

# APPLICATIONS

## Analysis of Methyl-t-Butyl Ether (MTBE) and related impurities per ASTM test method D5441 using Zebron<sup>TM</sup> ZB-DHA-PONA Gas Chromatography Column

Dr. Ramkumar Dhandapani\*, Zeshan Aqeel, and Tim Nelson  
Phenomenex, Inc., 411 Madrid Ave., Torrance, CA 90501 USA

\*Lead Scientist



**Ramkumar Dhandapani, Ph.D.**  
Product Manager - Gas Chromatography

*He has a PhD in Analytical Chemistry and a total of 14 years experience in chromatographic method development and troubleshooting. Ramkumar loves to write poems, read Shakespeare, and attend Shakespeare plays.*

### Introduction

Methyl-t-Butyl Ether (MTBE) is used as an additive for spark ignition fuels to enhance the octane performance. MTBE is a distilled product with a designed low amount of impurities, and the ASTM D5441 is a gas chromatography analysis method that is used to measure its purity. Running this test method verifies that no impurities were left during the manufacture of the MTBE nor were any contaminants introduced in its storage or shipment. Potential contaminants from the manufacturing process are C4 to C12 olefins and/or their dimers and trimers from unreacted feedstock, C1 to C4 alcohols, as well as ether isomers. Contaminants from shipment can practically be anything since truck containers are typically not sole product isolated and ship different products as needed for

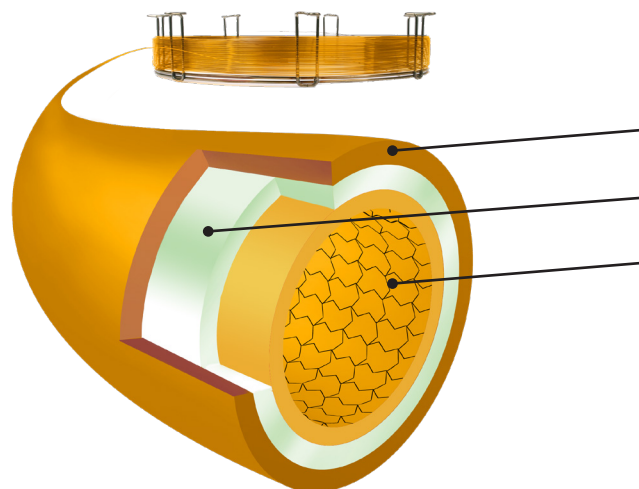
logistical efficiency. Even if a tanker is single product isolated there will be potential for contaminants from the loading and the tank cleaning process.

The purity of the MTBE is critical since any contamination will affect the performance of the spark ignition fuel. In this technical work, ASTM D5441 is run with the Zebron ZB-DHA-PONA gas chromatography column which is specially designed for the DHA test methods. A side by side comparison of commercially available columns is made to evaluate the peak shape and the separation of critical pairs.

**Table 1.**  
Zebron ZB-DHA-PONA Column Dimensional Options for Detailed Hydrocarbon Analysis (ASTM and alternative methods)

Part No.	Dimensions	Stationary Phase	Benefits
<b>7JE-G042-17</b>	50 m x 0.20 mm x 0.50 $\mu$ m	100 % Dimethylpolysiloxane	50 m column provides shorter run time while the 0.20 mm tighter ID provides higher efficiency
<b>7MG-G042-17</b>	100 m x 0.25 mm x 0.50 $\mu$ m	100 % Dimethylpolysiloxane	100 m length provides high plate count/efficiency
<b>7QG-G042-22</b>	150 m x 0.25 mm x 1.0 $\mu$ m	100 % Dimethylpolysiloxane	150 m with a 1.0 $\mu$ m thicker film provides better separation of lower boiling fractions and maintains high efficiency from the column length
<b>7AG-G042-22</b>	5 m x 0.25 mm x 1.0 $\mu$ m	5 % Phenyl 95 % Dimethylpolysiloxane	Optional tuning column provides phenyl selectivity in addition to true boiling point separation. This helps resolve certain aromatics from alkanes and alkenes

**Figure 1.**  
Benefits of ZB-DHA-PONA GC Column



#### Flexible Polyimide

Provides stability & flexibility at different temperatures

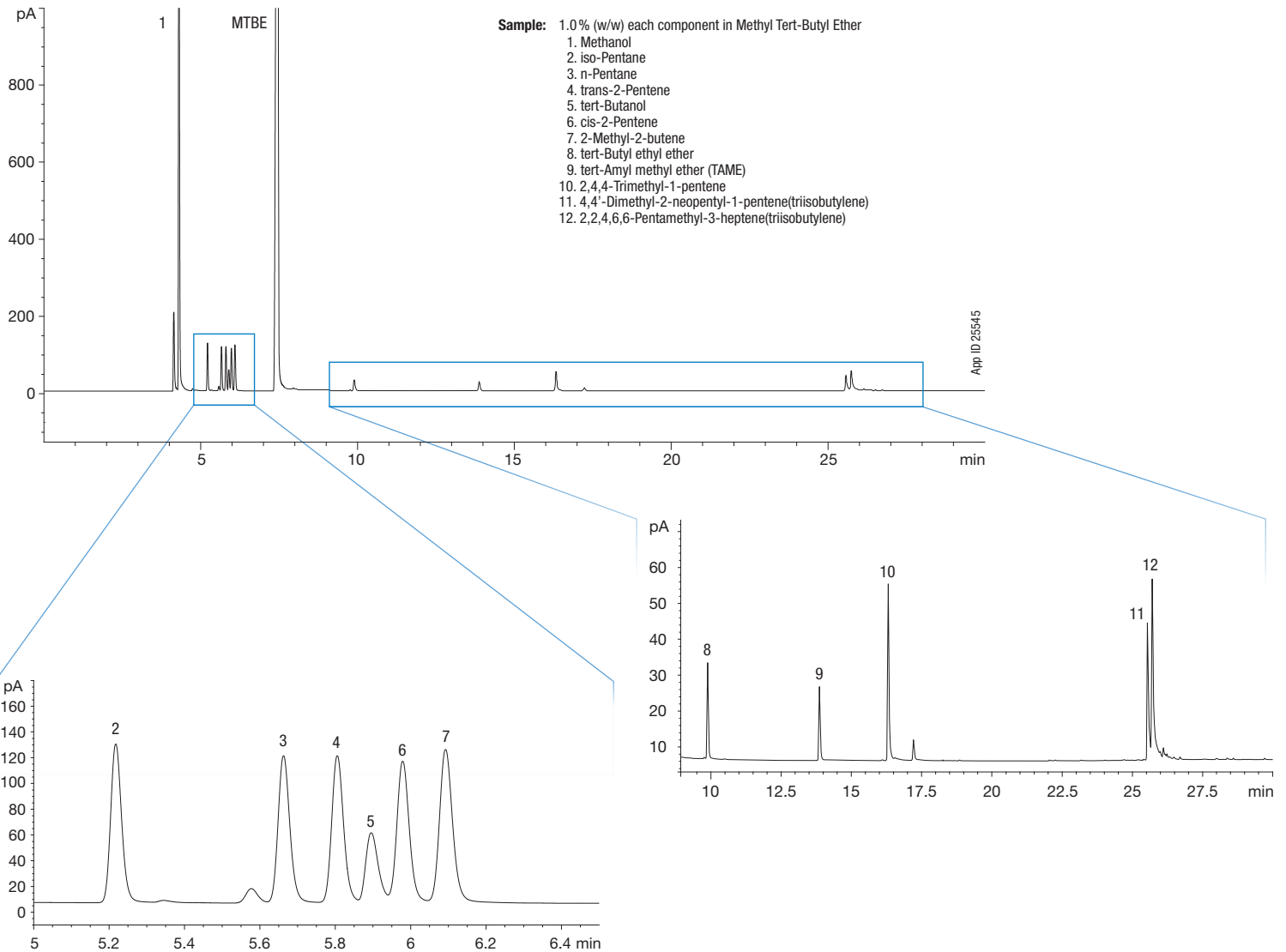
#### Specially Deactivated Fused Silica Surface

Gives excellent peak shape for polar & nonpolar compounds

#### Stationary Phase

- High efficiency dimension and consistent film thickness delivers excellent separation of paraffins, isoparaffins, olefins, naphthenes, aromatics, and polar compounds
- Special designed Engineered Self Cross-linking<sup>TM</sup> (ESC) stationary phase for low bleed with exceptional peak shape, resolution, and separation

**Figure 2.**  
 Analysis of MTBE contaminant mix with Zebron™ ZB-DHA-PONA by GC-FID\*\*



**Conditions for all examples:**

**Column:** Zebron ZB-DHA-PONA  
 Restek® Rtx®-DHA-50  
 Supelco® Petrocol®-DH 50.2  
 Agilent® HP®-PONA

**Phase:** 100% Dimethylpolysiloxane

**Dimensions:** 50 meter x 0.20 mm x 0.50 µm

**Part No.:** 7JE-G042-17

**Injection:** Pulse Split 50:1, 20 psi for 0.5 min.,  
 @ 200 °C, 0.5 µL

**Recommended Liner:** Zebron PLUS Z-Liner™

**Part No.:** AG2-OA03-01

**Carrier Gas:** Helium @ 0.9 mL/min (Constant Flow)

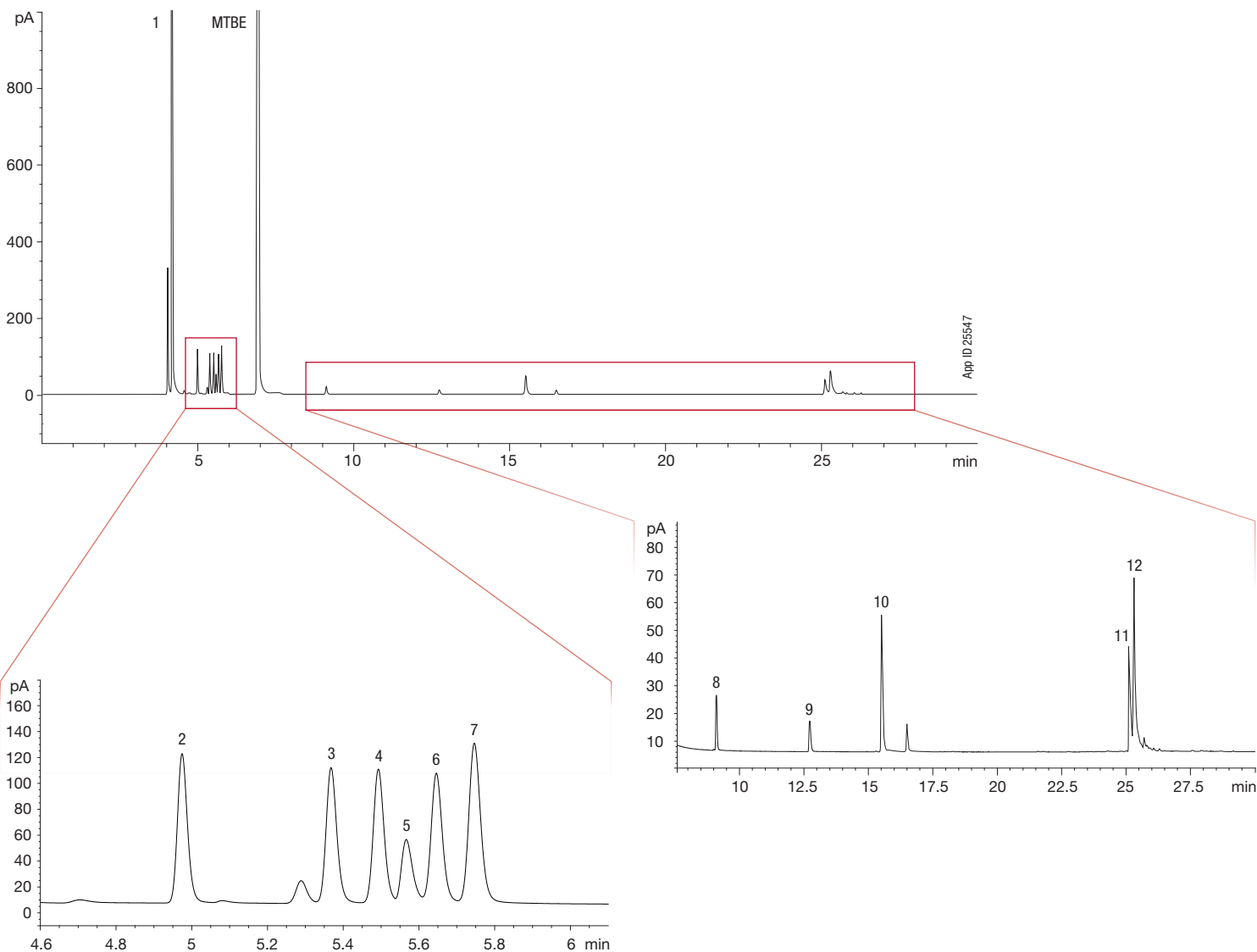
**Oven Program:** 40 °C (hold 13 min) to 180 °C at 10 °C/min (hold 3 min)

**Detector:** Flame Ionization (FID) @ 250 °C

\*\*test was run under equal and controlled conditions for a comparative analysis,  
 and the results are not representative of every column's performance.

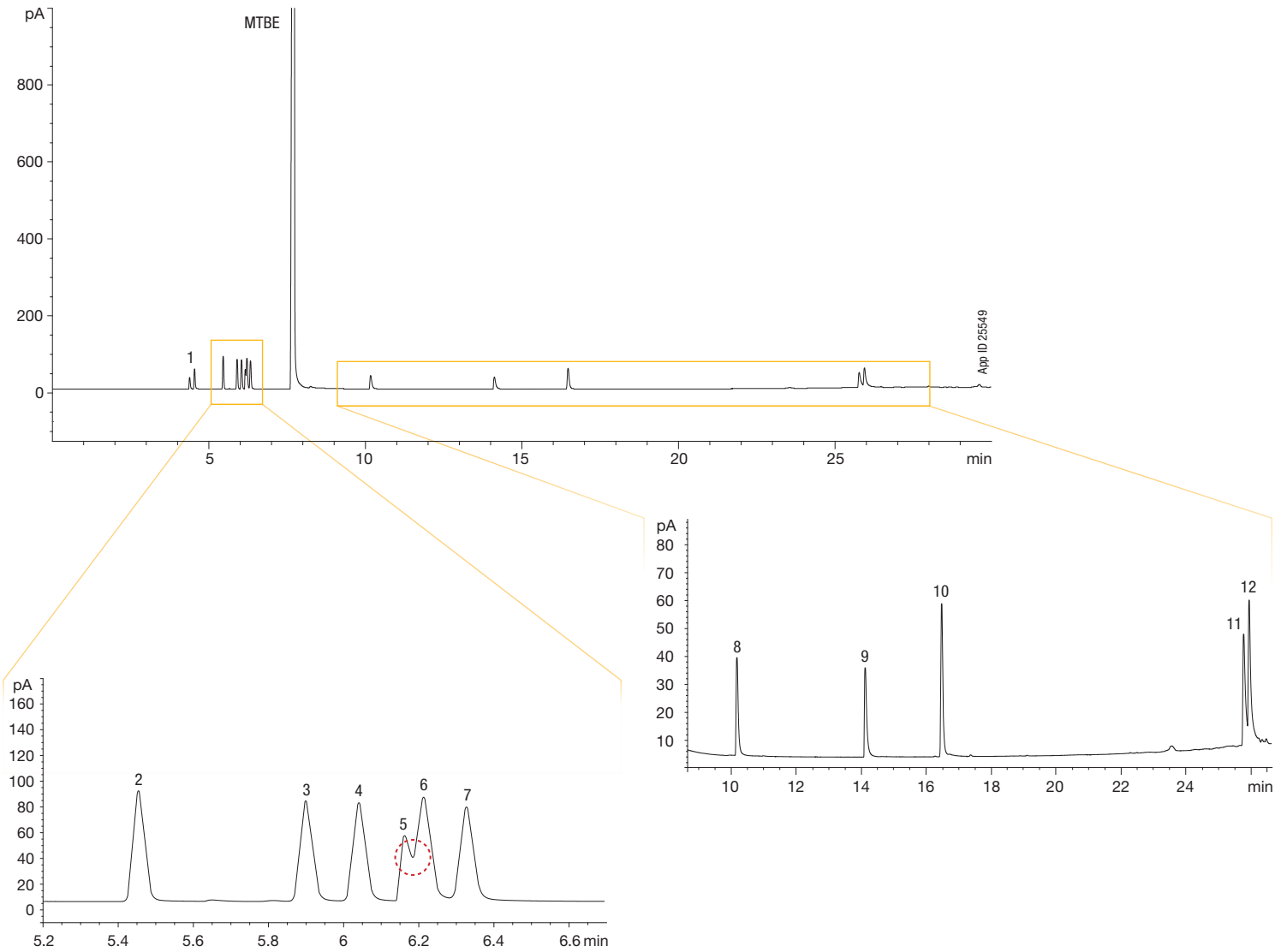
In addition to the Zebron™ ZB-DHA-PONA column, there were three competitive columns run using the same method and conditions.

**Figure 3.**  
Analysis of MTBE contaminant mix with Restek® Rtx®-DHA-50 Column\*\*



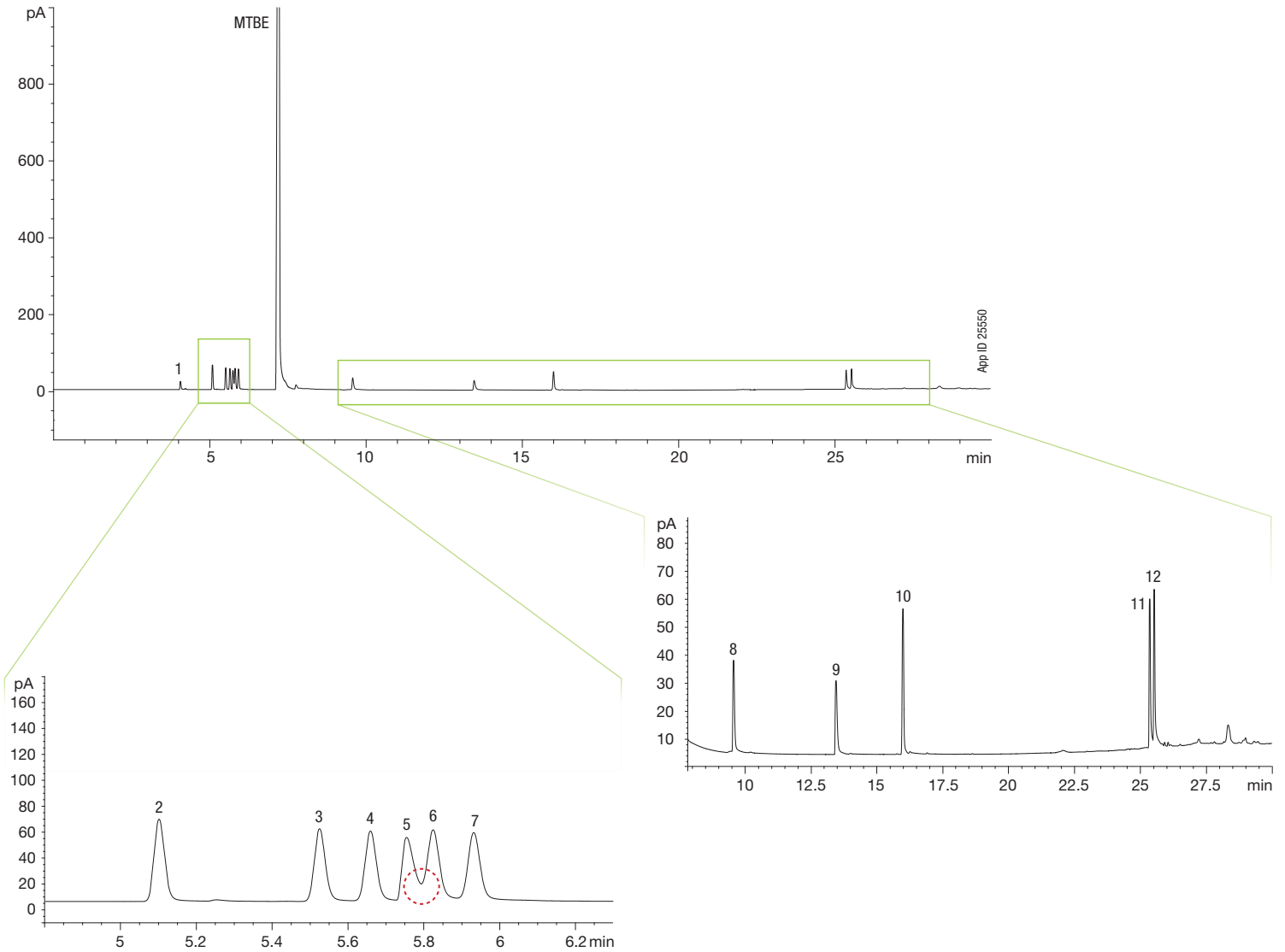
\*\*test was run under equal and controlled conditions for a comparative analysis, and the results are not representative of every column's performance.

**Figure 4.**  
Analysis of MTBE contaminant mix with Supelco<sup>®</sup> Petrocol<sup>®</sup>-DH 50.2 Column\*\*



\*\*test was run under equal and controlled conditions for a comparative analysis, and the results are not representative of every column's performance.

**Figure 5.**  
Analysis of MTBE contaminant mix with Agilent® HP®-PONA Column\*\*



\*\*test was run under equal and controlled conditions for a comparative analysis, and the results are not representative of every column's performance.

**Table 2.**

Resolution of mandated critical peaks per ASTM D5441 requirement in subsection 7.3 &amp; 11.2\*

Analyte Peaks	Resolution				
	ASTM Requirement	Zebron™ ZB-DHA-PONA	Restek® Rtx®-DHA	Supelco® Petrocol®-DH 50.2	Agilent® HP®-PONA
Trans-2-Pentene and Tert-Butanol	Not less than 1.3	1.6	1.4	2.1	1.7
Tert-Butanol and Cis-2-Pentene	Not less than 1.3	1.5	1.5	0.8	1.2

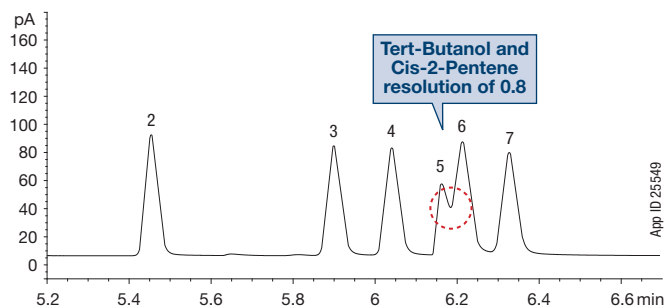
## Results and Discussion

MTBE is a volatile solvent with an ether functional group that has an oxygen with two lone pair of electrons. These lone pairs can give tailing peak shape if the GC column has activity in the middle fused-silica layer due to hydrogen bonding. Thus, a poorly deactivated column will cause asymmetric peaks for MTBE and any impurity that contains alcohol. Zebron ZB-DHA-PONA has a special deactivated fused silica surface that provides excellent peak shape for polar and nonpolar compounds (**Figure 1**).

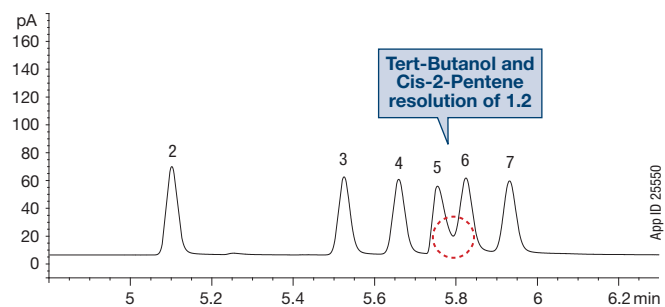
**Figure 6.**

Low boiling MTBE impurities

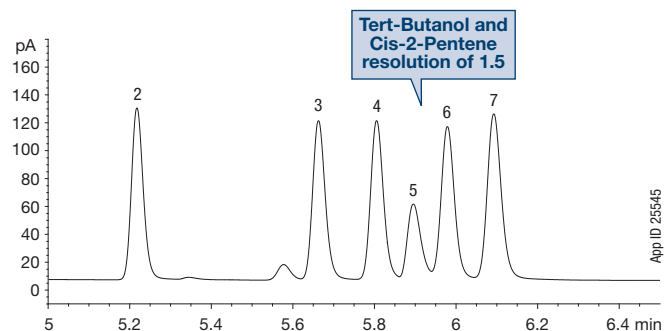
Supelco Petrocol-DH 50.2 Column\*\*



Agilent HP-PONA Column\*\*



Zebron ZB-DHA-PONA by GC-FID\*\*



The smaller 0.20mm inner diameter along with the 50-meter column length provides an efficient mass transfer of the complex analytes for great separation and resolution of critical pairs. The column's low polar 100% Dimethylpolysiloxane phase provided true boiling-point based separation. The ZB-DHA-PONA provides very good separation of low and high boiling impurities in the MTBE (**Figure 2**).

The ASTM D5441 test mandates a resolution requirement for two critical pairs in the MTBE analysis. There is a minimum resolution requirement of 1.3 between trans-2-Pentene and tert-Butanol as well as tert-Butanol and cis-2-Pentene. ZB-DHA-PONA GC column exceeds resolution requirement as per ASTM D5441 and also provides better separation than the competitors (**Table 2**). The test results show that Zebron ZB-DHA-PONA has good separation of low and high boiling impurities in MTBE versus the competitive columns (**Figure 3**).

A comparison of low boiling critical pairs of impurities in MTBE on various GC Columns highlights the challenges in meeting the 1.3 minimum resolution criteria for ASTM D5441 most specifically for **peaks 5 & 6**, tert-Butanol & cis-2-Pentene. Two out of the three competitive columns had significant coelution among two of the peaks (**Figure 3** and **Figure 4**).

## Conclusion

The Zebron ZB-DHA-PONA provided optimal separation of DHA critical pairs with symmetric peaks. The Zebron ZB-DHA-PONA with the 100% Dimethylpolysiloxane phase is a great selectivity to provide separation of the ASTM D5441 analytes.


\*\*test was run under equal and controlled conditions for a comparative analysis, and the results are not representative of every column's performance.

**Ordering Information**

**Zebtron ZB-DHA-PONA GC Columns**

ID(mm)	df(µm)	Temp. Limits °C	Part No.
<b>5-Meter</b>			
0.25	1.0	-60 to 340/360	<b>7AG-G042-22</b>
<b>50-Meter</b>			
0.20	0.50	-60 to 360/370	<b>7JE-G042-17</b>
<b>100-Meter</b>			
0.25	0.50	-60 to 360/370	<b>7MG-G042-17</b>
<b>150-Meter</b>			
0.25	1.0	-60 to 340/360	<b>7QG-G042-22</b>

Note: If you need a 5 in. cage, simply add a (-B) after the part number, e.g., 7HG-G010-11-B. Some exceptions may apply. Agilent 6850 and some SRI and process GC systems use only 5 in. cages.

- Australia**  
t: +61 (0)2-9428-6444  
auinfo@phenomenex.com
- Austria**  
t: +43 (0)1-319-1301  
anfrage@phenomenex.com
- Belgium**  
t: +32 (0)2 503 4015 (French)  
t: +32 (0)2 511 8666 (Dutch)  
beinfo@phenomenex.com
- Canada**  
t: +1 (800) 543-3681  
info@phenomenex.com
- China**  
t: +86 400-606-8099  
cninfo@phenomenex.com
- Denmark**  
t: +45 4824 8048  
nordicinfo@phenomenex.com
- Finland**  
t: +358 (0)9 4789 0063  
nordicinfo@phenomenex.com
- France**  
t: +33 (0)1 30 09 21 10  
franceinfo@phenomenex.com
- Germany**  
t: +49 (0)6021-58830-0  
anfrage@phenomenex.com
- India**  
t: +91 (0)40-3012 2400  
indiainfo@phenomenex.com
- Ireland**  
t: +353 (0)1 247 5405  
eireinfo@phenomenex.com
- Italy**  
t: +39 051 6327511  
italiainfo@phenomenex.com
- Luxembourg**  
t: +31 (0)30-2418700  
nlinfo@phenomenex.com
- Mexico**  
t: 01-800-844-5226  
tecnicomx@phenomenex.com
- The Netherlands**  
t: +31 (0)30-2418700  
nlinfo@phenomenex.com
- New Zealand**  
t: +64 (0)9-4780951  
nzinfo@phenomenex.com
- Norway**  
t: +47 810 02 005  
nordicinfo@phenomenex.com
- Portugal**  
t: +351 221 450 488  
ptinfo@phenomenex.com
- Singapore**  
t: +65 800-852-3944  
sginfo@phenomenex.com
- Spain**  
t: +34 91-413-8613  
espinfo@phenomenex.com
- Sweden**  
t: +46 (0)8 611 6950  
nordicinfo@phenomenex.com
- Switzerland**  
t: +41 (0)61 692 20 20  
swissinfo@phenomenex.com
- Taiwan**  
t: +886 (0) 0801-49-1246  
twinfo@phenomenex.com
- United Kingdom**  
t: +44 (0)1625-501367  
ukinfo@phenomenex.com
- USA**  
t: +1 (310) 212-0555  
info@phenomenex.com
- All other countries  
Corporate Office USA**   
t: +1 (310) 212-0555  
info@phenomenex.com

**Find Your Liner Online!**



Easily search by part numbers, applications, injection mode, or system manufacturer for quick selection in under 1 minute!

[www.phenomenex.com/FindLiner](http://www.phenomenex.com/FindLiner)

**Inlet Consumables Are Available Online!**



Need inlet seals, septa, or syringes? Explore hundreds of available parts online at:

[www.phenomenex.com/InletGC](http://www.phenomenex.com/InletGC)

Our Technical Nerds are available nearly 24/7.

**Live Chat today!**

▶ [www.phenomenex.com/chat](http://www.phenomenex.com/chat) ◀



**www.phenomenex.com**

Phenomenex products are available worldwide. For the distributor in your country, contact Phenomenex USA, International Department at [international@phenomenex.com](mailto:international@phenomenex.com)

**Terms and Conditions**

Subject to Phenomenex Standard Terms and Conditions which may be viewed at [www.phenomenex.com/TermsAndConditions](http://www.phenomenex.com/TermsAndConditions).

**Trademarks**

Zebtron, Z-Liner, and Be-Happy are trademarks of Phenomenex. Agilent and HP are registered trademarks of Agilent Technologies, Inc. Supelco and Petrocol are registered trademarks of Sigma-Aldrich Corporation. Restek and Rtx are registered trademarks of Restek Corporation.

**Disclaimer**

Phenomenex is not affiliated with Agilent Technologies, Sigma-Aldrich Corporation, or Restek Corporation. Comparative separations may not be representative of all applications. Results may not be representative of all applications.


FOR RESEARCH USE ONLY. Not for use in clinical diagnostic procedures.

© 2019 Phenomenex, Inc. All rights reserved.

**BE-HAPPY™**  
guarantee

Your happiness is our mission. Take 45 days to try our products. If you are not happy, we'll make it right.

[www.phenomenex.com/behappy](http://www.phenomenex.com/behappy)

 Having trouble reproducing this method? We would love to help! Visit [www.phenomenex.com/LiveChat](http://www.phenomenex.com/LiveChat) to get in touch with one of our Technical Specialists