Agilent 355 Sulfur Chemiluminescence Detector (355 SCD): Sulfur Compounds in Distillate Fuels

Technical Overview

Introduction

This technical overview discusses the analysis of commercial jet fuels for sulfur using an Agilent 355 Sulfur Chemiluminescence Detector (SCD). The sensitivity, selectivity, and linear response of the 355 SCD coupled with the separation capabilities of the Chrompack CP Sil 5 CB capillary column demonstrate the power of the Agilent 355 SCD as the ideal detector for low-level sulfur analysis.

Distillate fuels are generally divided into three types: jet fuels, diesel fuels, and heating oils. Jet fuels are typically blended from low-sulfur or desulfurized kerosene, cracked blending stocks, and hydrocracked blending stocks. The two basic types of jet fuels are naptha and kerosene.

Naptha jet fuel is primarily produced for military uses and consists of wide boiling range stock that extends through both gasoline and diesel ranges. Military JP-4, as illustrated below, has restrictions similar to ASTM type B fuel, with limitations on freezing point (–60 °F to –70 °F maximum), gravity (45 to 70 API), Reid Vapor Pressure (2.0 psi to 3.0 psi), and aromatic content (20 to 25 percent maximum). [1] The wide boiling range of 150 to 550 °F provides for great flexibility in blending kerosene, naptha, and low-octane gasoline. Commercial jet fuels are regulated to a narrower boiling point range of 350 to 550 °F and are typically sold as JP-5.

Sulfur requirements as specified in ASTM D 910 specify that total sulfur levels of commercial jet fuels be regulated to less than 500 ppm. [2] Lower levels are common in military fuels to avoid corrosional wear of engine parts from sulfur combustion products and to avoid conditions that may promote gum formations, which lower storage life.

The data in Figure 1 illustrate the sensitivity of the 355 SCD for trace level analysis of sulfur in a hydrocarbon matrix without interference. The equimolar response of the 355 SCD allows the operator the flexibility to use either an external standard method or an internal standard method for quantification of both individual components and total sulfur content.

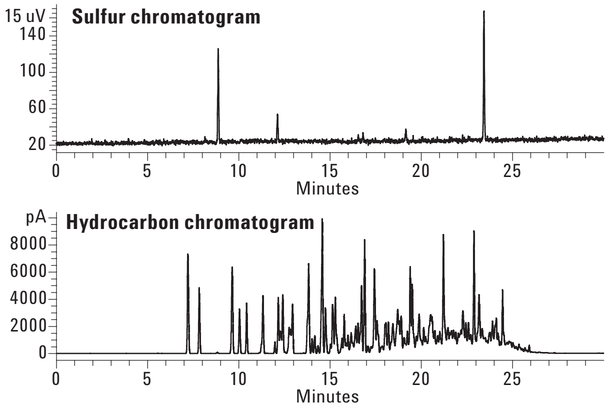

Figure 1. **Simultaneous FID / SCD chromatogram of JP-4 (split 1:10).**

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Figure 2 illustrates the use of an internal standard, in this case ethyl methyl sulfide (EMS 10.6 min), to quantify each peak, as well as the total sulfur content. EMS was spiked into the sample at 2.8 ppm as sulfur. Individual component analysis is accomplished by comparison of the analyte area to the internal standard area, and total sulfur content is calculated through summation of the total area of the unknown peaks. The JP-4 sample analyzed was found to have 8.3 ppm total sulfur content. The peaks at 8.8 and 12.2 minutes were confirmed to be carbon disulfide, and thiophene at 3.34 ppm and 2.3 ppm respectively.

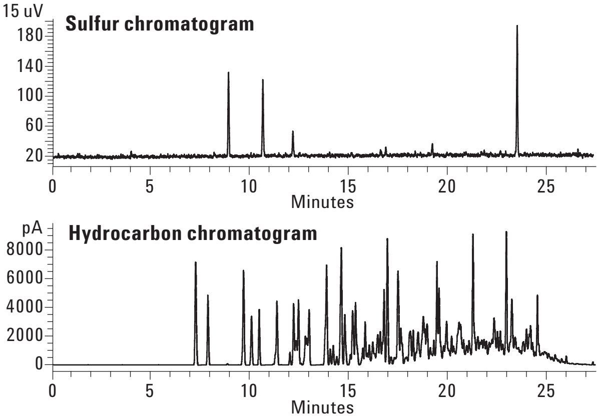

Figure 2. JP-4 FID / SCD chromatogram with internal standard (split 1:10).

All of the data were collected on a Agilent 6890 gas chromatograph with an Agilent 355 SCD in tandem on the flame ionization detector (FID) adaptor for the simultaneous collection of the hydrocarbon and sulfur chromatograms with no sample pretreatment, and no column splitting. This configuration provides the operator with the flexibility to monitor both the hydrocarbon and sulfur content of a sample simultaneously without requiring a separate detector port. The FID adapter samples approximately 10 percent of the effluent after the FID combustion, resulting in a 1:10 split to the SCD. In Figure 2, the 1:10 355 SCD split, coupled with the 1:10 injection split on the GC, result in a 1:100 sample split to the 355 SCD. The amount of sulfur arriving at the 355 SCD for the carbon disulfide peak is therefore 88 ppb, illustrating the extreme sensitivity of the 355 SCD. The column used was a Chrompack CP-Sil 5 CB, courtesy of Chrompack International. [3] The data were collected and analyzed by Agilent ChemStation version 4.02. Standard conditions for both analyses are summarized in Table 1.

Table 1. Chromatographic Conditions

Injection temperature	250 °C
Injection volume	1 µL
Initial temperature	40 °C
Initial time	2 min
Rate	10 °C / min
Final temperature	250 °C
Final time	2 min
Split rato	1:10
Flow mode	Constant flow
Column flow	2 mL / min
Column type	Chrompack CP-Sil 5 CB
Length	30 m
Internal diameter	0.32 mm
Film thickness	5 m

References

1. James H. Gary and Glenn E. Handwerk, “Petroleum Refining Technology and Economics,” Marcel Dekker Inc., New York, New York, 1984; Chapter 2.
2. Annual Book of ASTM Standards, Vol 05.01, ASTM D 910-90, Standard Specifications for Aviation Gasolines.
3. Chrompack International Herculesweg 8, P.O. Box 8033, 4330 EA Middleburg, The Netherlands.

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