Determining Aromatics in Finished Gasoline Using the Agilent 6820 GC System

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Abstract

A two-column Agilent 6820 gas chromatograph (GC), equipped with two flame ionization detectors (FID) and a 10-port valve, is used for the analysis of benzene, toluene, ethylbenzene, p/m-xylene, o-xylene, C9 and heavier aromatics, and total aromatics in finished gasoline. The internal standard used is 2-hexanone. This method requires two runs; the first is for benzene and toluene, and the second is for ethylbenzene, p/m-xylene, o-xylene, C9, and heavier aromatics.

Introduction

Benzene and aromatics are classified as carcinogens. Regulations limiting their concentration in finished gasoline are established worldwide [1]. In order to assess product quality and to meet the clean fuel regulations, it is necessary to create the required analytical methods for benzene and other aromatics. There are several methods available for the analysis of aromatics in gasoline. One method employs a single polar HP-INNOWax capillary column [2], and another uses a single nonpolar capillary column [3]. The latter method takes 90 minutes. The American Society for Testing and Materials (ASTM) has published analytical methods for the analysis of aromatics in gasoline. ASTM D5769 [4] employs gas chromatography/mass spectrometry (GC/MS) for the analysis of benzene, toluene, and total aromatic content in gasoline. ASTM D3606 [5] is a GC method for the analysis of benzene and toluene in finished motor and aviation gasoline, but this method is unable to analyze for C8 or heavier aromatics. ASTM D5580 [6] is another GC method for determining benzene, toluene, ethylbenzene, p/m-xylene, o-xylene, C9, heavier aromatics, and total aromatics in finished gasoline.

This application follows the ASTM D5580 method but is run using an Agilent 6820 GC. Another Agilent application note [8] cites that ASTM D4815 [7] and D5580 [6] were run on a single Agilent 6890N GC system.

Experimental

The configuration used for this application is listed in Table 1. A column micropacked with 1,2,3-tris-2-cyanoethoxypropane (TCEP) is used for preseparating aromatics from nonaromatics in the same boiling point range. A nonpolar HP-1 column is used for separating the aromatics.
Method Description

This method requires two runs for a complete aromatics analysis, as described below:

First Run

The sample containing the internal standard (ISTD) (2-hexanone) is injected into a precolumn containing micropacked polar TCEP. With the valve in the “OFF” position, C9 and lighter nonaromatics elute from this column and are vented. FID B is used to monitor this separation. See Figure 1A.

Before the elution of benzene from the TCEP column, immediately switch the valve to the “ON” position (switch valve at T1). This backflushes the TCEP column and transfers the remaining compounds to the nonpolar HP-1 column. Benzene, toluene, and the ISTD elute in boiling point order and are detected by FID A. See Figure 1B.

After elution of the ISTD from the HP-1 column, switch the valve to the “OFF” position (switch valve at T3). The HP-1 column-flow is now reversed to backflush the remainder of sample components (C8 and heavier aromatics, plus C10 and heavier nonaromatics) to FID A. See Figure 1C.

Second Run

The run is repeated a second time, allowing the C12 and lighter nonaromatics, benzene and toluene to elute from the TCEP column to the vent. FID B is used to monitor this separation. See Figure 1A.

Before the elution of ethylbenzene, immediately backflush the TCEP column, allowing the remaining sample components to enter the HP-1 column (switch valve at T2). The ISTD and C8 aromatics are thereby separated in boiling point order and are detected by FID A. See Figure 1B.

After the elution of o-xylene from the HP-1 column, immediately reverse the flow (switch valve at T4) to backflush C9 and heavier aromatics to FID A for detection. See Figure 1C.

Instrument Conditions

The instrument conditions are listed in Table 2.

Table 1. Configuration

<table>
<thead>
<tr>
<th>Hardware and software</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>G1180A 6820 GC</td>
<td>1</td>
</tr>
<tr>
<td>161 Split/Splitless inlet</td>
<td>1</td>
</tr>
<tr>
<td>215 Flame ionization detector (FID)</td>
<td>2</td>
</tr>
<tr>
<td>302 One manual controller</td>
<td>1</td>
</tr>
<tr>
<td>751 Installation and automation of one valve</td>
<td>1</td>
</tr>
<tr>
<td>800 10-port switch valve</td>
<td>1</td>
</tr>
<tr>
<td>872 Zero dead volume (ZDV) connection of a capillary column to a valve</td>
<td>2</td>
</tr>
<tr>
<td>870 Adjustable restrictor</td>
<td>1</td>
</tr>
<tr>
<td>874 Install valve downstream from the capillary inlet</td>
<td>1</td>
</tr>
<tr>
<td>335 Cerity NDS software</td>
<td>1</td>
</tr>
</tbody>
</table>

Columns

| 1909Z-623 Capillary column: HP-1, 30 m, 0.53 mm, 5-µm | 1 |
| TCEP (20%) micropacked column: 56 cm × 1/16-inch | 1 |

Standard

Aromatics standards

Table 2. Instrument Conditions

| Inlet | Split/Splitless, 200 ºC, split ratio: 11:1 |
| Detector | FID, 250 ºC, makeup: N2, 15 mL/min |
| Oven program | 50 ºC (10 min), 2 ºC/min, 120 ºC |
| Valve temperature | 80 ºC |
| HP-1 column flow | N2, 7 mL/min |
| TCEP precolumn flow | N2, 8 mL/min |
| Air flow | 350 mL/min |
| H2 flow | 40 mL/min |
| Valve switch times | T1 = 0.5 min, T2 = 1.6 min, T3 = 18.5 min, T4 = 29.5 min* |
| Precolumn | TCEP micropacked, 560 mm, 1.6-mm od, 0.38-mm id |
| Analytic column | HP-1, 30 m, 0.53 mm, 5 µm |

* Switch times should be determined for each GC system.
Results and Discussion

Valve Switch Time Setting

Appropriate valve switch time T1 and T2 must be determined experimentally. If switch time T1 and T2 are not set correctly (for example, switched too late), it is possible that part of the benzene and ethylbenzene will be vented. If switched too early, it may allow interfering compounds to enter the analytical column.

Setting valve switch time T1 and T2

Set valve to the “OFF” position, and then inject 1.0 µL of a calibration blend containing approximately 5% benzene, ethylbenzene, o-xylene, and 2-hexanone, respectively, in isoctane (the exact concentration need not be known). The correct time for T1 and T2 is just prior to the elution of benzene and ethylbenzene from the TCEP precolumn. The chromatogram is shown in Figure 2.

Setting valve switch time T3

Re-inject the calibration blend and turn the valve to backflush at time T1. The time when the ISTD returns to baseline is called T3, shown in Figure 3.

Setting valve switch time T4

Re-inject the calibration blend and backflush at time T2. The time when the o-xylene peak returns to the baseline is called T4, as shown in Figure 4.
Calibration
The experimental data yields correlation coefficients ($R^2$) >0.999 for each aromatic, accompanied by very low y-axis intercepts. A typical calibration curve for ethylbenzene is shown in Figure 5.

$$ y = 1.5506x - 0.0003 $$
$$ R^2 = 1 $$

Figure 5. Calibration curve for ethylbenzene.

For an optimum calibration, the absolute value of the y-intercept ($b_i$) must be at minimum. In this case, $A_i$ approaches zero when $w_i$ is less than 0.1 mass%. This means the mass% ($w_i$) calculated for an aromatic with zero peak area must be close to zero. The y-intercept can be tested by using Equation 1 below:

$$ w_i = \left(\frac{b_i}{m_i}\right) \times \left(\frac{w_s}{w_g}\right) \times 100\% $$

where:

$w_i$ = Mass% of aromatic compound $i$

$w_s$ = Mass of ISTD added, g

$w_g$ = Mass of gasoline sample, g

$m_i$ = Slope

$b_i$ = Intercept

$A_i$ = Area of the internal standard

The ASTM D5580 standard specifies that $w_i$ must be <0.02 mass% for benzene and 0.2 mass% for the other aromatics.

The following is an example of the y-intercept test using data from Figure 5.

For aromatic $i$ (ethylbenzene), $b_i = 0.0003$, $m_i = 1.5506$, a typical sample preparation may contain approximately $w_s = 0.8$ g (1 mL) of ISTD and $w_g = 7$ g (9 mL) of a gasoline sample. Substituting these values into Equation 1 yields:

$$ w_i = \left(\frac{0.0003}{1.5506}\right) \times \left(\frac{0.8 \text{ g}}{7 \text{ g}}\right) \times 100\% = 0.0022 \text{ mass\%} $$

Since $w_i = 0.0022$ mass% is less than 0.2 mass% (the ASTM D5580 specification), the y-intercept has an acceptable value for ethylbenzene.
Repeatability
Table 3 shows that observed repeatability meet or exceed ASTM D5580 specifications.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Observed ASTM D5580 specification</th>
<th>Repeatability *</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0.852 0.009</td>
<td>0.14-1.79</td>
</tr>
<tr>
<td>Toluene</td>
<td>6.229 0.014</td>
<td>2.11-10.08</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>1.614 0.009</td>
<td>1.57-2.65</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>3.370 0.049</td>
<td>0.77-3.92</td>
</tr>
</tbody>
</table>

* Difference between two runs

X = mass% of mean.

Conclusion
A two-column Agilent 6820 GC system equipped with 10-port switch valve, two FIDs, and Cerity NDS software is used for analysis of aromatics in gasoline. This system provides a simple approach for determining benzene, toluene, ethylbenzene, p/m-xylene, o-xylene, C9, heavier aromatics, and total aromatics. The Cerity NDS software is very easy to use for instrument control and data analysis. The results demonstrate that the observed data meet or exceed the calibration and repeatability specifications of the ASTM D5580 standard method.

References

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