An Improved Flame Photometric Detector for the Analysis of Dibenzothiophenes in Diesel, Distillates, and Feedstocks Using the Agilent 7890B Series GC

Application Note

Hydrocarbon processing industry

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Abstract

An Agilent 7890B Series GC equipped with a new high temperature Flame Photometric Detector (FPD) was used to determine the sulfur compound distribution of benzothiophenes in heavier fuels and feedstocks such as cycle oils and catalytic cracker feeds. A Capillary Flow Technology (CFT) Deans switch configuration was used to cut selected parts of a HP-1 column separation to a mid-polar DB-17HT column to help minimize quenching and to enhance separation of the sulfur compounds. Identification of many alky dibenzothiophenes in Light Cycle Oil (LCO) and other feedstocks was determined.

Introduction

The distribution of sulfur in various feedstocks is of great importance to the refining industry as processes are adjusted and optimized to meet clean fuel requirements. Sulfur levels in fuels and distillates are being driven lower by environmental regulation. Catalyst optimization for hydrotreating can also benefit from a knowledge of the distribution of dibenzothiophene class sulfur compounds. The new Flame Photometric Detector on the 7890B Series GC with its high temperature capability and improved sensitivity is an ideal, easy-to-use tool for the determination of sulfur in blending stocks such as light cycle oil (LCO). Detail on sulfur content is vital for optimal hydrotreating or hydrocracking conditions where profiling dibenzothiophenes is of particular importance to achieve the lowest sulfur levels in the final products. These include dibenzothiophene, methyl (C1) substituted dibenzothioiphenes, dimethyl (C2) dibenzothiophenes, C3, and C4 dibenzothiophenes. To achieve optimal results, the FPD must be operated at temperatures above 300 °C. A CFT Deans switch system where the Benzothiophene region is cut to a midpolar 30 m × 0.25 mm, 0.15 µm DB17 for additional separation and detection using the FPD was employed. This enhanced separation reduces the possibility for quenching caused by coelution with hydrocarbons.

Experimental

Figure 1 shows a diagram of the system used in this work. In an effort to minimize coelution which will occur with complex hydrocarbon feedstocks, a Deans switch is incorporated so that selected sections of a first dimension separation can be heart cut to undergo a secondary separation on a midpolar column. While this approach will not eliminate coelution, it can be significantly reduced leading to a better determination of sulfur distribution. The FPD can suffer from quenching effects when coelution with hydrocarbons occur. The new FPD+ has excellent sensitivity of 2.5 pg sulfur/second.

Hydrocarbon fuels or feedstocks such as diesel and LCO will elute completely with the configuration shown in Figure 1. When heavier feedstocks are injected, the columns and temperatures used in this work will not permit complete sample elution. Short 0.53 mm id columns with thin stationary phase could be used, however, separation would not be adequate and quenching effects would be severe in the boiling point range of interest for dibenzothiophenes. As with many purged CFT devices, the Deans switch can be backflushed allowing heavy feedstocks to be injected without damaging the higher resolution column sets that are normally used in such configurations. Backflush methods were used when analyzing the gas oil feedstocks. The Multimode inlet (MMI) was used for sample introduction in a temperature programmed split mode. This inlet was also well suited for backflush methods.

Typical parameters for nonbackflush and backflush methods are given in Tables 1 and 2, respectively.

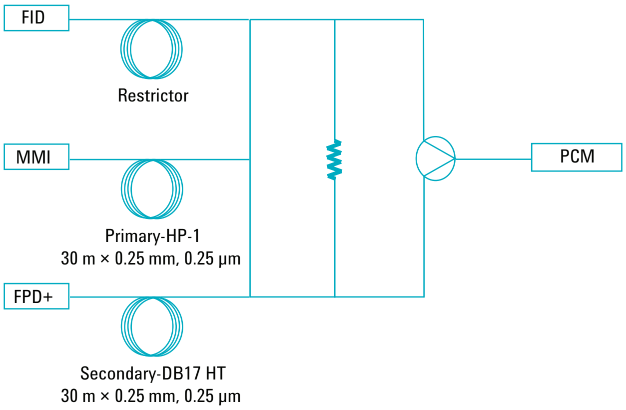
Agilent 7890B Series GC Deans Configuration with the FPD Plus

Figure 1. FPD + system with Deans switch.

Table 1. System Parameters

Gas chromatograph	Agilent 7890B Series GC
Injection port	Multimode Inlet (MMI)
MMI program	250 °C (0 minutes) to 350 °C at 50 °C/min
Split ratio	Variable, between 25–150 to 1
ALS	7693A, 1 µL
Oven program	40 °C (0 minutes) to 250 °C (10 minutes) at 10 °C/min, then 15 °C/min to 350 °C (10 minutes)
MMI	1.25 mL/min constant flow, 28.3 psi at 40 °C
PCM A-1	2.20 mL/min constant flow, 20.7 psi
FPD+	Transfer line, 325 °C to 360 °C Emission block, 150 °C Hydrogen 60 mL/min, Air 60 mL/min, Makeup 60 mL/min
FPD mode	Constant makeup + fuel
FPD data rate	5 Hz
Column 1	30 m × 0.25 mm, 0.25 µm HP-1
Column 2	30 m × 0.25 mm, 0.25 µm DB17-HT
Deans cut windows	18 to 24 minutes, 20 to 24 minutes, various

Table 2. Parameters for a Typical Backflush Method, Parameters not Listed are the Same as in Table 1

Flow program column 1 (MMI)	1.25 mL/min for 27 minutes then 100 mL/min to –3.6 mL/min
Flow program column 2 (PCM A-1)	2.2 mL/min for 27 minutes then 100 mL/min to 4 mL/min
Deans cut windows	23 to 25 minutes, 25 to 26 minutes, various
Sulfur standards	alkylated dibenzothiophenes

Results and Discussion

The FPD has undergone a redesign that enables it to operate at higher temperatures. A two zone heating configuration has been implemented where the emission block and transfer line temperatures are independent. Thermal isolation between these two zones allows the transfer line to be operated up to 400 °C while the emission block is kept at an optimal 150 °C. This makes it possible to analyze heavier feedstocks and distillates than would otherwise be possible. The transfer line is deactivated with an Agilent proprietary process leading to superior inertness which is critical to avoid adsorption or reaction of sulfur compounds with the transfer line wall.

Fuels and distillates analyzed in this work include transportation (highway) diesel, LCOs, and a cracked gas oil. The reactivity of dibenzothiophenes in hydrodesulfurization (HDS) reactions vary widely, making the distribution of these compounds of great interest to process engineers. This information assists in process optimization as well as the certification of final sulfur levels in finished products. Results are presented in order of sample final boiling point beginning with diesel and concluding with a gas oil feedstock having a final boiling point of over 540 °C.

The Deans switch was operated in a different mode that most are familiar with in classic 2D separations. Normally, a very narrow cut window is used to separate a single compound from a complex matrix of interfering compounds on a second column. In this work, wide cut windows of several minutes were typically used in order to transfer a group or class of compounds to the second column. This relied on the collective selectivity of the first and second dimension columns to separate the sulfur species from the hydrocarbons. Some coelution of hydrocarbons cannot be ruled out therefore some hydrocarbon quenching of the sulfur emission is possible. Compounds were identified from retention times by running individual pure standards. Sulfur standards were purchased from Chiron AS, Norway.

Highway Diesel

Highway diesel currently has a total maximum sulfur concentration of 15 ppm in the US. A significant amount of this sulfur can be present as various dibenzothiophenes. A calibration curve was constructed for 4,6 dimethyl dibenzothiophene (15.1% sulfur by weight), the most prominent sulfur species. The FPD shows quadradatic response due to emission from the active S2 species. The square root of area versus ppm of 4,6-dimethyldibenzothiophene linearizes the data and is plotted in Figure 2.

Figure 3 reveals C2 and C3 dibenzothiophenes in a Deans heart cut from 18 to 24 minutes. The bulk of remaining sulfur in highway diesel is represented by these compounds. Earlier cuts do not show any significant sulfur compounds. Based on the 4,6-DM DBT calibration, the sulfur content in this cut is approximately 1.5 ppm. Sulfur distributions in diesel has been extensively studied by a variety of techniques [1].

Light Cycle Oil

Next, light cycle oils were investigated. Two samples were choosen that received different processing and, therefore, expected to show different sulfur levels and compound distribution. Cut windows used for both samples were 18 to 24 minutes designed to capture the majority of dibenzothiophenes. The first sample, LCO1, shows a complex distribution where dibenzothiophene and 4-methy dibenzothiphene are the major species. FID and FPD+ chromatograms are shown in Figures 4A and 4B, respectively. The second sample, LCO2, shown in Figure 5, contains primarily dibenzothiophene and 4 methydibenzothiophene. Sulfur speciation in cycle oils has been widely studied [2,3].

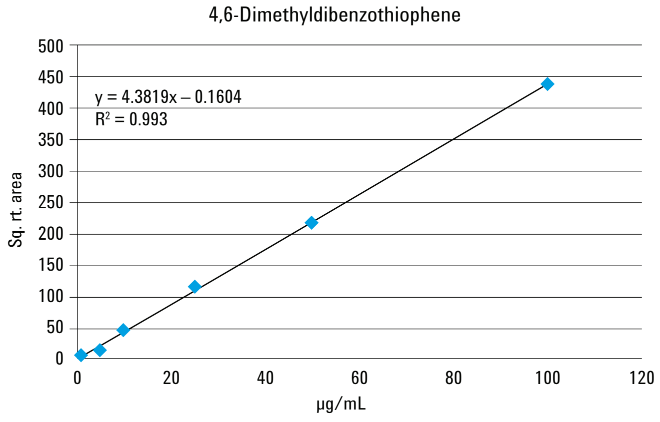

Figure 2. Calibration of 4,6 dimethy dibenzothiophene from 1 to 100 ppm. The split ratio is 25 to 1.

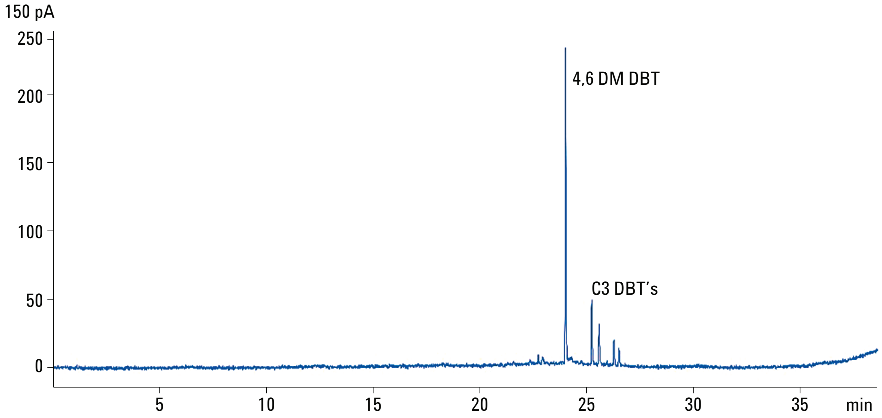

Figure 3. Highway diesel. Deans cut 18 to 24 minutes. Transfer line temperature: 325 °C, FPD emission block temperature: 150 °C.

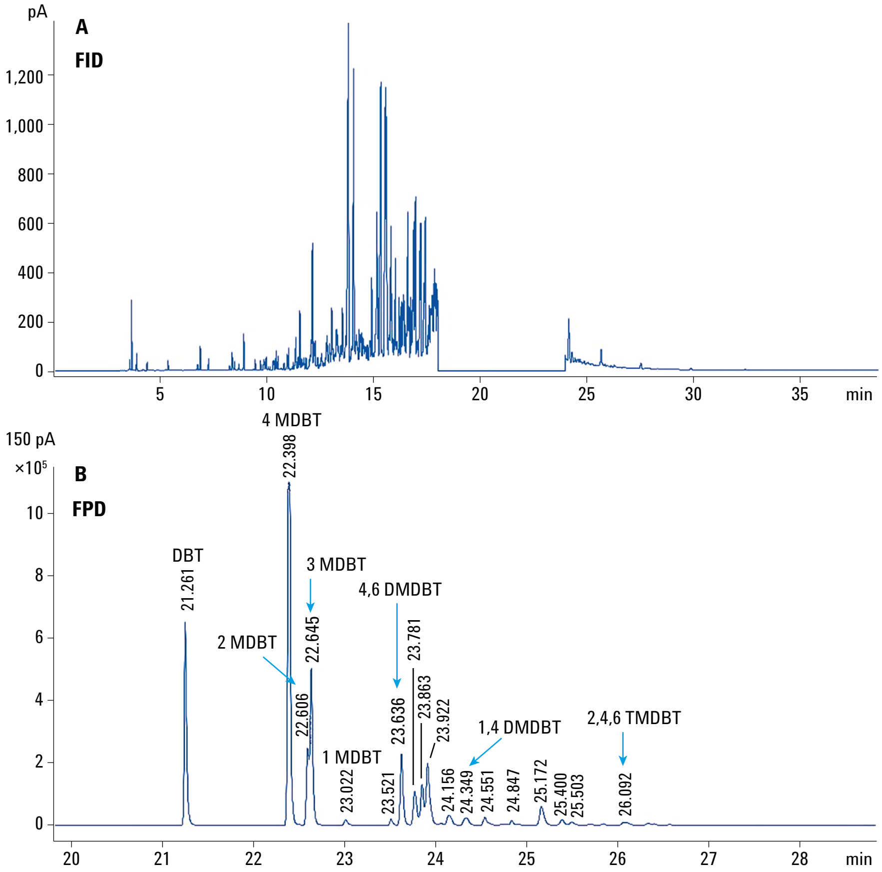

Figure 4. Analysis of substituted Dibenzothiophenes in LCO1 using a CFT Deans switch system and an Agilent 7890B Series GC FPD. Transfer line temperature: 350 °C, FPD emission block temperature: 150 °C. Column 1: 30 m × 0.25 mm, 0.25 µm HP-1ms, Column 2: 30 m × 0.25 mm, 0.15 µm DB-17HT. Deans cut 18 to 24 minutes.

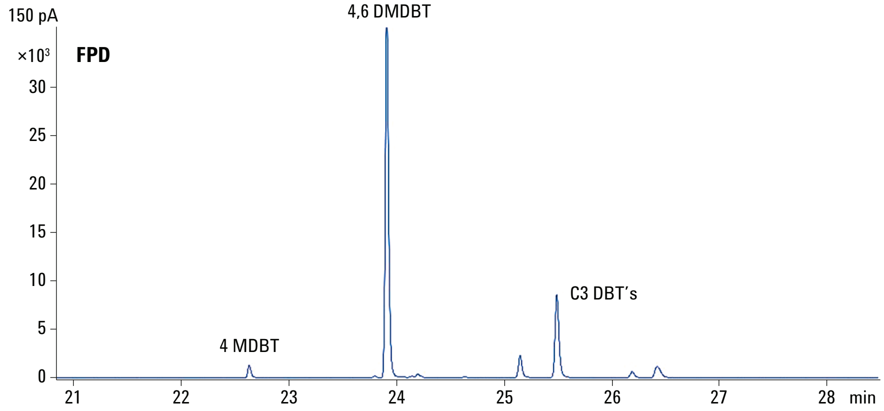

Figure 5. FPD chromatogram of sample LCO2 showing lower levels of dibenzothiophenes. Deans cut: 18 to 24 minutes.

Cracked Gas Oil

As is the case for many CFT devices such as purged unions and purged splitters, the Deans switch can be operated in a backflush mode. Therefore Deans heart cutting and backflushing can be combined in a single analysis. A GC method was developed that incorporates both of these features allowing injection of feedstocks with final carbon numbers of over 50. The gas oil used was first diluted 5 to 1 in toluene prior to injection. Typically, backflush will be programmed to occur at C30 or less to protect the column set and avoid the need for long runs or high tempeature bakeouts. Figure 6 shows the FID chromatogram to illustrate the timing of the heart cut and backflush. An FCC feed, such as the sample used, contains a significant amount of sulfur and shows a very complex distribution of higher molecular sulfur compounds especially in the boiling point ranges selected for this heart cut. This is evident in Figure 7. Benzonaphthothiophenes compounds may also be present in this fraction. Quenching is more likely to occur in this range given the increased coelution possibility. However, a number of compounds can be identified from retention times as shown in Figure 8 where the heart cut is 20 to 24 minutes. Such distributions can be useful to study the effect of steric hendrance caused by alkyl substitution [4]

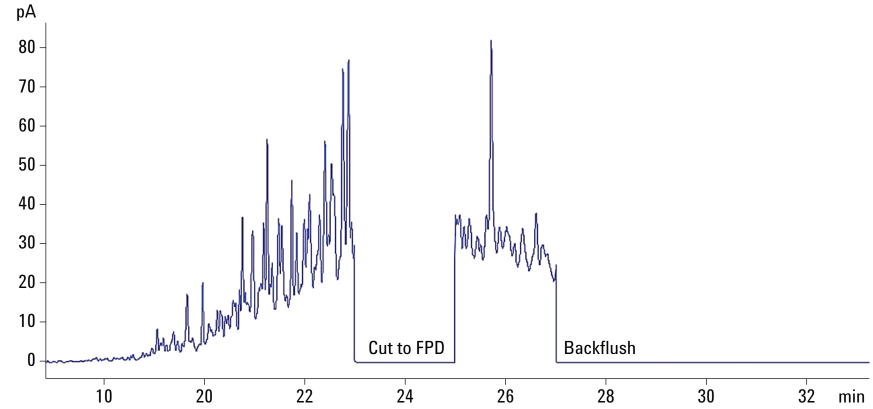

Figure 6. FID chromatogram of a cracked gas oil. Deans cut at 23 to 25 minutes and backflush beginning at 27 minutes are clearly visible.

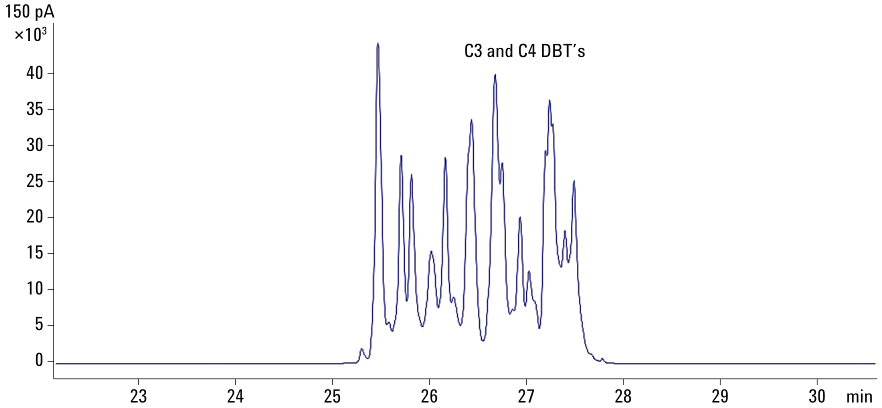

Figure 7. FPD 23 to 25 minute heart cut showing distribution of C3 and C4 alkyl dibenzothiophenes. FPD temperature: 360 °C.

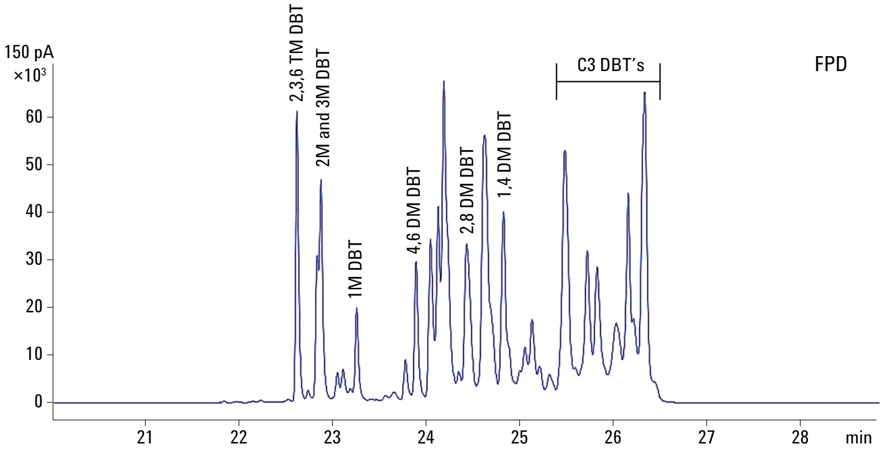

Figure 8. FPD 20 to 24 minute heart cut showing distribution of C2 and C3 alkyl dibenzothiophenes.

Conclusion

The new Flame Photometric Detector available on the Agilent 7890B Series GC is capable of operating at 400 °C which enables a new range of applications particularly for sulfur analysis of fuels, distillates, and feedstocks. To maximize selectivity and minimize coelution, a 2D separation system was used. Heart cuts were made from a nonpolar HP-1 or DB-1 column to a midpolar DB-17HT column. However, other column combinations can certainly be used as desired. CFT enables the Deans switch to be used in a backflush mode. Using backflush with the Deans switch allows heavy distillates and feedstocks with carbon numbers over C50 to be analyzed without damaging the column set with temperatures above 350 °C. Also, runtimes can be kept short with backflush of the heavy fraction. The system can successfully determine the distribution of alkyl dibenzothiophenes in a wide variety of distillates, fuels, and feedstocks.

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