

Application Note 47

Purity Analysis of MTBE Product by ASTM Test Method D5441 (High Resolution Capillary GC)

Methyl tert-butyl ether (MTBE) is an effective and increasingly important performance-enhancing additive for gasoline. Impurities in MTBE product, however, especially oxygenates and olefins, can adversely affect the value of MTBE as a gasoline additive. Consequently, the American Society for Testing and Materials (ASTM) has prepared a new analytical method, ASTM Test Method D5441, for determining the purity of MTBE product and quantifying the common impurities the product might contain (1).*

Key Words

- MTBE • gasoline additive • purity analysis
- high resolution capillary gas chromatography

The effectiveness of Method D5441 relies on high resolution capillary gas chromatography to separate several key impurities. Petrocol™ DH 50.2, Petrocol DH, and Petrocol DH 150 fused silica capillary columns (50 m x 0.20 mm I.D. x 0.50 µm film, 100 m x 0.25 mm I.D. x 0.50 µm film, 150 m x 0.25 mm I.D. x 1.0 µm film, respectively) demonstrate consistent ability to perform these key separations according to the requirements of the new method.

Method D5441 states that for a column to be considered acceptable for the analysis, it must resolve a qualitative mixture consisting of 1% each of tert-butanol, cis-2-pentene, and trans-2-pentene in MTBE with an R value of at least 1.3 between each pair of peaks (1). Figure A shows the analysis of MTBE Resolution Mix for ASTM D5441, our qualitative reference standard containing 1% each of trans-2-pentene, tert-butanol, and cis-2-pentene in MTBE, as described for evaluating column performance in the ASTM test method. Using a 100-meter Petrocol DH column, resolution between trans-2-pentene and tert-butanol and between tert-butanol and cis-2-pentene exceeds the method requirement of $R \geq 1.3$. Petrocol DH 50.2 and Petrocol DH 150 columns also will provide satisfactory results when used under the conditions summarized in Table 1.

In addition to columns and a column performance standard suitable for Method D5441, we have developed reference standards for identifying and quantifying contaminants in MTBE product. Our MTBE Contaminant Standards are quantitative reference standards containing common MTBE contaminants at 1% (Cat. No. 47942) or 0.1% (Cat. No. 47943) nominal weight in MTBE. Certificates of analysis describing lot-specific formulation, component purity (to at least 3 significant figures), and total weight percent composition (to at least 3 significant figures) are included with each standard. Figure B shows the analysis of the 1% standard, using a Petrocol DH column. Again,

the column provides excellent resolution, enabling the analyst to obtain highly accurate information about the composition of the mix.

We highly recommend Petrocol columns and the chemical standards described here to analysts monitoring MTBE product.

Table 1. Typical Conditions for MTBE Purity Analysis, per ASTM Method D5441

	Petrocol DH 50.2 50 m	Petrocol DH 100 m	Petrocol DH 150 150 m
Temperature			
Initial	40 °C	50 °C	60 °C
Initial Hold Time	13 min.	13 min.	13 min.
Program Rate	10 °C/min.	10 °C/min.	10 °C/min.
Final	180 °C	180 °C	180 °C
Final Hold Time	3 min.	7 min.	20 min.
Injection		Detection	
Temperature:	200 °C	Detector Type:	flame ionization
Sample Size:	0.1-0.5 µL	Temperature:	250 °C
Split Ratio:	200:1	Fuel Gas:	hydrogen, ~30 mL/min.
Carrier Gas:	helium, 20-24 cm/sec.	Oxidizing Gas:	air, ~300 mL/min.
		Make-Up Gas:	nitrogen, ~30 mL/min.

NOTE: These columns and conditions also are suitable for purity analyses of another important oxygenated additive, tert-amyl methyl ether (TAME).

Figure A. Resolution of Critical Contaminants Confirmed

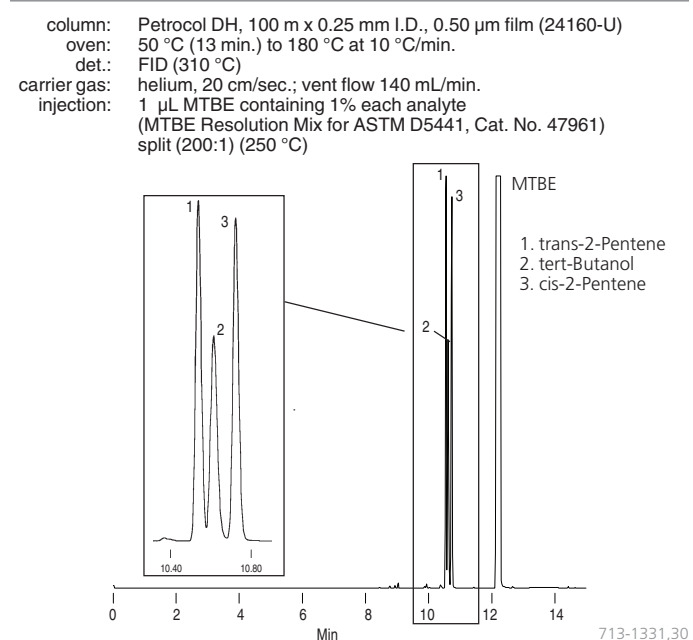
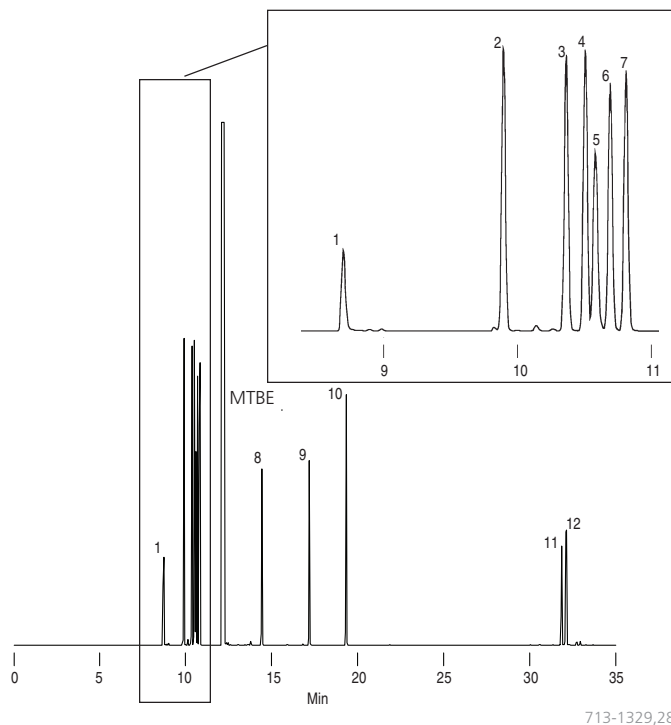


Figure B. MTBE Contaminants Standard Resolved

column: Petrocol DH, 100 m x 0.25 mm I.D., 0.50 µm film (24160-U)
 oven: 50 °C (13 min.) to 180 °C at 10 °C/min.
 det.: FID (310 °C)
 carrier gas: helium, 20 cm/sec.; vent flow 140 mL/min.
 injection: 1 µL MTBE containing 1% each analyte
 (MTBE Contaminants Mix A, Cat. No. 4-7942)
 split (200:1) (250 °C)



713-1329,28

Component	% Purity*	Wt. %*
1. Methanol	99.9	0.999
2. Isopentane	99.9	0.999
3. n-Pentane	98.7	0.999
4. trans-2-Pentene	99.9	1.029
5. tert-Butanol	99.9	0.999
6. cis-2-Pentene	97.9	1.029
7. 2-Methyl-2-butene	99.9	0.999
MTBE	99.9	88.891
8. tert-Butyl ethyl ether	97.9	1.029
9. tert-Amyl methyl ether (TAME)	98.7	1.030
10. 2,4,4-Trimethyl-1-pentene Triisobutylene Isomers:	99.9	0.999
11. 4,4-Dimethyl-2-neopentyl-1-pentene	99.9	0.469**
12. 2,2,4,6,6-Pentamethyl-3-heptene	99.9	0.529**

*Purity and weight % differ slightly from lot to lot, and will be listed on the data sheet included with the product.

**Isomer distribution (determined by capillary GC/FID analysis) and overall purity of triisobutylene isomers mix will be listed on the data sheet included with the product.

Ordering Information:

Description	Cat. No.
Petrocol Fused Silica Capillary Columns	
DH 50.2 Column 50 m x 0.20 mm I.D., 0.50 µm film	24133-U
DH Column 100 m x 0.25 mm I.D., 0.50 µm film	24160-U
DH 150 Column 150 m x 0.25 mm I.D., 1.0 µm film	24155

Standards for MTBE Product Purity Analyses

MTBE Contaminants Mix A 1 mL **47942**

Quantitative reference standard consisting of the following components at 1% nominal weight in MTBE:

tert-Amyl methyl ether
 tert-Butanol
 tert-Butyl ethyl ether
 Isopentane
 Methanol
 2-Methyl-2-butene
 n-Pentane

MTBE Contaminants Mix B 1 mL **47943**

Quantitative reference standard consisting of the following components at 0.1% nominal weight in MTBE:

tert-Amyl methyl ether
 tert-Butanol
 tert-Butyl ethyl ether
 Isopentane
 Methanol
 2-Methyl-2-butene
 n-Pentane

*Method D5441 is **not** intended for determination of MTBE in gasoline.

NOTE: A 150-meter Petrocol DH 150 column requires a head pressure of approximately 75 psi of helium for optimum linear velocity. The head pressure requirement can be reduced to approximately 50psi by using hydrogen as the carrier gas.

Petrocol is a trademark of Sigma-Aldrich Co.

Fused silica capillary columns manufactured under HP US Pat. No. 4,293,415.

Reference

1. *Analysis of Methyl tert-Butyl Ether (MTBE) by Gas Chromatography*, Test Method D5441, American Society for Testing and Materials, 1993.
 Obtain from ASTM, 1916 Race Street, Philadelphia, PA 19103 USA.

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