

High temperature Simdist analysis using the new MXT-1 HT Simdist phase

Jaap de Zeeuw and Gary Stidsen
Restek corporation, Bellefonte, PA, USA

 **HROMalytic** +61(0)3 9762 2034
ECHnology Pty Ltd
Australian Distributors; Importers & Manufacturers



Turning Visions into Reality
www.restek.com



Simulated Distillation

Determination of the boiling point distribution of the sample by using the gas chromatographic separation as a “simulation” for the distillation process

Biggest advantage:

Its Fast and Simple

Saves \$ and time



HROMalytic +61(0)3 9762 2034
ECHnology Pty Ltd
Australian Distributors; Importers & Manufacturers

Turning Visions into Reality
www.restek.com

Needs

- High temperature stable phases
 - reproducible boiling point measurement
 - Must be PDMS, for calibration with historical data
 - Constant retention times for reproducible calibration
 - Acceptable life time
- GC capillary columns that can withstand temperatures up to 450 C for longer periods



Turning Visions into Reality
www.restek.com

Challenges

- Fused silica solutions are not stable (column breakage)
- Commercial Metal columns
 - not consistent in retention/separation
 - not consistent in life time (develop bleed)
 - are very expensive



Turning Visions into Reality
www.restek.com

Simulated Distillation: what is this?

- Chromatographic procedure designed to mimic (simulate) the physical process of distilling crude oils and petroleum products
- Establishes a correlation between retention time and boiling point
- Results are used to control refining operations
- Results are also an indicator of the range of products that can be produce from a starting material and their potential yield



Turning Visions into Reality
www.restek.com

Why High Temperature Distillation?



Improved characterization of crude leads to better control of final product

- *Increased profit margin*

Increased gas oil yield

- *Increased profit margin*

Simulated Distillation: ASTM methods

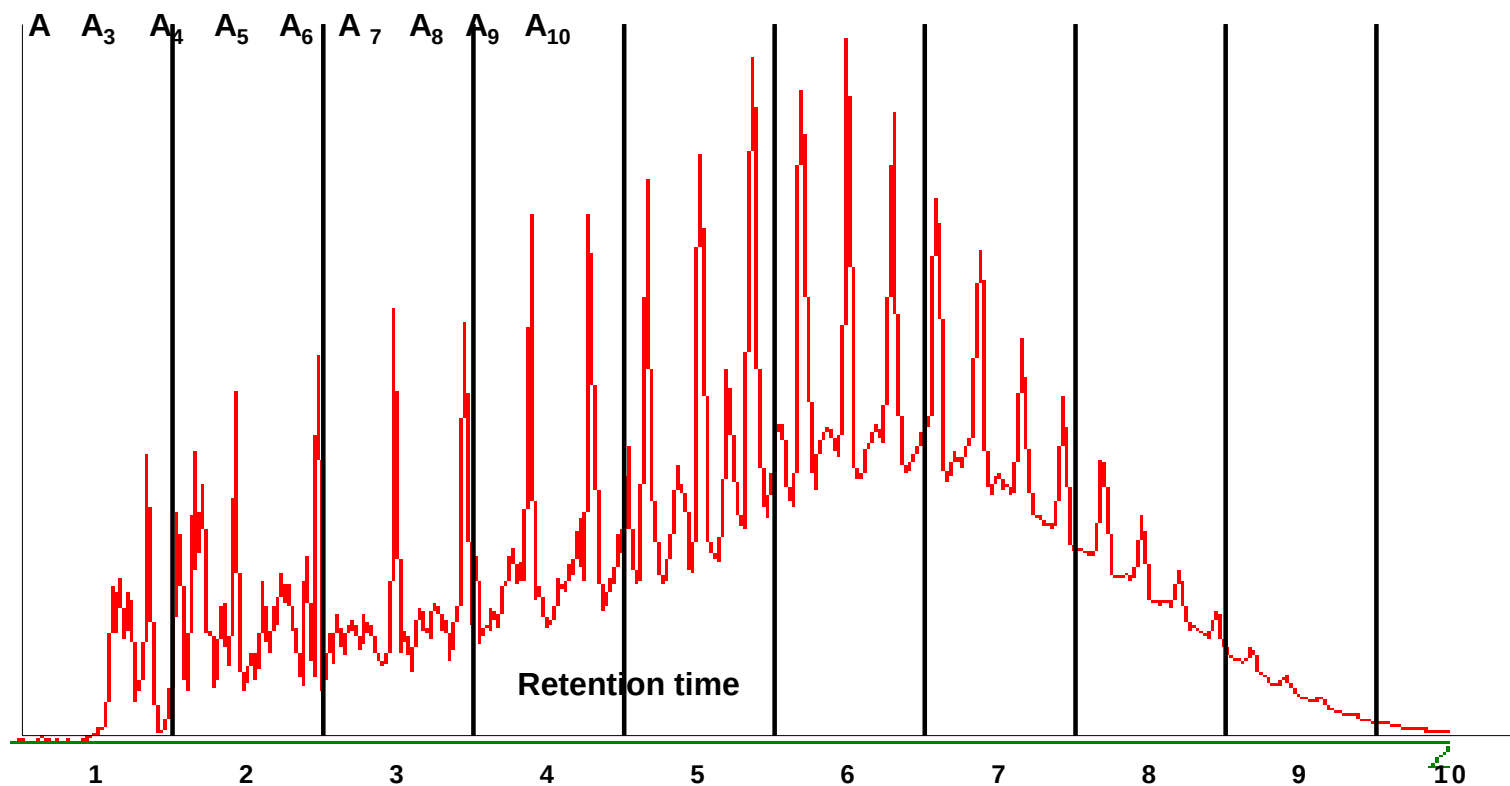
Methods can be classified by Boiling Point and Hydrocarbon ranges

ASTM nr	Range	Column	Injection
D2887	C5 - C44	0.88 - 3 μ m PDMS 10/0.53	neat
D7213 (2887-ext)	C5 - C60	0.15-1.2 μ m PDMS	diluted
D3710	gasoline upto C14	2.65 μ m PDMS 10/0.53	neat
D5307	crude upto C42	0.2 μ m PDMS, 5/0.53	diluted
D6352	C10- C90	0.2 μ m PDMS, 5/0.53	diluted
D7500	C7 - C110	0.2 μ m PDMS, 5/0.53	diluted
D7169	C5 -C100	0.2 μ m PDMS, 5/0.53	diluted



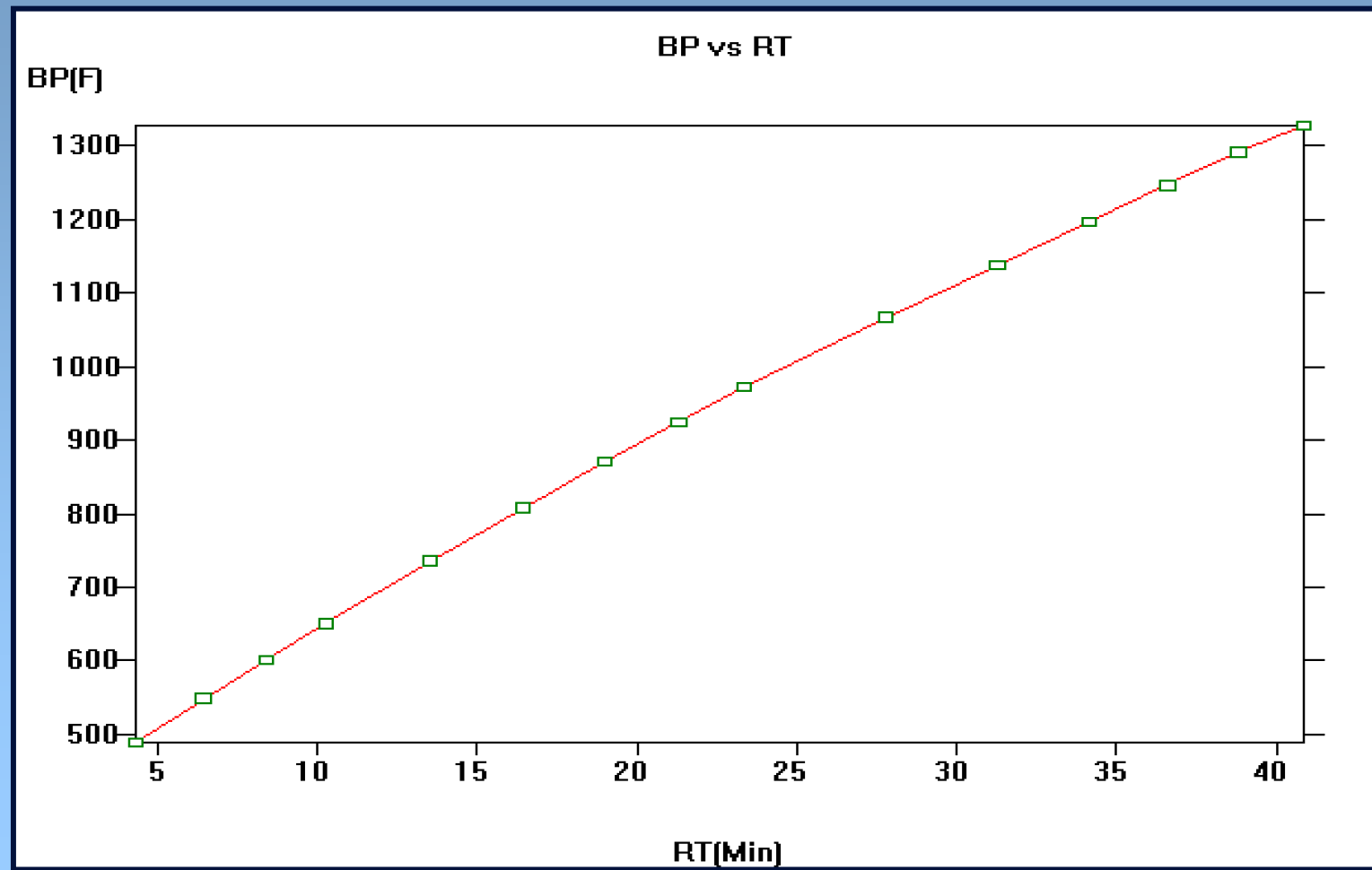
Turning Visions into Reality
www.restek.com

Simulated Distillation



The chromatogram of the sample is divided into time slices
The software determines the area count for each slice

Retention Time vs Boiling Point



Needs for accurate Simulated Distillation

- High temperature stable columns
- Low Bleed phases
- Sufficient loadability
- Reproducible quantification
 - Sample introduction
 - Integration



Turning Visions into Reality
www.restek.com

Simdist with fused silica: Big Problem area..

FS Standard fused silica column polyimide coated, type Inferno



Polyimide outside coating
seriously damaged

This will happen with ALL
fused silica columns

Boiling Range Distribution of Heavy Petroleum Products

Need to elute hydrocarbons from C4 up to C100 - C120

Short columns	5 m
High Flow rates	0.53mm
Stable at T >>400C	MXT
Low bleed	Siltek deactivation / Rxi technology
High efficiency	Smooth, defined metal surface



HROMalytic +61(0)3 9762 2034
ECHnology Pty Ltd
Australian Distributors; Importers & Manufacturers

Turning Visions into Reality
www.restek.com

Optimize strength/robustness of capillary
Application of MXT Metal capillary tubing



Turning Visions into Reality
www.restek.com

MXT tubing: extreme strong

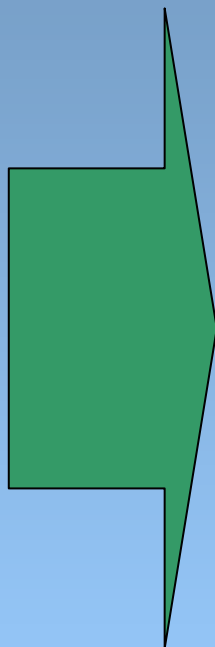


- Virtually unbreakable, self straightening
- Stable up to 450C
- Can be bended / coiled on small radius
- Stabilizes the stationary phase
- winded on standard cage
- special cutting tools available

For Simdist a MUST to use 0.53mm

MXT columns provide reliability: No column breakage possible!

New, easy accessible column cage



MXT is nicely winded on a cage:
Easy to install, handle and unwind..



HROMalytic +61(0)3 9762 2034
ECHnology Pty Ltd
Australian Distributors; Importers & Manufacturers

Turning Visions into Reality
www.restek.com

New columns for Simdist

Use Ultra Smooth MXT tubing, Siltek and Rxi basics, generating:

- Lowest bleed columns
- Highest efficiency

Outperforms both Agilent and Varian



Turning Visions into Reality
www.restek.com

For Simulated Distillation, we have to use pure 100% dimethyl siloxane: Stabilizing groups cannot be permitted.

- 100% PDMS provides best simulation of BP-range
- Results can be compared with “historical” data

PDMS can be stabilized by:

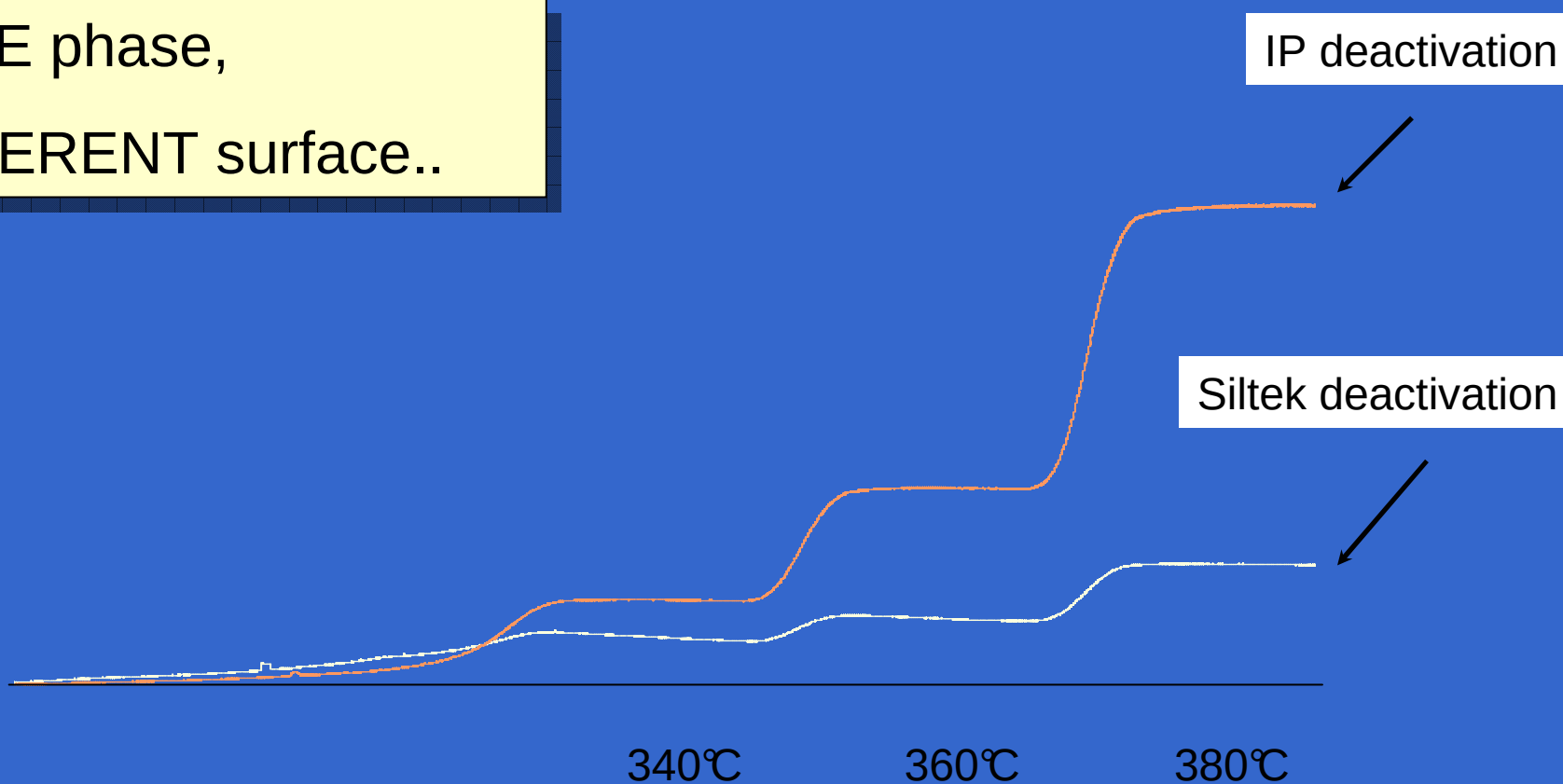
- Ladder technology (systematical cross-bonds between polymer chains)
- Surface deactivation



Turning Visions into Reality
www.restek.com

Bleed Comparison

SAME phase,
DIFFERENT surface..



Siltek deactivated surfaces STABILIZE the stationary phase;

- Lower bleed
- Higher T_{max}
- Reproducible retention times (less calibrations)
- Longer column life time

This is all IDEAL for SimDist applications..



HROMalytic +61(0)3 9762 2034
ECHnology Pty Ltd
Australian Distributors; Importers & Manufacturers

Turning Visions into Reality
www.restek.com

Advantages of Stabilized GC Phases for Simdist applications

- **Reduced noise operating high temperature FID systems**
 - improved determination higher hydrocarbons
 - Better end-point determination
- **Reproducible retention times/ calibration as the phase will not “bleed” out of the column..**
- **Longer column life time**
- **Short stabilization times**
- **Reduced detector contamination**

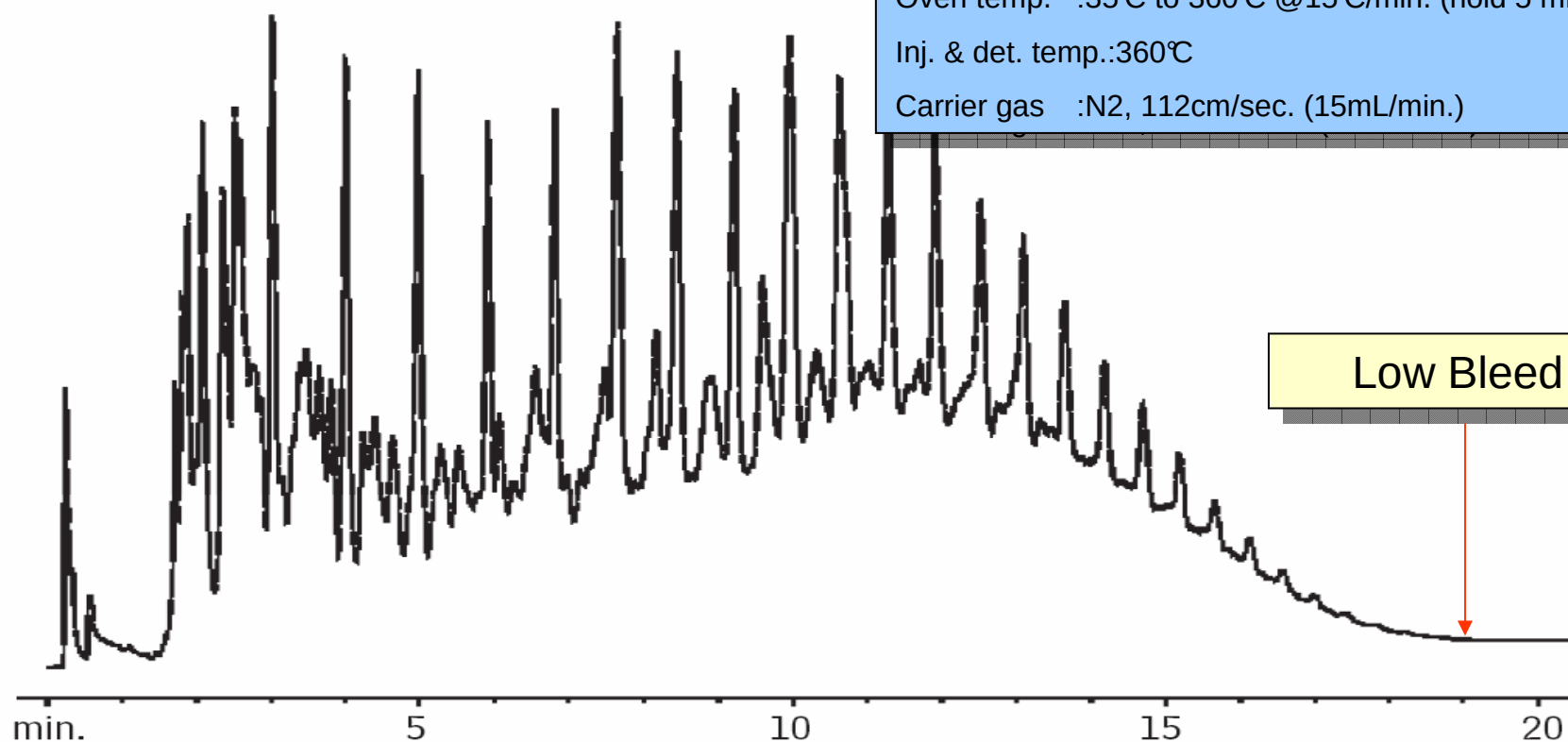


HROMalytic +61(0)3 9762 2034
ECHnology Pty Ltd
Australian Distributors; Importers & Manufacturers

Turning Visions into Reality
www.restek.com

D-2887 Simdis

Column :10m, 0.53mm ID, 2.65 μ m Rtx®-2887
Injection :Direct injection, 1.0 μ L of a 0.1 to 0.01 wt % hydrocarbon standard in carbon disulfide.
Oven temp. :35°C to 360°C @15°C/min. (hold 5 min.)
Inj. & det. temp.:360°C
Carrier gas :N2, 112cm/sec. (15mL/min.)



GC_PC00227



HROMalytic +61(0)3 9762 2034
ECHnology Pty Ltd
Australian Distributors; Importers & Manufacturers

Turning Visions into Reality
www.restek.com

ASTM spec

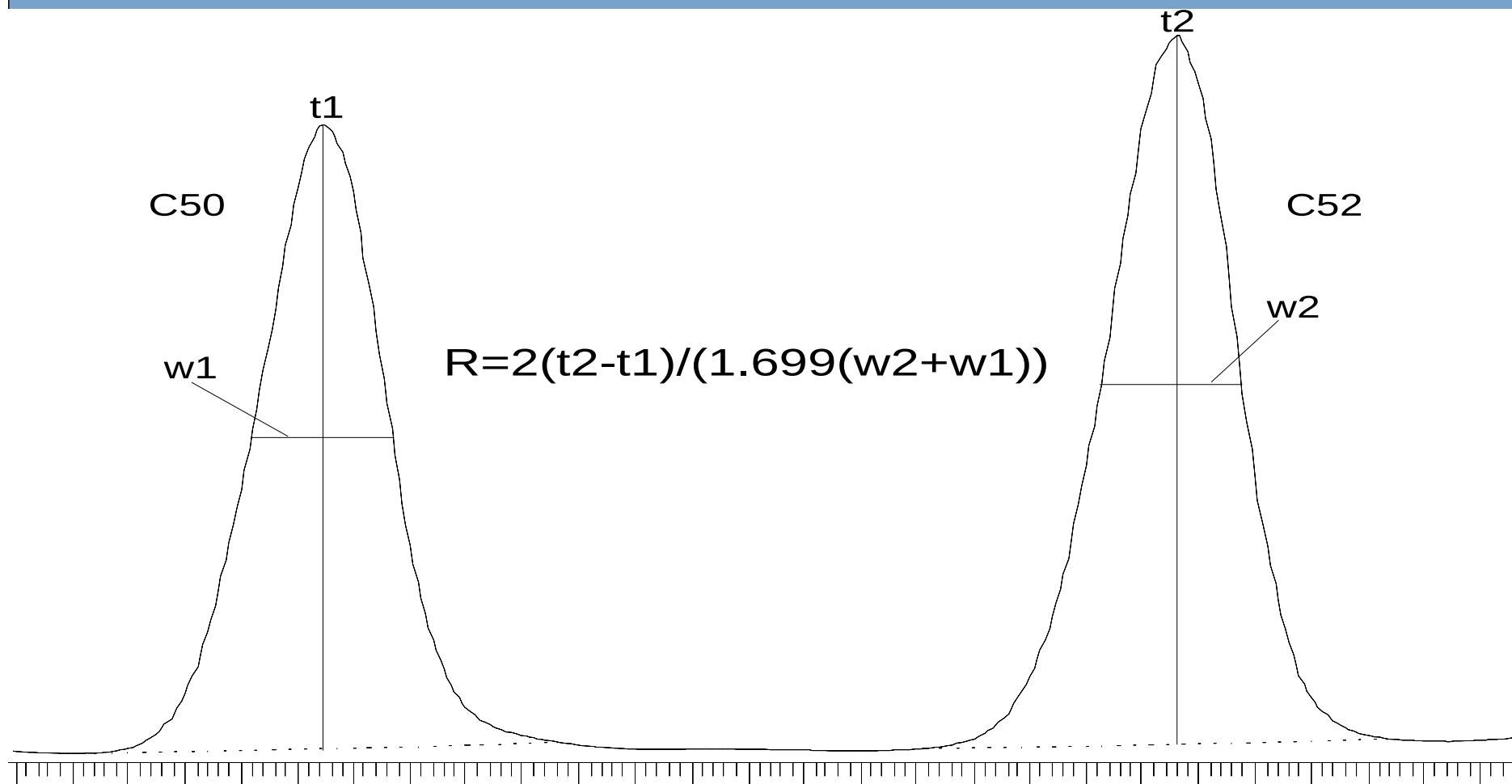
In order to be approved for ASTM D86 and 6352, 7169 and 7500:

Resolution between C50 and C52 > 2.0, running under ASTM conditions



Turning Visions into Reality
www.restek.com

C50 / C52 Resolution

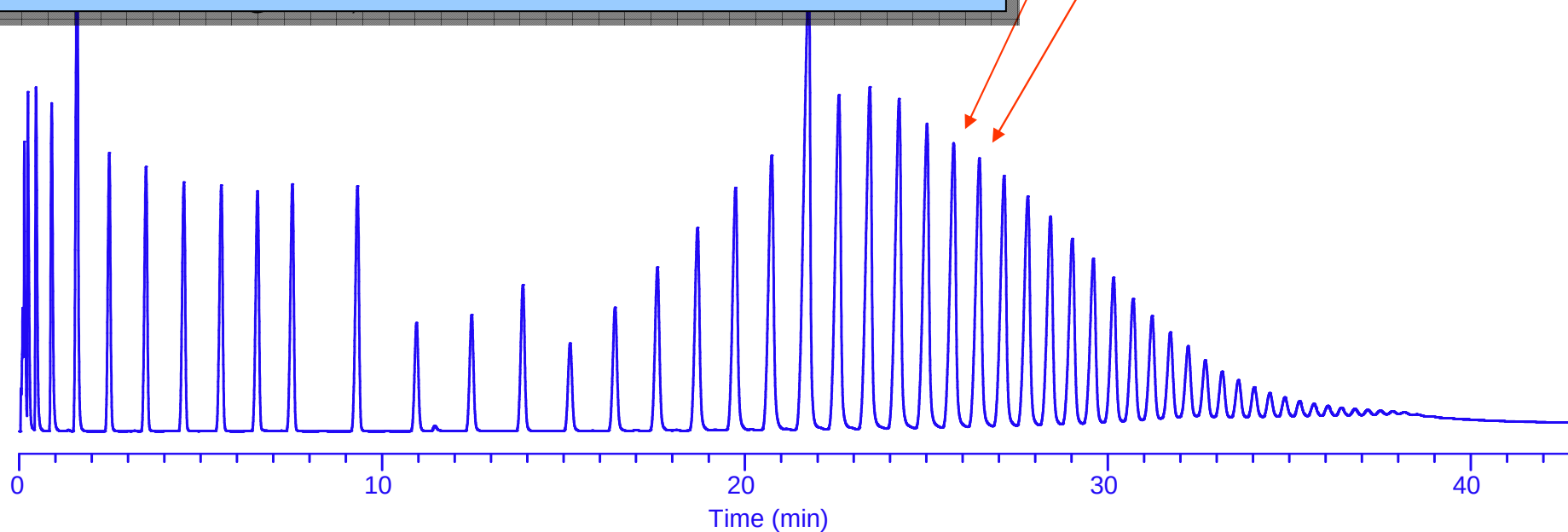


Resolution new MXT-1HT-Simdis

5m x 0.53 x 0.2 μ m

Column : MXT®-1HT Sim Dist, 5m, 0.53mm ID, 0.20 μ m
Instrument: : Shimadzu 2010
Sample : C5-C100, 1% in carbon disulfide;
Injection : 1 μ L via PTV; Inj. temp.: 53°C to 430°C @ 10°C/min. (hold 5 min.);
Carrier gas : He, constant flow; Flow rate: 18mL/min.;
Oven temp. : 50°C to 430°C @ 10°C/min. (hold 5 min.) ;
Det. : FID @ 430°C;

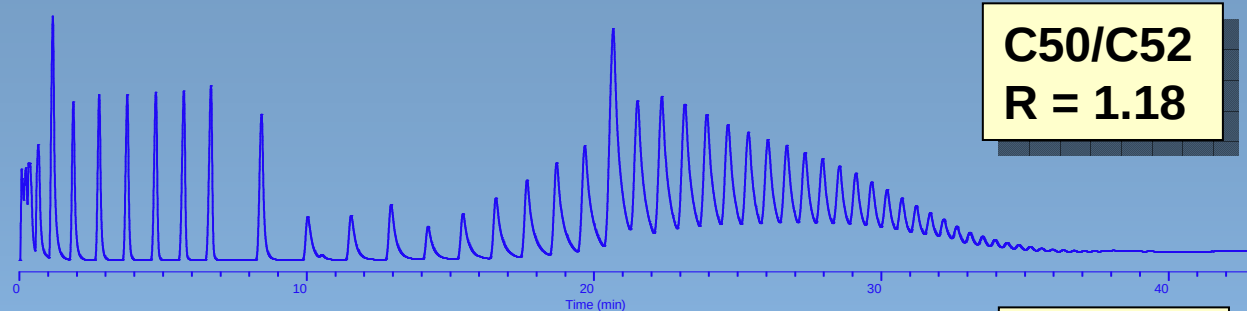
C50/C52
R = 2.45



HROMalytic +61(0)3 9762 2034
ECHnology Pty Ltd
Australian Distributors; Importers & Manufacturers

Turning Visions into Reality
www.restek.com

Comparison of Resolution values

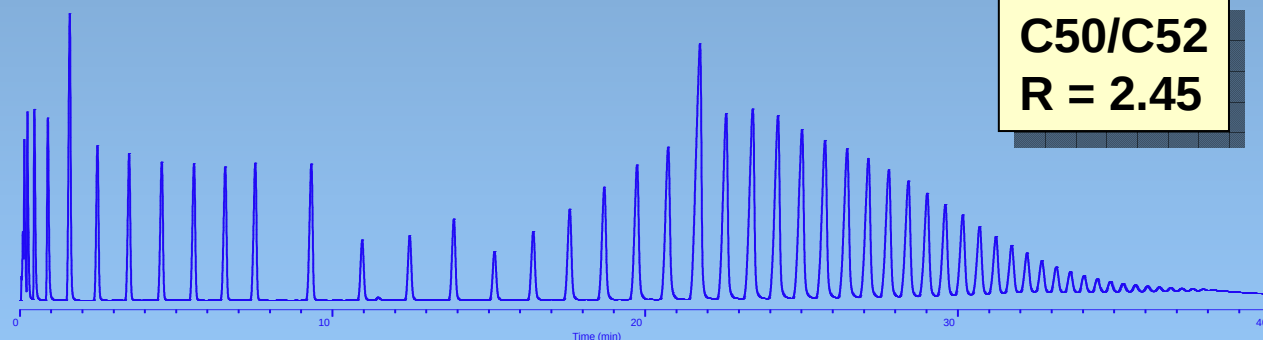


C50/C52
R = 1.18

Varian

5m x 0.53 x 0.17µm

NOT OK !

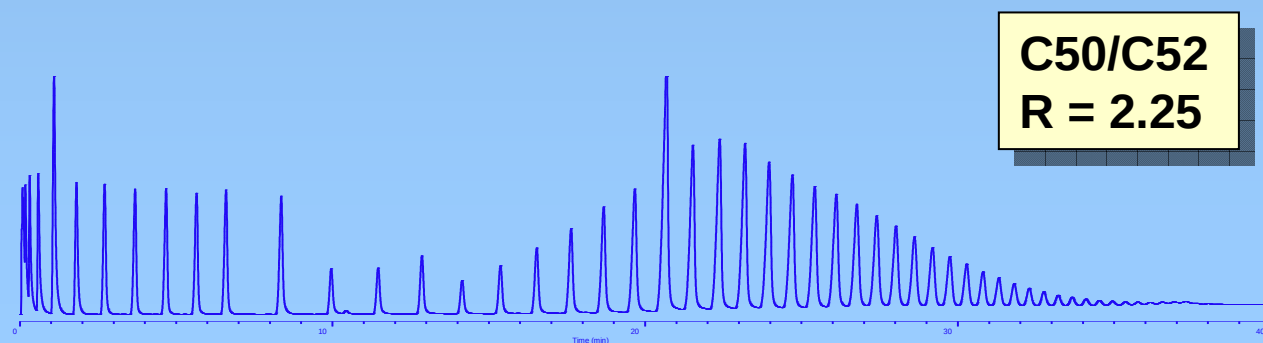


C50/C52
R = 2.45

Restek

5m x 0.53 x 0.2µm

OK



C50/C52
R = 2.25

J&W / Agilent

5m x 0.53 x 0.15µm

OK



HROMalytic +61(0)3 9762 2034
ECHnology Pty Ltd
Australian Distributors; Importers & Manufacturers

Turning Visions into Reality
www.restek.com

Resolution values

The height of this value means for the Restek MXT-1 HT Simdis:

- The surface is homogeneous and very smooth
- Smooth distribution of the PDMS phase over column length

Varian and Agilent have lower efficiencies, which means that columns do not standard fulfill ASTM requirements..
..many customers do NOT know or realize that..



Turning Visions into Reality
www.restek.com

Column stability / Life time / Nr. of analysis per column

Column life time in Simdist application usually is indirect proportional with the level of the bleeding

The LOWER the bleed, The LONGER the life time

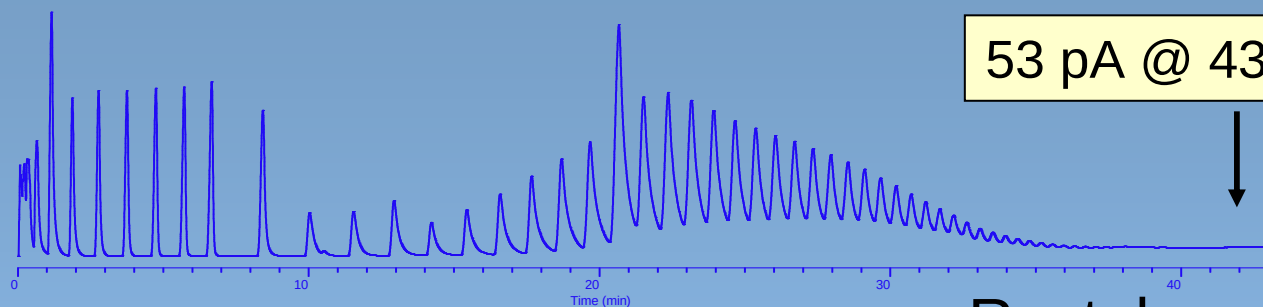


Turning Visions into Reality
www.restek.com

Comparison of Bleed values

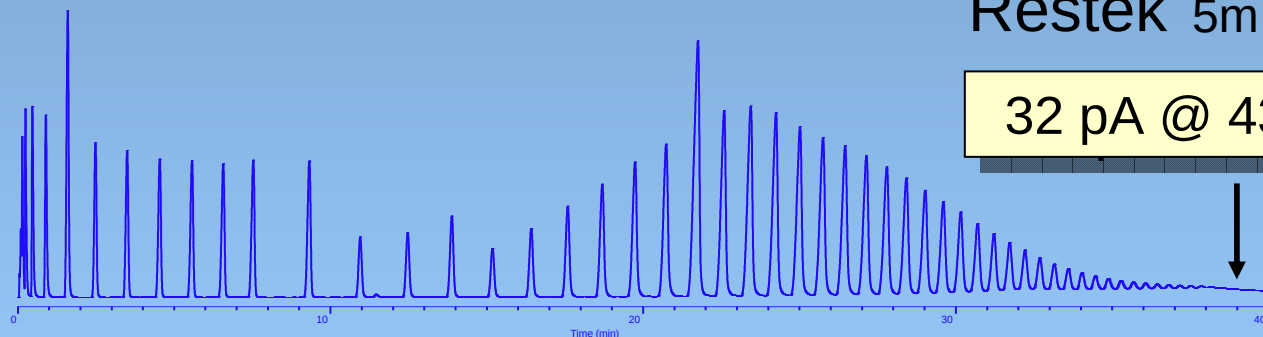
Varian 5m x 0.53mm x 0.17 μ m

53 pA @ 430 °C



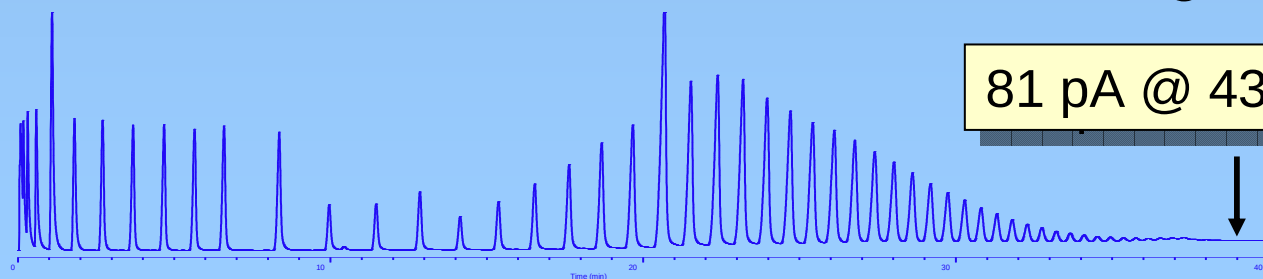
Restek 5m x 0.53mm x 0.2 μ m

32 pA @ 430 °C



J&W / Agilent 5m x 0.53mm x 0.15 μ m

81 pA @ 430 °C



Column life time

Column life time in Simdist application usually is indirect proportional with the level of the bleeding

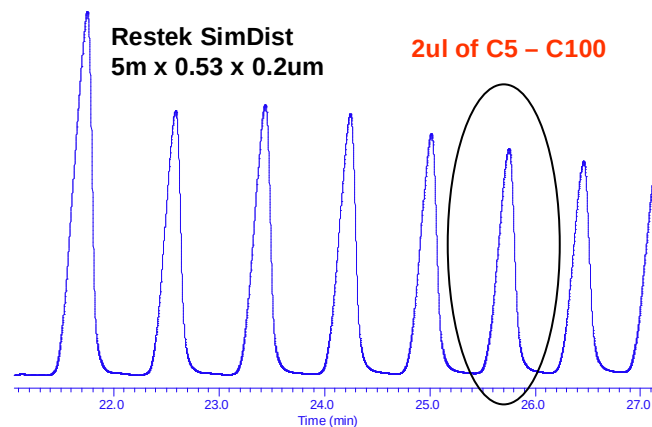
The LOWER the bleed, The LONGER the life time

If bleed is 2 x higher, the column loses its film 2 x faster resulting in..

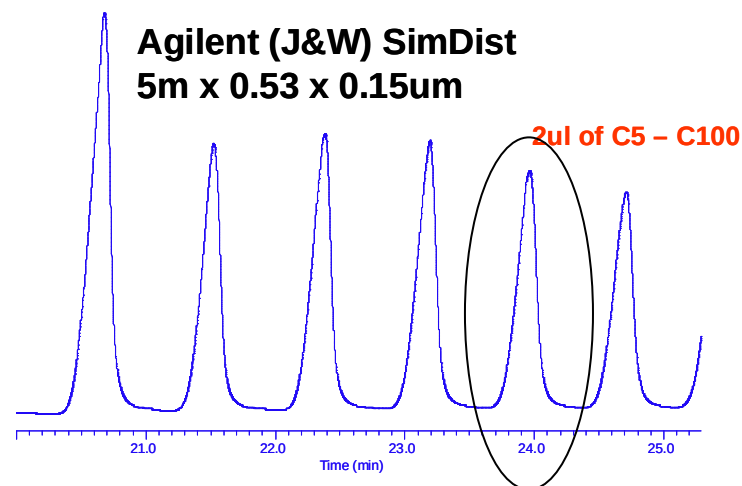
- faster decrease of retention times
- need more calibrations
- Needs 2x more columns for same number of analysis

Peak Skewness / symmetry of C50

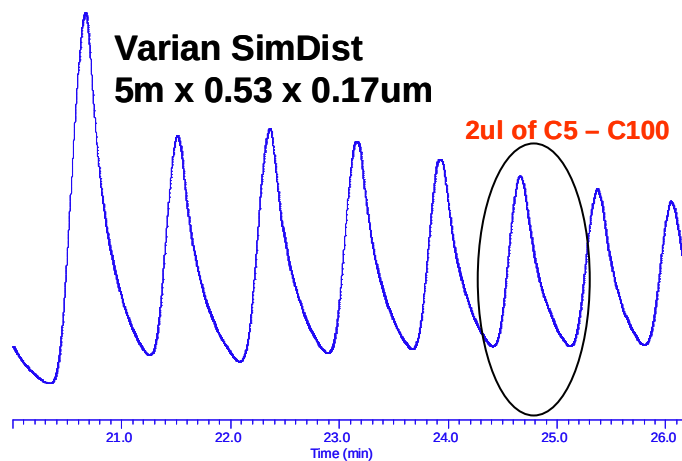
C40 marker



C40 marker



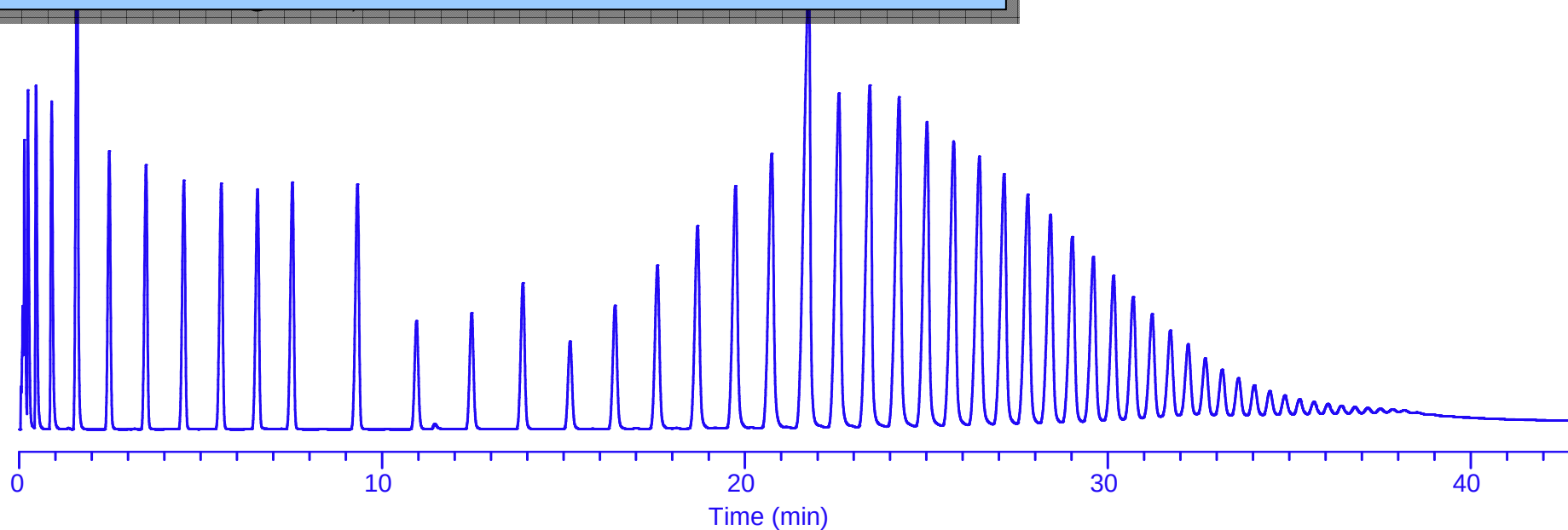
C40 marker



Note that the Restek column has
thickest film AND lowest bleed;
Overloading effects will be the smallest

Polywax 655 on the new MXT-1HT-Simdis

Column : MXT®-1HT Sim Dist, 5m, 0.53mm ID, 0.20µm
Instrument: : Shimadzu 2010
Sample : C5-C100, 1% in carbon disulfide;
Injection : 1µL via PTV; Inj. temp.: 53°C to 430°C @ 10°C/min. (hold 5 min.);
Carrier gas : He, constant flow; Flow rate: 18mL/min.;
Oven temp. : 50°C to 430°C @ 10°C/min. (hold 5 min.) ;
Det. : FID @ 430°C;

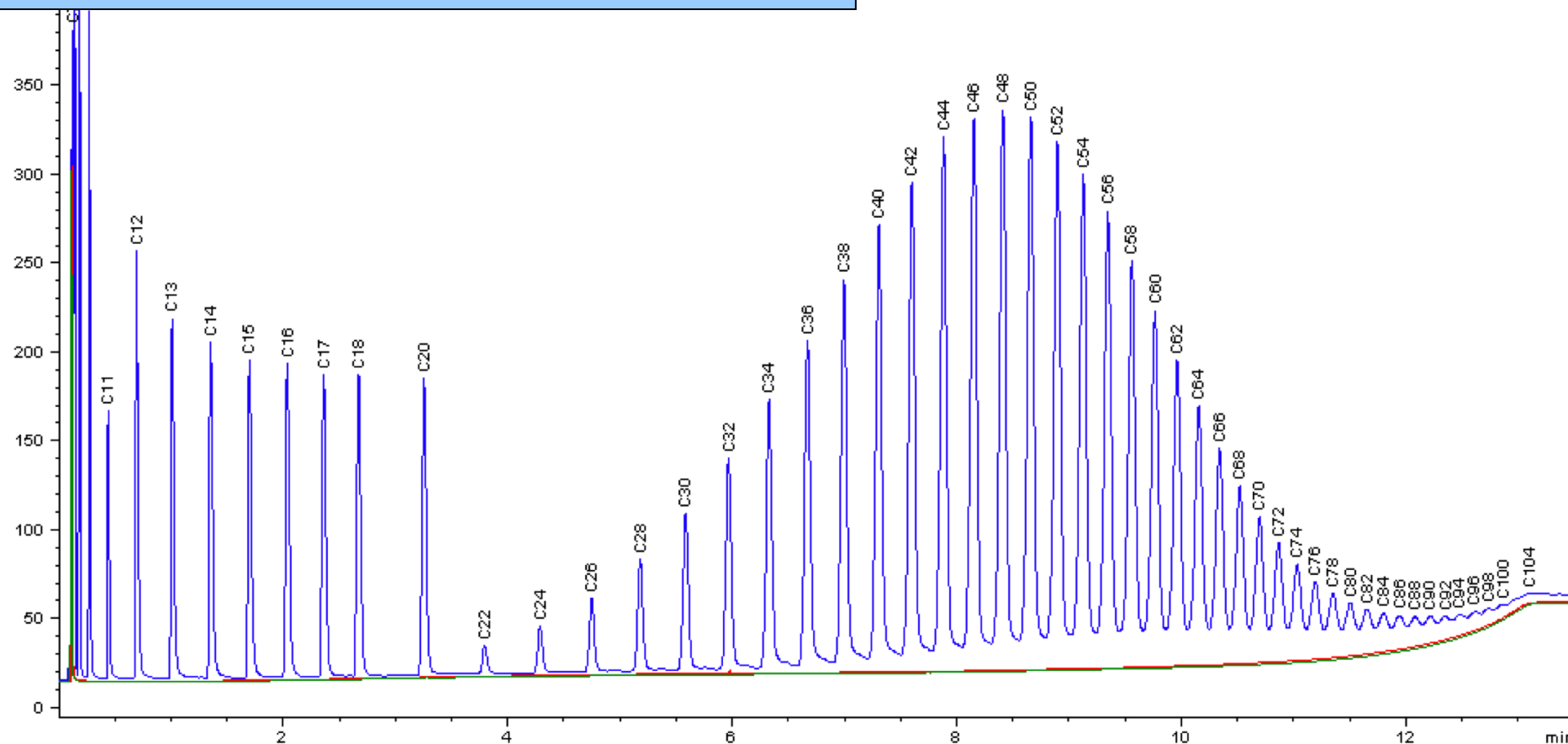


HROMalytic +61(0)3 9762 2034
ECHnology Pty Ltd
Australian Distributors; Importers & Manufacturers

Turning Visions into Reality
www.restek.com

Column Performance-ASTM D7169 (FAST GC)

Column : 5m .0.53mm 0.1u film HT-Simdist
Oven : 40C, +30%min => 430; 1 min



HROMalytic +61(0)3 9762 2034
ECHnology Pty Ltd
Australian Distributors; Importers & Manufacturers

Turning Visions into Reality
www.restek.com

Performance-ASTM D7169

Customer feedback on Beta testing, done by
Joaquin Lubkowitz, Separation systems.

Authority in petro – analysis field and ASTM

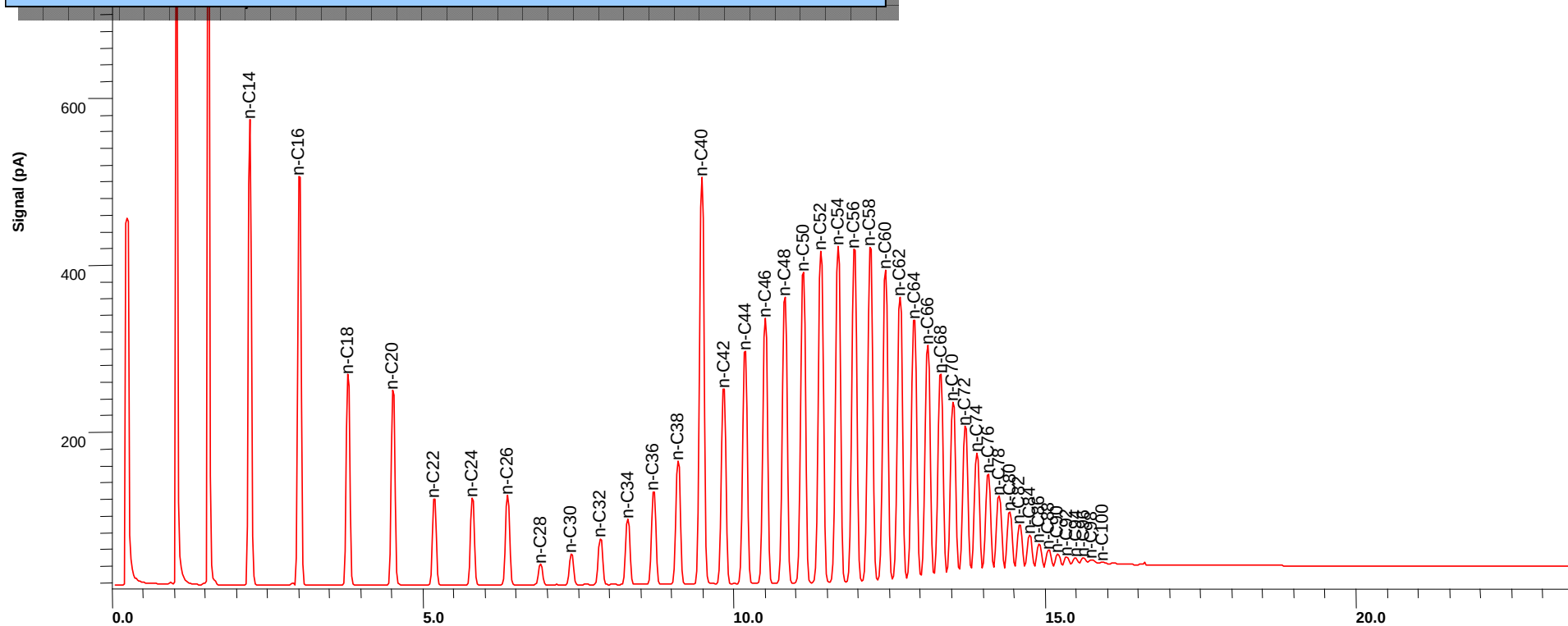


HROMalytic +61(0)3 9762 2034
ECHnology Pty Ltd
Australian Distributors; Importers & Manufacturers

Turning Visions into Reality
www.restek.com

C10-C100 calibration standard

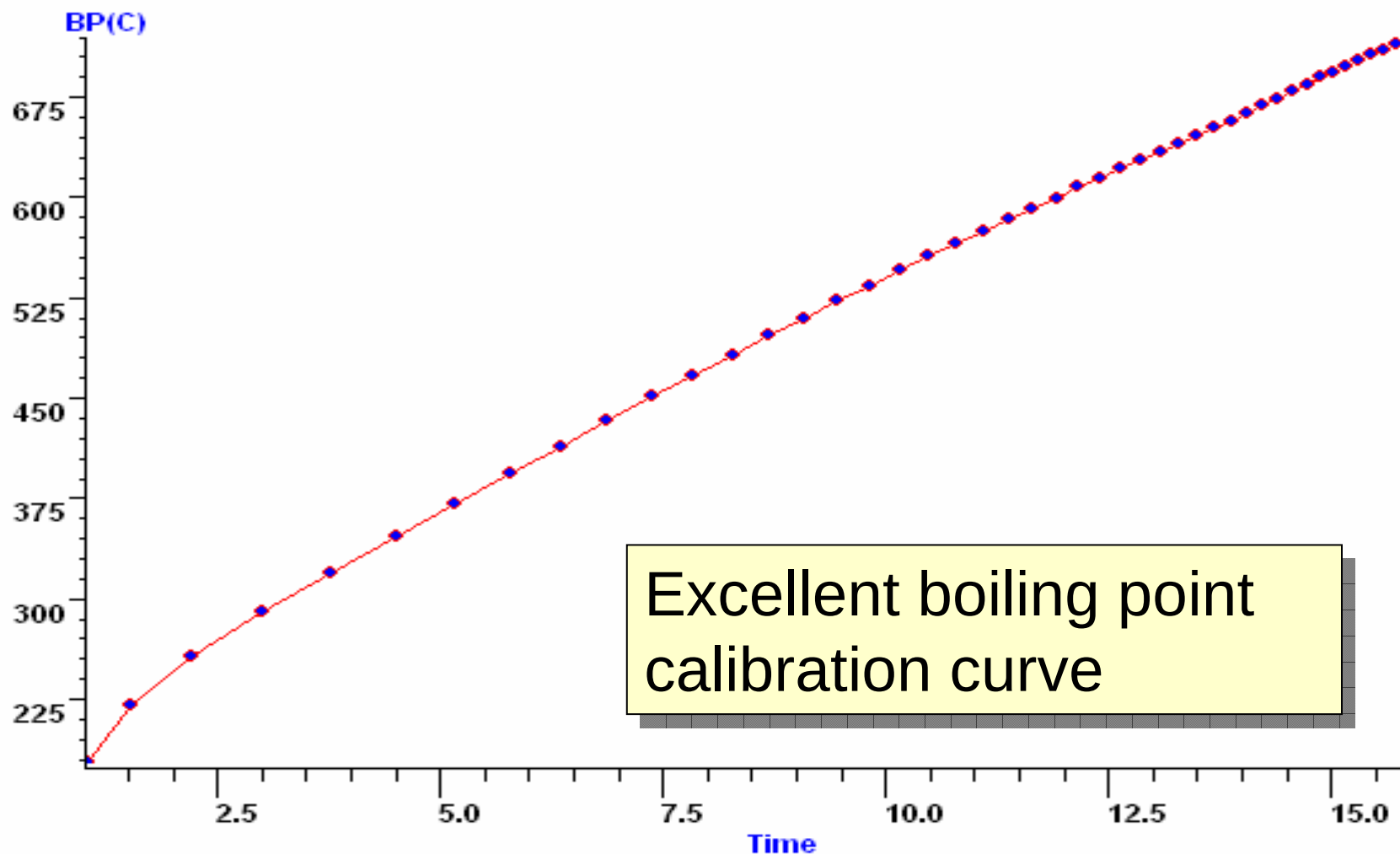
Column : 5m x 0.53mm MXT-1-HT Simdis
Inlet : Sep. systems 40C TO 430C AT 100°C/min
OVEN : 40°C TO 430°C 25C/MIN
Carrier : He, 20 mL/min

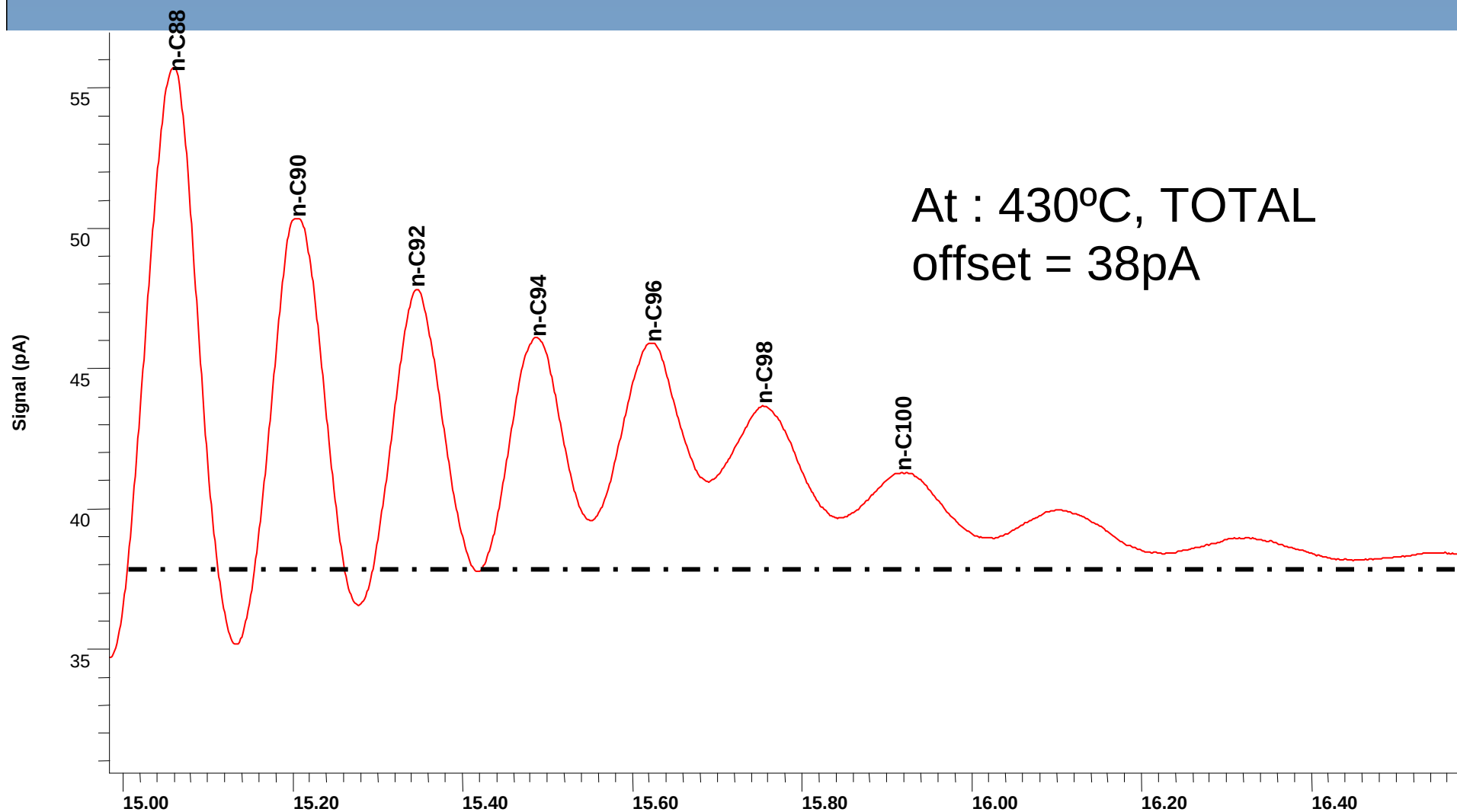


HROMalytic +61(0)3 9762 2034
ECHnology Pty Ltd
Australian Distributors; Importers & Manufacturers

Turning Visions into Reality
www.restek.com

Calibration curve C10-C100

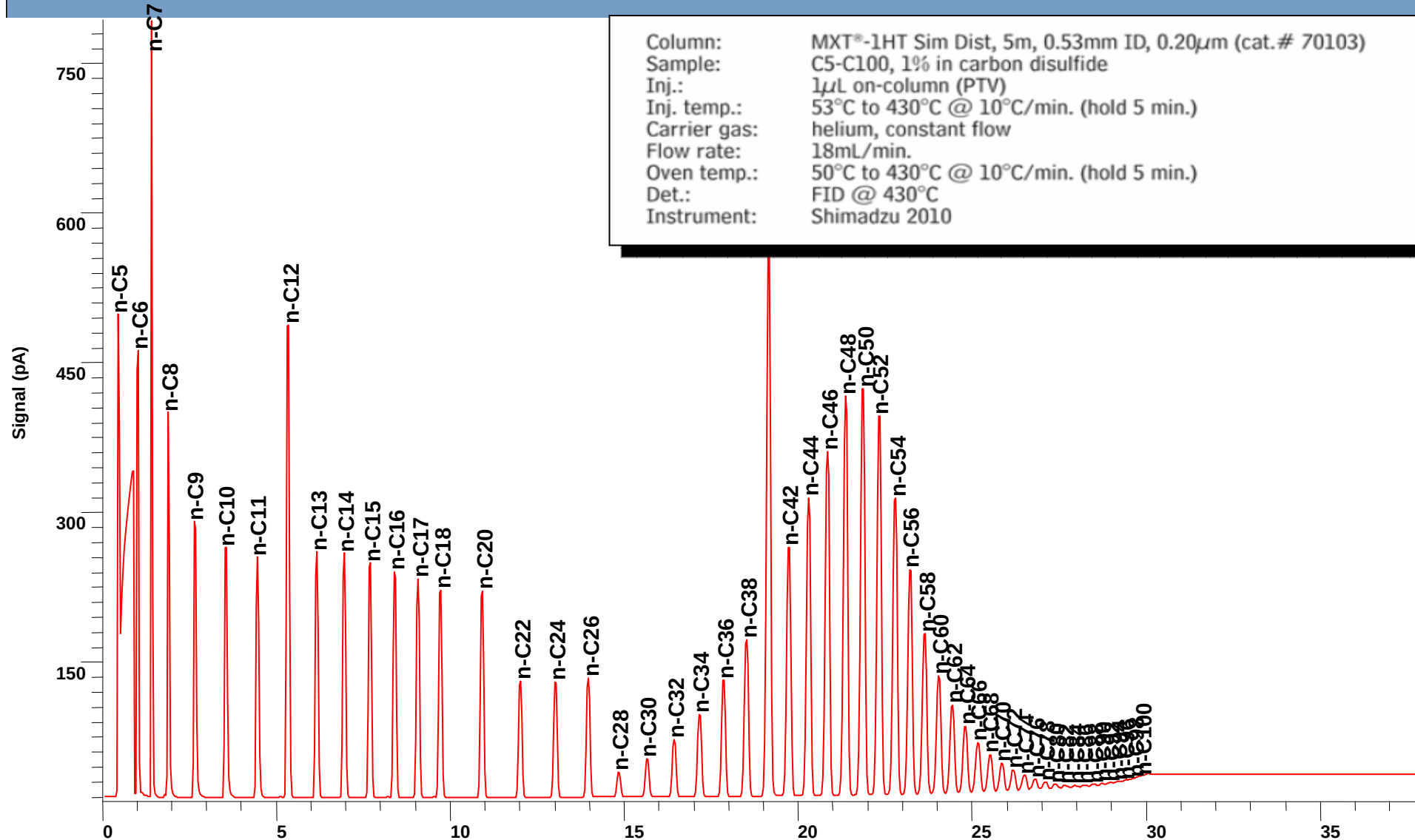




HROMalytic +61(0)3 9762 2034
ECHnology Pty Ltd
Australian Distributors; Importers & Manufacturers

Turning Visions into Reality
www.restek.com

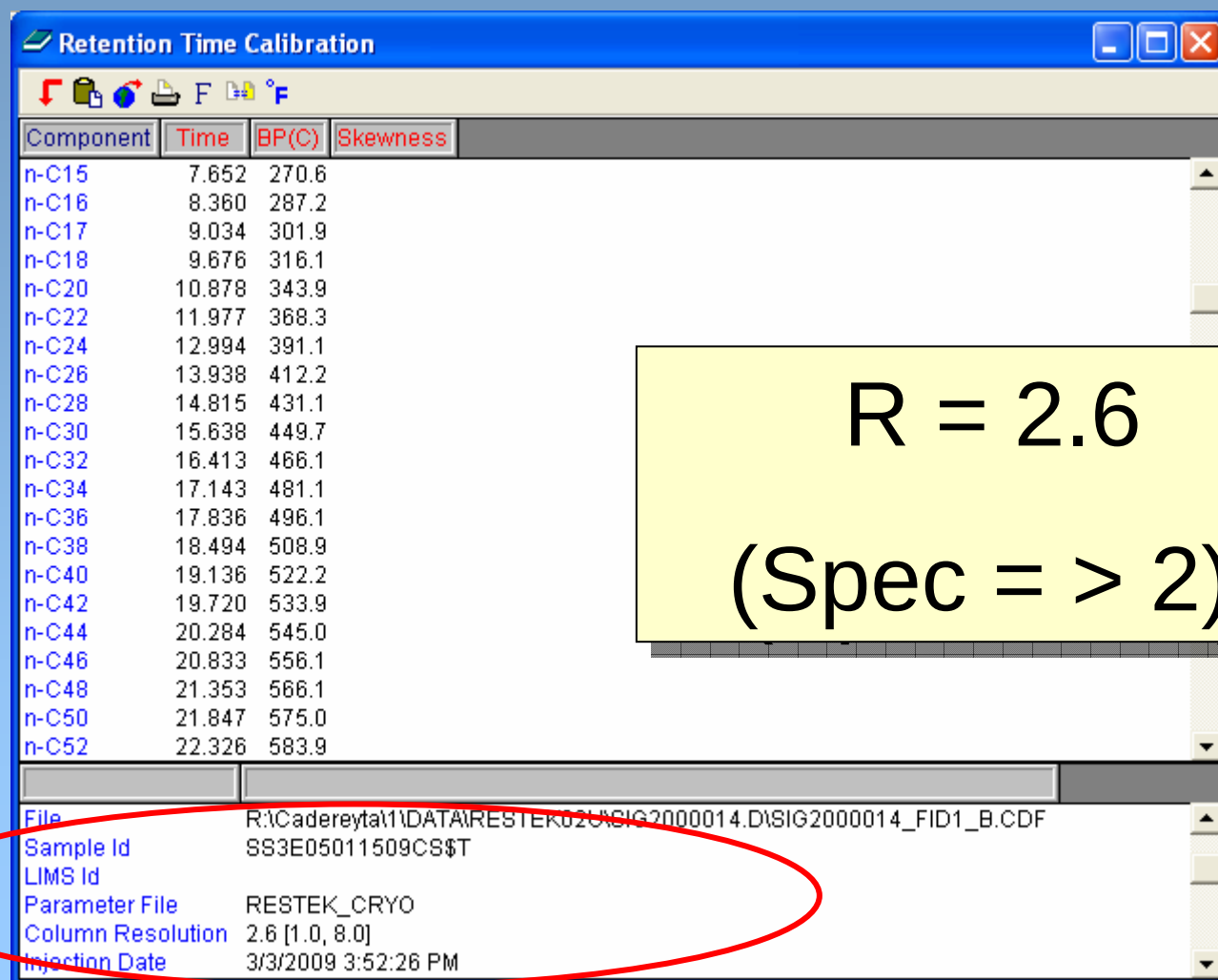
C5-C100



HRMalytic +61(0)3 9762 2034
ECHnology Pty Ltd
 Australian Distributors; Importers & Manufacturers

Turning Visions into Reality
www.restek.com

Column Resolution of C50-C52- at F lowrate of 25 mL/min



Retention Time Calibration

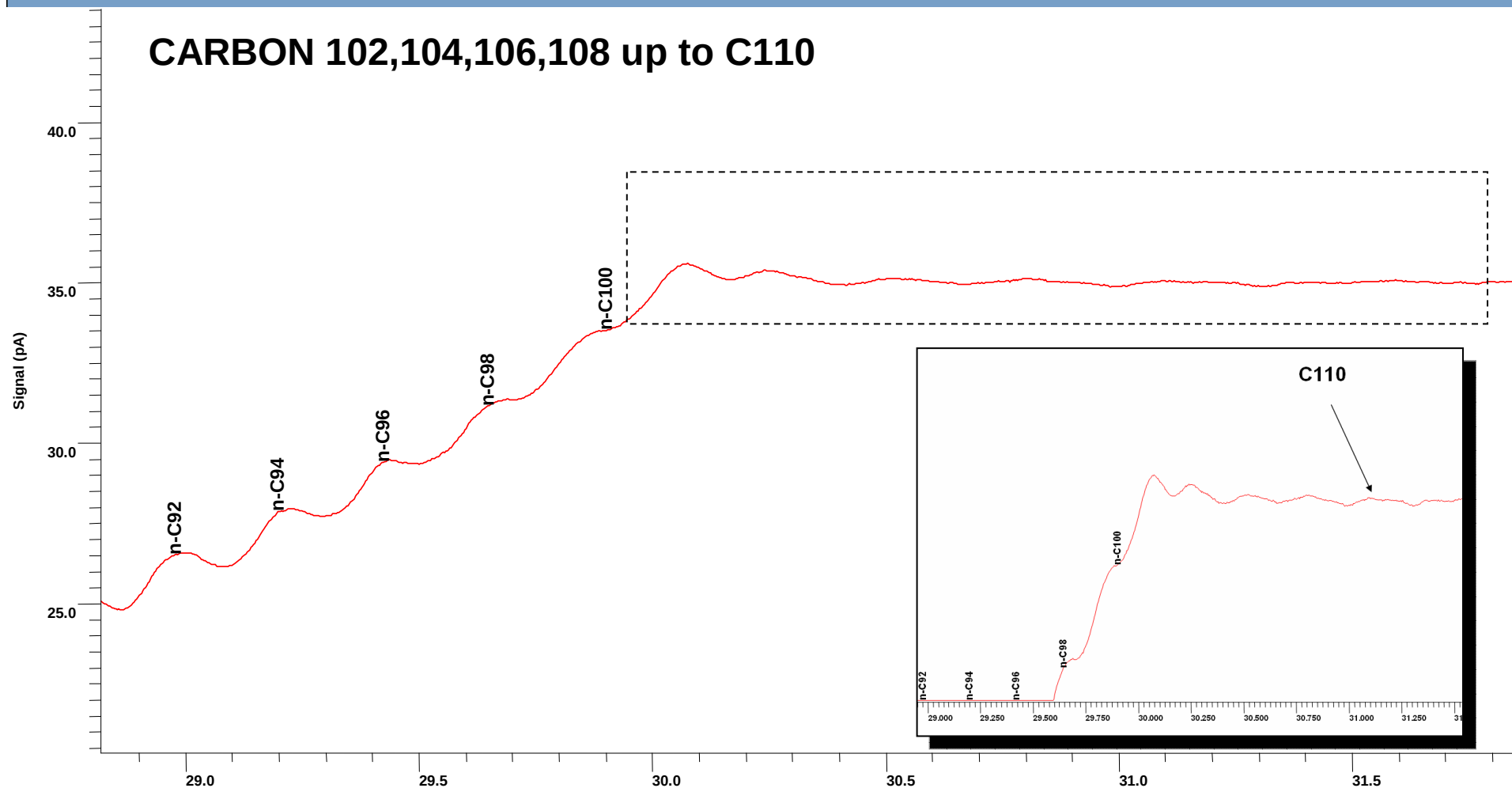
Component	Time	BP(C)	Skewness
n-C15	7.652	270.6	
n-C16	8.360	287.2	
n-C17	9.034	301.9	
n-C18	9.676	316.1	
n-C20	10.878	343.9	
n-C22	11.977	368.3	
n-C24	12.994	391.1	
n-C26	13.938	412.2	
n-C28	14.815	431.1	
n-C30	15.638	449.7	
n-C32	16.413	466.1	
n-C34	17.143	481.1	
n-C36	17.836	496.1	
n-C38	18.494	508.9	
n-C40	19.136	522.2	
n-C42	19.720	533.9	
n-C44	20.284	545.0	
n-C46	20.833	556.1	
n-C48	21.353	566.1	
n-C50	21.847	575.0	
n-C52	22.326	583.9	

File R:\Cadereyta\1\DATA\RESTEK02\USIG2000014.D\SIG2000014_FID1_B.CDF
Sample Id SS3E05011509CS\$T
LIMS Id
Parameter File RESTEK_CRYO
Column Resolution 2.6 [1.0, 8.0]
Injection Date 3/3/2009 3:52:26 PM

$R = 2.6$
(Spec = > 2)

Hydrocarbons eluting at 435 °C, 0.2 µL injection

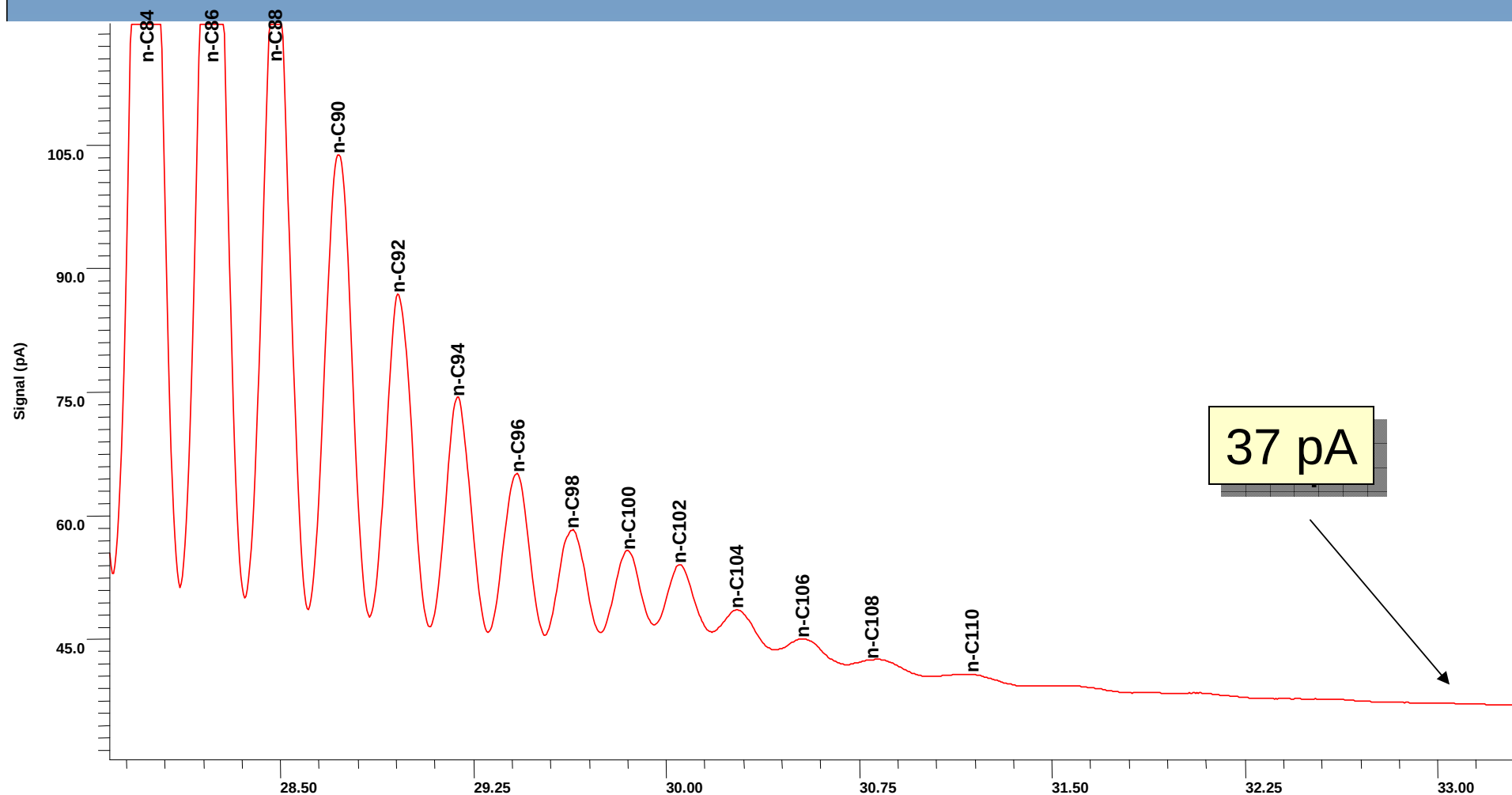
CARBON 102,104,106,108 up to C110



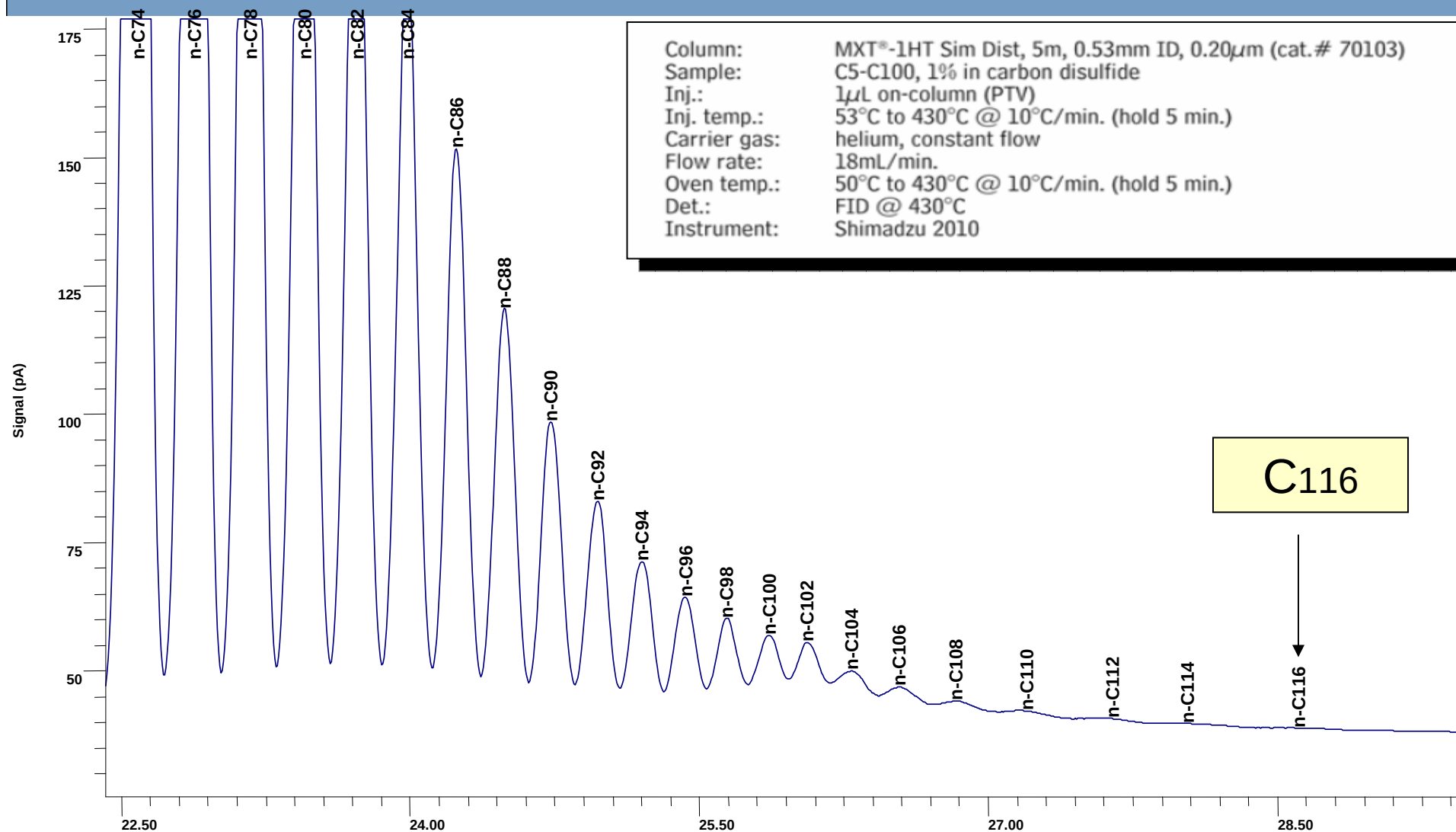
HROMalytic +61(0)3 9762 2034
ECHnology Pty Ltd
Australian Distributors; Importers & Manufacturers

Turning Visions into Reality
www.restek.com

C5-C110-Injection volume = 1 μ L



Extending to C116, Using a Small Liner



HROMalytic +61(0)3 9762 2034
ECHnology Pty Ltd
Australian Distributors; Importers & Manufacturers

Turning Visions into Reality
www.restek.com

Column Cutting

For installation in a PTV or on-column injector, the column inlet must be well-cut..



Turning Visions into Reality
www.restek.com

MXT Column Cutting

A special Tube “scorer” is developed..

Makes a perfect “cut” required for
“on-Column injection”..

For 0.25 - 0.53mm MXT

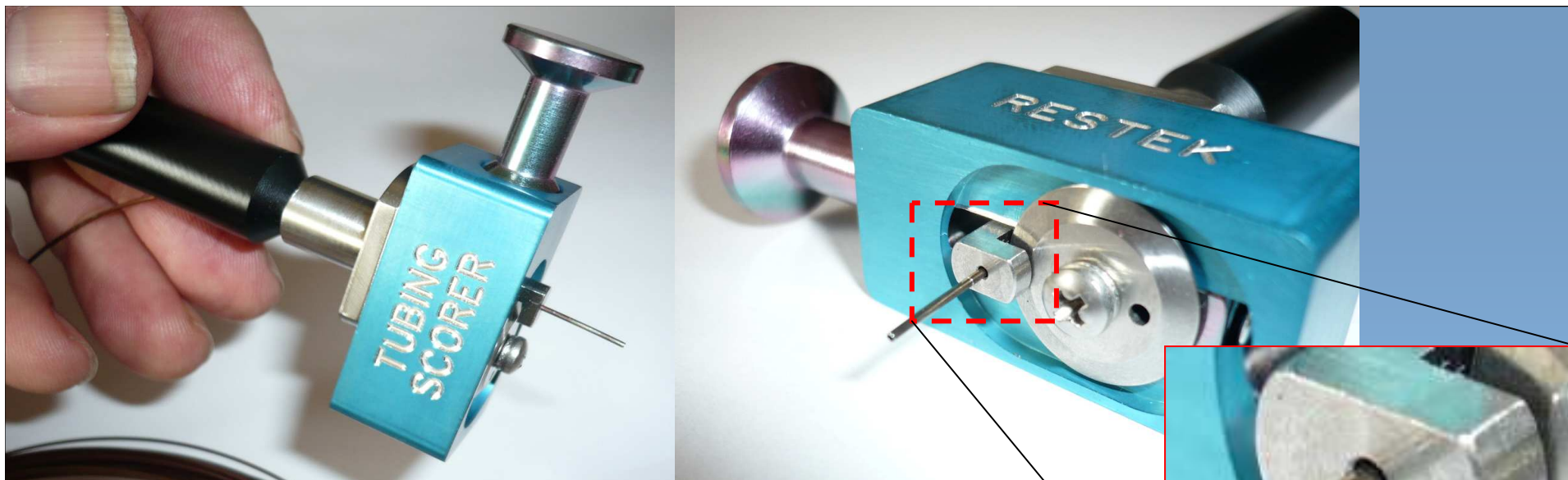


tubing scorer : 20523
replacement wheel: 20522

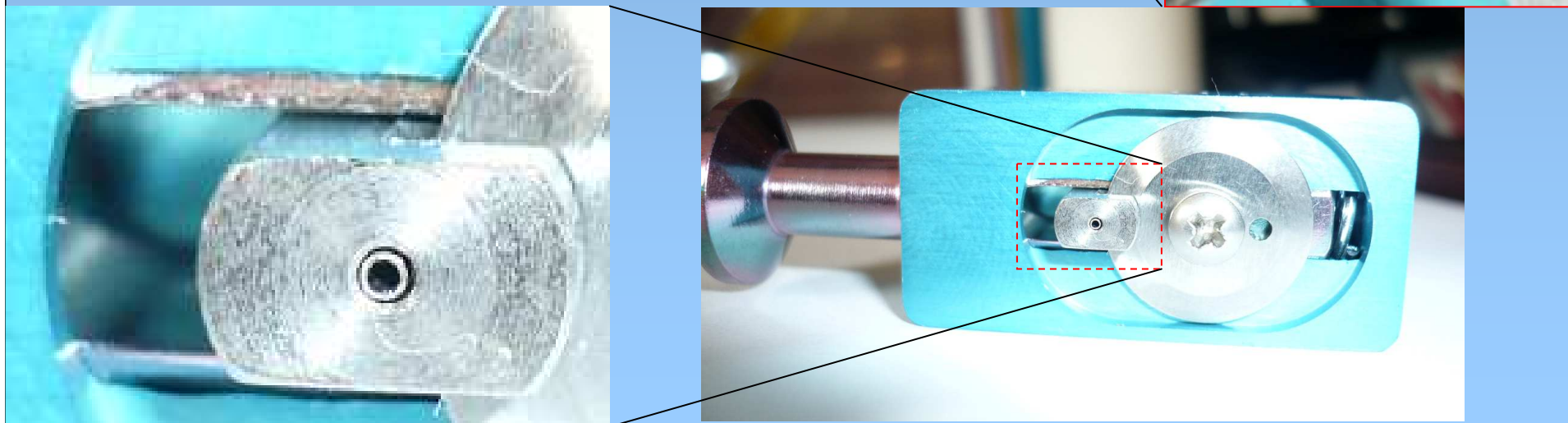


HRMalytic +61(0)3 9762 2034
ECHnology Pty Ltd
Australian Distributors; Importers & Manufacturers

Turning Visions into Reality
www.restek.com



For professional cutting of metal capillary columns



HROMalytic +61(0)3 9762 2034
ECHnology Pty Ltd
Australian Distributors; Importers & Manufacturers

Turning Visions into Reality
www.restek.com

Carrier gas considerations
Avoid introduction of oxidizers



HROMalytic +61(0)3 9762 2034
ECHnology Pty Ltd
Australian Distributors; Importers & Manufacturers

Turning Visions into Reality
www.restek.com

Impact of oxygen / moisture

- Increase of bleed
- Retention times drop fast
- Peaks will broaden
- Peaks will tail



Turning Visions into Reality
www.restek.com

Carrier Gas purification

Degradation reaction of stationary phase + water/oxygen develops exponentially with temperature..

Need: Pure gases



Need: Elimination of leaks



Summary

A new column has been developed for High Temp Simulated Distillation that offers:

Lower bleed:

- More analysis, lower cost per analysis

- Less calibrations

Higher capacity

- Less BP-shifting related to concentration effect

More Gaussian peak shape

- meets ASTM D7169 specs

Highly competitive Pricing



Turning Visions into Reality
www.restek.com

Acknowledgements

Barry Burger, Innovations Scientist

Chis English, Innovations Manager

Jan Pijpelink, Petrochemical marketing manager



Turning Visions into Reality
www.restek.com