Petrochemical

Applications note

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GC Analysis of Petroleum Products by Simulated Distillation, Using MXT® Sim Dist Columns

The American Society for Testing and Materials (ASTM) has released a new gas chromatographic (GC) method for petroleum distillation, "Boiling Range Distribution of Petroleum Distillates in the Boiling Range of 174°C to 700°C by Gas Chromatography (ASTM D6352)." This method extends the boiling point range specified in ASTM D2887 (55°C to 538°C). Determining the boiling range distribution of distillate fractions provides manufacturers with a better understanding of the composition of feed stocks and products related to petroleum refining processes.

Simulated distillation (Sim Dist) is a technique in which the GC is calibrated with alkane standards of published boiling points to perform a direct comparison to the boiling points of the sample components. Polyethylene standards such as Polywax® 655 or Polywax® 1000, which contain even-numbered hydrocarbons between C20 and C100, are used to calibrate the GC system. The retention times of the known alkanes are calibrated versus the published boiling points, and analysis of high molecular weight fractions are compared using special software. Analyzing high-boiling compounds (up to 700°C) requires an on-column or temperature-programmable injector to minimize injector discrimination, and a flame ionization detector (FID).

The capillary column used for the analysis is very important. The recommended column is coated with a non-polar methyl silicone phase that can withstand repeated cycles of high temperatures (430-450°C). However, the polyimide coating that maintains the flexibility of fused silica tubing rapidly breaks down at oven temperatures above 360°C and is unsuitable for high-temperature GC. Aluminum-clad tubing overcomes the problems associated with the polyimide, but has its own limitations. When repeatedly programmed to temperatures above 400°C, the aluminum sheath may become brittle. The most durable and inert capillary columns available are Restek MXT® columns, which are manufactured using Silcosteel® tubing—rugged metal tubing that is treated to provide the inertness of fused silica.

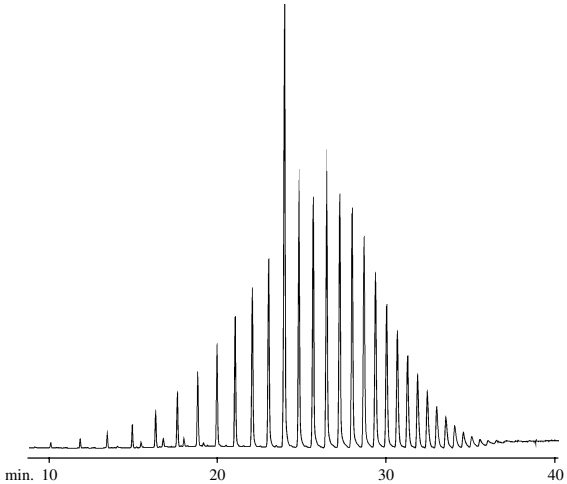
The liquid phase in the column also must withstand temperatures over 400°C, with minimum breakdown of the polymer. The phase must demonstrate low bleed and retention time stability that is repeatable with temperature programmed analysis. The methyl silicone polymer in the MXT®-1 Sim Dist column is synthesized to demanding quality control standards using a proprietary synthesis process. This process eliminates residual catalysts that could cause degradation and increase bleed from the polymer. The polymer then is carefully fractionated to remove low molecular weight fragments, providing a tight mono-modal distribution that results in extremely low bleed. The polymer is fully characterized for long-term reproducibility using techniques such as RI, FTIR, Kovats Indices, % crosslinking, coating efficiency, and a five-day thermal bake-out to ensure column longevity. Figure 1 shows the separation of Polywax® 655 on an MXT®-1 Sim Dist column.

Although the ASTM D6352 recommends a methyl silicone liquid phase, another phase also has gained acceptance by analysts performing simulated distillation—a carborane dimethyl polysiloxane, or MXT®-500 Sim Dist polymer. This has been designed by incorporating carborane into the backbone of the methyl silicone polymer chain to promote thermal stability (see Figure 2). The MXT®-500 Sim Dist stationary phase is the most stable phase available for high-temperature simulated distillation analyses and will outlast a 100% methyl silicone stationary phase. Figure 3 shows the separation of Polywax® 655 on the MXT®-500 column.

However, the trade-off for increased thermal stability produces a subtle polarity difference between the methyl silicone and the carborane stationary phase. The difference in polarity of the stationary phases causes a shift in the calculated boiling range

Figure 1

MXT®-1 Sim Dist Column Demonstrates Excellent Symmetry and Low Bleed for High-Temperature Sim Dist Calibration.



6m, 0.53mm ID, 0.15µm MXT®-1 (cat.# 70101). 1.0µL injection of Polywax® 655 in CS_2, cool on-column. **Oven temp.:** 40°C to 430°C @ 10°C/min. (hold 10 min.); **Det. temp.:** 430°C; **FID sensitivity:** 5 x 10^{-10} AFS; **Carrier gas:** hydrogen; **Linear velocity:** 45cm/sec. set @ 40°C.

distribution for petroleum samples containing aromatic hydrocarbons. The MXT®-500 Sim Dist stationary phase has increased relative retention of aromatic hydrocarbons compared to the methyl silicone MXT®-1 Sim Dist stationary phase. This causes the calculated boiling points of aromatics to be slightly higher using the MXT®-500 Sim Dist phase, although they are closer to the true value (see Table I).

While both columns can be operated to 430°C, the MXT®-500 Sim Dist column has lower bleed and longer lifetime. The MXT®-1 Sim Dist column offers methyl silicone polarity that matches published data.

Figure 2

MXT®-500 Sim Dist Polymer—designed by incorporating carborane into the backbone of the methyl silicone polymer chain to promote thermal stability.

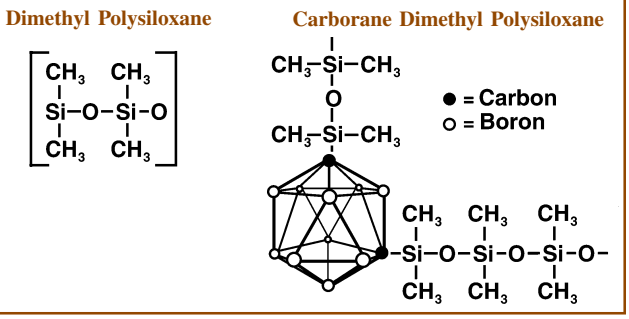


Table I

Differences in the Calculated Boiling Points of Aromatics Using the MXT®-500 Sim Dist Phase.

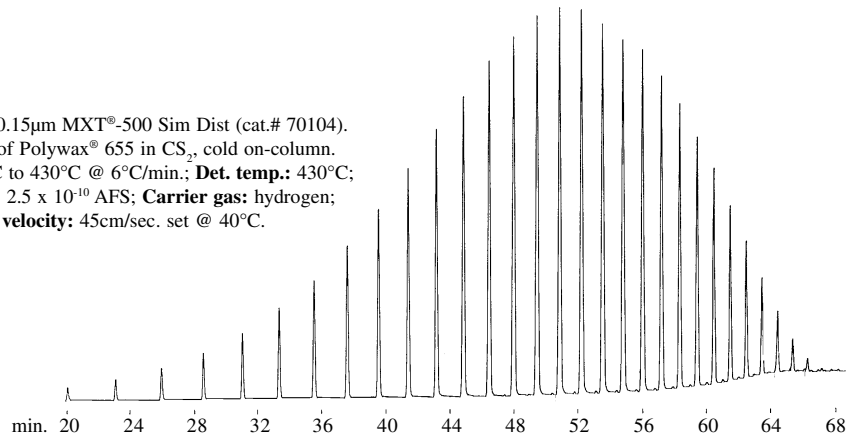
Compound	Boiling Point °C (°F)	MXT®-1 Δ °C (°F)	MXT®-500 Δ °C (°F)
toluene	128 (231)	-1 (-2)	8 (14)
p-xylene	157 (282)	-2 (-3)	4 (8)
naphthalene	236 (424)	-19 (-34)	-4 (-8)
acenaphthene	297 (534)	-28 (-51)	-11 (-19)
chrysene	465 (837)	-74 (-134)	-48 (-87)
coronene	543 (977)	-59 (-106)	-23 (-42)

High-temperature GC analyses challenge the limits of existing tubing and stationary phase technology. Restek's MXT® tubing is ideally suited to the task when compared to fused silica or aluminum clad tubing. The high temperatures necessary for simulated distillation analyses also push GC polymers to the limit of thermal stability. The MXT®-500 and MXT®-1 Sim Dist columns are proven performers under these extreme conditions. When properly conditioned to 430°C, these columns give stable baselines, low bleed, and repeatable retention times for simulated distillation and other high-temperature GC analyses.

Figure 3

MXT®-500 Sim Dist Column is an Excellent Choice for Lower Bleed and Extended Lifetime.

6m, 0.53mm ID, 0.15µm MXT®-500 Sim Dist (cat.# 70104).
1.0µL injection of Polywax® 655 in CS_2, cold on-column.
Oven temp.: 40°C to 430°C @ 6°C/min.; **Det. temp.:** 430°C;
FID sensitivity: 2.5 x 10^{-10} AFS; **Carrier gas:** hydrogen;
Linear velocity: 45cm/sec. set @ 40°C.



Product Listing

Description	Cat.#
MXT®-1 Sim Dist (6m, 0.53mm ID, 0.15µm)	70101
MXT®-500 Sim Dist (6m, 0.53mm ID, 0.15µm)	70104

Description	Cat.#
Polywax® Standard (655 Calibration Material, 1g)	36225
Polywax® Standard (1000 Material, 1g)	36227

Restek Trademarks: MXT, Silcosteel. ***Other Trademarks:*** Polywax (Petrolite Specialty Polymers Group).