

Petrochemical Applications note

cat.# 59587

Analyzing Oxygenates in Gasoline

The EPA issued a mandate for the use of oxygenate enhancers as gasoline additives in 1989. Congress passed *The Clean Air Act*, further solidifying the implementation of reformulated oxygenated gasoline, in 1990. Oxygenates increase the octane rating of gasoline but reduce harmful emissions into the atmosphere. The phase-in period for reformulated oxygenated fuel began in 1989 and continued until 1995. Requirements for oxygenated fuel depend on geographic location with strict regulations in non-attainment areas.¹

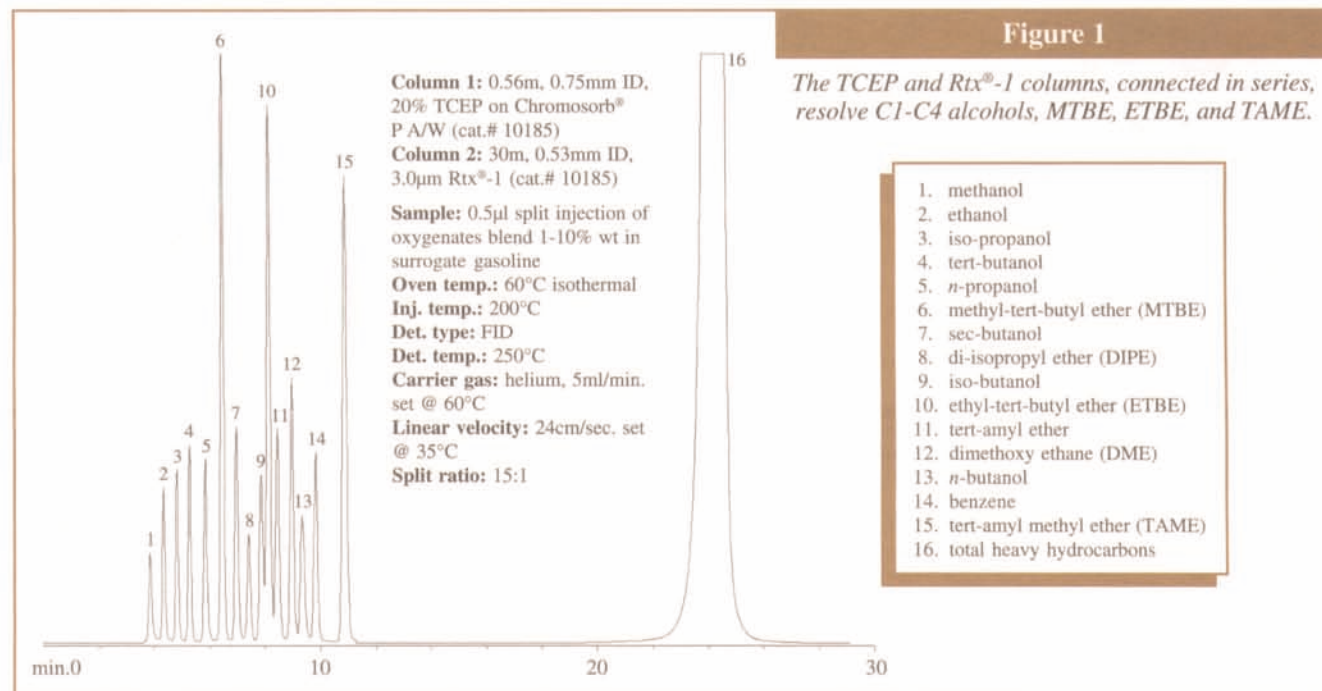
There are two GC methods which can be used for the measurement of the individual alcohols and ethers in gasoline. These two methods are the single-column OFID method^{2,3} and the

dual column ASTM method D4815-93.⁴ Restek now offers columns, calibration standards, and specially deactivated tubing for the analysis of alcohols and ethers in gasoline according to both ASTM and EPA methodology.

ASTM and EPA Method Column Selection

Oxygenate additives in gasoline could potentially consist of several ethers and/or alcohols with either methyl tert-butylether (MTBE), ethyl tert-butylether (ETBE), or ethanol being major constituents. 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 fused silica lined stainless steel (Silcosteel®) for transfer lines and the TCEP pre-column. Silcosteel® 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 components.

High purity standards are available for a 5-point calibration curve.

Restek now offers calibration standards that meet the method requirements found in all three oxygenates test methods, including ASTM D4815, ASTM D5599, and the EPA OFID. Restek's QA tests guarantee 99%+ individual compound purity required by ASTM and EPA procedures. After preparation using a NIST traceable balance, each solution undergoes extensive GC testing to assure that calibration mixes meet strict standards of accuracy. A data pack containing purity data and complete quality assurance documentation is available for each of these standards. All three methods specify using multi-point calibration with a minimum of five points for all 12 oxygenates. Quantitation of the individual oxygenates is performed using an internal standard such as 1,2-dimethoxyethane, present at 5 WT% level in all standards. The recommended concentration range of alcohols is determined by the concentrations typically expected in reformulated gasoline, whereas the

ethers are between 0.1 to 20 WT%. In addition, the total mass of oxygen content (including the internal standard), in each calibration mixture, must not exceed 30%. Restek's oxygenate in gasoline calibration standards meet or exceed all ASTM and EPA method specifications.

To meet the requirements of ASTM Test Method D 4815-93, an analyst must consider the sample handling system, calibration standards, and choice of columns. By implementing a low volume valve and small inner diameter Silcosteel® transfer lines, optimum resolution of oxygenates can be achieved. In addition, by using a Silcosteel® 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.

We offer the columns, calibration standards, and specially deactivated tubing specifically for the analysis of alcohols and ethers in gasoline according to ASTM and EPA methodology.

Product List

For ASTM D4815-93:

Rtx®-1
30m, 0.53mm ID, 3.0µm
cat.# 10185
or
MXT®-1 (Silcosteel®)*
30m, 0.53mm ID, 3.0µm
cat.# 70185
and
TCEP (Micropacked)
0.56m, 0.75mm ID
cat.# 19040

Valve Transfer Line:

**Silcosteel® Fused Silica Lined
Stainless Steel**
6 feet, 1/16" OD, 0.020" ID
cat.# 20524

OFID Procedure:

Rtx®-1
60m, 0.25mm ID, 1.0µm
cat.# 10156

*Have Questions?
Call Restek's technical
service staff at:
800-356-1688, ext. 4*

**A rugged Silcosteel® MXT®-1 column can be used as an alternative to a fused silica column in applications where column breakage is a concern.*



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ASTM D5599-94 Oxygenate Calibration Mixtures

ASTM Oxygenate Calibration Kit: cat.# 36223 and cat.# 36223-500 (w/data pack)
Includes 1ml each of the 9 mixes below, plus the ASTM Surrogate Base Gas, cat.# 36222.

Compound	Mix #1	Mix #2	Mix #3	Mix #4	Mix #5	Mix #6	Mix #7	Mix #8	Mix #9
tert-amyl methyl ether	—	13.5	—	4.50	1.00	9.00	—	18.0	—
butanol	2.00	1.00	0.80	0.50	0.10	—	—	—	—
sec-butanol	—	0.10	1.00	0.70	0.50	—	—	2.50	—
t-butanol	0.10	1.00	2.00	—	0.50	—	—	0.30	—
diisopropyl ether	0.50	1.00	0.30	2.00	—	0.10	—	—	—
1,2-dimethoxyethane (IS)	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00
ethanol	—	5.00	7.50	10.0	12.0	—	—	1.00	—
ethyl-tert-butyl ether	—	—	9.00	4.50	1.00	—	18.0	—	13.5
isobutanol	1.00	2.00	—	—	0.50	0.30	—	0.10	—
isopropanol	0.10	—	0.50	—	2.00	—	0.30	1.00	—
methanol	0.10	—	1.00	2.50	5.00	0.50	—	—	—
methyl-tert-butyl ether	17.0	—	—	—	1.00	15.0	6.00	—	11.5
t-pentanol	2.00	1.00	0.70	—	0.50	—	—	0.10	—
propanol	2.00	0.40	1.00	—	0.70	—	—	0.20	—
Total Oxygenates	29.80%	30.00%	28.80%	29.70%	29.80%	29.90%	29.30%	28.20%	30.00%
Surrogate Base Gasoline	70.20%	70.00%	71.20%	70.30%	70.20%	70.10%	70.70%	71.80%	70.00%
Quantity	Cat.#	Cat.#	Cat.#	Cat.#	Cat.#	Cat.#	Cat.#	Cat.#	Cat.#
each	36213	36214	36215	36216	36217	36218	36219	36220	36221
each w/data pk.	36213-500	36214-500	36215-500	36216-500	36217-500	36218-500	36219-500	36220-500	36221-500
5pk.	36213-510	36214-510	36215-510	36216-510	36217-510	36218-510	36219-510	36220-510	36221-510
5pk. w/data pk.	36213-520	36214-520	36215-520	36216-520	36217-520	36218-520	36219-520	36220-520	36221-520
10pk. w/data pk.	36313	36314	36315	36316	36317	36318	36319	36320	36321

Mixtures 1-9 prepared on a WT/WT% basis, 1ml ampul.

Restek also offers a complete set of standards for five-point calibration to meet ASTM and EPA calibration requirements (see our new product guide).

¹ Peaff, George, C&EN, September 26, 1994, pp 8-13.

² 40 CFR Part 30, Federal Register, 59(32): 7716-7878, Feb. 16, 1994.

³ ASTM Test Method D5599-94, *Determination of Oxygenates in Gasoline by Gas Chromatography and Selective Flame Ionization Detection*.

⁴ ASTM Test Method D4815-93, *Standard Test Method for Determination of MTBE, ETBE, TAME, DIPE, tertiary-amyl Alcohol and C1 to C4 Alcohols in Gasoline by Gas Chromatography*.

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Florasil® Cleanup for Organochlorine Pesticides & PCBs (# 59562)
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Extraction of PCBs Using Resprep™-C18-47 SPE Disks and Resprep™-6D (# 59564)
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Analyzing FAMES (# 59584)
Using Computer Modeling to Optimize FAME Analysis (# 59585)

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Aromatics in Reformulated Gasoline by GC/MS (# 59572)

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New Rtx®-I PONA Column for Analysis of Petroleum Products (# 59568)
Analyzing Oxygenates in Gasoline (# 59587)
Restek's Al₂O₃ PLOT Column (# 59569)
Rtx®-I: A New Bonded Packed Column for Simulated Distillation (# 59570)

Micro & Packed

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