

Evaluation of the Permanence of Flame Accelerating Material on Burned Material with GC-MS Analytical Techniques

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ABSTRACT

The aim of the work is to evaluate the permanence, understood as a presence detected by the analyzes, after a burn, of the flame-accelerating material used to start a fire, even in largely burnt residues, in order to be able to recognize, even in the investigative context, whether the fire was caused by an accident or if it was facilitated by the emission (voluntary or non-voluntary) of a flame-accelerating substance.

The analytical technique used to give answers to this is the use of the gas chromatograph-mass spectrometer (GC-MS), which allows to detect the presence of flame accelerators even in small quantities in the samples.

A series of burnt material samples will be reproduced in a controlled environment, originally containing flame-accelerating materials and then compared to burnt samples without flame-accelerating agents.

The results will be obtained through GC-MS analysis with the headspace (HS) and fiber (SPME) method, in order to evaluate, in greater detail, which of the two methods is the best performing to achieve the objective.

As final result, the SPME fiber is very performing for the goal to be achieved, because it is able to detail the flame accelerating compounds found.

1. INTRODUCTION

If we consider the destructive nature of the fire event, we understand how the investigation of the causes that originated it is an extremely complex activity that often sees the investigators but also the firefighting professionals, operating in the context of scenarios characterized by levels damage to structures and materials such as not to allow a reconstruction, if not partial, of the state of the places before the fire [1, 2].

The greater the ability to collect information on the scenario under investigation, interpreting, for example, the signs left by the fire or carrying out an appropriate activity for the search and identification of any accelerators present [3], and the higher the probability that the analysis of the event leads to the identification of the cause, through an objective reconstruction of the event [4, 5].

- It is obvious that the presence of flame accelerators (in this work we will evaluate benzene) gives important information to the analysis work as it directs investigations towards an arson or in any case a voluntary act [6].

In this work the "flame accelerator persistence" assumption will be considered valid if, following GCMS analysis of the sample [7], a benzene peak will still be visible in its spectrogram [8, 9].

This, transposed in the case of real activities, would allow us to affirm with a large degree of certainty that the benzene found in the sample contributed to the fire and that it was therefore introduced (voluntarily or not voluntarily) into the material which was then burned [10-12].

2. SUBSTANCES

Aromatic compounds are all those organic compounds, which contain one or more aromatic rings in their structure. The presence of these rings gives them particular reactivities [13].

Among the aromatic compounds, the main one is benzene, which has the brute formula C_6H_6 . Its structure is planar and has six carbon atoms arranged at the vertices of a regular hexagon [14].

Benzene is a natural constituent of petroleum, but it is also synthesized from other chemical compounds found in petroleum itself. It has remarkable solvent properties; at room temperature and atmospheric pressure it is in the form of a highly flammable colorless volatile liquid with a characteristic odor (Figure 1) [15].

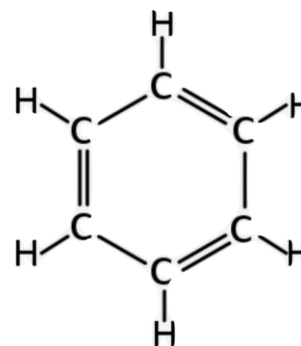


Figure 1. Benzene molecule

3. METHOD AND SEQUENCE OF OPERATIONS

To achieve the objectives of the Study, the AGILENT GC-MS was used [16].

An Agilent 7890A Series GC connected to a 5975C mass selective detector (combined) was used to carry out GC/MS analysis. Splitless injector and the interface were maintained at 300°C and 340°C respectively [17]. Helium gas was used as carrier gas (at constant inlet pressure). The oven temperature was programmed from 50°C to 350°C (2-10 min) at 10°C/min. The GC contained an HP-5MS 5% phenyl methyl siloxane phase fused silica column with a diameter of 15 m X 0.25 mm, 0.25 µm and was directly inserted into the ion source. A full scan at 70 eV from m/z 50 to 800 was carried out to obtain the electron impact (EI) spectra [18-20].

It is a Gas Chromatograph - Mass Spectrometer, used by the Regional Advanced CBRN team of the Milan Fire Headquarters, which provides the detailed molecular profile of organic compounds that are identified by comparison with standard compounds or mass spectra libraries (Figure 2).



Figure 2. Gas chromatograph

Four samples were prepared with 1ul of benzene in 1cm² of cotton tissue, plus 1 positive control and 1 negative control (blank) [21].

The HS extraction procedures for the VOCs were carried out using 20 mL headspace vials (Agilent, Santa Clara, USA) and 250 mL polypropylene vials (Plaszom, Orlenias, Brazil) with caps for sampling [22-23].

The SPME extraction of volatile compounds was carried out by manual solid-phase microextraction using a 1-cm long fiber (Supelco Co., Bellefonte, USA) coated with 30 µm divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) [24]. The fiber was exposed to the sample's headspace at 45°C for 60 min. Prior to the first extraction, the fiber was conditioned at 270°C for 1 h in the injector port of the gas chromatograph. Between analyses, the fiber was reconditioned at 240°C for 15 min (desorption time

of 4 min) [25-27].

Sequence of operations:

1. Samples I and II were burned, taking care of completely burning the tissue (Figure 3).

2. Samples III and IV (and the two controls) were closed in order to enhance benzene vapors;

3. The burned and unburned samples were analyzed by both headspace (HS) and fiber (SPME) methods (Figure 4);

4. The spectrograms obtained were compared in order to assess both the presence of benzene and the quality of the result with respect to the two techniques used [28].



Figure 3. The sample is burned

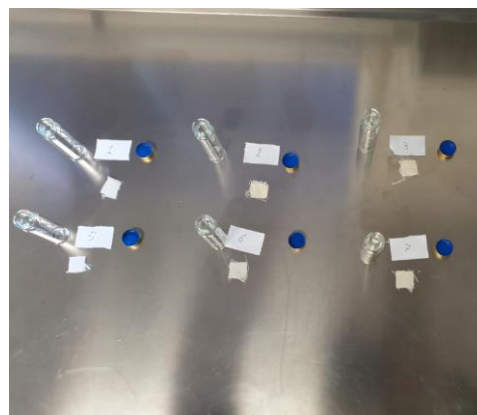


Figure 4. Preparation of the vials that will contain the sample for GC/MS analysis

4. RESULTS

Following analysis, the GC-MS curves turned out to be as follows (Figures 5-8).

Benzene was found in all 4 samples.

The obvious differences are explained in the conclusions.

Sample I – Burned HS

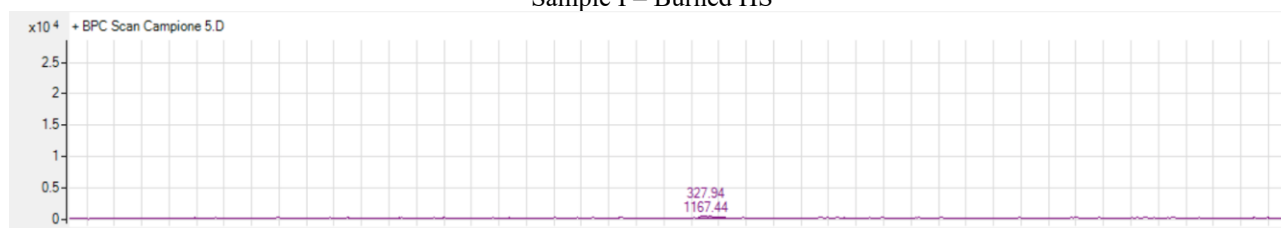


Figure 5. Sample I Spectrogram

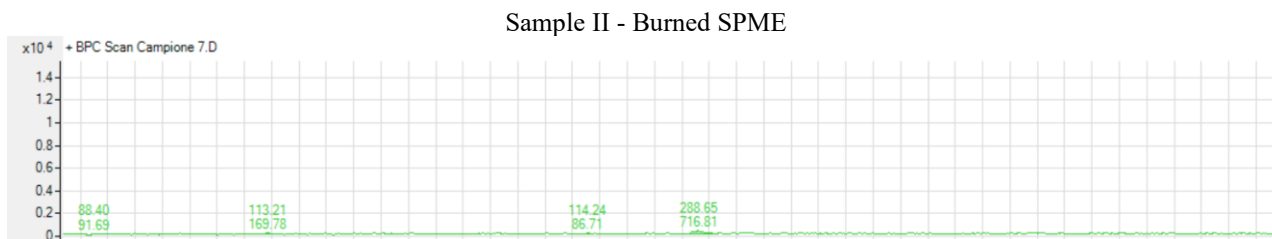


Figure 6. Sample II Spectrogram

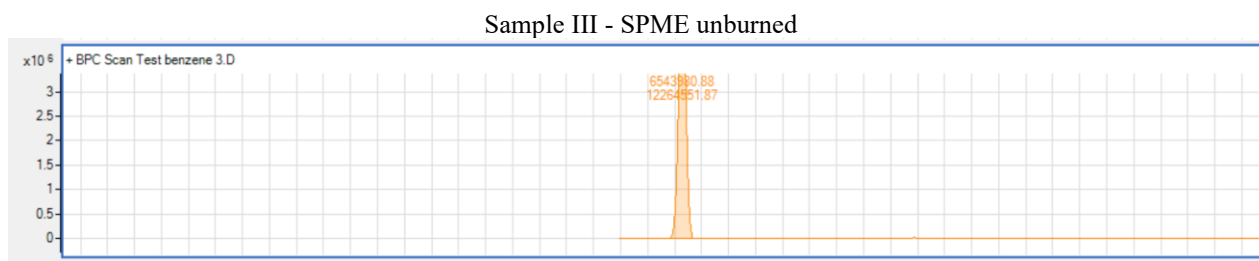


Figure 7. Sample III Spectrogram

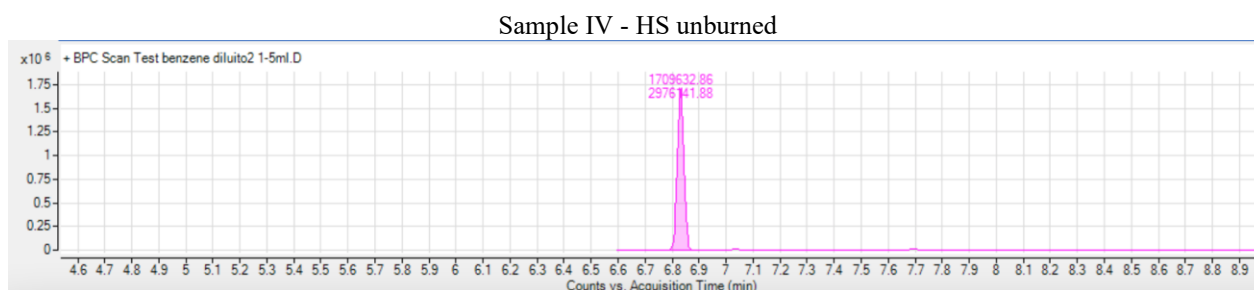


Figure 8. Sample IV Spectrogram

5. CONCLUSIONS

As expected, Flame Accelerating Compounds were found most strongly in the unburned III-SPME samples with a peak of $6,5 \times 10^{12}$ and in the unburned IV-HS sample with a peak of $1,7 \times 10^{12}$.

In the burned I-HS sample, benzene is found exclusively with a peak of $3,3 \times 10^6$, while in the burned II-SPME sample, a benzene peak of $2,9 \times 10^6$ is found, with another 3 peaks of flame accelerators which, in all other techniques, are not detected.

The abundance of the substance passing through the section of the column that reaches the mass spectrometer is used as the unit of measurement [29].

This means that:

- With analytical methods of GC-MS it is still possible to find flame accelerants after combustion of textile material;
- The SPME fiber is very performing for the goal to be achieved, because it is able to detail the flame accelerating compounds found [30].

These results, which will be the subject of subsequent studies, bring important perspectives in the field of flame accelerators research on combustible materials. The idea is to develop, starting from this base and with subsequent experiments, a method that enhances the presence of accelerators in order to make their presence even more evident.

In the case of development perspectives that are compatible with forensic work, great attention must be paid to the way in which the samples will be taken from the environment in order to minimize the evaporation of the accelerator.

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