IMPROVED RESOLUTION OF BENZENE (AND OTHER AROMATICS) AND OXYGENATES IN REFORMULATED GASOLINE USING A ONE-COLUMN APPROACH

The amount of benzene in gasoline is a concern because it is a known human carcinogen, and exposure to it has been linked to detrimental health effects. The challenge with the analysis lies in the complex composition of gasoline, which consists of hundreds of different compounds. Reformulated gasoline also contains additives to produce more complete combustion and subsequent lower emissions of harmful compounds.

These additives accomplish this by boosting the oxygen content, and are commonly referred to as "oxygenates." Ethanol is a commonly used oxygenate. Therefore, to measure benzene in reformulated gasoline, it must be resolved from the aliphatic hydrocarbons, other aromatics, ethanol, plus any other oxygenates. This typically requires the use of a two-column switching procedure.[1]

SLB-ILD3606 Chemistry

We developed SLB-ILD3606, a capillary gas chromatography (GC) column engineered for the determination of benzene (and other aromatics) and oxygenates in gasoline. Table 1 lists its specifications. It is a modified (inert) version of SLB-IL111, a GC column that employs an imidazolium dicationic ionic liquid stationary phase. This new column provides the unique selectivity of the extremely polar SLB-IL111, but with improved peak shapes for oxygenates, resulting in improved resolution for all analytes.

Table 1. Column Specifications

Application: Modified (deactivated) version of SLB-IL111 provides better inertness. Each column is tested to ensure resolution and sharp peak shapes of aromatics and alcohols. Excellent at separations involving benzene (and other aromatics) and oxygenates in petroleum products, such as gasoline. Also a good GCxGC column choice. Launched in 2015.

USP Code: None

Phase: Non-bonded; 1,5-di(2,3-dimethylimidazolium)pentane bis(trifluoromethylsulfonyl)imide

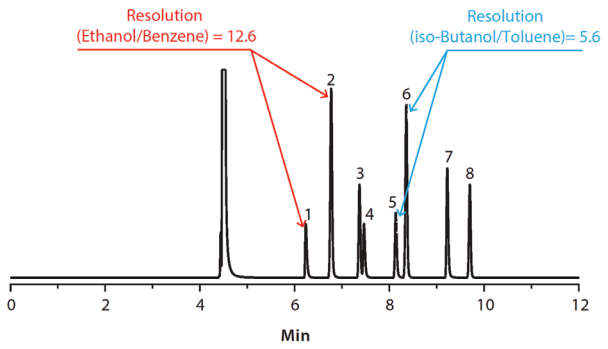
Temp. Limits: 50 °C to 260 °C (isothermal or programmed)

Aromatic and Alcohol Mix

To show selectivity and inertness capabilities, a mixture containing two aromatics, five alcohols, and one ketone was prepared in isooctane following the guidelines for a control standard to be used with ASTM® D3606. This mix was analysed using temperature programming, and the resulting chromatogram is shown in Figure 1. The inertness of the column resulted in sharp peak shapes for all alcohols, which in turn resulted in great resolution between ethanol and benzene (RS=12.6), and also between iso-butanol and toluene (RS = 5.6).

Figure 1: Aromatic and Alcohol Standard
column: SLB-ILD3606, 60 m × 0.25 mm I.D., 0.20 µm (29691-U)
oven: 50 °C (6 min), 15 °C/min to 265 °C (10 min)
inj. temp.: 250 °C
carrier gas: helium, 21 cm/sec detector: FID, 250 °C injection: 1 µL, 100:1 split
liner: 4 mm I.D., split type, cup design
sample: 8 analytes at various concentrations in isooctane

1. Ethanol
2. Benzene
3. sec-Butanol
4. n-Propanol
5. iso-Butanol
6. Toluene
7. n-Butanol
8. Methyl isobutyl ketone (MIBK)



Reformulated Gasoline Sample

Figure 2 shows the chromatogram resulting from the analysis of a reformulated gasoline sample on SLB-ILD3606. As shown:

- The extremely polar selectivity of this column resulted in the elution of benzene after the aliphatic portion, and also great resolution between benzene and ethanol
- Several other aromatic and oxygenate compounds are also fully resolved
- A few aromatics (e.g. p-/m-xylene) and oxygenates (e.g. MTBE, TAME) are partially resolved
- This column can be used up to 260°C, so allows the timely elution of the heavy polycyclic aromatic hydrocarbon (PAH) constituents in gasoline
- The phase stability of the SLB-ILD3606 column exhibits a stable baseline when subjected to a temperature ramp

These observations indicate the SLB-ILD3606 is an effective alternative to the two-column switching procedure currently required for the determination of benzene and other aromatics in reformulated gasoline

Conclusions

The measurement of benzene and oxygenate compounds in reformulated gasoline is a common application performed worldwide, both in on-site labs at industrial facilities and also in third-party testing labs. As shown, the SLB-ILD3606 column is able to resolve both benzene and toluene from oxygenates (such as alcohols, ketones, and ethers) and also the aliphatic portion of gasoline in a one-column set-up.

Reference

1. ASTM® D3606, Benzene and Toluene in Unleaded Gasoline and Aviation Fuel.

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Figure 2: Reformulated Gasoline
sample: reformulated gasoline (contains 10% ethanol) with 7 other oxygenates added (at 2.5-5%)
All other conditions the same as Figure 1

1. C5-C11 aliphatic hydrocarbons
2. Methyl tert-butyl ether (MTBE)
3. tert-Amyl butyl ether (TAME)
4. Ethanol
5. Benzene
6. sec-Butanol
7. n-Propanol
8. iso-Butanol
9. Toluene
10. n-Butanol
11. Ethylbenzene
12. Methyl isobutyl ketone (MIBK)
13. p-Xylene
14. m-Xylene
15. o-Xylene