

# The Effect of Weathering Time on the Change in the Gasoline Residues Composition

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## Abstract

The identification of flammable liquid residues in fire residues is a key finding to determine the cause of a fire and indicates that it was an intentional fire. Flammable liquids are subject to various changes over time, e.g. evaporation or microbial degradation. The article deals with the issue of the process of weathering of gasoline by the action of time in determining the causes of fires. The aim is to determine changes in the composition of gasoline residues in cotton carpet samples due to different weathering times. After various lengths of time (0-6 h) of weathering, residual substances from the gasoline were determined in the carpet fibers using the gas phase extraction method (headspace) in conjunction with gas chromatography and mass spectrometry (HS-GC-MS). The biggest changes were manifested in a reduction in the concentration of the most volatile compounds (alkylalkanes), which could subsequently lead to incorrect identification of the presence of a flammable liquid. Less significant changes in the specified amount occur in the group of alkyl derivatives of benzene (trimethylbenzene, ethylmethylbenzene), these substances are markers of the presence of gasoline in the samples. The results indicate the need for rapid sampling and subsequent timely analysis of fire residues in laboratories or their storage under conditions that prevent the degradation process.

**Keywords:** HS-GC-MS; fire accelerator; fire debris; fire investigation

## 1 Introduction

One of the important areas of fire protection and safety is to determine the causes of fires. Various types of fire accelerators are used to deliberately start fires, but the most common are flammable liquids. Gasoline is the most widely used fire accelerator because it is readily available, inexpensive, and highly flammable (Sampat et al., 2016).

Gasoline is a complex mixture of a wide range of volatile hydrocarbons (mainly alkanes, cycloalkanes, aromatic hydrocarbons, and alkenes) separated from crude oil. Gasoline is a middle distillate of crude oil containing C4 to C12 hydrocarbons. It contains ingredients that improve its properties (benzene and isooctane) as fuels. It is most often produced by fractional distillation from crude oil and treated by cracking (Mehaney et al., 2021; Morgan et al., 2010).

After a fire, it occurs due to combustion, thermal degradation, burning time, the presence of fire water, etc. to invalidate much of the evidence. Even with the growing presence of gasoline as a fire accelerator, its very presence at the site of the fire is not yet a definitive indicator of the deliberate nature of the fire. The increasing frequency of use of substances of petroleum origin makes it difficult to identify compounds from fire samples (Abel et al., 2018).

For a variety of reasons, depending on the extent of the fire, the degraded access, or the hazards that accompany the firefighting work, the fire detector must wait minutes, hours, or days before entering the fire site (Aliaño-González et al., 2018; Brassington et al., 2007). During this time, residues may undergo

various degradation processes that may alter the chemical composition of the liquid. The longer the analysis is delayed, the more the concentration of gasoline compound residues present decreases (Khan et al., 2018; Turner et al., 2018).

During a fire, the remnants of fire accelerators are exposed to various degradation processes, the action of which may prevent their identification (Sampat et al., 2016). Weathering process lies on a faster evaporation of volatile compounds. Residual more volatile compounds present at the fire are below the limit of quantification (LOQ). Less volatile, ie. more stable compounds, on the other hand, are determined in relatively higher amounts. All materials, especially flammable liquids, undergo a weathering process that releases volatile organic compounds (VOCs) (Turner, Goodpaster et al., 2012; Birks et al., 2017). Weathering and exposure to high temperatures can change the chemical composition of the residues, which can lead to modification of the analytical signal. Exposure to extreme temperatures can cause gasoline to weather to such an extent that its identification from a fire will be completely impossible (Willis et al., 2020).

Evaporation of gasoline components takes place at any temperature. Gasoline weathering is affected not only by ambient temperature but also by the time it takes place (Aliaño-González et al., 2018; Brassington et al., 2007).

Remnants of gasoline residues are often absorbed into porous materials, fittings, and structures. For this reason, it is necessary to pay increased attention when inspecting the fire site and to take samples from different places for this purpose (Aliaño-González et al., 2018). Volatility, dissolution, adsorption, biotransformation, photodegradation and microbial degradation are the main processes involved in hydrocarbon weathering (Brassington et al., 2007; Khan et al., 2018). The extent of hydrocarbon weathering also depends on the molecular weight of the petroleum hydrocarbons. The fastest hydrocarbon fractions with a higher number of carbon atoms in the chain, ranging from C10 to C19, are subject to the weathering process (Jonker et al., 2006).

At temperatures reached in fire conditions, it is difficult to detect even less volatile compounds, such as naphthalenes and higher alkylbenzenes, due to the weathering process. In the case of gasoline, lighter VOCs are the fastest to weather (Aliaño-González et al., 2018). When a sample of pure gasoline is exposed to severe weathering, the four compounds that form a characteristic group on the chromatograms are most often missing, namely ethylbenzene, *m*-xylene, *p*-xylene, and *o*-xylene (Hondrogiannis et al., 2019). Birks et al. (2007) and Willis et al. (2020) suggest that elevated temperatures should cause more than 50-75% weathering, especially for more volatile flammable liquids such as gasoline.

The aim of the paper is to determine the changes in the composition of gasoline residues in cotton carpet samples due to different weathering times using the gas phase extraction method (headspace) in conjunction with gas chromatography and mass spectrometry (HS-GC-MS). The assumption is that gasoline loses most of its signal strength after a few hours, after which its chemical composition changes significantly.

## 2 Material and Methods

A woven carpet measuring 80 × 150 cm, 100% cotton with a pile height of 0.5 cm, a fiber density of 1,400 g / m<sup>2</sup> and a weight of about 1.77 kg was used as a matrix for capturing gasoline. The carpet was cut into 5 × 5 cm samples. 5 ml of Natural-95 gasoline from the local Slovnaft petrol station was added to the carpet samples. The samples were allowed to weather under laboratory conditions at 20 ° C. Carpet fibers were removed at hourly intervals (from 0 h to 6 h), with an additional interval of 30 minutes, and then gasoline residues were determined analytically.

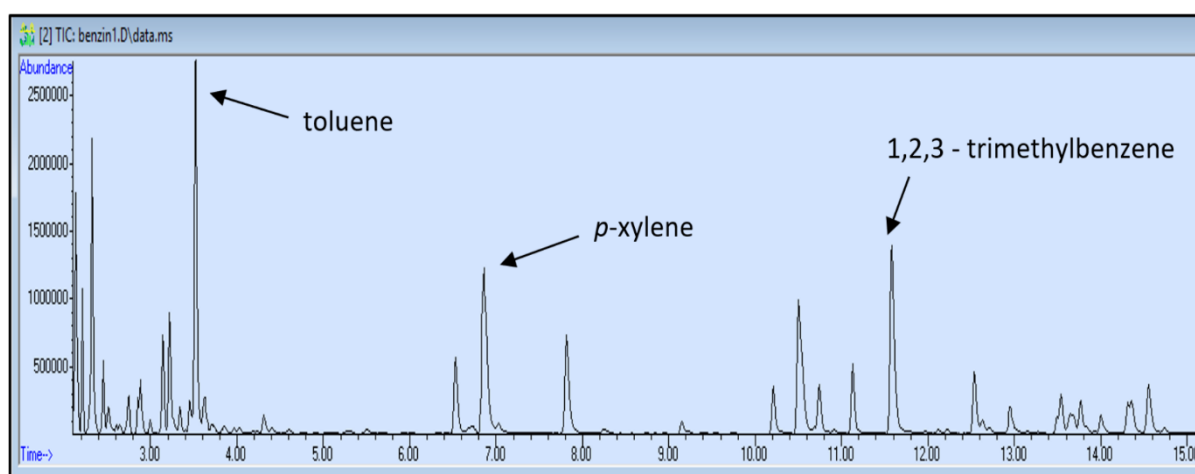
The analytical determination was based on the ASTM E1388-17 and ASTM E1618-14 methods. Residual volatile compounds were obtained by gas phase extraction (static headspace). The gas phase was subsequently analysed by gas chromatography with mass detection (HS-GC-MS). A Headspace Autosampler 7697A (Agilent) with an HP7890A gas chromatograph (Agilent) and a VL MSD 5975C mass spectrometer (Agilent) was used. The gas phase extraction took place at 60 ° C for 15 min and the gas phase was metered into the chromatographic column. The volatiles were separated on an HP 5MS column (30 m, 0.25 mm, 0.25 µm, Agilent) with a temperature program of 40 ° C for 4 min, a heating rate of 6 ° C / min to 250 ° C, with a carrier gas flow (He) 0.8 ml / min, in split mode 500 : 1. Mass

detection was performed at 70 eV electron ionization and conditions: source temperature 200 °C, detector temperature 150 °C.

The identification of the determined compounds was performed by comparing the measured mass spectra with the spectra in the NIST library database (Hodálík et al., 2020; Veřková et al., 2020). Changes in the amount of substances in the mixture were monitored by comparing the height and area of the peaks (Fig. 1 - Fig. 6).

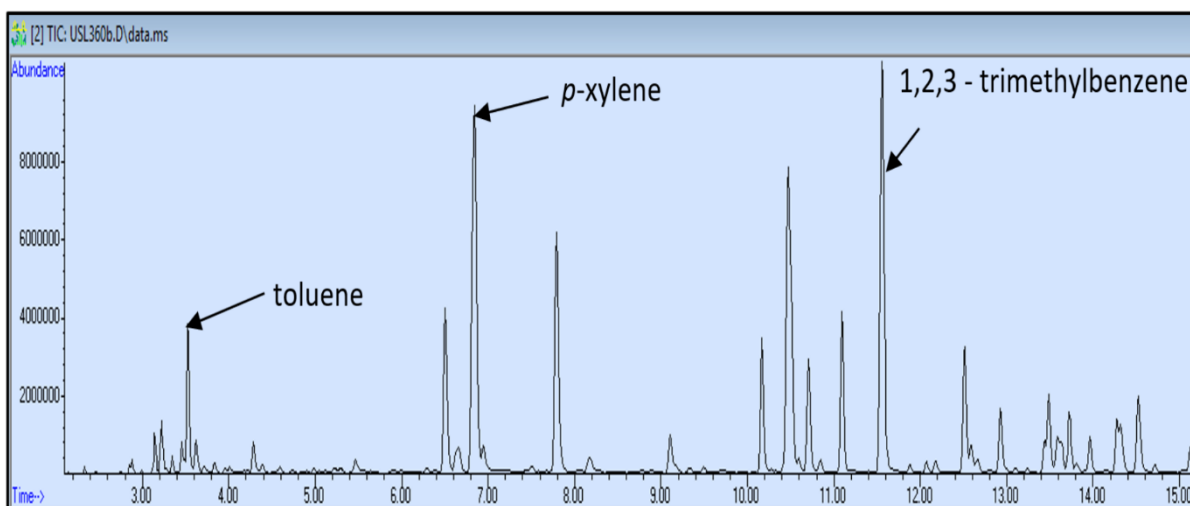
### 3 Results and Discussion

A comparison of the obtained chromatograms of pure carpet-fiber gasoline taken and sealed immediately (benzin1) with a sample of carpet-fiber gasoline exposed to weathering for 6 hours (USL 360) shows a significant difference at first sight. The intensities of the individual compounds, especially the more volatile ones, ie up to a retention time of about 4 minutes, are greatly reduced. A representative of the most volatile compounds category is toluene, which is shown in Figure 1 and 2.



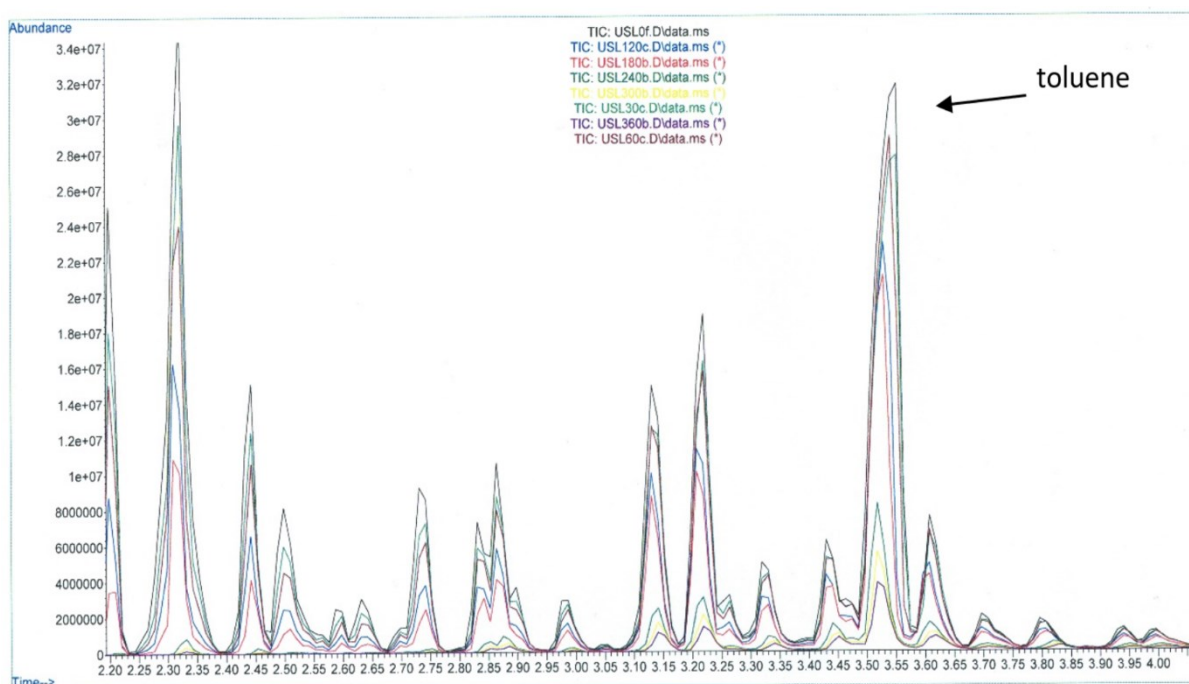
**Fig. 1** Part of the total chromatogram of pure gasoline with the retention time from 2 to 15 minute

The change occurs after the 5th minute (retention time), where the differences in this area are no longer so marked. A representative of this group of compounds is *p*-xylene. However, more pronounced differences reappear in the retention time area after the 10th minute. A member of this group is 1,2,3-trimethylbenzene. In this area, there is the opposite trend, i.e., an increase in individual intensities in samples that have been exposed to weathering for a long time. A comparison of the amounts of the compounds determined showed a decrease of 91.64% in toluene after 6 hours. The amount of *p*-xylene decreased from the reference sample of pure gasoline (benzin1) by 37.29% at (USL360b). In contrast, 1,2,3-trimethylbenzene increased USL360 by 37.41% over the reference sample. These substances were selected precisely because of their representativeness for the given areas of the chromatograms.



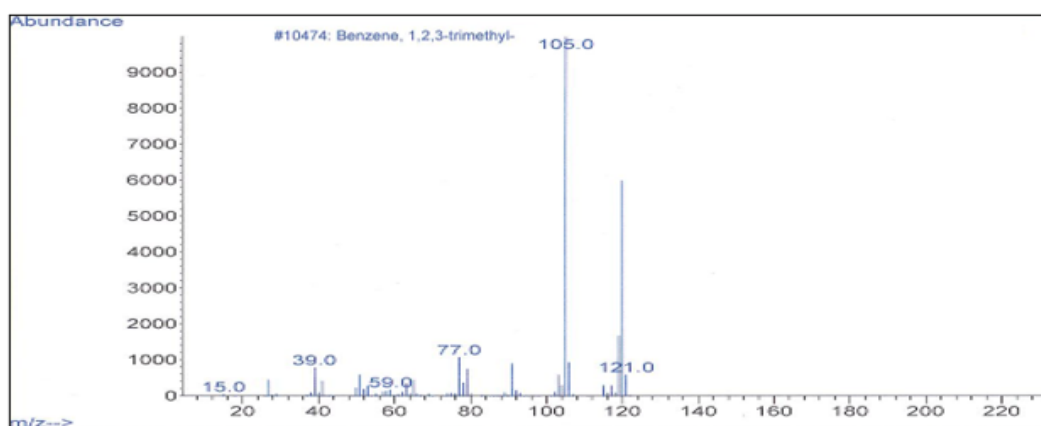
**Fig. 2** Part of the total chromatogram of gasoline weathered for 6 hours with the retention time from 2 to 15 minute

Figure 3 shows a portion of the chromatograms obtained by analysing weathered gasoline-treated cotton carpet fiber samples. Shown are those gasoline compounds which are more volatile, i.e. a group of aliphatic hydrocarbons and a C1 derivative of benzene (toluene). The peaks in the chromatogram marked in black characterize the compounds determined by analysis of reference samples (USL0f), which were taken and sealed in vials immediately after the addition of gasoline.



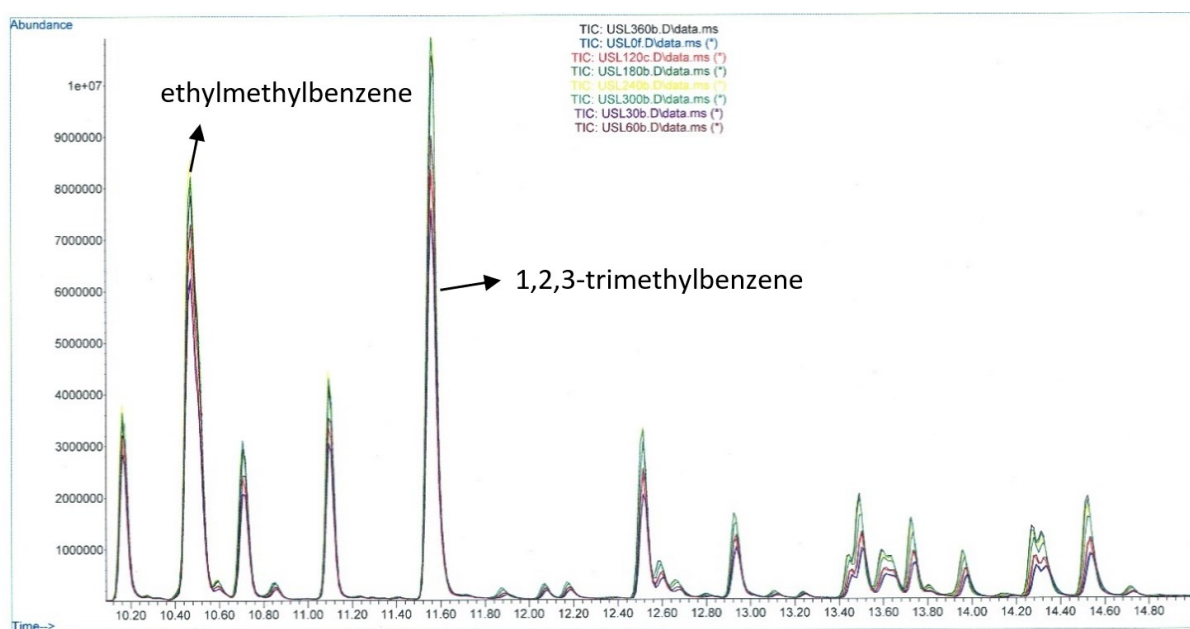
**Fig. 3** Part of the chromatogram of lighter hydrocarbons with the retention time from 2nd to 4th minute

As can be seen from the chromatogram, the most volatile compounds are e.g. toluene (time about 3.5 min) and alkylated alkanes, which are eluted first. Very small amounts of compounds were determined in the samples taken and closed later. The largest difference is noticeable for benzene with a retention time of about 2.3 min, where the largest amount was determined at (USL0f) and, conversely, the smallest amount was determined at sample USL360b (purple color).



**Fig. 4** Mass spectrum of 1,2,3 - trimethylbenzene (TMB)

The identified compound peaks were then compared with the NIST spectrum library. Figure 4 shows the mass spectrum of 1,2,3-trimethylbenzene (TMB).

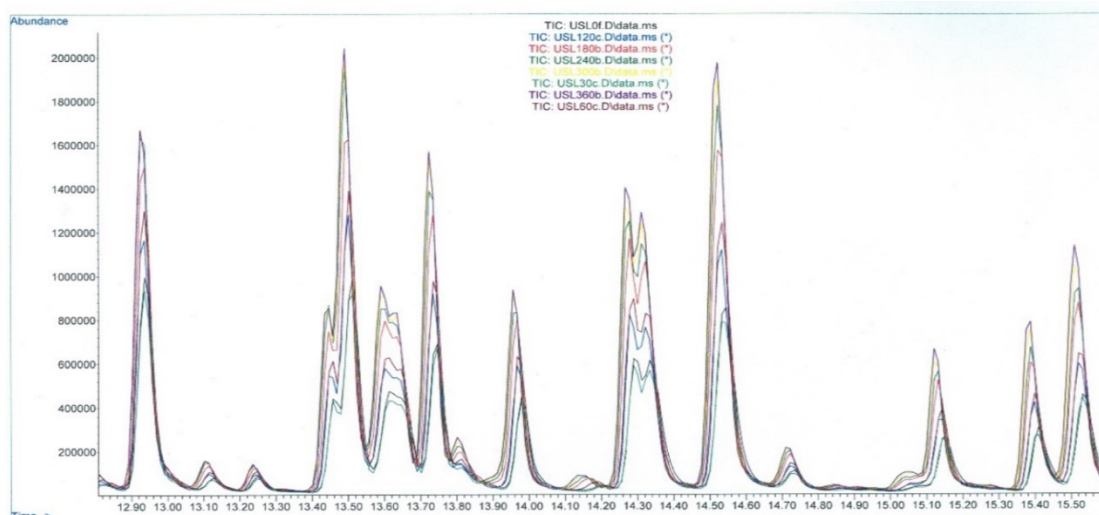


**Fig. 5** Part of the chromatogram showing the compounds ethylmethylbenzene and 1,2,3-trimethylbenzene (TMB)

Figure 5 shows the compounds ethylmethylbenzene and 1,2,3-trimethylbenzene (TMB), which are considered as the markers of a gasoline. As can be seen, there were no significant differences in the intensity of the two compounds during weathering after 6 hours. A similar finding was made by Chalmers et al. (2001) who investigated the negative effects of weathering to which the samples were intentionally exposed. They found that the least sensitive substances were 1,3,5-trimethylbenzene and ethylmethylbenzene.

If we compare the chromatogram belonging to the more volatile gasoline compounds (Fig. 3) with the one showing the less volatile heavier compounds (Fig. 6), it is possible to observe a trend that compounds with more carbon atoms in the chain are determined in larger amounts than with fewer carbon atoms in the chain.

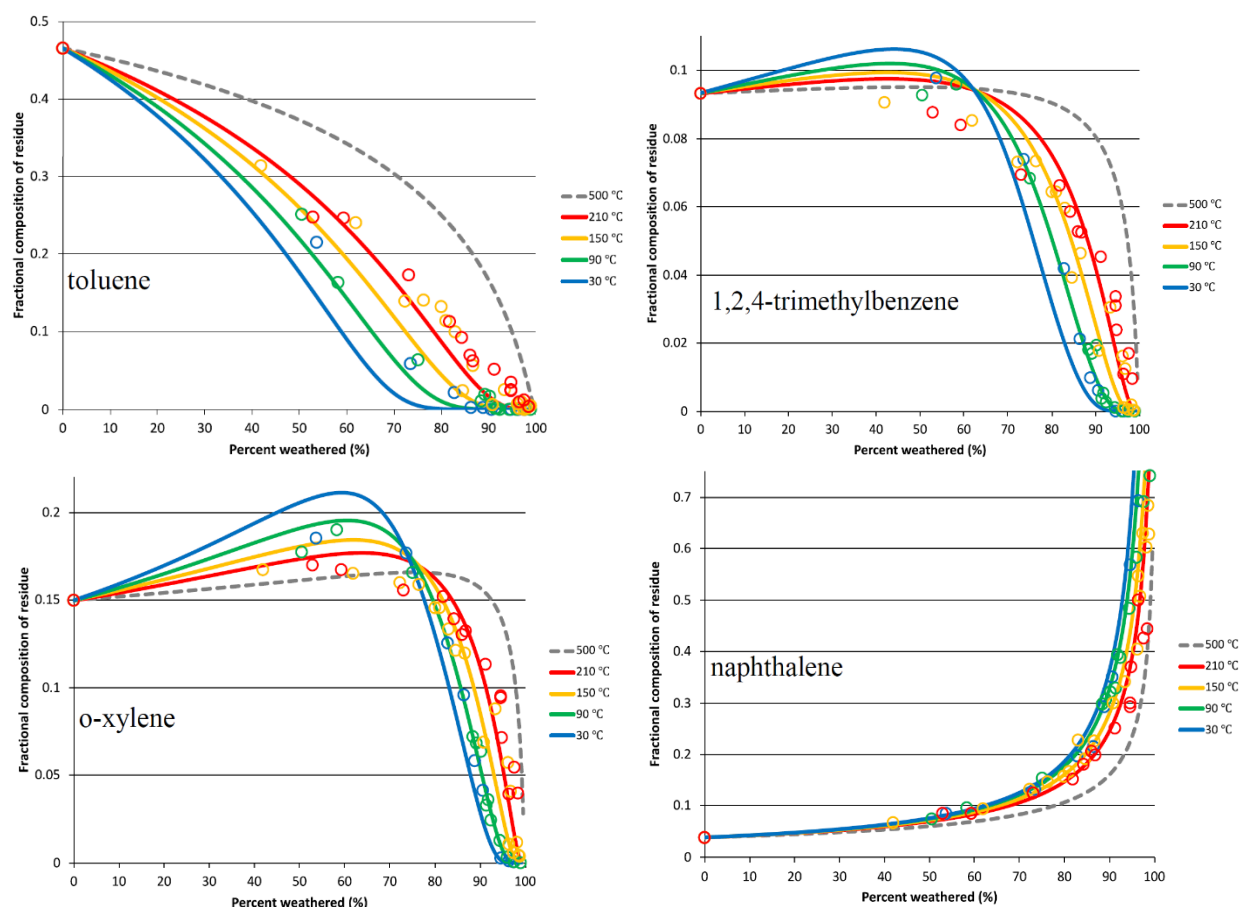
Looking at the course of the individual chromatograms, it is possible to observe a significant difference between the intervals of 180 and 240 minutes. From the above, it can be assumed that gasoline loses most of its signal intensity during the weathering process after a time ranging from 3 to 4 hours.



**Fig. 6** Part of the chromatogram of heavier hydrocarbons with the retention time from 12th to 16th minute

Aliaño-González et al. (2018) state, that a significant change is expected after a time of 0 to 6 hours with a significant decrease in signal intensities, which means that the weathering process is most pronounced after the first hours.

Borusiewicz et al. (2006) emphasize the fact that the determined intensities of compounds in the process of weathering with heat load (fire) differ significantly from unventilated samples, due to processes such as e.g. evaporation, pyrolysis and factors that are characteristic of fire.



**Fig. 7.** Comparison of four typical compounds in gasoline weathered as a function of temperature (Willis et al. (2020))



Our results also correspond to the results of the research of Willis et al. (2020), who investigated the weathering process for a mixed liquid from the compounds that occur in gasoline. Their results indicate a decrease in compounds as a function of temperature in Figures 7. Toluene is a characteristic representative compound from the most volatile compounds found in gasoline. Compounds such as 1,2,4-trimethylbenzene (TMB) and *o*-xylene are representative of the transition region that forms the transition between the volatile and most stable compounds. On the contrary, naphthalene is a typical compound from the group of the most stable compounds found in gasoline.

As can be seen in Figures 7, the most volatile component toluene decreases linearly with the extent of weathering and this decrease is more pronounced at lower temperatures. With 1,2,4-TMB, the amount more than doubles between zero and 90% weathering before reducing the composition above 90% weathering. In the case of *o*-xylene, the composition remains constant up to 50% weathering, at which point its composition decreases between 50 and 95% weathering at each temperature. In the case of naphthalene, the results show that at each temperature the composition increases slightly between zero and 75% weathering. The relative increase in the most stable compounds is due to the loss of those volatile components that evaporate faster. The least volatile components, which elute last from GC, show a sharp increase in the later stages of weathering.

Birks et al. (2017) also suggest that elevated temperatures in fires should cause weathering by more than 50-75%, especially for more volatile flammable liquids such as gasoline. One possible explanation for this phenomenon is absorption, which assumes that some of the original liquid is trapped in the pores of the substrate, and these relatively unventilated residues are then extracted during equilibrium conditions by Headspace extraction.

#### 4 Conclusions

In individual experiments, the weathering of absorbed gasoline in cotton carpet matrices was investigated. In this paper, we have chosen headspace gas phase extraction with gas chromatography and mass spectrometry (HS-GC-MS) as the analytical method. The determined compounds belong to the group of aliphatic hydrocarbons - alkanes, aromatic compounds - benzene derivatives and polycyclic aromatic hydrocarbons.

The analysis confirmed that lighter hydrocarbons are the fastest evaporating gasoline compounds. The largest difference in the changes in the intensity of the analytical signals can be observed after the time between four and five hours. After six hours of exposure of the samples to deliberate weathering, they significantly lost the strength of the analytical signal. In contrast, heavier hydrocarbons increased significantly in intensity six hours after the start of the experiment, and the peaks of these compounds increased.

Samples of residues obtained after a fire provide investigators with the causes of the fire with a wide range of interpretable evidence. If the extent of the destruction is modest, the source, fuel source and ignition source are generally identifiable. However, when the fire scene is largely destroyed and the flammable material is largely consumed, it is possible that investigators will gather and interpret little, if any, evidence. As part of the continuation of the research, samples exposed to combustion will be analysed.

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