GCxGC Columns

Your One Source for 2D Gas Chromatography

Rxi. GCColumns **Rtx.** GCColumns

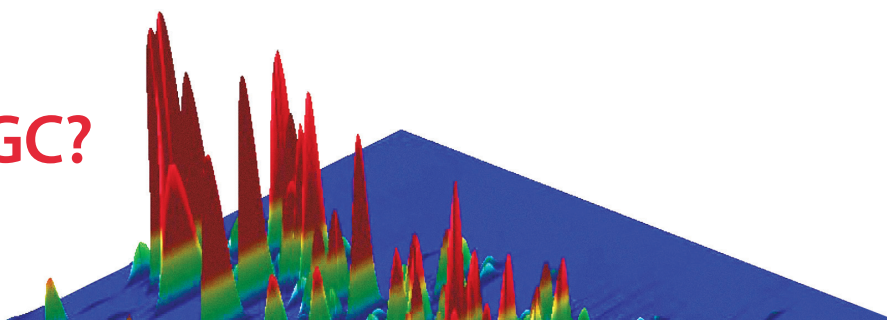**RESTEK** Innovative Chromatography Solutions

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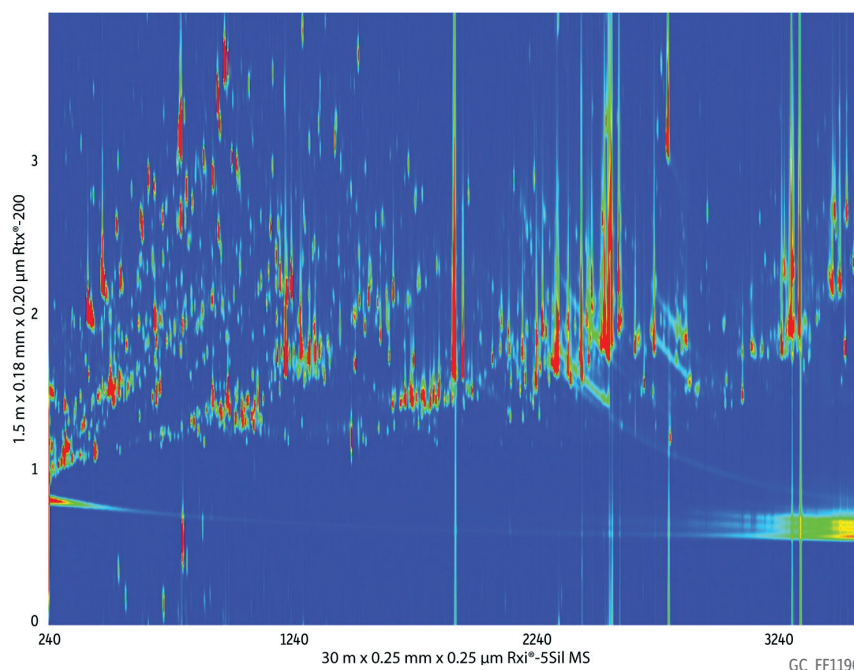1-800-267-8103 • sales@chromspec.com • tech@chromspec.com

Why Use GCxGC?

GCxGC is a powerful multidimensional GC technique that combines two independent separations to accurately analyze highly complex samples. GCxGC involves two columns with differing stationary phase selectivity (orthogonal) that are press-fitted together in series and separated by a modulator. The first (primary) column performs an initial separation, and its effluent is continually focused and "injected" in defined cycles by the modulator onto the second (secondary) column, where another separation occurs. By choosing a secondary column that is orthogonal (has different selectivity) to the primary column, it is possible to separate and identify analytes that cannot be separated by the primary column. And by keeping the secondary column very short, it is possible to maintain the separation produced by the primary column. Results generated through a series of high-speed chromatograms are plotted as a contour plot, sometimes known as a retention plane (Figure 1).

So, why use GCxGC? Because comprehensive two-dimensional gas chromatography allows you to perform separations that are simply not possible using standard one-dimensional chromatography! This brochure will show many examples from pesticides to petroleum.

Figure 1: In a contour plot like this plot of a sage QuEChERS extract cleaned with cSPE, the x axis represents the primary column retention time and the y axis represents the secondary column retention time.
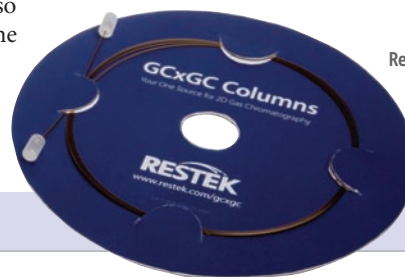

GC_FF1190

Column	Rxi®-5Sil MS 30 m, 0.25 mm ID, 0.25 µm (cat.# 13623)
	Rtx®-200 1.5 m, 0.18 mm ID, 0.20 µm (cat.# 45001)
Sample	
Diluent:	Toluene
Injection	
Inj. Vol.:	1 µL splitless (hold 1 min)
Liner:	Gooseneck Splitless (4mm) w/Wool (cat.# 22405)
Inj. Temp.:	250 °C
Purge Flow:	40 mL/min
Oven	
Oven Temp:	Rxi®-5Sil MS: 80 °C (hold 1 min) to 310 °C at 4 °C/min (hold 1.5 min)
	Rtx®-200: 90 °C (hold 1 min) to 320 °C at 4 °C/min (hold 1.5 min)
Carrier Gas	He, constant flow
Flow Rate:	1.8 mL/min
Modulation	
Modulator	
Temp. Offset:	25 °C
Second Dimension	
Separation Time:	4 sec
Hot Pulse Time:	1.2 sec
Cool Time	
between Stages:	0.8 sec
Detector	TOFMS
Transfer	
Line Temp.:	290 °C
Analyzer Type:	TOF
Source Temp.:	225 °C
Electron Energy:	70 eV
Mass Defect:	-20 mu/100 u
Solvent	
Delay Time:	4 min
Ionization Mode:	EI
Acquisition Range:	45 to 550 amu
Spectral	
Acquisition Rate:	100 spectra/sec
Instrument	LECO Pegasus 4D GCxGC-TOFMS
Notes	See application note GNAN1338 for extraction and cleanup details. A 1.5 m length of the Rtx®-200 column was trimmed from a 10 m column. Columns were connected with a Universal Press-Tight® Connector (cat.# 20429). See chromatogram GC_FF1192 for zoom.

visit **www.restek.com/gcxgc**

Why Use Restek GCxGC Columns?

- **Wide range of stationary phases offers orthogonal separations.**
- **High thermal stability increases system ruggedness.**
- **Unrivaled column inertness for accurate analysis of active compounds.**
- **0.15, 0.18, and 0.25 mm ID formats accommodate varying sample capacities, speeds, and detectors.**
- **Secondary columns come in convenient 2 m lengths for economical method development.**

Restek has been performing comprehensive two-dimensional gas chromatography since its commercial inception. Our Innovations lab boasts multiple instruments dedicated to GCxGC applications, and we are continually exploring new application areas—including environmental, food safety, petroleum, forensics, fragrance, natural products, tobacco, metabolomics, and dietary supplements.

Restek's GCxGC secondary columns can be matched with any Restek Rtx® or Rxi® primary column to create the perfect orthogonal separation for your application. We also offer a range of complementary GC accessories—including Sky™ inlet liners, the Restek Electronic Leak Detector, and Press-Tight® connectors—to boost your success with GCxGC. For a product listing and help pairing columns, see pages 13–16 or visit **www.restek.com/gcxgc-combo**

Restek secondary columns come in convenient 2 m lengths.

What is a GCxGC Modulator?

The modulator is the most important component of a GCxGC system. Its purpose is to trap effluent from the primary column and then release it in quick pulses to the secondary column for another separation. This fast focusing and reinjection of the sample onto the secondary column greatly enhances detectability (i.e., sharper peaks with increased height) while preserving the separation performed by the primary column.

The period between each pulse is called the modulation time (or second dimension separation time). Because the modulation time is so fast—typically 2–6 seconds—each peak from the primary column is effectively split into several "slices" (Figure 2) that are only 50–200 milliseconds wide. A very fast detector, such as a TOFMS, which can acquire hundreds of spectra per second, is needed to define peaks this narrow.

Thermal modulators are the most prevalent; they use cold jets to freeze the primary column effluent, and then quickly reheat it with hot jets to inject the effluent onto the secondary column. Mechanical valves as well as pneumatic and electrical devices are also available commercially.
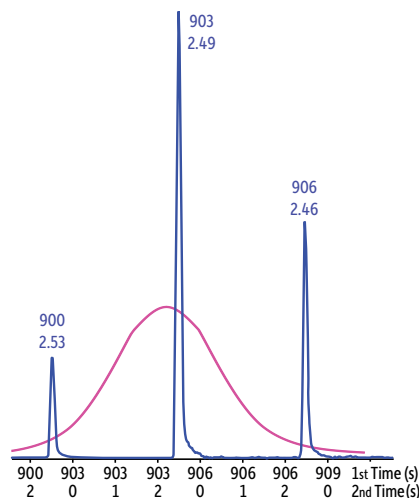

Figure 2: The low, wide peak (pink) shows what the primary column output might look like without modulation. The sharp peaks (blue) represent the same output had it been modulated. Note the decrease in peak width and increase in height (i.e., enhanced sensitivity). The labels above the blue peaks represent 1st dimension (long) and 2nd dimension (short) retention times in seconds.

Meet the Experts

Restek boasts not one, but three in-house GCxGC experts—Jack Cochran, Julie Kowalski, and Michelle Misselwitz—with over 15 years of combined experience. If you have any questions about GCxGC, consider them your personal technical resource for two-dimensional gas chromatography!

Jack Cochran
Director of New Business and Technology
jack.cochran@restek.com

Jack Cochran is a recognized expert in GC and GCxGC for the analysis of pesticides, PCBs, explosives, PAHs, PCDDs, PCDFs, BFRs, and similar priority pollutants in food, soils, sediments, air, water, and other matrices. He uses his years of real-world experience in method development, sample preparation, and analysis to help chromatographers worldwide and is still a "hands on" scientist, spending as much time in the laboratory as possible. Jack is frequently invited to speak at major scientific conferences— especially for his work with GC injection techniques, GCxGC, and QuEChERS— and is a founding member of the Multidimensional Chromatography Workshop, currently held annually in January at the Ontario Ministry of the Environment in Toronto. He serves on the Organizing Committee for the Florida Pesticide Residue Workshop / North American Chemical Residue Workshop and was the President in 2010. Jack is also an adjunct professor in the Forensic Science Program at The Pennsylvania State University.

Julie Kowalski
Senior Innovations Chemist
julie.kowalski@restek.com

Julie is a Senior Innovations Chemist who previously taught college-level chromatography and spectroscopy lectures and labs for 5 years in addition to working as a staff scientist. She has a B.S. in Chemistry, a Ph.D. in Analytical Chemistry, and professional experience that includes troubleshooting and method development for GC, GC-MS, GCxGC, LC, and LC-MS/MS. Her primary work for Restek has been in food safety applications, especially QuEChERS and GCxGC method development.

Michelle Misselwitz
Innovations Chemist
michelle.misselwitz@restek.com

Michelle is an Innovations Chemist at Restek Corporation with a B.S. in Chemistry. For the past several years, she has been generating applications data using new and existing products with the goal of providing a total solution for customers. With experience in GC and GC-MS as well as HPLC, she has worked with an emphasis on the environmental and food safety testing fields including GCxGC method development.

Restek Technical Service
Of course, if you have a question about GCxGC or any other type of analysis, you can also count on Restek's Technical Service team. They'll draw on their extensive experience in chemistry, chromatography, engineering, and related fields to solve your most challenging technical dilemmas. Whether you need help with setup and troubleshooting or column selection and method development, contact Restek Technical Service at **support@restek.com** or 1-814-353-1300, ext. 4.

Sales Representatives and Distributors
Restek maintains a regional sales staff and distributor network that covers over 100 countries across 6 continents. To place an order or set up a face-to-face meeting, visit **www.restek.com/Contact-Us** and find a distributor or representative near you.

PAHs in Seafood

Restek Primary Column:
Rxi®-17Sil MS 30 m, 0.25 mm ID, 0.25 µm

Restek Secondary Column:
Rxi®-1ms 1.2 m, 0.15 mm ID, 0.15 µm

In the wake of the 2010 Deepwater Horizon oil spill in the Gulf of Mexico, concerns over consumer safety increased the demand for rapid, accurate testing methods for polycyclic aromatic hydrocarbons (PAHs) in seafood. When the United States Food and Drug Administration (FDA) issued a protocol to reopen closed fishing waters, it included chemical testing of seafood for PAHs. But the NOAA sample preparation method that was proposed is extremely tedious, costly, and environmentally unfriendly due to the large number of solvents required. Using the QuEChERS approach, which offers complete seafood sample preparation in less than 2 hours, you can readily solve these issues. One-dimensional GC-MS, however, is still highly problematic due to the complexity of seafood samples.

By taking advantage of the separating power provided by GCxGC with time-of-flight mass spectrometry (TOFMS), it is easy to produce accurate qualitative and quantitative results for PAHs in complex samples, such as the mussel extract in Table I. An Rxi®-17Sil MS primary column produces optimized PAH separations while an Rxi®-1ms secondary column eliminates interference from the fatty acids and sterols in the seafood samples. While we did note slightly high recoveries for some compounds (e.g., fluoranthene) in a NIST mussel standard reference material, isobaric interferences can be ruled out as evidenced by the high efficiency separation of PAHs from matrix (Figure 3) and by good agreement between sample and reference spectra (Figure 4).

We've posted more information on this analysis, including sample preparation details, at ChromaBLOGgraphy (**www.restek.com/adv011**).

Table I: The QuEChERS sample preparation approach with GCxGC-TOFMS gave good recoveries for most PAHs in a NIST mussel sample.

PAH	Q Mass	NIST µg/kg	Average µg/kg by GCxGC	RSD%
Naphthalene-D8	136	ISTD	ISTD	ISTD
Naphthalene	128	9.68	63	5
2-Methylnaphthalene	142	8.1	8.6	15
1-Methylnaphthalene	142	5.8	5.4	8
Biphenyl	154	NA	4.2	1
2,6-Dimethylnaphthalene	156	NA	9.1	3
Acenaphthylene	152	NA	1.7	18
Acenaphthene-D10	162	ISTD	ISTD	ISTD
Acenaphthene	154	NA	3.3	22
2,3,5-Trimethylnaphthalene	170	NA	4.0	13
Fluorene	166	NA	8.8	8
Phenanthrene-D10	188	ISTD	ISTD	ISTD
Phenanthrene	178	74.4	113	5
Anthracene	178	2.46	8.1	8
1-Methylphenanthrene	192	17.6	29	12
Fluoranthene	202	287	376	5
Pyrene	202	186	229	4
Benzo(a)anthracene	228	31.1	39	9
Chrysene-D12	240	ISTD	ISTD	ISTD
Chrysene	228	123.6	199	5
Benzo(b)fluoranthene	252	41.5	53	0
Benzo(k)fluoranthene	252	18.95	22	12
Benzo(j)fluoranthene	252	21.4	18	3
Benzo(a)pyrene	252	9.73	12	5
Perylene-D12	264	ISTD	ISTD	ISTD
Perylene	252	6.80	5.0	3
Indeno(1,2,3-cd)pyrene	276	14.9	13	1
Benzo(ghi)perylene	276	23.7	20	10

ISTD = internal standard; NA = not analyzed by NIST

Figure 4: Good agreement between sample and reference spectra shows target PAHs were separated from isobaric interferences.

Caliper spectrum

Peak true (deconvoluted) spectrum

Reference spectrum

GC_FF1198

For complete conditions, visit www.restek.com and enter chromatogram GC_FF1198 in the search function.
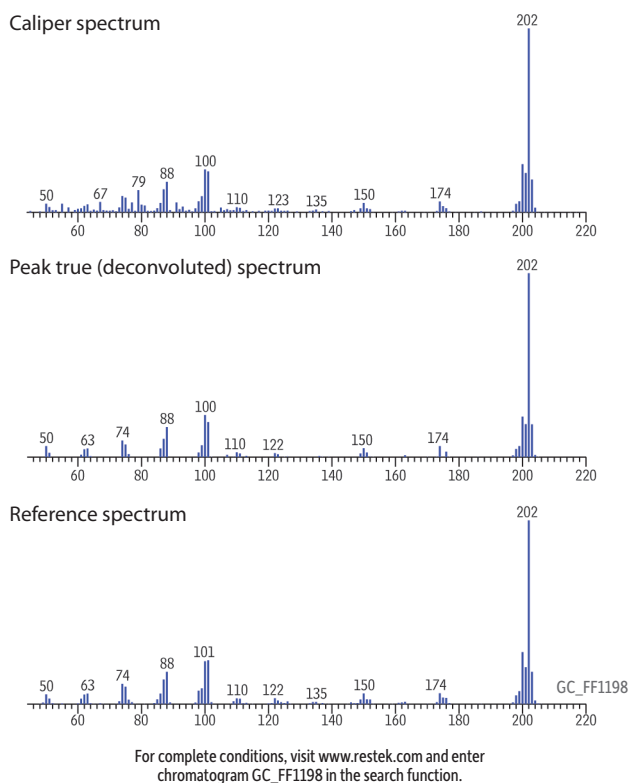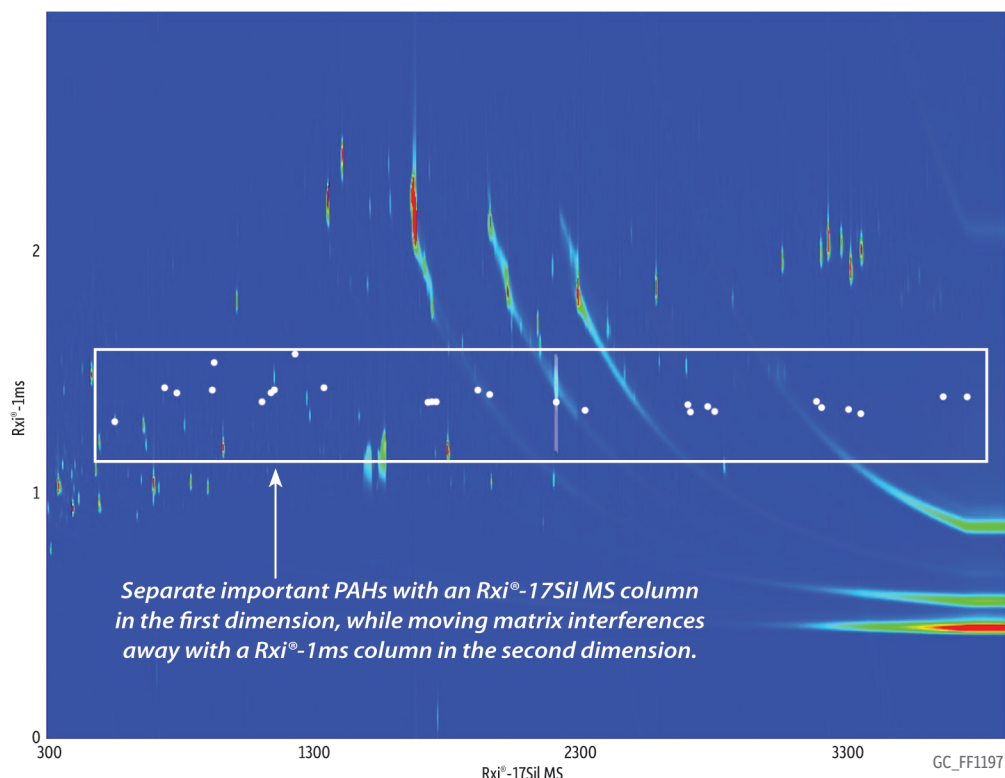
Figure 3: As shown in this contour plot for a QuEChERS extraction of a mussel sample, GCxGC-TOFMS allows you to separate PAHs from interferences that one-dimensional GC cannot.

Notes PAHs (shown in box) elute in a relatively narrow band and are identified by the white peak marker dots.

For complete conditions, visit www.restek.com and enter chromatogram GC_FF1197 in the search function.

Separate important PAHs with an Rxi®-17Sil MS column in the first dimension, while moving matrix interferences away with a Rxi®-1ms column in the second dimension.

Rxi®-1ms

Rxi®-17Sil MS

GC_FF1197

PCBs and BDEs

Restek Primary Column: Rxi®-XLB 30 m, 0.25 mm ID, 0.25 µm

Restek Secondary Column: Rxi®-17Sil MS 1 m, 0.15 mm ID, 0.15 µm with IP Deactivated Guard Column 0.2 m, 0.15 mm ID as a transfer line from secondary column to ECD
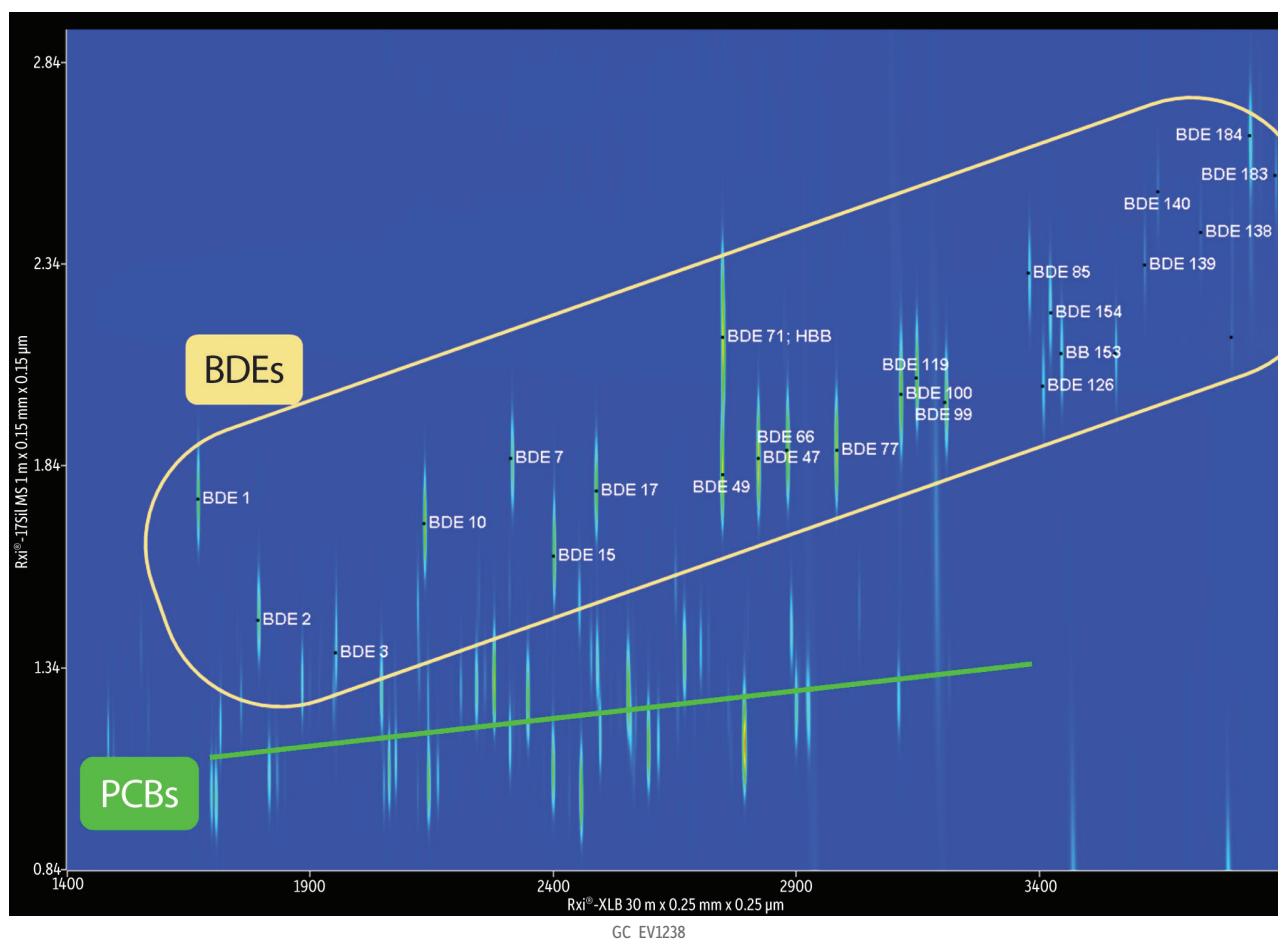
Polychlorinated biphenyls (PCBs) and brominated flame retardants (BFRs)—especially brominated diphenyl ethers (BDEs)—are persistent organic pollutants that have a variety of toxic effects on humans, other mammals, fish, and other biota. These harmful compounds are found worldwide in all environmental compartments, including air, water, soil, and sediments, making them some of the most commonly analyzed contaminants. But they are also difficult to analyze because PCBs and BDEs can coelute in one-dimensional GC analyses regardless of sample complexity. And if a non-specific electron capture detector (ECD) is used, it is impossible to achieve accurate quantification for all important congeners. Not even offline solid phase extraction cleanup methods like silica are helpful because PCBs and BDEs elute in the same solvent fraction.

With the proper set of complementary Restek primary and secondary columns, GCxGC-ECD allows you to fully separate PCBs and BDEs, resulting in accurate qualitative and quantitative data (Figure 5). This contour plot is also an excellent example of another important benefit of GCxGC—peak sharpening. This effect is afforded by the GCxGC modulator and can lead to a 3x to 10x increase in detectability, which is incredibly helpful for trace-level analyses like PCBs and BDEs in environmental samples.

Visit the Restek Chromatogram Library at **www.restek.com/chromatograms** to view more of our GCxGC work with PCBs and BDEs.

Figure 5: PCBs and BDEs are easily determined using GCxGC-ECD with Rxi®-XLB and Rxi®-17Sil MS columns. In a two-dimensional GC contour plot, compounds that line up on the x axis as shown here would coelute in one-dimensional GC.

GC_EV1238

Column: Rxi®-XLB 30 m, 0.25 mm ID, 0.25 µm (cat.# 13723): Rxi®-17Sil MS 1 m, 0.15 mm ID, 0.15 µm (cat.# 43820) with IP Deactivated Guard Column 0.2 m, 0.15 mm ID; **Sample:** Wellington BFR-PAR Mix: Aroclor; Diluent: isooctane; **Injection:** Inj. Vol.: 1.0 µL splitless (hold 1 min); Liner: Sky™ 4mm Single Taper Gooseneck w/Wool (cat.# 23303.5); Inj. Temp.: 250 °C; Purge Flow: 20 mL/min; **Oven:** Oven Temp: Rxi®-XLB: 80 °C (hold 1 min) to 120 °C at 10 °C/min to 300 °C at 3 °C/min: Rxi®-17Sil MS: 85 °C (hold 1 min) to 125 °C at 10 °C/min to 305 °C at 3 °C/min; **Carrier Gas:** He, corrected constant flow (2.0 mL/min); **Modulation:** Modulator Temp. Offset: 20 °C; Second Dimension Separation Time: 3.5 sec; Hot Pulse Time: 1.25 sec; Cool Time between Stages: 0.50 sec; **Detector:** µ-ECD @ 325 °C; Data Rate: 50 Hz; **Instrument:** Agilent/HP6890 GC; **Notes:** The Rxi®-17Sil MS column (cat.# 43820) is a 10 m column. A 1 m section was used as a second dimension column.: Guard column was connected using a Siltek® treated universal Press-Tight® connector (cat.# 20480).

Pesticides in Dietary Supplements

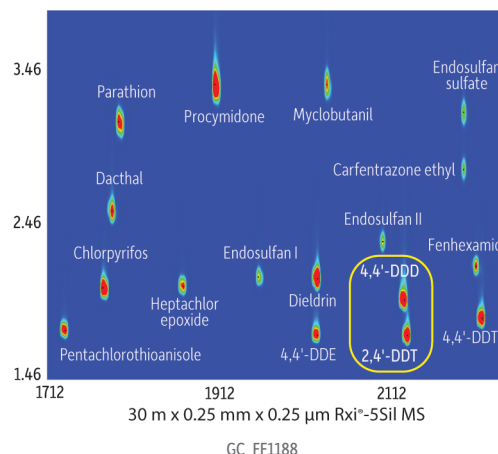**Restek Primary Column:** Rxi®-5Sil MS 30 m, 0.25 mm ID, 0.25 μm
Restek Secondary Column: Rtx®-200 1.5 m, 0.18 mm ID, 0.20 μm

Dietary supplement manufacturers must comply with the same current good manufacturing practice (cGMP) regulations that help ensure product safety for pharmaceuticals. And since many dietary supplements are botanically based, pesticide residue methods are among the new analyses being developed. Because plant-based samples are extremely complex, data integrity depends on removing or reducing matrix contributions as well as eliminating pesticide identification and quantification bias—tasks that one-dimensional GC-MS analysis simply cannot handle. The solution is to use comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry (GCxGC-TOFMS).

By combining GCxGC-TOFMS and an orthogonal set of Restek columns with QuEChERS and cSPE, you can easily quantify pesticides in dietary supplements—even compounds like 2,4'-DDT and 4,4'-DDD that have almost identical mass spectra and coelute on a single column (Figure 6). The separating power of GCxGC also allows production of high-quality mass spectra in complex dietary supplement extracts (Figure 7) while reducing matrix interferences and far improving accuracy relative to one dimensional GC-MS.
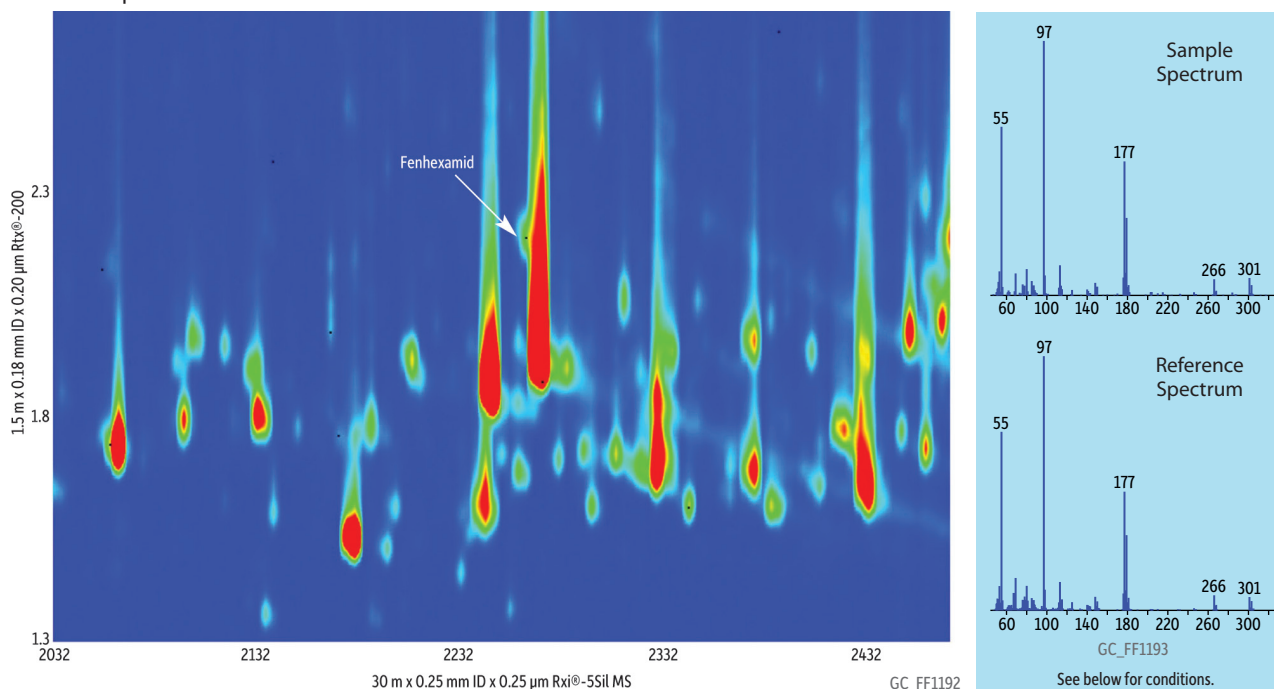
For complete procedures, download the full application note by visiting **www.restek.com** and searching for "GNAN1338".

Figure 6: As shown by the extensive spread along the x and y axes, a GCxGC analysis with Rxi®-5Sil and Rtx®-200 columns easily separates and quantifies compounds with isobaric interferences like 2,4'-DDT and 4,4'-DDD.

GC_FF1188

Column: Rxi®-5Sil MS 30 m, 0.25 mm ID, 0.25 μm (cat.# 13623); Rtx®-200 1.5 m, 0.18 mm ID, 0.20 μm (cat.# 45001); **Injector:** Splitless; **Detector:** MS-TOF

For complete conditions, visit www.restek.com and enter chromatogram GC_FF1188 in the search function.

Figure 7: GCxGC with orthogonal Restek columns is a powerful way to handle complex samples like dietary supplement extracts. Note the separation of fenhexamid in this sage extract from a major isobaric interference containing the quantification ion for fenhexamid (m/z 177). The contour plot reveals a distinct peak, and the sample spectrum for fenhexamid closely matches the reference spectrum.

GC_FF1192

GC_FF1193

See below for conditions.

Column: Rxi®-5Sil MS 30 m, 0.25 mm ID, 0.25 μm (cat.# 13623); Rtx®-200 1.5 m, 0.18 mm ID, 0.20 μm (cat.# 45001); **Sample:** Diluent: Toluene; **Injection:** Inj. Vol.: 1 μL splitless (hold 1 min); Liner: Gooseneck Splitless (4mm) w/Wool (cat.# 22405); Inj. Temp.: 250 °C; **Oven:** Oven Temp: Rxi®-5Sil MS: 80 °C (hold 1 min) to 310 °C at 4 °C/min (hold 1.5 min); Rtx®-200: 90 °C (hold 1 min) to 320 °C at 4 °C/min (hold 1.5 min); **Carrier Gas:** He, constant flow; Flow Rate: 1.8 mL/min; **Modulation:** Modulator Temp. Offset: 25 °C; Second Dimension Separation Time: 4 sec; Hot Pulse Time: 1.2 sec; Cool Time between Stages: 0.8 sec; **Detector:** TOFMS; Transfer Line Temp.: 290 °C; Analyzer Type: TOF; Source Temp.: 225 °C; Electron Energy: 70 eV; Mass Defect: -20 mu/100 u; Solvent Delay Time: 4 min; Ionization Mode: EI; Acquisition Range: 45 to 550 amu; Spectral Acquisition Rate: 100 spectra/sec; **Instrument:** LECO Pegasus 4D GCxGC-TOFMS; **Notes:** See application note GNAN1338 for extraction and cleanup details. A 1.5 m length of the Rtx®-200 column was trimmed from a 10 m column. Columns were connected with a Universal Press-Tight® Connector (cat.# 20429). See chromatogram GC_FF1190 for full scale view.

Halogenated POPs in Human Milk

Restek Primary Column: Rxi®-XLB 30 m, 0.25 mm ID, 0.25 µm

Restek Secondary Column: Rxi®-17Sil MS 1 m, 0.15 mm ID, 0.15 µm with IP Deactivated Guard Column 0.2 m, 0.15 mm ID as a transfer line from secondary column to ECD

Persistent organic pollutants (POPs) are a group of chemicals that include halogenated pesticides, brominated diphenyl ethers (BDEs), and polychlorinated biphenyls (PCBs). These chemicals can be distributed throughout the environment via soil, water, and air contamination, and once in the environment, they do not readily breakdown. Due to their lipophilic nature, halogenated POPs accumulate in the fatty tissue of animals and bioaccumulate up the food chain. According to the World Health Organization, human breast milk is an ideal matrix to monitor levels of POPs in the local environment. A high-resolution mass spectrometer is often used for the determination of halogenated POPs in breast milk extracts, but an HRMS is an expensive piece of equipment.

In contrast, comprehensive two-dimensional gas chromatography with an electron capture detector (ECD) offers a more cost-effective alternative due to the sensitivity of the ECD, coupled with the selectivity afforded by a multidimensional separation. Additionally, using the selective and sensitive ECD allows detection of multiple halogenated analytes down to femtogram (fg) amounts for each compound. Chromatographic resolution is very important when you don't have the ability to spectrally resolve analytes through mass spectrometry, and a GCxGC-ECD allows two independent separations in one analytical run (Figure 8). In a one-dimension GC analysis, some of the PCBs and BDEs will coelute; however, the second dimension Rxi®-17Sil MS column helps resolve BDEs from PCBs (Figure 9).

To learn how we developed our sample preparation technique for this analysis, search for "milk matters" at **blog.restek.com**

Figure 9: If not for the second-dimension Rxi®-17Sil MS column (which retains BDE 99), PCB 206 and BDE 99 would coelute.

Labels: Methoxychlor, BDE-100, BB-153, BDE-47, BDE-99, BDE-153, Endrin ketone, PCB 170, PCB 206, PCB 209, PCB 180, Coelution in one-dimensional GC!

Axes: Rxi®-17Sil MS 1 m x 0.15 mm x 0.15 µm / Time (s); Rxi®-XLB 30 m x 0.25 mm x 0.25 µm / Time (s)

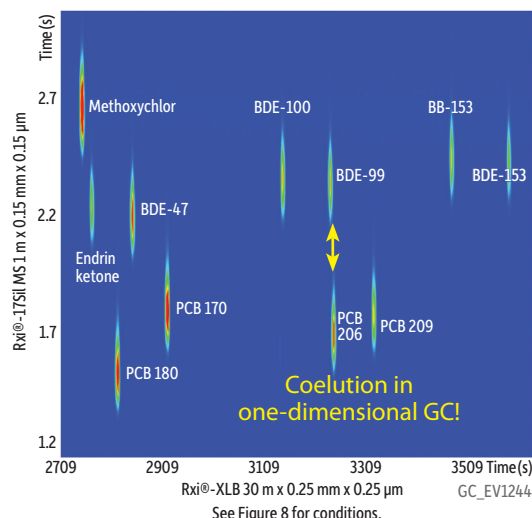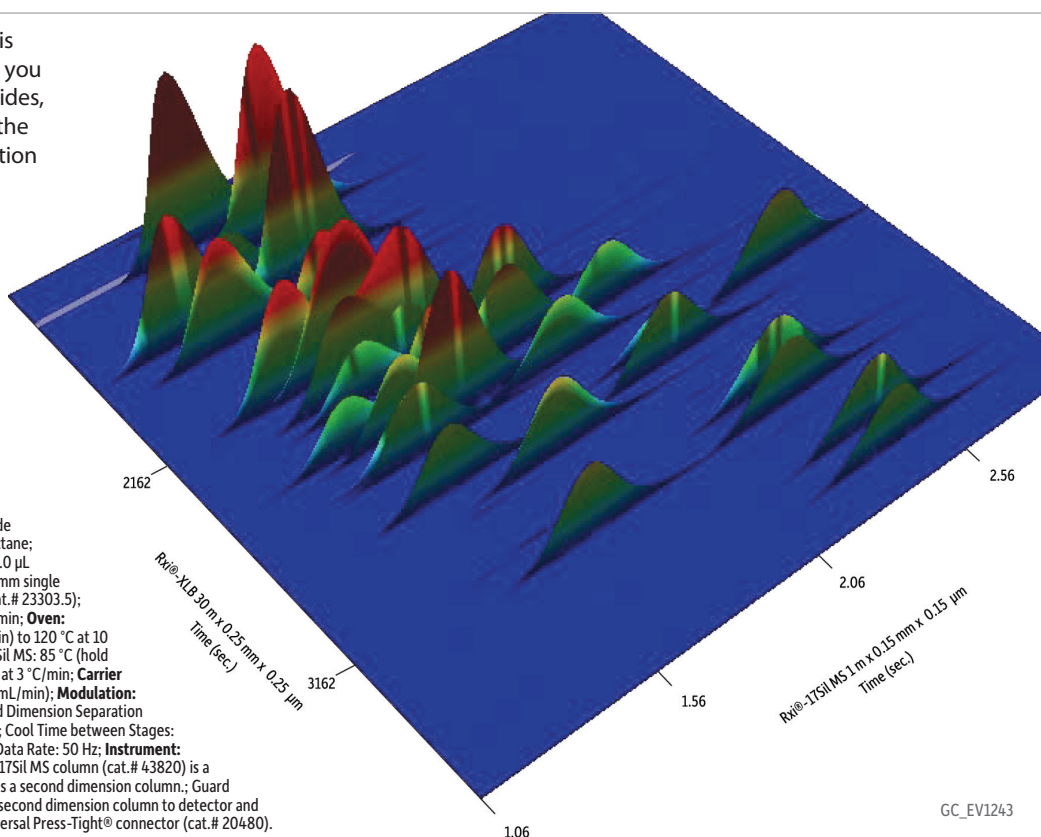See Figure 8 for conditions. GC_EV1244

Figure 8: As shown in this GCxGC-ECD surface plot, you can clearly resolve pesticides, PCBs, and BDEs without the expense of a high-resolution mass spectrometer.

Column: Rxi®-XLB 30 m, 0.25 mm ID, 0.25 µm (cat.# 13723); Rxi®-17Sil MS 1 m, 0.15 mm ID, 0.15 µm (cat.# 43820); with IP deactivated guard column 0.2 m, 0.15 mm ID; **Sample:** PBDE mix (cat.# 33098); PCB congener mix, Method 8082A (cat.# 32416); Organochlorine pesticide mix AB #1 (cat.# 32291); Diluent: Isooctane; Conc.: 250 pg/µL; **Injection:** Inj. Vol.: 1.0 µL splitless (hold 1.0 min); Liner: Sky™ 4 mm single taper/gooseneck inlet liner w/wool (cat.# 23303.5); Inj. Temp.: 250 °C; Purge Flow: 20 mL/min; **Oven:** Oven Temp: Rxi®-XLB: 80 °C (hold 1 min) to 120 °C at 10 °C/min to 300 °C at 3 °C/min; Rxi®-17Sil MS: 85 °C (hold 1 min) to 125 °C at 10 °C/min to 305 °C at 3 °C/min; **Carrier Gas:** He, corrected constant flow (2.0 mL/min); **Modulation:** Modulator Temp. Offset: 20 °C; Second Dimension Separation Time: 3.5 sec; Hot Pulse Time: 1.25 sec; Cool Time between Stages: 0.50 sec; **Detector:** µ-ECD @ 325 °C; Data Rate: 50 Hz; **Instrument:** Agilent/HP6890 GC; **Notes:** The Rxi®-17Sil MS column (cat.# 43820) is a 10 m column. A 1 m section was used as a second dimension column.; Guard column was used as transfer line from second dimension column to detector and connected using a Siltek® treated universal Press-Tight® connector (cat.# 20480).

GC_EV1243

Aromatics and Non-Aromatics in Crude Oil

Restek Primary Column: Rxi®-17Sil MS 30 m, 0.25 mm ID, 0.25 µm

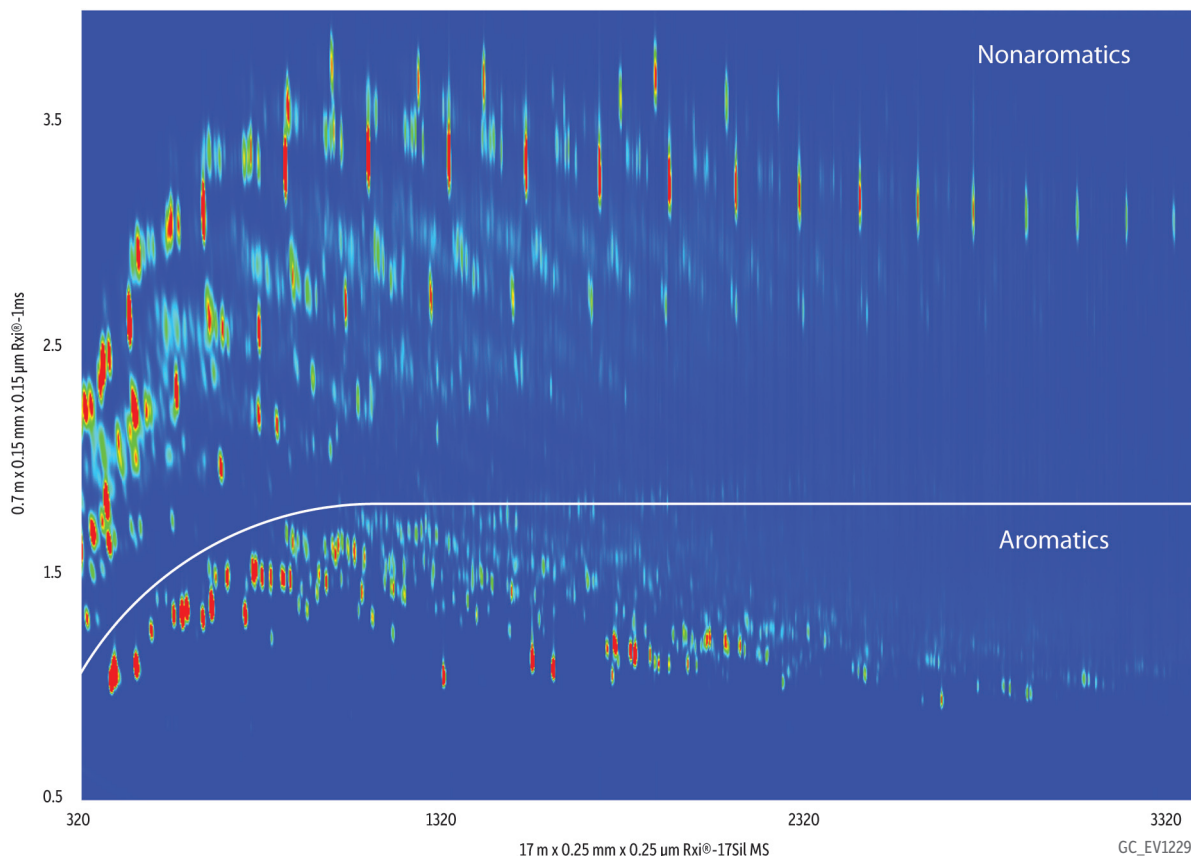**Restek Secondary Column:** Rxi®-1ms 1.2 m, 0.15 mm ID, 0.15 µm

Many aromatic compounds—for example, PAHs—are significant health hazards. As such, they are often targets for required measurement by the U.S. Environmental Protection Agency (EPA) and other environmental monitoring agencies. Unfortunately, these compounds, found in crude oils and petroleum distillates among many other sources, also coelute in one-dimensional GC analyses with non-aromatic compounds. Even with mass spectrometry detection, accurate identification and quantification is difficult or even impossible because of the sheer number of potential compounds and isobaric interferences, forcing analysts to apply off-line separation methods such as silica gel or liquid chromatography (LC) to grossly differentiate the aromatics and non-aromatics—prior to more specific characterization with GC. GCxGC offers a much simpler approach.

Using columns with different stationary phase selectivity in conjunction with either a GCxGC-TOFMS (Figure 10) or a GCxGC-FID, you can reliably separate aromatic and non-aromatic compounds in petroleum samples without employing complicated methodology. The key is that GCxGC offers a spectacular increase in peak capacity. Each separation performed by the first-dimension column—which would be the only separation in one-dimensional GC—is then further separated by a second column. When you look at a GCxGC contour plot, every set of resolved compounds aligned along the x axis represents a coelution had the sample be run using a standard GC analysis. The structured nature of a GCxGC chromatogram also offers a clear visual separation between compound classes. (In this case, the aromatics and nonaromatics present a broad example.)

For a closer look at the separation of the aromatic compounds in Figure 10, as well as additional discussion about resolving aromatic compounds, go to **blog.restek.com** and search "riser pipe".

Figure 10: GCxGC is not only able to resolve an incredibly high number of compounds due to increased peak capacity, but its structured nature also separates compounds into distinct groups for easy identification.

Cannabinoids in Marijuana

Restek Primary Column: Rxi®-17Sil MS 30 m, 0.25 mm ID, 0.25 µm

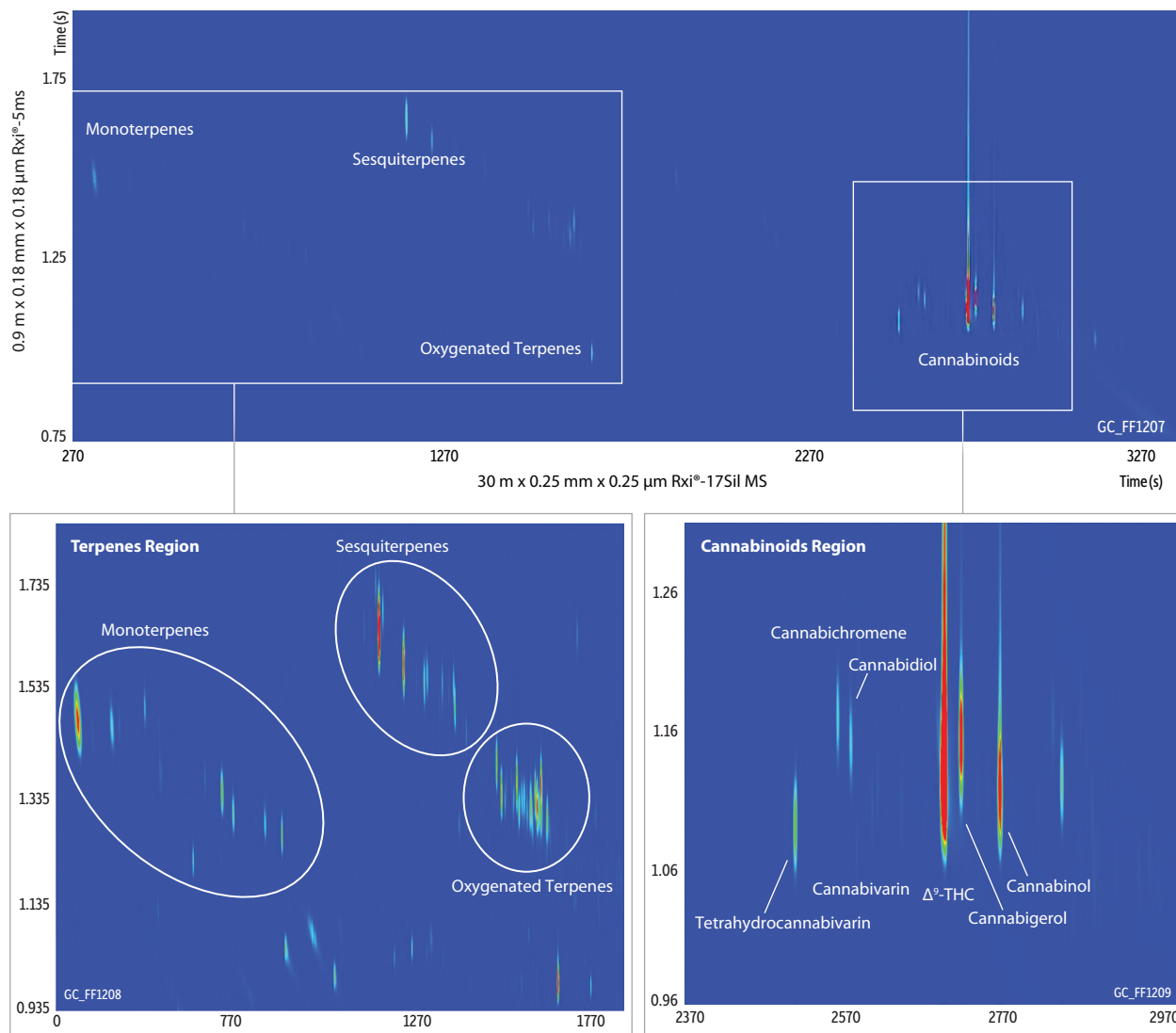**Restek Secondary Column:** Rxi®-5ms 0.9 m, 0.18 mm ID, 0.18 µm

With an increasing number of U.S. states enacting medical marijuana laws, interest in the topic of medical marijuana analysis has grown dramatically. Aside from checking for harmful levels of pesticides (see page 11), dispensaries need to know that their prescriptions are active and potent. To determine the viability of medical marijuana, you must clearly separate the cannabinoid compounds in your sample. Cannabinoid determination can be accomplished using conventional GC-MS, particularly for the "big three" (cannabidiol, 9-THC, cannabinol); however, GCxGC offers an added benefit: the structured chromatogram.

When analyzed using GCxGC, marijuana compound classes position themselves in specific, well-defined areas, forming what is known as a structured chromatogram (Figure 11). Note the clear separation of the terpenoid classes (which are thought to have therapeutic effects) and the cannabinoids, including cannabidiol (which has been shown to relieve convulsion, inflammation, anxiety, and nausea, as well as inhibit cancer cell growth). This clear separation helps with identification, of course, and it also makes discovery of new compounds within classes easier.

Figure 11: When analyzed with GCxGC, marijuana compound classes elute in specific, well-defined areas. Not only are the terpene classes well separated from each other, but they are also separated from the cannabinoids.

For complete conditions, visit www.restek.com and enter chromatogram GC_FF1207 in the search function.

Pesticides in Marijuana

Restek Primary Column: Rxi®-5Sil MS 30 m, 0.25 mm ID, 0.25 µm
Restek Secondary Column: Rtx®-200 1.3 m, 0.25 mm ID, 0.25 µm

Determining potency is certainly important for any prescription, but with medical marijuana, analysts must also look for the presence of harmful pesticides used by growers. Although most regulations do not require it at this time, the determination of pesticide content in medicinal marijuana will most likely gain prevalence in the near future. While many cannabis labs do purport to check for pesticides in marijuana, it is unlikely that their methods are capable of detecting anything but the highest levels. Only the most robust analytical methods—for example, QuEChERS extraction methodology, cartridge SPE cleanup, and GCxGC—can accurately determine trace levels of such a large number of pesticides from a sample as complex as marijuana.

Figure 12 shows an analysis of a standard of over 80 pesticides, including those reported to be found on marijuana or used in marijuana growing operations. Note the excellent separation along both axes, which indicates a highly orthogonal GCxGC column setup. Using QuEChERS to extract illicit marijuana samples, recoveries of spiked pesticides were very good as determined using GCxGC-TOFMS with just a few exceptions. Interestingly, but perhaps not surprisingly, incurred pesticides, even at ppm levels, were found in the illicit samples used for method development (Figure 13), highlighting the need for monitoring of medical marijuana and the high likelihood of such requirements being introduced in the near future.

Figure 12: With an Rxi®-5Sil MS primary column and an Rtx®-200 secondary column, you can easily and clearly determine over 80 pesticides using GCxGC.

Column: Rxi®-5Sil MS 30 m, 0.25 mm ID, 0.25 µm (cat.# 13623); Rtx®-200 1.3 m, 0.25 mm ID, 0.25 µm (cat.# 15020); **Sample:** Diluent: Toluene; **Injection:** Inj. Vol.: 1 µL splitless (hold 1 min); Liner: Sky™ 4mm Single Taper w/Wool (cat.# 23303.1); Inj. Temp.: 250 °C; Purge Flow: 40 mL/min; **Oven:** Oven Temp: Rxi®-5Sil MS: 80 °C (hold 1 min) to 310 °C at 5 °C/min; Rtx®-200: 85 °C (hold 1 min) to 315 °C at 5 °C/min; **Carrier Gas:** He, corrected constant flow (2 mL/min); **Modulation:** Modulator Temp. ; Offset: 20 °C; Second Dimension ; Separation Time: 3 sec; Hot Pulse Time: 0.9 sec; Cool Time ; between Stages: 0.6 sec; **Detector:** TOFMS; Transfer Line Temp.: 290 °C; Analyzer Type: TOF; Source Temp.: 225 °C; Electron Energy: 70 eV; Mass Defect: -20 mu/100 u; Solvent Delay Time: 5 min; Tune Type: PFTBA; Ionization Mode: EI; Acquisition Range: 45-550 amu; Spectral Acquisition ; Rate: 100 spectra/sec; **Instrument:** LECO Pegasus 4D GCxGC-TOFMS; **Notes:** Rtx®-200 (cat.# 15020) is a 15 m column. A 1.3 m section was used as the second dimension column.

For a peak list, visit www.restek.com and enter chromatogram GC_FF1205 in the search function.
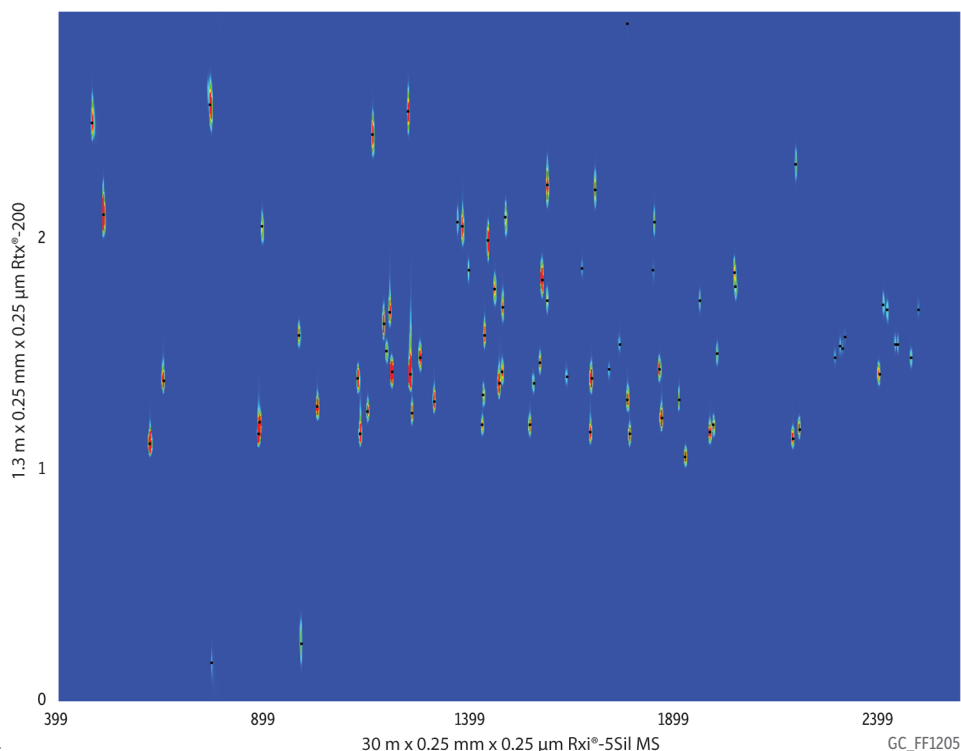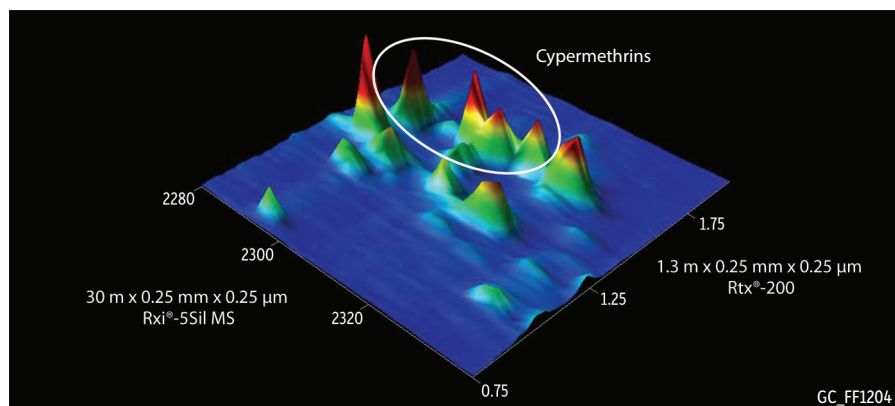

Figure 13: The presence of incurred cypermethrins in marijuana highlights the ability of GCxGC and QuEChERS to resolve pesticides from isobaric interferences in complex samples. (The peaks that are aligned here along the y-axis would have coeluted in one-dimensional GC.) It also serves as a powerful argument for pesticide testing in medical marijuana.

See Figure 12 for conditions.

Hydrocarbons in Gasoline

Restek Primary Column: Rtx®-DHA-150 150 m, 0.25 mm ID, 1.00 µm

Restek Secondary Column: Stabilwax® 1 m, 0.18 mm ID, 0.18 µm with IP deactivated guard column 0.2 m, 0.18 mm ID as a transfer line from secondary column to ECD

Detailed hydrocarbon analysis (DHA) of gasoline is crucial to ensuring a dependable fuel supply and efficient vehicle operation. DHA is usually accomplished using one-dimensional GC with a long, highly efficient column like the Rtx®-DHA, and the results are perfectly acceptable for standard refinery work. However, because gasoline is so exceedingly complex, it can make peak identification difficult. Coelutions can also be a concern with even slight system variation, especially for R&D. Using comprehensive two-dimensional GC gives you more accurate, more reliable results that are far easier to interpret.

A GCxGC system with a shorter primary column allows you to separate important petroleum compounds like aromatics—including toluene and xylenes—and oxygenates—including ethanol and MTBE—well away from the aliphatic components in gasoline for faster identification of target compounds (Figure 14). At the same time, that shorter column can compromise isomeric separations in the first dimension. But, with the longer Rtx®-DHA-150 primary column and the right modulator settings, you can perform "true peak capacity increase GCxGC" to maintain difficult isomer separations. Simply defined, this breakthrough technique is where the first-dimension separation is not intentionally compromised by suboptimum operation of the first-dimension column or modulation times that are too slow based on first-dimension peak widths. Specifically in a DHA analysis, using true peak capacity increase GCxGC means you not only get gross separation of aromatics and oxygenates from aliphatics for easy identification through a structured chromatogram, but you also maintain isomeric separations—as shown for *p*- and *m*-xylene in Figure 15—potentially helping resolve hundreds of additional components!

Learn more at **blog.restek.com** by searching for "true peak capacity increase".

Figure 14: GCxGC is capable of extremely efficient separations for hydrocarbons in gasoline while simultaneously providing a highly structured chromatogram where aromatics and oxygenates elute in the upper part of the retention plane, far away from the aliphatics.
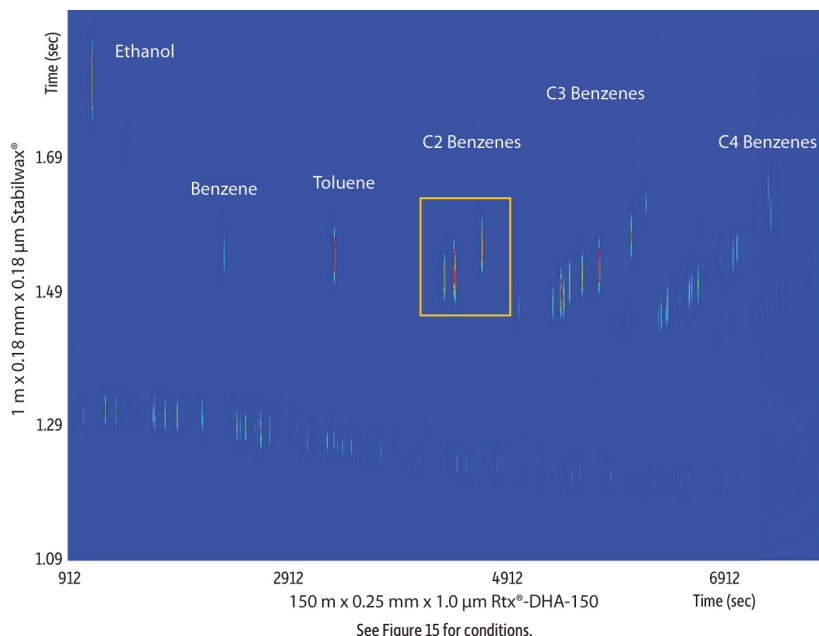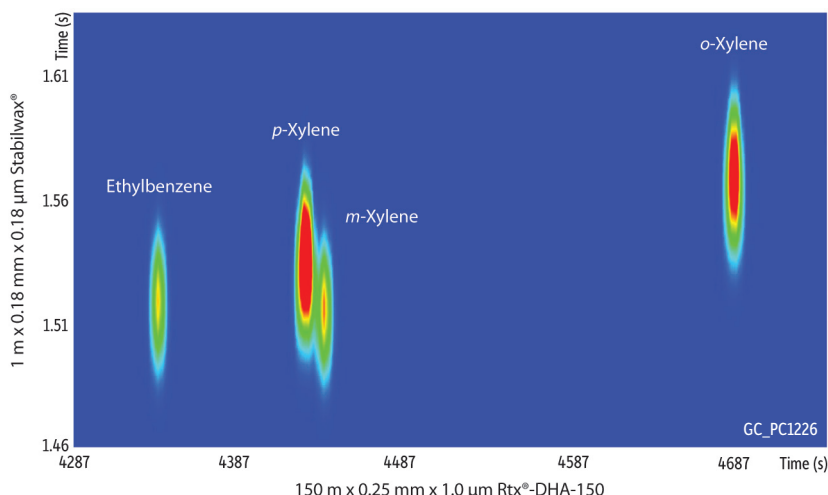

See Figure 15 for conditions.

Figure 15: As shown in this close-up of Figure 14, selection of a longer primary column and efficient modulator operation encourages "true peak capacity increase GCxGC" and permits the separation of isomers like *p*- and *m*-xylene.

Column: Rtx®-DHA-150 150 m, 0.25 mm ID, 1.00 µm (cat.# 10149); Stabilwax® 1 m, 0.18 mm ID, 0.18 µm (cat.# 15118); **Sample:** Gasoline; Conc.: "Neat" (undiluted); **Injection:**; Inj. Vol.: 0.1 µL split (split ratio 200:1); Liner: 4 mm split Precision® liner w/ semivolatiles wool (cat.# 21022-231.1); Inj. Temp.: 275 °C; **Oven:**; Oven Temp: Rtx®-DHA-150: 40 °C (hold 1 min) to 245 °C at 1 °C/min; Stabilwax®: 45 °C (hold 1 min) to 250 °C at 1 °C/min; **Carrier Gas:** He, corrected constant flow (1.8 mL/min); **Modulation:** Modulator Temp. Offset: 20 °C; Second Dimension; Separation Time: 3 sec; Hot Pulse Time: 0.8 sec; Cool Time; between Stages: 0.7 sec; **Detector:** FID @ 270 °C; Constant Column +; Constant Make-up: 50 mL/min; Make-up Gas Type: N2; Data Rate: 200 Hz; **Instrument:** LECO GCxGC-FID; **Notes:** The Stabilwax® column (cat.# 15118) is a 2 m column. A 1 m section was used as a second dimension column. IP deactivated guard column (cat.# 10102) is a 1 m column. A 0.2 m section was used as a transfer line from the second dimension column to the detector.

GC_PC1226

Your One Source for 2D Gas Chromatography

Primary GCxGC Columns
(In order of increasing polarity)

Phase	Length	ID	df	temp. limits	cat.#
Rxi-1ms	30 m	0.25 mm	0.25 µm	-60 to 330/350 °C	13323
Rxi-5Sil MS	30 m	0.25 mm	0.25 µm	-60 to 330/350 °C	13623
Rxi-XLB	30 m	0.25 mm	0.25 µm	30 to 340/360 °C	13723
Rxi-17Sil MS	30 m	0.25 mm	0.25 µm	40 to 340/360 °C	14123
Rtx-200	30 m	0.25 mm	0.25 µm	-20 to 320/340 °C	15023
Stabilwax	30 m	0.25 mm	0.25 µm	40 to 250/260 °C	10623

Secondary GCxGC Columns
(In order of increasing polarity)

Phase	Length	ID	df	temp. limits	cat.#
Rxi-1 MS	2 m	0.15 mm	0.15 µm	-60 to 330/350 °C	15114
	2 m	0.18 mm	0.18 µm	-60 to 330/350 °C	15120
	2 m	0.25 mm	0.25 µm	-60 to 330/350 °C	15127
Rxi-5Sil MS	2 m	0.15 mm	0.15 µm	-60 to 330/350 °C	15113
	2 m	0.18 mm	0.18 µm	-60 to 330/350 °C	15119
	2 m	0.25 mm	0.25 µm	-60 to 330/350 °C	15126
Rxi-XLB	2 m	0.15 mm	0.15 µm	30 to 340/360 °C	15115
	2 m	0.18 mm	0.18 µm	30 to 340/360 °C	15121
	2 m	0.25 mm	0.25 µm	30 to 340/360 °C	15128
Rxi-17Sil MS	2 m	0.15 mm	0.15 µm	40 to 340/360 °C	15110
	2 m	0.18 mm	0.18 µm	40 to 340/360 °C	15116
	2 m	0.25 mm	0.25 µm	40 to 340/360 °C	15123
Rtx-200	2 m	0.15 mm	0.15 µm	-20 to 320/340 °C	15111
	2 m	0.18 mm	0.18 µm	-20 to 320/340 °C	15117
	2 m	0.25 mm	0.25 µm	-20 to 320/340 °C	15124
Stabilwax	2 m	0.15 mm	0.15 µm	40 to 250/260 °C	15112
	2 m	0.18 mm	0.18 µm	40 to 250/260 °C	15118
	2 m	0.25 mm	0.25 µm	40 to 250/260 °C	15125

GCxGC Selectivity Kits

- Wide range of stationary phases helps ensure orthogonal separations; each kit includes one Rxi®-1ms, Rxi®-5Sil MS, Rxi®-17Sil MS, Rtx®-200, Rxi®-XLB, and Stabilwax® column.
- Comprehensive kit simplifies column selection for method developers and heavy GCxGC users alike.
- Convenient 2 m lengths are ideal for use as secondary columns in GCxGC analyses.
- Included Press-Tight® connectors offer a reliable, hassle-free installation.
- High thermal stability maximizes system ruggedness and sensitivity.
- Unrivaled column inertness means accurate analysis of active compounds.
- Choose 0.15, 0.18, or 0.25 mm ID format to accommodate your specific sample capacity, speed, and detector needs.

Description		qty.	cat.#
GCxGC (0.15 mm) Selectivity Kit		kit	15129
Includes (each product available separately)			
Rxi-1ms	2 m x 0.15 mm x 0.15 µm	ea.	15114
Rxi-5Sil MS	2 m x 0.15 mm x 0.15 µm	ea.	15113
Rxi-XLB	2 m x 0.15 mm x 0.15 µm	ea.	15115
Rxi-17Sil MS	2 m x 0.15 mm x 0.15 µm	ea.	15110
Rtx-200	2 m x 0.15 mm x 0.15 µm	ea.	15111
Stabilwax	2 m x 0.15 mm x 0.15 µm	ea.	15112
Universal Press-Tight Connectors	Deactivated	5-pk.	20429

Description		qty.	cat.#
GCxGC (0.18 mm) Selectivity Kit		kit	15130
Includes (each product available separately)			
Rxi-1ms	2 m x 0.18 mm x 0.18 µm	ea.	15120
Rxi-5Sil MS	2 m x 0.18 mm x 0.18 µm	ea.	15119
Rxi-XLB	2 m x 0.18 mm x 0.18 µm	ea.	15121
Rxi-17Sil MS	2 m x 0.18 mm x 0.18 µm	ea.	15116
Rtx-200	2 m x 0.18 mm x 0.18 µm	ea.	15117
Stabilwax	2 m x 0.18 mm x 0.18 µm	ea.	15118
Universal Press-Tight Connectors	Deactivated	5-pk.	20429

Description		qty.	cat.#
GCxGC (0.25 mm) Selectivity Kit		kit	15131
Includes (each product available separately)			
Rxi-1ms	2 m x 0.25 mm x 0.25 µm	ea.	15127
Rxi-5Sil MS	2 m x 0.25 mm x 0.25 µm	ea.	15126
Rxi-XLB	2 m x 0.25 mm x 0.25 µm	ea.	15128
Rxi-17Sil MS	2 m x 0.25 mm x 0.25 µm	ea.	15123
Rtx-200	2 m x 0.25 mm x 0.25 µm	ea.	15124
Stabilwax	2 m x 0.25 mm x 0.25 µm	ea.	15125
Universal Press-Tight Connectors	Deactivated	5-pk.	20429

Universal Press-Tight® Connectors

- Connect primary and secondary GCxGC columns.
- Deactivated Press-Tight® connectors maintain complete intertness for the GC flow path.
- Fit column ODs from 0.33–0.74 mm (Restek 0.1 mm–0.53 mm ID).

Description	5-pk.	25-pk.
Universal Press-Tight Connectors, Deactivated	20429	20430

For instructions on obtaining a reliable, leak-free seal and for ordering information, go to **www.restek.com/press-tight**

Restek Electronic Leak Detector

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

- 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.
- A convenient carrying and storage case.
- Easy to clean probe assembly.
- A universal charger set (US, European, UK, and Australian plugs included).

Backed by a 1-year warranty, the new Restek Leak Detector sets an industry standard for performance and affordability in hand-held leak detectors.

restek recommends

When your Leak Detector batteries need to be replaced, send the unit to us for a routine maintenance review to ensure continued sensitivity and reliability. We will replace not only the batteries, but also the probe and internal/external tubing. We will also recertify your unit. Contact Customer Service to send in your Leak Detector for maintenance (cat. #22839-R).

Leak Detector Facts

Detectable Gases:	Helium, nitrogen, argon, carbon dioxide, hydrogen	Operating Temp. Range:	32-120 °F (0-48 °C)
		Humidity Range:	0-97%
Battery:	Rechargeable Ni-MH internal battery pack (6 hours normal operation)	Warranty:	One year
		Certifications:	CE, Ex, Japan
		Compliance:	WEEE, RoHS

Limits of Detection

These gases can be detected with the Restek Electronic Leak Detector at the following leak rates.

Gas	Minimum Detectable Leak Rate (atm cc/sec.)	Indicating LED Light Color
Helium	1.0×10^{-5}	red LED
Hydrogen	1.0×10^{-5}	red LED
Nitrogen	1.4×10^{-3}	yellow LED
Argon	1.0×10^{-4}	yellow LED
Carbon Dioxide	1.0×10^{-4}	yellow LED

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
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.

Sky™ Inlet Liners

Patent pending

Sky™ 4.0mm ID Single Taper/Gooseneck Inlet Liner
w/ Wool
For Agilent GCs equipped with split/splitless inlets

ID x OD x Length	qty.	cat.#
Single Taper Gooseneck, Sky Technology, Wool, 4.0 mm x 6.5 mm x 78.5 mm	ea.	23303.1
Single Taper Gooseneck, Sky Technology, Wool, 4.0 mm x 6.5 mm x 78.5 mm	5-pk.	23303.5
Single Taper Gooseneck, Sky Technology, Wool, 4.0 mm x 6.5 mm x 78.5 mm	25-pk.	23303.25

Sky™ 4.0mm ID Single Taper/Gooseneck Inlet Liner
For Agilent GCs equipped with split/splitless inlets

ID x OD x Length	qty.	cat.#
Single Taper Gooseneck, Sky Technology, 4.0 mm x 6.5 mm x 78.5 mm	ea.	23302.1
Single Taper Gooseneck, Sky Technology, 4.0 mm x 6.5 mm x 78.5 mm	5-pk.	23302.5
Single Taper Gooseneck, Sky Technology, 4.0 mm x 6.5 mm x 78.5 mm	25-pk.	23302.25

Sky™ 4.0mm ID Cyclo Double Taper/Gooseneck Inlet Liner
For Agilent GCs equipped with split/splitless inlets

ID x OD x Length	qty.	cat.#
Cyclo Double Taper Gooseneck, Sky Technology, 4.0 mm x 6.5 mm x 78.5 mm	ea.	23310.1
Cyclo Double Taper Gooseneck, Sky Technology, 4.0 mm x 6.5 mm x 78.5 mm	5-pk.	23310.5
Cyclo Double Taper Gooseneck, Sky Technology, 4.0 mm x 6.5 mm x 78.5 mm	25-pk.	23310.25

Sky™ 4.0mm ID Precision® Inlet Liner w/ Wool
For Agilent GCs equipped with split/splitless inlets

ID x OD x Length	qty.	cat.#
Precision, Sky Technology, Wool, 4.0 mm x 6.3 mm x 78.5 mm	ea.	23305.1
Precision, Sky Technology, Wool, 4.0 mm x 6.3 mm x 78.5 mm	5-pk.	23305.5
Precision, Sky Technology, Wool, 4.0 mm x 6.3 mm x 78.5 mm	25-pk.	23305.25

Sky™ 4.0mm ID Cyclo Inlet Liner
For Agilent GCs equipped with split/splitless inlets

ID x OD x Length	qty.	cat.#
Cyclo, Sky Technology, 4.0 mm x 6.3 mm x 78.5 mm	ea.	23312.1
Cyclo, Sky Technology, 4.0 mm x 6.3 mm x 78.5 mm	5-pk.	23312.5
Cyclo, Sky Technology, 4.0 mm x 6.3 mm x 78.5 mm	25-pk.	23312.25

Also available for PerkinElmer, Shimadzu, Thermo Scientific, and Varian Instruments at www.restek.com/sky

Restek GCxGC Column Combination Guide

To achieve ideal results in a GCxGC analysis, it is imperative that your primary and secondary columns feature orthogonal phases capable of producing differing separations. Use the chart below to find the perfect combination of Restek columns to maximize the effectiveness of your GCxGC system.

Application Area	Primary Column		Secondary Column	
	Phase	Selectivity	Phase	Selectivity
Petrochemical	Rxi®-1ms	Non-polar	Rxi®-17Sil MS	Mid-polar, aromatic selective
Petrochemical	Rxi®-5Sil MS	Non-polar	Rxi®-17Sil MS	Mid-polar, aromatic selective
PAHs, environmental	Rxi®-17Sil MS	Mid-polar, aromatic selective	Rxi®-1ms	Non-polar
PAHs, environmental	Rxi®-17Sil MS	Mid-polar, aromatic selective	Rxi®-5Sil MS	Non-polar
PCBs, PBDEs, PAHs, environmental	Rxi®-XLB	Non-polar	Rxi®-17Sil MS	Mid-polar, aromatic selective
Mono-ortho, coplanar PCBs	Rxi®-1ms	Non-polar	Rxi®-XLB	Planar selective
Mono-ortho, coplanar PCBs	Rxi®-5Sil MS	Non-polar	Rxi®-XLB	Planar selective
Pesticides, nitroaromatics, halogenated compounds	Rxi®-1ms	Non-polar	Rtx®-200	Mid-polar, electronegative selectivity
Pesticides, nitroaromatics, halogenated compounds	Rxi®-5Sil MS	Non-polar	Rtx®-200	Mid-polar, electronegative selectivity
Pesticides, nitroaromatics, halogenated compounds	Rxi®-XLB	Non-polar	Rtx®-200	Mid-polar, electronegative selectivity
Flavors, fragrances	Rxi®-1ms	Non-polar	Stabilwax®	Polar
Flavors, fragrances	Rxi®-5Sil MS	Non-polar	Stabilwax®	Polar
Flavors, fragrances	Stabilwax®	Polar	Rxi®-1ms	Non-polar
Flavors, fragrances	Stabilwax®	Polar	Rxi®-5Sil MS	Non-polar

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