Evaluation of Headspace Solid Phase Microextraction of Diesel Fuel from Cotton Swabs for Forensic Analysis

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- There are no real or apparent conflicts or interest related to the content of this presentation.
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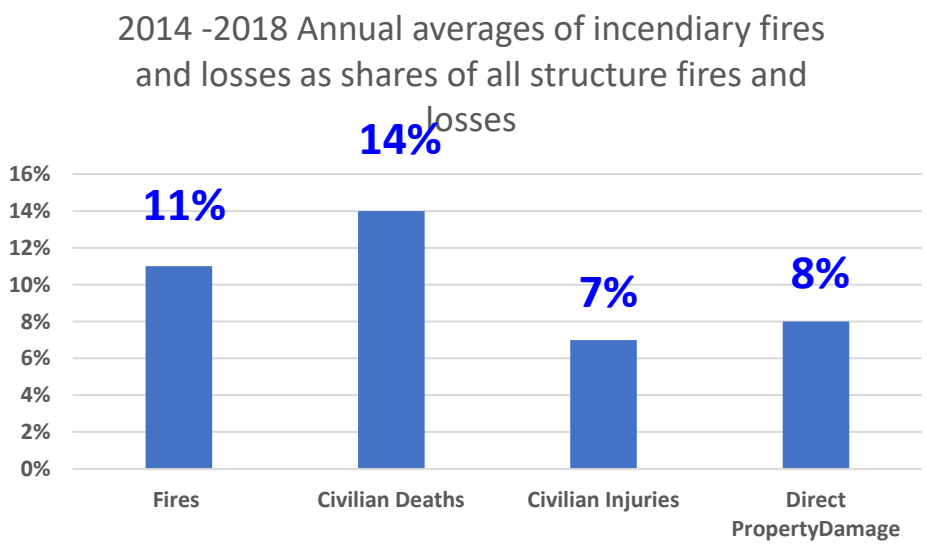
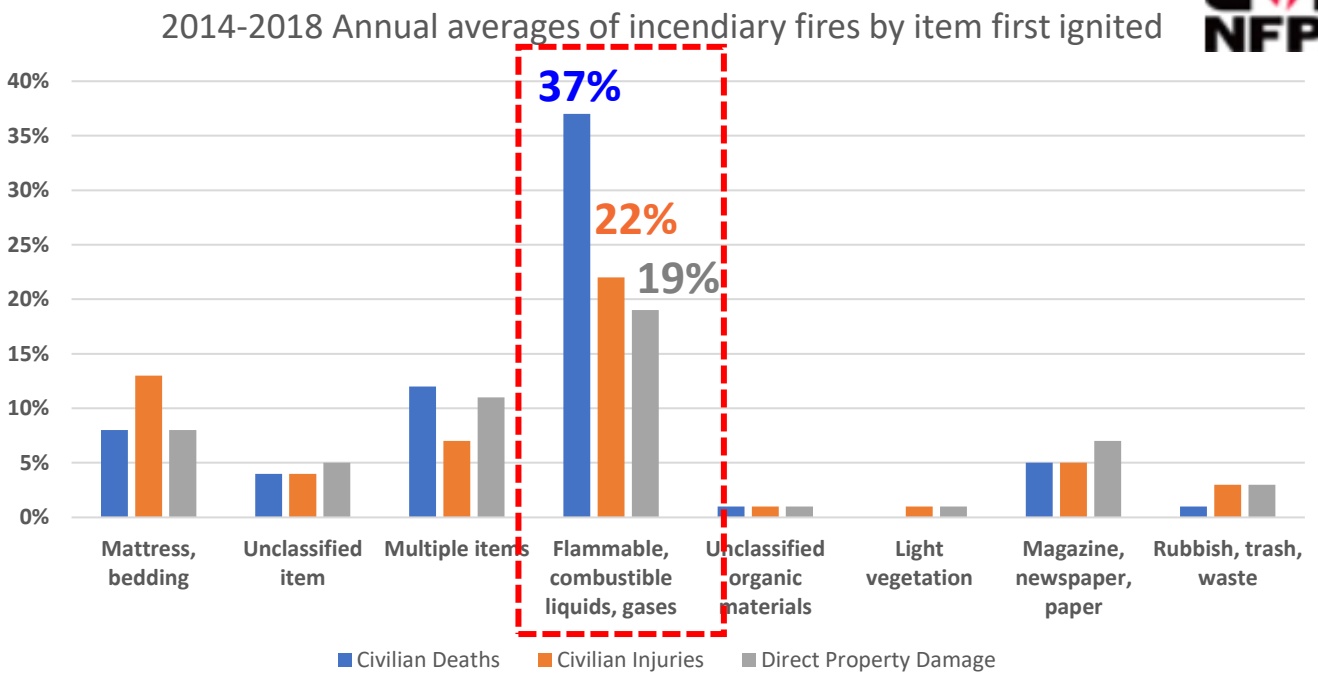
Ignitable Liquids in Fire Cases

- Annual average of 52,260 incendiary fires were reported (2014-2018)
- Annual casualties including 400 civilian deaths, 950 civilian injuries, and $815 million in direct property damage
- Gasoline, diesel, kerosene, mineral spirit, etc. are one of the most commonly-used ignitable liquids (ILs) in arson fires
  - ➢ Easy to obtain and transport
  - ➢ Volatility and flammability

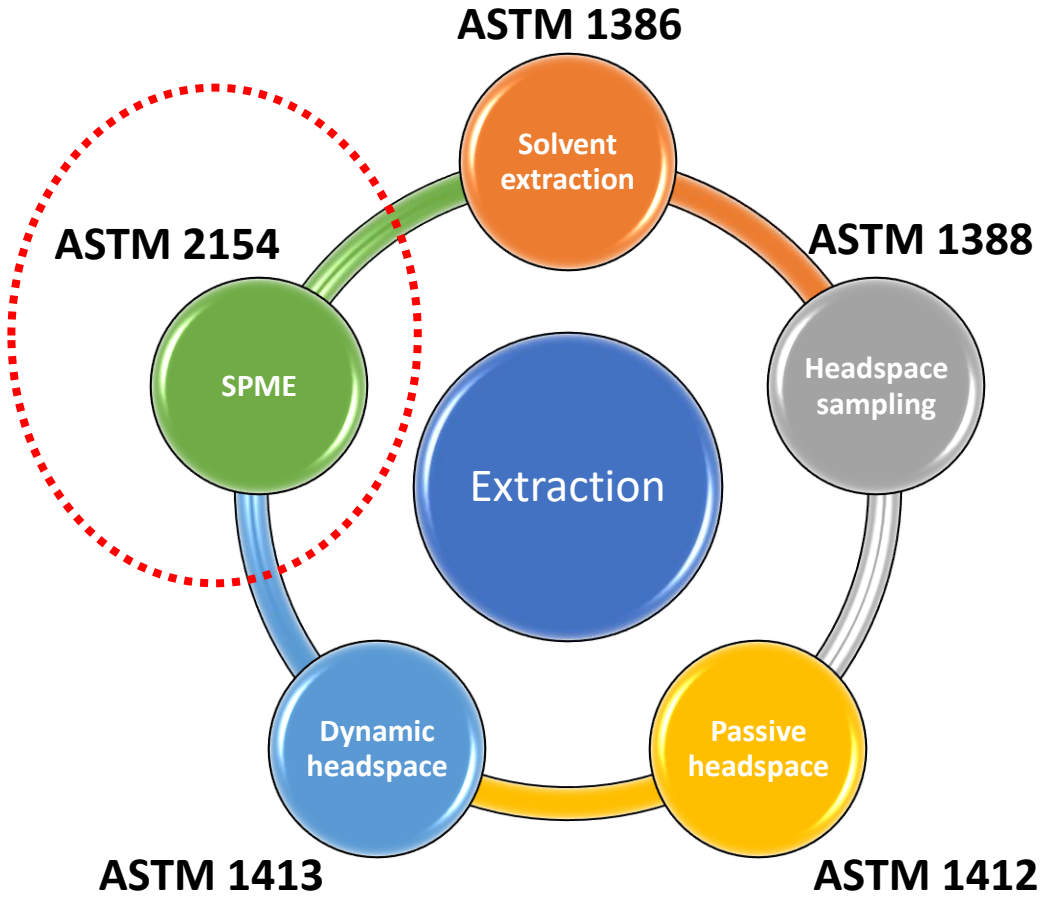




National Fire Protection Association (NFPA), Intentional Structure Fires. https://www.nfpa.org//-/media/Files/News-and-Research/Fire-statistics-and-reports/US-Fire-Problem/Fire-causes/osintentional.pdf, 2021.

Ignitable Liquids Analysis

- Gas chromatography and mass spectrometry (GC/MS) has been regarded as a “gold standard” for forensic ILs (ASTM E1618-19)
- **Sample preparation** to separate and pre-concentrate the small quantities of IL residues from the matrix



Standard Test Method for
Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography-Mass Spectrometry[1]

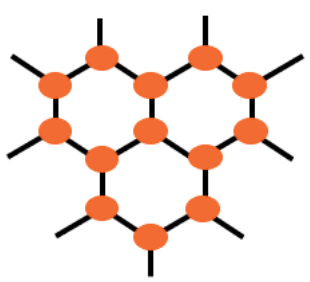
Solid Phase Microextraction (SPME)

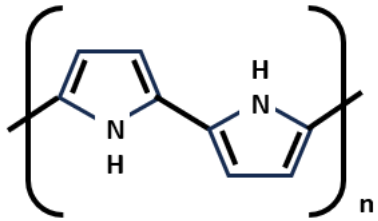
- First introduced in 1990
- Integrates sampling, isolation, concentration, and introduction into one single step
- Advantages:
  - solvent-free, fast, ease of operation, capability of automation, high sensitivity
  - Extraction of volatile and semi-volatile organic compounds
- Commercial SPME fibers:
  - Divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS), polydimethylsiloxane (PDMS), polydimethylsiloxane/divinylbenzene (PDMS/DVB), carboxen/polydimethylsiloxane (CAR/PDMS), polyacrylate (PA), etc.
  - Issues:
    - Fragility, thermal instability (operating temperatures between 240 – 280 °C), poor selectivity, expensive
- ***Development of new SPME fiber coatings***

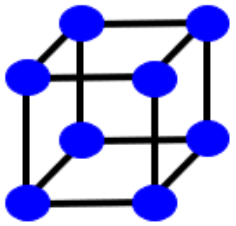
Novel SPME Fiber Coating Materials

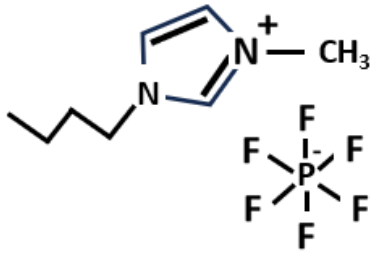
- Various materials used to fabricate SPME fiber coatings

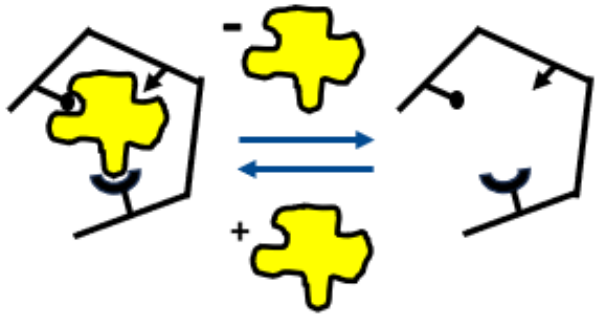
Carbon **Conductive polymers CPs** **Metal organic frameworks (MOF)** **Ionic liquids** **Molecular imprinted polymers… (MIPs)**











- Unique hydrophobic/hydrophilic structure, adjustable pore dimensions, and capability of being functionalized
- Ensure strong interaction between coating materials and analytes in the sample and the immobility of the coating materials on substrates

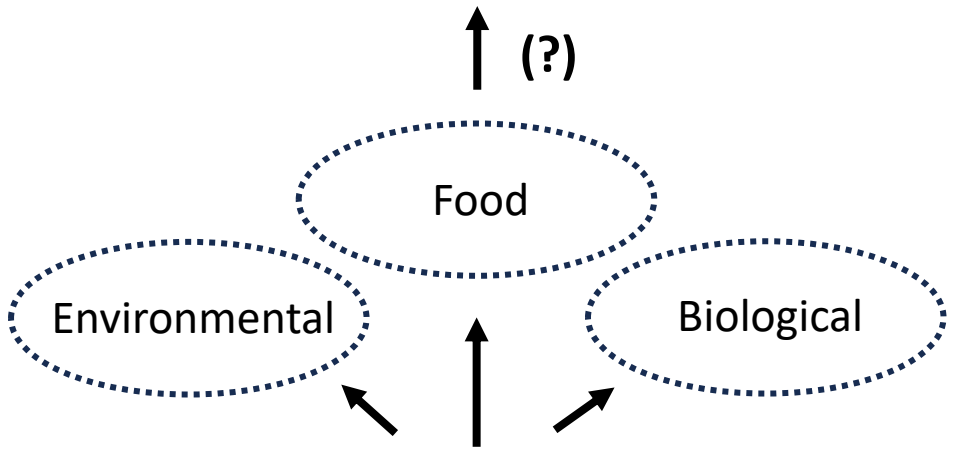
Carbon nanotubes (CNTs) as SPME fiber coating

- First invented in 1991
- Composed of single or multiple graphite sheets rolled into a cylinder(s)
- Morphology: SWCNTs, MWCNTs

Coating material (CNTs)

High length-to-diameter (≧1000) Large surface area	Significant **absorption** capacity
Non-covalent interactions	**Affinity** towards π-electron conjugated system and/or hydrophobic compounds
Thermal/mechanical stability	**Surface enhancement** for CPs
Capability of functionalization	**Homogeneous coating** and certain selectivity

Ignitable liquids



Robustness, sensitivity, better selectivity, improved thermal stability

Coating supports

(1) Fused silica
(2) Metal wires

Coating methods

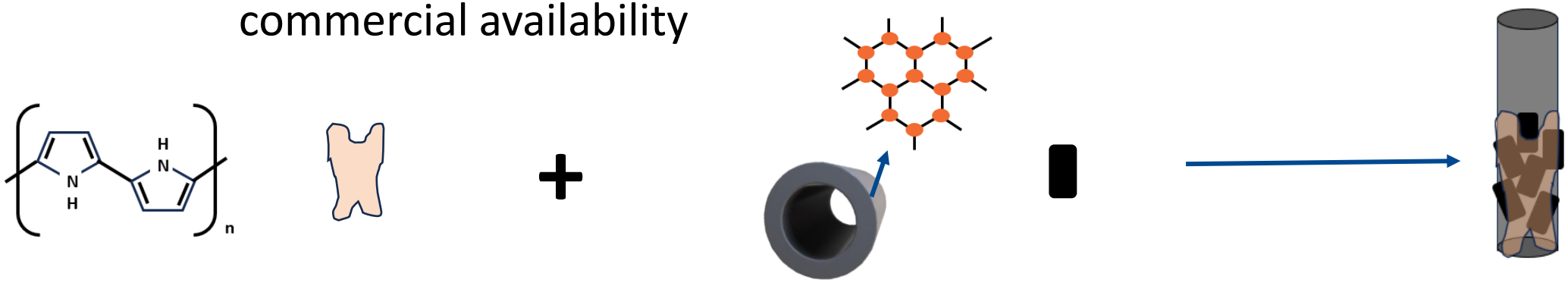
(1) Physical deposition
(2) Sol-gel technique
(3) Chemical bonding
(4) Electrochemical deposition

SPME

CNTs-SPME fiber

Preparation of PPy-CNT-SPME Fiber

- **Conductive polymer (CP) nanocomposites** as the coating material
  - **Pyrrole (Py)**
    - Ease of fabrication onto a metal support, environmental stability, commercial availability



Polypyrrole **Carbon nanotubes** **Nanocomposite**

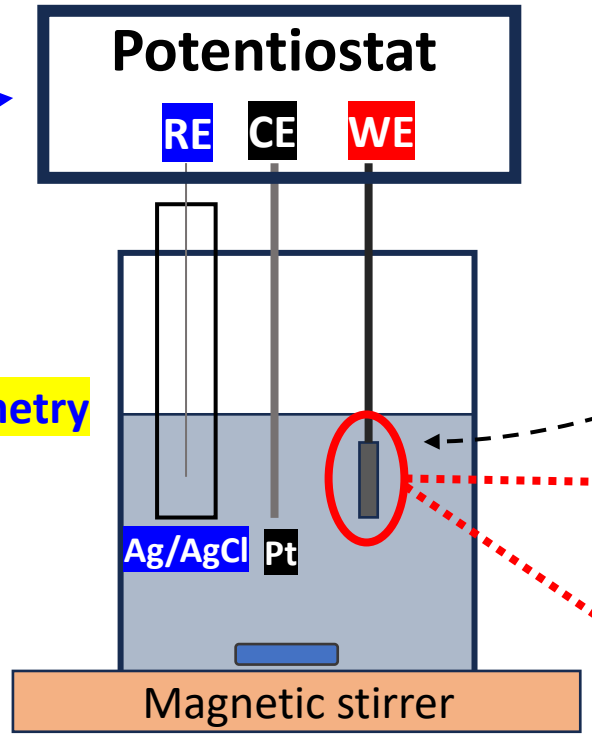
- **Electrochemical deposition** as the coating method
  - Flexibility, ease of control, mechanical strength
- **Stainless-steel fiber** as the supporting substrate
  - Unbreakable material

8 mg **CNTs** + 6 mL sodium dodecyl sulfate (0.2M) → Sonicate for 5 min

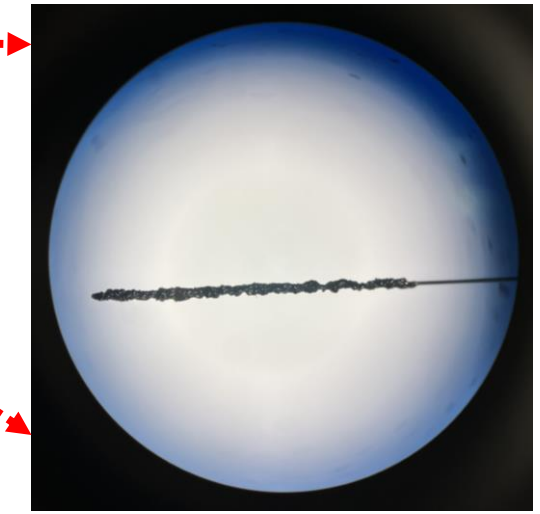
200 µl **Py** + 6 mL sodium chloride (1M) → Sonicate for 5 min

Sonicate for 5 min + Sonicate for 5 min → Mix and sonicate for 30 min

Cyclic voltammetry (CV)



CV parameter	Condition
Potential limits	0.1/0.8 V
Scan rate	0.05 V/s
Step	0.002 V
Scan number	1



PPy-CNT nanocomposite

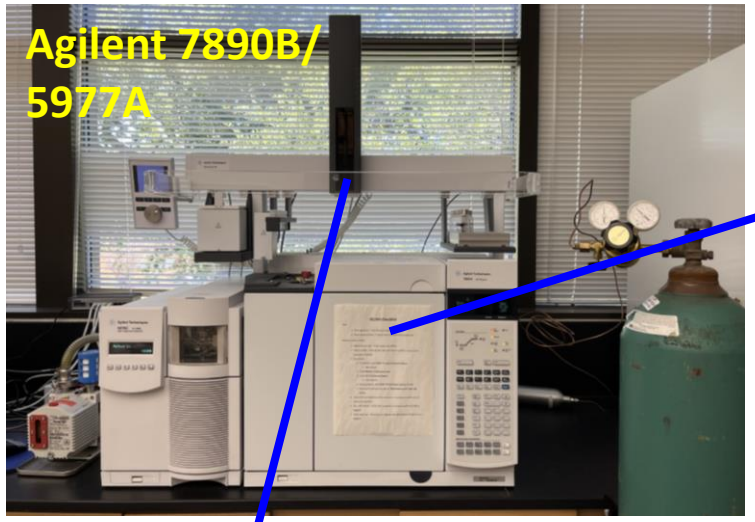
Preparation of Samples and Comparison Tests

- Samples
  - Neat diesel fuel: Serial dilution of the stock solution in the concentration range of 39 – 5,000 µg /mL in methanol (N = 8)
  - Spiked cotton swab: 5 µL of calibrator samples spiked onto 60 mg of cotton swab

- Comparison test

Extraction method	Procedure	Note
Solid phase microextraction (100 µm PDMS-SPME fiber)	Same as the PPy-CNT-SPME	ASTM E2154-15a
Passive headspace concentration (Activated charcoal strip)	• Neat diesel fuel: 625 µg of diesel fuel added to an unlined quart paint can • Spiked sample: 625 µg of diesel fuel spiked onto 3 g of cotton balls in an unlined quart paint can • Activated charcoal strip • Heated to 80°C/16 hours, desorbed by 1 mL pentane	ASTM E1412-19

HS-SPME-GC/MS Analysis



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

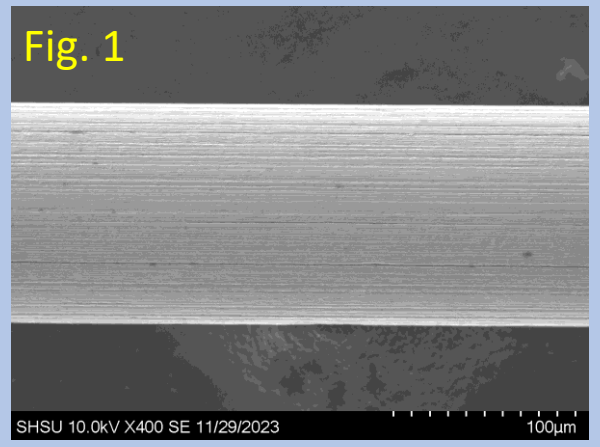
GC/MS parameters	Condition
Carrier gas	Helium (purity > 99.999%)
Flow rate (mL/ min)	1
Back inlet heater (˚C)	250
Back inlet mode	Splitless
GC oven initial temperature (˚C)	40
Hold time (min)	2
Rate #1 (˚C/min), Oven temperature #1 (˚C), Hold time #1 (min)	10, 150, 0
Rate #2 (˚C/min), Oven temperature #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

Scanning Electron Microscope (SEM) Analysis

Hitachi SU3500 variable-pressure SEM

Bare stainless-steel fiber

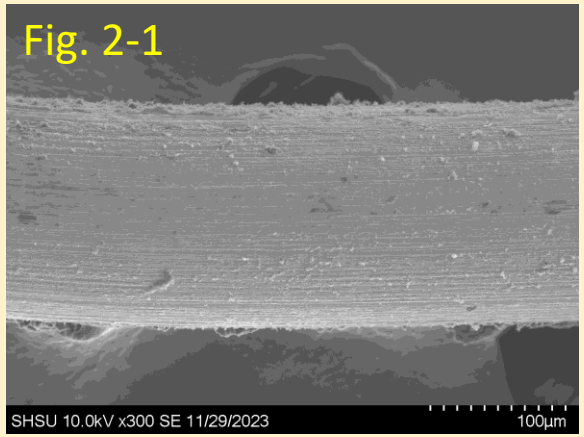
Fig. 1



10KV, 400x

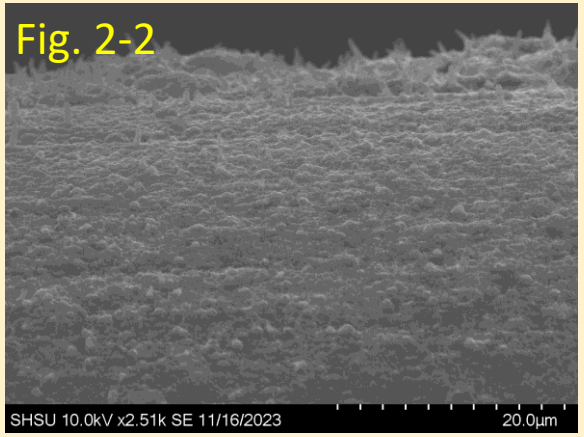
PPy-SPME fiber

Fig. 2-1



10KV, 300x

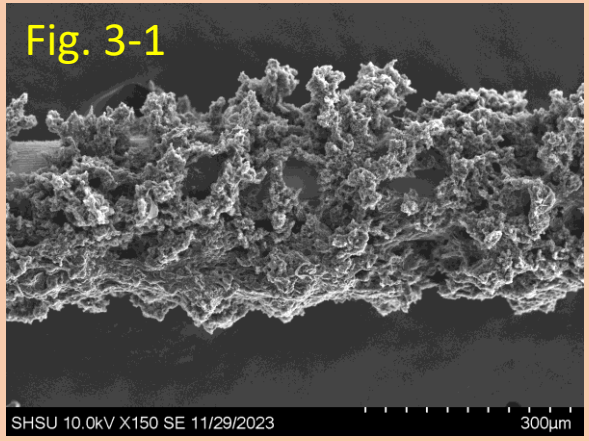
Fig. 2-2



10KV, 2,510x

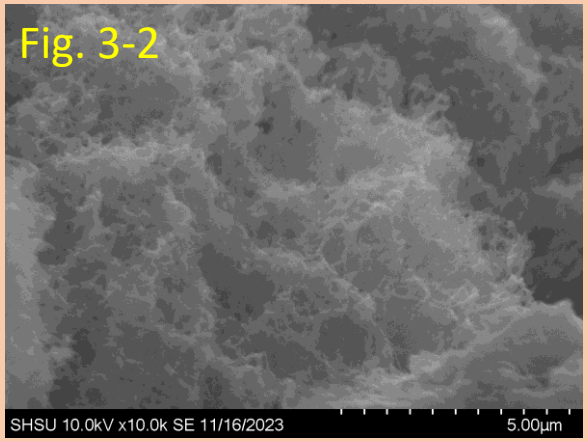
PPy-CNT-SPME fiber

Fig. 3-1



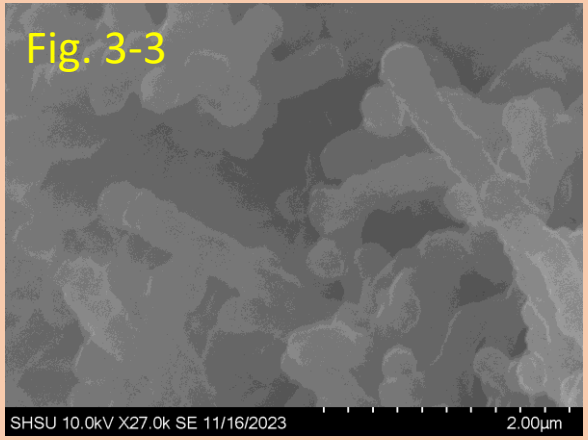
10KV, 150x

Fig. 3-2



10KV, 10,000x

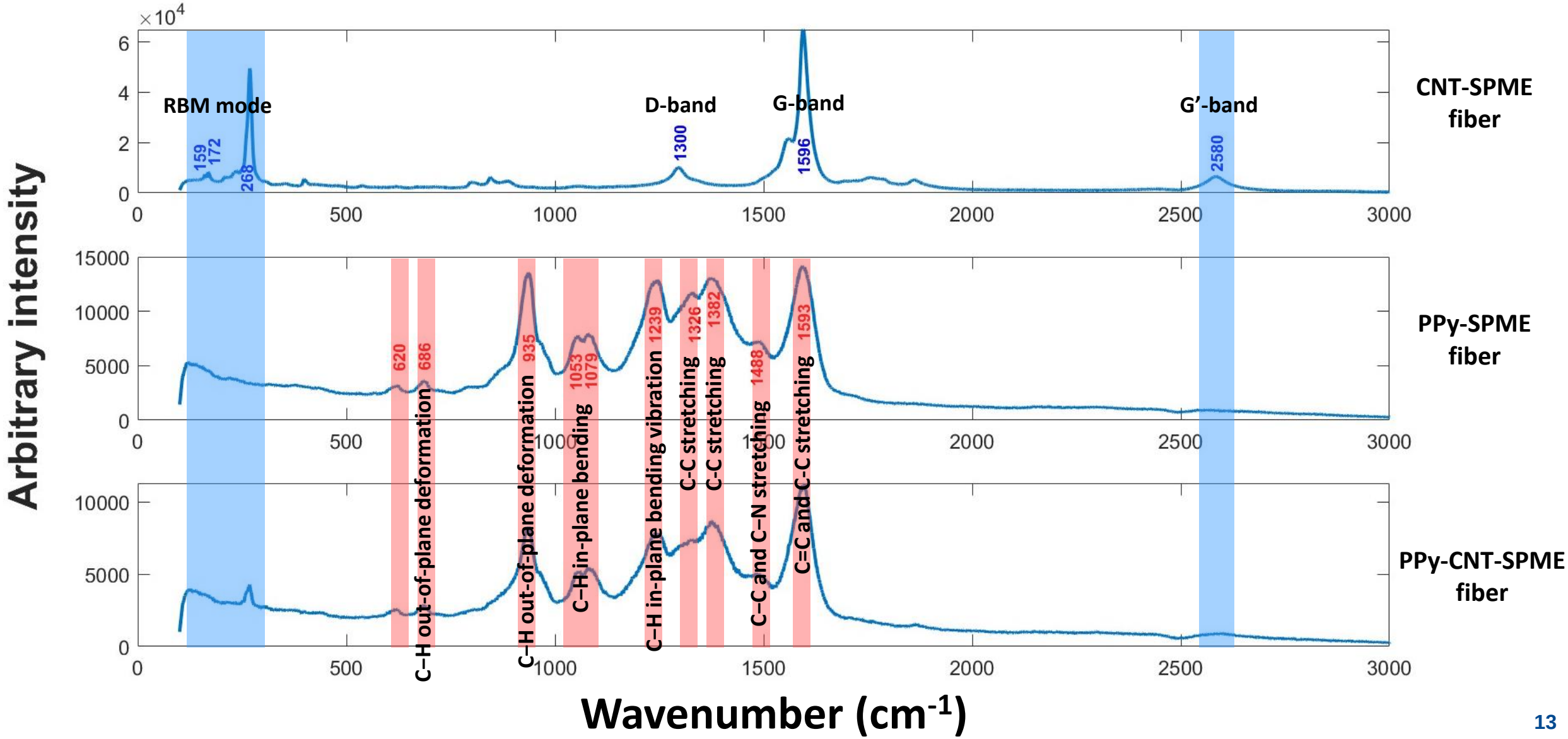
Fig. 3-3



10KV, 27,000x

Raman Microscope Analysis

inVia™ InSpect, Renishaw Raman confocal microscope



Calibration performance for n-Alkanes in Diesel Fuel

(a) Neat diesel fuel (Calibration range: 0.19 – 25 µg /20-mL HS vial)

n-Alkanes	Linear range [µg /20-mL HS vial]	Equation	Coefficient of determination, R^2	LOD [µg /20-mL HS vial]	Statistical significance		Lack of fit	
					F-test	P-value	F-test	P-value
C12	1.56 - 12.50	y = 3353.8x + 23328	0.96	0.19	266.75	1.54 E-08	0.34	0.72
C13	1.56 - 12.50	y = 6659.6x + 55072	0.96	0.19	208.79	5.00 E-08	0.49	0.63
C14	1.56 - 12.50	y = 10892x + 100240	0.94	0.19	167.14	1.45 E-07	0.59	0.57
C15	1.56 - 12.50	y = 25561x + 163800	0.97	0.19	271.78	1.41 E-08	0.25	0.78
C16	3.13 – 25.00	y = 64876x + 170000	0.98	0.19	397.23	2.22 E-09	3.07	0.10
C17	3.13 – 25.00	y = 77962x + 164920	0.99	0.19	820.97	6.24 E-11	0.72	0.51
C18	3.13 - 12.50	y = 96352x + 64467	0.99	0.19	956.93	9.52 E-09	9.38	0.02*
C19	3.13 - 12.50	y = 73478x - 7034.1	1.00	0.19	2002.10	7.28 E-10	4.74	0.07
C20	0.78 - 12.50	y = 59893x - 46203	1.00	0.19	4360.40	8.17 E-18	1.57	0.26

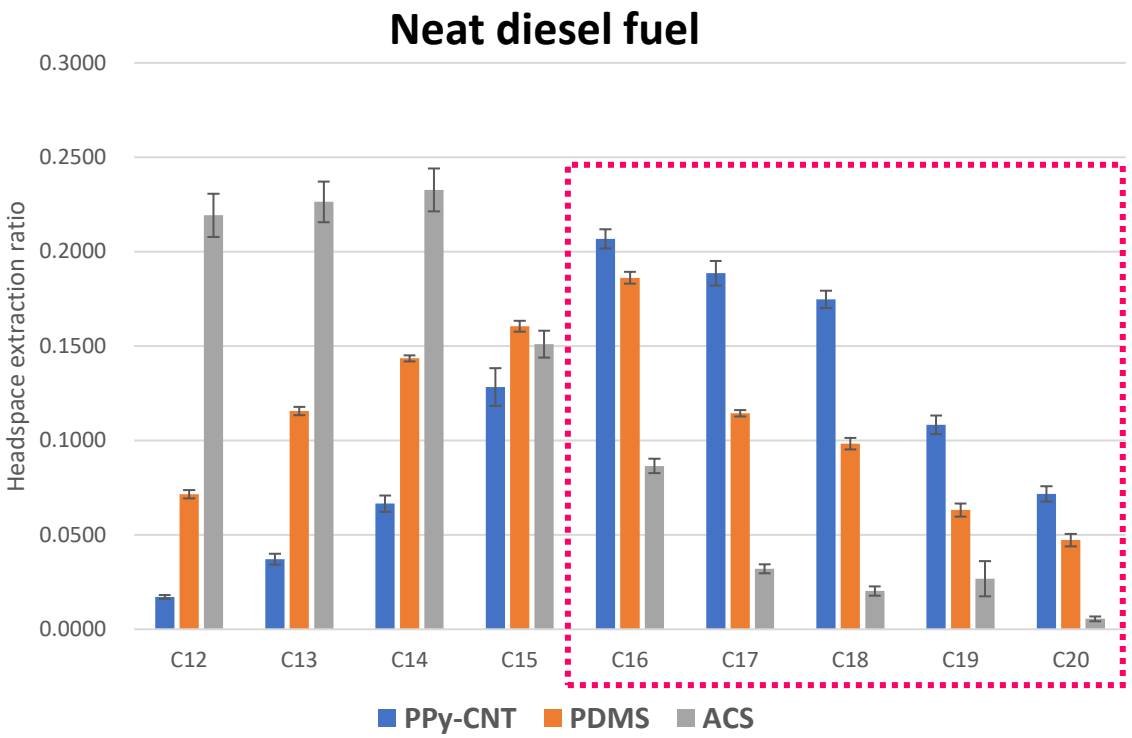
Note: * P-value > 0.01

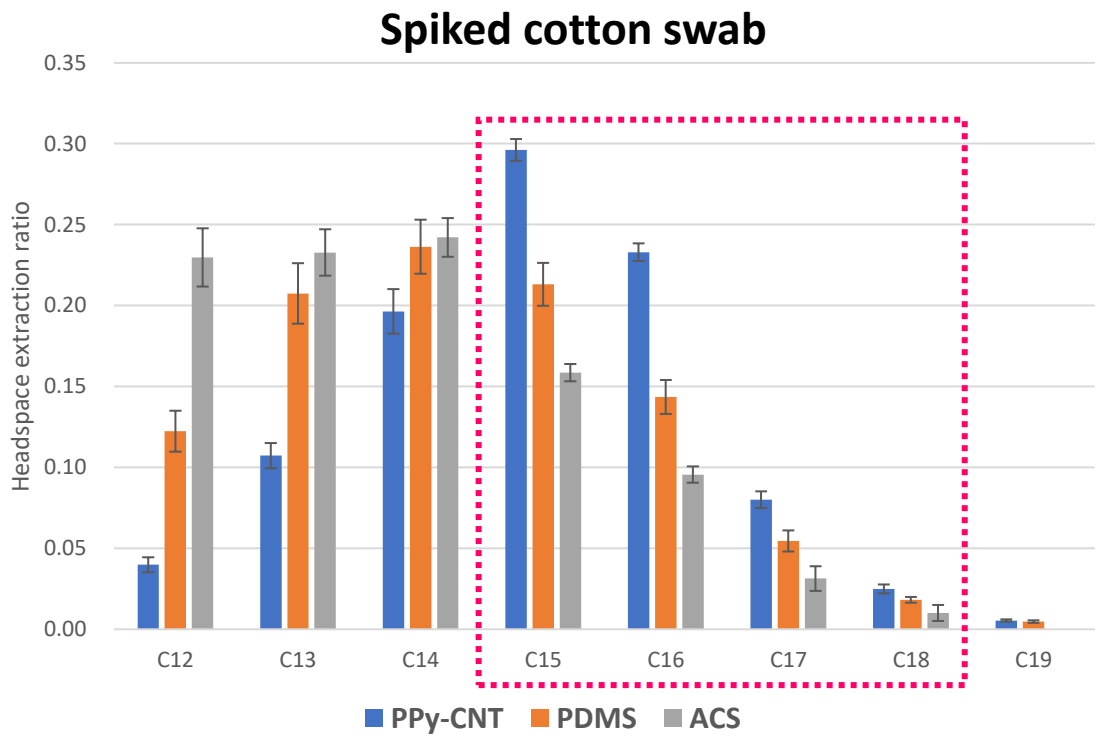
(b) Spiked cotton swabs (Calibration range: 0.19 – 25 µg /20-mL HS vial)

Normal alkanes	Linear range [µg /20-mL HS vial]	Equation	Coefficient of determination, R^2	LOD [µg /20-mL HS vial]	Statistical significance		Lack of fit	
					F-test	P-value	F-test	P-value
C12	3.13 - 25	y = 4942.6x + 14166	0.98	0.19	437.30	1.39 E-09	0.08	0.92
C13	3.13 - 25	y = 10610x + 47234	0.98	0.19	519.36	5.97 E-10	0.40	0.69
C14	3.13 - 25	y = 17883x + 107450	0.98	0.19	490.93	7.87 E-10	1.24	0.34
C15	0.39 - 6.25	y = 55133x + 17895	0.99	0.19	881.55	2.48 E-13	3.41	0.06
C16	0.19 - 12.50	y = 45977x + 18222	1.00	0.19	4967.5	1.89 E-24	0.09	0.99
C17	3.13 - 25	y = 29865x - 50867	0.99	0.19	676.40	1.63 E-10	0.49	0.63
C18	0.39 - 3.13	y = 5436.1x + 54.656	0.96	0.19	220.60	3.84 E-08	0.96	0.42
C19	0.39 - 3.13	y = 1121.9x + 157.64	0.92	0.19	107.77	1.13 E-06	0.71	0.52

Comparison of PPy-CNT-SPME Fiber with Other Extraction Technique

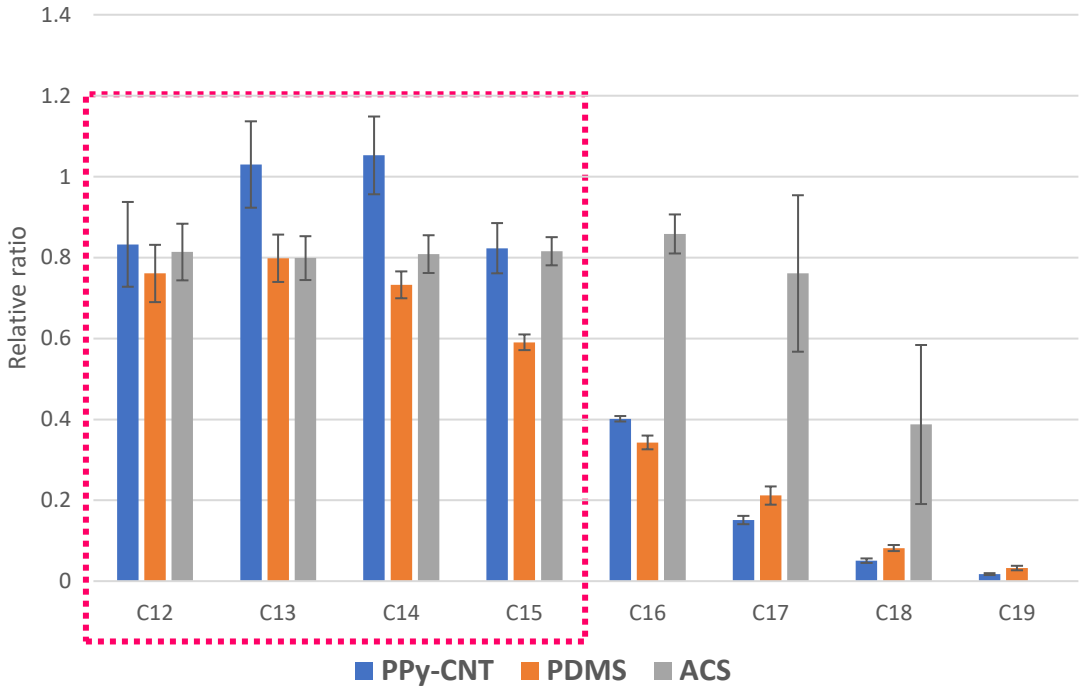
(a) Target compound ratio (TCR) (3.13 µg /20-mL HS vial)



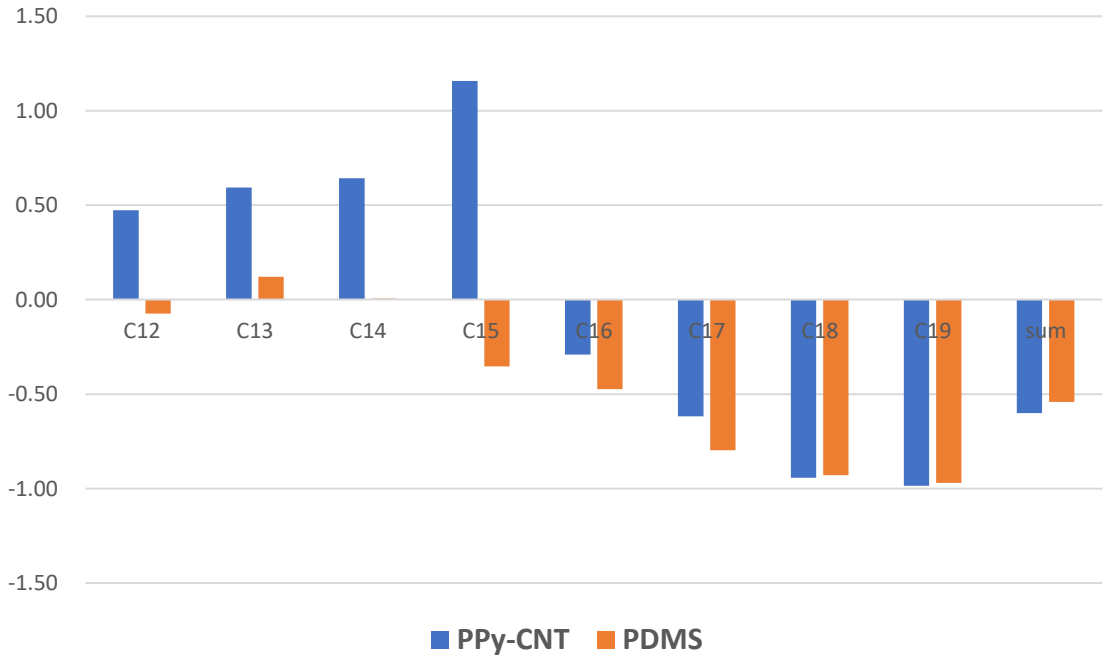


Comparison of PPy-CNT-SPME Fiber with Other Extraction Technique

(b) Relative ratio (RR) (3.13 µg /20-mL HS vial)



(c) Matrix effect (ME)



Diesel Fuel Profile with Exposure Time Elapsed in an Ambient Environment

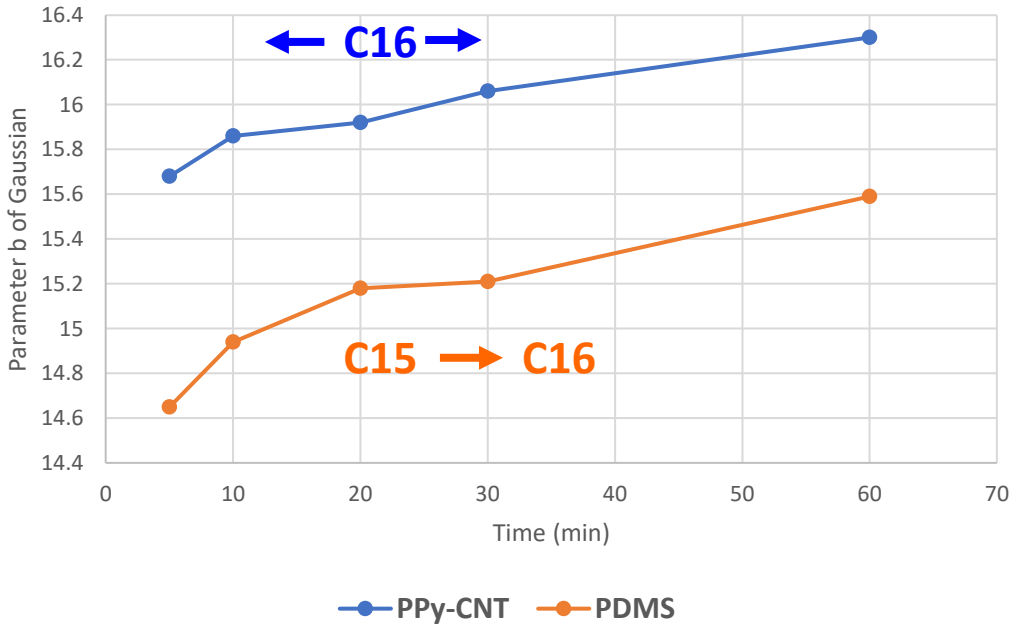
Centroid

$$y = \sum_{i=1}^{n} a_i e^{\left[-\left(\frac{x-b_i}{c_i}\right)^2\right]}$$

Amplitude Peak width

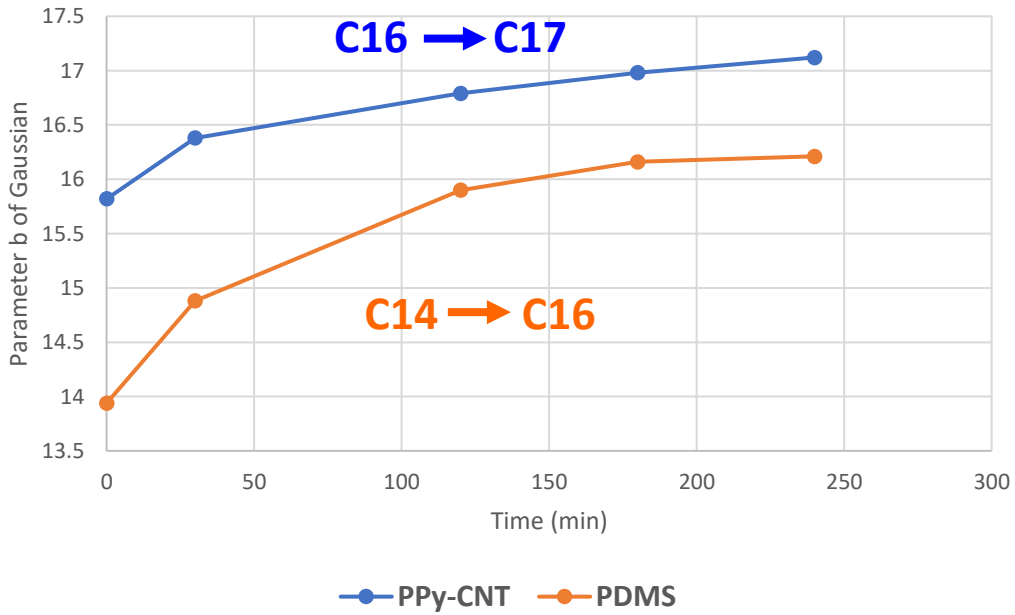
(a) Spiked samples with different exposure times

- 5 µL of 5,000 µg /mL calibrator sample spiked to a cotton swab
- 5, 10, 20, 30, and 60 minutes
- Diesel residues could be identified after being exposed for 1 hour



(b) Transferred samples with different deposition times on glass slides

- Deposit 5 µL of the 5,000 µg /mL calibrator sample to a glass slide
- 30, 120, 180, and 240 minutes
- Diesel residues deposited on a non-porous surface could be extracted and identified after being exposed for 4 hours



Conclusions

- PPy-CNT nanocomposite was successfully synthesized and coated on a metal wire for SPME through electrochemical deposition
  - Porous structure, high mechanical strength, controllable coating thickness
  - No need for any adhesives or oxidant
- PPy-CNT nanocomposite enhanced conductive polymer's extraction efficiency
- Good sensitivity (0.19 µg /20-mL; identification of diesel residues after 1 hour/4 hours of exposure) and linearity (0.78 – 25 and 0.19 – 25 µg /20-mL for neat diesel and spiked samples)
- Affinity towards heavier alkanes (>C15)
  - TCR C16 -C20 in neat diesel between 7.2 ± 0.4 and 20.7 ± 0.5 %
  - TCR C15 – C18 in spiked samples between 2.5 ± 0.3 and 29.6 ± 0.7 %
- Matrix effect was present when using cotton swabs as an evidence collection tool for diesel fuel
- Gaussian model can be used to characterize HS-SPME-GC/MS profiles of heavy petroleum distillate

Future work

- Assess the extraction capabilities in other ignitable liquids
- Evaluate matrix effect from other complex samples

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Thank you for your attention!

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