Application Note 5

Analyze Oxygenates in Gasoline and Similar Matrices, Using Single-Column Capillary GC

A single-column capillary GC analysis, using a 100 meter column, offers advantages over the currently-used two-column method for analyzing oxygenated additives in gasoline and other complex hydrocarbon mixtures. The single-column method eliminates valving, switching, and flow balancing problems, simultaneously provides information on PNA, PONA, and PIANO composition, and allows component quantification by area normalization rather than through the use of internal or external standards. Conditions for the analysis – and typical results – are described in this note.

Key Words:
● oxygenated compounds ● C1-C4 alcohols ● MTBE ● TAME
● complex hydrocarbon matrices ● gasoline ● reformate

The high toxicity of organically bound lead has lead to a mandate by the US Environmental Protection Agency to reduce the use of such compounds in gasoline. As a result, worldwide attention has turned to the use of oxygenated additives, specifically alcohols and ethers, as replacements for leaded additives to increase the octane rating of gasolines. Currently, the American Society for Testing and Materials (ASTM) specifies a multidimensional (dual-column) gas chromatographic approach, ASTM Test Method D4815, for separating oxygenated additives from interfering hydrocarbons in gasoline. We have found that, in many situations, a 100 meter fused silica capillary column provides sufficient resolution for separating the common oxygenated additives from components of complex hydrocarbon matrices, and eliminates the need for a multidimensional approach.

We analyzed samples of four common petroleum hydrocarbon streams – gasoline, naphtha, reformate, and alkylate – on our 100m x 0.25mm ID Petrocol™ DH fused silica capillary column, using a flame ionization detector and the conditions shown in Figure A (page 2). After completing detailed analyses of these samples, we added oxygenated compounds – C1-C4 alcohols, methyl tert-butyl ether (MTBE), and tert-amyl methyl ether (TAME) – then reanalyzed the samples under the same conditions and identified the oxygenates in the chromatograms. Figure A shows a chromatogram of an unleaded gasoline with the C1-C4 alcohols, MTBE, and TAME, added at levels of 0.05-0.10%, 1.0%, and 0.5%, respectively. Under the conditions employed, the 100 meter Petrocol DH column provided baseline separation of all but one of the oxygenates from major neighboring hydrocarbons. MTBE was 95% resolved from 2,3-dimethylbutane. A subambient initial column temperature (-25°C) was needed to resolve methanol from isobutane.

Separations of oxygenate- containing naphtha, reformate, and alkylate samples produced the same results. Although a subambient initial column temperature was needed to resolve methanol and isobutane, the other oxygenates were reasonably well separated with a 35°C initial temperature when isobutane was absent from the sample. With a 35°C initial temperature, however, the elution order of MTBE and 2,3-dimethylbutane was reversed and the separation was approximately 75%.

There are significant advantages to using a single column method, relative to a dual-column approach, for analyzing oxygenates in these complex hydrocarbon samples. Multidimensional systems are far more complicated, due to valving, switching, and flow balancing requirements. Also, a single column approach can simultaneously yield detailed hydrocarbon information (e.g., PNA, PONA, or PIANO analyses), and permits quantification of sample components by area normalization, rather than through the use of external or internal standards.

As always, there are compromises. The 100 meter column increases analysis time, relative to a dual-column approach. Also, high levels of oxygenates (i.e., 10-20%) could reduce the resolution of some components. In this situation, coupling the Petrocol DH column to an oxygen-specific detector, such as the O-FID, essentially eliminates interferences from closely eluting hydrocarbons and the need for a multidimensional approach.

The importance of oxygenated compounds to the petroleum industry will continue to increase, as will the importance of simple, accurate analyses for these compounds. In some situations, we feel the advantages of the single column analysis, as exemplified by the Petrocol DH column and the conditions shown here, make this a useful approach.

Ordering Information:

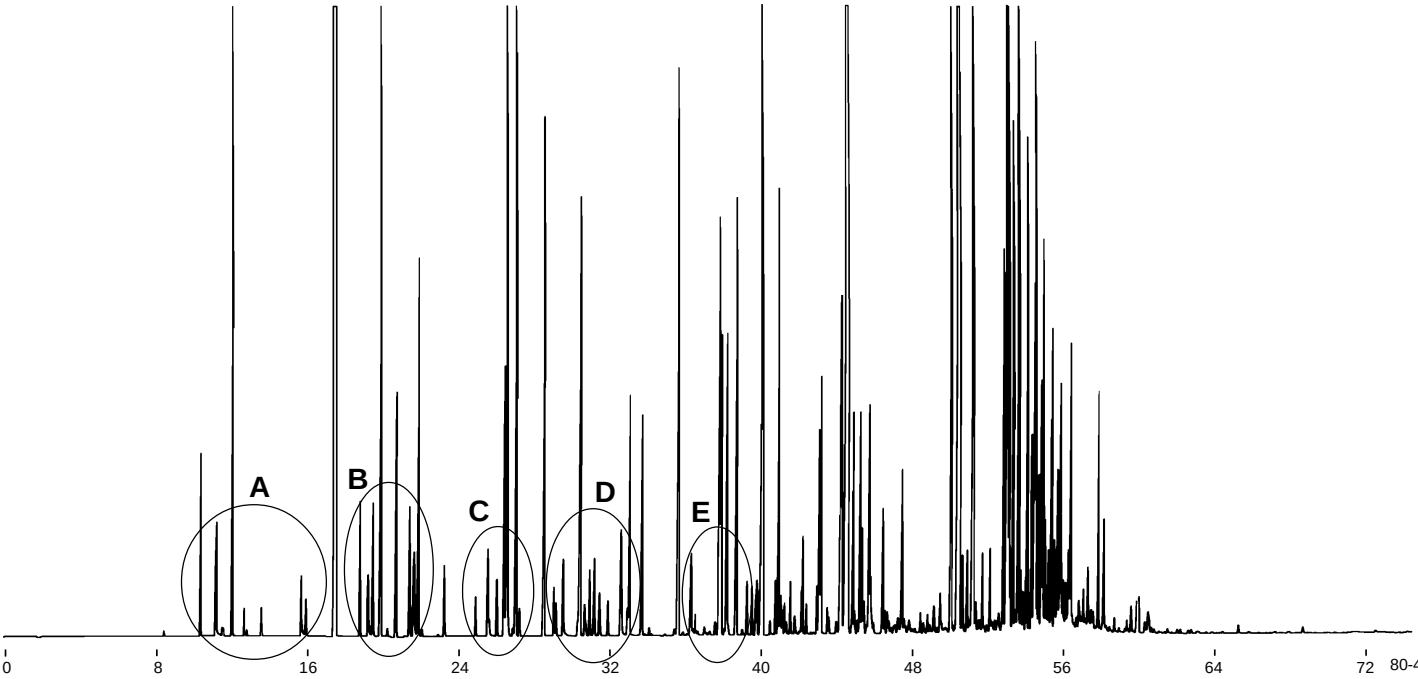
Petrocol DH Capillary Column

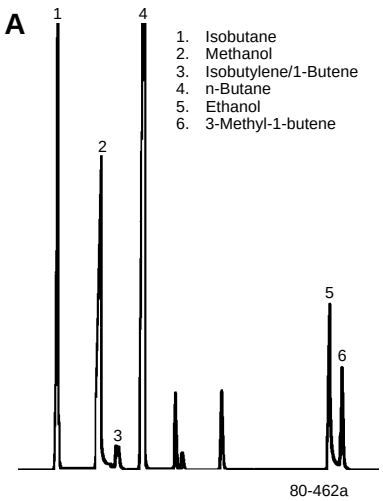
100m x 0.25mm ID fused silica, 0.50µm film	**24160-U**

Contact our Technical Service Department (phone 800-359-3041 or 814-359-3041, FAX 814-359-5468) for expert answers to your questions.

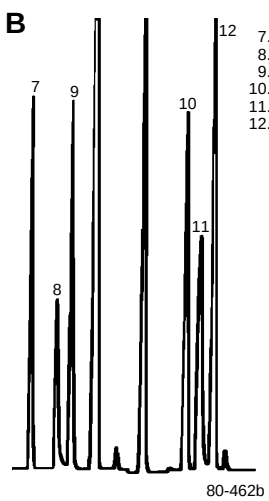
Figure A. Oxygenates in Gasoline

Column: **Petrocol DH, 100m x 0.25mm ID, 0.5µm film**
Cat. No.: **24160-U**
Oven: -20°C to 65°C at 2°C/min, then to 225°C at 25°C/min
Carrier: helium, 19cm/sec
Det.: FID, 275°C
Inj.: 0.5µL gasoline, 0.05-0.10% C1-C4 alcohols, 1.0% MTBE, 0.5% TAME added, split (100:1), 225°C

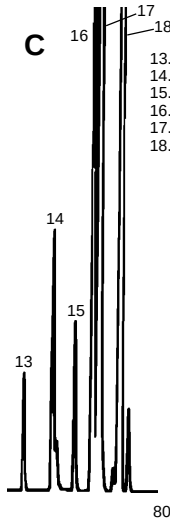




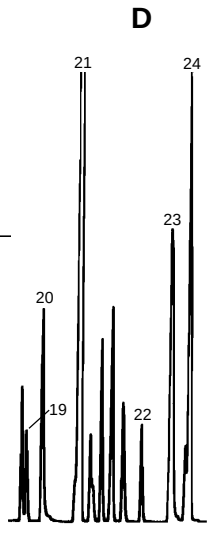
1. Isobutane
2. Methanol
3. Isobutylene/1-Butene
4. n-Butane
5. Ethanol
6. 3-Methyl-1-butene



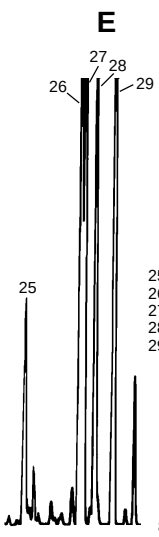
7. 1-Pentene
8. Isopropanol
9. 2-Methyl-1-butene
10. cis-2-Pentene
11. tert-Butanol
12. 2-Methyl-2-butene



13. Cyclopentene
14. n-Propanol
15. Cyclopentane
16. 2,3-Dimethylbutane
17. MTBE
18. 2-Methylpentane



19. 1-Hexene
20. sec-Butanol
21. n-Hexane
22. cis-2-Hexene
23. Isobutanol
24. Methylcyclopentane



25. n-Butanol
26. 2-Methylhexane
27. 2,3-Dimethylpentane
28. TAME
29. 3-Methylhexane

Notes