Fast GC Analyses of Volatiles

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Introduction

The primary aim of Fast GC is to maintain (compared to conventional GC) sufficient resolving power in a shorter time. Basically, Fast GC is accomplished by using a short column (reduces analysis time) with a narrow I.D. (offsets the loss of efficiency of the shorter column) while manipulating specific operating parameters, such as linear velocity and oven temperature ramp rates (1). The use of Fast GC has previously been demonstrated for several applications (2-7). In this space, Fast GC will be demonstrated for the analysis of volatiles using purge and trap (P&T).

Options for Decreasing Analysis Time for P&T Methods

The overwhelming number of samples that must be analyzed for the presence of volatiles is due to the ease with which many of these compounds are able to migrate through the environment, because of their water-soluble nature. Many regulatory agencies require constant monitoring for volatiles, resulting in heavy sample loads with short turnaround times. Therefore, laboratories are constantly looking for ways to reduce analysis times. Several options currently exist for decreasing analysis time.

1. Use two P&Ts for each GC. Synchronize so while the GC is analyzing the sample from one P&T, that P&T is in bake mode and the other P&T is purging the next sample. When the GC is ready, a sample is also ready for desorption so that the GC is never idle.
2. Use a P&T model that employs super high flow rates (i.e. 400 mL/min.) during the bake mode so that it is ready to purge the next sample sooner.
3. Convert the existing conventional GC method to a Fast GC method. Note that this option can be used with the current equipment found in most laboratories, or in combination with either (or both) option(s) listed above.

Converting Conventional GC to Fast GC for Waste Water Volatiles

Converting a conventional GC method to a Fast GC method is not as simple as just changing to a smaller I.D. column. Column dimensions, linear velocity, and oven temperature ramp rates must be optimized together. Changing only one parameter may decrease analysis time (desirable), but will likely cause a loss of resolution (undesirable). It is also critical to account for the reduced sample capacity of the smaller I.D. column.

A method for the analysis of volatiles from waste water samples (US EPA Method 624, commonly performed in the United States) on the SPB™-624 column was selected to illustrate the change from conventional GC to Fast GC. The optimized chromatogram obtained using conventional GC is shown in Figure 1. The analysis time is <18 minutes, peak shapes are good, and the mass spectrometer (MS) is able to mass resolve all analytes.

The column dimensions were changed to Fast GC dimensions, and then linear velocity and oven temperature ramp rates were optimized to produce the chromatogram shown in Figure 2 (parameters which were changed are highlighted). While analysis time is reduced to <10 minutes and the MS is still able to mass resolve all analytes, peak shape overall is not good. Why the poor chromatography? The reduced sample capacity of the smaller I.D. column was not accounted for.

The primary aim of Fast GC is to maintain (compared to conventional GC) sufficient resolving power in a shorter time

The capacity of the 0.18 mm I.D. column is significantly less than the 0.25 mm I.D. column, leading to sample overload. To alleviate this problem, the mass of sample reaching the column must be reduced. Diluting the sample, decreasing the injection volume, or increasing the split ratio are options to achieve this. The first two options are not as compatible with P&T methods as the third. Therefore, the split ratio was increased from 30:1 to 100:1, and then the linear velocity was optimized to achieve the chromatogram shown in Figure 3 (parameters which were changed are highlighted). Now, the short analysis time (<10 minutes) and mass resolution of all analytes is accompanied with improved peak shape of all analytes. This represents a vast improvement in analysis time (from over 17 minutes to under 10 minutes) compared to the conventional GC chromatogram in Figure 1.

(continued on page 9)

Did you know...?

Supelco currently offers a total of **nineteen columns in Fast GC dimensions,** covering twelve popular phases (SPB-624, VOCOL™, SLB™-5ms, Equity®-1701, TCEP, SP™-2560, Omegawax™ 100, SUPELCOWAX™ 10, Equity-1, SPB-1, Equity-5, and SPB-5). If increasing sample throughput is your goal, consider a change to a Supelco Fast GC column.

Figure 1. Waste Water Volatiles on the SPB-624

sample/matrix: each analyte at 50 ppb in 5 mL water
purge trap: VOCARB® 3000 "K" (24940-U)
purge: 40 mL/min. at 25 °C for 11 min.
dry purge: 2 min.
desorption pre-heat: 205 °C
desorption temp.: 210 °C for 2 min.
desorption flow: 40 mL/min.
bake.: 260 °C for 10 min.
transfer line/valve temp.: 110 °C
column: SPB-624, 30 m x 0.25 mm I.D., 1.4 µm (24255)
oven: 40 °C (2 min.), 7 °C/min. to 135 °C, 30 °C/min. to 230 °C (3 min.)
inj.: 150 °C
MSD interface: 200 °C
scan range: m/z = 35-400
carrier gas: helium, 1.1 mL/min.
injection: 30:1 split
liner: 0.75 mm I.D. SPME

Conventional GC Analysis, 30:1 Split

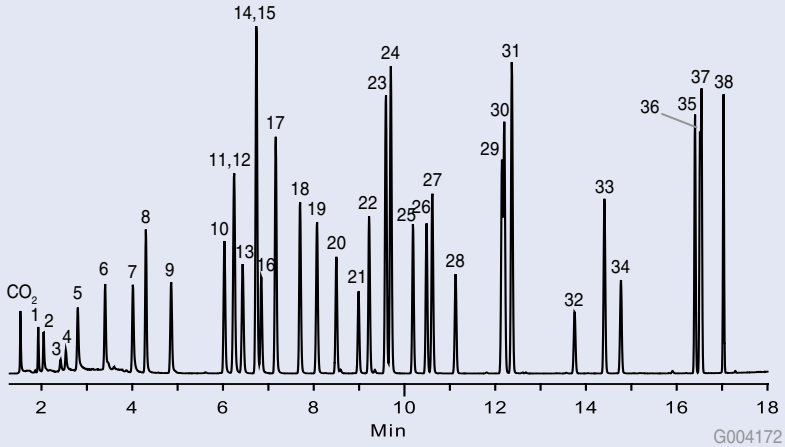


Figure 2. Waste Water Volatiles on the SPB-624

sample/matrix: each analyte at 50 ppb in 5 mL water
purge trap: VOCARB® 3000 "K" (24940-U)
purge: 40 mL/min. at 25 °C for 11 min.
dry purge: 2 min.
desorption pre-heat: 205 °C
desorption temp.: 210 °C for 2 min.
desorption flow: 40 mL/min.
bake.: 260 °C for 10 min.
transfer line/valve temp.: 110 °C
column: SPB-624, 20 m x 0.18 mm I.D., 1.0 µm (28662-U)
oven: 40 °C (1 min.), 11 °C/min. to 125 °C, 35 °C/min. to 230 °C (2 min.)
inj.: 150 °C
MSD interface: 200 °C
scan range: m/z = 35-400
carrier gas: helium, 1.2 mL/min.
injection: 30:1 split
liner: 0.75 mm I.D. SPME

Fast GC Analysis, 30:1 Split

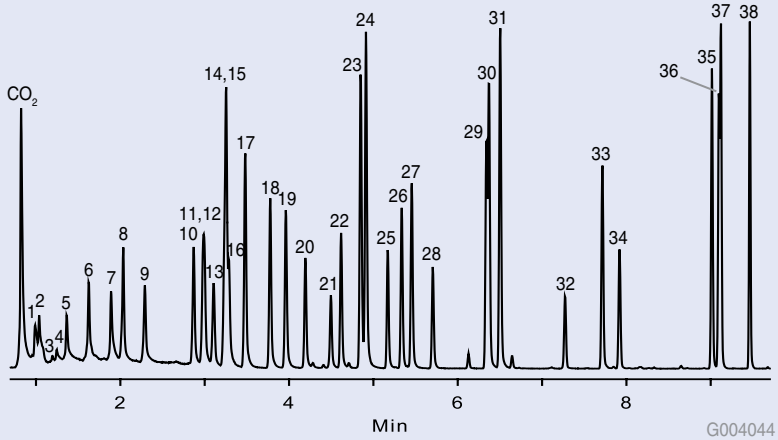
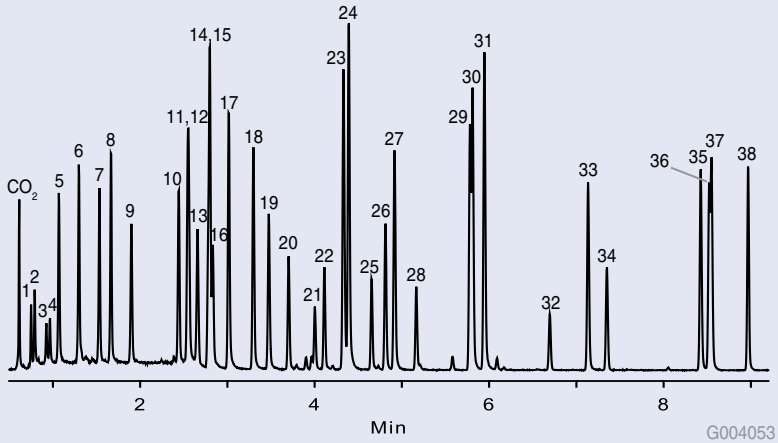


Figure 3. Waste Water Volatiles on the SPB-624

sample/matrix: each analyte at 50 ppb in 5 mL water
purge trap: VOCARB 3000 "K" (24940-U)
purge: 40 mL/min. at 25 °C for 11 min.
dry purge: 2 min.
desorption pre-heat: 205 °C
desorption temp.: 210 °C for 2 min.
desorption flow: 150 mL/min.
bake.: 260 °C for 10 min.
transfer line/valve temp.: 110 °C
column: SPB-624, 20 m x 0.18 mm I.D., 1.0 µm (28662-U)
oven: 40 °C (1 min.), 11 °C/min. to 125 °C, 35 °C/min. to 230 °C (2 min.)
inj.: 150 °C
MSD interface: 200 °C
scan range: m/z = 35-400
carrier gas: helium, 1.5 mL/min.
injection: 100:1 split
liner: 0.75 mm I.D. SPME

Fast GC Analysis, 100:1 Split



Peak IDs for Figures 1-3

1. Chloromethane
2. Vinyl chloride
3. Bromomethane
4. Chloroethane
5. Trichlorofluoromethane
6. 1,1-Dichloroethene
7. Methylene chloride
8. trans-1,2-Dichloroethene
9. 1,1-Dichloroethane
10. Chloroform
11. Dibromofluoromethane (surr.)
12. 1,1,1-Trichloroethane
13. Carbon tetrachloride
14. 1,2-Dichloroethane-d_4 (surr.)
15. Benzene
16. 1,2-Dichloroethane
17. Fluorobenzene (I.S.)
18. Trichloroethene
19. 1,2-Dichloropropane
20. Bromodichloromethane
21. 2-Chloroethyl vinyl ether
22. cis-1,3-Dichloropropene
23. Toluene-d_8 (surr.)
24. Toluene
25. trans-1,3-Dichloropropene
26. 1,1,2-Trichloroethane
27. Tetrachloroethene
28. Dibromochloromethane
29. Chlorobenzene-d_5 (I.S.)
30. Chlorobenzene
31. Ethylbenzene
32. Bromoform
33. 4-Bromofluorobenzene (surr.)
34. 1,1,2,2-Tetrachloroethane
35. 1,3-Dichlorobenzene
36. 1,4-Dichlorobenzene-d_4 (I.S.)
37. 1,4-Dichlorobenzene
38. 1,2-Dichlorobenzene

ordering: 800-247-6628 (US only) / 814-359-3441 technical service: 800-359-3041 (US and Canada only) / 814-359-3041

Figure 4. Solid Waste Volatiles on the VOCOL

sample/matrix: each analyte at 50 ppb in 5 mL water
purge trap: VOCARB 3000 "K" (24940-U)
purge: 40 mL/min. at 25 °C for 11 min.
dry purge: 2 min.
desorption pre-heat: 205 °C
desorption temp.: 210 °C for 2 min.
desorption flow: 40 mL/min.
bake: 260 °C for 10 min.
transfer line/valve temp.: 110 °C
column: VOCOL, 30 m x 0.25 mm I.D., 1.5 µm (24205-U)
oven: 40 °C (2 min.), 7 °C/min. to 125 °C, 12 °C/min. to 220 °C (5 min.)
inj.: 150 °C
MSD interface: 200 °C
scan range: m/z = 35-400
carrier gas: helium, 0.7 mL/min.
injection: 30:1 split
liner: 0.75 mm I.D. SPME

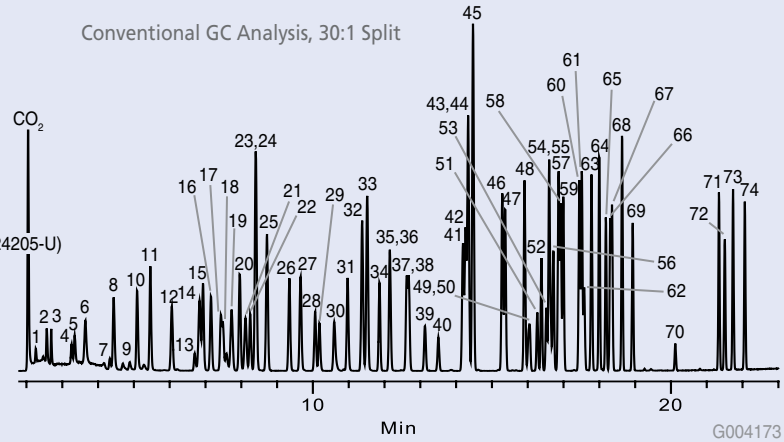


Figure 5. Solid Waste Volatiles on the VOCOL

sample/matrix: each analyte at 50 ppb in 5 mL water
purge trap: VOCARB 3000 "K" (24940-U)
purge: 40 mL/min. at 25 °C for 11 min.
dry purge: 1 min.
desorption pre-heat: 205 °C
desorption temp.: 210 °C for 1 min.
desorption flow: 46 mL/min.
bake.: 260 °C for 10 min.
transfer line/valve temp.: 110 °C
column: VOCOL, 20 m x 0.18 mm I.D., 1.0 µm (28463-U)
oven: 40 °C (0.8 min.), 19 °C/min. to 125 °C, 32 °C/min. to 220 °C (1 min.)
inj.: 150 °C
MSD interface: 220 °C
scan range: m/z = 35-400
carrier gas: helium, 1.4 mL/min.
injection: 30:1 split
liner: 0.75 mm I.D. SPME

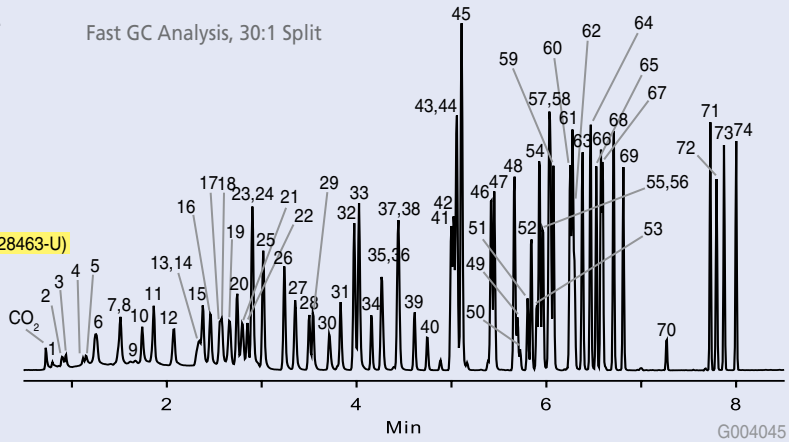
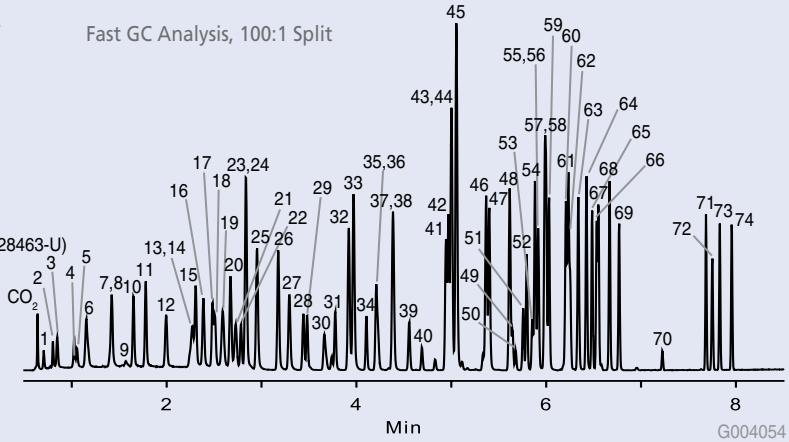


Figure 6. Solid Waste Volatiles on the VOCOL

sample/matrix: each analyte at 50 ppb in 5 mL water
purge trap: VOCARB 3000 "K" (24940-U)
purge: 40 mL/min. at 25 °C for 11 min.
dry purge: 1 min.
desorption pre-heat: 205 °C
desorption temp.: 210 °C for 1 min.
desorption flow: 150 mL/min.
bake.: 260 °C for 10 min.
transfer line/valve temp.: 110 °C
column: VOCOL, 20 m x 0.18 mm I.D., 1.0 µm (28463-U)
oven: 40 °C (0.8 min.), 19 °C/min. to 125 °C, 32 °C/min. to 220 °C (1 min.)
inj.: 150 °C
MSD interface: 220 °C
scan range: m/z = 35-400
carrier gas: helium, 1.5 mL/min.
injection: 100:1 split
liner: 0.75 mm I.D. SPME



Peak IDs for Figures 4-6

1. Dichlorofluoromethane
2. Chloromethane
3. Vinyl chloride
4. Bromomethane
5. Chloroethane
6. Trichlorofluoromethane
7. Acetone
8. 1,1-Dichloroethene
9. Iodomethane
10. Methylene chloride
11. trans-1,2-Dichloroethene
12. 1,1-Dichloroethane
13. 2-Butanone
14. 2,2-Dichloropropane
15. cis-1,2-Dichloroethene
16. Chloroform
17. Bromochloromethane
18. Dibromofluoromethane (surr.)
19. 1,1,1-Trichloroethane
20. 1,1-Dichloropropene
21. Carbon tetrachloride
22. 1,2-Dichloroethane-d_4 (surr.)
23. 1,2-Dichloroethane
24. Benzene
25. Fluorobenzene (I.S.)
26. Trichloroethene
27. 1,2-Dichloropropane
28. Bromodichloromethane
29. Dibromomethane
30. 4-methyl-2-pentanone
31. cis-1,3-Dichloropropene
32. Toluene-d_8 (surr.)
33. Toluene
34. trans-1,3-Dichloropropene
35. 1,1,2-Trichloroethane
36. 2-Hexanone
37. 1,3-Dichloropropane
38. Tetrachloroethene
39. Dibromochloromethane
40. 1,2-Dibromomethane
41. Chlorobenzene-d_5 (I.S.)
42. Chlorobenzene
43. Ethylbenzene
44. 1,1,1,2-Tetrachloroethane
45. m-Xylene & p-Xylene
46. o-Xylene
47. Styrene
48. Isopropylbenzene
49. Bromoform
50. cis-1,4-Dichloro-2-butene
51. 1,1,2,2-Tetrachloroethane
52. 4-Bromofluorobenzene (surr.)
53. 1,2,3-Trichloropropane
54. n-Propylbenzene
55. Bromobenzene
56. trans-1,4-Dichloro-2-butene
57. 1,3,5-Trimethylbenzene
58. o-Chlorotoluene
59. p-Chlorotoluene
60. tert-Butylbenzene
61. 1,2,4-Trimethylbenzene
62. Pentachloroethane
63. sec-Butylbenzene
64. p-Isopropyltoluene
65. 1,3-Dichlorobenzene
66. 1,4-Dichlorobenzene-d_4 (I.S.)
67. 1,4-Dichlorobenzene
68. Butylbenzene
69. 1,2-Dichlorobenzene
70. 1,2-Dibromo-3-chloropropane
71. 1,2,4-Trichlorobenzene
72. Hexachlorobutadiene
73. Naphthalene
74. 1,2,3-Trichlorobenzene

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(continued from page 6)

Converting Conventional GC to Fast GC for Solid Waste Volatiles

Fast GC is also compatible with more complex samples. A method for the analysis of volatiles from solid waste samples (US EPA Method 8260, also commonly performed in the United States) was selected as an example, this time using the VOCOL column. The optimized chromatogram obtained using conventional GC is shown in Figure 4. The analysis time is <23 minutes.

The column dimensions were changed to Fast GC dimensions, and then conditions were optimized to produce the chromatogram shown in Figure 5 (parameters which were changed are highlighted). While analysis time is reduced to <9 minutes, the shapes of the first several peaks are not good due to the lower capacity of the 0.18 mm I.D. column. Therefore, the split ratio was increased from 30:1 to 100:1, and then the linear velocity was optimized to achieve the chromatogram shown in Figure 6 (parameters which were changed are highlighted). Again, the short analysis time (<9 minutes) is accompanied with improved peak shapes. This represents a vast improvement in analysis time (from over 22 minutes to under 9 minutes) compared to the conventional GC chromatogram in Figure 4.

Fast GC of Hazardous Waste Site Volatiles

A method for the analysis of volatiles from hazardous waste site samples (US EPA Method OLM04.2 VOA) was selected to show the selectivity differences between the SPB-624 column and the VOCOL column. Optimized Fast GC chromatograms are shown in Figure 7 (SPB-624) and Figure 8 (VOCOL). Both show quick analysis times and good shapes of all peaks. Note the change in elution order for several peaks (10/11, 18/19, 31/32, 37/38, 47/48, and 49/50) due to the selectivity difference between the two columns.

Conclusion

Converting methods from conventional GC to Fast GC can result in decreased costs (less people and/or instruments are needed) and increased revenue (more samples can be processed). However, care must be taken to ensure that all Fast GC method parameters are optimized together. Changing only one may decrease analysis time (desirable), but will likely cause a loss of resolution (undesirable). With any Fast GC method, the reduced sample capacity of the smaller I.D. column must be accounted for so that unacceptable chromatography is not created.

Fast GC methods can be used with complex samples, and with any column, regardless of its selectivity. Furthermore, Fast GC is compatible with the current equipment found in most laboratories, and also with newer equipment that is designed for speed.

References

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(continued on page 10)

Featured Products

Description	Cat. No.
SPB-624 Fused Silica Columns	
20 m x 0.18 mm I.D., 1.0 µm	28662-U
30 m x 0.25 mm I.D., 1.4 µm	24255
VOCOL Fused Silica Columns	
20 m x 0.18 mm I.D., 1.0 µm	28463-U
30 m x 0.25 mm I.D., 1.5 µm	24205-U
VOCARB 3000 "K" Purge Traps	
Fits OI Analytical Eclipse 4660 / 4560	24940-U

Related Products

Description	Cat. No.
SPB-624 Fused Silica Columns	
60 m x 0.25 mm I.D., 1.4 µm	24256
30 m x 0.32 mm I.D., 1.8 µm	23323-U
60 m x 0.32 mm I.D., 1.8 µm	24251
30 m x 0.53 mm I.D., 3.0 µm	25430
60 m x 0.53 mm I.D., 3.0 µm	28663-U
75 m x 0.53 mm I.D., 3.0 µm	25432
105 m x 0.53 mm I.D., 3.0 µm	28664-U
VOCOL Fused Silica Columns	
10 m x 0.20 mm I.D., 1.2 µm	24129-U
60 m x 0.25 mm I.D., 1.5 µm	24154
30 m x 0.32 mm I.D., 1.8 µm	28464-U
60 m x 0.32 mm I.D., 1.8 µm	24217-U
60 m x 0.32 mm I.D., 3.0 µm	24157
30 m x 0.53 mm I.D., 3.0 µm	25320-U
60 m x 0.53 mm I.D., 3.0 µm	25381
105 m x 0.53 mm I.D., 3.0 µm	25358
60 m x 0.75 mm I.D., 1.5 µm	23313-U
VOCARB 3000 "K" Purge Traps	
Fits Tekmar Velocity XPT / 2000 / 4000	21066-U
Fits Tekmar 3000 / 3100	24920-U
Fits OI Analytical 4460	21131-U
Fits Dynatech "Dyna" Models	21085-U
Fits CDS Peak Master	21159

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Figure 7. Hazardous Waste Site Volatiles on the SPB-624

sample/matrix:	each analyte at 50 ppb in 5 mL water
purge trap:	VOCARB 3000 "K" (24940-U)
purge:	40 mL/min. at 25 °C for 11 min.
dry purge:	2 min.
desorption pre-heat:	205 °C
desorption temp.:	210 °C for 2 min.
desorption flow:	124 mL/min.
bake.:	260 °C for 10 min.
transfer line/valve temp.:	110 °C
column:	SPB-624, 20 m x 0.18 mm I.D., 1.0 µm (28662-U)
oven:	40 °C (1 min.), 11 °C/min. to 125 °C, 35 °C/min. to 230 °C (2 min.)
inj.:	150 °C
MSD interface:	200 °C
scan range:	m/z = 35-400
carrier gas:	helium, 1.2 mL/min.
injection:	100:1 split
liner:	0.75 mm I.D. SPME

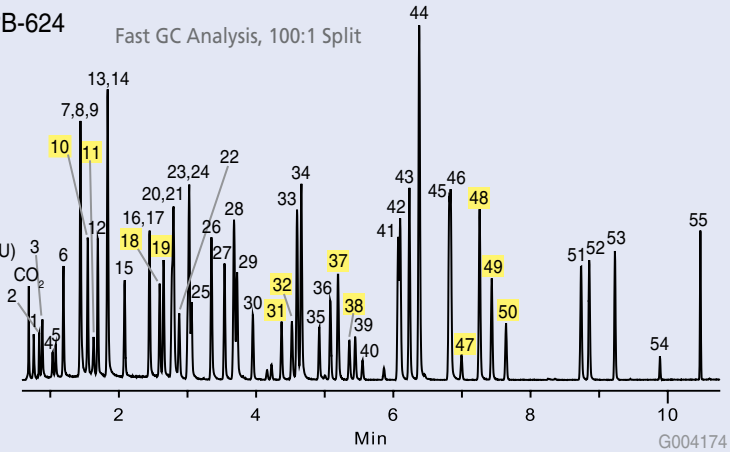
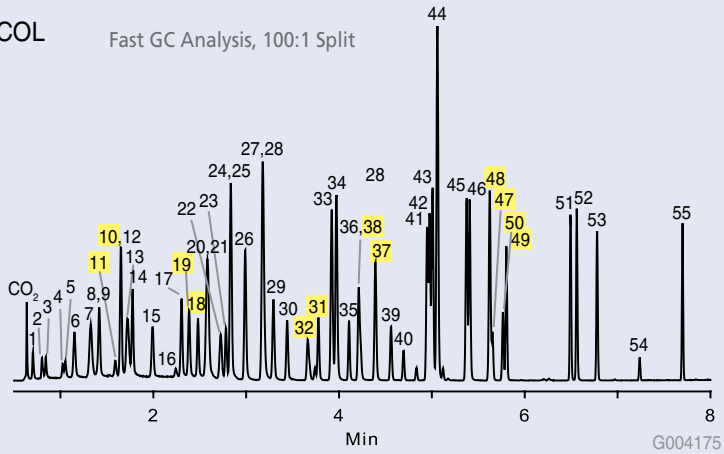


Figure 8. Hazardous Waste Site Volatiles on the VOCOL

sample/matrix:	each analyte at 50 ppb in 5 mL water
purge trap:	VOCARB 3000 "K" (24940-U)
purge:	40 mL/min. at 25 °C for 11 min.
dry purge:	2 min.
desorption pre-heat:	205 °C
desorption temp.:	210 °C for 2 min.
desorption flow:	150 mL/min.
bake.:	260 °C for 10 min.
transfer line/valve temp.:	110 °C
column:	VOCOL, 20 m x 0.18 mm I.D., 1.0 µm (28463-U)
oven:	40 °C (0.8 min.), 19 °C/min. to 125 °C, 32 °C/min. to 220 °C (1 min.)
inj.:	150 °C
MSD interface:	200 °C
scan range:	m/z = 35-400
carrier gas:	helium, 1.4 mL/min.
injection:	100:1 split
liner:	0.75 mm I.D. SPME



Peak IDs for Figures 7-8

1. Dichlorofluoromethane
2. Chloromethane
3. Vinyl chloride
4. Bromomethane
5. Chloroethane
6. Trichlorofluoromethane
7. 1,1,2-Trichloro-1,2,2-trifluoroethane
8. 1,1-Dichloroethene
9. Acetone
10. Carbon disulfide
11. Methyl acetate
12. Methylene chloride
13. Methyl-tert-butyl ether
14. trans-1,2-Dichloroethene
15. 1,1-Dichloroethane
16. 2-Butanone
17. cis-1,2-Dichloroethene
18. Bromochloromethane (I.S.)
19. Chloroform
20. 1,1,1-Trichloroethane
21. Cyclohexane
22. Carbon tetrachloride
23. 1,2-Dichloroethane-d_4 (surr.)
24. Benzene
25. 1,2-Dichloroethane
26. 1,4-Difluorobenzene (I.S.)
27. Trichloroethene
28. Methylcyclohexane
29. 1,2-Dichloropropane
30. Bromodichloromethane
31. cis-1,3-Dichloropropene
32. 4-Methyl-2-pentanone
33. Toluene-d_8 (surr.)
34. Toluene
35. trans-1,3-Dichloropropene
36. 1,1,2-Trichloroethane
37. Tetrachloroethene
38. 2-Hexanone
39. Dibromochloromethane
40. 1,2-Dibromomethane
41. Chlorobenzene-d_5 (I.S.)
42. Chlorobenzene
43. Ethylbenzene
44. m-Xylene & p-Xylene
45. o-Xylene
46. Styrene
47. Bromoform
48. Isopropylbenzene
49. 4-Bromofluorobenzene (surr.)
50. 1,1,2,2-Tetrachloroethane
51. 1,3-Dichlorobenzene
52. 1,4-Dichlorobenzene
53. 1,2-Dichlorobenzene
54. 1,2-Dibromo-3-chloropropane
55. 1,2,4-Trichlorobenzene

Did you know...?

The 2007 brochure *"Fast GC: A Practical Guide for Increasing Sample Throughput without Sacrificing Quality"* (T407096 JTW) contains valuable information concerning Fast GC principles that is not covered in this article. Included are practical considerations, theoretical discussions, a listing of columns in Fast GC dimensions, twenty-six chromatograms, a listing of related products designed to maximize performance, plus a list of literature for additional reading. Request a copy of this brochure on the attached postcard or contact Supelco Technical Service at 800-359-3041 (US and Canada only), 814-359-3041, or at ***techservice@sial.com***

Related Information

The Supelco *"Purge-and-Trap System Guide"* (T197916 BIN) contains both theory as well as troubleshooting information. Request a copy of this bulletin on the attached postcard or contact Supelco Technical Service at **800-359-3041** (US and Canada only), **814-359-3041**, or at ***techservice@sial.com*** (Available in electronic form only. Please provide email address.)