

# 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).\** (ChromFax No.: 394047)

### 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 (50m x 0.20mm ID x 0.50µm film, 100m x 0.25mm ID x 0.50µm film, 150m x 0.25mm ID x 1.0µm 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. 4-7942) or 0.1% (Cat. No. 4-7943) 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.

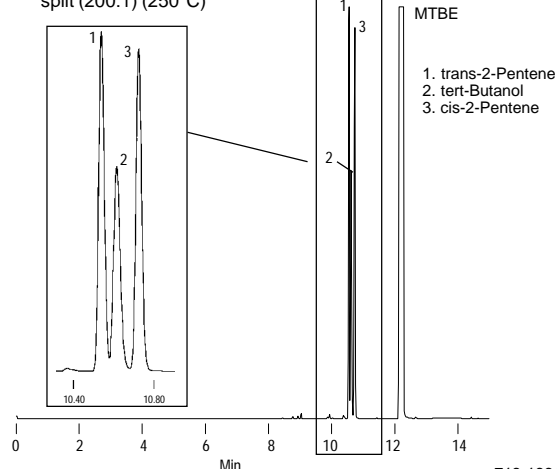
**Table 1. Typical Conditions for MTBE Purity Analysis, per ASTM Method D5441**

	Petrocol DH 50.2 50m	Petrocol DH 100m	Petrocol DH 150 150m
<b>Temperature</b>			
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
<b>Injection</b>		<b>Detection</b>	
Temperature:	200°C	Detector Type:	flame ionization
Sample Size:	0.1-0.5µL	Temperature:	250°C
Split Ratio:	200:1	Fuel Gas:	hydrogen, ~30mL/min
Carrier Gas:	helium, 20-24cm/sec	Oxidizing Gas:	air, ~300mL/min
		Make-Up Gas:	nitrogen, ~30mL/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**

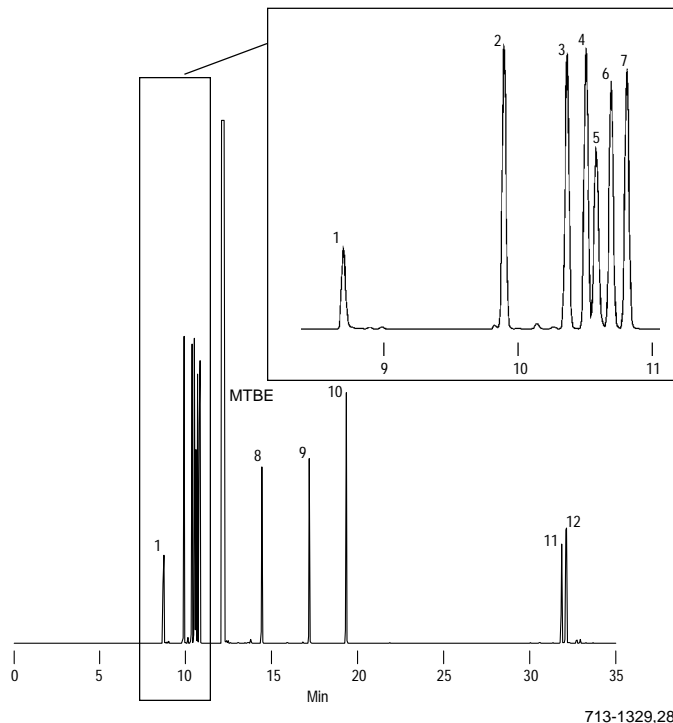
Column: Petrocol DH, 100m x 0.25mm ID, 0.50µm film  
Cat. No.: 24160-U  
Oven: 50°C (13 min) to 180°C at 10°C/min  
Carrier: helium, 20cm/sec; vent flow 140mL/min  
Det.: FID (310°C)  
Inj.: 1µL MTBE containing 1% each analyte (MTBE Resolution Mix for ASTM D5441, Cat. No. 4-7961) split (200:1) (250°C)



713-1331,30

## Figure B. MTBE Contaminants Standard Resolved

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



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	99.9	0.999
Triisobutylene Isomers:		
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:

### Petrocol Fused Silica Capillary Columns

DH 50.2 Column	
50m x 0.20mm ID, 0.50µm film	24133-U
DH Column	
100m x 0.25mm ID, 0.50µm film	24160-U
DH 150 Column	
150m x 0.25mm ID, 1.0µm film	24155

### Standards for MTBE Product Purity Analyses

MTBE Resolution Mix for ASTM D5441 1mL 47961

A qualitative reference standard containing 1% of each of the following components in MTBE, as described in ASTM Test Method D5441:

tert-Butanol  
 cis-2-Pentene  
 trans-2-Pentene

MTBE Contaminants Mix A 1mL 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 1mL 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

### Contact our Technical Service Department

(phone 800-359-3041 or 814-359-3041, FAX 814-359-5468) for expert answers to your questions.

\*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 75psi 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 Supelco, Inc.

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.

Note 47

For more information, or current prices, contact your nearest Supelco subsidiary listed below. To obtain further contact information, visit our website ([www.sigma-aldrich.com](http://www.sigma-aldrich.com)), see the Supelco catalog, or contact Supelco, Bellefonte, PA 16823-0048 USA.

ARGENTINA · Sigma-Aldrich de Argentina, S.A. · Buenos Aires 1119 AUSTRALIA · Sigma-Aldrich Pty. Ltd. · Castle Hill NSW 2154 AUSTRIA · Sigma-Aldrich Handels GmbH · A-1110 Wien  
 BELGIUM · Sigma-Aldrich N.V./S.A. · B-2880 Bornem BRAZIL · Sigma-Aldrich Quimica Brasil Ltda. · 01239-010 São Paulo, SP CANADA · Sigma-Aldrich Canada, Ltd. · 2149 Winston Park Dr., Oakville, ON L6H 6J8  
 CZECH REPUBLIC · Sigma-Aldrich s.r.o. · 186 00 Praha 8 DENMARK · Sigma-Aldrich Denmark A/S · DK-2665 Vallensbaek Strand FINLAND · Sigma-Aldrich Finland/YA-Kemia Oy · FIN-00700 Helsinki  
 FRANCE · Sigma-Aldrich Chimie · 38297 Saint-Quentin-Fallavier Cedex GERMANY · Sigma-Aldrich Chemie GmbH · D-82041 Deisenhofen GREECE · Sigma-Aldrich (o.m.) Ltd. · Ilioupoli 16346, Athens  
 HUNGARY · Sigma-Aldrich Kft. · H-1067 Budapest INDIA · Sigma-Aldrich Co. · Bangalore 560 048 IRELAND · Sigma-Aldrich Ireland Ltd. · Dublin 24 ISRAEL · Sigma Israel Chemicals Ltd. · Rehovot 76100  
 ITALY · Sigma-Aldrich s.r.l. · 20151 Milano JAPAN · Sigma-Aldrich Japan K.K. · Chuo-ku, Tokyo 100 038 KOREA · Sigma-Aldrich Korea · Seoul MALAYSIA · Sigma-Aldrich (M) Sdn. Bhd. · Selangor  
 MEXICO · Sigma-Aldrich Quimica S.A. de C.V. · 50200 Toluca NETHERLANDS · Sigma-Aldrich Chemie BV · 3330 AA Zwijndrecht NORWAY · Sigma-Aldrich Norway · Torshov · N-0401 Oslo  
 POLAND · Sigma-Aldrich Sp. z o.o. · 61-663 Poznań PORTUGAL · Sigma-Aldrich Quimica, S.A. · Sintra 2710 RUSSIA · Sigma-Aldrich Russia · Moscow 103062 SINGAPORE · Sigma-Aldrich Pte. Ltd.  
 SOUTH AFRICA · Sigma-Aldrich (pty) Ltd. · Jet Park 1459 SPAIN · Sigma-Aldrich Quimica, S.A. · 28100 Alcobendas, Madrid SWEDEN · Sigma-Aldrich Sweden AB · 135 70 Stockholm  
 SWITZERLAND · Supelco · CH-9471 Buchs UNITED KINGDOM · Sigma-Aldrich Company Ltd. · Poole, Dorset BH12 4QH  
 UNITED STATES · Supelco · Supelco Park · Bellefonte, PA 16823-0048 · Phone 800-247-6628 or 814-359-3441 · Fax 800-447-3044 or 814-359-3044 · email: [supelco@sial.com](mailto:supelco@sial.com)

H

Supelco is a member of the Sigma-Aldrich family. Supelco products are sold through Sigma-Aldrich, Inc. Sigma-Aldrich warrants that its products conform to the information contained in this and other Sigma-Aldrich publications. Purchaser must determine the suitability of the product for a particular use. Additional terms and conditions may apply. Please see the reverse side of the invoice or packing slip.