Applications of Purgeable Organic Compounds by US EPA Method 8260 Using Narrow-Bore Capillary Columns.

CHRIS M. ENGLISH, FRANK L. DORMAN, MARK LAWRENCE & DINESH PATWARDHAN.

Restek Corporation, 110 Benner Circle, Bellefonte, PA, 16823

ABSTRACT

Laboratories have been struggling to interface the high desorb flow (>10mL/min.) of the purge & trap concentrator with the lower flow requirements of the MS system. Conventional MS instruments run optimally when the flow of carrier gas into the ionizing chamber is 1mL/min. Flow rates higher than this will increase noise at a greater rate than the increase in sensitivity, resulting in a net loss of the signal-to-noise ratio. There are several options to accommodate the lower flow requirements of the MS. One approach is to employ a jet separator, which uses a vacuum pump to pull the carrier gas away from the analytes and allow a majority of sample to pass into the MS source. This approach is expensive and requires additional maintenance. The second method is to use a narrow-bore column with a split flow at the injection port. Columns with 0.18mm and 0.25mm IDs are run optimally at flow rates of 1mL/min., thereby providing a direct interface to the MS ion source.

This paper will discuss the setup of MS systems for volatile analysis—using a narrow-bore column with a split flow at the injection port. Applications on the 30m and 60m x 0.25mm ID and the 20 m x 0.18mm ID Rtx®-VMS column will be shown using high starting temperatures and electronic pressure control (EPC) for optimized runtimes.

INTRODUCTION

Narrow bore columns offer higher resolution compared to 0.53mm ID columns and are effective options for the analysis of volatile organic compounds. Since these columns are typically operated at low flow rates (1mL/min) they are not compatible with the fast desorb flow rates from the concentrator. To achieve compatibility, splitting of the desorb flow is common. With this technique, the trap is desorbed at flow rates ranging from 10 to 40mL/min with the flow split at the injection port delivering 1mL/min onto the column. The remaining flow exits through the split vent. With a split ratio of anywhere between 10:1 - 40:1 the column flow is compatible with the vacuum system of a mass spectrometer. A faster desorb flow rate results in narrower sample band width, these sharper peaks increase the chromatographic signal/noise ratio, however, splitting the flow at the injection port also decreases the amount of sample reaching the column, resulting in reduced sensitivity. The key to success using the narrow-bore columns is finding the optimum split flow that produces narrow peaks without a significant loss in sensitivity from splitting. There are two ways of increasing the amount of sample that reaches the detector: decrease the split flow & increase the purge volume (e.g. from 5mL to 25mL).

EXPERIMENTAL

Application #1 shows the analysis of US EPA Method 8260B using a 20m x 0.18mm ID x 1.0µm film, Rtx®-VMS column without the use of cyrogenic cooling. Resolution is greatly enhanced due to the increase in efficiency of the 0.18mm ID column. Desorb flow rates are set at 40mL/min for 1 minute. Many laboratories desorb under these conditions for 2 minutes, which is not necessary because the volatiles are quickly swept off of the trap in under a minute. One of the most important factors in optimizing the narrow-bore volatile analysis is adjusting the flow rate on the column. Most MS systems are designed for optimum sensitivity at 1mL/min; flow higher or lower will greatly compromise the method detection limit (MDL). For Application #1, the first gas—dichlorodifluoromethane—is set at a retention time of 1.03 minutes at 50°C which results in a column flow of 1 mL/min. Applications 2 & 3 also have specific information on setting the correct flow rate. With the use of Electronic Pressure Control (EPC) it is possible to run the instrument in constant flow over the course of the oven program, which can shave several minutes off of the analysis time compared to a system set up for constant pressure. All of these applications are run using EPC. When setting up a system for constant pressure, always adjust the flow

at the GC oven start temperature for a flow of ~ 1mL/min. At the beginning of the analysis, higher flows under constant pressure will equate to normal flows (closer to 1mL/min) as the temperature (and carrier gas viscosity) increases; however, maximum sensitivity is needed for the more volatile analytes since they have broader peak shapes (Applications #1,2 & 3). Also, higher flows at the start of the analysis, while the methanol/water are going into the MS, may cause excessive source pressure which will automatically shut off the filament. Application #2 uses the 60m x 0.25mm x 1.4µm film Rtx®-VMS column with an initial starting temperature of 60°C for the same compound list as shown in the 1st application. The injection port is set for a 20:1 split and constant flow is adjusted for 1.3mL/min. Again, the best way to set flows for these columns is with the retention time of dichlorodifluoromethane or an un-retained compound such as carbon dioxide, which easily can be used since its characteristic parent ion is 44. US EPA Method 8240 was developed to monitor almost 80 compounds in hazardous waste samples.

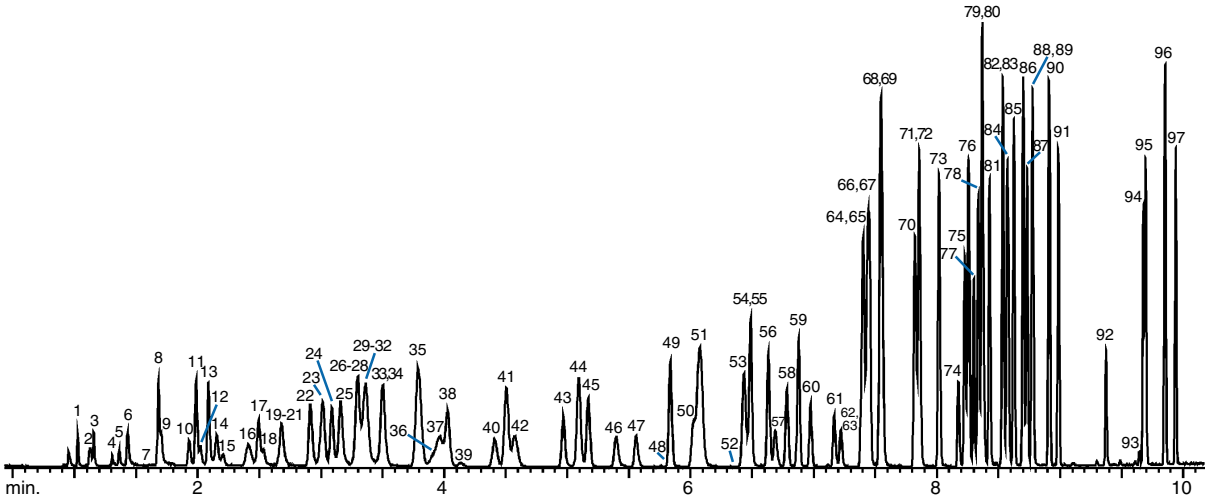
The Rtx®-VMS, 30m x 0.25mm x 1.4µm film column is a good choice for this shorter list of analytes. As with the 8260 compound list for both the 624 and VMS phases, care must be taken to avoid poor resolution between chlorobenzene-d5 and 1,1,1,2-tetrachloroethene, which share the chlorobenzene-d5 quantitation ion 117. Many laboratories change the chlorobenzene-d5 quantitation ion from 117 to 82 which eliminates the need for chromatographic resolution. Another solution is to replace the internal standard chlorobenzene-d5 for another compound, such as 4-bromofluorobenzene, which elutes in the same region of the chromatogram. These compounds can be chromatographically resolved on both the VMS and 624 phases using the proper GC oven program, but generally results in a longer runtime.

CONCLUSION

Choosing between the 0.25mm ID and the 0.18mm ID of the Rtx®-VMS column to interface with the MS ion source is a matter of preference. Customers running 100 or more analytes prefer the longer columns which offer higher starting temperatures and overall better resolution of target compounds. These applications help the analyst optimize runtimes, adjust column flows and be aware of coelutions of analytes sharing the same ions. This new column has excellent selectivity and a rapid cycle time for EPA Method 8260.

Application #1

Volatile Organics EPA Method 8260B Rtx®-VMS



20m, 0.18 mm ID, 1.00µm Rtx-VMS (cat.# 49914)
Compounds in at 10 ppb 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. @ 40 mL/min. @ ambient temperature
Dry Purge: 1 min. @ 40mL/min.
Desorb Preheat: 245°C
Desorb: 250°C for 2 min., Flow 10mL/min.
Bake: 260°C for 8 min.
Interface: transfer line 0.53mm ID Silcosteel MXT tubing
1: 40 split at injection port. 1mm ID sleeve.

Oven Program: 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 @ ~1.0 mL/min. constant flow
Adjust dichlorodifluoromethane to a retention times of 1.03 min. @ 50°C.
Detector: Hewlett-Packard 5973 Mass Selective Detetector
scan range 35 to 300 AMU

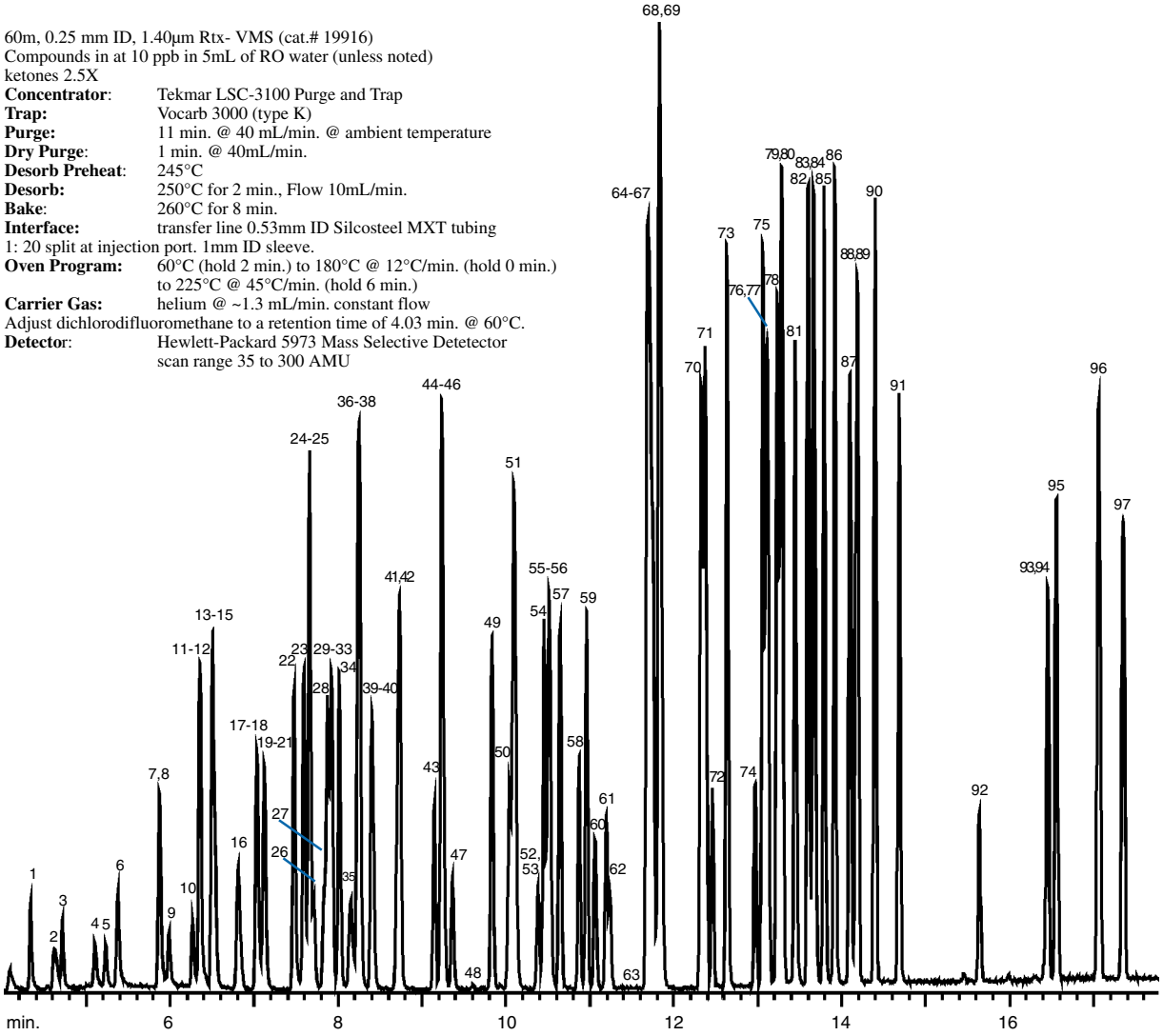
1. dichlorodifluoromethane
2. chloromethane
3. vinyl chloride
4. bromomethane
5. chloroethane
6. trichlorofluoromethane
7. ethanol (2500ppb)
8. 1,1-dichloroethene
9. carbon disulfide (40ppb)
10. allyl chloride
11. methylene chloride
12. acetone
13. *trans*-1,2-dichloroethene
14. methyl *tert*-butyl ether
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-penanone
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. 1,2,3-trichlorobenzene
96. naphthalene
97. 1,2,4-trichlorobenzene

Application #2

Volatile Organics EPA Method 8260B Rtx®-VMS

60m, 0.25 mm ID, 1.40µm Rtx- VMS (cat.# 19916)
Compounds in at 10 ppb in 5mL of RO water (unless noted)
ketones 2.5X

Concentrator: Tekmar LSC-3100 Purge and Trap
Trap: Vocarb 3000 (type K)
Purge: 11 min. @ 40 mL/min. @ ambient temperature
Dry Purge: 1 min. @ 40mL/min.
Desorb Preheat: 245°C
Desorb: 250°C for 2 min., Flow 10mL/min.
Bake: 260°C for 8 min.
Interface: transfer line 0.53mm ID Silcosteel MXT tubing
1: 20 split at injection port. 1mm ID sleeve.
Oven Program: 60°C (hold 2 min.) to 180°C @ 12°C/min. (hold 0 min.) to 225°C @ 45°C/min. (hold 6 min.)
Carrier Gas: helium @ ~1.3 mL/min. constant flow
Adjust dichlorodifluoromethane to a retention time of 4.03 min. @ 60°C.
Detector: Hewlett-Packard 5973 Mass Selective Detetector scan range 35 to 300 AMU



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. *tert*-butyl alcohol (100ppb)
15. methyl *tert*-butyl ether
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. methyl acrylate
28. propargyl alcohol (500ppb)
29. dibromofluoromethane (SMC)
30. tetrahydrofuran
31. carbon tetrachloride
32. 2-butanone
33. 1,1,1-trichloroethane
34. 1,1-dichloropropene
35. pentafluorobenzene(IS)
36. *tert*-amyl-methyl ether
37. benzene
38. isobutyl alcohol (500ppb)
39. 1,2-dichloroethane
40. isopropyl acetate
41. 1,4-difluorobenzene(SMC)
42. trichloroethene
43. dibromomethane
44. bromodichloromethane
45. 1,2-dichloropropane
46. methyl methacrylate
47. *n*-propyl acetate
48. 2-chloroethanol (2500ppb)
49. *cis*-1,3-dichloropropene
50. toluene-d8(SMC)
51. toluene
52. 4-methyl-2-penanone
53. pyridine (250ppb)
54. *trans*-1,3-dichloropropene
55. ethyl methacrylate
56. tetrachloroethene
57. 1,1,2-trichloroethane
58. dibromochloromethane
59. 1,3-dichloropropane
60. *n*-butyl acetate
61. 1,2-dibromoethane
62. 2-hexanone
63. 2-picoline (250ppb)
64. ethylbenzene
65. chlorobenzene-D5(IS)
66. chlorobenzene
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. *n*-propylbenzene
76. 1,1,2,2-tetrachloroethane
77. bromobenzene
78. 1,3,5-trimethylbenzene
79. 2-chlorotoluene
80. 1,2,3-trichloropropane
81. 4-chlorotoluene
82. *tert*-butylbenzene
83. 1,2,4-trimethylbenzene
84. pentachloroethane
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. 1,2,3-trichlorobenzene
96. naphthalene
97. 1,2,4-trichlorobenzene

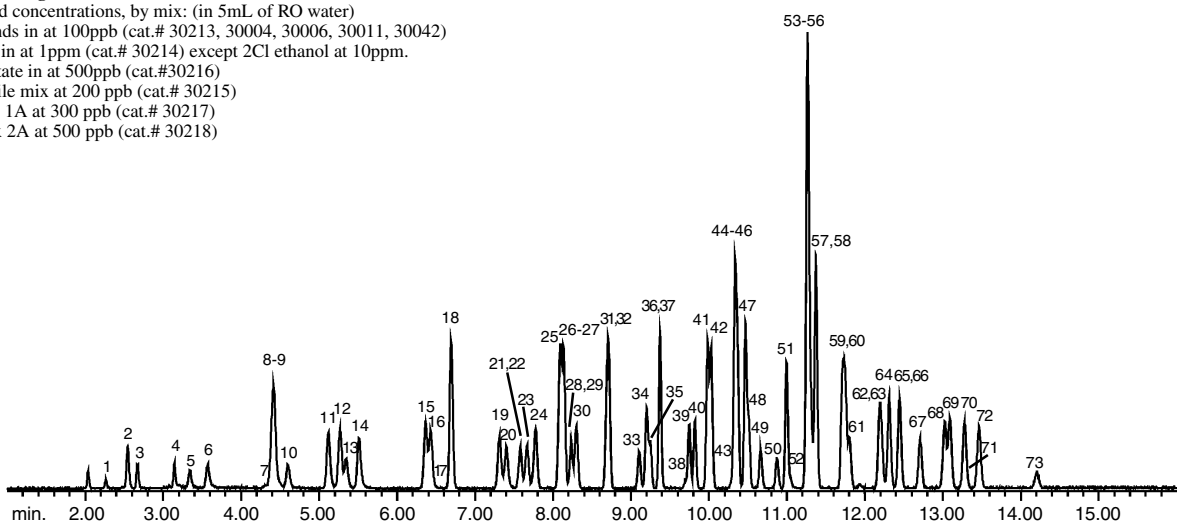
Application #3

Volatile Organics EPA Method 8240 (8260 Short List) Rtx®-VMS

Rtx®-VMS

30m, 0.25mm ID, 1.40µm
(cat.# 19915)

Instrumentation & Conditions
Carrier gas: 1.3mL/min. @ constant flow
Concentrator: Tekmar LSC-3000 Purge and Trap
Trap: Vocarb 3000 (type K) -- see concentrations in 5mL/RO
Purge: 11 min. @ 40mL/min. @ ambient temp.
Dry Purge: 1 min. @ 40mL/min. (MCS bypass)
Desorb Preheat: 245°C
Desorb: 250°C for 2 min., flow 15mL/min.
Bake: 260°C for 8 min.
Interface to GC: transfer line 0.32mm ID Siltek fused silica
1:20 split at injection port w/ 1mm ID sleeve.
GC: HP6890
Detector: HP5973 Mass Selective Detector
Oven Conditions: 40°C (hold 4 min.) to 90°C at 16°C/min. (no hold) to 210°C at 32°C/min. (hold 5 min.)
Adjust dichlorodifluoromethane to a retention time of 2.27 min. @ 40°C.
MS Scan Range: 35-300amu
compound concentrations, by mix: (in 5mL of RO water)
Compounds in at 100ppb (cat.# 30213, 30004, 30006, 30011, 30042)
Alcohols in at 1ppm (cat.# 30214) except 2Cl ethanol at 10ppm.
vinyl acetate in at 500ppb (cat.#30216)
8240 nitrile mix at 200 ppb (cat.# 30215)
8240 mix 1A at 300 ppb (cat.# 30217)
8240 Mix 2A at 500 ppb (cat.# 30218)



1. dichlorodifluoromethane
2. chloromethane
3. vinyl chloride
4. bromomethane
5. chloroethane
6. trichlorofluoromethane
7. ethanol
8. 1,1-dichloroethene
9. carbon disulfide
10. iodomethane
11. allyl chloride
12. methylene chloride
13. acetone
14. *trans*-1,2-dichloroethene
15. 1,1-dichloroethane
16. acrylonitrile
17. allyl alcohol
18. vinyl acetate
19. bromochloromethane
20. chloroform
21. carbon tetrachloride
22. propargyl alcohol
23. 1,1,1-trichloroethane
24. 2-butanone
25. benzene
26. propionitrile
27. methacrylonitrile
28. 1,2-dichloroethane-d4
29. isobutyl alcohol
30. 1,2-dichloroethane
31. trichloroethene
32. 1,4-difluorobenzene
33. dibromomethane
34. 1,2-dichloropropane
35. bromodichloromethane
36. methyl methacrylate
37. 1,4-dioxane
38. 2-chloroethanol
39. 2-chloroethyl vinyl ether
40. *cis*-1,3-dichloropropene
41. toluene-d8
42. toluene
43. pyridine
44. 4-methyl-2-pentanone
45. tetrachloroethene
46. *trans*-1,3-dichloropropene
47. ethyl methacrylate
48. 1,1,2-trichloroethane
49. dibromochloromethane
50. 1,2-dibromoethane
51. 2-hexanone
52. 2-picoline
53. chlorobenzene-D5
54. ethylbenzene
55. chlorobenzene
56. 1,1,1,2-tetrachloroethane
57. *m*-xylene
58. *p*-xylene
59. *o*-xylene
60. stryrene
61. bromoform
62. 4-bromo-1-fluorobenzene
63. *cis*-1,4-dichloro-2-butene
64. 1,1,2,2-tetrachloroethane
65. 1,2,3-trichloropropane
66. *trans*-1,4-dichloro-2-butene
67. pentachloroethane
68. 1,3-dichlorobenzene
69. 1,4-dichlorobenzene
70. benzyl chloride
71. malononitrile
72. 1,2-dichlorobenzene
73. 1,2-dibromo-3-chloropropane