ANALYSIS OF SULFUR CONTAINING COMPOUNDS IN PETROLEUM FUELS AND DISTILLATES USING DEANS SWITCHING WITH AN IMPROVED HIGH TEMPERATURE FLAME PHOTOMETRIC DETECTOR

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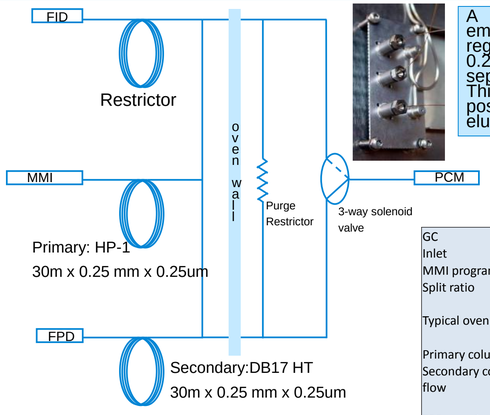
Introduction

The distribution of sulfur in various feedstocks is of great importance to the refining industry as they adjust processes to meet clean fuel requirements. Sulfur levels in fuels and distillates are being driven lower by environmental regulation. Catalyst optimization for various refining processes can also benefit from a knowledge of the distribution of dibenzothiophene class sulfur compounds. The new Flame Photometric Detector on the 7890B 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. Profiling dibenzothiophenes is of particular importance to achieve the lowest sulfur levels in final products. These include dibenzothiophene, methyl (C1) substituted dibenzothioiphenes, dimethyl (C2) dibenzothiophenes, C3, and C4 dibenzothiophenes. To analyze these materials and achieve optimal results, the FPD must be operated at temperatures above 300 °C.

Deans Switching for Optimal Separation



A CFT* deans switch system is employed where the Dibenzothiophene region is cut to the a mid- polar 30 m x 0.25 mm x 0.15 um DB17 for additional separation and detection using the FPD. This enhanced separation reduces the possibility for quenching caused by co-elution with hydrocarbons.

Typical System Parameters

GC	7890B
Inlet	MMI
MMI program	250 °C to 350 C at 50 °C/min
Split ratio	25-150 to 1
Typical oven program	40 °C (0 min) to 250° C (10 min) @ 10 °C/min then 15 °C/min to 350 °C (10 min)
Primary column flow	1.25 mL/min He @ constant flow
Secondary column flow	2.20 mL/min He @ constant flow
FPD transfer line	325° C to 360° C
FPD Emission block	150 °C

❑ Dibenzothiophenes identified from pure standards using retention time

FPD Designed for High Temperature Operation

- The FPD has two temperature controlled zones
  - ➢ Emission block
  - ➢ Transfer line
- The emission block is thermally isolated from the transfer line by a thin walled tube and purged gap. This makes high temperature operation possible.
- Maximum temperature is 400 °C for the transfer Line
- New range of applications are possible
- Deans Switch System used to minimize hydrocarbon quenching
- Backflushing can also be implemented with the deans system. This allows heavier feedstocks to be analyzed

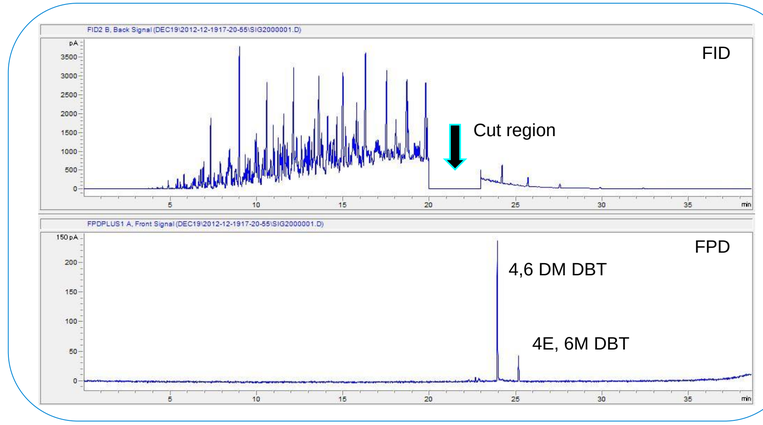
Specifications

- Sensitivity (Sulfur mode) 2.5 pgS/sec
- Sensitivity (Phosphorous mode) 45 fgP/sec
- Maximum Transfer line temp 400 °C
- Modes of operation
  - ➢ Constant makeup + fuel
  - ➢ Column + makeup = constant
  - ➢ Column + fuel = constant

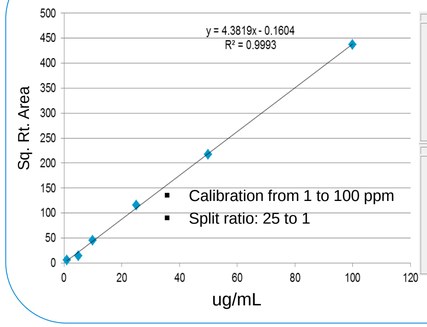
* CFT : Capillary Flow Technology

Dibenzothiophens in Diesel and LCO

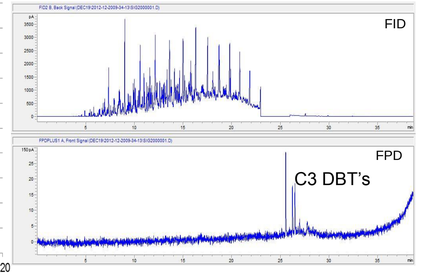
Low Sulfur Diesel



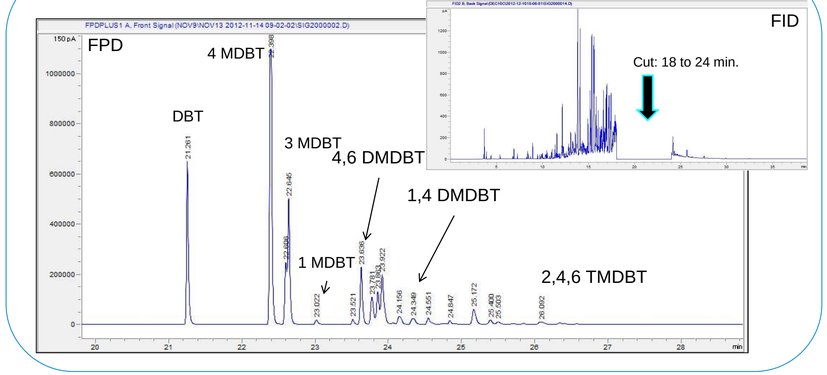
4,6 Dimethyldibenzothiophene



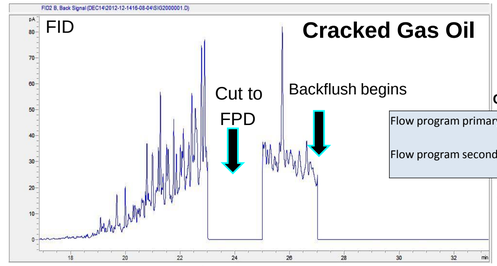
Diesel late cut: 23 to 26 min.



Light Cycle Oils



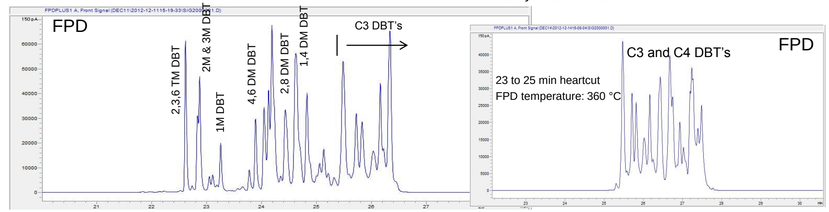
Backflushing for Gas Oil Feedstocks



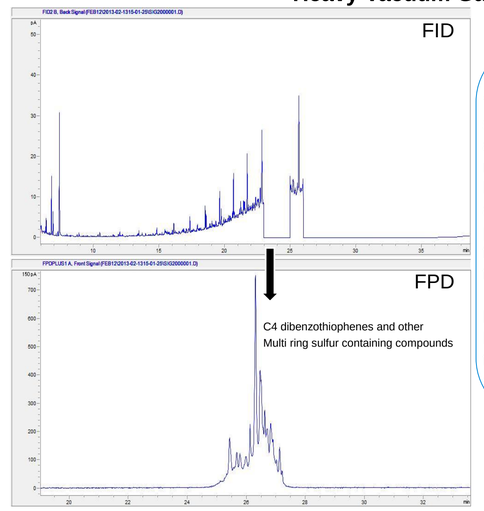
Column flow programs to enable backflush

Flow program primary column	1.25 mL/min for 27 min. , then 100 mL/min to -3.6 mL/min
Flow program secondary column	2.2 ml/min for 27 min. , then 100 mL/min to 4 mL/min.

This FCC feedstock shows a complex distribution of higher molecular weight alkylated dibenzothiophenes. Some quenching is likely given the increased possibility of hydrocarbon co-elutions.



Heavy Vacuum Gas Oil



This sample has a final boiling point of 620 °C from simulated distillation data. The sample was prepared in toluene diluted approximately 20 to 1. The deans cut was made from 23 to 25 minutes, with backflush of the primary column beginning at 26 minutes. Typically, backflush will be programmed to occur at approximately C30 to C35 to protect the column set and avoid the need for long runs or bake out times.

Higher boiling point heartcuts can be made by changing the column set to shorter thinner film columns. Some loss of separation power will result.

Summary

➢ **A Flame Photometric Detector available on the 7890B gas chromatograph is capable of operating at 400 °C which enables a new range of applications particularly in the sulfur analysis of fuels , distillates, and feedstocks.**

➢ **To maximize selectivity and minimize co-elution, a deans switch system is used. Heartcuts are made from a non-polar HP-1 or DB-1 column to a mid-polar DB-17HT column.**

➢ **CFT* enables the deans switch to be used in a backflush mode. Utilizing 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.**

➢ **The system determines the distribution of alkyl dibenzothiophenes in a wide variety of distillates, fuels, and feedstocks.**