APPLICATIONS

An Analytical Method Using the Zebron™ ZB-1 GC Column to Highlight the Opportunity to Resolve the Volatile Polar Sulfur Compounds in Petroleum Fuel

Tim Nelson
Phenomenex, Inc., 411 Madrid Ave., Torrance, CA 90501 USA

Tim Nelson
Global Marketing Manager
Fuels and Chemicals

Tim is an avid outdoorsman who loves to hike and ski. His most recent exploration is tall ship sailing in our local Pacific Ocean. Tim loves history and everything about the stars and space.

Introduction

Sulfur naturally resides in crude oil and so it then carries over to all its refined products, which includes gasoline, diesel, jet fuel, and fuel oils. Sulfur can be a noxious emission when it is burned in engines. It was not uncommon that even late into the 1970's to have the smell of eggs emit from an automobile. But worse than the smell, sulfur impairs the effectiveness of the catalyst in automobile emission control systems which then contributes to NOx and other ozone forming air pollution. There are ways to remove sulfur during the fuel refining process though it is very difficult and comes with a cost. One important benefit to removing the sulfur in the fuel, is that it allows for the advanced emission controls to work properly to reduce air pollution.

As a result, the new environmental regulations on sulfur levels in fuel are getting tighter and tighter. The sulfur content of gasoline and diesel fuels in Europe has been regulated to <10 ppm for over ten years now. Effective January 1, 2017, the U.S. Environmental Protection Agency (EPA) began requiring all U.S. gasoline to meet an annual 10 ppm average sulfur requirement as part of their new Tier 3 vehicle and fuel regulations. Jet fuel specifications now require total sulfur content to be less than 0.30 percent weight.

The International Maritime Organization's (IMO) Marine Environment Protection Committee will lower the maximum allowable sulfur content in marine fuel oil from 3.50% to 0.50%, which will go into effect on January 1, 2020. The average sulfur content of today's bunker heavy fuel oil (HFO) is above 2.5%. Only vessels that equip themselves with exhaust gas cleaning systems (scrubbers) will be able to continue burning these same higher sulfur level bunker fuels from the year 2020. Globally there are over 94,000 commercial vessels and due to the tighter regulation on fuel there is an increased demand for higher quality low sulfur marine fuels[1].

Most straight-run fuels produced through fractional distillation do not meet the quality value requirements for low sulfur and higher-octane, and therefore most of the crude unit fractions are further processed. Petroleum companies are now investing billions of dollars into older facilities to increase the refinery's production capacity for low sulfur fuels that are cleaner and higher value finished products. In addition, every day there are new quality challenges that refiners are facing with the changing sources of crude feedstock that need to be processed in these ever more complex refining facilities.

The refining facilities utilize catalytic reforming and isomerization processes to increase the fuel octane numbers. This upgrading of heavy hydrocarbon streams through hydrocracking into lighter hydrocarbon molecules utilize catalysts that are partially composed with costly metals. These precious metal catalysts are crucial to the operation's economic performance. Many of the contaminants in the feedstock are poisons that impair the performance of the expensive catalyst by reducing its activity, either via competitive adsorption onto active sites, or by alloy formation with active metal group sites. Catalyst with poisoned reactive sites can no longer function properly which then creates an increase in process costs and requires adjustments to the refining streams.

The sulfur contamination that can impair an automobile catalytic convertor for the same reason is also particularly harmful to the refinery catalyst systems. Sulfur species are a poison for the catalytic processes impairing the primary active phase. This impairment is mostly considered temporary, but their effect can be permanent depending on the process conditions. Sulfur may cause significant deactivation even at very low concentrations due to the formation of strong metal to sulfur bonds.

A more stringent pretreatment most likely is required to remove the harmful contaminants from hydrocarbon feedstocks that is essential to achieve the highest catalytic activity/selectivity. To select and optimize the best pretreatment, a thorough understanding of the contaminants is critical. A detailed sulfur compound speciation analysis of both the petroleum feedstock and the resulting processed fluids is therefore essential to understand what the refiner is up against. Sulfur speciation provides the needed details that are not provided from a "total sulfur" measurement analysis. A thoroughly complete sulfur speciation then allows the opportunity to optimize the operating parameters and the catalyst management strategies to provide a more stable and profitable operation.

For example, one especially difficult process fluid is Light Cycle Oil (LCO) which is used mostly as a diesel fuel blending component and it has a poor engine ignition performance due to high aromatics and it also has a high sulfur content that can typically range from 0.2 to 2+ percent weight. A detailed sulfur speciation of LCO can show that a significant portion of the sulfur is found in higher molecular weight aromatic molecules that are very difficult to desulfurize by typical processes. It is critical at many levels of these increasingly complex refining processes to map out the sulfur components through speciation analysis in order to utilize the right resources and optimize the process.

The Zebron ZB-1 100% dimethylpolysiloxane thick film GC capillary column is a proven approach for analyzing low level sulfur compounds by GC.

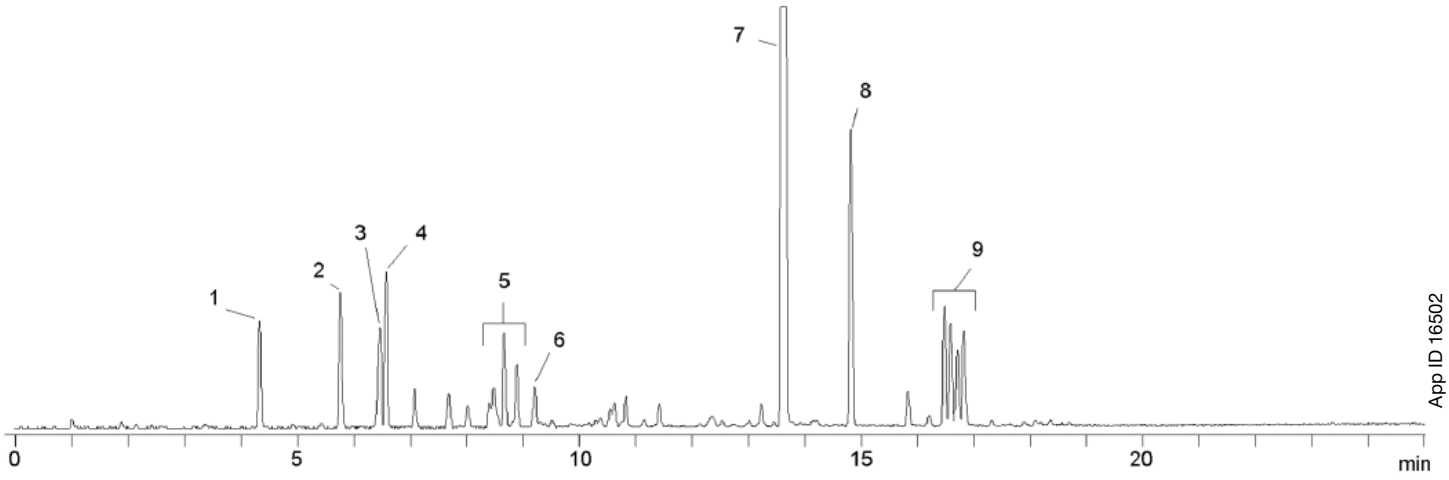
Materials and Methods

An analytical method using the Zebron ZB-1 GC column highlights the opportunities to resolve the volatile polar sulfur compounds.

Column: Zebron ZB-1
Phase: 100% Dimethylpolysiloxane
Dimensions: 30 meter x 0.32 mm x 3.00 µm
Part No.: 7HM-G001-36
Injection: Split 10:1 @ 270 °C, 1 µL
Carrier Gas: Helium @ 2 mL/min (constant flow)
Oven Program: 50 °C for 1 min to 300 °C @ 10 °C/min for 3 min
Detector: Sulfur (SCD) @ 320 °C

APPLICATIONS

Figure 1.
Separation of Sulfur Compounds by GC-SCD using a Zebron™ ZB-1 GC Column



Analytes:

1. Thiophene
2. Dimethyldisulfide
3. 2-Methyl-thiophene
4. 3-Methyl-thiophene
5. C2-Thiophenes
6. Diethylsulfide
7. Dibutylsulfide
8. Benzothiophene
9. C1-Benzothiophenes

Results

The Zebron ZB-1 GC column provides

- A short run time of less than 20 minutes (**Figure 1**)
- Good retention of low boiling sulfur compounds
- Elution of the higher molecular weight C1-Benzothiophenes (**Figure 1**)
- Optimal separation of critical pairs
- Symmetric peaks for challenging sulfur compounds

Discussion

The Zebron ZB-1 100% dimethylpolysiloxane GC capillary column with thick film is a proven approach to provide a true boiling-point based separation from the low-boiling sulfur components all the way up to the high-boiling sulfur heteroaromatics. In addition, the thicker film prevents potential tailing due to any secondary polar interaction of the sulfur with the active sites on the fused silica wall.

The Zebron ZB-1 has a special Engineered Self Cross-linking™ (ESC) stationary phase which:

- Provides low bleed in a thick film GC column
- Provides the needed retention to retain the volatile polar sulfur compounds
- Provides a secure inert platform for the van der Waals forces to create sharper peaks for the challenging sulfur compounds

Conclusion

All petroleum fuel is increasingly being regulated to even lower sulfur levels. Sulfur speciation is a great tool to help optimize the performance and profitability of the refining process. The Zebron ZB-1 column performs great at sulfur speciation when analyzing petroleum fuels. The test results show good resolution and symmetrical peak shape for polar and active sulfur compounds.

References

1. “REVIEW OF MARITIME TRANSPORT 2018”, United Nations Conference on Trade and Development, United Nations, 2018.

APPLICATIONS

Ordering Information
Zebron ZB-1

Zebron ZB-1 GC Columns			
ID(mm)	df(µm)	Temp. Limits °C	Part No.
10-Meter			
0.53	2.65	-60 to 340/360	7CK-G001-35
15-Meter			
0.25	0.10	-60 to 360/370	7EG-G001-02
0.25	0.25	-60 to 360/370	7EG-G001-11
0.25	1.00	-60 to 340/360	7EG-G001-22
0.32	0.25	-60 to 360/370	7EM-G001-11
0.32	1.00	-60 to 340/360	7EM-G001-22
0.53	0.15	-60 to 360/370	7EK-G001-05
0.53	0.50	-60 to 360/370	7EK-G001-17
0.53	1.50	-60 to 340/360	7EK-G001-28
30-Meter			
0.25	0.10	-60 to 360/370	7HG-G001-02
0.25	0.25	-60 to 360/370	7HG-G001-11
0.25	0.50	-60 to 360/370	7HG-G001-17
0.25	1.00	-60 to 340/360	7HG-G001-22
0.32	0.25	-60 to 360/370	7HM-G001-11
0.32	0.50	-60 to 360/370	7HM-G001-17
0.32	1.00	-60 to 340/360	7HM-G001-22
0.32	3.00	-60 to 340/360	7HM-G001-36
0.32	5.00	-60 to 340/360	7HM-G001-39
0.53	0.50	-60 to 360/370	7HK-G001-17
0.53	1.50	-60 to 340/360	7HK-G001-28
0.53	3.00	-60 to 340/360	7HK-G001-36
0.53	5.00	-60 to 340/360	7HK-G001-39
50-Meter			
0.25	0.50	-60 to 360/370	7JG-G001-17
60-Meter			
0.25	0.25	-60 to 360/370	7KG-G001-11
0.25	1.00	-60 to 340/360	7KG-G001-22
0.32	0.25	-60 to 360/370	7KM-G001-11
0.32	1.00	-60 to 340/360	7KM-G001-22
0.32	3.00	-60 to 340/360	7KM-G001-36
0.53	1.50	-60 to 340/360	7KK-G001-28
100-Meter			
0.25	0.50	-60 to 360/370	7MG-G001-17

Note: If you need a 5 in. cage, simply add a (-B) after the part number, e.g., 7HG-G001-11-B. Some exceptions may apply.
Agilent 6850 and some SRI and process GC systems use only 5 in. cages.

Zebron PLUS GC Inlet Liners

	Description	Application	Dimensions ID x L (mm)	Unit	Part No.
For Agilent® or Thermo Scientific® GC Systems					
	Single Taper Z-Liner™	Semi-volatiles, dirty samples	4 x 78.5	5/pk 25/pk	AG2-0A13-05 AG2-0A13-25
	Single Taper with Wool	Semi-volatiles	4 x 78.5	5/pk 25/pk	AG2-0A11-05 AG2-0A11-25

APPLICATIONS

Australia
t: +61 (0)2-9428-6444
auinfo@phenomenex.com

Austria
t: +43 (0)1-319-1301
anfrage@phenomenex.com

Belgium
t: +32 (0)2 503 4015 (French)
t: +32 (0)2 511 8666 (Dutch)
beinfo@phenomenex.com

Canada
t: +1 (800) 543-3681
info@phenomenex.com

China
t: +86 400-606-8099
cninfo@phenomenex.com

Denmark
t: +45 4824 8048
nordicinfo@phenomenex.com

Finland
t: +358 (0)9 4789 0063
nordicinfo@phenomenex.com

France
t: +33 (0)1 30 09 21 10
franceinfo@phenomenex.com

Germany
t: +49 (0)6021-58830-0
anfrage@phenomenex.com

India
t: +91 (0)40-3012 2400
indiainfo@phenomenex.com

Ireland
t: +353 (0)1 247 5405
eireinfo@phenomenex.com

Italy
t: +39 051 6327511
italiainfo@phenomenex.com

Luxembourg
t: +31 (0)30-2418700
nlinfo@phenomenex.com

Mexico
t: 01-800-844-5226
tecnicomx@phenomenex.com

The Netherlands
t: +31 (0)30-2418700
nlinfo@phenomenex.com

New Zealand
t: +64 (0)9-4780951
nzinfo@phenomenex.com

Norway
t: +47 810 02 005
nordicinfo@phenomenex.com

Portugal
t: +351 221 450 488
ptinfo@phenomenex.com

Singapore
t: +65 800-852-3944
sginfo@phenomenex.com

Spain
t: +34 91-413-8613
espinfo@phenomenex.com

Sweden
t: +46 (0)8 611 6950
nordicinfo@phenomenex.com

Switzerland
t: +41 61 692 20 20
swissinfo@phenomenex.com

Taiwan
t: +886 (0) 0801-49-1246
twinfo@phenomenex.com

United Kingdom
t: +44 (0)1625-501367
ukinfo@phenomenex.com

USA
t: +1 (310) 212-0555
info@phenomenex.com

All other countries
Corporate Office USA
t: +1 (310) 212-0555
info@phenomenex.com

www.phenomenex.com

Phenomenex products are available worldwide. For the distributor in your country, contact Phenomenex USA, International Department at international@phenomenex.com

TN65580119_W