Rapidly Analyze a Wide Range of Glycol Ethers by GC-MS Using the New Rxi®-1301Sil MS Column

By Rebecca Stevens and Chris English

Abstract

Chromatographic conditions were developed for a fast GC-MS glycol ether analysis on the Rxi®-1301Sil MS column. This cyano-based thin film column provides better resolution and faster run times than the thick film cyanopropylphenyl-type columns commonly used for speciation of the glycol ethers. The glycol ethers are high production volume industrial chemicals that often occur as complex mixtures of isomers. The Rxi®-1301Sil MS column is uniquely matched for the separation of these isomers while still producing narrow and symmetric peaks for the low molecular weight ethylene glycol ethers.

The Glycol Ethers

Glycol ethers are a broad class of commodity chemicals that find use in numerous applications. They are commonly used as ingredients in paints and coatings, cleaning products, and personal care products. This class of compounds is characterized by repeating ethylene (E-series) or propylene (P-series) glycol units terminated on one or both ends by alkyl ethers, phenyl ethers, or acetates (Figure 1). Glycol ethers are produced and used in enormous quantities, primarily in Western Europe, China, and the United States.

Their unique amphiphilic structure gives the glycol ethers favorable properties such as low volatility, strong solvent strength, high water solubility, and the ability to serve as coupling agents that promote the miscibility of aqueous and organic phases. These properties make glycol ethers a popular alternative to traditional oxygenated solvents such as ketones, ethers, and alcohols.

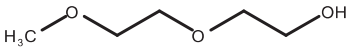
Toxicological studies indicate that the lower molecular weight E-series glycol ethers, such as ethylene glycol methyl ether (EGME), ethylene glycol ethyl ether (EGEE), and their acetates, may pose a more serious health hazard to humans and animals than their higher molecular weight counterparts.

The European Union and Canada have both adopted regulations limiting the use of glycol ethers in consumer products. In the EU, several of the glycol ethers are banned entirely while others are regulated to a specific concentration level. In 2010, Environment Canada (EC) published a reference method [1] for analysis of glycol ethers in consumer products including cleaners, degreasers, and coatings. This method addresses the most commonly used glycol ethers and describes an analytical approach for achieving the reporting limits set by Canadian regulation.

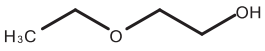
Figure 1: Structures of E-Series and P-Series Glycol Ethers

E-Series Glycol Ethers

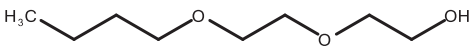
Ethylene glycol methyl ether



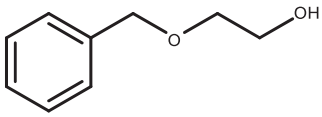
Diethylene glycol methyl ether



Ethylene glycol ethyl ether



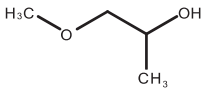
Diethylene glycol butyl ether



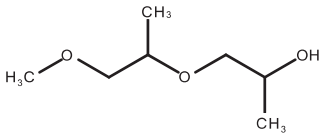
Ethylene glycol phenyl ether

Triethylene glycol methyl ether

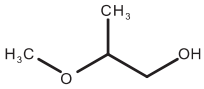
P-Series Glycol Ethers



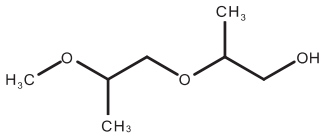
Propylene glycol methyl ether (α)



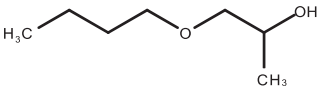
Dipropylene glycol methyl ether (α,α)



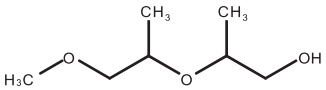
Propylene glycol methyl ether (β)



Dipropylene glycol methyl ether (β,β)



Propylene glycol butyl ether (α)



Dipropylene glycol methyl ether (α,β)

Glycol Ethers of Regulatory Importance are Well Resolved in Minimal Time

The Environment Canada reference method recommends a standard 624-type column in a 60 m x 0.32 mm x 1.80 µm format and a temperature program that spans 30 minutes for glycol ether analysis. The Rxi®-1301Sil MS column has very similar selectivity to that of 624-type columns as both are based on cyanopropylphenyl stationary phases; however, the thinner film and higher thermal stability of the Rxi®-1301Sil MS column provide good separations in a fraction of the time.

The Rxi®-1301Sil MS column in a 30 m x 0.25 mm x 0.25 µm format with optimized run conditions results in an analysis time of just 8 minutes. Using a fast temperature program, baseline resolution of the DPGME isomer group is possible and is comparable to, if not better than, the original method (Figure 2). The 0.25 µm film results in higher efficiency, narrow peaks, and, in turn, improved resolution with less retention. The Rxi®-1301Sil MS column also has a temperature limit of 320 °C, allowing for a high-temperature isothermal hold to remove any low-volatility sample components from the column. If these low-volatility contaminants are not removed during the analytical run they may elute in subsequent analyses as broad "ghost" peaks, possibly interfering with analytes of interest.

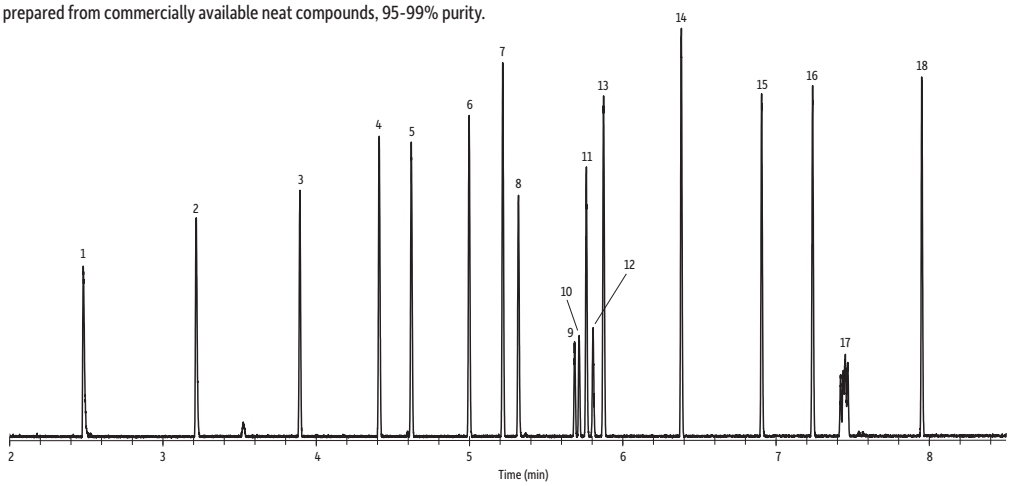
Faster run times can also be achieved using narrow-bore 30 meter 624-type columns with the same phase ratio, such as a 30 m x 0.25 mm x 1.4 µm format, which will maintain the same elution order. However, as shown in Figures 3 and 4, chromatographic resolution is reduced in exchange for speed in this situation, and coelution of the DPGME III isomer with DEGEE occurs. Poor resolution of the TPGME isomer group is also apparent. In contrast to 624-type columns, the Rxi®-1301Sil MS column provides better resolution of critical compounds for glycol ether analysis in a much faster analysis time.

Chromatograms were collected using a 200 amu scan range beginning at 20 amu in order to capture the low mass fragments generated by electron ionization of the glycol ethers. The glycol units fragment readily and even the higher molecular weight P-series compounds do not produce abundant ions greater than 150 amu. A high scan speed was employed to achieve enough points across the narrow peaks.

Figure 2: An Rxi®-1301Sil MS column provides excellent separation of glycol ethers of regulatory importance three times faster than under the EC method conditions while maintaining baseline resolution of the DPGME isomers.

Peaks	tR (min)	Conc. (µg/mL)	Common Name
1. EGME	2.483	100	Ethylene glycol methyl ether
2. EGEE	3.218	100	Ethylene glycol ethyl ether
3. Perfluoro TEGME (IS)	3.894	100	Perfluoro triethylene glycol methyl ether
4. PnPGE	4.412	100	Propylene glycol propyl ether
5. PGMA	4.622	100	Propylene glycol methyl ether acetate
6. EGBE	4.998	100	Ethylene glycol butyl ether
7. PGBE	5.218	100	Propylene glycol butyl ether
8. DEGME	5.320	100	Diethylene glycol methyl ether
9. DPGME I	5.685	100	Dipropylene glycol methyl ether
10. DPGME II	5.715		Dipropylene glycol methyl ether
11. DEGEE	5.763	100	Diethylene glycol ethyl ether
12. DPGME III	5.807		Dipropylene glycol methyl ether
13. 1,2-DCB-D4 (IS)	5.876	100	1,2-Dichlorobenzene-D4
14. EGHE	6.383	100	Ethylene glycol hexyl ether
15. DEGBE	6.907	100	Diethylene glycol butyl ether
16. EGPhE	7.239	100	Ethylene glycol phenyl ether
17. TPGME isomers	7.451	100	Tripropylene glycol methyl ether
18. DEGHE	7.952	100	Diethylene glycol hexyl ether

Standard was prepared from commercially available neat compounds, 95-99% purity.



GC_PC1280

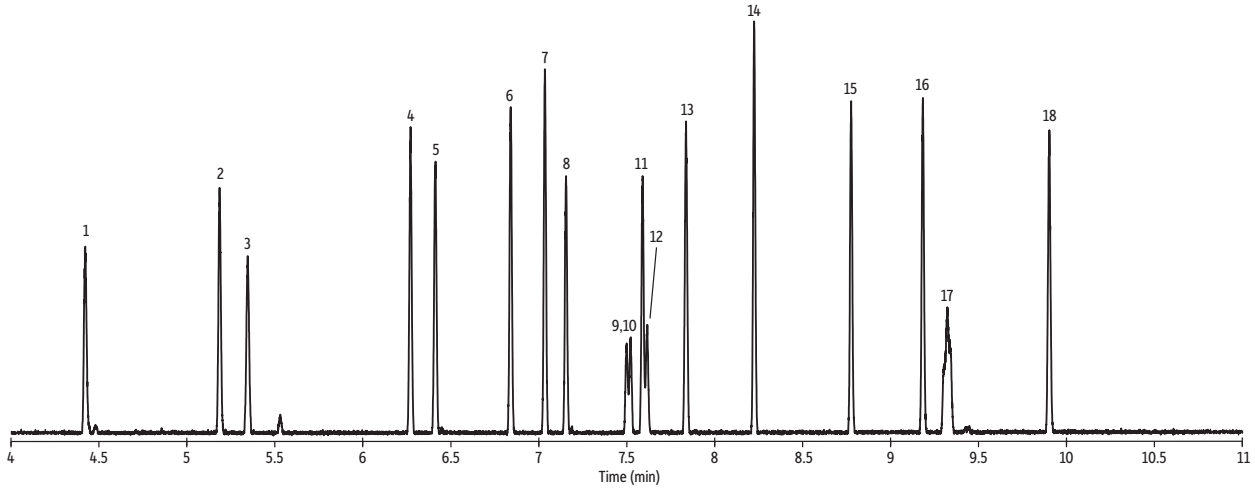
Column	Rxi®-1301Sil MS, 30 m, 0.25 mm ID, 0.25 µm (cat.# 16094)
Sample	
Diluent:	Methanol
Conc.:	100 ppm
Injection	
Inj. Vol.:	1 µL split (split ratio 30:1)
Inj. Temp.:	260 °C
Oven	
Oven Temp.:	40 °C (hold 2 min) to 300 °C at 27 °C/min (hold 3 min)
Carrier Gas	He, constant flow
Flow Rate:	1.3 mL/min
Linear Velocity:	41.05 cm/sec @ 40 °C
Detector	MS

Scan Program:	Group	Start Time (min)	Scan Range (amu)	Scan Rate (scans/sec)
	1	2	20-220	29
Transfer Line Temp.:	300°C			
Analyzer Type:	Quadrupole			
Source Type:	Inert			
Source Temp.:	230 °C			
Quad Temp.:	150 °C			
Electron Energy:	70 eV			
Solvent Delay Time:	2 min			
Tune Type:	PFTBA			
Ionization Mode:	EI			
Instrument	Agilent 7890A GC & 5975C MSD			

Figure 3 : Analysis of glycol ethers on a conventional 624-type (30 m x 0.25 mm x 1.4 µm) column from another vendor showing the longer analysis time required and coelution of DEGEE with a DPGME isomer.

	Peaks	tR (min)	Conc. (µg/mL)	Common Name
1.	EGME	4.423	100	Ethylene glycol methyl ether
2.	EGEE	5.186	100	Ethylene glycol ethyl ether
3.	Perfluoro TEGME (IS)	5.346	100	Perfluoro triethylene glycol methyl ether
4.	PnPGE	6.272	100	Propylene glycol propyl ether
5.	PGMA	6.412	100	Propylene glycol methyl ether acetate
6.	EGBE	6.841	100	Ethylene glycol butyl ether
7.	PGBE	7.036	100	Propylene glycol butyl ether
8.	DEGME	7.156	100	Diethylene glycol methyl ether
9.	DPGME I	7.510	100	Dipropylene glycol methyl ether
10.	DPGME II	7.510	100	Dipropylene glycol methyl ether
11.	DEGEE	7.591	100	Diethylene glycol ethyl ether
12.	DPGME III	7.616		Dipropylene glycol methyl ether
13.	1,2-DCB-D4 (IS)	7.838	100	1,2-Dichlorobenzene-D4
14.	EGHE	8.225	100	Ethylene glycol hexyl ether
15.	DEGBE	8.777	100	Diethylene glycol butyl ether
16.	EGPhE	9.184	100	Ethylene glycol phenyl ether
17.	TPGME isomers	9.324	100	Tripropylene glycol methyl ether
18.	DEGHE	9.903	100	Diethylene glycol hexyl ether

Standard was prepared from commercially available neat compounds, 95-99% purity.



GC_EX1133

Column	
Sample	
Diluent:	Methanol
Conc.:	100 ppm
Injection	
Inj. Vol.:	1 µL split (split ratio 30:1)
Inj. Temp.:	260 °C
Oven	
Oven Temp.:	40 °C (hold 2 min) to 240 °C at 27 °C/min (hold 6 min)
Carrier Gas	He, constant flow
Flow Rate:	1.3 mL/min
Linear Velocity:	41.05 cm/sec @ 40 °C
Detector	MS
Mode:	Scan

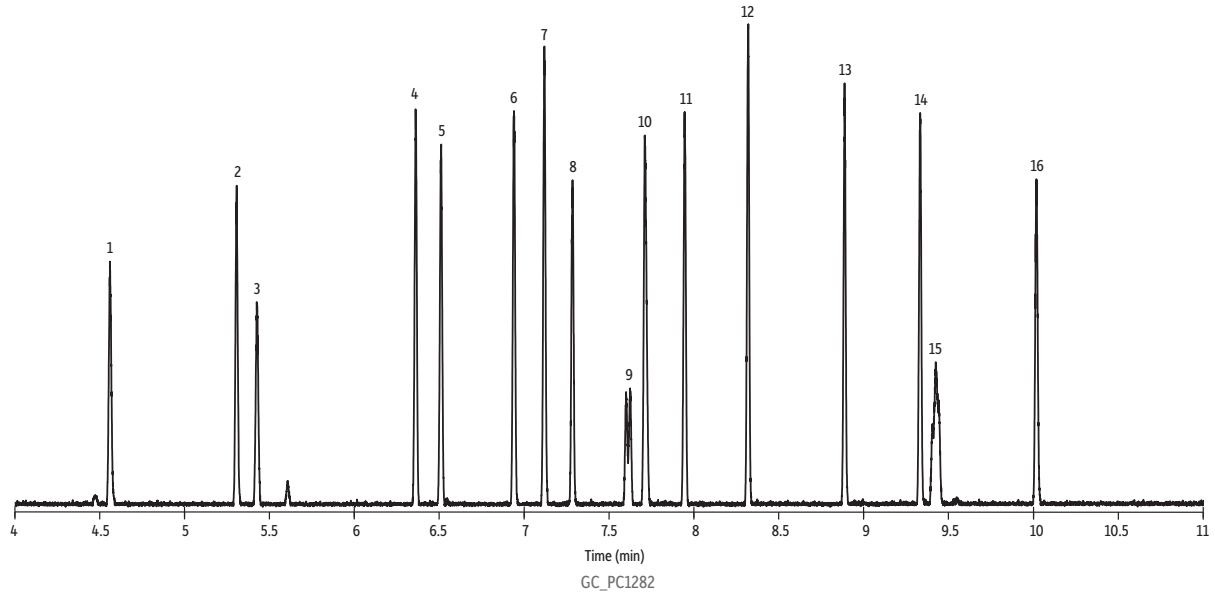
Scan Program:	Group	Start Time (min)	Scan Range (amu)	Scan Rate (scans/sec)
	1	2	20-220	29

Transfer Line Temp.:	250 °C
Analyzer Type:	Quadrupole
Source Type:	Inert
Source Temp.:	230 °C
Quad Temp.:	150 °C
Electron Energy:	70 eV
Solvent Delay Time:	2 min
Tune Type:	PFTBA
Ionization Mode:	EI
Instrument	Agilent 7890A GC & 5975C MSD

Figure 4: Analysis of glycol ethers on an Rtx®-624 column (30 m x 0.25 mm x 1.4 µm) showing the same analysis time and coelution issues associated with thick film cyanopropylphenyl columns

Peaks	t_R (min)	Conc. (µg/mL)	Common Name
1.EGME	4.561	100	Ethylene glycol methyl ether
2. EGEE	5.306	100	Ethylene glycol ethyl ether
3. Perfluoro TEGME (IS)	5.427	100	Perfluoro triethylene glycol methyl ether
4. PnPGE	6.362	100	Propylene glycol propyl ether
5. PGMA	6.511	100	Propylene glycol methyl ether acetate
6. EGBE	6.940	100	Ethylene glycol butyl ether
7. PGBE	7.119	100	Propylene glycol butyl ether
8. DEGME	7.285	100	Diethylene glycol methyl ether
9. DPGME I + DPGME II	7.613	100	Dipropylene glycol methyl ether
10. DEGEE + DPGME III	7.713	100	Diethylene glycol ethyl ether
11. 1,2-DCB-D4 (IS)	7.946	100	1,2-Dichlorobenzene-D4
12. EGHE	8.319	100	Ethylene glycol hexyl ether
13. DEGBE	8.880	100	Diethylene glycol butyl ether
14. EGPhE	9.333	100	Ethylene glycol phenyl ether
15. TPGME isomers	9.427	100	Tripropylene glycol methyl ether
16. DEGHE	10.018	100	Diethylene glycol hexyl ether

Standard was prepared from commercially available neat compounds, 95-99% purity.



See Figure 3 for conditions.

Rapid Analysis is Achieved Using a Thin Film Column Alternative

The Rxi®-1301Sil MS column is based on the same stationary phase chemistry as the Rxi®-624Sil MS column, but it is made in a thin film format (0.25 µm). This combination of selectivity and film thickness provides an ideal solution for fast GC-MS analysis of a wide range of glycol ethers, making the Rxi®-1301Sil MS column ideal for the analysis of comprehensive lists of glycol ether compounds.

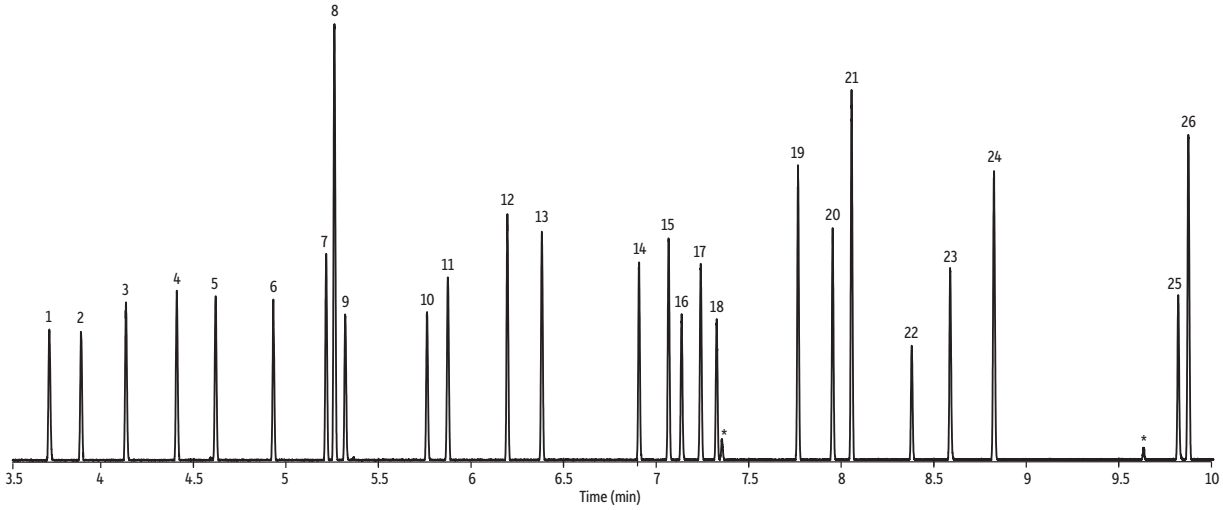
Figure 5 shows the optimized separation of 24 glycol ethers and two internal standards on the Rxi®-1301Sil MS column. Perfluorinated glycol ethers, such as fluorinated triethylene glycol methyl ether (perfluoro-TEGME), are commercially available and represent candidates for functionally similar surrogates or internal standards for applications where isotope-labeled standards are not practical or are unnecessary.

While column bleed can be a concern with some stationary phases, the Rxi®-1301Sil MS column can be used with confidence. At the maximum method temperature of 300 °C, column bleed is minimal and does not interfere with mass spectral compound identification. Low column bleed is critical to the operation of sensitive mass selective detectors and allows full scan spectra to be collected without interference from bleed ions.

Figure 5: The optimized selectivity and efficiency of thin film Rxi®-1301Sil MS columns provides good separation of many key compounds for glycol ether analysis.

Peaks	t_R (min)	Conc. (µg/mL)	Common Name
1. EGiPE	3.723	100	Ethylene glycol isopropyl ether
2. Perfluoro TEGME (IS)	3.894	100	Perfluoro triethylene glycol methyl ether
3. EGPE	4.137	100	Ethylene glycol propyl ether
4. PnPGE	4.411	100	Propylene glycol propyl ether
5. PGMA	4.621	100	Propylene glycol methyl ether acetate
6. EGEA	4.933	100	Ethylene glycol ethyl ether acetate
7. PGBE	5.218	100	Propylene glycol butyl ether
8. DEGDME	5.263	100	Diethylene glycol dimethyl ether
9. DEGME	5.322	100	Diethylene glycol methyl ether
10. DEGEE	5.763	100	Diethylene glycol ethyl ether
11. 1,2-DCB-D4 (IS)	5.876	100	1,2-dichlorobenzene-D4
12. EGBEA	6.197	100	Ethylene glycol butyl ether acetate
13. EGHE	6.384	100	Ethylene glycol hexyl ether
14. DEGBE	6.909	100	Diethylene glycol butyl ether
15. TEGDME	7.069	100	Triethylene glycol dimethyl ether
16. TEGME	7.138	100	Triethylene glycol methyl ether
17. EGPhE	7.242	100	Ethylene glycol phenyl ether
18. PGPhE	7.328	100	Propylene glycol phenyl ether
19. DEGBEA	7.768	100	Diethylene glycol butyl ether acetate
20. DEGHE	7.955	100	Diethylene glycol hexyl ether
21. DEGDBE	8.057	100	Diethylene glycol dibutyl ether
22. TEGBE	8.382	100	Triethylene glycol butyl ether
23. TetraEGME	8.590	100	Tetraethylene glycol methyl ether
24. TEGDA	8.826	100	Triethylene glycol diacetate
25. PentaEGME	9.822	100	Pentaethlylene glycol methyl ether
26. EGDPhE	9.877	100	Ethylene glycol diphenyl ether

*Indicates a minor isomer. Standard was prepared from commercially available neat compounds, 95-99% purity.



GC_PC1279

See Figure 2 for conditions.

Conclusion

The new Rxi®-1301Sil MS column from Restek provides a significant opportunity to improve glycol ether analysis. While 624-type columns are often used for this work, the Rxi®-1301Sil MS column allow separations to be achieved in much faster analysis times. Glycol ethers of regulatory concern can be analyzed in just 8 minutes while still achieving good separations of key isomers. Labs interested in reducing analysis times for current methods based on 624-type columns should consider adoption of the Rxi®-1301Sil MS column into their testing programs. The Rxi®-1301Sil MS column offers high thermal stability and very low bleed, ensuring optimal performance for glycol ether analysis.

References

[1] Environment Canada, En14-33/2010E-PDF, Reference method for the analysis of 2-butoxyethanol (2-BE) and other glycol ethers (GEs) in selected products (automotive and household cleaners, paints, paint strippers and solvents), 2010. http://www.ec.gc.ca/Publications/EC1E3FFB-61ED-4317-91CC-36FF5F66949C%5CReferenceMethodForTheAnalysisOf2Butoxyethanol2BE-AndOtherGlycolEthersGEs.pdf (Accessed February 20, 2015).

RESTEK®
Pure Chromatography

Questions about this or any other Restek® product?
Contact us or your local Restek® representative (www.restek.com/contact-us).

www.restek.com

Lit. Cat.# GNAR2147B-UNV