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Short communication

Post-mortem test for low-boiling arson residues of gasoline by gas chromatography–ion-trap mass spectrometry

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Abstract

Using headspace capillary GC–MS with ion-trap detection, the additive in motor gasoline, MTBE (methyl *tert.*-butyl ether), was spotted in the blood from five victims of arsons set off with motor gasoline. In the brain from a death of a fire started by ignited isoparaffins, a number of branched C8 alkanes were found. Since 80 control samples of accidental fires, started by non-chemical means, tested negative for MTBE or isoparaffins, the data suggested that post-mortem exams for low-boiling organics may offer a new concept for arson analysis.

1. Introduction

Fires may cause large losses of humans, houses and goods. To spot an arson is, hence, a main issue, and an approach of such a task is to search a fire debris sample for accelerant residues. However, to reveal in this material the chemical that may have started a fire is an analytical challenge. There are many reasons for this: the large number of possible accelerants, changes in their relative composition during a fire, the formation of pyrolysis products that are the same as the target compounds, and also sampling and test problems [1,2].

Reports on the use of post-mortem samples for arson analysis seem not to be present, but volatile organics in body fluids of fire victims have been studied [3–5]. In the course of such tests, I found in the blood of a suspected arson death a low-boiling substance, used as an additive in motor gasoline. Since this organic perhaps could serve as an easily recognized marker for gasoline being used as an arson accelerant, post-mortem blood from victims in fires started by a known chemical product or by non-chemical means were tested for volatile compounds. The data of the work showed that body remains protect low-boiling substances from evaporation during a fire, and that a post-mortem exam could offer a new approach for arson analysis.

2. Experimental

2.1. Materials

Routine post-mortem specimens, sent from all over Sweden to our laboratory, were used for the arson analysis. Details about the sampling, preservative added, and container employed are given in an earlier report [6].

In the study reported here post-mortem samples from 87 fires were tested. Five of these (fires C–G in Fig. 2) were known at the time of the

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analysis to have been started by motor gasoline, and in two fires (fire B in Fig. 1 and fire H in Fig. 3) some unspecified arson accelerants were suspected. Fire B, the arson initiating this work, killed three persons and, also, caused complete demolition of a villa. Any search for accelerant residues in the ashes was, therefore, not possible. Fires C–G occurred in villas (D,F) or in cars (A,C,G), and killed seven humans; three persons died in fire F. Fire H took place in a 8-flat apartment house, which was completely ruined, and the event carried off one victim, a suspected arsonist. He had shortly before the disaster been seen in a gas station shopping a 5-l container labeled "Miljöanpassad Bensin" (Alkylate Distillate). However, no search of the ashes for accelerants could be done. Blood samples from a single dead in each of 80 fires, which were accidental or without sign of any chemical being involved, were used as controls. Fire A in Fig. 1 started by an accident in a flat.

2.2. Analytical methods

The determinations were done by direct headspace capillary GC–ion-trap MS, and run under two different conditions. In the first part of the study, including 27 blood samples, I used the version of the technique in which the analytes were separated in a polar stationary phase of the capillary [7]. Even though this method served well for the aromatic hydrocarbons and polar organics, it was not ideal for the apolar, low-boiling ones because of their short retention times. When it appeared that such substances could be spotted in arson cases and perhaps used as markers for a gasoline accelerant, the remaining 60 samples, as well as those of all arson deaths, were tested by a capillary with an apolar stationary phase [6]. The retention index (RI) values for some organics discussed in the text were based on the assay with the apolar stationary phase of the GC capillary, run under non-isothermic conditions, and on the use of the C3–C13 n-alkanes as standards [6].

3. Results

Fig. 1 shows the data from two deaths, one of an arson but without the accelerant specified (fire B) and the other of an accidental fire (fire A). As seen both victims displayed in the blood very similar alkane and aromatic hydrocarbon patterns. The two chromatograms differed, though, in one regard. The arson victim held

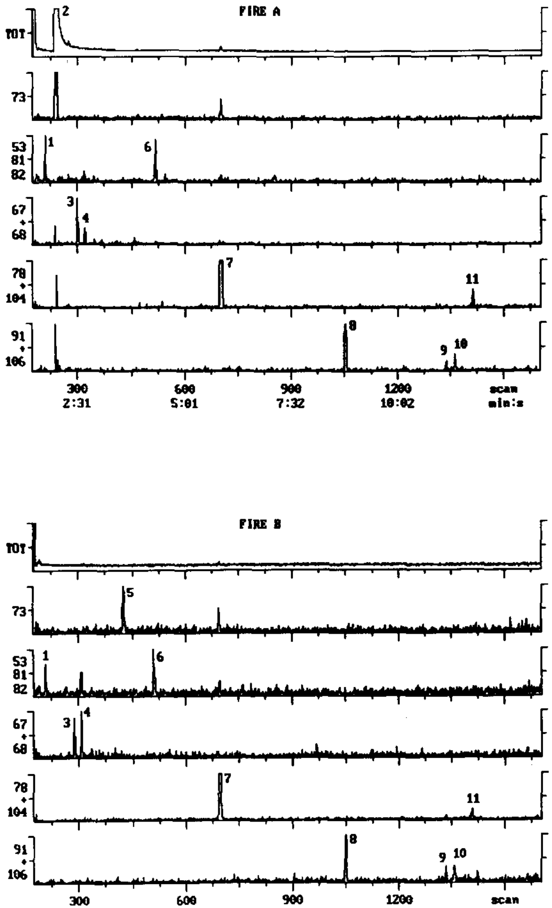

Fig. 1. Total-ion current and reconstituted mass chromatogram of volatile organics in the blood of two deaths, one caused by an accidental fire of a flat (fire A) and the other by an arson of a villa (fire B). Peaks: 1 = 1,3-butadiene, 2 = ethanol, 3 = furan, 4 = isoprene, 5 = methyl *tert.*-butyl ether (MTBE), 6 = 2-methylfuran, 7 = benzene, 8 = methylbenzene, 9 = ethylbenzene, 10 = 1,3- and/or 1,4-dimethylbenzene, and 11 = styrene.

MTBE (peak 5; RI = 553), an organic not found in the blood from the dead in the accidental fire. A similar pattern of MTBE and aromatic hydrocarbons was found in the blood from all three arson deaths of fire B.

To see if MTBE could be used as an arson marker for motor gasoline, blood samples from deaths of five fires that had been set off on purpose with this accelerant were tested. The results in Fig. 2 show that, in addition to benzene and a number of alkylbenzenes, all samples contained MTBE. Along with some aromatic hydrocarbons, the ether was also found in the two additional deaths of fire F. None of the samples held isooctane or any other C8 isoparaffins.

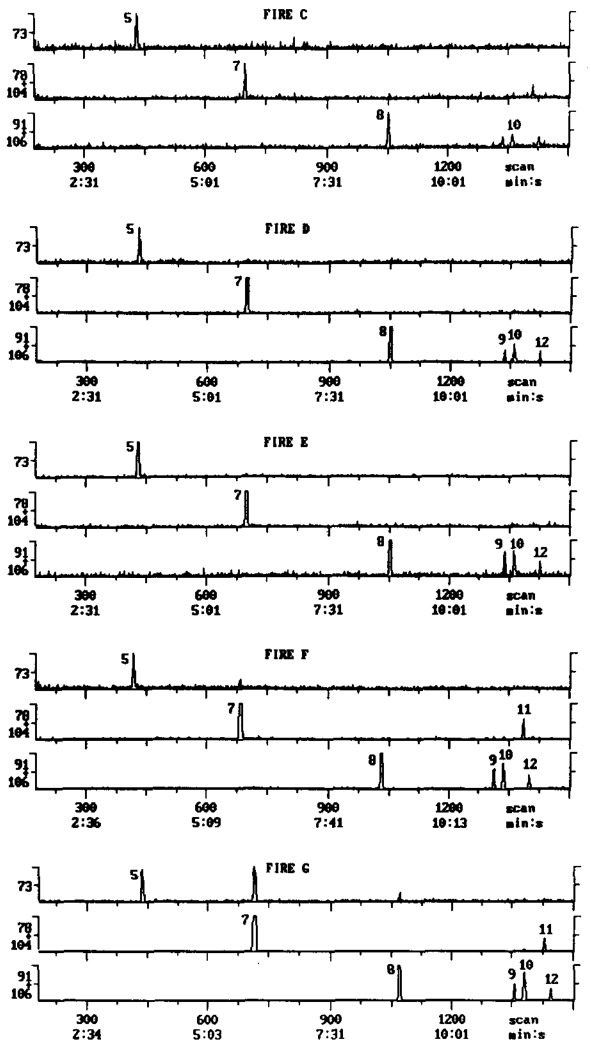

Fig. 2. Total-ion current and reconstituted mass chromatogram of volatile organics in the blood of five deaths caused by fire of cars (fire C,E,G) and of villas (fire D,F) with motor gasoline used as the arson accelerant. Peaks: 5,7–11 = legend of Fig. 1 and 12 = 1,2-dimethylbenzene.

At the time of the arson analysis of the body remains of fire H, gasoline was the suspected accelerant. However, none of the post-mortem samples had MTBE, but as shown in Fig. 3, brain tissue contained a number of branched hydrocarbons. These appeared at RI values in the range 689–761 on the mass chromatogram, which was very similar to that formed by the isoparaffin reference liquid and later alleged arson accelerant. Among the alkanes, 2,2,4-trimethylpentane (isooctane) and 2,3,4-trimethylpentane were spotted also in the blood of the dead.

To study what organics were deposited in the blood of victims of non-arsons, 80 control samples were examined. Of these 48 tested positive for benzene (RI = 648), which showed up either sole or along with one or several of the other alkylbenzenes (RI = 755–885) and furans shown in Fig. 1. However, none of the controls contained MTBE or any branched C8 alkanes.

4. Discussion

Gasoline is an accelerant often found in routine arson investigations, and the development of methods for its identification has, therefore, evoked some interest [1,2,8]. The common use of fire debris as test material presents, however, a number of problems. One is caused by the formation of pyrolysis products, from burning plastics [8,9] or other solid materials [8], that are the same as many of the target compounds in gasoline. On a gas chromatogram most of these contaminants, notably aromatic hydrocarbons, appear with RI values above 755 (toluene) [8]. However, as shown in the present

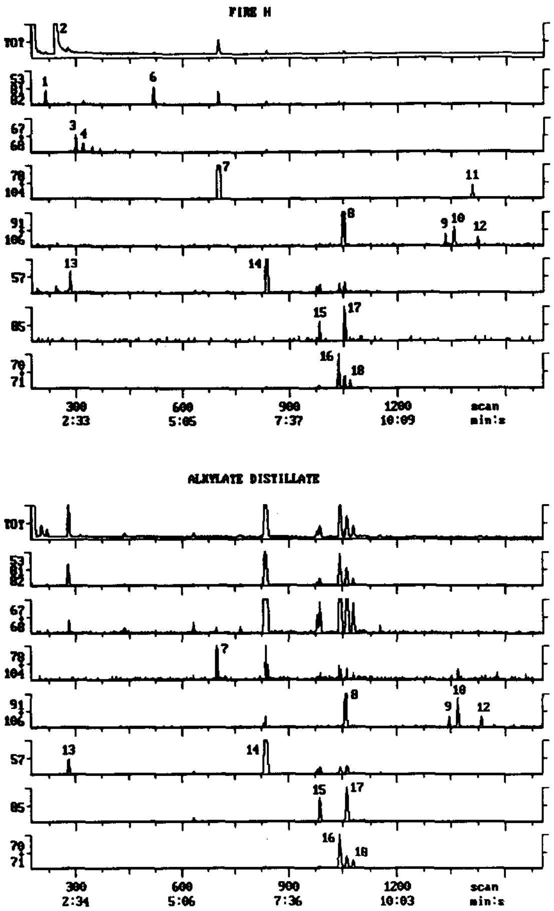

Fig. 3. Total-ion current and reconstituted mass chromatogram of volatile organics in the brain of a death caused by fire of an apartment house (fire H), and in the alleged arson accelerant (alkylate distillate). Peaks: 1–11 = legend of Fig. 1, 12 = legend of Fig. 2, 13 = 2-methylbutane, 14 = 2,2,4-trimethylpentane, 15 = 2,4-dimethylhexane, 16 = 2,3,4-trimethylpentane, 17 = 2,3,3-trimethylpentane, and 18 = 2,3-dimethylhexane.

work, the post-mortem samples do not seem to be very useful for spotting gasoline residues within this RI range; aromatic hydrocarbons were commonly found in human material of non-arson fires.

Compounds more specific for gasoline, except for benzene (RI = 648), are those with RI values below 755, showing up in an area of the gas chromatogram that is less contaminated by pyrolysis products [8]. However, because of their fairly high-volatile properties, these organics will be subject to evaporative loss or depletion during a fire, and their value as arson markers in a fire debris sample, therefore, becomes limited [8]. In the post-mortem samples, on the other hand, the low-boiling MTBE (b.p. 55.2°C) and some C8 isoparaffins (b.p. 99–116°C) were retained and spotted in the RI range 553–755.

MTBE is added to motor gasoline not to be stored in a rock basin, and its concentration in both the unleaded and leaded fuel is about 10% (leaded gasoline is banned in Sweden). The ether is not known to be formed as a pyrolysis product, and neither was it found in the controls of the present work. MTBE should, hence, be useful as an arson marker. Also the finding in post-mortem samples of C8 isoparaffins, which appear on the chromatogram in the "alkylate region" (RI = 500–800) free of most pyrolysis products [8], may indicate an arson.

The possibility that MTBE stems from a source other than arson residues of motor gasoline should be kept in mind. The ether may, thus, show up in the body fluids from a sniffer of gasoline or of the liquid fuel (T-Bränsle) used for outdoor cooking. It has also been found in a victim exposed to a fatal amount of car exhaust gas [6]. Even though MTBE might be deposited in the body fluids of car drivers also after accidental inhalation of gasoline fumes, no data seem to be reported in the literature on the relation between the presence of the ether in body fluids and domestic exposure to the fuel. However, if MTBE may appear in the blood under such conditions it should be a rare event. For according to Swedish law, gas stations have to be equipped with a special device for protecting a customer from exposure to gasoline vapor while he is tanking his vehicle. Also, none of the 80 non-arson controls in this study exhibited MTBE in the blood. Another possible false positive result of MTBE could arise in connection with its clinical use for dissolving gallstones. However, since the ether is instilled locally into the gallbladder, systemic absorption of it from the biliary tract may be negligible [10]. Finally, some types of rubber septa, joint to the specimen containers, free MTBE into the headspace [6]. Great care should, therefore, be given to the choice and control of the sampling tools.

This work showed that body remains protected high-volatile organics from evaporation during a fire; even 1,3-butadiene, which boils already at −4.5°C, was found in nine deaths. This is a phenomenon that makes body fluids or organs from a victim useful for spotting arson specific compounds, which otherwise may not be detected. The simplicity and low cost of the method should render it feasible for routine use. No special attempts have to be made to locate the start of a fire or to gather specimens; to reveal the cause of death, post-mortem samples are taken anyway at the autopsy and sent to a forensic laboratory. Even though the test method requires a high sensitivity, the low-cost mass spectrometer used in the present work was good enough for spotting MTBE with a limit of detection at 0.03 μmoles per liter of blood [6]. Moreover, the common arson analysis of a fire debris sample entails that the chemist use some method for pattern recognition [8,11] to sort out the complex system of GC peaks of a likely accelerant from those of pyrolysis products. The arson marker, MTBE or C8 isoparaffins, inhaled along with other gases during a fire and deposited in a biological matrix, can, on the other hand, easily be identified on the chromatogram simply by vision.

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