

Environmental Applications

Optimized Volatiles Analysis Ensures Fast VOC Separations

By Michelle Misselwitz, Gary Stidsen, and Chris English

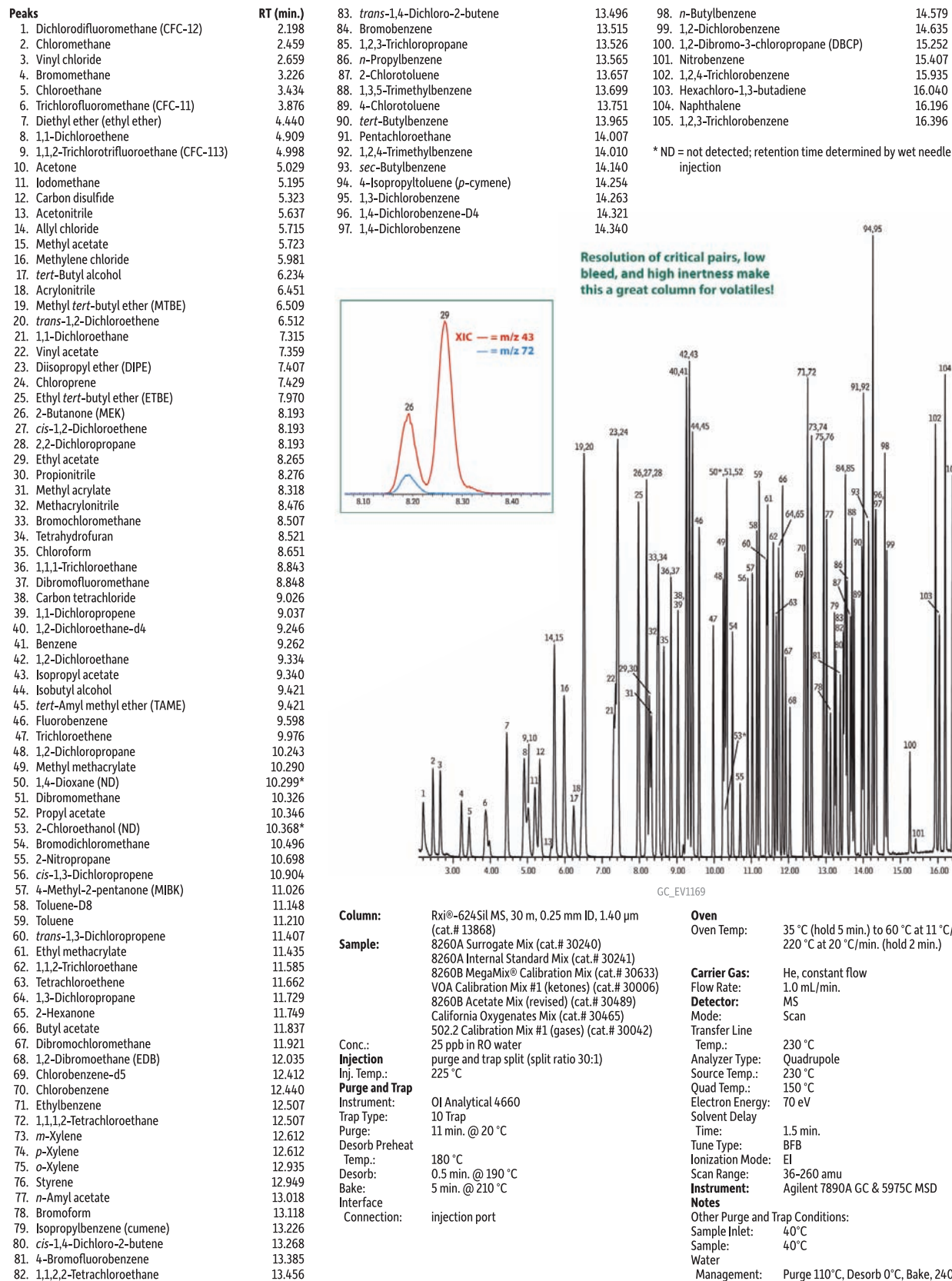
- Optimized analysis allows for 36 runs per 12-hour shift, increasing instrument productivity.
- Rxi®-624Sil MS column inertness gives sharper peaks and more accurate data.
- High temperature stability reduces bleed profile, resulting in lower detection limits.

Optimized methods for the analysis of volatile organic compounds (VOCs) can be time-consuming to develop because compound lists can be extensive and analytes vary significantly in chemical characteristics. For example, target compounds in EPA Method 8260 for solid waste matrices include volatiles that range from light gases (Freon®) to larger aromatic compounds (trichlorobenzenes). These differences make column selectivity, thermal stability, and inertness critical to resolving volatiles. Often, “624” type columns are chosen for their selectivity, but thermal stability is usually poor, which can result in phase bleed that decreases detector sensitivity. New Rxi®-624Sil MS columns offer reliable resolution of critical VOC pairs and also provide lower bleed and greater inertness than other columns. In order to provide optimized conditions for labs analyzing VOCs, we established parameters that ensure good resolution, while reducing downtime by syncing purge and trap cycles with instrument cycles. In addition, we present comparative data that demonstrate why Rxi®-624Sil MS columns are the best choice for volatiles analysis.

Resolve Critical Pairs and Reduce Downtime

In order to achieve desired separations and minimize downtime between injections, several critical pairs were chosen for computational modeling using Pro ezGC software. The temperature program initially determined by the software was 35 °C (hold 5 min.) to 120 °C @ 11 °C/min. to 220 °C @ 20 °C/min. (hold 2 min.). While this provided the best resolution of critical pairs, it also extended the analysis time to 19 min. Since the purge and trap cycle time was 16.5 min., we tested other conditions to see if adequate resolution could be maintained, while using a faster instrument cycle time that more closely matched the purge and trap cycle time, in order to maximize sample throughput. In other calculations, the software suggested changing temperature ramps at 60 °C; therefore, a program of 35 °C (hold 5 min.) to 60 °C @ 11 °C/min. to 220 °C @ 20 °C/min. (hold 2 min.) was tested. This final program reduced instrument downtime by better synchronizing injection and analysis cycles, and also provided excellent resolution of volatile compounds (Figure 1). Testing of faster conditions determined that the initial hold of 5 minutes at 35 °C was critical for the best separation of early eluting compounds, such as the gases, as well as a favorable elution of methanol between gas compounds.

Figure 1 Rxi®-624Sil MS columns resolve methyl ethyl ketone and ethyl acetate, a separation not obtained on other 624 columns.



Not all “624s” are Equivalent

While optimizing instrument conditions can improve sample throughput, obtaining adequate resolution depends largely on column selectivity, thermal stability, and inertness. Rxi®-624Sil MS columns are optimized across these parameters, and therefore provide reliable separation of critical VOCs.

Lower Bleed Means Improved Sensitivity and Longer Column Lifetime

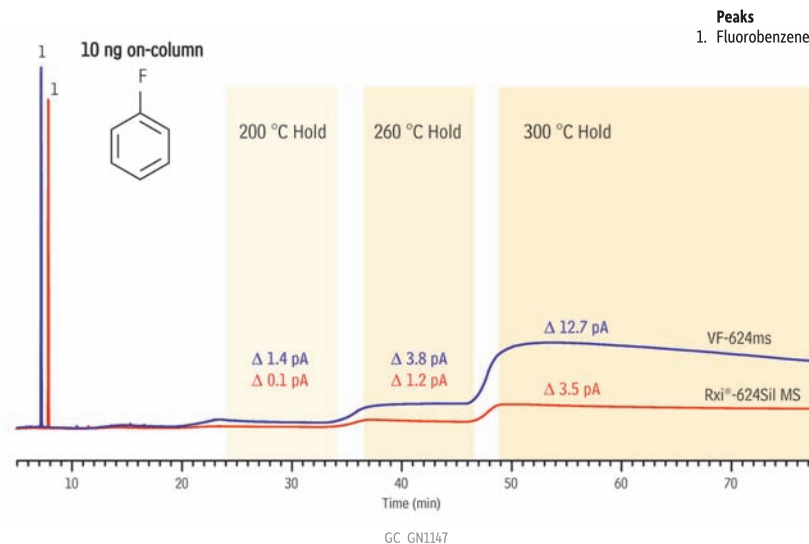
While 624 type columns generally provide good selectivity for most volatiles, they are limited by their low thermal stability. Poor thermal stability results in phase bleed that can reduce column lifetime, decrease detector sensitivity (especially ion trap mass spectrometers), and interfere with the quantification of later eluting compounds. Rxi®-624Sil MS columns have the highest thermal stability and lowest bleed among 624 type columns due to the incorporation of phenyl rings in the polymer backbone (Table I, Figure 2). The conjugated ring system of this silarylene phase provides a more rigid structure that increases thermal stability compared to nonsilarylene phases.

Table I The Rxi®-624Sil MS column has the highest thermal stability of any 624 column.

Column	Manufacturer	Highest Temperature Limit (Isothermal)
Rxi-624Sil MS	Restek	320 °C
VF-624ms	Varian	300 °C
DB-624	Agilent J&W	260 °C
ZB-624	Phenomenex	260 °C

Figure 2 The Rxi®-624Sil MS column has the lowest bleed of any column in its class and provides true GC/MS capability.

Bleed Comparison of Rxi®-624Sil MS and VF-624ms

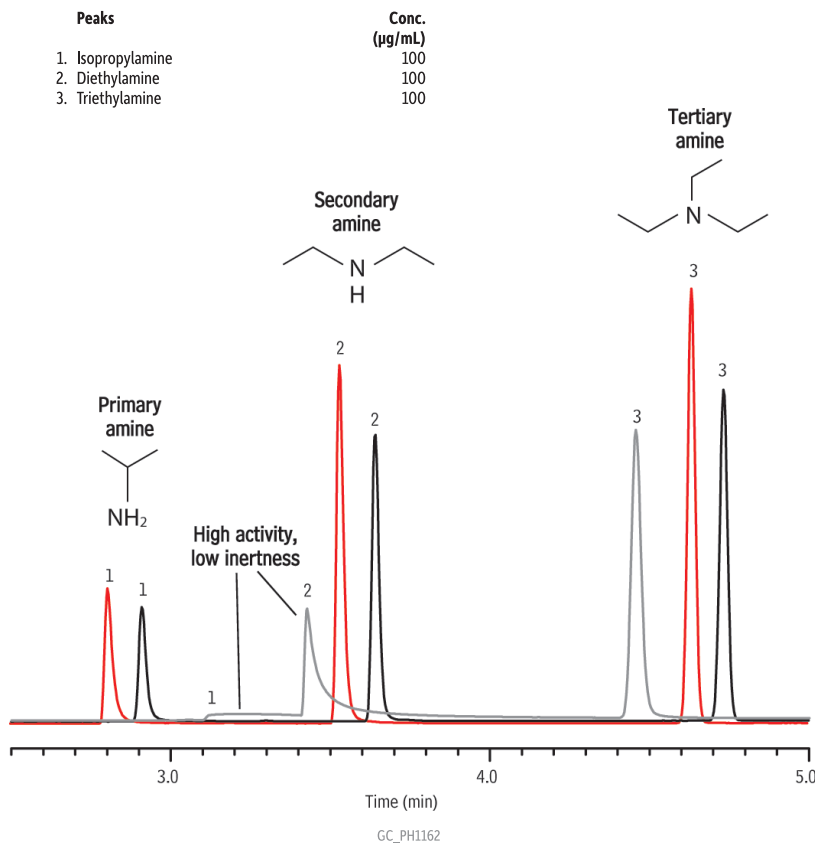


Column Rxi®-624Sil MS (see notes), 30 m, 0.25 mm ID, 1.4 μm (cat.# 13868)
Sample Fluorobenzene (cat.# 30030)
Diluent: methanol
Conc.: 200 μg/mL
Injection
Inj. Vol.: 1 μL split (split ratio 20:1)
Liner: 4mm Split Liner with Wool (cat.# 20781)
Inj. Temp.: 220 °C
Oven
Oven Temp: 40 °C (hold 5 min.) to 60 °C at 20 °C/min. (hold 5 min.) to 120 °C at 20 °C/min. (hold 5 min.) to 200 °C at 20 °C/min. (hold 10 min.) to 260 °C at 20 °C/min. (hold 10 min.) to 300 °C at 20 °C/min. (hold 20 min.)
Carrier Gas He, constant flow
Linear Velocity: 40 cm/sec.
Detector FID @ 250 °C
Instrument Agilent/HP6890 GC
Notes Columns are of equivalent dimensions and were tested after equivalent conditioning.

Better Peak Shape Means More Accurate Results

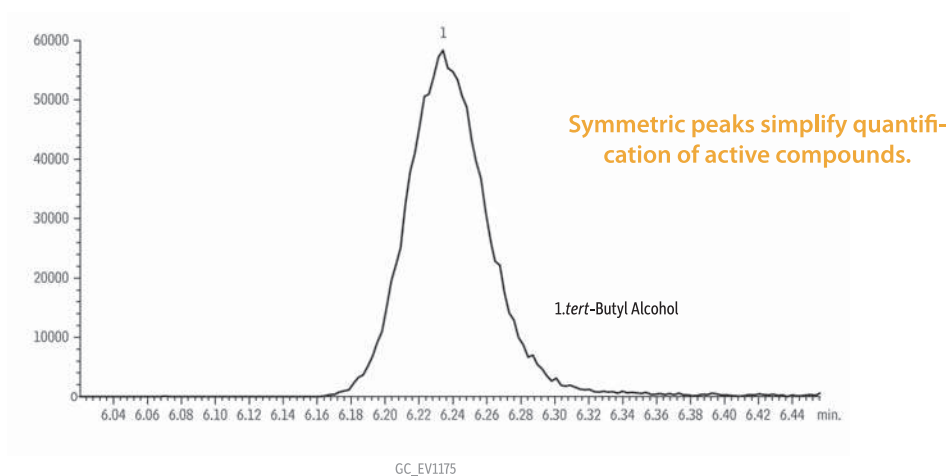
Rxi®-624Sil MS columns are the most inert 624 column available. Figure 3 shows the differences between vendor columns using primary amines, which are good indicators of column activity. The unique Rxi® deactivation results in symmetric peaks with minimal tailing, which improves quantitative accuracy. Minimizing tailing is especially important with concentration techniques, such as purge and trap, since the act of desorbing analytes off of the packing material results in some tailing. If a column is not inert, additional tailing due to column activity can magnify this problem. The sharp, symmetric peaks seen on Rxi®-624Sil MS columns allow greater resolution, higher signal-to-noise ratios, and more accurate results for active volatiles such as alcohols (Figure 4).

Figure 3 Highly inert Rxi®-624Sil MS columns provide better peak shape and more accurate results for active compounds.



Column Rxi®-624SilMS, 30 m, 0.32 mm ID, 1.8 µm (cat.# 13870)
Sample
Diluent: DMSO
Conc.: 100 µg/mL
Injection
Inj. Vol.: 1 µL split (split ratio 20:1)
Liner: 5mm Single Gooseneck with Wool (cat.# 22973-200.1)
Inj. Temp.: 250 °C
Oven
Oven Temp: 50 °C (hold 1 min.) to 200 °C at 20 °C/min. (hold 5 min.)
Carrier Gas He, constant flow
Linear Velocity: 37 cm/sec.
Detector FID @ 250 °C
Instrument Agilent/HP6890 GC

Figure 4 Obtain more accurate results for active volatiles, such as alcohols, by using highly inert Rxi®-624Sil MS columns.



Column Rxi®-624Sil MS, 30 m, 0.25 mm ID, 1.40 µm (cat.# 13868)
Sample
 Conc.: 25 ppb in RO water
Injection purge and trap split (split ratio 30:1)
 Inj. Temp.: 225 °C
Purge and Trap
 Instrument: OJ Analytical 4660
 Trap Type: 10 Trap
 Purge: 11 min. @ 20 °C
 Desorb Preheat Temp.: 180 °C
 Desorb: 0.5 min. @ 190 °C
 Bake: 5 min. @ 210 °C
Interface
 Connection: injection port
Oven
 Oven Temp: 35 °C (hold 5 min.) to 60 °C at 11 °C/min. to 220 °C at 20 °C/min. (hold 2 min.)
Carrier Gas He, constant flow
 Flow Rate: 1.0 mL/min.
Detector MS
 Mode: Scan
 Transfer Line Temp.: 230 °C
 Analyzer Type: Quadrupole
 Source Temp.: 230 °C
 Quad Temp.: 150 °C
 Electron Energy: 70 eV
 Solvent Delay Time: 1.5 min.
 Tune Type: BFB
 Ionization Mode: EI
 Scan Range: 36-260 amu
Instrument Agilent 7890A GC & 5975C MSD
Notes Other Purge and Trap Conditions:
 Sample Inlet: 40 °C

Conclusions

Labs interested in optimizing resolution and sample throughput can adopt the conditions established here on Rxi®-624Sil MS columns to maximize productivity and assure accurate, reliable results.

PATENTS & TRADEMARKS

Restek patents and trademarks are the property of Restek Corporation. Other trademarks appearing in Restek literature or on its website are the property of their respective owners.