A New Megabore GC Column for the Adsorption and Chromatographic Separation of Oxygenates in Hydrocarbon Matrices.

Allen K. Vickers and Daron Decker
Agilent Technologies, 91 Blue Ravine Road, Folsom, CA 95630, USA

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Abstract

Depending on the degree of specific information that is required, gas chromatographic (GC) analysis of petrochemical samples can be very difficult to accomplish. Detailed hydrocarbon (HC) type analysis of gasoline for example will typically require the use of a long, narrow-bore (i.e., high efficiency) GC column, and even though hours are spent for complete elution of a sample, it is known that there are still co-elutions that occur on any single GC separation column.

For a less detailed analysis which requires that only "like" HC types are separated (e.g., saturated HC 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 +30% 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 would be 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 new megabore (0.53 mm I.D.) GC column, GS-OxyPLOT, that that can be used for the analysis of oxygentate HC's in C1-C5 gas streams, reformualted 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.

Solute	MTBE	Iso-Buteraldehyde	Methanol	Acetone
RI*	1236	1368	1418	1450

*150°C

  - Upper temperature limit 350°C with no column bleed
  - Stabilized phase coating, minimizing particle generation and detector spiking

Need more information? www.agilent.com/chem/oxyplot1

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 in a WCOT column, 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

GS-OxyPLOT and ASTM Methods

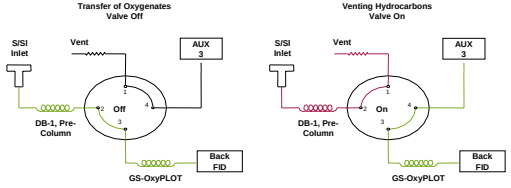
Three ASTM standardized methods* that GS-OxyPLOT is specifically designed for:

- 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

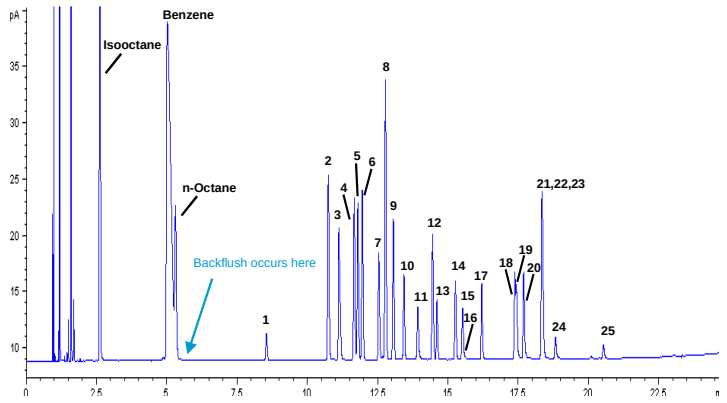
*These are "proposed methods" (i.e., do not have method designation numbers) that are destine for approval by ASTM Committee D2. These methods have already been accepted by, and are being implemented in petrochemical refineries around the world.

ASTM Method D7059

- Determination of Methanol in Crude Oils By Gas Chromatography with Flame Ionization Detection



Hydrocarbons and Oxygenates with GS-OxyPLOT



GC Conditions

Column 1: DB-1

25 m x 0.53 mm I.D. x 1.0 µm

P/N 125-102J

Column 2: GS-Oxy-PLOT

10 m x 0.53 mm I.D.
P/N 115-4912

Carrier gas: Helium
Injection volume: 1 µL

Oven

- Initial temp: 50 °C
- Initial hold: 5 min
- Ramp rate: 10 °C/min
- Final temp: 240 °C

Detector: FID

- Temperature: 250 °C

Inlet: Split/splitless

- Temperature: 225 °C
- Split Ratio: 10:1
- Column flow: 11 mL/min

Note: GC analyzer conditions will vary depending on sample matrix type and type of valve/Fluidic Switch configuration being utilized.

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. s-Butyl Alcohol
24. n-Butyl Alcohol
25. 2-Methyl-2-pentanol

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