Fast Analysis of Volatiles by Gas Chromatography Using US EPA Methods 502.2 & 8021

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ABSTRACT

Traditionally, column development has relied on analyzing a list of compounds using all existing stationary phases, and then choosing the column that produces the best separation. Also, with the recent changes in US EPA methods for the analysis of volatile compounds using GC/PID-ELCD, many laboratories struggle to achieve resolution of a continually expanding compound list. All of the current phases available for these types of analyses suffer from lack of resolution between critical compounds, and many suffer from low thermal stability and long analysis times. With the aid of computer stationary phase modeling, existing polymers, combinations of polymers, and new functionalities can be tailored to the application—to give unsurpassed separation of specific compounds of interest.

Disinfectant by-products of drinking water, known as the trihalomethanes (THM), are the most commonly found contaminants in the public water supply. They must be well resolved from other target analytes to prevent poor compound quantitation of "real-world" samples. All other currently available columns either have unacceptable resolution or coelutions of these ubiquitous compounds with other analytes in the method compound list. This paper will discuss an alternative Volatile GC column that addresses these issues. It is designed using computer modeling and results in a column with unsurpassed resolution and fast analysis for all compounds listed in US EPA Methods 502.2 and 8021. Method-specific chromatograms will be presented, including "added" compounds commonly requested with these analysis.

INTRODUCTION

US EPA Methods 502.2 and 8021 employ purge and trap to concentrate volatile contaminants in water, soil and wastewater. While purge and trap significantly increases sensitivity relative to other sample introduction techniques, it has its downside. Early eluting volatile compounds typically exhibit broad peak shapes due to inefficient sample transfer from the trap to the gas chromatograph (GC). This distorted peak shape decreases resolution between closely eluting compounds, placing demands on the analytical system and GC operating conditions.

US EPA GC methods for the determination of volatiles often recommend the use of photoionization detector (PID) and an electrolytic conductivity detector (ELCD) installed in series on the GC system. The PID responds to aromatics, alkene, alkynes and oxygenates. The ELCD detector is sensitive to halogenated compounds. Therefore, it is allowable to have coelutions on an analytical column as long as they can be resolved using separate detectors. The most problematic of these two detectors is the ELCD because of the characteristic peak tailing; sensitivity can be increased on the ELCD, but not without a sacrifice in peak shape. Optimization of this detector results in minimized tailing and maximized sensitivity. Even under these conditions, choosing an analytical column that can give reasonable separation of these halogenated compounds is difficult.

The Rtx®-VGC column is specifically designed to analyze volatiles using GC/PID/ELCD. The phase is optimized to achieve excellent separation of gases and early eluting compounds, specifically the four critical trihalomethanes (chloroform, bromodichloromethane, dibromochloromethane and bromoform). The column also provides unsurpassed separation in the fastest analysis time and cycle time, thereby increasing sample throughput.

EXPERIMENTAL

Several factors contribute to the total analysis time of volatile separations, such as purge and trap cycle time, GC runtime, GC oven cool down time (time it takes for the GC to cool down to the initial oven temperature) and column length. Long purge and trap cycles result from lengthened purge times, dry purges, long desorb times, and long trap bakes. Long oven cycle times result from low initial oven temperatures (from subambient to 35°C), slow temperature program rates, and low column operating temperatures. Although cryofocusing improves the separation of early eluting compounds, most environmental laboratories do not use it because it increases cost and cycle time. And, while a certain column length is necessary for separation, a column that is too long can increase analysis time and cost without a significantly increasing resolution.

The Rtx®-VGC provides the best GC separations and fastest analysis time of target compounds found in US EPA Method 8021 & 502.2. Application #1 shows the Rtx®-VGC as the primary column and the Rtx-VRX as a confirmation column. The target list includes commonly analyzed, but unregulated compounds, such as methyl-*tert*-butyl ether (MTBE) and Freon® 113. This application shows the separation of the gases and the trihalomethanes — there are no coelutions using the PID/ELCD detectors in series.

Application #2 shows the analysis of the 8021A / 502.2 compound list without the addition of Freon® 113. This allows for a 50°C starting temperature which greatly reduces the total cycle time — that is the time it takes for the GC to complete the oven cycle and come back down to starting temperature. The time it takes a Hewlett-Packard 5890 GC oven to cool from 205°C down to 35°C is 9 minutes. That time, added to the analysis time in Application #1 of 28 minutes results in the fastest possible total cycle time of 37 minutes. Application #2 has a final temperature of 200°C and a starting temperature of 50°C. The time it takes for the oven to cool down is 4 minutes. The application has a total cycle time of under 30 minutes, significantly faster than any other column available. For instance, the VRX stationary phase requires a starting temperature of 40°C. This combined with the 28 minute runtime ensures that the total cycle time can not be faster than 35 minutes. This faster sample throughput allows environmental laboratories to make at least 4 more runs-per-day over other volatile columns with better data quality.

Client compound lists may remain the same as the compound list given by Method 601/602, however, the calibration criteria and low detection limits of Method 8021 are enforced. Application #3 illustrates a common list of compounds analyzed by GC/PID-ELCD, along with the addition of 2-chloro-ethyl-vinyl ether. The starting temperature to aquire these chromatogram was 40°C with a runtime of 20 minutes.

These chromatograms (Application #5) incorporated a broader range of analytes, many of those compounds are found in US EPA Method 8021B, along with other requested compounds such as 1 & 2 methyl-naphthalene. There are 72 target compounds in this list, coelutions on the Rtx®-VGC are resolved on the Rtx®-502.2 column. Even with the addition of the semi-volatile methylnaphthalenes the runtime is still under 30 minutes.

CONCLUSION

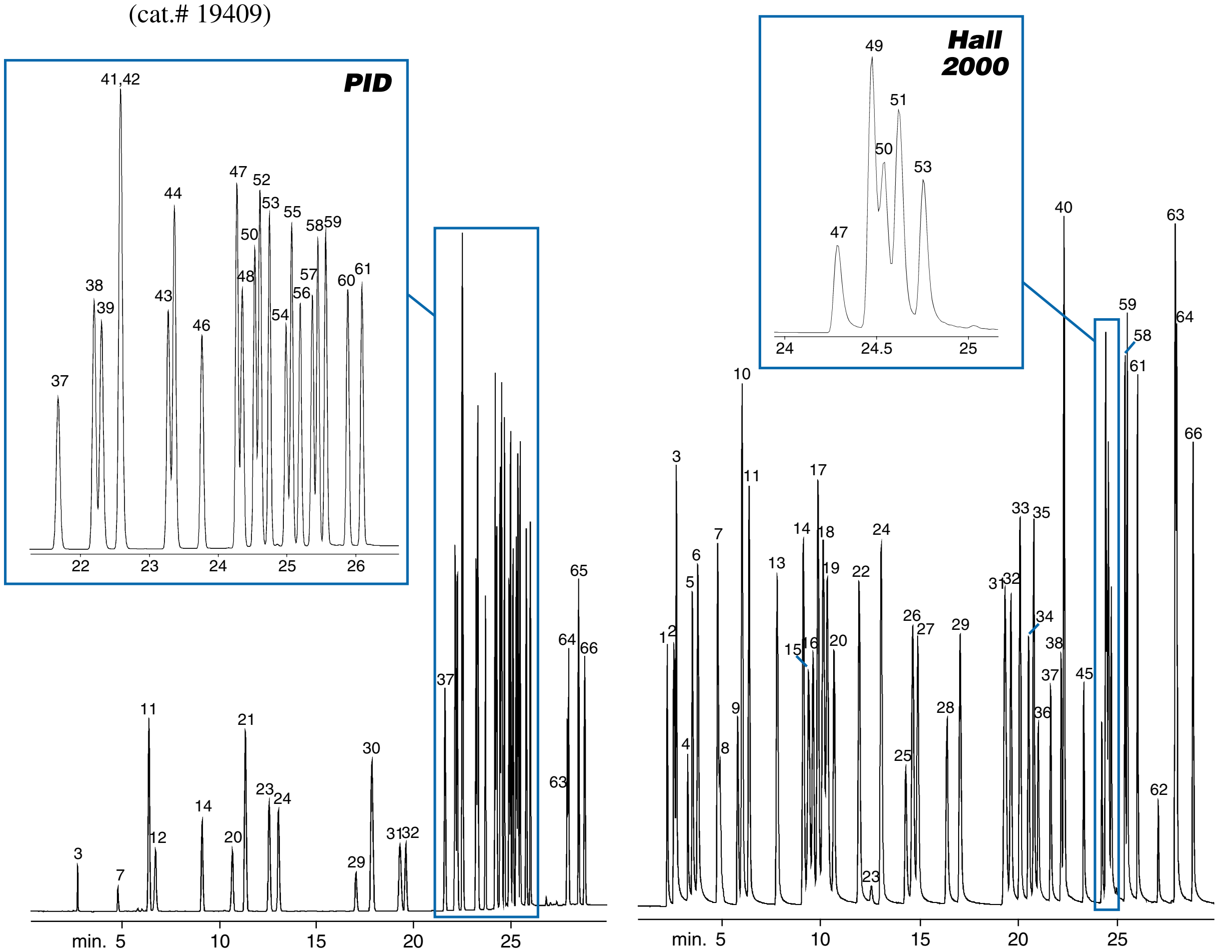
Disinfectant by-products of drinking water – known as the trihalomethanes (THMs) – are the most commonly found contaminants in the public water supply. These four compounds: chloroform, bromodichloromethane, dibromochloromethane and bromoform are found in all treated municipal drinking water. The THMs must be well resolved from other volatile organic pollutants to prevent poor quantitation, inaccurate data, or mis-identification. All other columns exhibit partial or complete coelutions of the THM's with other target analytes even under optimized conditions. The Rtx®-VGC column provides better than 85% resolution of the THMs from other volatile compounds (application #1).

The Rtx®-VGC column provides 30% resolution of 1,1,2,2-tetrachloroethane/2-chlorotoluene and greater than 60% resolution of all other volatile compounds found in US EPA Methods 502.2 and 8021. This column provides the best resolution in less time than any other column commercially available.

Application #1

Volatile Organics EPA Method 8021 Rtx®-VGC

Rtx®-VGC
75m, 0.45mm ID, 2.55µm
(cat.# 19409)



1. dichlorodifluoromethane
2. chloromethane
3. vinyl chloride
4. bromomethane
5. chloroethane
6. trichlorofluoromethane
7. 1,1-dichloroethene
8. Freon® 113
9. allyl chloride
10. methylene chloride
11. *trans*-1,2-dichloroethene
12. methyl *tert*-butyl ether
13. 1,1-dichloroethane
14. *cis*-1,2-dichloroethene
15. 2,2-dichloropropane
16. bromochloromethane
17. chloroform
18. carbon tetrachloride
19. 1,1,1-trichloroethane
20. 1,1-dichloropropene
21. benzene
22. 1,2-dichloroethane
23. fluorobenzene (SS)
24. trichloroethene
25. dibromomethane
26. 1,2-dichloropropane
27. bromodichloromethane
28. 1-bromo-2-chloroethane (SS)
29. *cis*-1,3-dichloropropene
30. toluene
31. tetrachloroethene
32. *trans*-1,3-dichloropropene
33. 1,1,2-trichloroethane
34. dibromochloromethane
35. 1,3-dichloropropane
36. 1,2-dibromoethane
37. 1-chloro-3-fluorobenzene (SS)
38. chlorobenzene
39. ethylbenzene
40. 1,1,1,2-tetrachloroethane
41. *m*-xylene
42. *p*-xylene
43. *o*-xylene
44. stryrene
45. bromoform
46. isopropylbenzene
47. bromobenzene
48. *n*-propylbenzene
49. 1,1,2,2-tetrachloroethane
50. 2-chlorotoluene
51. 1,2,3-trichloropropane
52. 1,3,5-trimethylbenzene
53. 4-chlorotoluene
54. *tert*-butylbenzene
55. 1,2,4-trimethylbenzene
56. *sec*-butylbenzene
57. *p*-isopropyltoluene
58. 1,3-dichlorobenzene
59. 1,4-dichlorobenzene
60. *n*-butylbenzene
61. 1,2-dichlorobenzene
62. 1,2-dibromo-3-chloropropane
63. hexachlorobutadiene
64. 1,2,4-trichlorobenzene
65. naphthalene
66. 1,2,3-trichlorobenzene

20ppb in 5mL of RO water.
primary column: 75m, 0.45mm ID, 2.55µm Rtx®-VGC (cat.# 19409)
confirmation column: 75m, 0.45mm ID, 2.55µm Rtx®-VRX (cat.# 19309)
Concentrator: Tekmar LSC-3000 Purge and Trap
Trap: Vocarb™ 3000;
Purge: 11 min. @ 40mL/min.
Dry purge: 1 min. @ 40mL/min. (MCS by-passed with Silcosteel® tubing [cat.# 21035])
Desorb preheat: 245°C;
Desorb: 250°C for 2 min.
Bake: 260°C for 8 min.
Interface: direct
Transfer line: 0.32mm ID Siltek™ tubing
GC: Finnigan 9001
Oven temp.: 35°C (hold 4 min.) to 75°C @ 3°C/min. (hold 2 min.) to 175°C @ 21°C/min. to 205°C @ 35°C/min. (hold 5 min.)
Carrier: helium 11mL/min., constant pressure
Adjust dichlorodifluoromethane to a retention time of 2.28 min. @ 35°C on the Rtx-VGC column.
Detectors: µGold Tandem PID/HALL
PID: makeup 7mL/min., purge 7mL/min., set @ 0.35mV, base temp 200°C.
Hall 2000: RxnGas 25mL/min., RxnTemp.: 940°C, propanol flow 470µL/min.

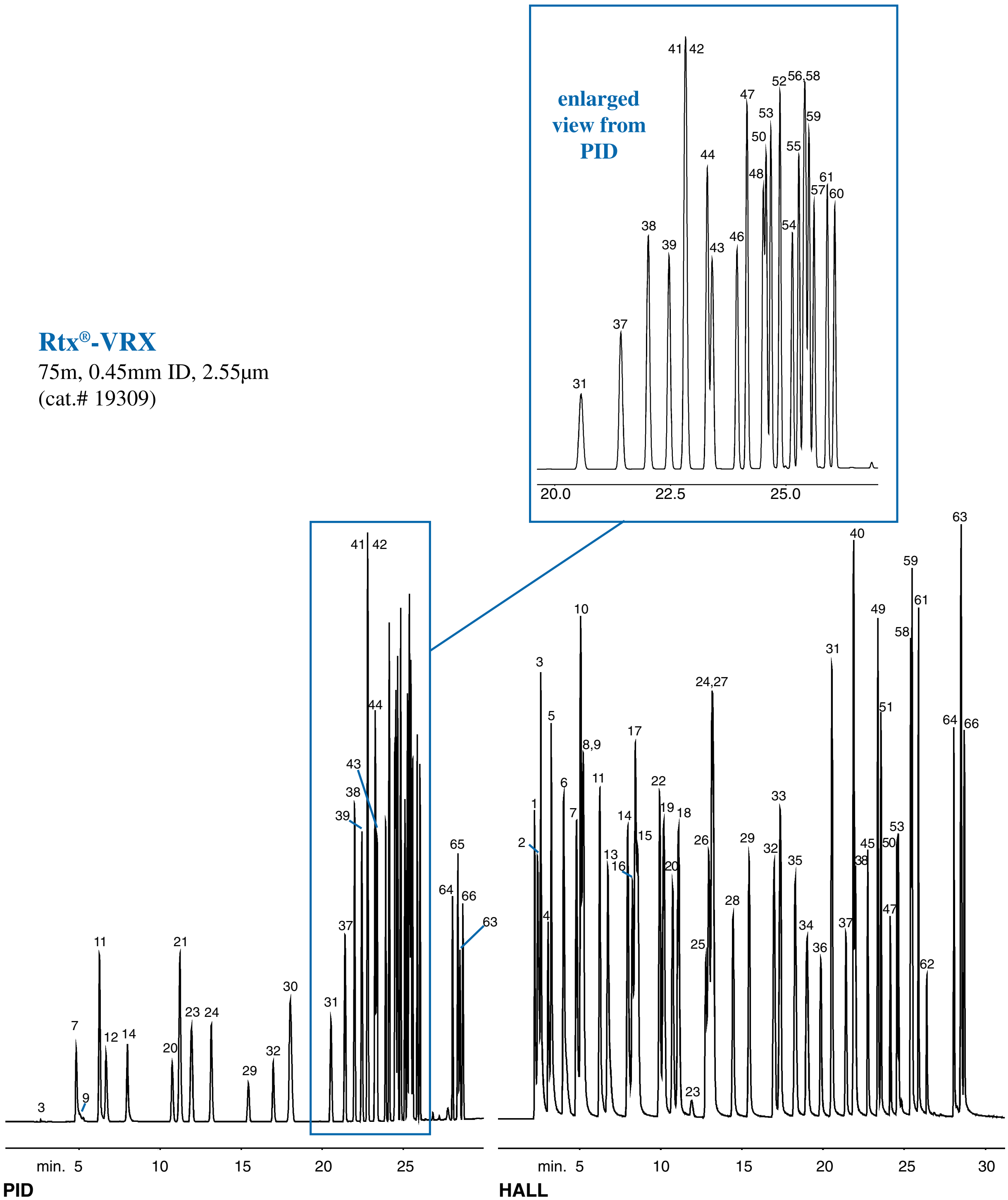
Acknowledgement: *Finnigan 9001 GC, µGold Tandem Photoionization Detector & Hall 2000 Detector provided courtesy of ThermoQuest/CE Instruments, 2215 Grand Avenue Parkway, Austin, TX 78728.*

Application #1

Volatile Organics EPA Method 8021 Rtx®-VRX

Confirmational column to the Rtx®-VGC

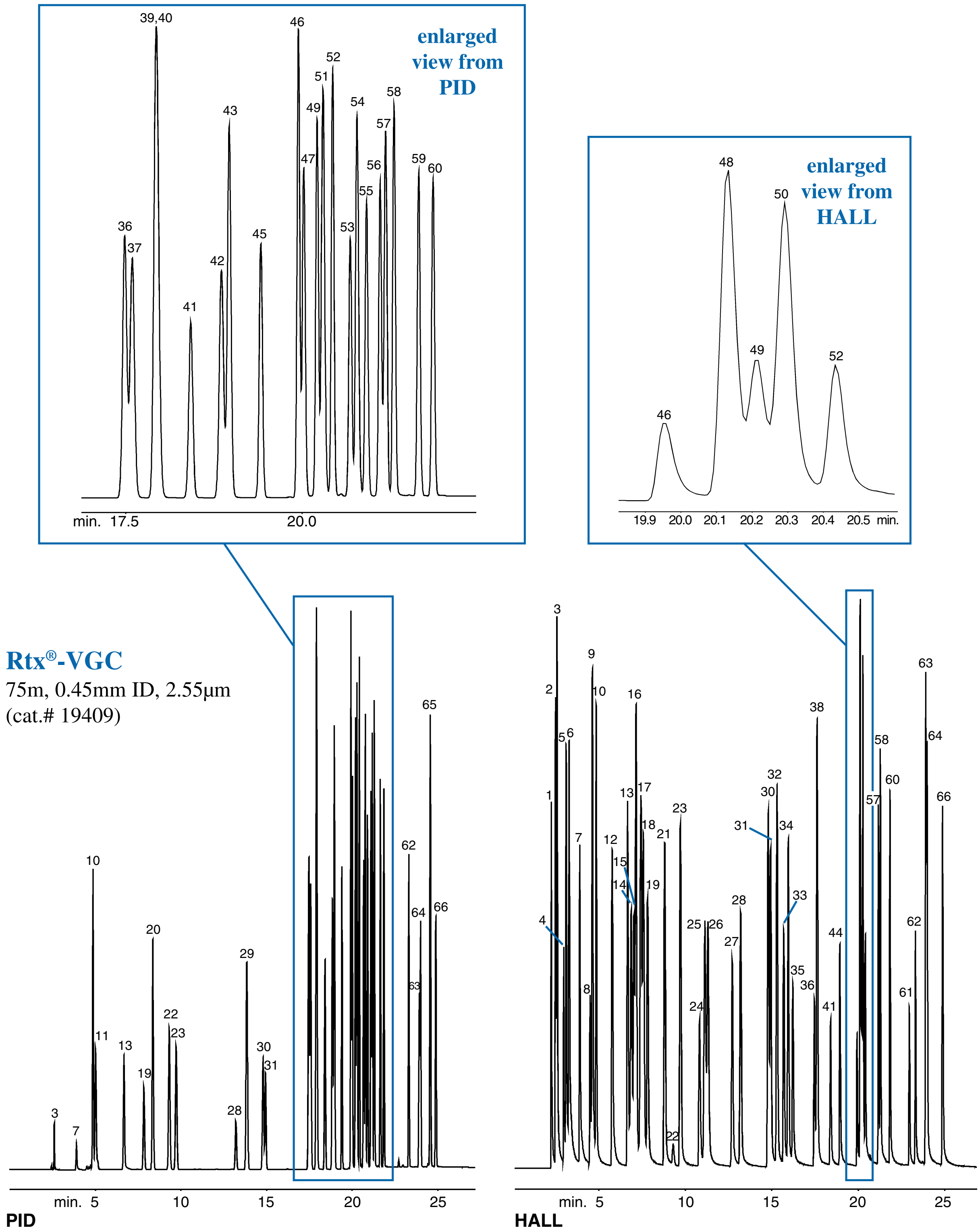
Rtx®-VRX
75m, 0.45mm ID, 2.55µm
(cat.# 19309)



Acknowledgement: *Finnigan 9001 GC, µGold Tandem Photoionization Detector & Hall 2000 Detector provided courtesy of ThermoQuest/CE Instruments, 2215 Grand Avenue Parkway, Austin, TX 78728.*

Application #2

Volatile Organics EPA Method 8021A/502.2 Rtx®-VGC



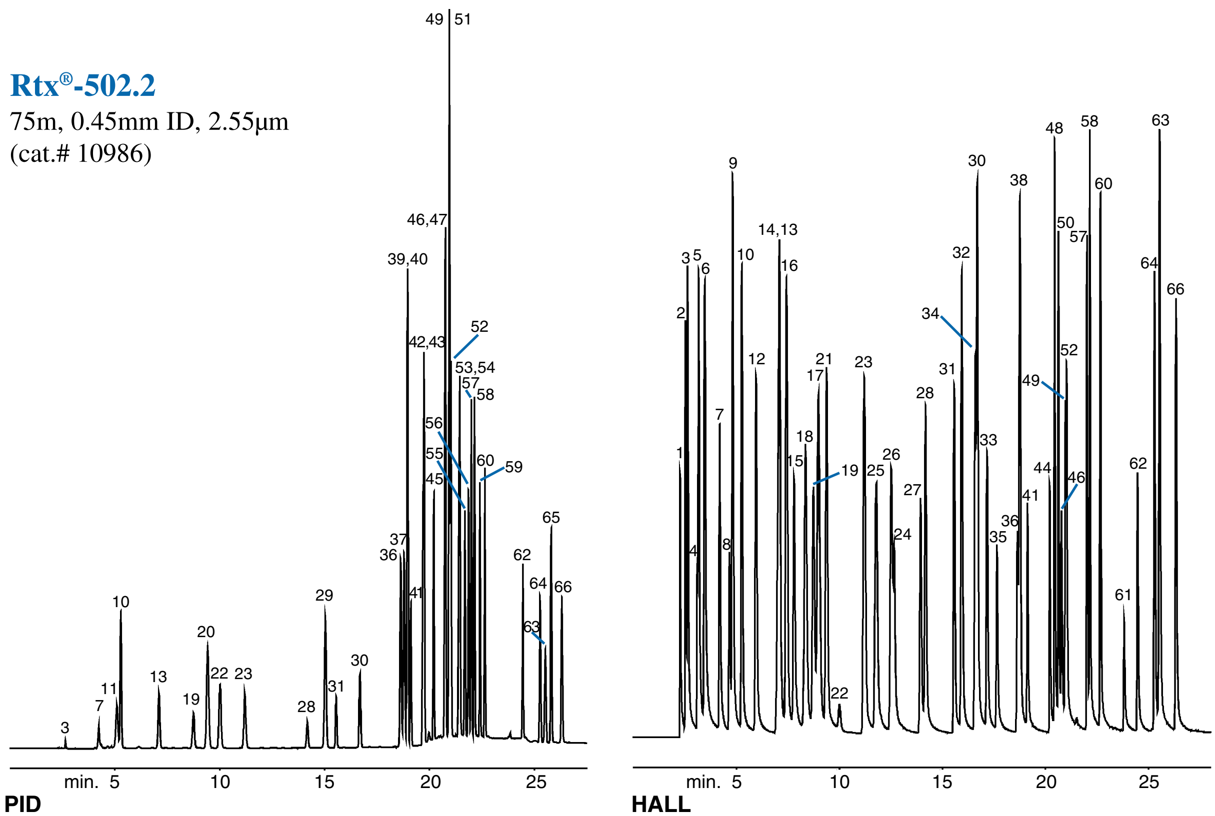
Rtx®-VGC
75m, 0.45mm ID, 2.55µm
(cat.# 19409)

Acknowledgement: *Finnigan 9001 GC, µGold Tandem Photoionization Detector & Hall 2000 Detector provided courtesy of ThermoQuest/CE Instruments, 2215 Grand Avenue Parkway, Austin, TX 78728.*

Application #2

Volatile Organics EPA Method 8021A/502.2 Rtx®-502.2

Confirmational column to the Rtx-VGC.



1. dichlorodifluoromethane
2. chloromethane
3. vinyl chloride
4. bromomethane
5. chloroethane
6. trichlorofluoromethane
7. 1,1-dichloroethene
8. allyl chloride
9. methylene chloride
10. *trans*-1,2-dichloroethene
11. methyl *tert*-butyl ether
12. 1,1-dichloroethane
13. *cis*-1,2-dichloroethene
14. 2,2-dichloropropane
15. bromochloromethane
16. chloroform
17. carbon tetrachloride
18. 1,1,1-trichloroethane
19. 1,1-dichloropropene
20. benzene
21. 1,2-dichloroethane
22. fluorobenzene (SS)
23. trichloroethene
24. dibromomethane
25. 1,2-dichloropropane
26. bromodichloromethane
27. 1-bromo-2-chloroethane (SS)
28. *cis*-1,3-dichloropropene
29. toluene
30. tetrachloroethene
31. *trans*-1,3-dichloropropene
32. 1,1,2-trichloroethane
33. dibromochloromethane
34. 1,3-dichloropropane
35. 1,2-dibromoethane
36. chlorobenzene
37. ethylbenzene
38. 1,1,1,2-tetrachloroethane
39. *m*-xylene
40. *p*-xylene
41. 1-chloro-2-fluorobenzene(SS)
42. *o*-xylene
43. stryrene
44. bromoform
45. isopropylbenzene
46. bromobenzene
47. *n*-propylbenzene
48. 1,1,2,2-tetrachloroethane
49. 2-chlorotoluene
50. 1,2,3-trichloropropane
51. 1,3,5-trimethylbenzene
52. 4-chlorotoluene
53. *tert*-butylbenzene
54. 1,2,4-trimethylbenzene
55. *sec*-butylbenzene
56. *p*-isopropyltoluene
57. 1,3-dichlorobenzene
58. 1,4-dichlorobenzene
59. *n*-butylbenzene
60. 1,2-dichlorobenzene
61. 1,2-dibromo-3-chloropropane
62. 2-bromo-1-chlorobenzene (SS)
63. hexachlorobutadiene
64. 1,2,4-trichlorobenzene
65. naphthalene
66. 1,2,3-trichlorobenzene

primary column:	75m, 0.45mm ID, 2.55µm Rtx-VGC (cat.# 19409)
confirmation column:	75m, 0.45mm ID, 2.55µm Rtx-502.2 (cat.# 10986)
Concentration of Analytes:	10ppb in 5mL of RO water
Concentrator:	Tekmar LSC3100 Purge and Trap
Trap:	Vocarb3000
Purge:	11 min. @ 40mL/min.
DryPurge:	1 min. @ 40mL/min.
Desorb Preheat:	245°C
Desorb:	250°C for 2 min
Bake:	260°C for 8 min
Interface:	direct connection from concentrator to column
Transfer line:	Siltek 0.32 fused silica transfer line direct to columns w/ Press-Tight "Y" connector

Gas Chromatograph:	Finnigan 9001
Carrier Gas:	Helium @ ~10 mL/min. constant pressure

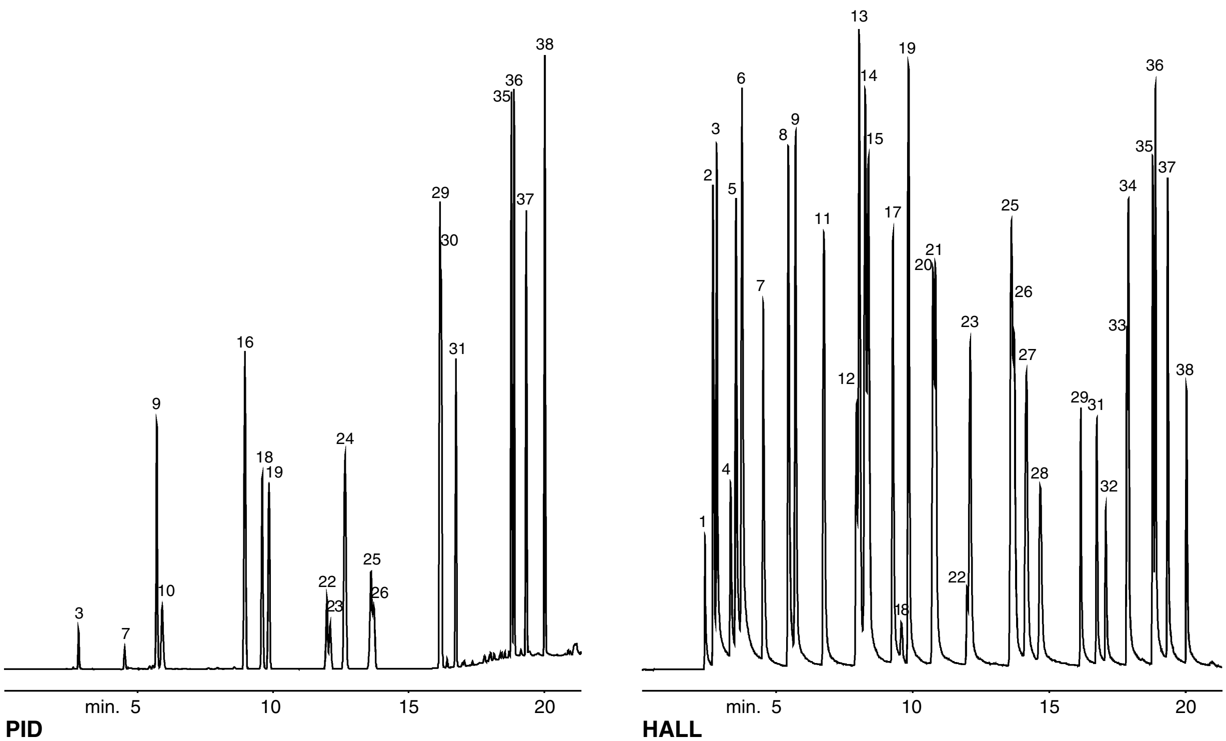
Adjust dichlorodifluoromethane to a retention time of 2.28 min. @ 50°C on the Rtx-VGC column.

Oven temp.:	50°C (hold 2 min.) to 70 @ 2°C/min. to 130 @ 9°C/min. to 200 @ 40°C/min. (final hold 5 min.)
Detectors:	uGold Tandem PID/Hall PID: makeup 7mL/min., purge 7mL/min., set @ 0.35mV base temp 200°C. Hall2000: RxnGas 25mL/min., RxnTemp.940°C, Propanol Flow 470 µL/min.

***Acknowledgement:** Finnigan 9001 GC, µGold Tandem Photoionization Detector & Hall 2000 Detector provided courtesy of ThermoQuest/CE Instruments, 2215 Grand Avenue Parkway, Austin, TX 78728.*

Application #3

Volatile Organics EPA Method 601/602 Rtx®-VGC



1. dichlorodifluoromethane
2. chloromethane
3. vinyl chloride
4. bromomethane
5. chloroethane
6. trichlorofluoromethane
7. 1,1-dichloroethene
8. methylene chloride
9. *trans*-1,2-dichloroethene
10. methyl *tert*-butyl ether
11. 1,1-dichloroethane
12. bromochloromethane (SS)
13. chloroform
14. carbon tetrachloride
15. 1,1,1-trichloroethane
16. benzene
17. 1,2-dichloroethane
18. fluorobenzene (SS)
19. trichloroethene
20. 1,2-dichloropropane
21. bromodichloromethane
22. 2-chloroethyl vinyl ether
23. *cis*-1,3-dichloropropene
24. toluene
25. tetrachloroethene
26. *trans*-1,3-dichloropropene
27. 1,1,2-trichloroethane
28. dibromochloromethane
29. chlorobenzene
30. ethylbenzene
31. 1-chloro-2-fluorobenzene (SS)
32. bromoform
33. 1,4-dichlorobutane (SS)
34. 1,1,2,2-tetrachloroethane
35. 1,3-dichlorobenzene
36. 1,4-dichlorobenzene
37. 1,2-dichlorobenzene
38. 4-bromo-1-chlorobenzene (SS)

suggested surrogates: peaks 18, 31, & 38

primary column: 75m, 0.45mm ID, 2.55µm Rtx-VGC (cat.# 19409)
confirmation column: 75m, 0.45mm ID, 2.55µm Rtx-502.2 (cat.# 10986)*
concentration of analytes: 10ppb in 5ml of RO water
Concentrator: Tekmar LSC3100 Purge and Trap
Trap: Vocarb3000
Purge: 11 min. @ 40mL/min.
Dry Purge: 1 min. @ 40mL/min.
Desorb Preheat: 245°C
Desorb: 250°C for 2 min.
Bake: 260°C for 8 min.
Interface: Direct connection from concentrator to column
Transfer line: Silcosteel Tubing
Gas Chromatograph: Finnigan 9001
Carrier Gas: helium @ ~10 mL/min. constant pressure
Adjust dichlorodifluoromethane to a retention time of 2.47 min. @ 40°C.
Oven temp.: 40°C (hold 2 min.) to 58°C @ 4°C/min. to 90°C @ 10°C/min (hold 5 min.) to 220°C @ 40°C/min (hold 5 min.)
Detectors: uGold Tandem PID/Hall
PID: makeup 7mL/min., purge 7mL/min., set @ 0.35mV base temp 200°C.
Hall 2000: RxnGas 25mL/min., Rxn Temp. 940°C, Propanol Flow 470µL/min.

Acknowledgement: *Finnigan 9001 GC, µGold Tandem Photoionization Detector & Hall 2000 Detector provided courtesy of ThermoQuest/CE Instruments, 2215 Grand Avenue Parkway, Austin, TX 78728.*

Application #4

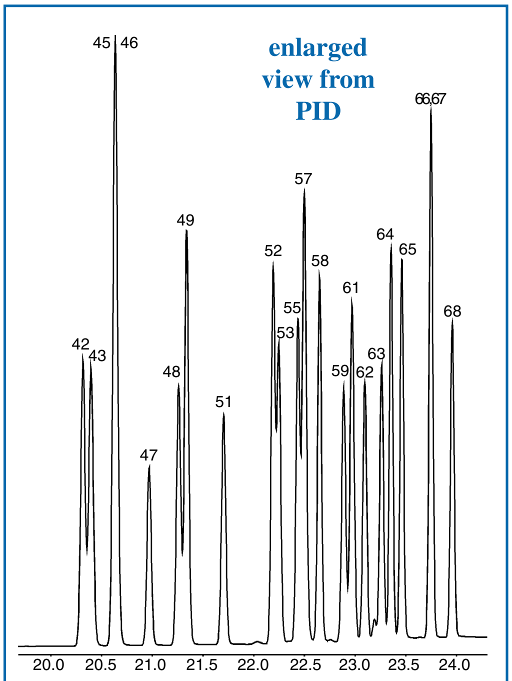
Volatile Organics EPA Method 8021B Rtx®-VGC

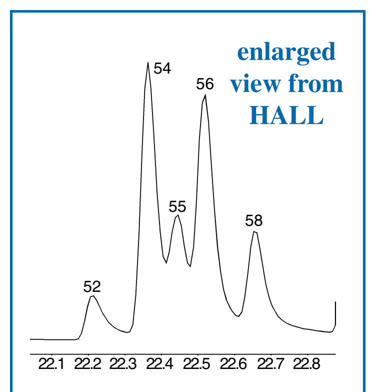
primary column:	75m, 0.45mm ID, 2.55µm Rtx-VGC (cat.# 19409)
confirmation column:	75m, 0.45mm ID, 2.55µm Rtx-502.2 (cat.# 10986)
Concentration of Analytes:	10 ppb in 5 mL of RO Water
Concentrator:	Tekmar LSC-3000 Purge and Trap
Trap:	Vocarb 3000
Purge:	11 min. @ 40 mL/min.
Dry Purge:	1 min. @ 40mL/min. (MCS bypassed using Silcosteel tubing)
Desorb Preheat:	245°C ,Flow 10mL/min.
Desorb:	250°C for 2 min.
Bake:	260°C for 8 min.
Interface:	direct using 0.32 mm ID Siltek transfer line
GC:	Finnigan 9001
Carrier Gas:	helium @ ~10 ml/min constant pressure

Adjust dichlorodifluoromethane to a retention time of 2.40 min. @ 45°C on the Rtx-VGC column.

Oven Program:	45°C (hold 4 min.) to 70°C @ 2°C/min. to 210°C @ 20°C/min. (hold 10 min.)
Detectors:	uGold Tandem PID/HALL **PID:** makeup 7mL/min., purge 7mL/min., set @ 0.35mV base temp. 200°C. **Hall 2000:** RxnGas 25mL/min., RxnTemp.940°C, Propanol Flow 470 µL/min.

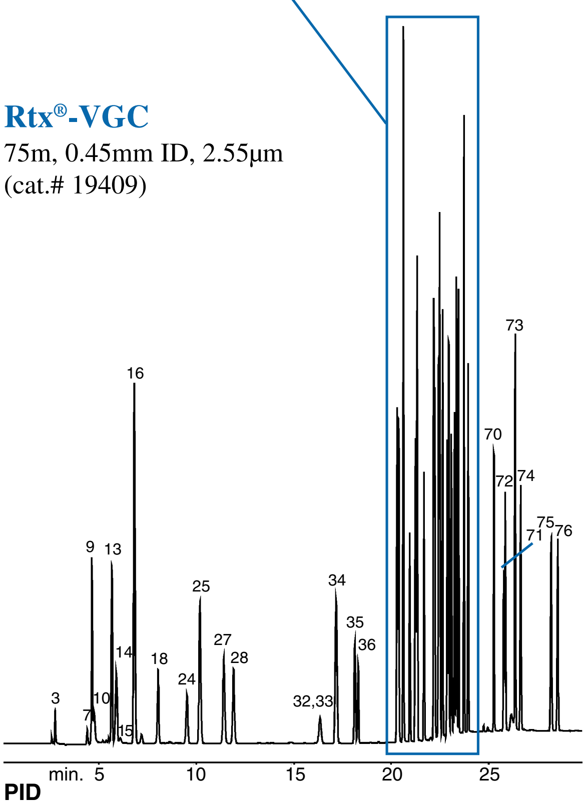
Acknowledgement: *Finnigan 9001 GC, µGold Tandem Photoionization Detector & Hall 2000 Detector provided courtesy of ThermoQuest/CE Instruments, 2215 Grand Avenue Parkway, Austin, TX 78728.*

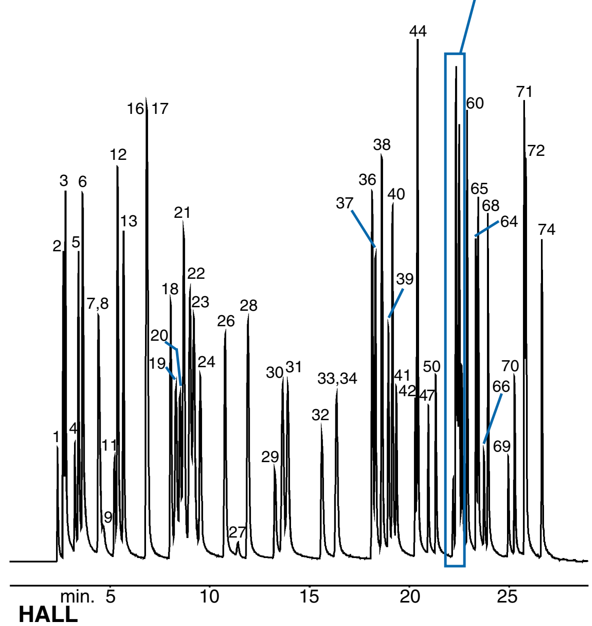




Rtx®-VGC

75m, 0.45mm ID, 2.55µm
(cat.# 19409)

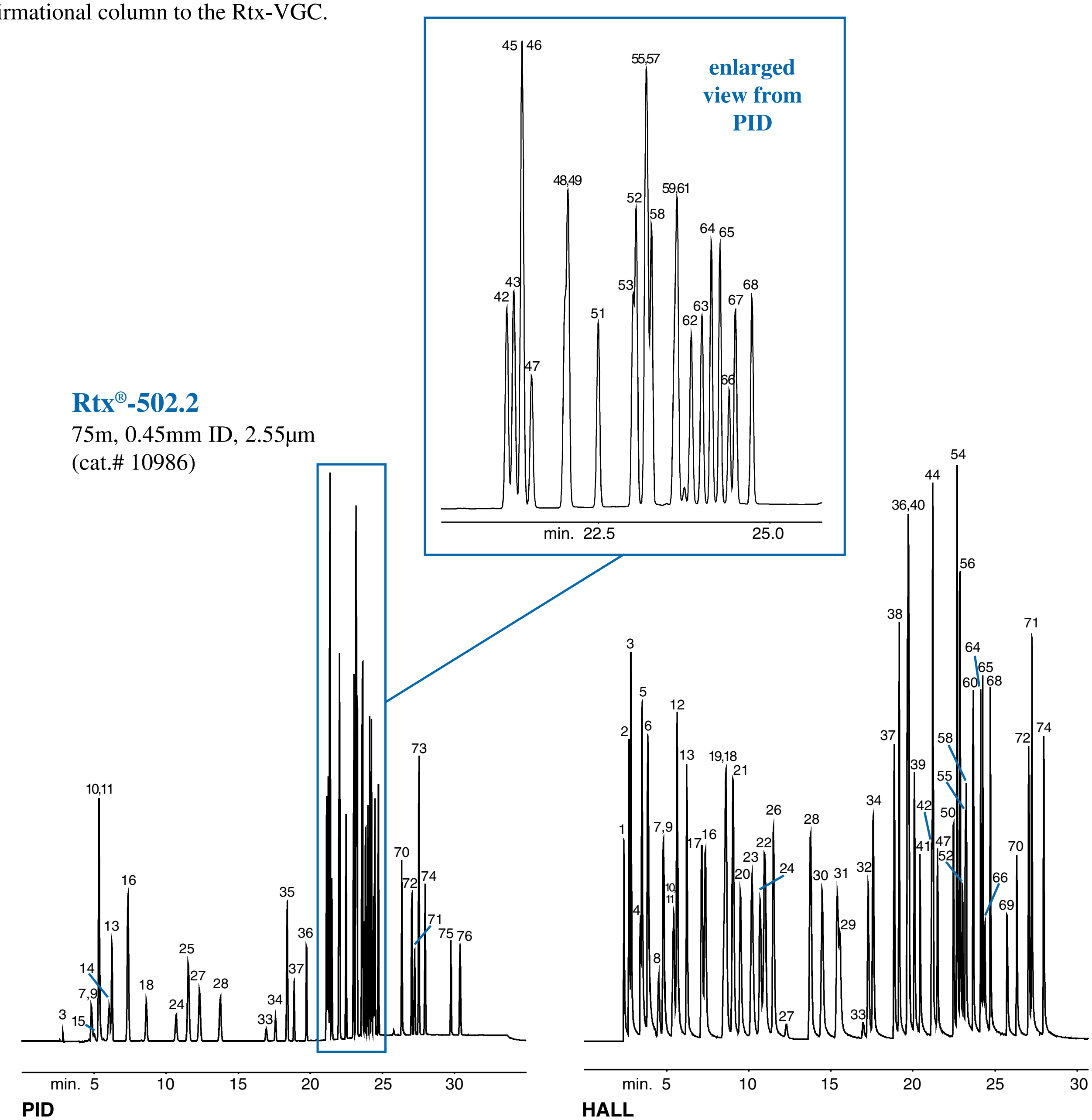




Application #4

Volatile Organics EPA Method 8021B Rtx®-502.2

Confirmational column to the Rtx-VGC.



1. dichlorodifluoromethane
2. chloromethane
3. vinyl chloride
4. bromomethane
5. chloroethane
6. trichlorofluoromethane
7. 1,1-dichloroethene
8. Freon 113
9. chloromethyl methyl ether
10. iodomethane (40ppb)
11. allyl chloride
12. methylene chloride
13. *trans*-1,2-dichloroethene
14. methyl *tert*-butyl ether
15. *tert*-buyl alcohol (40ppb)
16. chloroprene
17. 1,1-dichloroethane
18. *cis*-1,2-dichloroethene
19. 2,2-dichloropropane
20. bromochloromethane
21. chloroform
22. carbon tetrachloride
23. 1,1,1-trichloroethane
24. 1,1-dichloropropene
25. benzene
26. 1,2-dichloroethane
27. fluorobenzene (SS)
28. trichloroethene
29. dibromomethane
30. 1,2-dichloropropane
31. bromodichloromethane
32. 1-bromo-2-chloroethane (SS)
33. 2-chloroethyl vinyl ether
34. *cis*-1,3-dichloropropene
35. toluene
36. tetrachloroethene
37. *trans*-1,3-dichloropropene
38. 1,1,2-trichloroethane
39. dibromochloromethane
40. 1,3-dichloropropane
41. 1,2-dibromoethane
42. chlorobenzene
43. ethylbenzene
44. 1,1,1,2-tetrachloroethane
45. *m*-xylene
46. *p*-xylene
47. 1-chloro-2-fluorobenzene(ss)
48. *o*-xylene
49. stryrene
50. bromoform
51. isopropylbenzene
52. bromobenzene
53. *n*-propylbenzene
54. 1,1,2,2-tetrachloroethane
55. 2-chlorotoluene
56. 1,2,3-trichloropropane
57. 1,3,5-trimethylbenzene
58. 4-chlorotoluene
59. *tert*-butylbenzene
60. pentachloroethane
61. 1,2,4-trimethylbenzene
62. *sec*-butylbenzene
63. *p*-isopropyltoluene
64. 1,3-dichlorobenzene
65. 1,4-dichlorobenzene
66. benzyl chloride
67. *n*-butylbenzene
68. 1,2-dichlorobenzene
69. 1,2-dibromo-3-chloropropane
70. 2-bromo-1-chlorobenzene (ss)
71. hexachlorobutadiene
72. 1,2,4-trichlorobenzene
73. naphthalene
74. 1,2,3-trichlorobenzene
75. 2-methylnaphthalene (40ppb)
76. 1-methylnaphthalene (40ppb)

Acknowledgement: *Finnigan 9001 GC, µGold Tandem Photoionization Detector & Hall 2000 Detector provided courtesy of ThermoQuest/CE Instruments, 2215 Grand Avenue Parkway, Austin, TX 78728.*

Application #3

Volatile Organics EPA Method 601/602 Rtx®-502.2

Confirmational column to the Rtx-VGC.

Rtx®-502.2
75m, 0.45mm ID, 2.55µm
(cat.# 10986)