Application Note: 52284

Simplification of the ASTM D3606 Method for the Determination of Benzene and Toluene in Gasoline

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Key Words

- TRACE 1310 GC
- Chromeleon Data System
- ASTM D3606 Method
- Benzene
- Gasoline Analysis
- Toluene

Introduction

Benzene is used as an additive into gasoline to increase octane rating and prevent engine knocking. Being a toxic air pollutant known to have carcinogenic effects, knowledge of its concentration can be of aid in the assessment of possible health hazards to persons handling and using gasoline.

The U.S. Federal Clean Air Act and the European Community specifications mandate a level of benzene in gasoline below 1% in volume.[1] To meet the specific limits of benzene, an accurate quantitative determination of the compound is essential.

The ASTM D3606 method is designed to determine benzene and toluene content in motor and aviation gasoline using packed columns and a thermal conductivity detector (TCD).[2] The following methodology describes the determination of these components in gasoline, using the Thermo Scientific TRACE 1310 GC in a split/splitless-backflush configuration using capillary columns and flame ionization detection (FID), for a simpler fully automated analysis. The SSL/backflush injector used in this paper is a user-installable, compact and self-sufficient module featuring all the required hardware components and the electronic carrier gas controls.

Materials and Methods

A TRACE™ 1310 GC configured with a Split/Splitless (SSL) module with backflush and a FID detector has been used. A Thermo Scientific TraceGOLD TG-5MS 15 m × 0.53 mm × 1 µm 5 phenil-methilpolisyloxane pre-column (P/N: 26098-2860) and a 30 m × 0.25 mm × 0.4 µm Thermo Scientific TraceGOLD TG-TCEP (P/N: 26069-3190) analytical column were used. The two are connected via the new SSL backflush module using standard capillary column ferrules and nuts, as in Figures 1 and 2. The calibration standards were acquired as a kit from Restek™ Corporation (P/N: 30673).

The carrier gas is Helium with a constant flow of 2.5 mL/min. The analysis is performed in split mode with a split flow of 100 mL/min, for a split ratio of 40.

The oven program consists of a starting temperature 40 °C for 4 min., then 10 °C/min up to 65 °C, then 50 °C/min up to 130 °C with a final hold time of three minutes. Total run time is 10 minutes, and the system can inject a sample every 13 minutes. The autosampler used was a Thermo Scientific AS 1310. One microliter of sample is injected. All the data were acquired and processed with the Thermo Scientific Dionex Chromeleon data system.

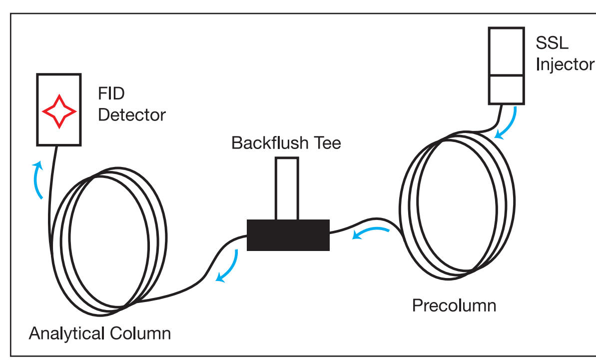

Figure 1: Column flow when backflush is *OFF*. Carrier gas flows from the injector to the detector.

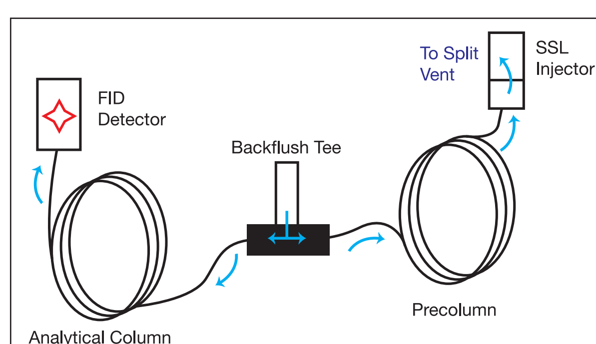

Figure 2: Column flow when backflush is *ON*. Carrier gas is provided to both columns by the mid-point T-connection of the SSL-backflush module.

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Analytical Procedure

The sample is injected via autosampler into the GC, with the backflush flow set to *OFF*, and passes through the less polar TraceGOLD 5MS pre-column first where components are separated according to their boiling points. The lighter compounds elute first and are then transferred into the analytical polar TCEP column and detected by the FID. In this specific case, after benzene, toluene and the non-aromatic compounds up to n-Octane have eluted, the backflush system is switched on, and the heavier components that were still in the TraceGOLD 5MS precolumn are backflushed to the vent without reaching the analytical column. The backflush is turned on at 4 minutes. The resulting chromatograms are shown in Figures 3 and 4.

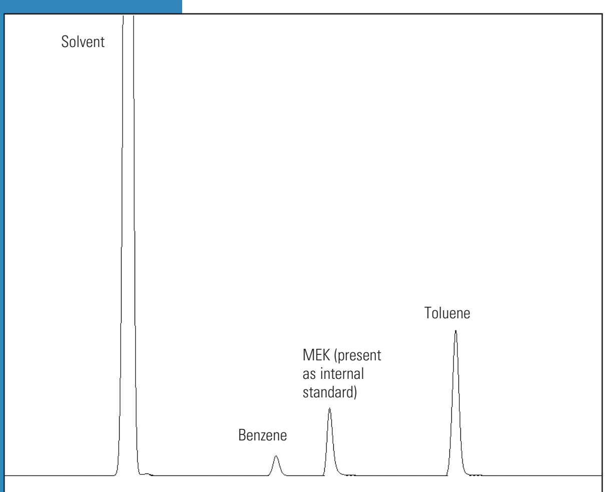

Figure 3: Calibration mix chromatogram, showing excellent sensitivity and perfect peak shapes

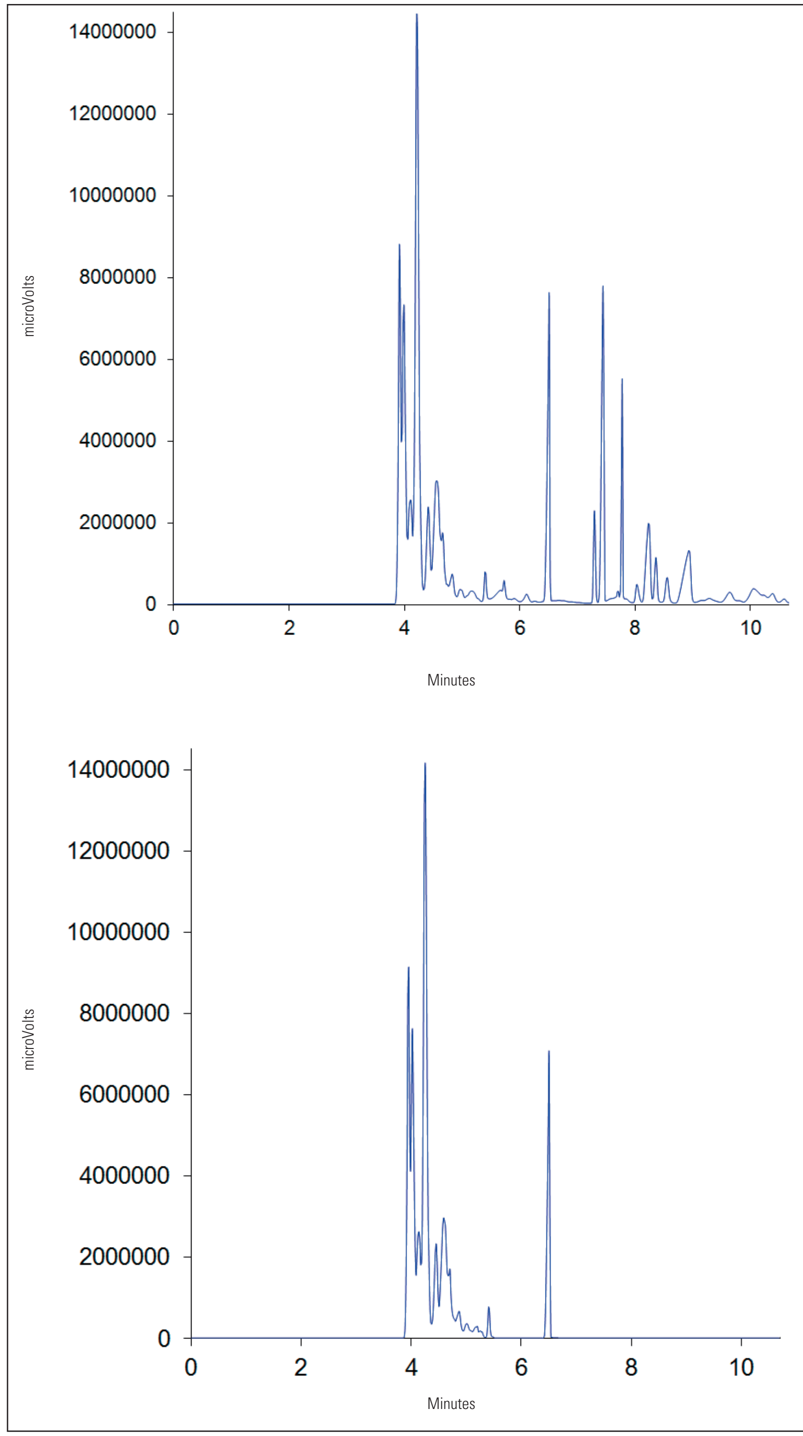

Figure 4: Real gasoline sample chromatogram without backflush (top) and with backflush (bottom). In the bottom chromatogram, the heavier matrix components are eliminated, leaving the column and the detector cleaner.

Results

Seven standard samples were used to build the calibration curve. They cover a 0.06 to 5% volume concentration range for benzene and a 0.5 to 20% volume concentration range for toluene. The calibration curve is linear with a R^2 of 0.999 for both compounds (Figures 5 and 6).

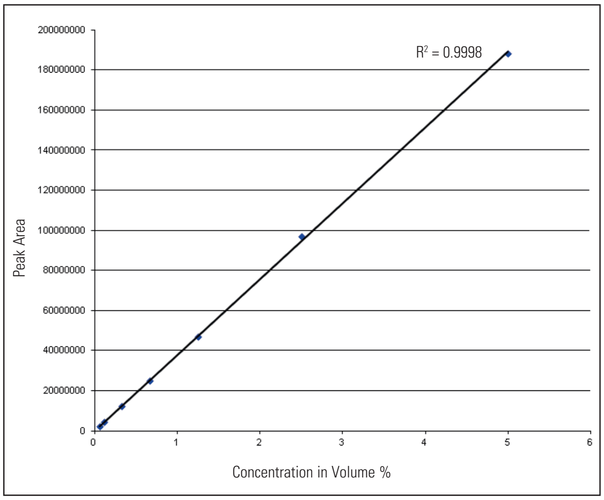

Figure 5: Calibration curve for benzene

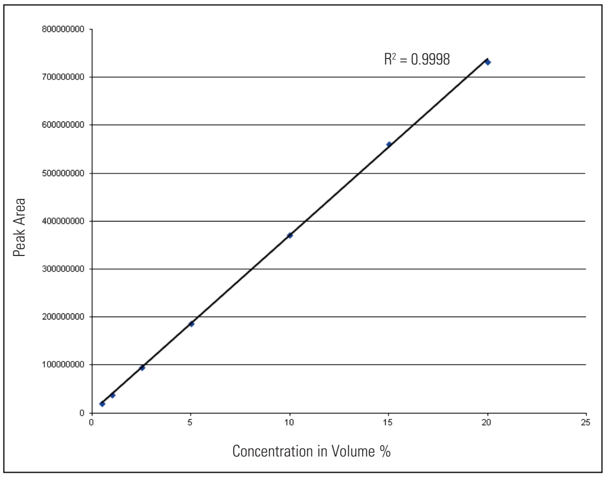

Figure 6: Calibration curve for toluene

Subsequently, a common retail gasoline sample with no alcohol content has been analyzed. The average content in benzene was 0.57% in volume and 5.84% in volume in toluene. To validate the system robustness, a total of 170 runs of the gasoline samples were performed in this study.

The repeatability was tested on 150 samples following the ASTM method specifications*. The total area RSD% was 1.21 for benzene and 1.26 for toluene confirming exceptional system stability.

Only two samples out of 150 exceeded the repeatability calculated values, respectively 0.027 and 0.195 for benzene and toluene (Table 1). This is well within the ASTM limit of one case in twenty being higher than the repeatability calculated values.

The reproducibility, as stated in the ASTM** method, was tested on a second system running 20 samples. No value outside the reproducibility test range values, respectively 0.12 and 0.77 for benzene and toluene, was observed (Table 1). Both repeatability and reproducibility exceeded the requirements of the ASTM D3606 method.

Repeatability — **ASTM D3606 Specifications (x is the average content)**

Compound	Average Content	Calculated Value	Range	% (V/V)
Benzene	0.57	0.027	0.1–0.5 >1.5	0.03 (x) + 0.01 0.03
Toluene	5.84	0.195	1.7–9 >9	0.03 (x) + 0.02 0.03

Reproducibility — **ASTM D3606 Specifications (x is the average content)**

Compound	Average Content	Calculated Value	Range	% (V/V)
Benzene	0.58	0.12	0.1–0.5 >1.5	0.13 (x) + 0.05 0.28 (x)
Toluene	5.84	0.77	1.7–9 >9	0.12 (x) + 0.07 1.15

Table 1: Repeatability and reproducibility

**The difference between successive test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the calculated values in the table only in one case in 20.*

***The difference between two, single and independent results, obtained by a different operator working in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the calculated values in the table only in one case in 20.*

Finally, to exclude the presence of non-eluted components retained into the system after a long batch of samples, a blank sample was analyzed at the end of the sequence (Figure 7). The chromatogram of the blank sample shows a clean baseline.

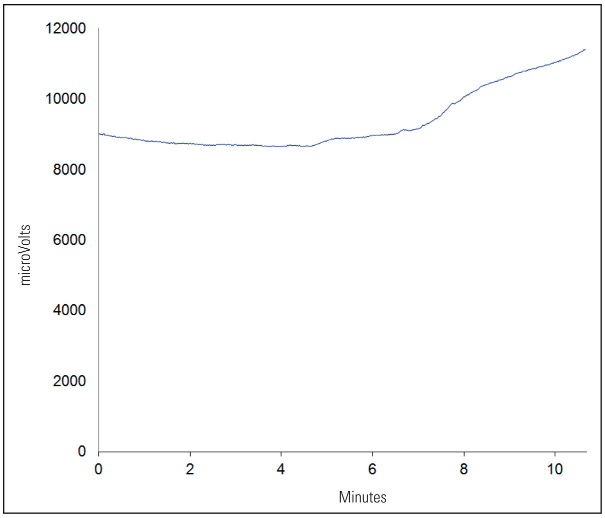

Figure 7: Blank sample chromatogram after 150 gasoline samples

Conclusions

ASTM D3606 is the standard method for benzene and toluene determination in gasoline. It implies the use of packed columns and TCD detector and, as such in most refineries, a gas chromatograph is dedicated to this analysis even if the number of daily runs is often limited to a handful of samples.

With the present application, we show the possibility to perform gasoline analysis with excellent repeatability and reproducibility using the innovative TRACE 1310 gas chromatograph.

Its Ic-SSL (Instantaneously Connect-split/splitless injector) with backflush capabilities represents a simple, compact and convenient hardware solution to keep the analytical column and the detector cleaner; the backflush timing is part of the instrumental method guaranteeing constant retention time for reliable reproducibility. Adopting an FID detector and capillary columns, this solution eliminates the need for a dedicated instrument or expensive packed column sets.

Moreover, the TRACE 1310 GC is a versatile system that can be easily switched to other applications. By simply changing injector and detector modules, different methods can be run on the same platform in a matter of a few minutes.

References

1. Federal Clean Air Act, http://www.epa.gov/air/caa/.
2. ASTM Standard D3606, "ASTM D3606 - 10 Standard Test Method for Determination of Benzene and Toluene in Finished Motor and Aviation Gasoline by Gas Chromatography", DOI: 10.1520/D3606-10, www.astm.org.

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