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Alternatives for Separating Volatile Organic Compounds by Capillary GC

C. Woolley, R. Shirey, J. Desorcie

Using identical analytical conditions, we compared the performance of three 60m x 0.25mm ID capillary columns for separating 60 volatile organic compounds (VOCs) listed in US EPA Method 502.2: an SPB-624 column (1.4µm film), a VOCOL column (1.5µm phase film), and an SPB-Octyl column (1.0µm film). The SPB-624 column provided the highest column efficiency and, except for m- and p-xylene, complete resolution with MS or PID/ELCD detection. The VOCOL column provided the lowest column efficiency and longest retention times, but the fewest coelutions, and near-complete resolution with MS or PID/ELCD detection. The SPB-Octyl column provided high column efficiency and a unique elution order.

Volatile organic compounds (VOCs) are among the most common chemical pollutants tested for in soil, sludge, drinking water, and wastewater, and emphasis currently is being placed on determining and controlling VOC contaminants in outdoor and indoor air (e.g., US Environmental Protection Agency Method TO-14). The great number and chemical diversity of VOCs which can be present in these samples demands capillary GC columns that are capable of separating almost 100 compounds. This high separating power usually is accomplished with long (75 or 105 meters) 0.53mm ID columns, but narrow diameter columns (0.25mm ID) with shorter lengths (30 or 60 meters) also can be effective. Columns with specially developed bonded stationary phases provide the polar, polarizable, and dispersive interactions needed to separate large numbers of VOCs. Columns with different bonded stationary phases also can elute VOCs in different orders, or can separate pairs of VOCs that cannot be separated by other columns.

Using identical analytical conditions, we examined the performance of three 60m x 0.25mm ID capillary columns for separating 60 VOCs listed in US EPA Method 502.2: an SPB™-624 column (1.4µm film), a VOCOL™ column (1.5µm phase film), and an SPB-Octyl column (1.0µm film) (see Figure A). Our findings are summarized here.

SPB-624 Column

The SPB-624 column is a key column for separating VOCs extracted from drinking water, wastewater, indoor or outdoor air, and soil/sludge. SPB-624 columns also are commonly used to separate volatile organic flavor and fragrance additives, and residual solvents in industrial or pharmaceutical products. These columns can be used with purge-and-trap, headspace, or solid phase microextraction (SPME) systems. Under the conditions we used, the SPB-624 column provided the highest column efficiencies and a unique selectivity for certain VOCs that typically coelute on VOCOL columns (Table 1). Most coeluting VOCs could be resolved by using MS (extracted ions), PID/ELCD, or FTIR. Only m- and p-xylene (35/36) were not resolved.

VOCOL Column

The VOCOL column is standard in the industry for separating environmental VOCs. It is widely used in purge-and-trap GC-PID/ELCD and purge-and-trap GC-MS systems, in US EPA Methods 502.2, 524.2, 624, 8020, TO-14, 8260, and CLP-VOA. The VOCOL column provided the lowest Trennzahl values, yet, due to the designed selectivity of the stationary phase, it produced the fewest coelutions (Table 2). The VOCOL column provided superior separation of substituted benzenes (40-55) and of halogenated alkanes and alkenes (11-19). Coeluting VOCs were resolved by using MS, PID/ELCD, or FTIR, again with the exception of m- and p-xylene. Relative to SPB-624, the VOCOL column reversed the elution order for a few compounds (Table 2), because the VOCOL column's higher mean polarity creates a stronger interaction with the longer retained VOCs.

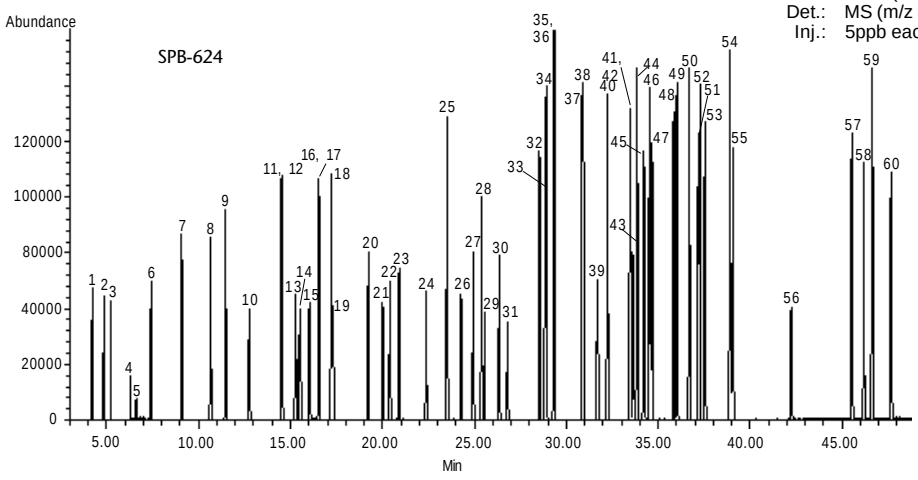
Table 1. Column Performance: SPB-624 Column

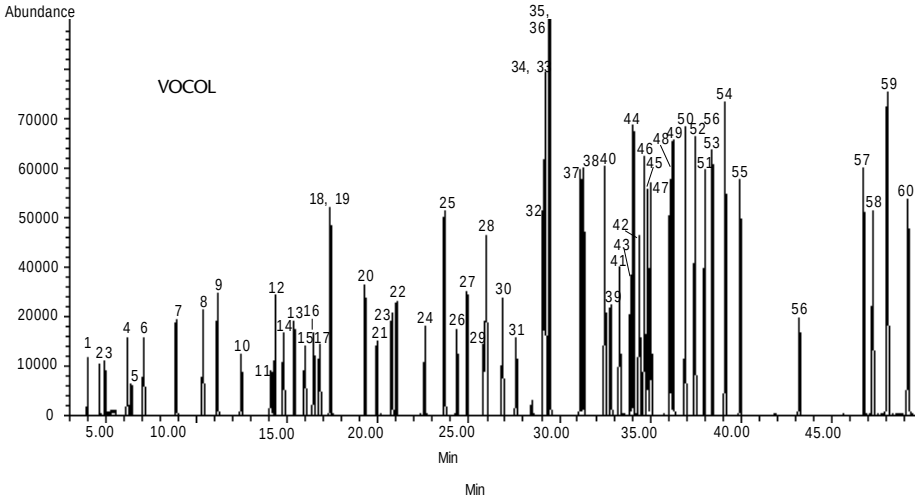
Trennzahl Values (Separation Numbers)	
between vinyl chloride (3) and tetrachloroethene (28)	211
between chlorobenzene (32) and 1,2,3-trichlorobenzene (60)	204
Unique Separations	
tetrachloroethene/1,3-dichloropropane (28/29)	
chlorobenzene/1,1,1,2-tetrachloroethane - ethylbenzene (32/33-34)	

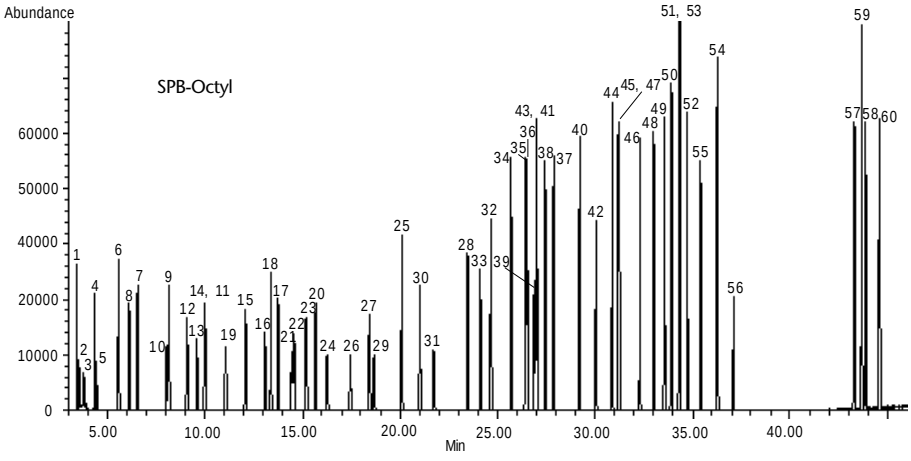
VOCs Resolved by Selective Detection	**MS**	**PID/ELCD**
Coeluting		
2,2-dichloropropane/cis-1,2-dichloroethene (11 / 12)	yes	yes
1,1-dichloropropene/carbon tetrachloride (16/17)	yes	yes
m-xylene / p-xylene (35/36)	no	no
1,1,2,2-tetrachloroethane and bromobenzene (41/42)	yes	yes
Partially Coeluting		
benzene/1,2-dichloroethane (18/19)	yes	yes
1,1,1,2-tetrachloroethane/ethylbenzene (33/34)	yes	yes
o-xylene/styrene (37/38)	yes	no
1,3-dichlorobenzene/p-isopropyltoluene (51/52)	yes	yes

Figure A. Volatile Organic Compounds on Three Capillary Columns (VOCs Listed in US EPA Method 502.2)

Column: **SPB-624, 60m x 0.25mm ID, 1.4µm film**
Cat. No.: **24256**
VOCOL, 60m x 0.25mm ID, 1.5µm film
24154
SPB-Octyl, 60m x 0.25mm ID, 1.0µm film
24233-U
Oven: 35°C (4 min) to 200°C at 4°C/min, hold 10 min
Det.: MS (m/z = 45-300), 300°C
Inj.: 5ppb each analyte in methanol, splitless (2 min), 250°C







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. 1,1,-Dichloroethane
11. 2,2-Dichloropropane
12. cis-1,2-Dichloroethene
13. Bromochloromethane
14. Chloroform
15. 1,1,1-Trichloroethane
16. 1,1-Dichloropropene
17. Carbon tetrachloride
18. Benzene
19. 1,2-Dichloroethane
20. Trichloroethene
21. 1,2-Dichloropropane
22. Dibromomethane
23. Bromodichloromethane
24. cis-1,3-Dichloropropene
25. Toluene
26. trans-1,3-Dichloropropene
27. 1,1,2-Trichloroethane
28. Tetrachloroethene
29. 1,3-Dichloropropane
30. Dibromochloromethane
31. 1,2-Dibromoethane
32. Chlorobenzene
33. 1,1,1,2-Tetrachloroethane
34. Ethylbenzene
35. m-Xylene
36. p-Xylene
37. o-Xylene
38. Styrene
39. Bromoform
40. Isopropylbenzene
41. 1,1,2,2-Tetrachloroethane
42. Bromobenzene
43. 1,2,3-Trichloropropane
44. n-Propylbenzene
45. 2-Chlorotoluene
46. 1,3,5-Trimethylbenzene
47. 4-Chlorotoluene
48. tert-Butylbenzene
49. 1,2,4-Trimethylbenzene
50. sec-Butylbenzene
51. 1,3-Dichlorobenzene
52. p-Isopropyltoluene
53. 1,4-Dichlorobenzene
54. n-Butylbenzene
55. 1,2-Dichlorobenzene
56. 1,2-Dibromo-3-chloropropane
57. 1,2,4-Trichlorobenzene
58. Hexachlorobutadiene
59. Naphthalene
60. 1,2,3-Trichlorobenzene

795-0459, 0465, 0462

SPB-Octyl Column

The SPB-Octyl column (50% n-octyl/50% methyl polysiloxane phase) was designed for detailed separations of petroleum hydrocarbons and PCB congeners. The bonded phase is less polar than polydimethylsiloxane (e.g., SPB-1) and is only slightly more polar than the totally hydrocarbon nonbonded phase, squalane. The column provides high theoretical plates, even at subzero temperatures, and increases the retention of halogenated aromatics and alkenes (Table 3). Relative to VOCOL and SPB-624 columns, the SPB-Octyl column greatly shifted the elution order for many VOCs (Table 3). It was the only column to separate m- and p-xylene (Figure A).

Table 2. Column Performance: VOCOL Column

Trennzahl Values (Separation Numbers)		
between vinyl chloride (3) and tetrachloroethene (28)		197
between chlorobenzene (32) and 1,2,3-trichlorobenzene (60)		130
Unique Separations		
2,2-dichloropropane/cis-1,2-dichloroethene (11/12)		
1,1-dichloropropene/carbon tetrachloride (16/17)		
o-xylene / styrene (37/38)		
1,1,2,2-tetrachloroethane/bromobenzene (41/42)		
p-isopropyltoluene/1,3-dichlorobenzene (52/51) (elution order reversed, relative to SPB-624)		
VOCs Resolved by Selective Detection	**MS**	**PID/ELCD**
Coeluting		
benzene/1,2-dichloroethane (18/19)	yes	yes
1,1,1,2-tetrachloroethane/ethylbenzene (33/34)	yes	yes
m-xylene/p-xylene (35/36)	no	no
Partially Coeluting		
tetrachloroethene/1,3-dichloropropane (28/29)	yes	yes
chlorobenzene/1,1,1,2-tetrachloroethane - ethylbenzene (32 / 33-34)	yes	no
Elution Order Reversed, Relative to SPB-624		
chloroform / bromochloromethane (14/13)		
bromodichloromethane / dibromomethane (23/22)		
isopropylbenzene/bromoform (40/39)		
p-isopropyltoluene/1,3-dichlorobenzene (52/51)		

Based on this study, we concluded that the SPB-624 column provided the highest column efficiency (Trennzahl values), the most coelutions, and near-complete resolution with MS or PID/ELCD detection. The VOCOL column provided the lowest column efficiency and longest retention times, but the fewest coelutions, and near-complete resolution with MS or PID/ELCD detection. The SPB-Octyl column provided high column efficiency and a unique elution order. m-Xylene and p-xylene were resolved, but 2-chlorotoluene/4-chlorotoluene and 1,4-dichlorobenzene/1,3-dichloro-benzene were not resolved. One of these three columns should prove ideal for almost any analysis of these and other VOCs.

Table 3. Column Performance: SPB-Octyl Column

Trennzahl Values (Separation Numbers)		
between vinyl chloride (3) and tetrachloroethene (28)		200
between chlorobenzene (32) and 1,2,3-trichlorobenzene (60)		165
Unique Separations		
m-xylene / p-xylene (35/36)		
1,2,3-trichloropropane/n-propylbenzene (43/44)		
1,1,1,2-tetrachloroethane/chlorobenzene - ethylbenzene (33/32-34)		
High Resolution and Reversed Elution Order, Relative to SPB-624 and VOCOL		
cis-1,2-dichloroethene/2,2-dichloropropane (12/11)		
1,2-dichloroethane/benzene (19/18)		
1,3-dichloropropane/tetrachloroethene (29/28)		
styrene/o-xylene (38/37)		
VOCs Resolved by Selective Detection	**MS**	**PID/ELCD**
Coeluting		
chloroform/2,2-dichloropropane (14/11)	yes	no
1,2,3-trichloropropane/ 1,1,2,2-tetrachloroethane (43/41)	yes	no
2-chlorotoluene/4-chlorotoluene (45/47)	no	no
1,3-dichlorobenzene/1,4-dichlorobenzene (51/53)	no	no
Partially Coeluting		
1,1-dichloroethane/trans-1,2-dichloroethene (10/9)	yes	yes
1,2-dichloropropane/dibromomethane (21/22)	yes	no
bromoform/trichloropropane - 1,1,2,2-tetrachloroethane (39/43-41)	yes	no
Elution Order Reversed, Relative to SPB-624 and VOCOL		
8/7, 10/9, 13/12, 18/17, 33/32, 38/37, 55/54, 59/58		
Elution Greatly Reduced		
19, 39, 43, 41		
Elution Greatly Increased		
20, 25, 28		

Ordering Information:

Description	Cat. No.
SPB-624 Capillary Column 60m x 0.25mm ID, 1.4µm film	**24256**
VOCOL Capillary Column 60m x 0.25mm ID, 1.5µm film	**24154**
SPB-Octyl Capillary Column 60m x 0.25mm ID, 1.0µm film	**24233-U**
EPA 524.2 VOC Mix 200µg/mL each analyte in 1mL methanol	**47932**

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