The Design of High Temperature Capillary Gas Chromatography Columns Based on Polydimethylsiloxane

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Outline

Background

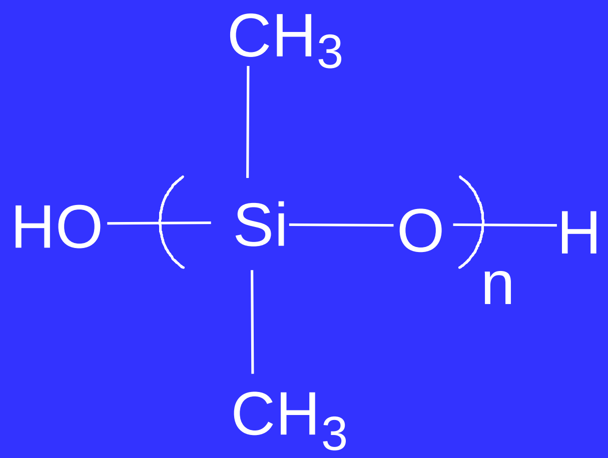
Definition of Terminology

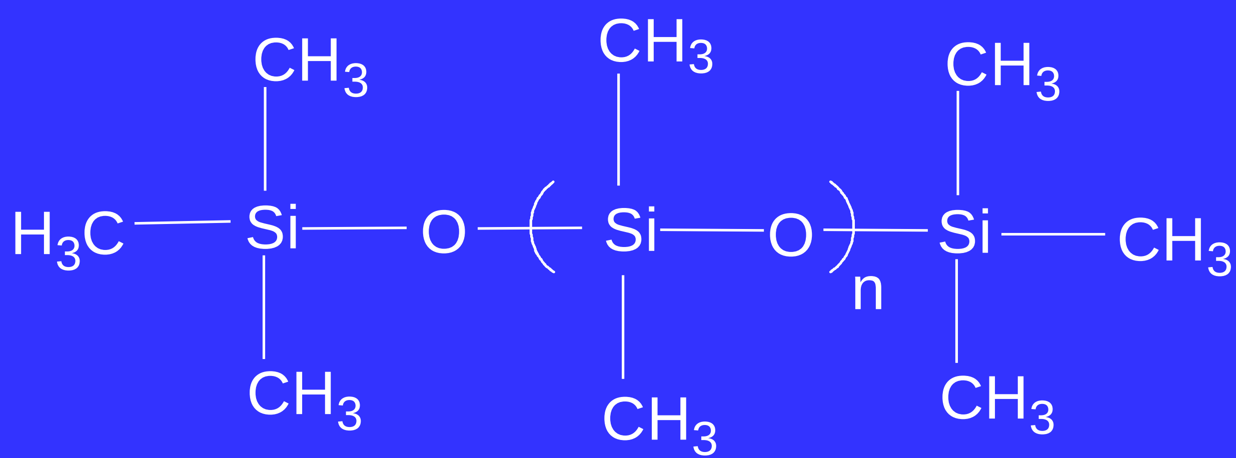
Unique Attributes of High Temperature Column

Applications

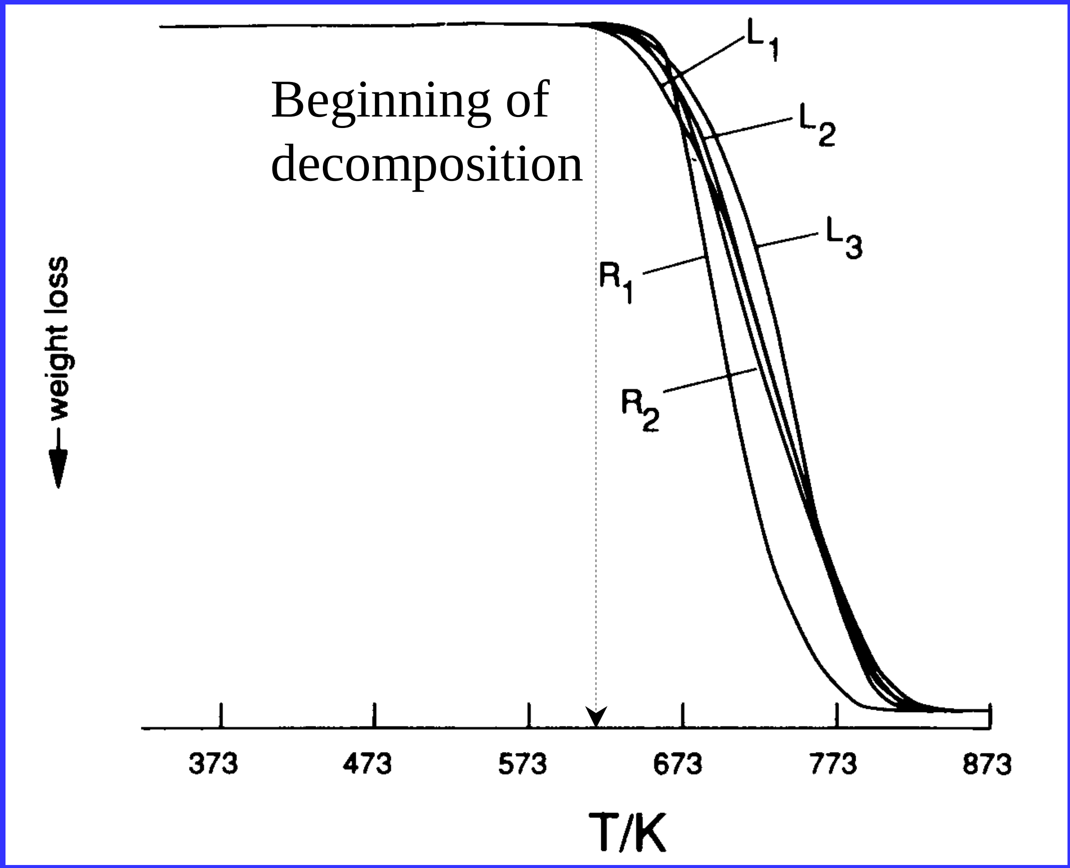
Conclusions

Polydimethylsiloxane





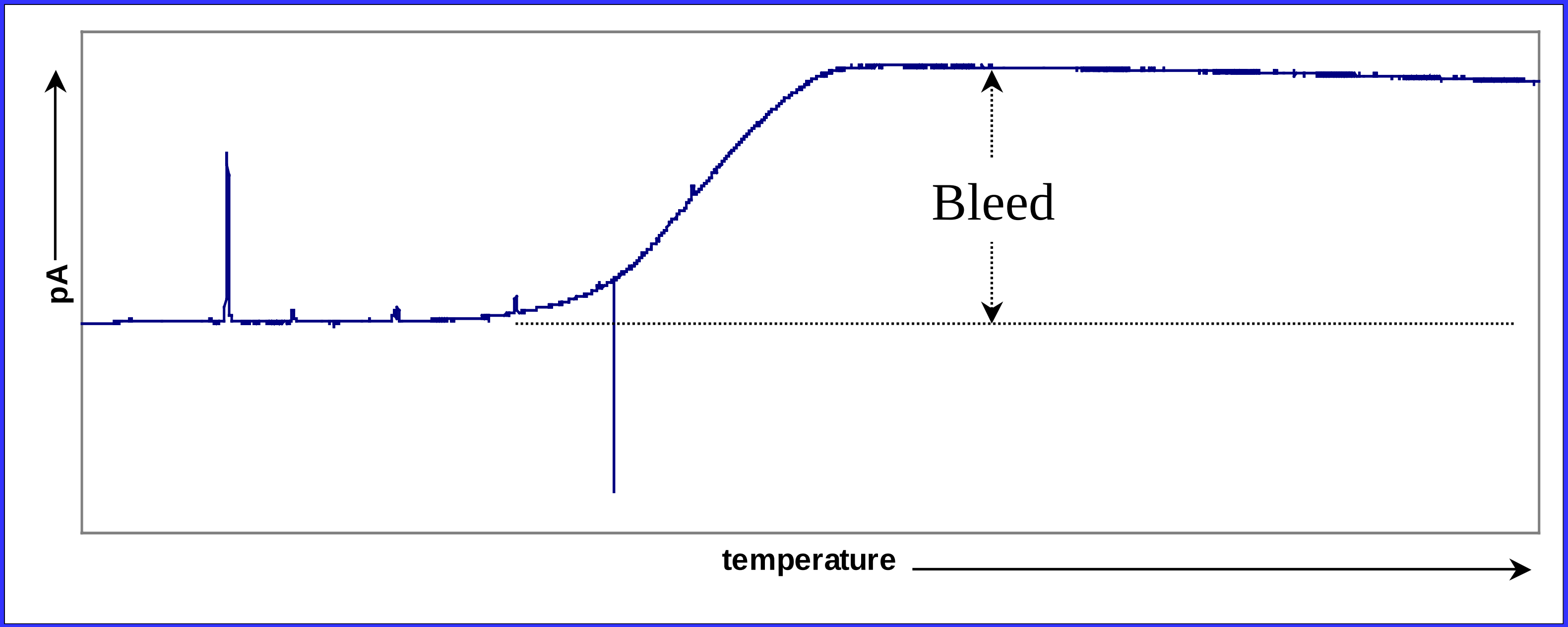
Thermal Stability of PDMS



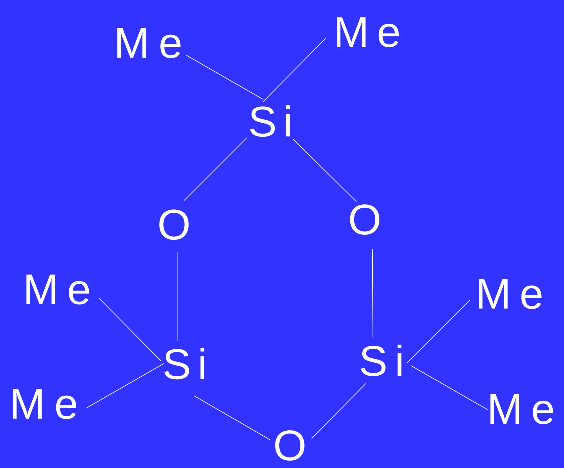
Adapted from Siloxane Polymers, ed. Clarson & Semlyen, 1993.

Bleed

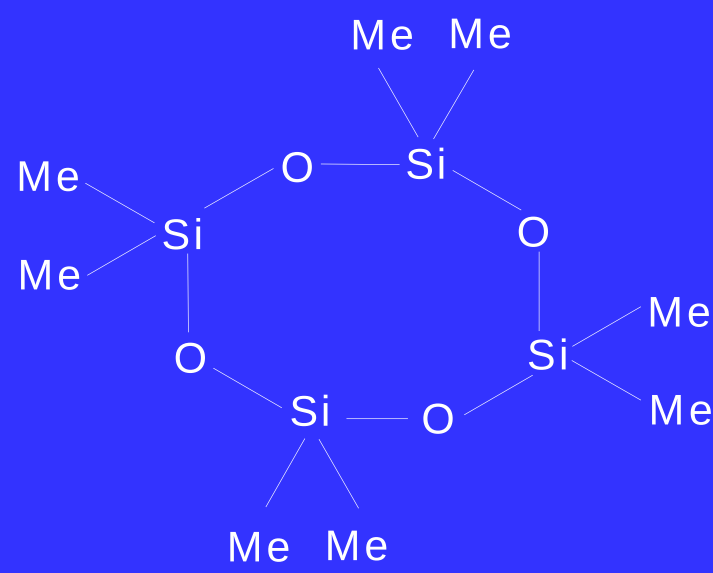
- Chromatography of "loose" silicones from the column



Typical Chemical Structure of Bleed



D_3



D_4

Challenge

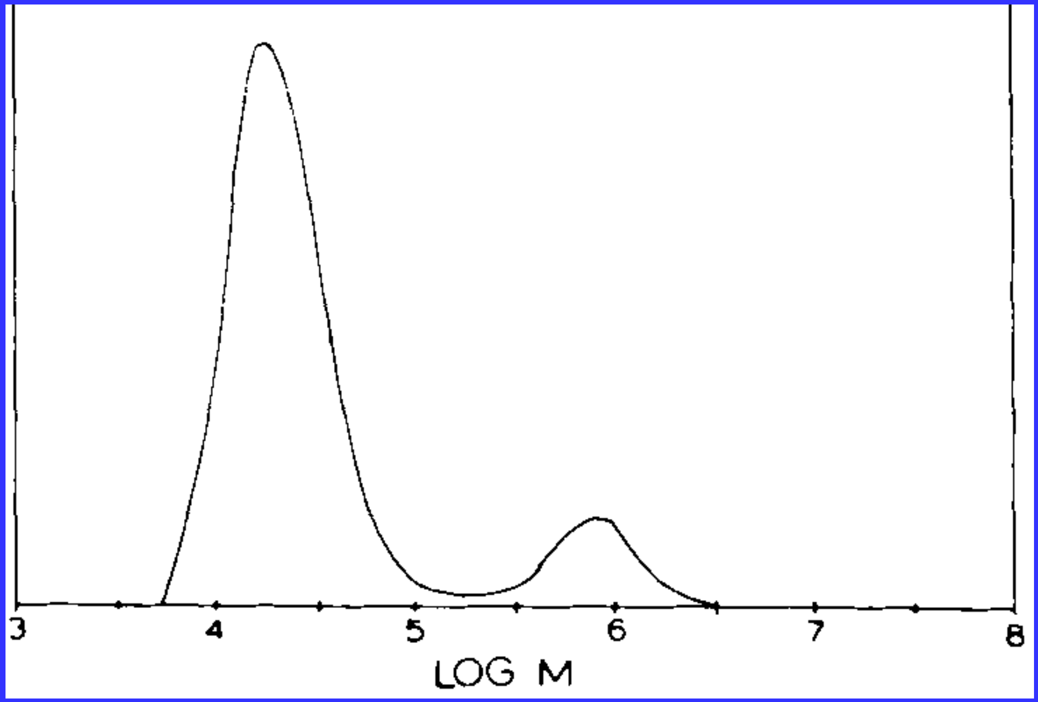
- Since the decomposition temperature for PDMS is 343°C, it is a challenge to make a column that is stable and has low bleed at 380°C.

Origin of Bleed

- Polymer Synthesis
- Oligomers that are “created” in a column’s lifetime

Origin of Bleed...

- Polymer Synthesis



Adapted from Inorganic Polymers, Mark, Allcock, & West 1992.

Polymer Synthesis

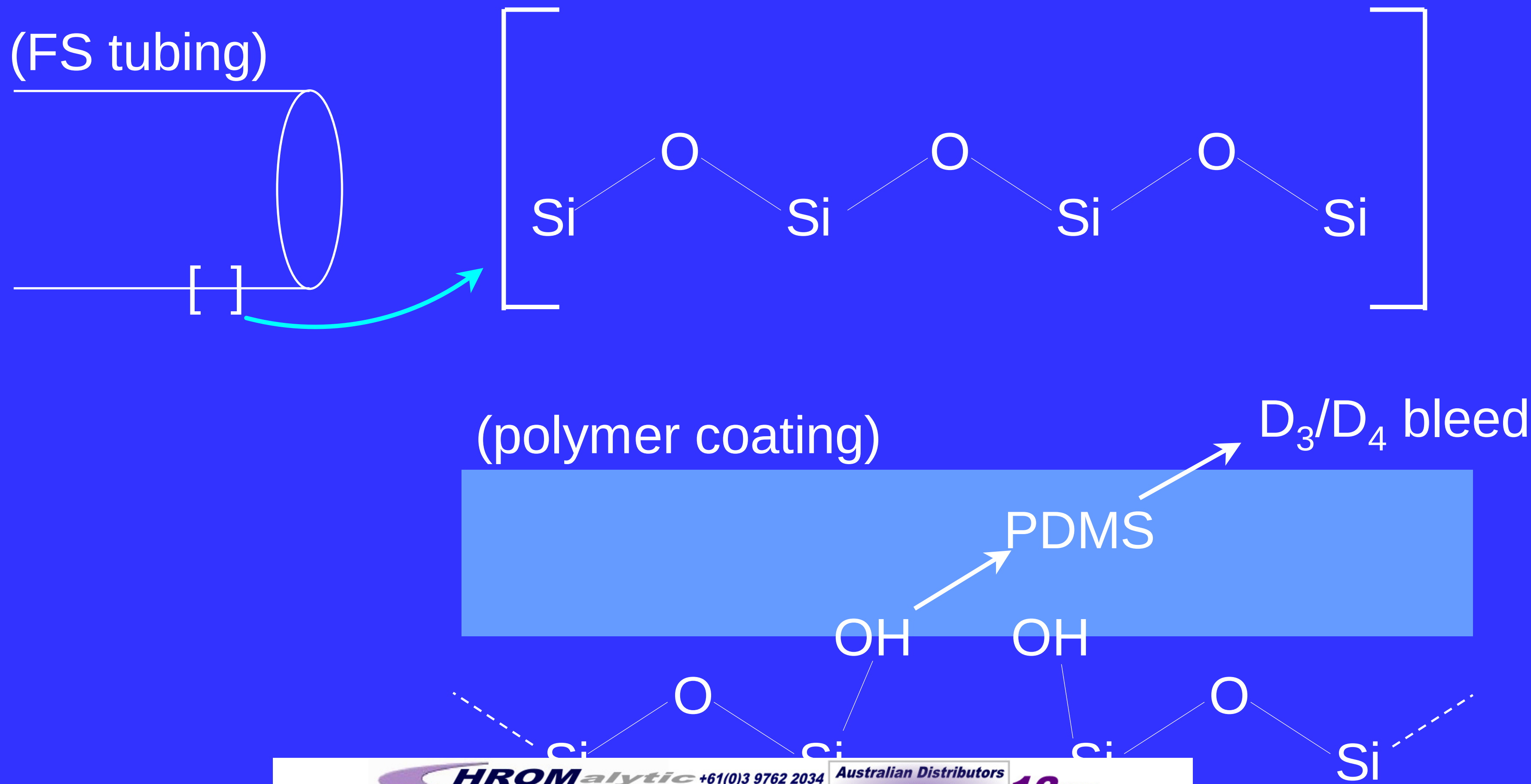
- Silicone Polymers can be synthesized using well known catalysts (KOH, HCl) under equilibration polymerization conditions.
- We use newer, more advanced catalysts, better synthetic techniques.

Origin of Bleed...

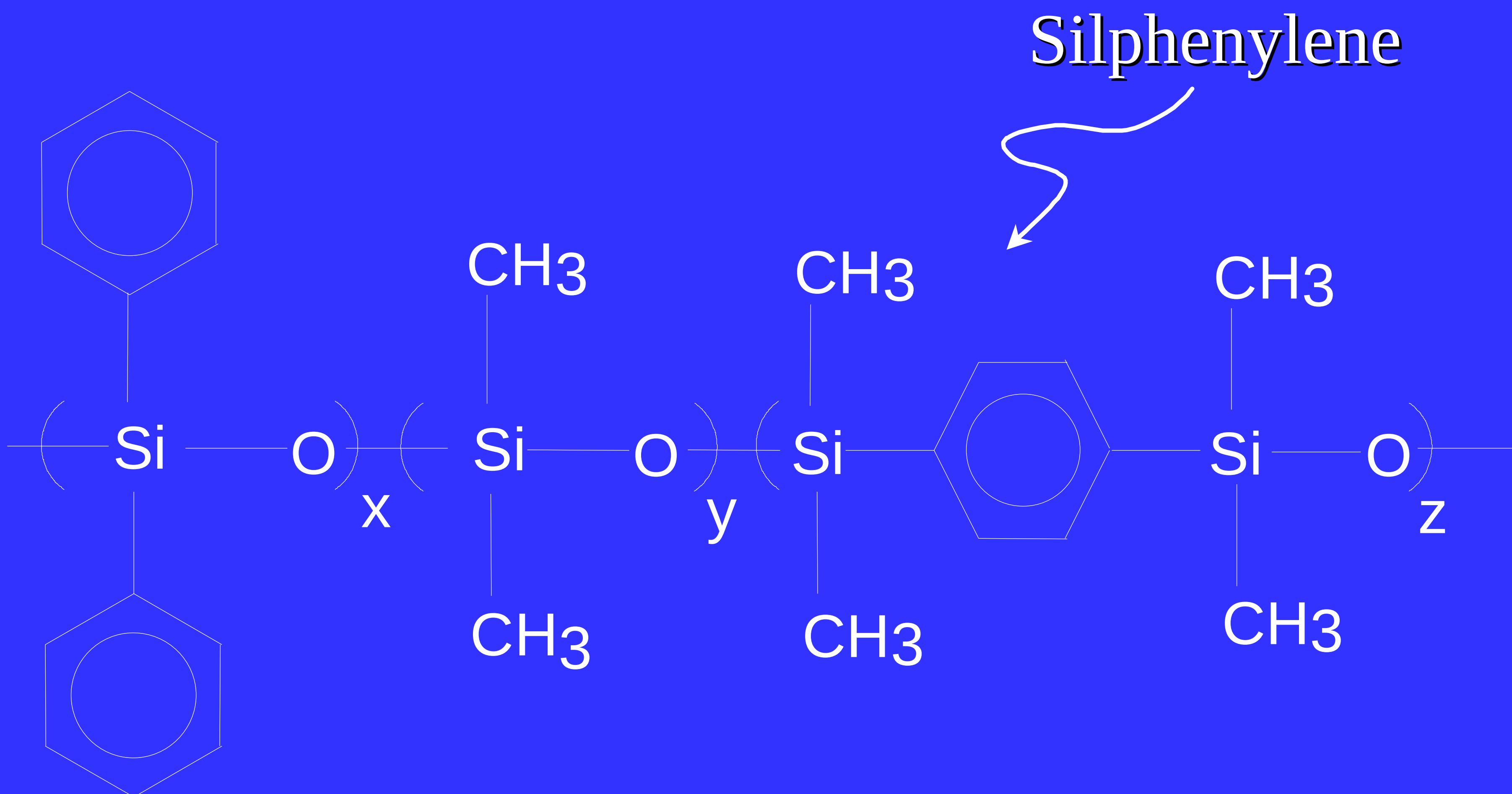
- Polymer Synthesis
- Oligomers that are "created" in a column's lifetime

Origin of Bleed...

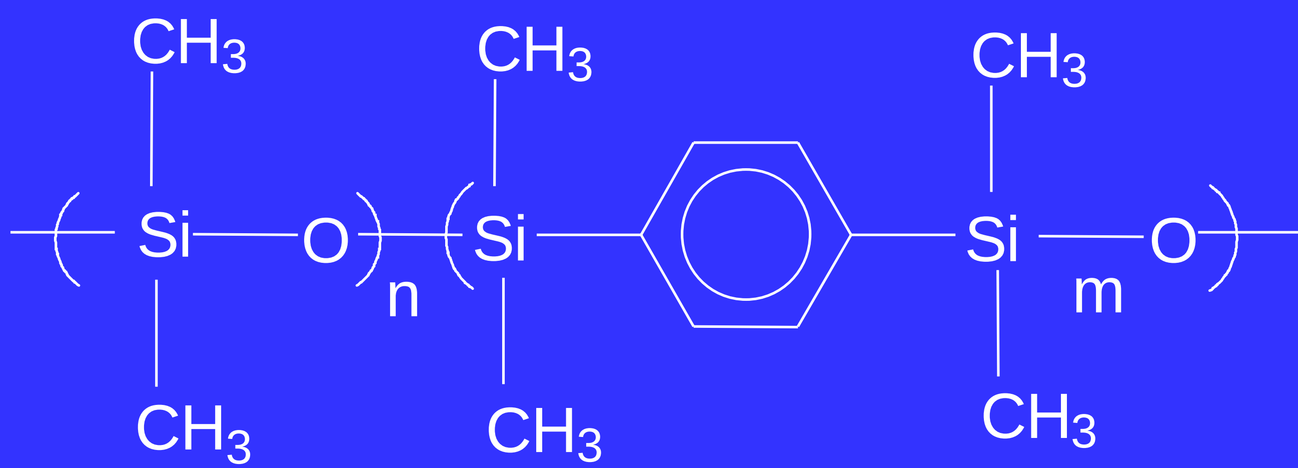
- Oligomers that are “created” in a column’s lifetime



Enhancement of Thermal Stability by Using "Additives"



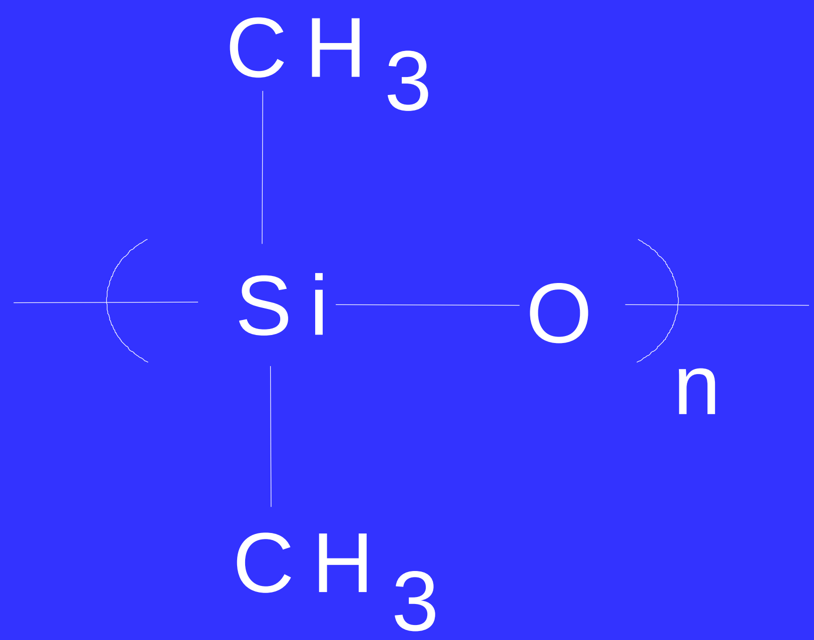
Additives...



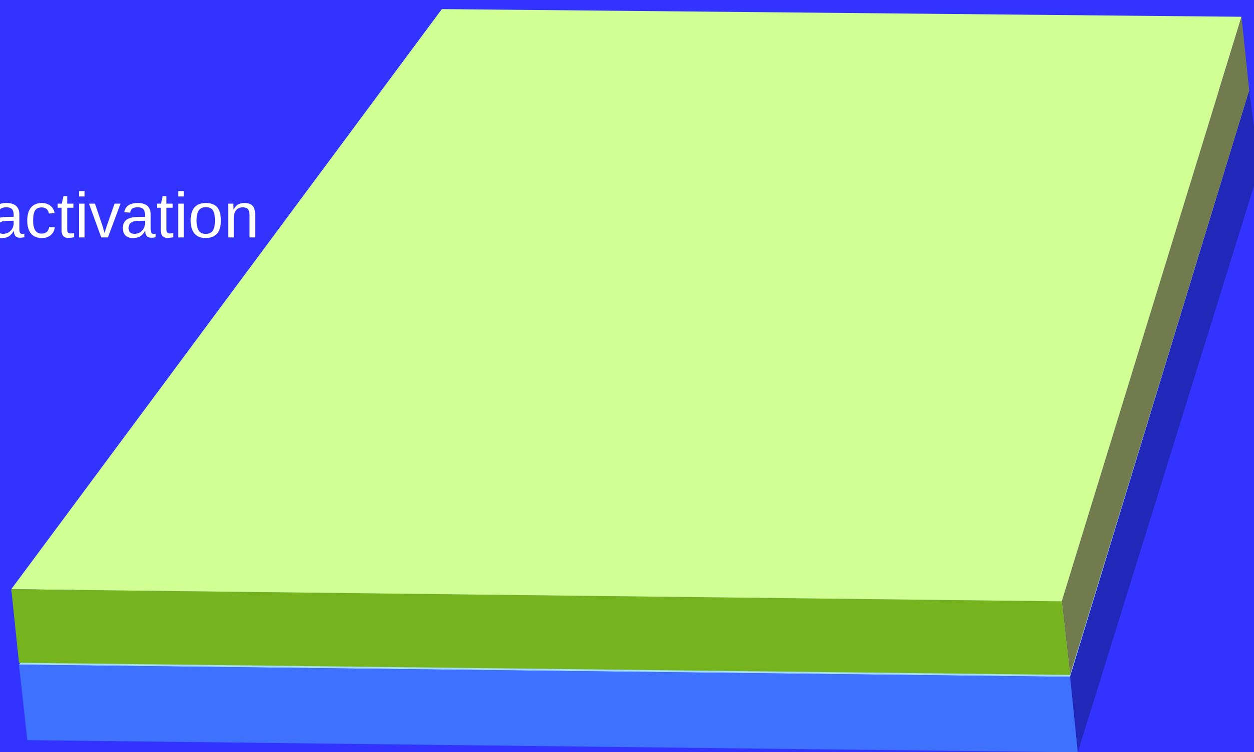
- A column with true "One" selectivity cannot be obtained by having silphenylene in the backbone.

Stx™-1 HT

- The polymer or the phase is PDMS.

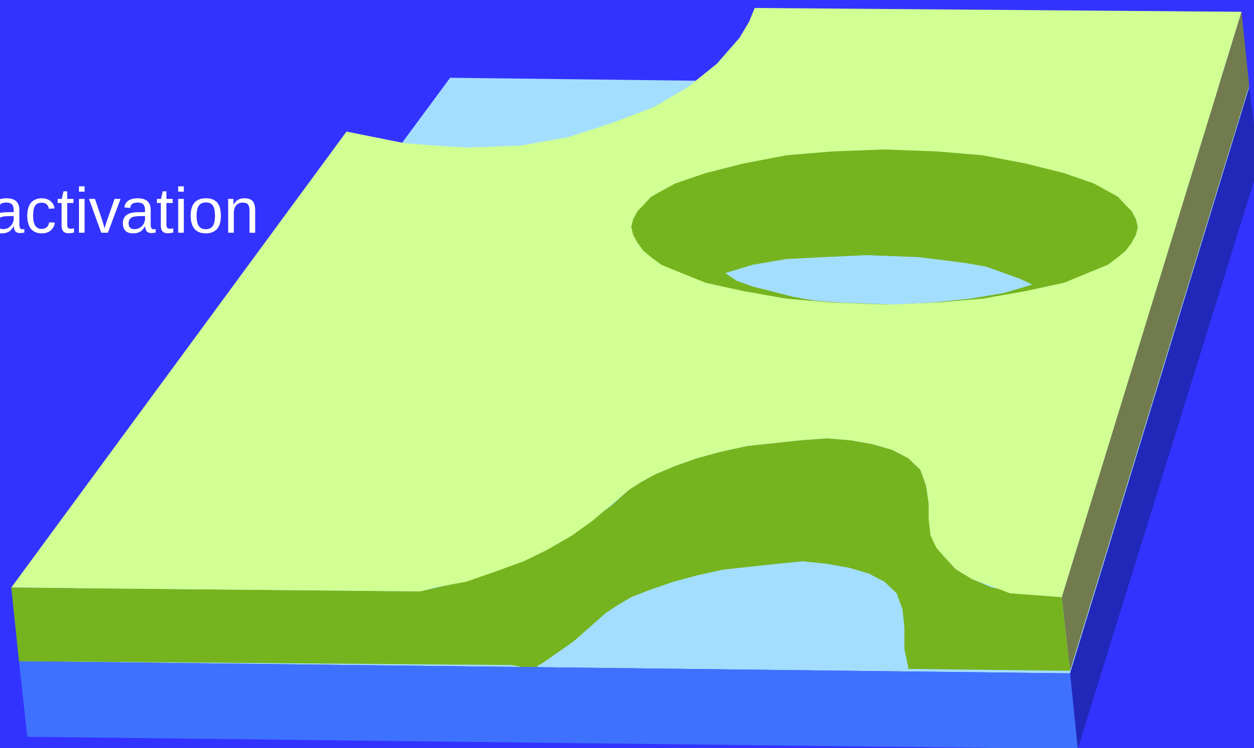


Origin of Bleed...



Origin of Bleed...

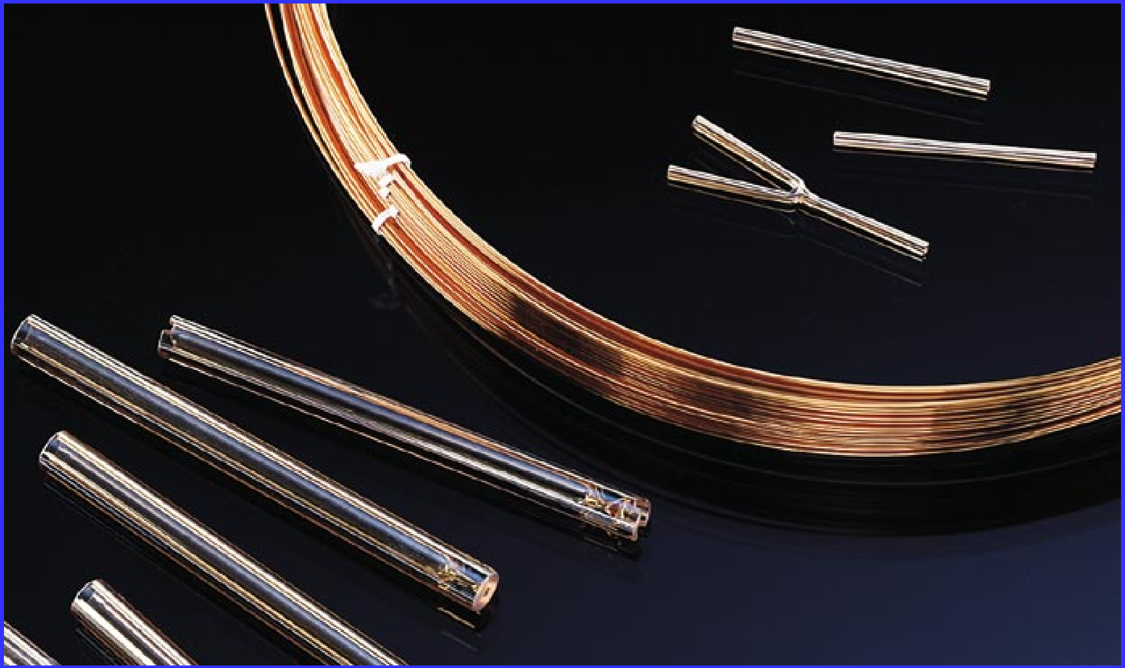
deactivation



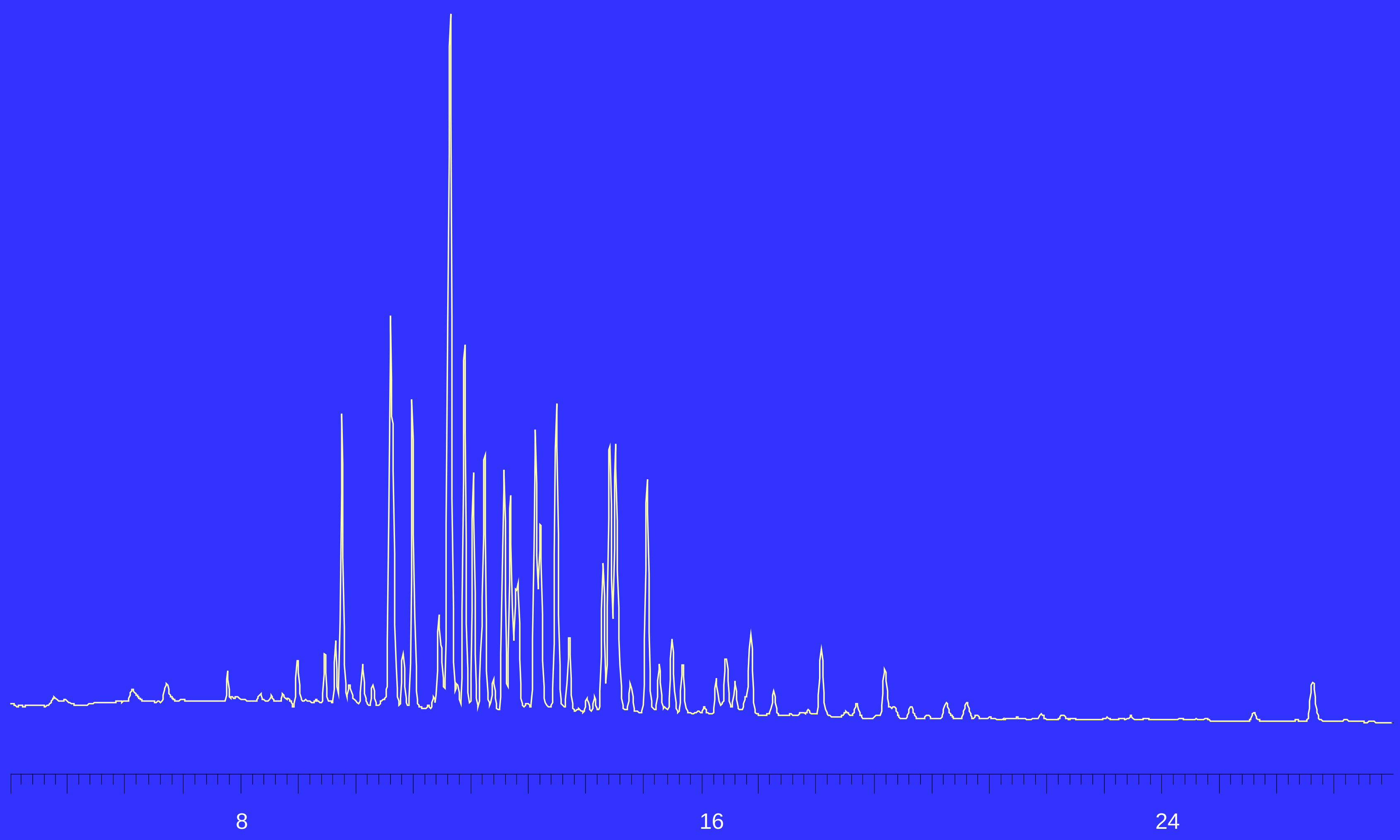
fused silica

Deactivation of the Fused Silica Surface

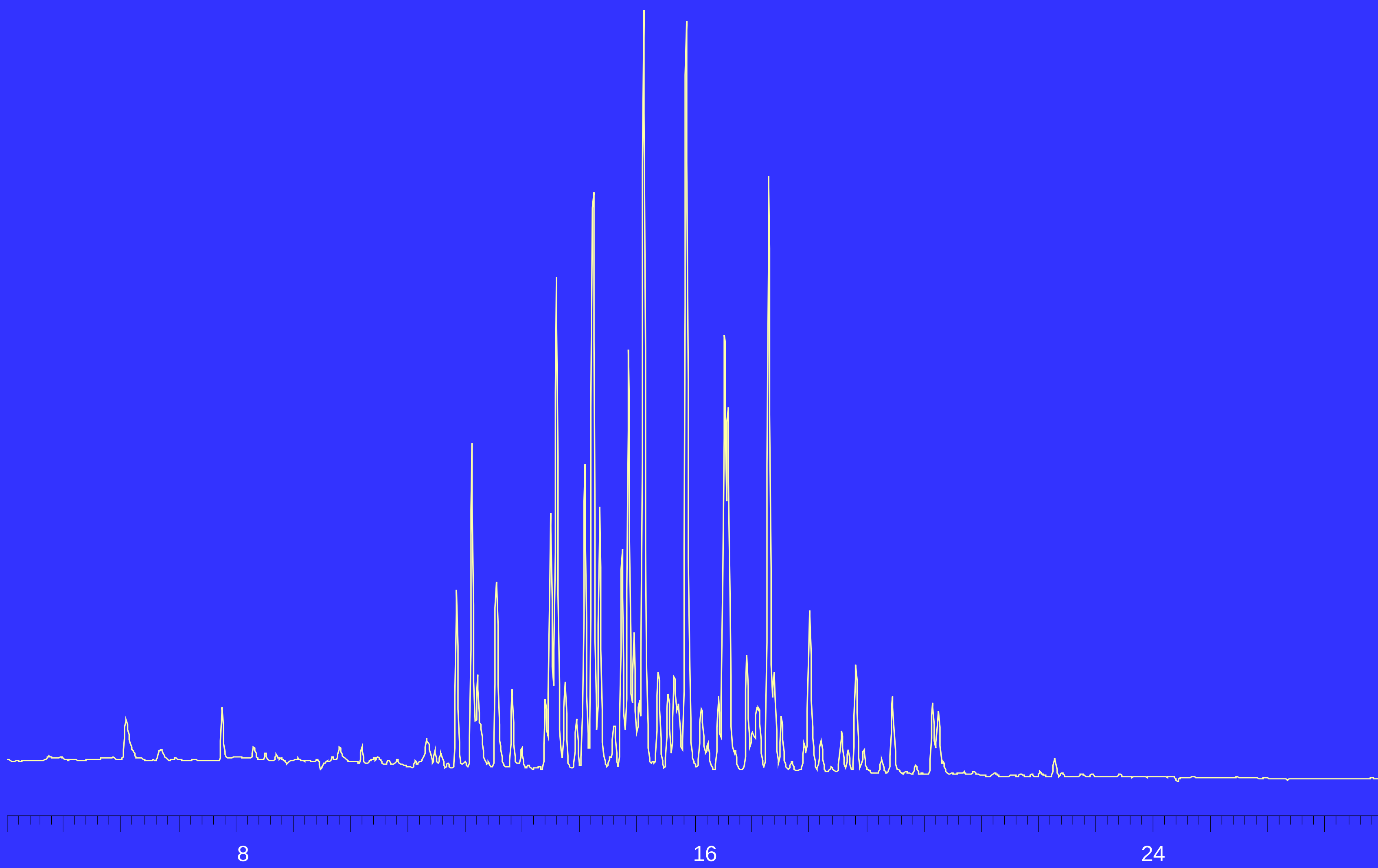
- We are using an advanced deactivation called Siltek™. It is a deposition process, unlike silazane or silicone deactivation.



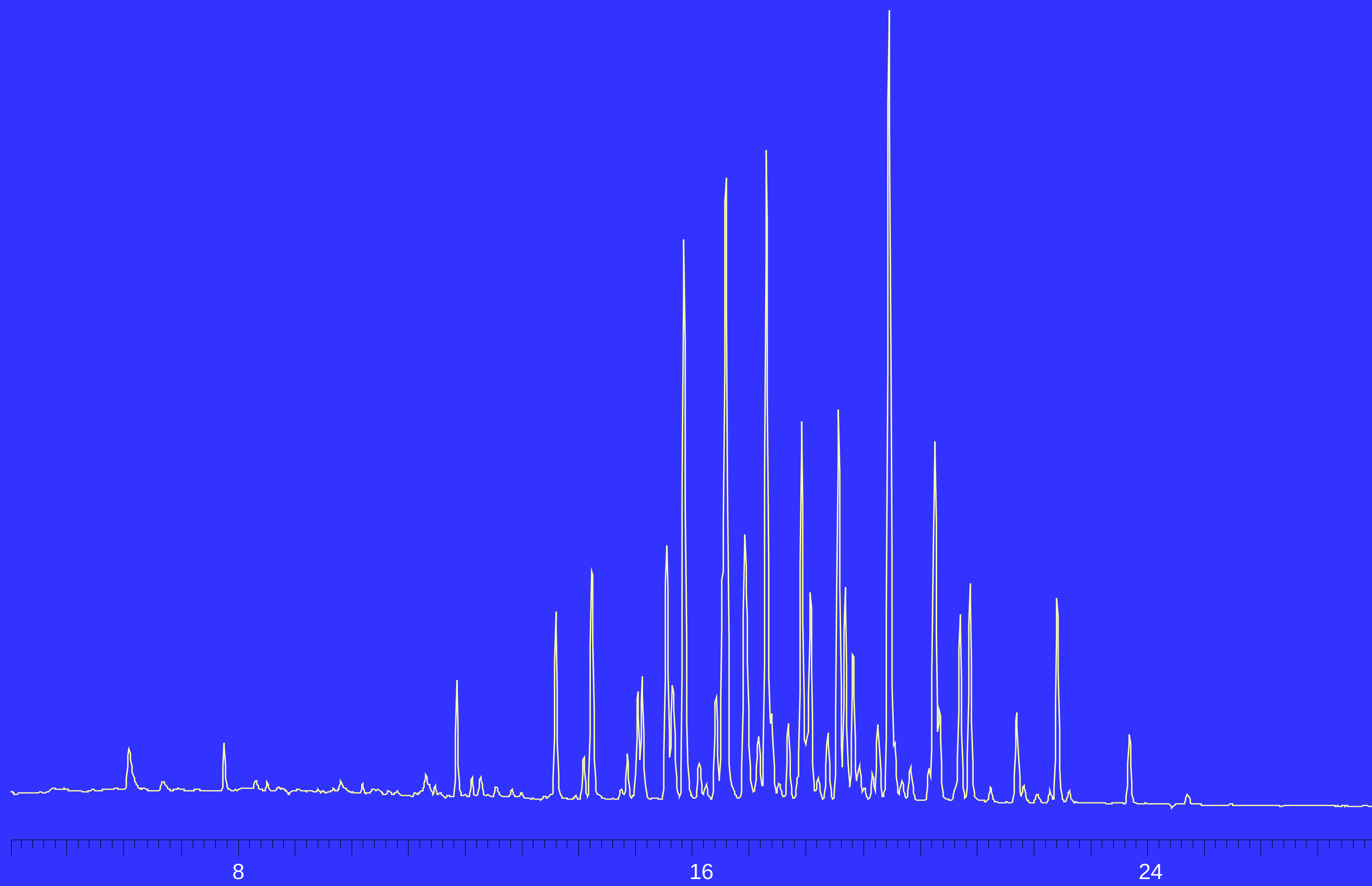
Aroclor® 1242



Aroclor® 1254



Aroclor® 1260



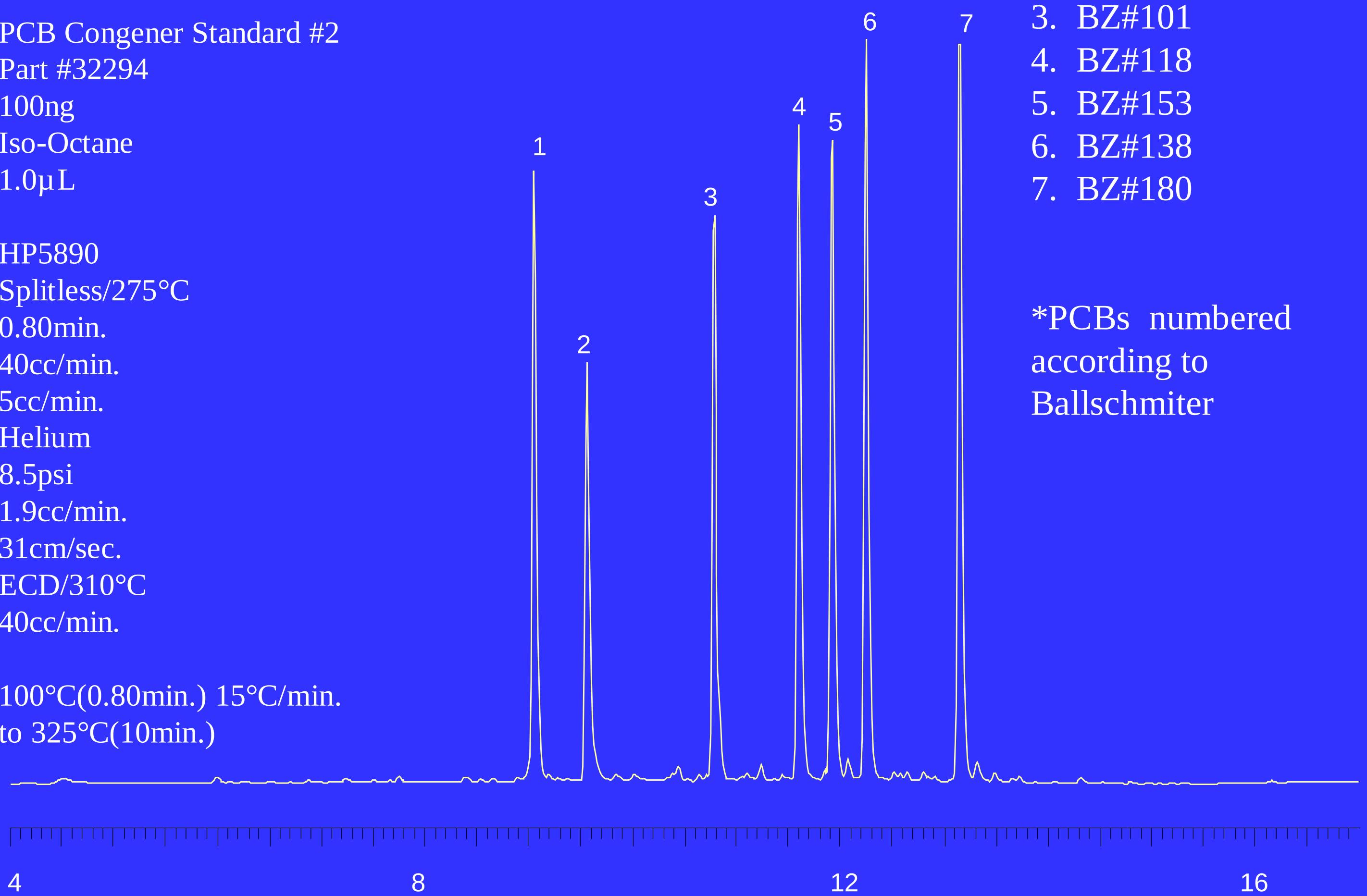
Aroclor® Run Conditions

Column:	Stx-HT1
Serial #:	215041
Description:	30m, 0.32mmID, 0.10µm
Sample:	Aroclor Solutions Part #32009, 32011, 32012
Concentration:	400ppb
Solvent:	Hexane
Sample Size:	1.0µL
Instrument:	HP5890
Injector:	Splitless/275°C

Splitless Hold Time:	1.0min.
Split Vent Flow:	40cc/min.
Septa Purge:	5cc/min.
Carrier Gas:	Helium
Head Pressure:	8.5psi
Column Flow Rate:	1.9cc/min.
Linear Velocity:	31cm/sec.
Detector:	ECD/310C
Make up Gas Flow:	40cc/min.
Temp. Program:	75°C(1.0min.) 15°C/min. to 150°C(0) 5°C/min. 300°C(10min.)

PCB Congeners

Column:	Stx-HT1
Serial #:	215041
Description:	30m, 0.32mmID, 0.10µm
Sample:	PCB Congener Standard #2 Part #32294
Concentration:	100ng
Solvent:	Iso-Octane
Sample Size:	1.0µL
Instrument:	HP5890
Injector:	Splitless/275°C
Splitless Hold Time:	0.80min.
Split Vent Flow:	40cc/min.
Septa Purge:	5cc/min.
Carrier Gas:	Helium
Head Pressure:	8.5psi
Column Flow Rate:	1.9cc/min.
Linear Velocity:	31cm/sec.
Detector:	ECD/310°C
Make up Gas Flow:	40cc/min.
Temp. Program:	100°C(0.80min.) 15°C/min. to 325°C(10min.)



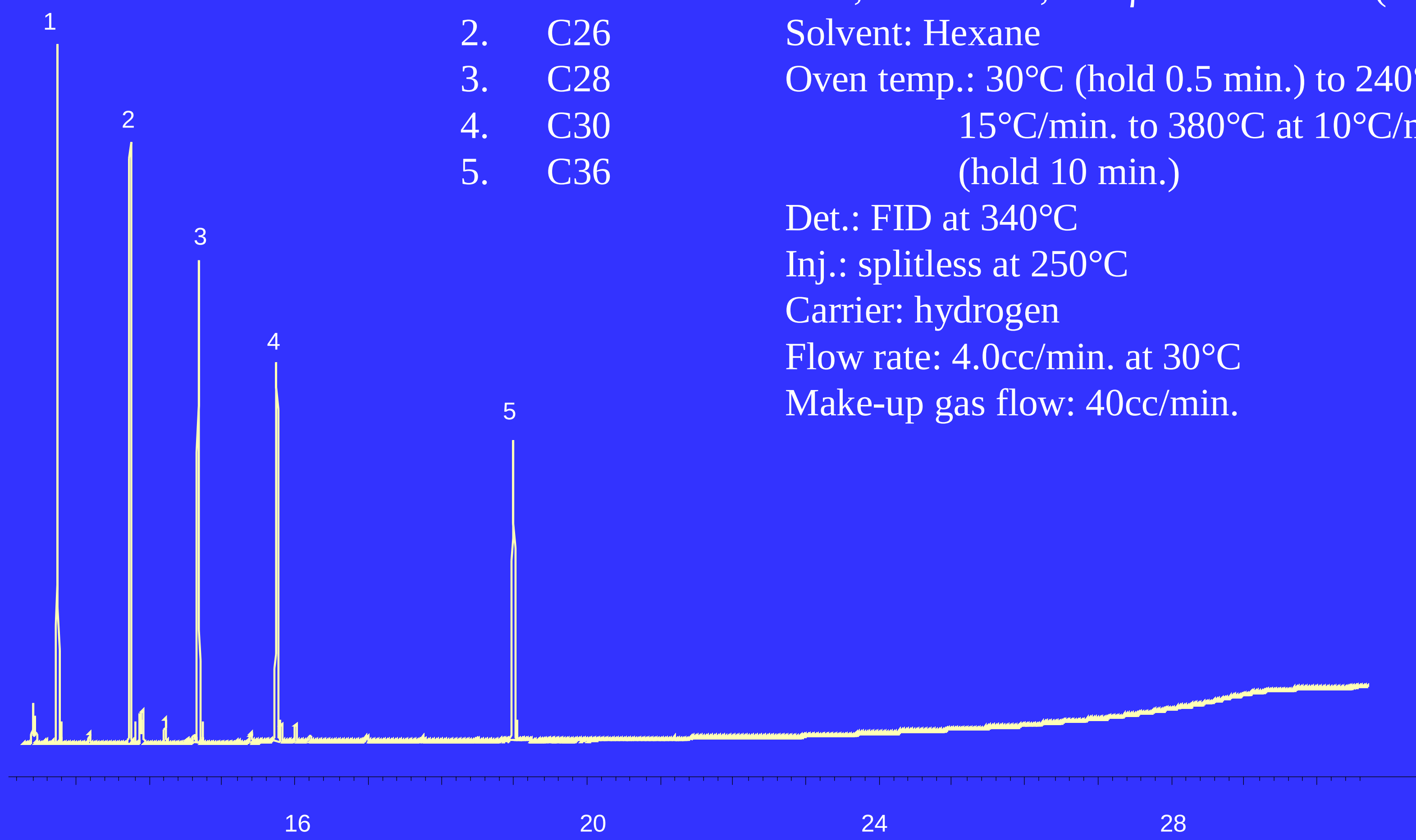
Elution Order:
1. BZ#28
2. BZ#52
3. BZ#101
4. BZ#118
5. BZ#153
6. BZ#138
7. BZ#180

*PCBs numbered according to Ballschmiter

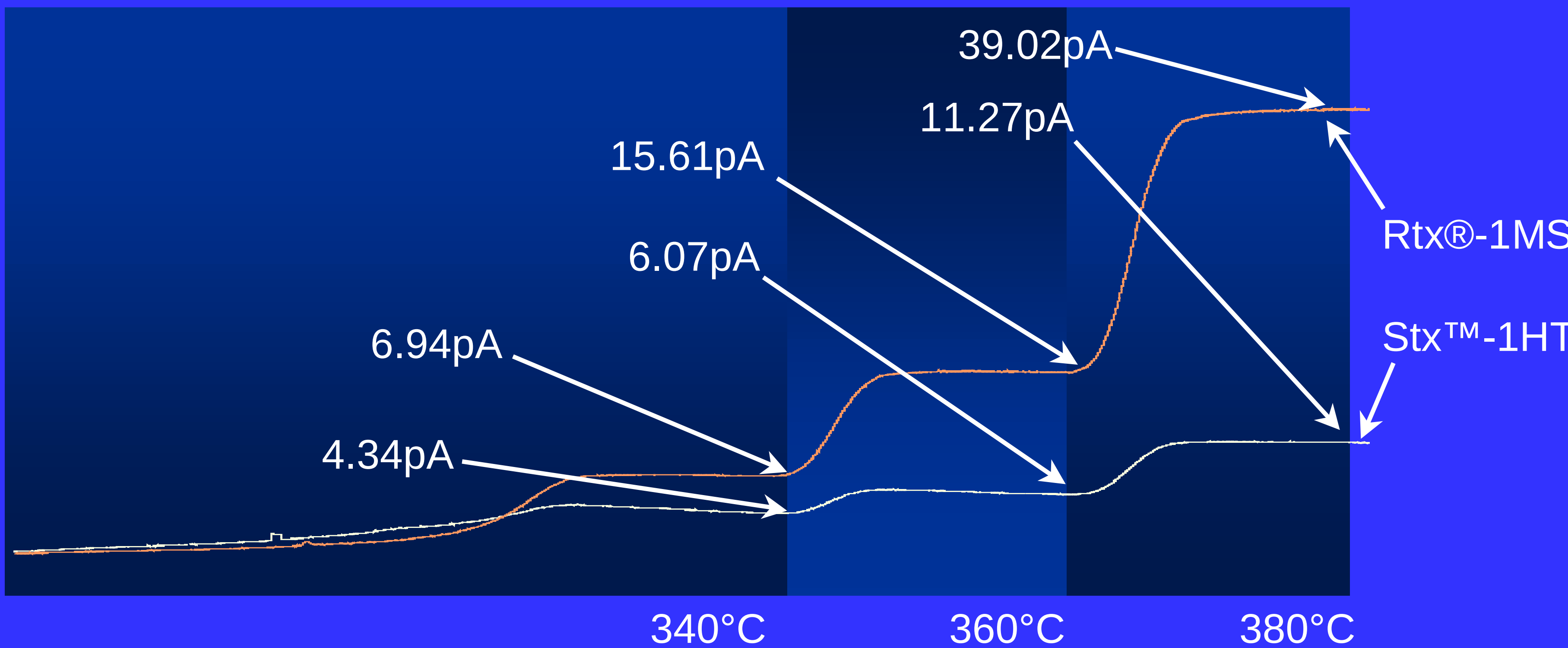
10ppm Aliphatics

1. C24
2. C26
3. C28
4. C30
5. C36

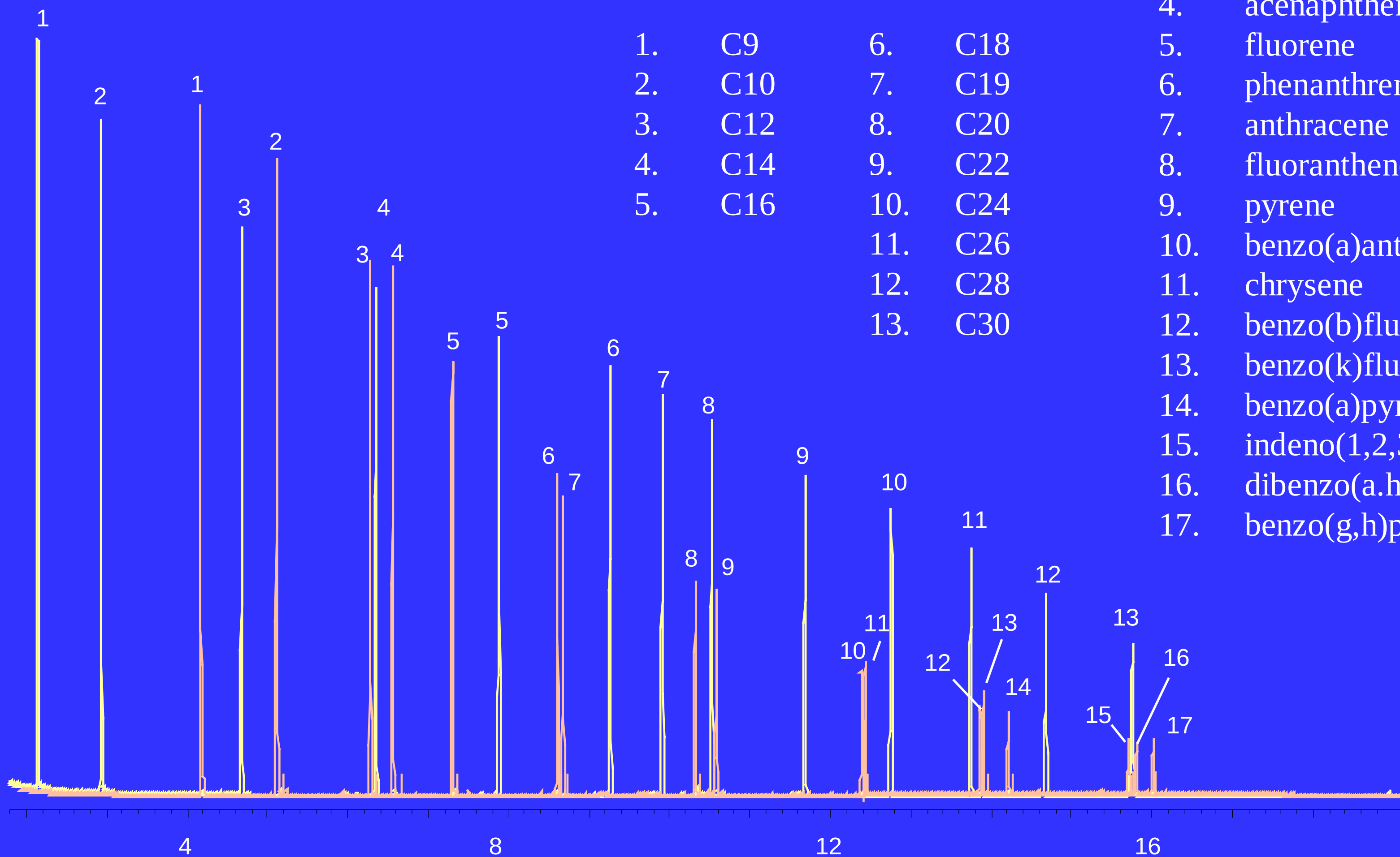
30m, 3.32mmID, 0.01µm Stx™-1HT (cat.# 11709)
Solvent: Hexane
Oven temp.: 30°C (hold 0.5 min.) to 240°C at 15°C/min. to 380°C at 10°C/min. (hold 10 min.)
Det.: FID at 340°C
Inj.: splitless at 250°C
Carrier: hydrogen
Flow rate: 4.0cc/min. at 30°C
Make-up gas flow: 40cc/min.



Bleed Comparison



50ppm Hydrocarbons



Aliphatic hydrocarbons:

1.	C9	6.	C18
2.	C10	7.	C19
3.	C12	8.	C20
4.	C14	9.	C22
5.	C16	10.	C24
		11.	C26
		12.	C28
		13.	C30

Aromatic Hydrocarbons:

1. napthalene
2. 2-methylnaphthalene
3. acenaphthylene
4. acenaphthene
5. fluorene
6. phenanthrene
7. anthracene
8. fluoranthene
9. pyrene
10. benzo(a)anthracene
11. chrysene
12. benzo(b)fluoranthene
13. benzo(k)fluoranthene
14. benzo(a)pyrene
15. indeno(1,2,3-cd)pyrene
16. dibenzo(a.h)anthracene
17. benzo(g,h)perylene

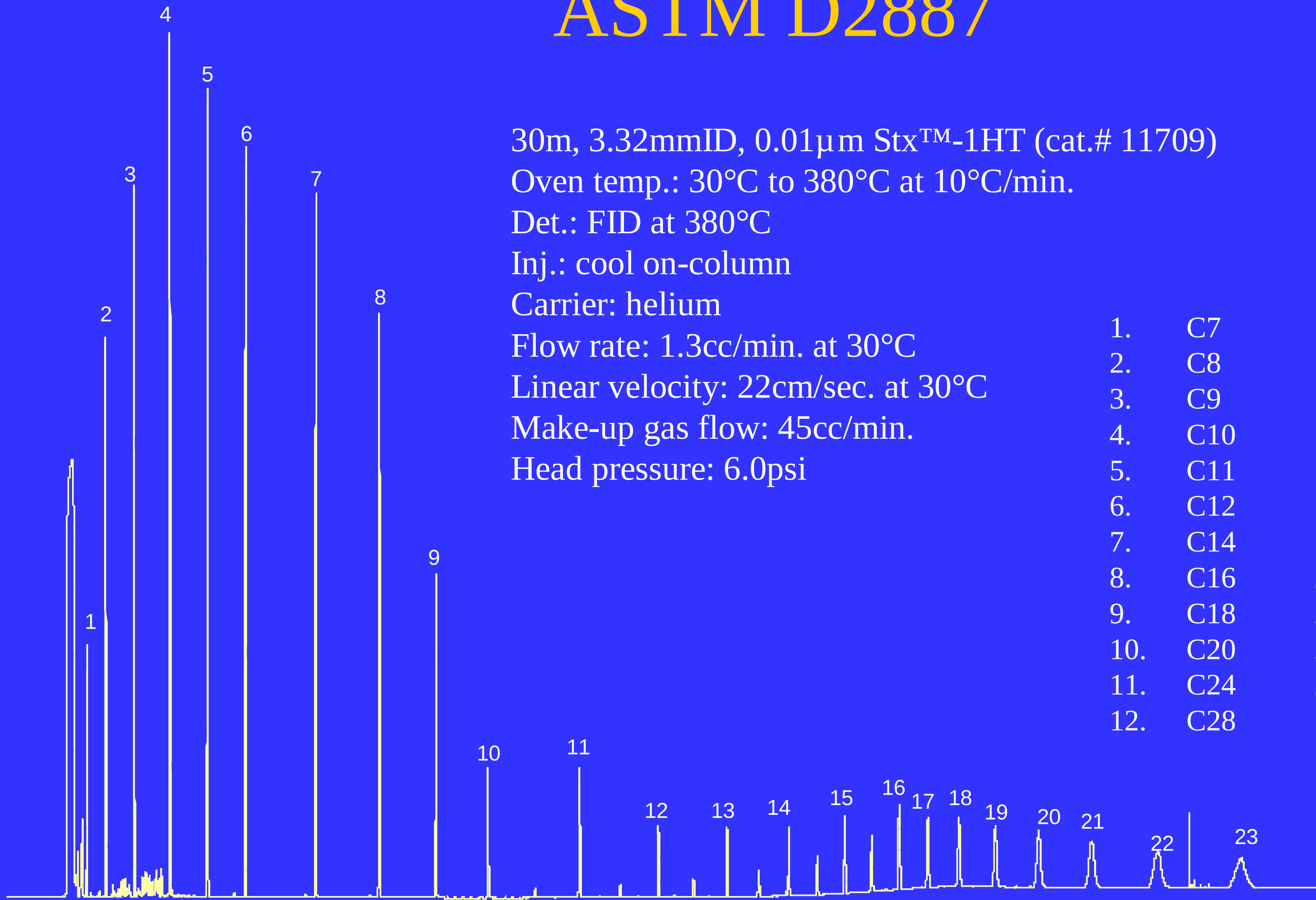
Analysis Conditions

30m, 3.32mmID, 0.01µm Stx™-1HT (cat.# 11709)
Oven temp.: 30°C (hold 0.5 min.) to 240°C at
15°C/min. to 380°C at 10°C/min.
(hold 10 min.)
Det.: FID at 340°C
Inj.: splitless at 250°C
Carrier: hydrogen
Flow rate: 4.0cc/min. at 30°C
Make-up gas flow: 40cc/min.

1.0µL injections of MA EPH Aliphatic Hydrocarbon standard (cat.# 31459, solvent: hexane) & MA EPH Aromatic Hydrocarbon standard (cat.# 31458, solvent: methylene chloride) @ 50ppm concentration.

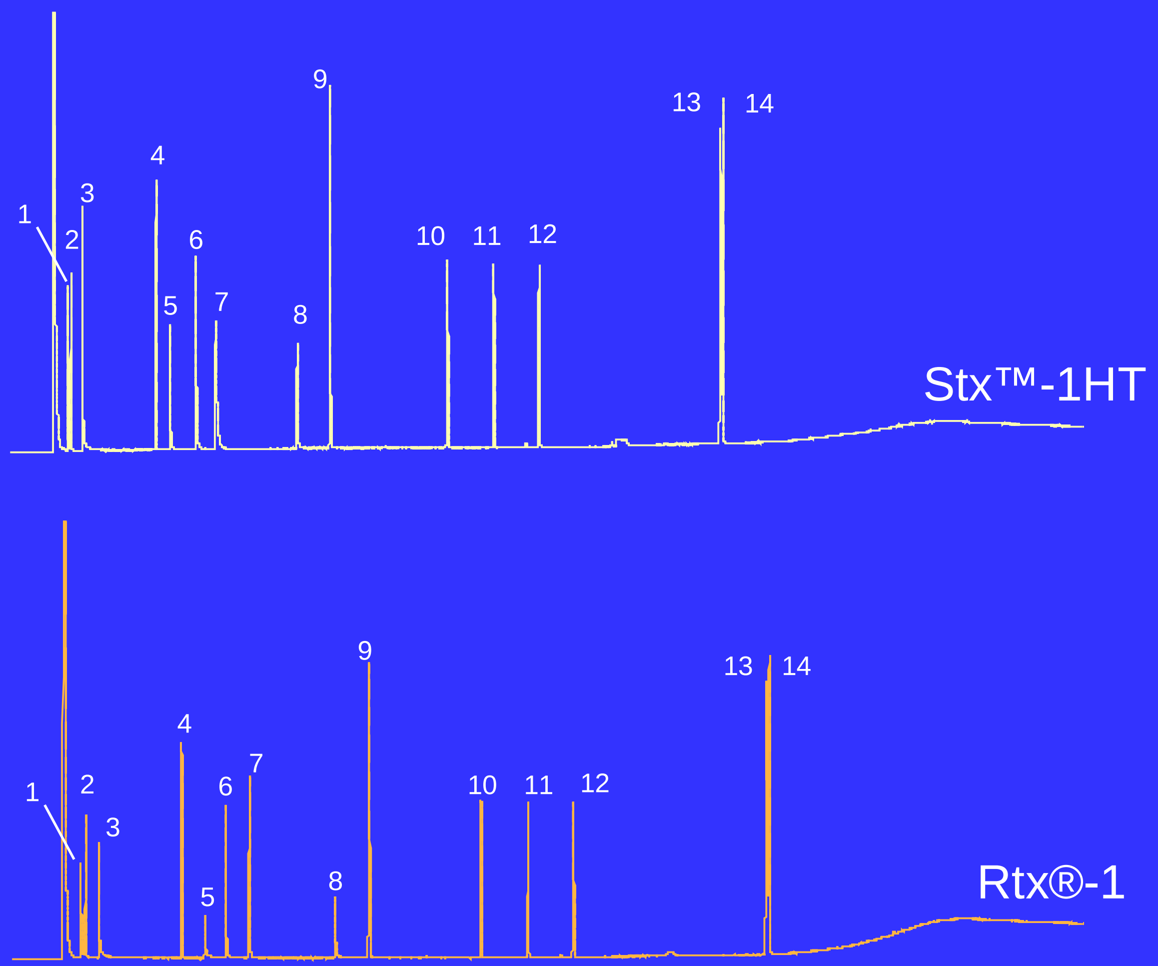
ASTM D2887

30m, 3.32mmID, 0.01µm Stx™-1HT (cat.# 11709)
Oven temp.: 30°C to 380°C at 10°C/min.
Det.: FID at 380°C
Inj.: cool on-column
Carrier: helium
Flow rate: 1.3cc/min. at 30°C
Linear velocity: 22cm/sec. at 30°C
Make-up gas flow: 45cc/min.
Head pressure: 6.0psi



1.	C7	13.	C32
2.	C8	14.	C36
3.	C9	15.	C40
4.	C10	16.	C44
5.	C11	17.	C46
6.	C12	18.	C48
7.	C14	19.	C50
8.	C16	20.	C52
9.	C18	21.	C54
10.	C20	22.	C56
11.	C24	23.	C58
12.	C28		

XTI Mix on Rtx-1 & Stx-1HT



1. 1,2-hexanediol
2. nitro-di-N-propylamine
3. benzoic acid
4. C14
5. 2,4-dinitrophenol
6. nitrophenol
7. nitroaniline
8. pentachlorophenol
9. carbazole
10. C20
11. C21
12. C22
13. benzo(b)fluoranthene
14. benzo(k)fluoranthene

Summary

- Definitions
- The design of low bleed & stable column system was discussed
- Several applications were shown