Environmental Applications

Optimized Volatiles Analysis Ensures Fast VOC Separations

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- 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.

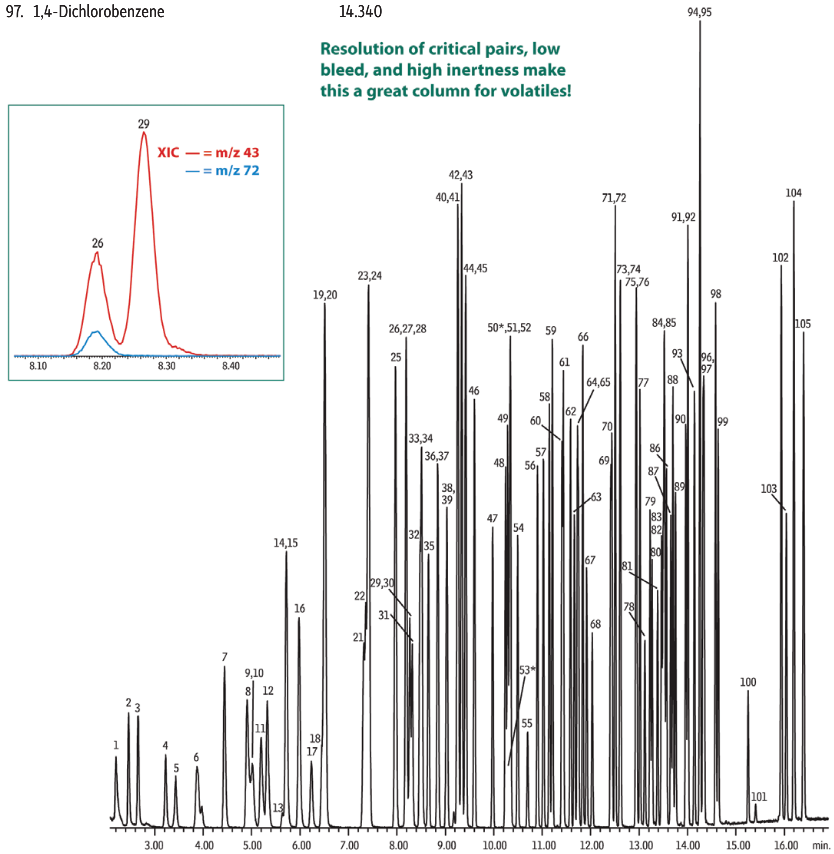
Resolve Critical Pairs and Reduce Downtime

In order to achieve desired separations and minimize downtime between injections, several critical pairs were chosen for computational modeling using Pro *ez*GC 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.

Peaks	RT (min.)
1. Dichlorodifluoromethane (CFC-12)	2.198
2. Chloromethane	2.459
3. Vinyl chloride	2.659
4. Bromomethane	3.226
5. Chloroethane	3.434
6. Trichlorofluoromethane (CFC-11)	3.876
7. Diethyl ether (ethyl ether)	4.440
8. 1,1-Dichloroethene	4.909
9. 1,1,2-Trichlorotrifluoroethane (CFC-113)	4.998
10. Acetone	5.029
11. Iodomethane	5.195
12. Carbon disulfide	5.323
13. Acetonitrile	5.637
14. Allyl chloride	5.715
15. Methyl acetate	5.723
16. Methylene chloride	5.981
17. *tert*-Butyl alcohol	6.234
18. Acrylonitrile	6.451
19. Methyl *tert*-butyl ether (MTBE)	6.509
20. *trans*-1,2-Dichloroethene	6.512
21. 1,1-Dichloroethane	7.315
22. Vinyl acetate	7.359
23. Diisopropyl ether (DIPE)	7.407
24. Chloroprene	7.429
25. Ethyl *tert*-butyl ether (ETBE)	7.970
26. 2-Butanone (MEK)	8.193
27. *cis*-1,2-Dichloroethene	8.193
28. 2,2-Dichloropropane	8.193
29. Ethyl acetate	8.265
30. Propionitrile	8.276
31. Methyl acrylate	8.318
32. Methacrylonitrile	8.476
33. Bromochloromethane	8.507
34. Tetrahydrofuran	8.521
35. Chloroform	8.651
36. 1,1,1-Trichloroethane	8.843
37. Dibromofluoromethane	8.848
38. Carbon tetrachloride	9.026
39. 1,1-Dichloropropene	9.037
40. 1,2-Dichloroethane-d4	9.246
41. Benzene	9.262
42. 1,2-Dichloroethane	9.334
43. Isopropyl acetate	9.340
44. Isobutyl alcohol	9.421
45. *tert*-Amyl methyl ether (TAME)	9.421
46. Fluorobenzene	9.598
47. Trichloroethene	9.976
48. 1,2-Dichloropropane	10.243
49. Methyl methacrylate	10.290
50. 1,4-Dioxane (ND)	10.299*
51. Dibromomethane	10.326
52. Propyl acetate	10.346
53. 2-Chloroethanol (ND)	10.368*
54. Bromodichloromethane	10.496
55. 2-Nitropropane	10.698
56. *cis*-1,3-Dichloropropene	10.904
57. 4-Methyl-2-pentanone (MIBK)	11.026
58. Toluene-D8	11.148
59. Toluene	11.210
60. *trans*-1,3-Dichloropropene	11.407
61. Ethyl methacrylate	11.435
62. 1,1,2-Trichloroethane	11.585
63. Tetrachloroethene	11.662
64. 1,3-Dichloropropane	11.729
65. 2-Hexanone	11.749
66. Butyl acetate	11.837
67. Dibromochloromethane	11.921
68. 1,2-Dibromoethane (EDB)	12.035
69. Chlorobenzene-d5	12.412
70. Chlorobenzene	12.440
71. Ethylbenzene	12.507
72. 1,1,1,2-Tetrachloroethane	12.507
73. *m*-Xylene	12.612
74. *p*-Xylene	12.612
75. *o*-Xylene	12.935
76. Styrene	12.949
77. *n*-Amyl acetate	13.018
78. Bromoform	13.118
79. Isopropylbenzene (cumene)	13.226
80. *cis*-1,4-Dichloro-2-butene	13.268
81. 4-Bromofluorobenzene	13.385
82. 1,1,2,2-Tetrachloroethane	13.456
83. *trans*-1,4-Dichloro-2-butene	13.496
84. Bromobenzene	13.515
85. 1,2,3-Trichloropropane	13.526
86. *n*-Propylbenzene	13.565
87. 2-Chlorotoluene	13.657
88. 1,3,5-Trimethylbenzene	13.699
89. 4-Chlorotoluene	13.751
90. *tert*-Butylbenzene	13.965
91. Pentachloroethane	14.007
92. 1,2,4-Trimethylbenzene	14.010
93. *sec*-Butylbenzene	14.140
94. 4-Isopropyltoluene (*p*-cymene)	14.254
95. 1,3-Dichlorobenzene	14.263
96. 1,4-Dichlorobenzene-D4	14.321
97. 1,4-Dichlorobenzene	14.340
98. *n*-Butylbenzene	14.579
99. 1,2-Dichlorobenzene	14.635
100. 1,2-Dibromo-3-chloropropane (DBCP)	15.252
101. Nitrobenzene	15.407
102. 1,2,4-Trichlorobenzene	15.935
103. Hexachloro-1,3-butadiene	16.040
104. Naphthalene	16.196
105. 1,2,3-Trichlorobenzene	16.396

* ND = not detected; retention time determined by wet needle injection



GC_EV1169

Column: Rxi®-624Sil MS, 30 m, 0.25 mm ID, 1.40 µm (cat.# 13868)
Sample: 8260A Surrogate Mix (cat.# 30240)
8260A Internal Standard Mix (cat.# 30241)
8260B MegaMix® Calibration Mix (cat.# 30633)
VOA Calibration Mix #1 (ketones) (cat.# 30006)
8260B Acetate Mix (revised) (cat.# 30489)
California Oxygenates Mix (cat.# 30465)
502.2 Calibration Mix #1 (gases) (cat.# 30042)
Conc.: 25 ppb in RO water
Injection purge and trap split (split ratio 30:1)
Inj. Temp.: 225 °C
Purge and Trap
Instrument: OI 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
Sample: 40°C
Water Management: Purge 110°C, Desorb 0°C, Bake, 240°C

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

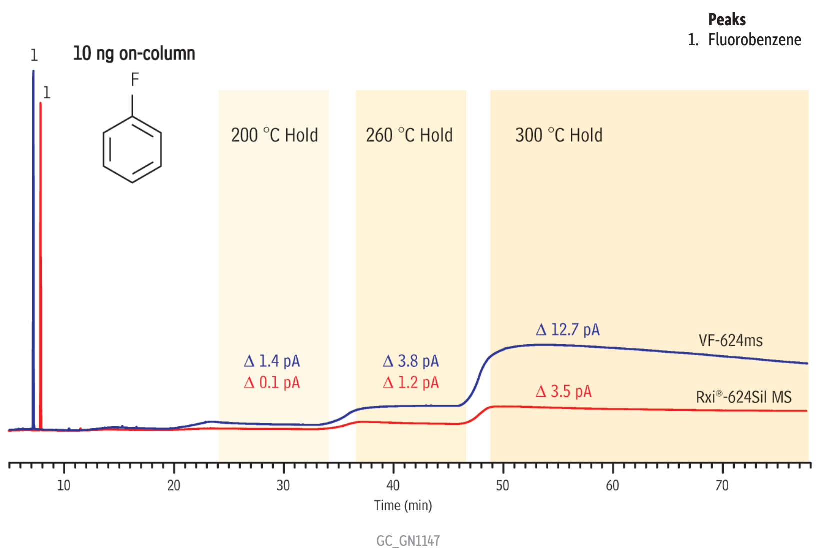
While 624 type columns generally provide good selectivity for most volatiles, they are limited by their low thermal stability. Poor thermal stability results in phase bleed that can reduce column lifetime, decrease detector sensitivity (especially ion trap mass spectrometers), and interfere with the 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 ºC**
VF-624ms	Varian	300 ºC
DB-624	Agilent J&W	260 ºC
ZB-624	Phenomenex	260 ºC

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



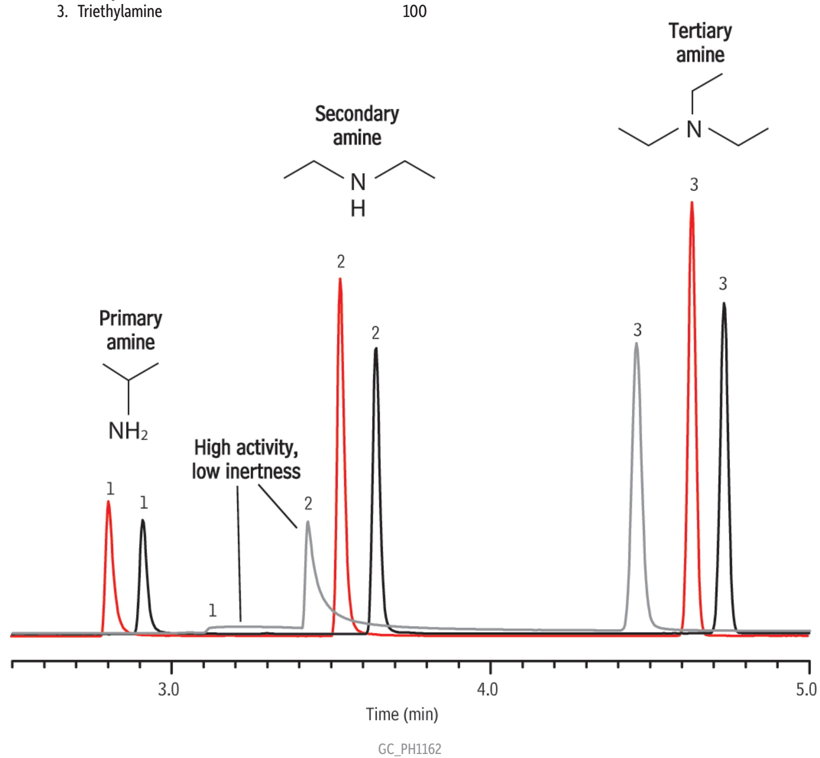
Column	Rxi®-624Sil MS (see notes), 30 m, 0.25 mm ID, 1.4 µm (cat.# 13868)
Sample	Fluorobenzene (cat.# 30030)
Diluent:	methanol
Conc.:	200 µg/mL
Injection	
Inj. Vol.:	1 µL split (split ratio 20:1)
Liner:	4mm Split Liner with Wool (cat.# 20781)
Inj. Temp.:	220 °C
Oven	
Oven Temp:	40 °C (hold 5 min.) to 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).

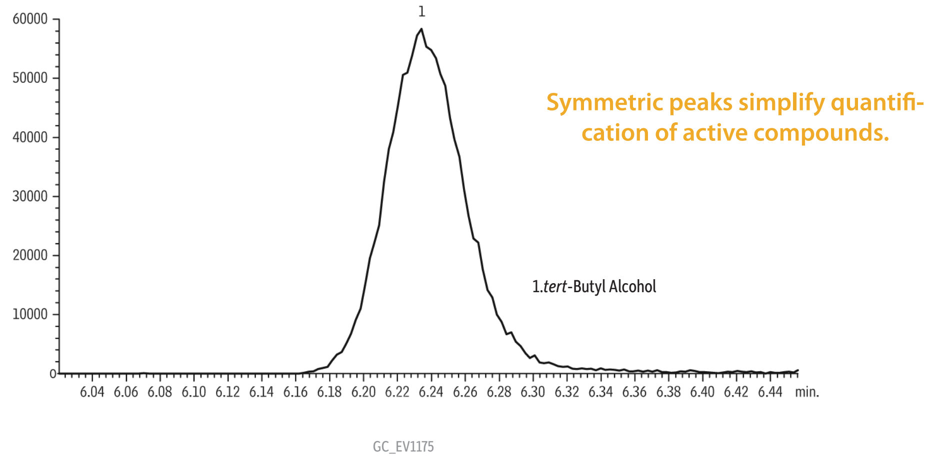
Figure 3 Highly inert Rxi®-624Sil MS columns provide better peak shape and more accurate results for active compounds.

Peaks	Conc. (µg/mL)
1. Isopropylamine	100
2. Diethylamine	100
3. Triethylamine	100



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:	OI 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.

Lit. Cat.# EVAN1271

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