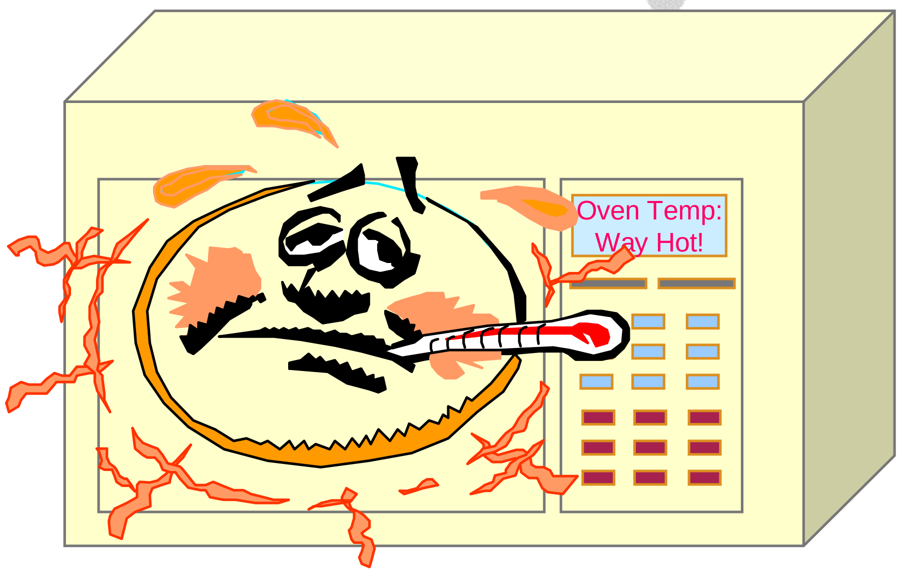
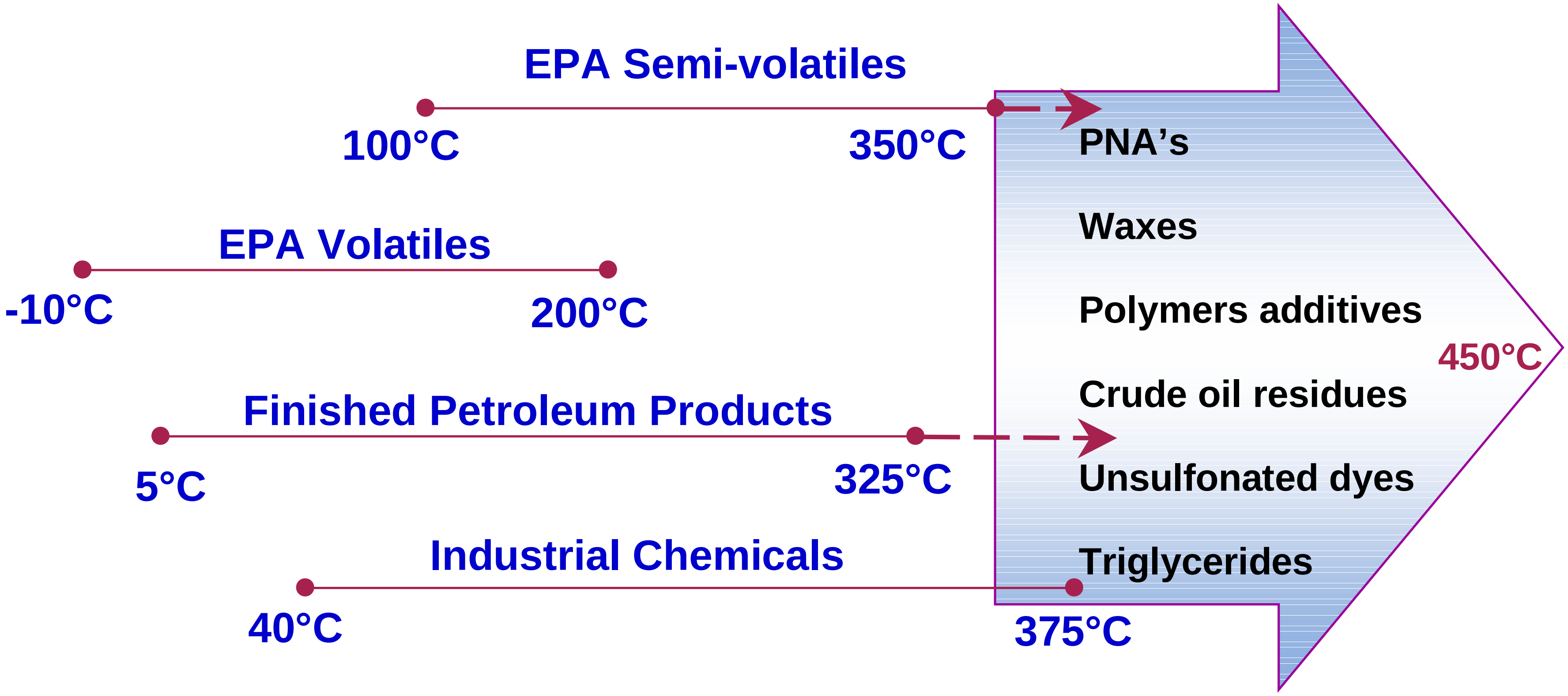
Helpful Hints and Tricks for High Temperature GC Analysis



Agilent Technologies
Innovating the HP Way

What is High Temperature GC?



Typical GC Analysis Temperatures

Why High Temperature GC?

- Fast versus LC techniques
- Simple versus SFC
- High resolution
- Stable - Good endurance - Rugged

Sample Requirements

Must be a vapor at or below 450°C

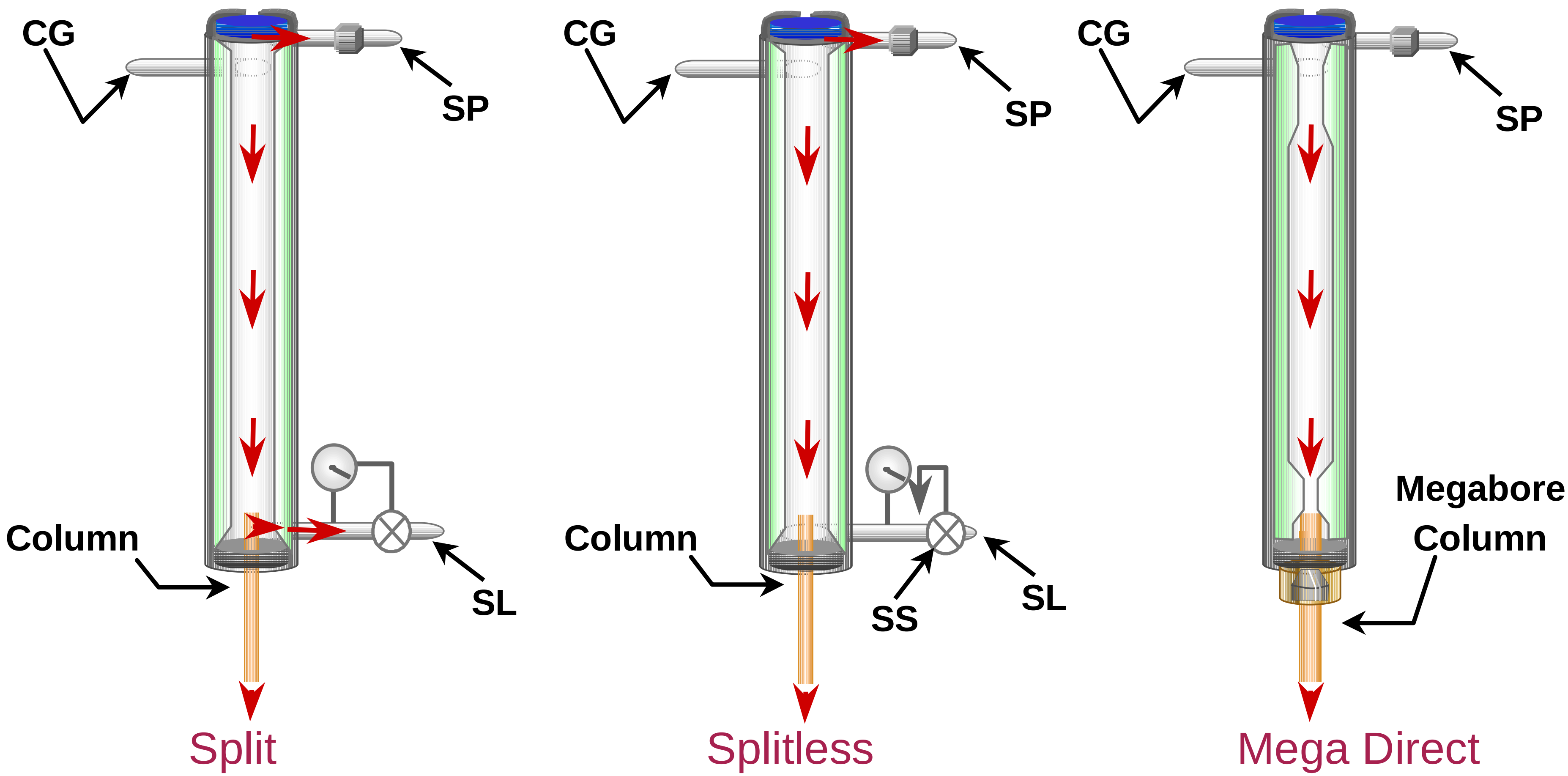
Must be soluble in a suitable solvent *or* can be vaporized from sample matrix

Must be stable at elevated temperatures

Essential Equipment for High Temperature GC

- **450°C maximum temperature zones**
- **Ultra high purity helium carrier gas**
- **Constant flow control**
- **Short, thin film column**
- **PTV or on-column injector**

Classic Capillary Vaporization Injectors



CG = **Carrier gas inlet**
SP = **Septum purge outlet**
SL = **Split flow outlet**
SS = **Splitless solenoid valve**

Problems with Split/Splitless and Direct Vaporization Injectors in HTGC

Potential for backflash of solvent

$$V \propto nT/P$$

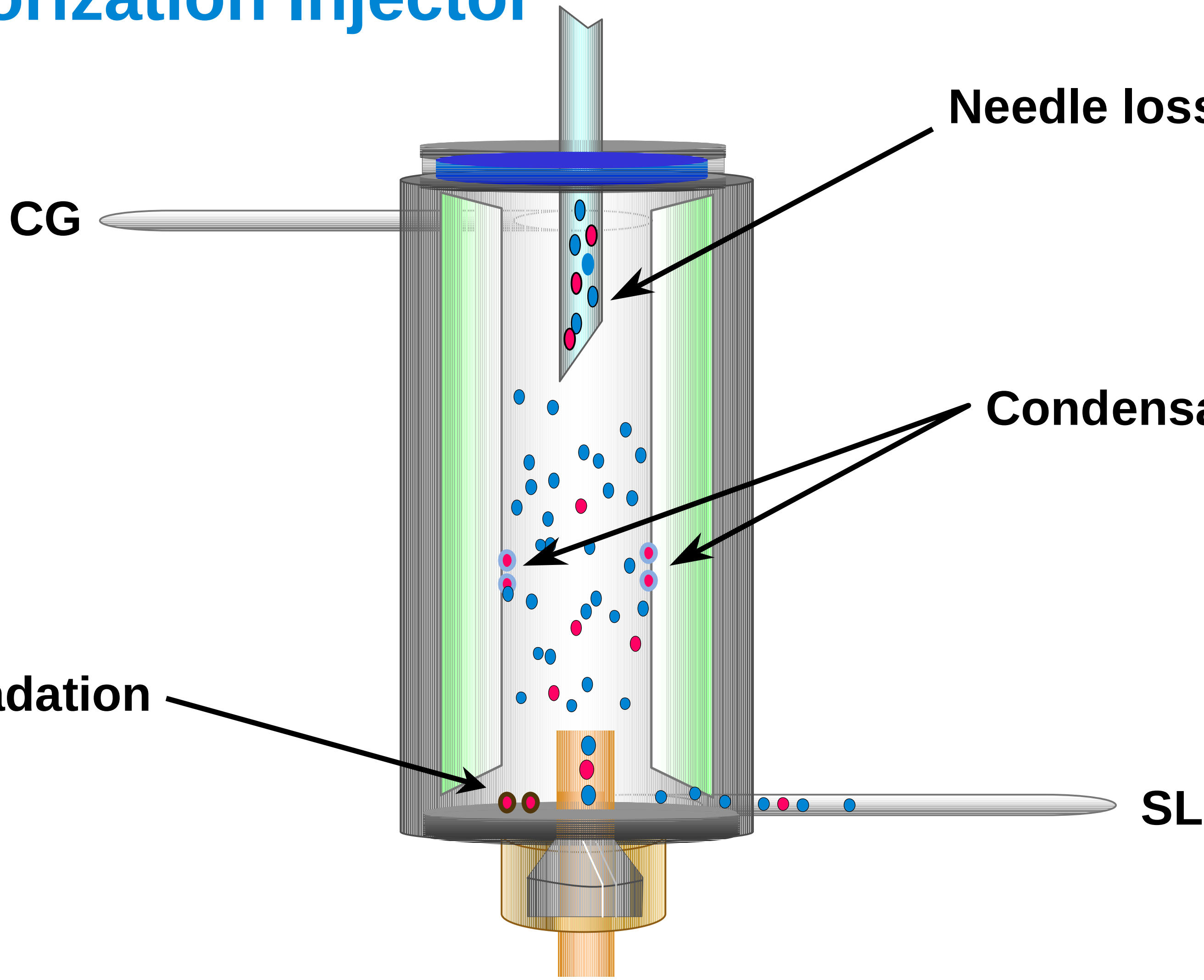
(1 µL CS_2 $\Rightarrow$ 807 µL vapor @ 400°C / 2psi)

Solute discrimination

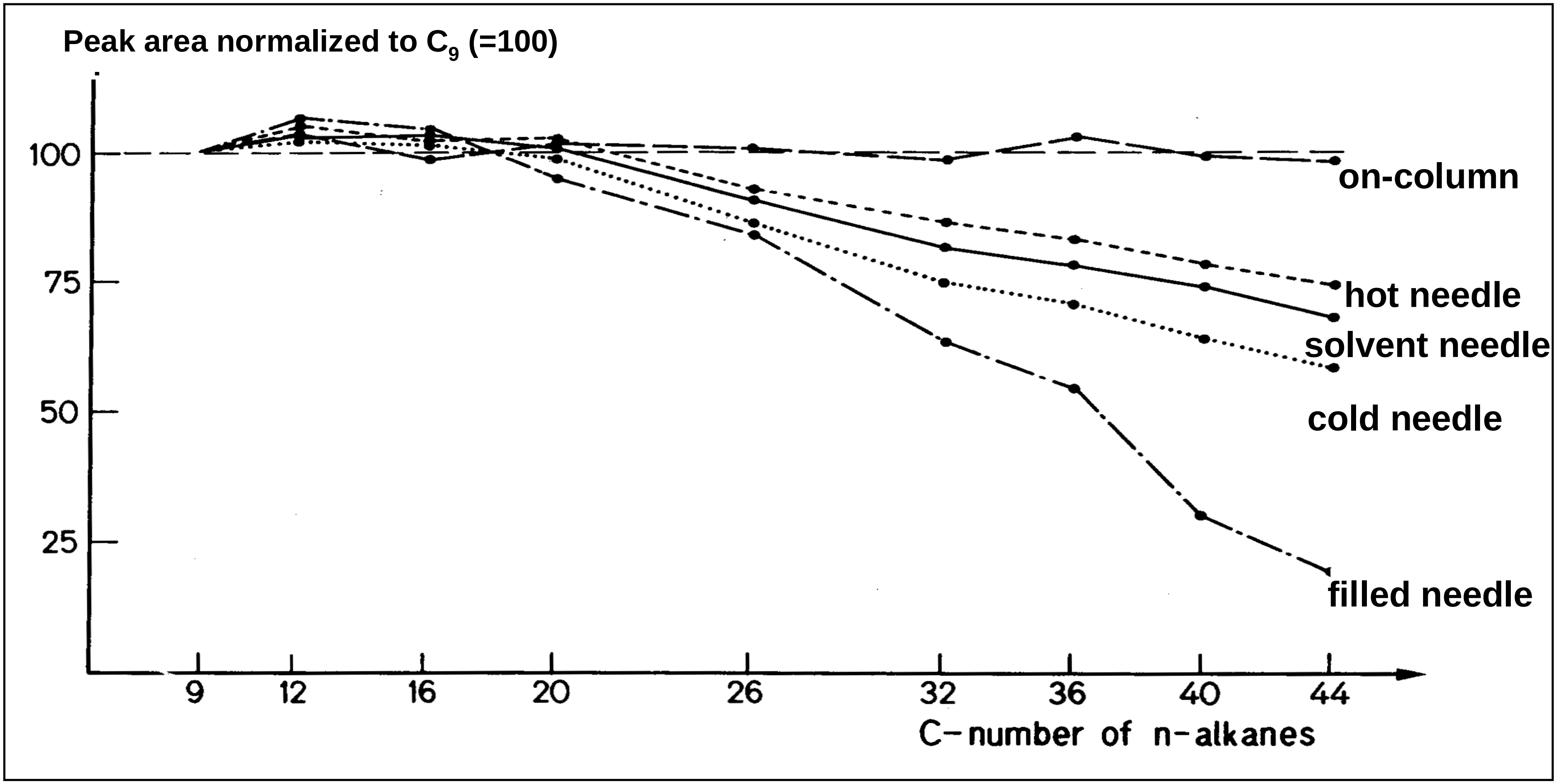
Solute Discrimination

Loss of solute(s) relative to the actual amount in the original sample. Discrimination can occur in the preliminary preparation of the sample such as evaporation or precipitation of the solutes(s) of interest. In the chromatographic analysis of a sample, discrimination can occur during any of the 3 primary processes. These are solute losses during the injection, chromatographic separation and detection. Discrimination can affect all solutes equally or, more likely, it will show a greater affect to a particular sub-group/class of solutes in the sample.

Sources of Solute Discrimination in a Vaporization Injector



Solute Discrimination in a Split Injector



Inj: 350°C, 1µL split injection 1:15

Column: SE52 10 m x 0.30 mm I.D., 0.09 µm

Oven: 25 to 310°C

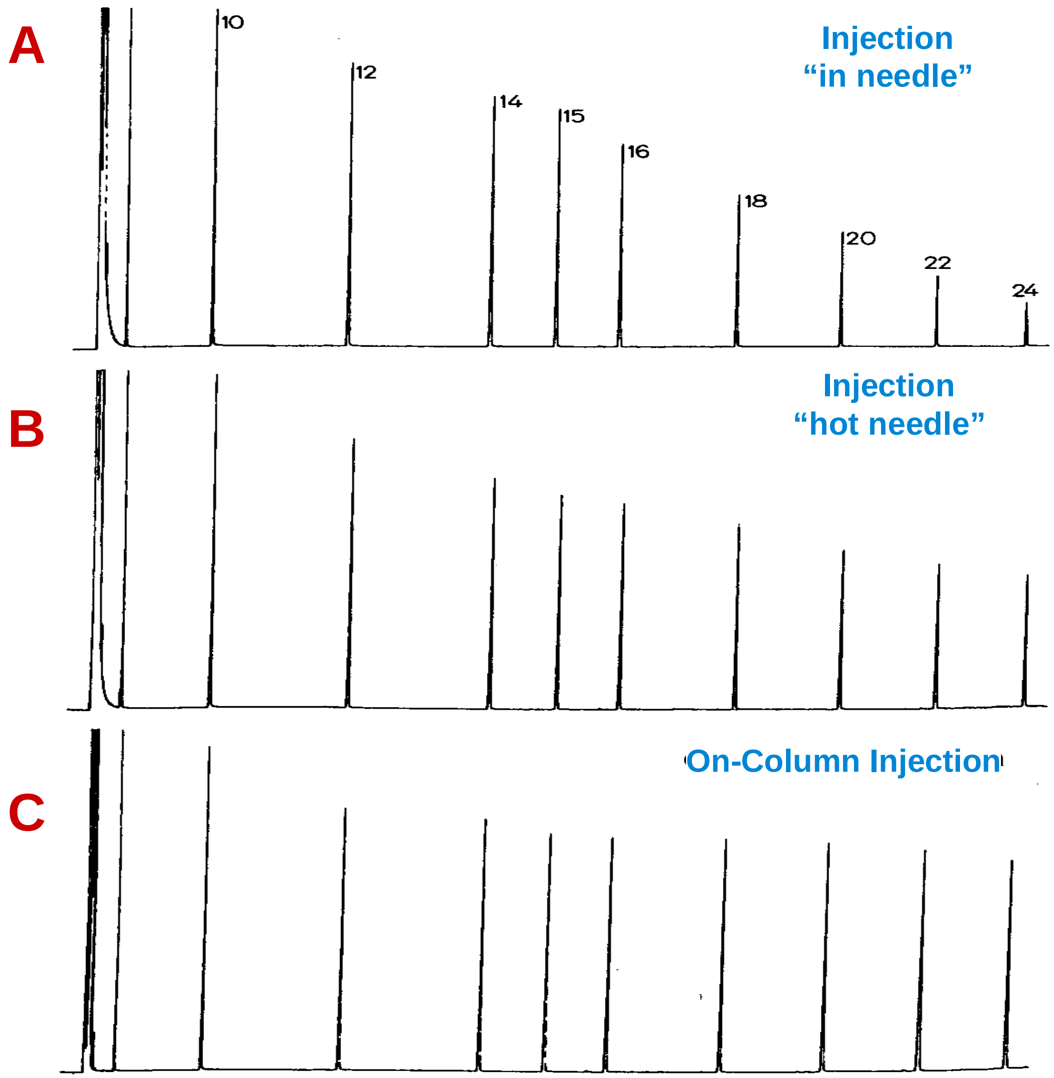
K.Grob Jr. and H.P. Neukom. J.HRC & CC (1979) 15

Evaluation of Inlet Discrimination

Column: SE 52
20m x 0.30 mm I.D., 0.18 µm
80°C, 5°/min, 240°C

Chromatograms A & B
Split injections
1µL, C_{10} - C_{24} n-Alkanes
in Hexane, 1:40

Chromatogram C
on-column injection
0.1µL



K.Grob Jr. and H.P. Neukom. J.HRC & CC, 3 (1979) 109

Some Comments Concerning Splitless or Direct Injections and HTGC

Upper temperature limit is too low -- broad peaks result from the slow transfer from the inlet to the column

Discrimination, although not as bad as split injections is still a problem

Thermal decomposition of components within the inlet can be a problem

Addition of silanized glass wool or other thermal mass "enhancers" do not seem to help encourage rapid vaporization of high molecular weight solutes

Tips for using Splitless or Direct Injectors in HTGC

(If you think you must)

Keep injector temperature as *reasonably* hot as possible

Use a high boiling solvent and minimize volume

Use inert liners with restricted openings

Optimize carrier gas flow rate (helium or hydrogen) -- pressure pulsing is helpful

Glass wool *is not* usually recommended

Run discrimination sample probe to discern limitations

Preferred Injectors for HTGC
Utilize Cool Injection Modes

The sample is injected into a controlled temperature environment

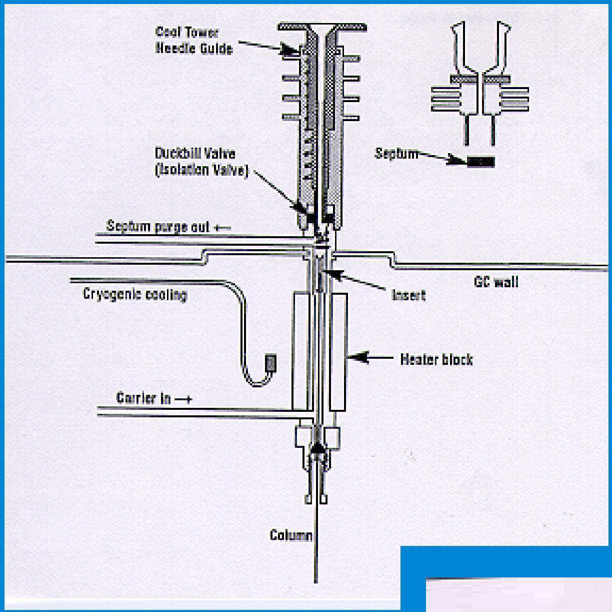
PTV and Cool On-Column injection

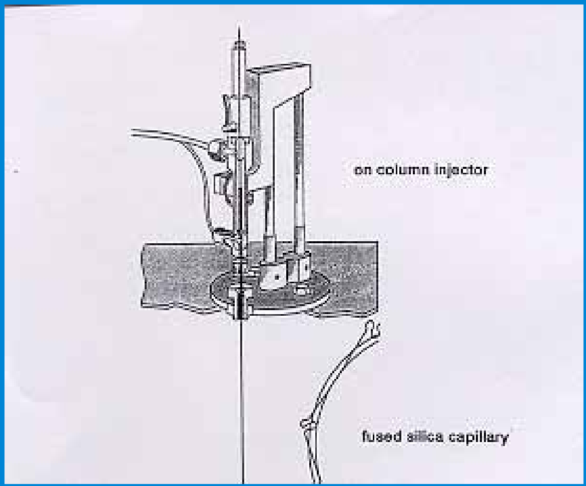
The solute bands need refocusing prior to beginning the separation

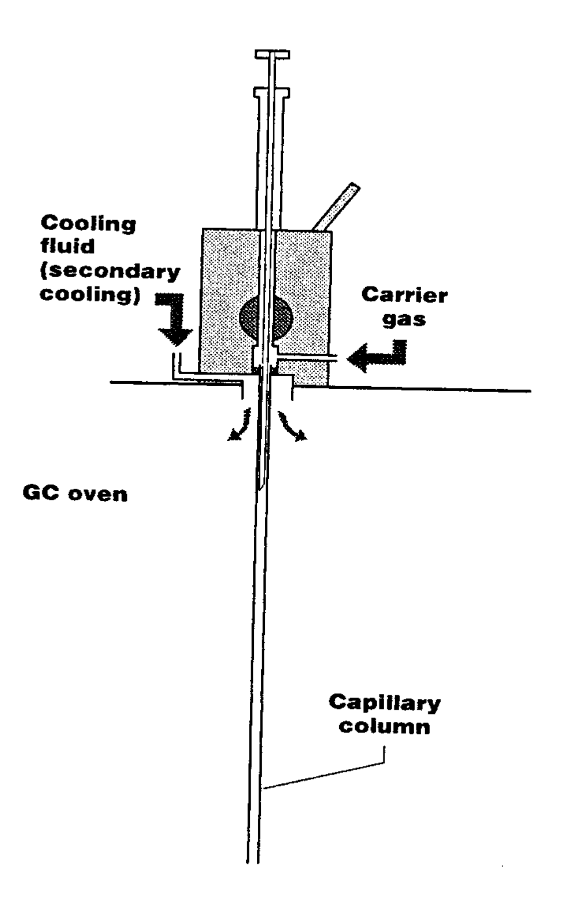
Cool On-Column Injection

- Clean samples
- Thermally labile solutes
- High boiling solutes
- Refocusing

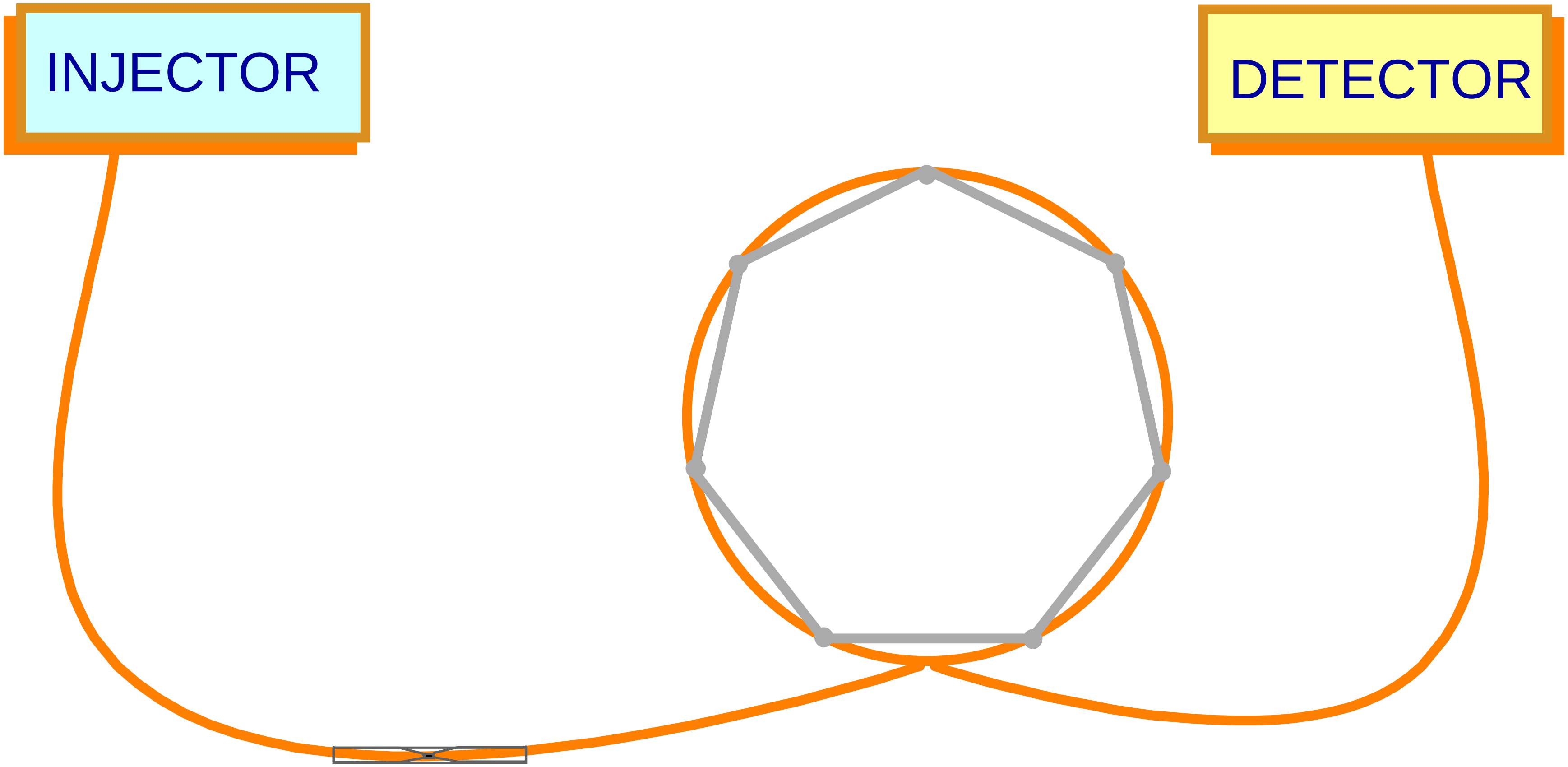
Cool On-Column Injectors



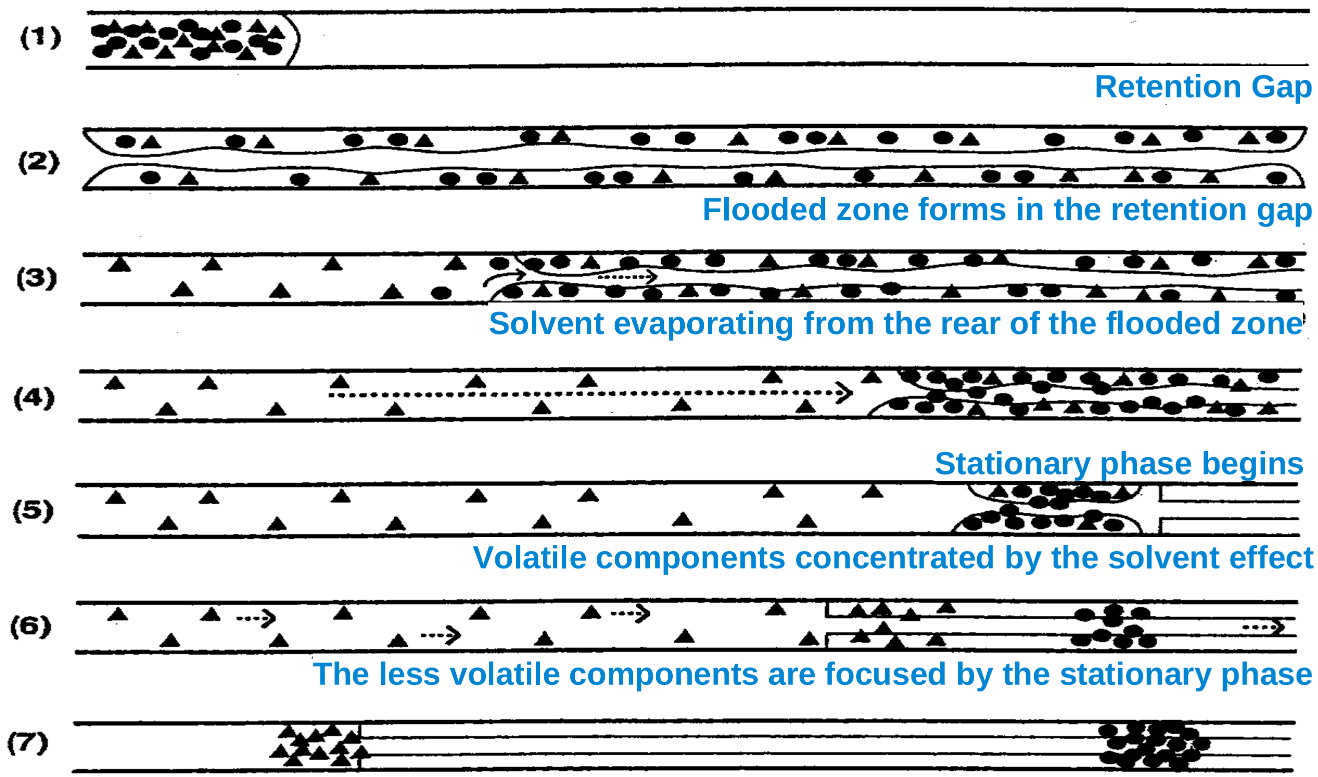




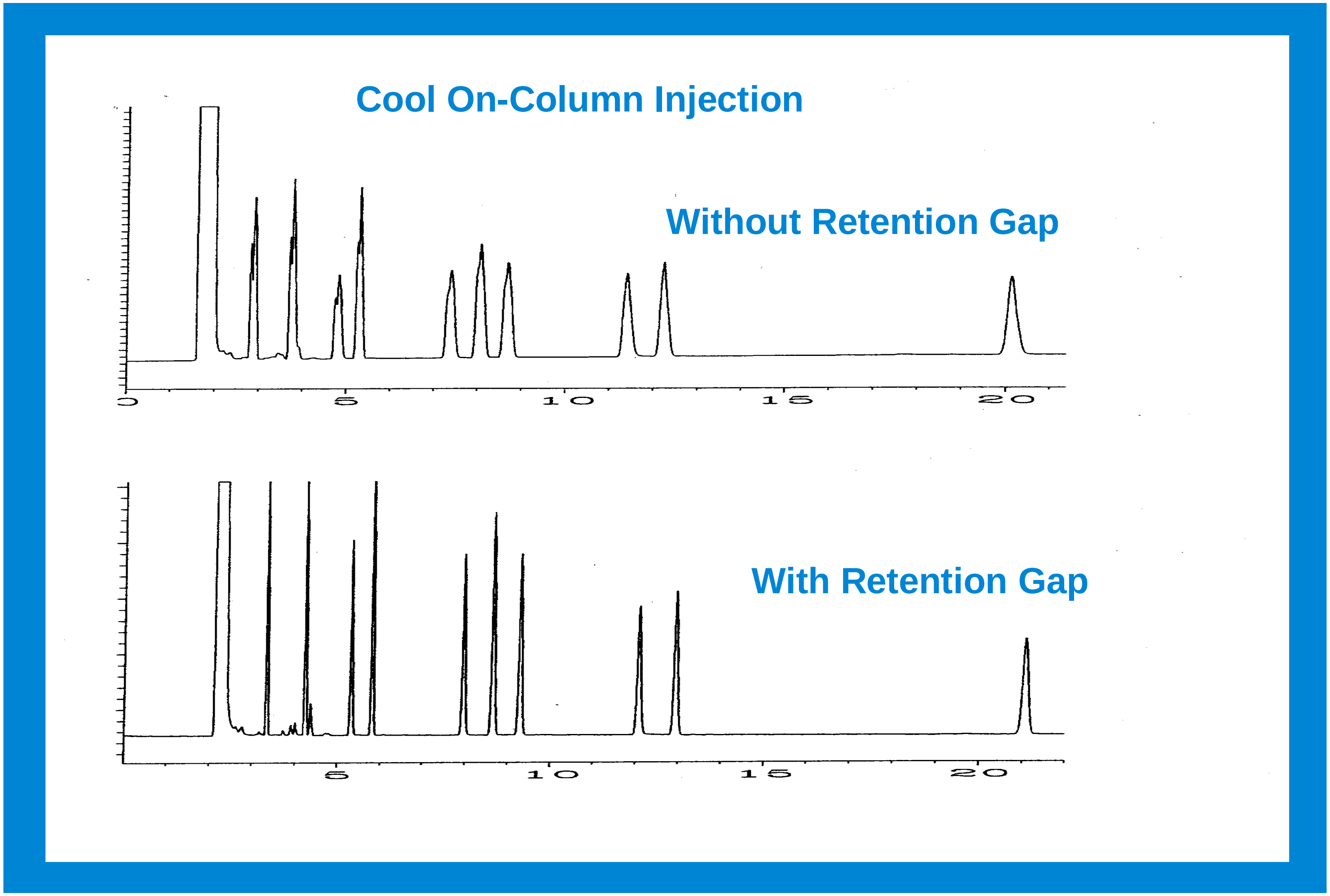
Retention Gap



Retention Gap



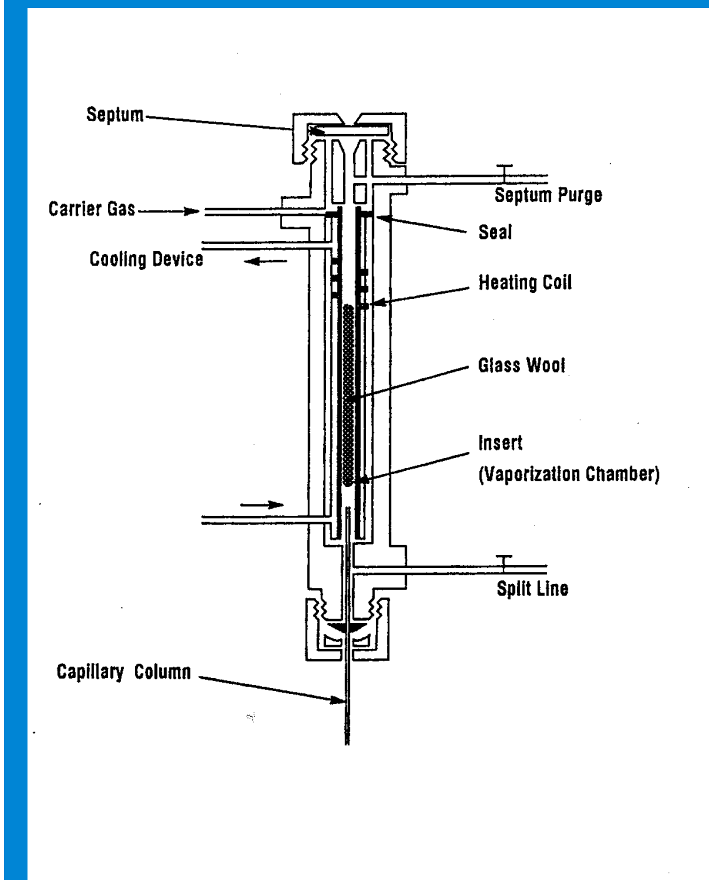
Cool On-Column Injection Refocusing

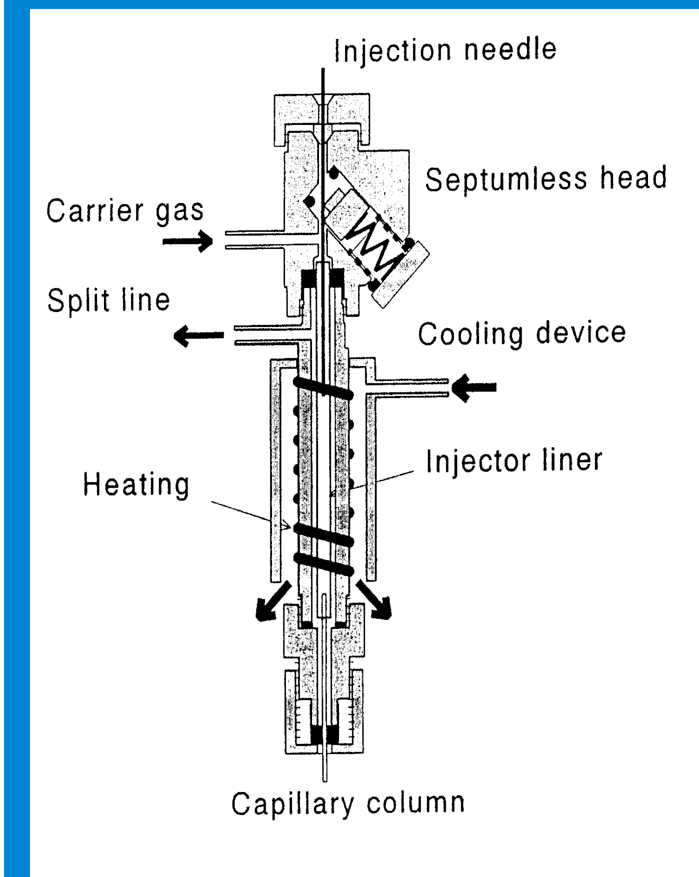


PTV Injectors- Functional Features

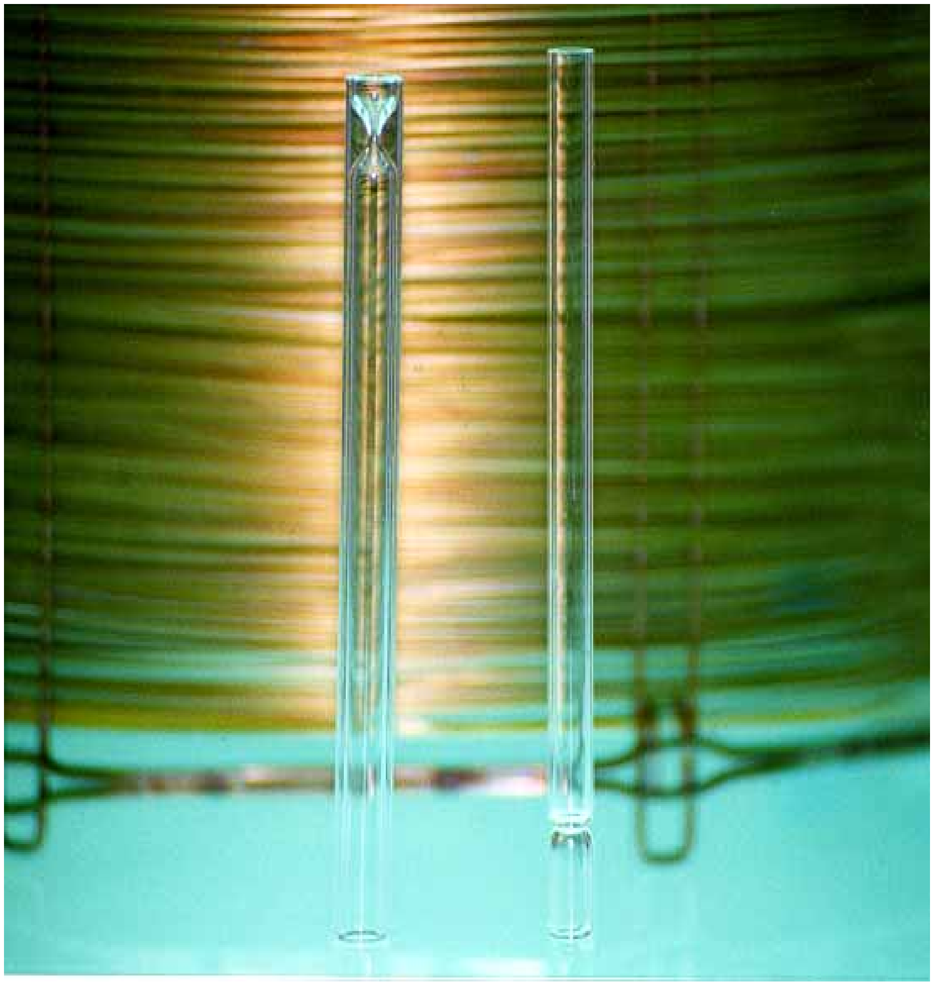
- **Low thermal mass**
- **Rapid heating and cooling**
- **Lower internal volume**
- **Packing options**
- **Split vent timing**

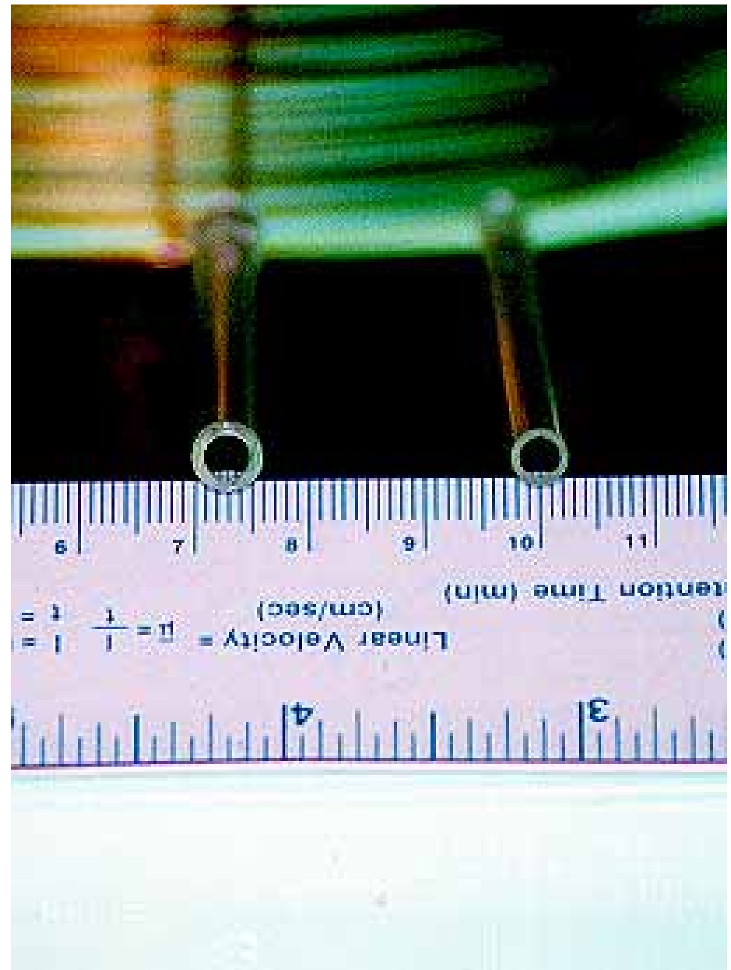
Programmable Temperature Vaporization Injectors





Liner Volume is Smaller for the PTV Injector



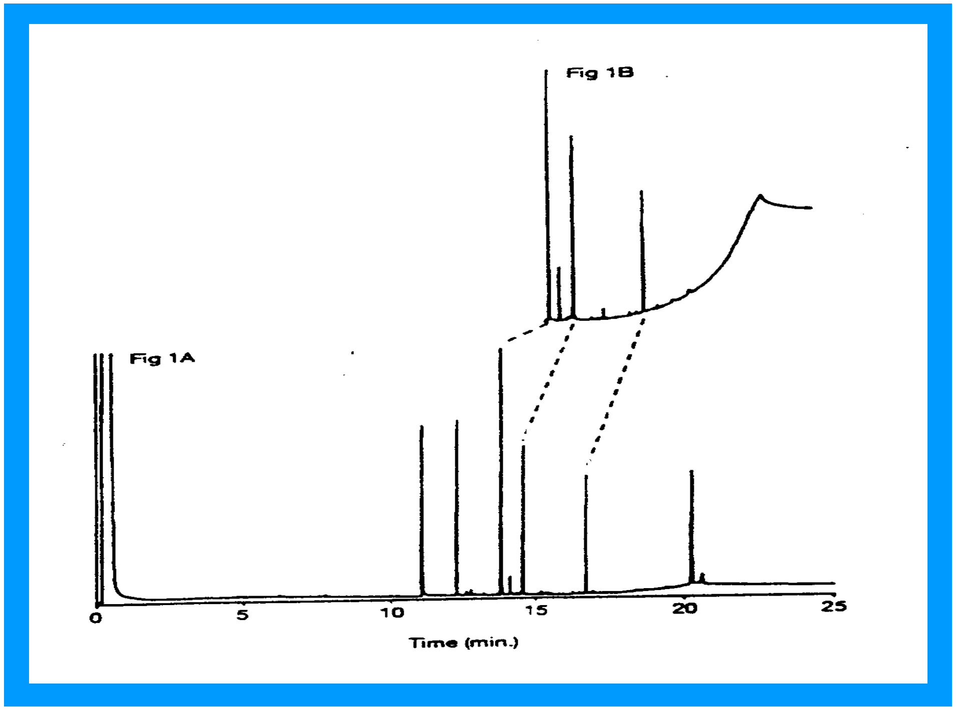


Guidelines for Optimizing PTV Parameters

$T_{initial}$	- At or below solvent boiling point
Rate	- Dependent on column capacity, solvent and sample stability -- As fast as possible
T_{final}	- As hot as possible without causing solute degradation

Final PTV Injector

- Polymer additive mixture
- 1. Cyasorb 531
- 2. Tinuvin 770
- 3. Irganox 1076
- 4. Tinuvin 144
- 5. DSTDP
- 6. Irganox 1010



- Oven: 40° to 400°C @ 20°/min
- 1A. PTV program: 35 to 600°C @ 8°C/s
- 1B. PTV program: 35 to 400°C @ 8°C/s

C.A. Cramers,et.al, American Lab, Aug. 1995, 38 - 44

Advantages of Cool On-Column and PTV in HTGC

Cool On-Column	PTV
• Inexpensive • Easily optimized • Can be used with all column types • Greatly reduces chances of solute degradation • High analytical precision	• Better choice for dirty samples • Does not need a retention gap • Temperature range extended over full range of the GC • Minimum inlet discrimination • Uses standard microliter syringes • Range of solutes that can be analyzed is broad

Disadvantages of Cool On-Column and PTV in HTGC

Cool On-Column	PTV
• Needs retention gap -- upper limit temperature range • Range of solute is limited for low boiling points • Dirty samples spoil retention gap • Special syringe needed	• Expensive • Optimization of injector parameters can be difficult • Septum bleed can be an issue • Solute degradation can occur

Break Number 1

For Questions and Answers

Press *1 on Your Phone to

Ask a Question

Essential Equipment for High Temperature GC

- 450°C maximum temperature zone
- Ultra high purity helium carrier gas
- PTV or on-column injector
- Constant flow control
- Short, thin film column

Thin Film Columns Because...

- For any given compound with a high molecular weight (i.e., large K_C), reasonable retention times will only be obtained if the phase ratio (β) is large (i.e., thin stationary phase).

$$K_C = k\beta$$

$$K_C = \frac{\text{conc. solute in stationary phase}}{\text{conc. solute in gas phase}}$$

Short Columns Because...

- **Sometimes methodology requires it.**
- **Practicality demands it.**

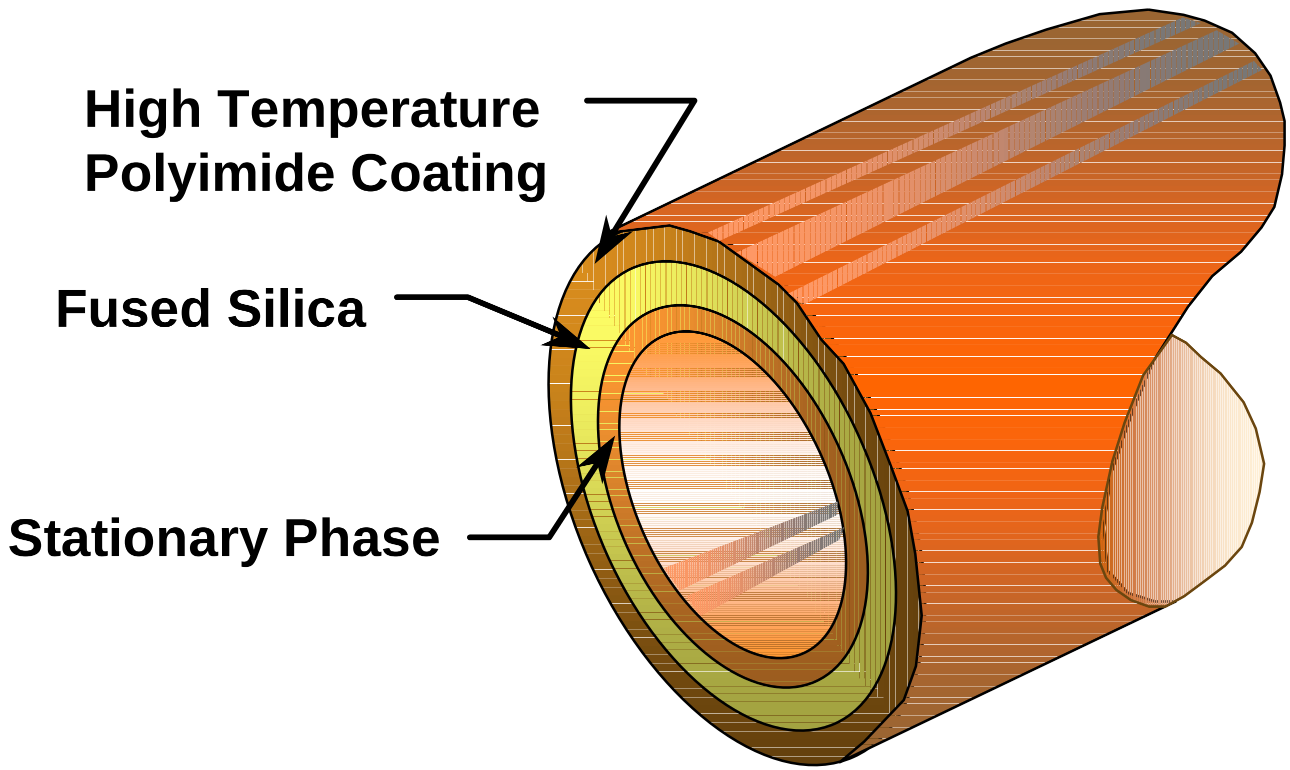
$$R_S = \frac{\sqrt{N}}{4}\left(\frac{k}{k+1}\right)\left(\frac{\alpha - 1}{\alpha}\right)$$

The Necessary Column Requirement

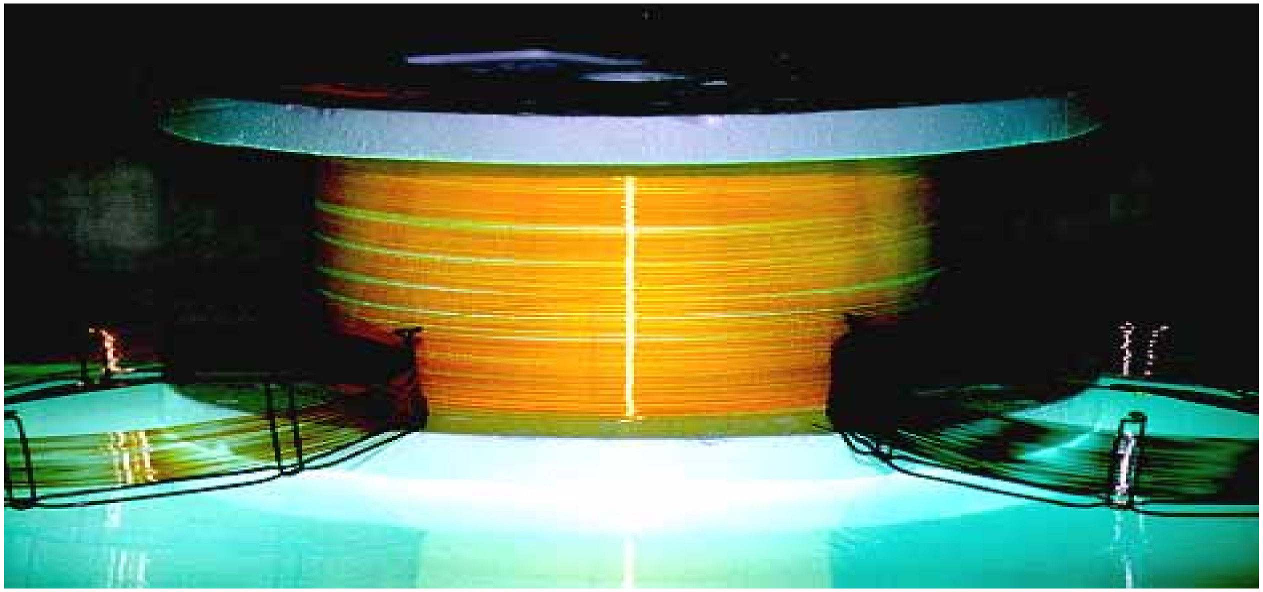
It must be able to take the heat.

Column Types for High Temperature GC

Polyimide Coated Fused Silica

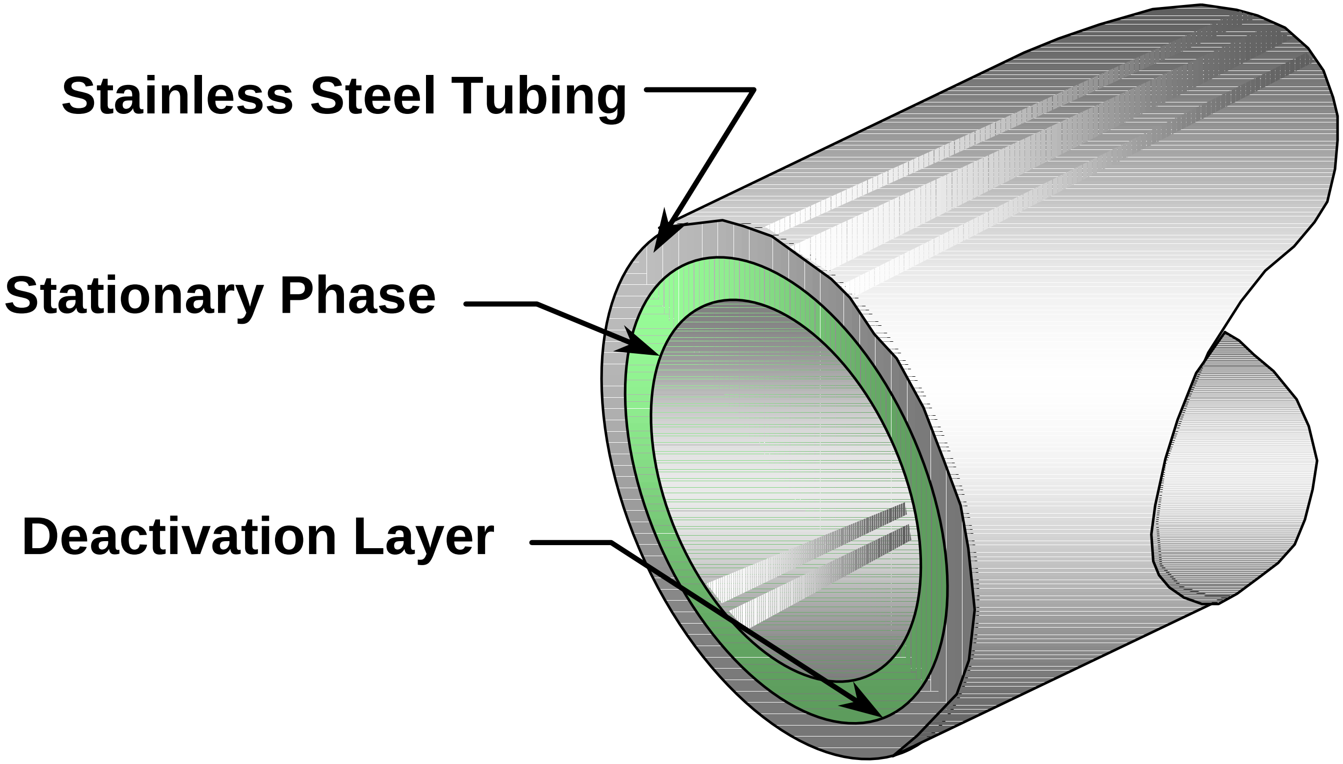


High Temperature versus Standard

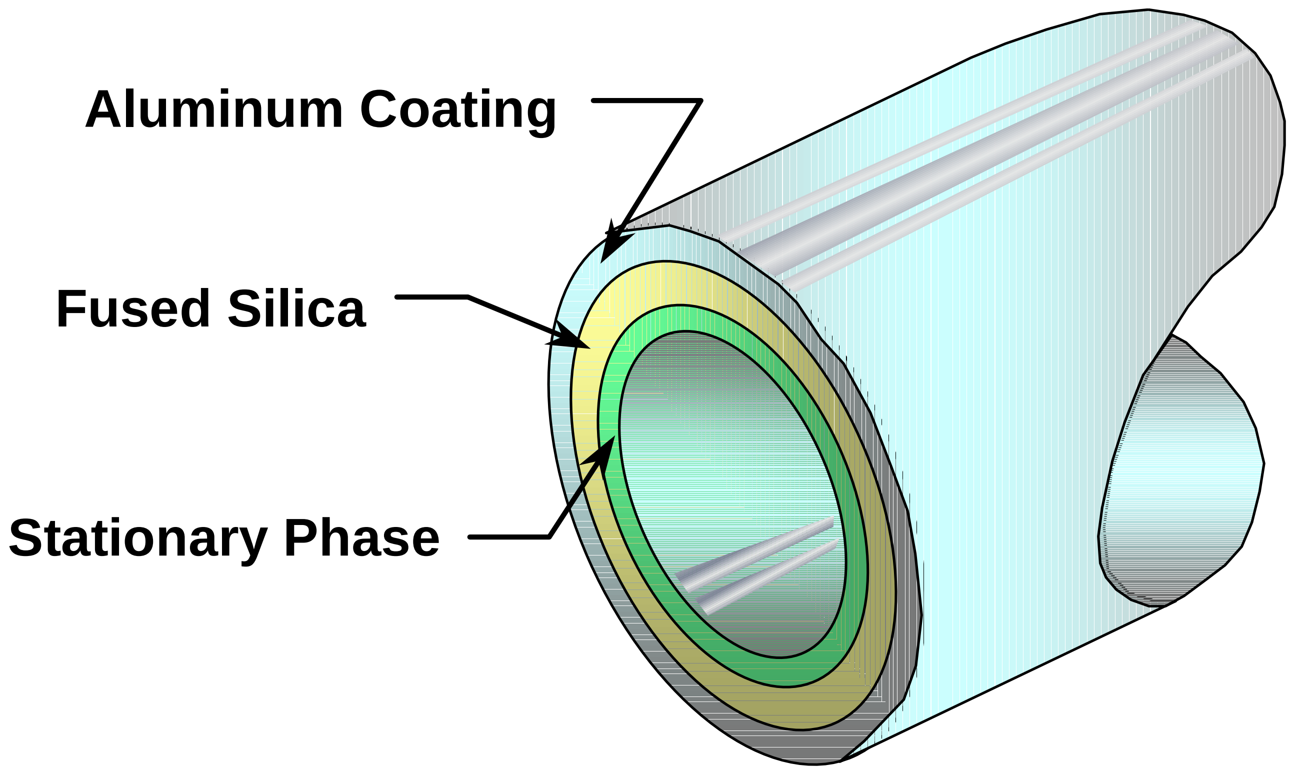


- **Color is function of cure temperature during manufacturing**
- **Color is also a function of polyimide resin type**
- **Inner coating determines chromatographic performance**
- **The tubing is often the temperature limiting parameter**

Stainless Steel Column



Aluminum Clad Fused Silica



Column Type

Standard	HT	Steel
360°C	400°C	450°C
Best chromatographic performance.	Less than optimal chromatographic performance.	Comparable performance, depends on thermal history.
All diameters	0.25 and 0.32 mm I.D.	0.53 mm I.D.
Easy to cut.	Easy to cut.	Different to cut.
Easy to connect to retention gap.	Difficult to connect to retention gap.	Difficult to connect to retention gap.

Aluminum Clad Columns

Good chromatographic performance

Variety of sizes

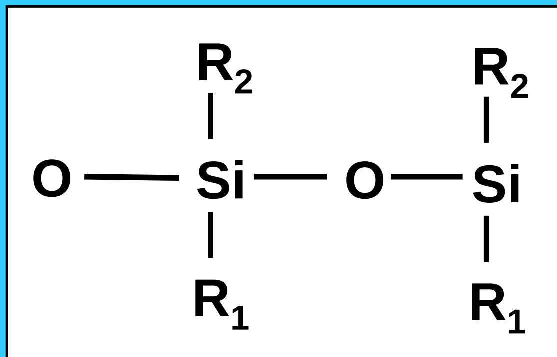
Different to cut

Difficult to install retention gap

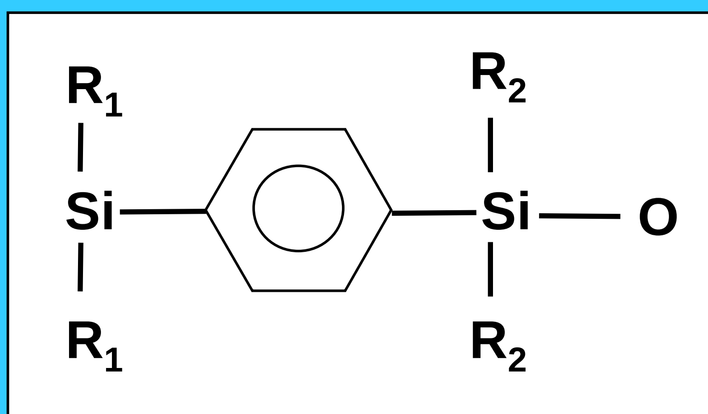
Aluminum sheath known to be unstable

Expensive

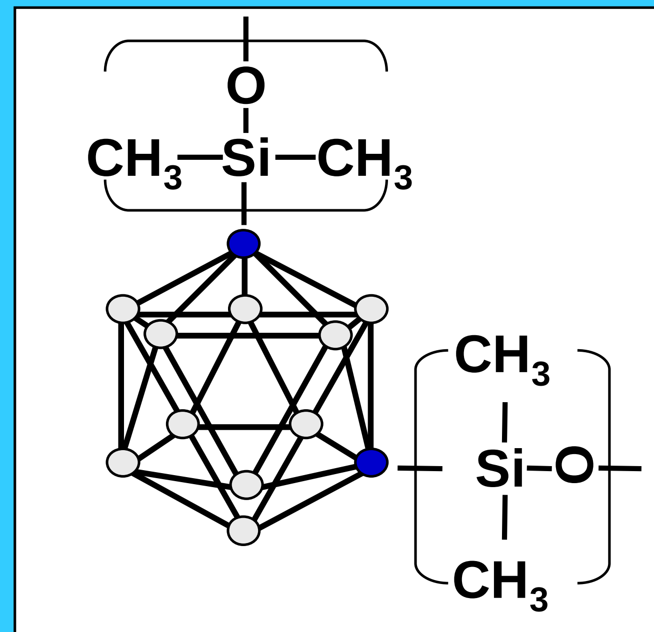
Stationary Phases



Polysiloxanes 430°to 450°C (max)



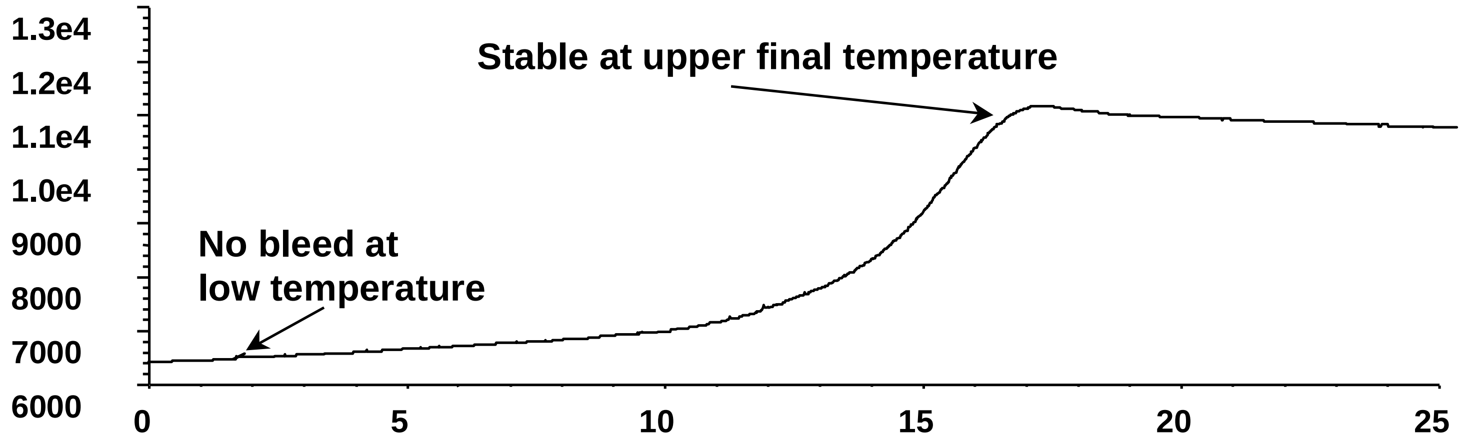
Arylenes 360°C (max)

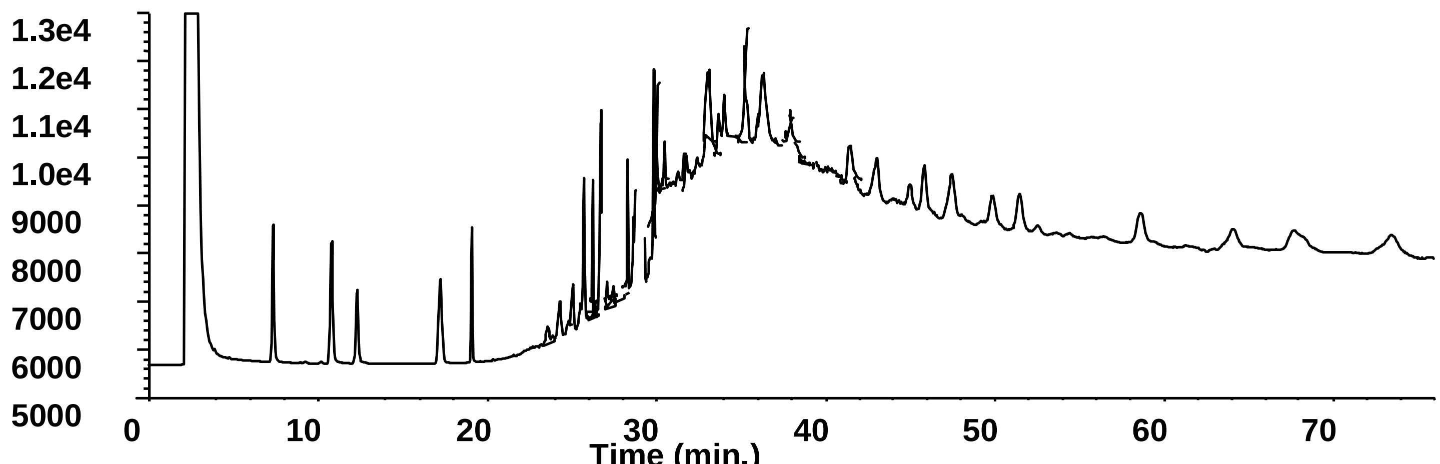


Carboranes 480°C (max)

Column Bleed in HTGC

High bleed is inevitable at high temperature





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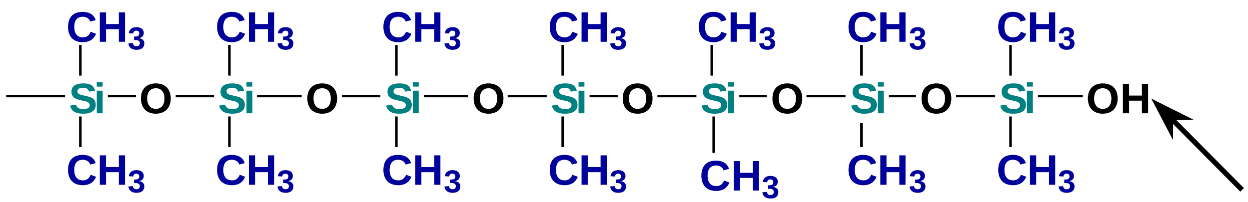
Siloxane Polymer End-Capping

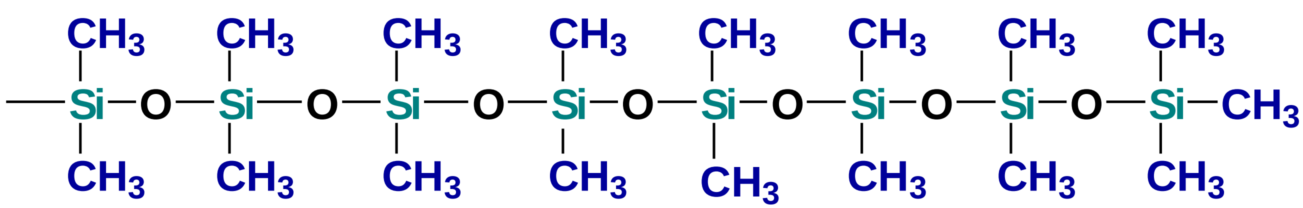


Not end-capped

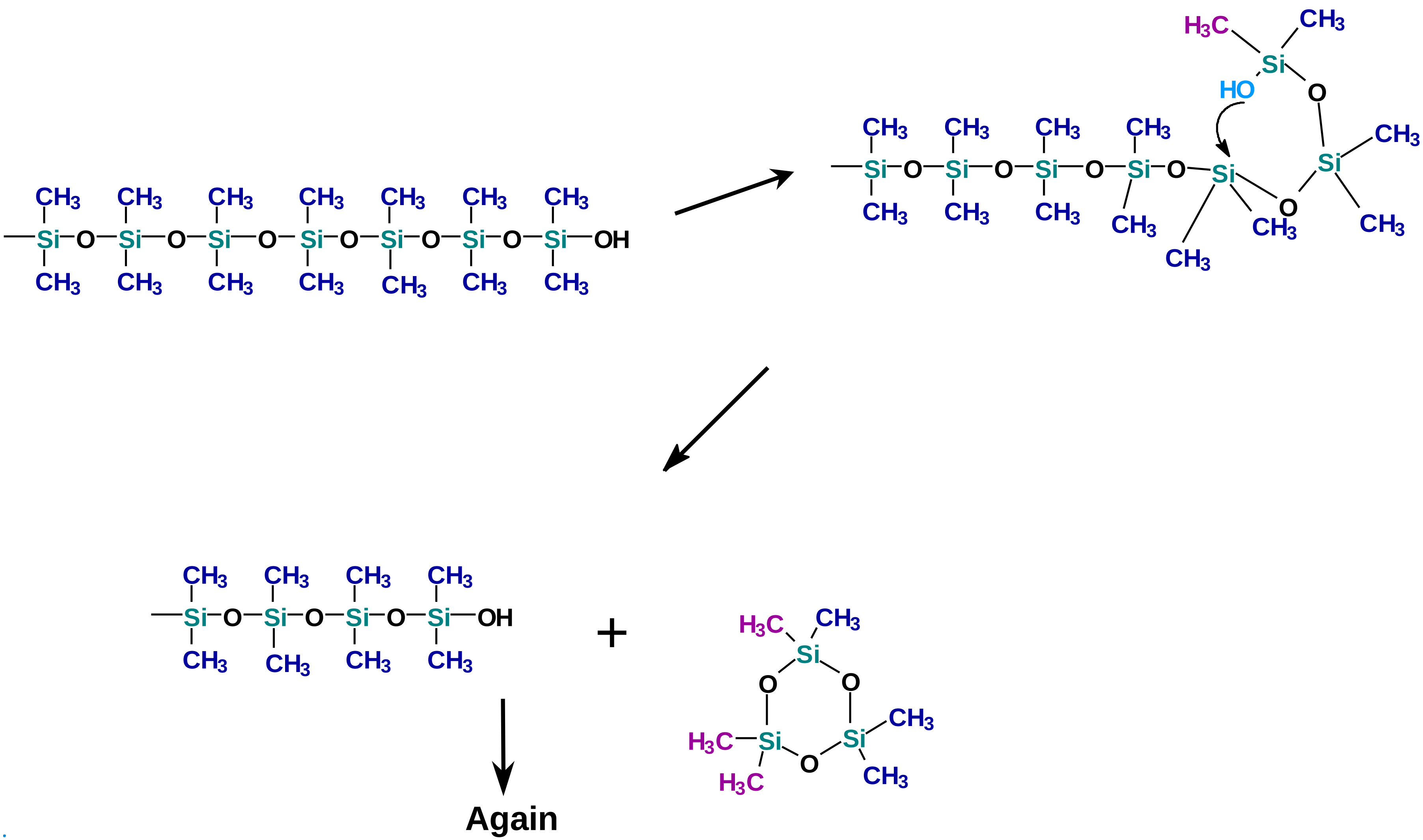
1. Higher bleed
2. Increased activity

Trimethylsilane end-capped

1. Increased stability
2. Reduced activity



“Back biting” Mechanism of Bleed Formation



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Choosing a Phase That Can Take the Heat

Dimethylpolysiloxane is a good “HT” choice

Arylene polymers will extend the range of some mid-polarity columns -- slightly

The best way to reduce bleed is to have ***less*** phase

Choosing the Dimensions That Can Take the Heat

Length has a direct affect on run time: amount of the distribution that elutes and the temperature of elution.

Short, widebore columns will need special flow control restrictions such as EPC to eliminate gas pressure problems

Important Reminders About HTGC and Bleed

Oxygen damage can be rapid at high temperatures with massive bleed

Inertness of column degrades at higher temperature

The column will lose phase with continual use so R_S and k change with time

Stable, reproducible bleed can be managed

Break Number 2

For Questions and Answers

Press *1 on Your Phone to

Ask a Question

Applications for High Temperature GC

- PNA's
- Triglycerides
- Azo Dyes (Unsulfonated)
- Surfactants
- Simulated Distillation

Alkylethoxylate Surfactant

Neodol 91-6 (Shell)

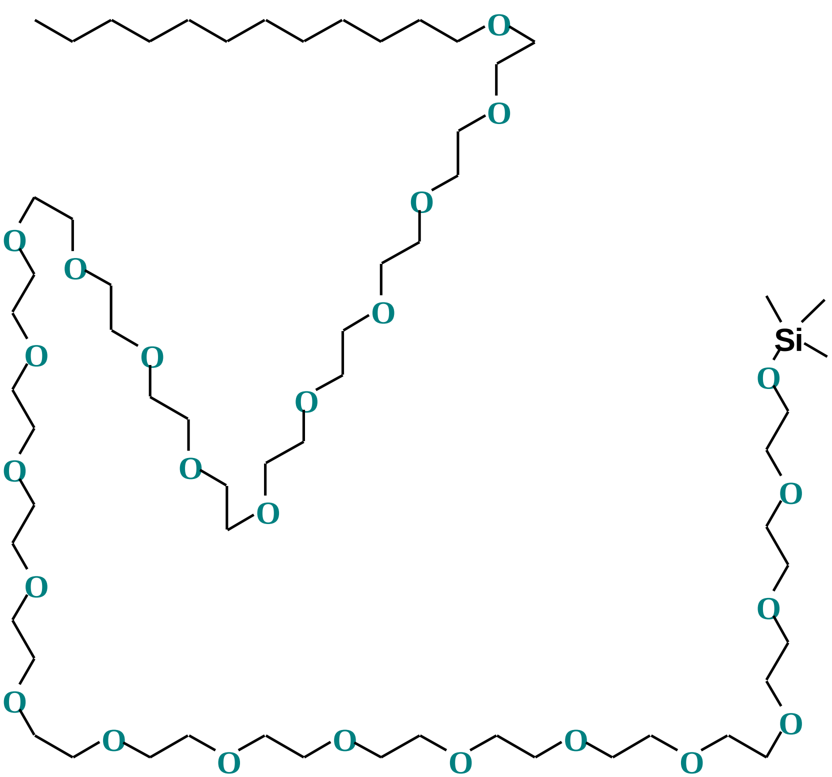
$RO(CH_2CH_{2O})xH$

R = C_9, C_{10}, C_{11}

X = 6 (Target Mole %)

For $C_{10}H_{21}O(EO)xOTMS$

X = 1	Mw = 274
X = 10	Mw = 670
X = 20	Mw = 1110
X = 23	Mw = 1242

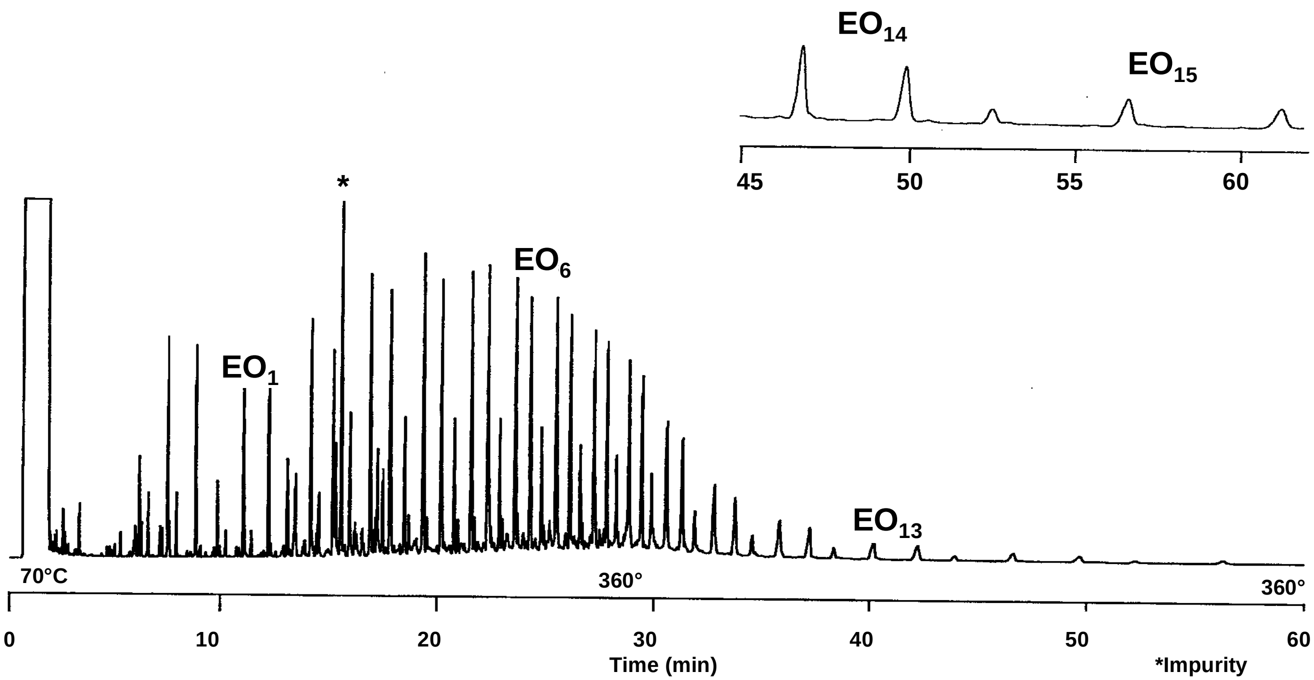


$C_{12}EO_{23}TMS$

M = 1271

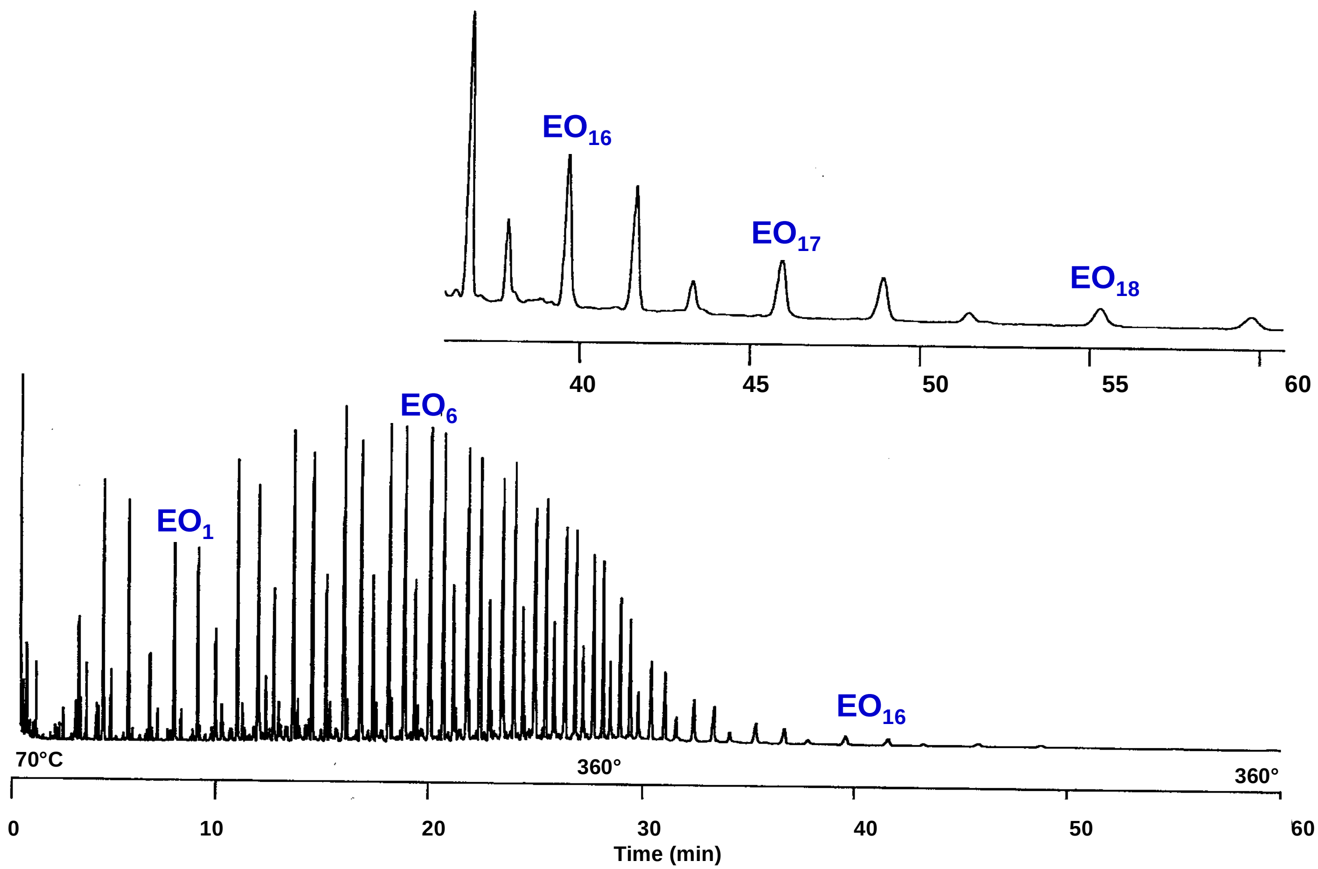
Neodol 91-6 TMS

DB-XLB, 15 m x 0.25 mm, 0.1 µm (5.5 psi)



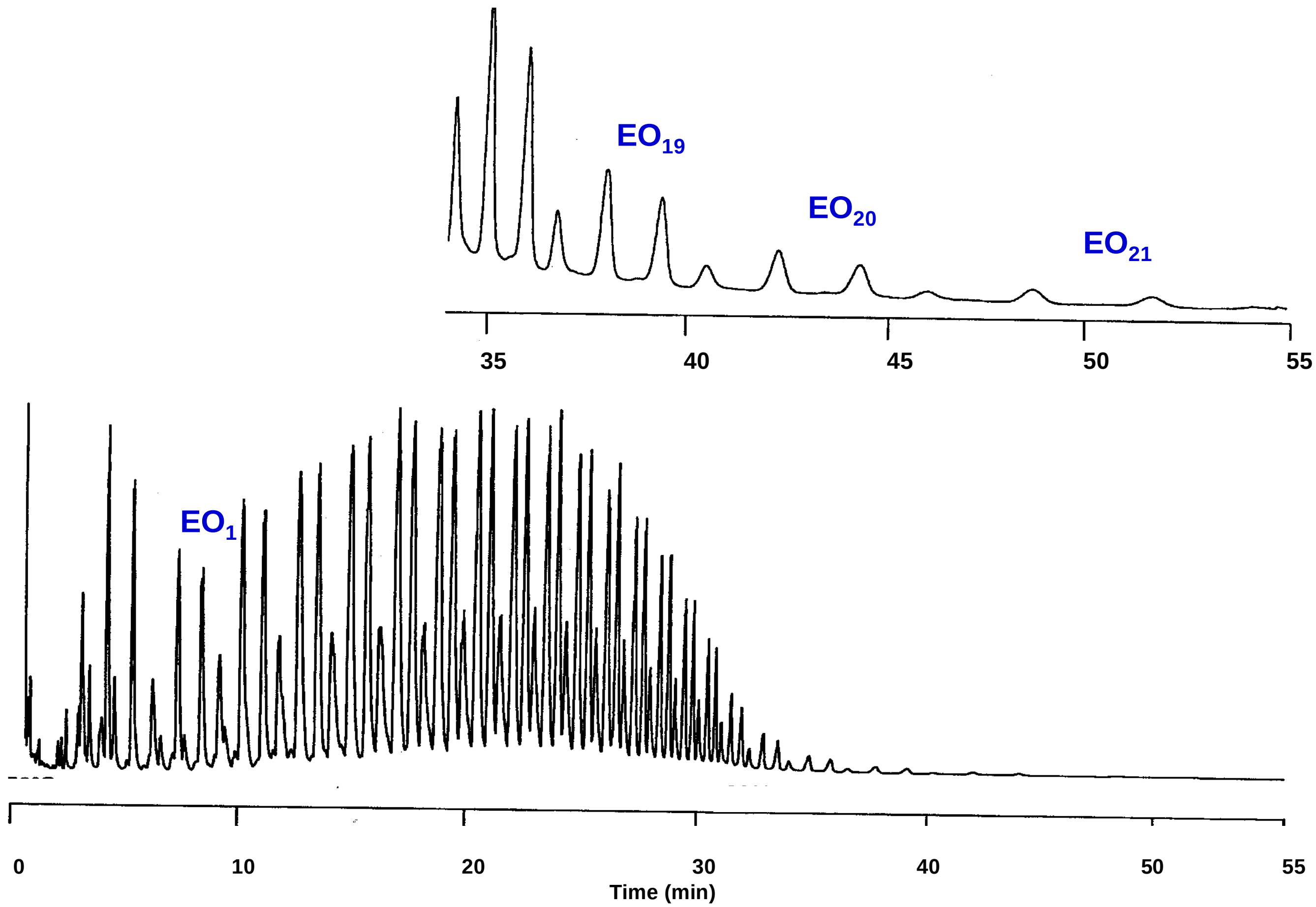
Neodol 91-6 TMS

DB-XLB, 7.5 m x 0.25 mm, 0.1 µm (5 psi)



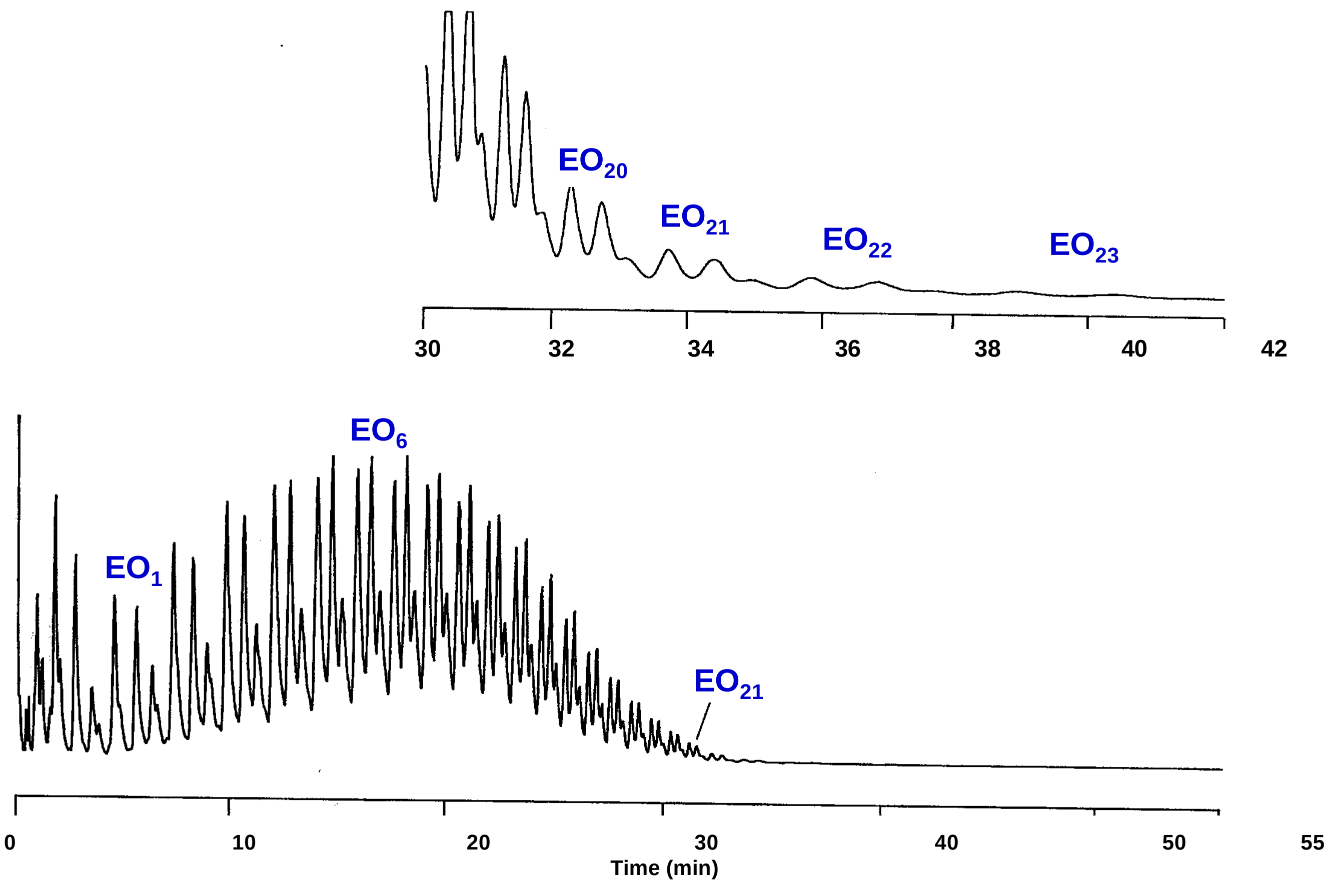
Neodol 91-6 TMS

DB-XLB, 3 m x 0.25 mm, 0.1 µm (5 psi)



Neodol 91-6 TMS

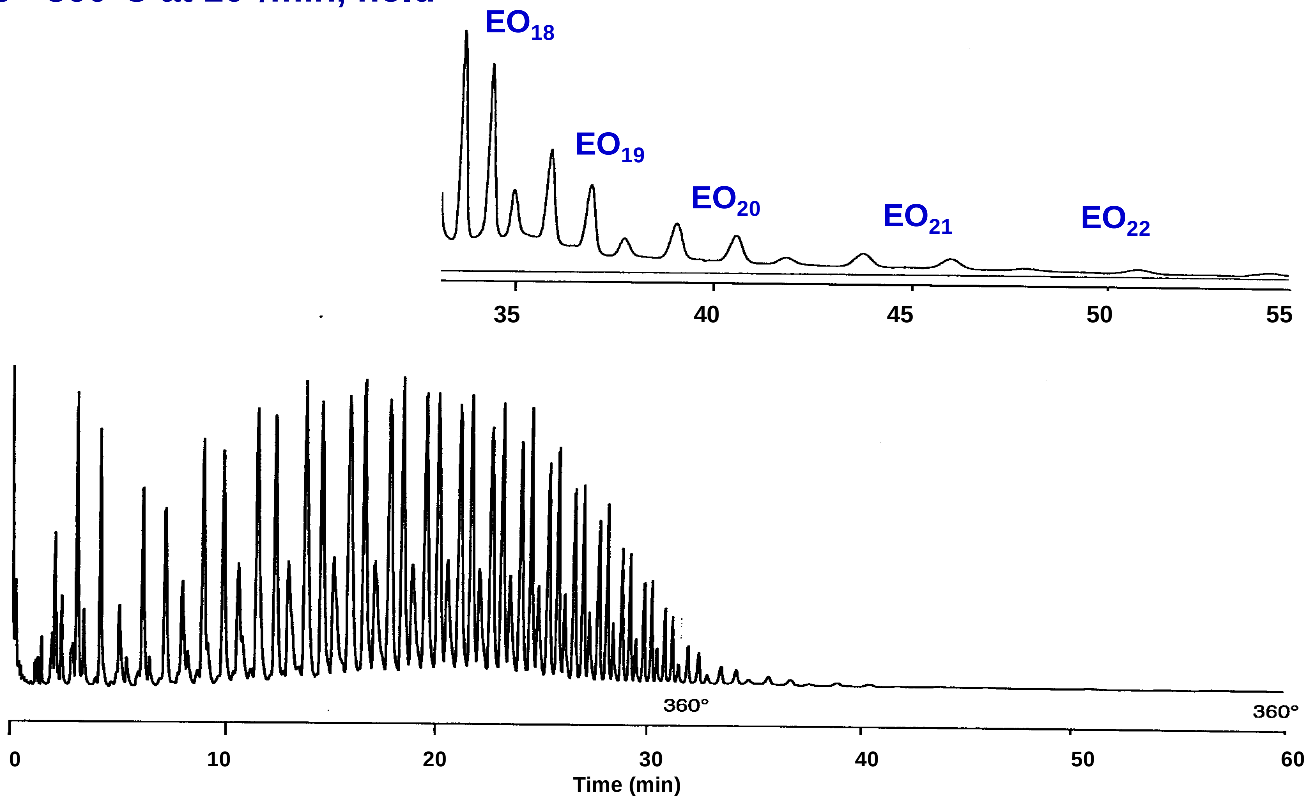
DB-XLB, 1.5 m x 0.25 mm, 0.1 µm (5 psi)



What About Temperature?

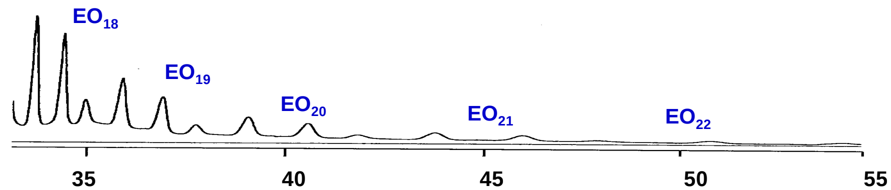
Neodol 91-6 TMS

DB-XLB, 3 m x 0.25 mm, 0.1 µm
50 - 360°C at 10°/min, hold

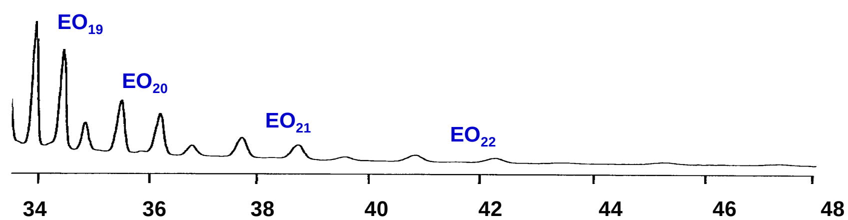


What About Temperature?

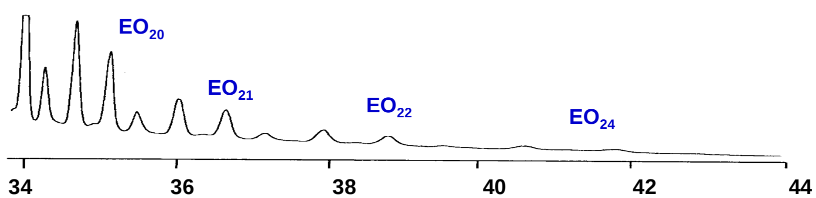
Neodol 91-6 TMS
DB-XLB, 3 m xm 0,25 mm, 0.1 µm
50 - 360°C at 10°/min, hold



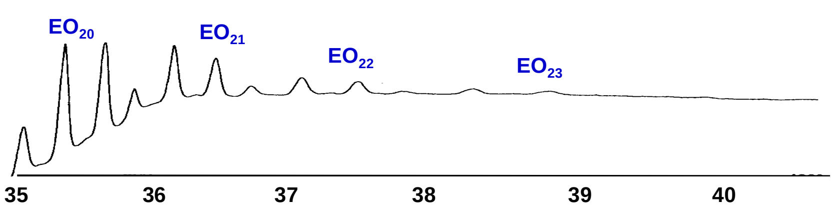
Neodol 91-6 TMS
DB-XLB, 3 m xm 0,25 mm, 0.1 µm
50 - 375°C at 10°/min, hold



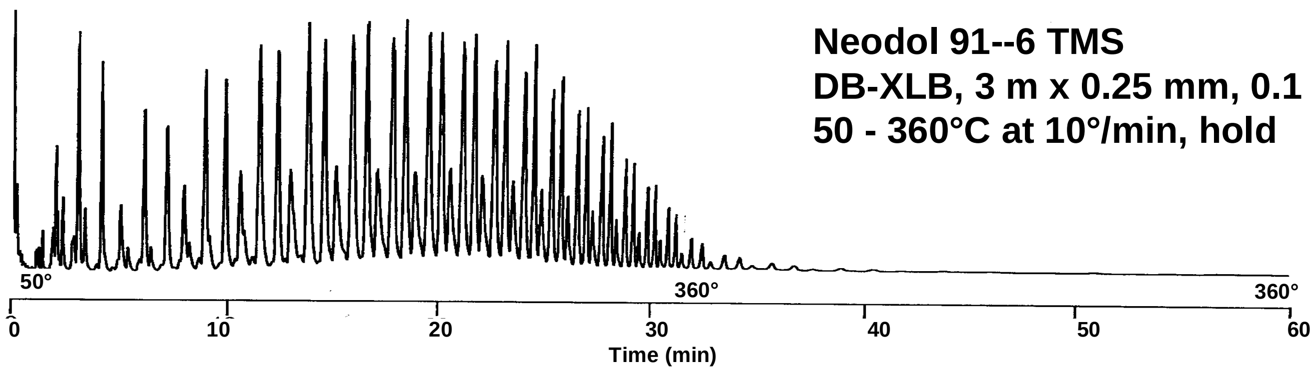
Neodol 91-6 TMS
DB-XLB, 3 m xm 0,25 mm, 0.1 µm
50 - 385°C at 10°/min, hold



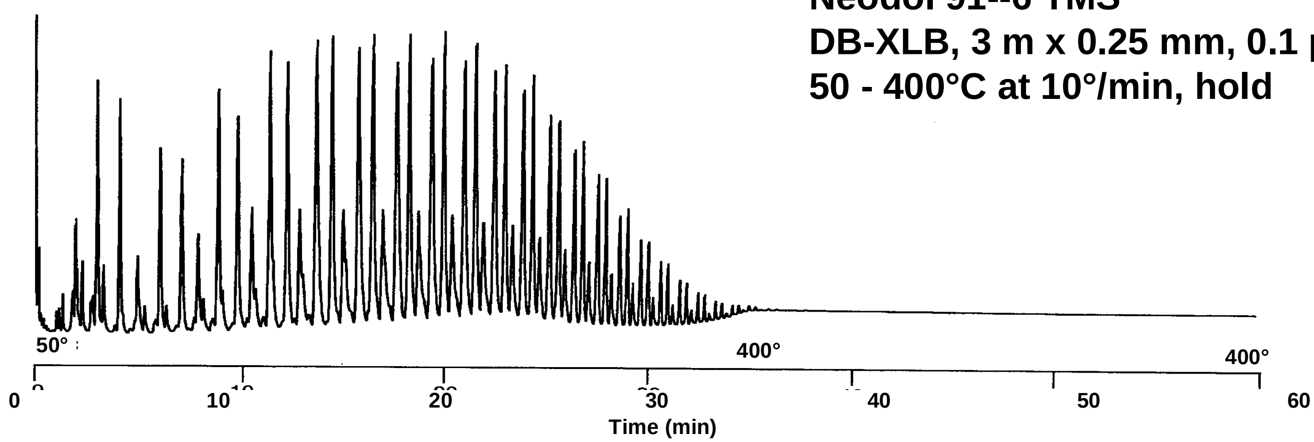
Neodol 91-6 TMS
DB-XLB, 3 m xm 0,25 mm, 0.1 µm
50 - 400°C at 10°/min, hold



But… What Else Happens With High Temperature?



Neodol 91--6 TMS
DB-XLB, 3 m x 0.25 mm, 0.1 µm
50 - 360°C at 10°/min, hold



Neodol 91--6 TMS
DB-XLB, 3 m x 0.25 mm, 0.1 µm
50 - 400°C at 10°/min, hold

Simulated Distillation
"Sim Dist"

- **A combined GC method and computer program for the calculation of boiling range distribution by the chromatographic analysis**

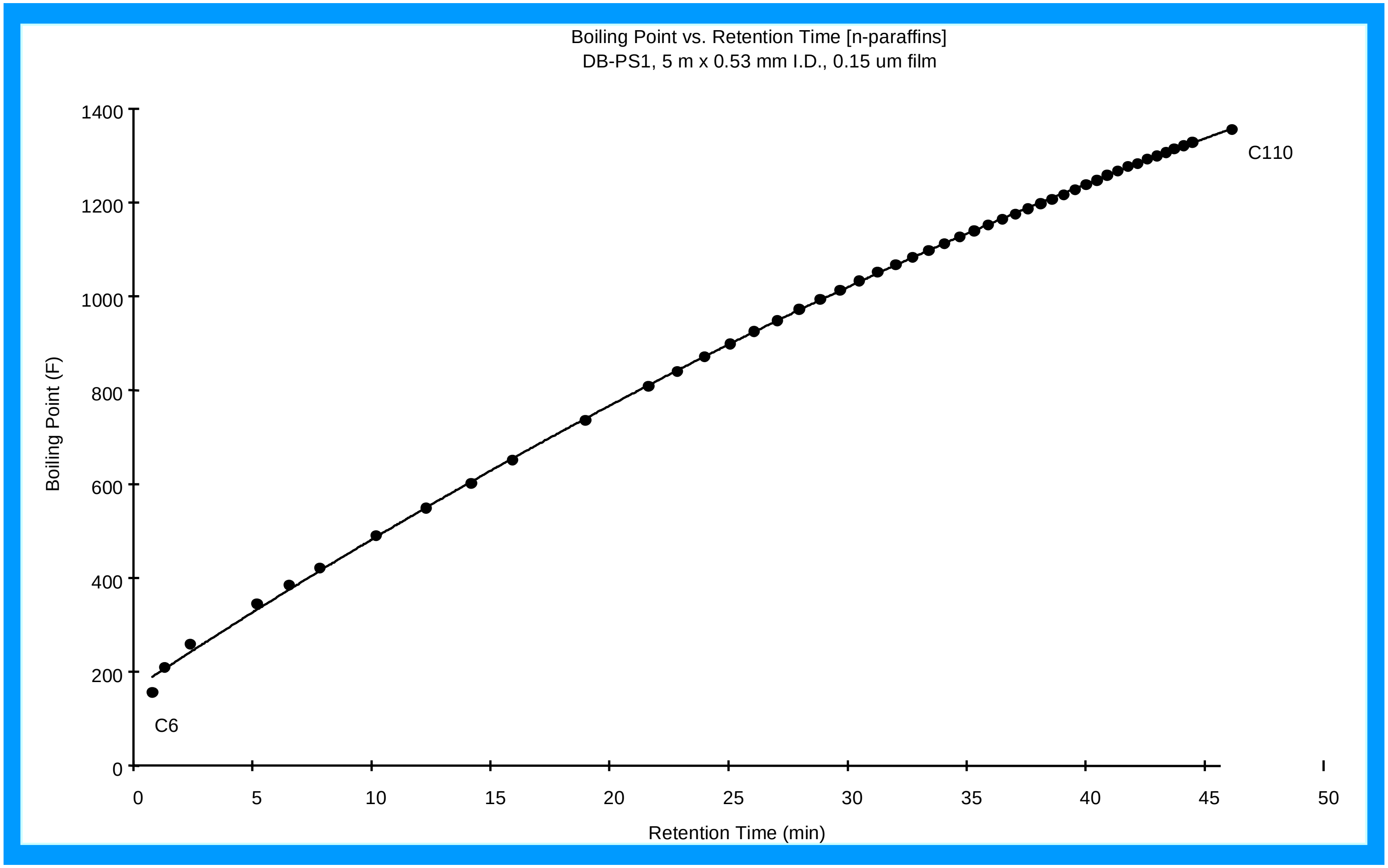
Boiling Points of Normal Paraffins

Carbon Number	Boiling Point (°F)*	Carbon Number	Boiling Point (°F)*	Carbon Number	Boiling Point (°F)*
2	-127.5	26	774	66	1175
3	-44	28	808	68	1186
4	32	30	840	70	1197
5	97	32	871	72	1207
6	156	34	898	74	1216
7	209	36	925	76	1227
8	259	38	948	78	1238
9	303	40	972	80	1247
10	345	42	993	82	1258
11	385	44	1013	84	1267
12	421	46	1033	86	1276
13	455	48	1051	88	1283
14	489	50	1067	90	1292
15	520	52	1083	92	1299
16	549	54	1098	94	1306
17	576	56	1112	96	1314
18	601	58	1126	98	1321
20	651	60	1139	100	1328
22	696	62	1152	110	1355
24	736	64	1164	120	1382

***Atmospheric Equivalent Boiling Point (AEBP) as described in API Project 44.**

Simulated Distillation

Retention Time vs Bpt.



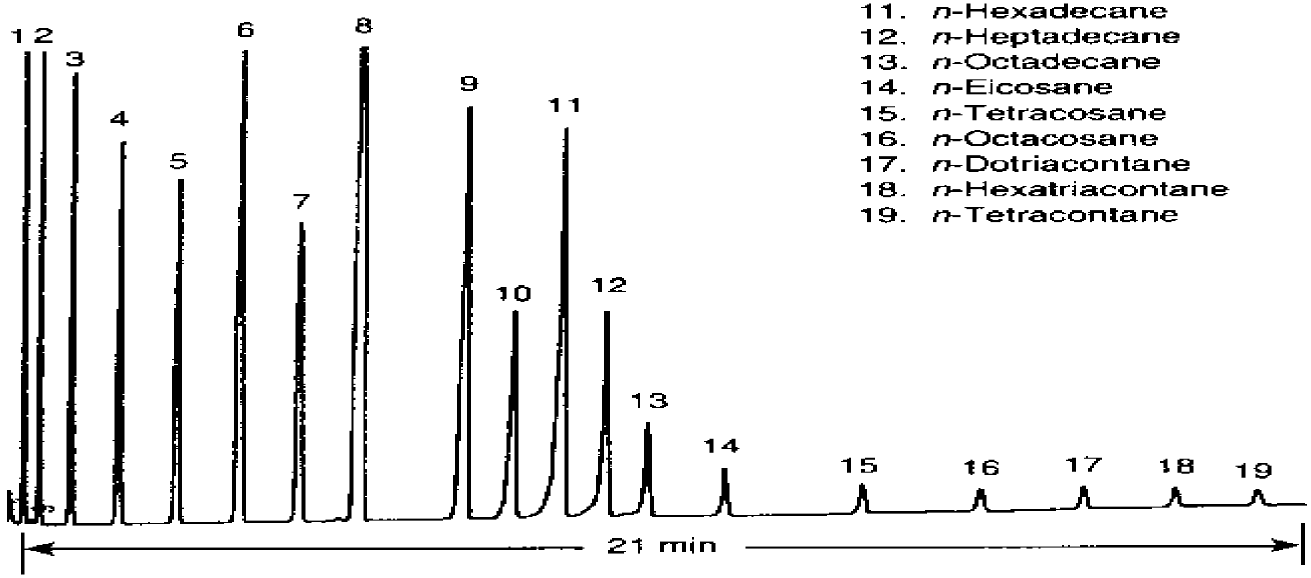
Column Characteristics for Sim Dist

- Megabore diameter (0.53 mm I.D.)
- Dimethylpolysiloxane stationary phase
- Film thickness ranging from the 0.09 - 3.0 µm
- Fused silica (polyimide or Al clad) and Metal
- Low resolution (lengths 5-10 meters)

Simulated Distillation

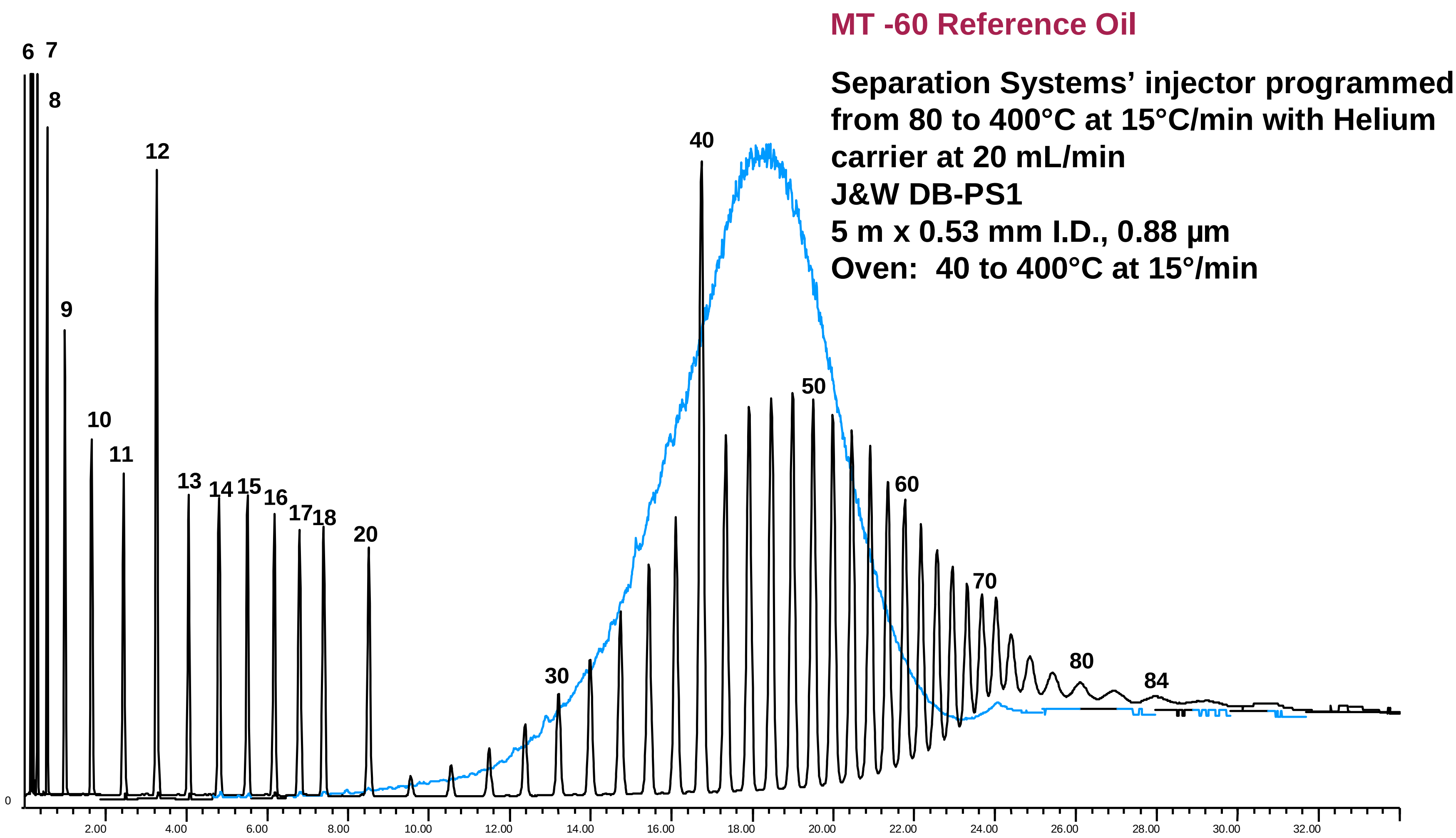
Column: **DB-2887**
10 m x 0.53 mm I.D., 3.0 µm
J&W P/N: **125-2814**
Carrier: Helium at 7 mL/min
Oven: 35-350°C at 15°/min
Injector: Megabore Direct
Detector: FID
Nitrogen makeup gas
at 30 mL/min

1. *n*-Pentane
2. *n*-Hexane
3. *n*-Heptane
4. *n*-Octane
5. *n*-Nonane
6. *n*-Decane
7. *n*-Undecane
8. *n*-Dodecane
9. *n*-Tetradecane
10. n-Pentadecane
11. *n*-Hexadecane
12. *n*-Heptadecane
13. *n*-Octadecane
14. *n*-Eicosane
15. *n*-Tetracosane
16. *n*-Octacosane
17. *n*-Dotriacontane
18. *n*-Hexatriacontane
19. *n*-Tetracontane



C166

Extended Method 2887



Peak ID denotes n-Alkane carbon number

Chromatogram courtesy of Joaquin Lubkowitz, Separation Systems, Inc.., Gulf Breeze, FL

Extreme GC

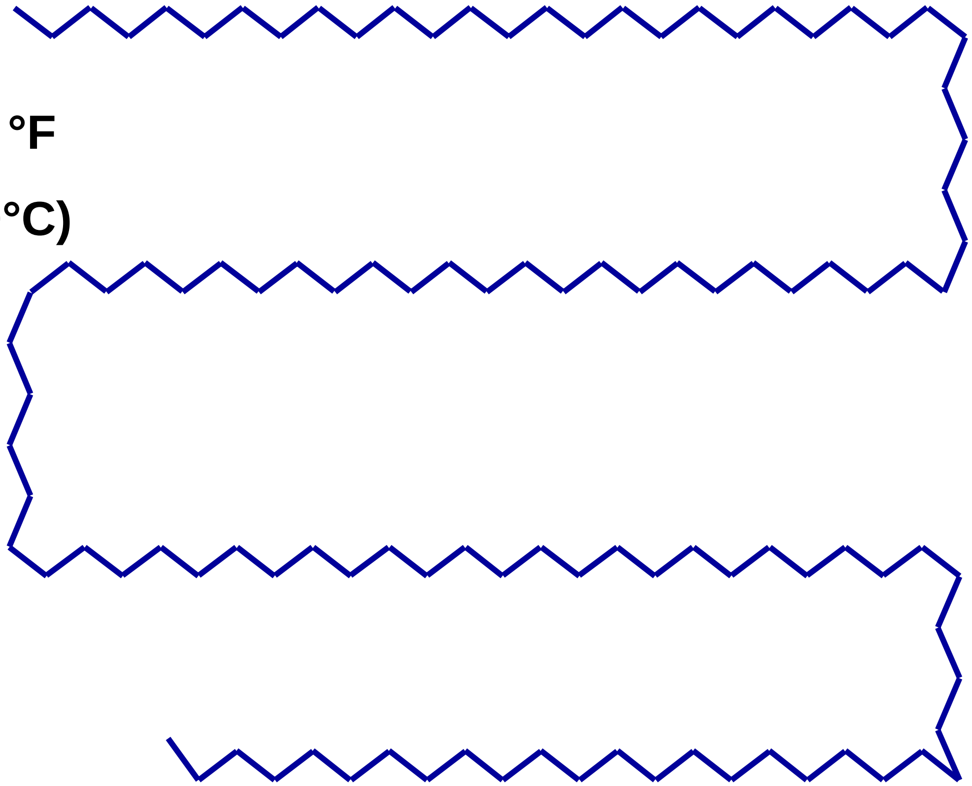
C_5 - C_{100}

Analysis is run similar to D2887

Boiling point range 156°F - 1328 °F

(69°C - 720°C)

Requires cryogenic oven

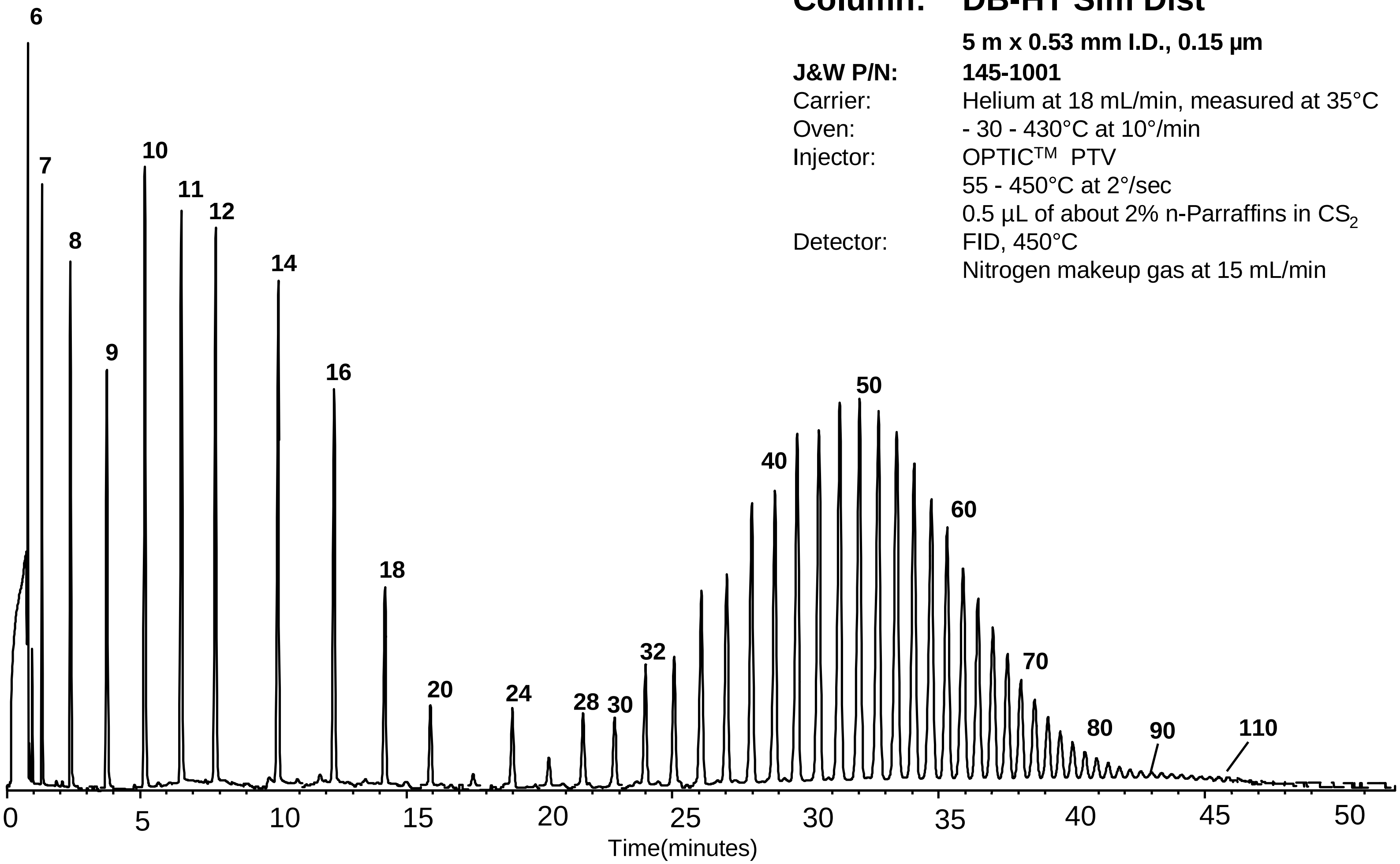


$C_{110}H_{222}$

M= 1544

High Temp Sim Dist Analysis

n-Paraffins



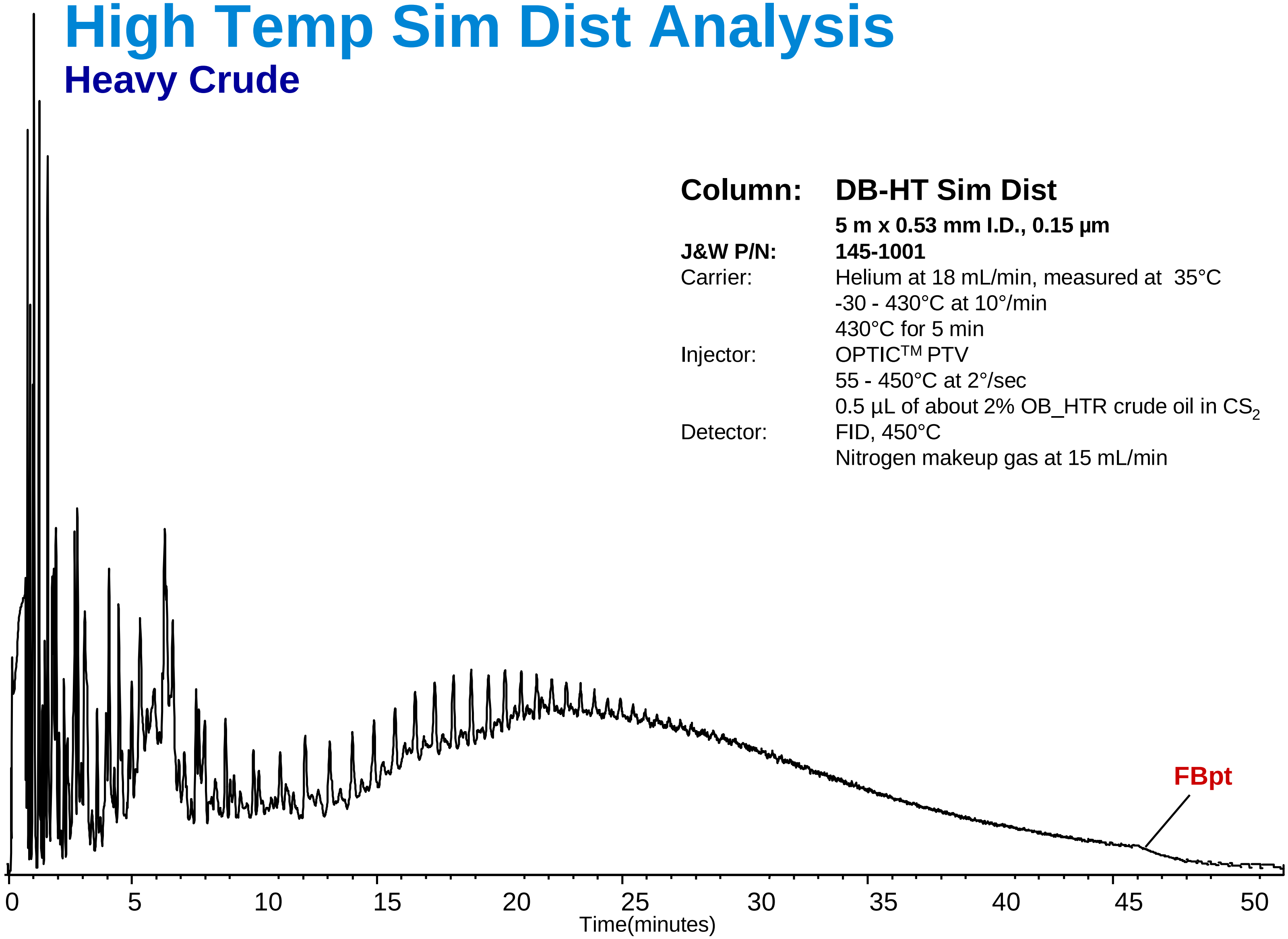
Column:	**DB-HT Sim Dist**
	5 m x 0.53 mm I.D., 0.15 µm
J&W P/N:	**145-1001**
Carrier:	Helium at 18 mL/min, measured at 35°C
Oven:	- 30 - 430°C at 10°/min
Injector:	OPTIC™ PTV
	55 - 450°C at 2°/sec
	0.5 µL of about 2% n-Parraffins in CS_2
Detector:	FID, 450°C
	Nitrogen makeup gas at 15 mL/min

n-Paraffin standard showing distillation range from C_6 to C_{110} on DB-HT Sim Dist

High Temp Sim Dist Analysis

Heavy Crude

Column: **DB-HT Sim Dist**
5 m x 0.53 mm I.D., 0.15 µm
J&W P/N: **145-1001**
Carrier: Helium at 18 mL/min, measured at 35°C
-30 - 430°C at 10°/min
430°C for 5 min
Injector: OPTIC™ PTV
55 - 450°C at 2°/sec
0.5 µL of about 2% OB_HTR crude oil in CS_2
Detector: FID, 450°C
Nitrogen makeup gas at 15 mL/min



Simulated distillation of a full range reference crude oil (OB-HTR)

General Maintenance Issues Significant to HTGC

Oxygen is a Polymer Pathogen - always use a quality O_2 scrubber

High quality septa are essential -- “high temp septa” usually means low sealability

Use high quality graphite ferrules to minimize out gassing and leaks

Be aware of syringe carry over due to poor solubility solutes

Maintenance Issues Related to Sample Residue Accumulation

Residues will cause tailing, loss of resolution and noisy elevated detector signal

Trim guard column -- replace when less than 1 meter long (2 coils)

PTV liners can be recycled with a muffle furnace

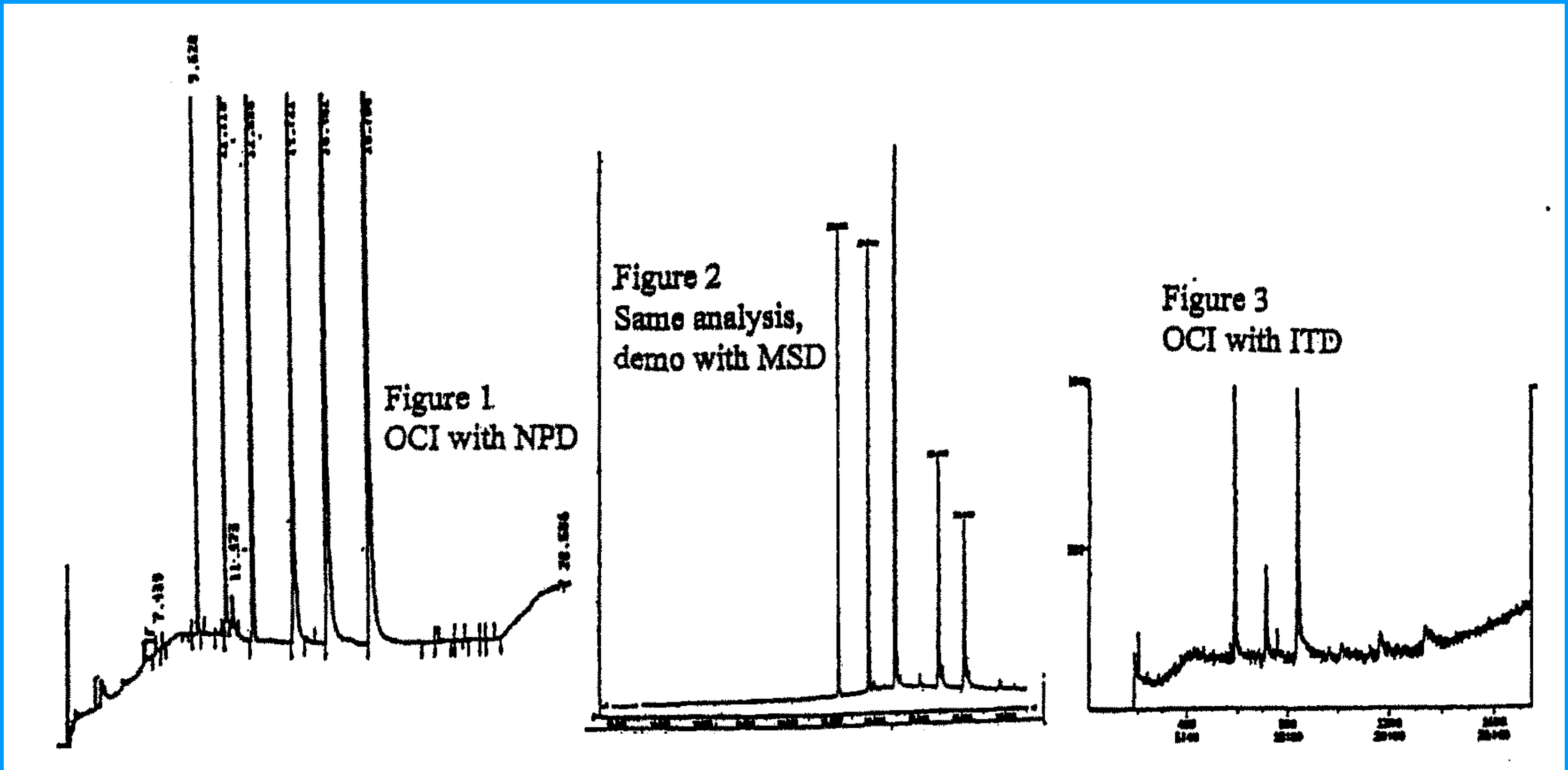
Maintenance Issues for HTGC Detectors

Extreme temperature causes rapid degradation of polymeric materials

Column bleed leaves “silicon powder” build-up in/on detector

Poor detector heat profile can cause poor resolution and sample losses

Poor Detector Design for High Molecular Weight Solutes



Final Remarks About HTGC

Precise and accurate

Capillary columns have amazing robustness

While not necessarily new -- HTGC equipment is more dependable

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