Improved High Temperature Simulated Distillation (ASTM D6352 and D7169) Using Zebron™ ZB-1XT SimDist Metal GC Columns

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An improved method for high temperature simulated distillation based upon ASTM D7169 is presented using the Zebron ZB-1XT SimDist column. This column utilizes a Glass Infusion™ Technology that results in more improved efficiency, resolution, and unmatched column-to-column reproducibility. This technology also allows simulated distillation methods, such as ASTM D6352 and D7169, to be extended from C100 to C120 while still meeting all the system suitability requirements.

Introduction

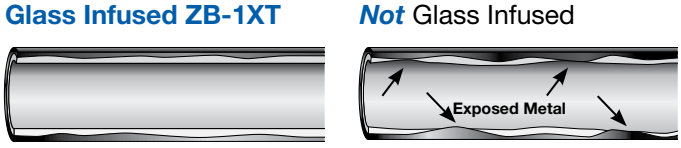
The two current ASTM Methods for high temperature simulated distillation only analyze to C90 or C100, which limit a refinery's ability to optimize a production run. The new Zebron ZB-1XT SimDist column allows the boiling range of these methods to be extended to C120 to better classify an incoming crude. In this article, we will explain how the new Glass Infusion Technology allows the Zebron ZB-1XT SimDist metal column to extend simulated distillation analysis up to C120, while still meeting the performance criteria outlined in the methods.

Results

Glass Infusion Technology

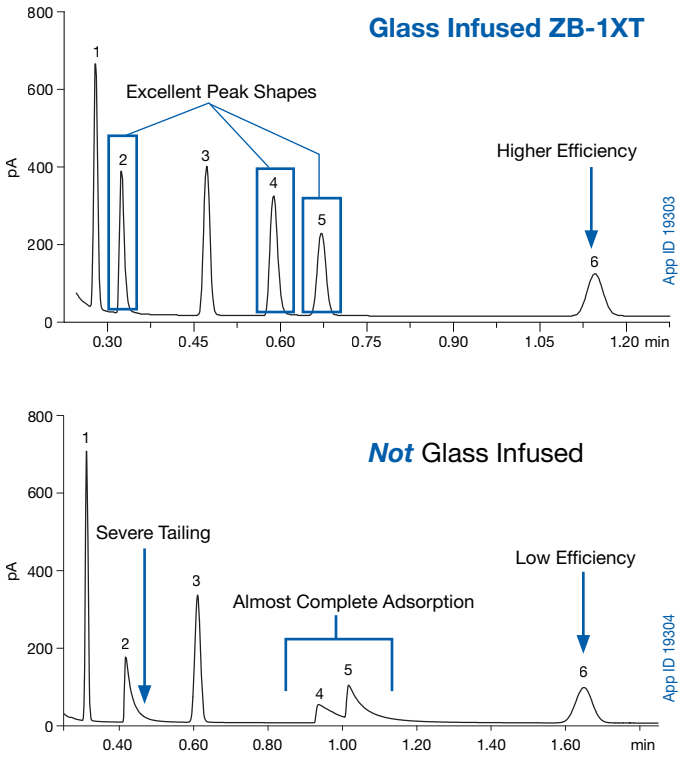
The new Zebron ZB-1XT SimDist metal columns employ a new type of bonding called Glass Infusion Technology. The Glass Infusion process starts by depositing a thick, uniform layer of glass that completely covers the internal metal surfaces of the column **(Figure 1).** The column on the left represents the Zebron ZB-1XT SimDist with Glass Infusion Technology where the metal surface is completely covered by a smooth glass layer. This provides a consistent surface for bonding the stationary phase. The column on the right is non-glass infused with areas of exposed metal accented by arrows. These exposed metal surfaces result in abnormal bonding of the stationary phase which affects chromatographic performance, decreases column efficiencies, and results in inconsistent performance between columns.

Figure 1.
Depiction of a Zebron ZB-1XT SimDist column with Glass Infusion Technology and non-glass infused column



The complete coating and bonding is measured with an aggressive test mix that includes acidic and basic compounds. These active compounds probe the column surface and indicate columns with poor performance. Examples are shown in **Figure 2** where the non-glass infused column shows tailing peaks as well as absorption due to the interaction with the exposed metal and/or glass surface. In comparison, the Zebron ZB-1XT SimDist column shows sharp, symmetrical peaks, indicating a complete and effective bonding. For quality purposes, all Zebron ZB-1XT SimDist columns are individually QC tested to ensure that all columns meet our high standards. In contrast, some manufacturers batch test their columns, which can lead to poor column-to-column reproducibility.

Figure 2. Active test mix on Zebron ZB-1XT SimDist and alternative column. Labeled peaks are 1) Undecane, 2) 4-Chlorophenol, 3) Tridecane, 4) 1-Undecanol , 5) Dicyclohexylamine, and 6) Pentadecane. Analytes are 250 µg/mL each in hexane; 1.0 µL split 100:1 at 250 °C. Oven temperature is 130 °C isothermal with FID at 325 °C and a column flow of hydrogen at 1.93 mL/min constant pressure.



Benefits of Glass Infusion Technology to High Temperature Simulated Distillation Analysis

Glass Infusion Technology provides great benefits when applied to high temperature simulated distillation methods, including improved performance for system suitability requirements and increased column lifetime.

Improved lifetime is attained by two key factors. The first is higher initial resolution, which gives a larger buffer for contamination before failing the key resolution requirements. The second is the stability of the bonded phase to the higher temperatures used in distillation methods. Columns that have these advantages will provide longer lifetime, which results in less instrument downtime, fewer columns purchased, and greater productivity.

APPLICATIONS

An example of extended lifetime is shown in **Figure 3** where resolution of C50/52 is shown over time on three different manufacturer's simulated distillation columns, Phenomenex, Varian, and Restek. The columns were tested by injecting a POLYWAX® test mix. After two hours at 400 °C, the resolution of C50/C52 was measured. The POLYWAX injection and C50/52 measurement were repeated for a total of 90 hours.

The minimum resolution requirements listed in ASTM Method D6352 is 2.0. **Figure 3** shows that the Phenomenex Zebron column starts with a resolution value of 2.5 and maintains resolution above 2.3 for the 90 hours of testing. The Varian column shows good initial resolution, but falls below 2.3 after less than 80 hours at 400 °C. This causes it to be close to failing the method requirement. The Restek column started with a much lower resolution than either the Zebron or the Varian column. At just over 70 hours, this column comes very close to failing the minimum resolution requirement.

High Temperature Distillation up to C120

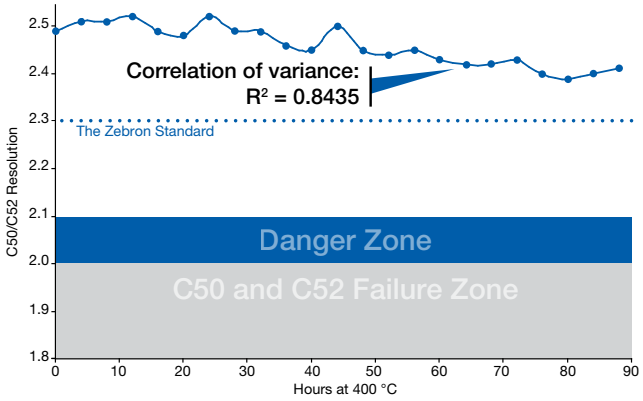
To see how the Zebron ZB-1XT SimDist could be used to improve existing ASTM simulated distillation methods, we investigated the analysis of samples containing hydrocarbons up to C120, while still maintaining the system suitability requirements of ASTM D7169. The Zebron ZB-1XT SimDist easily surpassed all of the requirements of the method **(Table 1)**. The resolution requirement of 1.8 between C50/C52 was easily met, with the Zebron ZB-1XT SimDist column achieving a resolution of 2.55. The method also specifies that the peak skew for any peak between C12 and C24 should be between 1.8 and 2.4. The Zebron ZB-1XT SimDist showed near perfect peak shape for C12 of 0.99.

Table 1. Method requirements for ASTM D7169 and values obtained using ZB-1XT column.

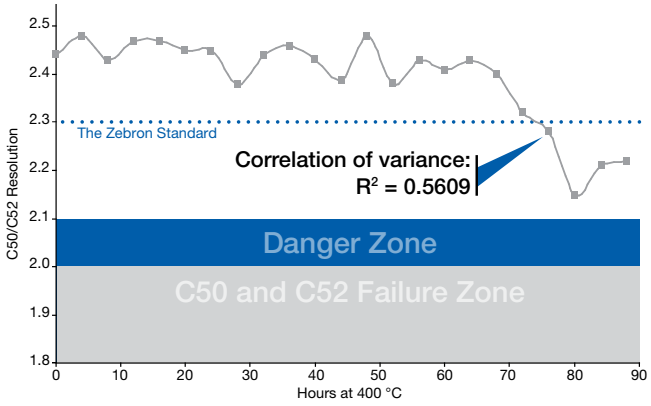
Method Requirement	ZB-1XT Value	Pass
Resolution of C50 / C52 is between 1.8 and 4.0	2.55	√
Peak skew for any peak from C12-C24 is between 0.8 and 1.2	Skew for C12 = 0.99	√
C100 elute on temperature ramp	Up to C120 elute on ramp	√

Figure 3. Resolution over time at elevated temperatures.
1.0 µL of POLYWAX® 1000 was injected on-column at 53 °C. The oven was set to 50 °C to 430 °C @ 10 °C/min for 20 min with an FID temperature of 450 °C. The carrier gas was helium at a constant flow of 30 mL/min

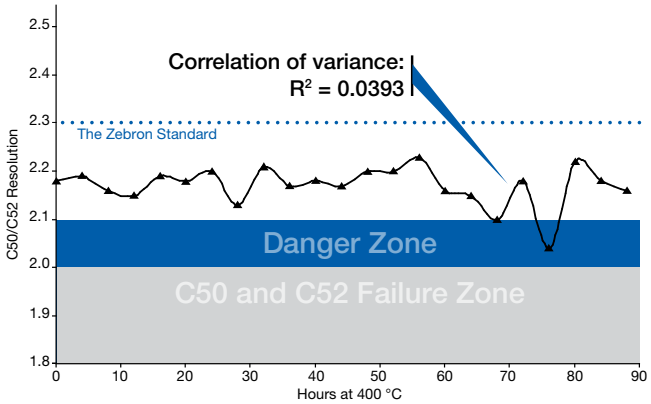
Zebron ZB-1XT SimDist
5 m x 0.53 mm x 0.09 µm



Varian™ CP-SimDist UltiMetal
5 m x 0.53 mm x 0.09 µm



Restek® MXT®-1HT Sim Dist
5 m x 0.53 mm x 0.10 µm



Comparative separations may not be representative of all applications.

Figure 4. ASTM D7169 standard using a Zebron ZB-1XT SimDist column of 5 meter x 0.53 mm x 0.09 µm dimensions with elution of C120 on the temperature ramp to 430 °C. The sample was ASTM D2887 calibration mix with POLYWAX® 1000 in CS_2. The 1.0 µL injection was on-column at 38 °C. Helium carrier gas was at a constant flow of 34 mL/min. The oven was set from 35 °C to 430 °C @ 9 °C/min for 10 min with an FID temperature of 450 °C.

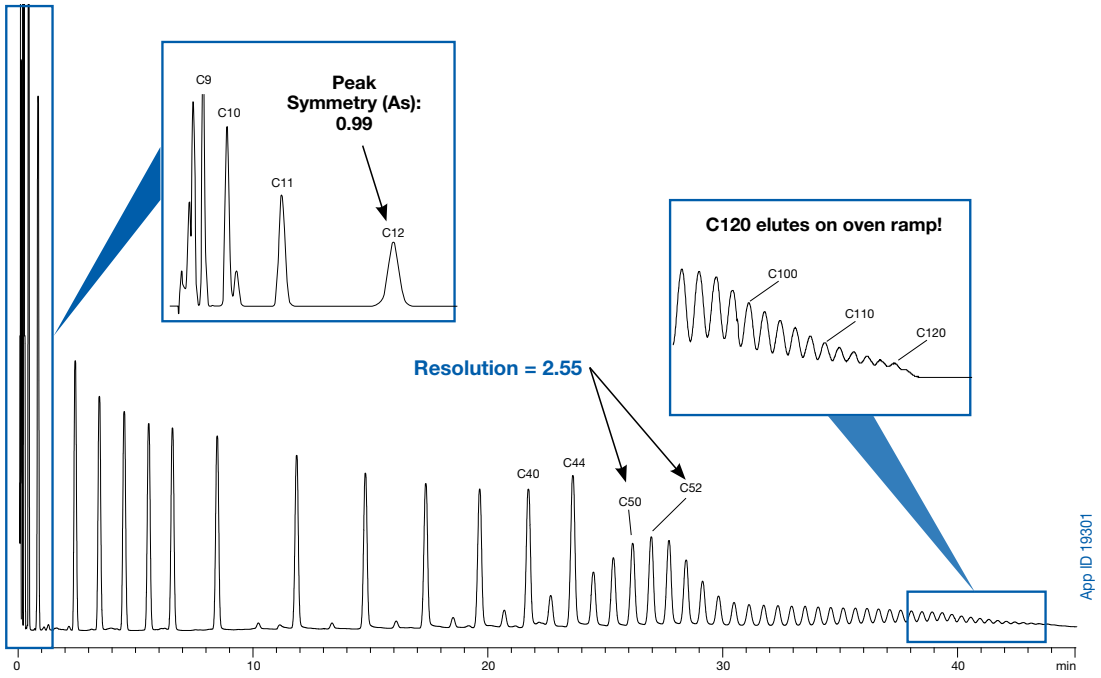
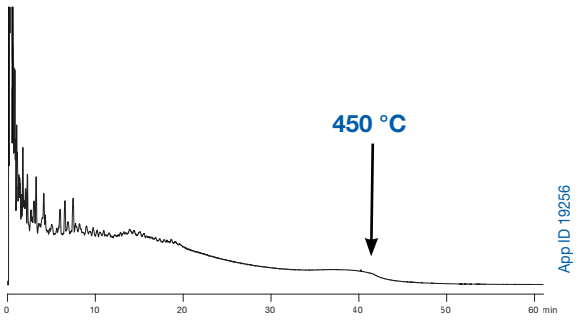


Figure 5. Chromatogram of Yeates Crude Oil showing elution of compounds at 450 °C. A 1.0 µL volume was injected on-column at 38 °C. Helium carrier gas was set to a constant flow of 15 mL/min. The oven was programmed from 35 °C to 450 °C @ 10 °C/min for 20 min with an FID temperature of 450 °C.



The third method requirement specifies that peaks must elute on the temperature ramp in order to be quantified. The last required compounds for ASTM method D6352 and D7169 are C90 and C100, respectively. However, in many cases, the incoming crude samples are composed of material with hydrocarbons above C100. In order to determine the optimum cracking process, it would be helpful to characterize the higher boiling fractions.

By optimizing both column dimensions and the GC conditions, we were able to develop a separation that allowed for C120 to be eluted on the temperature program, with a final oven temperature of only 430 °C **(Figure 4)**. This method provides more extensive characterization of samples than the customary ASTM method D7169 and can result in better process planning and increased refinery yields.

The increased temperature stability of the Zebron ZB-1XT SimDist phase is an advantage when analyzing raw materials that have large amounts of very high boiling points, like crude oil **(Figure 5)**. The high temperature stability allows for elution of compounds in excess of C120, which reduces carry over, prevents contamination, extends column lifetime, and minimizes maintenance.

Conclusion

The Zebron ZB-1XT SimDist metal column is an ideal column for simulated distillation analysis. By utlizing Glass Infusion Technology, it provides superior column-to-column reproducibility and extended lifetimes when compared to alternative columns. This consistency is guaranteed by individually QC testing all columns. This improved performance results in less instrument downtime, fewer columns purchased, and increased productivity.

This Zebron ZB-1XT SimDist metal column also allows for extended analysis up to C120. With an extended analysis range, higher boiling point compounds will elute off the column instead of deteriorating column and system lifetime by remaining as residues. This allows for better sample identification and can aid in process planning, reduction of waste, and increase product yields, all of which directly affect the bottom line.

For further information on Zebron ZB-1XT SimDist metal columns or the applications seen here, please contact your Phenomenex representative.

APPLICATIONS

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Phenomenex products are available worldwide. For the distributor in your country, contact Phenomenex USA, International Department at international@phenomenex.com

Ordering Information

Zebron™ ZB-1XT SimDist Metal GC Columns

ID(mm)	df(µm)	Temp. Limits °C	Part No.
5-Meter			
0.53	0.09	-60 to 450	7AK-G026-55
0.53	0.15	-60 to 450	7AK-G026-05
10-Meter			
0.53	0.15	-60 to 450	7CK-G026-05
0.53	0.88	-60 to 450	7CK-G026-49
0.53	2.65	-60 to 400	7CK-G026-35

Easy Seals

Part No.	Description	Unit
Standard, single groove for splitless applications, 0.8 mm dia. inlet hole		
AG0-8619	Easy Seal Inlet Base Seal, Gold Plated, for Agilent GCs	2/pk
AG0-8620	Easy Seal Inlet Base Seal, Gold Plated, for Agilent GCs	10/pk

Ceramic Scoring Wafers

Part No.	Description	Unit
AG0-4718	Ceramic Scoring Wafer	2/pk

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