Upgrade to a Faster D2887 Analysis with a GC Accelerator Kit

Reduce Analysis Time to 9 Minutes in a 120 V GC

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Abstract

The results of a simulated distillation analysis are vitally important to the operation of refineries globally. For the analysis of petroleum samples within the boiling point range from 55.5 ˚C to 538 ˚C, ASTM D2887 is a standard method that has been accepted and is used industry-wide. This application note will demonstrate how a creative use of the Restek GC Accelerator oven insert kit can permit analysts using Agilent 6890/7890 GCs with 100/120 V ovens to successfully migrate from D2887's slower Procedure A conditions to the accelerated Procedure B conditions without new instrumentation or software, resulting in a 9-minute analysis time that meets all method requirements.

Introduction

The distribution of boiling point temperatures of petroleum products or liquid fuels is one of the properties that govern the quality of these products. That distribution is also used for the optimization of refinery processes and the characterization and prediction of other physical parameters of the fuels. Traditionally, the boiling point distribution range is determined using classical physical distillation, which results in volumetrically measurable fractions of known boiling point ranges. A major disadvantage of physical distillation is that it can be a labor-intensive, time-consuming process that requires large sample volumes.

However, simulated distillation (SimDist) can be a much more efficient alternative. SimDist analysis is a gas chromatographic technique designed to provide the same information as a physical distillation. The SimDist approach is simpler and faster, and it can be automated. It also requires significantly less sample.

ASTM D2887 [1] is a SimDist method, published by ASTM International (formerly the American Society for Testing and Materials), for analyzing samples with a boiling point range of 55.5 °C to 538 °C (C5-C44). The method contains two procedures: Procedure A and Procedure B, which each include several options that offer a variety of column choices and analytical conditions. The boiling point range for ASTM D2887 includes light crudes, naphtha, and kerosene, and Procedure B allows for a variety of biodiesel mixtures (B5, B10, and B20).

Procedure B was developed to significantly reduce the analysis time of the original method by taking advantage of faster oven heating rates, high flows, and open tubular capillary columns. A 0.53 mm ID column facilitates the use of high flow rates, and a thick film provides the sample loading capacity to allow neat samples to be injected without sacrificing peak shape due to overloading. The oven heating rate is 35 °C/min from 40 °C to 350 °C. An Agilent GC equipped with a 100/120 V oven cannot meet these aggressive oven heating rates, especially at temperatures greater than 250 °C, so typically analysts are restricted to using the longer Procedure A methods, which often take more than 20 minutes. This study investigated a novel use of the Restek GC Accelerator oven insert kit to increase the oven ramp rate of an Agilent GC with a 100/120 V oven in order to meet the requirements for Procedure B oven ramp rates.

Experimental

Sample

The instrument was set up with a GC Accelerator (plate only) installed and evaluated against the method requirements using an ASTM D2887-12 calibration standard (cat.# 31674). The configuration was further evaluated using a reference gas oil (RGO) standard. RGO oil is an oil sample with a certified boiling range distribution. It is run to evaluate the system prior to analyzing samples. The RGO values must be in agreement with the published values for the lot of RGO that is used (Separation Systems, reference gas oil, lot #1, batch #2, cat.# SD-016-05).

Analysis Conditions

As shown in Table I, the D2887 analysis conditions followed ASTM Method D2887-16a [1], Procedure B, Column Option 2. The sample amount was reduced from 0.1 µL to 0.05 µL.

For this study, a 10 m, 0.53 mm ID, 2.65 µm film thickness MXT-1HT SimDist column was cut to the 5 m length called for by the Procedure B, Column 2 method. A custom 5 m column is available (contact your Restek representative and request cat.# 573912).

The PTV purge flow was turned on near the end of the analysis (at 8 minutes) to mitigate the potential for sample carryover, while allowing enough time to achieve reproducible and representative sample transfer from the inlet to the column.

Table I: D2887 Analysis Conditions

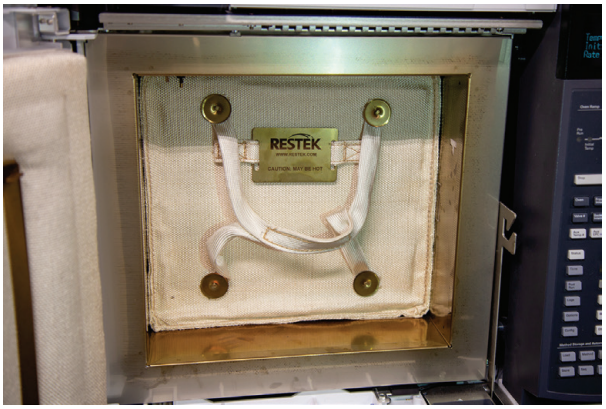
	ASTM D2887 Procedure B, Column 2 Option
Column	5 m x 0.53 mm x 2.65 µm MXT-1HT SimDist
Inlet	PTV 100 °C to 350 °C at 35 °C/min, purge flow 100 mL/min at 8 min
Flow Conditions	Helium, 35 mL/min, constant flow
Oven Program	40 °C to 350 °C at 35 °C/min with GC Accelerator plate installed
Detector	FID @ 360 °C Air 400 mL/min, hydrogen 40 mL/min, make-up gas (nitrogen) at 5 mL/min
Sample	ASTM D2887-12 calibration standard (Restek, cat.# 31674); Reference gas oil (Separation Systems, lot# 1, batch #2, cat.# SD-016-05)
Sample Size	0.05 µL injection, autosampler, D2887 standard sample was heated 5 min at 40 °C prior to injection
Liner	Topaz 2.0 mm ID single baffle CIS4/TDU inlet liner (cat.# 23283)
Injection	Splitless, 0.05 µL injection, autosampler, slow sample drawing speed, fast injection

Instrument Setup and GC Accelerator Installation

An Agilent 7890B equipped with a 120 V oven was used for this study. This particular GC is designed for two column analyses; therefore, it has two inlets and two detectors. For this experiment, the column was installed at the back PTV inlet and the back FID detector. This was to facilitate the novel use of the GC Accelerator kit.

The GC Accelerator oven insert kit (cat.# 23849) comes with one plate insert, one large block insert, and one small block insert and was originally intended to be installed in an Agilent GC to accommodate a column installed in the front or back inlet positions, the front or back detector positions, or principally, for use with a mass spectrometer. Installed in this way, however, a 120 V oven is unable to achieve the 35 °C/min ramp rate called for by the method at the upper oven temperature range (300-350 °C).

Figure 1: GC Accelerator plate insert placed behind the front inlet/detector positions.

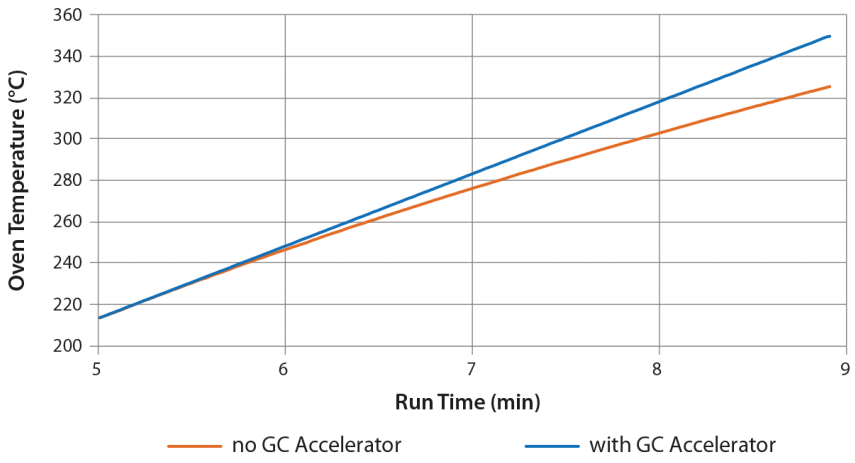


In this study, only the plate insert was used, and it was installed behind the front inlet and detectors in the GC oven (Figure 1). This position further reduced the volume of the oven and allowed the oven to meet the accelerated oven ramp rate required for this method (Figure 2). With the plate installed in this position, there is no room for the large or small block inserts, so they were not used.

Data Analysis Software

Since the required data analysis for actual samples can be a mathematically labor-intensive process, the results are routinely evaluated using one of the commercially available SimDist software packages. In this study, Dragon SimDist software developed by Envantage was used. The software comes pre-built with all the data calculations, performance measurement tools, and reporting requirements for all normal and high-temperature simulated distillation analyses.

Figure 2: Overlay of actual oven temperatures with no GC Accelerator (orange) and with the GC Accelerator plate insert installed (blue) when ramping oven temperature at 35 °C/min from 40 °C to 350 °C (the D2887-16a, Procedure B required oven profile). Without the GC Accelerator plate, the actual oven temperature after 250 °C does not meet the required oven temperature.

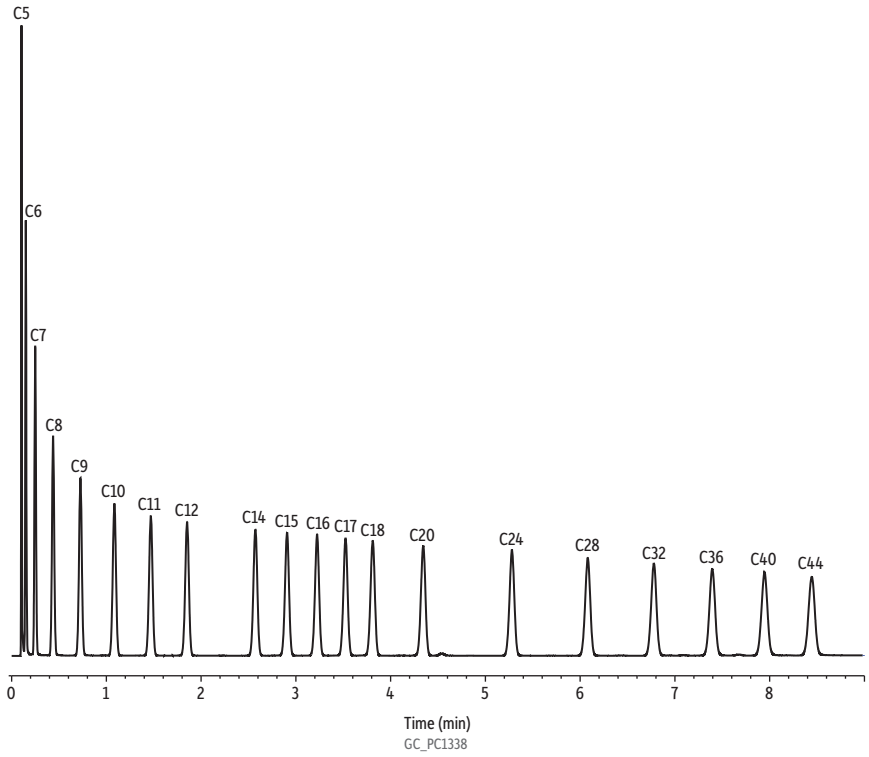


Results and Discussion

D2887 Analysis of Retention Time Calibration Standard

The setup described here was initially tested using a calibration standard and evaluated against the method requirements for skewness (asymmetry at 10%) and sample discrimination. The chromatogram is shown below in Figure 3. Table II demonstrates how this novel setup permits an analyst with an Agilent 100/120 V oven to meet Method D2887 skewness and discrimination requirements. Measuring the ratio of a given peak's area to the area of decane (C10) provides a measure of discrimination, or unintended loss of signal for a given compound, where a value of 1 is ideal. The skewness, or asymmetry, of the peak is a measure of potential column overloading where again, a value of 1 represents a perfectly symmetrical peak.

Figure 3: D2887 analysis of a calibration standard following method D2887-16a, Procedure B, Column 2 conditions (Table I) using the GC Accelerator plate in a 120 V GC oven.



Column	See notes
Sample	ASTM D2887-12 calibration standard (cat.# 31674)
Diluent:	Carbon disulfide
Conc.:	1% w/w
Injection	
Inj. Vol.:	0.05 µL PTV splitless
Liner:	Topaz 2.0 mm ID single baffle CIS4/TDU inlet liner (cat.# 23283)
Inlet Temp. Program:	100 °C to 350 °C at 35 °C/min
Oven	
Oven Temp.:	40 °C to 350 °C at 35 °C/min
Carrier Gas	He, constant flow
Flow Rate:	35 mL/min
Detector	FID @ 360 °C
Instrument	Agilent 7890B GC
Notes	The analytical column used here is a 5 m section cut from a 10 m, 0.53 mm ID, 2.65 µm MXT-1HT SimDist column. A 5 m length can be ordered by contacting your Restek representative and requesting custom part number 573912. The analysis was run in a 120 V oven using the plate insert from a GC Accelerator kit (cat.# 23849) in order to meet the aggressive oven ramp rate.

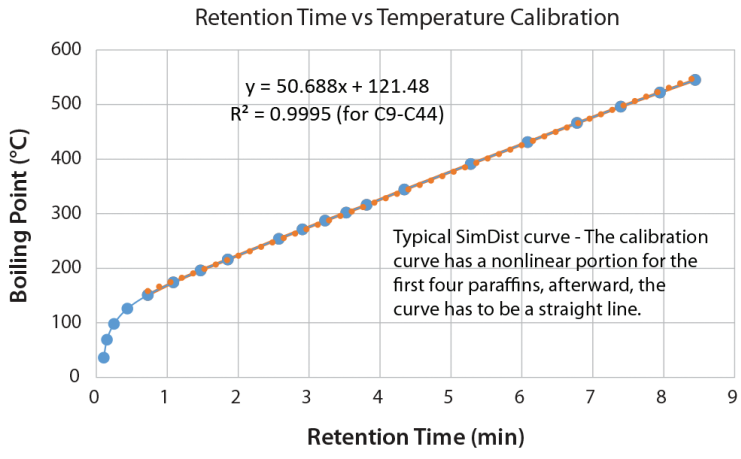
Table II: Evaluation of the chromatogram in Figure 3 for skewness (asymmetry at 10%) and sample discrimination (Cx/C10 area ratio). All the method requirements were met.

Compound	Structural Name	Boiling Point (°C)	Time	Area	Cx/C10 Area Ratio	Cx/C10 Spec	Asymmetry (10%)	Asymmetry Spec
n-Pentane	C5	36	—	—	—	—	—	—
n-Hexane	C6	69	0.15	8665	0.93	0.9-1.1	1.06	0.8-1.3
n-Heptane	C7	98	0.249	9239.3	0.99	0.9-1.1	1.04	0.8-1.3
n-Octane	C8	126	0.438	9267.2	0.99	0.9-1.1	1.01	0.8-1.3
n-Nonane	C9	151	0.726	9495.9	1.01	0.9-1.1	1.00	0.8-1.3
n-Decane	C10	174	1.085	9362.1	1.00	0.9-1.1	0.98	0.8-1.3
n-Undecane	C11	196	1.469	9314.8	0.99	0.9-1.1	0.98	0.8-1.3
n-Dodecane	C12	216	1.852	9318.9	1.00	0.9-1.1	0.97	0.8-1.3
n-Tetradecane	C14	254	2.573	9379.6	1.00	0.9-1.1	0.97	0.8-1.3
n-Pentadecane	C15	271	2.907	9318.7	1.00	0.9-1.1	0.96	0.8-1.3
n-Hexadecane	C16	287	3.224	9363.1	1.00	0.9-1.1	0.97	0.8-1.3
n-Heptadecane	C17	302	3.524	9344.4	1.00	0.9-1.1	0.97	0.8-1.3
n-Octadecane	C18	316	3.811	9363.9	1.00	0.9-1.1	0.96	0.8-1.3
n-Eicosane	C20	344	4.344	9355.8	1.00	0.9-1.1	0.96	0.8-1.3
n-Tetracosane	C24	391	5.28	9520.4	1.02	0.9-1.1	0.98	0.8-1.3
n-Octacosane	C28	431	6.081	9374.2	1.00	0.9-1.1	0.97	0.8-1.3
n-Dotriacontane	C32	466	6.778	9259.2	0.99	0.9-1.1	0.98	0.8-1.3
n-Hexatriacontane	C36	496	7.394	9253.6	0.99	0.9-1.1	0.98	0.8-1.3
n-Tetracontane	C40	522	7.946	9252.5	0.99	0.9-1.1	0.97	0.8-1.3
n-Tetratetracontane	C44	545	8.445	9277.6	0.99	0.9-1.1	0.97	0.8-1.3

When plotting retention times against boiling points, it is typical to observe a curve that is nonlinear for the first four paraffins (C5-C8), but the plot must be linear from C9-C44. Figure 4 illustrates the performance of the method under the conditions and the setup used in this study. The results show the expected performance for D2887 analysis.

If the GC oven had not been able to achieve or maintain the necessary temperature program, the variation would result in a nonlinear curve, especially for the later eluting compounds where the temperature lag would be more pronounced. The agreement shown is further evidence that the novel use of the GC Accelerator plate insert upgrades performance to meet the accelerated method conditions, allowing labs to speed up their D2887 analyses using the thoroughly vetted and approved method conditions found in Procedure B with their existing 100/120 V GC oven.

Figure 4: Boiling point/retention time dependency of normal paraffins obtained from the D2887 analysis shown in Figure 3. This calibration curve has a typical SimDist profile—a nonlinear portion for the first four paraffins, followed by a linear response across the rest of the calibration range. Any deviation from the linear oven heating rate would be observed on the calibration curve.



Analysis of Reference Gas Oil (RGO) Sample

Using the certified RGO sample and the Dragon SimDist software package, the setup was evaluated to determine if it would produce results that agreed with the published boiling points, which is required by the method to evaluate a system prior to the analysis of test samples. An initial instrument blank was also collected to demonstrate system cleanliness.

Figure 5 illustrates the chromatogram from D2887 analysis of the RGO sample using the GC Accelerator plate with data analysis performed by the software package overlaid. Table III shows the passing results from the analysis, demonstrating that the GC Accelerator plate insert allowed the 100/120 V GC oven to meet the method requirements.

Figure 5: Overlay of blank (blue) and RGO (green) D2887 analyses using the conditions from Table I. The overlay is from the Dragon SimDist software, labeled with a determination of initial boiling point (IBP) and final boiling point (FBP). The red curve is the distillation curve generated from the data points.

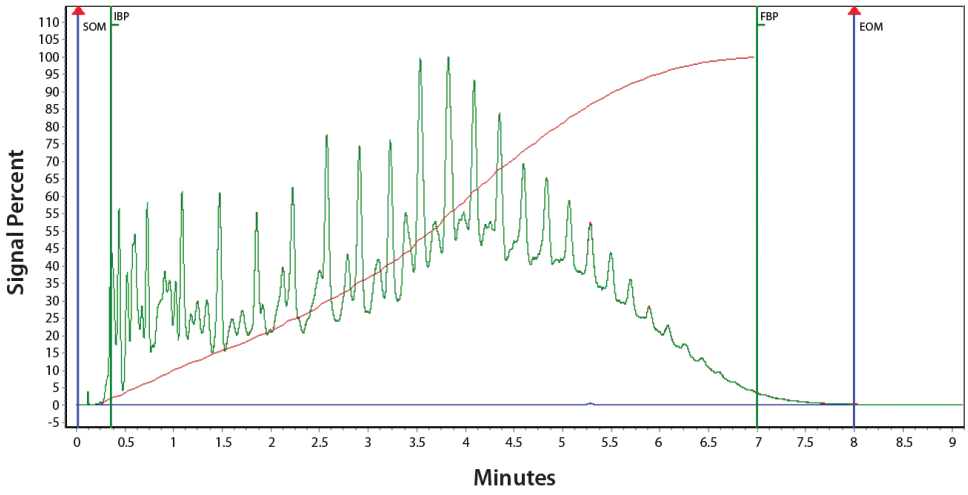


Table III: Dragon SimDist report of D2887 analysis of RGO sample. All the percent mass increments are in good agreement and within the permitted deviation range from the certified RGO values.

Reference Gas Oil QC Detail - Type: RGO, Lot# 2					
Percent Off	**Certified BP Temp (°C)**	**Temp Window (°C)**	**Actual BP Temp (°C)**	**Variance**	**Result**
IBP	115.556	7.611	113.961	-1.594	-PASSED-
10	175.556	4.111	174.216	-1.340	-PASSED-
20	223.889	4.833	222.207	-1.682	-PASSED-
30	259.444	4.667	258.292	-1.152	-PASSED-
40	288.889	4.278	288.846	-0.043	-PASSED-
50	312.222	4.278	311.961	-0.262	-PASSED-
60	331.667	4.278	331.19	-0.477	-PASSED-
70	353.333	4.278	353.626	0.293	-PASSED-
80	377.778	4.278	378.145	0.367	-PASSED-
90	406.667	4.278	407.524	0.857	-PASSED-
95	428.333	4.278	429.713	1.380	-PASSED-
FBP	475.556	11.778	476.986	1.431	-PASSED-

Method Precision (Repeatability)

The method's repeatability was measured from nine replicate injections of RGO oil and a coefficient of variation was calculated from these values. A coefficient of variation, or relative standard deviation, is expressed as the standard deviation divided by the average of data set in percent. The data set, shown in Table IV, resulted in a spread below 0.5%, which demonstrates acceptable method precision.

Table IV: Dragon SimDist values for nine replicate injections of RGO with calculated standard deviations and relative standard deviations.

Percent Off	Certified BP Temp (°C)	Temp Window (°C)	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Std. Dev.	% RSD
0.5	115.6	7.6	114.0	114.9	114.7	115.2	114.2	115.0	114.0	115.3	115.5	0.6	0.5
10	175.6	4.1	174.2	175.7	175.1	176.0	175.1	175.9	174.9	175.6	176.0	0.6	0.3
20	223.9	4.8	222.2	225.1	223.9	225.5	224.6	225.5	224.1	224.5	225.3	1.1	0.5
30	259.4	4.7	258.3	260.5	259.6	260.9	260.2	260.8	259.8	260.0	260.7	0.8	0.3
40	288.9	4.3	288.9	290.0	289.5	290.3	289.9	290.2	289.7	289.8	290.2	0.5	0.2
50	312.2	4.3	312.0	312.7	312.4	312.9	312.7	312.9	312.6	312.6	312.9	0.3	0.1
60	331.7	4.3	331.2	331.5	331.5	331.7	331.6	331.6	331.5	331.5	331.6	0.1	0.0
70	353.3	4.3	353.6	354.0	353.9	354.2	354.1	354.1	354.0	354.0	354.1	0.2	0.0
80	377.8	4.3	378.2	378.4	378.4	378.5	378.5	378.5	378.4	378.4	378.5	0.1	0.0
90	406.7	4.3	407.5	407.6	407.6	407.8	407.8	407.7	407.7	407.7	407.7	0.1	0.0
95	428.3	4.3	429.7	429.8	429.8	429.9	429.9	429.9	429.9	429.9	429.9	0.1	0.0
99.5	475.6	11.8	477.0	477.1	477.3	477.1	477.2	477.1	477.2	477.2	477.2	0.1	0.0

Conclusion

A novel use of the GC Accelerator oven insert kit in an Agilent instrument with a 120 V oven upgraded the instrument's performance to achieve the accelerated D2887-16 Procedure B method conditions where the oven ramp rate is 35 °C/min from 40 °C to 350 °C. All the method requirements were met in for the D2887 analyses performed, making this a viable option for labs wanting to take advantage of a faster 9-minute analysis time, while still using the industry-accepted method conditions established in ASTM method D2887-16.

References

[1] ASTM D2887-16a, Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography, ASTM International, West Conshohocken, PA, 2016. https://www.astm.org/Standards/D2887.htm

ASTM D2887-12 Calibration Standard (20 components)

Designed to serve as a column resolution text mixture, as well as a calibration mixture for retention time (RT) versus boiling point (bp) calibration.

American Society for Testing and Materials (ASTM International) Method D2887-12 is used to determine the boiling range distribution of petroleum products and fractions having a final boiling point of 538 °C (1,000 °F) or lower, a boiling range greater than 55 °C (131 °F), and a vapor pressure sufficiently low to permit sampling at ambient temperature.

Certified reference materials (CRMs) manufactured and QC-tested in ISO-accredited labs satisfy your ISO requirements.

(C5) *n*-Pentane (109-66-0)
(C6) *n*-Hexane (110-54-3)
(C7) *n*-Heptane (142-82-5)
(C8) *n*-Octane (111-65-9)
(C9) *n*-Nonane (111-84-2)
(C10) *n*-Decane (124-18-5)
(C11) *n*-Undecane (1120-21-4)
(C12) *n*-Dodecane (112-40-3)
(C14) *n*-Tetradecane (629-59-4)
(C15) *n*-Pentadecane (629-62-9)
(C16) *n*-Hexadecane (544-76-3)
(C17) *n*-Heptadecane (629-78-7)
(C18) *n*-Octadecane (593-45-3)
(C20) *n*-Eicosane (112-95-8)
(C24) *n*-Tetracosane (646-31-1)
(C28) *n*-Octacosane (630-02-4)
(C32) *n*-Dotriacontane (544-85-4)
(C36) *n*-Hexatriacontane (630-06-8)
(C40) *n*-Tetracontane (4181-95-7)
(C44) *n*-Tetratetracontane (7098-22-8)

1% w/w in carbon disulfide, 1 g solution/ampul	cat.# 31674 (ea.)

No data pack available.

Topaz 2.0 mm ID Single Baffle CIS4/TDU Inlet Liner for Agilent GCs equipped with CIS4/PTV inlets

ID x OD x Length	qty.	cat.#
Single Baffle, Premium Deactivation, Borosilicate Glass		
2.0 mm x 3.0 mm x 78 mm	10-pk.	23283

* 100% SATISFACTION GUARANTEE: If your Topaz inlet liner does not perform to your expectations for any reason, simply contact Restek Technical Service or your local Restek representative and provide a sample chromatogram showing the problem. If our GC experts are not able to quickly and completely resolve the issue to your satisfaction, you will be given an account credit or replacement product (same cat.#) along with instructions for returning any unopened product. (Do not return product prior to receiving authorization.) For additional details about Restek's return policy, visit **www.restek.com/warranty**

GC Accelerator Oven Insert Kit

for Agilent 6890 and 7890 instruments

- Get the same GC separation in less time—use a GC Accelerator kit and the *EZ*GC method translator to accurately convert methods to a scaled-down column format.
- Scaled-down methods let you speed up analysis time and increase sample throughput without capital investment.
- GC Accelerator kit installs easily without damaging the GC column or interfering with the MS interface.

Designed with GC-MS users in mind, the GC Accelerator kit provides a simple way to speed up sample analysis. By reducing oven volume, these inserts allow faster ramp rates to be attained, which reduces oven cycle time and allows for increased sample throughput and more capacity to process rush samples. When faster ramp rates are used, existing methods can be accurately scaled down to smaller, high-efficiency, narrow-bore columns using Restek's *EZ*GC method translator. With a scaled-down column, a properly translated method, and a GC Accelerator kit, you can obtain the same chromatographic separation—often with greater sensitivity—in a fraction of the time without making a capital investment.

Description	qty.	cat.#
GC Accelerator Oven Insert Kit for Agilent 6890 and 7890 instruments	kit	23849

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