Gas Chromatographic Analysis of Aromatic Hydrocarbons in Gasoline by Column Switching-Back Flushing Technique and Normalization Method

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Abstract A simple and efficient method based on the technique of capillary column switching-back flushing was developed for the detailed analysis of aromatic hydrocarbons in gasoline. The early eluting components from a pre-column and the components of interest eluting from an analytical column are all directed to a flame ionization detector through a tee piece which facilitates the quantitation of aromatic hydrocarbons in gasoline by normalization method. Real samples were analyzed and RSD ≤3%. The operation is simple and easy and the switching time window is ±5 s.

Key words gas chromatography, capillary column, column switching, normalization, aromatic hydrocarbon, gasoline

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The analysis of aromatic hydrocarbons is important for quality control of gasoline. Conventional method using a long PONA capillary column for the separation and analysis of the complex mixtures suffer from the interference of a large number of substances especially the target components at low concentration. The techniques of multidimensional gas chromatography and column switching strategies which are effective for the analysis of certain analytes in complex matrix have been applied to analyze the components of interest in oil products. With a very polar pre-column aromatic hydrocarbons are retained far behind the aliphatics of similar volatility and can then be switched into a non-polar column for further analysis. However the early eluting components of the sample are pre-vented and external or internal standards have to be used for quantitation which could probably give rise to several disadvantages such as poor repeatability less accuracy as well as troublesome operation particularly under the circumstance of manual operation.

In the present work a simple method based on the technique of capillary column switching-back flushing was developed for the analysis of gasoline. The early eluting substances and the components of interest eluting from analytical column are all led to the same detector through a tee piece which permits the quantitation of aromatic hydrocarbons in gasoline by normalization method. The standards and real samples were analyzed with the apparatus for evaluation of the method and the comparable results were obtained.

1 Experimental
1.1 Instrumental set-up
A Shimadzu gas chromatograph 14A Shimadzu Co., Japan was used. The instrument was equipped with a split-splitless injector, the split ratio was set at 1:

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30°C and a flame ionization detector FID. A chromatograph workstation KeFen Dalian China was used for data processing. The flowchart of the device is shown in Fig. 1. Nitrogen was used as both the carrier gas and the auxiliary gas and both of them were in constant flow mode. A six-port Valco valve VICI USA T_max ≤ 225 °C was employed as switching valve. The pre-column was a 30 m × 0.32 mm i.d. × 0.3 μm OV-2330 fused silica capillary column Restek USA and the analytical column was a 30 m × 0.53 mm i.d. × 1.2 μm OV-1 FS capillary column KeFen Dalian China. A narrow-bore capillary tubing of 4 m × 0.20 mm i.d. was used for resistance matching. A narrow-bore 0.8 mm i.d. tee of SST316 with low dead volume was specially made for the device.

![Flowchart of the method](image)

1. constant flow controller 2. resistor 3. tee piece 4. pre-column 5. analytical column 6. 6-port valve 7. FID.

The temperature program was as follows 40 °C for 3.5 min then 25 °C/min to 100 °C and finally 8 °C/min to 150 °C hold for 10 min. The temperature of injector and detector was 280 °C. The flow rates of carrier gas and auxiliary gas were 1.8 ml/min and 2 ml/min respectively.

### 2 Results and discussion

#### 2.1 Method optimization

Column switching has been previously applied for the analysis of complex petrochemical samples. In most cases only target components are introduced into FID with external or internal standards employed for quantitation. In addition when a micro-packed column of OV-2330 or TCEP is used as the pre-column the time-error of group-cutting to be granted is limited to only 0.2 s – 0.4 s easily leading to large error when column retention suffers a little variation.

By using a highly polar OV-2330 capillary column for group separation benzene eluted after n-C_10 while all the other aromatic hydrocarbons eluted after n-C_11. A 30 m long capillary column gave a wider time window for valve switching since the retention distance between benzene and n-C_10 became as large as 12 s which permitted a ± 5 s error of cutting in practical operation. The aromatic hydrocarbons and heavier aliphatics ≥ n-C_11 were back flushed into the second non-polar column for further analysis. The oven temperature was programmed at 25 °C/min immediately after the valve switching till 100 °C in order to sharpen the chromatographic band before its entry into the second column.

The micro-tee plays a very important role in the method. When the effluent from one of the columns is directed to the detector the gas flow from the other channel plays the role of make-up gas which
thereby eliminates dead volume and avoids peak tailing. As all peaks from both columns are detected with the same detector under the same conditions normalization method can be employed for quantitative analysis which simplifies the routine analysis of benzene and other aromatic hydrocarbons in gasoline.

2.2 Evaluation of the apparatus

Comparing the data obtained with a single pre-column with those obtained with the method mentioned above see Table 1 we can know that they are almost identical which implies no sample loss during valve switching.

Table 1: Comparison of the analytical data obtained with a single pre-column (S) to those with column switching-back flushing technique (T)

<table>
<thead>
<tr>
<th>Method</th>
<th>Component and mass percentage in gasoline</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n-pentane</td>
<td>n-decane</td>
</tr>
<tr>
<td>S</td>
<td>11.43</td>
<td>4.25</td>
</tr>
<tr>
<td>T</td>
<td>11.71</td>
<td>4.13</td>
</tr>
</tbody>
</table>

The analysis of a gasoline sample from catalytic cracking process was completed in 15 min. To verify the allowable error of switching time switching times of 2.80 min 2.85 min 2.90 min 2.95 min and 3.00 min were employed successively. Table 2 indicates that the time window for valve switching is ±5 s with RSD≤4%.

Table 2: Contents of aromatic hydrocarbons in catalytic gasoline under different cutting time

<table>
<thead>
<tr>
<th>Switching time min</th>
<th>Component and mass percentage in gasoline</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>benzene</td>
<td>toluene</td>
</tr>
<tr>
<td>2.80</td>
<td>0.66</td>
<td>6.60</td>
</tr>
<tr>
<td>2.85</td>
<td>0.62</td>
<td>6.43</td>
</tr>
<tr>
<td>2.90</td>
<td>0.65</td>
<td>6.83</td>
</tr>
<tr>
<td>2.95</td>
<td>0.69</td>
<td>6.61</td>
</tr>
<tr>
<td>3.00</td>
<td>0.68</td>
<td>6.20</td>
</tr>
<tr>
<td>Average</td>
<td>0.66</td>
<td>6.53</td>
</tr>
</tbody>
</table>

The aromatic hydrocarbons of two real samples were determined with the method see Table 3. The results are in good agreement with those obtained by the ASTM D 4420-89 method.

3 Conclusion

A novel and simple method using a single injection and normalization method of quantitation was proposed for routine analysis of aromatic hydrocarbons in gasoline. Satisfactory results for a run was obtained within 15 min. A novel device consisting of two streams of carrier gas passing through a tee piece with each gas acting as the make-up gas for the other was designed and used to reduce the connector dead volume and improve effectively the peak shape.

References

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