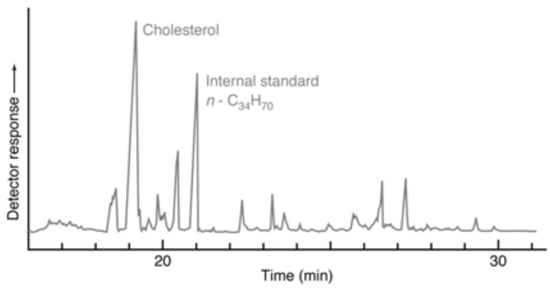
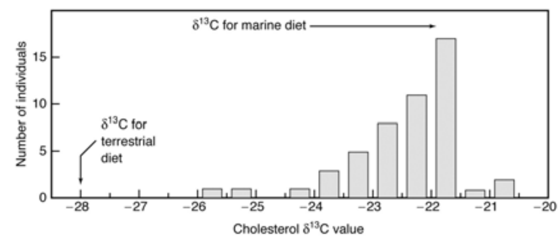
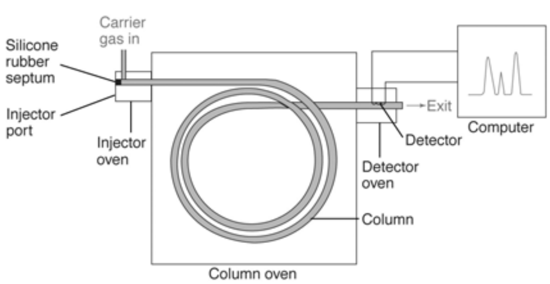
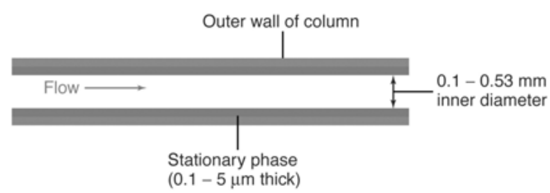
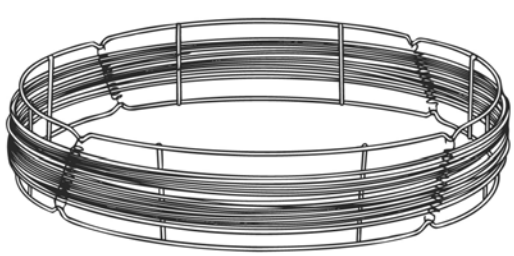

Cholesterol
Internal standard
n - $C_{34}H_{70}$
Detector response ⟶
20
30
Time (min)


$\delta^{13}C$ for marine diet
$\delta^{13}C$ for terrestrial diet
Number of individuals
Cholesterol $\delta^{13}C$ value

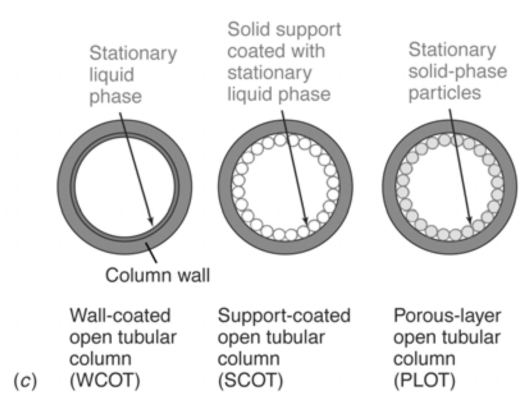

Carrier gas in
Silicone rubber septum
Injector port
Injector oven
Column oven
Column
Detector oven
Detector
Exit
Computer


Outer wall of column
Flow
0.1 – 0.53 mm inner diameter
Stationary phase (0.1 – 5 μm thick)

(a)



(b)


Stationary liquid phase
Solid support coated with stationary liquid phase
Stationary solid-phase particles
Column wall
Wall-coated open tubular column (WCOT)
Support-coated open tubular column (SCOT)
Porous-layer open tubular column (PLOT)

(c)

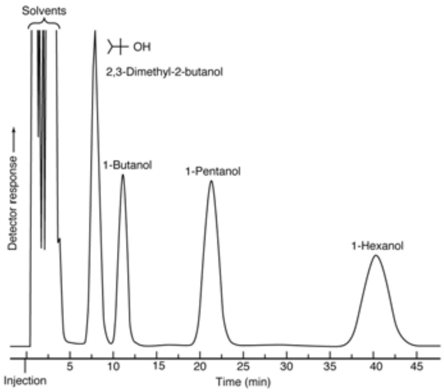
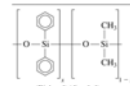
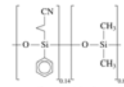
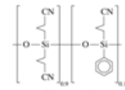
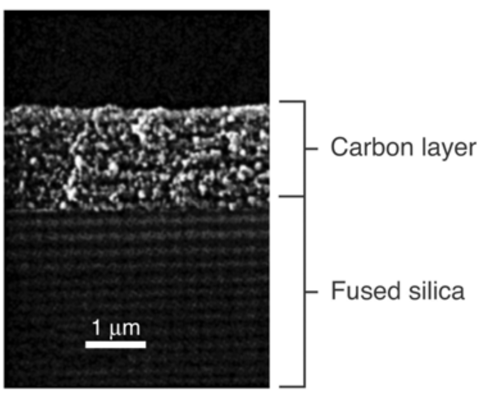


Table 24-1 Common stationary phases in capillary gas chromatography

Structure	Polarity	Temperature range (°C)
 (Diphenyl)$_x$(dimethyl)$_{1-x}$ polysiloxane	$x = 0$ Nonpolar $x = 0.05$ Nonpolar $x = 0.35$ Intermediate polarity $x = 0.65$ Intermediate polarity	−60°−320° −60°−320° 0°−300° 50°−370°
 (Cyanopropylphenyl)$_{0.14}$ (dimethyl)$_{0.86}$ polysiloxane	Intermediate polarity	−20°−280°
$-[CH_2CH_2-O]_n-$ Carbowax (poly(ethylene glycol))	Strongly polar	40°−250°
 (Biscyanopropyl)$_{0.9}$ (cyanopropylphenyl)$_{0.1}$ polysiloxane	Strongly polar	0°–275°



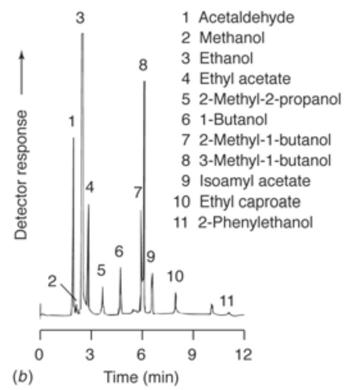
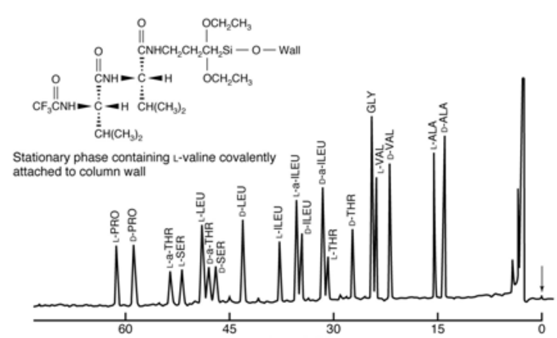
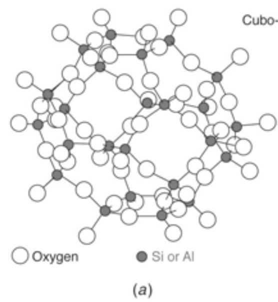


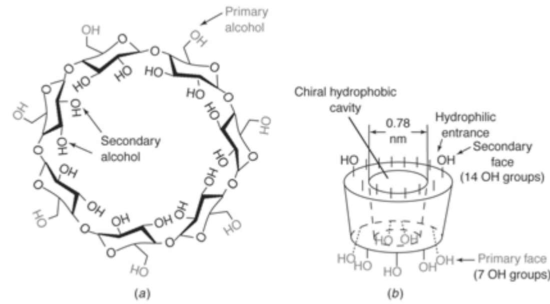
Table 24-2 Polarity of solutes

Nonpolar	Weak intermediate polarity
Saturated hydrocarbons	Ethers
Olefinic hydrocarbons	Ketones
Aromatic hydrocarbons	Aldehydes
Halocarbons	Esters
Mercaptans	Tertiary amines
Sulfides	Nitro compounds (without α-H atoms)
CS_2	Nitriles (without α-atoms)
Strong intermediate polarity	**Strongly polar**
Alcohols	Polyhydroxyalcohols
Carboxylic acids	Amino alcohols
Phenols	Hydroxy acids
Primary and secondary amines	Polyprotic acids
Oximes	Polyphenols
Nitro compounds (with α-H atoms)	
Nitriles (with α-H atoms)	

SOURCE: Adapted from H. M. McNair and E. J. Bonelli, *Basic Gas Chromatography* (Palo Alto, CA: Varian Instrument Division, 1968).







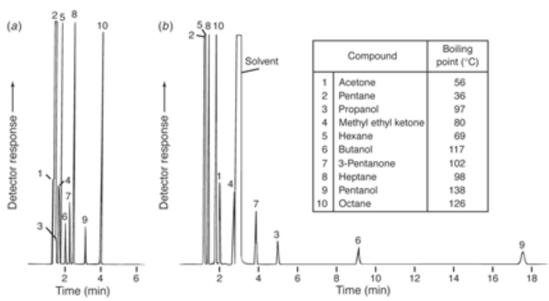
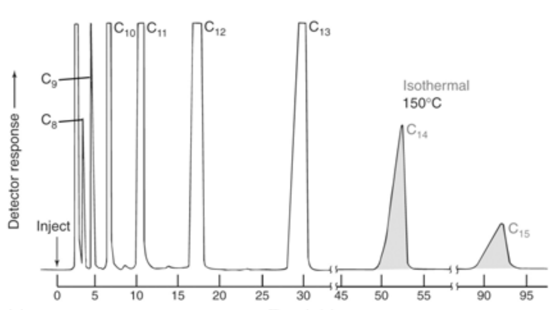


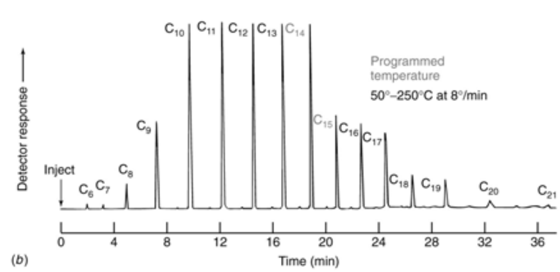
Table 24-3 Retention indexes for several compounds on common stationary phases

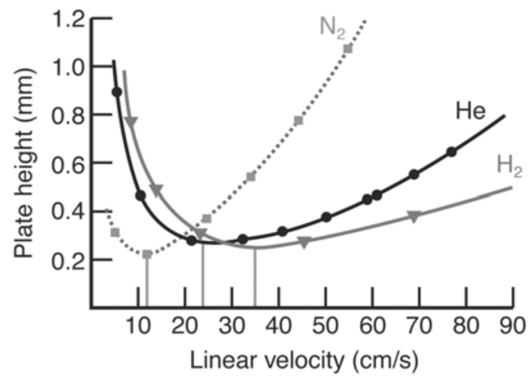
Phase	Retention index[a]				
	Benzene b.p. 80°C	Butanol b.p. 117°C	2-Pentanone b.p. 102°C	1-Nitropropane b.p. 132°C	Pyridine b.p. 116°C
Poly(dimethylsiloxane)	657	648	670	708	737
$(Diphenyl)_{0.05}(dimethyl)_{0.95}$-polysiloxane	672	664	691	745	761
$(Diphenyl)_{0.35}(dimethyl)_{0.65}$-polysiloxane	754	717	777	871	879
$(Cyanopropylphenyl)_{0.14}$-$(dimethyl)_{0.86}$polysiloxane	726	773	784	880	852
$(Diphenyl)_{0.65}(dimethyl)_{0.35}$-polysiloxane	797	779	824	941	943
Poly(ethylene glycol)	956	1 142	987	1 217	1 185
$(Biscyanopropyl)_{0.9}$-$(cyanopropylphenyl)_{0.1}$-polysiloxane	1 061	1 232	1 174	1 409	1 331

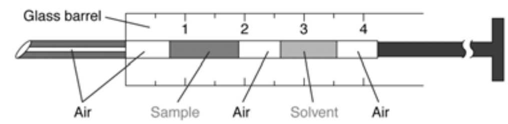
a. For reference, boiling points for various alkanes are hexane, 69°C; heptane, 98°C; octane, 126°C; nonane, 151°C; decane, 174°C; undecane, 196°C. Retention indexes for the straight-chain alkanes are fixed values and do not vary with the stationary phase: hexane, 600; heptane, 700; octane, 800; nonane, 900; decane, 1 000; undecane, 1 100.

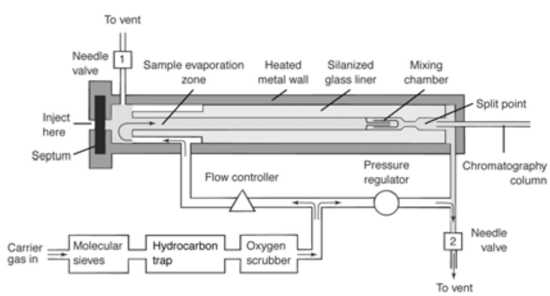
SOURCE: Restek *Chromatography Products Catalog*, 1993–94, Bellefonte, PA.

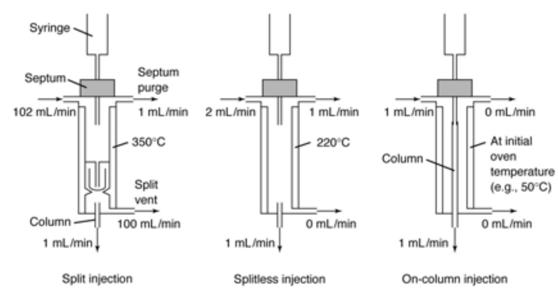


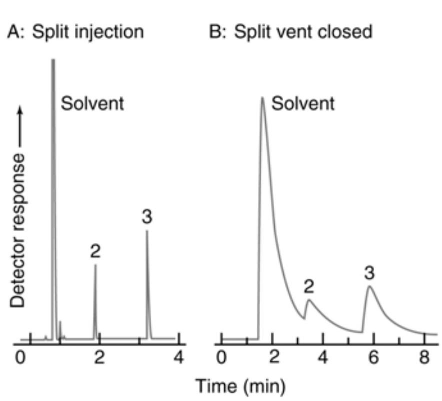



1.2
1.0
0.8
0.6
0.4
0.2
Plate height (mm)
N2
He
H2
10 20 30 40 50 60 70 80 90
Linear velocity (cm/s)


Glass barrel
1 2 3 4
Air
Sample
Air
Solvent
Air


To vent
Needle valve
1
Sample evaporation zone
Heated metal wall
Silanized glass liner
Mixing chamber
Split point
Inject here
Septum
Flow controller
Pressure regulator
Chromatography column
Carrier gas in
Molecular sieves
Hydrocarbon trap
Oxygen scrubber
2
Needle valve
To vent


Syringe
Septum
Septum purge
102 mL/min
1 mL/min
350°C
Split vent
Column
100 mL/min
1 mL/min
2 mL/min
1 mL/min
220°C
0 mL/min
1 mL/min
1 mL/min
0 mL/min
Column
At initial oven temperature (e.g., 50°C)
0 mL/min
1 mL/min
Split injection
Splitless injection
On-column injection


A: Split injection
B: Split vent closed
Solvent
Solvent
Detector response
2
3
2
3
0 2 4
0 2 4 6 8
Time (min)

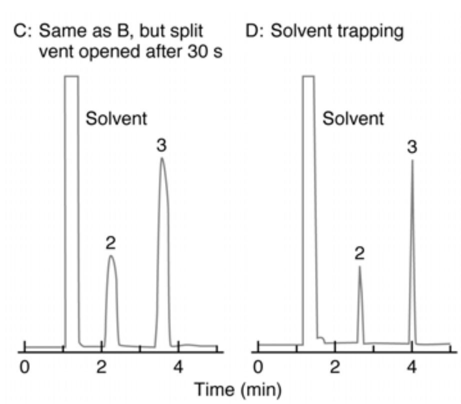

C: Same as B, but split vent opened after 30 s
D: Solvent trapping
Solvent
Solvent
3
2
3
2
0 2 4
0 2 4
Time (min)

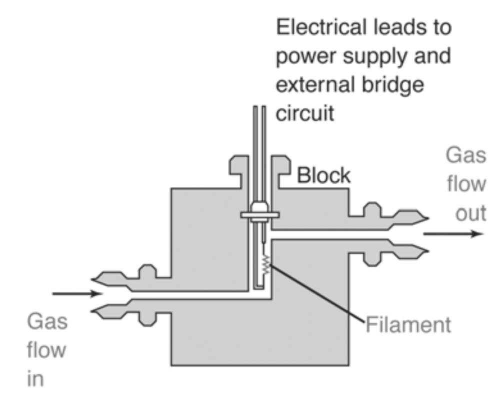
Table 24-4 Thermal conductivity at 273 K and 1 atm

Gas	Thermal conductivity J/(K · m · s)
H_2	0.170
He	0.141
NH_3	0.021 5
N_2	0.024 3
C_2H_4	0.017 0
O_2	0.024 6
Ar	0.016 2
C_3H_8	0.015 1
CO_2	0.014 4
Cl_2	0.007 6

The energy per unit area per unit time flowing from a hot region to a cold region is given by

$$\text{Energy flux } (\text{J}/(\text{m}^2 \cdot \text{s})) = -\kappa(dT/dx)$$

where κ is the thermal conductivity [units = J/(K · m · s)] and dT/dx is the temperature gradient (K/m). Thermal conductivity is to energy flux as the diffusion coefficient is to mass flux.



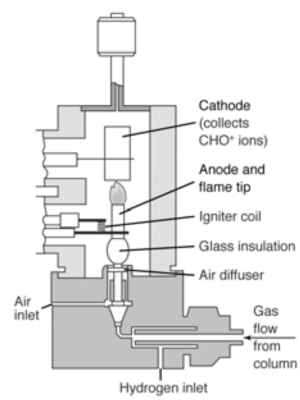
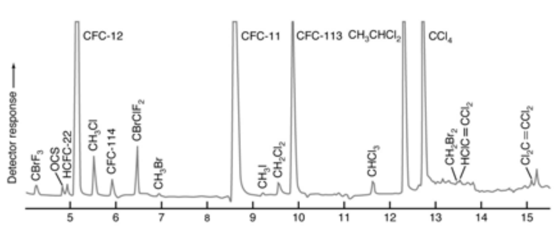
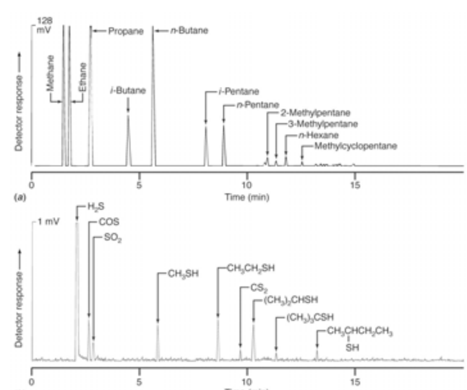


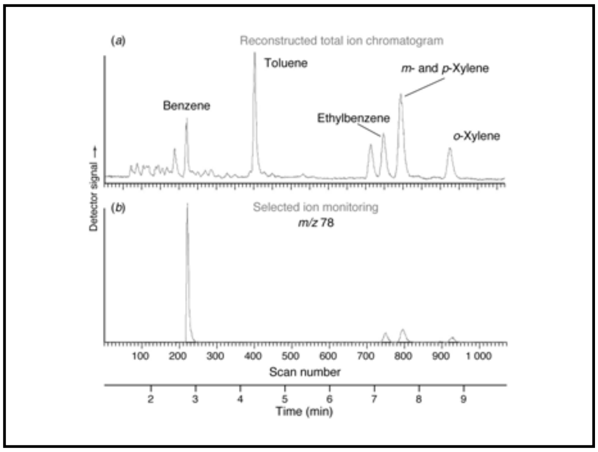
Table 24-5 Detection limits and linear ranges of gas chromatography detectors

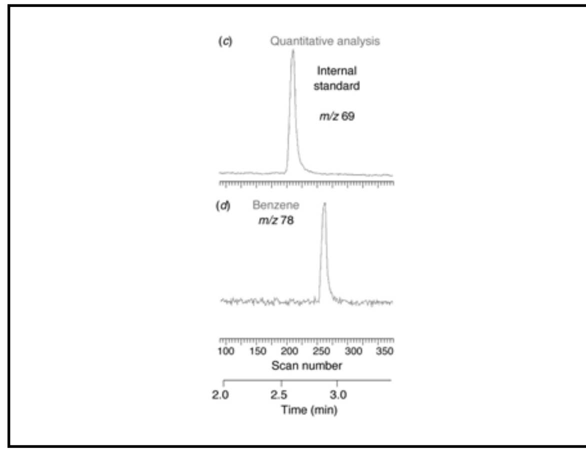
Detector	Approximate detection limit	Linear range
Thermal conductivity	400 pg/mL (propane)	$>10^5$
Flame ionization	2 pg/s	$>10^7$
Electron capture	As low as 5 fg/s	10^4
Flame photometric	<1 pg/s (phosphorus)	$>10^4$
	<10 pg/s (sulfur)	$>10^3$
Nitrogen-phosphorus	100 fg/s	10^5
Sulfur chemiluminescence	100 fg/s (sulfur)	10^5
Fourier transform infrared	200 pg to 40 ng	10^4
Mass spectrometric	25 fg to 100 pg	10^5

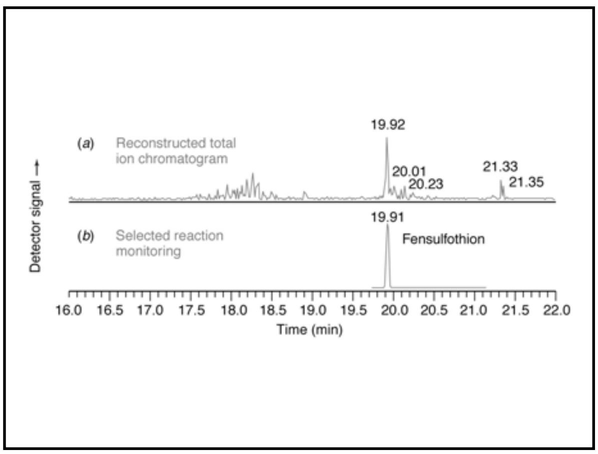
SOURCE: Most data are from D. G. Westmoreland and G. R. Rhodes, "Detectors for Gas Chromatography," *Pure Appl. Chem.* **1989**, *61*, 1147.

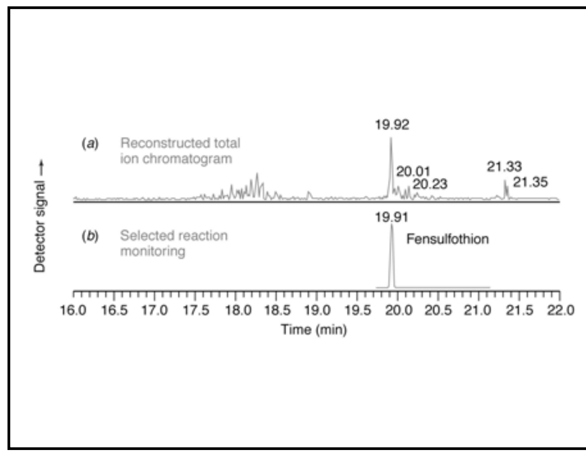


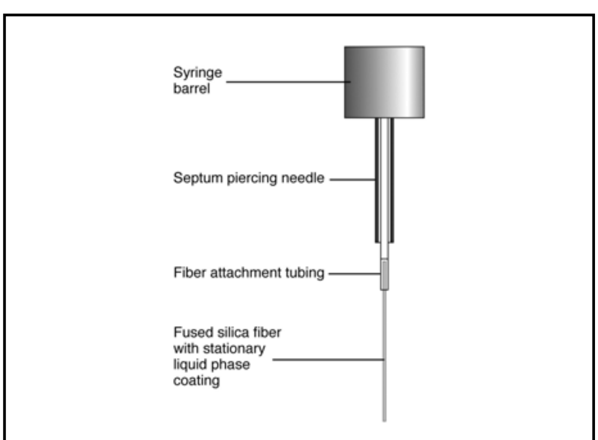


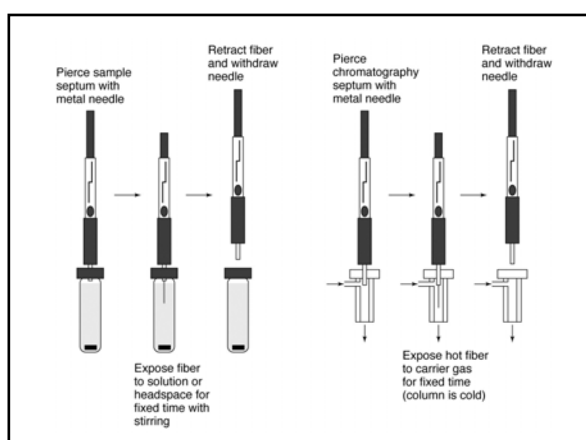

(a)
Reconstructed total ion chromatogram
Toluene
m- and p-Xylene
Benzene
Ethylbenzene
o-Xylene
Detector signal →
(b)
Selected ion monitoring
m/z 78
100 200 300 400 500 600 700 800 900 1 000
Scan number
2 3 4 5 6 7 8 9
Time (min)

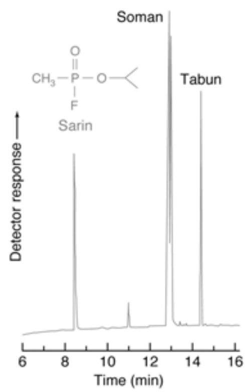

(c)
Quantitative analysis
Internal standard
m/z 69
(d)
Benzene
m/z 78
100 150 200 250 300 350
Scan number
2.0 2.5 3.0
Time (min)


(a)
Reconstructed total ion chromatogram
19.92
20.01
20.23
21.33
21.35
Detector signal →
(b)
Selected reaction monitoring
19.91
Fensulfothion
16.0 16.5 17.0 17.5 18.0 18.5 19.0 19.5 20.0 20.5 21.0 21.5 22.0
Time (min)


(a)
Reconstructed total ion chromatogram
19.92
20.01
20.23
21.33
21.35
Detector signal →
(b)
Selected reaction monitoring
19.91
Fensulfothion
16.0 16.5 17.0 17.5 18.0 18.5 19.0 19.5 20.0 20.5 21.0 21.5 22.0
Time (min)


Syringe barrel
Septum piercing needle
Fiber attachment tubing
Fused silica fiber with stationary liquid phase coating


Pierce sample septum with metal needle
Retract fiber and withdraw needle
Pierce chromatography septum with metal needle
Retract fiber and withdraw needle
Expose fiber to solution or headspace for fixed time with stirring
Expose hot fiber to carrier gas for fixed time (column is cold)



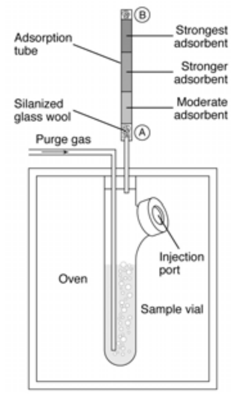


Table 24-6 Gas chromatography column comparisons[15]

Description	Thin-film narrow-bore	Thick-film narrow-bore	Thick-film wide-bore
Inner diameter	0.10–0.32 mm	0.25–0.32 mm	0.53 mm
Film thickness	~0.2 μm	~1–2 μm	~2–5 μm
Advantages	High resolution Trace analysis Fast separations Low temperatures Elute high b.p. compounds	Good capacity Good resolution (4 000 plates/m) Easy to use Retains volatile compounds Good for mass spectrometry	High capacity (100 ng/solute) Good for thermal conductivity and infrared detectors Simple injection techniques
Disadvantages	Low capacity (≤1 ng per solute) Requires high sensitivity detector (not mass spectrometry) Surface activity of exposed silica	Moderate resolution Long retention time for high b.p. compounds	Low resolution (500–2 000 plates/m) Long retention time for high b.p. compounds