

The Analysis of Monocyclic Aromatic Hydrocarbons by ASTM D7504 on the Agilent 8850 GC System

Conventional and high-speed approaches using helium or hydrogen carrier gas

Author

Scott Hoy
Agilent Technologies, Inc.

Abstract

This application note highlights the speed and precision of the Agilent 8850 single-channel GC applied to both a conventional separation (39 minutes) and fast separation (6.05 minutes) of common aromatic contaminants described in ASTM D7504.¹ Also shown is the use of the Agilent method translator software to convert the conventional method into the fast method for users interested in exploring additional variations of ASTM D7504. The precision of both methods was evaluated using three different purchased standard mixtures analyzed over 20 consecutive replicate injections each. The system yielded excellent precision for both methods with calculated concentration RSDs below 1.0% for all non-trace-level compounds. The fast method yielded a benzene peak in the *p*-xylene standard with an average ($n = 20$) RMS signal-to-noise ratio (S/N) of 60 at a concentration of 14 ppmw, indicating an approximate benzene MDL of less than 1.0 ppmw.

Introduction

ASTM D7504 is a landmark method in the global chemicals industry for both quality control of finished products and process control of feed and intermediate streams. The method establishes the purity of the simplest monocyclic aromatic hydrocarbon species, including benzene, toluene, ethylbenzene, and the xylene isomers. These compounds are widely used in fuels, as solvents, and as building blocks to produce more-specialized chemicals and materials. The key challenge of ASTM D7504 is the separation of the small ethylbenzene and *m*-xylene peaks from the large *p*-xylene peak in bulk *p*-xylene samples.

This application note explores the analysis of monocyclic aromatic hydrocarbons by ASTM D7504 through two different approaches using the Agilent 8850 GC. The first approach follows a conventional application using helium carrier gas and a long column with a thick polyethylene glycol (or "wax") phase and a total run time of 39 minutes. Examples of this

and other similar approaches have been previously published using the Agilent 6850, 8860, 8890, and 9000 GCs.²⁻⁵ The second approach is a faster method that uses hydrogen carrier gas and a shorter and narrower wax column to yield a total run time of 6.05 minutes. The fast method maintains sufficient resolution of the ethylbenzene/*p*-xylene/*m*-xylene triplet without sacrificing method precision.

Designed after the classic Agilent 6850 GC but leveraging the latest technology, the Agilent 8850 GC features a single powerful channel in the same small footprint. The aromatic solvent purity methods were popular applications on the 6850 because the small footprint enabled labs to increase their sample throughput while maintaining true instrument redundancy. In the development of this application note, the conventional separation was initially developed on a 6850 GC before being further refined on the 8850 GC, and Figure 1 shows the separation of the *p*-xylene check standard (described in the Experimental section) on both instruments.

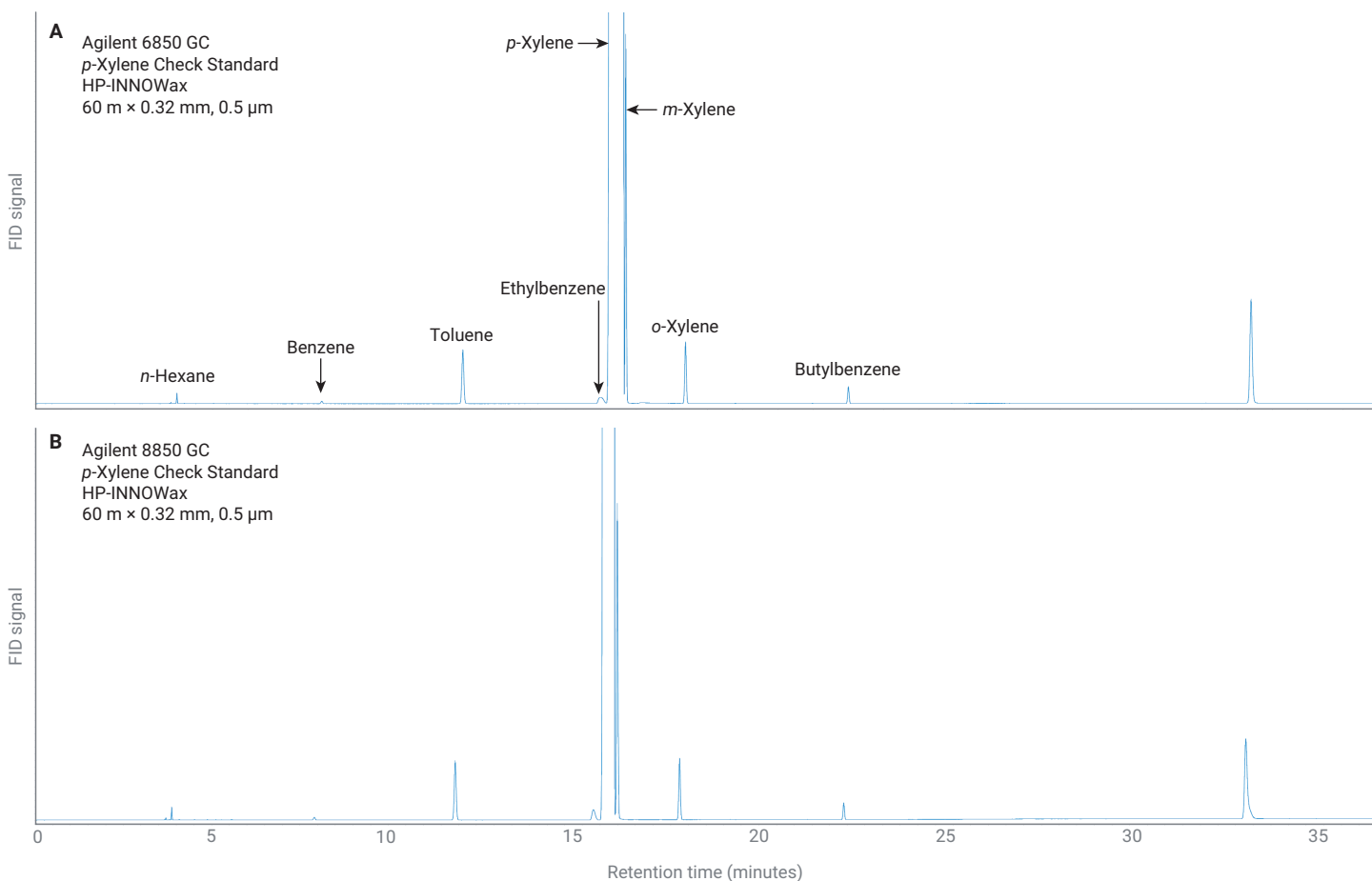


Figure 1. Chromatograms of the *p*-xylene check standard analyzed on the Agilent 6850 GC (A) and the Agilent 8850 GC (B).

The 8850 GC combines a small-volume column oven with the same sixth-generation electronic pneumatic control (EPC) technology that drives the flagship 8890 GC. This combination of thermal agility and pneumatic precision enables the 8850 GC to greatly accelerate conventional methods. It also comes with the full slate of GC Intelligence features present in the Agilent 8890 and 9000 Intuvo GCs, including Blank Evaluation and Peak Evaluation, which can aid in warning users of degrading chromatographic conditions, and Early Maintenance Feedback (EMF) counters that can track the number of injections and time elapsed since maintenance was last performed. These features help users not only achieve success, but also sustain performance to extend instrument uptime.

The EMF counters on the 8850 GC are particularly useful for fast methods where inlet consumables (such as septa and liners) experience more wear over a given time owing to the enhanced throughput. Figure 2 shows the EMF counter tracking liner injections with the option to enable a popup warning on the GC when a time or injection limit is reached. These counters come preconfigured with recommended limits for Agilent-brand consumables and can be changed by the user for their specific needs. The EMF trend plots are accessible through both the GC front touch panel and the browser interface, and in OpenLab CDS.

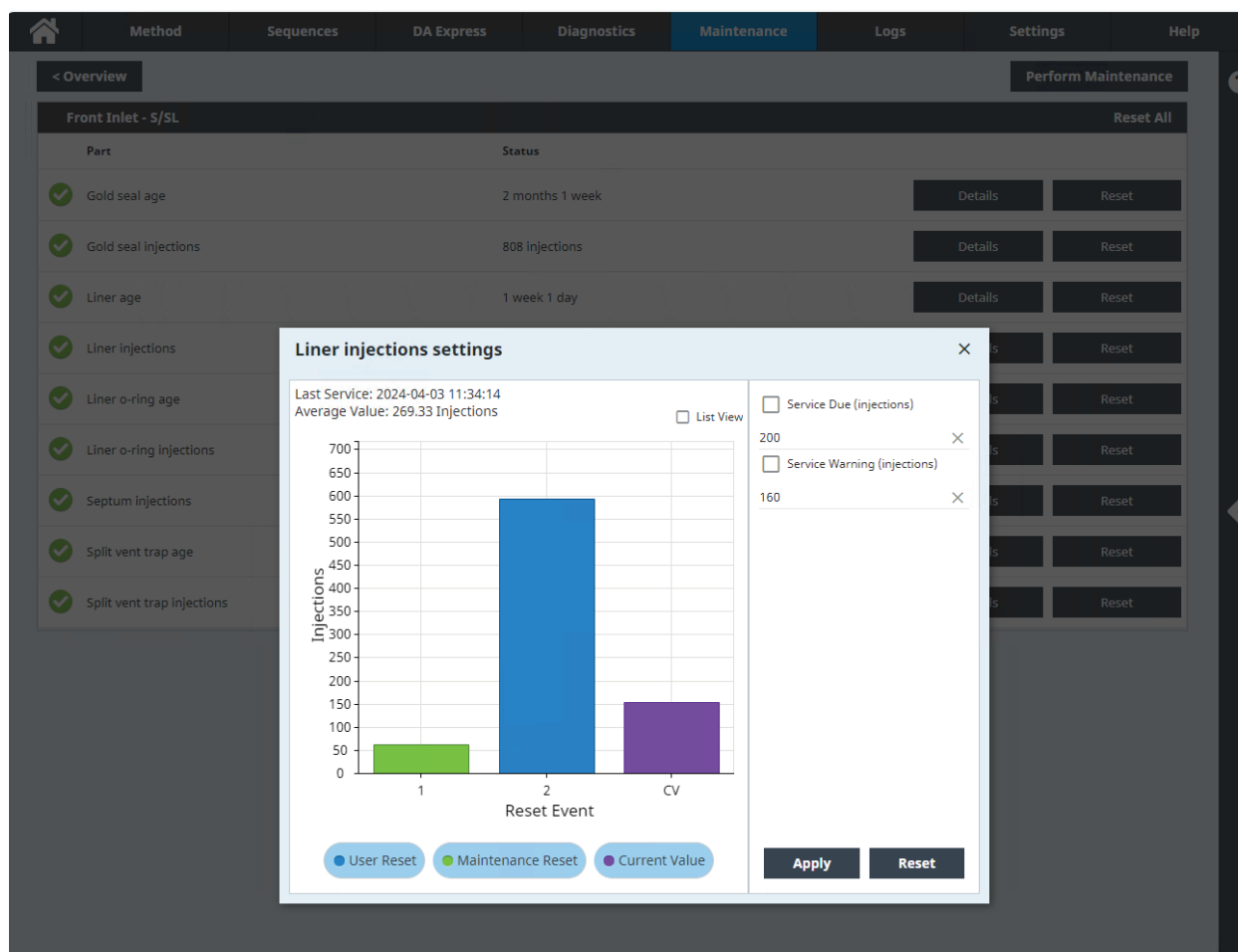


Figure 2. EMF counter tracking inlet liner age by number of injections since the last liner replacement on the Agilent 8850 GC.

In addition to instrument performance insights, the 8850 GC also tracks energy and gas consumption. Figures 3 and 4 show examples of trend plots of helium consumption and power usage each day during part of the development of this application note. It is not uncommon for quality control

laboratories running ASTM D7504 to dedicate many GCs to the method for increased redundancy and throughput, and power and gas consumption data on a per-GC level can help quickly identify potential outlier behavior for investigation.

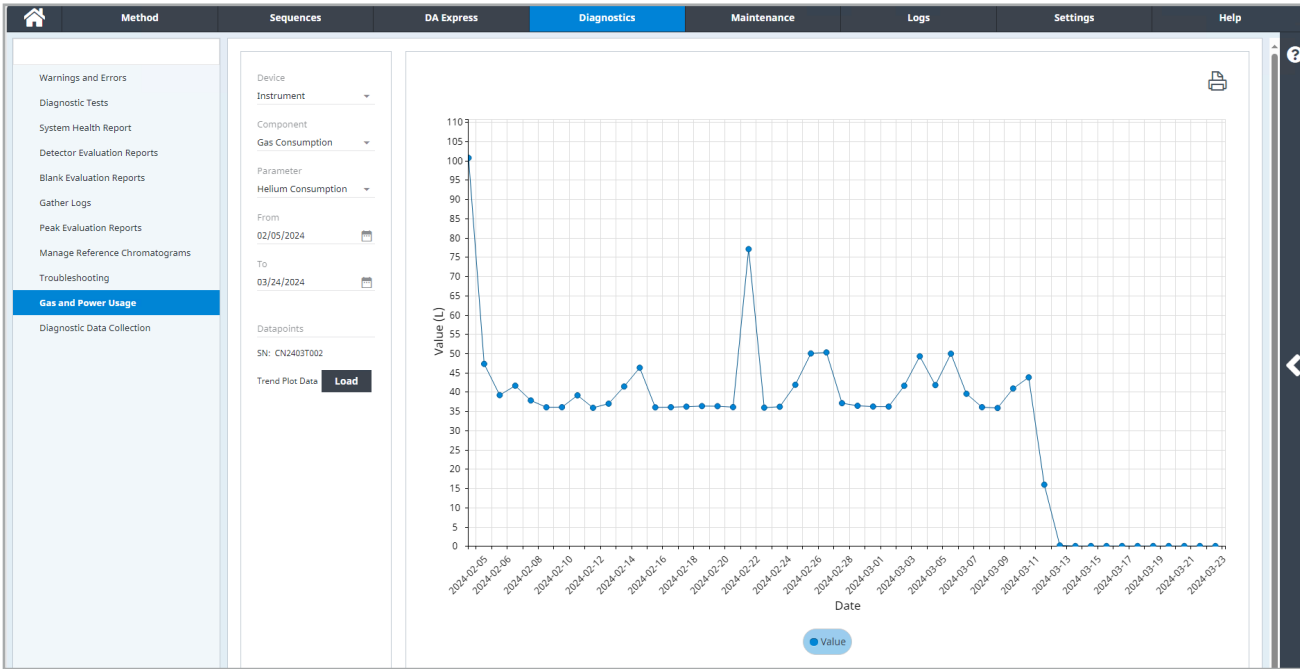


Figure 3. Daily gas consumption (helium) of the Agilent 8850 GC used during development of this application note. 2024-03-13 shows the drop in He consumption as method development transitioned to focusing on H₂ carrier gas.

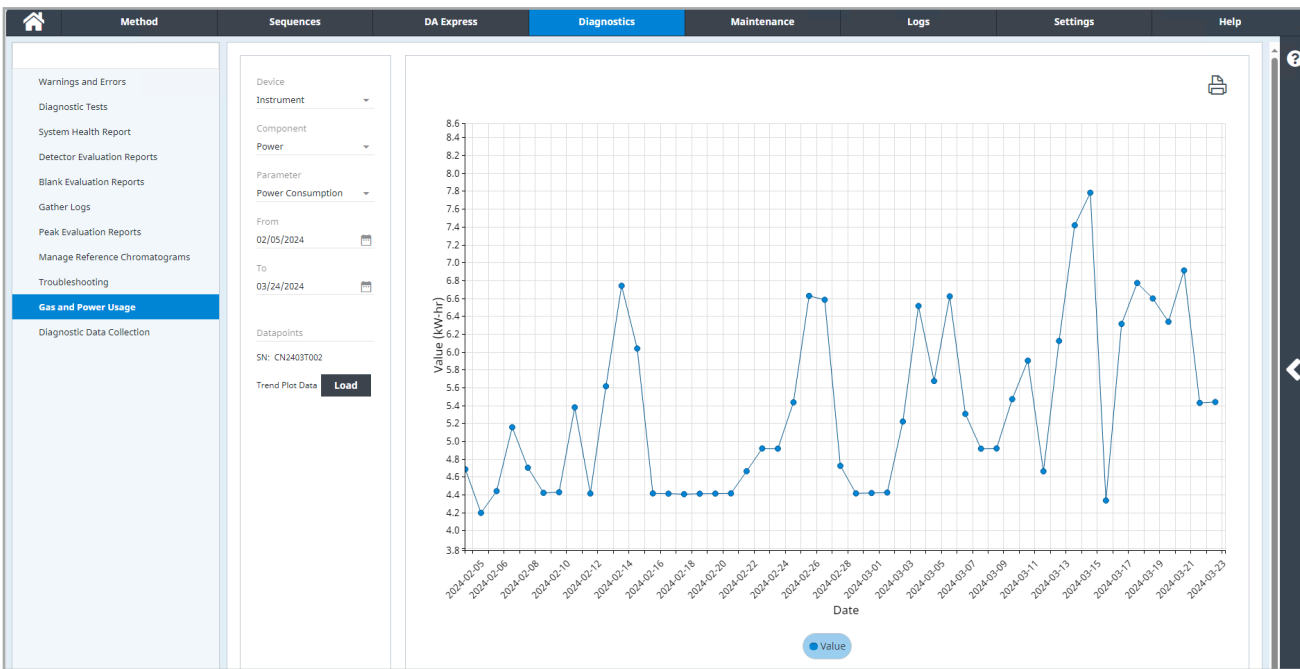


Figure 4. Daily power consumption of the Agilent 8850 GC used during development of this application note.

Experimental

An 8850 GC was configured with an Agilent 7650A autosampler, split/splitless (SSL) inlet, and a flame ionization detector (FID). The conventional method used an Agilent HP-INNOWax, 60 m × 0.32 mm, 0.5 µm column (part number 19091N-2161E) and helium carrier gas; the fast method used a 20 m × 0.18 mm, 0.18 µm HP-INNOWax column (part number 19091N-5771E) and hydrogen carrier gas. Instrument configuration and consumables for both methods can be found in Table 1; method parameters for both methods can be found in Table 2.

Check standards containing common contaminants for benzene, toluene, and *p*-xylene were purchased from Spectrum Quality Standards (part number 7504CK-BZ, 7504CK-T, and 7504CK-PX, respectively); their compositions are shown in Table 3. A precision study was conducted for both the conventional and fast method, consisting of twenty consecutive replicate injections of each check standard. Data acquisition and analysis were conducted using Agilent OpenLab CDS 2.7.

Table 1. Instrument configuration and consumables for the conventional and fast methods.

Configuration		
	Conventional Method	Fast Method
Sampler	Agilent 7650A Automated Liquid Sampler (ALS)	Agilent 7650A Automated Liquid Sampler (ALS)
Inlet	Split/Splitless	Split/Splitless
Column	Agilent HP-INNOWax, 60 m × 0.32 mm, 0.5 µm (p/n 19091N-2161E)	Agilent HP-INNOWax, 20 m × 0.18 mm, 0.18 µm (p/n 19091N-5771E)
Detector	FID	FID
Carrier Gas	Helium	Hydrogen
Consumables		
Inlet Septa	Agilent Nonstick Advanced Green (p/n 5183-4759)	
Inlet Liner	Agilent Ultra-Inert, low pressure drop split liner with glass wool (p/n 5190-2295)	
ALS Syringe	Agilent Blue Line, 5 µL, fixed needle, 23-26s/42/cone (p/n G4513-80206)	
Carrier Gas Filter	Agilent Gas Clean purifier kit for carrier gas, 1/8 in (p/n CP17976)	
FID Gas Filter	Agilent Gas Clean purifier kit for FID, 1/8 in (p/n CP736530)	

Table 2. Method parameters for the conventional and fast methods.

	Conventional Method	Fast Method
Run Time	39 minutes	6.05 minutes
ALS and Inlets		
Carrier Gas	Helium, 2.1 mL/min constant flow	Hydrogen, 1.5 mL/min constant flow
Septum Purge	3 mL/min	6 mL/min
Injection Volume	0.6 µL	0.2 µL
Mode	Split, 100:1	Split, 500:1
Temperature	260 °C	260 °C
Oven Program		
Initial Temperature	60 °C	50 °C
Initial Hold	10 minutes	1 minute
Ramp 1 Rate	5 °C/min	40 °C/min
Ramp 1 Setpoint	150 °C	100 °C
Ramp 1 Hold	–	–
Ramp 2 Rate	50 °C/min	50 °C/min
Ramp 2 Setpoint	200 °C	240 °C
Ramp 2 Hold	10 minutes	1 minute
Detector		
Data Rate	20 Hz	50 Hz
Temperature	260 °C	260 °C
Air	400 mL/min	400 mL/min
Hydrogen	30 mL/min	30 mL/min
Make-up (N ₂)	25 mL/min	25 mL/min

Table 3. Compositional breakdown of benzene, toluene, and *p*-xylene check standards.

	Benzene Check Standard	Toluene Check Standard	<i>p</i> -Xylene Check Standard
Concentration (ppmw)			
<i>n</i> -Hexane	502	–	27
Benzene	Balance	159	14
Toluene	102	Balance	320
1,4-Dioxane	10	–	–
Ethylbenzene	–	205	85
<i>p</i> -Xylene	50	97	Balance
<i>m</i> -Xylene	50	108	1,251
Cumene	10	–	–
<i>o</i> -Xylene	30	10	296
Propylbenzene	202	24	–
Butylbenzene	100	–	74

Results and discussion

Conventional D7504 method

Figure 5 shows the separation of all three check standards using the conventional method configuration with a 60 m × 320 μm, 0.5 μm HP-INNOWax column. This method successfully elutes all compounds in the benzene, toluene, and *p*-xylene standards in approximately 23 minutes. Two additional peaks are present at the end of the *p*-xylene chromatogram due to the tendency of *p*-xylene to slowly oxidize in air. These oxidative products can carry over into successive runs as "ghost peaks", along with other potential

contaminants in the sample, if not completely eluted before the next injection. To help counteract potential carryover, the oven was ramped beyond the normal method final temperature of 150 °C. This was accomplished by removing the 10-minute hold at 150 °C and instead quickly ramping the oven from 150 to 200 °C at 50 °C/min and holding at 200 °C for 10 minutes. Note that this application note was developed using a 120 V model 8850 GC; the 230 V model offers even faster oven ramp rates. Despite this difference, the 120 V Agilent 8850 GC handles the fast ramp with excellent precision as evidenced by the retention time repeatability of the large contaminant peak at 31 minutes (0.0018% RSD, n = 20).

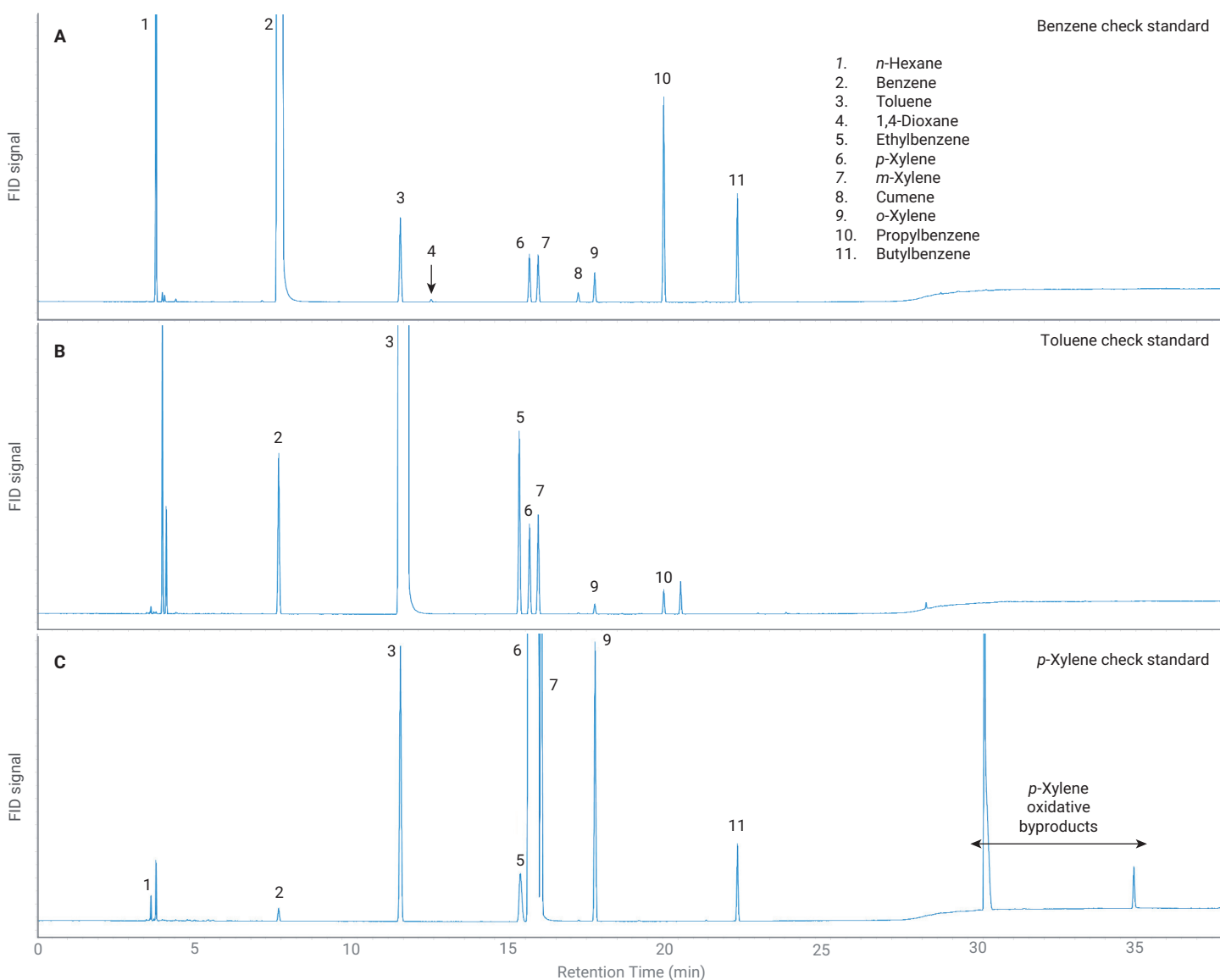


Figure 5. Conventional method separation of the benzene (A), toluene (B), and *p*-xylene (C) check standards.

A precision study was conducted to evaluate the repeatability of the method by injecting twenty consecutive replicates of each check standard with blank injections between each group of replicates. The results of the precision study are shown in Table 4. Light aromatic molecules can be challenging to analyze with precision due to their relatively high vapor pressures and susceptibility to swings in the local environmental conditions. This can result in increased variability in the amount of sample injected by the

autosampler, as evidenced by the higher peak area %RSD results for the compounds in the benzene check standard compared to the toluene and *p*-xylene check standards. ASTM D7504 uses a normalized quantification process, which helps overcome this challenge, and the resulting precision of the calculated concentration results is less than 1.0 %RSD for all non-trace molecules in all three standards with *n* = 20 replicate measurements per standard.

Table 4. Results of the conventional method precision study.

	Benzene Check Standard (n = 20)					
	Concentration (ppmw)	Average RMS S/N	RT Average (min)	RT %RSD	Peak Area %RSD	%Mass %RSD
<i>n</i> -Hexane	502	17,235	3.8885	0.011	2.88	0.72
Benzene	Balance	9,721,787	8.0008	0.0274	2.85	0.00
Toluene	102	1,304	11.8929	0.0158	2.81	0.32
1,4-Dioxane	10	44	12.9036	0.0277	2.37	2.73
<i>p</i> -Xylene	50	739	16.1223	0.0087	2.81	0.37
<i>m</i> -Xylene	50	729	16.407	0.008	2.68	0.55
Cumene	10	152	17.7228	0.0073	2.19	1.40
<i>o</i> -Xylene	30	459	18.2612	0.0067	2.61	0.81
Propylbenzene	202	3,187	20.5218	0.0046	2.82	0.64
Butylbenzene	100	1,711	22.9378	0.0033	2.87	0.77
	Toluene Check Standard (n = 20)					
	Concentration (ppmw)	Average RMS S/N	RT Average (min)	RT %RSD	Peak Area %RSD	%Mass %RSD
Benzene	159	2,506	7.9078	0.008	1.54	0.41
Toluene	Balance	5,376,842	12.1279	0.0123	1.57	0.00
Ethylbenzene	205	2,919	15.7896	0.0059	1.66	0.29
<i>p</i> -Xylene	97	1,404	16.1265	0.0067	1.65	0.28
<i>m</i> -Xylene	108	1,568	16.4113	0.0062	1.65	0.33
<i>o</i> -Xylene	10	165	18.2643	0.0059	1.36	0.77
Propylbenzene	24	388	20.5246	0.0035	1.73	0.73
	<i>p</i> -Xylene Check Standard (n = 20)					
	Concentration (ppmw)	Average RMS S/N	RT Average (min)	RT %RSD	Peak Area %RSD	%Mass %RSD
<i>n</i> -Hexane	27	921	3.8885	0.0166	1.00	0.94
Benzene	14	199	7.906	0.0123	0.84	0.81
Toluene	320	4,130	11.8959	0.0099	0.78	0.49
Ethylbenzene	85	732	15.8226	0.0196	0.75	0.17
<i>p</i> -Xylene	Balance	4,600,116	16.3998	0.0122	0.76	0.00
<i>m</i> -Xylene	1,251	21,670	16.5071	0.0061	0.78	0.10
<i>o</i> -Xylene	296	4,258	18.2729	0.0044	0.77	0.10
Butylbenzene	74	1,164	22.9403	0.0023	0.84	0.29

Fast D7504 method

While the 8850 GC brings value to conventional D7504 methodology, its true potential is revealed when applied to a more challenging separation. By increasing the oven ramp rate, reducing the oven hold times, and using hydrogen instead of helium as carrier gas, the ASTM D7504 separation can be greatly accelerated. Faster oven ramp rates do result in a reduction in resolution that must be offset to ensure acceptable separation of the ethylbenzene/*p*-xylene/*m*-xylene region. This was accomplished by decreasing the column internal diameter from 320 μm to 180 μm , which greatly increases the efficiency of the separation (the peaks get sharper) and, by extension, the overall resolution. The impact of sharper peaks on increasing resolution can be large enough that column length can also be reduced to further speed up the method.

To aid users in navigating the impact of changing columns and method parameters, Agilent provides the method translator along with other additional useful GC calculators with every GC system, and they are also available to be downloaded online. The method translator (Figure 6) allows a user to input their existing method parameters, column attributes, carrier gas, and oven program steps, and calculate the appropriate parameters that will yield a nearly identical separation when using a different column and carrier gas. In addition to a raw translation, the method translator can also output method parameters to yield a desired speed gain or to maximize separation efficiency (peak sharpness). Figure 6 shows the method translator being used to convert the conventional D7504 method parameters to a faster method using hydrogen carrier gas and a 20 m \times 0.18 μm HP-INNOWax column.

Method Translator

Speed gain: 10.2294

Translate

Best Efficiency

Last file imported:

Original Method Parameters

Gas: He

Calculated Method Parameters

Gas: H2

Parameter	Original Method Parameters	Calculated Method Parameters
Length (m)	60 m	20 m
Inner Diameter (μm)	320 μm	180 μm
Film Thickness (μm)	0.50 μm	0.18 μm
Phase Ratio	159.25	249.25
Inlet Pressure (gauge)	17.587 psi	18.311 psi
Outlet Flow (mL/min)	2.1 mL/min	1.4766 mL/min
Average Velocity (cm/s)	29.248 cm/sec	63.72 cm/sec
Outlet Pressure (abs)	14.696 psi	14.696 psi
Holdup Time	3.419 min	0.52313 min
Outlet Velocity (cm/s)	48.628 cm/sec	108.06 cm/sec

#	Ramp Rate ($^{\circ}\text{C}/\text{min}$)	Final Temp ($^{\circ}\text{C}$)	Final Time (min)
Init		60	10
1	5	150	0
2	50	200	10

Total Run Time: 39.00 min

#	Ramp Rate ($^{\circ}\text{C}/\text{min}$)	Final Temp ($^{\circ}\text{C}$)	Final Time (min)
Init		60	0.98
1	51.147	150	0
2	511.47	200	0.98

Total Run Time: 3.82 min

Pressure Units: PSI

Original Column Capacity: 7.01

Translated Column Capacity: 0.61

The column capacity of the translated method is 9% of the original column capacity. You may need to adjust your injection volume.

Figure 6. The Agilent method translator converts the conventional method parameters to yield the same separation using a different column and hydrogen carrier gas.

The method translator shows a new total run time of 3.82 minutes, approximately ten times faster than conventional D7504. By rounding the translated oven ramp rate to 50 °C/min, rounding the initial and final hold times to 1 minute each, and reducing the new bakeout rate from 511.47 °C/min back down to 50 °C/min, the oven program can be simplified to a single ramp yielding a new total run

time of 4.8 minutes. Further tuning of these parameters was done to enhance the *p*-xylene/*m*-xylene separation by slowing the ramp during their elution window. Additionally, the final oven temperature was raised to 240 °C to help elute potential contaminants. The final method parameters are shown in Table 2, and the resulting check standard separations are shown in Figure 7.

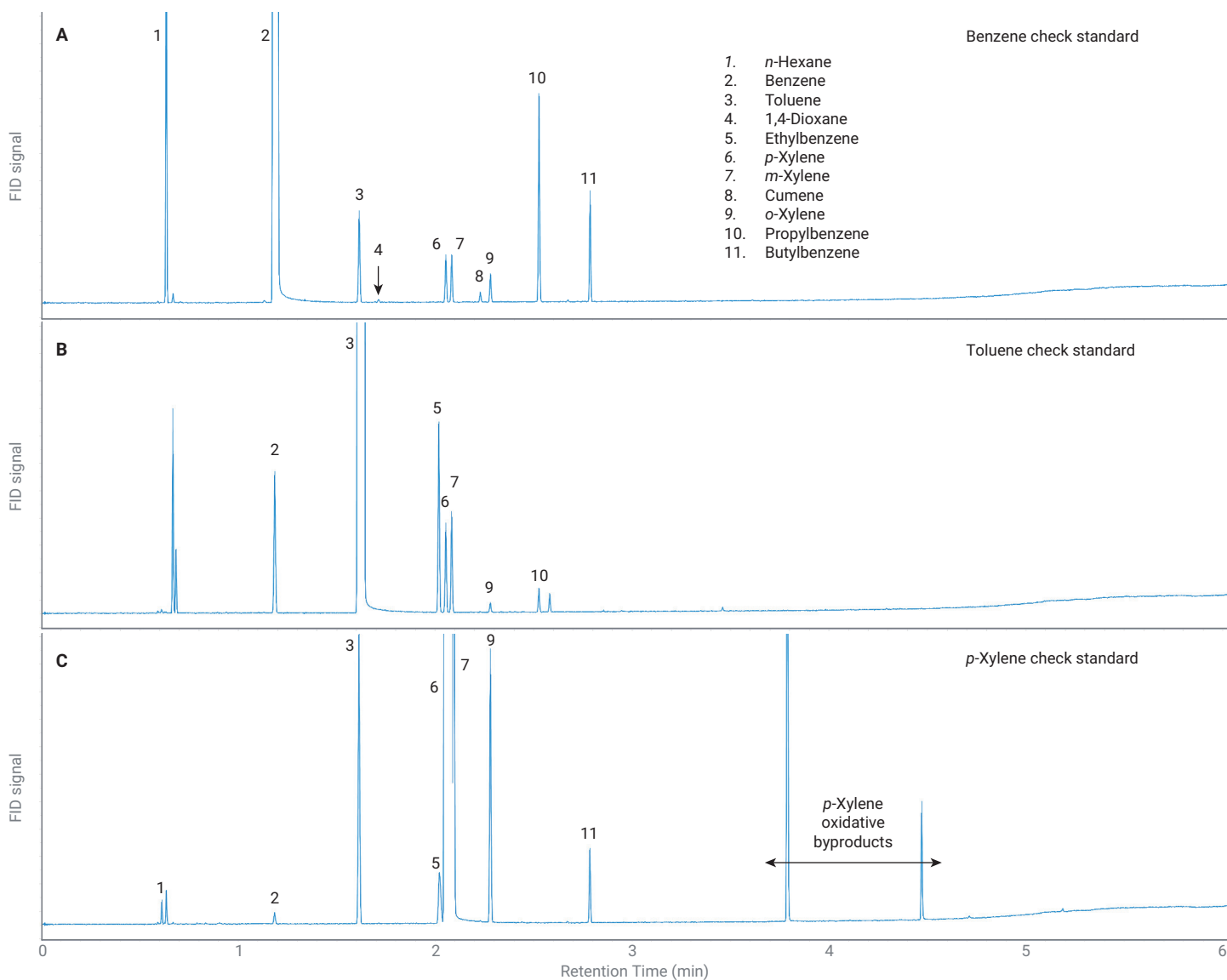


Figure 7. Fast method separation of the benzene (A), toluene (B), and *p*-xylene (C) check standards.

A key parameter output by the method translator is the translated column capacity. This is crucial to successfully separating the ethylbenzene/*p*-xylene/*m*-xylene peak triplet in *p*-xylene samples. In this case, the method translator indicates the new column has 9% the capacity of the conventional method column, meaning that the fast method inlet and ALS parameters must be adjusted to inject approximately 90% less sample. This was accomplished by reducing the injection volume from 0.6 to 0.2 μ L and increasing the split ratio from 100:1 to 500:1, resulting in a 93% reduction in sample loading.

The same precision study done on the conventional method was also done on the fast method (in 1/5 of the time); the results are shown in Table 5. Except for the trace compounds, the resulting concentration precision for each compound was less than 1.0 %RSD. The direct impact of the sixth-generation EPCs and agile oven control is evident in the retention time precision of the fast method, where ethylbenzene, *p*-xylene, and *m*-xylene elute in a window of 4.3 seconds, compared to the conventional method where the elution window is 41.1 seconds.

Table 5. Results of the fast method precision study.

	Benzene Check Standard (n = 20)					
	Concentration (ppmw)	Average RMS S/N	RT Average (min)	RT %RSD	Peak Area %RSD	%Mass %RSD
<i>n</i> -Hexane	502	3,263	0.6327	0.0078	1.82	0.19
Benzene	Balance	3,010,035	1.1953	0.0313	1.76	0.00
Toluene	102	458	1.6127	0.0221	1.76	0.88
1,4-Dioxane	10.1	15	1.7117	0.0442	6.31	6.70
<i>p</i> -Xylene	50.3	241	2.0527	0.0179	1.84	1.00
<i>m</i> -Xylene	50.3	237	2.0824	0.0167	1.75	0.97
Cumene	10.1	49	2.2278	0.0176	3.59	4.13
<i>o</i> -Xylene	30.2	145	2.2792	0.0154	1.74	1.90
Propylbenzene	202	1,026	2.5258	0.0167	1.68	0.37
Butylbenzene	99.7	548	2.7848	0.0171	1.87	0.62
	Toluene Check Standard (n = 20)					
	Concentration (ppmw)	Average RMS S/N	RT Average (min)	RT %RSD	Peak Area %RSD	%Mass %RSD
Benzene	159	707	1.1837	0.024	2.09	0.46
Toluene	Balance	2,150,591	1.6349	0.0451	2.48	0.00
Ethylbenzene	205	952	2.0171	0.0205	2.35	0.26
<i>p</i> -Xylene	97.3	452	2.0527	0.0187	2.34	0.42
<i>m</i> -Xylene	108	502	2.0824	0.0181	2.36	0.39
<i>o</i> -Xylene	10	50	2.279	0.0184	2.15	1.88
Propylbenzene	24.2	122	2.5257	0.0135	2.47	0.97
	<i>p</i> -Xylene Check Standard (n = 20)					
	Concentration (ppmw)	Average RMS S/N	RT Average (min)	RT %RSD	Peak Area %RSD	%Mass %RSD
<i>n</i> -Hexane	27	169	0.633	0.0099	2.06	1.57
Benzene	14	60	1.1838	0.0338	2.12	2.03
Toluene	319.9	1,484	1.6126	0.023	2.05	0.22
Ethylbenzene	84.6	254	2.0216	0.0271	1.61	0.76
<i>p</i> -Xylene	Balance	1,857,116	2.0812	0.0422	2.06	0.00
<i>m</i> -Xylene	1,251.4	7,495	2.0938	0.0254	1.99	0.67
<i>o</i> -Xylene	296.2	1,400	2.2797	0.0173	2.00	0.16
Butylbenzene	73.9	385	2.7845	0.0136	2.08	0.48

A key highlight of the fast method precision is benzene in the *p*-xylene check standard, which is present at 14 ppmw with an average RMS S/N of 60. This indicates an approximate benzene method detection limit of 0.7 ppmw (S/N = 3) and method quantitation limit of 2.3 ppmw (S/N = 10), despite injecting 93% less sample onto the column. Figure 8 shows

the overlaid benzene peak of all 20 consecutive replicate *p*-xylene check standard injections. Users requiring more sensitivity for trace compounds can reduce the inlet split ratio to inject more at the cost of reduced resolution of the ethylbenzene/*p*-xylene/*m*-xylene triplet.

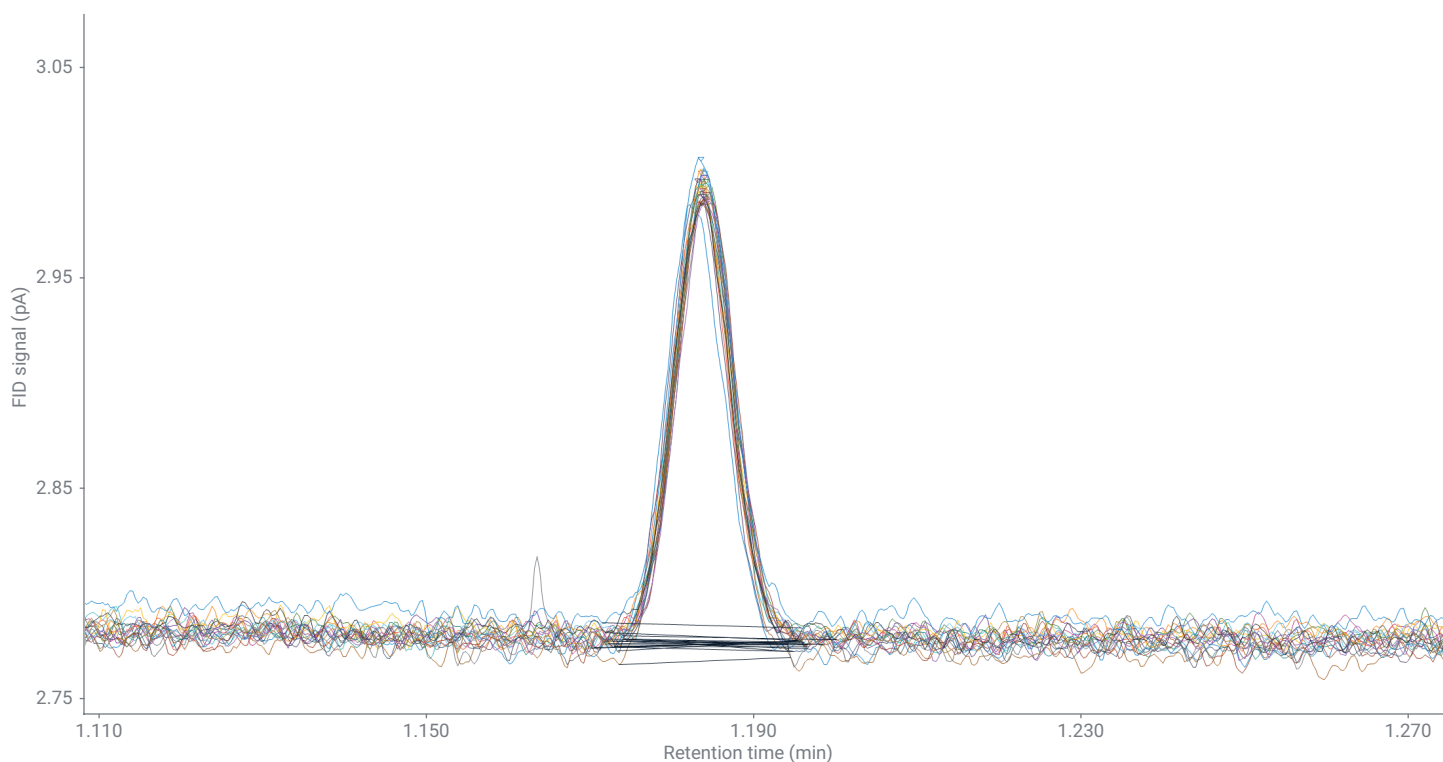


Figure 8. Overlay of 20 consecutive replicates of the fast method *p*-xylene check standard showing benzene at 14 ppmw with an average RMS S/N of 60.

Conclusion

The Agilent 8850 GC was shown to be robust and precise when applied to both a conventional approach and a high-speed adaptation of ASTM D7504. All non-trace-level components in all three standards using both methods yielded precision below 1.0% RSD across 20 consecutive replicate injections. Benzene was measured at 14 ppmw with an average RMS S/N of 199 using the conventional method and 60 using the fast method, indicating an approximate method detection limit below 1.0 ppmw for both methods. At half the width of the Agilent 8890 GC, using two Agilent 8850 GCs in the same footprint offers true independent redundancy of single-channel test methods. The full suite of GC Intelligence features on the Agilent 8850 GC facilitates enhanced remote monitoring and diagnostics of the instrument, and the Early Maintenance Feedback counters help maximize instrument uptime.

References

1. ASTM D7504-23, Standard Test Method for Trace Impurities in Monocyclic Aromatic Hydrocarbons by Gas Chromatography and Effective Carbon Number, ASTM International, West Conshohocken, PA, **2023**.
www.astm.org
2. McCurry, J. D. A Unified Gas Chromatographic Method for Aromatic Solvent Analysis, *Agilent Technologies application note*, publication number 5988-3741EN, August **2001**.
3. Zhang, Y. A Unified Method for the Analysis of Monocyclic Aromatic Solvents Using the Agilent 8860 GC System and On-Board Data Processing, *Agilent Technologies application note*, publication number 5994-1586EN, September **2022**.
4. Pan, J.; Wieder, L.; McCurry, J. Optimizing Productivity and Reliability for Monocyclic Aromatic Hydrocarbon Purity Analysis According to ASTM D7504 on the Agilent 8890 GC System, *Agilent Technologies application note*, publication number 5994-0597EN, January **2019**.
5. Chemical Purity Analysis, *Agilent Technologies application brief*, publication number 5991-7220EN, September **2016**.

www.agilent.com/gc/8850

DE65256369

This information is subject to change without notice.

© Agilent Technologies, Inc. 2024
Printed in the USA, May 15, 2024
5994-7409EN