them also include oxygenated compounds. Therefore, the hypothesis is that the chemical composition of these ILs may be altered by the acid. Apart from that, it is important to bear in mind that some other ILs could only be acidified, but not chemically modified. This means mixed with acid, and hence with an increase of protons present in the solution, but remaining its main compounds unchanged.



**Table 1.** List of initially preselected ILs with their compositions (as declared by manufacturers in their labels) and the subjective observations of the spectral changes (after acid alteration/acidification) are showed. The n-alkane range was indicated following the criterion showed in reference [13]. The ILs highlighted in grey are the selected ILs for further study. The majority compounds (indicated as %, v/v) identified by GC–MS in the further studied ILs are also included. The identified minority compounds (< 1% and < 2%, v/v, respectively) in Universal Thinner and Bitumen of Judea are also declared in the Supplementary material (Table S1). Experimental conditions as explained in Section 2.1. All compounds were identify using NIST 05 library (matching > 85%). It was not possible to identify the complete composition of bitumen of Judea after 96 h of reaction by this methodology.

IL	Declared composition	Spectral changes (after 23 h of reaction)	Identified compounds in neat ILs by GC–MS	New identified compounds in acidified ILs by GC–MS (after 96 h of reaction)
<b>Epoxy thinner</b>	Aromatic compounds, esters and alcohols	Several changes	1-methoxy-2-propyl acetate (18%); <i>p/m</i> -xylene (14.9%); methyl alcohol (13.8%); <i>o</i> -xylene (8%); ethylbenzene (7.8%); isopropyl alcohol (6.3%); and minority compounds (< 1%): toluene; acetic acid, butyl ester; 1-butanol, 3-methoxy-, acetate; 2-methyloctane; 3-methyloctane; nonane; benzene, (1-methylethyl).	Acetic acid, 1-methylethyl ester; 2-propanol, 1-methoxy-; 1-butanol, 3-methoxy-; benzene, 1-ethyl-4-(1-methylethyl)-; benzene, 1,3-dimethyl-5-(1-methylethyl)-; benzene, 1,4-dimethyl-2-(1-methylethyl)-; benzene, 2,4-dimethyl-2-(1-methylethyl)-; benzene, 1-ethyl-3,5-diisopropyl-; benzene, 1,4-dimethyl-2,5-bis(1-methylethyl)-.
<b>Oxirite thinner</b>	Xylenes and acetic acid, butyl ester	Several changes	<i>p</i> -xylene (50%); ethylbenzene (20%); methyl alcohol (13%); <i>o</i> -xylene (8%); acetic acid, butyl ester (5%); and minority compounds (< 1%): 1-butanol; hexanedioic acid; bis(2-ethylhexyl) ester; toluene; 2-methyloctane; 3-	Hexane; cyclohexane ethyl-; 3-methyldodecane; 2,2,6-trimethyldecane; 2,2-dimethyloctane; benzene, 1,3,5-triethyl-; benzene, 2,4-dimethyl-1-(1-methylpropyl).

			methyloctane; nonane.	
<b>Universal thinner</b>	Toluene, aromatic compounds, light alkanes (C <sub>4</sub> –C <sub>9</sub> ) and methyl alcohol	Some changes	Toluene (50,4%); methyl alcohol (20,8%); 1,2,3-trimethylbenzene (10,6%); bis(2-ethylhexyl) hexanedioate (4,8%); benzene, 1-ethyl-3-methyl- (4,8%); benzene, 1-ethyl-2-methyl- (3,7%); benzene, propyl- (1,2%).	Benzene, (2-methylpropyl)-; benzene, 1-methyl-2-propyl-; benzene, 1-methyl-2-(1-methylethyl)-; benzene, 1-(1,1-dimethylethyl)-3-methyl-; benzene, 1-ethenyl-4-ethyl-; naphthalene.
<b>Bitumen of Judea</b>	Aromatic compounds (mainly xylenes), medium alkanes (C <sub>9</sub> –C <sub>13</sub> )	Several changes	Methyl alcohol (11,9%); <i>m</i> -xylene (11,0%); acetic acid, butyl ester (8,1%); ethylbenzene (3,9%)	–
<b>Acrylic rubber solvent</b>	Aromatic compounds and light alkanes (C <sub>4</sub> –C <sub>9</sub> )	Only changes in band intensity		
<b>Synthetic solvent</b>	Aromatic compounds and light alkanes (C <sub>4</sub> –C <sub>9</sub> )	Apparently not		
<b>White spirit</b>	Light and medium alkanes (C <sub>9</sub> –C <sub>13</sub> )	Apparently not		
<b>Turpentine</b>	Medium alkanes (C <sub>9</sub> –C <sub>13</sub> ), aromatic compounds and trementine	Apparently not		
<b>Liquid paraffin</b>	Alkanes	Apparently not		
<b>Kerosene</b>	Heavy alkanes (C <sub>8</sub> –C <sub>20</sub> and above)	Apparently not		

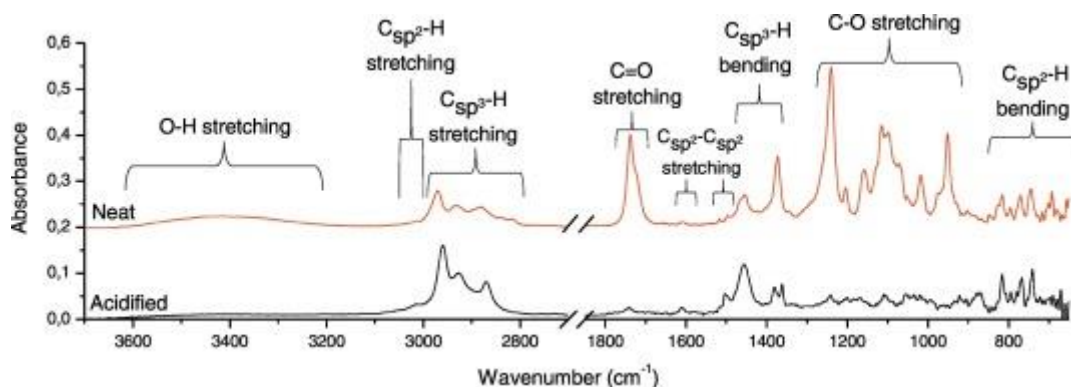
First, neat ILs were measured by ATR-FTIR. Then, each IL was mixed with sulfuric acid. After 23 h, aliquots from each mixture were measured, and spectra were compared. Table 1 shows the main subjective observations about changes produced in their IR spectra. Some of the preselected ILs (i.e., thinners and bitumen of Judea) showed clear modifications in their IR absorption spectra, which manifested as the appearance or disappearance of several bands in spectra of acidified samples (more information and figures in the section below). Therefore, these thinners and the Bitumen of Judea were chosen to further study in this work. Apparently, the non-chosen ILs did not show spectral changes (at the naked eye). It does not mean that those unselected ILs are not affected by sulfuric acid. It only signifies that after 23 h of reaction, there are not observable changes in their IR spectra. In fact, as was previously suggested for diesel fuel acidified samples [10], [12], the sulfonation of aromatic compounds is produced slowly [14], taken several days (keeping still the solutions during the experiments) to modify their proportions. Therefore, turpentine, acrylic rubber and synthetic solvents, which supposedly have aromatic compounds, could show modifications in their compositions at longer exposition times.

## 3.2. Study of spectroscopic, chromatographic and chemical characteristics of the selected ILs

### 3.2.1. Epoxy thinner

First of all, spectroscopic characteristics of neat epoxy thinner were studied. Fig. 1 shows the IR spectrum of neat epoxy thinner. Having in mind the band assignment reported in the literature [15], [16], and the declared composition (Table 1), the following band assignment is proposed: a wide band can be seen from  $3600$  to  $3200\text{ cm}^{-1}$  which may be related to O-H stretching of alcohol compounds. Bands included in the range  $3000$ – $2800\text{ cm}^{-1}$  could be assigned to Csp<sup>3</sup>-H stretching, while bands between  $1475$  and  $1360\text{ cm}^{-1}$  may be related to Csp<sup>3</sup>-H symmetric and asymmetric bends. Both groups of bands could be associated to several type of compounds such as aromatic, alcohols or esters. The band at  $1740\text{ cm}^{-1}$  could be related to C=O stretching of esters. In the range  $1330$ – $970\text{ cm}^{-1}$ , the spectrum shows several bands that may be related to C-O stretching of esters and alcohols. Bands between  $830$  and  $690\text{ cm}^{-1}$  may correspond with Csp<sup>2</sup>-H out-of-plane bends of different aromatic compounds depending on their different substitution. In order to confirm the actual composition, GC-MS analyses were carried out. Table 1 depicts the complete chemical composition of the selected neat ILs

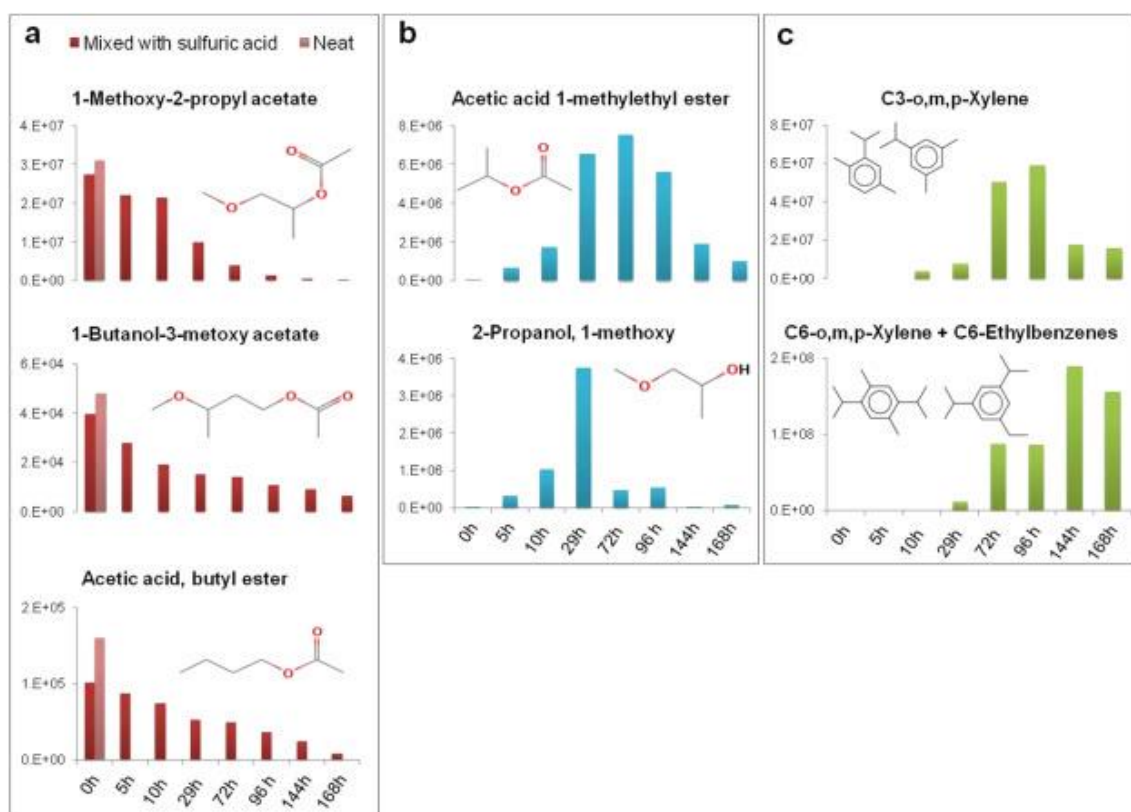
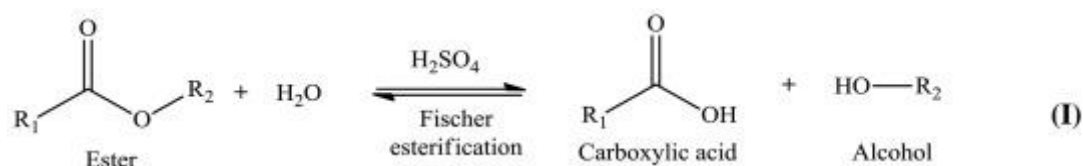
obtained by GC–MS. Ester compounds (1-methoxy-2-propyl acetate; acetic acid, butyl ester; and 1-butanol, 3-methoxy-, acetate), alcohols (isopropyl alcohol and methyl alcohol) and aromatic compounds (xylenes, ethylbenzene and toluene) are in a greater proportion in epoxy thinner, as was declared by the manufacturer. There are also some non-reported alkanes among the minority compounds of epoxy thinner, which could show Csp<sup>3</sup>-H bands in the neat IR spectrum.



**Fig. 1.** Spectrum of neat epoxy thinner and spectrum of acidified epoxy thinner after 1056 h (44 days) of reaction with sulfuric acid.

Then, acidified epoxy thinner was studied. Fig. 1 also shows a spectrum of an acidified sample after several days of reaction. The most remarkable changes are found in bands at around 3600–3200 cm<sup>-1</sup>, as well as in bands at 1740 cm<sup>-1</sup> and at around 1330–970 cm<sup>-1</sup>. They are related to O-H, C=O and C-O stretching [15], [16]. All these bands disappear or decrease over time. As mentioned above, these bands may be related to alcohol and ester compounds, which could be modified by the treatment with sulfuric acid. Some extra GC–MS tests were carried out in order to obtain more information about the behaviour of those compounds and about possible by-products of the reaction between this IL and sulfuric acid (see Table 1). These analyses showed the immediate disappearance of the original alcohol compounds: isopropyl alcohol and methyl alcohol. Both original alcohols are soluble in aqueous solutions (methyl alcohol more than isopropyl alcohol) [17]. Therefore, they could be migrating at the beginning of the reaction to the aqueous part of the mixture. In addition, the analysis showed the gradual disappearance over time of the original ester compounds: 1-methoxy-2-propyl acetate, acetic acid, butyl ester and 1-butanol, 3-methoxy-, acetate (Fig. 2a). It is well-known that sulfuric acid can catalyse ester hydrolysis producing carboxylic acid and

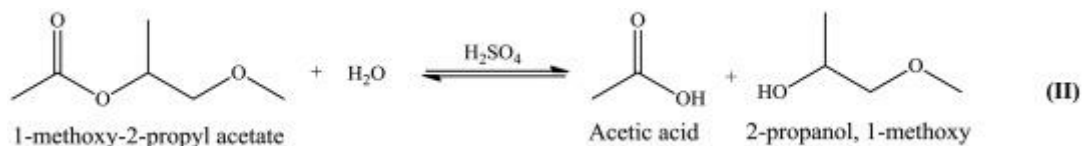
alcohol, as can be seen in Reaction I. Such processes are reversible and concentration dependent equilibrium is established [18], [19].



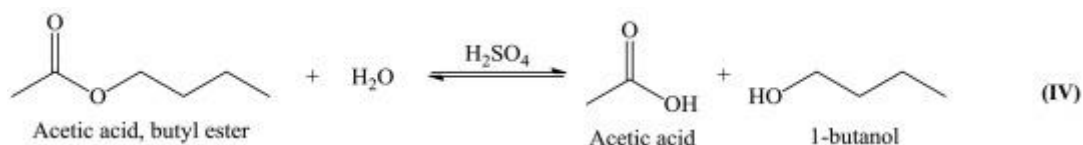
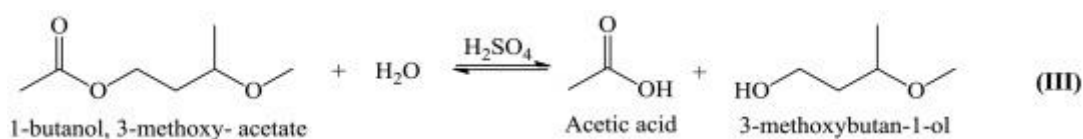
**Fig. 2.** Monitoring of the presence of original compounds and by-products formed in acidified samples of epoxy thinner. Quantity of each compound was represented as signal intensity (abundance). In a) neat analysis was performed without sulphuric acid addition and  $t = 0$  was the measure just after the addition of sulphuric acid to the sample (after some few seconds).

The GC-MS tests also showed that two new by-products were immediately produced (see Table 1): acetic acid, 1-methylethyl ester (also named as isopropyl acetate) and 2-propanol, 1-methoxy- (also named as methoxyisopropanol). Both new compounds increased their abundances during first 72 and 29 h of reaction, respectively, and then decreased to almost their disappearance (Fig. 2b). Reaction II shows the

possible origin of 2-propanol, 1-methoxy-, which also would justify the progressive disappearance of 1-methoxy-2-propyl acetate.



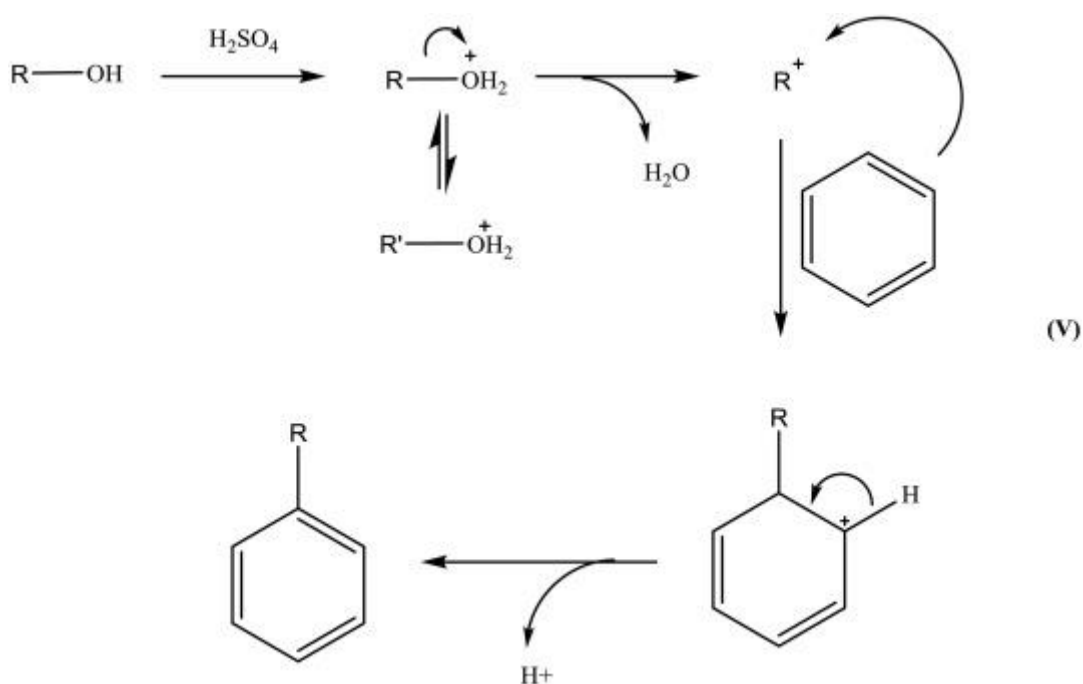
Similar reaction mechanisms could explain the behaviour of the other two original ester compounds (see Fig. 2 and Reactions III and IV):



Furthermore, Reaction I could also occur in its reverse way, as Fischer esterification (Reaction I, to the left) [18]. The concentration of the required compounds (mainly the no presence of water, which would be consumed during ester hydrolysis, and the presence of new carboxylic acids) for these reactions involves different product distribution (dynamic equilibrium). Therefore, carboxylic acids such as acetic acid produced in Reactions II, III and IV may also react with the new alcohols (in this case, these new alcohols are less soluble than the original ones, hence they do not pass quickly into the aqueous phase) to produce new ester compounds. This would explain the presence of the other above mentioned new by-product, the acetic acid, 1-methylethyl ester from acetic acid and an alcohol.

Additionally, other new compounds were observed in acidified epoxy thinner samples (Table 1). They were identified as di-, tri- and tetra-substituted benzene compounds. They seem to be toluene, ethylbenzene and xylenes, but with additional isopropyl substitutions. They are produced after some hours from the start of the reaction and their abundances increased gradually over time (Fig. 2c). A hypothesis about their production could be that the initial aromatic compounds of epoxy thinner undergo Friedel-Crafts alkylation reactions, adding isopropyl groups [20]. These isopropyl groups might be produced from the acid catalysed hydrolysis of one of the by-products, the

acetic acid, 1-methylethyl ester [21]. This would explain why acetic acid, 1-methylethyl ester abundance increased, and after some hours, it starts to decrease (Fig. 2b). Hence, the production of the new isopropyl aromatic derivatives is explained via Friedel–Crafts alkylation between aromatic residues and isopropyl carbocations (see Reaction V), which are produced from that ester.

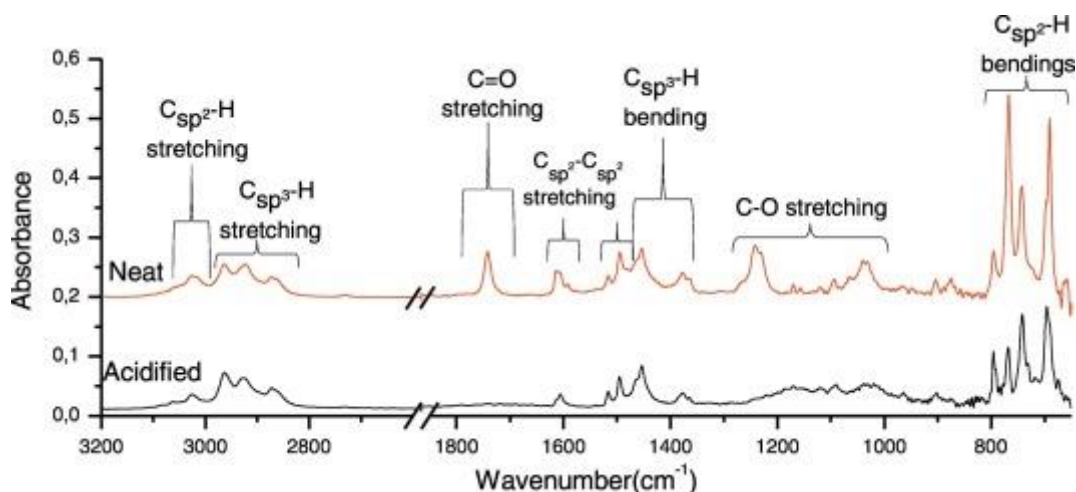


In addition, as can be seen in Fig. 2c, some of these new compounds started to decrease at long reaction times, maybe as a consequence of additional alkylation over those new compounds. All these reactions would explain the chemical composition modifications, and hence spectral and chromatographic characteristics, of epoxy thinner when is mixed with sulfuric acid. In addition, and as was indicated above, the sulfonation of some aromatic compounds could also be produced at longer reaction times [14]. These sulfonated compounds would turn to be enough polar to migrate to the aqueous phase. Moreover, alkanes are not supposed to be modified by sulfuric acid [10]. Indeed, the GC–MS and ATR-FTIR analyses do not show changes related to alkanes, as can be appreciated in the IR spectrum of Fig. 1. Nevertheless, it can be observed an increase in its intensity over reaction time (e.g.,  $2970\text{ cm}^{-1}$  and  $1454\text{ cm}^{-1}$  bands in Fig. 1). That fact can be explained by a concentration effect. If alcohol compounds (and, where appropriate, sulfonated aromatic compounds) are migrating to the aqueous phase, the whole volume of the organic solution is reduced (this fact is noticeable with the naked

eye). As a consequence, having the same amount of alkanes results in a bigger band while the reaction progress. This effect has also been observed in other of the IR spectra of the four selected ILs (see below).

### 3.2.2. Oxirite thinner

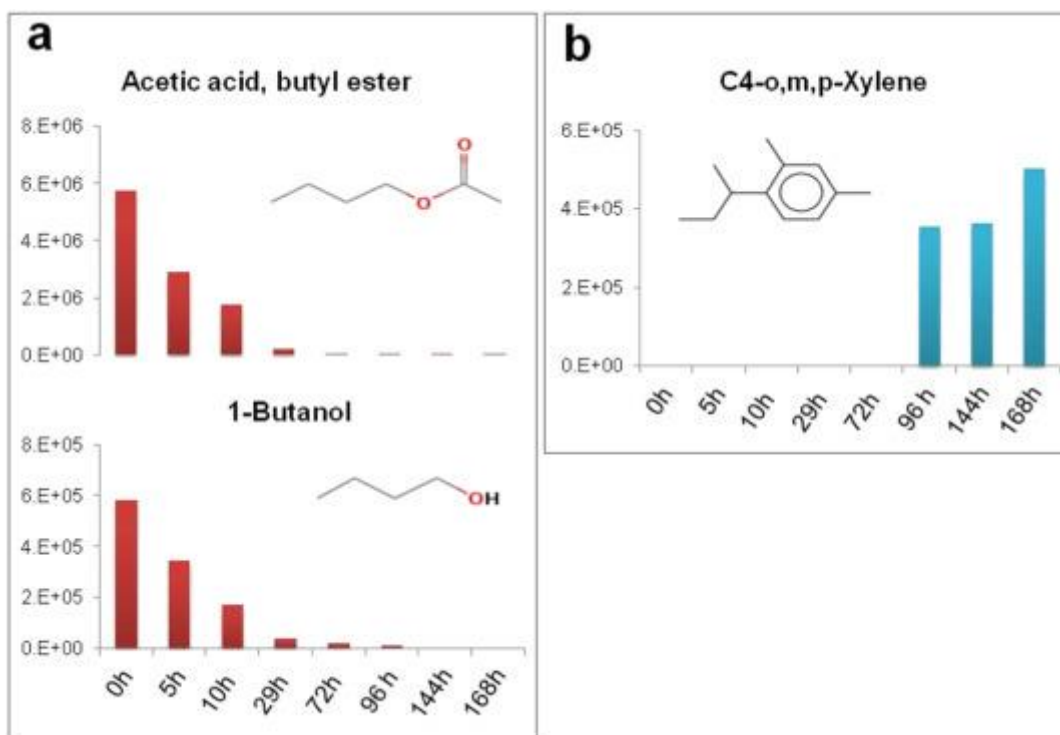
Looking at Fig. 3, main bands present in the neat spectrum of oxirite thinner can be described. Bands in the ranges between  $3000$  and  $2800\text{ cm}^{-1}$  and those appearing around  $1475$ – $1360\text{ cm}^{-1}$  may be related to  $\text{C}_{\text{sp}^3}\text{-H}$  stretching and  $\text{C}_{\text{sp}^3}\text{-H}$  bends of  $\text{CH}_3$  and  $\text{CH}_2$  groups, respectively. Bands among  $3100$ – $3000\text{ cm}^{-1}$  ( $\text{C}_{\text{sp}^2}\text{-H}$  stretching),  $1625$ – $1575\text{ cm}^{-1}$  and  $1525$ – $1475\text{ cm}^{-1}$  ( $\text{C}_{\text{sp}^2}\text{-C}_{\text{sp}^2}$  stretching) and  $830$ – $690\text{ cm}^{-1}$  ( $\text{C}_{\text{sp}^2}\text{-H}$  out-of-plane bend) can be related to several type of compounds, such as aromatic compounds [15], [16]. Lastly, the band around  $1740\text{ cm}^{-1}$  ( $\text{C}=\text{O}$  stretching) and those in the range  $1330$ – $1050\text{ cm}^{-1}$  ( $\text{C}-\text{O}$  stretching) can be assigned to esters [15], [16]. Unlike epoxy thinner's spectrum, in this case the percentage of aromatic compounds determined by GC–MS analysis was higher (Table 1), consequently bands related to  $\text{C}_{\text{sp}^2}\text{-H}$  stretching can be seen in its IR spectrum. In addition, other non-declared compounds such as alcohols, esters, aromatics and alkanes were detected by GC–MS, some of them in minority amount (Table 1).



**Fig. 3.** Spectrum of neat oxirite thinner (on the top) and spectrum of acidified oxirite thinner after 44 days of reaction with sulfuric acid without moving the sample (at the bottom).



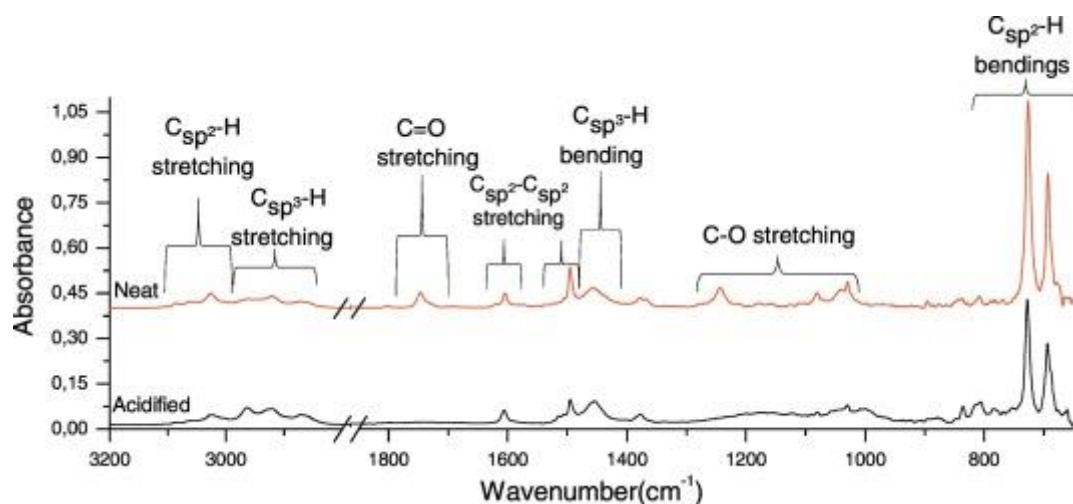
After acidification, this thinner also showed a modified IR spectrum (Fig. 3). The main differences were in the bands at  $1740\text{ cm}^{-1}$  and around  $1330\text{--}970\text{ cm}^{-1}$  (mainly the band at  $1240\text{ cm}^{-1}$ ), which disappeared. In order to obtain additional chemical information and figure out the occurring chemical reactions, GC–MS analyses were carried out (Table 1). The original methyl alcohol disappeared immediately, probably due to its solubility in the aqueous phase, as suggested before. 1-butanol and acetic acid, butyl ester decreased their abundances over the reaction time (Fig. 4a). The decreasing of acetic acid, butyl ester can be related to the ester hydrolysis, as explained before (Reaction IV). However, that reaction produces 1-butanol as by-product. Hence, in that moment, it was not possible to explain the observed decreasing of this compound. In addition to these modifications, several aromatic compounds with alkyl substituents such as benzene, 2,4-dimethyl-1-(1-methylpropyl) or benzene, 1,3,5-triethyl- appeared after some reaction days (see Fig. 4b, and Fig. S1 in Supplementary material). The production of these by-products could also be explained as above (Reaction V), though, unlike the previous case, butanol (the initial one and the one produced from the hydrolysis of the acetic acid, butyl ester) should be the source of alkyl groups instead of isopropanol. In this case, an isomerization process of the n-butyl into a sec-butyl (represented as R and R' in Reaction V) was produced. As explained above, a Friedel Craft alkylation between aromatic and sec-butyl carbocations was occurred, obtaining 2-sec-butyl-m-Xylene (or other alkyl by-products, which cannot be identified unequivocally because of their similar mass spectra) starting at 96 h, as shows Fig. 4b. Consequently, now it is possible to explain the 1-butanol abundance decreasing, as well as the rest of chemical modifications after the addition of sulfuric acid to this thinner.



**Fig. 4.** Monitoring of the presence of original compounds and by-products formed in acidified samples of oxirite thinner. Quantity of each compound was represented as signal intensity (abundance).

### 3.2.3. Universal thinner

The IR spectrum of neat universal thinner showed bands in the ranges 3000–2800  $\text{cm}^{-1}$  (Csp<sup>3</sup>-H stretching) and 1475–1360  $\text{cm}^{-1}$  (Csp<sup>3</sup>-H bends), which may be assigned to alkanes (Fig. 5). Bands between 3100 and 3000  $\text{cm}^{-1}$  can be related to Csp<sup>2</sup>-H stretching, those between 1625–1575  $\text{cm}^{-1}$  and 1525–1475  $\text{cm}^{-1}$  can be assigned to Csp<sup>2</sup>-Csp<sup>2</sup> stretching, while bands around 830–690  $\text{cm}^{-1}$  could be related to Csp<sup>2</sup>-H out-of-plane bends [15], [16]. All of them can be related to aromatic compounds. Furthermore, bands appearing between 1260 and 970  $\text{cm}^{-1}$  arise from C-O stretching, and the band at 1740  $\text{cm}^{-1}$  could be related to C=O stretching [15], [16]. GC-MS analysis showed the complete chemical composition of neat universal thinner (Table 1). As can be seen (Table 1 and Table S1 in Supplementary material), main compounds in this solvent are aromatic compounds, besides alcohols, specifically methyl alcohol and 2-hexanol, and some ketone such as 3-penten-2-one, 4-methyl-

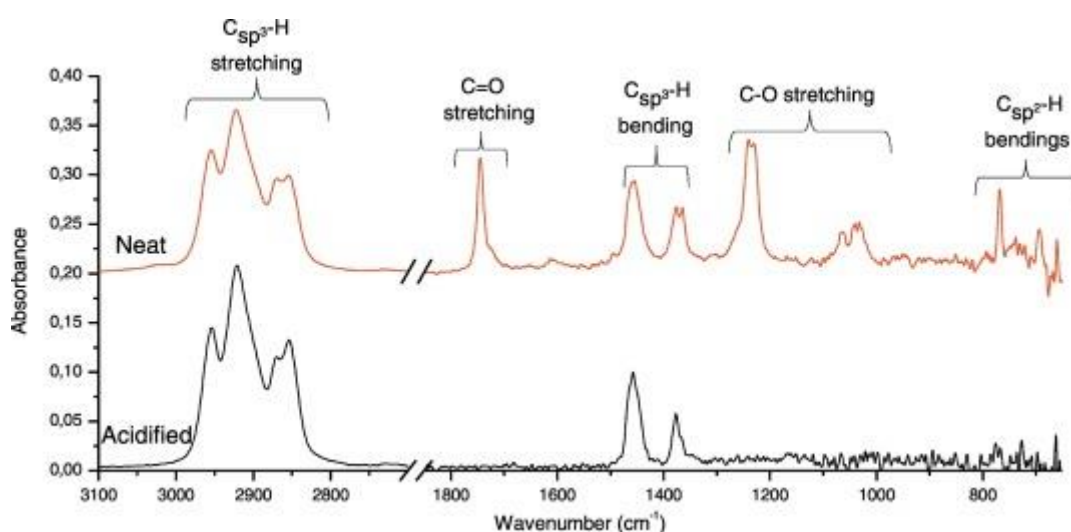


**Fig. 5.** Spectrum of neat universal thinner (on the top) and spectrum of acidified universal thinner after 44 days of reaction with sulfuric acid without moving the sample (at the bottom).

Looking at the spectrum of acidified universal thinner in Fig. 5, it can be observed that bands related to C=O and C-O disappeared over reaction time. Those bands could be related to ketones and alcohols. GC-MS analysis showed that methyl alcohol disappeared immediately after mix sulfuric acid with this thinner. However, 2-hexanol and 3-penten-2-one, 4-methyl- disappeared over reaction time (see Fig. S2 in Supplementary material). Methyl alcohol could pass into the aqueous solution from the beginning of the reaction, as a response of their higher solubility in the aqueous phase. And 2-hexanol could react similarly to the above mentioned cases of isopropanol and butanol, and then its isomerized form may react alkylating aromatics (Reaction V) [22]. This would explain the production of new aromatic derivatives. In addition, the amount decreasing over reaction time of the ketone suggests a similar reaction. Carbocations would be formed from the ketone and the sulfuric acid catalyst [19]. The carbocation is attacking aromatic compounds to also produce the new by-products of this reaction. Depending on the monomer structures and the reaction conditions, an alcohol, a diaryl-compound or a mixture of both could be obtained. Lastly, Fig. 5 shows that the bands related to alkanes have higher intensity in the acidified IL spectrum than those bands in the neat IL spectrum. This could happen due to alkanes are concentrating more and more, since some original compounds have migrated to the aqueous phase.

### 3.2.4. Bitumen of Judea

The neat spectrum of bitumen of Judea (Fig. 6) shows bands between 3000 and 2800  $\text{cm}^{-1}$ , related to  $\text{C}_{\text{sp}^3}\text{-H}$  stretching, and bands appearing around 1475–1360  $\text{cm}^{-1}$ , assigned to  $\text{C}_{\text{sp}^3}\text{-H}$  bends. In addition, there are some bands around 830–690  $\text{cm}^{-1}$ , assigned to  $\text{C}_{\text{sp}^2}\text{-H}$  out-of-plane bends, and a band at 1745  $\text{cm}^{-1}$  ( $\text{C}=\text{O}$  stretching), and those between 1330 and 1050  $\text{cm}^{-1}$  ( $\text{C}-\text{O}$  stretching) [15], [16]. The manufacturer compound declaration and the GC–MS analysis (Table 1 and Table S1 in the Supplementary material) revealed a big amount of alkanes, a little amount of aromatic compounds, and the presence of alcohols, ketones and esters.



**Fig. 6.** Spectrum of neat bitumen of Judea (on the top) and spectrum of acidified bitumen of Judea after 44 days of reaction with sulfuric acid without moving the sample (at the bottom).

IR absorbance bands corresponding to alkanes barely change during the reaction, as it can be seen in the acidified IL spectrum in Fig. 6. As was indicated above, alkanes are not affected by sulfuric acid. In spite of that, the acidified spectrum of this IL is quite different to its neat spectrum since bands related to ester, ketone and alcohol, and those to aromatic compounds disappeared over reaction time. As was observed in the results obtained by GC–MS, once again methyl alcohol disappeared immediately, and 1-butanol, methyl isobutyl ketone, and acetic acid, butyl ester, among others, disappeared after some days (Fig. S3 in Supplementary material). As was hypothesized above, methyl alcohol could pass into the aqueous phase, and is producing ester hydrolysis. However, by this GC–MS methodology was not possible to obtain the complete composition of bitumen of Judea after 96 h of reaction because of the huge

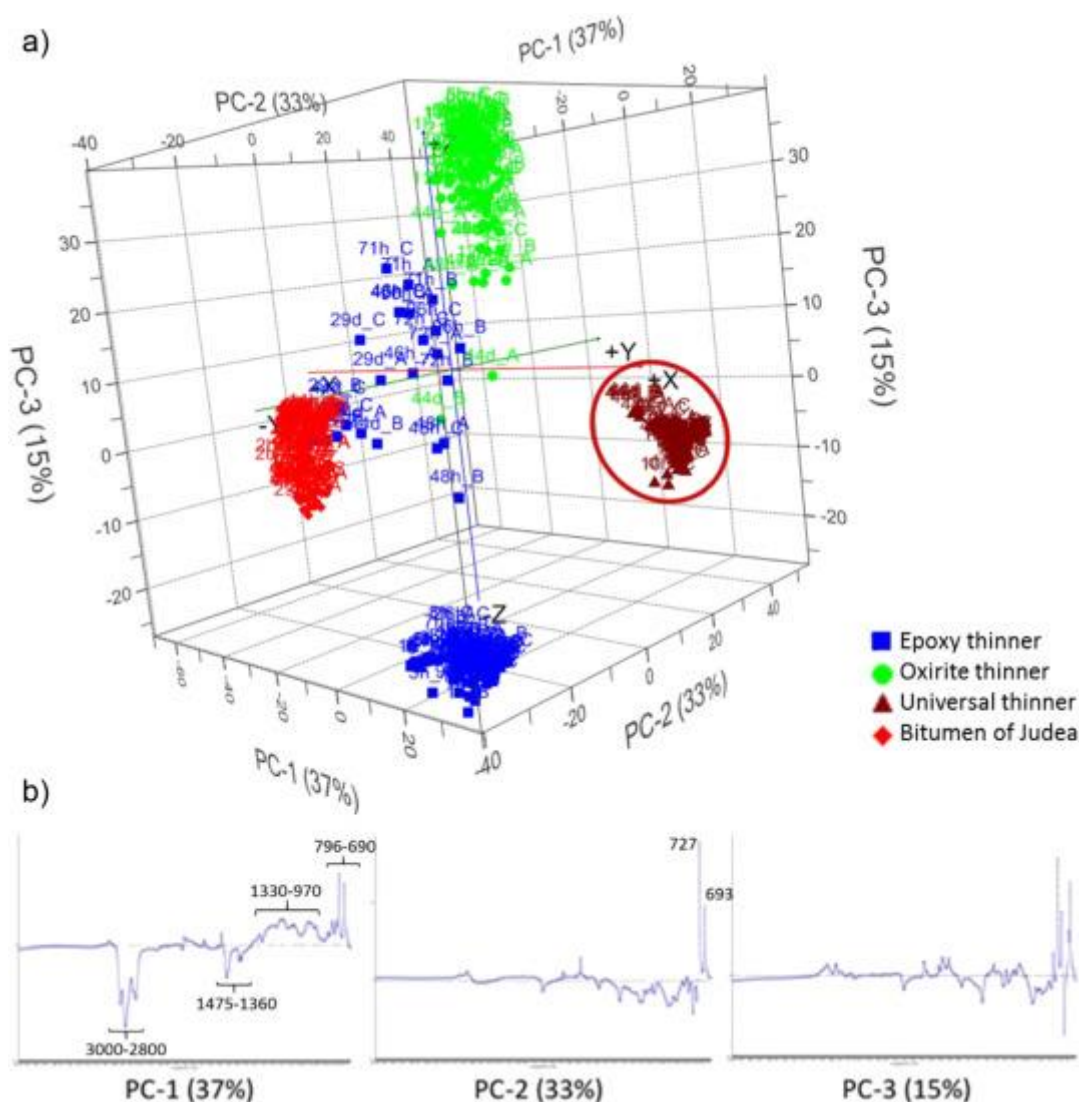
amount of overlapped peaks in some parts of the chromatogram. Therefore, it is not possible to confirm the production of carbocations and new alkylated by-products (Friedel–Crafts reaction), although it could be expected a similar behaviour.

### 3.3. ILs exposed to sulfuric acid during long reaction times: potential impact in casework

As it was discussed above, the ester, alcohol and ketone compounds contained in the studied ILs will be removed or transformed into other products, only remaining alkanes and aromatic compounds. Therefore, the chemical composition of the studied ILs could tend to be very similar after a long exposition to sulfuric acid. This fact could preclude a complete identification of the IL used in a real casework.

In order to provide an objective interpretation of the data, a chemometric analysis based on a PCA (exploratory technique) including all the samples (neat and acidified IR spectra) was carried out. As it can be seen in Fig. 7a, 85% of the variance of all data was explained using PC-1, PC-2 and PC-3. Four different groups, each one related to one of the ILs studied, can be seen. Universal thinner (inside the brown line) is present in one group separated from the other three ILs. However, there are regions where epoxy thinner (blue squares) is almost overlapped with oxirite thinner (green circles) and bitumen of Judea (red diamonds). Some acidified samples of epoxy thinner (after 1–3 days of reaction) overlaps with oxirite thinner, while samples of bitumen of Judea and epoxy thinner appear closer at longer reaction times (29 and 44 days). This confirms the initial assumption, where some spectra of the studied acidified ILs (especially the ones exposed to longer acidification times) could be very similar to other acidified or neat samples. According to the loadings plot (Fig. 7b), bands related to alkanes and aromatic compounds, the non- or less- affected compounds, are influencing stronger in this PCA. Universal thinner samples can be differentiated from the other samples mainly because of PC-2, which puts on its positive side those samples which have bands related to toluene ( $693\text{ cm}^{-1}$  and  $727\text{ cm}^{-1}$ ) [9]. In fact, this compound is in great amount in this thinner. PC-1 makes it possible to distinguish oxirite thinner and bitumen of Judea. Bands appearing on its positive side are common in oxirite thinner, as its aromatic compounds ( $796\text{--}690\text{ cm}^{-1}$ ) and oxygenated compounds ( $1330\text{--}970\text{ cm}^{-1}$ ), while bitumen of Judea appears on the negative side of PC-1, influenced by bands in the ranges  $3000\text{--}2800\text{ cm}^{-1}$  and  $1475\text{--}1360\text{ cm}^{-1}$ , which can be related to its huge amount of alkanes. As epoxy thinner is constituted by alkanes, oxygenated and aromatic compounds (and these compounds remain longer times in its composition), it is overlapped with oxirite thinner

and bitumen of Judea. Although it is possible to classify most of the analysed samples looking at their chromatograms/IR spectra or applying a simple PCA to their IR spectra, additional discriminant analyses should be applied in order to avoid false negatives/positive or the misidentification of some samples in casework.



**Fig. 7.** a) scores plot of all samples studied. It includes PC-1, PC-2 and PC-3 as well as the percentage of variance that each of them explains; b) loadings plot of a).

#### 4. Conclusions and future trends

The original chemical composition of the three thinners studied and bitumen of Judea is modified when they are mixed with sulfuric acid. As a consequence, their IR absorption spectra and GC–MS data are also modified regarding to their neat ones. Ester

compounds are subjected to hydrolysis reaction. In addition, Fischer esterification could happen, producing new ester compounds from alcohols and carboxylic acids. Oxygenated compounds contained in those ILs such as alcohols, esters and ketones, react in presence of sulfuric acid producing several by-products. Some alcohols (highly soluble in water) pass immediately into the aqueous phase, meanwhile others (e.g., 1-butanol or 2-propanol, 1-methoxy-) are subjected to protonation, producing alkyl groups. Similar reactions affect to ketones. Aromatic compounds attack to these alkyl groups producing new alkylated compounds. At longer times of reaction, aromatic compounds might be sulfonated, as was suggested in previous works. Lastly, alkanes do not show modifications, as expected. Additionally, it has been shown that the very much modified samples of the studied ILs could be misclassified since, after long acid treatments, their chemical compositions could become almost identical to each other. The proposal of discriminant analyses might address this issue. Regarding the non-selected ILs for an in-depth studied of this work, some of them could be only acidified (hence, not altered by the acid), while others could be slightly modified (their main chemical compounds) at longer reaction times. Therefore, a closer look at them should be taken.

This information could be crucial in forensic casework to detect, classify and identify correctly the studied ILs, even if they have been altered by acid intentionally, or to avoid false negatives. However, it is also important to mention that new classification schemes including acidified ILs should be published. Furthermore, it would be advisable to expand the study to other ILs of potential use in arsons in order to know the chemical modifications produced when mixing them with sulfuric acid. They should also be studied after an arson/fire event in order to validate and make more useful all the information exposed in this work.

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