Evaluation of Stationary Phases for the Analysis of Volatiles by US EPA Methods 8260 & 524.2.

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Abstract

There are many columns that are currently used for the analysis of volatile environmental pollutants by GC/MS. Most of the stationary phases that are offered have adequate selectivity, bleed and inertness for the most common methods. Problems occur when starting temperatures & oven ramp rates are increased. Laboratories that increase runtimes without carefully checking the mass-spectra of each coeluting analyte may compromise data integrity.

This paper will compare four common stationary phases to a new volatile-mass / spec phase for separation of isomeric pairs using high oven starting temperatures and a rapid final oven ramp rate. Other common analytes that share ions will also be presented.

Introduction

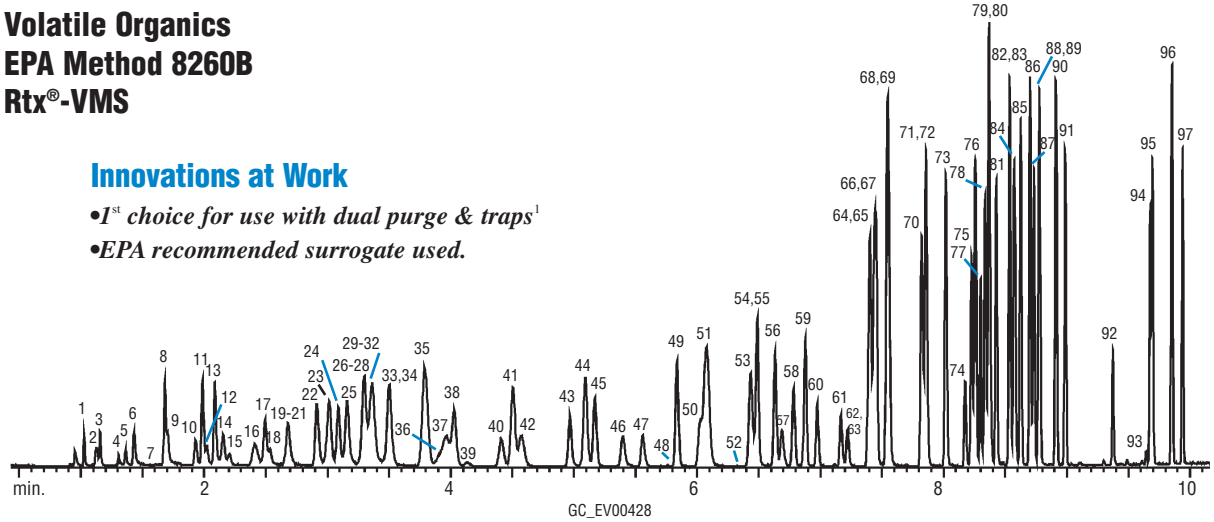
Chromatographic and purge & trap cycle times have been the limiting factor for volatile analysis for many years. With the advent of interfacing two purge & trap concentrators onto one GC/MS, analysts are now interested in columns with sub-ten-minute runtimes.

The Rtx-VMS chromatogram shown below spectrally resolves all of the target compounds in under 10 minutes. Faster runtimes are possible by substituting chlorobenzene-D5 with an alternate internal standard. This solution works for the VMS phase but will not work for other phases since the resolution of isomers is compromised. This paper will compare other phases run under these conditions for separation of isomeric pairs.

Volatile Organics
EPA Method 8260B
Rtx®-VMS

Innovations at Work

- *1st choice for use with dual purge & traps*[1]
- *EPA recommended surrogate used.*



GC_EV00428

20m, 0.18 mm ID, 1.00µm Rtx®-VMS (cat.# 49914)
Compounds in at 10ppb in 5mL of RO water
unless otherwise noted, ketones in at 2.5X

Concentrator:	Tekmar LSC-3100 Purge and Trap
Trap:	Vocarb 3000 (type K)
Purge:	11 min. @ 40mL/min. @ ambient temperature
Dry purge:	1 min. @ 40mL/min.
Desorb preheat:	245°C
Desorb:	250°C for 2 min., Flow 40mL/min.
Bake:	260°C for 8 min.
Interface:	transfer line 0.53mm ID Silcosteel® tubing 1:40 split at injection port. 1mm ID sleeve.
Oven temp.:	50°C (hold 4 min.) to 100°C @ 18°C/min. (hold 0 min.) to 230°C @ 40°C/min. (hold 3 min.)
Carrier gas:	helium @ ~1.0mL/min. constant flow

Adjust dichlorodifluoromethane to a retention time of 1.03 min. @
50«M,29[Degreeered Trademark]»C.

Detector:	HP 5973 MSD
Scan range:	35-300amu

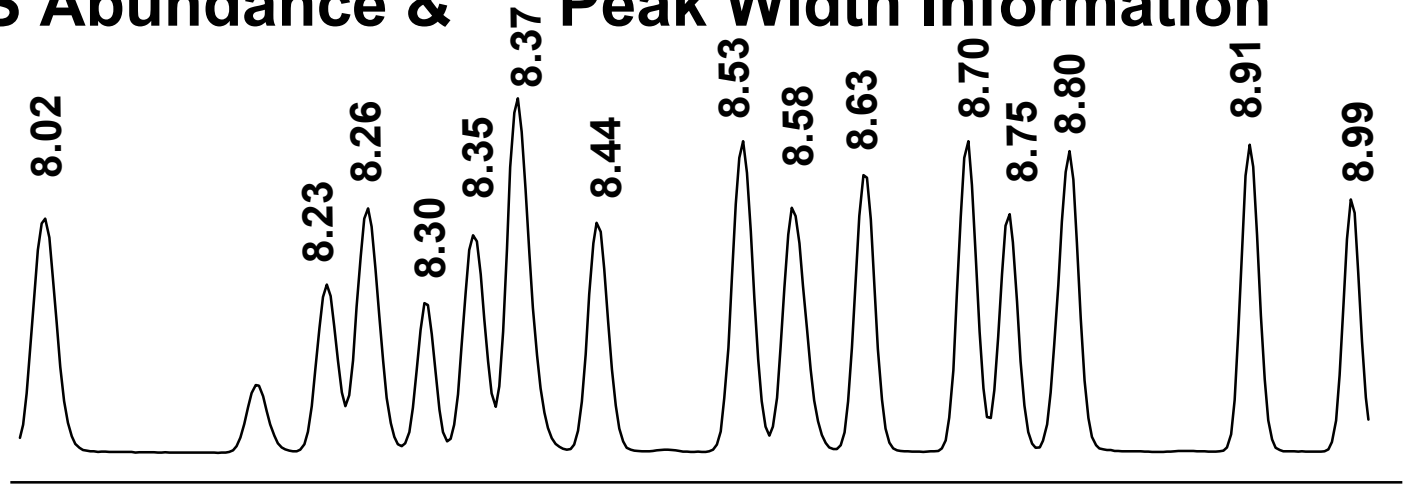
1. dichlorodifluoromethane
2. chloromethane
3. vinyl chloride
4. bromomethane
5. chloroethane
6. trichlorofluoromethane
7. ethanol (2500ppb)
8. 1,1-dichloroethene
9. carbon disulfide (40ppb)
10. allyl chloride
11. methylene chloride
12. acetone
13. *trans*-1,2-dichloroethene
14. methyl *tert*-butyl ether
15. *tert*-butyl alcohol (100ppb)
16. diisopropyl ether
17. 1,1-dichloroethane
18. acrylonitrile
19. vinyl acetate
20. allyl alcohol (250ppb)
21. ethyl-*tert*-buyl ether
22. *cis*-1,2-dichloroethene
23. 2,2-dichloropropane
24. bromochloromethane
25. chloroform
26. ethyl acetate
27. carbon tetrachloride
28. methyl acrylate
29. propargyl alcohol (500ppb)
30. dibromofluoromethane (SMC)
31. tetrahydrofuran
32. 1,1,1-trichloroethane
33. 2-butanone
34. 1,1-dichloropropene
35. benzene
36. pentafluorobenzene (IS)
37. *tert*-amyl-methyl ether
38. 1,2-dichloroethane
39. isobutyl alcohol (500ppb)
40. isopropyl acetate
41. trichloroethene
42. 1,4-difluorobenzene (SMC)
43. dibromomethane
44. 1,2-dichloropropane
45. bromodichloromethane
46. methyl methacrylate
47. *n*-propyl acetate
48. 2-chloroethanol (2500ppb)
49. *cis*-1,3-dichloropropene
50. toluene-d8(SMC)
51. toluene
52. pyridine (250ppb)
53. tetrachloroethene
54. 4-methyl-2-pentanone
55. *trans*-1,3-dichloropropene
56. 1,1,2-trichloroethane
57. ethyl methacrylate
58. dibromochloromethane
59. 1,3-dichloropropane
60. 1,2-dibromoethane
61. *n*-butyl acetate
62. 2-hexanone
63. 2-picoline (250ppb)
64. chlorobenzene-D5 (IS)
65. chlorobenzene
66. ethylbenzene
67. 1,1,1,2-tetrachloroethane
68. *m*-xylene
69. *p*-xylene
70. *o*-xylene
71. stryrene
72. bromoform
73. isopropylbenzene
74. 4-bromo-1-fluorobenzene (SMC)
75. bromobenzene
76. *n*-propylbenzene
77. 1,1,2,2-tetrachloroethane
78. 2-chlorotoluene
79. 1,3,5-trimethylbenzene
80. 1,2,3-trichloropropane
81. 4-chlorotoluene
82. *tert*-butylbenzene
83. pentachloroethane
84. 1,2,4-trimethylbenzene
85. *sec*-butylbenzene
86. *p*-isopropyltoluene
87. 1,3-dichlorobenzene
88. 1,4-dichlorobenzene-d4 (IS)
89. 1,4-dichlorobenzene
90. *n*-butylbenzene
91. 1,2-dichlorobenzene
92. 1,2-dibromo-3-chloropropane
93. nitrobenzene (250ppb)
94. hexachlorobutadiene
95. 1,2,4-trichlorobenzene
96. naphthalene
97. 1,2,3-trichlorobenzene

1A.L. Hilling and G. Smith, Environmental Testing & Analysis, 10(3), 15-19, 2001.

Rtx-VMS Abundance & Peak Width Information

The EZ-GC® computer program allows up to 100 compounds to be modeled on a single stationary phase under varying GC conditions & column dimensions with an excellent level of both precision and accuracy. Retention time, abundance, and peak width were loaded into EZ-GC®. The abundance and peak width values were determined from the Rtx-VMS chromatogram which was run using an HP5973 GC/MS system (see GC_EV00428 for specific conditions).

Rtx-VMS Abundance & Peak Width Information



Rtx-VMS Compounds Examined	RT (min.)	Peak Wi	MS Abundance (x 1000)
isopropylbenzene	8.02	0.045	440
bromobenzene	8.23	0.058	340
n-propylbenzene	8.26	0.055	460
1,1,2,2-tetrachloroethane	8.30	0.05	290
2-chlorotoluene	8.35	0.04	400
1,3,5-trimethylbenzene	8.37	0.045	440
1,2,3-trichloropropane	8.37	0.06	180
4-chlorotoluene	8.44	0.04	400
tert-butylbenzene	8.53	0.05	550
1,2,4-trimethylbenzene	8.58	0.055	440
sec-butylbenzene	8.63	0.045	525
p-isopropyltoluene	8.70	0.055	545
1,3-dichlorobenzene	8.75	0.04	460
1,4-dichlorobenzene	8.80	0.04	475
n-butylbenzene	8.91	0.055	501
1,2-dichlorobenzene	8.99	0.04	475

Peak Widths & Abundance Determined from Purge and Trap Analysis.

Rtx-VMS Model versus Actual Analysis

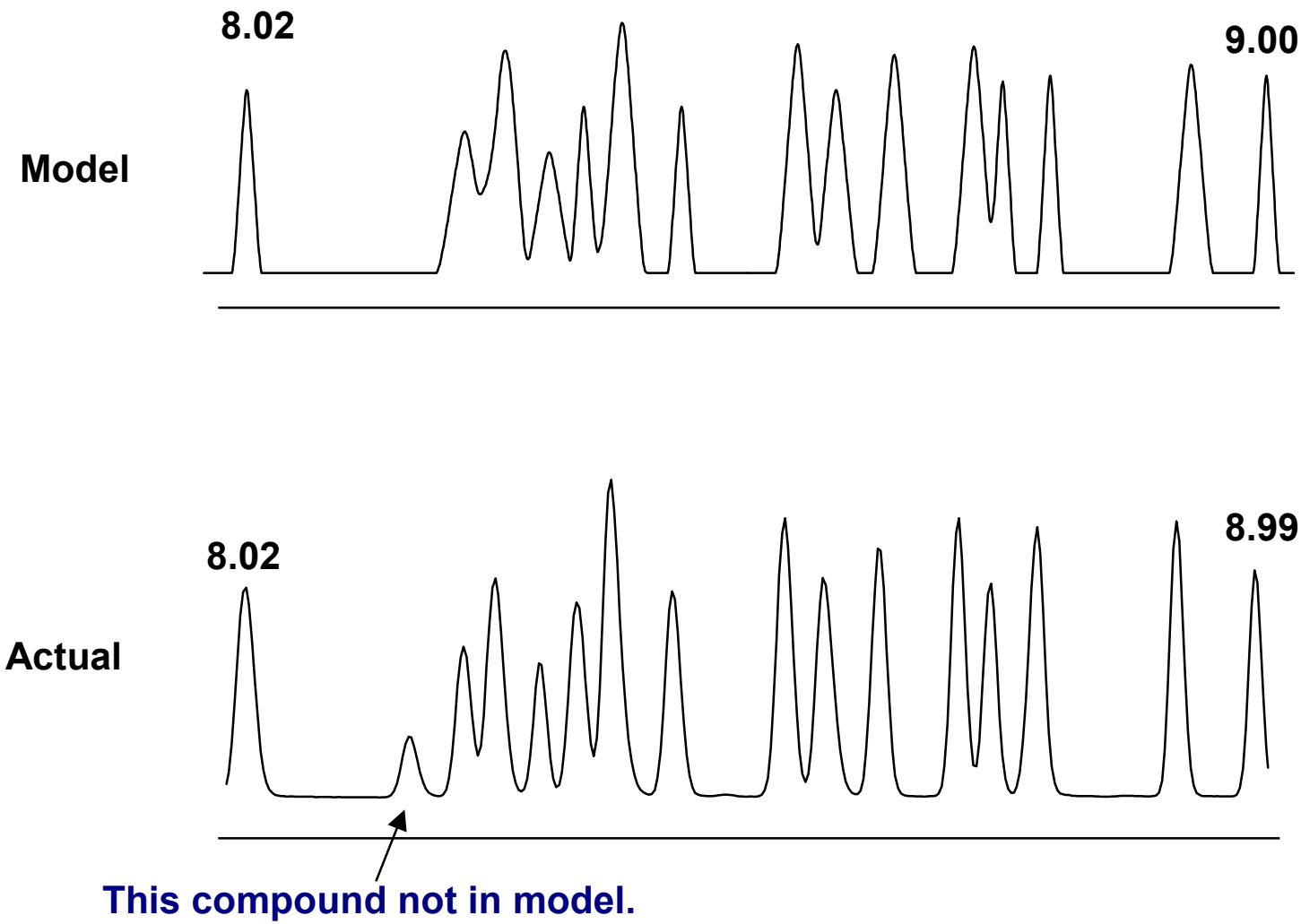
Using retention time indices specific to each of the stationary phases in combination with the abundance values & peak widths values from the VMS phase; model chromatograms were produced. Since column efficiency may change with each stationary phase – only differences in retention time will be examined. The abundance and peak width information was loaded into the program to produce sample chromatograms as a visual aid only.

The first step in the column comparison was to determine the effectiveness of EZ-GC® by comparing our known VMS chromatogram with a model. Retention times were collected for these compounds under fast and slow conditions and were entered into EZ-GC®. The application chromatogram was modeled using this fast/slow data. The diagram below shows the difference between the actual chromatogram and the model to be 0.01 minutes.

Rtx-VMS Model versus Actual Analysis

Rtx-VMS 20 m x 0.180 mm x 1.0 µm

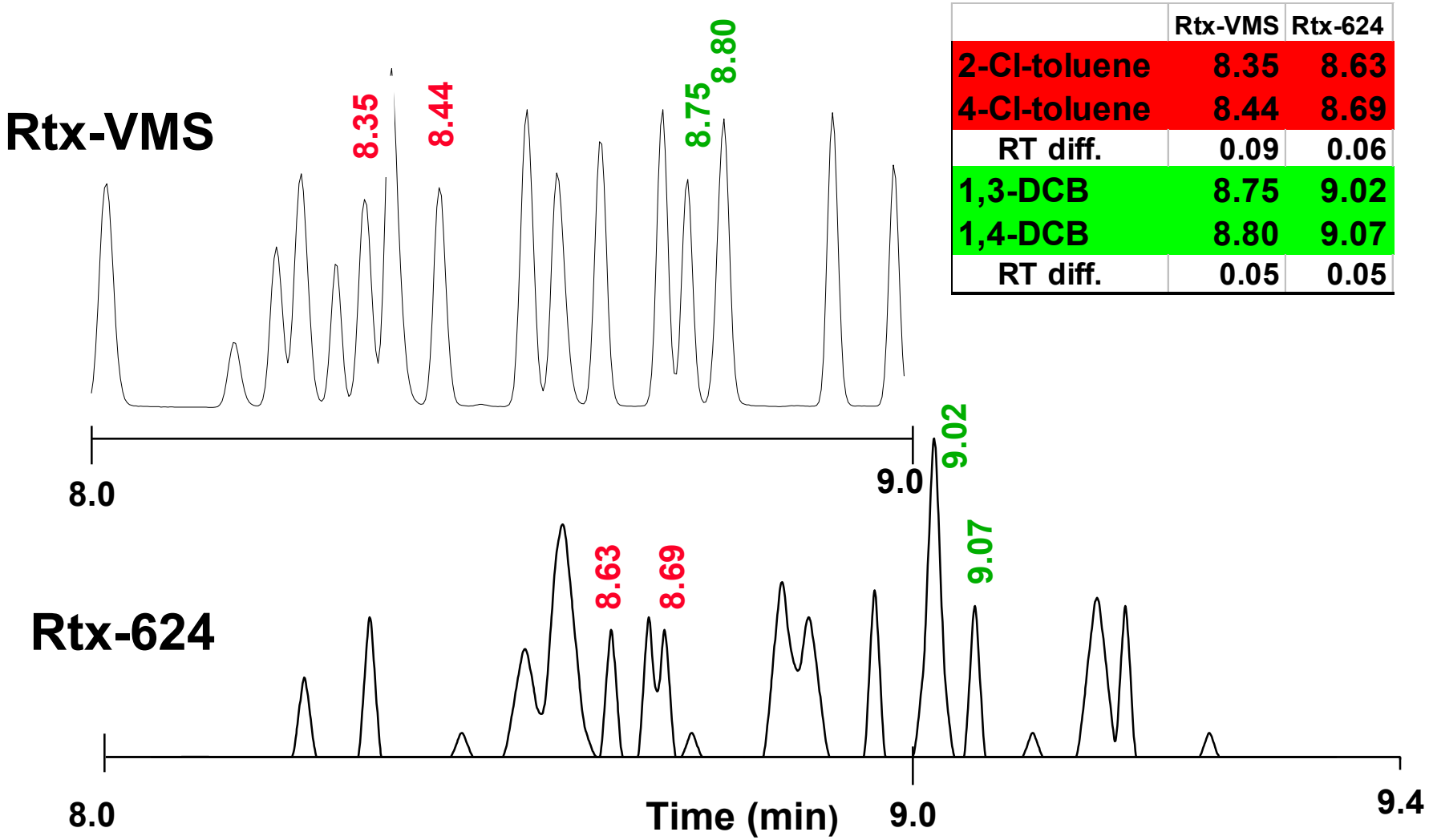
50°C (4) @ 18°C/min to 100°C @ 40°C/min to 230°C (1) Flow : ~ 1.0 ml/min



Rtx-VMS Compared to the Rtx-624

The change in retention between the chlorotoluenes modeled on the VMS & 624 phases is 0.03 minute, which in reality, constitutes a significant difference since this data is produced with a 20m x 0.18mm ID column with a 40°C/minute oven ramp rate. A faster final oven ramp rate is possible using the VMS phase since these compounds are well separated. Using a 60m x 0.53mm ID x 3.0df column for a direct comparison the difference between these phases is 0.9 minute. The 624 phase is suitable for fast dual-purge & trap applications. Analytes that share ions and coelute on the 624 phase and are resolved by the VMS include: ether/ethanol, vinyl acetate/ethyl-tert-butyl-ether & t-butyl alcohol/methyl-tert-butyl-ether. Several of these compounds require a lower starting oven temperature (35°C) using the VMS phase which is not shown in this application.

Rtx-VMS Compared to the Rtx-624

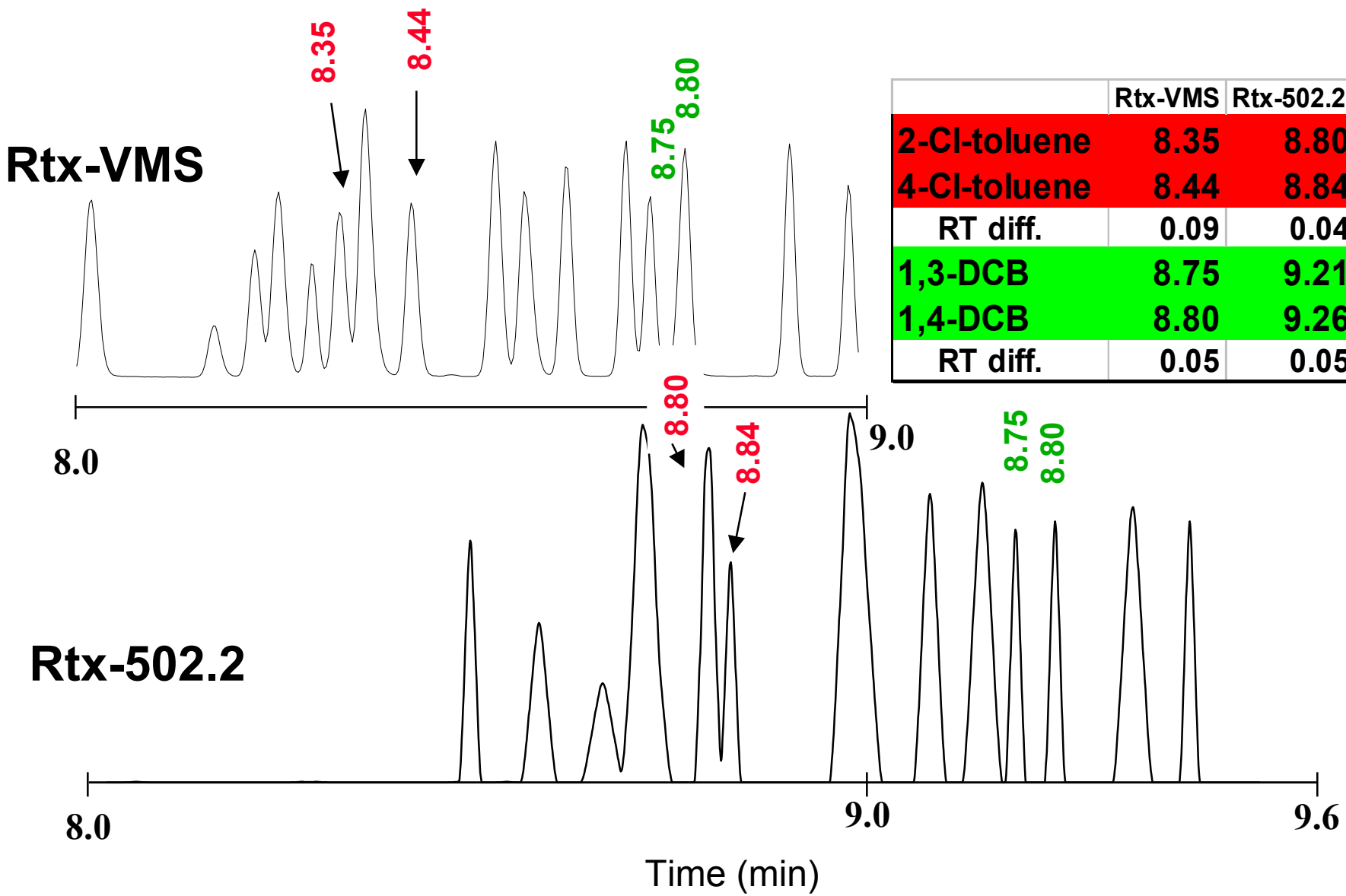


	Rtx-VMS	Rtx-624
2-Cl-toluene	8.35	8.63
4-Cl-toluene	8.44	8.69
RT diff.	0.09	0.06
1,3-DCB	8.75	9.02
1,4-DCB	8.80	9.07
RT diff.	0.05	0.05

Rtx-VMS Compared to the Rtx-502.2

The Rtx-502.2 is a cross-bonded diphenyl-methyl containing polysiloxane, which is particularly resistive to oxidative breakdown and exhibits lower bleed compared to the cyanopropyl-phenyl polysiloxanes (624phase). The disadvantage is the difficult resolution between bromomethane and chloroethane. Although our model indicates partial resolution between the chlorotoluenes under these run-conditions, linearity is effected over the concentration range. Slower final oven ramp rates will resolve these isomers, but it will sacrifice runtime.

Rtx-VMS Compared to the Rtx-502.2

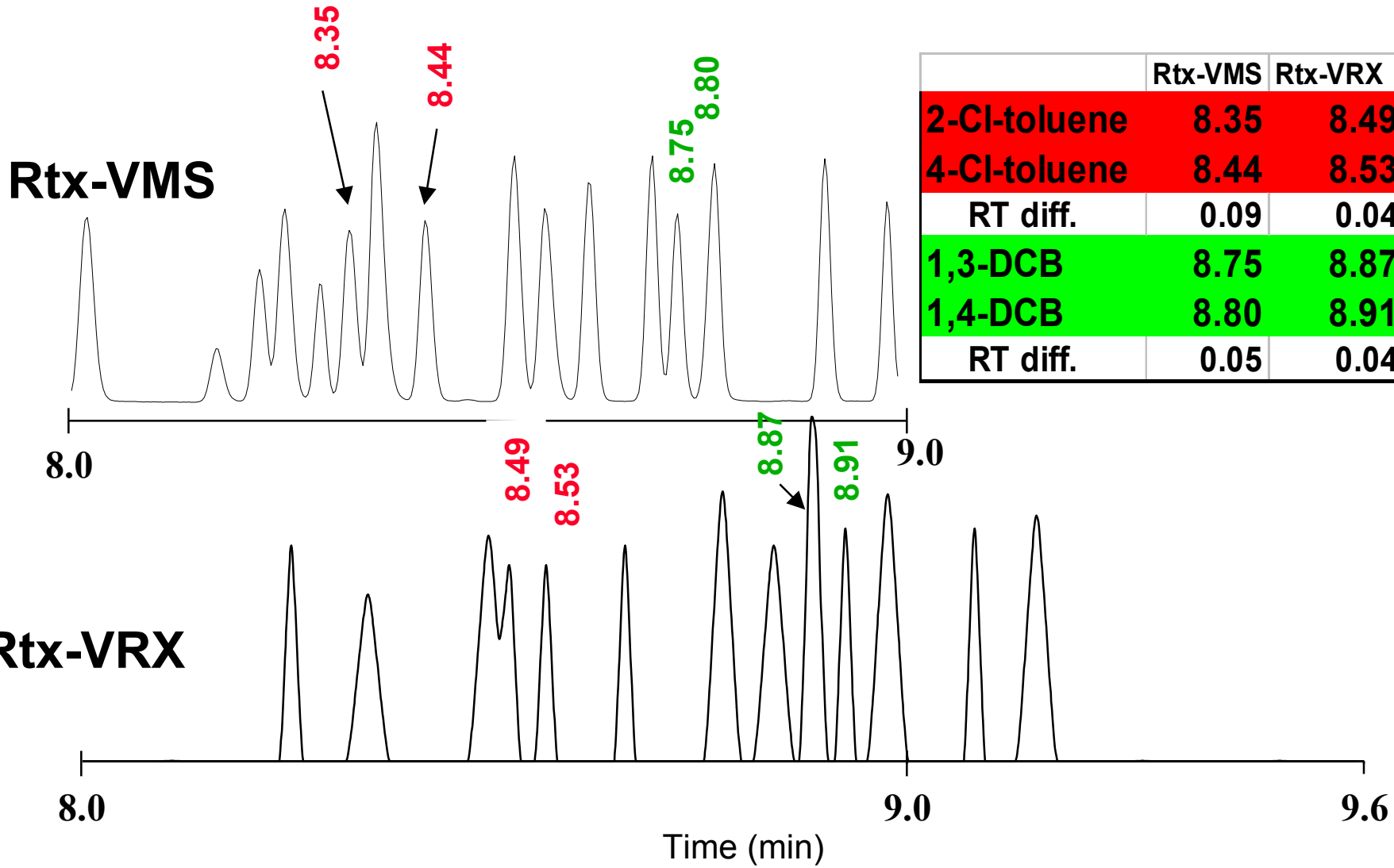


	Rtx-VMS	Rtx-502.2
2-Cl-toluene	8.35	8.80
4-Cl-toluene	8.44	8.84
RT diff.	0.09	0.04
1,3-DCB	8.75	9.21
1,4-DCB	8.80	9.26
RT diff.	0.05	0.05

Rtx-VMS Compared to the Rtx-VRX

The Rtx-VRX incorporates a low percentage of pentafluorobenzylpropyl- polysiloxane, which gives this column similar characteristics to an Rtx-1, only it resolves close eluting GC pairs such as 2,2-dichloropropane & chloroform. It is possible to do fast dual purge and trap applications using this phase as long as the recommended EPA internal standard, chlorobenzene-d5 is substituted with another compound. As shown in the direct comparison the Rtx-VMS does out-perform the VRX stationary phase for this application.

Rtx-VMS Compared to the Rtx-VRX

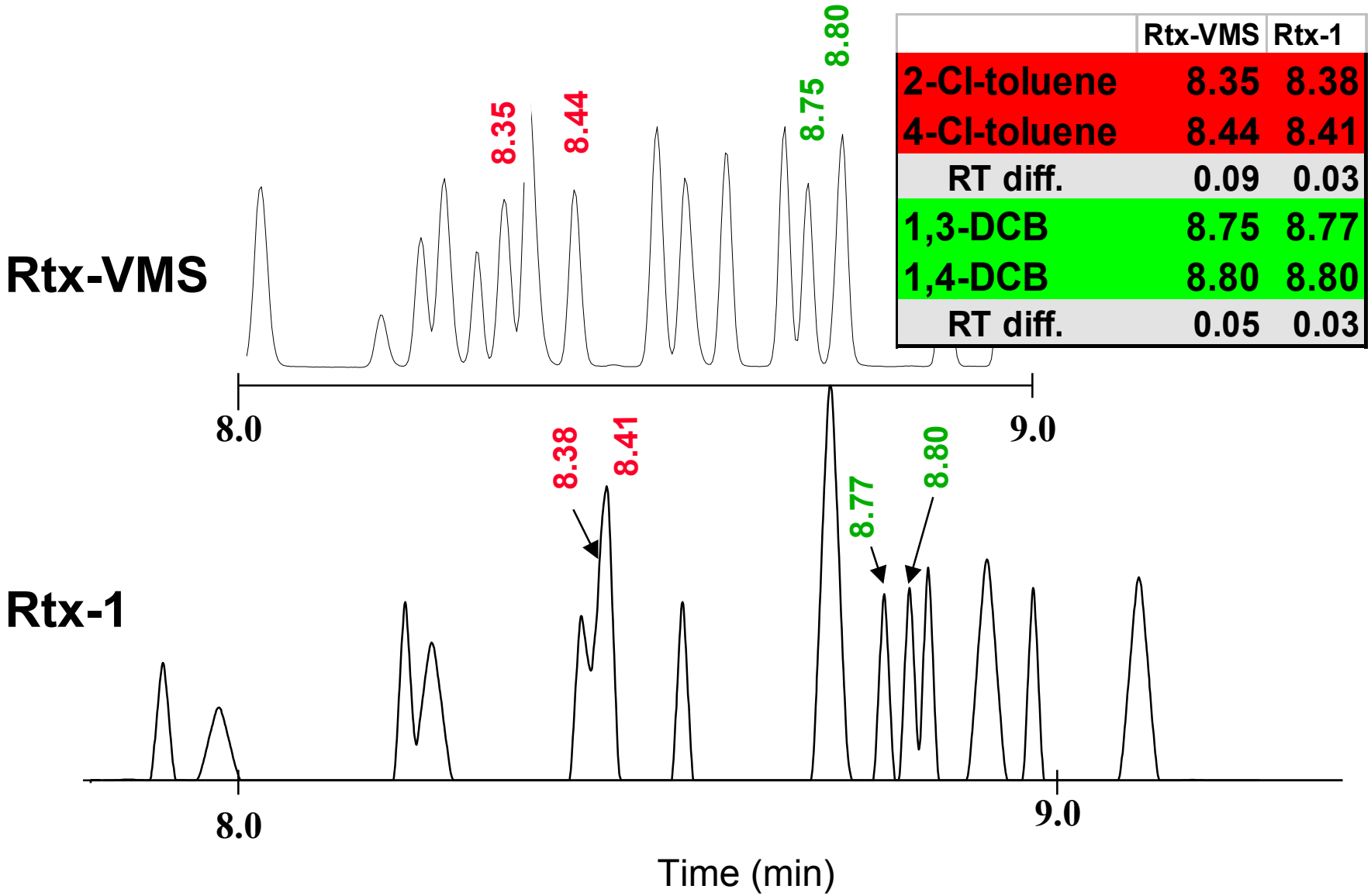


	Rtx-VMS	Rtx-VRX
2-Cl-toluene	8.35	8.49
4-Cl-toluene	8.44	8.53
RT diff.	0.09	0.04
1,3-DCB	8.75	8.87
1,4-DCB	8.80	8.91
RT diff.	0.05	0.04

Rtx-VMS Compared to the Rtx-1

Although the 100% dimethyl-polysiloxane (Rtx-1) polymer is unchallenged for air analysis, this phase does not perform well for fast purge and trap analysis. Like the VRX phase chlorobenzene-d5 & 1,1,1,2-tetrachloroethane are poorly resolved as are the isomers shown.

Rtx-VMS Compared to the Rtx-1



	Rtx-VMS	Rtx-1
2-Cl-toluene	8.35	8.38
4-Cl-toluene	8.44	8.41
RT diff.	0.09	0.03
1,3-DCB	8.75	8.77
1,4-DCB	8.80	8.80
RT diff.	0.05	0.03

The VMS phase has the best resolution of isomeric pairs and other target compounds for US EPA Method 8260B.

Rtx-VMS – Best Resolution of Isomeric Pairs.

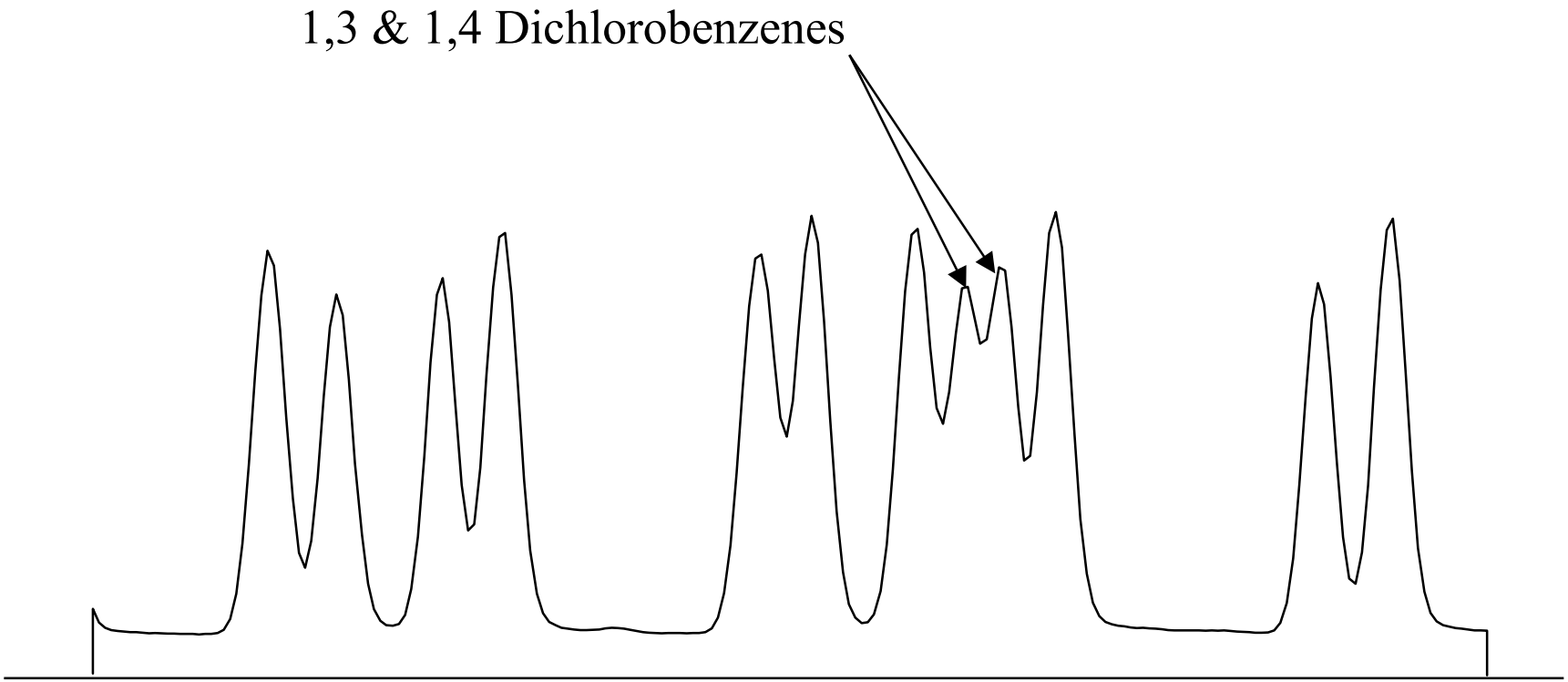
COMPOUND	Shared Ions	Rtx-VMS	Rtx-624	Rtx-502.2	Rtx-VRX	Rtx-1
Chlorobenzene-d5	117	7.34	7.62	7.90	7.34	7.25
1,1,1,2-tetrachloroethane	117	7.42	7.70	7.93	7.39	7.24
RT diff.		0.08	0.08	0.07	0.04	0.01
2-chlorotoluene	126,91	8.35	8.63	8.80	8.49	8.38
4-chlorotoluene	126,91	8.44	8.69	8.84	8.53	8.41
RT diff.		0.09	0.06	0.04	0.04	0.03
1,3-dichlorobenzene	146	8.75	9.02	9.21	8.87	8.77
1,4-dichlrorobenzene	146	8.80	9.07	9.26	8.91	8.80
RT diff.		0.05	0.05	0.05	0.04	0.03

A Candidate for Volatile Applications Fails for Resolution of the DCBs.

One of our attempts to build a column suitable for fast volatile analysis met all of the design criteria except for the resolution between the dichlorobenzenes.

Experimental Fluorinated Phase

A Candidate for Volatile Applications Fails for Resolution of the DCBs.



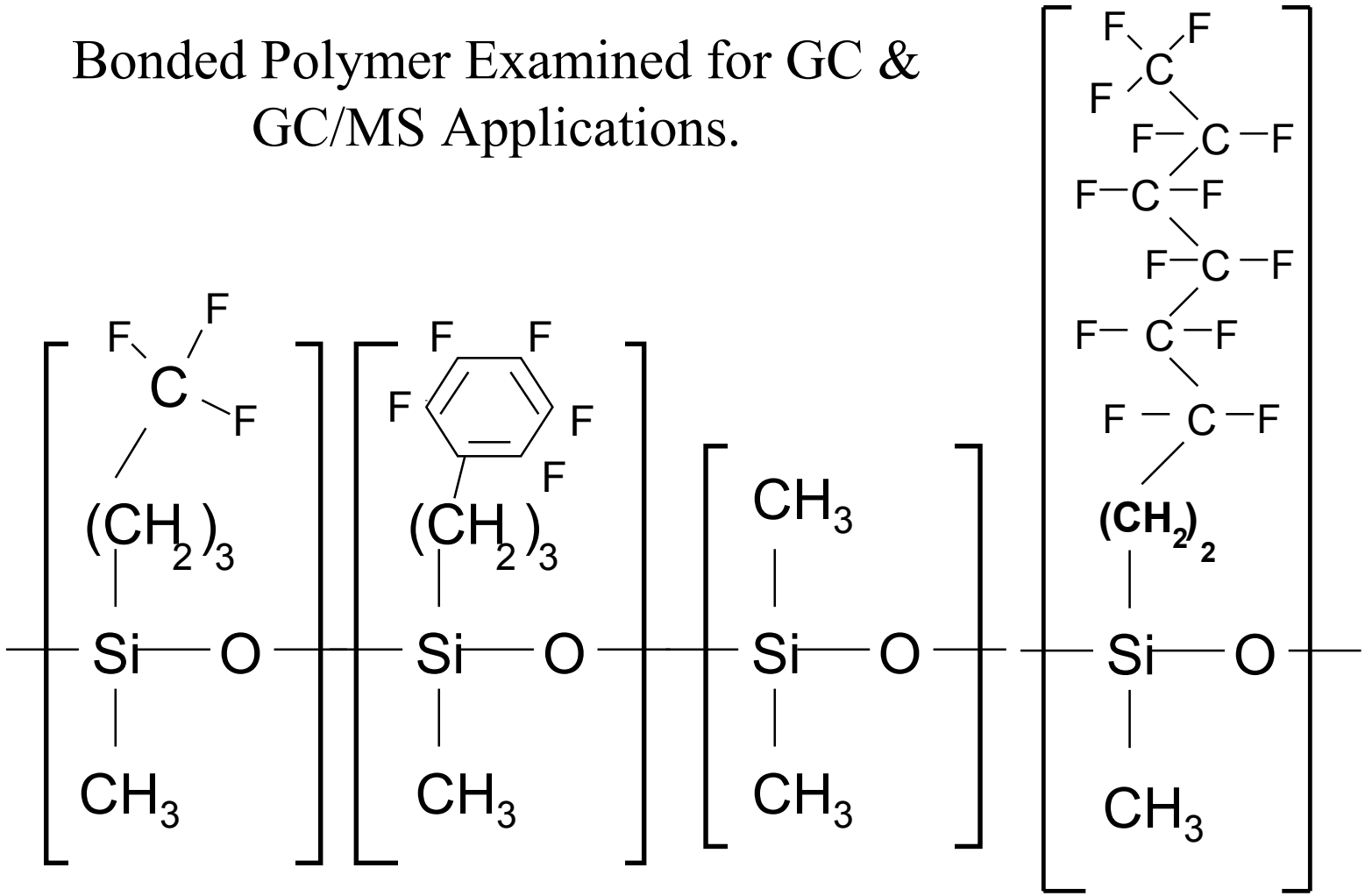
Experimental Fluorinated Phase

Bonded Polymer Examined for Volatile Applications.

This phase was built based on predictions of separation. The separation criteria was met on all accounts except for the dichlorobenzenes. The first step in designing a new column is to start with functionalities that the target analytes are soluble in. The better the solubility between the analyte and the phase the better the chances of resolving these compounds.

Experimental Fluorinated Phase

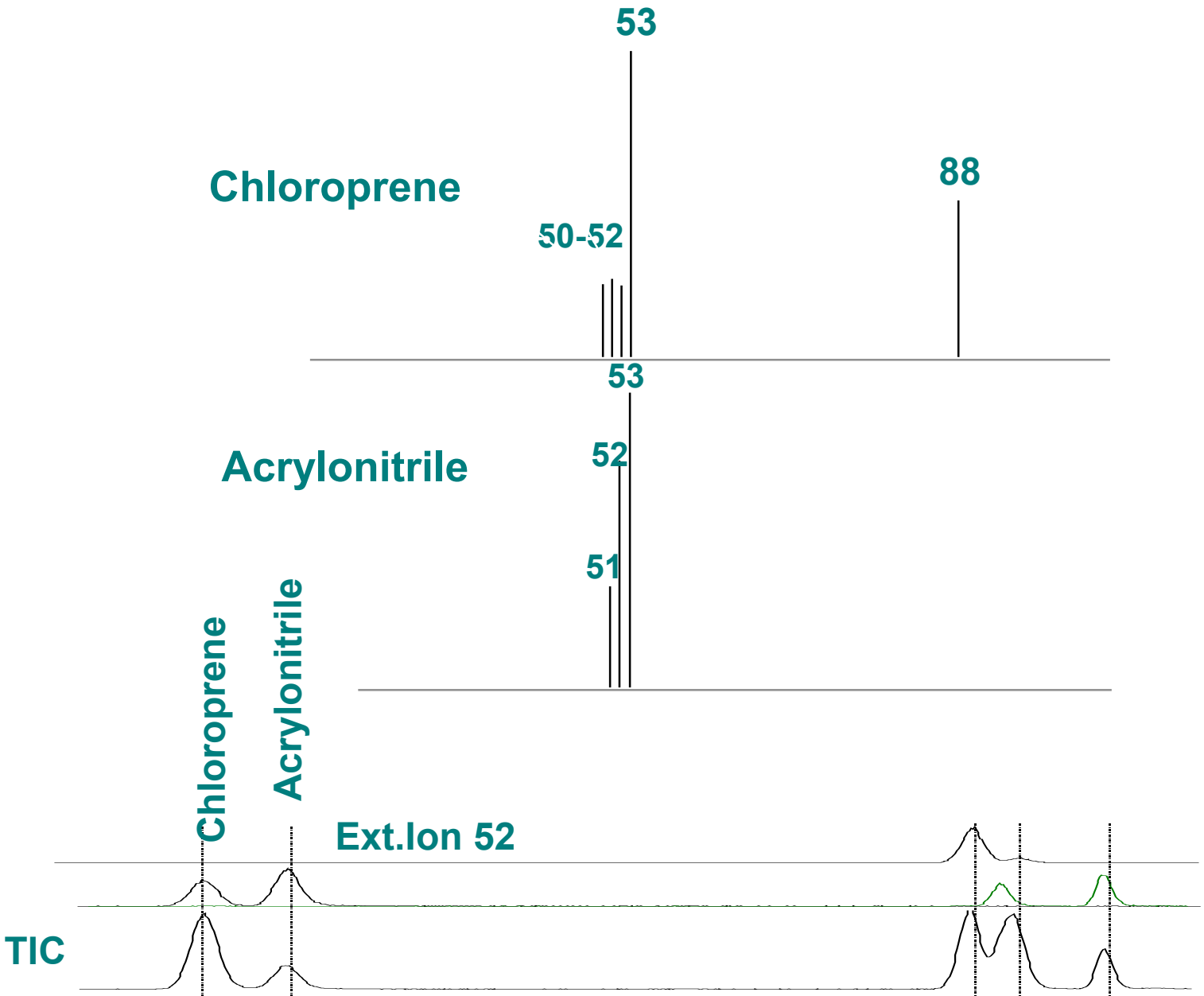
Bonded Polymer Examined for GC & GC/MS Applications.



Rtx-VMS Column Meets Design Criteria

The successful polymer known as the VMS phase not only met the resolution criteria for the isomeric pairs but also exceeded separations of critical pairs. The percentage of functionality was adjusted to resolve chloroprene and acrylonitrile.

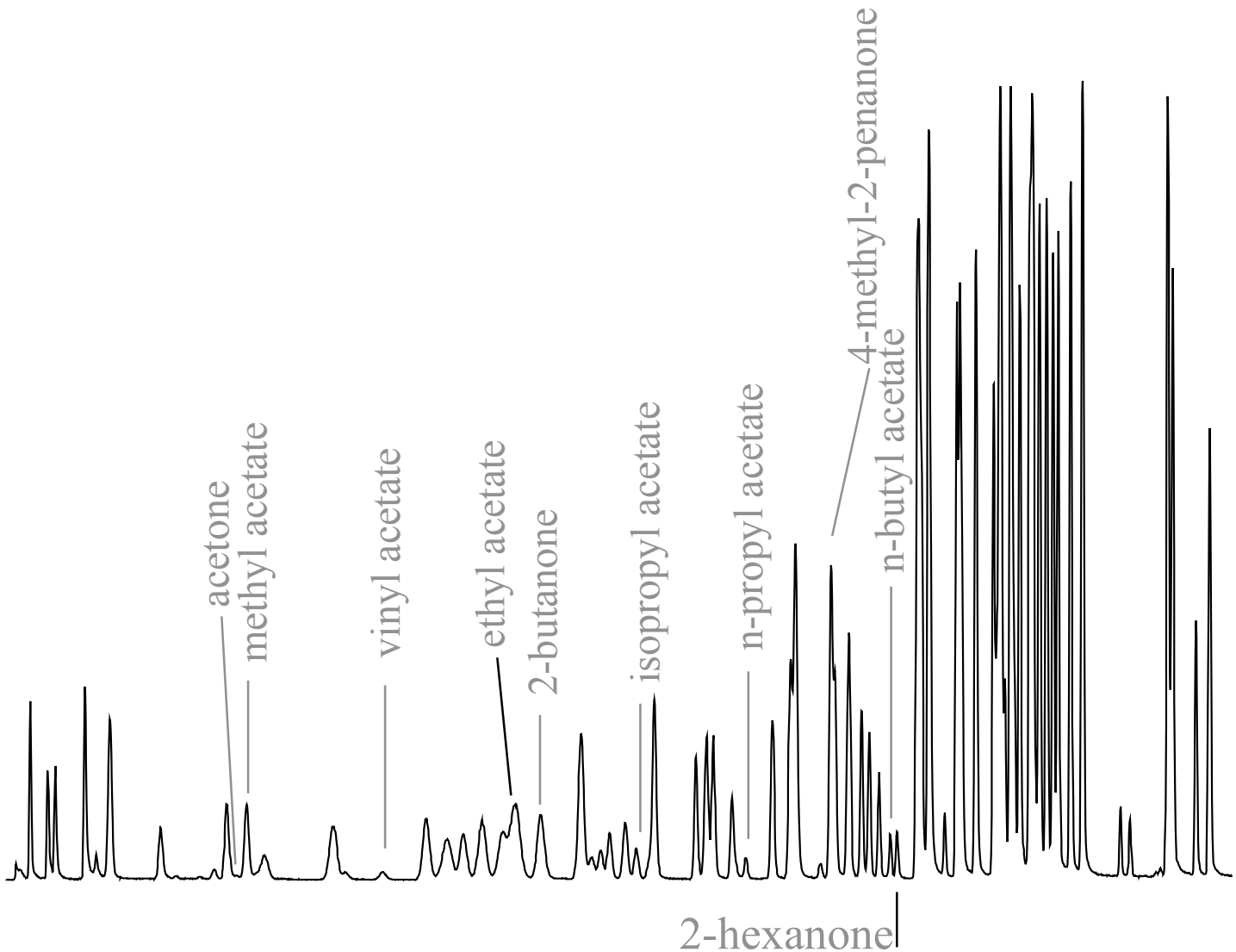
Rtx®-VMS Critical Pairs with Common Ions



Rtx-VMS Resolution of Acetates & Ketones.

Since the acetates and ketones share the spectral ion 43 its important that these analytes are resolve. The diagram shows the elution of the most commonly analyzed acetates and ketones.

Acetates & Ketones Share ion 43



Rtx-VMS Designed for EPA Method 8260B

The Rtx-VMS column was designed to address the increasing number of analytes listed in EPA Method 8260B, and also is a good choice for separating compounds listed in EPA Method 524.2, revision IV. The major difference between the Rtx-VMS phase and others such as the “624,” “502.2,” and “VRX” is its overall selectivity and the distance between isomeric pairs like 2/4-chlorotoluene. A faster final oven ramp rate is possible because these compounds elute farther apart on the Rtx-VMS phase, preventing a partial coelutions that would interfere with quantitation. Using the EPA-suggested surrogates the analysis time is under 10 minutes making this the clear choice for fast GC applications.

For More Information...

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