Two-Dimensional Gas Chromatographic Analysis of Trace Benzene in Styrene

Application

HPI

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Abstract

A two-dimensional gas chromatographic method for the analysis of trace benzene in styrene is described. This method employs the Agilent 6890N GC system equipped with a Deans switch device. The method can be used in a prefractionator mode to analyze trace benzene in styrene according to the proposed ASTM method [1]. It can also be used in a heart-cutting mode to transfer more precisely just the benzene peak from the primary column to the secondary column. The Agilent 6890N electronic pneumatics control and flow calculation software are used for setting up the precise flows and pressures required. Excellent calibration and sensitivity of this system is demonstrated in both prefractionator mode and heart-cutting mode, and the interference can be greatly reduced by the heart-cutting.

Introduction

The American Society of Testing and Materials (ASTM) method D5135 uses a single column GC to measure the overall purity of styrene, including benzene down to 1000 ppm [2]. However, industry now desires to lower the benzene content in styrene to 10 ppm. Styrene also contains trace amounts of C_8 and C_9 hydrocarbons that cannot be separated from trace benzene with a single GC column. A fast analytical method for trace benzene in styrene is needed for final product inspections, process control, establishing specifications, and research work.

ASTM has proposed a two-dimensional gas chromatography (2-D GC) method to completely separate trace levels of benzene from other contaminants in styrene. This method operates in a prefractionator mode where the primary column retains the high boiling styrene components while the low boiling contaminants (including benzene) are transferred to a second column. After the transfer is complete, the benzene is easily separated from the interfering hydrocarbons on the second column. This method uses two columns of different polarity coupled together with a device that allows one or more discrete effluent segments to be transferred from the first to the second column. There are two different switching devices that can be used with this method. The first device uses a rotary valve to transfer the benzene from column one to column two. The second uses a fluidic switch to transfer the benzene. The fluidic switch is similar in design to the Agilent Deans switch for the 6890N GC system. While the Agilent Deans switch works well as a prefractionator, it can also be used in a heart-cutting mode to offer more precise transfer of benzene from the first column to the second column, thus further improving chromatographic resolution.

Two-dimensional GC is an old idea that was first demonstrated by Deans over 30 years ago. Although the Deans switch approach was useful, it did not gain widespread use because of problems associated with unreliable column connections, column flow drift, oven temperature imprecision, and column variability [3]. These problems caused poor overall retention time (RT) precision, thus forcing the analyst to use very wide cut times to ensure transfer of the target analyst from column one to column two. These wider cut times resulted in the transfer of more interference peaks and a loss in overall resolution.

Advanced technology of the Agilent 6890N GC improves the performance of 2-D GC. It makes the construction of 2-D GC systems much simpler and easier to use. Modern column connections have low dead volume and are inert and reliable. The Agilent 6890N electronic pneumatics control (EPC) and oven controls provide better RT precision that allows narrower cut times for better resolution and quantitative precision. New Deans Switch Software used for calculating pressures makes the 2-D GC method development faster and easier.

Experimental

Deans Switch System Design

Heart-Cutting Mode

Figure 1 shows the Agilent 6890N GC system configured with the Deans switch hardware. The sample is injected into the split/splitless (S/S) inlet and is initially separated on the non-polar methyl silicone (HP-1) primary column. With the fluidic switch in the "off" position, the pneumatics control module (PCM) delivers 8.54 mL/min of helium through the lower flow path. This supplies 6.54 mL/min of helium to the secondary column coated with a polar polyethylene glycol (INNOWax) phase. The remaining 2 mL/min is used to divert to the HP-1 column eluent to flame ionization detector (FID) A.

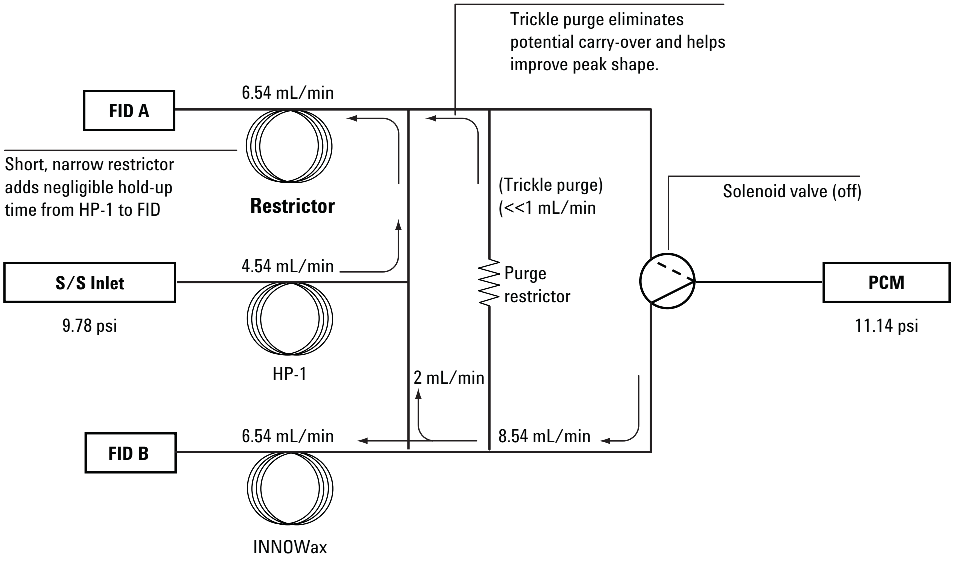


Figure 1. Solenoid valve off - no heart-cutting.

Figure 2 shows the flow path when heart-cutting with the Deans switch. Just before the benzene and any unresolved hydrocarbons elute from the HP-1 column, the fluidic switch is set to the “on” position. Helium from the PCM is now directed through the upper flow path so that 6.54 mL/min goes through the restrictor and 2 mL/min diverts the benzene and the hydrocarbons from the HP-1 column to the INNOWax column. The benzene is then separated from the hydrocarbons by the INNOWax column and detected on FID B. After the peaks are loaded onto the INNOWax column, the fluidic switch is returned to the “off” position shown in Figure 1, so that any peaks still on the HP-1 column are eluted to FID A.

Prefractional Mode

The Agilent 6890N Deans switch can also be used as a prefractionator. With the solenoid valve in the “on” position (Figure 2), the sample is injected into the S/S inlet and a partial separation is made on the nonpolar HP-1 column. The PCM delivers 8.54 mL/min of helium through the upper flow path. This supplies 6.54 mL/min of helium to the restrictor and 2 mL/min transfers fractions that are boiling point equal or less than benzene to the INNOWax secondary column.

When the benzene and lighter compounds are transferred to the INNOWax column, the fluidic switch is set to the “off” position, shown in Figure 1. The PCM delivers 8.54 mL/min of helium through the lower flow path. This supplies 6.54 mL/min of helium to the INNOWax column to separate the benzene from the hydrocarbons with detection on FID B.

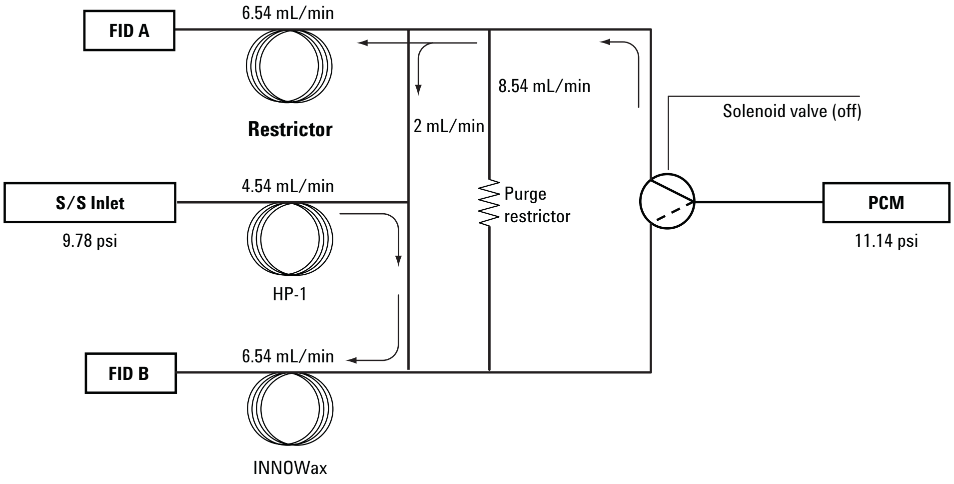
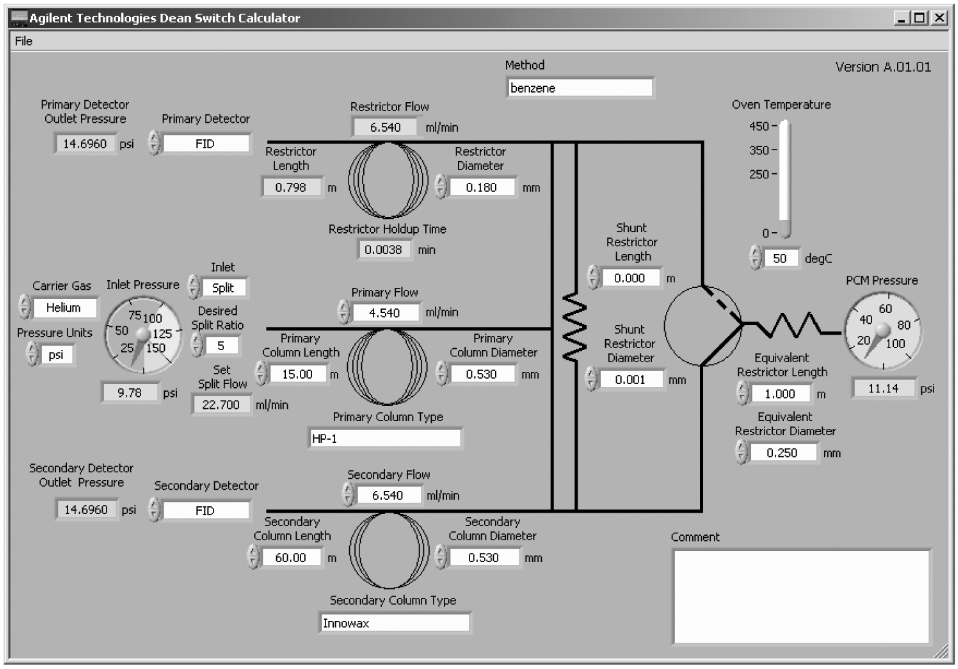


Figure 2. Solenoid valve on heart-cutting from HP-1 to INNOWax column.

Method Development Tool - Deans Switch Calculator

A powerful method development tool, Deans Switch Calculator, is used to easily set the correct column flows, inlet pressure, PCM pressure, and restrictor size. After the method parameters are decided, they are entered into designated fields in the software (shown in Figure 3). The Deans Switch Calculator will then determine the pressure needed to obtain the desired flow rates from the primary column inlet and the PCM. The software will also calculate the dimension for the fixed restrictor.


Agilent Technologies Dean Switch Calculator

Version A.01.01

Method	benzene	
Primary Detector Outlet Pressure	14.6960	psi
Primary Detector	FID	
Restrictor Flow	6.540	ml/min
Restrictor Length	0.798	m
Restrictor Diameter	0.180	mm
Restrictor Holdup Time	0.0038	min
Oven Temperature	50	degC
Shunt Restrictor Length	0.000	m
Carrier Gas	Helium	
Inlet Pressure	9.78	psi
Inlet	Split	
Desired Split Ratio	5	
Set Split Flow	22.700	ml/min
Pressure Units	psi	
Primary Flow	4.540	ml/min
Primary Column Length	15.00	m
Primary Column Diameter	0.530	mm
Primary Column Type	HP-1	
Shunt Restrictor Diameter	0.001	mm
PCM Pressure	11.14	psi
Equivalent Restrictor Length	1.000	m
Equivalent Restrictor Diameter	0.250	mm
Secondary Detector Outlet Pressure	14.6960	psi
Secondary Detector	FID	
Secondary Flow	6.540	ml/min
Secondary Column Length	60.00	m
Secondary Column Diameter	0.530	mm
Secondary Column Type	Innowax	
Comment		

Figure 3. Deans Switch Calculator.

Hardware Configuration

The details of the system hardware for this analysis are listed in Table 1.

Table 1. Agilent 6890 Hardware Configuration

Standard 6890GC hardware		
G1540N	Agilent 6890N series GC	1
112	Capillary split/splitless inlet with EPC control	1
210	FID with EPC control	2
309	PCM with EPC control	1
G2613A	Agilent 7683 autoinjector	1
2310-0129	Deans switch kit	1
Columns		
Primary column	HP-1 15 m, 0.53 mm, 3.0 µm (p/n 19095Z-421)	1
Secondary column	INNOWax 60 m, 0.53 mm, 1.0 µm (p/n 9095N-126)	1
Data system		
G2070A	Agilent multitechnique ChemStation rev. A.08.01	
Optional consumables		
5812-3442	Merlin microseal high-pressure septum	
5182-0875	5-µL fixed straight needle autoinjector syringe for Merlin Microseal	
5183-4647	Inlet liner optimized for split operation	
Standards		
	Benzene, 99.8% minimum purity	
	Styrene, the highest purity available, but not less than 99.6%	

Instrument Conditions

Instrument conditions are listed in Table 2.

Table 2. Instrument Conditions

Split/Splitless inlet	Split mode, with 5:1 split ratio
Temperature	250 °C
Pressure	9.78 psi helium
Split ratio	5:1
HP-1 Column flow	4.54 mL/min, constant pressure mode
INNOWax column flow	6.54 mL/min, constant pressure mode
PCM	11.1psi
FID Temperatures	250 °C
Oven temperature program	50 °C for 4 min, 20 °C/min to 220 °C, for 2 min
FID H_2 flows	40 mL/min
FID Air flows	450 mL/min
FID Makeup gas (He) flows	45 mL/min

Results and Discussion

Heart-Cutting Mode

Agilent Deans switch design can be used in a heart-cutting mode, the results show very good sensitivity, precision, and linearity. The heart-cutting mode can precisely transfer just the benzene peak from the primary column to the secondary column.

Sensitivity

Figure 4 shows a chromatogram of 1-ppm benzene in styrene. It demonstrates the very good performance of the Agilent Deans switch system for sensitive and quantitative detection of 1-ppm benzene in styrene.

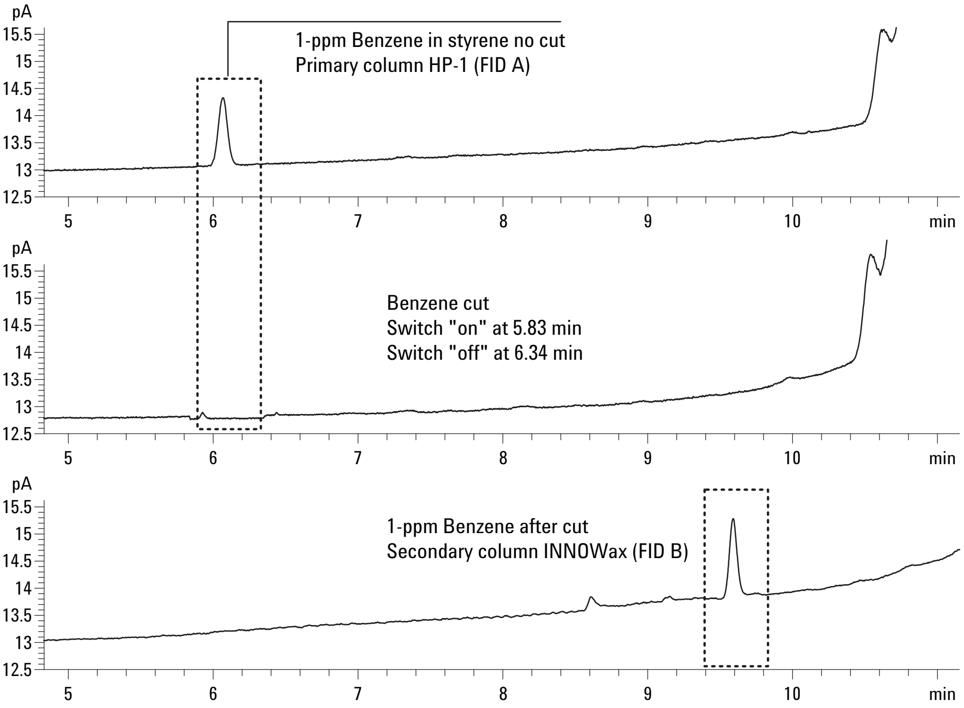


Figure 4. Benzene 1-ppm in styrene can be detected at good signal to noise (S/N) with heart-cutting mode.

Precision

Table 3 shows the excellent RT and detector response repeatability when heart-cutting with the Agilent Deans switch for this method.

Table 3. Repeatability of 2-D GC Method with Heart-Cutting Model

	1-ppm Benzene in styrene		10-ppm Benzene in styrene		100-ppm Benzene in styrene		1000-ppm Benzene in styrene	
	Area	RT	Area	RT	Area	RT	Area	RT
Run 1	5.4	9.589	55.2	9.555	569.6	9.557	5848.8	9.556
Run 2	5.4	9.566	55.7	9.553	572.5	9.556	5898.8	9.555
Run 3	5.4	9.560	55.2	9.555	567.5	9.556	5920.5	9.555
Run 4	5.4	9.561	55.5	9.557	569.5	9.556	5886.1	9.555
Run 5	5.4	9.560	55.4	9.557	570.9	9.554	5821.2	9.556
Average	**5.4**	**9.567**	**55.4**	**9.5554**	**570**	**9.561**	**5875.08**	**9.5554**
SD	**0.00**	**0.01**	**0.190**	**0.0015**	**1.6565**	**0.0023**	**35.6111**	**0.0005**
%RSD	**0.00**	**0.12**	**0.34**	**0.02**	**0.29**	**0.02**	**0.61**	**0.01**

Linearity

Regression statistics of four-point linear calibration curve for benzene containing 1-ppm to 1000-ppm in styrene is shown in Figure 5.

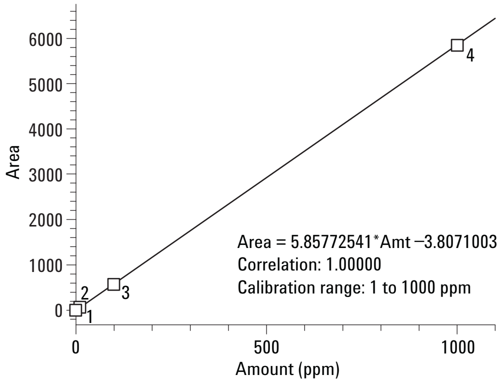


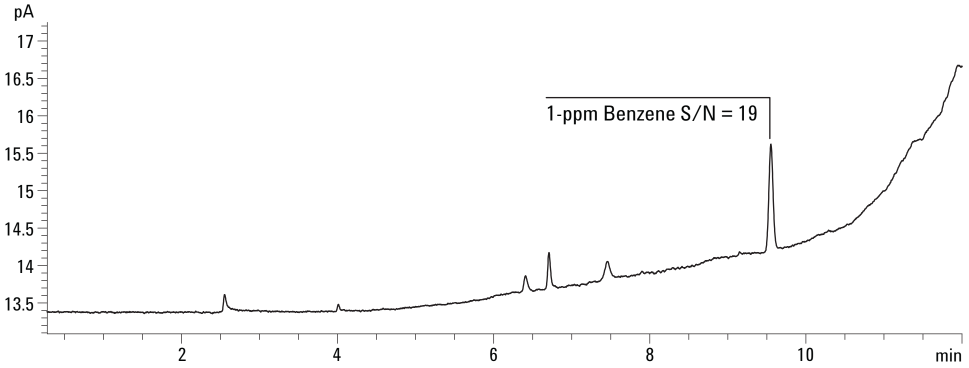
Figure 5. Calibration for styrene containing 1- to 1000-ppm benzene with heart-cutting mode.

Prefractionator Mode

Agilent Deans switch design can be used in a prefractionator mode to analyze trace benzene in styrene according to the proposed ASTM method. The result demonstrates excellent sensitivity and precision.

Sensitivity

Figure 6 shows a chromatogram of 1-ppm benzene in styrene. The 1 ppm of benzene is easily detected at good S/N.



1-ppm Benzene S/N = 19

Figure 6. Benzene 1-ppm in styrene

Precision

Table 4 shows a very good repeatability for calibration standards from 1-ppm to 1000-ppm benzene when using the Agilent Deans switch as a prefractionator.

Table 4. Repeatability of 2-D Method with Prefractionator Model

	1-ppm Benzene in styrene		**10-ppm Benzene in styrene**		**100-ppm Benzene in styrene**		**1000-ppm Benzene in styrene**	
	Area	RT	Area	RT	Area	RT	Area	RT
Run 1	5.3	9.552	54.1	9.540	543.4	9.547	5492.1	9.498
Run 2	5.3	9.550	54.0	9.540	543.8	9.547	5492.8	9.500
Run 3	5.3	9.542	53.8	9.541	538.3	9.544	5489.7	9.504
Run 4	5.3	9.544	53.4	9.545	539.1	9.545	5507.7	9.522
Run 5	5.2	9.540	53.9	9.548	538.5	9.544	5525.9	9.544
Average	**5.3**	**9.546**	**53.8**	**9.543**	**540.6**	**9.545**	**5501.6**	**9.514**
SD	**0.04**	**0.005**	**0.2**	**0.003**	**2.4**	**0.001**	**13.7**	**0.017**
%RSD	**0.76**	**0.05**	**0.45**	**0.03**	**0.45**	**0.01**	**0.25**	**0.18**

Linearity

Figure 7 shows a calibration for styrene containing 1 to 1000-ppm benzene with prefractionator mode.

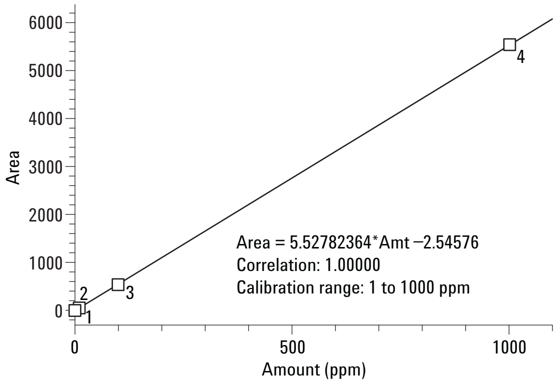


Figure 7. **Calibration for styrene containing 1- to 1000-ppm benzene with prefractionator mode.**

The Comparison Between Heart-Cutting Mode and the Prefractionator Mode

Comparing heart-cutting technique to the prefractionator technique, the former one can greatly reduce interference, because the heart-cutting can precisely transfer just the benzene and any co-eluting compounds from the primary column to the secondary column. While in the prefractionator mode, all compounds that elute before benzene on the HP-1 column are also transferred to the INNOWax column. These extra compounds are a potential source of interference on the INNOWax column. To show that heart-cutting can reduce potential interference, a styrene sample was spiked with 1000 ppm of natural gasoline to increase the amount and number of hydrocarbons. This sample was run using both the heart-cutting mode and the prefractionator mode. Figures 8 and 9 show the results of this experiment.

On the nonpolar primary column (HP-1), the components elute in boiling point order and the benzene peak co-elutes with hydrocarbons that have boiling points similar to benzene. After heart-cutting to the polar INNOWax column, the benzene is easily separated from the less polar hydrocarbons as shown in Figure 8. In the prefractionator mode, the benzene and all lighter compounds are transferred to the polar INNOWax column, on which there are hydrocarbons peaks including benzene peaks as shown in Figure 9. This demonstrates that heart-cutting greatly reduces the number of potential interferences for this method.

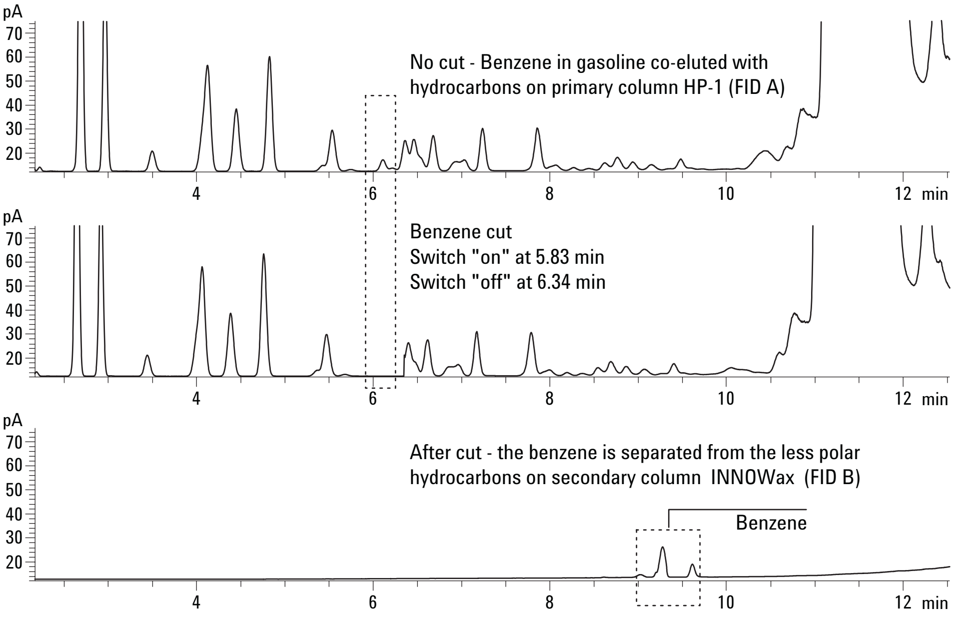


Figure 8. **One thousand ppm gasoline in styrene with heart-cutting mode with reduced hydrocarbon peaks in the lower chromatogram.**

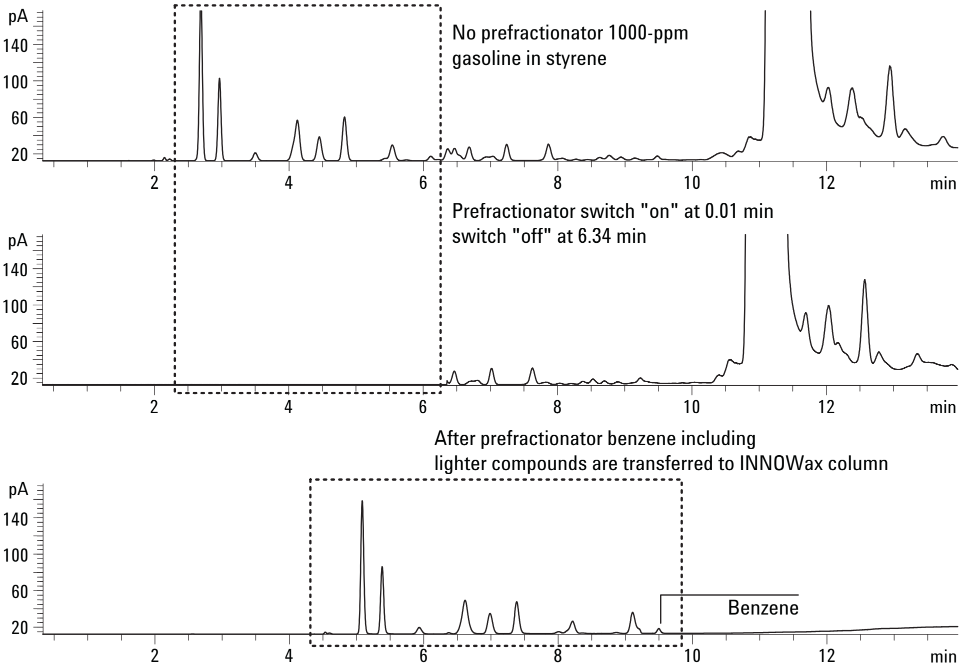


Figure 9. **One thousand ppm gasoline in styrene with prefractionator mode. A larger number of peaks are observed in the lower chromatogram.**

Conclusions

An easy and reliable 2-D GC system with a simplified Deans switch can be used in a prefractionator mode and in a heart-cutting mode to analyze trace benzene in styrene. In this system the Agilent 6890 EPC provides better RT precision that allows narrower cut times for better resolution and quantitative precision. Deans Switch Calculator makes the method development faster and easier. As the results have demonstrated, prefractionator and heart-cutting modes have an excellent calibration, linearity, and repeatability. The heart-cutting can greatly reduce the interference and benzene co-eluted with hydrocarbons on the nonpolar primary column and can be completely separated after heart-cutting to the polar secondary column. The system was able to detect 1-ppm benzene in styrene with excellent signal to noise.

References

1. Proposed ASTM Method “Proposed Standard Test Method for Trace Benzene in Aromatic Hydrocarbons by Capillary Gas Chromatography.”
2. ASTM Method D5135-02 “Standard Test Method for Analysis of Styrene by Capillary Gas Chromatography”, Vol. 6.04, ASTM, 100 Bar Harbor Drive, West Conshohocken, PA 19428 USA.
3. W. Bertsch, Two-Dimensional Gas Chromatography. Concepts, Instrumentation, and Applications - Part 1: Fundamentals, Conventional Two-Dimensional Gas Chromatography, Selected Applications, (1999) *J. High Resol. Chromatogr.* **22**, 647-665.

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