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Analysis of Sulfur Compounds in Hydrocarbon Fuels using Gas Chromatography with Pulsed Flame Photometric Detection

Introduction

Most analyses of sulfur in finished fuels are performed due to regulatory agency requirements. The primary concerns regarding the sulfur content in fuels are the effects of oxidized sulfur species resulting from fuel combustion. The two primary areas of concern are the effects on health and downstream equipment. In both cases, the corrosive nature of the sulfur gases is responsible for the adverse effects. In the future, the quantity of sulfur permitted in fuels will probably be reduced due to its role in pollution formation.

Most of the analytical techniques currently used for sulfur determination are designed to give a total sulfur content number with no determination of the specific sulfur compounds present. The identity of the sulfur containing compounds may be important in determining the origin of the sulfur containing compounds and the most efficient method of removing these compounds.

Most analyses of crude oil sulfur content and the resulting refined products are currently performed by X-ray fluorescence (XRF). XRF is a rapid and relatively inexpensive method for determining the total sulfur content of a hydrocarbon liquid, and the matrix effects are not serious for this application. XRF gives only a bulk measurement of the sulfur content of the oil, so it is not an appropriate method if speciation of the sulfur compounds is desired.

A gas chromatograph/mass spectrometer system (GC/MS) may be used for the analysis of the sulfur compounds in fuels, but the sensitivity of the mass spectrometer may be lower than desired in the full scan mode. Setting up a mass spectrometer in the selected ion monitoring mode for this type of analysis requires a skilled operator to properly select the ions monitored and the acquisition parameters to develop a method that is free from interferences. In addition, the sensitivity of the mass spectrometer for individual compounds can be affected by the presence of coeluting major components. If a major component elutes from the column with a trace component, the ionization efficiency of the trace component may be significantly reduced.

The sulfur chemiluminescence detector (SCLD or SCD) is often used for the speciation of sulfur compounds in fuels. The SCLD is sensitive and selective, but it can be a difficult detector to keep operating at peak efficiency. The detector requires considerable maintenance and a skilled operator to produce optimal results. This is a difficult detector to use in a mobile laboratory or other field installation.

The flame photometric detector (FPD) is a detector that has been used for a considerable period of time for the analysis of sulfur compounds in fuels. The FPD is a selective detector if a narrow bandpass filter is used to reduce interferences; however, this also reduces the sensitivity of the detector by limiting the emitted light reaching the photomultiplier tube. The FPD can also suffer from quenching effects when major hydrocarbon compounds elute with trace sulfur compounds. The quenching reduces the sulfur response, limiting the sensitivity and dynamic range of the detector. The FPD can also suffer from flameouts, where solvents or major hydrocarbon compounds eluting from the column change the air to fuel ratio enough to cause the flame to be extinguished.

The pulsed flame photometric detector (PFPD) reduces the problems associated with the other detectors used to determine speciated sulfur in fuels. The PFPD uses a hydrogen and air mixture at a flow rate that will not support continuous combustion. The combustor is filled with an ignitable gas mixture, the flame is ignited, the flame propagates through the combustor, and it burns out when all the fuel is consumed (Figure 1). The cycle is repeated continuously at a rate of 3–4 hertz. The PFPD adds a time dimension to the emission analysis in addition to the wavelength selectivity in a conventional FPD. Figure 2 shows the emission profiles of a hydrocarbon, phosphorus, and sulfur. Hydrocarbon emission shows little delay, phosphorus emission shows a slight delay, and the sulfur emission occurs over a significantly delayed time period. By analyzing a specific time slice of the emitted radiation, the selectivity of the detector is significantly enhanced. For example, if the time slice from 10–24 milliseconds is analyzed, the majority of the emission is from sulfur with only a small contribution from phosphorus and no hydrocarbon contribution.
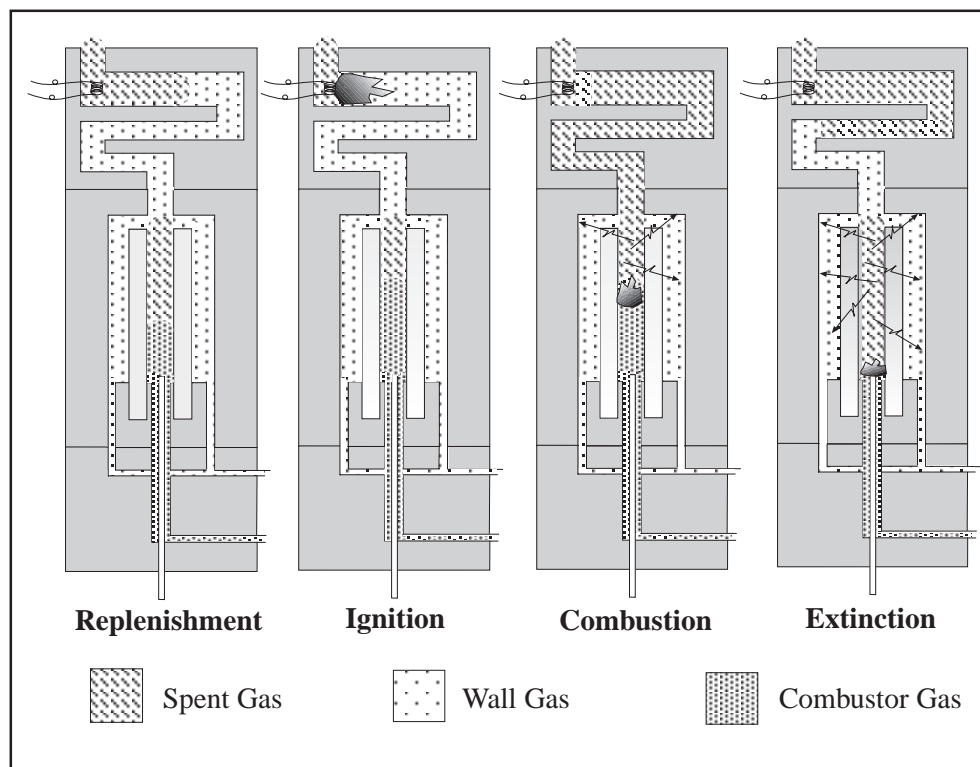

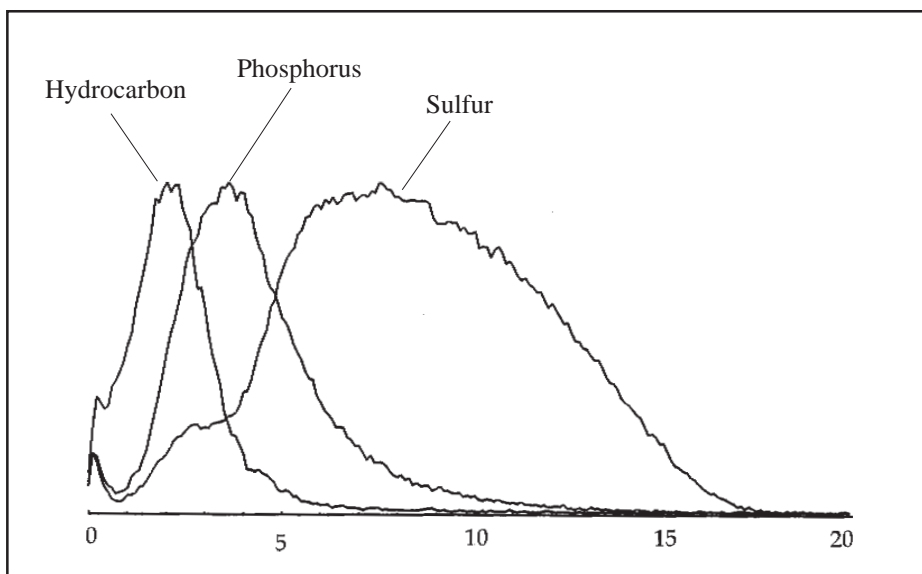Figure 1. Four Phase Cycle of Propagating Flame

Figure 2. Emission in the PFPD

A diagram of the OI Analytical Model 5380 PFPD is shown in Figure 3. The combustion of the gas mixture begins after it has filled the volume of the detector and reaches the ignitor. The flame then propagates through the combustor, the heteroatoms are excited and emit, the emitted light passes through the light pipe and filter, then is amplified by the photomultiplier tube. The signal from the photomultiplier tube is then passed into the detector controller electronics where it is processed and a 0 to 1 volt analog signal is then output to the gas chromatograph data system. Changing the filter and photomultiplier tube changes the selectivity for various heteroatoms.

A properly optimized PFPD is significantly more selective than the standard FPD since using time slices as well as filters increases selectivity. The PFPD is also more sensitive than a FPD for sulfur analysis, although this is somewhat application and compound dependent. Another advantage of the PFPD is its equimolar response to sulfur, so the determining factor for the intensity of emission is the mass of sulfur present with little effect from the chemical form of the sulfur. Equal masses of sulfur in a thiophenic compound, a mercaptan, or a thiazole will give the same emission intensity. This allows quantitation of sulfur in a number of compounds using a single standard. Quenching is reduced in the PFPD compared to the standard FPD. Flameouts are no longer a problem since the ignitor is on constantly and the flame is ignited whenever a combustible mixture reaches the ignitor.
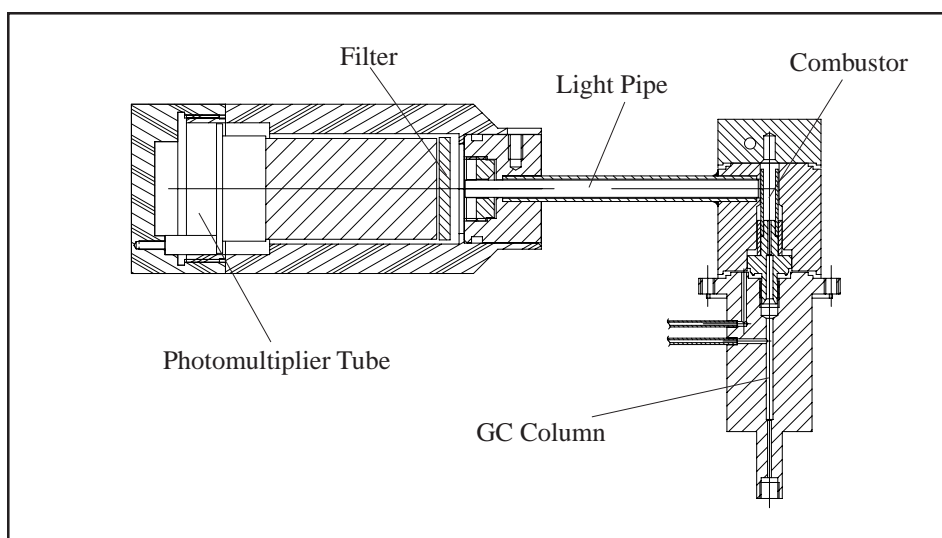

Figure 3. Diagram of the OI Analytical Pulsed Flame Photometric Detector

One minor disadvantage of the PFPD is that like the FPD the sulfur response is not linear but quadratic. This can be handled by the data system by constructing a quadratic calibration curve, which is possible with almost all current data systems, or by using the linearization function built into the OI Analytical Model 5380 PFPD Detector Controller. When the linearization in the controller option is selected, the digital signal processor in the controller is used to mathematically convert the quadratic response into a linear response.

Results and Discussion

An OI Analytical Model 5380 PFPD was mounted on a Hewlett-Packard Model 6890 Gas Chromatograph fitted with a split/splitless injection port. Data was collected using Hewlett-Packard ChemStation GC Software. The samples were injected in split mode using the split ratio necessary to keep the peaks on scale, usually a 100:1 to 150:1 split ratio. The column used for all samples was a 30 m x 0.25 mm I.D. J&W DB-5MS column with a 0.25 micron phase thickness. The samples were injected at 35°C with a 5 minute hold time, then the temperature was ramped up at 5°C per minute until all the compounds had eluted.

Figures 4 and 5 are sulfur chromatograms of regular unleaded gasoline and super regular unleaded gasoline from 1992. The primary sulfur compounds in these samples are thiophenes and benzothiophenes. Note that there is a much higher concentration of thiophene and substituted thiophenes in the super regular unleaded gasoline. This is not surprising since aromatics were common octane enhancers during this time, and thiophenes may be formed during the platforming process if sulfur is present in the feedstock of a platforming unit. For comparison, Figures 6, 7, and 8 are sulfur chromatograms of regular unleaded, super regular unleaded, and premium unleaded gasolines collected in 1997. The overall sulfur content of these gasolines is lower than the 1992 gasolines, especially the more highly refined premium unleaded.

GC: HP 6890
Injector: Split/Splitless
Injection Mode: Split mode, 100:1 split
Injector Temp: 270°C
Column: J&W DB-5 ms, 30 m x 0.25 mm, 0.25 μm phase
Column Flow: 1 mL/min, constant flow mode
Oven: 35°C for 1 min, 5°C/min to 170°C, 2 min hold
Detector: OI Analytical Model 5380 PFPD
                 Pulse rate - 4 Hz, Photomultiplier tube - R1924, Filter - BG12
Detector Temp: 300°C

A.   Thiophene
B. C_1-Thiophenes
C. C_2-Thiophenes
D. C_3-Thiophenes
E.   Benzothiophene
F. C_1-Benzothiophenes
G. C_2-Benzothiophenes
H. C_3-Benzothiophenes
I.   Dibenzothiophene
J. C_1-Dibenzothiophenes
K. C_2-Dibenzothiophenes
L. C_3-Dibenzothiophenes
M.   Alkyl Sulfides and
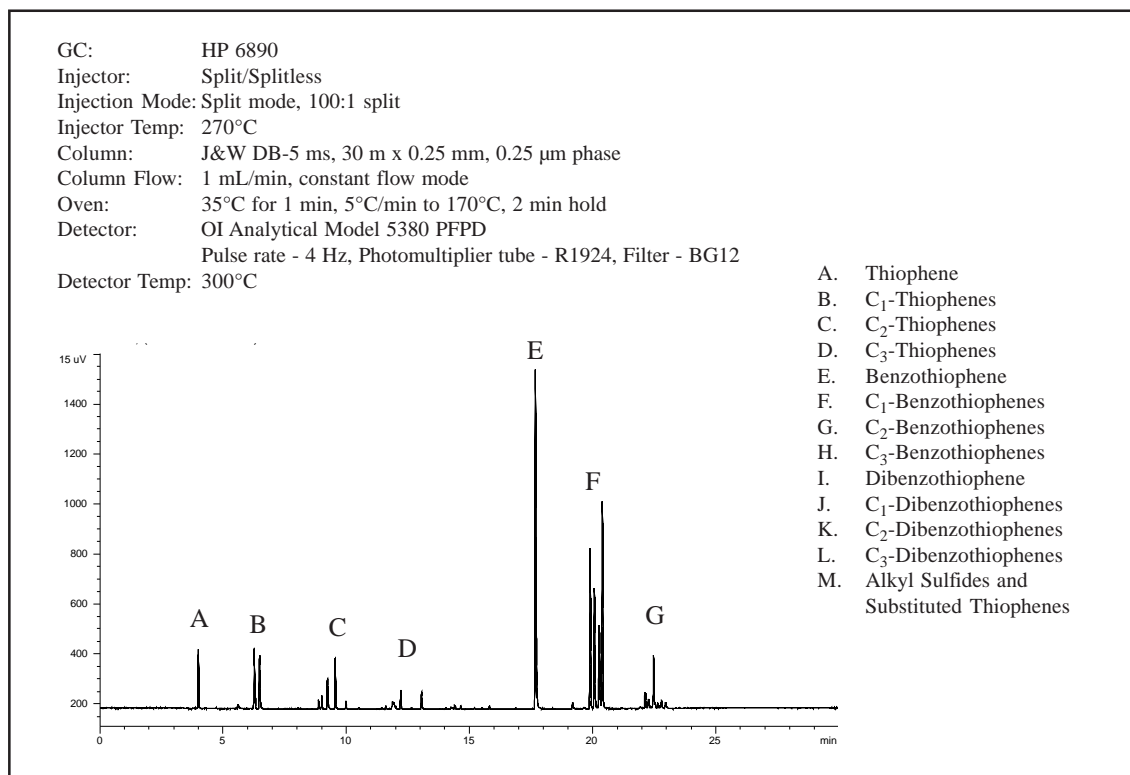   Substituted Thiophenes

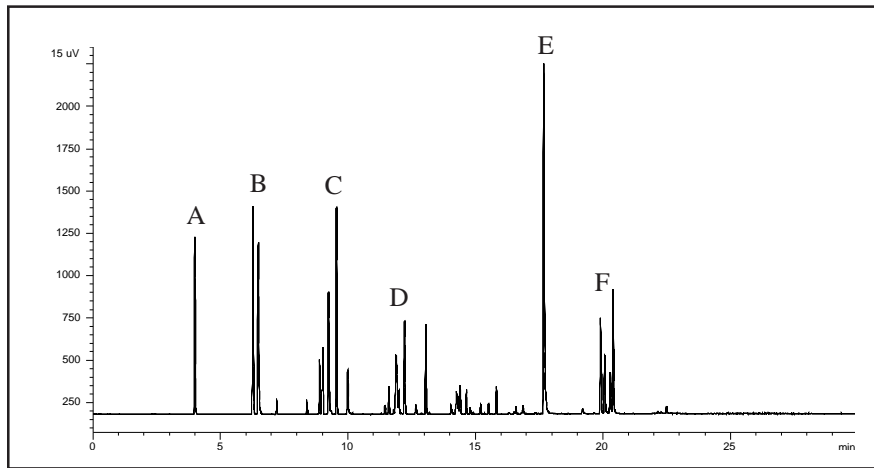Figure 4. Regular Unleaded Gasoline (1992)

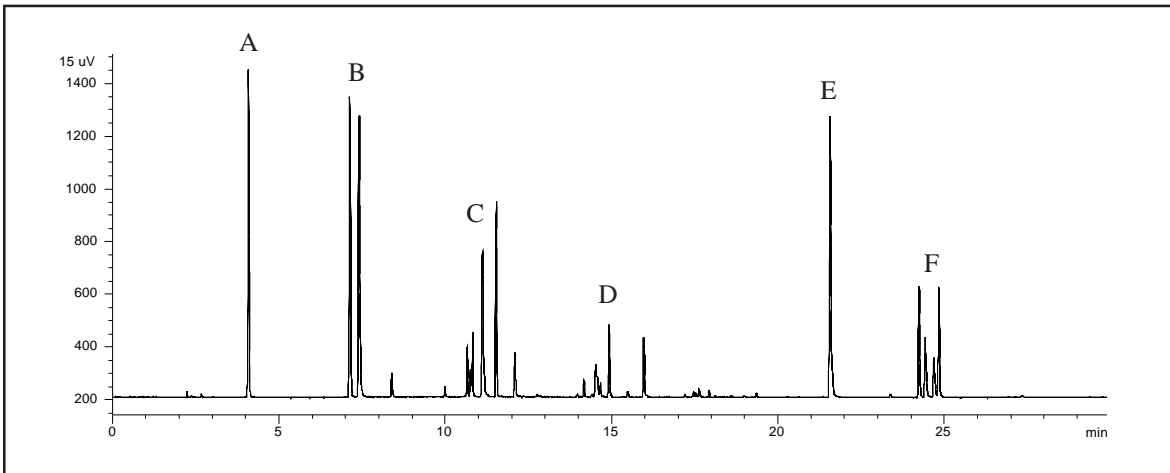Figure 5. Super Regular Unleaded Gasoline (1992) (same conditions as Figure 4)

Figure 6. Company E Regular Unleaded Gasoline (1997) (same conditions as Figure 4)
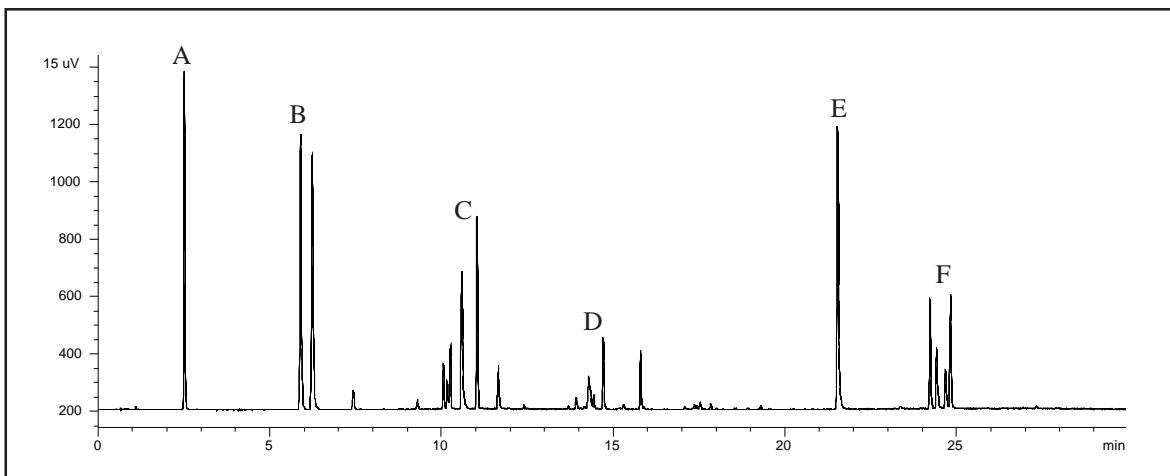

Figure 7. Company E Midrange Unleaded Gasoline (1997) (same conditions as Figure 4)
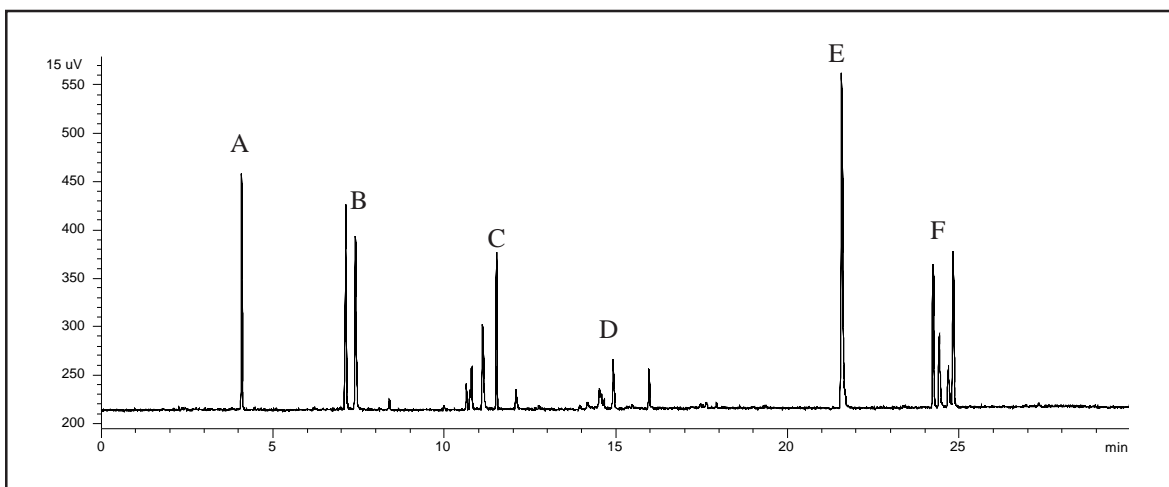
Figure 8. Company E Super Unleaded Gasoline (1997) (same conditions as Figure 4)

Figures 9 and 10 are sulfur chromatograms of diesel fuels from two different companies. Diesel fuel is a less volatile, higher boiling fraction of crude oil than gasoline, so the sulfur compounds in diesel fuels are generally higher molecular weight compounds than those in gasoline. The lightest sulfur compounds in the diesel fuels are the benzothiophenes, with a significant portion of the sulfur compounds existing in the form of dibenzothiophenes. The diesel fuel from Company S is higher is sulfur content than the diesel fuel from Company DS. In addition, the diesel fuel from company DS has a higher proportion of heavier sulfur compounds.

GC: HP 6890
Injector: Split/Splitless
Injection Mode: Split mode, 100:1 split
Injector Temp: 270°C
Column: J&W DB-5 ms, 30 m x 0.25 mm, 0.25 μm phase
Column Flow: 1 mL/min, constant flow mode
Oven: 35°C for 1 min, 5°C/min to 220°C, 2 min hold
Detector: OI Analytical Model 5380 PFPD
                 Pulse rate - 4 Hz, Photomultiplier tube - R1924, Filter - BG12
Detector Temp: 300°C

A. Thiophene
B. C_1-Thiophenes
C. C_2-Thiophenes
D. C_3-Thiophenes
E. Benzothiophene
F. C_1-Benzothiophenes
G. C_2-Benzothiophenes
H. C_3-Benzothiophenes
I. Dibenzothiophene
J. C_1-Dibenzothiophenes
K. C_2-Dibenzothiophenes
L. C_3-Dibenzothiophenes
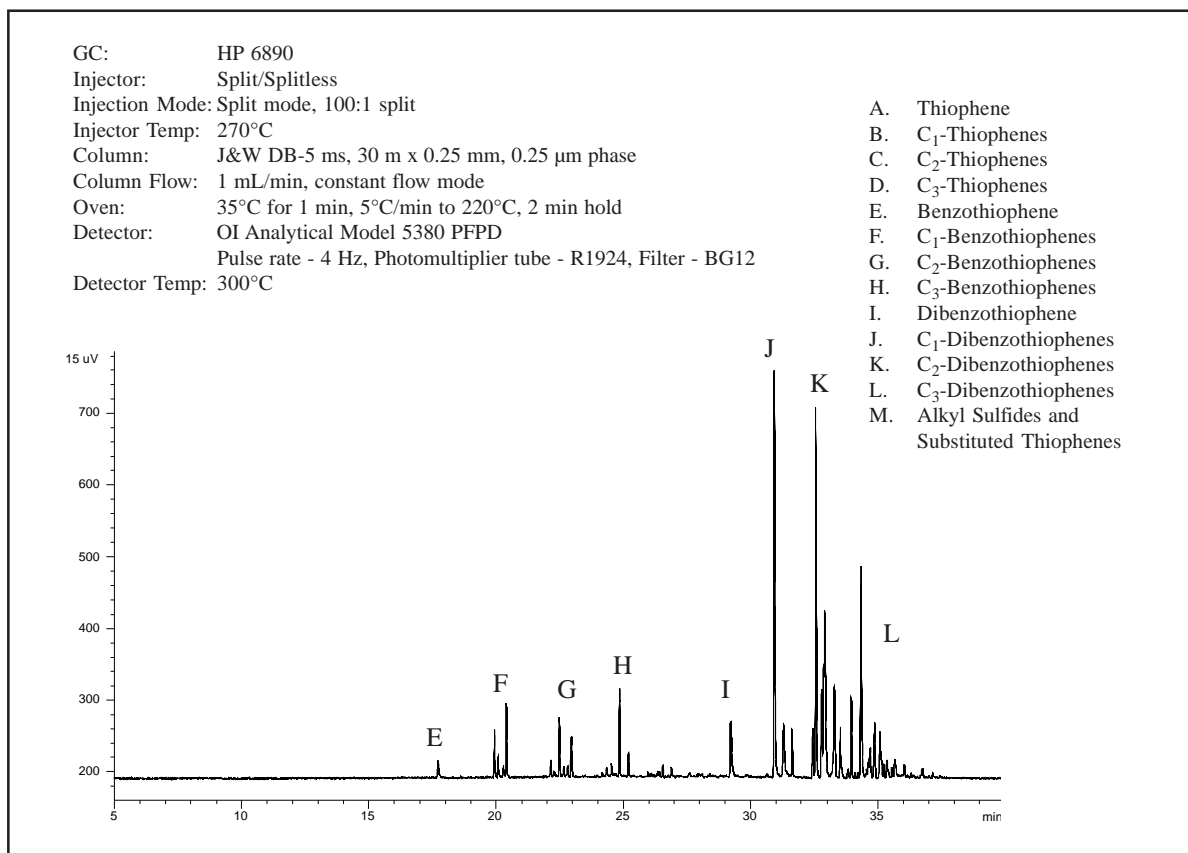M. Alkyl Sulfides and
    Substituted Thiophenes

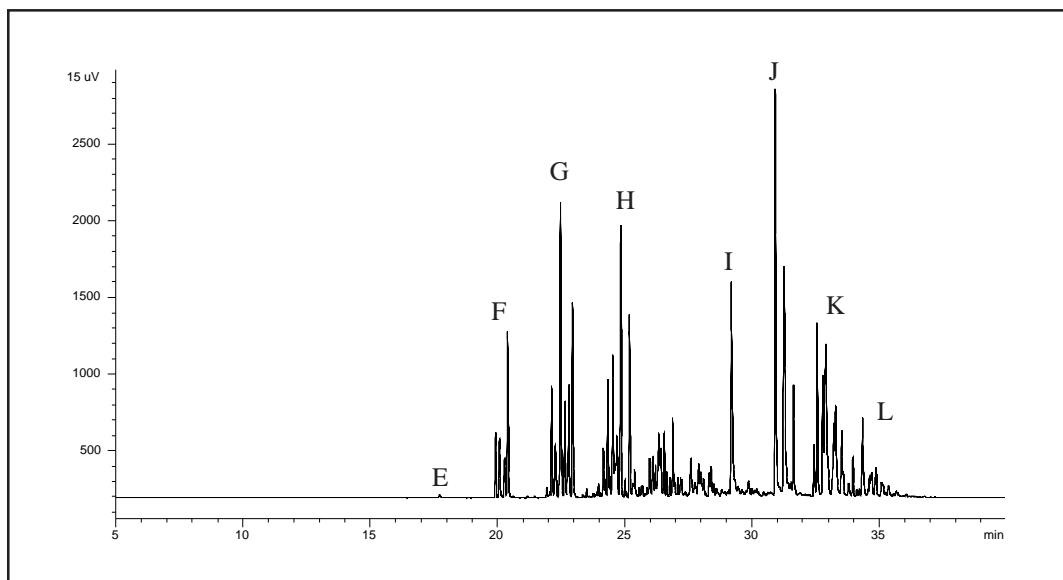Figure 9. Company DS Diesel Fuel (1992)

Figure 10. Company S Diesel Fuel (1992) (same conditions as Figure 9)

Figures 11 and 12 are the sulfur chromatograms from two samples of kerosene, a high sulfur kerosene and a desulfurized kerosene. The chromatograms clearly show the difference in the sulfur content of the two kerosenes. The low sulfur kerosene has a very low concentration of alkyl substituted benzothiophenes. The high sulfur kerosene has alkyl substituted thiophenes, alkyl substituted benzothiophenes, and acyclic sulfur compounds present. Kerosene is intermediate in volatility between gasoline and diesel fuel, and the distribution of sulfur compounds shows this with heavier compounds than the gasoline samples and a high molecular weight cutoff lower than diesel fuel.

Figure 13 is a sulfur chromatogram of a fuel oil sample. This is the heaviest crude oil fraction analyzed, and the distribution of sulfur compounds reflects this. The sulfur compounds are higher molecular weight on the average than the other samples. There is also a larger "hump," or contribution from the unresolved organic component thaat contains sulfur. The sulfur compounds in the heavier diesel fuel from Company S are similar to those in the fuel oil, but the diesel fuel has a higher proportion of lighter sulfur compounds and a smaller hump.
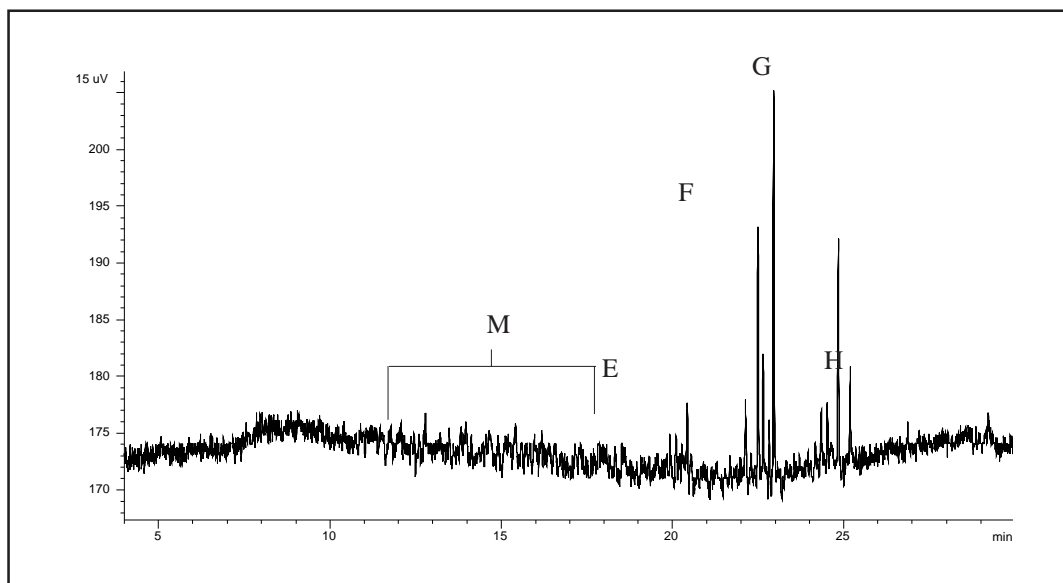

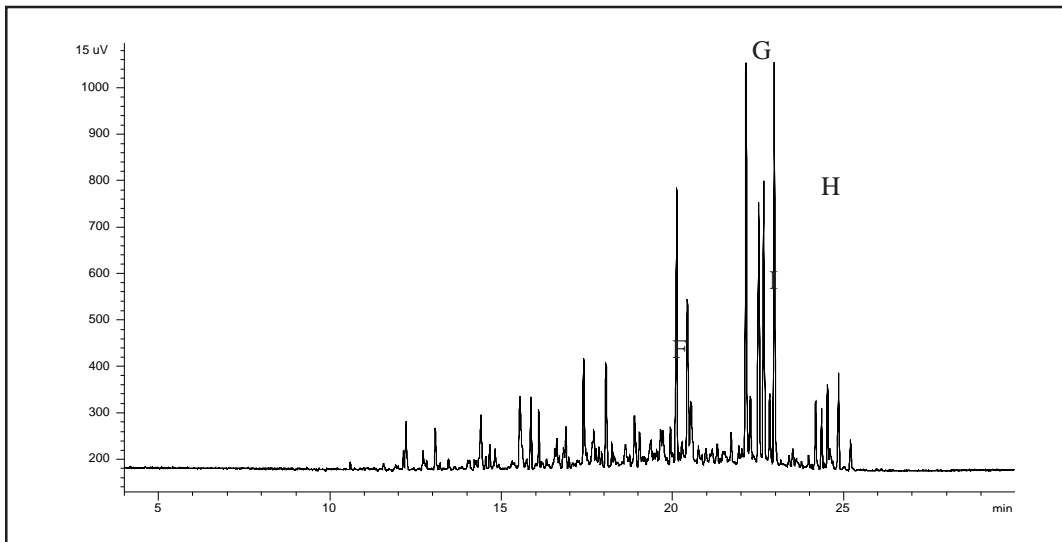Figure 11. High Sulfur Kerosene (same conditions as Figure 4)

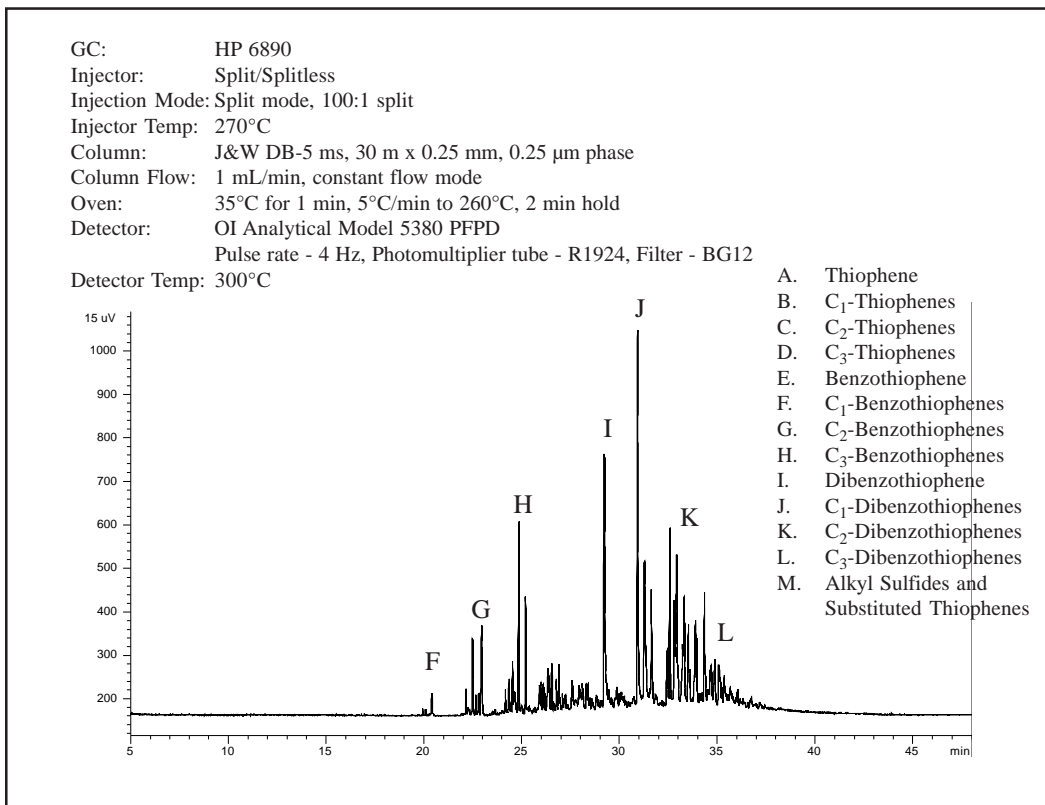Figure 12. Low Sulfur Kerosene (same conditions as Figure 4)

GC: HP 6890
Injector: Split/Splitless
Injection Mode: Split mode, 100:1 split
Injector Temp: 270°C
Column: J&W DB-5 ms, 30 m x 0.25 mm, 0.25 μm phase
Column Flow: 1 mL/min, constant flow mode
Oven: 35°C for 1 min, 5°C/min to 260°C, 2 min hold
Detector: OI Analytical Model 5380 PFPD
                Pulse rate - 4 Hz, Photomultiplier tube - R1924, Filter - BG12
Detector Temp: 300°C

A.   Thiophene
B. C_1-Thiophenes
C. C_2-Thiophenes
D. C_3-Thiophenes
E.   Benzothiophene
F. C_1-Benzothiophenes
G. C_2-Benzothiophenes
H. C_3-Benzothiophenes
I.   Dibenzothiophene
J. C_1-Dibenzothiophenes
K. C_2-Dibenzothiophenes
L. C_3-Dibenzothiophenes
M.   Alkyl Sulfides and
     Substituted Thiophenes

Figure 13. Fuel Oil

Conclusion

The pulsed flame photometric detector is an excellent detector for the analysis of sulfur compounds in hydrocarbon fuels. Sulfur compounds may be analyzed over a wide volatility range and a wide concentration range. The detector is very selective for sulfur in this sample matrix and there are no obvious interfering peaks. There was no evidence of quenching of the sulfur response in these samples even though there was a high concentration of hydrocarbons present.