

Analyzing Oxygenates in Gasoline

Using TCEP and Rtx[®]-1/MXT[®]-1 Columns

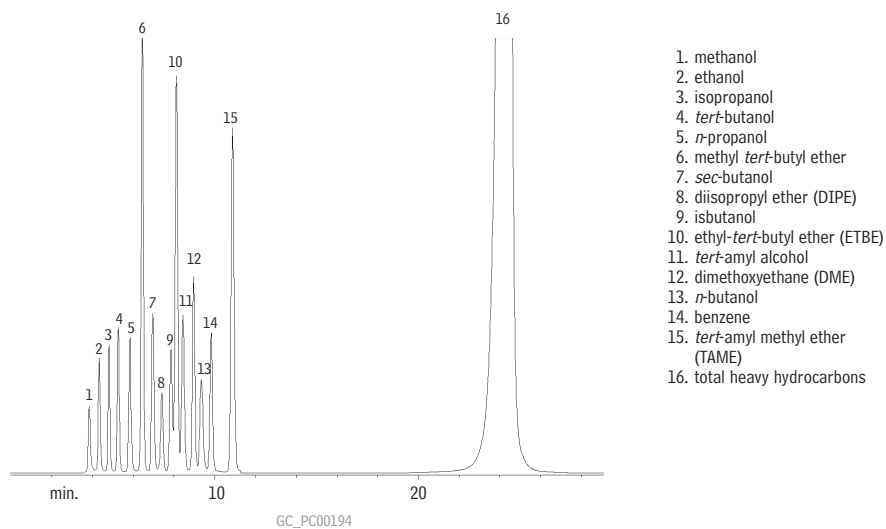
Oxygenate additives in gasoline potentially consist of several ethers and/or alcohols with either methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE), or ethanol being major constituents. Two GC methods can be used for the measurement of the individual alcohols and ethers in gasoline: the single-column OFID method^{1,2} and the dual column ASTM method D4815-93.³ Restek offers columns and specially deactivated tubing for the analysis of alcohols and ethers in gasoline according to both ASTM and EPA methodology.

ASTM Test Method D4815-93 specifies the use of two columns, a micro-packed pre-column of 1,2,3-tris-2-cyanoethoxy-propane (TCEP), and an analytical capillary column of methyl silicone (Rtx[®]-1 or MXT[®]-1). These columns are configured with a 10-port valve to accomplish the heartcutting and backflushing necessary in order to resolve oxygenates from hydrocarbons present in gasoline. The sample is first directed to the TCEP column. This column has high retention for polar oxygenates, while the more volatile hydrocarbons are vented. The valve is then actuated, backflushing the remaining sample to the Rtx[®]-1 or MXT[®]-1 column where separation of oxygenates occurs. After the elution of the last oxygenate (*tert*-amyl methyl ether), the valve is redirected and remaining heavy hydrocarbons are backflushed from the Rtx[®]-1 column as a single peak. A separation example of all the specified alcohols and ethers appears in Figure 1.

Fused silica lined stainless steel improves peak shapes for alcohols.

In order to achieve optimum peak width in this valve system, small diameter sample transfer tubing is recommended to minimize band broadening and resolution loss. Because alcohols can adsorb on both the stainless steel transfer line tubing and TCEP pre-column stainless steel surface, Restek recommends using Silcosteel[®] treated* stainless steel for transfer lines and the TCEP pre-column. Silcosteel[®] treated

Figure 1 TCEP and Rtx[®]-1 columns, connected in series, resolve C1-C4 alcohols, MTBE, ETBE, and TAME.



0.56m, 0.75mm ID 20% TCEP on Chromosorb[®] P A/W (cat.# 19040) and
30m, 0.53mm ID, 3.0 μ m Rtx[®]-1 (cat.# 10185) connected in series
0.5 μ L split injection of oxygenates blend 1–10% wt in surrogate gasoline

Oven temp.: 60°C
Inj. / det. temp.: 200°C / 250°C (FID)
Carrier gas: helium, 5mL/min. set @ 60°C
Split ratio: 15:1

*Silcosteel[®] treatment is a proprietary surface treatment for passivating steel and stainless steel. U.S. Patent 6,511,760.

tubing provides the inertness of fused silica tubing, resulting in excellent peak shape for the oxygenates (Figure 1). The Restek TCEP micropacked column is prepared using 0.75mm ID tubing, which gives a more reproducible retention time than columns prepared from smaller ID tubing. This column also produces a slightly longer and more reproducible valve time (i.e., 0.28 minutes), which helps when initially setting this critical parameter. For methods using the oxygen-specific OFID, a 60-meter Rtx[®]-1 column will resolve the oxygenated compounds.

Summary

To meet the requirements of ASTM Test Method D4815-93, an analyst must consider the sample handling system and choice of columns. By implementing a low volume valve and small ID Silcosteel[®] treated transfer lines, optimum resolution of oxygenates can be achieved. In addition, by using a Silcosteel[®] treated 0.75mm ID TCEP pre-column and the Rtx[®]-1 or MXT[®]-1 analytical column, optimum resolution can be attained. For the OFID procedures, Restek offers a low-bleed, 60-meter Rtx[®]-1 or MXT[®]-1 methyl silicone column.

References

1. 40 CFR Part 30, Federal Register, 59(32): 7716-7878, Feb. 16, 1994.
2. ASTM Test Method D5599-94, *Determination of Oxygenates in Gasoline by Gas Chromatography and Selective Flame Ionization Detection.*
3. ASTM Test Method D4815-93, *Standard Test Method for Determination of MTBE, ETBE, TAME, DIPE, tertiary-amy Alcohol and C1 to C4 Alcohols in Gasoline by Gas Chromatography.*

References not available from Restek.

For ASTM D4815-93:

Rtx[®]-1 Column (fused silica) (Crossbond[®] 100% dimethyl polysiloxane)

ID	df (μm)	temp. limits	length	cat. #
0.53mm	3.00	-60 to 270/290°C	30-Meter	10185

MXT[®]-1 Column (Silcosteel[®] treated stainless steel) (Crossbond[®] 100% dimethyl polysiloxane)

ID	df (μm)	temp. limits	length	cat. #
0.53mm	3.00	-60 to 285°C	30-Meter	70185

Micropacked TCEP Column

	ID	OD	Temp. Range	0.56-Meter
20% TCEP on 80/100 Chromosorb [®] PAW	0.75mm	1/16"	0–120°C	19040

Valve Transfer Line:

Silcosteel[®] Treated Coiled 304 Grade Stainless Steel Tubing†

ID	OD	cat. #
0.020" (0.51mm)	1/16" (1.59mm)	20593

†Silcosteel[®] treated and siloxane deactivated. For Silcosteel[®] treatment only, add-279 to the cat. #.

Minimum order is 5 ft. Price breaks are available at 25 ft., 200 ft., and 400 ft.

For OFID Procedure:

Rtx[®]-1 Column (fused silica) (Crossbond[®] 100% dimethyl polysiloxane)

ID	df (μm)	temp. limits	length	cat. #
0.25mm	1.00	-60 to 320/340°C	60-Meter	10156

Restek Trademarks:
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Silcosteel, Restek logo.

Other Trademarks:
Chromosorb (Celite Corp.)

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