

## Abstract

Determinations of low levels of sulfur and oxygen containing components in fuel processing streams are of keen interest to the petrochemical and chemical industries.

Both species are increasingly being monitored as both impurities and deliberate additives in highly regulated environments. Certain sulfur containing species can have a rapid, deleterious and costly impact on the catalysts used in petroleum cracking. For the chemical industry feed stocks with sulfur containing impurities can lead to contaminated downstream product.

In natural gas processing the deliberate addition and monitoring of sulfur containing odorant additives has important safety implications. Natural gas odorant additives such as methyl mercaptan are added at the 10 to 50 ppm range requiring testing on an ongoing basis.

Re-formulated gasolines need to be monitored for trace level impurities such as methyl tert butyl ether that have historically led to ground water contamination from leaking underground storage tanks.

Recent developments in gas chromatographic analysis using 2 D GC technology, electronic pressure control and highly selective PLOT (porous layer open tubular) columns help reduce some of these difficult analyses to routine practice.

For a less detailed analysis which requires that only "like" HC types are separated (e.g., saturated HC (hydrocarbon) separated from unsaturated HC, PIONA, etc.) then high selectivity columns are required; usually multiple columns with a valve (or valves) to direct solutes eluting from one column of a lower selectivity, to a column with higher selectivity toward the solute types.

For the case of oxygenated compounds added to gasoline (e.g. lower alcohols, ethers and ketones), a detailed HC analysis can be accomplished with modest quantitative success. Problems can arise however when a HC solute closely elutes to the oxygenated solutes and one is at a much higher concentration than the other. This can be a common situation for reformulated gasoline that can have +20% of ethanol added to the fuel. Also, lower concentration oxygenates need to be quantitatively measured. It is primarily for these reasons that a multi-column approach is favored. In this case a column capable of high retention of the oxygenates is desirable. This approach allows potential HC "background inference" to elute first, while trapping the oxygenates, then with a valve switch, perform a chromatographic separation of the oxygenates from the trapping column via temperature program desorption.

Demonstrated here is a megabore (0.53 mm I.D.) GC column, GS-OxyPLOT, that can be used to analyze C1-C5 HC streams, re-formulated gasoline and crude oil in new ASTM methods for the determination of oxygenated compounds in HC samples.

## What is GS-OxyPLOT?

• A 10 m x 0.53 mm I.D., Porous Layer Open Tubular (PLOT) Capillary Column

• The stationary phase is a "proprietary, salt deactivated adsorbent".

• Key characteristics are:

✓ Strong selectivity to oxygenated hydrocarbons

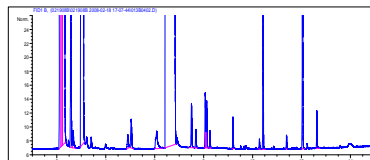
✓ Upper temperature limit of 350 °C with no column bleed

✓ Stabilized phase coating minimizing particle generation and detector spiking

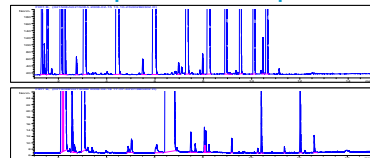
Solute	MTBE	Iso-buteraldehyde	Methanol	Acetone
RI @150°C	1236	1368	1418	1450

## GS-OxyPLOT and Sulfur Species

### Spectrum Mix GS-OxyPLOT



### GS-OxyPLOT C5-16 Carbon Ladder/Spectrum Mix Comparison



### Observed Retention Times on DB-1 and GS-OxyPLOT for C5-C16 alkanes and sulfur species

Compound	Ret. Time DB-1	Ret. Time GS-OxyPLOT	SP	Compound	Ret. Time DB-1	Ret. Time GS-OxyPLOT	SP
Decalin	1.00	1.00	100	Diethyl sulfide	1.00	1.00	100
Decane	2.00	2.00	200	Diethyl disulfide	2.00	2.00	200
Nonane	3.00	3.00	300	Diethyl trisulfide	3.00	3.00	300
Nonane	4.00	4.00	400	Diethyl tetrasulfide	4.00	4.00	400
Octane	5.00	5.00	500	Diethyl pentasulfide	5.00	5.00	500
Octane	6.00	6.00	600	Diethyl hexasulfide	6.00	6.00	600
Heptane	7.00	7.00	700	Diethyl heptasulfide	7.00	7.00	700
Heptane	8.00	8.00	800	Diethyl octasulfide	8.00	8.00	800
Hexane	9.00	9.00	900	Diethyl nonasulfide	9.00	9.00	900
Hexane	10.00	10.00	1000	Diethyl decasulfide	10.00	10.00	1000
Pentane	11.00	11.00	1100	Diethyl undecasulfide	11.00	11.00	1100
Pentane	12.00	12.00	1200	Diethyl dodecasulfide	12.00	12.00	1200
Butane	13.00	13.00	1300	Diethyl tridecasulfide	13.00	13.00	1300
Butane	14.00	14.00	1400	Diethyl tetradecasulfide	14.00	14.00	1400
Propane	15.00	15.00	1500	Diethyl pentadecasulfide	15.00	15.00	1500
Propane	16.00	16.00	1600	Diethyl hexadecasulfide	16.00	16.00	1600
Ethane	17.00	17.00	1700	Diethyl heptadecasulfide	17.00	17.00	1700
Ethane	18.00	18.00	1800	Diethyl octadecasulfide	18.00	18.00	1800
Methane	19.00	19.00	1900	Diethyl nonadecasulfide	19.00	19.00	1900
Methane	20.00	20.00	2000	Diethyl eicosasulfide	20.00	20.00	2000

Alkanes less retained

Sulfur species more retained

### Interesting Observations

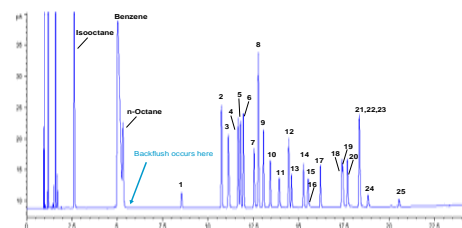
- Sulfur species are retained on GS-OxyPLOT
- high selectivity for some sulfur species
- more relative retention for lower boiling sulfur species vs. methyl silicone column
- shift in retention may be useful for shifting sulfur species away from hydrocarbon interferences
- preliminary results are encouraging

## GS-OxyPLOT "Electronic" Selective Interactions

### Distinct Advantages

- Adsorption interactions are much stronger than the polar/non-polar interactions in "liquid" stationary phases.
- Oxygenated hydrocarbons, un-retained on siloxane columns, even at sub-ambient temperatures, exhibit high retention in the GS-OxyPLOT column at GC oven temperatures above ambient
- Non-polar solutes are essentially un-retained except for their vapor pressure interaction at a given oven temperature
- Ideal column for selective solute-value cut applications
- Column phase is surprisingly inert to the polar compounds it so strongly interacts with.
- Good for low concentration, quantitative GC analysis

## Hydrocarbons and Oxygenates with GS-OxyPLOT



### GC Conditions

**Column 1:** DB-1 25 m x 0.53 mm x 1.0 µm P/N 125-102J

**Column 2:** GS-OxyPLOT 10 m x 0.53 mm P/N 115-4912

**Oven:** Initial Temp: 50 °C  
 Initial hold: 5 min  
 Ramp rate: 10 °C  
 Final Temp: 240 °C

**Detector:** FID @ 250 °C

**Inlet:** Split/Splitless 225 °C  
 Split Ratio 10:1  
 Column flow 11 mL/min

**Carrier Gas:** Helium

**Injection Vol.:** 1 µL

### Compound I.D.

1. Dimethyl ether
2. Diethyl ether
3. Acetaldehyde
4. Ethyl t-butyl ether
5. Methyl t-butyl ether
6. Diisopropyl ether
7. Propionaldehyde
8. Tert-amyl methyl ether
9. Propyl ether
10. Isobutylaldehyde
11. Butylaldehyde
12. Methanol
13. Acetone
14. Isovaleraldehyde
15. Valeraldehyde
16. Methyl Ethyl Ketone
17. Ethanol
18. 1-Propanol
19. Isopropyl Alcohol
20. Allyl Alcohol
21. Isobutyl Alcohol
22. t-Butyl Alcohol
23. n-Butyl Alcohol
24. n-Butyl Alcohol
25. 2-Methyl-2-pentanol

## GS-OxyPLOT and ASTM Methods

Three ASTM standardized methods\* that GS-OxyPLOT is specifically designed for:

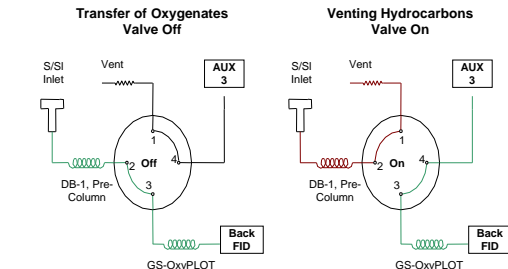
• Determination of C1 to C5 Oxygenates at Trace Levels in High Ethanol Content Gasoline Streams by Multidimensional Chromatography with Flame Ionization Detection

• Determination of Oxygenates in Ethene, Propene, C4 and C5 Hydrocarbon Matrices by Gas Chromatography and Flame Ionization Detection

\*These are "proposed methods" that are destined for balloting by ASTM Committee D2. The method below has been accepted by, and is being implemented in petrochemical refineries around the world.

### ASTM Method D7059

• Determination of Methanol in Crude Oils by Gas Chromatography with Flame Ionization Detection



## Conclusions

• GS-OxyPLOT shows high selectivity for low boiling sulfur species found in hydrocarbon feed stocks

• Retention shift away from HC interferences may be possible

• GS-OxyPLOT is highly selective for oxygenate species

• ASTM proposed applications include the determination of trace level C1-C5 oxygenates in reformulated gasoline and the determination of oxygenates in C2-C5 hydrocarbon matrices

• ASTM D7059 current 2 D GC method for determination of methanol in crude oils with flame ionization detection

Please leave your business card to receive a reprint of this poster and more information about GS-OxyPLOT, and the analysis of oxygenates using Agilent Technologies instrumentation