

**Keywords**

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 Quenching

**Changes to the Standard PFPD Sulfur Configuration To Reduce Hydrocarbon Quenching in Gasoline Samples**

**Introduction**

The OI Analytical Pulsed Flame Photometric Detector (PFPD) shown in Figure 1 has become a preferred gas chromatography (GC) detector for detection and quantitation of sulfur compounds in matrices ranging from foods, flavors, and fragrances to petroleum products and fine chemicals. The standard PFPD configuration for sulfur analysis uses a 2-mm quartz combustor, hydrogen-rich gas mixture, and 250 °C detector base temperature to produce conditions within the detector that extend sulfur emission lifetime, maximize sulfur sensitivity, and optimize sulfur-hydrocarbon selectivity. Using these conditions, individual sulfur peaks in the low-ppb range can be easily detected and quantified in most matrices.

Gasoline samples contain high concentrations of many low-molecular-weight hydrocarbon species that elute early in the chromatogram and can interfere with (i.e., quench) low levels of sulfur under normal PFPD conditions, and on the static flame photometric detectors (FPDs). By changing to the larger 3-mm combustor, a slightly more air-rich gas mixture, and more polar GC column, the hydrocarbon interference can be greatly minimized, and in some cases, completely eliminated. This application note describes how simple changes to the chromatography and standard PFPD sulfur configuration can lower sulfur detection limits in gasoline 20-fold, and how modifications to the gate setting can further minimize any residual hydrocarbon interference.

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Figure 1. OI Analytical Model 5380 Pulsed Flame Photometric Detector (PFPD)

## Hydrocarbon Quenching

The common terms “hydrocarbon quenching” and “quenching” on the PFPD refer to sulfur signal reduction by the presence of a co-eluting hydrocarbon peak. Two conditions must occur for quenching to take place: the sulfur compound must co-elute with a hydrocarbon, and the hydrocarbon must be present at very high concentrations.

Quenching occurs because the hydrocarbon consumes all the available oxygen during the combustion process. This results in incomplete combustion and formation of excess CO, rather than complete oxidation of hydrocarbon to CO<sub>2</sub>. When a sulfur compound co-elutes with the hydrocarbon under these conditions, the formation of CO allows competing side reactions to occur.



These sulfur-scavenging side reactions reduce the sulfur amount that is otherwise available for forming the sulfur emitting species, S<sub>2</sub>\*. Because less sulfur is available to form S<sub>2</sub>\*, the observed sulfur signal becomes reduced or quenched. The degree of sulfur signal suppression can vary with the amount of hydrocarbon present. In some cases, the quenching effect may be very minimal or barely noticeable. In other cases, the sulfur signal may be completely lost.

Hydrocarbon quenching is identified by the presence of baseline dips in the sulfur chromatogram. These dips are caused by quenching of the background emission due to trace amounts of sulfur present in the gases, ferrules, stainless steel, etc. or slight imperfections in the fused silica. These baseline dips indicate the presence of a high concentration of hydrocarbon that may suppress the S<sub>2</sub>\* signal when a sulfur compound co-elutes. Figure 2 illustrates baseline dips caused by hydrocarbon quenching of the background emission.

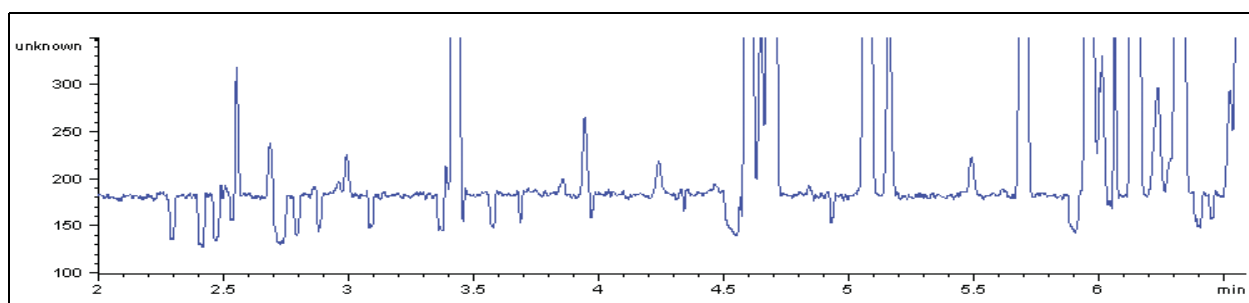


Figure 2. Expanded baseline of a PFPD chromatogram from the analysis of sulfur in gasoline acquired using standard sulfur conditions (2-mm combustor and hydrogen-rich combustor gas). The dips in the baseline indicate high concentrations of hydrocarbon present that may suppress the S<sub>2</sub>\* signal if there are co-eluting sulfur compounds.

The degree of quenching can be confirmed using PFPDView, an optional postacquisition processing software program available with the PFPD. PFPDView allows the user to view each individual sulfur or hydrocarbon emission after analysis, and determine whether quenching has taken place. As shown in Figure 3, the shape of the sulfur emission and the presence of a high-concentration hydrocarbon confirm a quenching event. A normal sulfur emission extends to a full 25 msec (when using a 2-mm combustor), but the emission delay becomes shortened when the S<sub>2</sub>\* signal has been quenched.

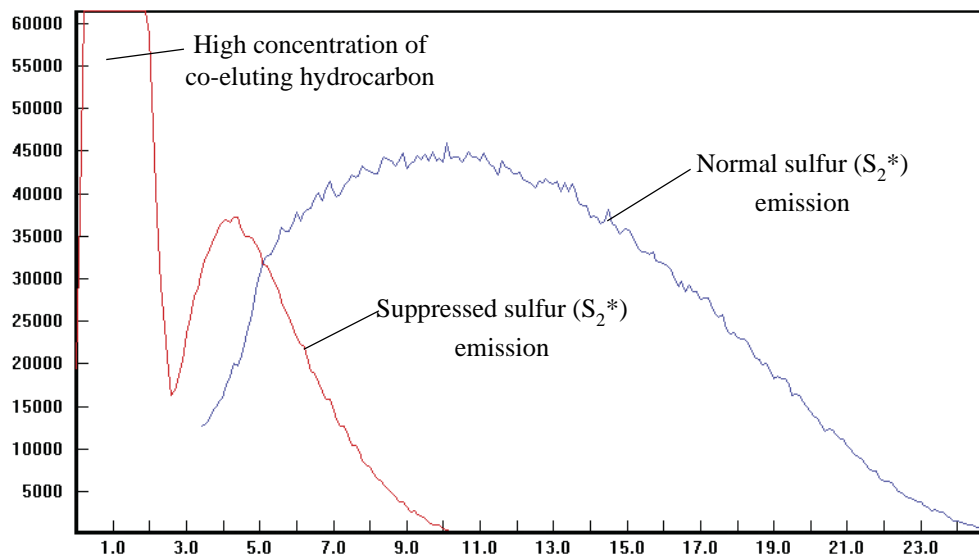


Figure 3. Overlaid emission profiles from PFPDView illustrating a normal, non-quenched sulfur emission (blue) and a sulfur emission that experienced significant quenching (red) from the co-eluting hydrocarbon

In most applications, the matrix contains insufficient hydrocarbon to cause significant quenching. However, gasoline contains many low-molecular-weight compounds eluting early in the chromatogram that can interfere with detecting co-eluting sulfur compounds. This project combines two different approaches to produce analytical conditions that greatly reduce, and in some cases, completely eliminate this hydrocarbon quenching effect in the chromatographic analysis of gasoline by the PFPD.

## Gas Chromatography Techniques to Reduce Quenching

### *Split Ratio*

Two GC techniques are commonly used to reduce or minimize quenching: an increase in the split ratio used at the injector, and proper column selection. Increasing the split ratio is simple and easy to accomplish. It decreases the amount of hydrocarbon introduced to the detector, allowing sufficient oxygen for complete combustion, and reducing the possibility of competing side reactions. The one disadvantage to increasing the split ratio is that it also decreases the amount of sulfur transferred to the PFPD, thereby raising detection limits.

When used alone, increasing the split ratio significantly reduces quenching and is a good choice for analyzing high-sulfur gasoline, such as the sample shown in Figure 4. With a 10:1 split ratio, the sulfur signal in this high-sulfur gasoline saturated the PFPD detector throughout much of the first half of the chromatogram, and significant quenching was observed in the baseline. With a split ratio of 200:1, all of the sulfur peaks were on scale, no quenching of any of the sulfur emissions was observed, and quantitation of both the individual sulfur peaks and total sulfur content was possible.

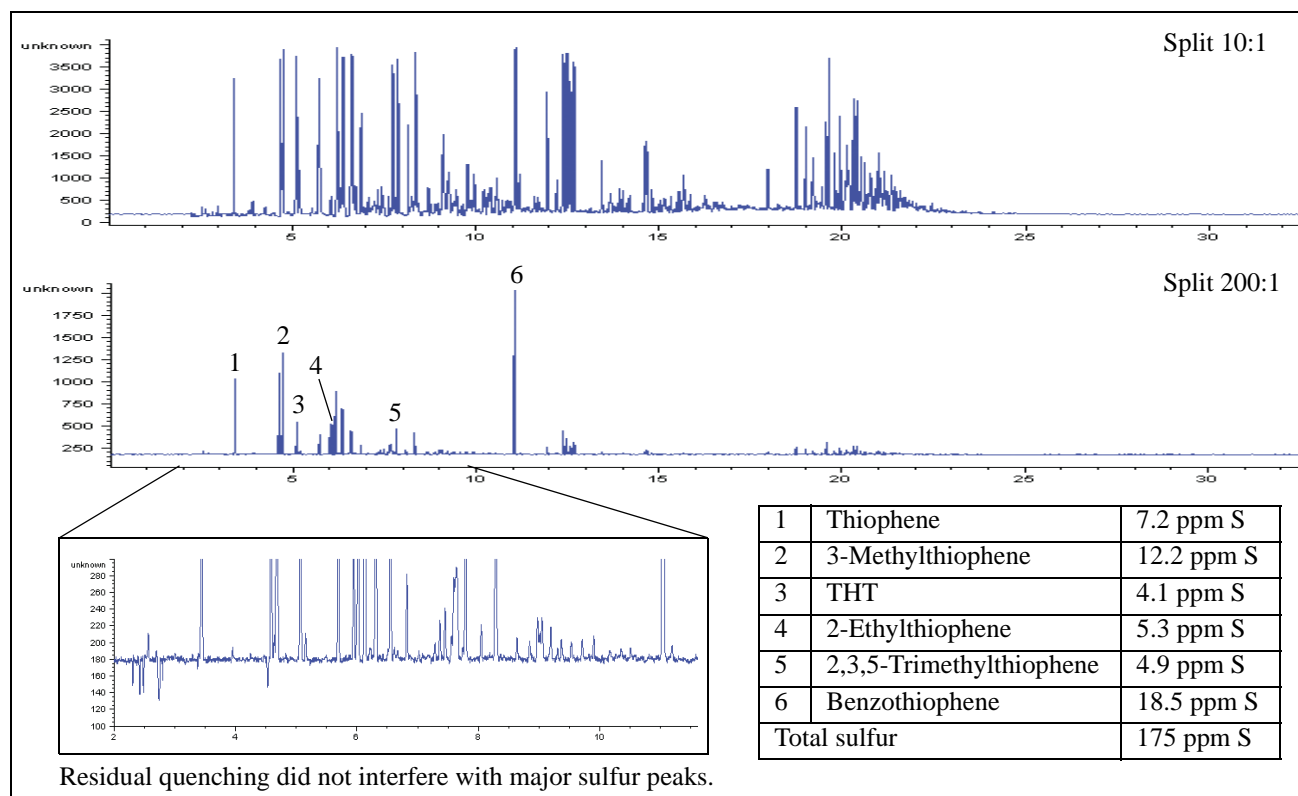


Figure 4. PFPD sulfur chromatograms from the analysis of a high-sulfur gasoline using two different split ratios. At 200:1 all sulfur peaks were on scale and no sulfur signal quenching was observed.

### Column Selection

Increasing the split ratio is ineffective for gasoline samples that contain low sulfur levels because detection limits may be raised and sulfur peaks are not detected. However, proper column selection can minimize the quenching effect. Gasoline contains only a limited number of critical pairs of sulfur-hydrocarbon compounds subject to quenching. These critical pairs occur early in the chromatogram where the highest concentration of hydrocarbons elute and where quenching is most likely to be a problem. For example, thiophene is an important, early-eluting sulfur compound in gasoline, but it co-elutes with benzene on most nonpolar phenylmethylpolysiloxane columns, as shown in Figure 5. If the sulfur and hydrocarbon peaks can be separated, the interference can be reduced. Methylthiophene and toluene are another example of a critical pair that co-elute on non-polar GC columns typically used for gasoline analysis.

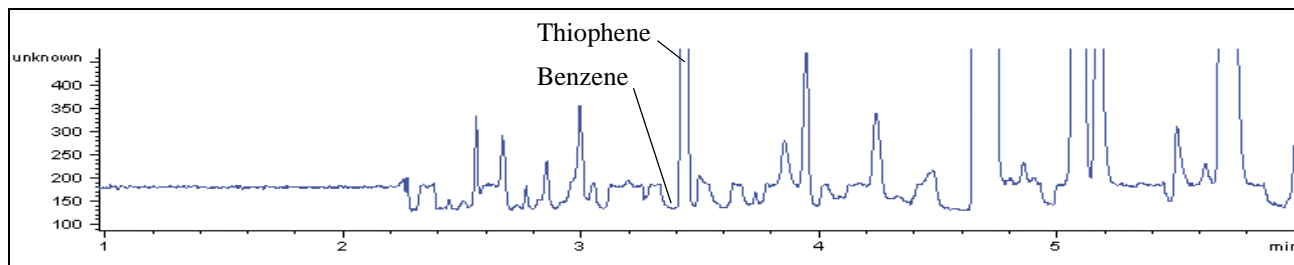


Figure 5. PFPD sulfur chromatogram of gasoline analyzed on a 5% phenylmethylpolysiloxane column using a 1- $\mu$ L injection and a 10:1 split ratio, illustrating the co-elution of thiophene and benzene. The dip in the sulfur baseline identifies the benzene. The thiophene signal has been slightly reduced by benzene, but is still visible in the chromatogram.

A slightly more polar GC column with a thick film and a slower GC program can be used to chromatographically separate the critical pairs. If the sulfur peak can be chromatographically resolved from the hydrocarbon, quenching does not occur. Figure 6 shows the PFPD sulfur chromatogram of the same gasoline analyzed on a more polar,

thick-film column using similar conditions (1- $\mu$ L injection and 10:1 split ratio). This type of column provides better separation between the thiophene-benzene and the methylthiophene-toluene, and minimizes the potential for quenching. Several types of columns have been proven successful for this separation such as Rtx<sup>®</sup>-17, DB-17, Rtx-35, and DB-35.

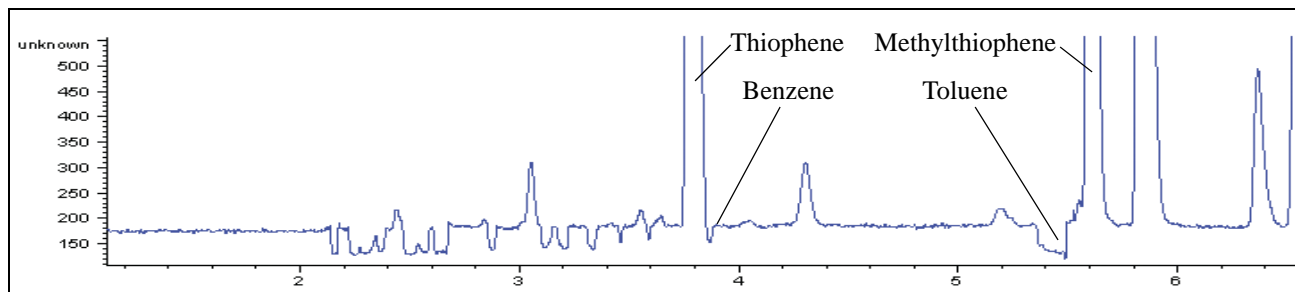


Figure 6. PFPD sulfur chromatogram of gasoline analyzed on a slightly more polar, thick-film column using a 1- $\mu$ L injection and a 10:1 split ratio, illustrating the separation of the thiophene-benzene and the methylthiophene-toluene

### Adjustments to the PFPD Configuration To Reduce Quenching

Selecting a more polar GC column minimizes the potential for quenching by spatially separating the hydrocarbon from sulfur, but it does not directly address the root cause for quenching. To do so, changing the combustion conditions within the detector that cause quenching is necessary.

#### Combustor Size

The relatively-cool conditions inside the PFPD combustor body tend to favor the extended lifetime of the sulfur emitting species,  $S_2^*$ . The standard PFPD sulfur configuration uses a 2-mm quartz combustor to extend this emission delay and maximizes sulfur-hydrocarbon selectivity. However, switching to the larger, 3-mm combustor creates flame conditions that favor hotter post-pulsed flame temperatures, and create thermodynamic conditions unfavorable for scavenging sulfur atoms and forming COS (i.e., quenching). The post-pulse flame temperature is hotter because heat transfer to the internal combustor walls is less effective. The hotter conditions promote more complete combustion of the hydrocarbons, and less potential for forming COS and quenching.

Figure 7 shows an example of how effective this can be. Gasoline was analyzed on the PFPD using 2-mm and 3-mm combustors. Using identical GC conditions (1- $\mu$ L injection, 25:1 split ratio, DB-17 column), the 3-mm combustor produced dramatically improved results with very little quenching. The level of quenching with the 3-mm combustor and 25:1 split ratio was very similar to that seen with a 2-mm combustor and 200:1 split ratio, indicating a potential ten-fold improvement in sensitivity by simply changing the combustor size.

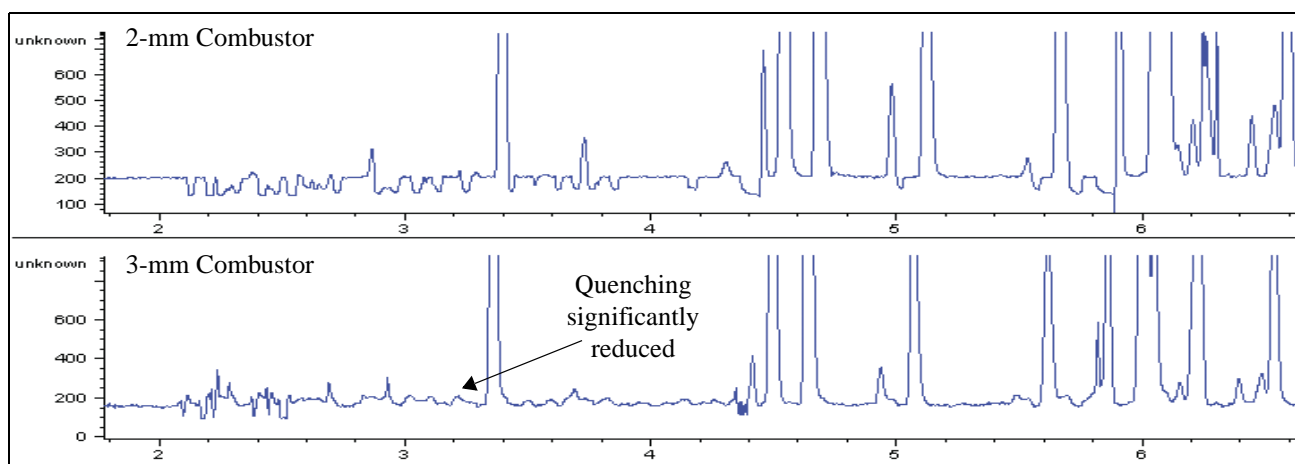


Figure 7. PFPD sulfur chromatograms of a gasoline analyzed using 2-mm and 3-mm combustors (1- $\mu$ L injection, 25:1 split ratio, DB-17 column). Simply switching to the 3-mm combustor dramatically reduced the quenching and potentially increases sensitivity ten-fold.

### Hydrogen-Air Combustion Gas Ratio

In addition to using the 3-mm combustor, a slightly more air-rich combustor gas also favors more complete hydrocarbon combustion and further heats the post-pulsed flame gases to suppress COS formation. By increasing the air in the hydrogen-air combustion gas mixture by 1.0 to 1.5 mL/minute, any remaining CO converts to CO<sub>2</sub>, suppressing formation of COS through side reactions and reducing or completely eliminating quenching.

The increased airflow, together with the 3-mm combustor and more polar, thick-film column, dramatically reduce, and in some cases completely eliminate quenching, as illustrated in Figure 8. The bottom trace shows the PFPD sulfur chromatogram of gasoline analyzed using a 1- $\mu$ L injection, 10:1 split ratio, and Rtx-35 column. The PFPD was configured with a 3-mm combustor and the airflow was increased by 1.0 mL/minute. The top chromatogram shows the same gasoline analyzed with a 2-mm combustor, no additional air, and a Rtx-5 column. With the 2-mm combustor, an increased split ratio to 200:1 was necessary to achieve significant reduction in quenching (Figure 4). Using the 3-mm combustor and increased air nearly eliminated quenching. With the new conditions, a 10:1 split ratio can be used with a 20-fold increased sensitivity.

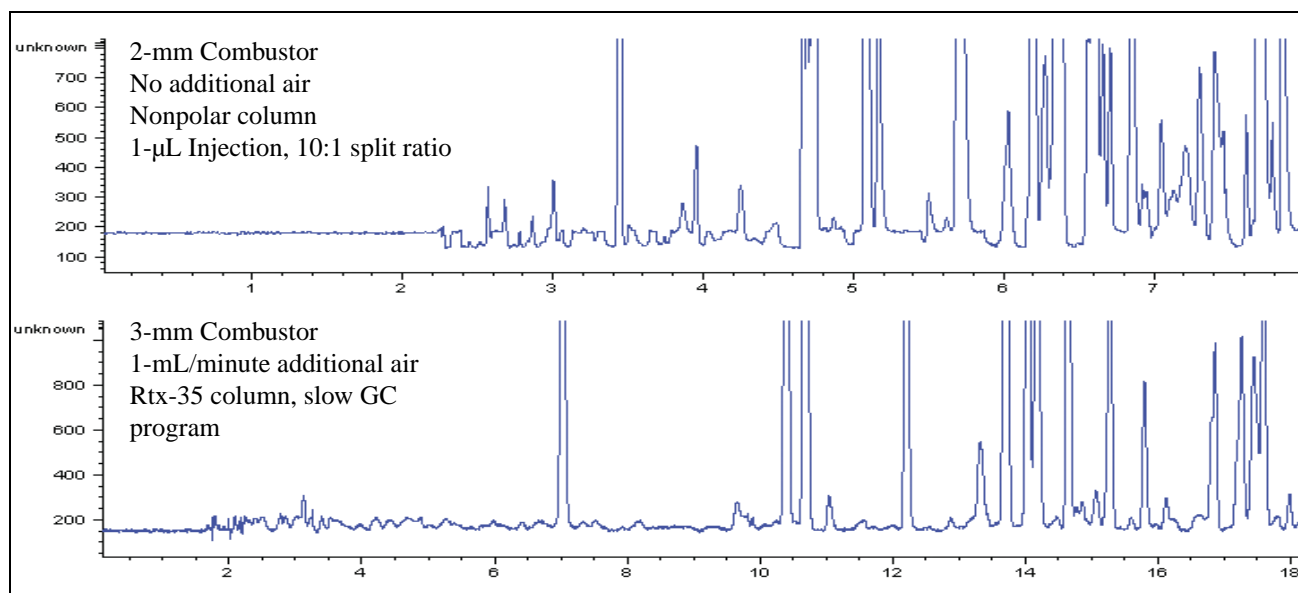


Figure 8. Baseline expansions of two PFPD sulfur chromatograms from analyzing the same gasoline using original conditions (top) and optimized conditions (bottom). The chromatograms illustrate how hydrocarbon quenching can be nearly eliminated and sensitivity improved 20-fold with only slight modifications to PFPD operating conditions. (Baseline scales are not the same because of differences in the column and GC program.)

### Gate Selection

In addition to the steps described previously, adjusting the sulfur gate mitigates any residual baseline disruption. If any incompletely-combusted hydrocarbon remains, the flame propagation through the combustor may be slowed, causing “gate invasion,” i.e., the hydrocarbon emission creeps into the sulfur gate and appears as a slightly-disrupted baseline. To avoid any residual gate invasion from the hydrocarbon, the starting time for the sulfur gate can be moved from 6 msec (the standard setting) to 8 or 10 msec, as shown in Figure 9. Although the sulfur gate has been reduced by 4 msec, the overall detector sensitivity is not affected and signal-to-noise ratio remains unchanged.

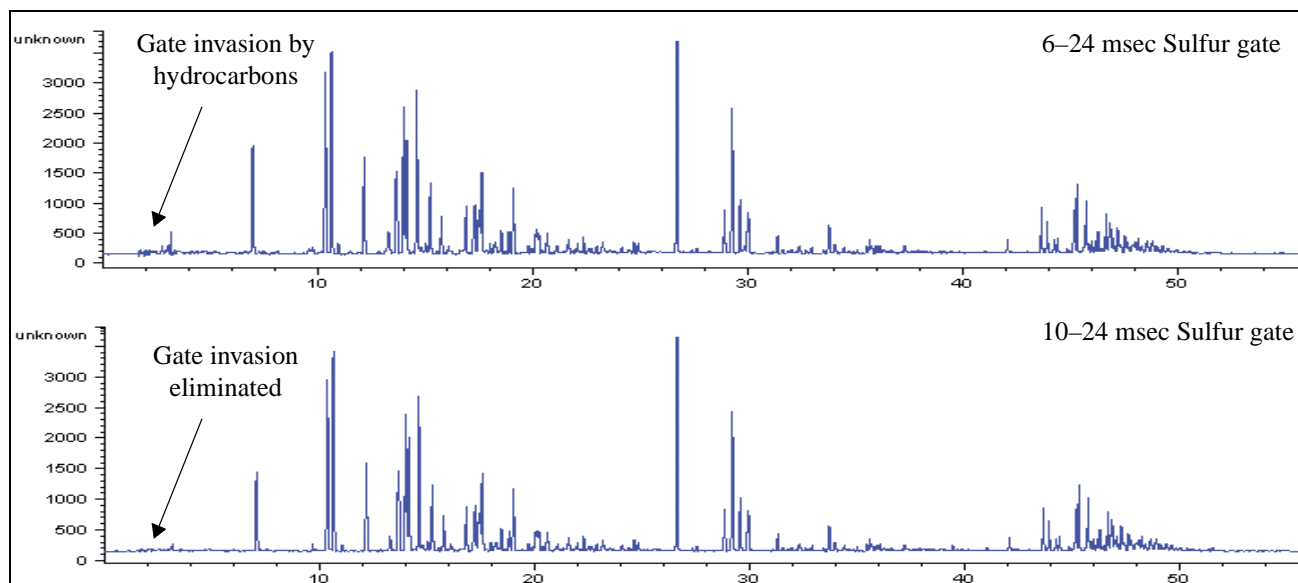


Figure 9. PFPD sulfur chromatograms of gasoline acquired using the optimized conditions (3-mm combustor, increased air, and Rtx-35 column) and two different sulfur gate settings. Starting the sulfur gate at 10 msec instead of 6 msec eliminates gate invasion but does not affect overall PFPD sensitivity.

Since the quenching effect is greatest at the end of the sulfur gate (see Figure 3), moving the stop time for the gate from 24 msec to 18 msec can also be used to minimize or eliminate quenching.

The optimized conditions were used to analyze a low-sulfur gasoline (5-ppm total sulfur) with a 1- $\mu$ L injection, 10:1 split ratio, and Rtx-35, thick-film column (Figure 10). No quenching of the sulfur signal by the high hydrocarbon background was observed despite the complete saturation of the hydrocarbon channel for much of the analytical run.

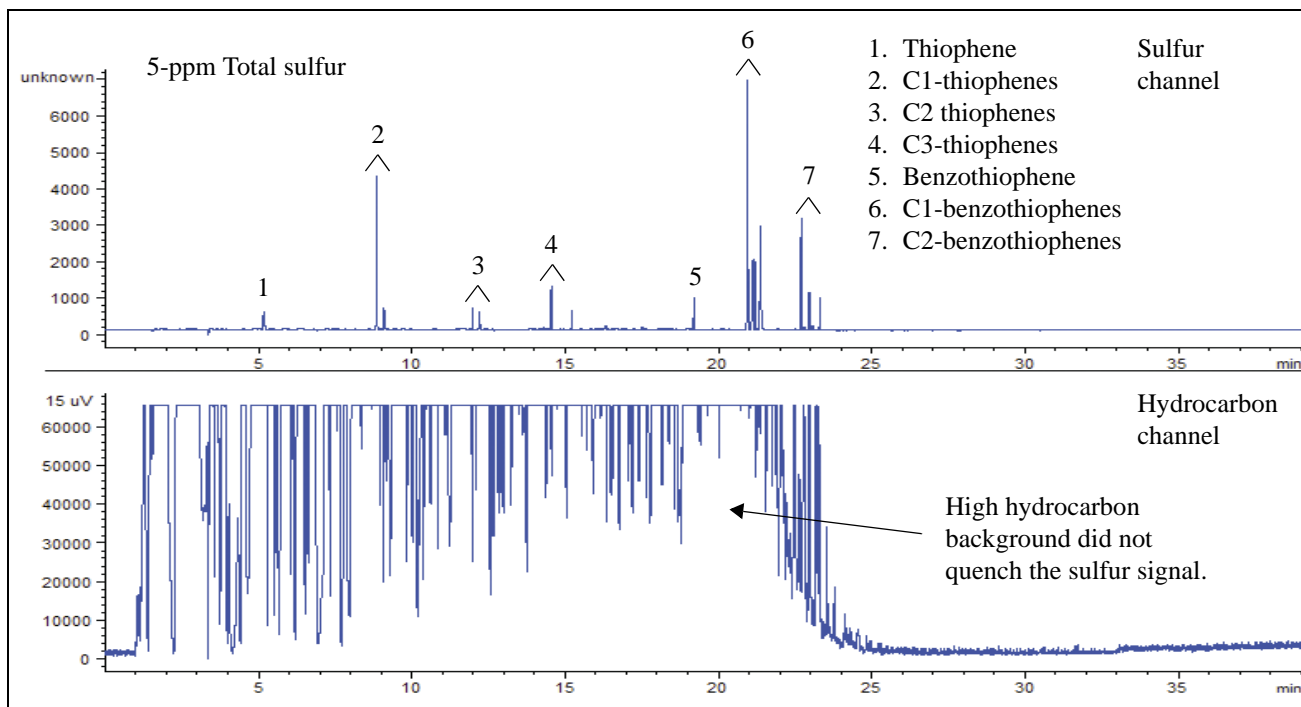


Figure 10. Simultaneous sulfur and hydrocarbon chromatograms of a 5-ppm total sulfur gasoline analyzed using the optimized PFPD conditions. No quenching of the sulfur signal by the high hydrocarbon background was observed despite the complete saturation of the hydrocarbon channel for much of the analytical run.

## Conclusions

Using the conditions described here, low-level sulfur analysis in gasoline on the PFPD is possible with hydrocarbon quenching greatly reduced, or in some cases, completely eliminated, an application not possible on the static FPD. A slightly more polar, thick-film chromatography column spatially separates the critical sulfur-hydrocarbon pairs and minimizes co-elution. The 3-mm combustor and increased air in the combustion gas support complete hydrocarbon combustion, minimizing the potential for competing side reactions that are the root cause of quenching. Careful selection of the sulfur gate start and stop times eliminates residual gate invasion, and avoids the delayed portion of the sulfur emission where quenching potential is greatest. Lastly, the optional PFPDView software program is an invaluable tool for identifying and confirming quenching events and for method development.

## Acknowledgement

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