「Application Note」

Analysis of Benzene, Toluene, Ethylbenzene, o-Xylene and Other Aromatics in Gasoline by ChroZen GC According to ASTM D5580

- GC Application

Abstract

Aromatic compounds including BTEX (benzene, toluene, ethylbenzene and xylene) are used for gasoline to increase its octane rating. However, the emission is highly toxic and it triggers to form the ozone which is very harmful for human being. To regulate these pollutants, the % content of benzene and total aromatic compounds in gasoline is managed by fuel regulations.

ASTM D5580 is mainly for determining % concentration of benzene and total aromatic compounds in finished motor gasoline and the coverage range[1)] is written at the bottom of the page.

In this application note, aromatic compounds in gasoline are analyzed and the % concentration is determined by ChroZen GC with 10-port switching valve according to ASTM D5580.

ChroZen GC is the optimized system for determination of benzene, toluene, ethylbenzene, p/m-xylene, o-xylene, C9 and heavier aromatics in finished gasoline by complying with ASTM D5580.

[1)] 0.1 ~ 5 % for benzene, 1 ~ 15 % for toluene, 0.5 ~ 10 % for C_8 aromatics (ethylbenzene, xylenes), 5 ~ 30 % for C_9 and heavier aromatics, 10 ~ 80 liquid volume % for total aromatics.

Instruments and Software

· ChroZen GC System

Item	Description	Part No.
Oven	ChroZen GC Mainframe Assembly with UPC Detector Board Unit	6701012502
UPC	UPC Packed Manifold Block Assembly for ChroZen GC	6701012660
Inlet	Capillary Inlet Assembly for ChroZen GC	6701012550
Detector	FID Assembly for ChroZen GC	6701012590
	TCD Assembly for ChroZen GC	6701012570
Liquid Autosampler	ChroZen PAL LSI system for liquid injection	6501011590
	Mounting Kit for ChroZen GC	PAL3-Kit-YI6700
Valve	Automatic Gas Valve, 2 pos/10 port, Micro-electric actuator type with 250 ul sample loop	6501011280
	Valve Control Case for ChroZen GC	6701012750
CDS	YL-Clarity software for single instrument of YCM GC	5301011020
	Autosampler control of YL-Clarity	5301011040
Column	20% TCEP on 80/100 Chromosorb PAW	19040
	Rxi-1 (30 m, 0.53 mm ID, 5µm)	10179

Figure 1. ChroZen GC

Columns

Column 1 : 20% TCEP on 80/100 Chromosorb PAW (0.56 m, 0.75 mm ID, 1/16” OD)

Column 2 : Rxi-1 (30 m, 0.53 mm ID, 5 µm)

Standards

ASTM® D5580 Quantitative Calibration Kit

① D5580 Quantitative Calibration Mix 1-5

(Part No. 47740U – 47744U)

- Benzene
- Toluene
- Ethylbenzene
- 2-Hexanone — ISTD
- o-Xylene
- 1,2,4-Trimethylbenzene
- 2,2,4-Trimethylpentane(iso-octane)—Solvent

② Valve Timing Calibration Blend

(Part No. 47731U)

- Benzene
- Toluene
- Ethylbenzene
- 2-Hexanone — ISTD
- o-Xylene
- 2,2,4-Trimethylpentane(iso-octane)—Solvent

Sample preparation

Take 1 mL of 2-hexanone (internal standard) in a 10 mL of volumetric flask and dilute with gasoline to the volume.

Instrument Conditions

Table 1. GC Conditions

GC Conditions	
Inlet	200°C
	Column 1 : 20% TCEP on 80/100 Chromosorb PAW (0.56 m, 0.75 mm ID, 1/16" OD) / N_2 10 mL/min, 36.520 psi
	Column 2 : Rxi-1 (30 m, 0.53 mm ID, 5 µm) / Split 1:11 / N_2 10 mL/min, 9.373 psi
Oven	40°C (8 min) -> 2°C / min -> 50°C (5 min) -> 3°C / min -> 120°C (8.7 min)
Detector	FID : 250°C
	Air : 300 mL/min
	H_2 : 35 mL/min
	Make up (N_2) : 20 mL/min
Valve (GSV / 10 port / 250 µL)	Method A : 80 °C / Switching time(On) : 5.20 min / Reset time(Off) : 27 min
	Method B : 80 °C / Switching time(On) :14.65 min / Reset time(Off) : 36 min

Table 2. Liquid Autosampler Conditions

Autosampler Conditions (PAL-LSI System)	
Pre Wash	Wash solvent - 4 µL
	Wash cycle – 3 times
Load Sample	Air Gap Volume - 0 µL
	Sample Rinse Cycles – 3 times
	Filling Strokes Count/Volume – 5 times / 3 µL
Inject Sample	Injection Mode – Normal
	Injection Flow Rate – 100 µL/s
	Injector Penetration Speed – 100 mm/s
Post Wash	Wash solvent - 4 µL
	Wash cycle – 3 times

Summary of Test Method

We analyzed aromatic compounds in gasoline by ChroZen GC with a switching valve and two columns; micro-packed TCEP as pre-column and PDMS (Dimethylpolysiloxance) non-polar column. There are two methods in ASTM D5580. You can determine benzene, toluene and 2-hexanone (ISTD) through method A and ethylbenzene, 2-hexanone (ISTD), o-xylene and C_9 and heavier aromatics through method B.

< Method A >

: Determination of benzene, toluene and 2-hexonone (ISTD)

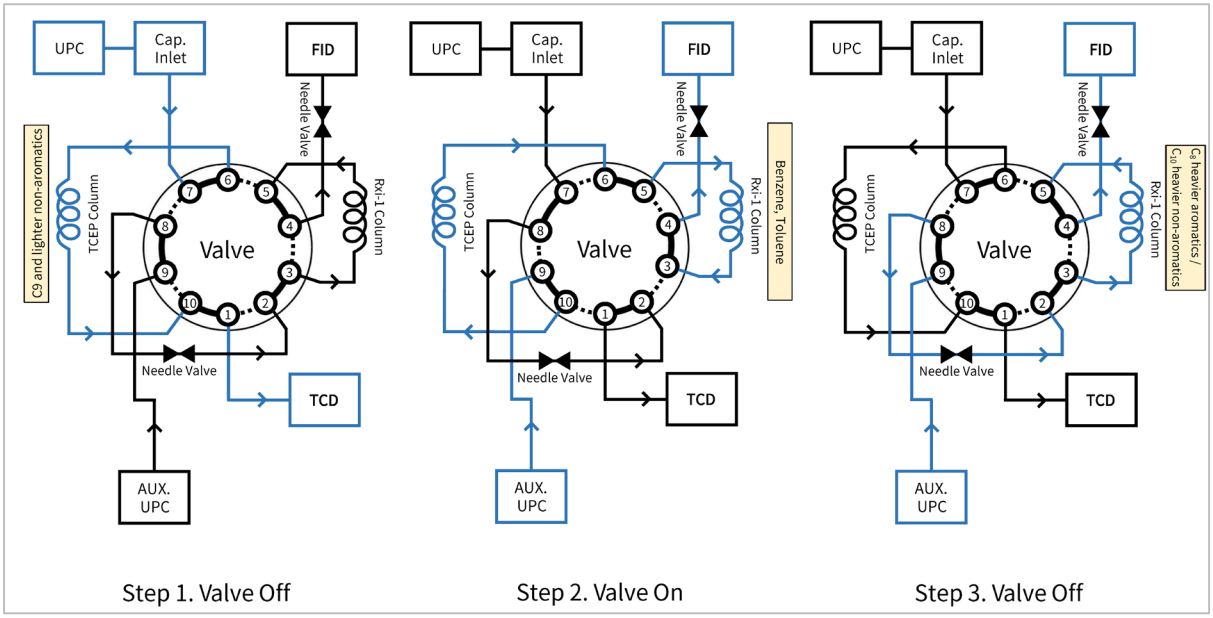


Figure 2. Switching position of 10-port valve for method A

Step 1. Valve off

When sample is injected in the valve off state, C9 and lighter non-aromatic hydrocarbons are vented from TCEP column to TCD as an extra detector for monitoring the separation while aromatic compounds are retained on TCEP column.

Step 2. Valve on

Right before the elution of benzene from TCEP column, switch the valve to on and then

aromatic compounds are backflushed to non-polar PDMS column. FID detects benzene, toluene and 2-hexanone in order.

Step 3. Valve off

Right after the detection of 2-hexanone by FID, the valve position is changed to off and C_8 and heavier aromatic compounds and C_{10} and heavier non-aromatic compounds are backflushed and detected as the composite peaks.

< Method B >

: Determination of ethylbenzene, 2-hexanone (ISTD), o-xylene

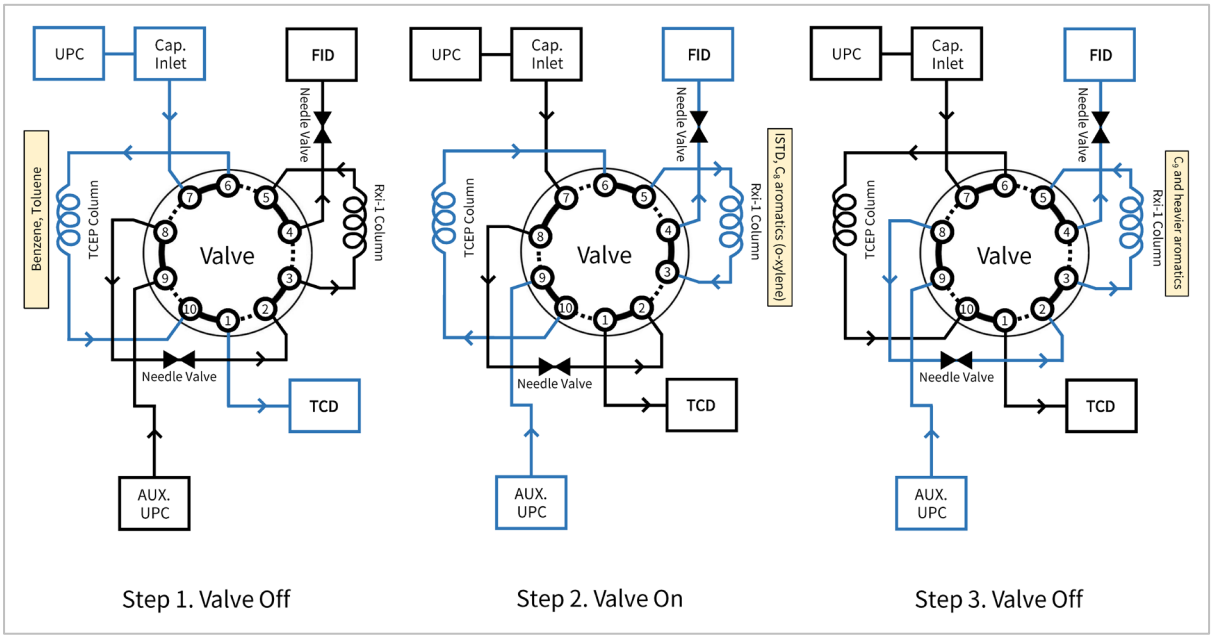


Figure 3. Switching position of 10-port valve for method B

Step 1. Valve Off

In method B, benzene and toluene are vented from TCEP column when valve is off position and they are monitored by TCD.

Step 2. Valve On

Right before the elution of ethylbenzene from TCEP column, the valve is switched to

backflush and 2-hexanone, ethylbenzene and o-xylene are detected by FID in order.

Step 3. Valve Off

Right after the o-xylene is detected by FID, remained compounds such as C_9 and heavier aromatic compounds are backflushed and detected by FID as the composite peak.

Determining Backflush Time

< Backflush time T1 and T3 for Method A >

According to method A and B, they need two backflush times each. For method A, one is the time before the elution of benzene and another is the time after 2-hexanone. With the valve off, the valve timing calibration blend is injected to find the retention time of each compound on TCD. The chromatogram is shown in Figure 4-1. The first appropriate valve backflush time (T1) is to subtract 6 seconds from the time to start elution of benzene. Inject the valve timing calibration blend again and backflush after T1 to detect peaks by FID. The solvent (2,2,4-trimethylpentane) is detected on TCD chromatogram, shown in Figure 4-2. After the complete exhaust of 2-hexanone (ISTD), reset the valve to off position (T3). The ethylbenzene and o-xylene are backflushed and eluted as the composite chromatogram peaks. See Figure 4-3.

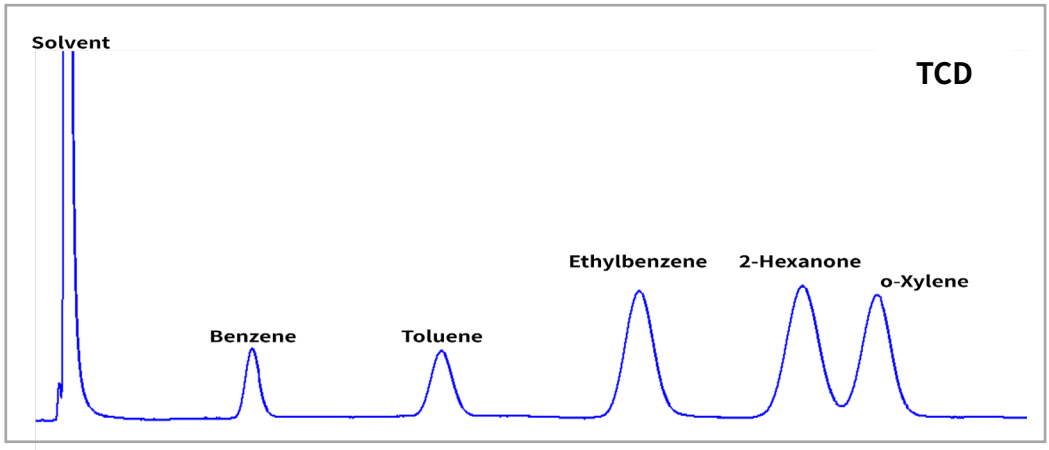


Figure 4-1. Chromatogram of valve timing calibration blend on TCD when "valve off"

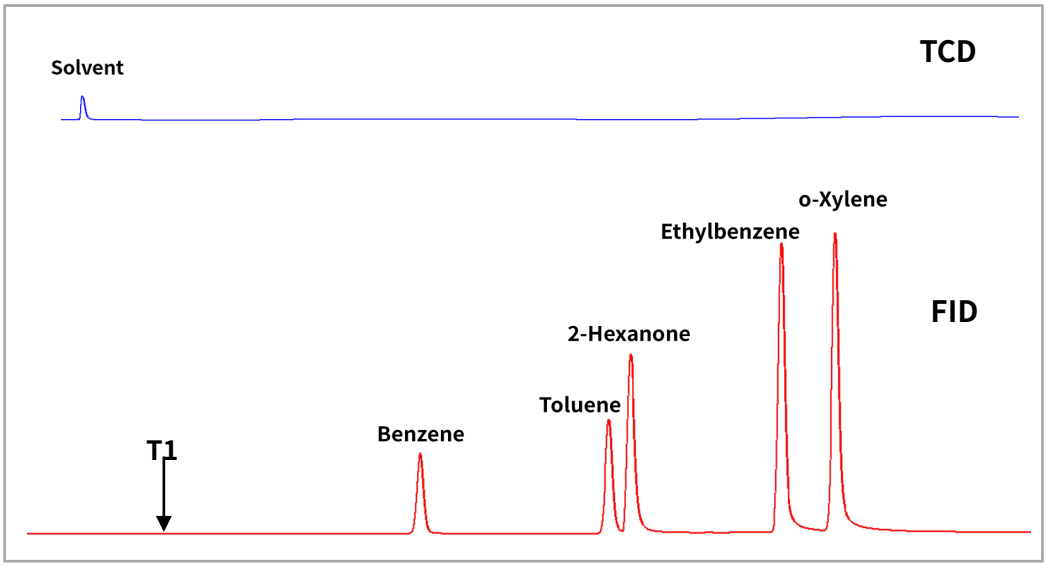


Figure 4-2. Chromatogram of valve timing mix when switching the valve at T1

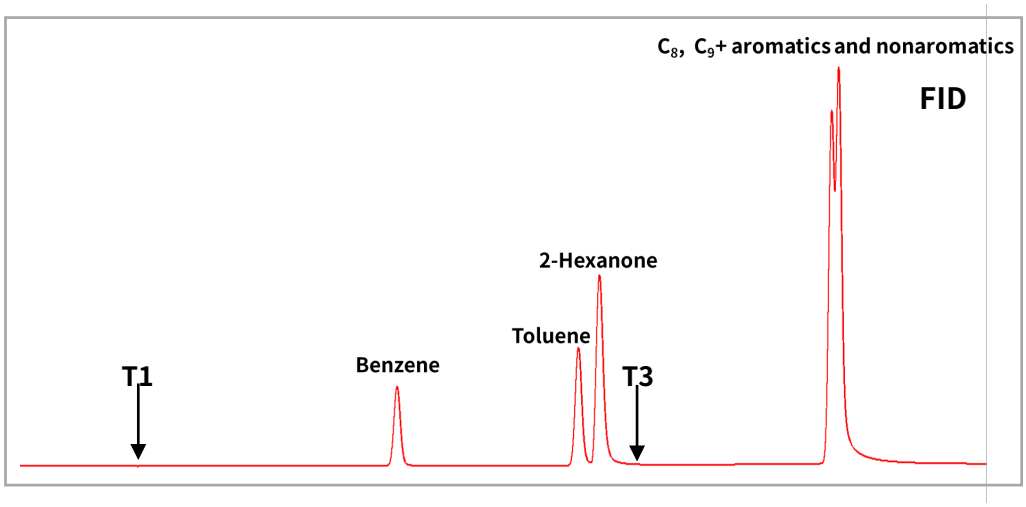


Figure 4-3. Chromatogram of valve timing mix when switching the valve at T1 and T3

< Backflush time T2 and T4 for Method B >

With the valve off, the valve timing calibration blend is injected to find the retention time of each compound on TCD. The chromatogram is shown in Figure 4-1. The first backflush time is set as the time subtracting 6 seconds from the time to start elution of ethylbenzene. As you can see, the peaks which are eluted after T2 are shown on FID chromatogram in Figure 5-1. Also you can find solvent, benzene, toluene peaks in order on TCD chromatogram. After the o-xylene is completely detected by FID, the valve is reset to off position (T4). The chromatogram is shown in Figure 5-2.

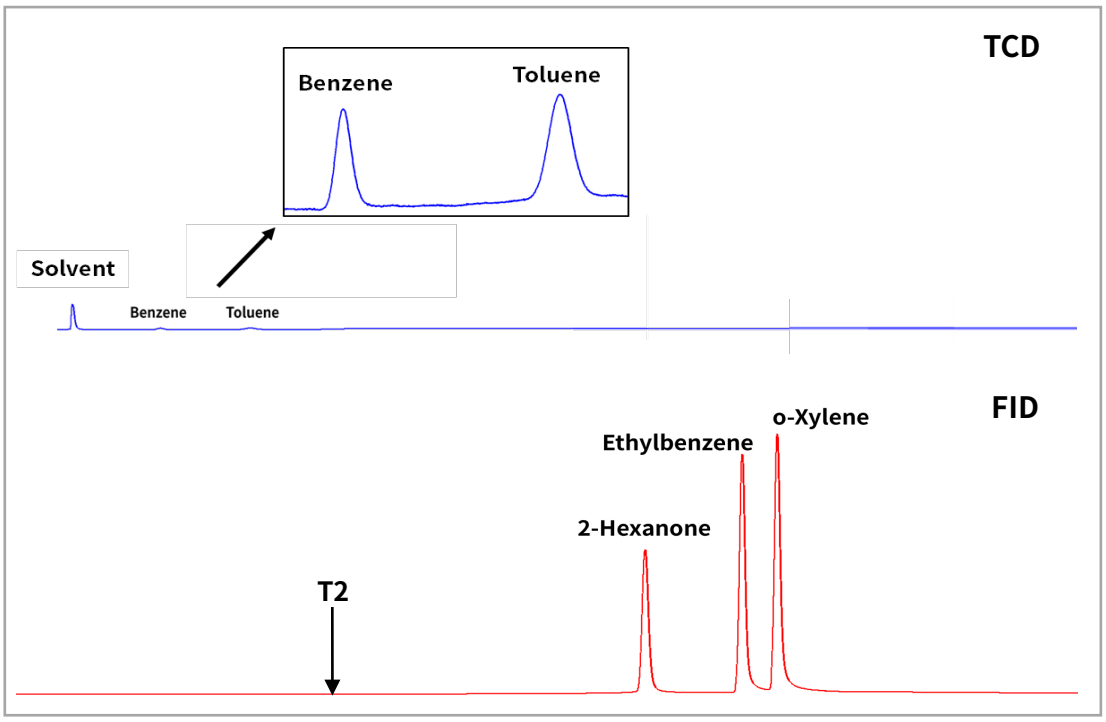


Figure 5-1. Chromatogram of valve timing mix when switching the valve at T2

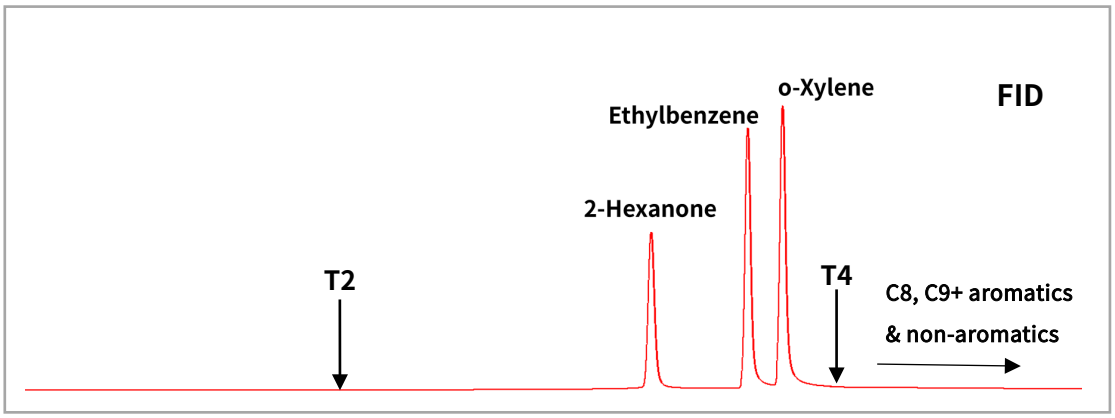


Figure 5-2. Chromatogram of valve timing mix when switching the valve at T2 and T4

Calibration Curve

The calibration curve should be plotted by five-point and the correlation coefficient for each compound must be over 0.990. If it is lower than 0.990, the calibration curve needs to be re-established.

The calibration mixtures of benzene (0.1, 0.5, 1.0, 2.0, 5.0%), toluene (1.0, 2.5, 5.0, 10.0, 15.0%), ethylbenzene, o-xylene and 1,2,4-trimethylbenzene (0.5, 1.0, 2.5, 5.0, 10.0%) were used for calibration curve. According to the result shown in Figure 7, the correlation coefficients of all mixture are greater than 0.990 which satisfies ASTM specifications good enough.

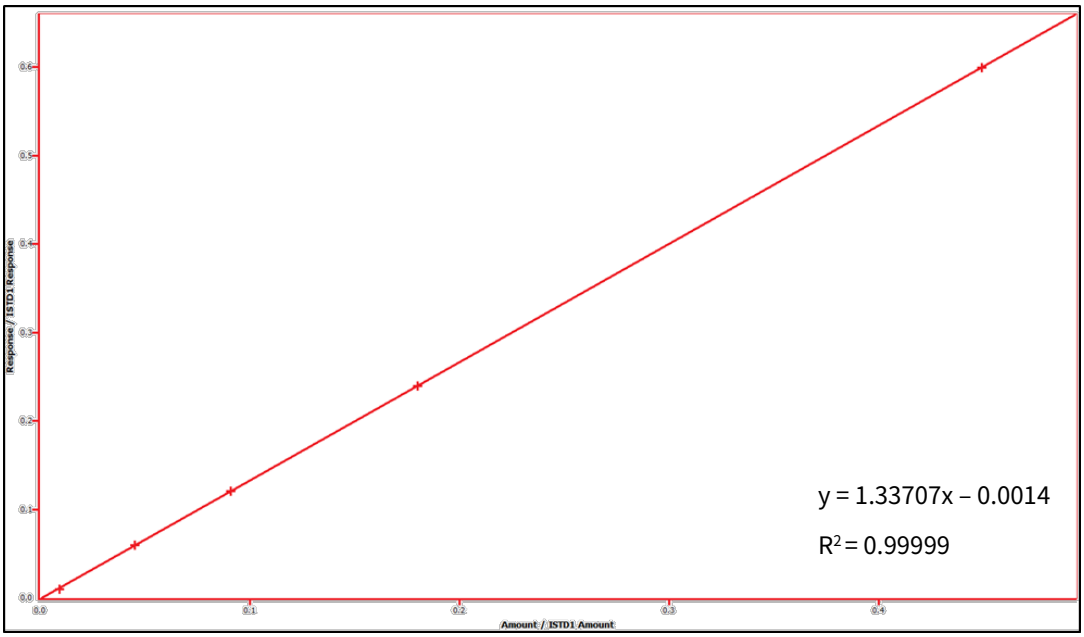


Figure 6. Calibration curve of benzene

The absolute value of the y-intercept must be at a minimum and the mass % of benzene must be less than 0.02 and it must be less than 0.2 mass % of other aromatics for an optimum calibration. Each parameter is described on the following equation. If the calculated mass % exceeds the regulation, it is required to re-establish the calibration curve or check the condition of instrument.

The equation to determine mass % is as follows.

$$Wi = (bi / mi) * (Ws / Wg) * 100$$

W_i : mass of aromatic i (%)

Ws : mass of internal standard (g)

Wg : mass of gasoline sample (g)

The following calculation is an example of benzene from Figure 10 (b_i = 0.0014, m_i = 1.33707)

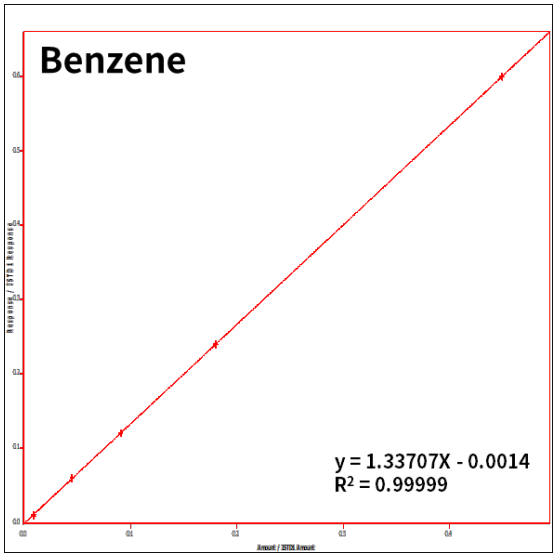
mass of internal standard (Ws) = 0.8 g (1 mL)

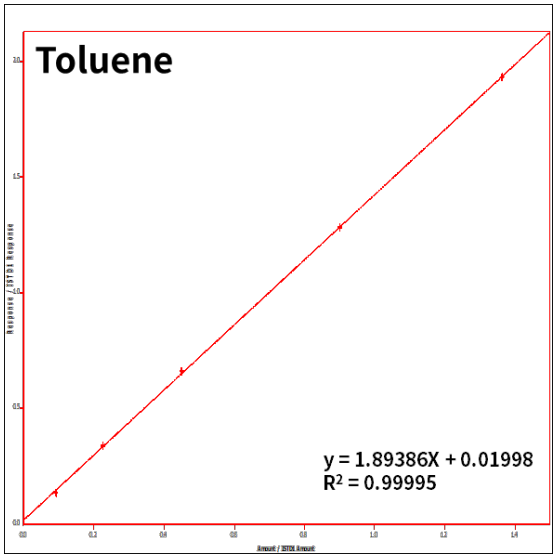
mass of gasoline sample (Wg) = 6.75 g (9.0 mL)

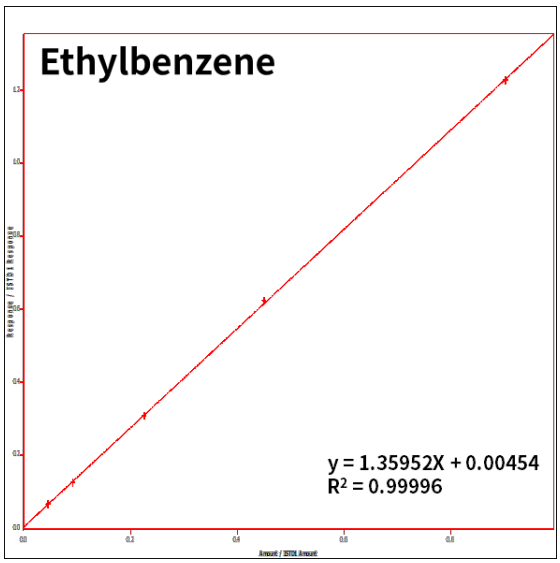
$$W_i = (0.0014/1.33707) * (0.8 /6.75) * 100 = \mathbf{0.01241\ mass\%}$$

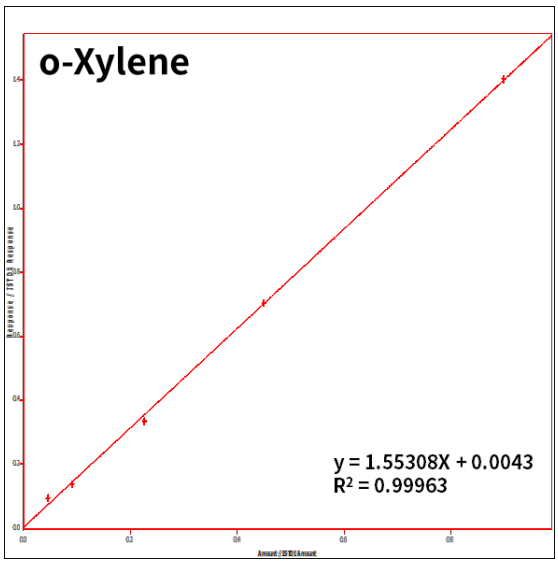
$$W_i < 0.02\ mass\%$$

Mass % of aromatics are resulted 0.012 mass % for benzene, 0.131 mass % for toluene, 0.040 mass % for ethylbenzene, 0.033 mass % for o-xylene, 0.077 mass % for 1,2,4-trimethylbenzene each. It is satisfied with the acceptance criteria of ASTM D5580 as < 0.02 mass % for benzene, < 0.2 mass % for other aromatic compounds.









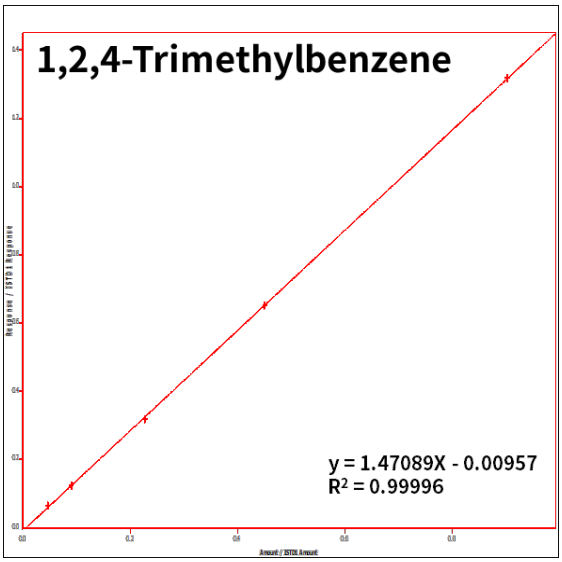


Figure 7. Calibration curves of aromatic compounds

Result

The repeatability in 5 sequences is about 0.37-0.85 %RSD, shown on the Table 3. Also, the mass % of all aromatics in gasoline sample is under the limit of ASTM D5580 which is represented on the Table 4.

Table 3. Peak area repeatability of gasoline sample (n=5)

No.	Peak area (pA.s)			
	Benzene	Toluene	Ethyl benzene	o-Xylene
1	806.68	4848.37	1914.20	1695.22
2	803.33	4781.04	1905.90	1703.77
3	803.25	4858.51	1915.35	1703.71
4	800.76	4895.71	1888.73	1698.44
5	808.10	4849.61	1911.55	1722.75
%RSD	0.37	0.85	0.85	0.63

Table 4. Repeatability of gasoline sample

Compound	ASTM D5580 specification		Observed	
	Range (mass %)	Repeatability	Mass%	*Repeatability
Benzene	0.14-1.79	$0.0265(X^{0.65})$	0.519	0.008
Toluene	2.11-10.08	$0.0301(X^{0.5})$	2.212	0.051
Ethylbenzene	0.57-2.65	0.029	1.109	0.076
o-Xylene	0.77-3.92	$0.0296(X^{0.5})$	0.809	0.003

X = mass %

* Difference between maximum and minimum mass %

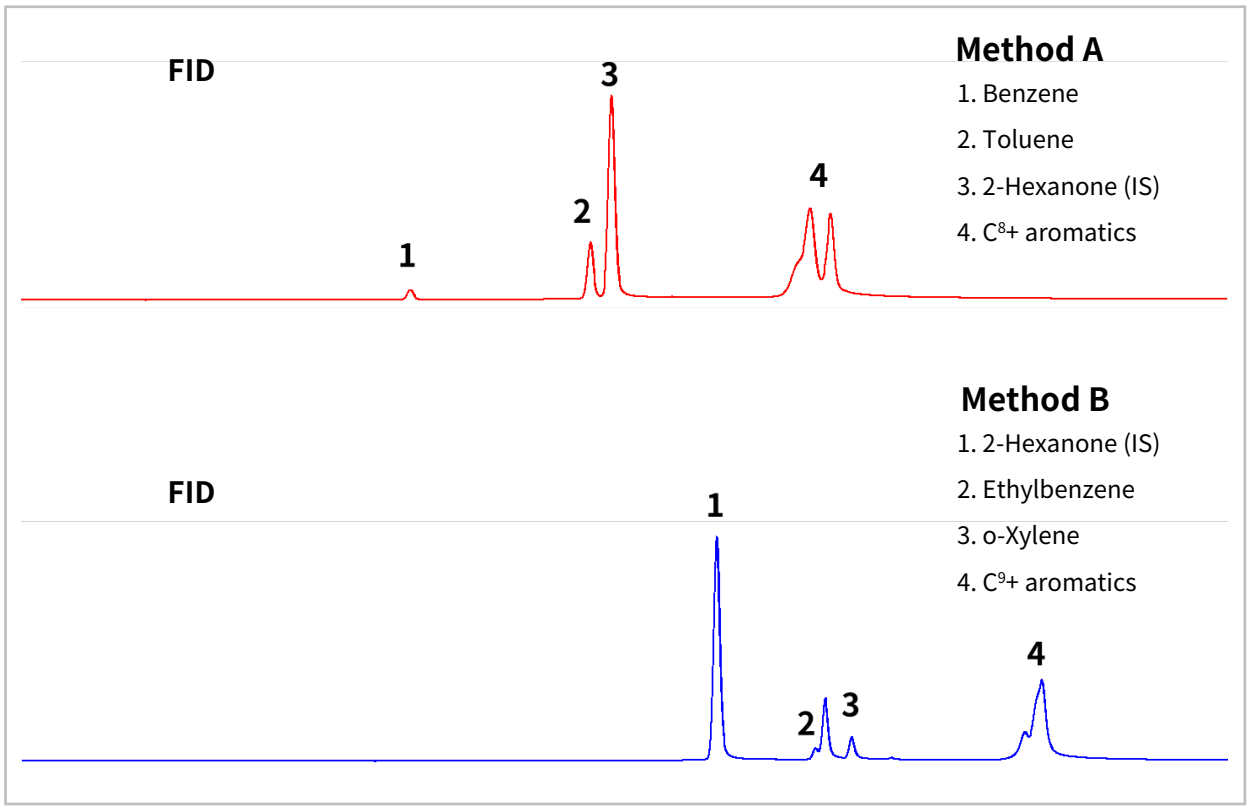


Figure 8. Chromatogram of gasoline sample

Conclusion

The ChroZen GC with 10-port valve shows the great repeatability and linearity for analysis of aromatic compounds in gasoline while satisfying ASTM D5580. In conclusion, it is proven that the ChroZen GC with 10-port valve is an optimized system for determination of benzene, toluene, ethylbenzene, p/m-xylene, o-xylene, C9 and heavier aromatics and total aromatics in finished gasoline by complying ASTM D5580.

Reference

- ASTM D5580 Standard test method for determination of Benzene, Toluene, Ethylbenzene, p/m-Xylene, o-Xylene, C_9 and heavier aromatics and total aromatics in finished gasoline by gas chromatography

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