

The Design of High Temperature Metal Capillary Gas Chromatography Column Based on Polydimethylsiloxane

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Outline

Background

Column Bleed

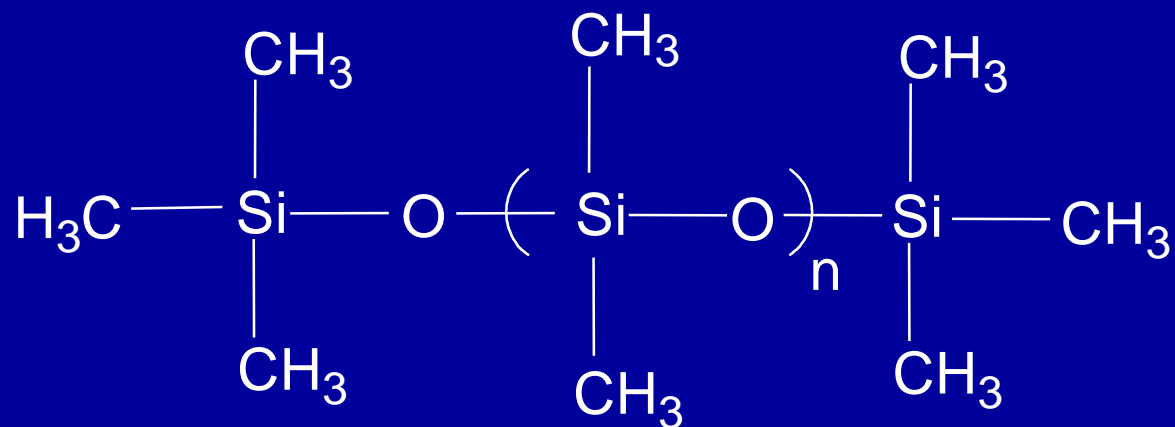
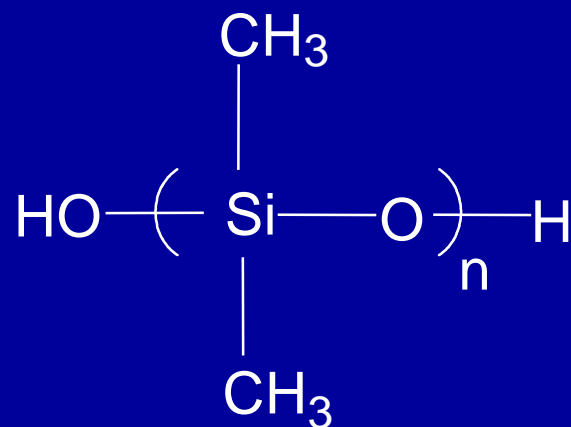
Column Selectivity

Unique Attributes of High Temperature Column

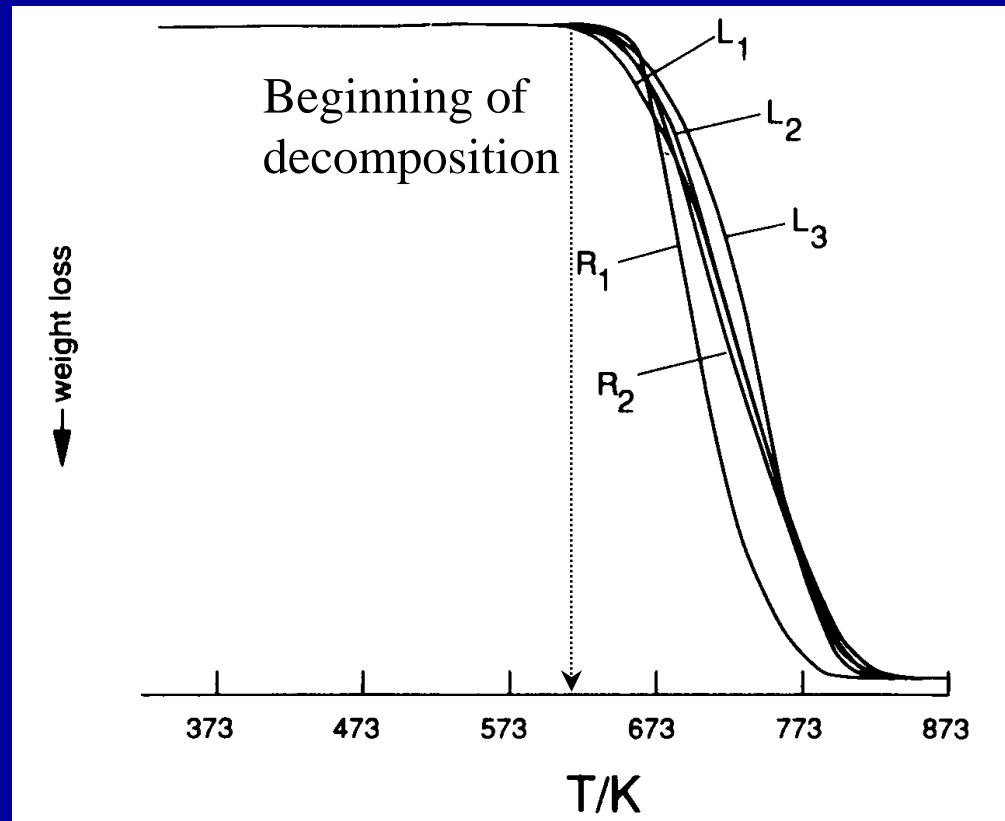
Applications

Conclusions

Polydimethylsiloxane

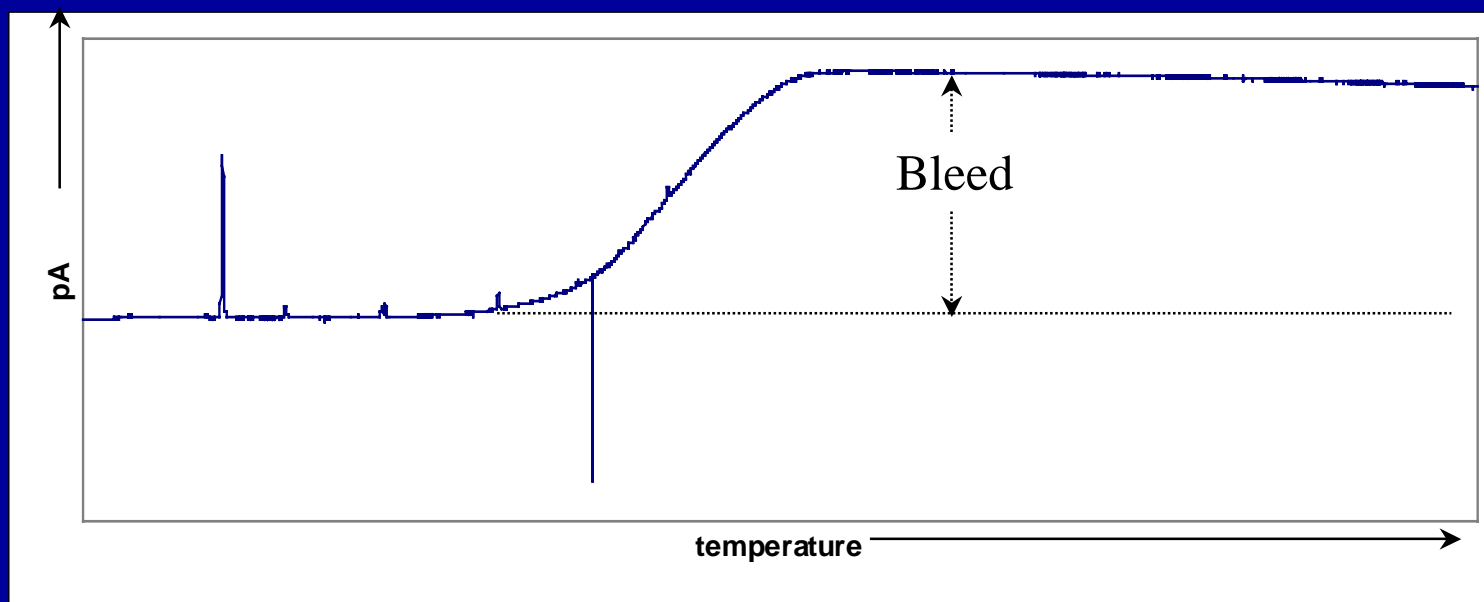


Thermal Stability of PDMS



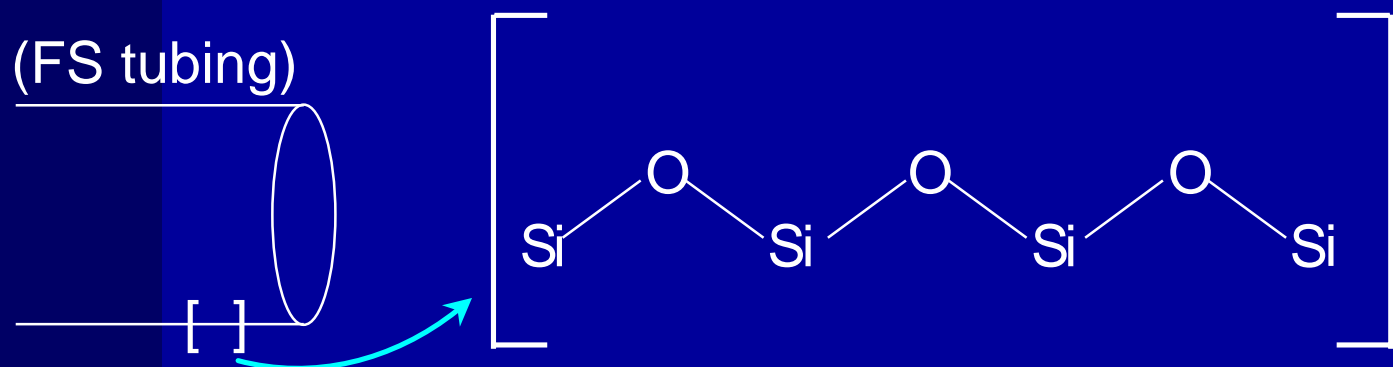
Adapted from Siloxane Polymers, ed. Clarson & Semlyen, 1993.

Bleed



Origin of Bleed

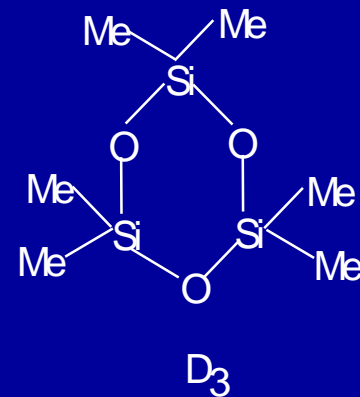
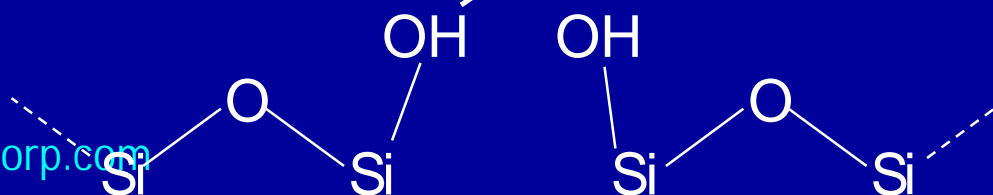
- Oligomers that are created in a column's lifetime



(polymer coating)

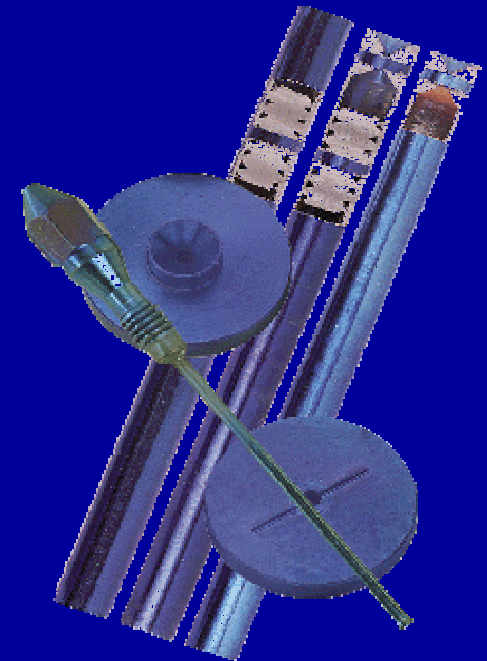
D₃/D₄ bleed

PDMS



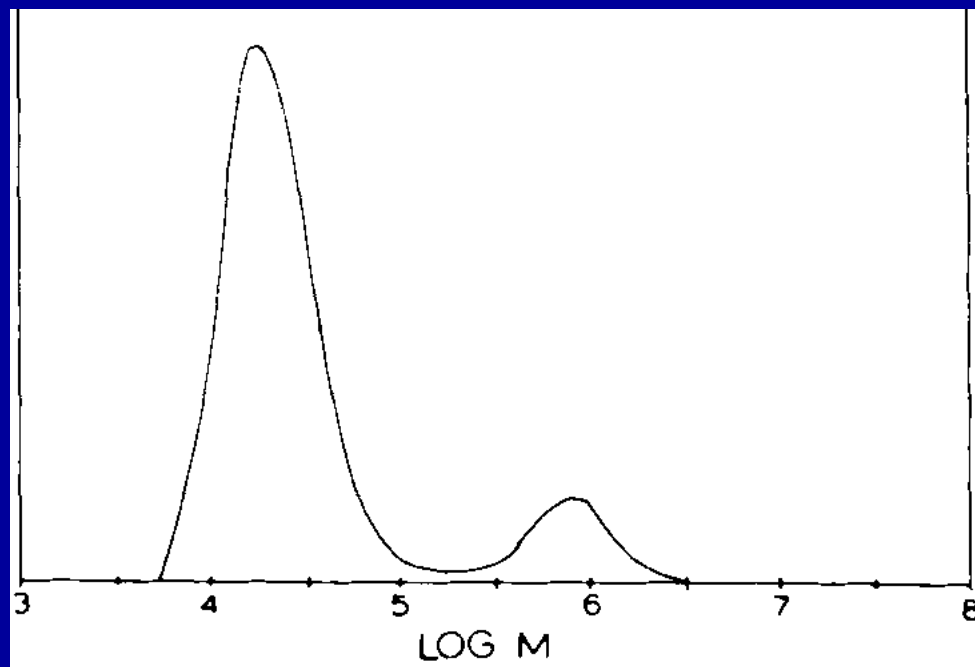
Deactivation of Metal Columns

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



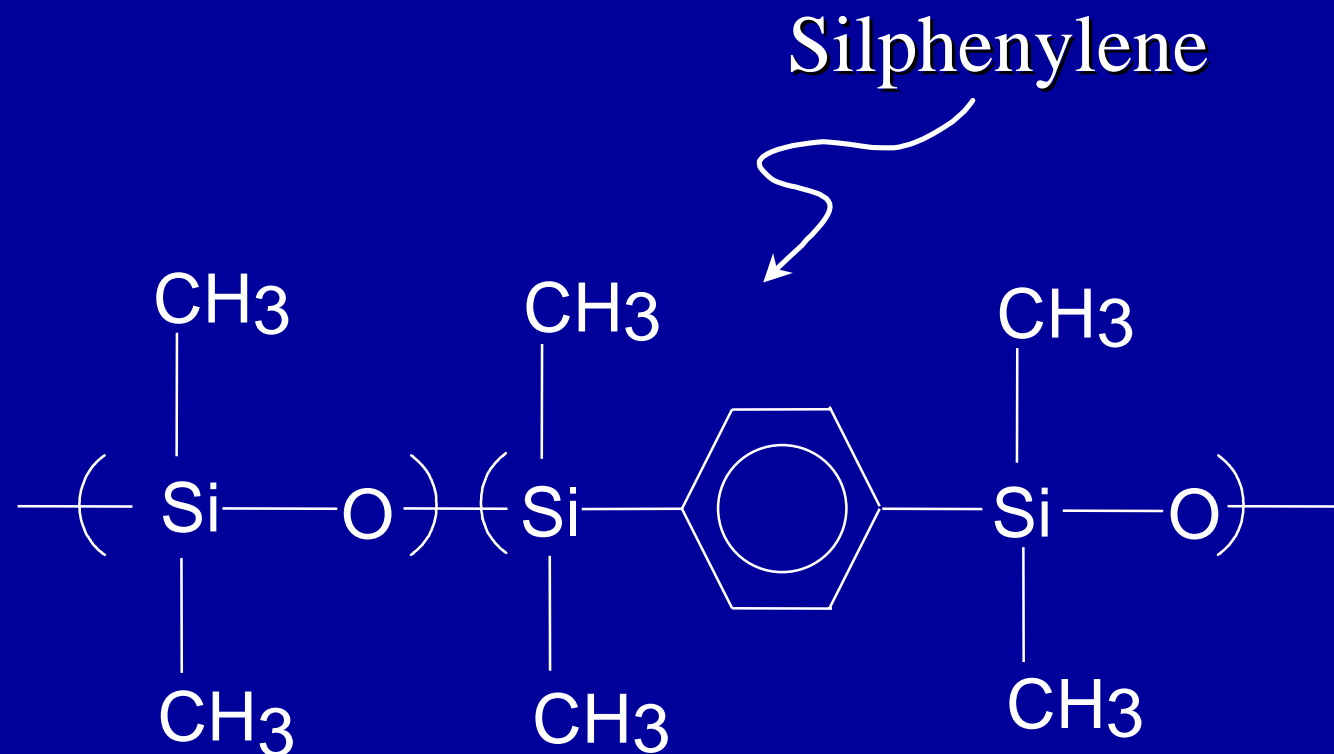
Origin of Bleed

- Polymer Synthesis



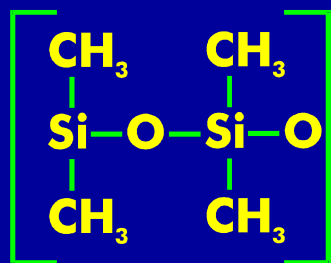
Adapted from Inorganic Polymers, Mark, Allcock, & West 1992.

Enhancement of Thermal Stability by Using Additives

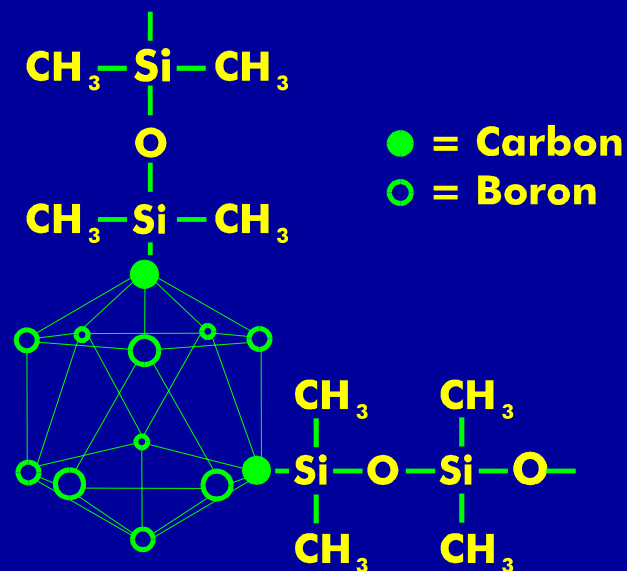


Stationary Phases for High Temperature Simulated Distillation

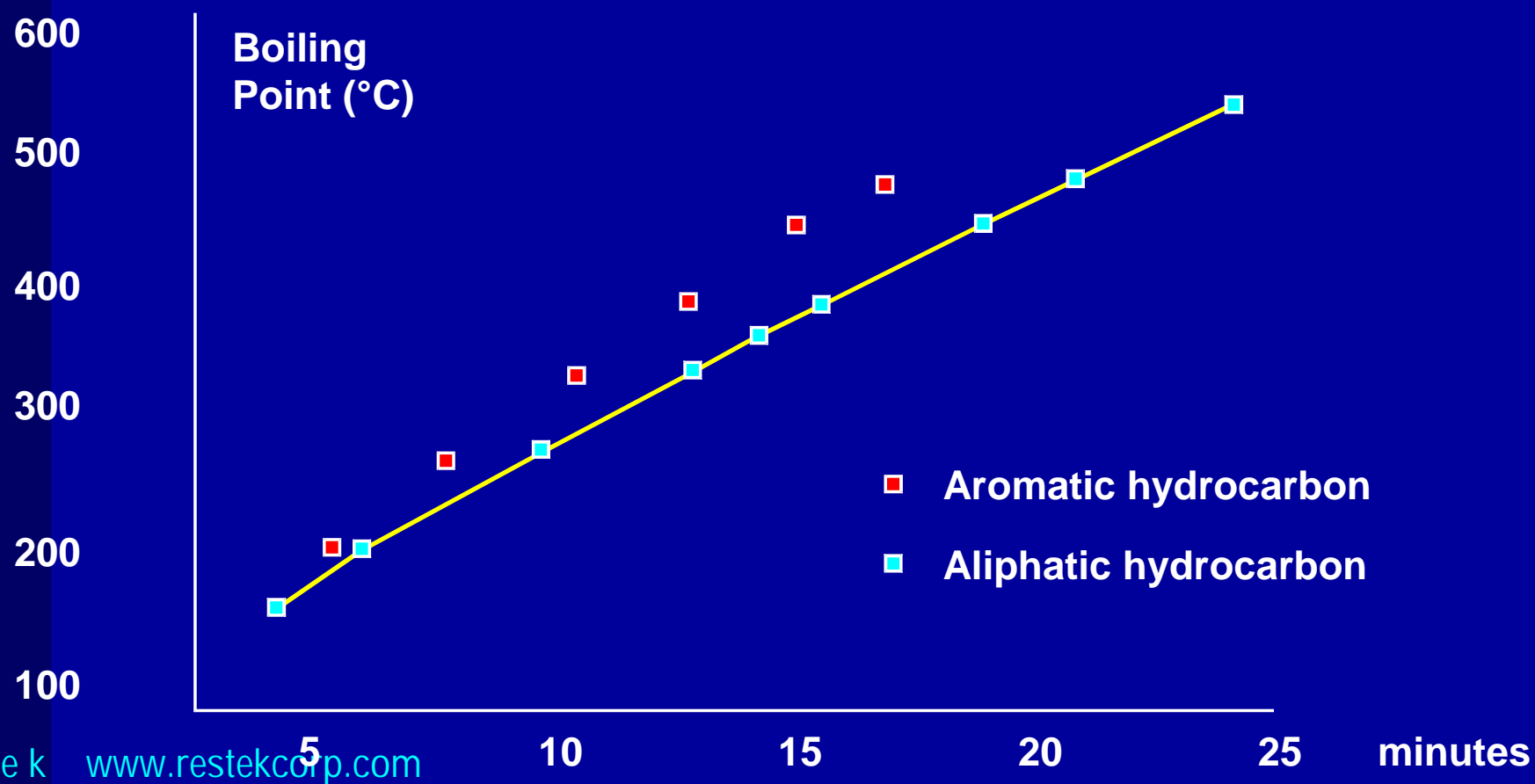
Dimethyl Polysiloxane



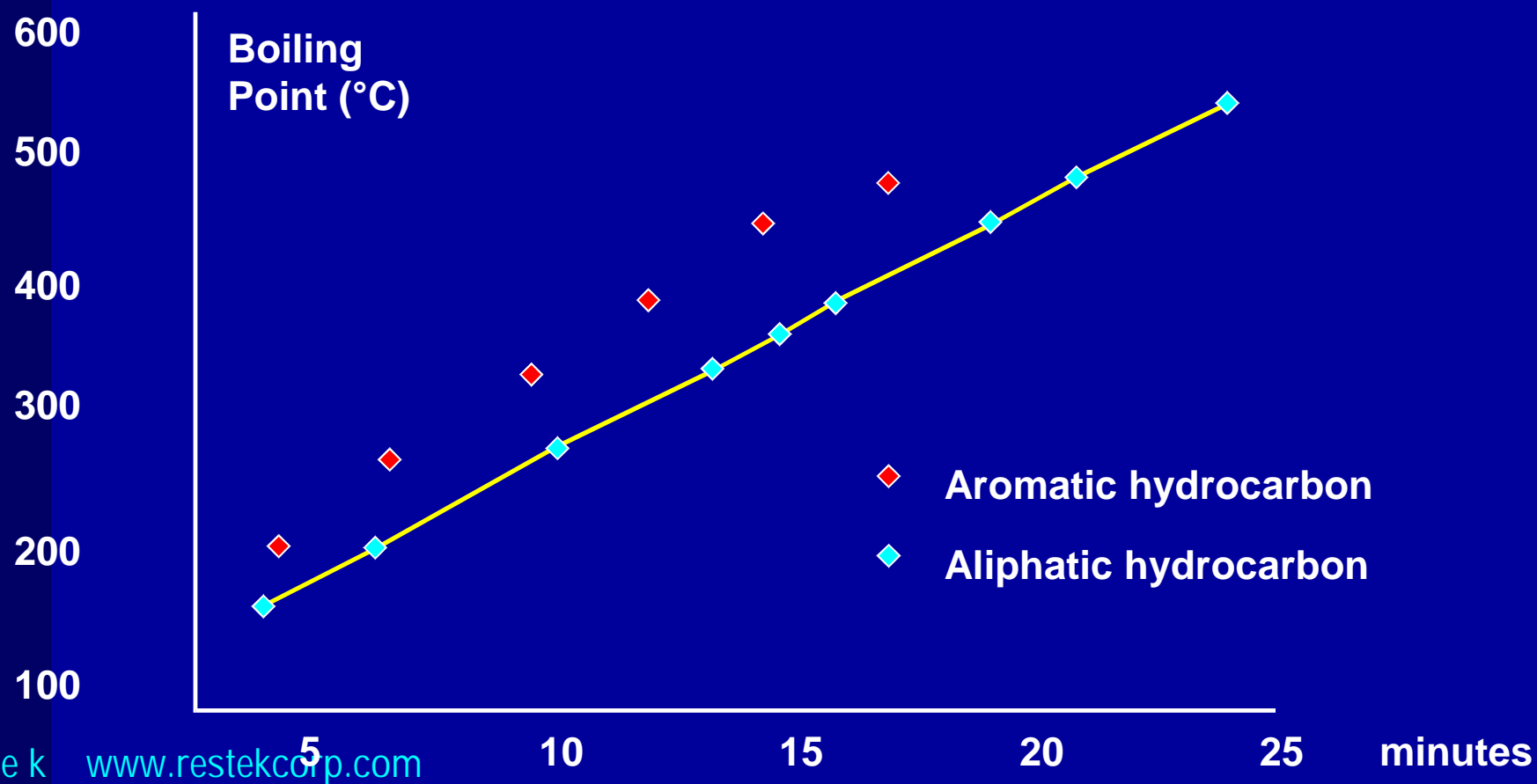
Carborane Dimethyl Polysiloxane



Retention According to BP methyl silicone



Retention According to BP carborane



Published vs Calculated BP for Aromatics

Compound	Published BP (°C)	Calculated BP	
		Dimethyl <u>Polysiloxane</u>	Carborane Dimethyl <u>Polysiloxane</u>
naphthalene	217	201	180
acenaphthalene	279	249	222
phenanthrene	340	300	275
anthracene	340	302	277
pyrene	393	342	321
chrysene	448	382	363
benzo-a-pyrene	477	414	410

High Temperature Simulated Distillation

- ASTM Method D 6352-02 is used for the determination of the boiling range distribution of petroleum distillate fractions.
- The method specifies the use of a short, wide bore, thin film capillary column.
- The upper temperature of the analysis is set at 400°C.

Column Design

- Method criteria: 5 m x 0.53mm ID x 0.10um
- Stainless steel tubing
- Treated with Siltek Deactivation
- A high temperature, non-polar stationary phase was developed that was able to withstand 430°C while producing minimal bleed.
- Matching the McReynolds requirements of the method.

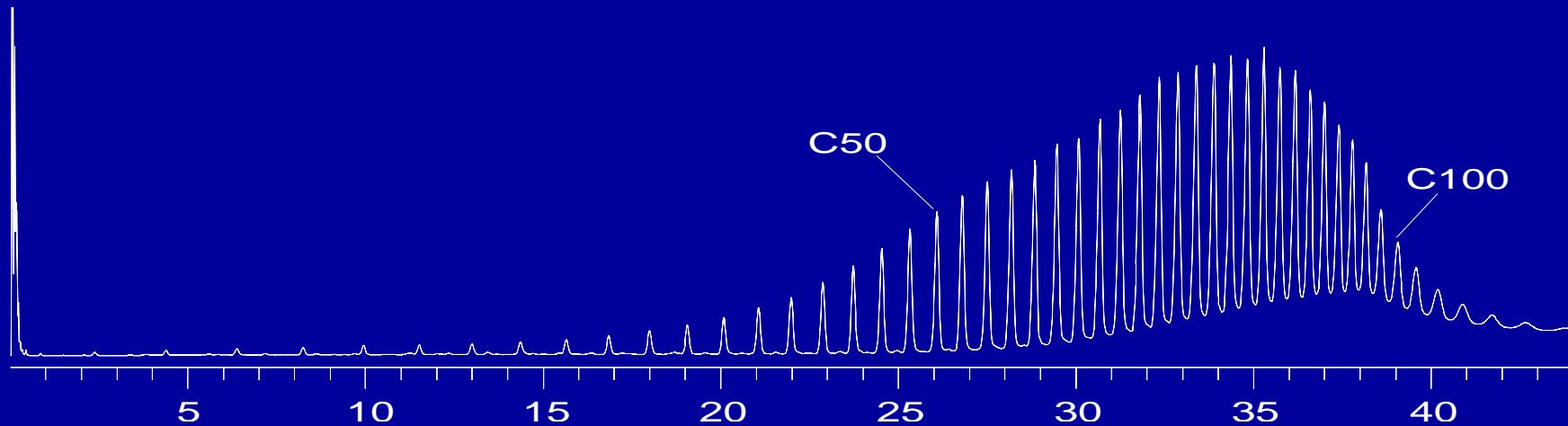
Experimental Design

- A lifetime study was performed by repetitively injecting a standard mixture designed for ASTM D2887 calibration.
- A Polywax 1000 sample was injected and resolution between C50 and C52 was calculated according to the method.
- Record kept of the retention time for C52 and the bleed at 430°C over the course of the experiment.
- Repeated until the column resolution fell below ASTM D6352-02 specifications.

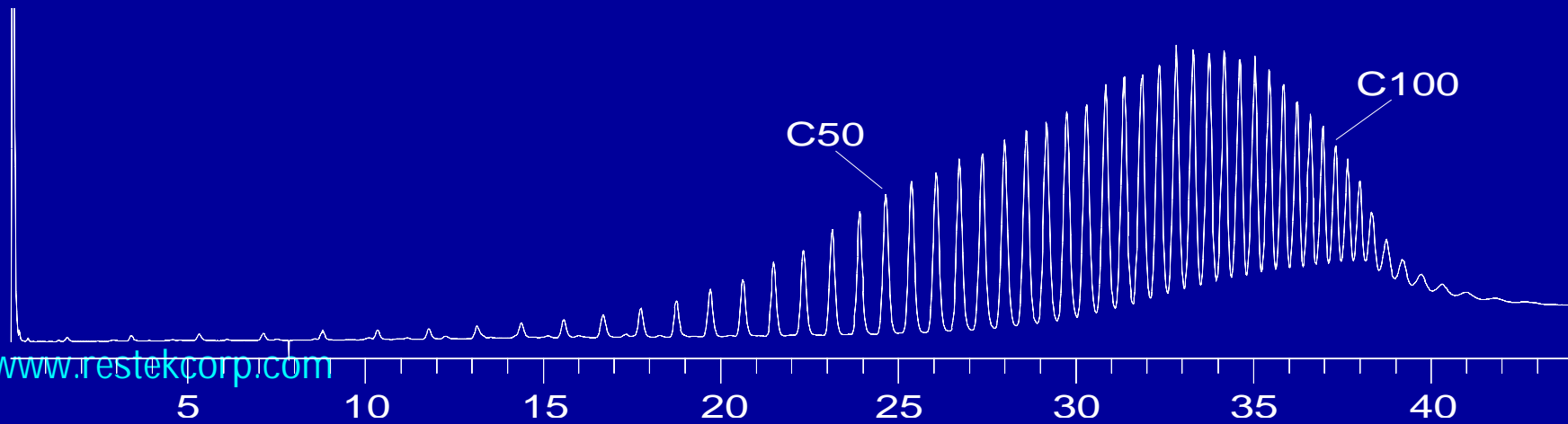
GC Conditions

- D2887 sample
 - 40°C to 430°C at 70°C/minute
 - Hold at 430°C for 10 minutes
- Polywax 1000 sample
 - 50°C to 430°C at 10°C/ minute
 - Hold at 430°C for 6 minutes
- Carrier Gas – Helium, 1.8psi (14ml/min)
- Sample – 0.2uL, 2% sample in Carbon Disulfide
- Cold On Column Injection with Oven Tracking

Polywax 1000 – Run #1



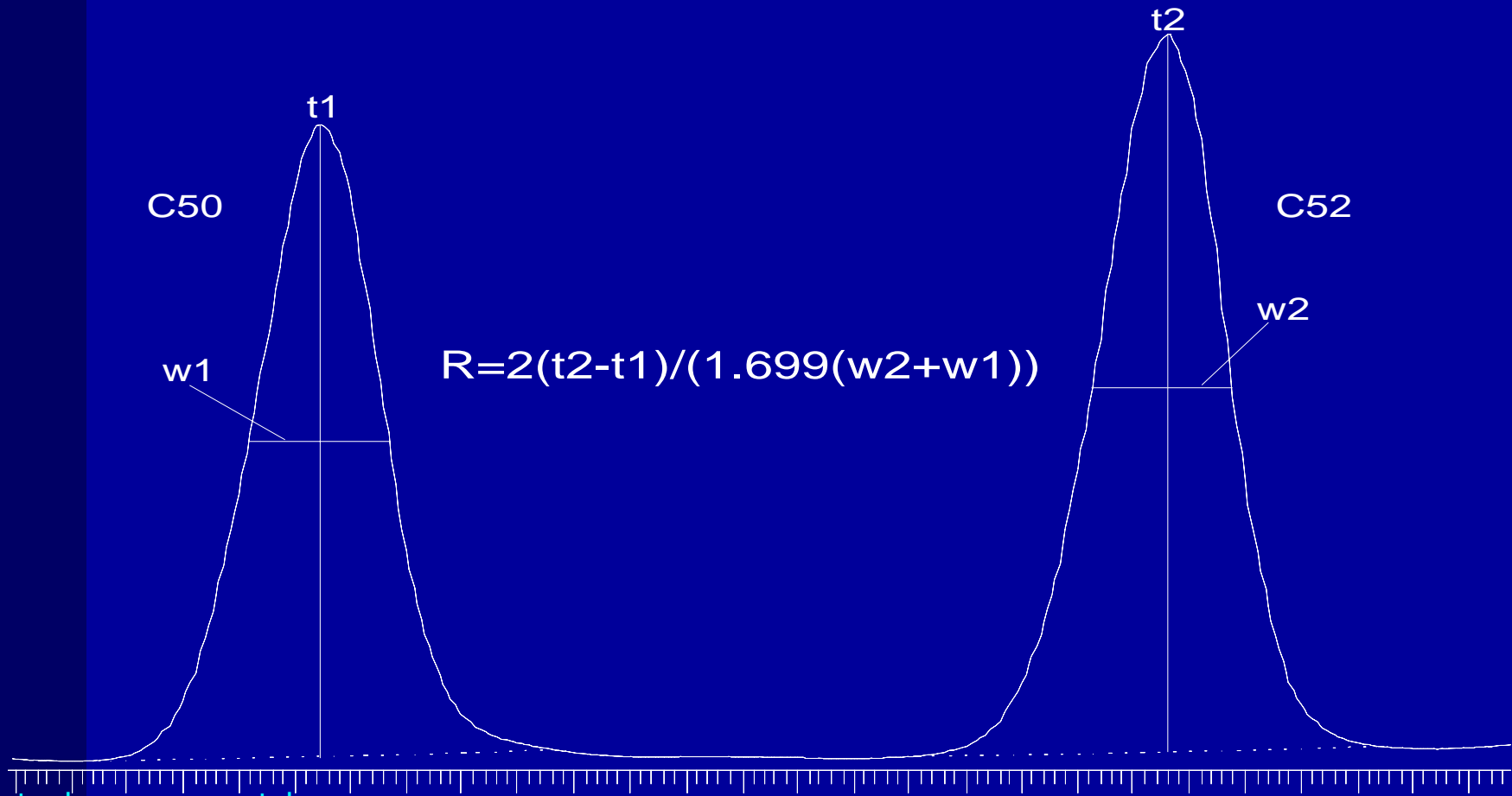
Polywax 1000 – Run #400



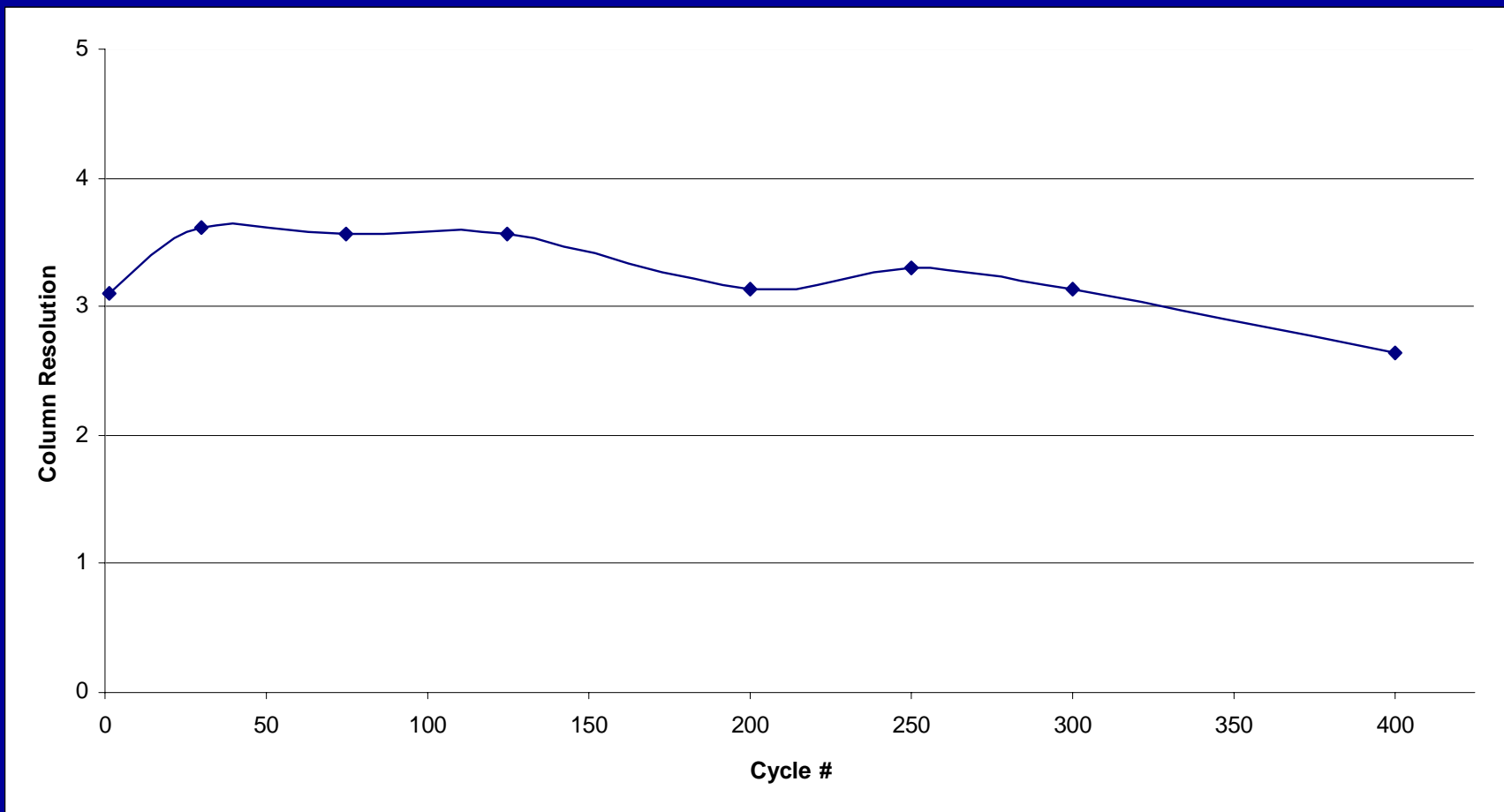
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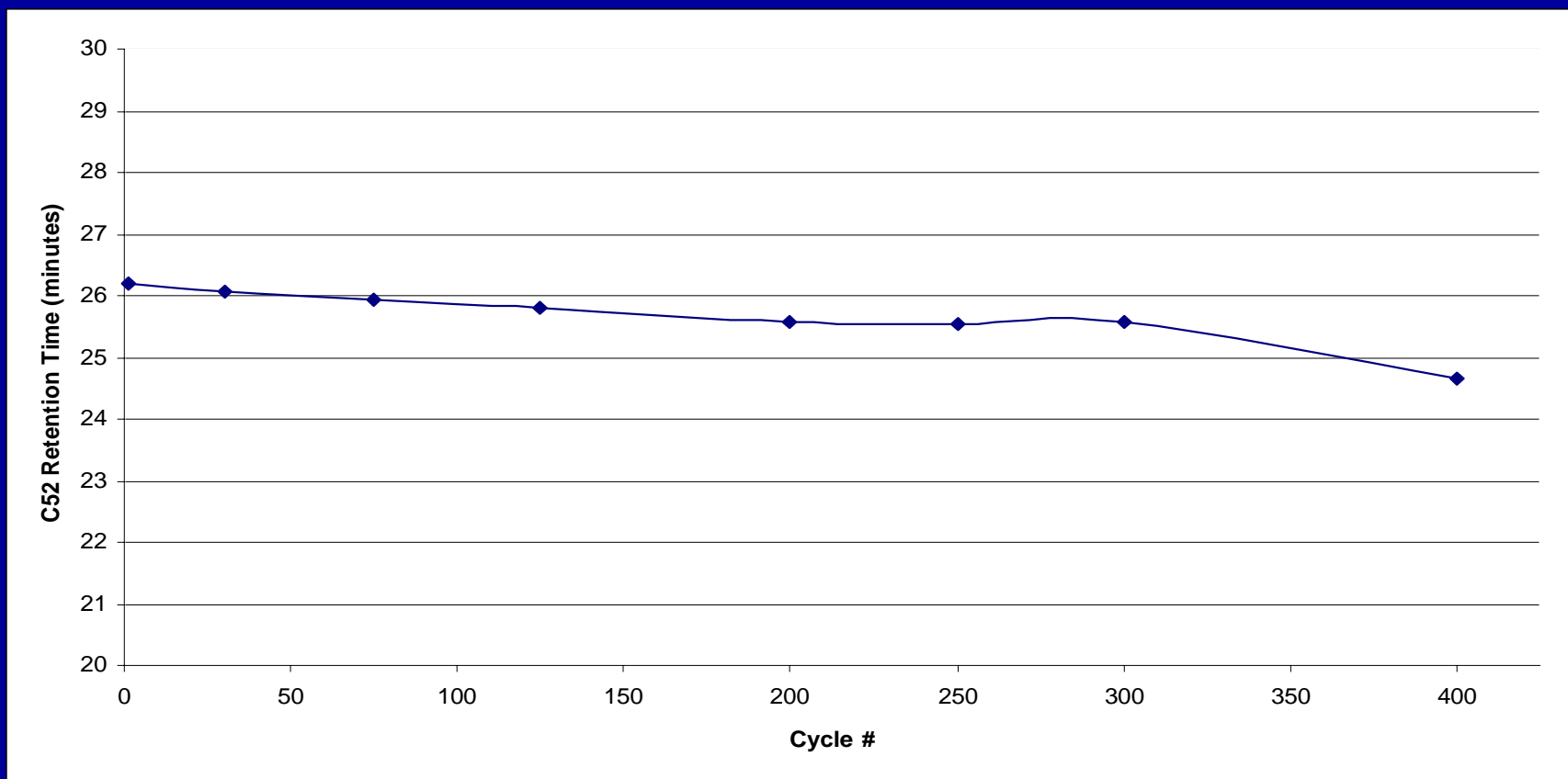
C50 / C52 Resolution – Run #1



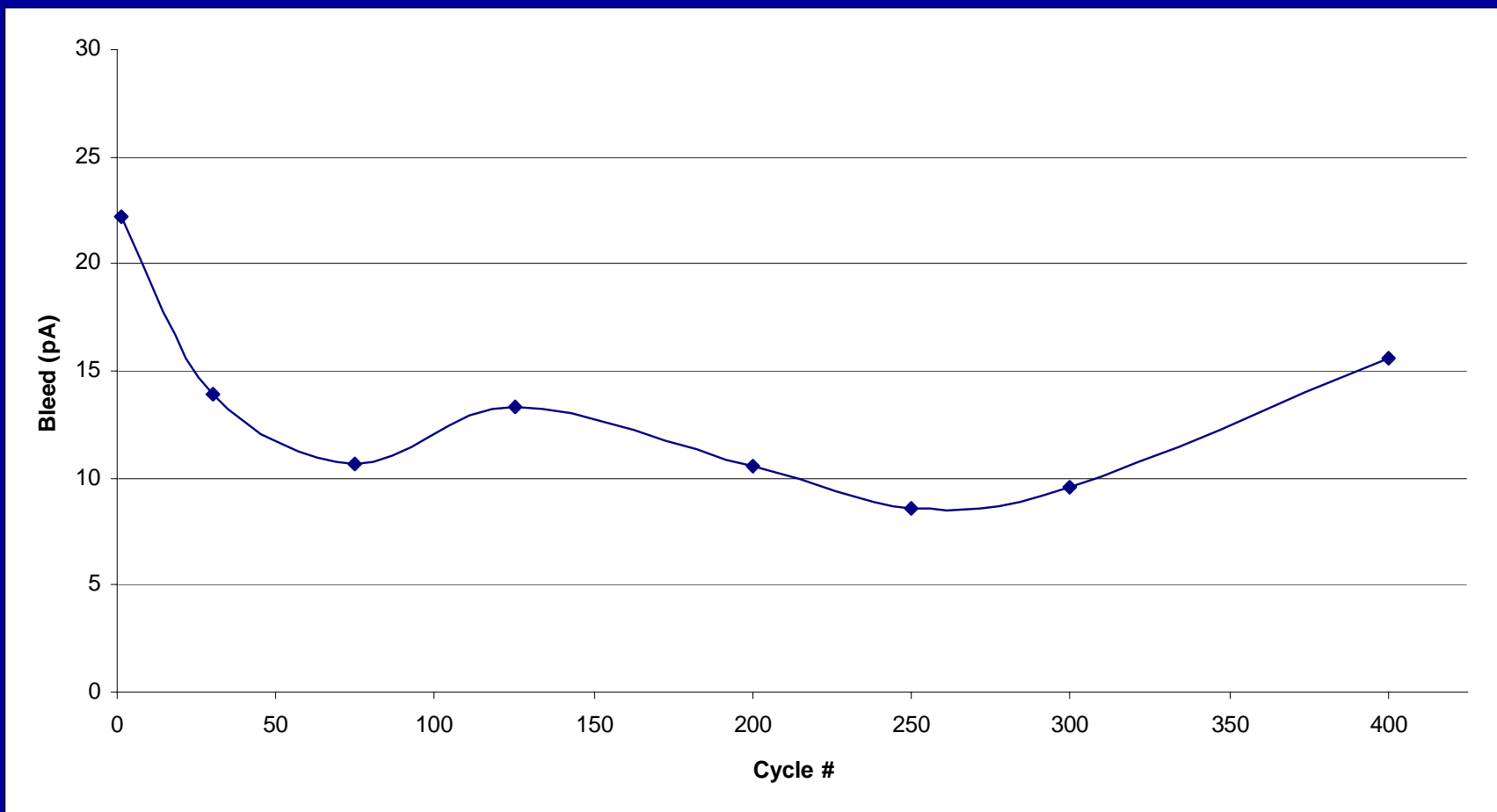
C50 / C52 Resolution



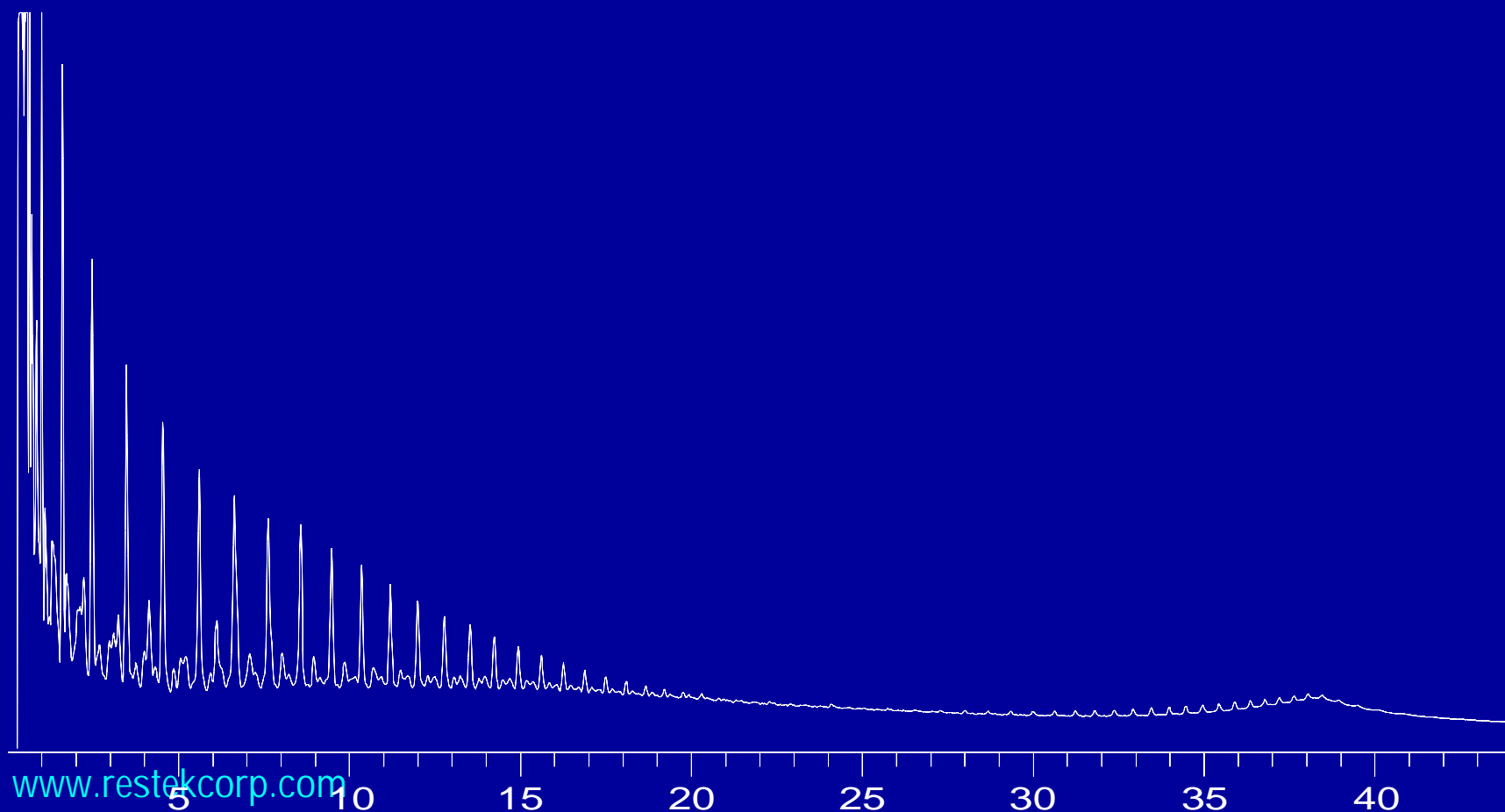
C52 Retention Time Stability



Column Bleed Stability



Pennsylvania Light Crude Oil



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Summary

- The MXT-1HT column demonstrates superior performance due to Siltek Deactivation and our in-house polymer synthesis.
- The MXT-1HT has the selectivity of polydimethylsiloxane.
- Able to withstand 400 cycles at 430°C and still retain good column efficiency and low bleed.
- Column demonstrated low bleed and adequate separating efficiency to resolve hydrocarbons in a crude oil sample.