High-Speed Gas Chromatography
or
Fast GC

- The reason for Fast GC is the openness of the wall coated column (greater gas permeability) results in a substantially smaller pressure drop per length of column.

- This phenomena causes:

1. Use longer column for complex samples
2. Use of higher flow rate

$$t_{R1} = \frac{L}{u}(k_l + 1)$$

t_{R1} = Retention time

L = Column length

K_1 = Retention factor

u = average carrier-gas velocity

$$\ln k = \frac{A}{T_c} + B$$

A & B = constants that are unique for every compound and for every stationary-phase type and phase volume ratio

T_c = Column temperature

- Plots of ln *k* versus *1/Tc* are known as *van't Hoff plots.*
- These plots are reasonably linear over a limited temperature range and are very useful for addressing the effects of column temperature and temperature program on analysis time and column selectivity. Note that retention is very sensitive to temperature, and typically a 15–20°C increase in column temperature will result in a twofold reduction in solute retention factors.

Problems with HSGC

1. Conventional GC instruments are inadequate
2. Peak capacity np (number of perfectly spaced peaks that will fit in a chromatogram with a specified resolution Rs) is reduced with shorter columns as described by

$$n_p = 1 + \frac{\sqrt{L/H}}{4R_s} \ln\left(\frac{t_{Rl}}{t_M}\right)$$

t_M = holdup time for the column

$$H_{\min} = r\sqrt{\frac{1 + 6k + 11k^2}{3(k+1)^2}}$$

$$u_{\text{opt}} = \frac{j D_{\text{G}}}{r}\sqrt{\frac{48(k+1)^2}{1 + 6k + 11k^2}}$$

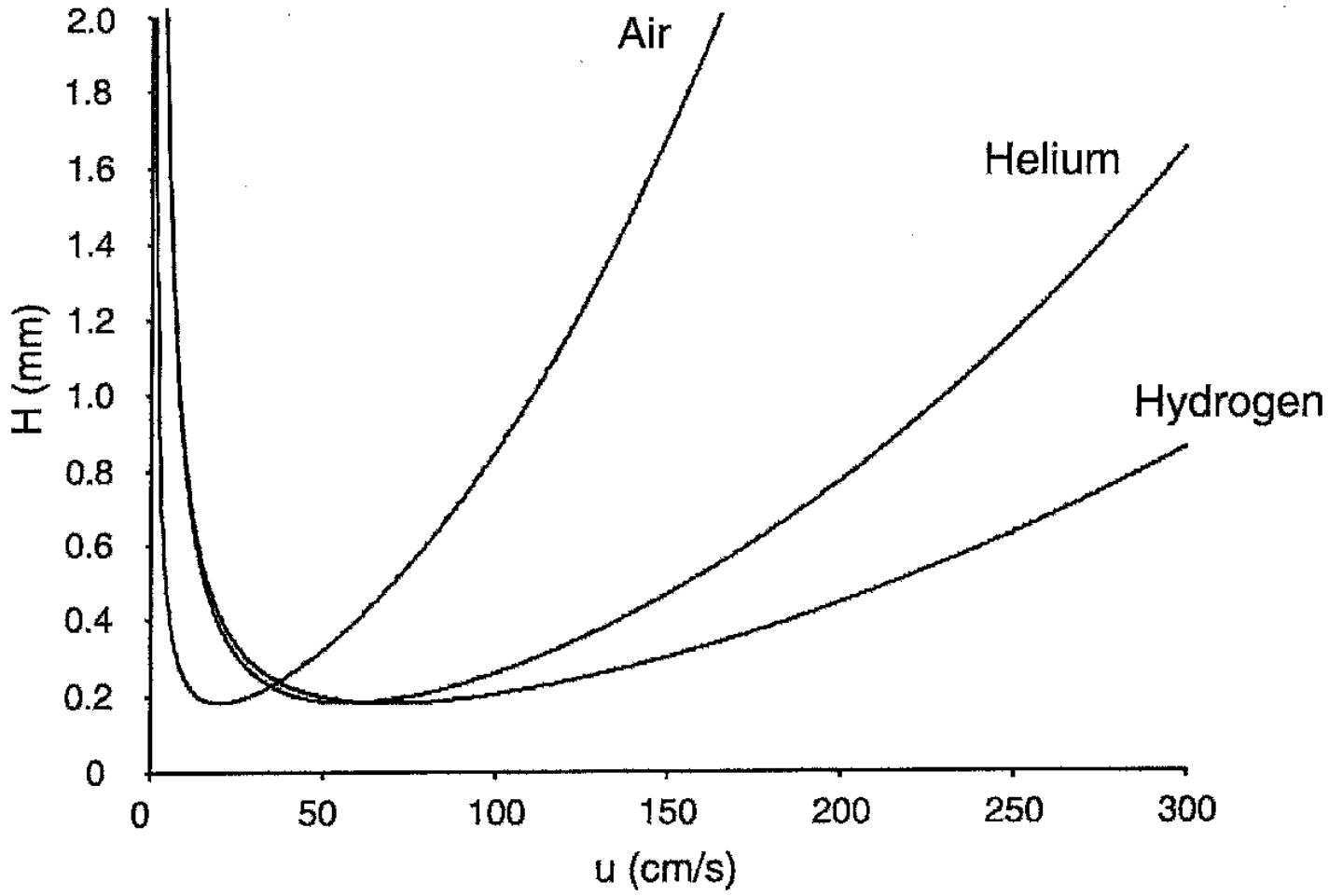
where r is the column radius, D_G is the binary diffusion coefficient of the solute in the carrier gas, k is the solute retention factor, and j is the Martin–James gas compressibility correction for the column inlet and outlet pressures P_i and P_o, respectively:

$$j = \frac{3(P^2 - 1)}{2(P^3 - 1)}$$

$$P = \frac{p_{\text{i}}}{p_{\text{o}}}$$

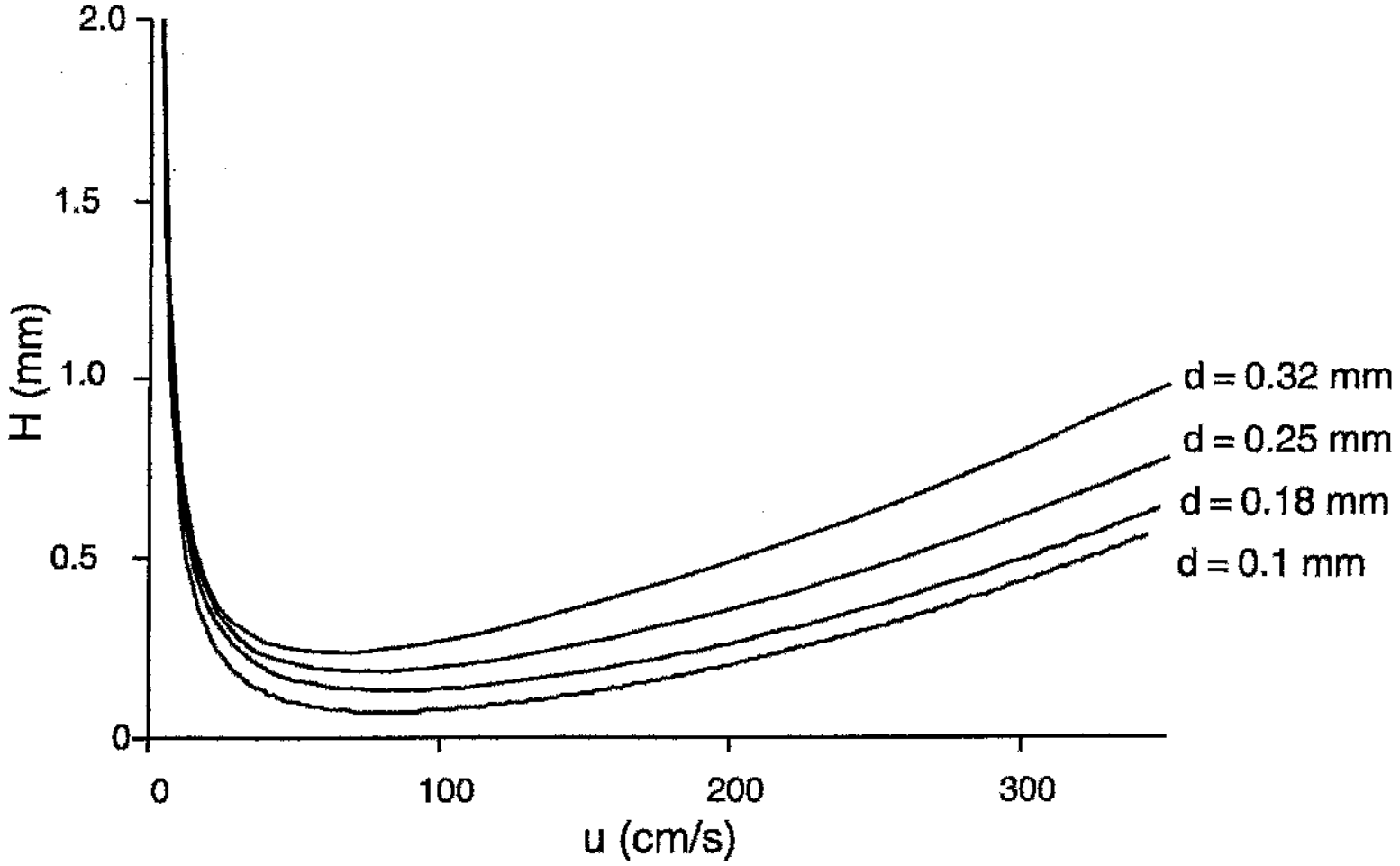
From first equation it is clear that smaller column radius favors greater column efficiency (smaller plate height), and from second equation that small column radius and large binary diffusion coefficients favor high optimal carrier gas velocity, both of which are desirable for HSGC.

Golay plots for air, hydrogen, and helium as carrier gases using a 10-mlong, 0.25-mm-i.d. thin-film column.



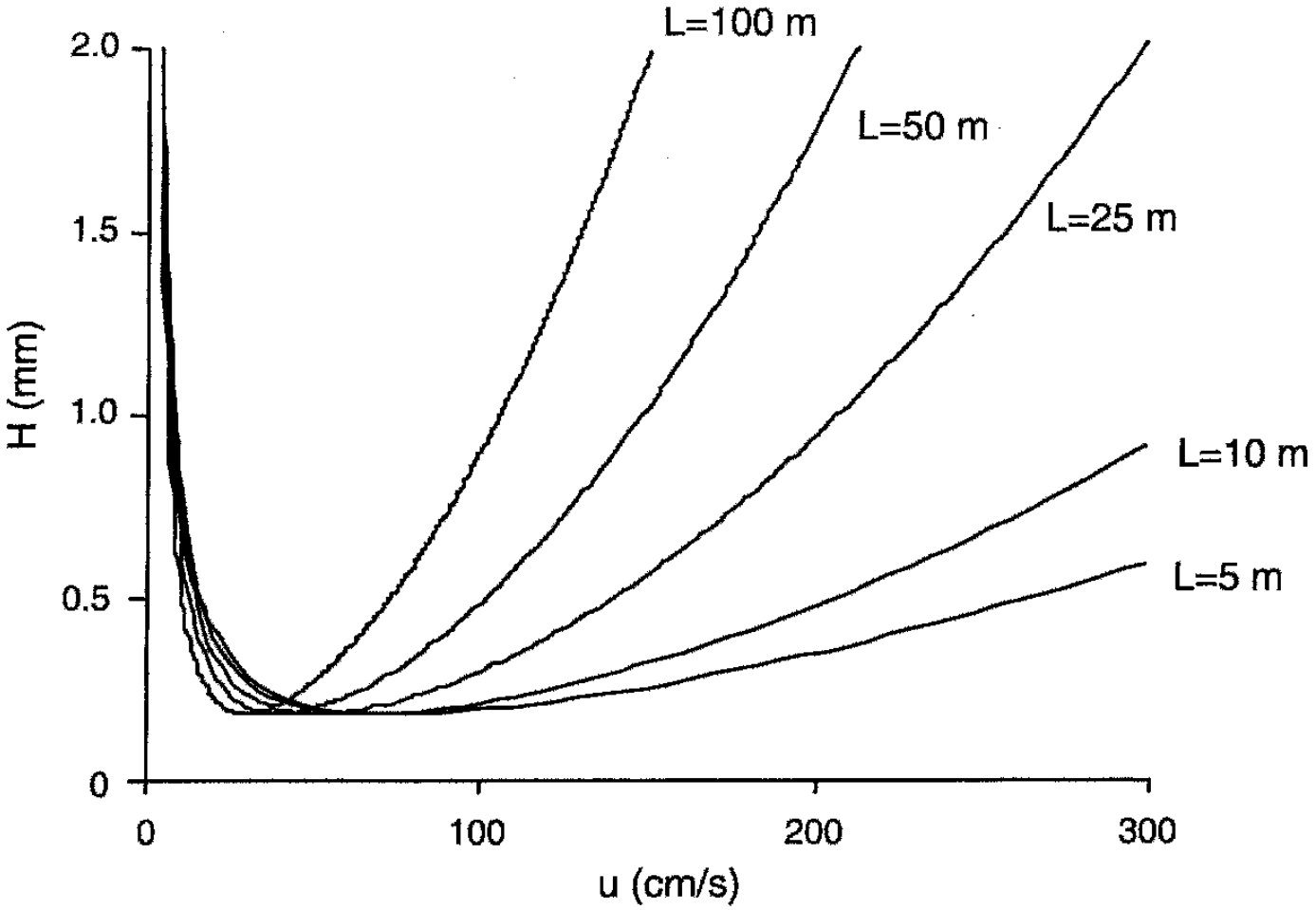
- Note that the slope is inversely proportional to *jDG.* This explains why efficiency with helium as carrier gas decreases more rapidly with increasing *u than with hydrogen. Thus, hydrogen become progressively more* useful as a carrier gas for HSGC as the gas velocity increases. Air and nitrogen are particularly poor for HSGC, since u_{opt} *is low and significant departure from* u_{opt} *results in a large loss in efficiency.*

Golay plots for 10-m-long, thin-film columns of various diameters using hydrogen as carrier gas. A binary diffusion coefficient of 0.4 cm2/s and a retention factor of 2.0 are assumed.



The values of H_{min} *decrease, and the values of* u_{opt} *increase with decreasing column radius, and substantially faster separations* can be obtained with the microbore (0.1-mm-i.d.) column.

Golay plots for 0.20-mm-i.d thin-film columns of various lengths using hydrogen as carrier gas. A binary diffusion coefficient of 0.4 cm2/s and a retention factor of 2.0 are assumed.



- It is frequently observed that shorter columns are more efficient than longer ones at higher flow rates.
- This is explained entirely by gas compression effects. A decrease in *j caused by an increase in inlet pressure associated with longer* columns results in a shift in u_{opt} *to smaller values.*
- In addition to a shift to lower u_{opt} values, the slope of the right-hand flank of the plots in Figure 5.3 is larger for longer columns. This results in substantially greater efficiency for shorter columns when operated at the relatively high average carrier-gas velocities used for HSGC. However, the total number of theoretical plates and thus the column resolving power decreases steadily with decreasing column length.

INSTRUMENTATION

Sources of Extracolumn Band Broadening

$$\sigma_{ec}^2 = \frac{\Delta t^2 u^2}{(k+1)^2}$$

$$H_{ec} = \frac{\Delta t^2 u^2}{L(k+1)^2}$$

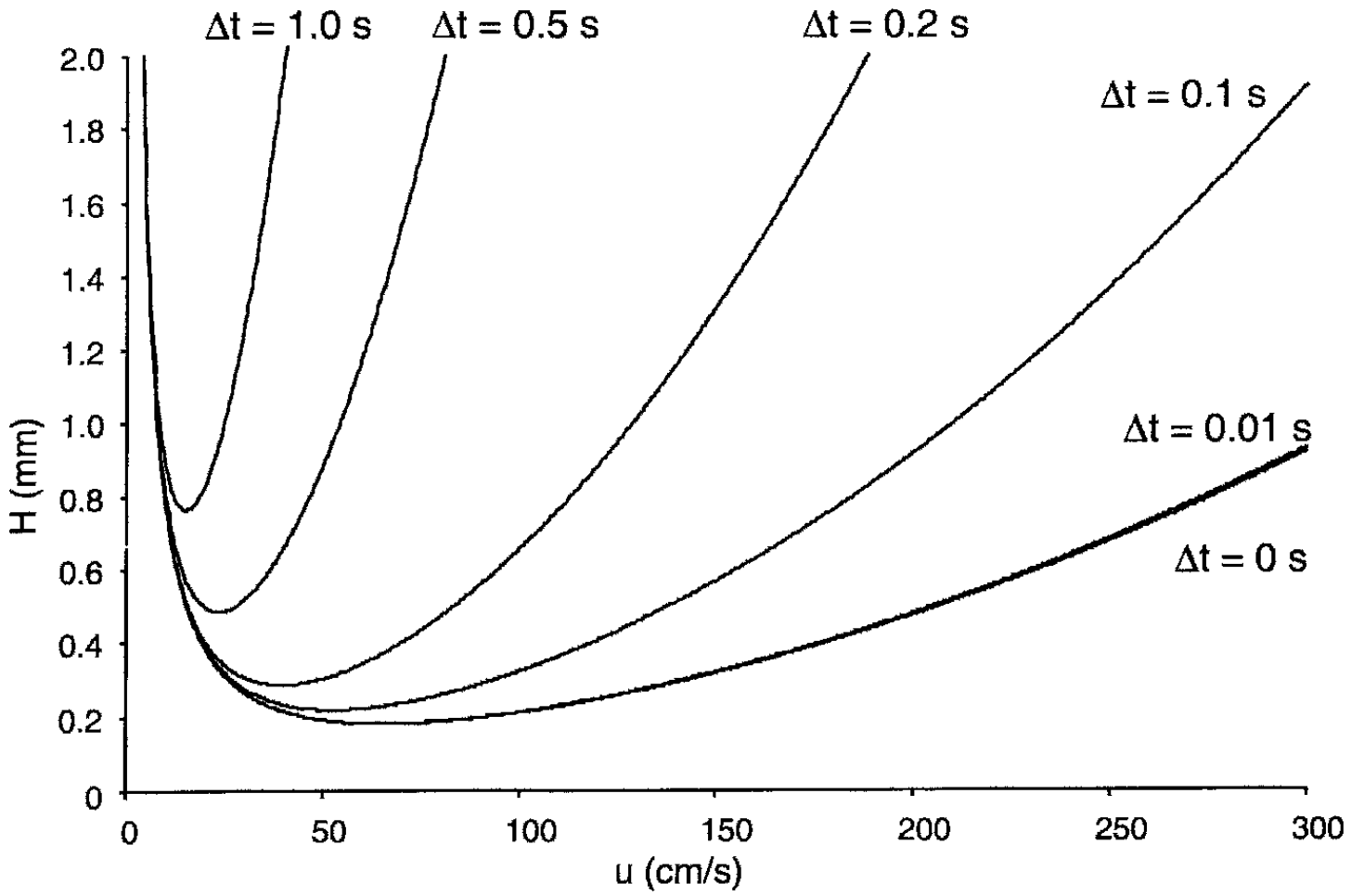
Δt: the total instrumental dead time

H_{ec} = H extra column

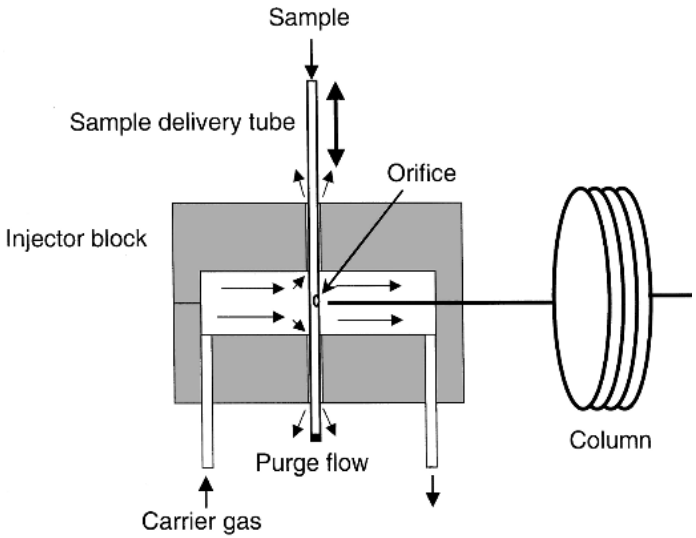
For HSGC with thin-film columns and high flow rates, Equations 5.8 and 5.10 are combined to give Equation 5.11 for plate height considering extracolumn band broadening:

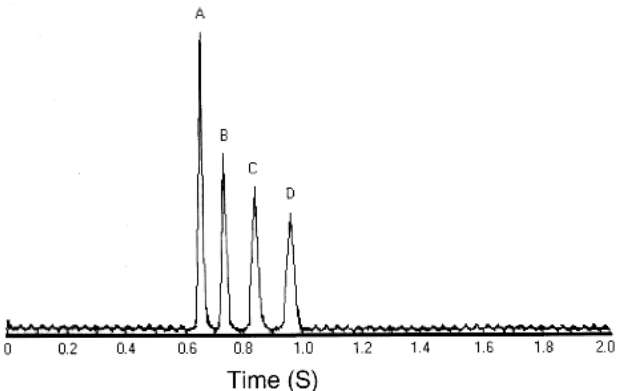
$$H = \frac{1 + 6k + 11k^2}{24(k+1)^2} \frac{r^2}{j D_G} u + \frac{\Delta t^2}{L(1+k)^2} u^2$$

Inlet system

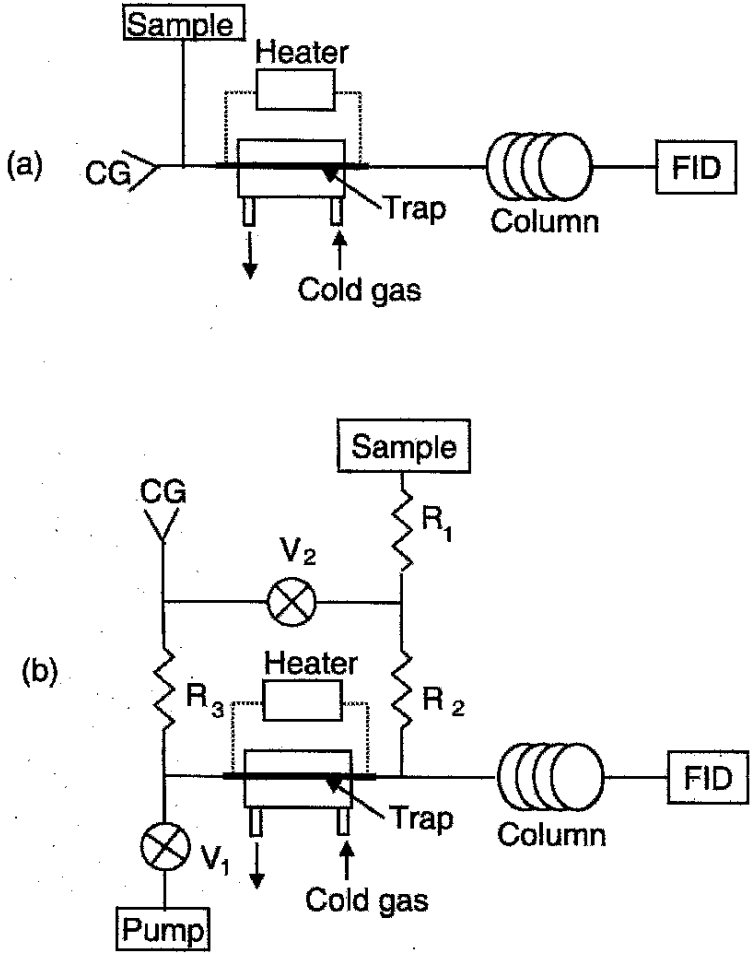


Sample vapor is delivered continuously from a small orifice in the side of the sample delivery tube. A variable-speed motor or a stepper motor is used to translate the sample delivery tube so that the orifice passes the end of the column. The width of the injected sample plug is controlled by the velocity of the sample delivery tube. Only when the orifice is aligned with the end of the column will sample vapor be delivered to the column. Using a microstepper motor to move the sample delivery tube, very reproducible vapor plugs can be obtained with a wide range of plug widths.



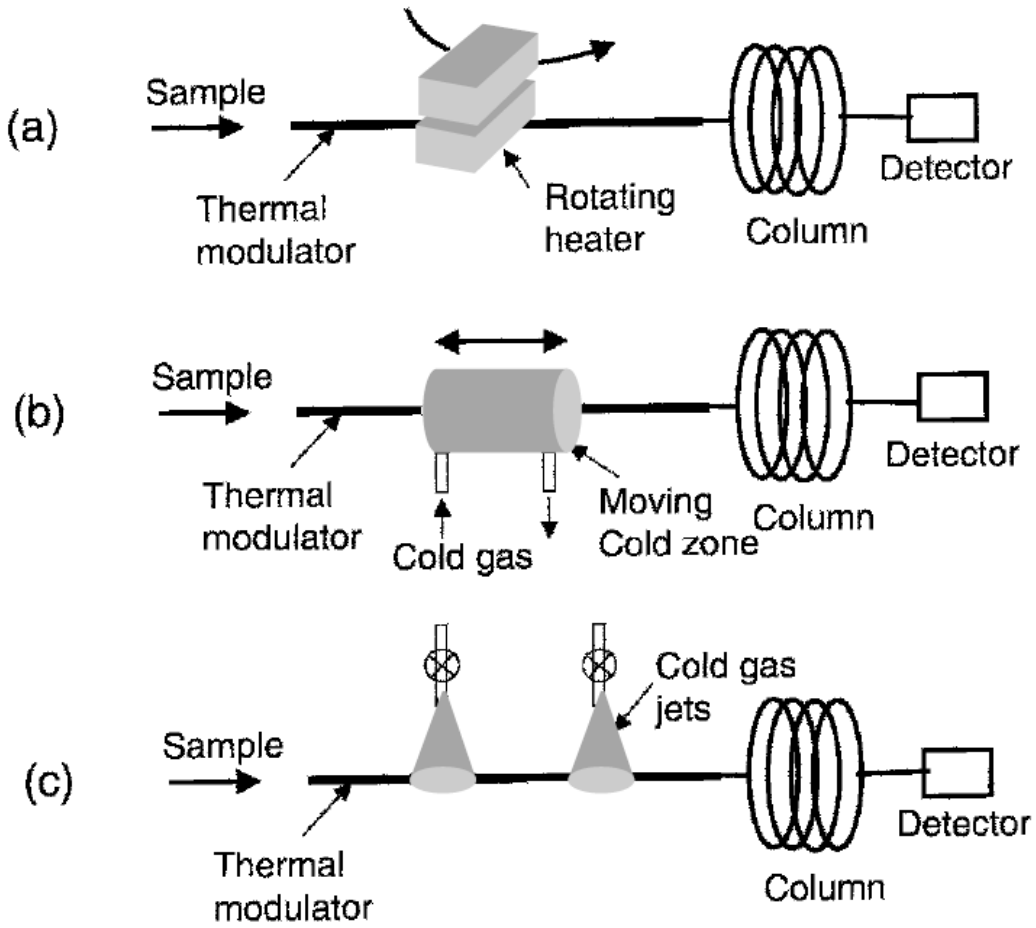


For sample collection, the trap tube is cooled to −50 to −100°C. Trapped compounds slowly creep through the cold-trap tube at rates that depend on the component vapor pressure at the trapping temperature and the gas flowrate through the trap. Eventually, each compound breaks through the downstream end of the trap tube, and this sets the upper limit on sample collection time.

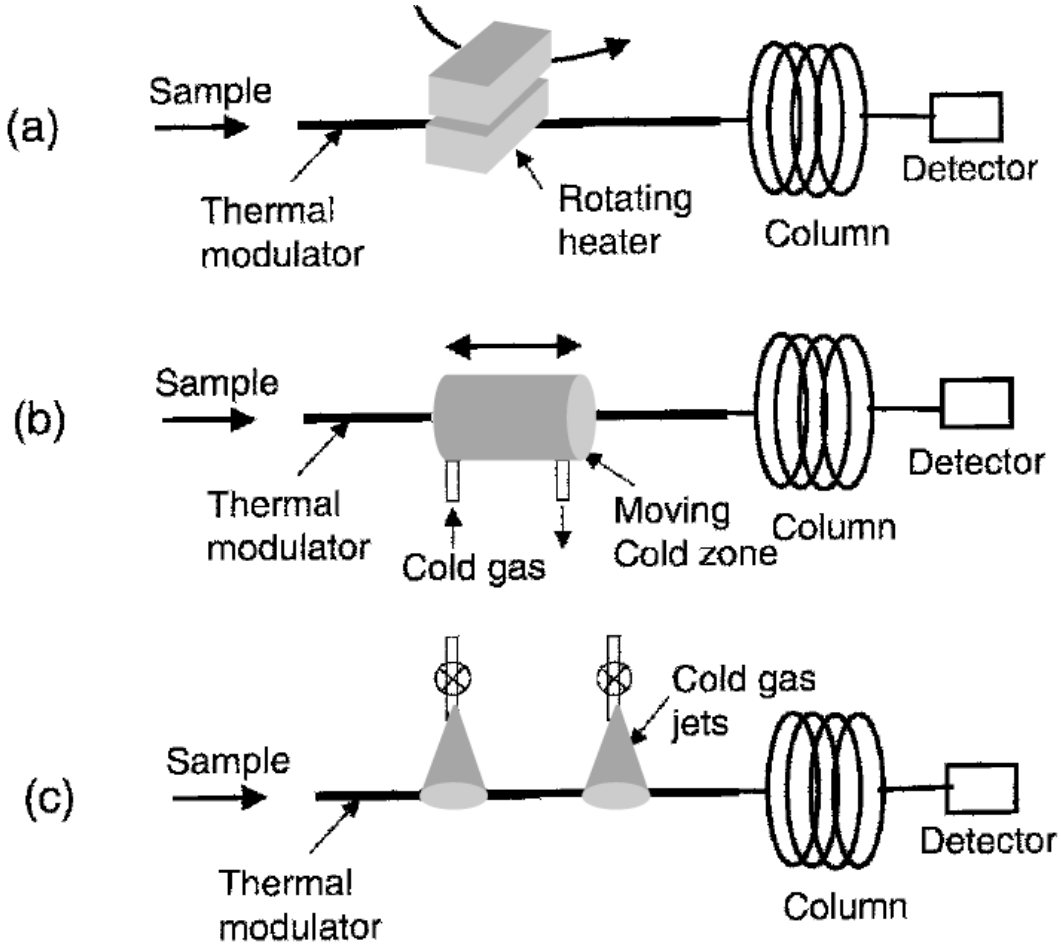


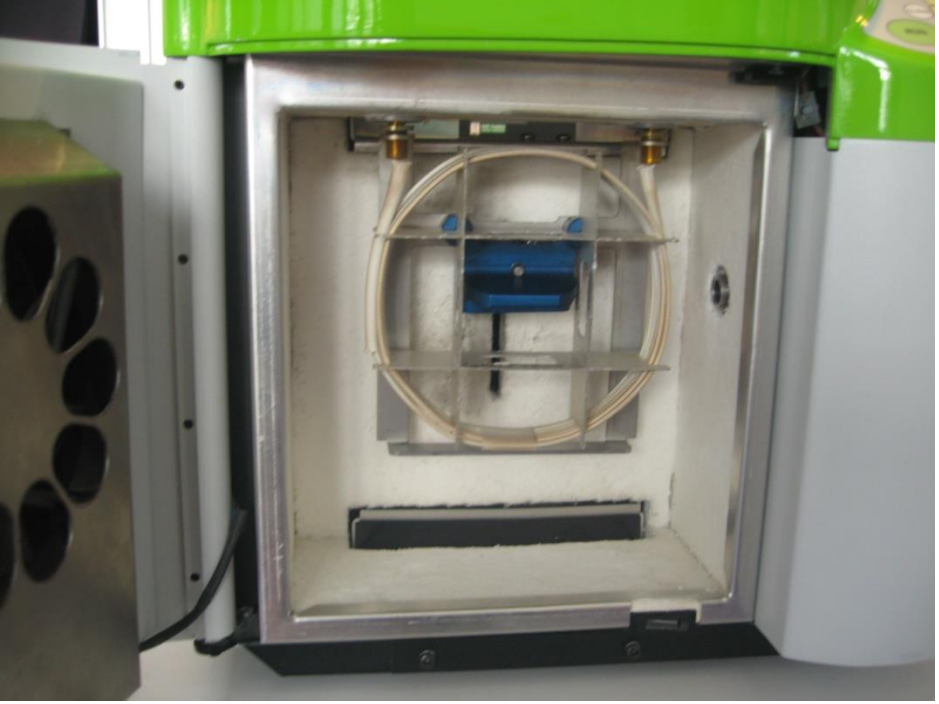
Phase-Coated Thermal Modulators

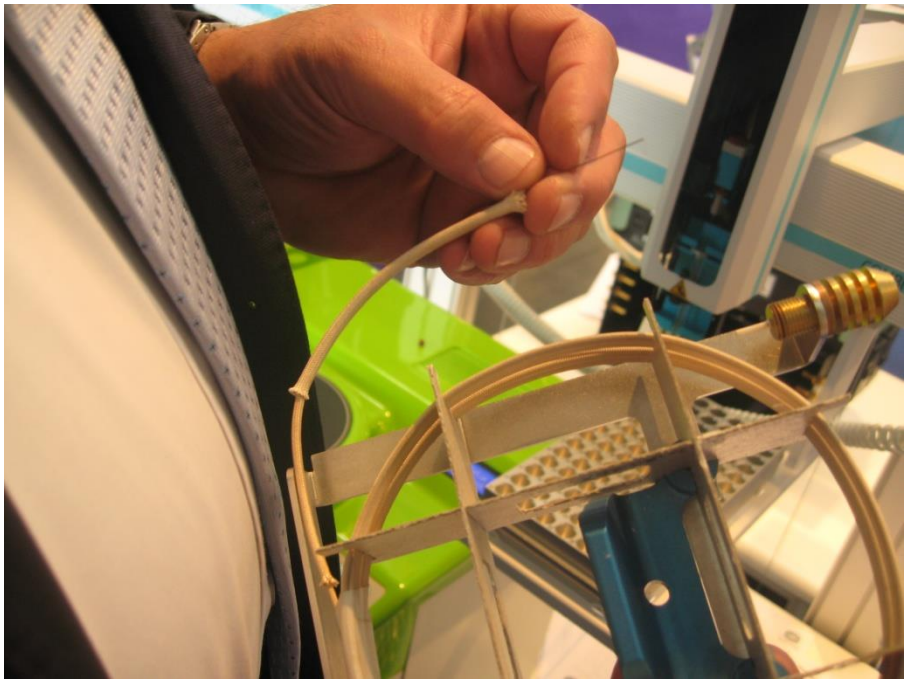
- If a segment of a coated gas chromatographic column is operated at a lower temperature than the oven, or if the stationary phase film is thicker in that portion of the column, the increased retention factors for mixture components in the segment result in reduced migration velocities, and thus sample accumulation occurs in the segment.


(a)
Sample
Thermal modulator
Rotating heater
Column
Detector
(b)
Sample
Thermal modulator
Cold gas
Moving Cold zone
Column
Detector
(c)
Sample
Thermal modulator
Cold gas jets
Column
Detector

If a segment of a coated gas chromatographic column is operated at a lower temperature than the oven, or if the stationary phase film is thicker in that portion of the column, the increased retention factors for mixture components in the segment result in reduced migration velocities, and thus sample accumulation occurs in the segment.







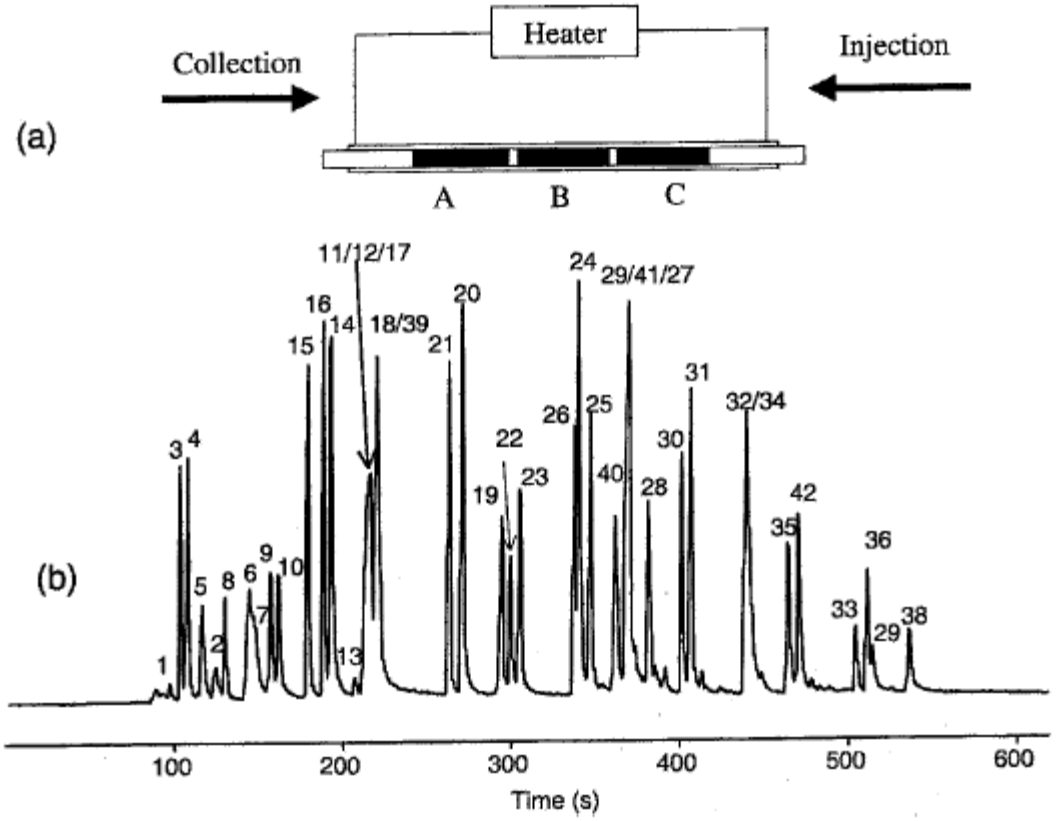
DETECTORS FOR HSGC

Open-Cell Flame Detectors

- Open-cell, flame-based detectors typically have response times of a few milliseconds or less if the capillary separation column is passed through the burner tip and positioned just below the base of the flame. Thus, *t is small, and* σ^2 ec from the detector usually is negligible relative to other extracolumn sources of band broadening. While many HSGC studies have used the FID, few data areavailable for other flame-based detectors such as the flame thermionic detector and the flame photometric detector. These detectors should be suitable for HSGC.

Closed-Cell Detectors

- For closed-cell detectors, including the photoionization detector, the electroncapture detector and the TCD, extracolumn band broadening can be excessive unless specially designed devices with small cell volume are used or the detector is operated at subambient pressure. At reduced column outlet pressure, the carriergas velocity in the detector is increased, and the cell is swept out more quickly.
- Extra gas, called *makeup gas, can be introduced into the detector cell to sweep* the cell more rapidly and reduce peak broadening and distortion.


(a)
Collection
Heater
Injection
A
B
C
(b)
1
2
3
4
5
6
7
8
9
10
11/12/17
13
14
15
16
18/39
19
20
21
22
23
24
29/41/27
25
26
40
28
30
31
32/34
35
42
33
29
36
38
100
200
300
400
500
600
Time (s)