Development of a Novel Nanocomposite using Polypyrrole and Single-walled Carbon Nanotubes for Headspace Solid Phase Microextraction of Alkanes in Forensic Ignitable Liquid Analysis

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ABSTRACT

This poster presents an electropolymerization method to prepare a nanocomposite consisting polypyrrole (PPy) and carbon nanotubes (CNTs) on a stainless-steel wire for solid phase microextraction (SPME) of alkanes in ignitable liquids (ILs).
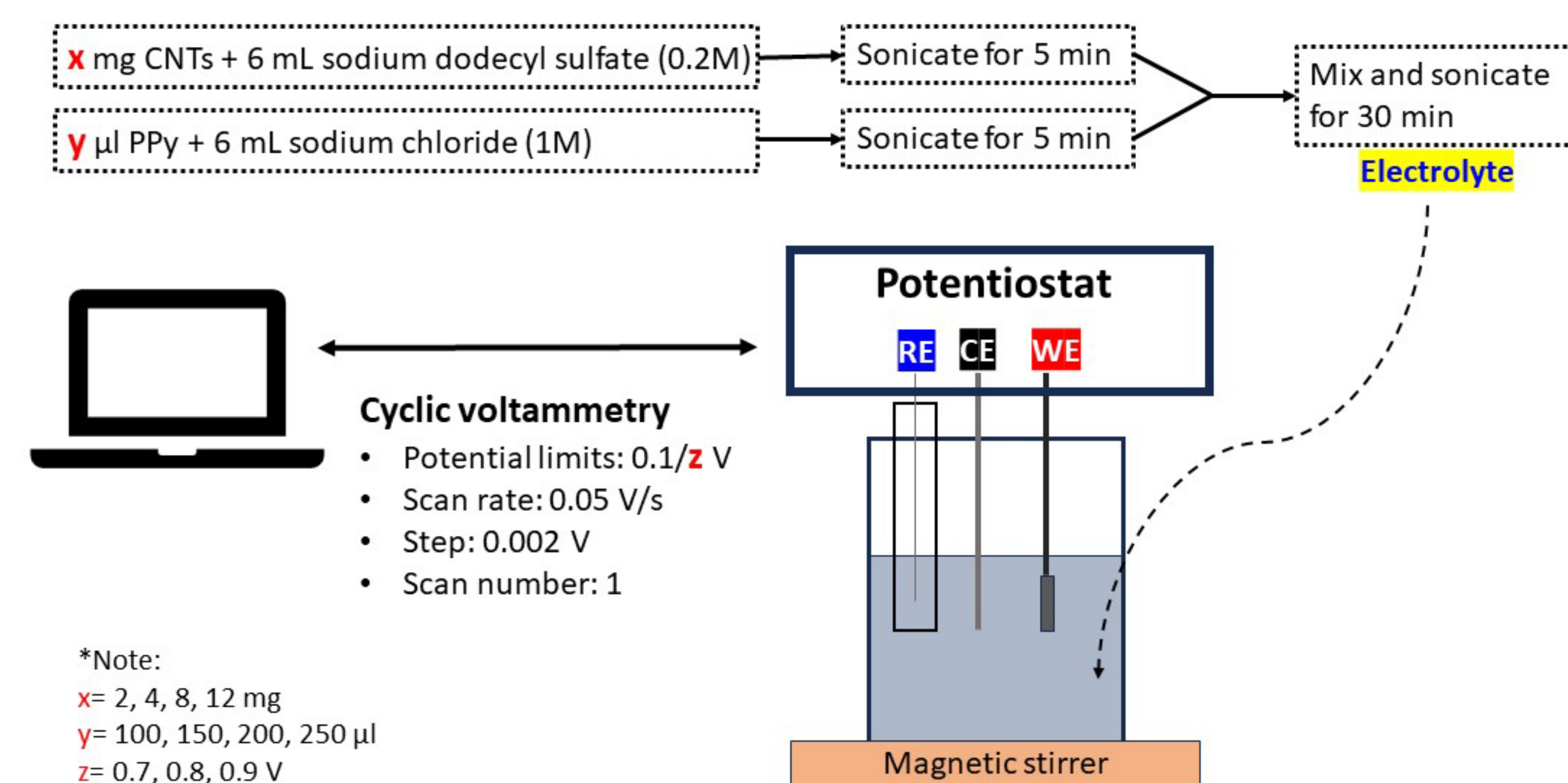
INTRODUCTION

As reported in the 2022 Arson Incident Report by the United States Bomb Data Center (USBDC), approximately 25% of the fire-related incidents were listed as incendiary fires [1]. Petroleum-based ILs are commonly-used in arsons because they are cheap and easily obtainable at gas stations.

In order to separate and concentrate the traces of ILs from matrices of fire debris or evidence collection tools, such as humidified cotton swabs, headspace sampling approaches have been adopted by forensic laboratories. Solid phase microextraction (SPME) was invented by Pawliszyn in 1990. This technique uses a polymer-based sorbent to absorb the analytes from the headspace above the sample. The sorbent, i.e., the SPME fiber, is housed in a syringe-like device. The analytes are then thermally desorbed from the SPME fiber in the injection port of a gas chromatograph. The partition coefficient of the analyte between the stationary phase and the sample matrix determines the extraction efficiency of the SPME fiber, including the capacity and selectivity towards target compounds in the samples.

Polypyrrole (PPy) can be synthesized based on electropolymerization from aqueous solutions. The PPy film is porous and its applications in serving as SPME fiber coating has been reported [2]. Carbon nanotubes (CNTs), discovered by Iijima in 1991, is a material consisting of carbon atoms being arranged in hexagons [3]. The carbons form cylindrical graphitic sheet and are wrapped up into the shape of tubing. The CNTs offer large surface-to-volume ratio, mechanical strength, and thermal stability, which make them attractive as SPME coating material.

In this study, a nanocomposite consisting of PPy and CNTs are synthesized via electrochemical approach for SPME. The experimental conditions including the amount of PPy, CNTs, and the voltage of cyclic voltammetry method are discussed. Saturated alkanes reference is utilized to test the extraction performance of the PPy-CNT-SPME fiber. The proposed SPME coating method shows promising as a SPME extraction medium for ILs analysis.

RESULTS & DISCUSSIONS

Figure 1. The proposed electropolymerization procedure for the preparation of the PPy-CNT-SPME fiber.

*Note:
x= 2, 4, 8, 12 mg
y= 100, 150, 200, 250 μl
z= 0.7, 0.8, 0.9 V

Cyclic voltammetry
- Potential limits: 0.1/**z** V
- Scan rate: 0.05 V/s
- Step: 0.002 V
- Scan number: 1

Figure 3. Comparison of TICs of (a) C7-C30 saturated alkanes reference and (b) diesel fuel standard (25 μg/20-mL HS vial) extracted by the Ppy-CNT-SPME fiber.
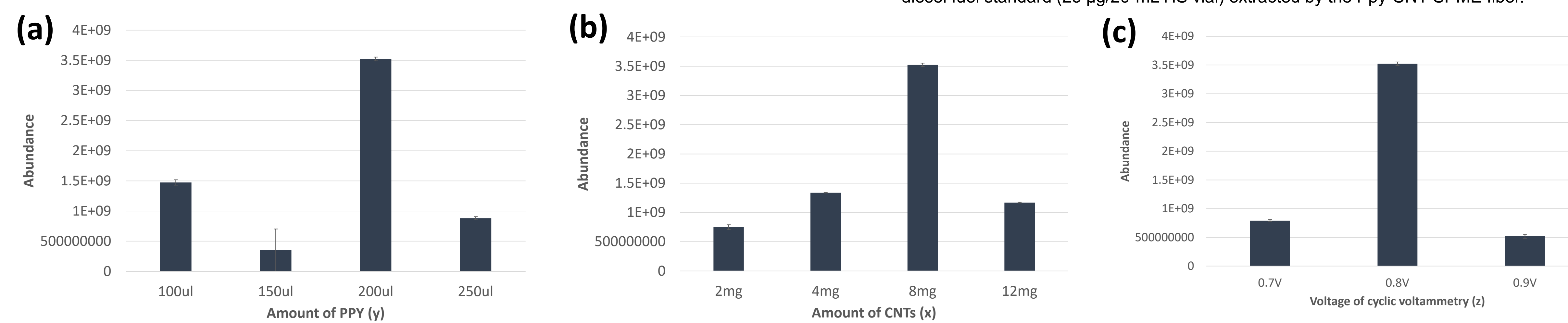

Figure 2. Comparison of peak area vs. (a) amount of PPy (with 8mg of CNTs and 0.8 V of cyclic voltammetry); (b) amount of CNTs (with 200 μl of PPy and 0.8 V of cyclic voltammetry); (c) voltage of cyclic voltammetry (with 200 μl of PPy and 8 mg of CNTs) used for the preparation of the PPy-CNT-SPME fiber.

- The cyclic voltammetry was performed one cycle for the synthesis of PPy-CNTs composite. Multiple cycles of cyclic voltammetry caused the PPy-CNT-SPME fiber coating being too thick and resulting to damage to the fiber upon retraction into the SPME holder.
- The use of a magnetic stirrer with moderate stirring speed (600-700 rpm) helped to maintain the suspension of CNTs in the electrolyte and increase the homogeneity of the synthesized fiber coating.
- Loosely-bonded PPy-CNTs composite was removed by rinsing the SPME fiber with DI water after the electropolymerization procedure, which avoided the contamination of GC injection port and column during sample injection process.

MATERIALS & METHODS (1/2)

Fiber preparation Stainless-steel fibers (0.13mm-o.d.x 5cm-length) were purchased from Hamilton (Reno, NV, USA). A potentiostat (Metrohm DropSens, Oviedo, Spain) with a three-electrode configuration was utilized for the preparation of the PPy-CNT-SPME fiber coating. Each stainless-steel fiber was served as the working electrode. The counter electrode was a platinum wire with a diameter of 0.3 mm (Thermo Scientific Chemicals, Waltham, MA, USA). The reference electrode was a silver and chloride titrations (Ag/AgCl) (4M potassium chloride, KCl) (Thermo Scientific Chemicals) electrode, which was stored in 1M sodium sulfate (Na2SO4) (Supelco Inc.). The procedure of the electropolymerization of the PPy-CNT-SPME fiber coating is demonstrated in Figure 1. The tested parameters included the amount of PPy (y=100, 150, 200, 250 μl), CNTs (x=2, 4, 8, 12 mg), and the voltage of cyclic voltammetry (z=0.7, 0.8, 0.9 V).

Sample C7 - C30 saturated alkanes reference (1,000 μg/mL each component in hexane) (Supelco Inc., Bellefonte, PA, USA) was utilized for the evaluation of the extraction performance of the PPy-CNT-SPME fiber (N=2). Diesel fuel standard (unweathered, 5,000 μg/mL methylene chloride) (Restek, Bellefonte, PA, USA) was used as a real IL sample to test the extraction capability of the PPy-CNT-SPME fiber.

HS-SPME extraction The PPy-CNT-SPME fiber was installed onto a PAL autosampler. The parameters for the HS-SPME extraction are listed in Table 1. A blank analysis was conducted before a new sequence of runs to confirm that the carry-over of analytes has been removed.
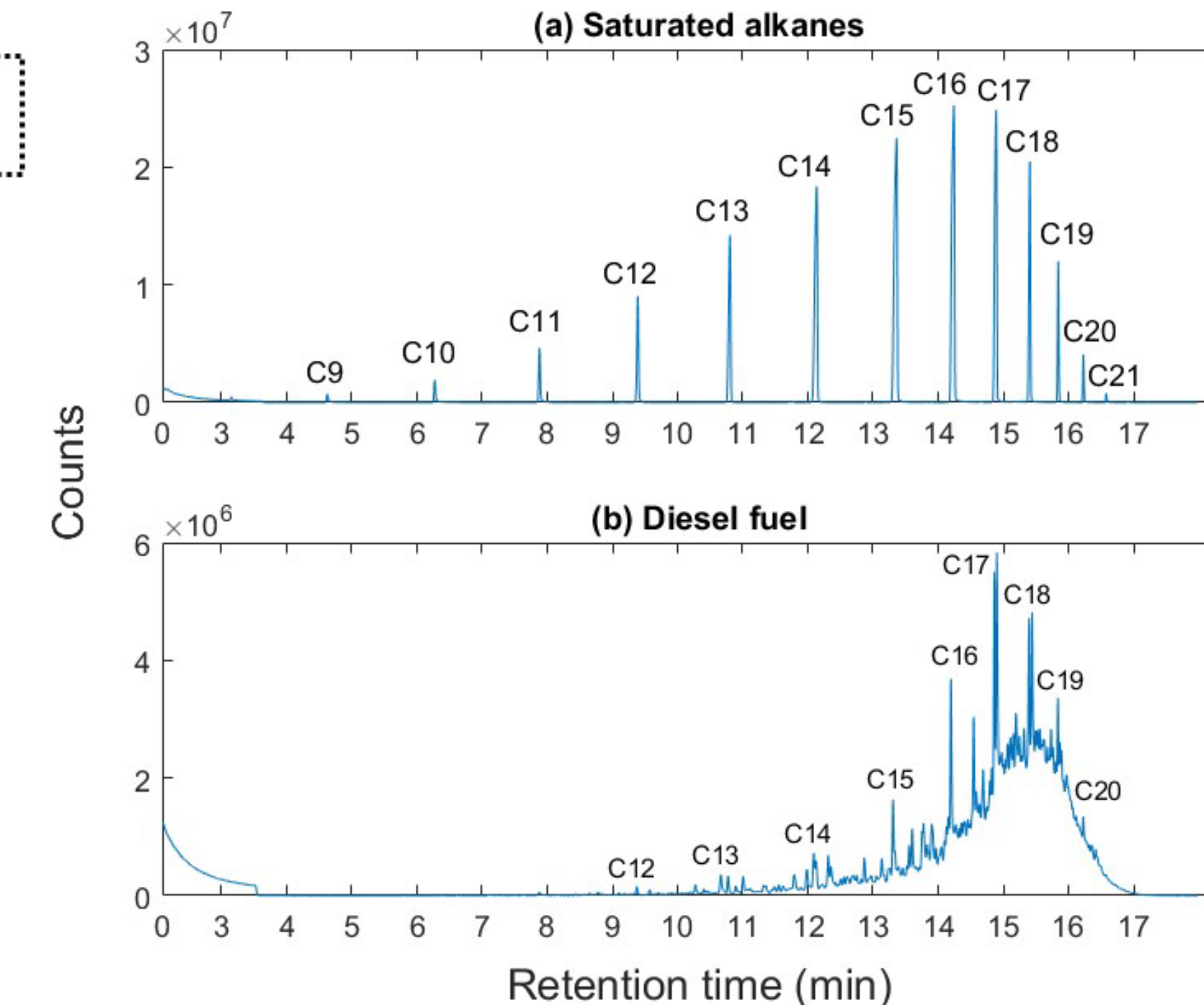
MATERIALS & METHODS (2/2)

GC/MS analysis The GC/MS analysis was performed on an Agilent 7890B gas chromatograph coupled with a 5977A mass spectrometer (Agilent Technologies, Santa Clara, CA). The settings of GC/MS are shown in Table 2. The chromatographic separation was conducted on a HP-5ms capillary column with a dimension of 30 m-length × 0.25 mm-inner diameter × 0.1 μm-film thickness (Agilent Technologies). The total analysis time was 17 min.

Table 1.	HS-SPME steps	Condition
	Pre-fiber conditioning temperature (˚C)	250
	Pre-fiber conditioning time (s)	60
	Pre-incubation time (s)	300
	Incubation temperature (˚C)	80
	Agitator speed (rpm)	250
	Extraction time (s)	120
	Desorption time (s)	120
	Post-fiber conditioning temperature (˚C)	250
	Post-fiber conditioning time (s)	600

Table 2.	GC/MS parameters	Condition
	Carrier gas	Helium (purity > 99.999%)
	Flow rate (mL/ min)	1
	Back inlet heater (˚C)	250
	Back inlet mode	Splitless
	GC oven initial temperature (˚C)	40
	Hold time (min)	2
	Rate #1 (˚C/min), Oven temperature #1 (˚C), Hold time #1 (min)	10, 150, 0
	Rate #2 (˚C/min), Oven temperature #2 (˚C), Hold time #2 (min)	30, 300, 0
	Ion source	EI
	Source temperature (˚C)	230
	Quad temperature (˚C)	150
	Electron energy (eV)	70.3
	Solvent delay (min)	2
	Scan mass (m/z)	45-450

CONCLUSIONS

- The optimal experimental condition for the electrochemical synthesis of the PPy-CNT-SPME composite is 200 μL of PPy, 8 mg of CNTs, and 0 V to +0.8 V of cyclic voltammetry.
- The PPy-CNT-SPME fiber was capable of extracting diesel fuel with a concentration of 25 μg/20-mL HS vial (heavy petroleum distillate based on the ASTM E1618-19 IL classification scheme).
- The proposed electrochemical method was simple, fast, cost-effective, and reduced organic solvent-consumed.

REFERENCES

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