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

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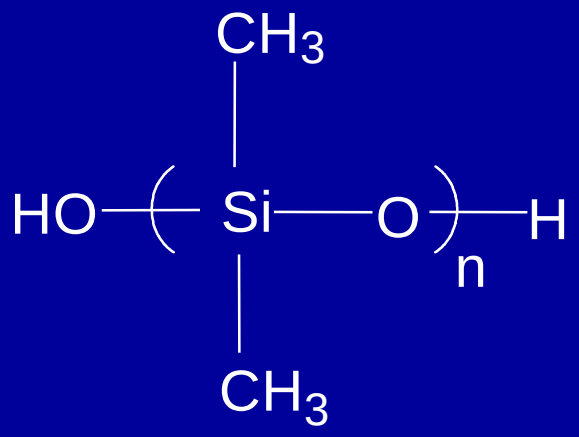
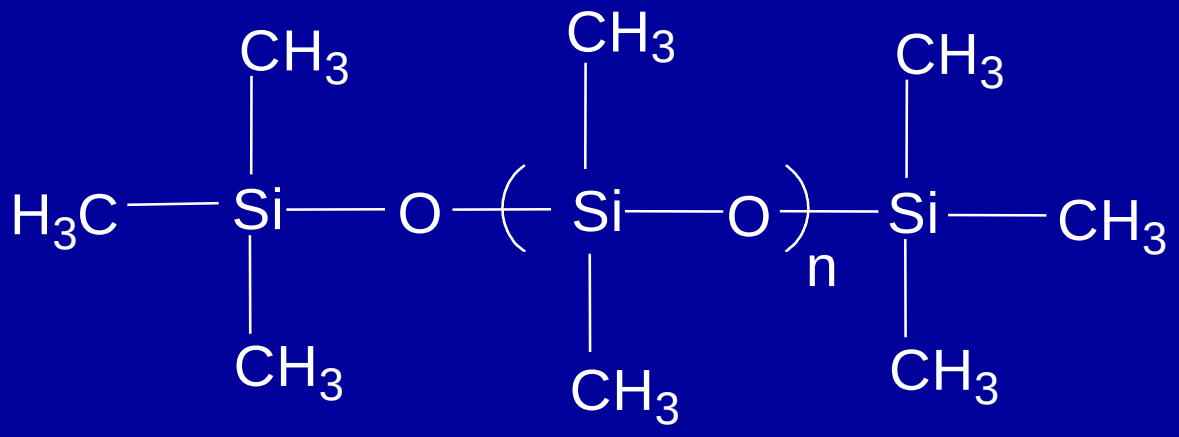
Outline

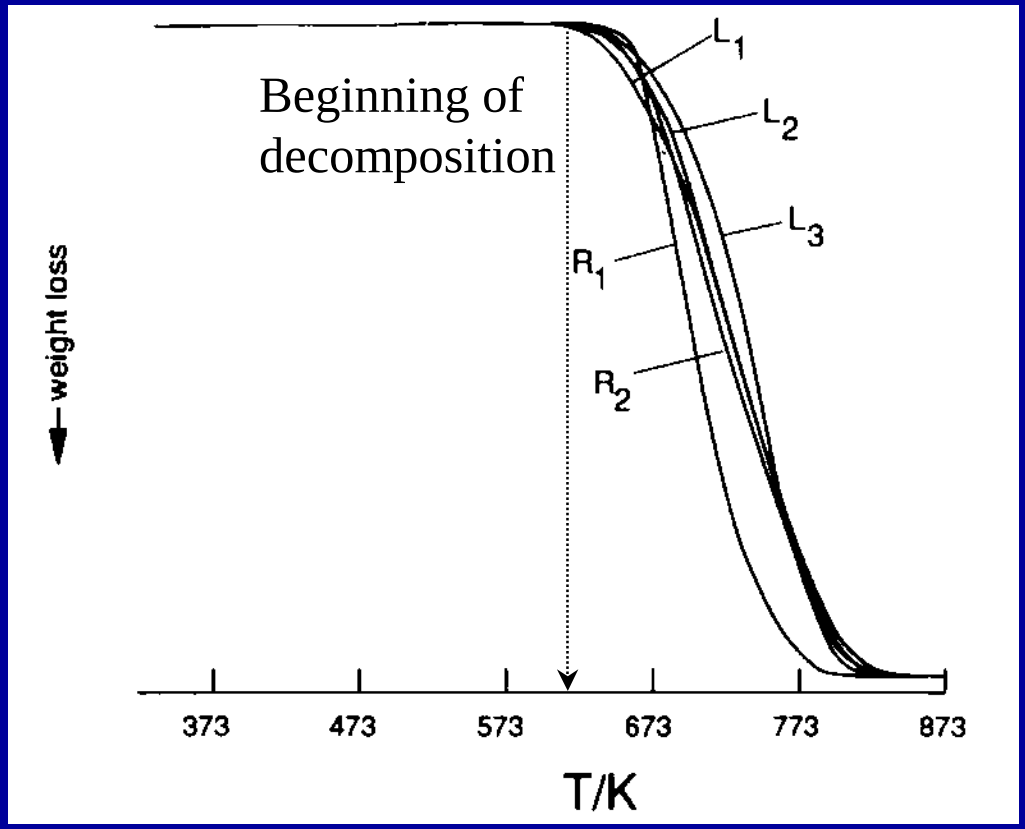
Background
Column Bleed
Column Selectivity
Unique Attributes of High Temperature Column
Applications
Conclusions

Polydimethylsiloxane





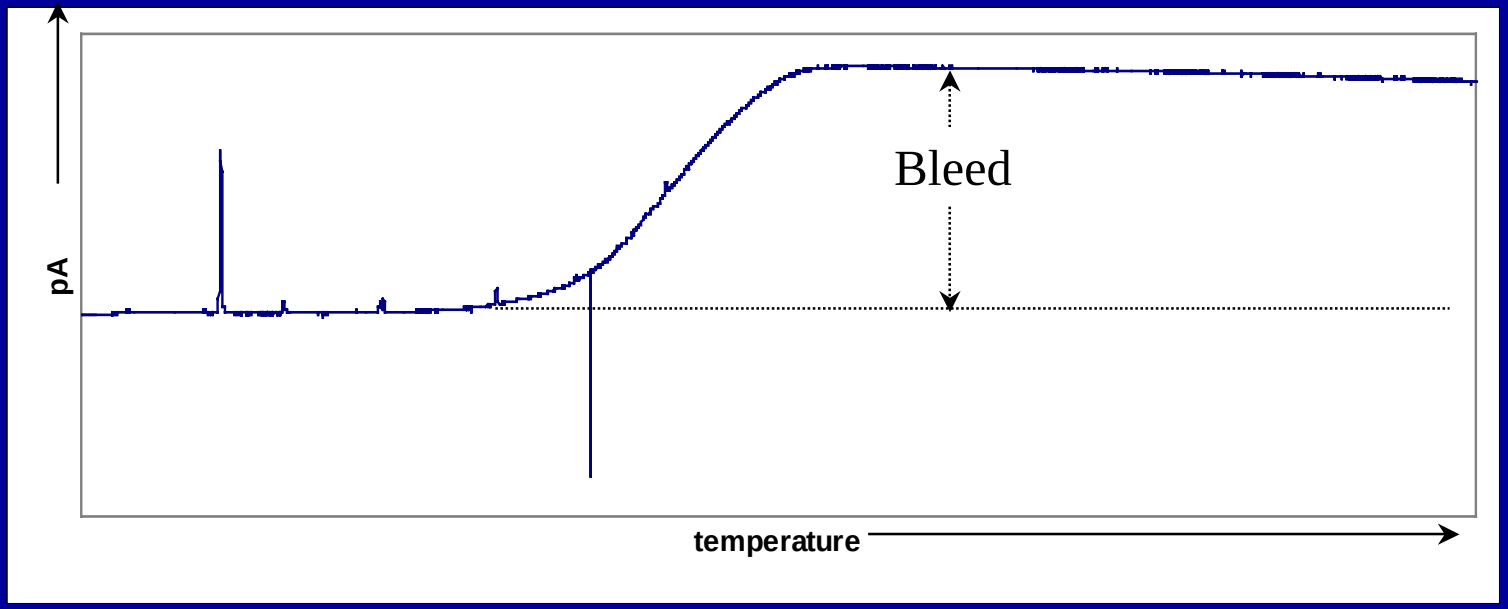
Thermal Stability of PDMS



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

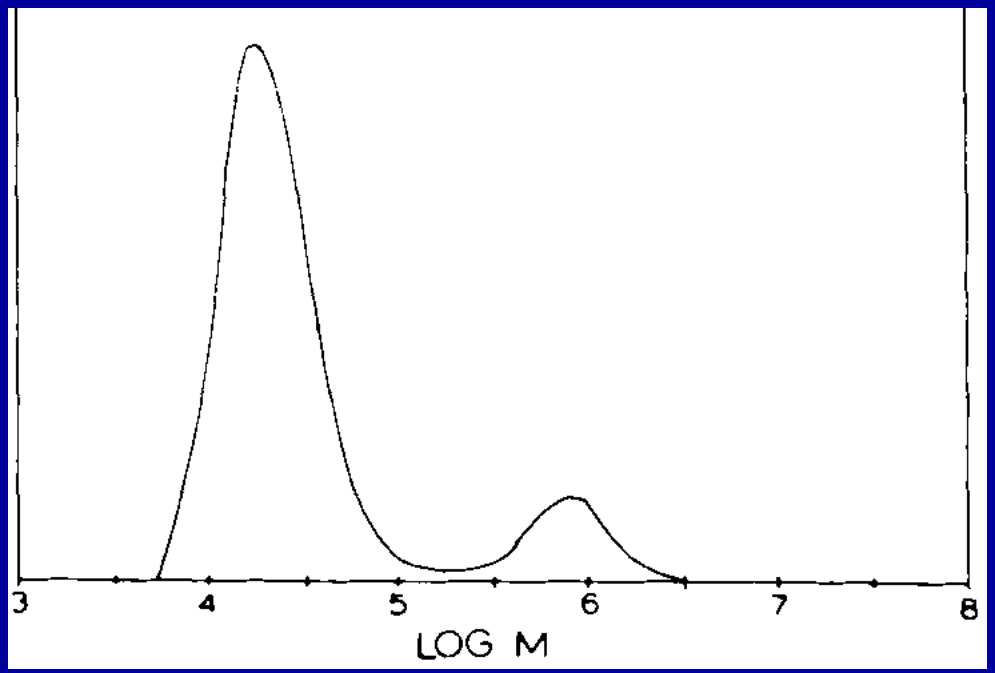
Bleed

- Chromatography of silicone “bleed” from the gas chromatography column under temperature programming



Origin of Bleed...

- Polymer Synthesis



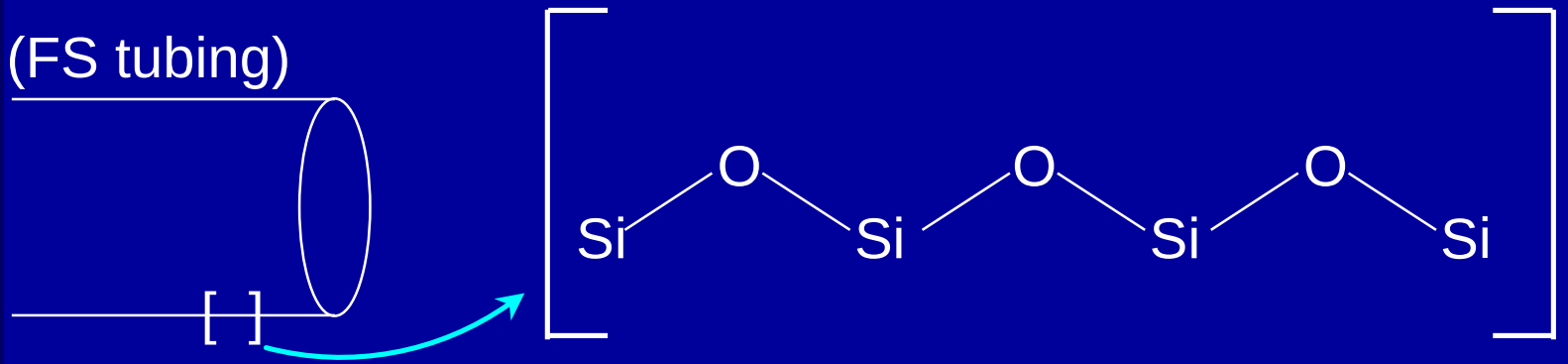
Adapted from Inorganic Polymers, Mark, Allcock, & West 1992.

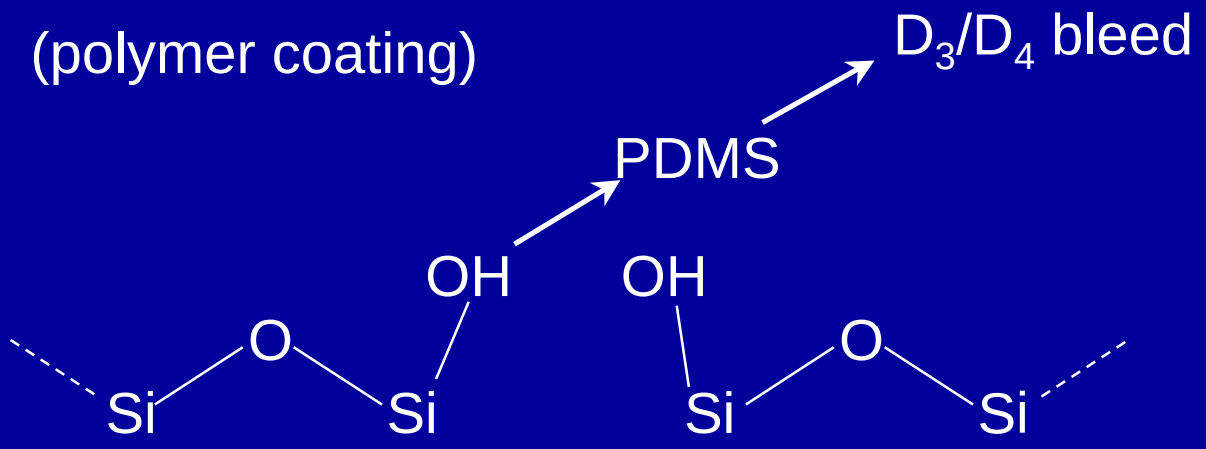
Polymer Synthesis

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

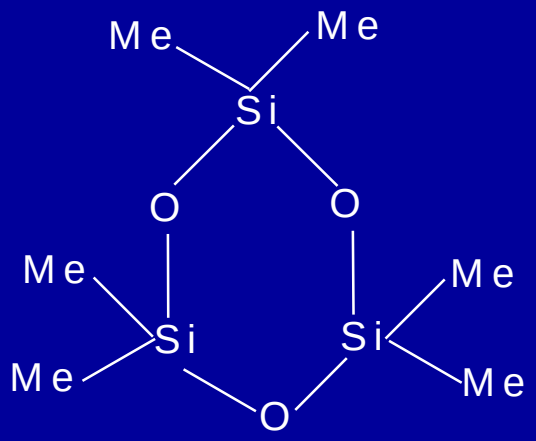
Origin of Bleed...

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

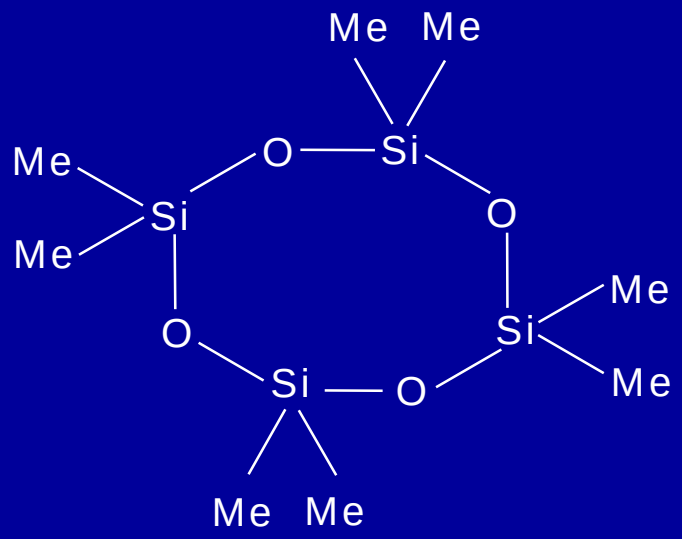




Typical Chemical Structure of Bleed



D_3



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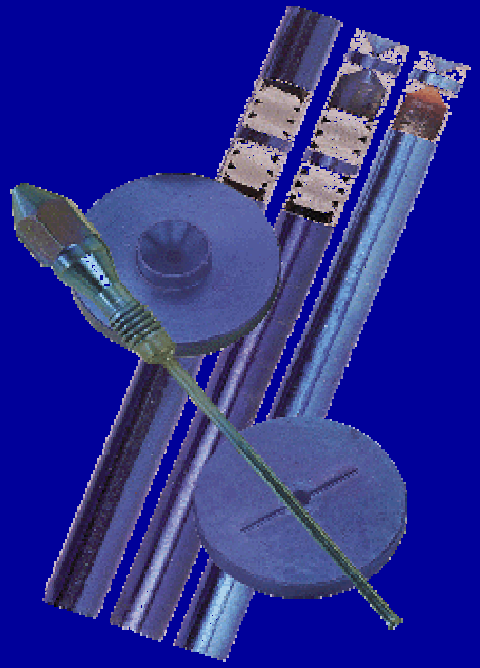
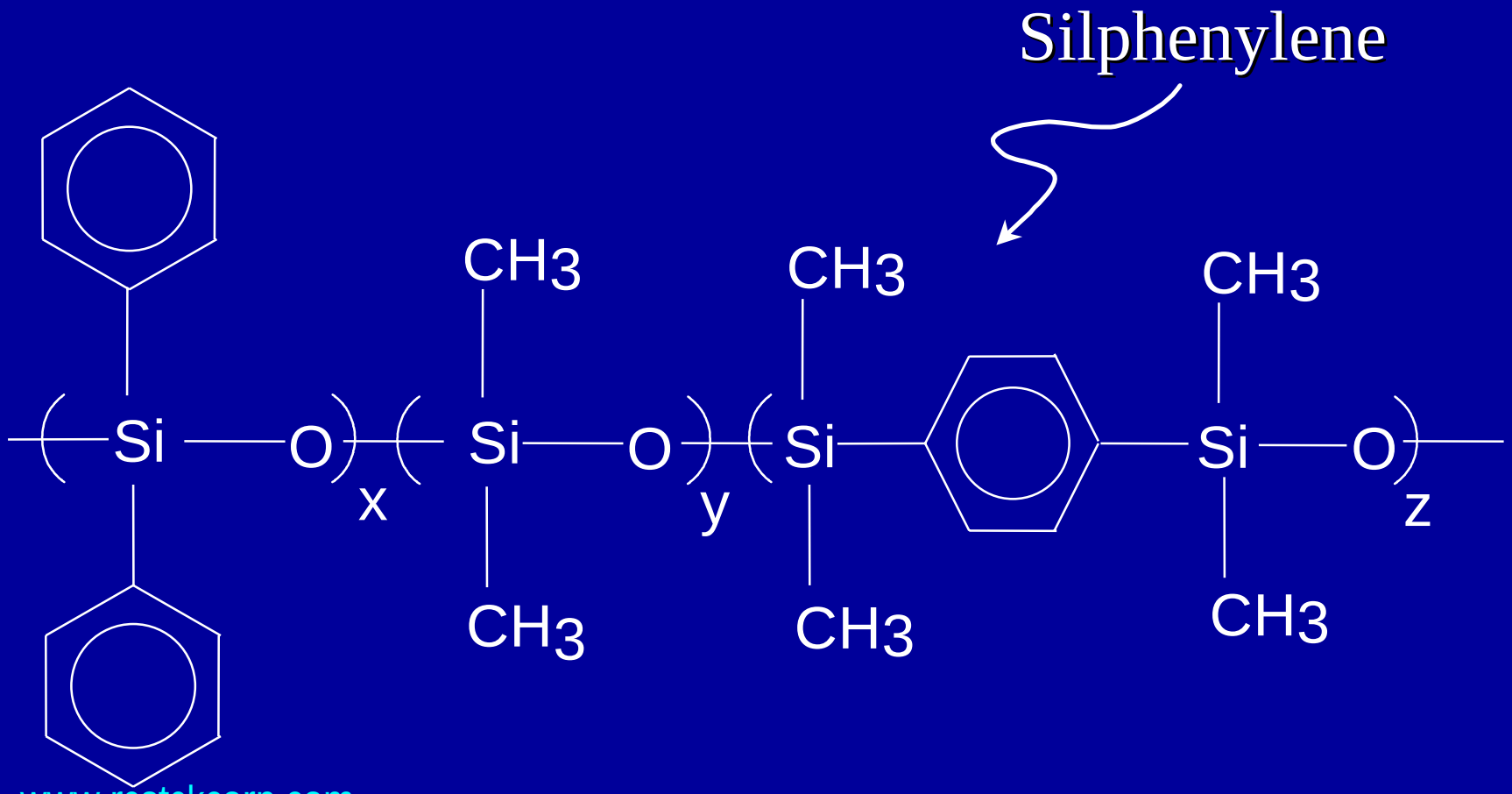
Deactivation of Metal Columns

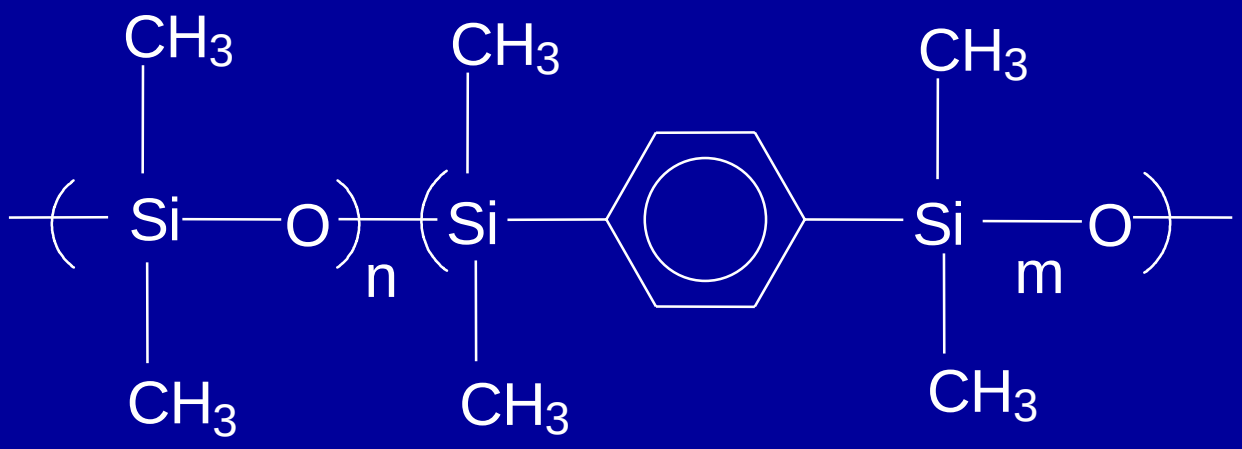
- We are using an advanced deactivation called Siltek™. It is a deposition process, unlike silazane or silicone deactivation.



Enhancement of Thermal Stability by Using "Additives"



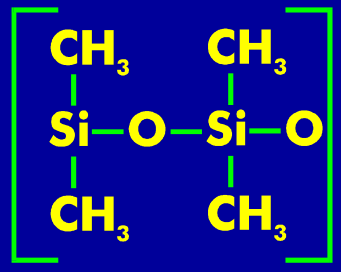
Additives...



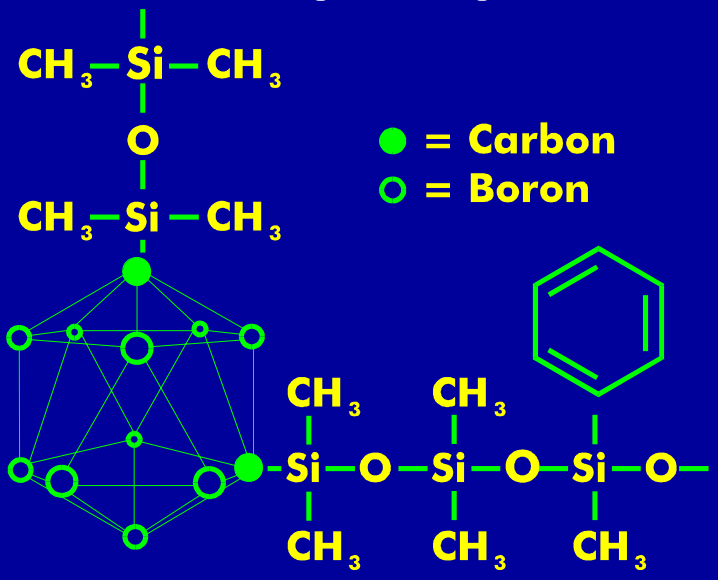
- A column with true Polydimethylsiloxane selectivity cannot be obtained by having silphenylene in the backbone.

Stationary Phases for High Temperature Simulated Distillation

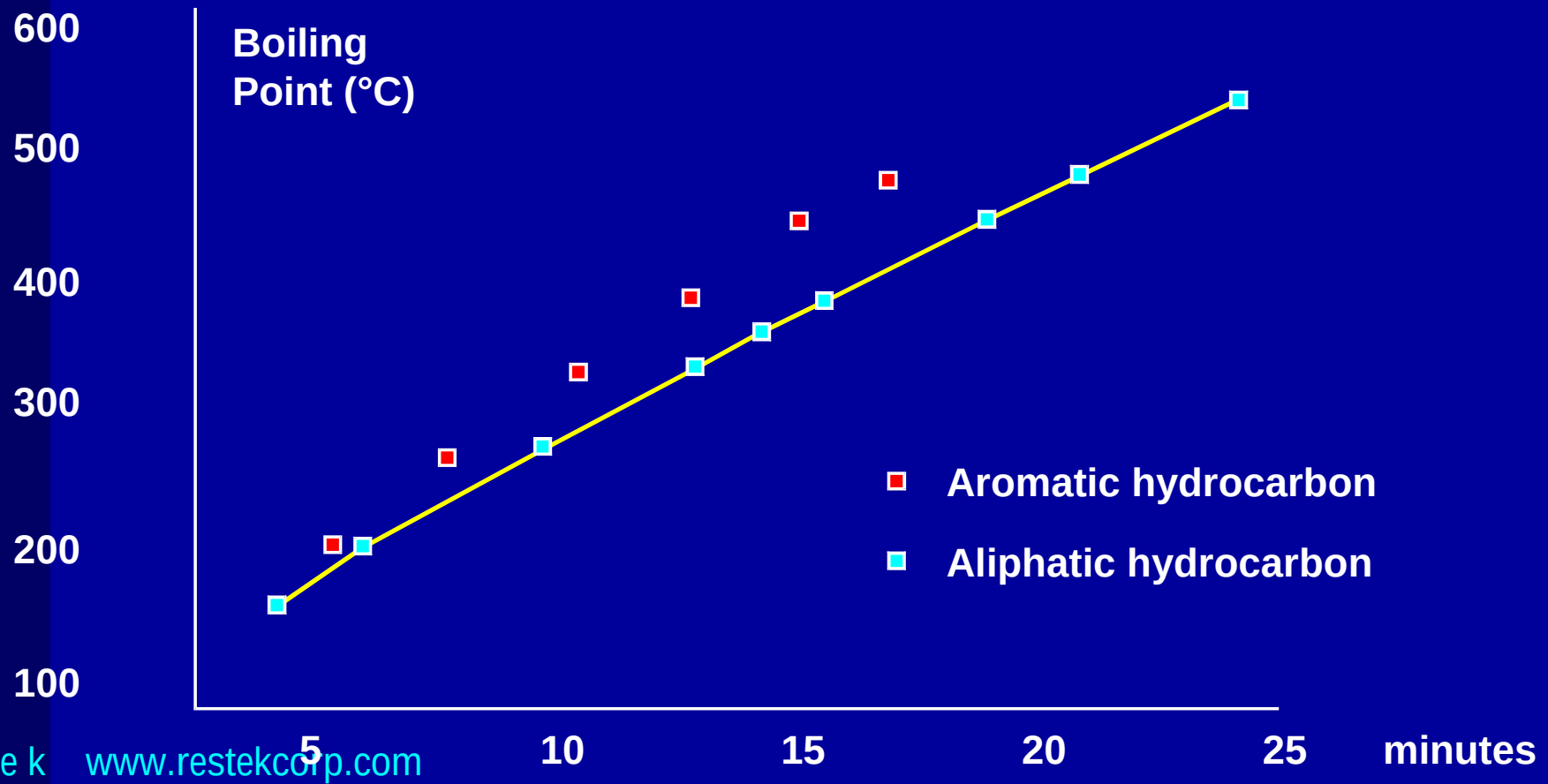
Dimethyl Polysiloxane



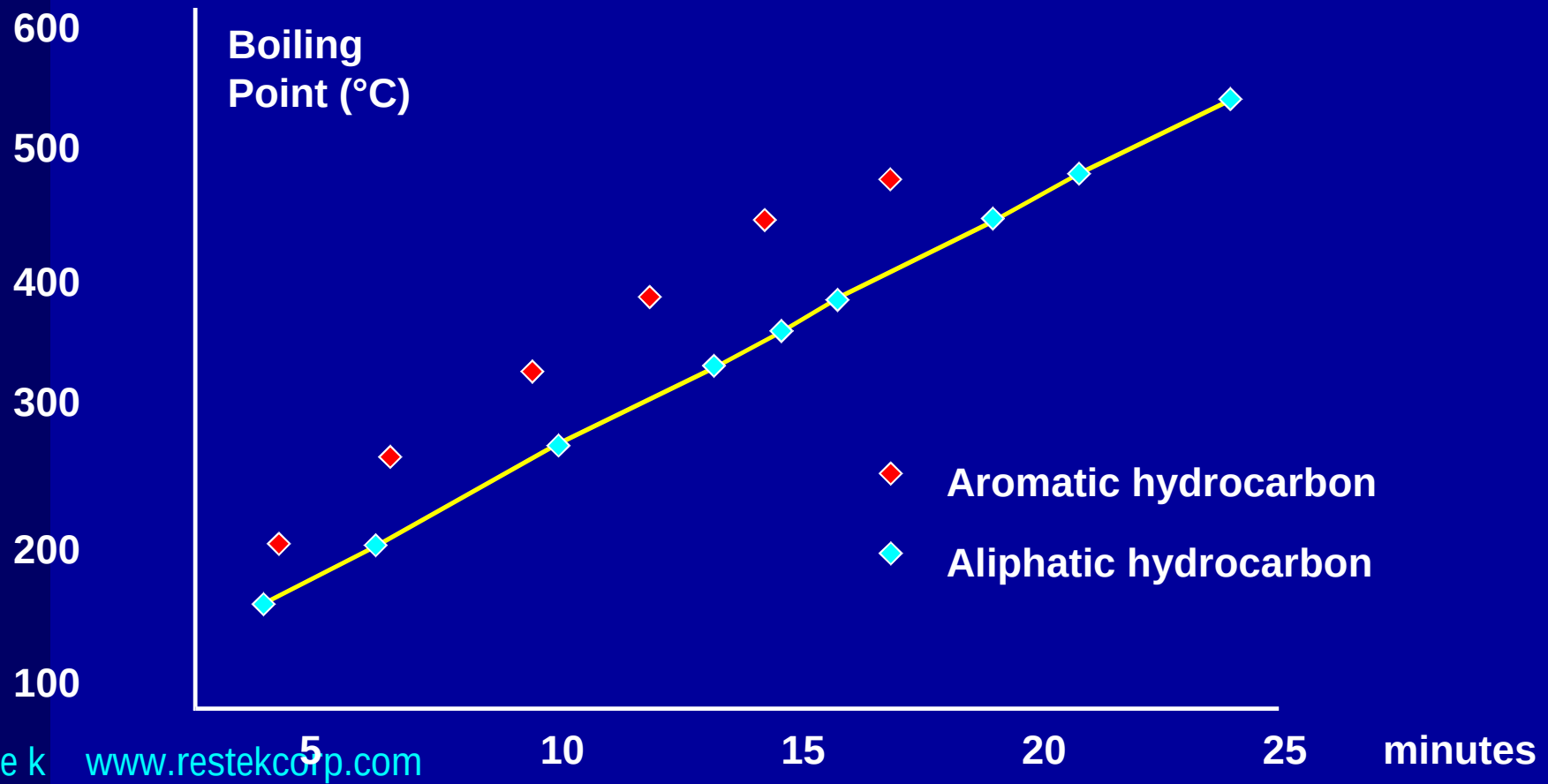
Carborane Dimethyl Polysiloxane



Retention According to BP methyl silicone



Retention According to BP carborane



Effect of Stationary Phase on Calculated BP

Aromatic Hydrocarbon	Published BP[1] (°C)	Calculated BP		
		Rtx-1	UCW-982	OV-101
benzene	80	81.3	82	80.3
p-xylene	139	138.6	140.2	137.7
naphthalene	218	204.6	206.9	204.3
acenaphthalene	280	252.7	255.6	252.2
anthracene	342	304.1	307.2	303.4
chrysene	447	385.6	389.2	384.9
dibenzo(a,h)anthracene	524	452.3	455.7	450.4

[1] from API Project 44

Published vs Calculated BP for Aromatics

Compound	Published BP (°C)	Calculated BP	
		Dimethyl Polysiloxane	Carborane Dimethyl Polysiloxane
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 6352-98 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^{o}C over the course of the experiment.
- Repeated until the column resolution fell below ASTM D6352-98 specifications.

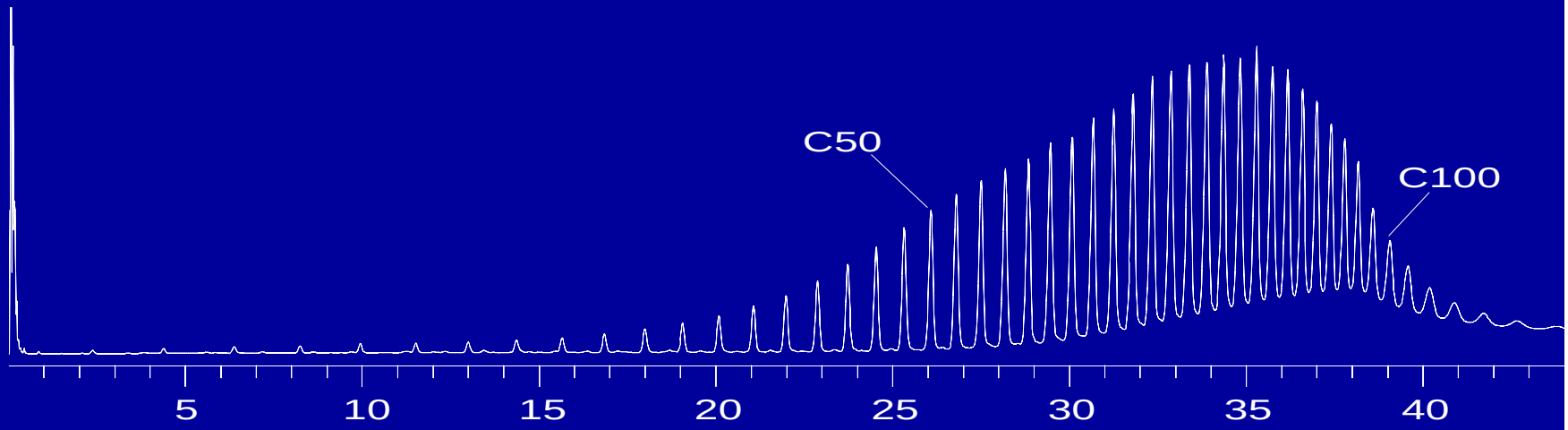
GC Conditions

- 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

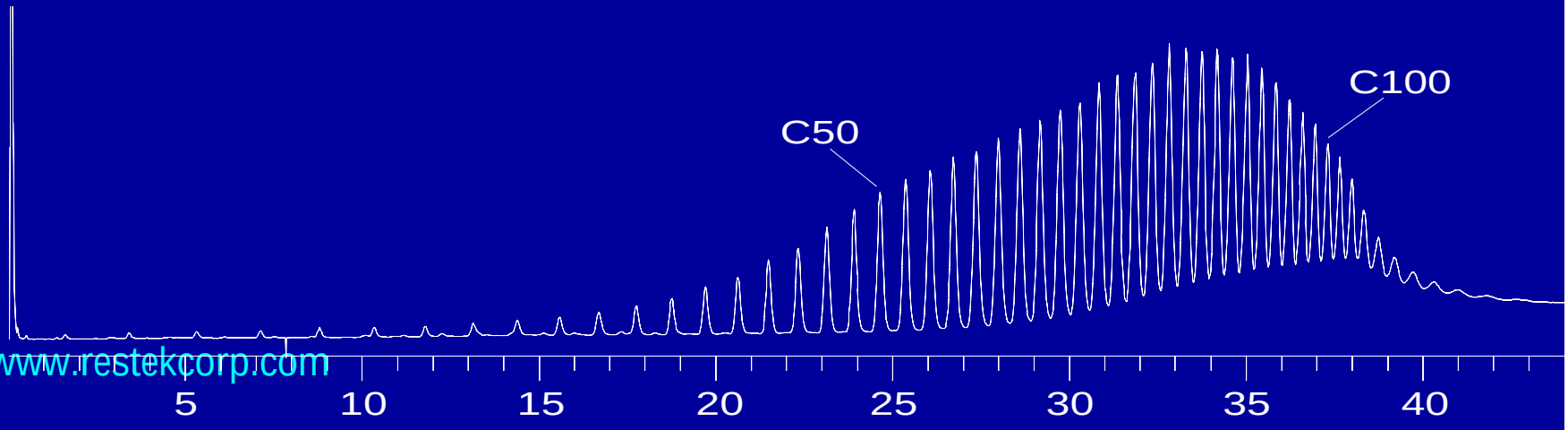
Results

- Column demonstrated consistent performance for 400 analyses at temperatures 30^{o} higher than method specifications.
- Column resolution for C50/C52 did not fall below the specifications of the method until approximately 350 injections.

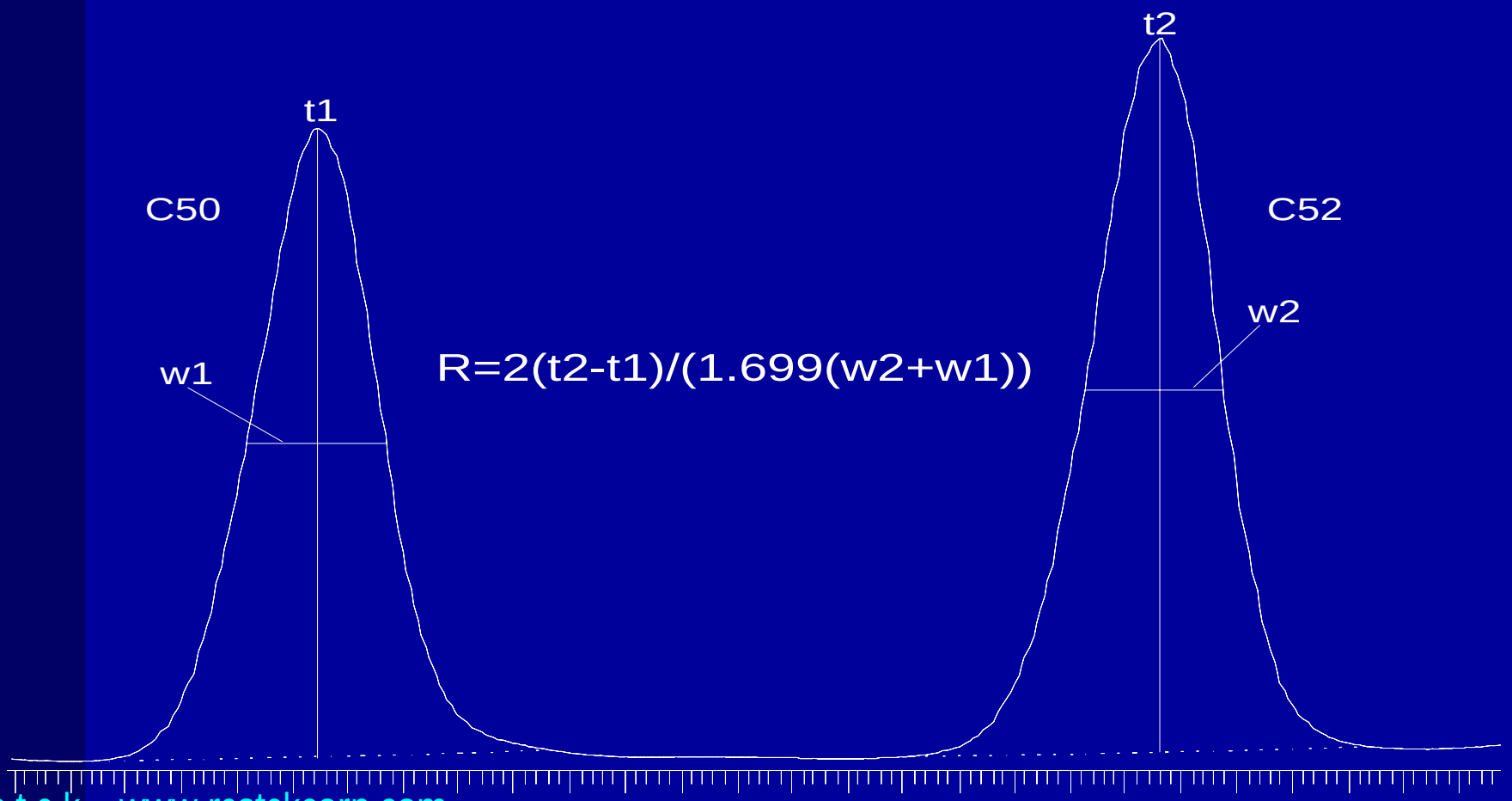
Polywax 1000 – Run #1



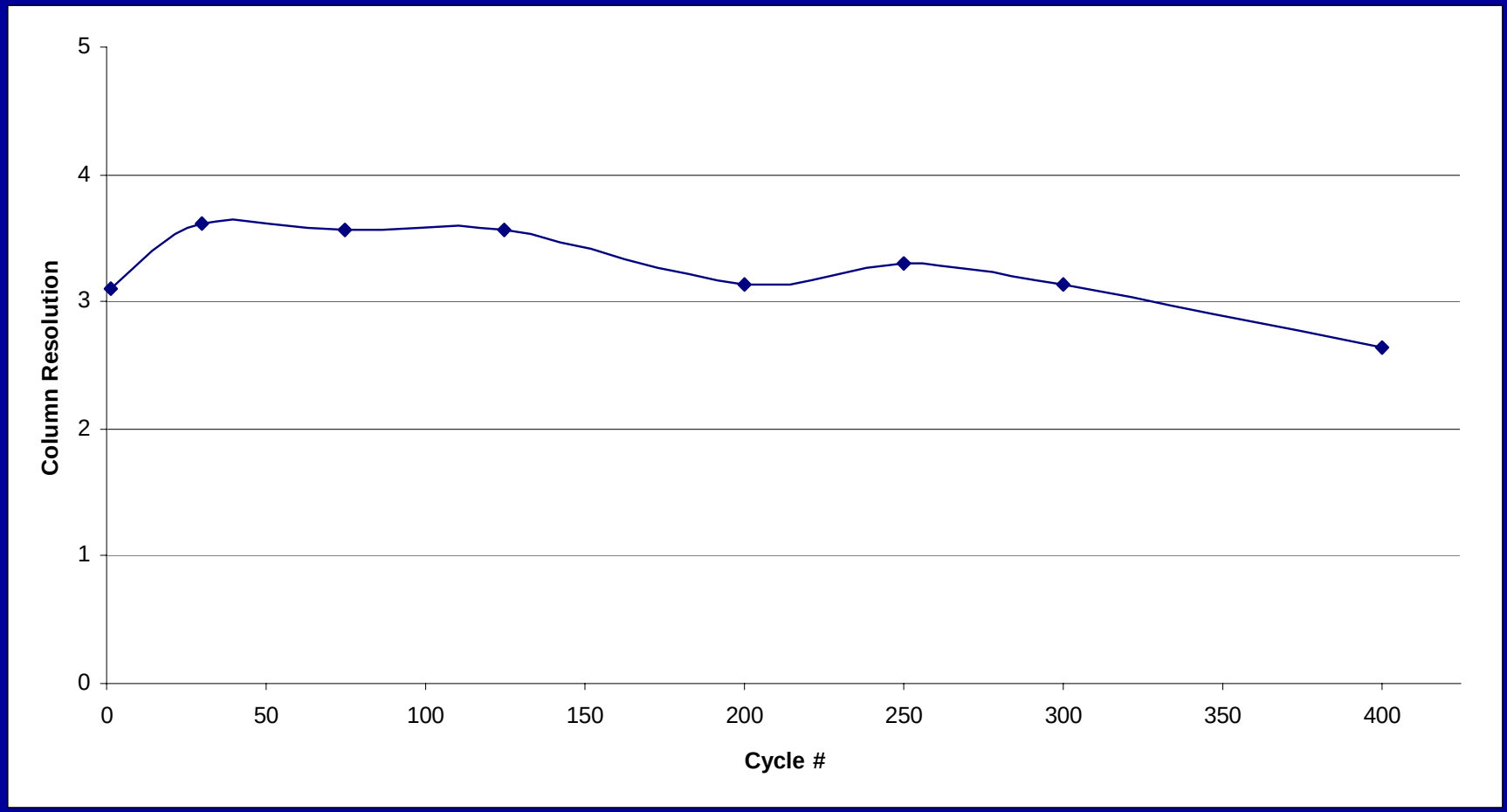
Polywax 1000 – Run #400



C50 / C52 Resolution – Run #1



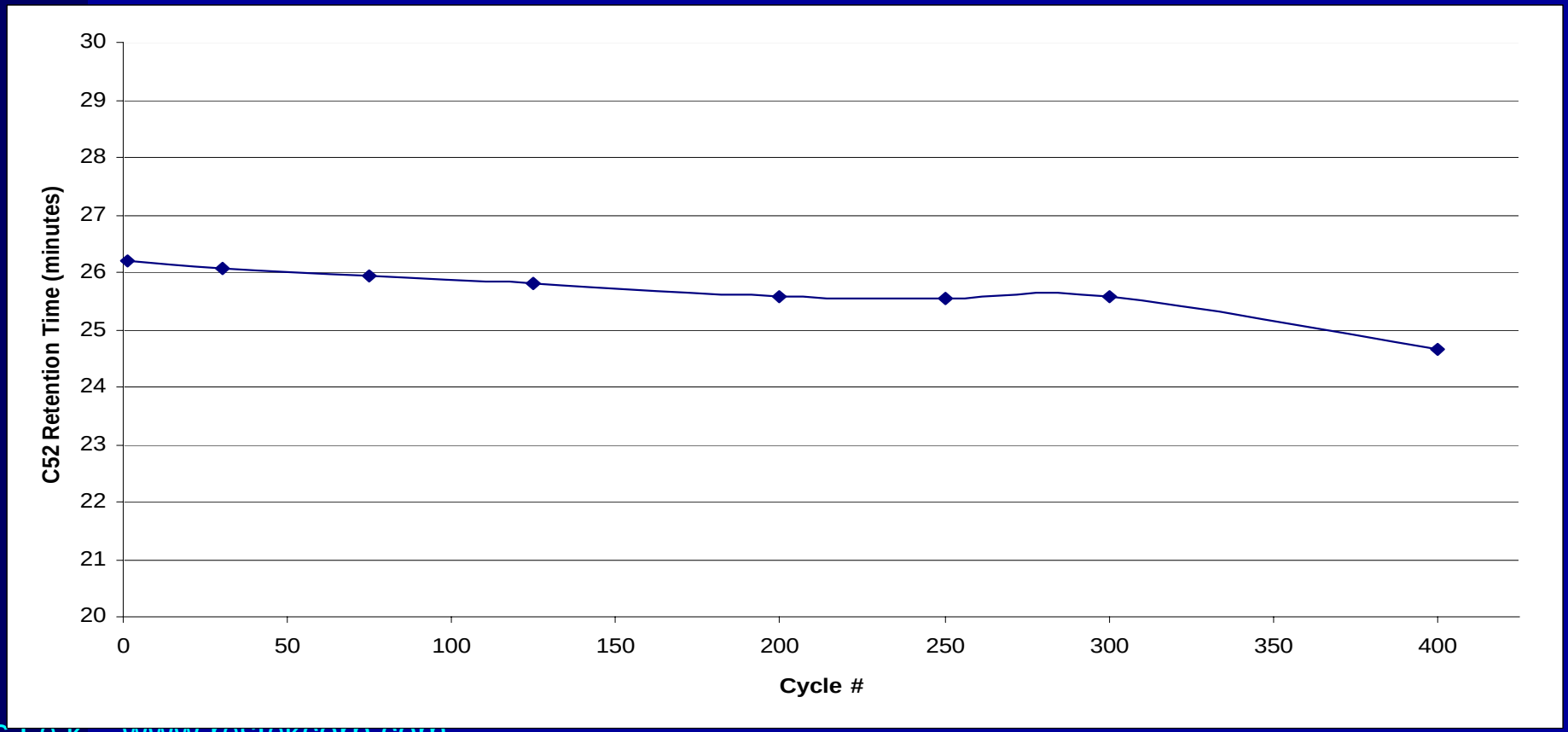
C50 / C52 Resolution



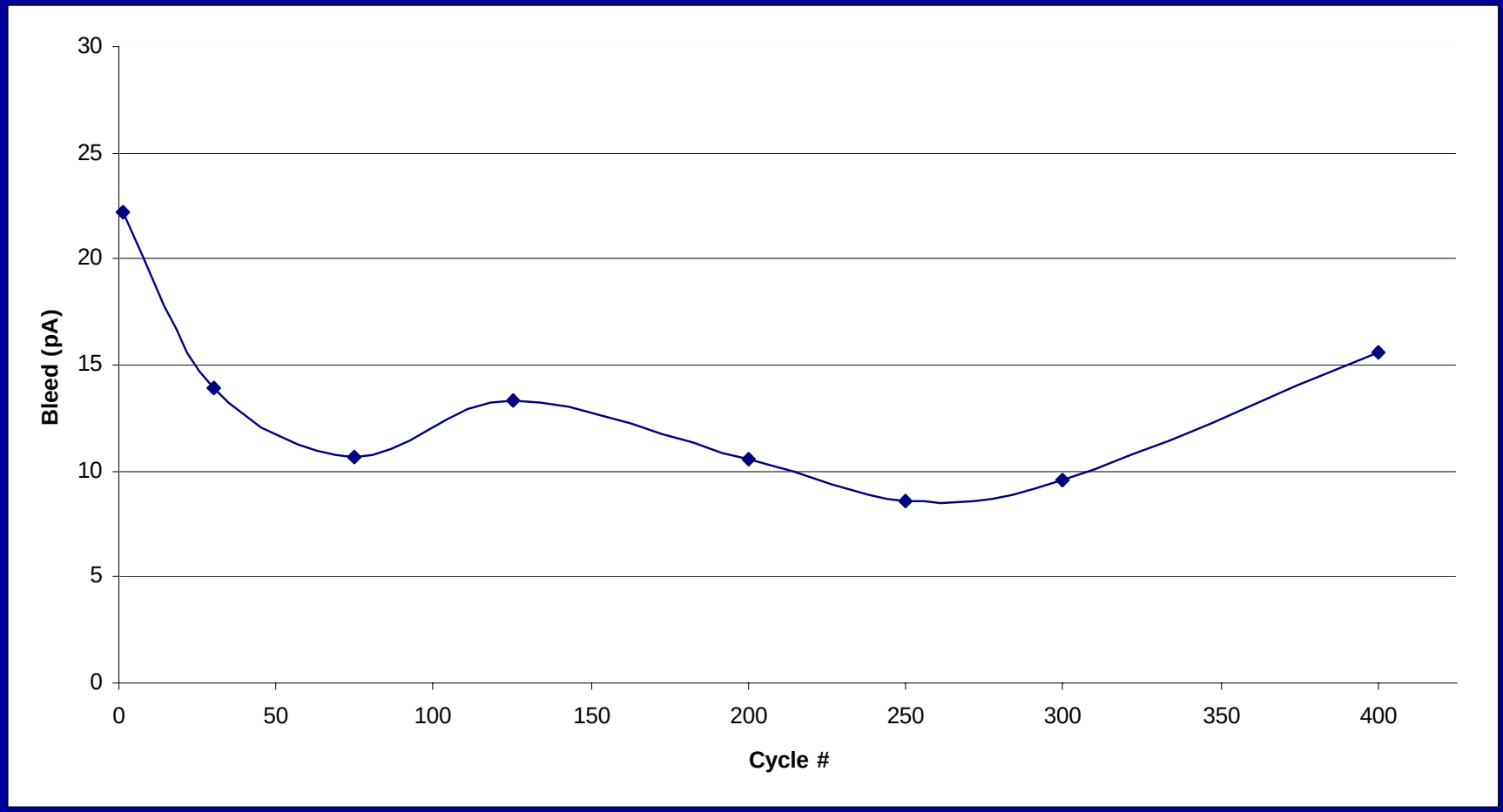
Column Stability

- C52 retention time was monitored to ensure that significant amounts of stationary phase were not being lost due to thermal cycling.
- After 400 injections the retention time of C52 moved approximately 1.4 minutes.
- Column bleed at 430°C was monitored to ensure that the phase had not undergone significant thermal decomposition.
- Bleed values were consistently low and did not interfere with the analysis.

C52 Retention Time Stability



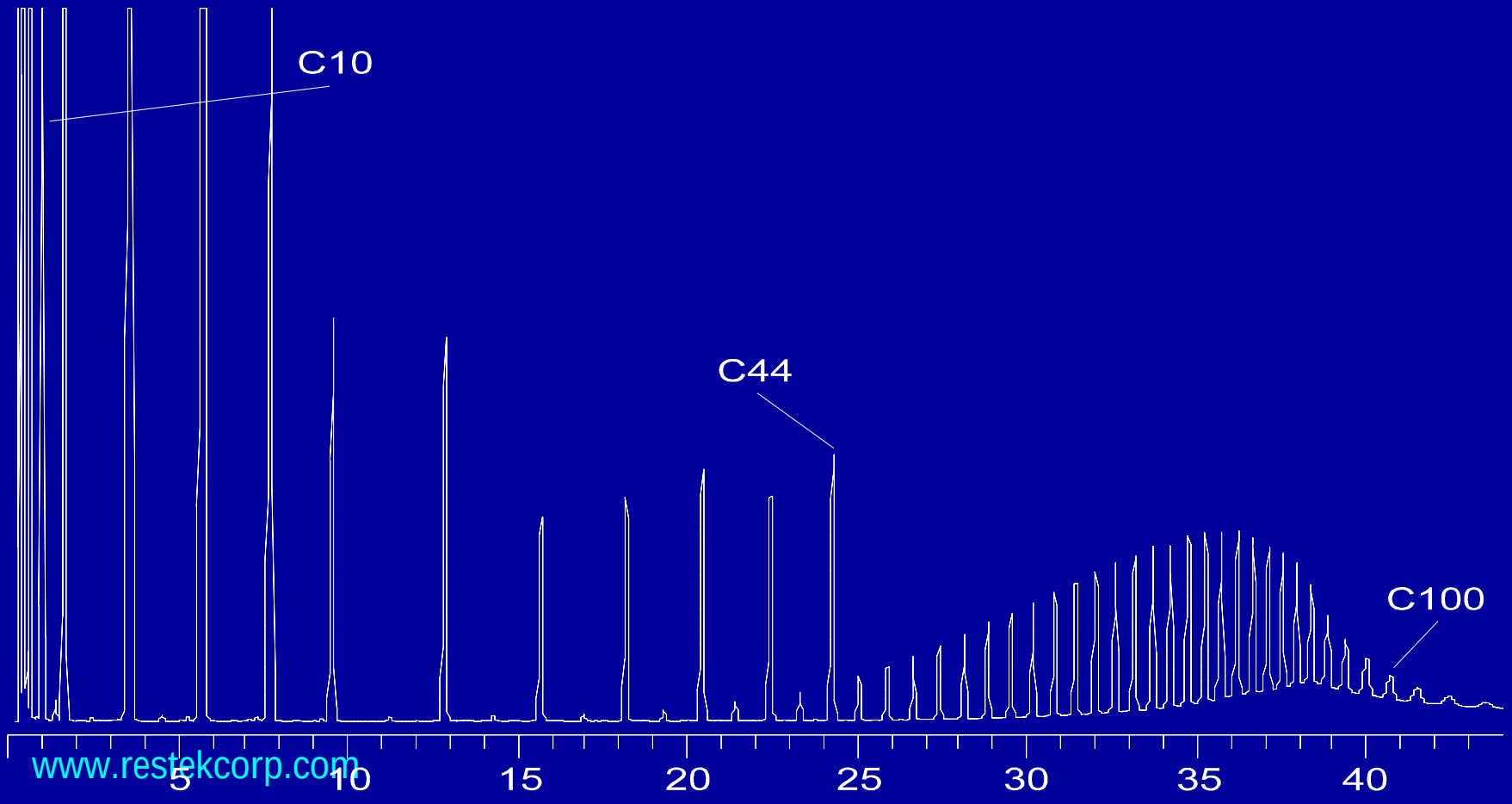
Column Bleed Stability



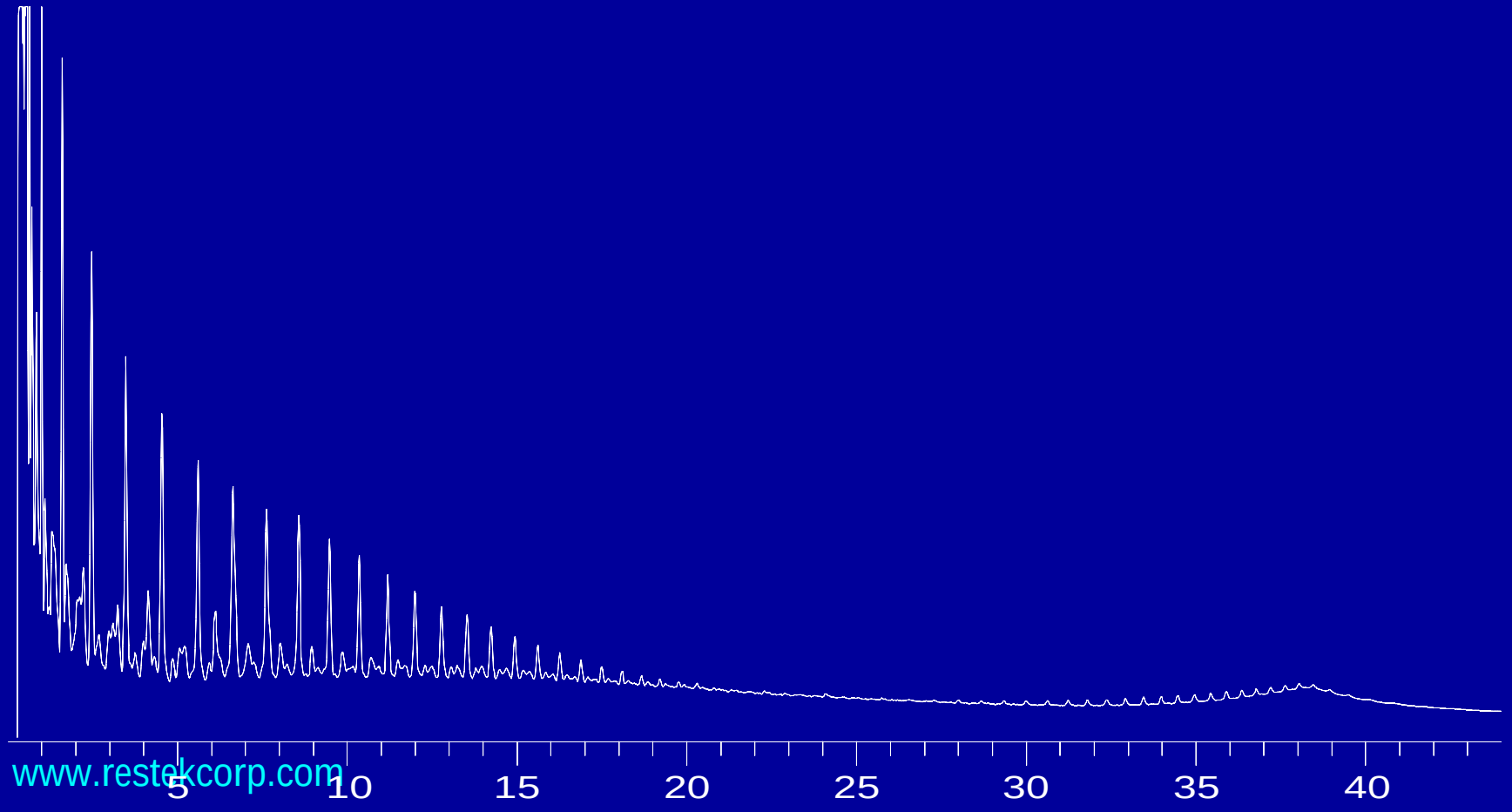
Column Performance after 400 Cycles

- After 400 cycles to 430°C, a Polywax 1000 sample gave a column resolution value of 2.7
- A mixed sample of the D2887 standard and Polywax 1000 was injected to calibrate the column for C10 through C100.
- A diluted sample of Pennsylvania light crude oil was then analyzed and compared to the calibration mixture.
- Adequate resolution of the hydrocarbons in the crude oil sample was obtained even though the column was below the minimum resolution criteria of the method.

C10 to C100 Calibration



Pennsylvania Light Crude Oil



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.