

# Optimizing Productivity and Reliability for Monocyclic Aromatic Hydrocarbon Purity Analysis According to ASTM D7504 on the Agilent 8890 GC System

## Authors

Jie Pan, Lukas Wieder, and  
James McCurry  
Agilent Technologies, Inc.  
Wilmington, DE

## Abstract

This Application Note highlights the use of a dual-channel Agilent 8890 GC configured with two Agilent J&W DB-HeavyWAX columns for the analysis of monocyclic aromatic hydrocarbons in accordance with ASTM method D7504<sup>1</sup>. Sample throughput was increased by 100 % using dual-simultaneous injection of different samples on each GC channel. Retention time locking (RTL) was used to get precise retention time agreement on each channel, making peak identification and calibration easier and more reliable. The system demonstrates excellent separation between compounds of interest, and allows for quantification ranging from 0.0004 to 99.9787 weight %. The precision observed for replicate analysis of several different aromatic solvents exceeded ASTM repeatability requirements.

## Introduction

Monocyclic aromatic hydrocarbons are important commodity chemicals used to manufacture polymers, additives, and specialty chemicals. ASTM Committee D16 designates purity specifications for many of these chemicals. The ASTM D7405 method supports these specifications using gas chromatography (GC) to measure overall chemical purity and the concentrations of key impurities. To simplify the technique while maintaining precision, the D7504 method eliminates sample preparation and instrument calibration using Effective Carbon Number (ECN) responses. For this technique to be effective, sample components from 0.0001 to >99.9 weight % must be detected in a single run.

These analyses are often performed in manufacturing quality control laboratories, where sample throughput is as important as analysis precision. Both concerns can be addressed using dual-simultaneous injection and RTL on the 8890 gas chromatograph. A 100 % increase in sample throughput can be achieved by simultaneously running two samples on a single GC configured with two identical channels. Precision is improved by applying RTL to this method, allowing the GC to produce nearly identical retention times between each channel. This makes it easier to compare results while avoiding errors in misidentification of key impurities. Furthermore, any instrument running this method can be retention time locked, allowing direct comparison of results between labs.

## Equipment

An 8890 GC was configured with dual split/splitless inlets and dual flame ionization detectors (FIDs) to create two identical flowpaths using J&W DB-HeavyWAX columns. Sample introduction was performed using dual Agilent 7693A Automatic Liquid Samplers (ALS). Table 1 shows the details of this configuration, including consumables. Agilent OpenLab ChemStation was used for all instrument control, data acquisition, and data analysis.

## Chemicals and reagents

The following chemicals were purchased from Sigma-Aldrich (St. Louis, MO, USA): carbon disulfide (ACS reagent  $\geq 99.9\%$ ), *n*-nonane (anhydrous  $\geq 99\%$ ), toluene, 1,4-dioxane (anhydrous 99.8%), ethylbenzene (anhydrous 99.8%), *p*-xylene (HPLC grade 99+%), *o*-xylene (HPLC grade 98%), styrene (analytical standard), *m*-xylene (anhydrous 99+%), cumene (99%), 2-ethyltoluene (99%), 3-ethyltoluene (99%), 1,4-diethylbenzene (96%), butylbenzene (99+%), and 4-ethyltoluene (purity  $\geq 95.0\%$  GC).

**Table 1.** 8890 GC configuration for dual-simultaneous analysis using ASTM D7504.

Front channel	
Sampler	7693A Automated Liquid Sampler (ALS)
Inlet	Split/splitless
Column	J&W DB-HeavyWAX, 60 m $\times$ 0.320 mm, 0.25 $\mu$ m (p/n 123-7162)
Detector	FID
Back channel	
Sampler	7693A Automated Liquid Sampler (ALS)
Inlet	Split/splitless
Column	J&W DB-HeavyWAX, 60 m $\times$ 0.320 mm, 0.25 $\mu$ m (p/n 123-7162)
Detector	FID
Consumables	
Inlet septa	Nonstick Advanced Green (p/n 5183-4759)
Inlet liner	Ultra-Inert, low pressure drop split liner w/ glass wool (p/n 5190-2295)
ALS syringes	10 $\mu$ L ALS syringe, 23s/42/cone (p/n G4513-80230)
Column ferrules	Short graphite for 0.32 mm columns, 10/pk (p/n 5080-8853)

## GC operating conditions

Table 2 shows the operating conditions for these measurements. These setpoints are the same as those published in the ASTM D7504 method.

**Table 2.** Operating conditions for ASTM D7504.

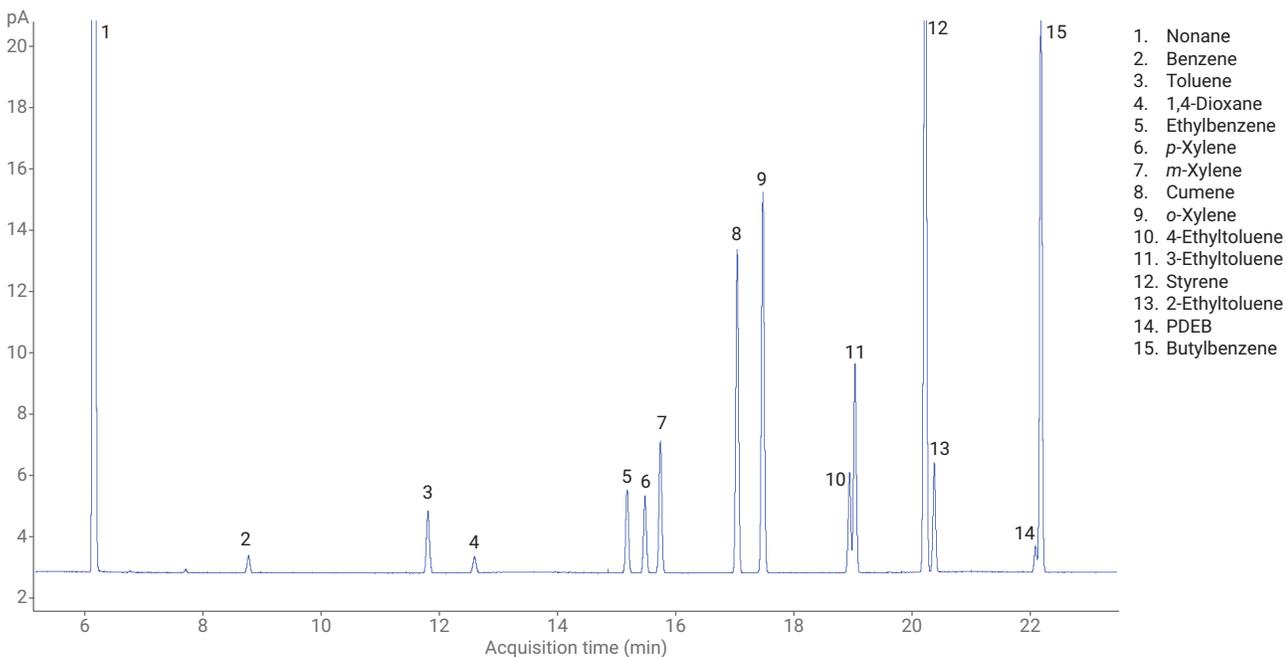
ALS and Inlets	
Sample size	0.6 $\mu$ L
Carrier gas	Helium, 1.2 mL/min constant flow
Mode	Split, split ratio 100:1
Temperature	270 $^{\circ}$ C
Oven temperature	
Initial temperature	60 $^{\circ}$ C
Initial hold time	10 minutes
Ramp rate	5 $^{\circ}$ C/min
Final temperature	150 $^{\circ}$ C
Final hold time	2 minutes
Detector	
Temperature	300 $^{\circ}$ C
Air flow	400 mL/min
Hydrogen flow	30 mL/min
Make-up ( $N_2$ ) flow	25 mL/min

## RTL calibration

An RTL calibration solution was prepared in 2 mL of carbon disulfide by adding one drop of 15 solvents: *n*-nonane, benzene, toluene, 1,4-dioxane, ethylbenzene, *p*-xylene, *m*-xylene, cumene, *o*-xylene, 4-ethyltoluene, 3-ethyltoluene, styrene, 2-ethyltoluene, *p*-diethylbenzene (PDEB), and butylbenzene. This standard was used to develop the RTL calibration, and to assess the separation of each compound.

## Results and discussion

Figure 1 shows a chromatogram of the carbon disulfide solution containing an aggregate of aromatic solvents and impurities. For most compounds, baseline resolution was achieved. Two pairs are only partially resolved. The first pair, 4-ethyltoluene and 3-ethyltoluene, are also not resolved in the ASTM method (D7504 Impurities in Ethylbenzene) and, with 2-ethyltoluene, are reported as total ethyltoluene. A second pair, PDEB and 2-butylbenzene are also only partially resolved. This does not present a problem since these two components are not typically found together in the same material.



**Figure 1.** Chromatogram of the 15 compounds analyzed by the ASTM D7504 method.

## RTL

RTL calibration was performed using *o*-xylene as the target peak. Figure 2 shows the five RTL calibration runs with the retention times of *o*-xylene indicated, and Figure 3 shows the RTL calibration table. These calibration runs do not have to be repeated by anyone wishing to lock this method on the 8890 systems. To use this RTL calibration:

- Create a new method with the conditions outlined in Table 1.
- Use the ChemStation RTL software to create new RTL calibration.
- Enter the data shown in Figure 3.

The GC can then be locked by running the sample containing *o*-xylene and using the RTL software to relock the method. The general theory and use of RTL are detailed in previous publications<sup>2,3</sup>.

Retention Time Locking Calibration

	Pressure	Ret Time
Run 1	9.44	19.619
Run 2	10.62	18.512
Run 3	11.8	17.585
Run 4	12.98	16.721
Run 5	14.16	15.973

Pressure Units: psi

Desired Ret Time: 17.585

Min relock pressure: 7

Max relock pressure: 16

Column: 2

Compound Name: *o*-xylene

OK Cancel Print Help

Figure 3. RTL calibration using *o*-xylene as the RTL target peak.

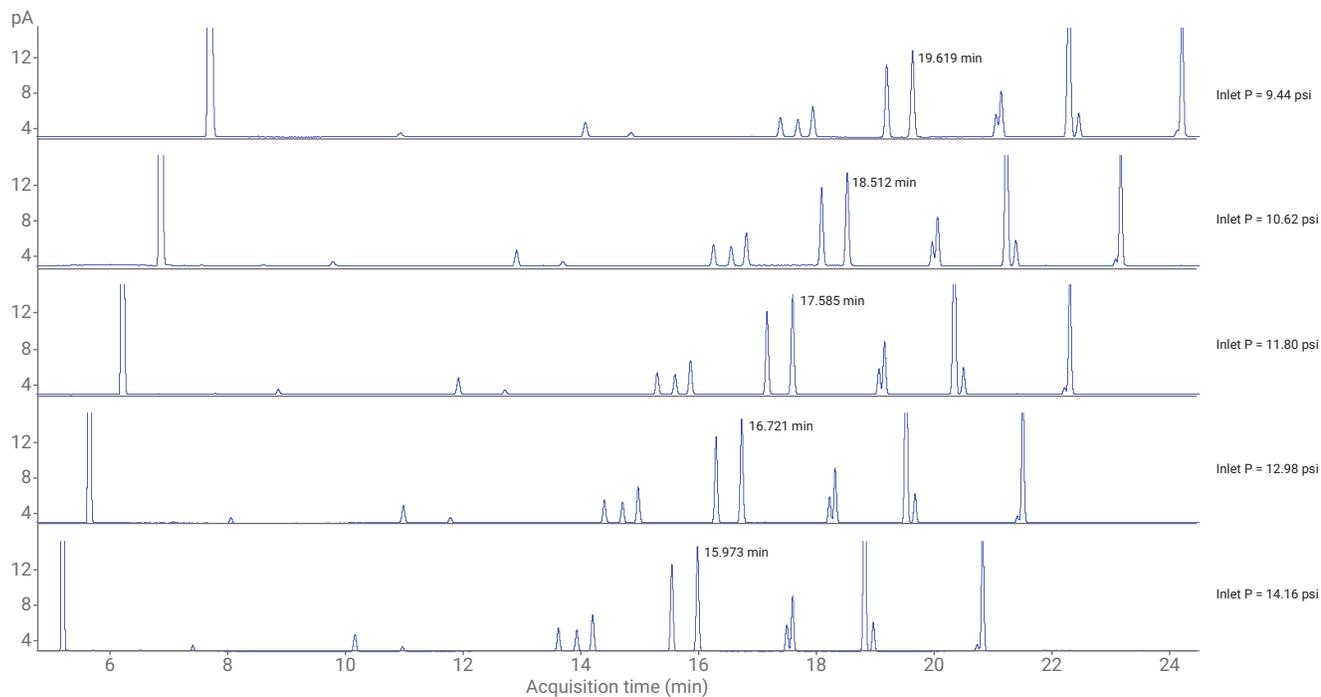
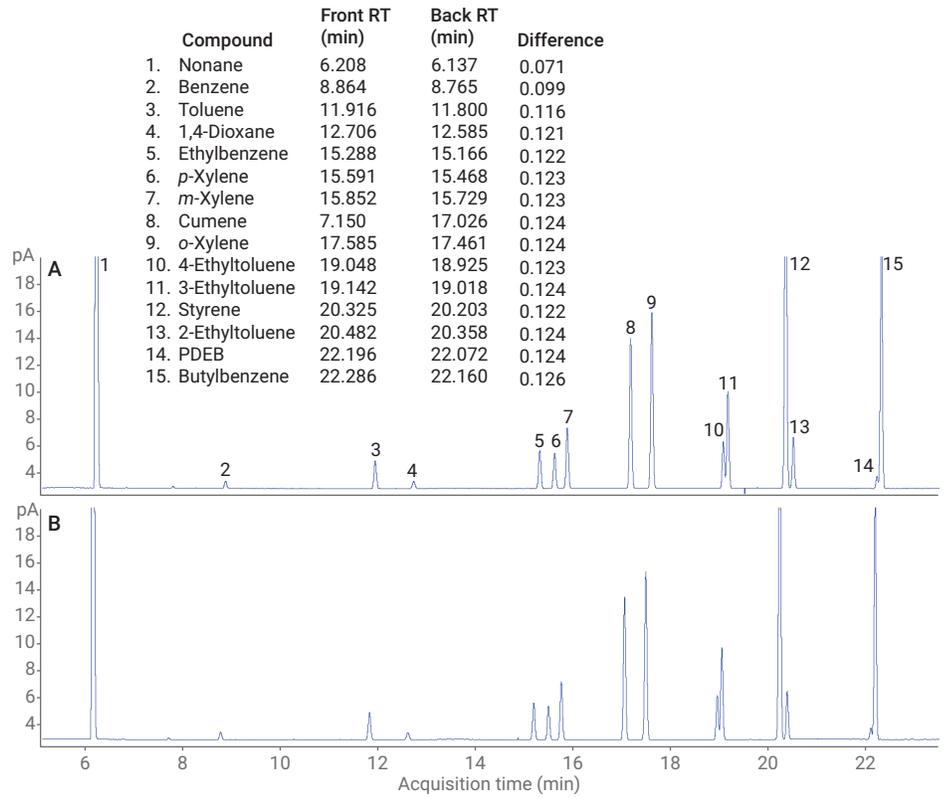


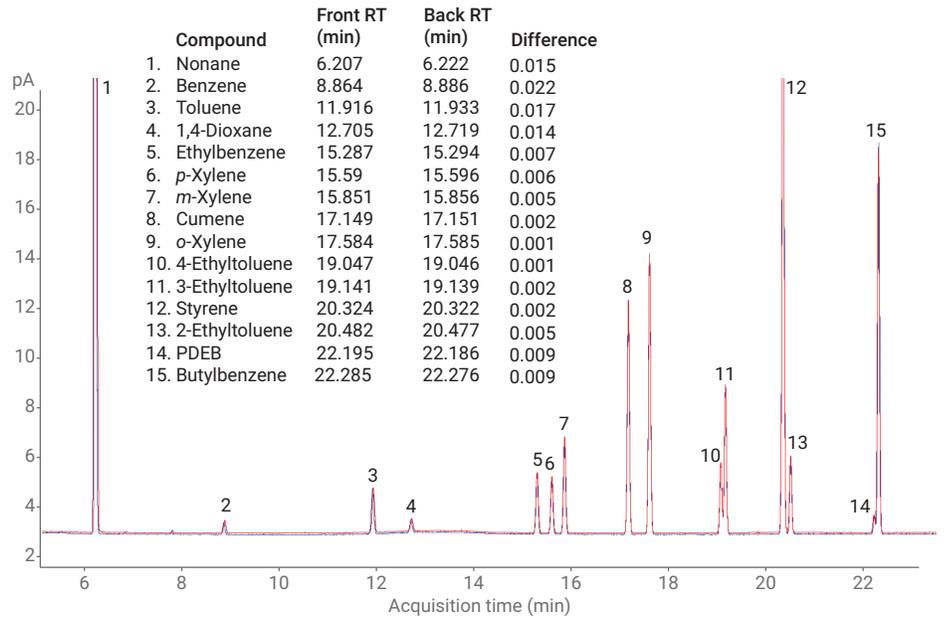
Figure 2. RTL calibration runs using *o*-xylene as the RTL target peak.

The GC was retention time locked using an *o*-xylene target retention time of 17.585 minutes. Figure 4 shows chromatograms on the front and back columns before locking. Retention time differences for most compounds exceeded 0.1 minutes between each column. Figure 5 shows an overlay of the chromatograms after the columns were locked. Excellent retention time agreement was observed for each channel, with differences typically below 0.01 minutes.

It is not always necessary to use *o*-xylene to perform RTL. Analysts who want to use this method for samples not containing *o*-xylene can select a different compound as the RTL target peak. Compounds that do not elute near temperature program transitions can serve as RTL target peaks.



**Figure 4.** Without using RTL, chromatograms of 15 compounds analyzed by the ASTM D7504 method, front and back.



**Figure 5.** Using RTL, overlay of 15 compounds analyzed by the ASTM D7504 method, front and back.

### Benzene purity analysis

Figure 6 shows the chromatogram of benzene analyzed with the ASTM D7504 method using *o*-xylene as the RTL target peak. Results in Table 3 show the weight % of benzene and its impurities. The content of nonaromatics was calculated by summing all peaks from 0 to 8 minutes. Since the method was retention time locked, the same nonaromatic peak sum window was used for the analysis of toluene, ethylbenzene, *p*-xylene, and styrene as well. Observed repeatability (*r*) of the most prominent compounds passed the ASTM repeatability standards.

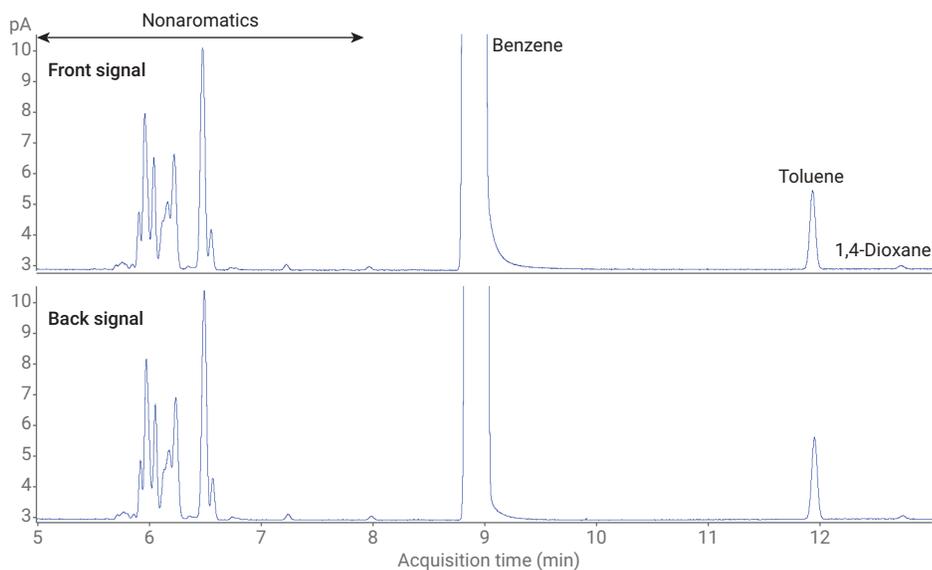


Figure 6. Benzene solvent with RTL.

Table 3. Benzene purity and impurities.

Compound	Results (wt %)		Reproducibility ( <i>r</i> )		Pass
	Front channel	Back channel	Observed	ASTM specification	
Nonaromatics	0.0714	0.0717	0.0003	0.0026	yes
Benzene	99.9193	99.9189	0.0004	0.0085	yes
Toluene	0.0008	0.0008	0.0000	0.0036	yes
1,4-Dioxane	0.0012	0.0012	0.0000	Not reported by ASTM	

### Toluene purity analysis

Figure 7 shows the chromatogram of toluene analyzed with the ASTM D7504 method using *o*-xylene as the RTL target peak. The results in Table 4 show the purity of toluene and the target impurities calculated in weight %.

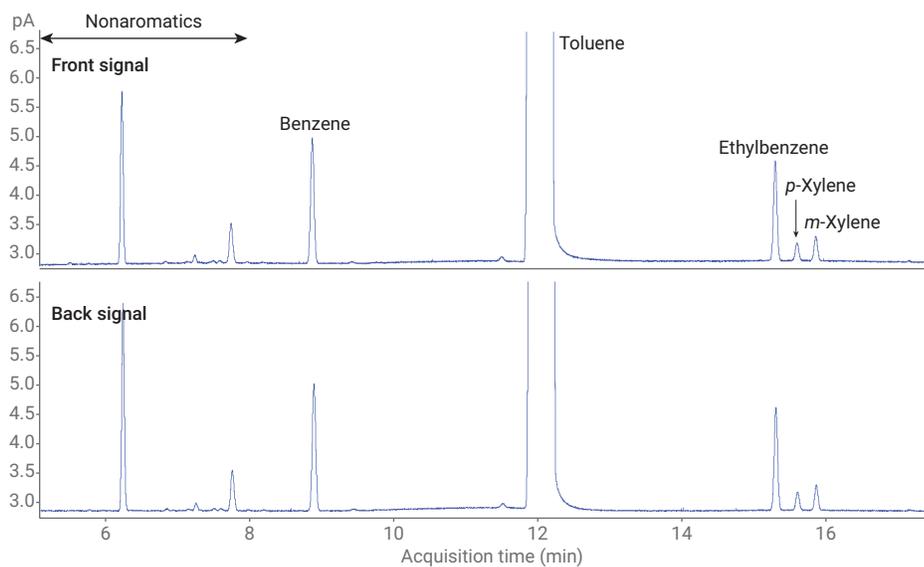


Figure 7. Toluene solvent with RTL.

Table 4. Toluene purity and impurities.

Compound	Results (wt %)		Reproducibility (r)		Pass
	Front channel	Back channel	Observed	ASTM specification	
Nonaromatics	0.0099	0.0111	0.0013	0.0032	yes
Benzene	0.0065	0.0064	0.0001	0.0008	yes
Toluene	99.9760	99.9748	0.0012	0.0068	yes
Ethylbenzene	0.0053	0.0053	0.0000	0.0014	yes
<i>p</i> -Xylene	0.0010	0.0010	0.0000	0.0018	yes
<i>m</i> -Xylene	0.0014	0.0014	0.0000	0.0020	yes

## Ethylbenzene purity analysis

Figure 8 shows the chromatogram of ethylbenzene analyzed with the ASTM D7504 method using *o*-xylene as the RTL target peak. Results in Table 5 show the purity of ethylbenzene and its impurities in weight %.

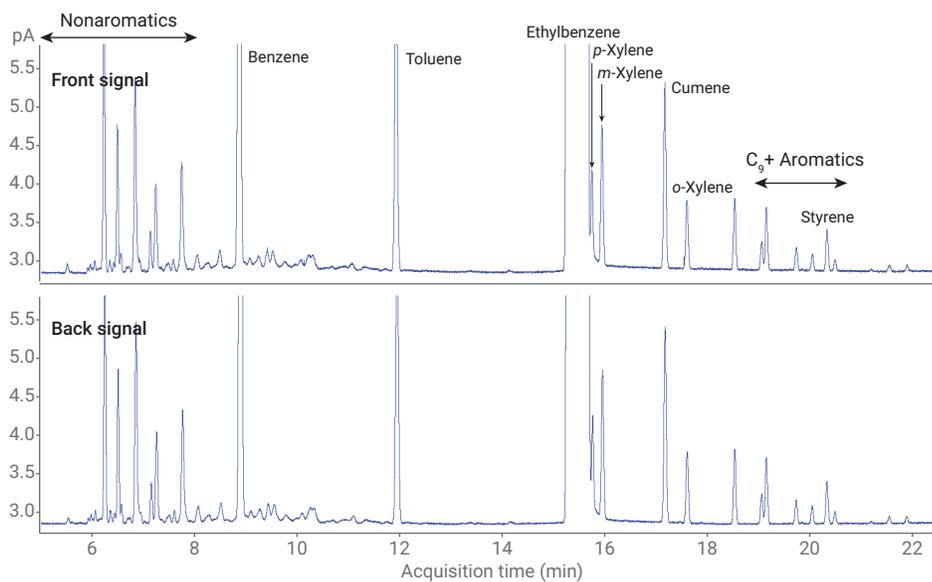


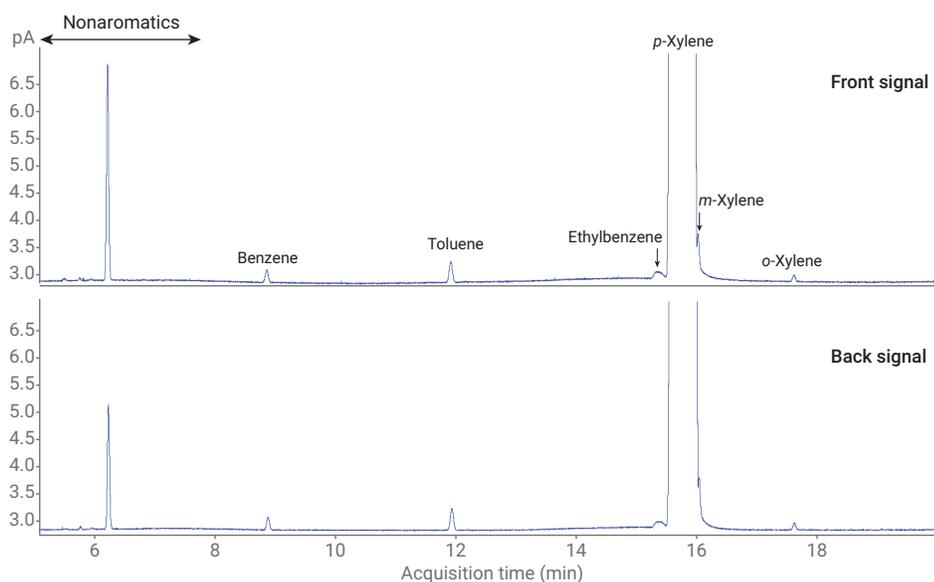
Figure 8. Ethylbenzene solvent with RTL.

Table 5. Ethylbenzene purity and impurities.

Compound	Results (wt %)		Reproducibility (r)		Pass
	Front channel	Back channel	Observed	ASTM specification	
Nonaromatics	0.0386	0.0379	0.0007	0.0047	yes
Benzene	0.0470	0.0464	0.0006	0.0069	yes
Toluene	0.0133	0.0129	0.0004	0.0015	yes
Ethylbenzene	99.8797	99.8804	0.0007	0.0146	yes
<i>p</i> -Xylene	0.0041	0.0042	0.0001	0.0086	yes
<i>m</i> -Xylene	0.0053	0.0054	0.0001	0.0004	yes
Cumene	0.0071	0.0072	0.0001	0.0003	yes
<i>o</i> -Xylene	0.0027	0.0027	0.0000	0.0007	yes
Styrene	0.0015	0.0018	0.0003	Not reported in by ASTM	
C <sub>9</sub> + Aromatics	0.0007	0.0010	0.0003	0.003	yes

### ***p*-Xylene purity analysis**

Figure 9 shows the chromatogram of *p*-xylene analyzed with the ASTM D7504 method using *o*-xylene as the RTL target peak. Results in Table 6 show the purity of *p*-xylene and its impurities in weight %.



**Figure 9.** *p*-Xylene solvent with RTL.

**Table 6.** *p*-Xylene purity and impurities.

Compound	Results (wt %)		Reproducibility (r)		Pass
	Front channel	Back channel	Observed	ASTM specification	
Nonaromatics	0.0150	0.0124	0.0026	0.0029	yes
Benzene	0.0008	0.0007	0.0001	0.0005	Yes
Toluene	0.0014	0.0013	0.0001	0.0009	Yes
Ethylbenzene	0.0008	0.0007	0.0001	0.0006	Yes
<i>p</i> -Xylene	99.9787	99.9813	0.0026	0.0034	Yes
<i>m</i> -Xylene	0.0028	0.0031	0.0003	0.0014	Yes
<i>o</i> -Xylene	0.0004	0.0004	0.0000	0.0003	Yes

## Styrene purity analysis

Figure 10 shows the chromatogram of styrene analyzed with the ASTM D7504 method using *o*-xylene as the RTL target peak. Results in Table 7 show the purity of styrene and its impurities in weight %.

As shown in Tables 3–7, ASTM repeatability standards are met for all compounds in each solvent.

## Conclusions

The 8890 GC combined with the HP-HeavyWax Column was shown to successfully run ASTM D7504 for the determination of monocyclic aromatic solvent purity with a high degree of precision. A 100 % increase in sample throughput was demonstrated using an 8890 GC configured with two identical channels, allowing the simultaneous analysis of two samples. Adding RTL technology to the method enables easy comparison of results between instruments and different laboratories, and improves consistency of results over time. Locked retention times are especially useful for this method when identifying closely eluting isomers such as  $C_8$  aromatics. This retention time locked method meets the need for a fast and simple yet effective method, improving productivity and reliability in today's production laboratories.

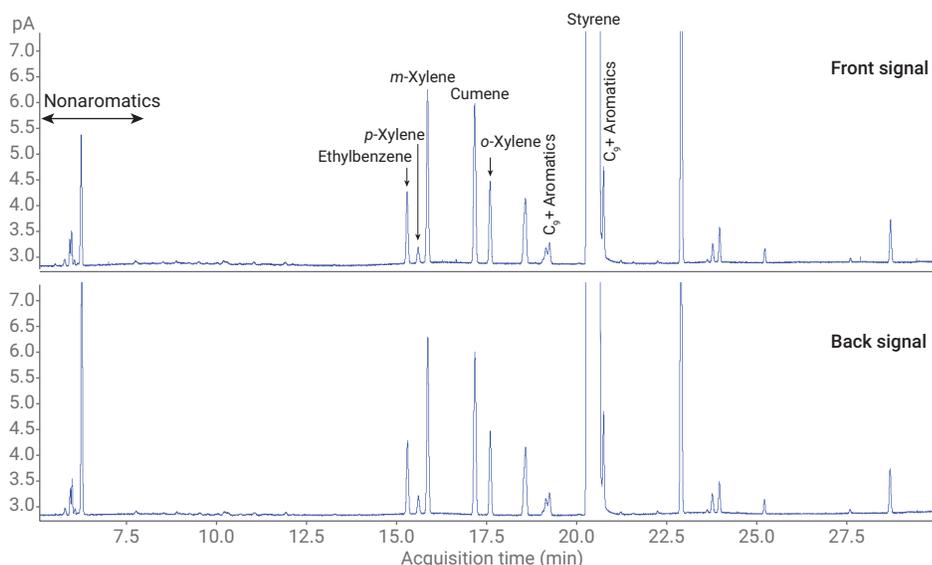


Figure 10. Styrene solvent with RTL.

Table 7. Styrene purity and impurities.

Compound	Results (wt %)		Reproducibility (r)		Pass
	Front channel	Back channel	Observed	ASTM specification	
Nonaromatics	0.0087	0.0111	0.0024	0.0044	Yes
Ethylbenzene	0.0044	0.0043	0.0001	0.0005	Yes
<i>p</i> -Xylene	0.0012	0.0012	0.0000	0.0018	Yes
<i>m</i> -Xylene	0.0104	0.0104	0.0000	0.0009	Yes
Cumene	0.0110	0.0110	0.0000	0.0003	Yes
<i>o</i> -Xylene	0.0053	0.0053	0.0000	0.0005	Yes
Styrene	99.9580	99.9556	0.0024	0.0059	Yes
$C_9+$ Aromatics	0.0011	0.0010	0.0001	0.0027	Yes

## References

1. ASTM D7504-18, Standard Test Method for Trace Impurities in Monocyclic Aromatic Hydrocarbons by Gas Chromatography and Effective Carbon Number, ASTM International, West Conshohocken, PA, **2018**, [www.astm.org](http://www.astm.org)
2. Giarrocco, V.; Quimby, B. D.; Klee, M. S.; Retention Time Locking: Concepts and Applications, *Agilent Technologies Application Note 228-392*, publication number 5966-2469E, December **1997**.
3. McCurry, J. D. A Unified Gas Chromatographic Method for Aromatic Solvent Analysis, *Agilent Technologies Application Note*, publication number 5988-3741EN, August **2001**.

[www.agilent.com/chem](http://www.agilent.com/chem)

This information is subject to change without notice.

© Agilent Technologies, Inc. 2019  
Printed in the USA, January 8, 2019  
5994-0597EN

 **Agilent**  
Trusted Answers