Development of Carbon Nanotubes Assisted Solid-phase Microextraction for Fire Debris Analysis

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ABSTRACT

This poster presents a novel carbon nanotube - assisted solid phase microextraction (CNT-SPME) fiber coupled with headspace gas chromatography and mass spectrometry (HS-GC/MS) to determine gasoline residues in fire debris samples. The devised CNT-SPME fiber enables simple, fast, reliable, mechanically robust, and durable analysis of fire debris samples.

INTRODUCTION

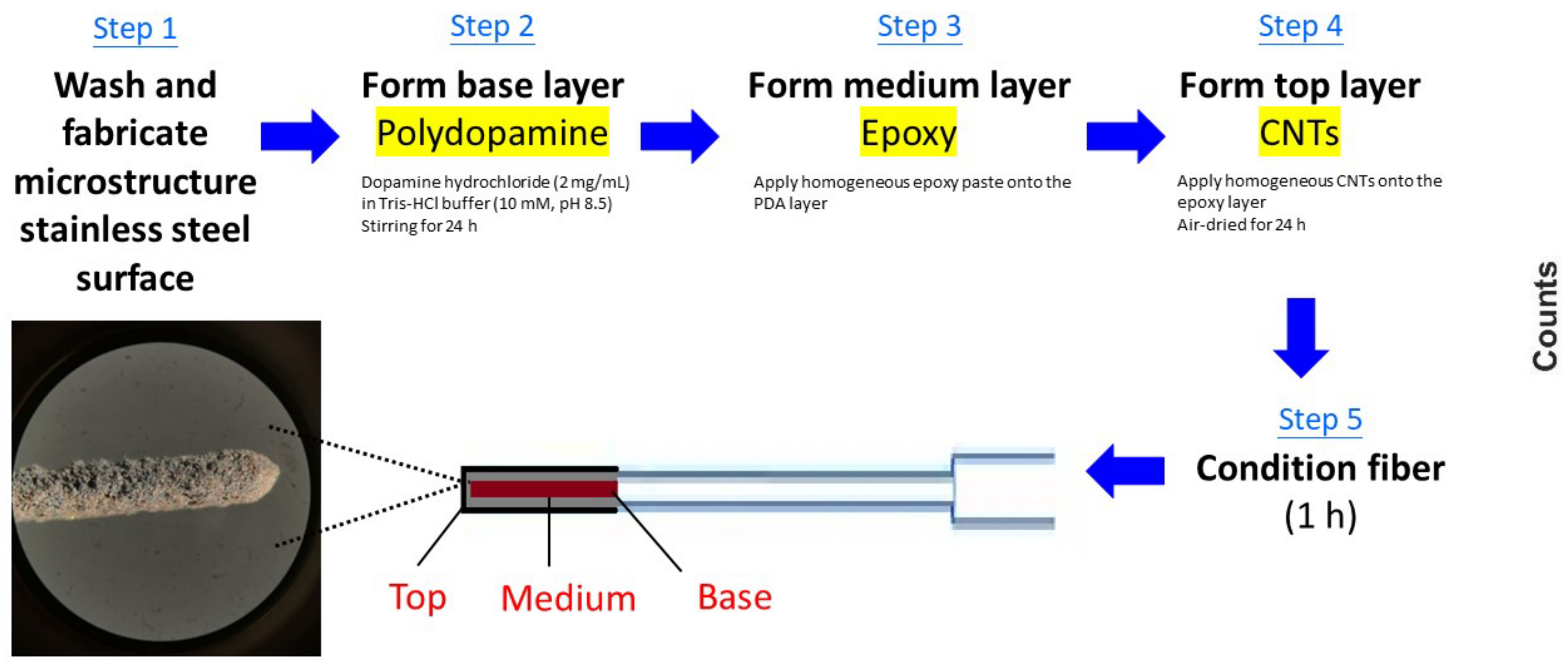
Between 2014 and 2018, an estimated 52,260 intentionally set fires were reported to the United States municipal fire departments annually, according to the National Fire Protection Association (NFPA) [1]. Due to the features of readiness and easy transportation, gasoline has become the most widely used ignitable liquid (IL) to initiate fires by arsonists.

Solid phase microextraction (SPME), introduced by Pawliszyn et al. in 1990 [2], has been standardized by the American Society for Testing and Materials (ASTM) for the isolation of trace IL residues from fire debris samples prior to gas chromatography and mass spectrometry (GC/MS) analysis since 2001. SPME offers rapid, non-destructive, and solvent-free extraction of volatile compounds from fire debris samples. Moreover, the procedure is reusable, automated, and highly sensitive to trace IL residues caused by combustion and firefighting activities at the fire scenes. However, commercial SPME fibers are expensive, fragile, and easily breakable during sample extraction and thermal desorption at the GC injection port because the fibers are mostly made from fused silica.

Carbon nanotubes (CNTs) are introduced by Iijima in 1991 [3]. CNTs are formed by rolling up one or more graphite sheet(s) into a cylinder. Single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) are two conformations of the CNTs. The advantages of the CNTs include a large surface area, high tensile strength, thermal stability, and mechanical robustness. The non-covalent forces of the CNTs, such as hydrogen bonding, van der Waals forces, electrostatic forces, and π-π stacking, provide strong adsorption of aromatic compounds, whose structure contains π-electron conjugated systems.

In this study, a novel CNT-SPME fiber is proposed to extract gasoline residues in fire debris samples. The devised CNT-SPME fiber combined with GC/MS offers promising opportunities for the detection of gasoline in fire debris samples to support fire investigation.

RESULTS AND DISCUSSION



Step 1
Wash and fabricate microstructure stainless steel surface

Step 2
Form base layer
Polydopamine
Dopamine hydrochloride (2 mg/mL) in Tris-HCl buffer (10 mM, pH 8.5)
Stirring for 24 h

Step 3
Form medium layer
Epoxy
Apply homogeneous epoxy paste onto the PDA layer

Step 4
Form top layer
CNTs
Apply homogeneous CNTs onto the epoxy layer
Air-dried for 24 h

Step 5
Condition fiber
(1 h)

Figure 1. Physically-attached procedure for the preparation of the proposed CNT-SPME fiber.

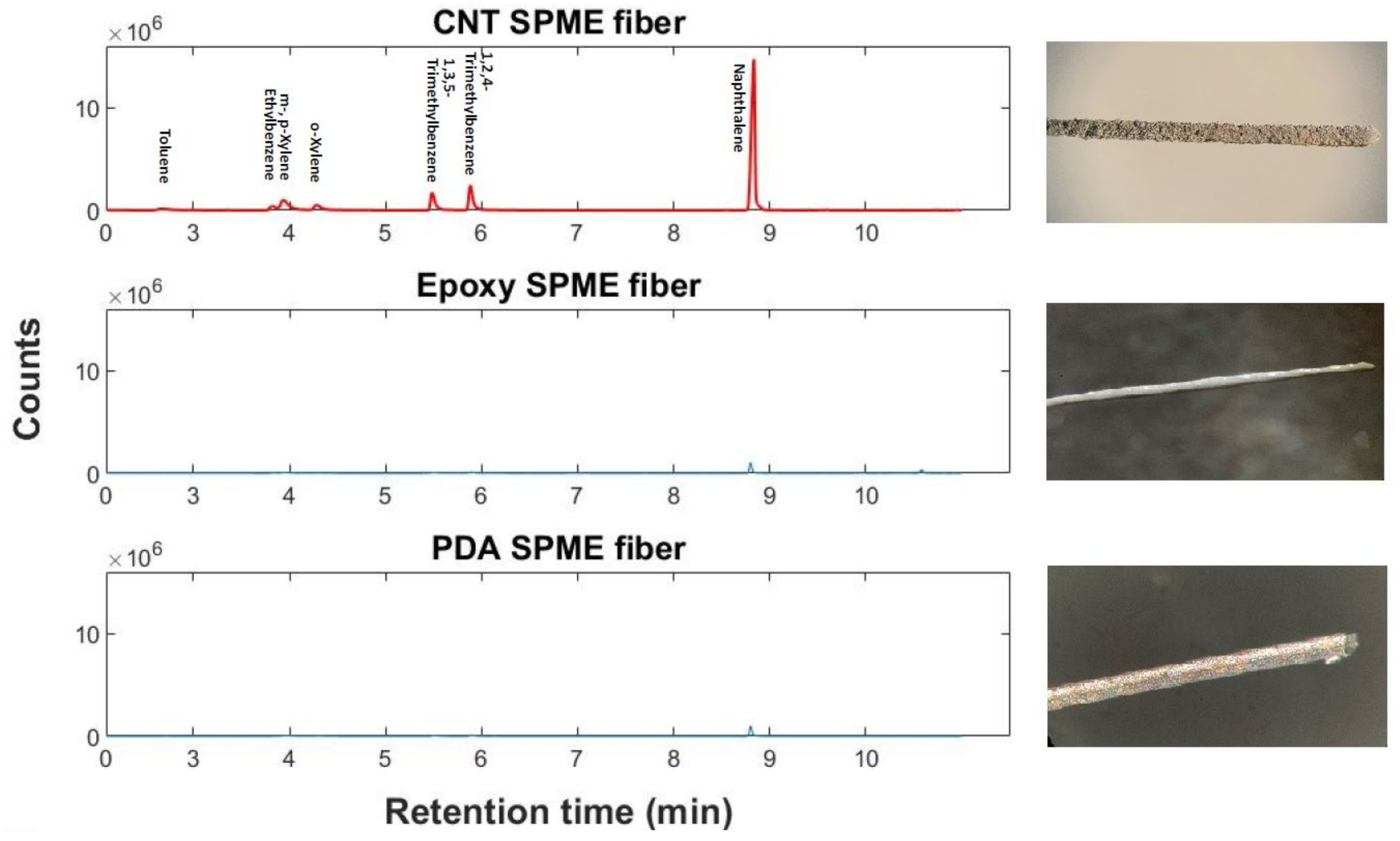


Figure 2. Comparison of the extraction performance of PDA, epoxy, and CNT-SPME fiber for 5 µL of gasoline range organic standard solution in a 20-mL HS vial.

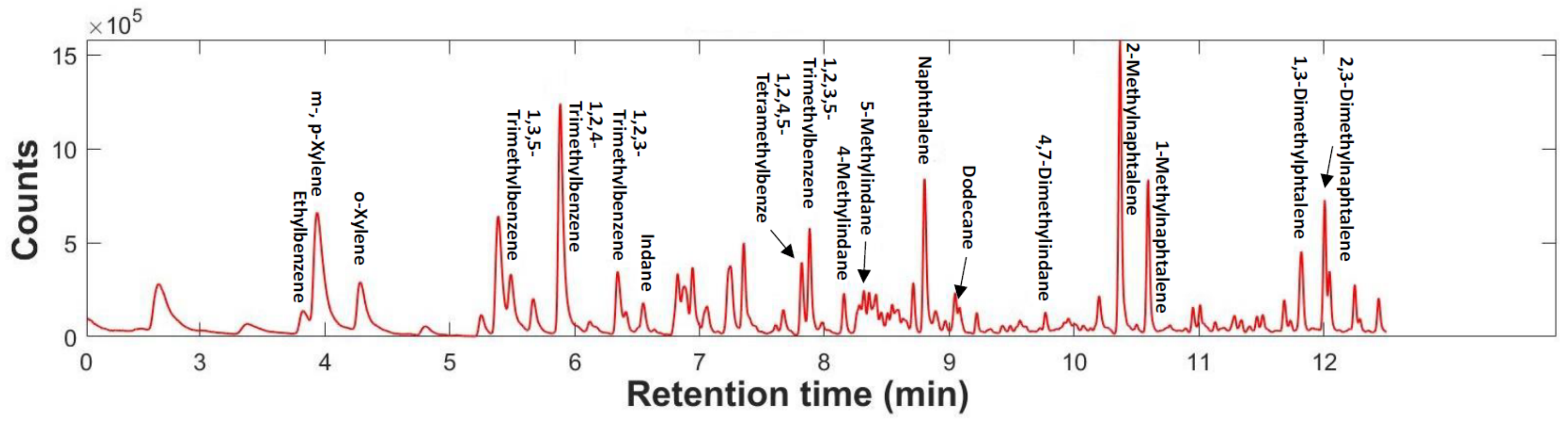


Figure 3 (Upper). Extraction performance of the CNT-SPME fiber for 100 µg of the gasoline standard solution in a 20-mL HS vial.

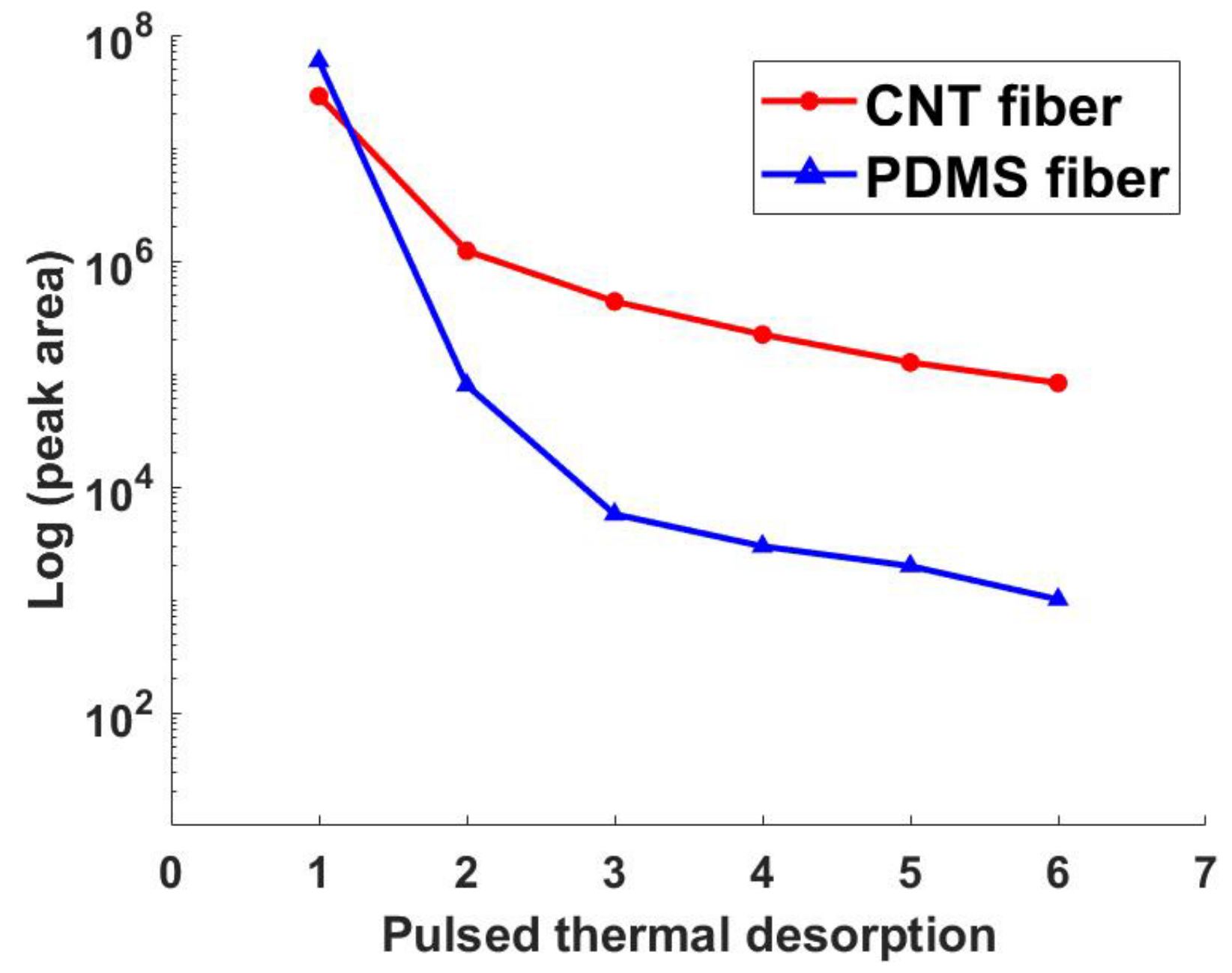


Figure 4 (Right). Comparison of peak area on a logarithmic scale vs. the numbers of times of pulsed thermal desorption using the CNT-SPME fiber and a 100 µm PDMS fiber to extract 50 µg of the gasoline standard solution in a 20-mL HS vial.

- The capability of CNTs to extract gasoline range organics was confirmed by comparing the extraction performance of PDA (base layer) and epoxy (medium layer)-SPME fibers (Figure 2). Based on the identification criteria defined by ASTM E1618-19, gasoline standard could be successfully determined by the CNT-SPME-GC/MS analysis in this study (Figure 3).
- Gasoline target analytes could still be detected at a sixth desorption analysis when using the CNT-SPME fiber as the extraction medium (Figure 4).
- Analytical performance of the CNT-SPME fiber:
  - ■ Neat gasoline samples:
    Calibration equation: $y=154500x+338714$; $R^2 = 0.99$; limit of detection (LOD) = 0.4µg/20-mL HS vial; calibration range: 0.4-50 µg/20-mL HS vial.
  - ■ Simulated fire debris samples:
    Calibration equation: $y=69573x+260288$; $R^2 = 0.99$; LOD = 3.1µg/20-mL HS vial; calibration range: 3.1-50 µg/20-mL HS vial.
- Average %RSDs of calibrators at the 95% confidence interval were 3.7 ± 1.3 and 4.2 ± 3.6 for neat gasoline samples and simulated fire debris samples, respectively.

CONCLUSIONS

- The CNT-SPME fiber showed good linearity range, LODs, and reproducibility.
- The CNT-SPME fiber showed stronger binding affinity towards gasoline target analytes than a PDMS-SPME fiber.
- The service life of the CNT-SPME fiber was longer than that of a PDMS-SPME fiber (more than 100 analyses).
- The CNT-SPME fiber eliminates extraneous signals in the chromatograms due to degraded materials from the fiber coating.
- Low-cost and easily-made features enable batch production and massive usage.

REFERENCES

[1] National Fire Protection Association (NFPA), Intentional Structure Fires. https://www.nfpa.org//-/media/Files/News-and-Research/Fire-statistics-and-reports/US-Fire-Problem/Fire-causes/osintentional.pdf, 2021. (accessed 9 November 2022).

[2] C.L. Arthur, J. Pawliszyn, Solid phase microextraction with thermal desorption using fused silica optical fibers, Anal. Chem. 62(19) (1990) 2145-2148. https://doi.org/doi.org/10.1021/ac00218a019.

[3] S. Iijima, Helical microtubules of graphitic carbon, Nature. 354(6348) (1991) 56-58. https://doi.org/doi:10.1038/354056a0.

MATERIALS AND METHODS

Fiber preparation A lab-built SPME fiber assembly was constructed using a stainless-steel wire with 0.18 mm-diameter × 5.0 cm-long. The stainless-steel wire was mounted into a SPME device, and the exposed fiber was trimmed to 1.0 cm. The preparation of the CNT-SPME was accomplished by a physically-attached method (Figure 1).

Sample preparation Gasoline standard (20,000 µg /mL in methanol) was used as a stock solution of the neat gasoline samples. The working solutions were prepared by serial dilution of the stock solution in the concentration range of 78 - 10,000 µg /mL in methanol (N = 8). Five µL of each calibrator sample was transferred to a 20-mL HS vial (Supelco Inc.) for HS-SPME-GC/MS analysis.

To prepare the burned substrate samples, approximately 16 cm^2 of a Nylon carpet was burned by a butane torch (Bernzomatic, Chilton, WI) for 1 min in the air. After the burned sample was cooled to room temperature, 300 mg of the burned sample was measured and placed into a 20-mL HS vial. Five µL of each calibrator sample was added to the burned substrate sample in the 20-mL HS vial for HS-SPME-GC/MS analysis.

Triplicate analyses were performed for all neat gasoline and simulated fire debris samples.

Instrumental analysis The HS-SPME analysis was performed on an Agilent 7890B gas chromatograph (Agilent Technologies, Santa Clara, CA) coupled with a 5977A mass spectrometer (Agilent Technologies). The settings of GC/MS are shown in Table 1.

The optimal parameters of the PAL sampler for HS-SPME of gasoline samples are listed in Table 2. Blank samples were extracted with the SPME fibers between runs.

A pulsed thermal desorption experiment (N = 6) was performed through two phases to investigate the binding capability of the CNT-SPME fiber towards the aromatic compounds in gasoline (Table 2). The first phase was performed only once. The second phase was repeated five times.

Table 1. GC/MS settings

Oven program steps	Condition
GC oven initial temperature	40 ˚C
Hold time	2 min
Rate #1, Oven temperature #1, Hold time #1	10 ˚C/min, 150 ˚C, 0 min
Rate #2, Oven temperature #2, Hold time #2	30 ˚C/min, 300 ˚C, 0 min

Table 2. HS-SPME settings

HHS-SPME step	Condition		
	Optimal condition	Pulsed thermal desorption	
		Phase 1	Phase 2
Pre-fiber conditioning temperature (°C)	250	250	250
Pre-fiber conditioning time (s)	60	60	0
Pre-incubation time (s)	300	300	10
Incubation temperature (°C)	80	80	80
Extraction time (s)	120	900	10
Desorption time (s)	120	10	10
Post-fiber conditioning temperature (°C)	250	250	250
Post-fiber conditioning time (s)	600	0	0

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