Fast Analysis of Fire Debris Using an Agilent 5975T LTM GC/MSD with Capillary Trap Sampling (CTS)

Application Note

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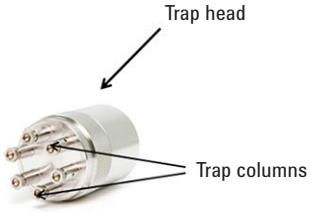
Abstract

This application note describes the development of an innovative method for the confirmation of fire accelerants using the Agilent Capillary Trap Sampler (CTS), which is based on capillary column absorbing principles. CTS has the advantage of rapid sampling of airborne debris and toxic compounds within 1 minute. The study used 97 RON (Research Octane Number) octane gasoline as a standard, and compared the aromatic compounds (m/z = 91) in the sample to those in the standard in order to qualify the accelerant type. Results confirmed that this is an effective method for confirming accelerant types.



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Introduction

Arson is a crime that can cause serious property damage, injury, and sometimes death. Fires of suspicious origins are investigated to determine whether or not the cause was intentional. Laboratory analysis of fire debris can be used to search for traces of accelerants that could have been used to start a fire. These include: gasoline, kerosene, diesel, heating oils, alcohols, and mineral and white spirits. Samples of debris from fires are routinely analyzed for traces of hydrocarbon accelerants. Mass spectrometery is used to identify and eliminate the interference of pyrolysis products in the resulting chromatograms. The hydrocarbon type is determined by comparing the sample chromatogram to standards. Individual mass chromatograms of key ions are typically reviewed to make this comparison. However, a good comparison is not always possible because the sample is severely fire damaged making it difficult to get a sample. Therefore, sample collection is a critical step preceding analysis. The samples must be collected from the fire origination point because this is the only place where traces of accelerant, if used, would be found. Before the development of CTS, Solid Phase Microextraction (SPME), has been the scientific choice for sample collection. One advantage of SPME is that it has good concentrating ability [1]. However, it also has the disadvantage of requiring more than 30 minutes to aquire a trace content sample.

This study details the development of an airborne sampling technique using CTS based on the same principles as SnifProbe [2]. CTS can process a sample within a few seconds to several minutes and it can easily be used on-site. One sample can be analyzed within minutes using an Agilent 5975T LTM GC/MS System. Since gasoline is a common fire accelerant, this study attempted to identify gasoline in fire debris samples.

CTS is a 6-port trap column airborne sampler. It can accommodate six trap columns simultaneously with different polarities. Customized column selection provides more flexibility in application. This application note explores using a Pora PLOT Q column as the trap column. The performance evaluation is compared to the Shanghai Key Laboratory of Crime Scene Evidence, Institute of Forensic Science's conventional SPME method. The verification tests were done by six Shanghai fire stations.

Experimental

Reagents and chemicals

All the chemicals used in this study are from Shanghai Key Laboratory of Crime Scene Evidence, Institute of Forensic Science. Commonly used fire accelerants: 97 RON gasoline, kerosene, and small organic solvents.

Equipment and materials

The analysis was performed on an Agilent 5975T LTM GC-MS equipped with TSP (G4381A). The sample was prepared using a CTS system, and the compounds were separated on an Agilent HP-5 ms LTM column, 10 m × 0.18 mm, 0.18 µm).

Instrument conditions

Table 1. Instrumentation and Conditions of Analysis

Instrumentation	
GC/MS system	Agilent 5975T LTM GC/MS System
Inlet	Split/splitless, with TSP
Column	Agilent HP-5ms LTM 10 m × 0.18 mm, 0.18 µm
Guard column	1 m deactivated blank column connected to the injector.
Experimental conditions	
Inlet temperature	220 °C
Injection mode	Split, 20:1; manual
Carrier gas	Helium
Constant flow	1.4 mL/min
LTM oven temperature	40 °C (0.8 minutes), 12 °C/min, 50 °C (0.4 minutes), 30 °C/min, 100 °C (0 minutes), 90 °C/min, 180 °C (0 minutes), 120 °C/min, 220 °C
Transfer line temperature	230 °C
Ion source	230 °C
Quad. temperature	150 °C
Ionization mode	EI
Scan mode	full scan, *m/z* 45–300 u
EMV mode	Gain factor
Gain factor	5.00
Resulting EM voltage	1,430 V
Solvent delay	0.1 minutes

Sample preparation

The sample was prepared using direct headspace gas sampling with CTS. A specific volume of liquid gasoline was injected into a 5-L glass bottle, then equilibrated for six hours to vaporize the gasoline components.

Results and Discussion

Trap column selection and CTS work conditions optimized

This study required a short trap column with sufficient absorbing volume. Therefore, a Pora PLOT series column was selected. To match the Agilent standard ferrules, we used 0.32-mm and 0.53-mm columns as trap columns. Considering the micro vial height and ease of removal, 20-mm columns are suitable. Therefore, an Agilent Pora Plot Q column (20 × 32 mm, 20 µm) was chosen because it can absorb most components in gasoline. CTS pump test conditions were 60 mL/min for 1 minute because these settings produce good results for the samples tested.

Identification of gasoline

Gasoline is a mixture of hydrocarbons, although some may contain significant quantities of ethanol and some may contain small quantities of additives such as tertiarybutylmethyl ether as agents to increase the octane rating. The hydrocarbons consist of a mixture of *n*-paraffins, naphthenes, olefins, and aromatics. Naphthenes, olefins, and aromatics increase the octane rating of the gasoline whereas the *n*-paraffins have the opposite effect. The aromatics consist mostly of a mixture of benzene, toluene, and xylenes. The gasoline composition can vary significantly depending on the source of the crude oil, its processing method, and its intended use. Because aromatic compounds are a typical specification marker of gasoline, this study used aromatic compounds as the main specification for identification of gasoline. We compared the components of the samples to gasoline standards.

Gasoline standard preparation

A 1-µL amount of 97 RON octane gasoline was placed in a 5-L glass bottle to vaporize. After vaporization, 60 mL of headspace air were sampled. Figure 1 shows the total ion chromatogram (TIC) of the gasoline. As the figure illustrates, almost all visible peaks were aromatics. Table 1 lists the main trapping components of gasoline. Components were identified with the assistance of the AMDIS software in NIST EPA library. The AMDIS software allows some overlap peaks to be ignored, and the rapid 5975T method to be used.

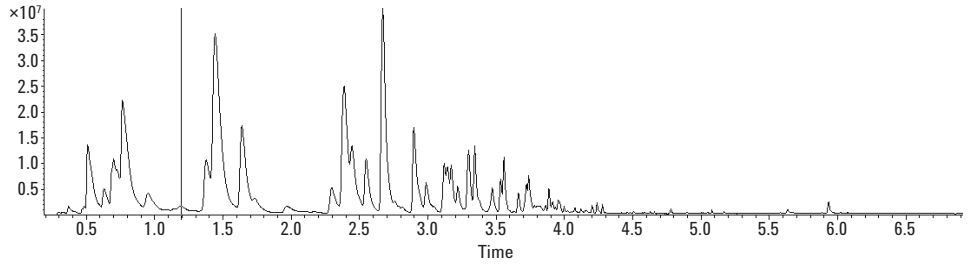

Figure 1. TIC of 97# gasoline with six columns.

Table 1. Main Trapping Components of 97# Gas Oil (Identified by AMDIS-NIST EPA Library)

RT (min)	Chemical name	CAS no.
0.1971	Cyclohexane	110-82-7
0.2617	Benzene	71-43-2
0.2942	1-Hexanol, 2-ethyl-	104-76-7
0.3932	3-Penten-2-one, 4-methyl-	141-79-7
0.5626	Toluene	108-88-3
0.5927	Methanethiol	74-93-1
1.2132	Ethylbenzene	100-41-4
1.4395	Benzene, 1,3-dimethyl-	108-38-3
1.4427	*p*-Xylene	106-42-3
1.449	Benzaldehyde	100-52-7
1.6385	*o*-Xylene	95-47-6
1.9574	1-Hexanol, 2-ethyl-	104-76-7
1.9735	Benzene, propyl-	103-65-1
2.0009	Benzene, 1,2,4-trimethyl-	95-63-6
2.3802	Propane, 2-methoxy-2-methyl-	1634-04-4
2.3878	Benzene, (1-methylethyl)-	98-82-8
2.6849	Benzene, 1,3,5-trimethyl-	108-67-8
2.7638	Decane	124-18-5
2.9869	Indane	496-11-7
3.0518	Indene	95-13-6
3.1181	Benzene, 1-methyl-4-(1-methylethyl)-	99-87-6
3.1194	Benzene, 1-methyl-2-propyl-	1074-17-5
3.1199	Benzene, 1-methyl-3-propyl-	1074-43-7
3.1384	Decane, 4-methyl-	2847-72-5
3.142	Benzene, 1-methyl-2-(1-methylethyl)-	527-84-4
3.144	Benzene, butyl-	104-51-8
3.147	Benzene, 1,2-diethyl-	135-01-3
3.1696	Benzene, 1,2,3,4-tetramethyl-	488-23-3
3.2238	Decane, 2-methyl-	6975-98-0
3.2902	Benzene, 1,3-diethyl-	141-93-5
3.2986	Benzene, 1-ethyl-2,4-dimethyl-	874-41-9
3.3018	Benzene, 1-methyl-3-(1-methylethyl)-	535-77-3
3.4612	Undecane (ID#:1120-21-4)	1120-21-4
3.4629	Benzene, 1-ethyl-2,3-dimethyl- (ID#:933-98-2)	933-98-2
3.4752	Benzene, 1-ethyl-3,5-dimethyl- (ID#:934-74-7)	934-74-7
3.556	Benzene, 1,2,4,5-tetramethyl-	95-93-2
3.6624	^{1}H-Indene, 2,3-dihydro-5-methyl-	874-35-1
3.7189	^{1}H-Indene, 1-methyl-	767-59-9
3.7224	Benzene, 1,2,3,5-tetramethyl-	527-53-7
3.7383	Naphthalene	91-20-3
3.8857	Benzene, pentamethyl-	700-12-9
3.9574	Dodecane	112-40-3
3.9708	Benzene, 1,3-dimethyl-5-(1-methylethyl)-	4706-90-5
4.0252	^{1}H-Indene, 2,3-dihydro-4,7-dimethyl-	6682-71-9
4.1201	Naphthalene, 2-methyl-	91-57-6
4.238	Tridecane	629-50-5
4.2532	Biphenyl	92-52-4
4.4327	Tetradecane	629-59-4
4.4606	Naphthalene, 1-ethyl-	1127-76-0
4.4687	Naphthalene, 1,5-dimethyl-	571-61-9
4.4782	Naphthalene, 1,8-dimethyl-	569-41-5
4.5065	Naphthalene, 1,4-dimethyl-	571-58-4
4.5412	Naphthalene, 1,3-dimethyl-	575-41-7
4.6212	Butylated Hydroxytoluene	128-37-0
4.6592	Naphthalene, 1,6,7-trimethyl-	2245-38-7

Compare CTS method with their conventional lab method

In China, a SPME method with GC/MS is the forensic standard. The sample preparation time is 40 minutes and the GC/MS running time is 40 minutes with a VF-5ms (30 m × 0.25 mm, 0.25 µm). Using an Agilent 5975T GC/MS with an HP-5ms column (10 m × 0.18 mm, 0.18 µm), we were able to reduce the running time approximately 5 fold. The CTS method requires only 1 minute, which is an improvement in sample preparation. Figure 2 is a TIC and EIC chromatogram of a SPME method for gas oil. All of the main components can be aligned using either method. Therefore, a CTS sampling technique can replace SPME in practical applications.

Real case study

Several real samples from the field provided by the Shanghai forensic institute were tested in this study. User reports were provided by several fire stations. In these reports, CTS was successfully used for gasoline, banana oil samples, and so forth. It was determined that all of the main components from fire debris caused by gasoline could be matched with the gasoline standard.

Gasoline identification in fire debris

A special group in gasoline is aromatic compounds, such as toluene and xylenes with short arms to long arms. They all have the characteristic ion *m/z* 91. These masses are the molecular weights of the most abundant aromatic compounds found in the gasoline. The aromatic compounds were compared as they are the most characteristic compounds in gasoline. There is no extra solvent wash step and only airborne samples were used in the CTS sampling technique, so there was minimal interference in the GC/MS chromatogram with a low matrix effect. This advantage provides a good basis for gasoline identification.

Figure 3 is an overlap EIC of gasoline standard and gasoline residue from fire debris. The black chromatogram (big) is a typical gasoline chromatogram and blue (small) is sample. Burned denim was the fire sample used for analysis. Figure 3 shows good correlation of the two chromatograms. Comparing the components relative contents and types shows that the fire was caused by gasoline.

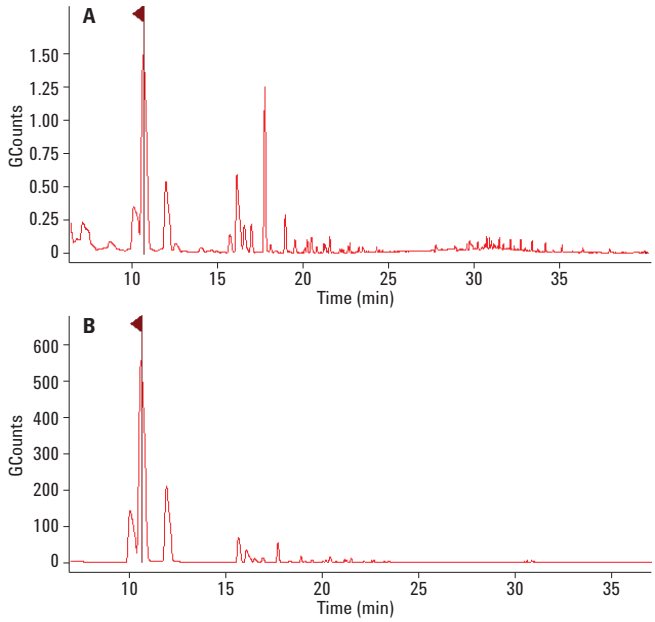

Figure 2. SPME results for 97# gasoline. A) TIC and B) EIC of m/z 91.

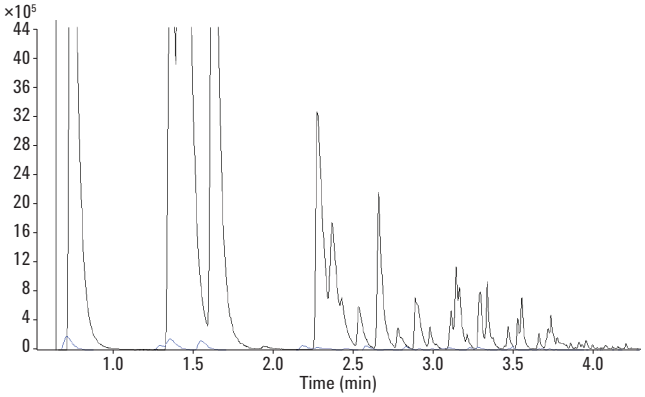

Figure 3. Mass chromatograms of fingerprints of gasoline (m/z 91). Gasoline standards (black) and fire debris caused by gasoline (blue).

Banana oil identification

Banana oil, also called thinner, is often used as a paint dilution. Since it is readily available, it is often used as a fire accelerant. Its main components are xylenes and some butyl acetates. The primary distinction between gasoline and banana oil is the content of xylenes. Banana oils typically have a high content of xylenes, as well as butyl acetates. The CTS technique allowed direct sampling for one minute. Two trap columns were injected into the GC/MS. Figure 4 shows an overlap EIC of the gasoline standard and banana oil. CTS helped provide a good backup for crime evidence.

Extended applications of CTS

CTS can also be applied to the detection of aviation kerosene and diesel. Figure 5 presents a TIC of diesel and Figure 6 gives a TIC of aviation kerosene. Table 2 shows the light components of diesel, and Table 3 lists the light components of aviation kerosene.

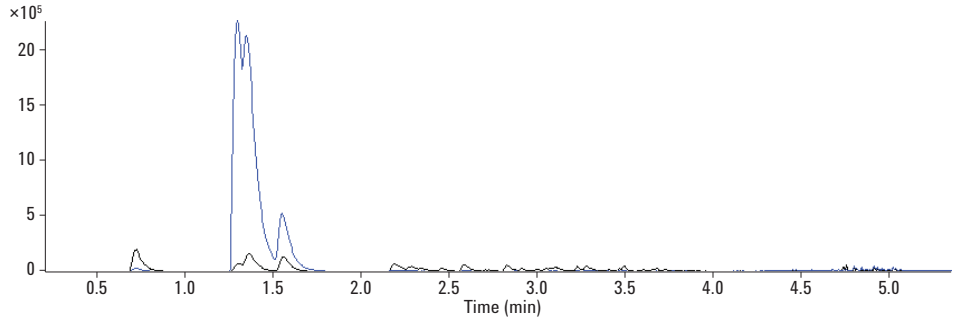

Figure 4. Mass chromatogram of banana oil and gasoline (m/z 91), banana oil (blue), gasoline (black). Both are samples from the field.

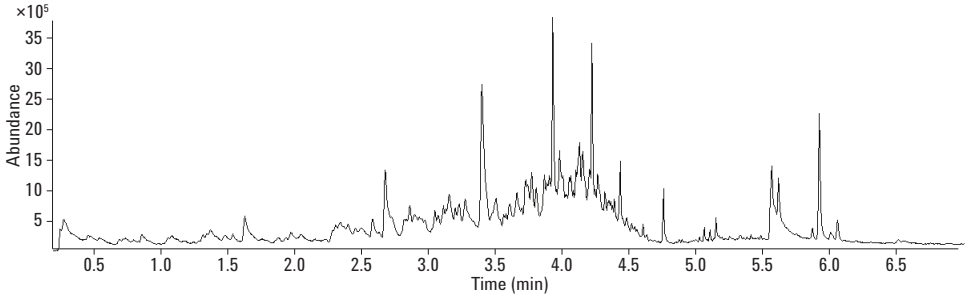

Figure 5. TIC of diesel by CTS sampling.

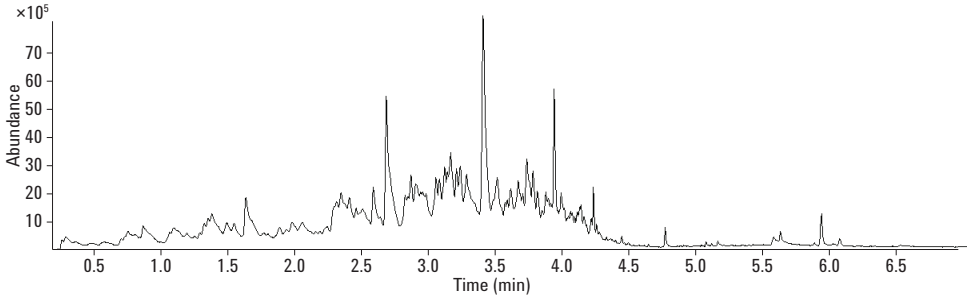

Figure 6. TIC of aviation by CTS sampling.

Table 2. Light Components of Diesel

R.T. (min)	Chemicalname
0.3657	*n*-Hexane
0.4755	2,2,4-Trimethylpentane
0.4938	3-Methylhexane
0.5580	Methylcyclohexane
0.7169	Toluene
0.7328	3-Methylheptane
0.8747	*n*-Octane
1.0725	1-Octanol
1.3585	Ethylbenzene
1.3613	*m*-Xylene
1.3887	3-Methyloctane
1.5599	*o*-Xylene
1.6429	*n*-Nonane
2.2007	*n*-Propylbenzene
2.2968	*m*-Ethyltoluene
2.3224	2-Methylnonane
2.4682	o-Ethyltoluene
2.5940	1,3,5-Trimethylbenzene
2.6909	*n*-Decane
2.8321	Isopropylbenzene
3.1623	*sec*-Butylbenzene
3.2449	*p*-Isopropyltoluene
3.4103	*n*-Undecane
3.6915	*tert*-Butylbenzene
3.9416	*n*-Dodecane
4.2332	*n*-Tridecane
4.4445	*n*-Tetradecane
4.6145	*n*-Pentadecane
4.6437	2,6-di-t-Butyl-4-methylphenol(BHT)

Table 3. Light Components of Aviation Kerosene

R.T. (min)	Chemical name
0.2366	Acetaldehyde
0.3708	*n*-Hexane
0.4750	3-Methylpentane
0.5670	Methylcyclohexane
0.6018	1-Octene
0.7086	3-Methylhexane
0.7355	3-Methylheptane
0.8716	*n*-Octane
1.2929	Ethylbenzene
1.3539	*m*-Xylene
1.3837	3-Methyloctane
1.6375	*n*-Nonane
1.8590	Isopropylbenzene
1.8877	2-Ethyl-1-hexanol
2.1905	*n*-Propylbenzene
2.2895	*m*-Ethyltoluene
2.3461	2-Methylnonane
2.5150	1-Decene
2.5876	1,3,5-Trimethylbenzene
2.6866	*n*-Decane
2.8264	*o*-Ethyltoluene
2.9200	*o*-Methystyrene
3.0861	*n*-Butylbenzene
3.0904	Toluene
3.1598	*sec*-Butylbenzene
3.2415	*p*-Isopropyltoluene
3.4096	*n*-Undecane
3.6866	*ter*t-Butylbenzene
3.8483	Naphthalene
3.9421	*n*-Dodecane
4.2335	*n*-Tridecane
4.4443	*n*-Tetradecane
4.6445	2,6-di-t-Butyl-4-methylphenol (BHT)

Conclusion

Capillary Trap Sampling (CTS) allows a direct comparison of standard compounds to hydrocarbons and other organics vaporized from burned material samples, to determine the type of accelerant used in a fire. An excellent correlation can be obtained, since the matrix compounds of the sample can be eliminated by the selectivity of CTS sampling with the transportable Agilent 5975T LTM GC/MSD. The CTS airborne sampling technique and 5975T GC/MSD technology provides a fast and reliable method for fire accelerant identification.

Reference

1. J.A. Lloyd and P.L. Edmiston "Preferential Extraction of Hydrocarbons from Fire Debris Samples by Solid Phase Microextraction" *J. Forensic Sci.* Jan. 2003, Vol. **48**, No. 1.

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