TECHNICAL NOTE

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Detection of Trace Levels of Gasoline in Arson Cases by Gas Chromatography-Mass Spectrometry with an Automatic On-Line Thermal Desorber

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ABSTRACT: A method for the analysis of trace levels of gasoline in arson debris using an automatic thermal desorber (TD) and commercial Tenax adsorbent tubes is described. First, a static headspace screening test is performed by gas chromatography using a flame ionization detector (GC-FID). Suspected gasoline is reanalyzed by gas chromatography-mass spectrometry (GC-MS). Gasoline traces smaller than 10 μL in a 1 liter volume are analyzed by a dynamic heated headspace procedure with thermal desorption and GC-MS after adsorption on 45 mg Tenax tubes. The desorption of adsorbed vapors is carried out by heating the tubes; the analytes are focused in cryogenic units cooled with liquid nitrogen. The cryofocused vapor sample is flash-heated for injection into the capillary column of the GC. The dynamic heated headspace technique (TD-GC-MS) is suitable for analyses of trace amounts of gasoline (0.1−10 μL in 1 liter volume).

KEYWORDS: criminalistics, forensic science, gasoline, gas chromatograph, thermal desorption, arson, debris, trap, cryo, GC-MS, chemical analysis

Liquid accelerants such as gasoline are frequently used in setting fires. Gasoline findings represent about 40% of positive cases in this laboratory. Gas chromatography (GC) is a widely used technique for the analysis of accelerants. General sample preparation methods for fire debris analysis include steam distillation, solvent extraction, direct (static) heated headspace and dynamic heated headspace. A debris sample containing a large amount of volatile accelerant can be quickly analyzed by the direct headspace procedure. Dynamic headspace enrichment is used for identifying accelerants at trace levels [*1,2*]. A method based on thermal elution and on-column injection with charcoal trap and cryogenic focusing has been reported as an appropriate tool for the enrichment

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of accelerant vapors [*3*]. In this laboratory, the screening test with flame ionization detector is more sensitive than analysis with a quadrupole mass selective detector. The aim of this work was to improve the sensitivity of the mass spectrometric analysis and to develop a practical and sensitive method for the analysis of trace amounts of gasoline in fire debris. The analysis was performed by using commercial Tenax tubes for trapping and an automated thermal desorber with cryofocusing units connected on-line with a capillary gas chromatograph, a mass spectrometer (MS) and a work station.

Experimental

Sampling

Standards—Filter papers impregnated with 1.0 μL, 0.5 μL and 0.1 μL of gasoline (Neste, Finland) were placed into nylon bags (Rilsan Nylon 11, 30 cm × 60 cm, wall thickness 0.04 mm; Petersen-Bach, Danmark) approximately 1 liter in volume. The bag was tied in a knot and sealed with a nylon band (polyamide 66, Panduit). The standard samples were heated in an oven at 100°C for 30 min and analyzed thereafter by direct static (injection volume 1 mL) and dynamic headspace procedures. In the dynamic headspace analyses commercial sealed glass Tenax tubes (45 mg, 70 mm × 6 mm o.d., SKC Inc.) were used for trapping. The adsorbent was held in position by plugs of glass wool. The ends of a tube were cut and the trap was baked at 260°C for 30 min before use. A hypodermic needle was connected to one end of the Tenax tube with silicone rubber tubing. Accelerant vapors were adsorbed by drawing different amounts of vapor from the nylon bag through the trap using a suction pump (capacity 100 mL/min, SKC Inc.) attached to the other end of the tube (Fig. 1). Cotton gloves were used in handling the tubes in order to avoid contamination.

Fire Debris Samples—Fire debris samples from crime scenes were heated in a microwave oven (700 W, 0.5−2 min), or in a convection oven (100°C, 30 min). The heating time depended on the moisture of the sample. The sample was heated as long as the bag distended or the moisture condensed on a wall of the bag. If the sample sparked in a microwave oven it was transferred to the convection oven. The adsorption was performed in the same manner as the standards.

Desorption

Compounds were desorbed by an automatic on-line thermal desorber (5010 GT, Tekmar Inc., Cincinnati, Ohio) and the analytes were collected into two cryogenic units cooled with liquid nitrogen. By heating the cold trap the sample was introduced to the GC column. The operating principle of the thermal desorber is illustrated in Fig. 1. The operating parameters of the TD are given in Table 1.

Heated aluminum-clad fused silica capillary transfer line is used as the interface between the desorber and the capillary column of the GC. The transfer line and the column are connected with a glass press-fit connector (0.32 mm/0.32 mm, HNU-Nordion Oy Ltd., Finland) inside the GC oven.

GC and MS Parameters

Two Hewlett-Packard 5890 gas chromatographs were used, one with a flame ionization detector (FID) for the screening test and the other with a Hewlett-Packard 5970 quadrupole mass selective detector (MSD) for the final detection. Fused silica capillary columns (25 m × 0.32 mm i.d., 0.25 μm film of NordiBond-54 5% phenyl 1% vinyl

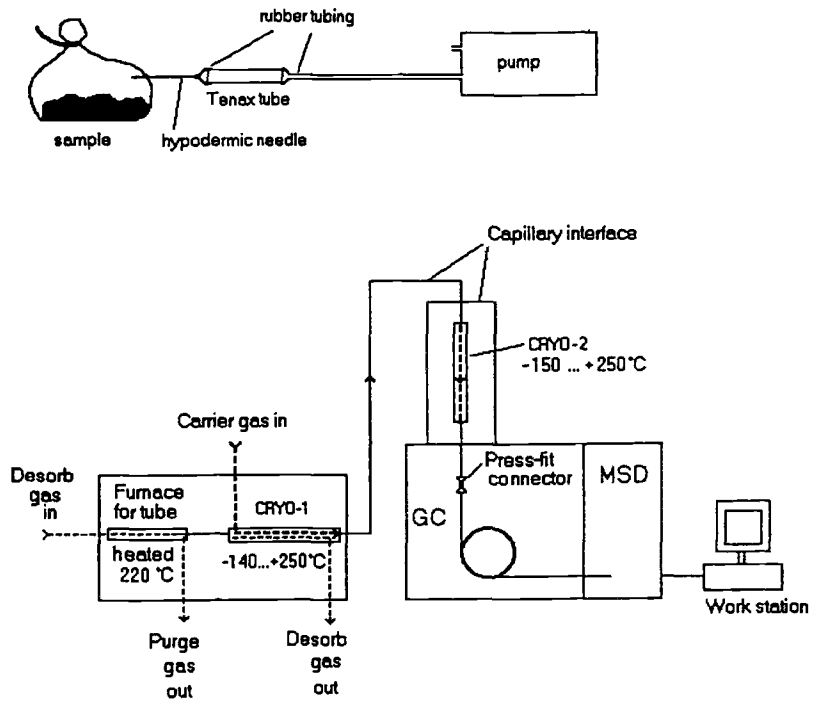

FIG. 1—(Top) *Sample trapping from a nylon bag and* (bottom) *Schematic diagram of thermal desorption and cryogenic focusing system in conjunction with GC-MS and a work station: After the collection of accelerant vapors, the Tenax tube is set to a furnace chamber of the desorber. The trap is purged with helium to remove water. The cryogenic units (CRYO-1 and CRYO-2) are cooled with liquid nitrogen. Analytes are desorbed from the adsorbent tube at a high desorb gas flow rate onto the CRYO-1 by heating the furnace. Analytes are transferred from the CRYO-1 to the CRYO-2 by heating the CRYO-1. The cryofocused sample is introduced to the column of the GC by flash-heating the CRYO-2. At the end of the program the trap is purged and baked for reusing.*

methylsilicone, HNU-Nordion Oy, Finland) were used in both GCs. The temperature program was the same in both GCs: 35°C (2 min), 10°C/min to 270°C (5 min). The temperature of the transfer line between the GC and the MSD was 270°C. Electron impact ionization (70 eV) and selected ion monitoring (SIM) were used. Nine ions characteristic for compounds in gasoline (Table 2) were selected to achieve high sensitivity and to minimize background. The ions were changed by the computer during the run. The dwell time was 100 ms/ion leading to 1.7 . . . 6.3 cycles per second depending on the number of ions. The report macro consists of the total ion chromatogram and nine different extracted ion profiles, for comparing selected hydrocarbon patterns of the sample to the gasoline standard.

Results and Discussion

In this laboratory a GC-FID screening run with static heated headspace sampling is performed as the first step for all routine fire debris analyses. Samples with suspected gasoline are reanalyzed using the GC-MS method of Smith [*4*]. Static headspace is not sensitive enough to identify trace quantities of gasoline with GC-MS. Dynamic headspace followed by thermal elution and on-column injection, combined with cryogenic focusing, eliminates this problem (Fig. 2).

TABLE 1—*Thermal desorber conditions.*

Desorption gas (He) pressure	p = 20 Psi
Desorption gas (He) flow rate	v = 10 mL/min
Carrier gas (He) pressure	p = 8 Psi
Transfer line temperature	T = 220°C
8-port valve temperature[a]	T = 270°C

Temperature program of the thermal desorber.

Furnace READY temperature	T = 40°C
Purge time	t = 5.00 min
DESORB temperature and time[b]	T = +220°C, t = 10 min
Cryo-1 temperature	T = −140°C
TRANSFER temperature and time[c]	T = +250°C, t = 5 min
Cryo-2 temperature	T = −150°C
INJECT temperature and time[d]	T = +250°C, t = 0.75 min
Bake temperature and time	T = +260°C, t = 15 min

[a]8-port valve controls the purge, desorb and carrier gas flow depending on the valid operation mode of the thermal desorber.

[b]DESORB: temperature and heating time of the furnace for desorbing the adsorbed vapors from the Tenax trap.

[c]TRANSFER: analytes are transferred from the cryo-1 to the cryo-2 by heating the cryo-1.

[d]Injection is performed during 0.75 minutes while the temperature of cryo-2 rises from −150°C to +250°C.

With the dynamic headspace technique there is a risk of overloading the column. The collection time of accelerant vapors into Tenax tube should be known. The screening analysis with static headspace and GC-FID produces information for the proper trap loading time. The trapping times were determined on the basis of the GC-FID screening test peaks-on-scale attenuator values (Table 3).

The sensitivity of the method can be greatly improved by increasing the trapping time. However, in order to minimize matrix interferences from air, and also from pyrolysis products, the threshold for routine analyses was adjusted to 100 mL trapping volume and 1 minute trapping time. Bertsch and Sellers have reported the detection of gasoline components from a 2 L sample of urban air [*5*]. We analyzed the ambient air of the laboratory and detected heavy gasoline components from a 1 L air sample (collected in 10 min). The threshold (100 mL and 1 min trapping) was matched to the screening test with a static headspace analysis by GC-FID; 0.1 μL of gasoline standard in a 1 L volume was detectable with 1 minute trapping (Fig. 2) and smaller amounts than 0.1 μL of gasoline per liter were not observed on the screening test with the GC-FID. Larger amounts of gasoline, more than 10 μL per liter were detectable on GC-MS with static

TABLE 2—*Selected ions and monitoring times on MS runtable.*

Compounds	Ions (m/z)	Monitoring time (min)
Aliphatics	43, 57	2.0–6.7
Alkylbenzenes (toluene, xylenes, ethylbenzene etc.	91, 105 and 119	3.0–10.2 and 6.7–10.2
Styrene (and also alkylbenzenes)	104	3.0–10.2
Naphthalenes (naphthalene and methylnaphthalenes)	128 and 142	10.2–12.0 and 12.0–16.0
Tetraethyllead	237	10.2–12.0

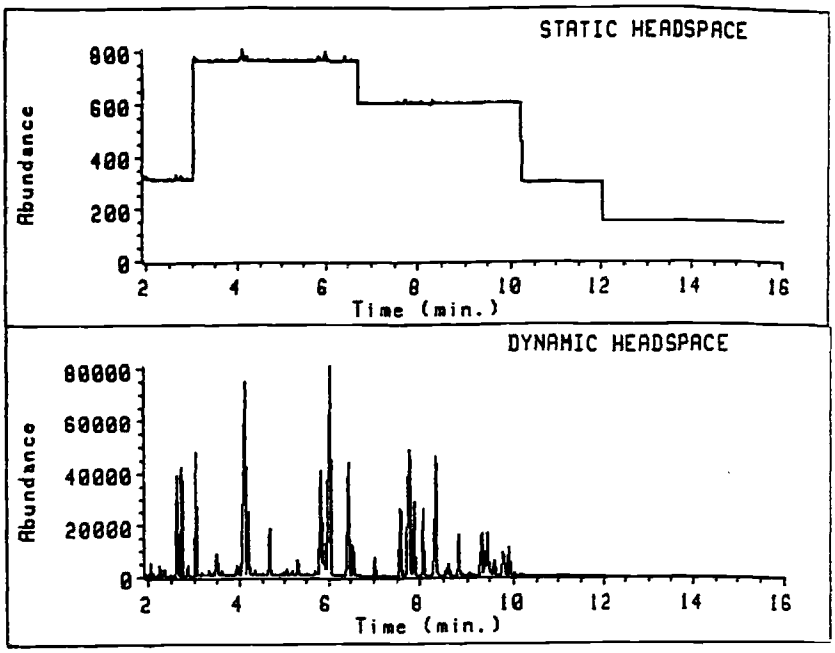

FIG. 2—*Total ion chromatograms of gasoline standard 0.1 μL/1 liter volume:* (Top) *Static heated headspace, injection 1 mL; the "stairs" in the baseline are created by the SIM windows listed in Table 2.* (Bottom) *Dynamic heated headspace, trapping time 1 minute through a Tenax adsorbent tube; stairs are not evident due to attenuation.*

headspace. The dynamic heated headspace method (TD-GC-MS) is useful for the gasoline quantities of 0.1 to 10 μL per liter volume.

The main advantage of the method is the easy use of both commercial traps and the automated on-line thermal desorber. With the use of commercial tubes, there is neither the need to prepare traps nor wash the adsorbent. A new Tenax tube need only be baked in the furnace of the TD prior to use. The desorption and the baking process at the end of the temperature program usually purges the traps well enough for reuse. If a trap has been overloaded rebaking may be necessary. Figure 3 illustrates the baselines of a Tenax tube before and after trapping the fire debris sample (from case example 3).

By comparing these baselines at the same scale as a sample chromatogram, it can be observed that the peaks of the baselines are negligible. The tubes were successfully reused, but it is recommended to check the background of the tube before trapping.

The disadvantage of the method is the length of analysis. Eight to nine analyses per

TABLE 3—*Trapping times and volumes passed through the Tenax adsorbent tube compared to the GC-FID screening test attenuator values.*

Static GC-FID att: 2	Dynamic Trapping Time	Dynamic Trapping Volume
2	2 s	3 mL
1	5 s	8 mL
0	15 s	25 mL
−1	30 s	50 mL
−3	60 s	100 mL

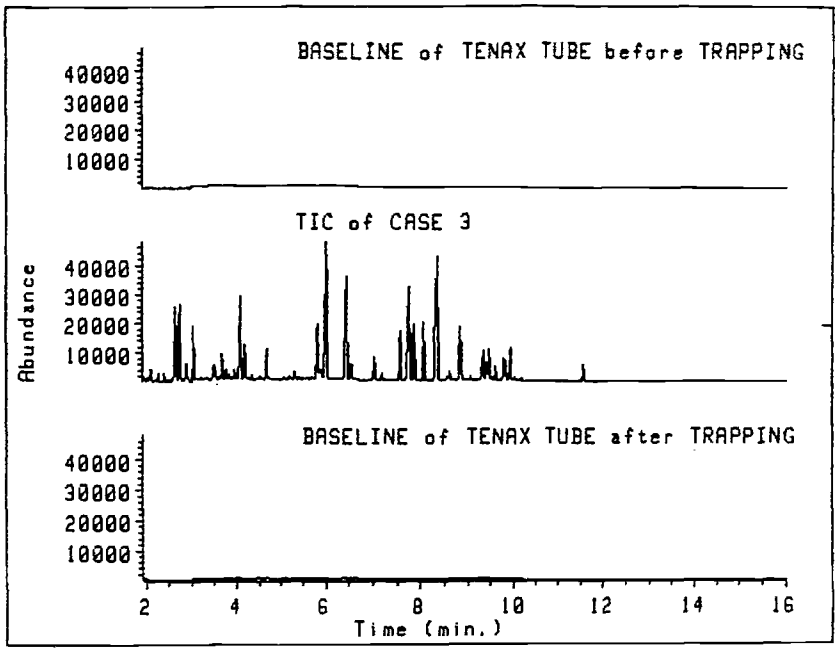

FIG. 3—*Baseline of a commercial Tenax tube before and after trapping the sample at the same scale as the total ion chromatogram (TIC).*

day can be performed with this method, half of which are background analyses. One analysis by TD-GC-MS takes about 45 min. An analysis with static headspace takes approximately 30 min. Furthermore, sample handling, checking the backgrounds of the tubes and printing the results takes additional time.

Case Examples

The technique was successfully introduced into routine casework, as illustrated by the following examples. These samples were collected by law enforcement officers and transported to the laboratory in sealed nylon bags.

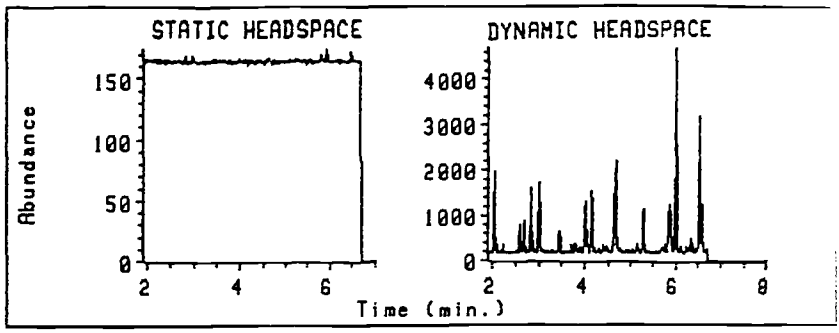

FIG. 4—*Ion m/z 57 chromatograms of a fire debris sample. Static headspace (1 mL) and dynamic headspace (trapping 10 s on a Tenax tube) sampling.*

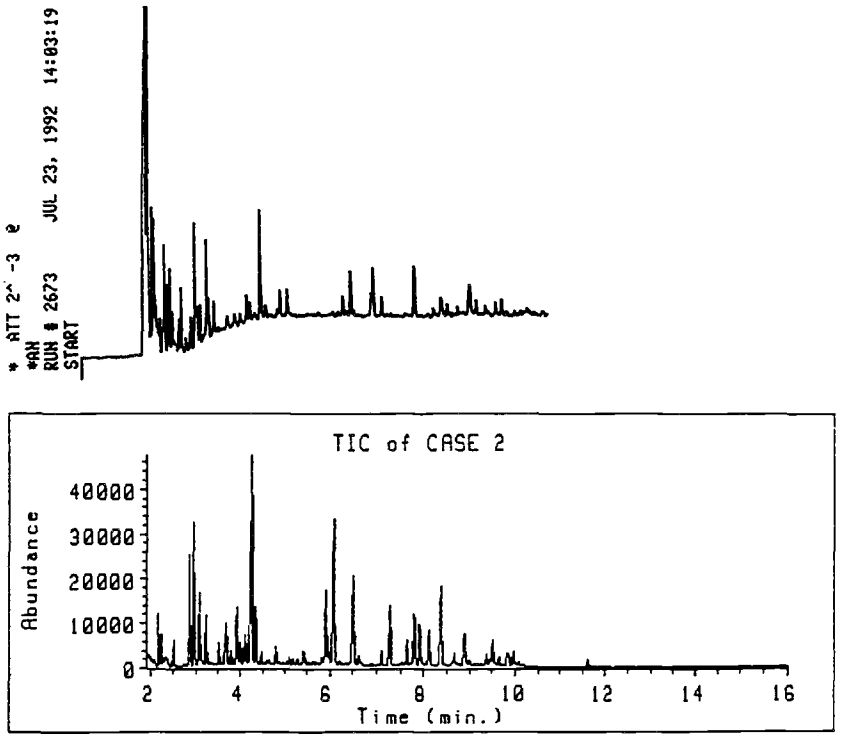

FIG. 5—(Top) *Gas chromatogram of the GC-FID screening test of a weak arson sample, attenuator* 2^{-3} (Bottom) *Total ion chromatogram (TIC) of the same sample (trapping time 60 s).*

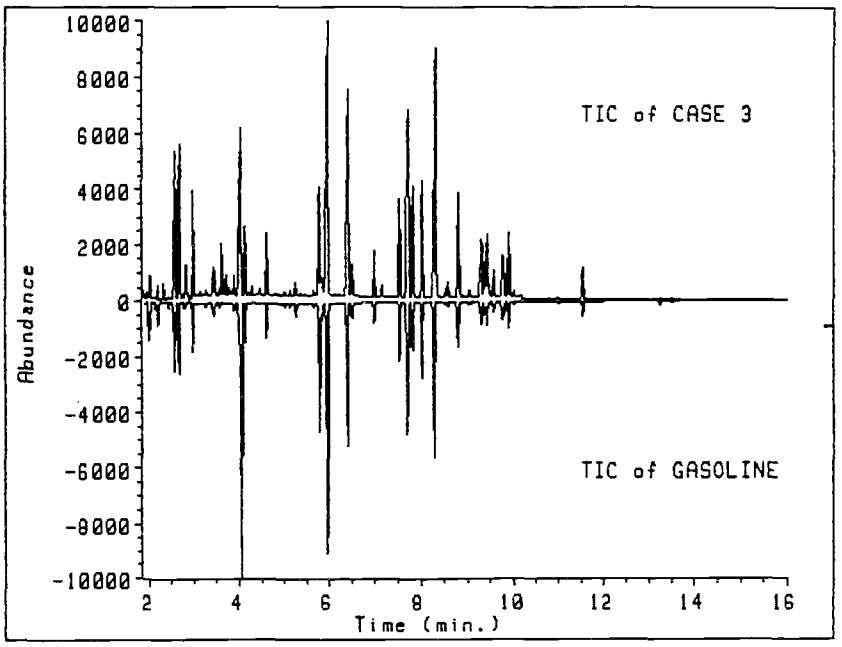

FIG. 6—*Total ion chromatogram (TIC) of an arson sample compared with gasoline standard. Trapping time 20 s on a Tenax tube.*

Case 1—Residue from the wooden floor of a burnt restaurant represents a sample where gasoline has partially evaporated. Fig. 4 illustrates the difference between results obtained at ion m/z 57 by direct static headspace and dynamic headspace procedures. The lighter compounds of gasoline are not observed by the static headspace technique but easily detected by the dynamic headspace enrichment.

Case 2—A fire burnt down the storage shed of a students' residential home. Five samples were taken from separate rooms. Fig. 5 (top) illustrates the result of the static headspace analysis with GC-FID of one of those samples. A weak hydrocarbon mixture with matrix compounds is observed on the chromatogram. The sample was reanalyzed using the dynamic headspace technique with 1 minute trapping and GC-MS. The total ion chromatogram (TIC) of this analysis is shown in Fig. 5 (bottom). On the basis of the TIC and extracted ion profiles it was concluded the sample contained gasoline.

Case 3—The sample consisted of a piece of charred carpet from the hall of an apartment. The comparison of normalized TICs is represented in Fig. 6.

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