Electrospun polyacrylonitrile nanofibers as miniaturized layer materials for ultra-thin layer chromatography

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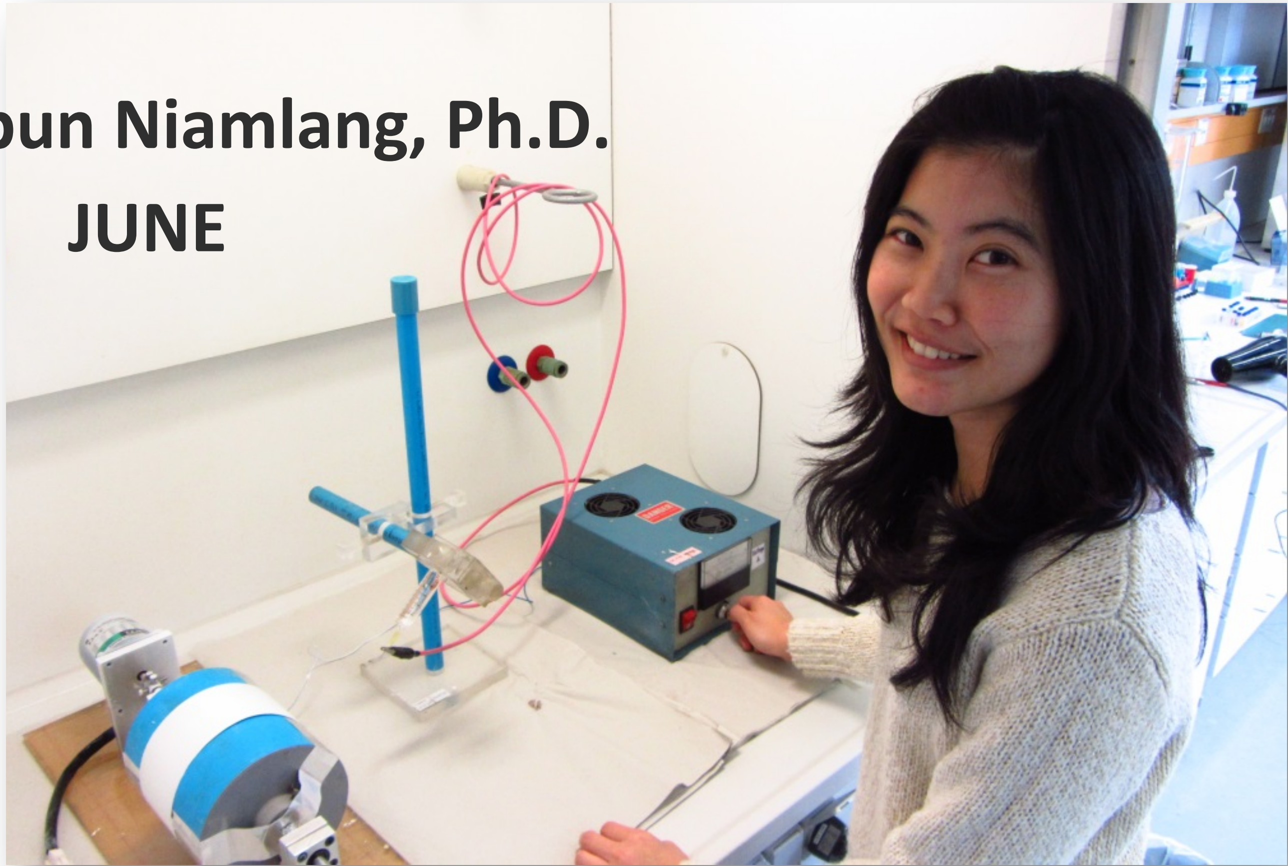
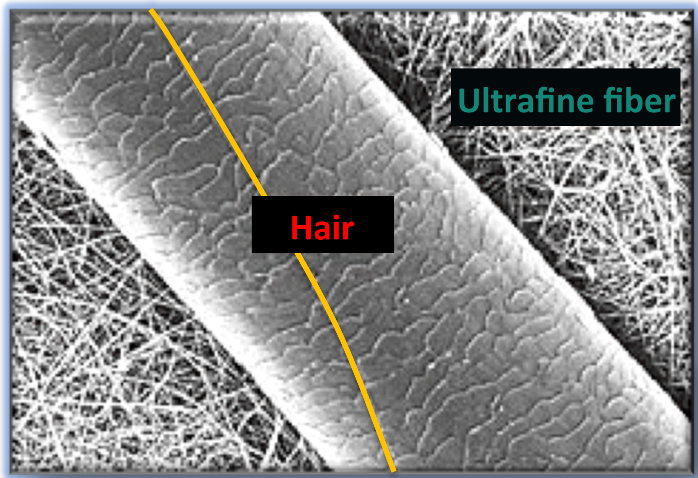
JUNE



Nanofibers

Fibers with diameters less than 1000 nanometers.



Advantages of Ultrafine fibers

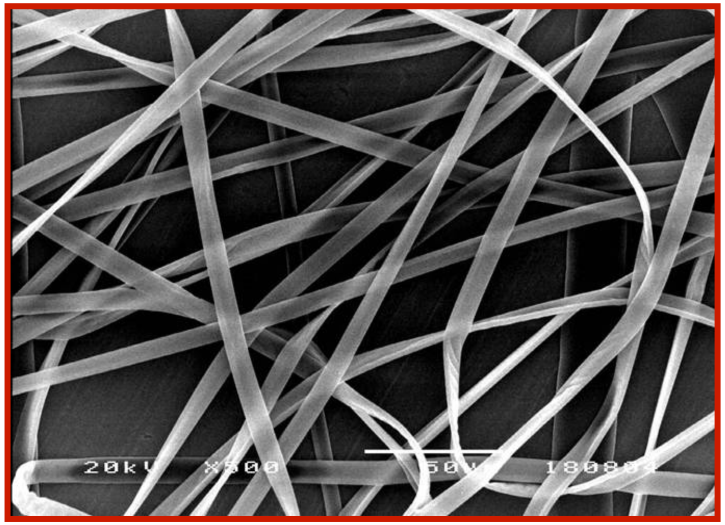
- Large surface area to volume ratio
- Large length to diameter ratio
- High porosity with small pore size
- Flexibility for surface functionalization

Applications

- Composite reinforcements
- Capacitors
- Drug delivery systems
- Energy storage
- Filter

Electrospinning (electrostatic spinning)

- A process capable of producing ultra-fine fibers with diameters in the range of nanometers to micrometers by using an electrical force applied to polymer solution or polymer melt.



Electrospun Polystyrene Fibers

Polymer solution/melt → Fibers

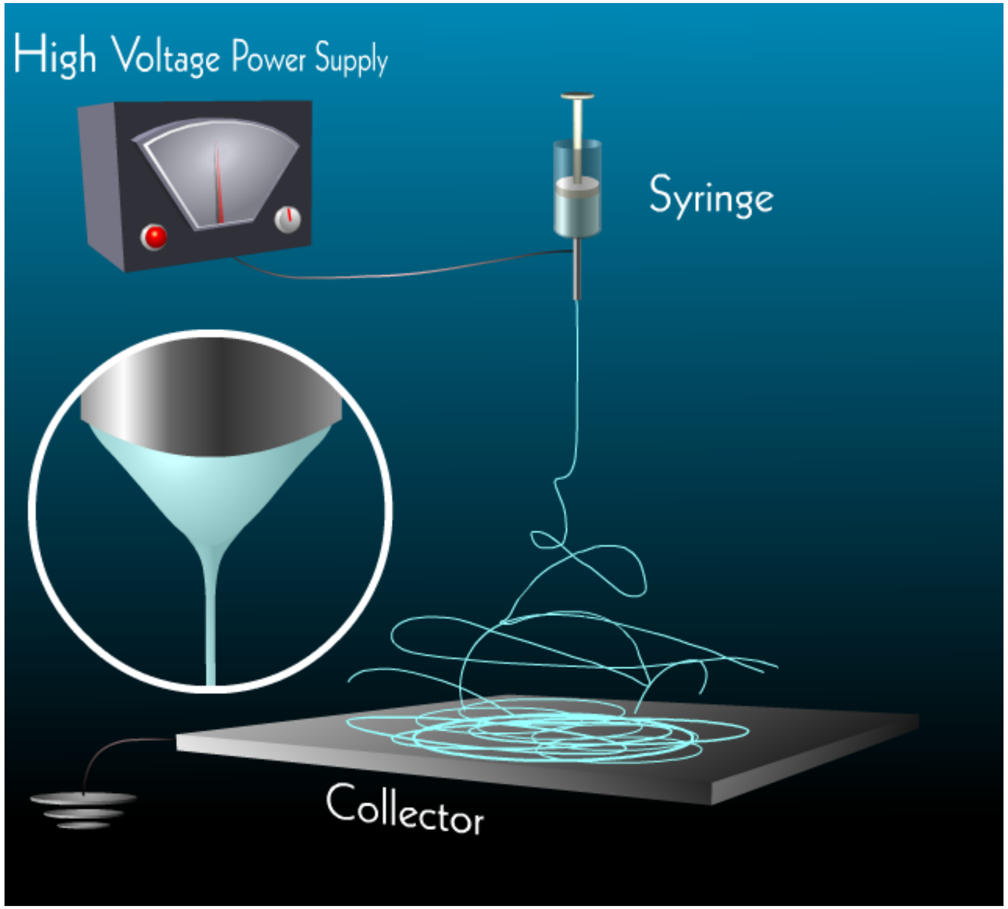
Produces fibers with diameter = 40-2000 nm

Advantages

- Fast process
- Simple process
- Require less materials

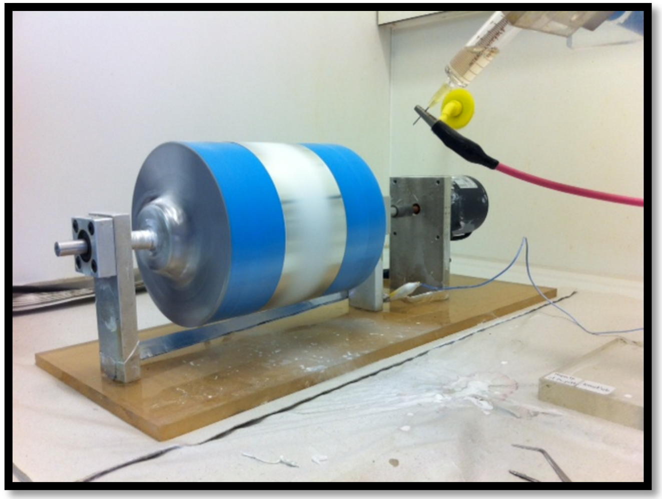
A. Frenot, I.S. Chronakis, Current Opinion in Colloid and Interface Science 8 (2003) 64-75

Electrospinning Apparatus



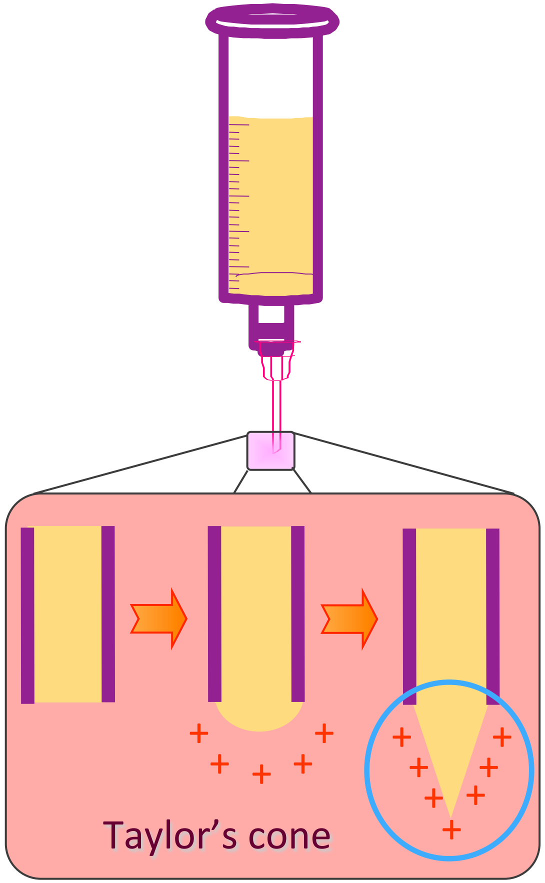
Components

- A high voltage supplier
- A capillary tube with a needle of small diameter
- A metal collector



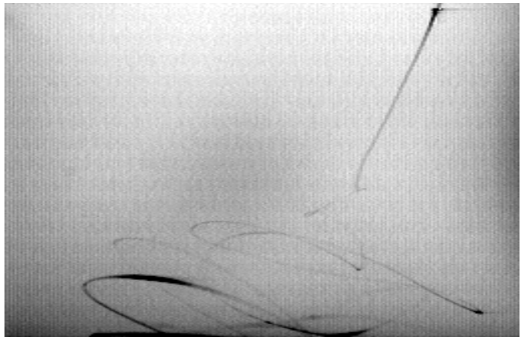
Fiber Formation in Electrospinning

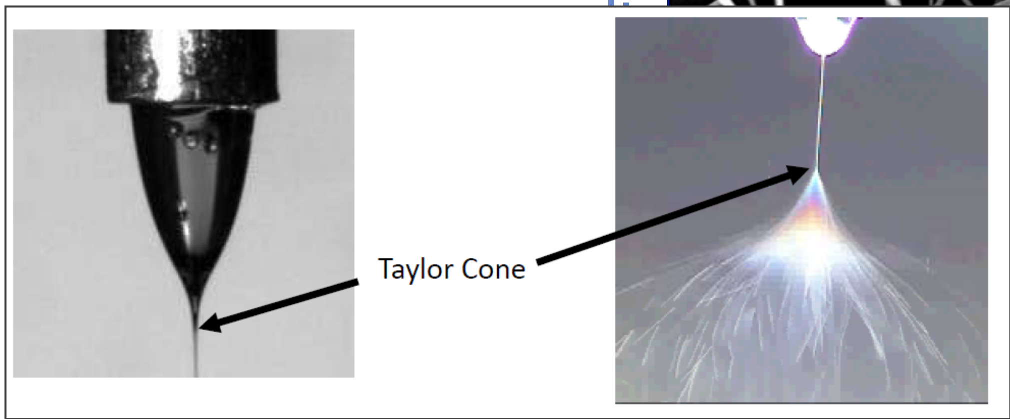
1. Initiation of the jet



2. Continuous flow of the jet

Bending Instability

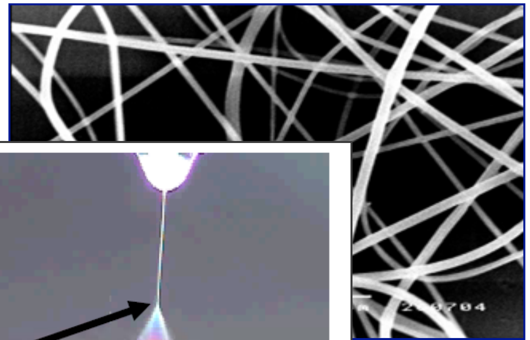




3. Solidification of the jet

Charged jet thins down
Dries out / solidifies

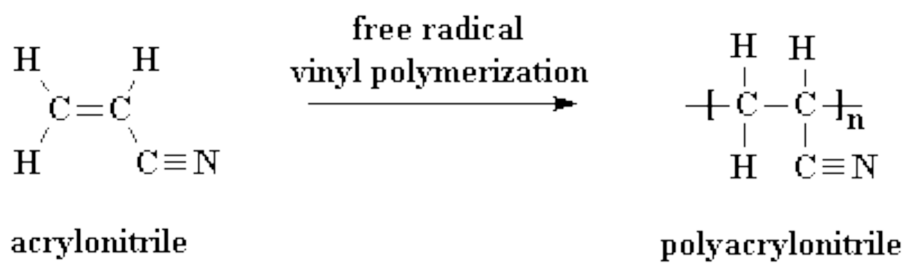
Fibers



Parameters of Electrospinning Process

- The ability of polymer solution to form uniform fibers is depend on many parameters:
  - Solution properties
    - concentration
    - viscosity
    - conductivity
    - surface tension
  - Processing conditions
    - electrical potential
    - collection distance
  - Ambient conditions
    - temperature
    - humidity

Polymer matrix: Polyacrylonitrile (PAN)



Applications

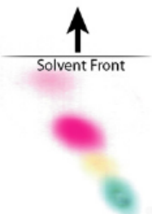
- carbon fiber
- hot gas filtration systems
- outdoor awnings
- fiber reinforced concrete.
- knitted clothing
- like socks and sweaters
- outdoor products like tents

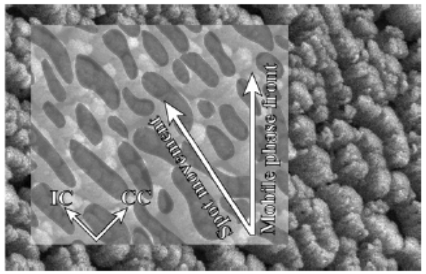
PAN is one of the versatile polymers that is widely used for making ***membranes*** due to its good solvent resistance property. It has been used as a substrate for ***reverse osmosis (RO) and nanofiltration (NF).***

Stationary phase for UTLC

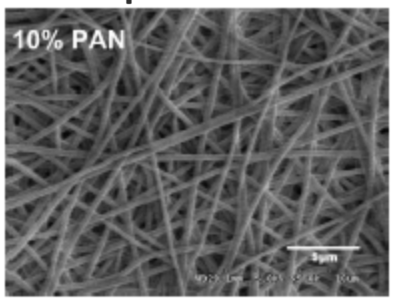
Parameter	TLC	HPTLC	UTLC
Plate size (cm)	20 × 20	10 × 10	6 × 3.6
Layer thickness (mm)	0.1–0.25	0.1 or 0.2	0.01
Particle size (µm)	10–12	4–6	Monolithic
Particle size range (µm)	5–20	4–8	
Maximum value for Z_f (cm)	7–15	3–7	1–3
Separation time (min)	30–200	3–20	1–5
Average plate height (µm)	35–75	23–25	
Typical application volume (spots) (µl)	1–5	0.1–0.5	0.01–0.1
Initial spot diameter (maximum) (mm)	3–6	1–1.5	0.5–1
Detection limits (reflectance)			
UV–vis (ng)	1–5	0.1–0.5	0.5
Fluorescence (pg)	50–100	5–10	5

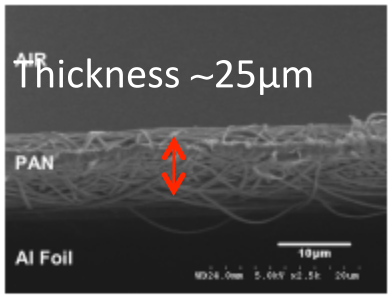
Silica Monoliths

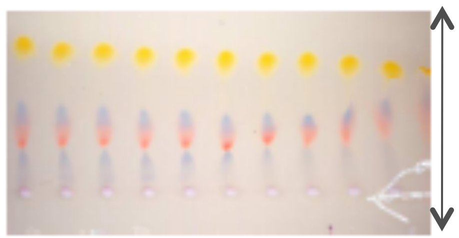




Electrospun nanofiber





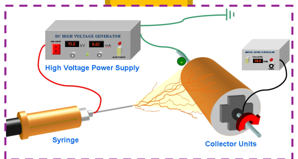


Immigration distance ~ 20mm

Experimental

staple fiber

In DMF

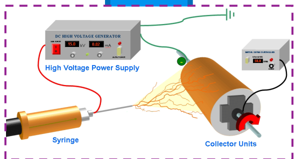


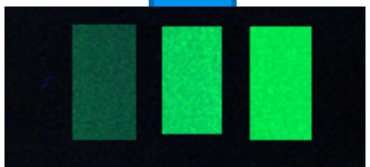
e-spun PAN

Vary - electrostatic field
- collecting time
- concentration of UV_{254}

staple fiber

In DMF





e-spun PAN-UV_{254}

Separation of 7 preservative compounds and non-alcohol beverage

Fluorescent indicator UV_{254}

manganese activated zinc silicate

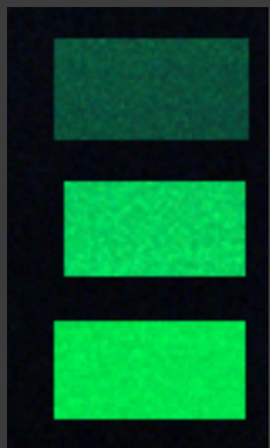
Morphology & Size of PAN nano phase

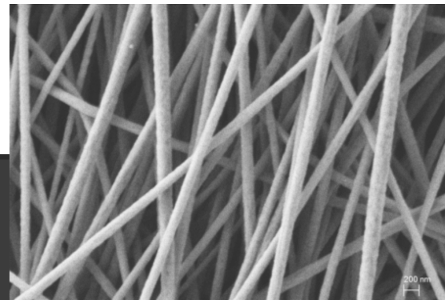
Applied voltage	Diameters of individual fibers ± SD (nm)			
	-	1% UV_{254}	5% UV_{254}	10% UV_{254}
16 kV	224±65	177±48	179±50	181±40
18 kV	181±58	155±53	161±48	165±45
20 kV	160±43	149±60	152±38	154±48

1% UV_{254}

5% UV_{254}

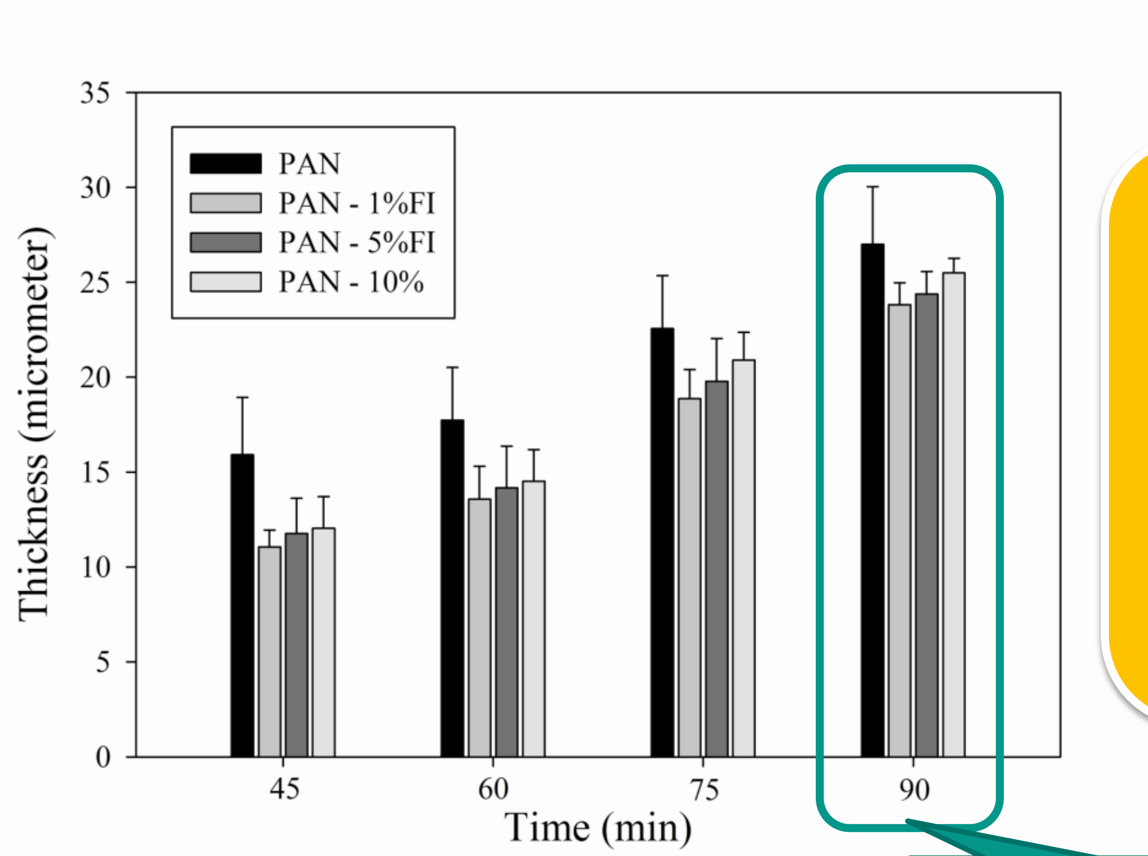
10% UV_{254}





SEM image of PAN nanofiber phase with UV_{254} which was spun under condition; 18kV/10cm and 10% of UV_{254}

Electrospinning time and thickness



There are beads along with the nanofibers when the spinning time reached 120min

Selected spinning time

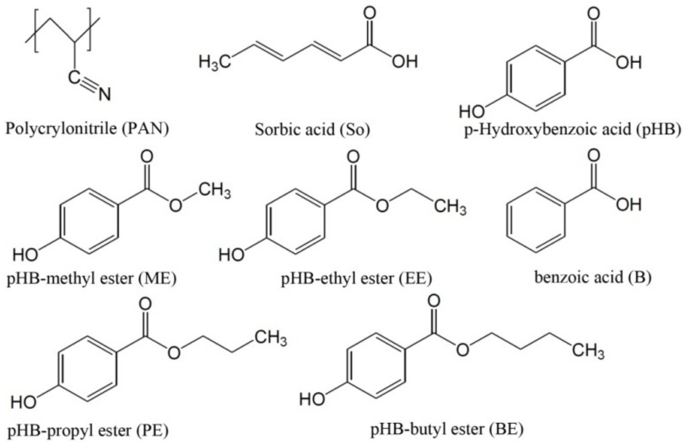
Thickness of electrospun PAN nanofiber phases and h different amounts of fluorescence indicator UV_{254} (1%, 5% and 10%) at different collecting times (45-90 min)

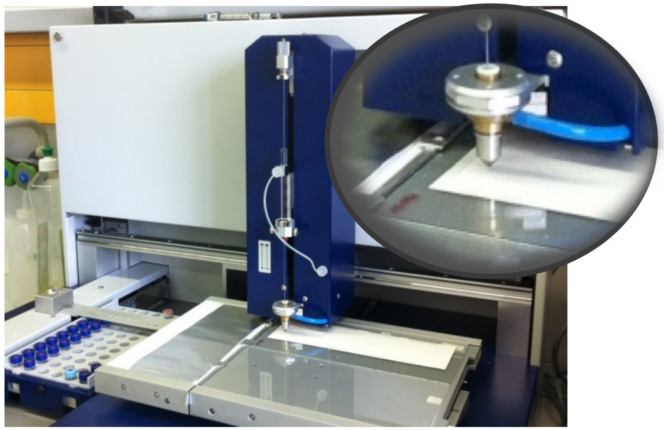
Application

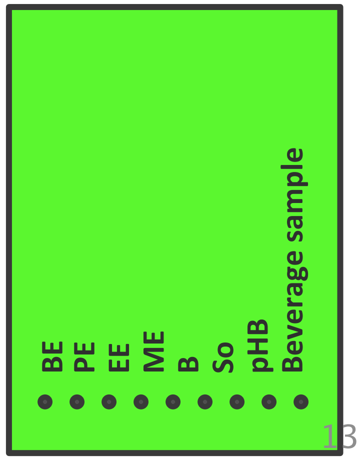
7 preservative compounds

ATS4
Adjust the volume to 10nL

8 tracks of each 7 preservative compounds and beverage sample



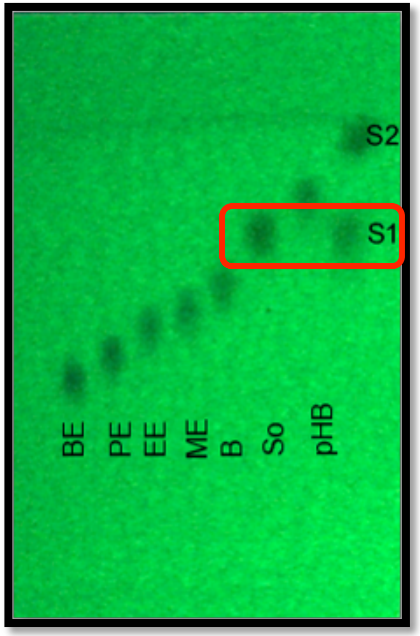




Separation of Preservatives

- **Stationary phase – E-spun PAN-10%UV254 nanofiber phase**
- **Mobile phase – water:acetonitrile 13:7 with 0.1M of tetra-n-butylammonium phosphate, 1ml**

	A) Electrospun PAN nanofibers with 10% UV_{254}			B) HPTLC plate silica gel CN		
	hR_F	*%RSD*	N	hR_F	*%RSD*	N
BE	17	1.3	9044	40	0.10	3937
PE (E216)	24	1.5	6745	46	0.65	4161
EE (E214)	31	2.1	3822	54	0.86	6568
ME (E218)	40	1.5	6005	58	0.40	5112
B (E210)	45	2.2	3711	65	0.19	4136
So (E200)	48	2.5	4984	76	0.40	3783
pHB	56	3.9	3997	83	0.55	5263
Beverage	86	1.0	2214	96	1.16	3139
Sample	47	2.6	6233	76	0.47	3025



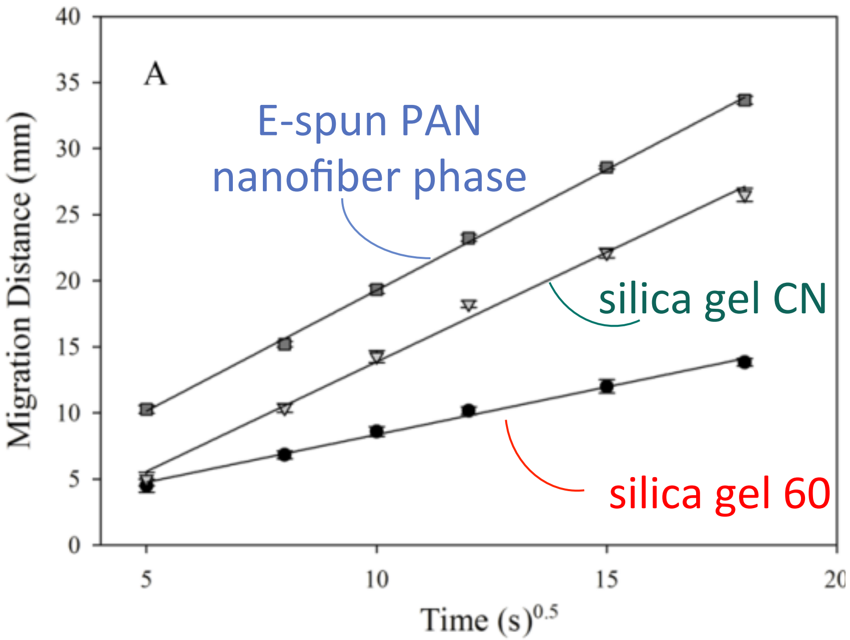
$$R = \frac{2(D_{R2} - D_{R1})}{(w_2 + w_1)}$$

D_{R1}, D_{R2} = the retention distance of two adjacent peaks 1 and 2

w_1, w_2 = the widths of two adjacent peaks 1 and 2,

Stationary phase	BE/PE	PE/EE	EE/ME	ME/B	B/So	So/pHB
A) Electrospun PAN nanofibers with 10% UV_{254}	1.04	1.26	0.97	1.34	1.82	1.16
B) HPTLC plate silica gel CN	1.45	1.41	1.33	0.49	0.56	1.43

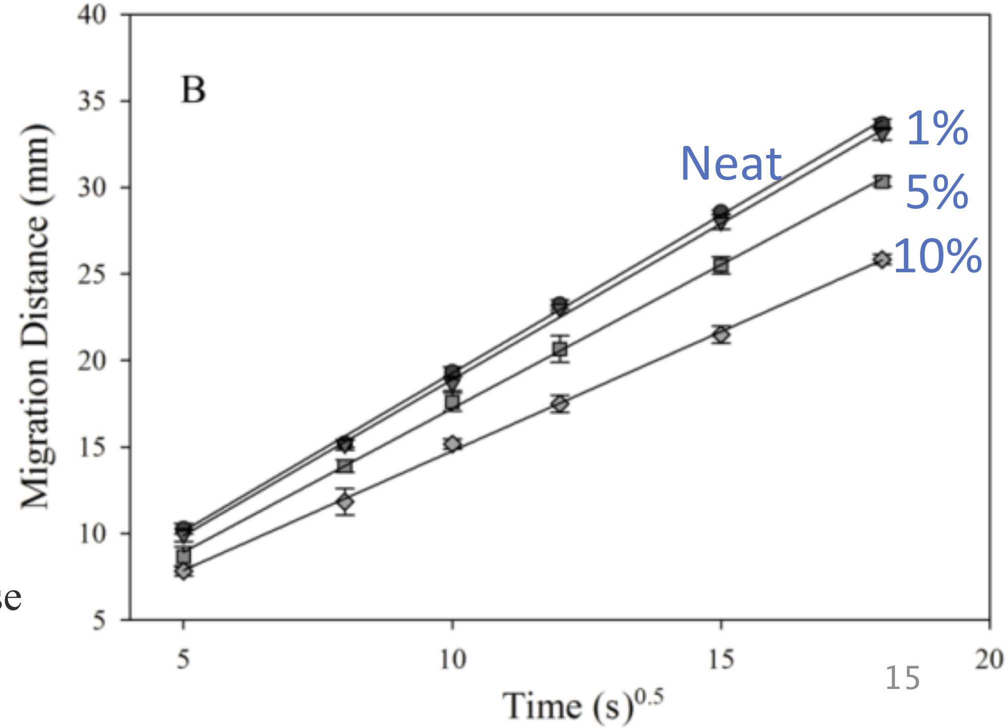
Comparison of Mobile Phase Velocities



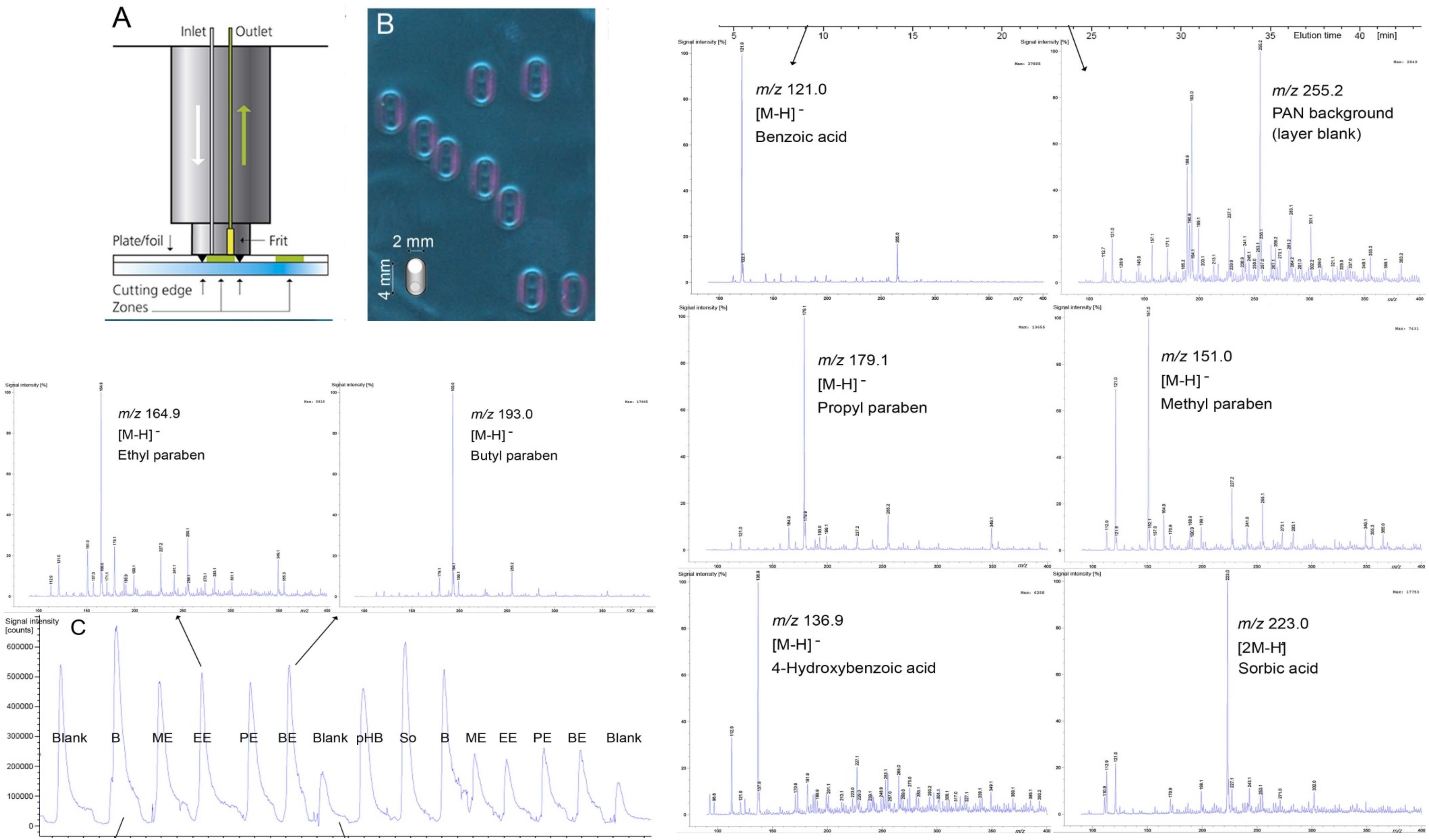
$$Z_f^2 = \kappa t \; ; \quad Z_f = \frac{\gamma R t \cos\theta}{2\eta}$$

$$\kappa = 2K_0 d_p(\gamma/\eta)\cos\phi$$

Z_f = the distance traveled by the solvent front,
t = the development time,
κ = the velocity constant;
K_0 = the permeability constant of the layer,
d_p = the average particle size,
γ = the surface tension of the mobile phase,
ϕ = the contact angle between the mobile phase and the layer.



Compound confirmation by mass spectrometry

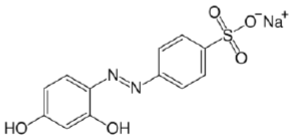


Conclusions

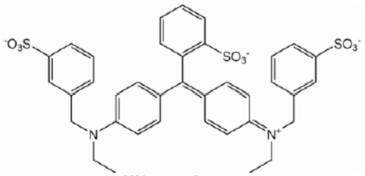
- The electrospun PAN nanofibers are effective as the stationary phase for thin layer chromatography.
- The devices have been shown to decrease time of analysis and volume of solvent needed.
- The visualization of preservatives on the stationary phase was easily done by put UV_{254} indicator directly into polymer solution.
- ESI-MS spectra were successfully recorded from the nanofiber phases after development and a good detect ability was observed. The regular elution head cleaning after each elution could be skipped as the layer material was still intact after elution.

Thank you

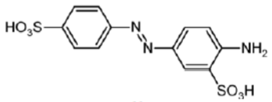
Application



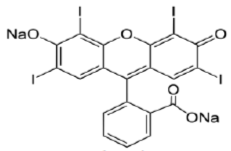
Chrysoine resorcinol
(E103)



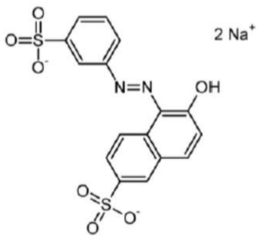
Brilliant Blue FCF
(E133)



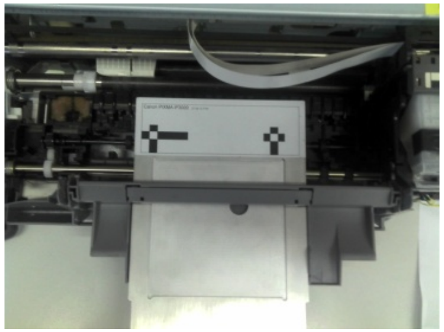
Fast Yellow AB
(E105)

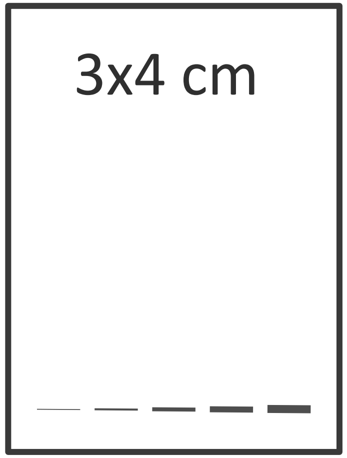


Erythrosine
(E127)



Orange GGN
(E111)





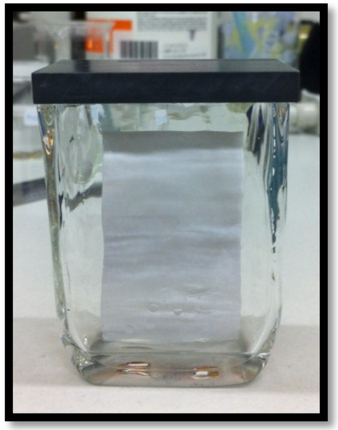
5 water-soluble food dyes

A modified Canon Printer

5 tracks of 3 mm bands
Mixture std solution

Separation of water soluble food dyes

- Mobile phase - MeOH:Toluene:NH_4OH 25% 40:57:3 ; 1ml
- Development time ≈ 8 min

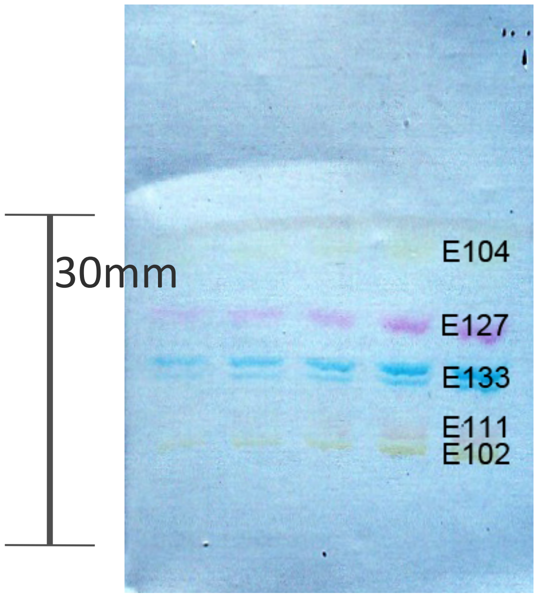


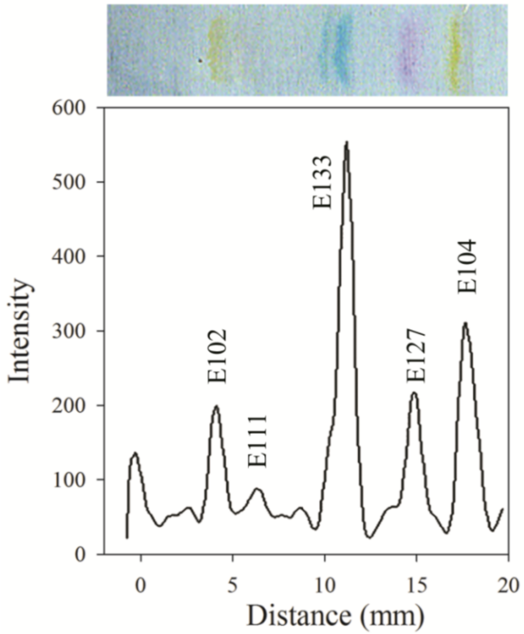
4.5×1.5×5.5 cm

$$hR_F = \frac{Z_s}{Z_f} \times 100 \quad ; \quad N = 16\left(\frac{Z_s}{w}\right)^2$$

hR_F = Retention factor x 100;
Z_s = migration distance of sample;
Z_f = migration of front solvent

N =plate number
w = width of spot





	hR_f	%sd	N
E104	28	1	8345
E127	35	4	8286
E133	53	15	46760
E111	68	16	9596
E102	89	5	6002