Introduction to Biodiesel

Today, as oil prices climb and pollution levels soar, there is significant worldwide interest in alternative fuels. Biodiesel is one of the most popular alternative fuels available today. It may be used in engines, either pure or blended with diesel fuel, to reduce exhaust pollutants. It can be produced easily from sunflowers, soy, rapeseed, tallow, lard, yellow grease, and other sources. Chemically, it is the product obtained when a vegetable oil or animal fat is reacted with an alcohol in the presence of a catalyst, such as sodium or potassium hydroxide, to produce fatty acid methyl esters (FAMEs).

Methods used to test the quality of biodiesel fuels can be categorized into three types based on the target compounds: ASTM D6584 and EN 14105 test for total glycerin, EN 14103 tests for FAMEs, and EN 14110 tests for residual methanol. These methods may be performed using either fused silica or metal columns, but the column chosen must have extremely high temperature tolerance. Restek offers both fused silica and metal columns designed specifically for high temperature biodiesel analysis. These columns, the Rtx®-Biodiesel TG, MXT®-Biodiesel TG, Stabilwax®, and Rtx-1® column lines, offer outstanding performance for biodiesel testing.

Rtx®-Biodiesel TG Columns (fused silica)

- Linearity for all reference compounds exceeds method requirements.
- Low column bleed at high temperatures.
- For glycerin and glycerides analysis, according to ASTM D6584 and EN 14105 methods.

Description	temp. limits	cat.#
10m, 0.32mm ID, 0.10µm	to 330/380°C	10292
10m, 0.32mm ID, 0.10µm with 2m x 0.53mm ID Retention Gap	to 330/380°C	10291
15m, 0.32mm ID, 0.10µm	to 330/380°C	10294
15m, 0.32mm ID, 0.10µm with 2m x 0.53mm ID Retention Gap	to 330/380°C	10293

Biodiesel Calibration Standards

Volume is 1mL/ampul. Concentration is µg/mL in pyridine.

Compound	Conc.	cat.#
(s)-(-)-1,2,4-butanetriol	1,000	33024
(s)-(-)-1,2,4-butanetriol	1,000	33032
diolein (1,3-di[*cis*-octadecenoyl]glycerol)	5,000	33022
glycerin	500	33020
monolein (1-mono[*cis*-9-octadecenoyl]-rac-glycerol)	5,000	33021
monopalmitin	5,000	33026
tricaprin (1,2,3-tricaprinoylglycerol)	8,000	33025
tricaprin (1,2,3-tricaprinoylglycerol)	8,000	33033
triolein (1,2,3-Tri[*cis*-octadecenoyl]glycerol)	5,000	33023

Diesel/Biodiesel 80:20 Blend Standard

The biodiesel component is methyl soyate.

5,000 µg/mL in methylene chloride, 1 mL/ampul	cat.# 31880 (ea.)

Silylation Derivatization Reagents

Compound	CAS #	cat.#
MSTFA (N-methyl-N-trimethylsilytrifluoroacetamide)		
10-pk. (10x1g)	24589-78-4	35600
25g vial	24589-78-4	35601

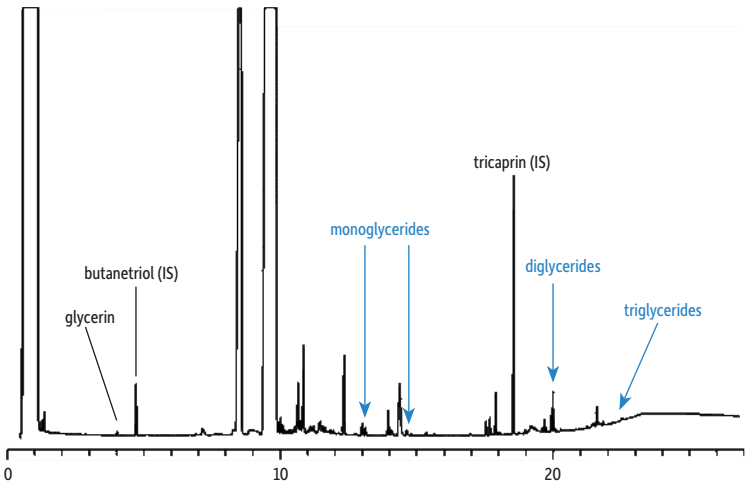
Analyzing Total Glycerin in Biodiesel

Rtx®-Biodiesel TG Fused Silica Columns

Glycerin in biodiesel falls out of solution, causing gumming in fuel systems and malfunctioning of engine parts, which eventually leads to inferior engine performance. Total glycerin presents itself in two forms: free glycerin and bound glycerin in the form of glycerides. Derivatization is required for analysis, and both ASTM D6584 and EN 14105 use N-methyl-N-trimethylsilytrifluoroacetamide derivatization reagent.

A 10 m x 0.32 mm ID Rtx®-Biodiesel TG column with a 2 m x 0.53 mm ID retention gap is ideal for glycerin analysis. The retention gap is factory-coupled using Restek's unique Alumaseal® connector. The data in Figure 1 show the elution of glycerin, monoglycerides, diglycerides, and triglycerides in B100 biodiesel following ASTM Method D6584, utilizing cool on-column injection. The Rtx®-Biodiesel TG column provides good resolution and signal-to-noise ratios for mono-, di-, and triglycerides.

Figure 1 The Rtx®-Biodiesel TG column meets resolution criteria and shows excellent response for determining glycerin in biodiesel.



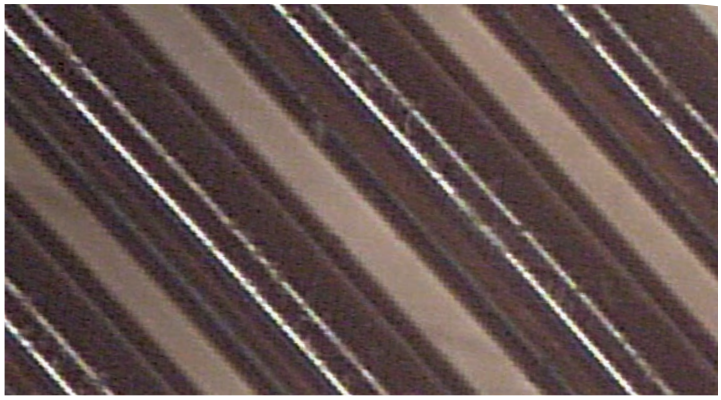
Column	Rtx®-Biodiesel TG, 10 m, 0.32 mm ID, 0.10 µm connected to 2 m x 0.53 mm Hydroguard® tubing using Alumaseal® connector (cat.# 10291)
Sample	biodiesel (B100) plus monoolein, diolein, triolein, glycerin, butanetriol, tricaprin
Injection	1 µL, cool on-column
Inj. temp.:	oven track
Carrier Gas	hydrogen, constant flow
Flow rate:	4 mL/min.
Oven temp.:	50 °C (hold 1 min.) to 180 °C @ 15 °C/min. (hold 7 min.) to 230 °C @ 30°C/min. to 380 °C @ 30 °C/min. (hold 5 min.)
Detector	FID
Det. temp.:	380 °C

Comparing Fused Silica to Metal

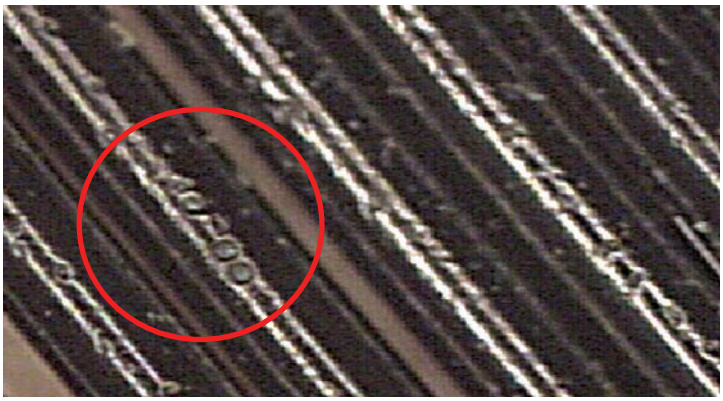
High temperature applications shorten the lifetime of fused silica columns due to deterioration of the polyimide resin used to make the columns. When fused silica columns are exposed to oven temperatures over 400 °C the polyimide coating becomes brittle and the deactivation of the column is compromised. Figure 2 shows the effect of cycling a commercially available fused silica column to 430 °C for 5 minutes 100 times. Although the column was labeled as stable up to 430 °C, the polyimide coating shows damage. The inertness of the column also deteriorates as shown by the loss of peak symmetry for the internal standard butanetriol over multiple injections (Figure 3).

Metal MXT®-Biodiesel TG columns are a better alternative to fused silica columns. As shown in Figure 3, they clearly outperform high temperature fused silica columns under the cycling conditions required for biodiesel analysis. Metal MXT®-Biodiesel TG columns offer greater stability and longer column lifetimes compared to fused silica columns.

Figure 2 Fused silica columns, labeled as stable up to 430 °C, show significant pitting and breakdown.



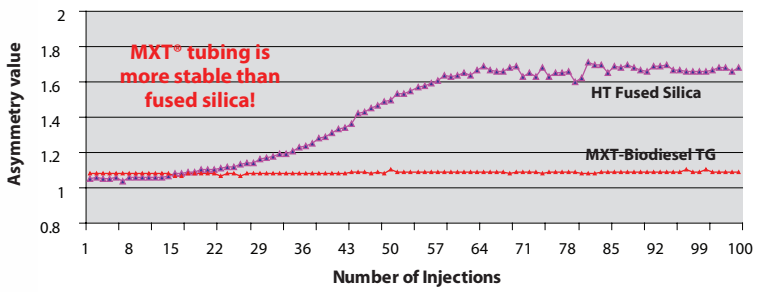
Before



After

100 temperature cycles to 430 °C totaling 500 minutes at maximum temperature.

Figure 3 Stable peak shape for internal standard butanetriol on MXT®-Biodiesel TG columns gives more accurate quantification.



Metal Column Solutions: Two Options for Increased Stability and Performance

- 0.32 mm MXT®-Biodiesel TG column with a 0.53 mm retention gap, factory-coupled with an MXT® low-dead-volume connector
- 0.53 mm MXT®-Biodiesel TG column with a built-in 0.53mm Integra-Gap® integrated retention gap

The primary advantage of using metal MXT® columns is that they are more stable at high temperatures than fused silica columns. This means they will exhibit lower bleed, improving analytical performance, and have longer lifetimes, making them a cost-effective option. They also can be brought to high temperatures (430 °C) allowing nonvolatile material to be heated off of the column, removing carryover contamination and improving cycle times.

Metal MXT®-Biodiesel TG columns are offered in the same column dimensions as their fused silica counterparts. Two different column configurations are available for cool on-column injection: 1) a 10 m (or 15 m) x 0.32 mm ID MXT®-Biodiesel TG column factory-coupled to a 2 m x 0.53 mm retention gap using an MXT® connector, and 2) a 14 m x 0.53 mm ID MXT®-Biodiesel TG column with a built-in 2 m x 0.53 mm ID Integra-Gap® integrated retention gap.

Target analytes resolve well and the solvent and triglyceride peaks show excellent symmetry on both columns (Figures 4 and 5), but the 0.53 mm MXT ®-Biodiesel TG column with the Integra-Gap® integrated retention gap eliminates the need for a connector, making connector-related leaks a thing of the past. Peak shape for butanetriol is very good, demonstrating inertness, and the resolution and responses for the mono-, di- and triglycerides are excellent. The leak-proof 0.53 mm MXT®-Biodiesel TG column with the Integra-Gap® integrated retention gap is the ultimate biodiesel solution (Figure 6).

Figure 4 Derivatized B100 samples resolve well on the 15 m x 0.32 mm MXT®-Biodiesel TG column, which is factory coupled to a 0.53 mm retention gap using an MXT® low-dead-volume connector.

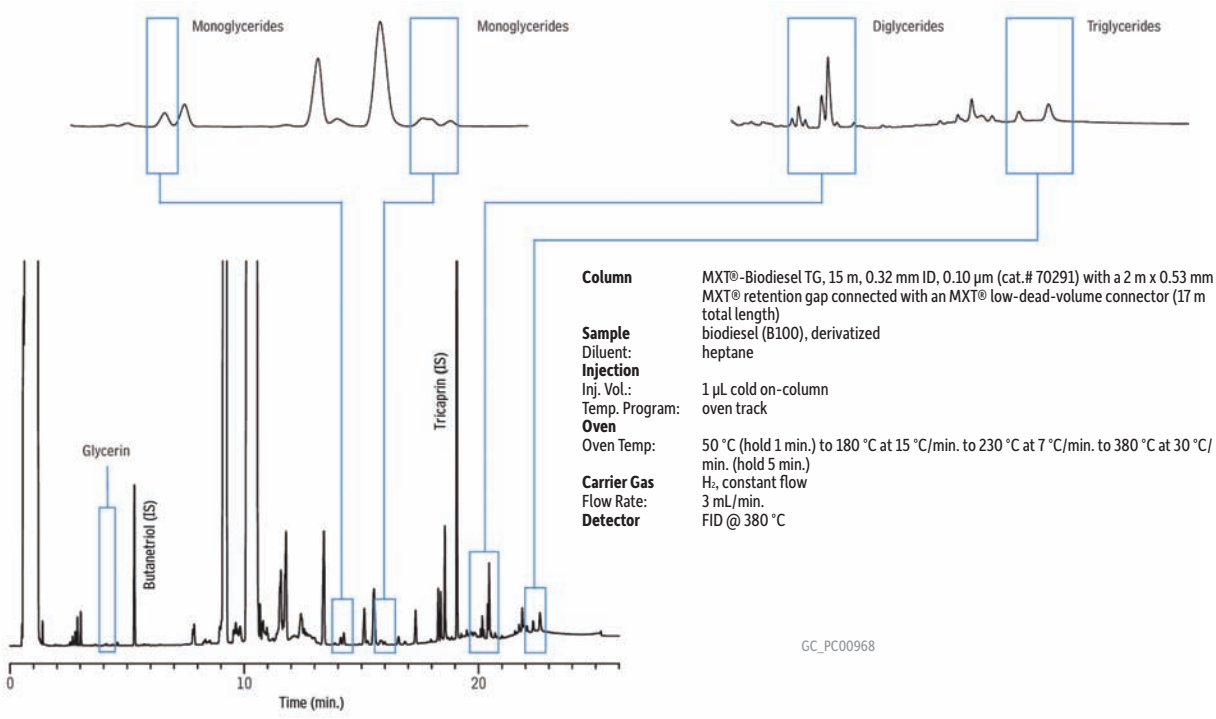
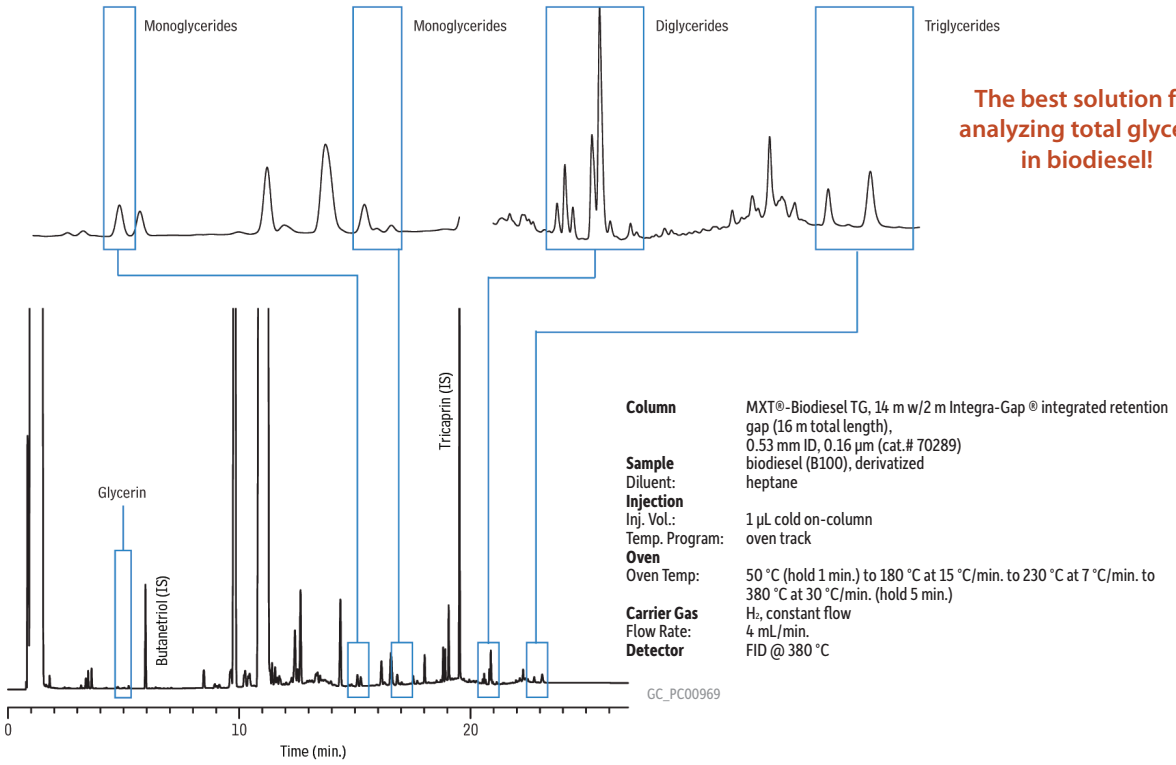


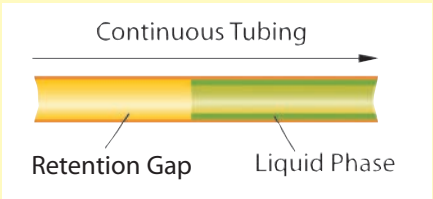
Figure 5 Excellent chromatographic quality and resolution on the 0.53 mm MXT®-Biodiesel TG column with the Integra-Gap® integrated retention gap.



The best solution for analyzing total glycerin in biodiesel!

Figure 6 The Ultimate Biodiesel Solution: MXT®-Biodiesel TG column with Integra-Gap® integrated retention gap.

The 0.53 mm MXT®-Biodiesel TG columns are an innovative alternative to using a 0.32 mm column coupled to a 0.53 mm retention gap. Restek applied the Integra-Gap® integrated retention gap technology to the 0.53 mm MXT®-Biodiesel TG columns, eliminating the column coupling. These 100% leak-proof columns feature a built-in retention gap, reducing the risk of peak broadening and tailing, and guaranteeing the user many analyses without downtime.



MXT®-Biodiesel TG Columns (Siltek® treated stainless steel)

- Fast analysis times and sharp mono-, di-, and triglyceride peaks.
- Stable at 430 °C for reliable, consistent performance.
- Integra-Gap® built-in retention gap on 0.53 mm ID column eliminates column coupling completely.

Description	temp. limits	cat.#
14m, 0.53mm ID, 0.16µm with 2m Integra-Gap*	-60 to 380/430°C	70289
10m, 0.32mm ID, 0.10µm	-60 to 380/430°C	70292
10m, 0.32mm ID, 0.10µm with 2m x 0.53mm Retention Gap**	-60 to 380/430°C	70290
15m, 0.32mm ID, 0.10µm	-60 to 380/430°C	70293
15m, 0.32mm ID, 0.10µm with 2m x 0.53mm Retention Gap**	-60 to 380/430°C	70291
2m, 0.53mm ID, Retention Gap	-60 to 380/430°C	70294

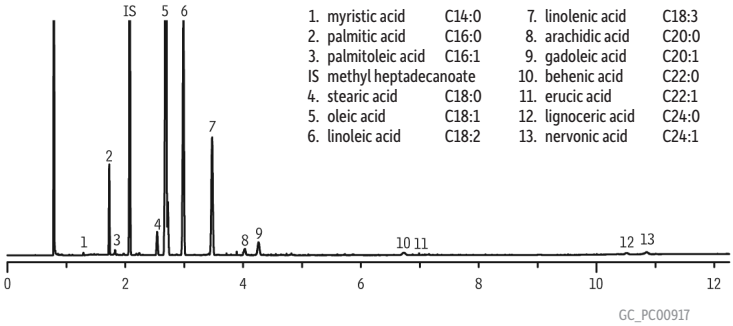
Columns are on a 7" diameter 11-pin cage. To order a 3.5" coil, add suffix -273 to the part number.
*Total column length = 16 meters.
**Connected with low-dead-volume MXT connector.

Analyzing FAMEs in Biodiesel

FAMEs are the desired end product of biodiesel production and they are analyzed to determine the percent of usable fuel in the final product. A Stabilwax® fused silica GC column affords excellent peak symmetry, resolution, and reproducibility for determining the FAMEs and linolenic acid methyl ester content in B100 biodiesel fuel, following European standard method EN 14103.

As shown in Figure 7, C14:0-C24:1 FAMEs and linolenic acid methyl ester can be determined in less than 11 minutes using a 30 m x 0.32 mm ID x 0.25 µm Stabilwax® column. Particularly notable are the stability of the baseline, excellent peak symmetry, and baseline resolution of all compounds of interest. The Stabilwax® column shows excellent peak shape for all FAMEs, even at low concentrations, which is critical for accurate quantification (Table I).

Figure 7 Stable baselines, excellent peak symmetry, and rapid, baseline resolution of all compounds characterize FAMEs analyses on a Stabilwax® column.



1.	myristic acid	C14:0	7.	linolenic acid	C18:3
2.	palmitic acid	C16:0	8.	arachidic acid	C20:0
3.	palmitoleic acid	C16:1	9.	gadoleic acid	C20:1
IS	methyl heptadecanoate		10.	behenic acid	C22:0
4.	stearic acid	C18:0	11.	erucic acid	C22:1
5.	oleic acid	C18:1	12.	lignoceric acid	C24:0
6.	linoleic acid	C18:2	13.	nervonic acid	C24:1

Column:	Stabilwax®, 30 m, 0.32 mm ID, 0.25 µm (cat.# 10624)
Sample:	rapeseed source of biodiesel (B100), prepared according to European Method EN 14103
Inj.:	1.0 µL split (split ratio 100:1), Cyclosplitter® inlet liner (cat.# 20706)
Inj. temp.:	250 °C
Carrier gas:	hydrogen, constant flow, 3 mL/min.
Linear velocity:	60 cm/sec.
Oven temp.:	210 °C (hold 5 min.) to 230 °C @ 20 °C/min. (hold 5 min.)
Det.:	FID
Det. temp.:	250 °C

Table I Sources of FAMEs in B100 biodiesel fuel (% m/m).

		Soy	Tallow	Rapeseed	Yellow Grease
Myristic acid	C14:0	0.21	1.7	0.11	0.68
Palmitic acid	C16:0	11.24	25.5	4.1	16.35
Palmitoleic acid	C16:1	0.2	3.27	0.27	1.23
Stearic acid	C18:0	4.04	14.41	1.8	9.32
Oleic acid	C18:1	21.93	40.34	58.57	47.8
Linoleic acid	C18:2	53.84	12.02	22.2	20.01
Linolenic acid	C18:3	7.29	0.99	13.26	2.93
Arachidic acid	C20:0	0.36	0.4	0.79	0.46
Gadoleic acid	C20:1	0.26	1.03	1.79	0.39
Behenic acid	C22:0	0.45		0.57	0.44
Erucic acid	C22:1			0.13	0.23
Lignoceric acid	C24:0	0.16	0.34	0.3	0.24
Nervonic acid	C24:1		0.17	0.54	

Stabilwax® Columns (fused silica)
(polar phase; Crossbond® Carbowax® polyethylene glycol)

ID	df	temp. limits	length	cat. #
0.32mm	0.25µm	40 to 250/260°C	30-Meter	10624

Analyzing Methanol in Biodiesel

Methanol is commonly used to produce biodiesel by derivatizing the fatty acids to methyl esters. The amount of residual methanol must be determined because engine performance can be negatively affected if the methanol concentration in the final product is too high. Methanol in biodiesel is quantified using a headspace method (e.g. EN 14110). We recommend an Rtx®-1 column (30 m, 0.32 mm ID, 3 µm) for this analysis. The selectivity of the Rtx®-1 column is ideal for resolving methanol from interfering peaks in biodiesel fuels.

Conclusion

Whether testing for glycerin, FAMEs, or methanol, Restek can supply the high quality chromatography products required for biodiesel testing. We offer an array of metal and fused silica GC columns designed for high performance biodiesel analysis, including our innovative MXT®-Biodiesel TG column with an Integra-Gap® integrated retention gap (Table II). Our columns, accessories, and analytical reference materials are designed to improve analytical quality, simplify lab work, and increase productivity. Rely on Restek for innovative solutions to your biodiesel testing needs.

Rtx®-1 Columns (fused silica)
(nonpolar phase; Crossbond® 100% dimethyl polysiloxane)

ID	df	temp. limits*	length	cat. #
0.32mm	3.00µm	-60 to 280/300°C	30-Meter	10184

Table II GC column selection guide for biodiesel fuel methods.

Fused Silica GC Columns	Description	Injection Type	ASTM D6584 Free and Total Glycerin	EN 14103 Ester and Linoleic Acid Methyl Esters	EN 14105 Free and Total Glycerin and Mono, Di, and Triglycerides	EN 14110 Methanol
Rtx-Biodiesel TG (max temp. 380°C)	15 m, 0.32 mm ID, 0.1 µm with 2 m x 0.53 mm ID retention gap	cool on-column	10293	—	10293	—
Rtx-Biodiesel TG (max temp. 380°C)	15 m, 0.32 mm ID, 0.1 µm	PTV**	10294	—	10294	—
Rtx-Biodiesel TG (max temp. 380°C)	10 m, 0.32 mm ID, 0.1 µm with 2 m x 0.53 mm ID retention gap	cool on-column	10291	—	10291	—
Rtx-Biodiesel TG (max temp. 380°C)	10 m, 0.32 mm ID, 0.1 µm	PTV**	10292	—	10292	—
Stabilwax	30 m, 0.32 mm ID, 0.25 µm	split/splitless	—	10624	—	—
Rtx-1	30 m, 0.32 mm ID, 3.0 µm	headspace	—	—	—	10184
Metal (MXT) GC Columns						
*MXT-Biodiesel TG (max temp. 430°C)	14 m, 0.53 mm ID, 0.16 µm with 2 m Integra Gap	cool on-column	70289	—	70289	—
MXT-Biodiesel TG (max temp. 430°C)	15 m, 0.32 mm ID, 0.1 µm with 2 m x 0.53 mm ID retention gap	cool on-column	70291	—	70291	—
MXT-Biodiesel TG (max temp. 430°C)	15 m, 0.32 mm ID, 0.1 µm	PTV**	70293	—	70293	—
MXT-Biodiesel TG (max temp. 430°C)	10 m, 0.32 mm ID, 0.1 µm with 2 m x 0.53 mm ID retention gap	cool on-column	70290	—	70290	—
MXT-Biodiesel TG (max temp. 430°C)	10 m, 0.32 mm ID, 0.1 µm	PTV**	70292	—	70292	—

*Recommended for total glycerin analysis. **PTV=programmed temperature vaporizer.

GC Accessories

BTO® Septa

- Usable to 400 °C inlet temperature.
- Precision molding assures consistent, accurate fit.
- Partial predrilled CenterGuide design.
- Preconditioned and ready to use.
- Do not adhere to hot metal surfaces.
- Packaged in precleaned glass jars.
- Each batch GC/FID tested.
- Bleed and temperature optimized; ideal for demanding GC and GC/MS applications.

Septum Diameter	50-pk.	100-pk.
5mm CenterGuide	27100	27101
6mm (1/4")	27102	27103
9mm CenterGuide	27104	27105
9.5mm (3/8")	27106	27107
10mm	27108	27109
11mm (7/16") CenterGuide	27110	27111
11.5mm CenterGuide	27112	27113
12.7mm (1/2") CenterGuide	27114	27115
17mm CenterGuide*	27116	27117
Shimadzu Plug	27118	27119

Note: Due to the injection port temperatures, Restek recommends using only BTO septa in Thermo Scientific instruments.
*For 17 mm injectors, the maximum temperature is 330 °C.

Parker Balston® PEM Hydrogen Generators

- Proton Exchange Membrane (PEM) cell eliminates the need for liquid electrolytes.
- Reliably generate 99.9995% pure hydrogen—for better chromatography.
- Eliminates high-pressure cylinders—greater convenience and improved lab safety.

Specifications

Purity:	99.9995% pure hydrogen	Outlet Port:	1/8" compression
Delivery Pressure:	10-100 psig ± 1 psig (69-689 kPa ± 7kPa)	Electrical Requirements:	100-230 VAC/50-60 Hz

Description	Model #	Capacity	qty.	cat.#
Hydrogen Generator	H2PEM-100	100cc/min.	ea.	23065
Hydrogen Generator	H2PEM-165	165cc/min.	ea.	23066
Hydrogen Generator	H2PEM-260	260cc/min.	ea.	23067
Hydrogen Generator	H2PEM-510	510cc/min.	ea.	23068
Replacement and Maintenance Components for Hydrogen Generators (for all models listed above)				
Replacement Desiccant Cartridge for H2PEM Generators			ea.	23069
6-Month Maintenance Kit for H2PEM Generators *Includes: 1 deionizer cartridge, 1 water filter, 3 environmental filters*			kit	23070
24-Month Maintenance Kit for H2PEM Generators *Includes: 1 deionizer cartridge, 1 water filter, 3 environmental filters, 1 water level sensor, 1 water pump, and 1 desiccant cartridge*			kit	23071

- Dimensions: 17.12" x 13.46" x 17.95"
- 40 lb. dry weight

Don't let a small leak turn into a costly repair—protect your instrument and analytical column by using a Restek Leak Detector.

Restek Electronic Leak Detector

Features & Benefits include:

- Optimized sample flow path.
- New ergonomic, hand-held design.
- Rugged side grips for added durability.
- Handy probe storage for cleanliness and convenience.
- Longer lasting battery, up to 6 hours of continuous use.
- Automatic shut-off.

Leak Detector Facts

Detectable gases:	helium, nitrogen, argon, carbon dioxide, hydrogen
Battery:	Rechargeable Ni-MH internal battery pack
Operating Temp. Range:	32°-120°F (0°-48°C)
Humidity Range:	0-97%
Warranty:	one year
Certifications:	CE, Ex, Japan
Compliance:	WEEE, RoHS

Description	qty.	cat.#
Leak Detector with Hard-Sided Carrying Case and Universal Charger Set (US, UK, European, Australian)	ea.	22839
Leak Detector Routine Maintenance Review†	ea.	22839-R
Soft-Side Storage Case	ea.	22657
Small Probe Adaptor	ea.	22658

Avoid using liquid leak detectors on a GC! Liquids can be drawn into the system.

*Caution: The Restek Electronic Leak Detector is designed to detect trace amounts of hydrogen in a noncombustible environment. It is NOT designed for determining leaks in a combustible environment. A combustible gas detector should be used for determining combustible gas leaks under any condition. The Restek Electronic Leak Detector may be used for determining trace amounts of hydrogen in a GC environment only.

†Routine maintenance includes inspection of the probe tip, internal/external tubing and a battery replacement.

Also available in money-saving 50-packs!

Capillary Ferrules for 1/16-Inch Compression-Type Fittings

Graphite Ferrules

- Preconditioned to eliminate out-gassing.
- High-purity, high-density graphite.
- Stable to 450 °C.

Vespel®/Graphite Ferrules

- 60%/40% Vespel®/graphite blend, offering the best combination of sealing and ease of workability.
- Stable to 400 °C.

Ferrule ID	Fits Column ID	qty.	Graphite	Vespel/Graphite
0.5mm	0.32mm	10-pk.	20201	20212
0.8mm	0.45/0.53mm	10-pk.	20202	20213

For more ferrule choices visit us at **www.restek.com/biodiesel**

FID Replacement Jets

- Available untreated or Siltek® treated, for maximum inertness.

Capillary Adaptable FID Replacement Jet for Agilent 5890/6890/6850 GCs

Description	Similar to Agilent part #	qty.	cat.#	qty.	cat.#
Standard, 0.011-Inch ID Tip	19244-80560	ea.	20670	3-pk.	20671
High-Performance Siltek Treated, 0.011-Inch ID Tip	19244-80560	ea.	20672	3-pk.	20673

Capillary Dedicated FID Replacement Jet for Agilent 6890/6850/7890 GCs

Description	Similar to Agilent part #	qty.	cat.#	qty.	cat.#
Standard, 0.011-Inch ID Tip	G1531-80560	ea.	21621	3-pk.	21682
High-Performance Siltek Treated, 0.011-Inch ID Tip	G1531-80560	ea.	21620	3-pk.	21683
High-Temperature, 0.018-Inch ID Tip	G1531-80620	ea.	23078	3-pk.	23079

RESTEK

Lit. Cat.# PCFL1409-UNV

Restek U.S. • 110 Benner Circle • Bellefonte, PA 16823 • 814-353-1300 • 800-356-1688 • fax: 814-353-1309 • **www.restek.com**
Restek France • phone: +33 (0)1 60 78 32 10 • fax: +33 (0)1 60 78 70 90 • e-mail: restek@restekfrance.fr
Restek GmbH • phone: +49 (0)6172 2797 0 • fax: +49 (0)6172 2797 77 • e-mail: info@restekgmbh.de
Restek Ireland • phone: +44 (0)2890 814576 • fax: +44 (0)2890 814576 • e-mail: restekireland@aol.com
Restek Japan • phone: +81 (3)6459 0025 • fax: +81 (3)6459 0025 • e-mail: ryosei.kanaguchi@restek.com
Thames Restek U.K. LTD • phone: +44 (0)1494 563377 • fax: +44 (0)1494 564990 • e-mail: sales@thamesrestek.co.uk

ISO 9001:2008 cert.# FM80397