Reverse Flow Split/Splitless Injector: Simplification of ASTM D3606 and D4815 Methods

Stefano Pelagatti[1], Paolo Magni[1], Massimo Santoro[1], Fausto Pigozzo[1], Andrea Caruso[1], Eric Phillips[2] [1]Thermo Fisher Scientific, Milan, Italy, [2]Thermo Fisher Scientific, Austin, TX

Overview

Purpose: We propose two modified methods for the determination of the content of benzene and toluene and detection of MTBE and oxygenates in gasoline with the new Thermo Scientific TRACE 1310 GC in a configuration that is simpler and more versatile than the one proposed by the classic ASTM methods.

Methods: The analytes content is determined using an Instant Connect Split/Splitless injector with backflush, a Flame Ionization Detector and capillary columns. An autosampler is used to operate the GC in an automated way.

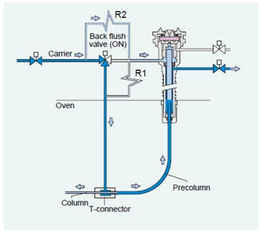
Results: With the new TRACE™ 1310 GC it is possible to quantify the content of benzene and toluene and MTBE in gasoline with a simpler configuration with results that match or exceed those of the original method in terms of repeatability.

Introduction

A number of complex mixture analyses are today resolved using GC multi-column switching solutions. Even if the analytical flow is apparently simple, these solutions require rather complex hardware from a constructions stand point. Typical complex analysis involving two analytical columns and flow switching systems can be replaced by this reverse flow split/splitless solution with a large savings in terms of capital investment, system set-up, and user training. The backflush solution adopted here enables the user to reverse the flow between the precolumn and the analytical column, eliminating heavy or "undesired" compounds, protecting the column and detector while cutting down non-productive times, thus increasing throughput.

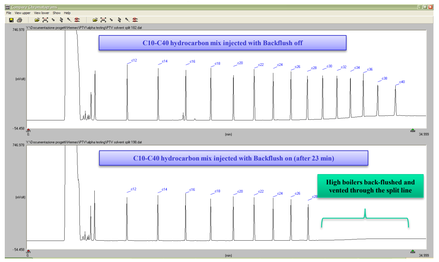
FIGURE 1. TRACE 1310 GC System

FIGURE 2. Instant Connect Split/Splitless Injector with Backflush (SSL-BKF) Schematics



In Figure 2, the pneumatic scheme of the SSL-BKF is presented. The three way valve enables the flow to reverse into the precolumn without affecting the separation into the analytical column. The compounds still in the precolumn are vented while those into the analytical column are separated and then sent to the detector. This approach is much easier compared to the balanced pressure one, while still enabling precise cuts in the chromatogram, as shown in Figure 3, where the backflush efficiency has been tested on an C10-C40 hydrocarbon standard mix.

FIGURE 3. Effects of Backflush on Hydrocarbon Mix



ASTM D3606 method overview
Benzene is used as an additive into gasoline to increase octane rating and prevent engine knocking. Being a toxic air pollutant, knowledge of its concentration can be of aid in the assessment of possible health hazards to persons handling and using gasoline. 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.

ASTM D4815 method overview
Methyl Tertiary Butyl Ether (MTBE) and other oxygenates can be added to gasoline to increase octane number and to reduce emissions. Type and concentration of various oxygenates are specified and regulated to ensure acceptable commercial gasoline quality. The ASTM D4815 method employs a valve to vent the first fraction of the eluted mixture and a backflush to eliminate the highest boiling compounds

The following methodology describes the determination of these components in gasoline, using the TRACE 1310 GC in a split/splitless-backflush configuration using capillary columns and flame ionization detector (FID), for a simpler fully automated analysis.

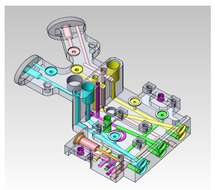
The Instant Connect SSL-Backflush Module

The instant connect SSL backflush module, shown in Figure 4, is one of the innovative features of the TRACE 1310 GC. The modules can be easily swapped by the user to ensure extreme versatility. Their plug-in concept allows the user to mount modules and replace them in a few minutes and be readily operative after installation. The instant connect SSL backflush module includes the injector body, the backflush lines and electronics for temperature and carrier gas control in a compact and self sufficient build. The whole backflush pneumatics are integrated into the manifold, as presented in Figure 5, without the need of external tubing and connections, minimizing the risk of leaks. The injector body and filters can be quickly accessed for easy maintenance and substitution of parts.

The instant connect SSL injector features a further optimized thermal profile developed to avoid sample discrimination, thus allowing the broadest range of analytes to be accurately injected. The unique injector head guarantees minimum thermal stress to the septum, therefore reducing its bleeding and extending septa lifetime.

FIGURE 4. Instant Connect SSL-BKF Module

FIGURE 5. BKF Pneumatics Built in the Manifold



Methods

ASTM D3606
The sample is injected via autosampler into the GC with the backflush flow set to OFF, and passes through the less polar Thermo Scientific TraceGOLD TG-5MS 15 m × 0.53 mm × 1 µm pre-column (P/N: 26098-2860) first where components are separated according to their boiling points. The lighter compounds elute first and are then transferred into the 30 m × 0.25 mm × 0.4 µm Thermo Scientific TraceGOLD TG-TCEP (P/N: 26069-3190) analytical polar column and detected by the FID. 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. 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. 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 precolumn are backflushed to the vent without reaching the analytical column. The backflush is turned on at 3 minutes. The resulting chromatograms are shown in Figures 6 and 7. Total run time is 10 minutes, and the system can inject a sample every 13 minutes.

FIGURE 6. GC Run without Backflush

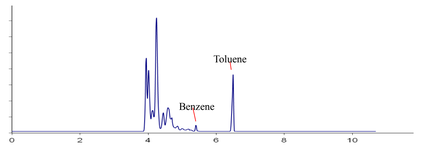
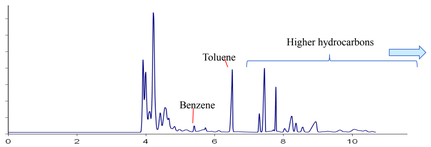


FIGURE 7. GC Run with Backflush

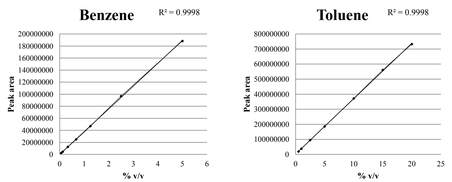


ASTM D4815
The sample is injected via an autosampler into the GC, with the backflush flow set to OFF, and passes through the polar Thermo Scientific TRACE TR-WAX precolumn to separate the oxygenates from the heaviest compounds that are backflushed. The compounds eluted from the first column are transferred to a Thermo Scientific TRACE TR-1 column (100% methyl poly siloxane) and detected by the FID. In this specific case, the backflush system is turned on after the Tert Amyl Methyl Ether peak (TAME) has eluted .The backflush is turned on at 8 minutes, and the total run time is 16 minutes.

Results

ASTM D3606
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 0.9998 for both compounds (Figure 8) .

FIGURE 8. Calibration Curves for Benzene and Toluene

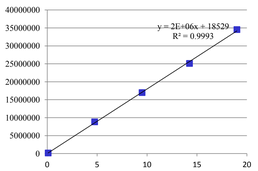


The average content in benzene was 0.57 % in volume and 5.84 % in volume of toluene. To validate the system robustness and measure the system repeatability and reproducibility, a total of 170 runs of the gasoline samples were performed in this study. The repeatability was tested on 150 samples following the ASTM method specifications. Both repeatability and reproducibility exceeded the requirements of the ASTM D3606 method. The total area RSD% was 1.21 for benzene and 1.26 for toluene confirming exceptional system stability.

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. The chromatogram of the blank sample showed a clean baseline.

ASTM D4815
The calibration consisted of 5 points from 0.095 % to 19% w/w content in MTBE. The calibration curve is linear with an R^2 of 0.9993. A gasoline sample has been analyzed and showed an average content in MTBE of 7.4 % w/w. The method repeatability was tested on 70 consecutive injections of this sample, with an area RSD% of 1.85.

FIGURE 9. Calibration Curve for MTBE and Concentrations Injected



MTBE Conc % w/w	Peak Area
0,095	161910
4,75	8835716
9,5	16989185
14,25	25109963
19	34541998

Conclusion

ASTM D3606 and ASTM D4815 are the standard methods for benzene and toluene and MTBE and other ethers and alcohols determination in gasoline. They imply 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.

The proprietary instant connect split/splitless injector with backflush capabilities represents a compact and convenient hardware solution to keep the analytical column and the detector cleaner. 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.