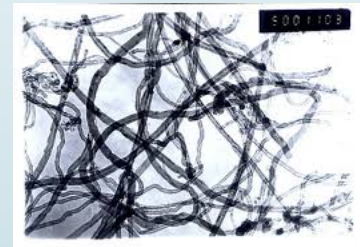
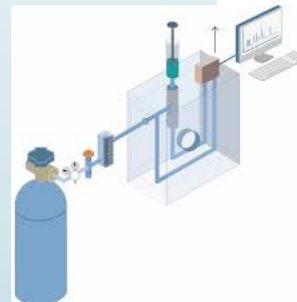
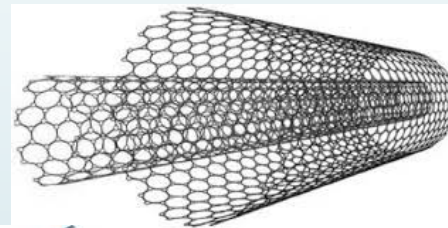


Gas Chromatography and Sample Preconcentration on Self-Assembled Carbon Nanotubes



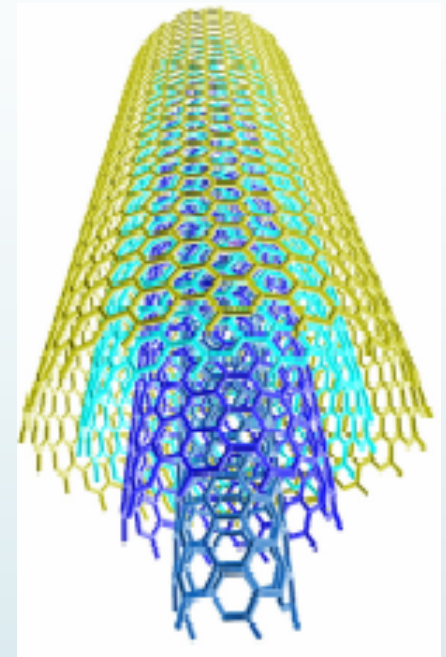
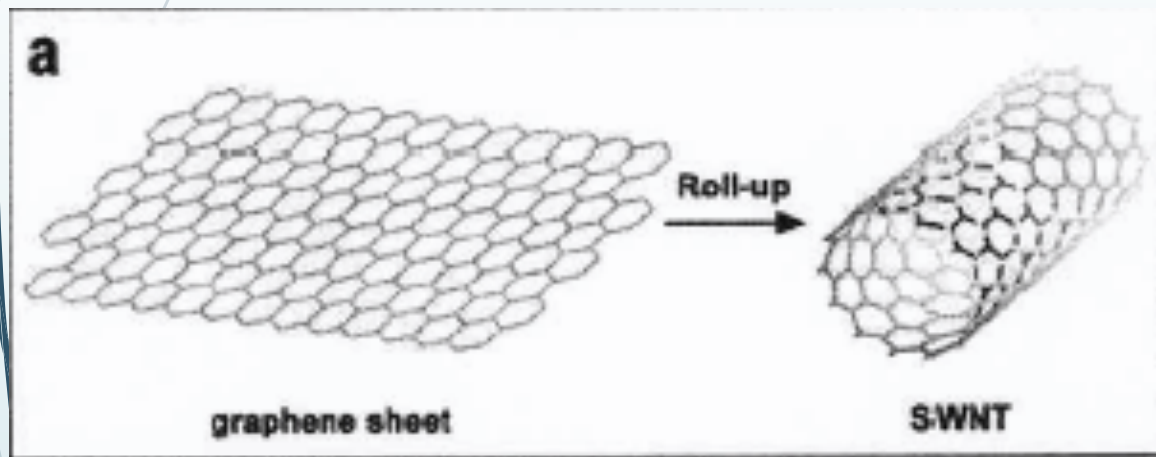
Traditional Carbon Sorbents in Chemical Processing

Type	Name	SurfaceArea (m ² /g)
Activated Carbon		500-1200
Molecular Sieves (Permanent gases application)	Carbosieve B	117
	Carbosieve S-III	1000
	Carbosieve S-II	1000
	Carboxen 1000	1200
	Carboxen 1001	500
	Carboxen 1002	1100
Porous Carbon	Carb I	1200
	Carb II	400
Graphitized Carbon Black As Supports in packed GC columns	Carbopack F	5
	Carbotrap F	5
	Carbograph 3	6-7
	Carbopack C	12
	Carbotrap C	12
	Carbograph 2	10-12
	Carbopack B	100
	Carbotrap B	100

Introduction

3

Carbon nanotubes are formed by rolling up layers of graphene sheets into hollow seamless cylinders of nano diameters.

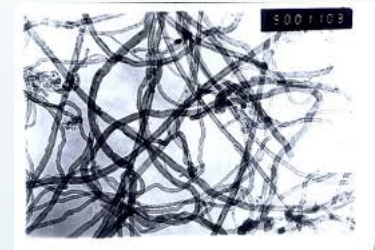
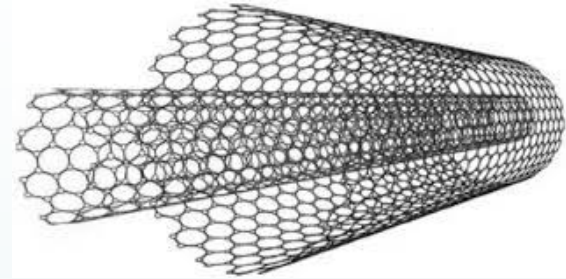


Several concentric shells: Multi-walled CNTs (10 – 70 nm).

Single shelled: Single-walled CNTs (0.5 – 2 nm).

Why Carbon Nanotubes? Why Nano-scale?

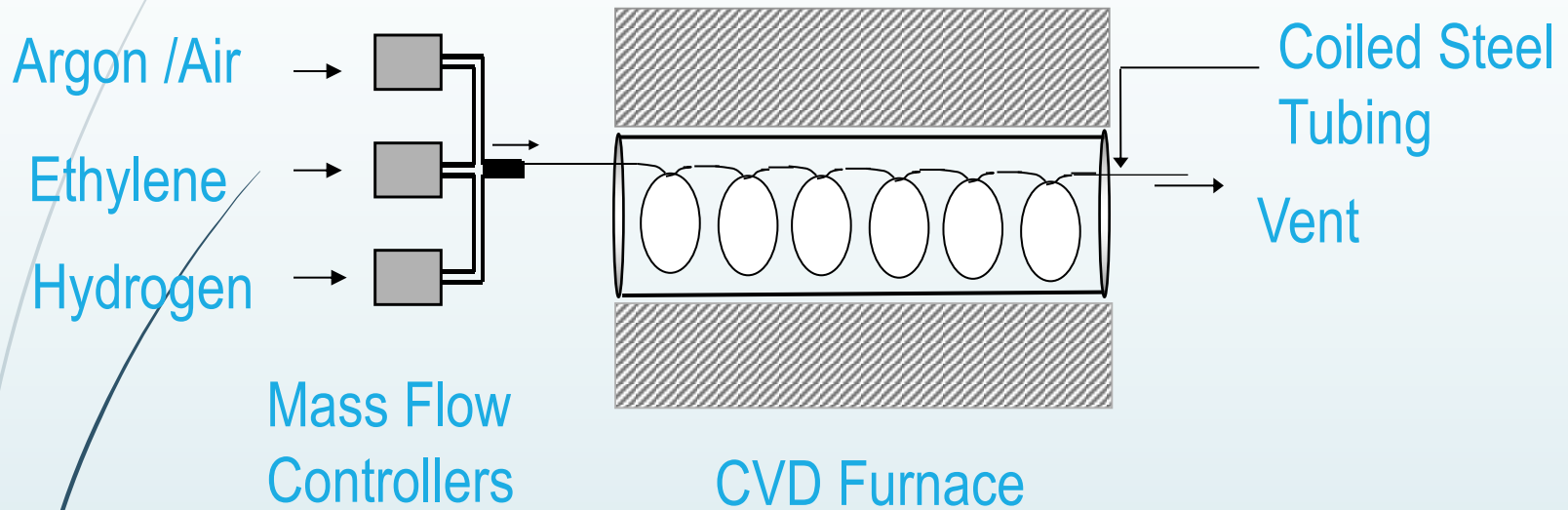
- High surface areas
- Greater interaction of analytes
- Higher capacities
- Fast – Adsorption/desorption
- nano-scale interactions.
- Improving assay sensitivity, selectivity and resolution



Challenges in Large Scale Self Assembly

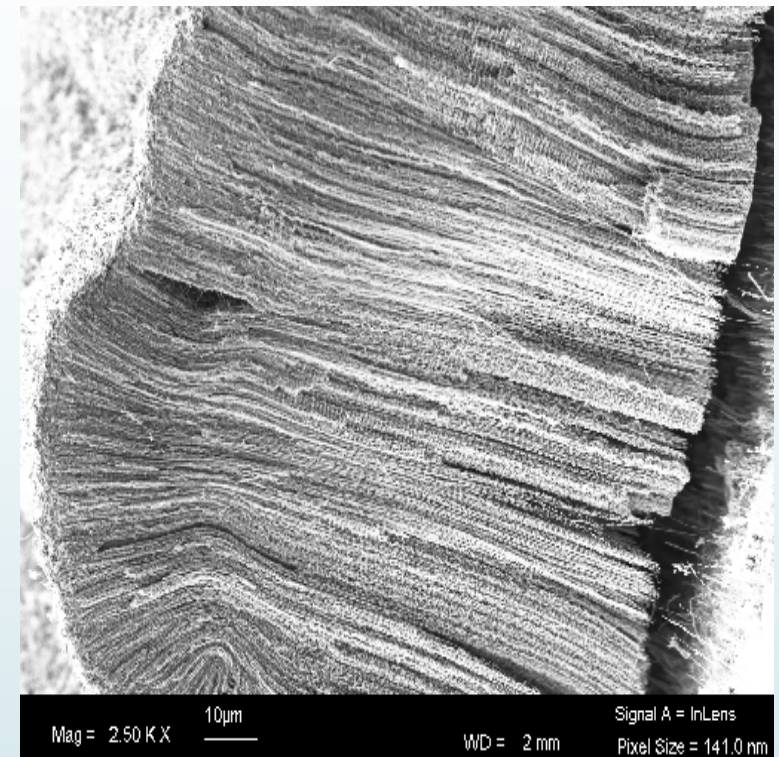
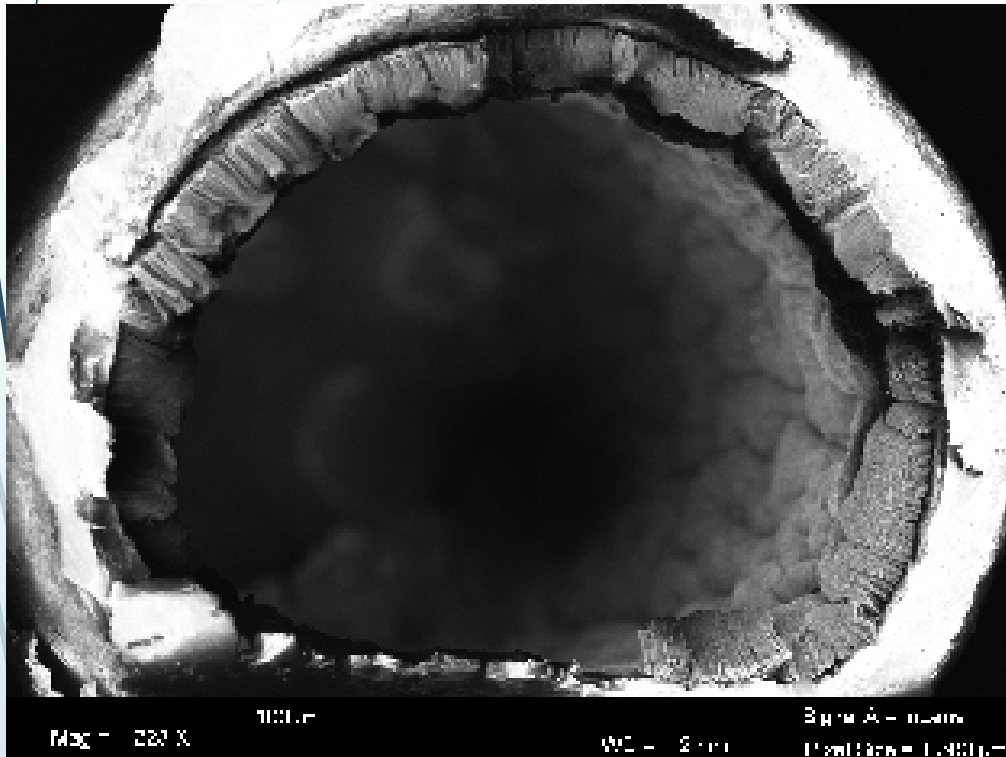
- Laying down of nano-sized catalyst uniformly over the substrate
- Achieve Surface coverage of CNTs over the entire substrate
- Selective growth of CNTs & avoid amorphous carbon formation
- Controlling kinetics / morphology of the deposition

Scaling Up Self-assembly



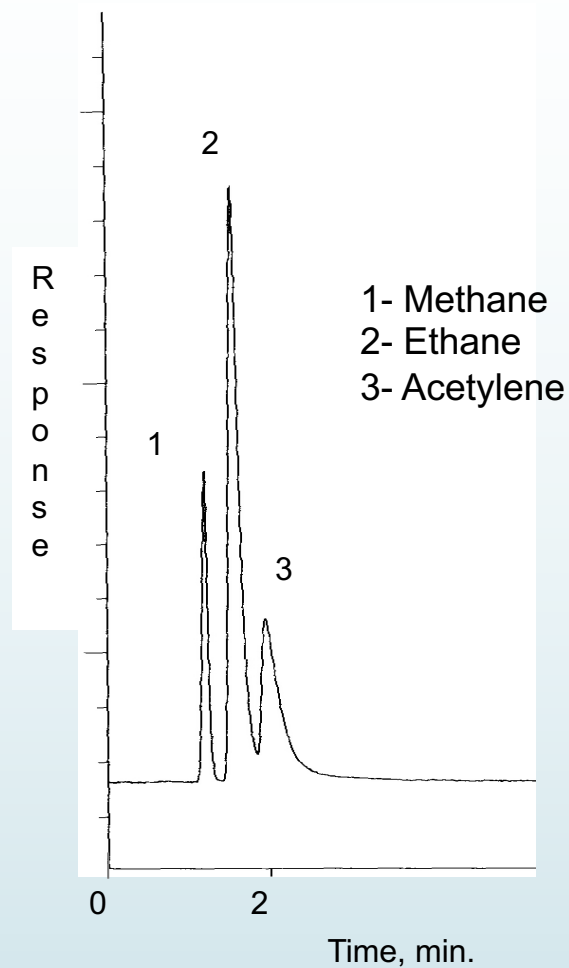
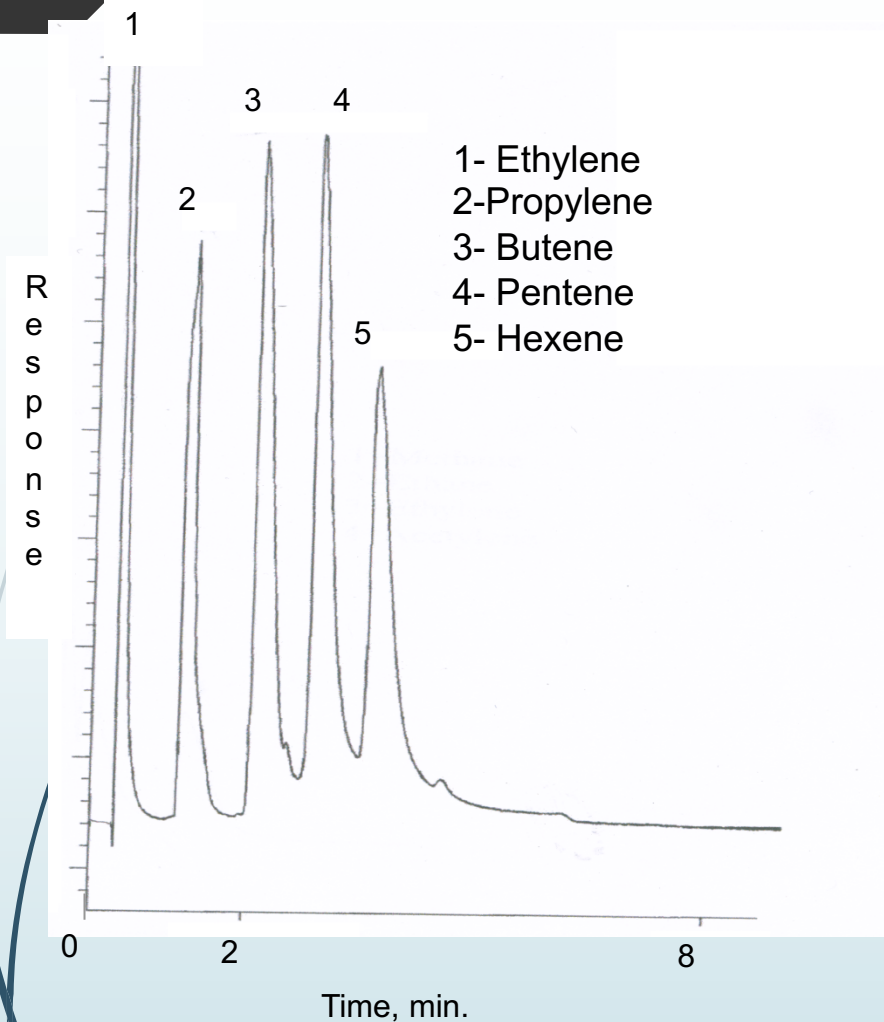
Length: 1-3 m

Cross Section of Steel tubing Showing Radially Aligned CNTs anchored to the surface



Previous Research: Separations on MWNT column

8



Ref: C.Saridara, S.Mitra; Anal. Chem. 2005, 77, 7094 -7097.

Self-assembly Process

Surface Conditioning

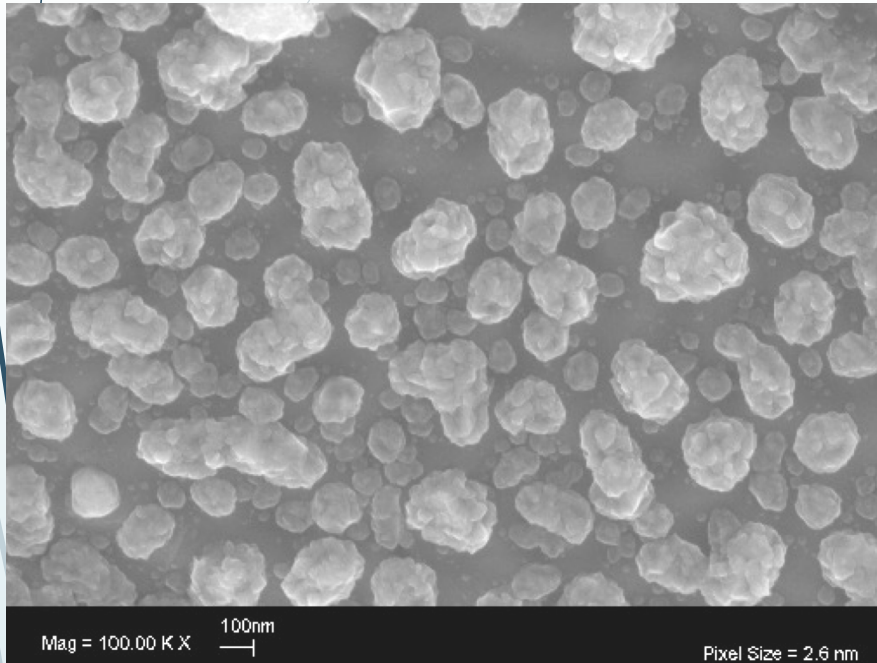
Oxidation (air), Reduction (H_2)
700°C, 45 min, 65 sccm

Chemical Vapor Deposition

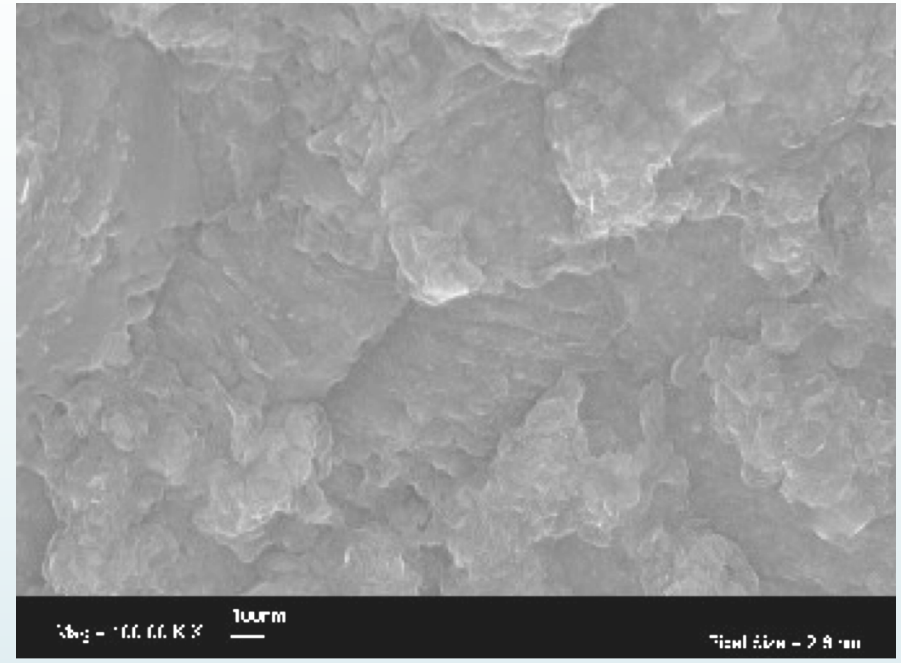
Deposition (C_2H_4)
700°C, 1 – 30 min,
5 – 20sccm, 40 psig

Surface Conditioning of Surface of Steel Tubing

10



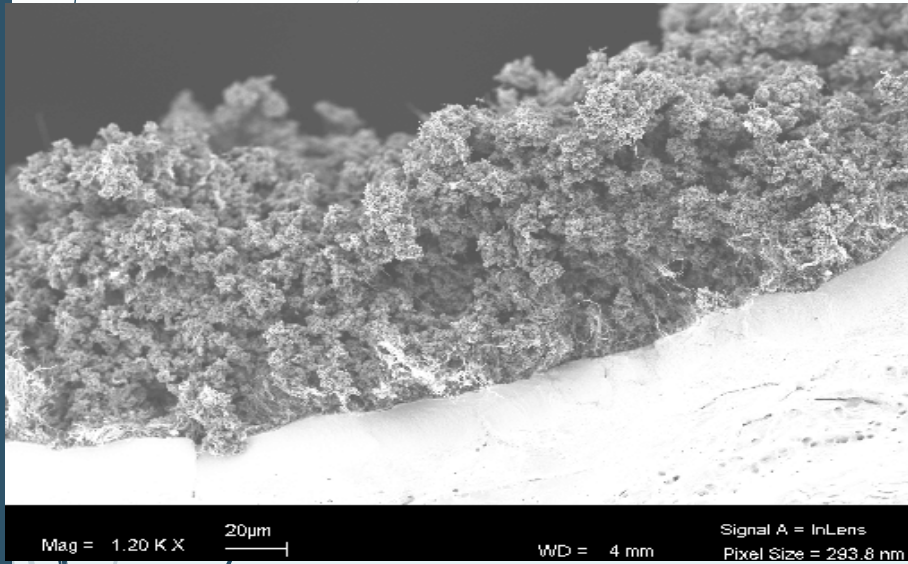
500°C



700°C

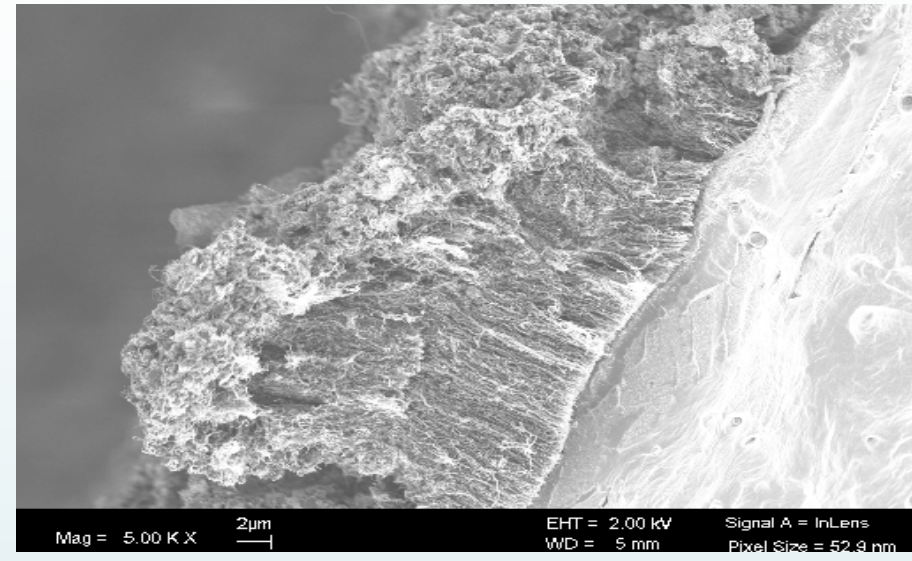
- Generation & Activation of Nano sized catalyst on the surface.

Surface Conditioning : CNT Morphology



500°C

➤ Resulted in higher amounts of amorphous carbon



700°C

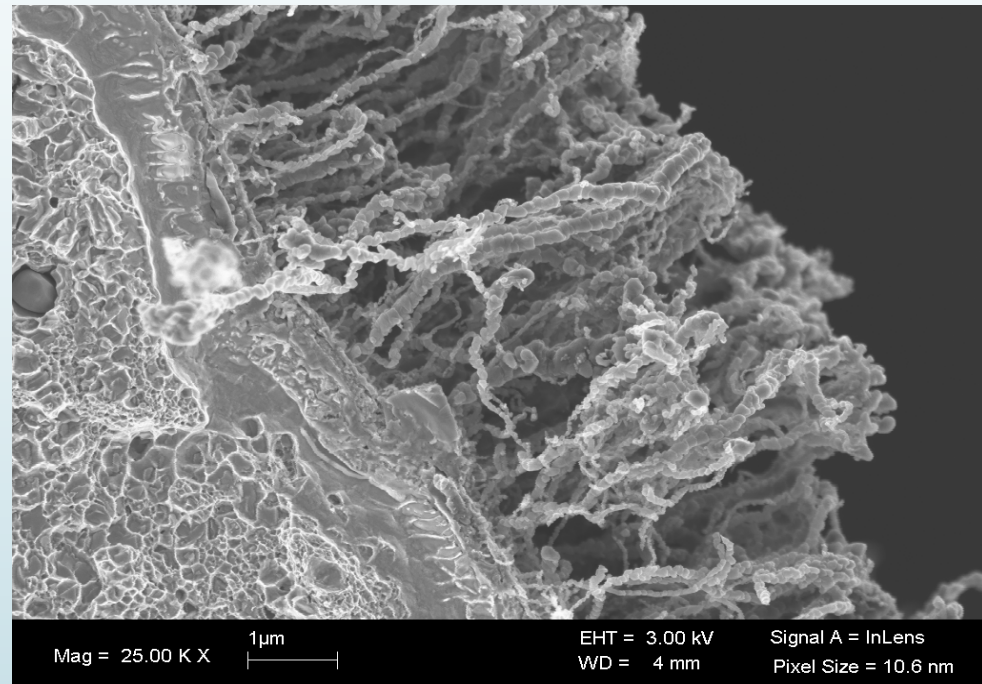
➤ Resulted in higher amounts of CNTs

CNT Morphology With CO as Precursor

12

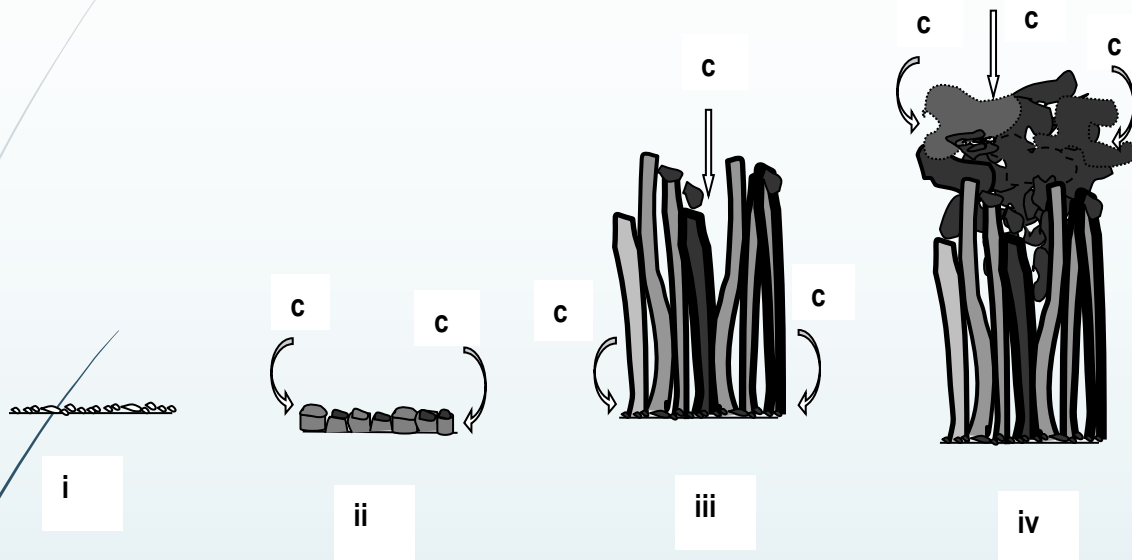
CVD Time (mins)	Thickness (cm) of CO CVD coating along the length in the inside of Stainless Steel tubing (μms)				
	5	12.5	25	35	45
5	0	0	0	0	0
30	4 - 5	1 - 2	6 - 7	2 - 3	1 - 2
60	25 - 30	10 - 15	8 - 12	2 - 4	1 - 2

- MWNTs with nodes
- Requires relatively long time for coverage
- Diameter of CNTs wide



Mechanism of Growth – Why Overcoat of C on CNT with

¹³
 C_2H_4 ?



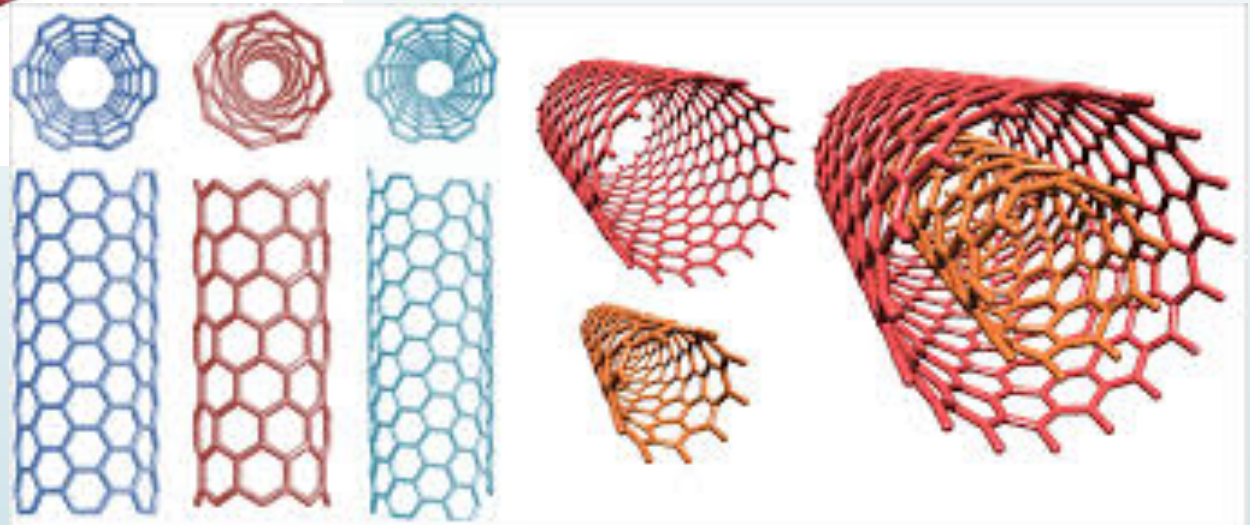
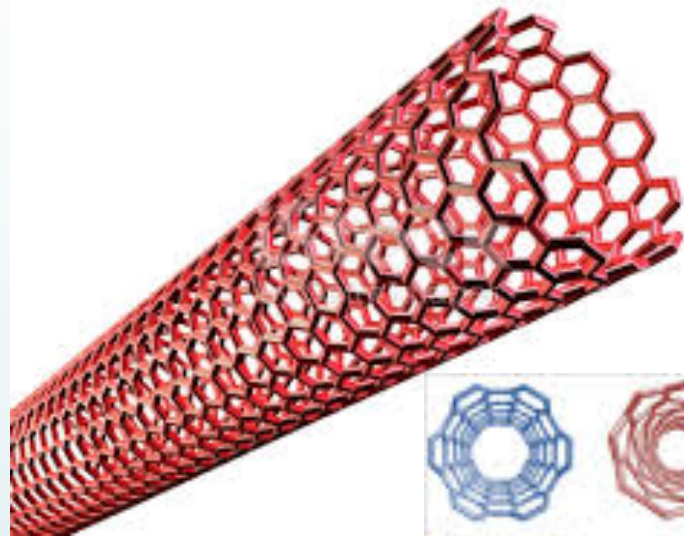
(i) Diffusion of carbon into the granular catalyst metal surface.

(ii) Precipitation of carbon to form tubules

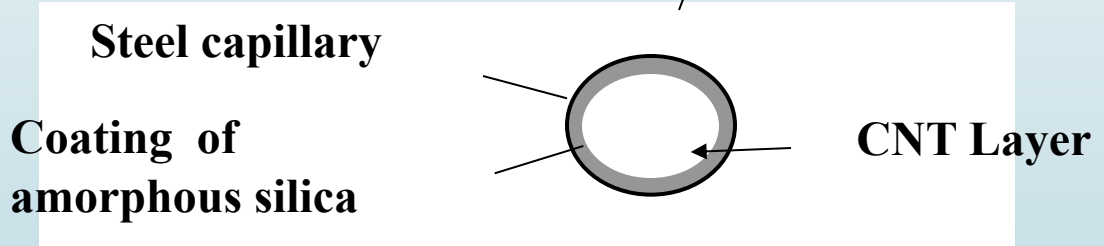
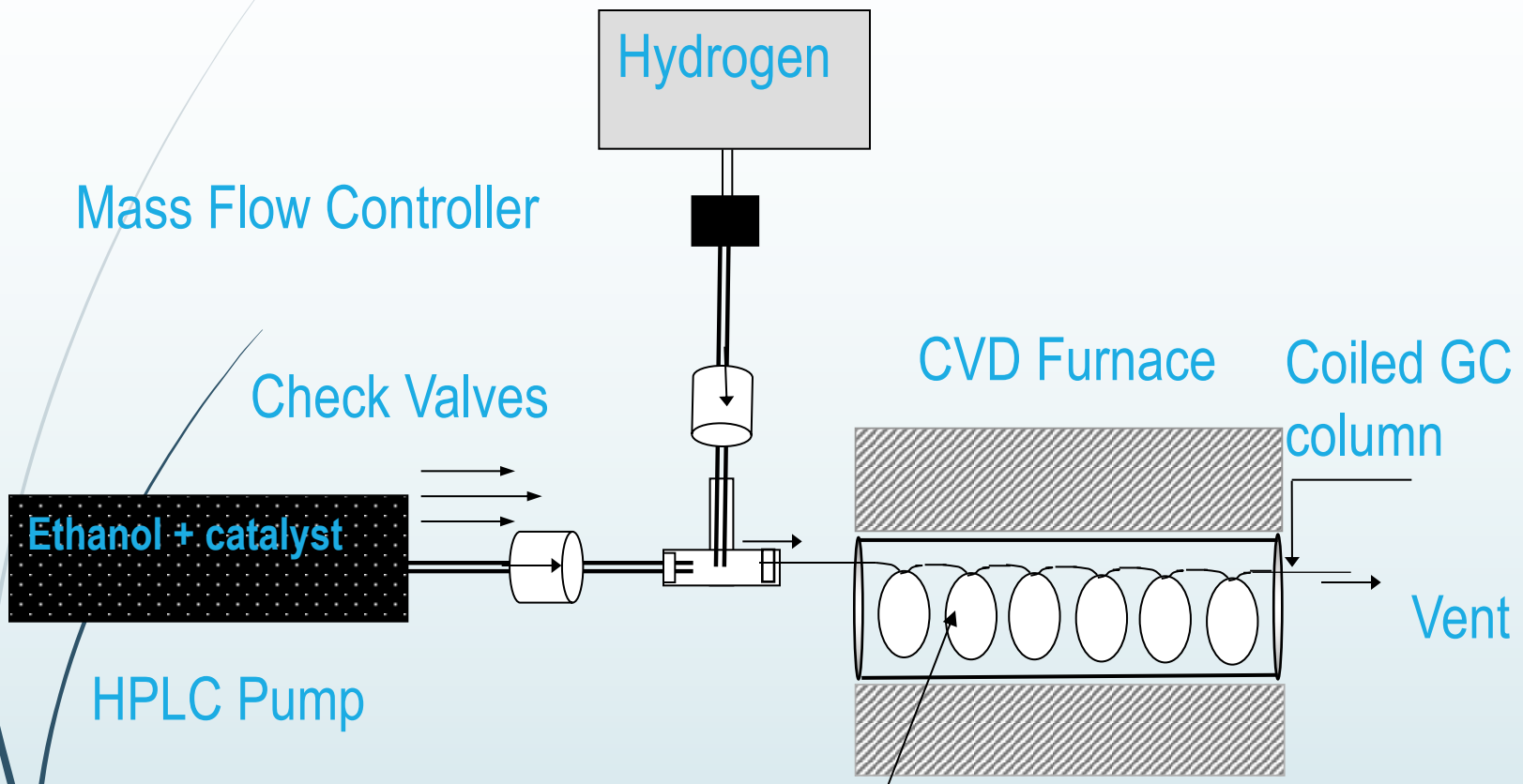
(iii) Growth of (hollow) MWNTs and solid CNFs from the tubules.

(iv) Formation of amorphous carbon structures at the tips of the CNT's due to the lack of accessibility of the bulk metal surface – BASE GROWTH MECHANISM

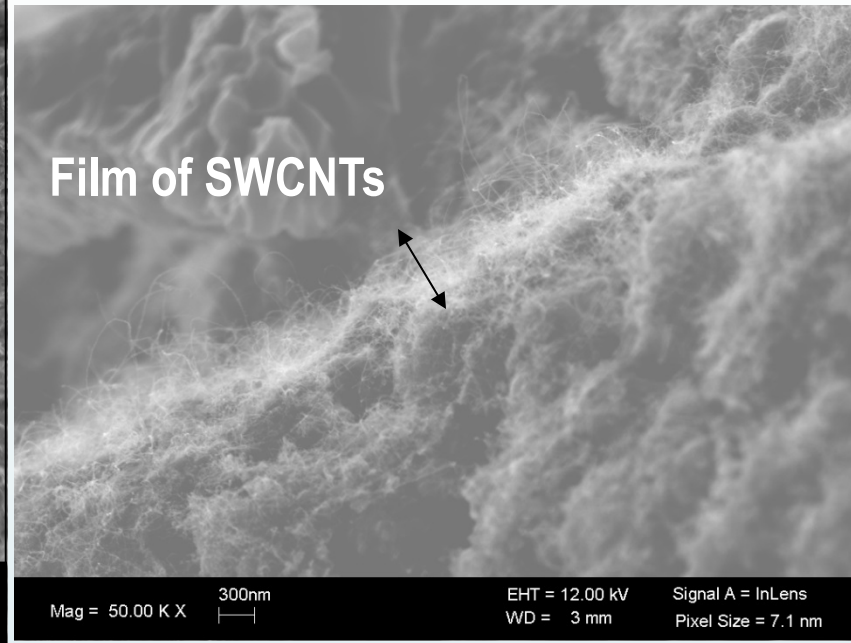
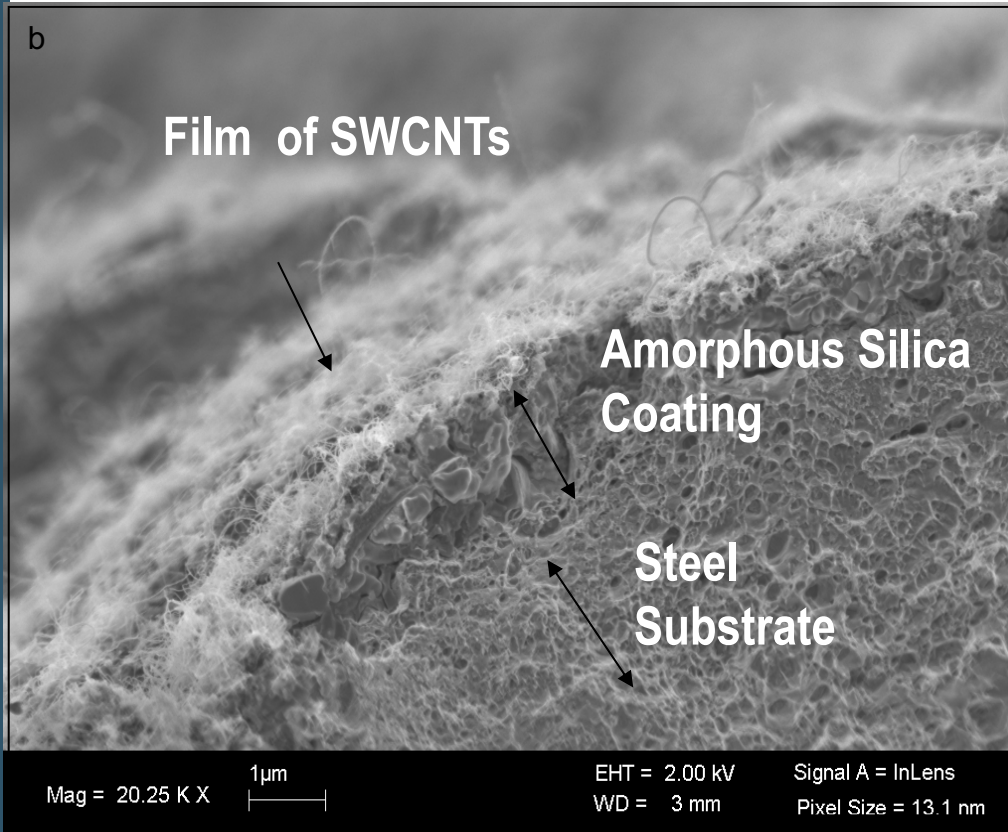
Growing Single Walled Nanotubes



One-Step, Selective SWCNT Synthesis via CVD

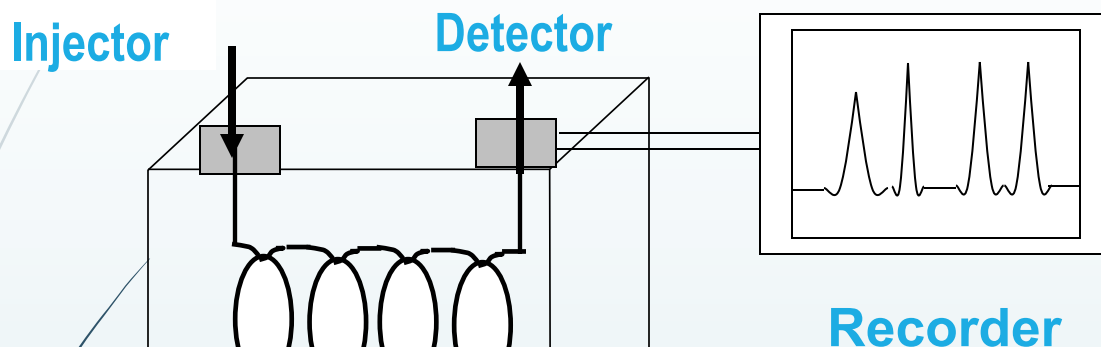


SWCNT film upon the silica lined steel substrate



- **Silica lined surface proved critical for the formation of SWCNT as it restricted the interaction of Fe in steel which is known to catalyze the MWCNT formation**
- Same conditions: Steel substrates resulted in MWCNTs with few thin diameter SWCNTs which could not be detected by Raman

SWCNTs for GC separations



Gas Chromatograph

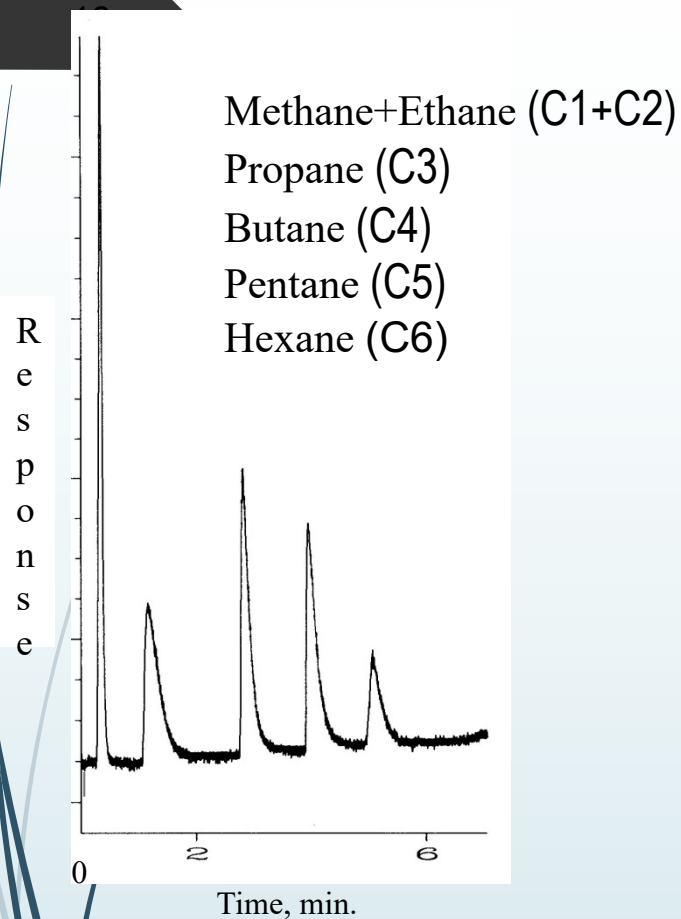
Silica Lined Steel capillary

Layer of carbon nanotubes

Capillary Tube Length : 0.75 m, 0.53 mm ID

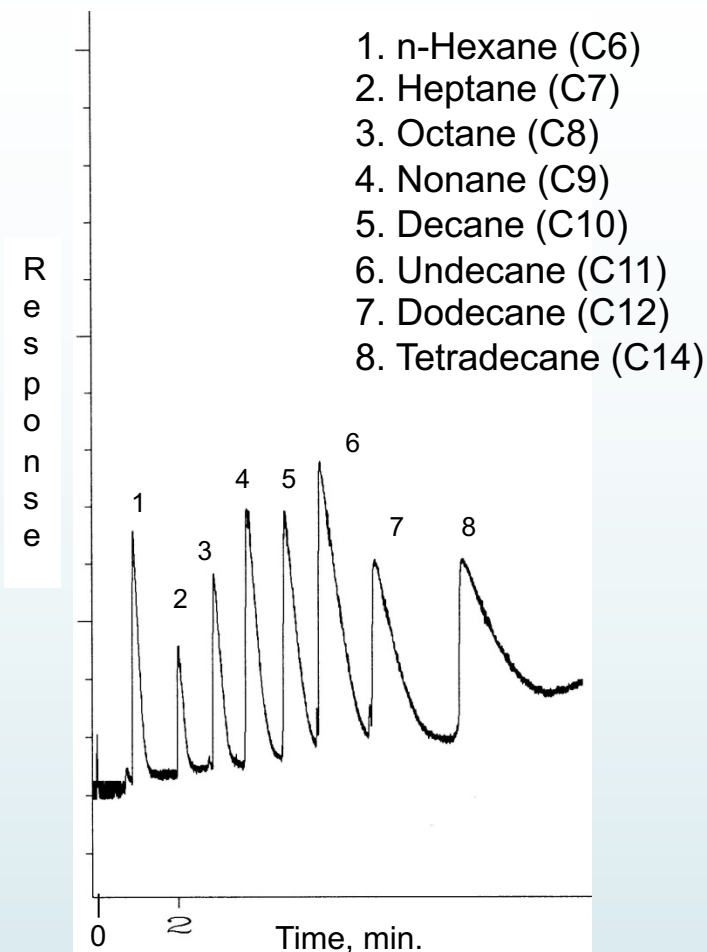
Gas Chromatography

a



1

b



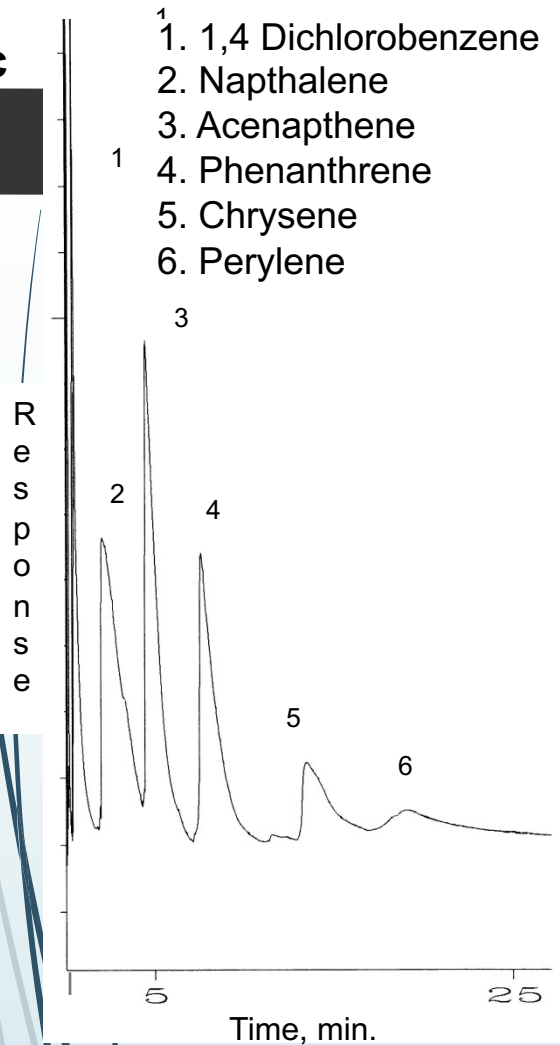
a) ppm level of alkanes std, 30°C, 0.5min, at 40°C/min. to 250°C, flow rate - 1.5 ml/min, 20 µl inj. b) high mol. wt. n-alkanes, 120°C, 0.1min, at 40°C/min. to 425°C, 5 min; flow rate - 5.0 ml/min, Split 1:20, Vapor injected (ppb level Conc's)

Retention time repeatability data (n=5) for the separation of n-alkanes mixture

19

Solute	Avg. Retention time (min)	RSD (%)
n-Hexane	0.87	4.43
Heptane	1.92	2.54
Octane	2.75	2.71
Nonane	3.51	1.77
Decane	4.42	0.82
Undecane	5.25	0.87
Dodecane	6.57	1.47
Tetradecane	8.74	3.31

C



➤ The high surface area of the SWCNT media, the possibility to self-assemble a nano sized film, and its high thermal stability (>425°C)

➤ Permitted separations of gases & higher molecular weights at higher temperatures.

➤ Thus it was possible to extend the range of conventional chromatography on the same column.

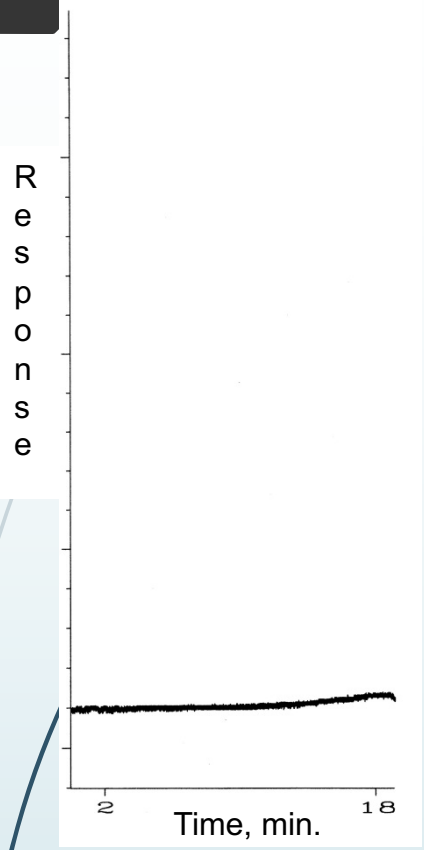
c) Separation of PAH mix, 0.6 ul, 1:20 split ratio, Oven temp. 125°C at 30°C/min. to 425°C, 10 min.

Retention time repeatability data for the separation of PAH mixture (n=5)

Solute	Avg. Retention time (min)	RSD (%)
1,4 dichlorobenzene	0.35	2.02
Napthalene	1.96	0.63
Acenaphthene	3.88	1.79
Phenanthrene	6.39	1.34
Chrysene	10.84	2.15
Perylene	13.58	2.25

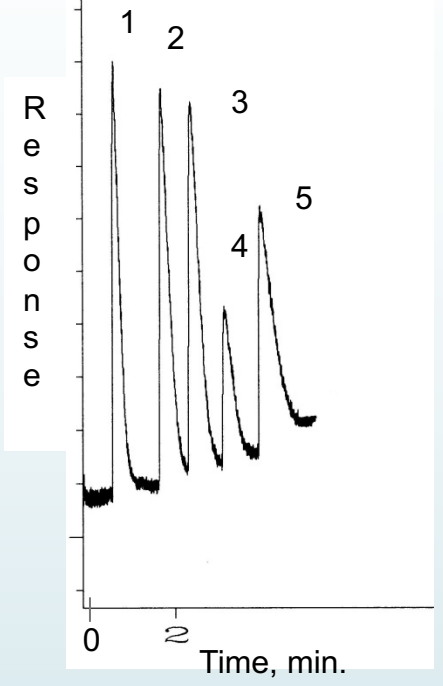
d

22



e

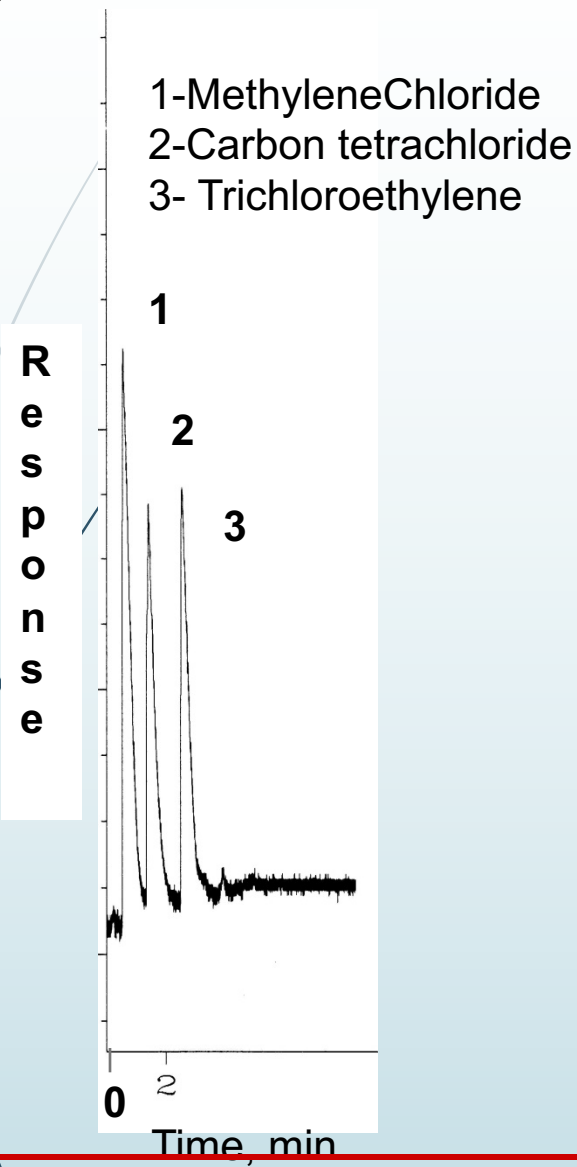
- 1-Benzene
- 2-Toluene
- 3- Ethylbenzene
- 4- O-Xylene
- 5- Nonane



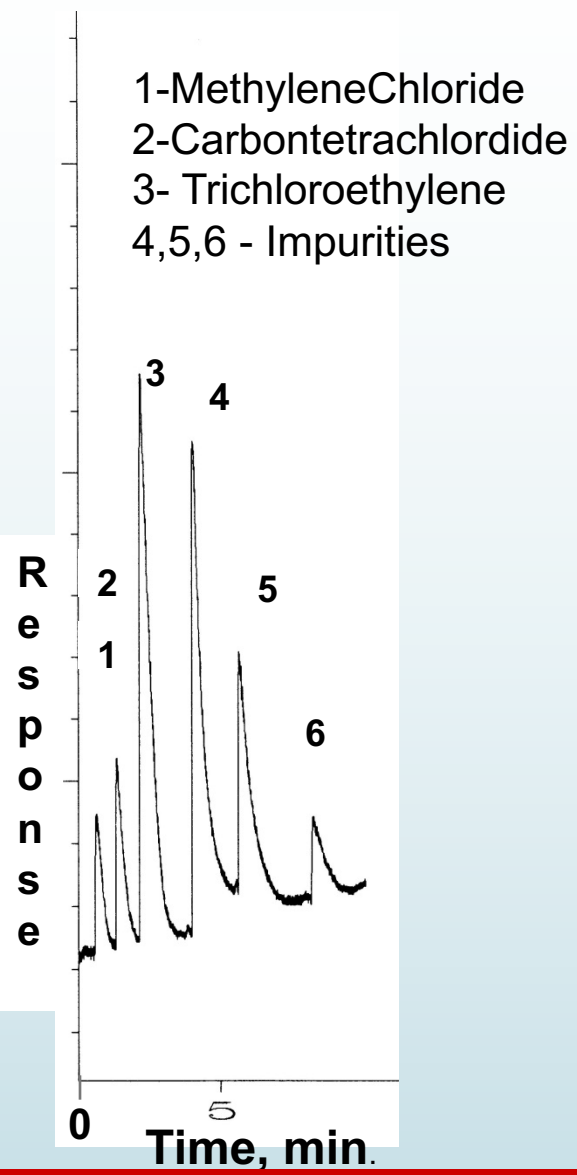
d) column bleed test 30°C, 2 min, at 30°C / min to 425°C, 4 min. **e) aromatics**, 120°C for 0.1 mins, 45°C/min. to 300°C/min., flow rate - 5.7 ml/min. Split ratio 1:20, Vapor injected (ppb level Conc's)

chlorohydrocarbons, conditions: 60oC for 0.5 mins, 45oC/min. to 240oC/min, flow rate of carrier gas was 4.0 ml/min. h) chlorohydrocarbons with few impurities, conditions: 60oC for 0.5 mins for 45C/min to 325C, flow rate – 5 ml/min

f

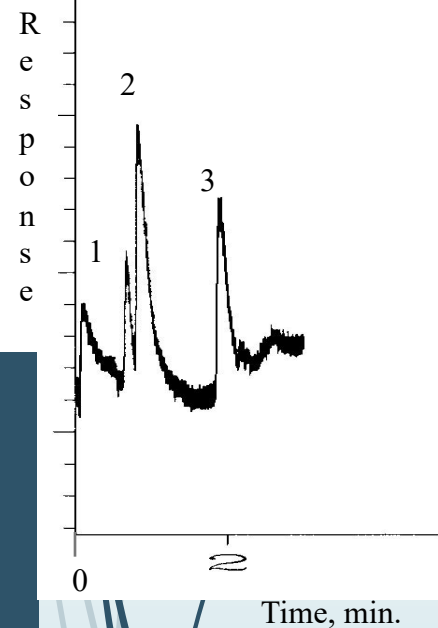


g

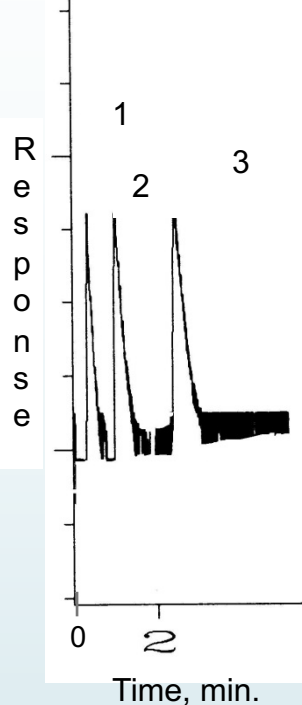


h

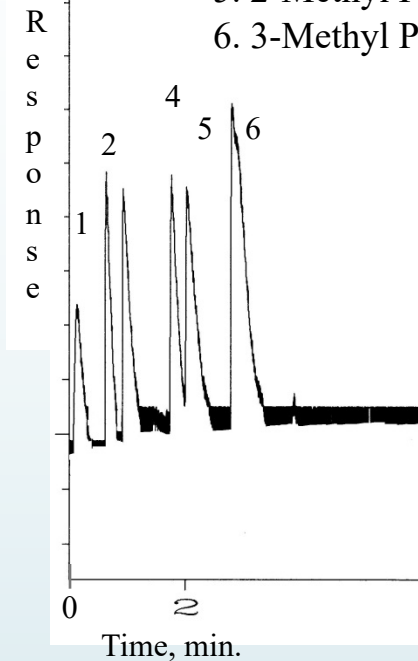
- 1- Methanol
- 2- Ethanol
- 3- Propanol

**i**

1. Acetone
2. 2-pentanone
3. Isobutyl isobutyrate

**j**

1. Isobutane
2. 2,2-Dimethyl Propane
3. 2-Methyl Butane
4. 2,2- Dimethyl Butane
5. 2-Methyl Pentane
6. 3-Methyl Pentane

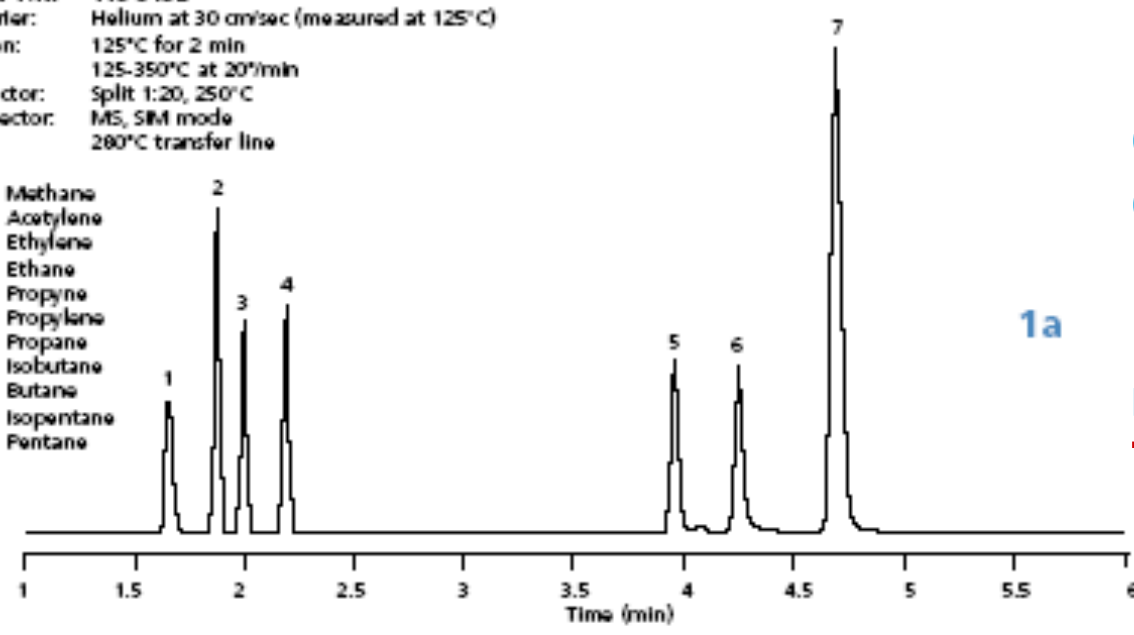


f) alcohols, 120°C for 0.5mins, 40°C/min. to 250°C, flow rate 5.7ml/min. **g) Ketones**, 145°C for 0.1mins, 45°C/min. to 300°C, flow rate - 5.0ml/min **h) isomers of branched H.C's**, 50°C for 0.25 mins, 20°C/min. to 200°C/min, 250 µl inj., flow rate - 2.7ml/min, ppm level

Hydrocarbons

Column: GS-CarbonPLOT
30 m x 0.32 mm I.D., 1.5 µm
J&W P/N: 113-3132
Carrier: Helium at 30 cm/sec (measured at 125°C)
Oven: 125°C for 2 min
125-350°C at 20°/min
Injector: Split 1:20, 250°C
Detector: MS, SIM mode
280°C transfer line

- 1. Methane
- 2. Acetylene
- 3. Ethylene
- 4. Ethane
- 5. Propyne
- 6. Propylene
- 7. Propane
- 8. Isobutane
- 9. Butane
- 10. Isopentane
- 11. Pentane

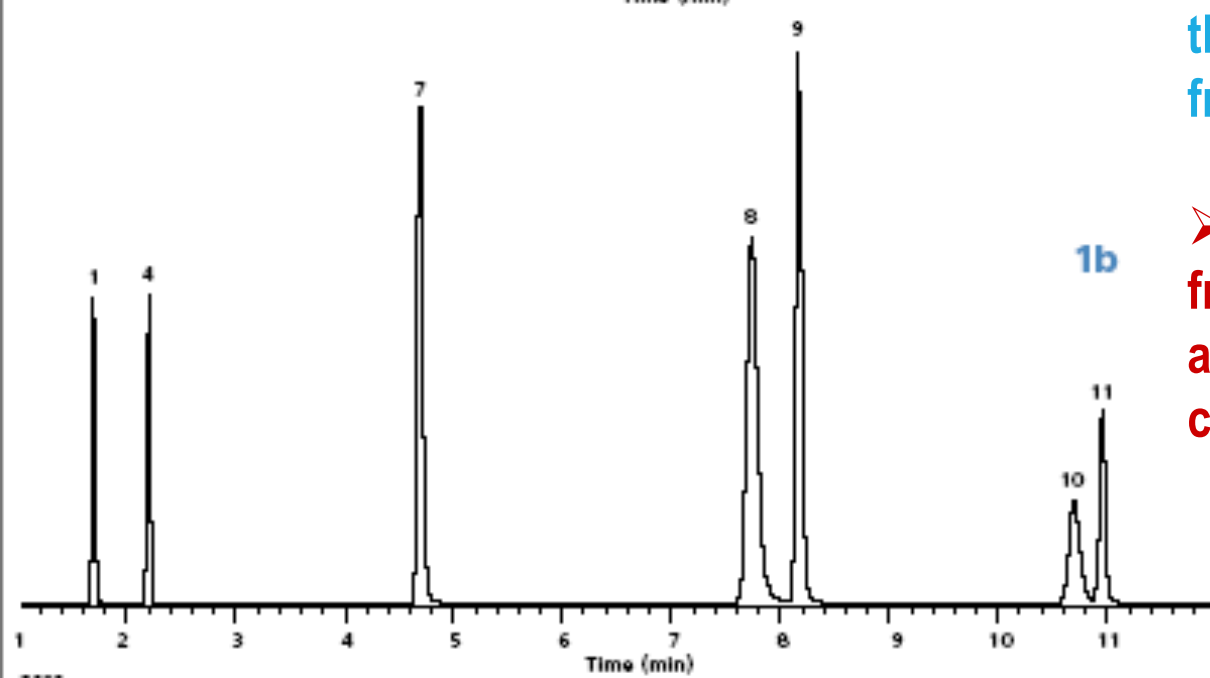


1a

➤ Chromatograms from Commercial Carbon based GC Columns from Agilent.

➤ The stationary phase is bonded, monolithic carbon layer. Max Temp. stability is 360 C

➤ All the available applications on this column were sent on request from a Technical Service Rep.

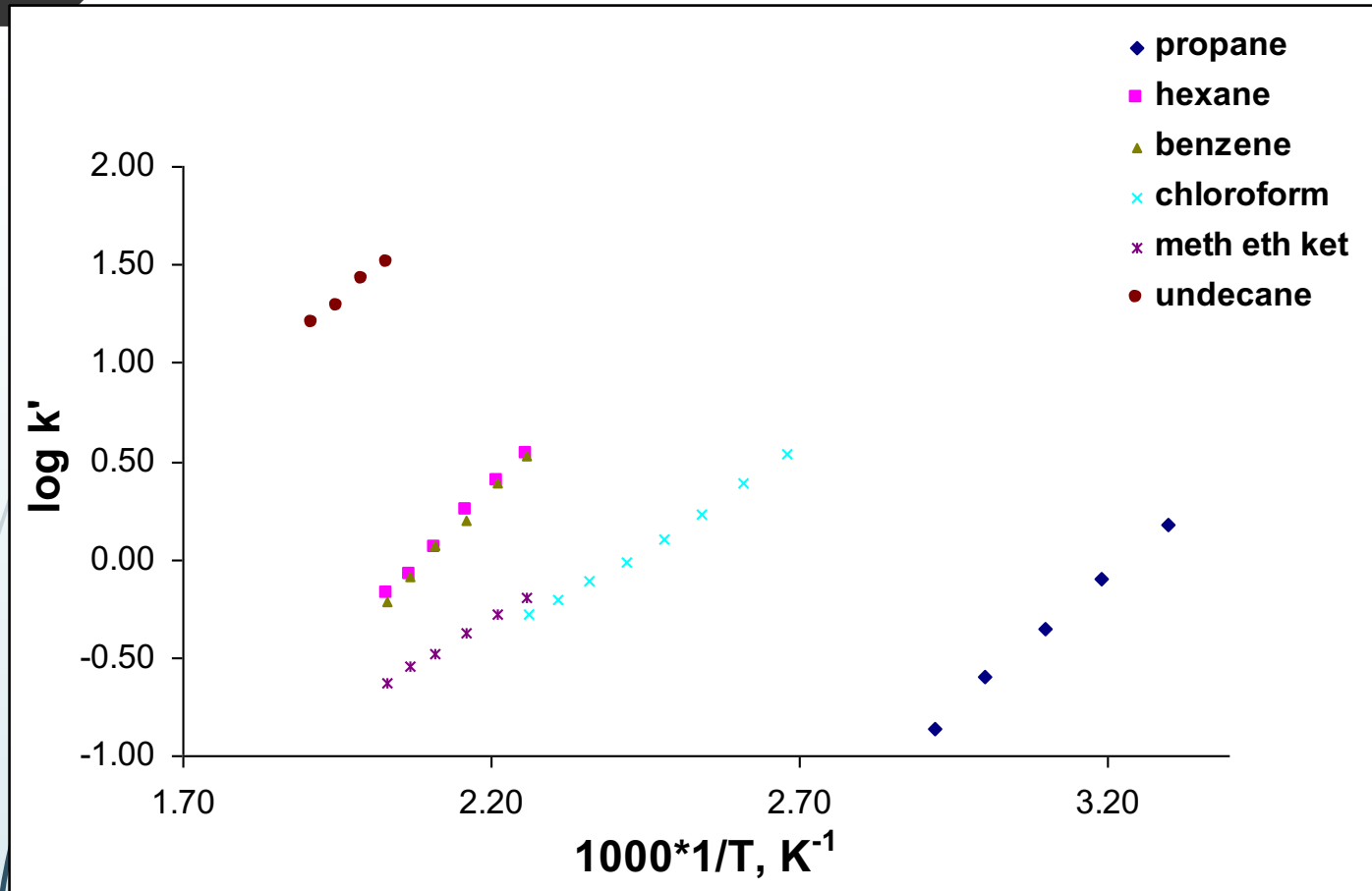


1b

➤ They show separations ranging from gases until Mol. Wts. as high as just Benzene on the same column.

Van't Hoff Plots on SWCNT Column

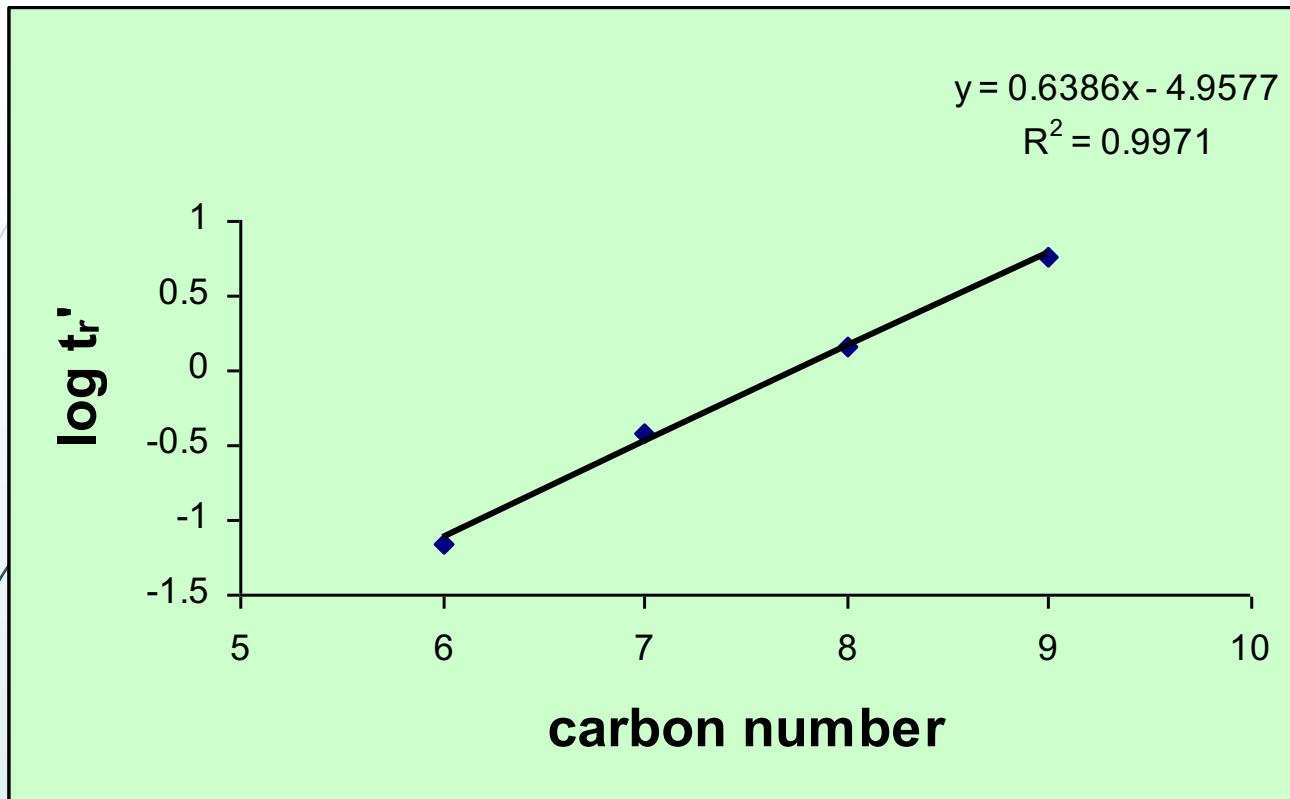
26



➤ A linear Plot suggests that the column follows classical chromatographic behavior

Plot of Homologous series

27



Conditions: 110°C, 4.5ml/min flow rate, 10 ul sample loop

➤ A linear Plot suggests Classical Chromatographic behavior

Column Efficiency

28

$$N = \frac{5.55 t_R^2}{w_{1/2}^2}$$

Solute	Column efficiency (N)	Capacity Factor (k')	Temp. (°C)
Pentane	759	3.270	130
Dichloromethane	745	4.486	50
Toluene	785	7.283	200
O-Xylene	793	10.962	240
Ethylbenzene	689	6.216	230
Nonane	625	13.915	270

➤ The above column efficiency is for 0.75 m length of column. For a meter length of column the N is about 1000. This is comparable to commercial GC Columns

McReynolds Constant – Indicator of Polarity of a stationary Phase

- Mc Reynolds Constant is difference between the retention index (I^P) on a particular phase and on a non polar reference phase (I^{NP}) usually squalane (C_{30}) hydrocarbon.

$$\Delta I_x = I^P - I^{NP}$$

The retention index, I , is defined by

$$I = 100 [\log t'_{rx} - \log t'_{rn} / \log t'_{rn+1} - \log t'_{rn}] + 100n$$

- Where t'_{rx} is the adjusted retention time for the sample; t'_{rn} and t'_{rn+1} are the adjusted retention times for the n -alkanes eluting just before, and just after the sample, respectively; and n is the number of carbon atoms in the n -alkane eluting at t'_{rn} .

Evaluation of McReynolds Constants for Column Polarity

30

Probe	benzene	1-butanol	2-pentanone	1-nitropropane	pyridine
I for SWNT	589.7	689.5	752.2	-	874.9
I for Squalane	653	590	627	652	699
ΔI	-63 (x')	100 (y')	125 (z')	(u')	176 (s')

- A solute's retention index on squalane is primarily reflective of its partial pressure with respect to the n-alkanes,
- a difference in its retention index on other column is indicative of specific solute interaction with that stationary phase.

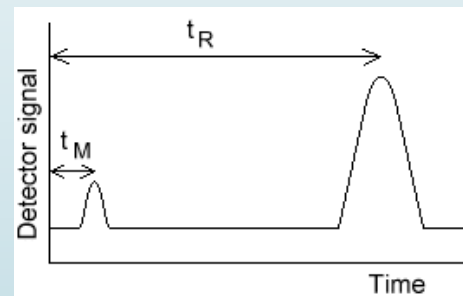
Comparison of Capacity factors (k') on SWCNT and packed Carbopack-CTM column

31

Sample	SWNT- k'	Carbopack- k'	Temp.
Hexane	3.390	4.005	180
Benzene	3.125	2.562	180
Methylethylketone	0.531	1.500	180
Chloroform	3.450	3.048	100
Propane	1.508	1.625	30

➤ Capacity factor (k') is a measure of sample retention on the sorbent. Results show that the capacity of 300 nm SWCNT film is comparable to the 0.35 g packed sorbent material.

$$k'_A = \frac{t_R - t_M}{t_M}$$



Gas Chromatography: Heats of Sorption

32

$$F \cdot t_R = V_R \quad \text{Retention Volume}$$

$$F \cdot t_M = V_M \quad \text{Dead Volume}$$

$$V'_R = V_R - V_M \quad \text{Adjusted Retention Volume}$$

$$V_N = j V'_R \quad \text{Net Retention Volume, since mobile phase is compressible}$$

$$J = \frac{3((P_i/P)^2 - 1)}{2((P_i/P)^2 - 1)} \quad \text{Pressure gradient factor}$$

$$V_N = (t_R - t_m) \cdot F \cdot T/T_f \cdot j$$

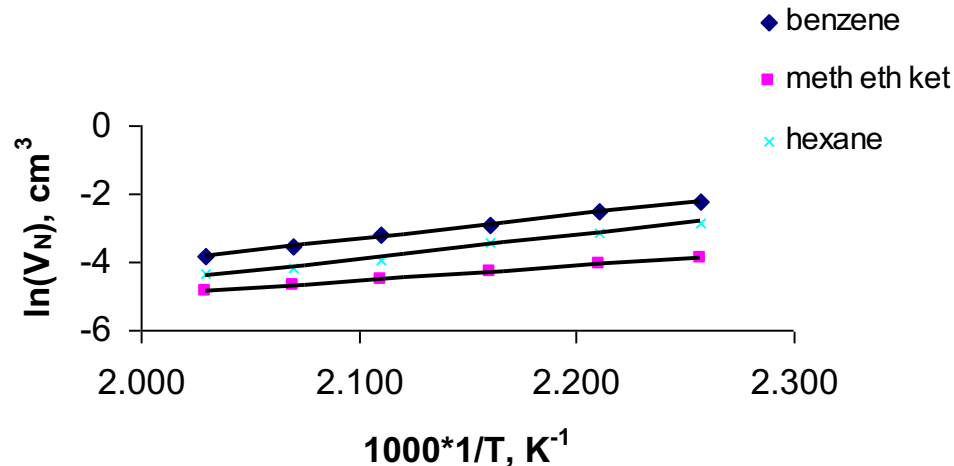
$$\ln V_N = \ln(RTn_s) + \Delta S/R - \Delta H/RT$$

ΔH (differential enthalpy of adsorption) and ΔS can be calculated from slope and intercept of the plot of $\ln V_N$ versus $1/T$

Intercept = $(\ln(RTn_s) + \Delta S/R)$, at infinite dilution region the first term can be neglected.

Heats of Adsorption

33



Sample	SWNT- ΔH_s (kJ.mol ⁻¹)	Carbopack-C- ΔH_s (kJ.mol ⁻¹)
Hexane	59.53	19.18
Benzene	55.88	16.0
Methyl ethyl ketone	39.12	14.88

➤ Isosteric Heats of Sorption is a measure of Sorbent-Sorbate Interaction. Data suggests stronger Interaction of organic compounds with SWCNT phase relative to the Carbopack-C Sorbent

Advantages of CNTs in GC Separations

34

- Possibility to Self-assemble on a Scaled up level & able to tweak the thickness. **Critical for Chemical Processing applications not possible with other sorbents.**
- It was possible to **extend the range of conventional chromatography** on the SWCNT column by separating gases as well as high molecular weights such as PAH's on the same column. This is unheard of in the conventional Gas-solid stationary phase materials.
- The SWCNT phase demonstrated **high thermal stability** ($> 425^{\circ}\text{C}$) than the conventional Gas-solid stationary phase materials.
- Gas Chromatography **Separations of varied polar analytes** was possible.
- Evaluation of capacity factors as well as heats of sorption demonstrated **strong sorbate-sorbent interactions** of analyte on the SWCNT phase.
- The single layer of atoms on the SWCNT framework may facilitate **nano-scale interactions with the analyte** thus proving it to be a high performance GC stationary phase material.

Homologous Series Plot

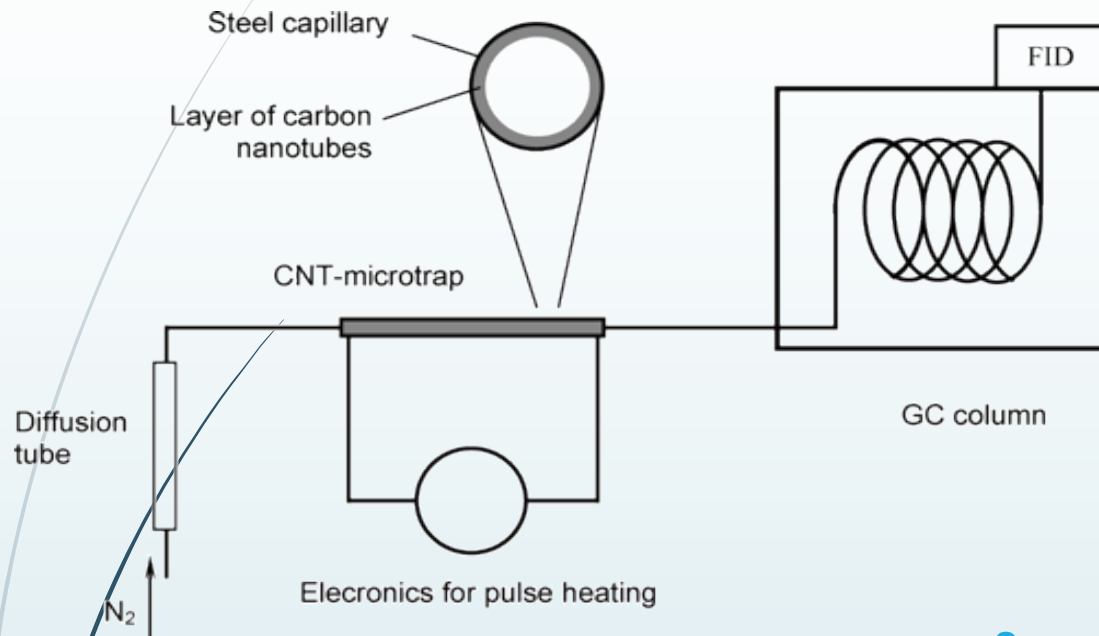
sample	carbon no.	RT (tr)	tm	tr'=tr - tm	log tr'
hexane	6	0.12	0.052	0.068	-1.1674911
heptane	7	0.427	0.052	0.375	-0.4259687
octane	8	1.468	0.052	1.416	0.1510633
nonane	9	5.923	0.052	5.871	0.7687121

Thickness of the CVD coating (CNT, CNT+ C) along the length at various CVD durations

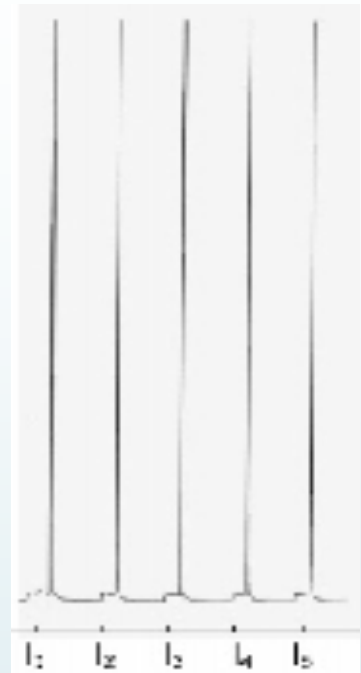
CVD duration (min)	Thickness (Average \pm SD) of CVD coating (μm) along the length (cm)					
	(cm) 10		30		40	
	CNT+C	CNT	CNT+C	CNT	CNT+C	CNT
1	4 ± 1	4 ± 1	15 ± 4	13 ± 4	7 ± 4	6 ± 3
5	55 ± 7	25 ± 7	65 ± 7	40 ± 7	35 ± 7	25 ± 7
15	100 ± 7	35 ± 7	175 ± 14	60 ± 14	65 ± 7	50 ± 7

VOC Nano Concentrator

37



Schematic of the experimental set up of microtrap



Sequence of desorption peaks generated using the CNT microtrap with toluene.

Ref: C.Saridara, R.Bruk, Z.Iqbal, S.Mitra, Anal. Chem. 2005, 77, 1183-1187