27-1 How do gas-liquid and gas-solid chromatography differ?

The stationary phase in GLC is a liquid at operating temperature while it is a solid in GSC. Primarily, GSC is used for separation of polar compounds that are usually not retained in GLC like hydrogen sulfide, nitrogen oxides, sulfur dioxide, carbon mono and dioxide, as well as other gases.

27-2 What is meant by retention volume?

The retention volume of a solute is defined as its retention time times average flow rate.

\[ V_R = t_R F \]

27.3 What is meant by temperature programming in GC? Why is it frequently used?

Temperature programming in gas chromatography is the main technique used to optimize a separation. In TPGC, the temperature of the column is increased as a function of time. The program is designed in order to fully and efficiently separate compounds that differ significantly in boiling points. Initially low boiling compounds are separated at low temperatures followed by increasing the temperature to allow the separation of other compounds. The increase in temperature can be linear, stepwise, parabolic or combinations so that best separations are obtained. It is frequently used in GC because it is the major tool for optimization of a separation.

27-4. What is the difference between a concentration-sensitive and a mass-sensitive detector?

A concentration sensitive detector responds to concentration of analytes, which means that the same concentration of analytes will result in same signal value. However, mass sensitive detectors respond to number of active groups in the molecule.

27-5. Are the following detectors mass or concentration sensitive? (a) thermal conductivity, (b) electron capture, (c) flame ionization.

<table>
<thead>
<tr>
<th>Detector</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal Conductivity Detector</td>
<td>Concentration sensitive</td>
</tr>
<tr>
<td>Flame ionization Detector</td>
<td>Mass Sensitive</td>
</tr>
<tr>
<td>Electron Capture Detector</td>
<td>Mass Sensitive</td>
</tr>
</tbody>
</table>

27-6. Describe the principles of operation for the detectors listed in Question number 27-5.

a. TCD

This is a nondestructive detector which is used for the separation and collection of solutes to further perform some other experiments on each purely separated component. The heart of the detector is a heated filament which is cooled by helium
carrier gas. Any solute passes across the filament will not cool it as much as helium does because helium has the highest thermal conductivity. This results in an increase in the temperature of the filament which is related to concentration. The detector is simple, nondestructive, and universal but is not very sensitive and is flow rate sensitive.

b. Flame Ionization Detector (FID)

This is one of the most sensitive and reliable destructive detectors. Separate two gas cylinders, one for fuel and the other for \( O_2 \) or air are used in the ignition of the flame of the FID. The fuel is usually hydrogen gas. The flow rate of air and hydrogen should be carefully adjusted in order to successfully ignite the flame.

The FID detector is a mass sensitive detector where solutes are ionized in the flame and electrons emitted are attracted by a positive electrode which is shown as a current and a signal is obtained.

The FID detector is not responsive to air, water, carbon disulfide. This is an extremely important advantage where volatile solutes present in water matrix can be easily analyzed without any pretreatment.

c. Electron Capture Detector (ECD)

This detector exhibits high intensity for halogen containing compounds and thus has found wide applications in the detection of pesticides and polychlorinated biphenyls. The mechanism of sensing relies on the fact that electronegative atoms, like halogens, will capture electrons from a \( \beta \) emitter (usually \( ^{63}\text{Ni} \)). In absence of halogenated compounds, a high current signal will be recorded due to high ionization of the carrier gas which is \( \text{N}_2 \), while in presence of halogenated compounds the signal will decrease due to lower ionization.

27-7. What are the major advantages and the principal limitations of each of the detectors listed in Question

a. TCD characteristics include:

- Rugged
- Wide dynamic range \((10^5)\)
- Nondestructive
• Insensitive ($10^{-8}$ g/s)
• Flow rate sensitive
• Almost Universal

b. FID characteristics include:

• Rugged
• Sensitive ($10^{-13}$ g/s)
• Wide dynamic range ($10^7$)
• Signal depends on number of carbon atoms in organic analytes which is referred to as mass sensitive rather than concentration sensitive
• Weakly sensitive to carbonyl, amine, alcohol, amine groups
• Not sensitive to non-combustibles - H$_2$O, CO$_2$, SO$_2$, NO$_x$
• Destructive

c. ECD characteristics include:

• Electrons from a $\beta$-source ionize the carrier gas (nitrogen)
• Organic molecules containing electronegative atoms capture electrons and decrease current
• Simple and reliable
• Sensitive ($10^{-15}$ g/s) to electronegative groups (halogens)
• Largely non-destructive
• Insensitive to amines, alcohols and hydrocarbons
• Limited dynamic range ($10^2$)
• Mass sensitive detector

27-8. What is the packing material used in most packed GC columns?
Most packing materials are composed of a solid support that is usually a diatomaceous earth particles coated with a stationary phase like OV-x or carbowax.

27-9. How do the following open tubular columns differ?
(a) PLOT columns (b) WCOT columns (c) SCOT columns

a. A PLOT column is an open tubular column with the interior surface covered with a layer of a porous support. It is used for GSC separations.

b. WCOT columns are capillary columns with their inner surfaces coated with a thin film of liquid stationary phase.

c. SCOT columns are capillary columns in which a solid support is first affixed to their inner surfaces followed by coating the support with a liquid stationary phase. The amount of the stationary phase used in SCOT columns are much greater than that used in WCOT columns which allows a higher sample capacity of the SCOT columns.

27-10. What are megapore columns? Why are they manufactured?

Megapore columns are open tubular columns that have internal diameters greater than 500 \( \mu \text{m} \). They are used in situations where a large sample is to be separated since megapore columns tolerate sample sizes close to packed columns.

27-11. What are the advantages of fused-silica capillary columns compared with glass or metal columns?

Fused silica capillary columns are advantageous as compared to glass or metal columns since fused silica columns are easier to manufacture, can be reproducibly drawn to very small diameters and practically any length, and very pure fused silica materials are available which results in very clean columns. FSOT columns are easy to work with in terms of trimming, coiling, etc.

27-12. What properties should the stationary-phase liquid for GC possess?

Liquid Stationary Phases should have the following characteristics:

- Low volatility
- High decomposition temperature (thermally stable)
- Chemically inert (reversible interactions with solvent)
- Chemically attached to support (to prevent bleeding)
- Appropriate \( k' \) and \( \alpha \) for solutes to obtain good resolution
27-13. Why are gas chromatographic stationary phases often bonded or cross-linked? What do these terms mean?

Stationary phases in GLC are usually bonded to solid support or cross-linked in order to prevent bleeding of the stationary phase. Bonding means to covalently attach the stationary phase molecules to solid support while crosslinking means to chemically attach stationary phase molecules to each other, usually by a polymerization process.

27-14. What is the effect of stationary-phase film thickness on gas chromatograms?

Stationary phase film thickness has the following effects in GC:

a. As film thickness increases, efficiency decreases.

b. As film thickness increases, sample capacity increases.

c. As film thickness increases, retention increases which allows the separation of highly volatile solutes that have very small and close retention times.

27-15. What are retention indexes? Describe how they are determined.

The retention index, was proposed as a parameter for identifying solutes from chromatograms. The retention index for any given solute can be derived from a chromatogram of a mixture of that solute with at least two normal alkanes (chain length >four carbons) having retention times that bracket that of the solute. By definition, the retention index for a normal alkane is equal to 100 times the number of carbons in the compound regardless of the column packing, the temperature, or other chromatographic conditions. The retention index system has the advantage of being based upon readily available reference materials that cover a wide boiling range. The retention index of a compound is constant for a certain stationary phase but can be totally different for other stationary phases. In finding the retention index, a plot of the number of carbons of standard alkanes against the logarithm of the adjusted retention time is first constructed. The value of the logarithm of the adjusted retention time of the unknown is then calculated and the retention index is obtained from the plot.

27-16. What is meant by GC/MS? Why is it important?

In GC/MS, the mass spectrometer is coupled to the outlet of the GC column where effluents are ionized and fragmented through the mass spectrometer. The mass spectrometer separates the fragments according to molecular mass and thus provides a full spectrum for each compound (peak in GC), which presents excellent undoubtful identification of compounds.

27-17. A polar compound is gas chromatographed on an SE-30 (very nonpolar) column and then on a Carbowax 20M (very polar column). How will $K = C_S/C_M$ vary between the two columns?
The distribution constant of the polar compound on carbowax 20M will be much greater than the distribution constant of the same polar compound on SE-30. Retention is increased as the polarity of an analyte approaches that of the stationary phase. Therefore, $K_{\text{carbowax}}$ will be much greater than $K_{\text{SE-30}}$.

27-18.
Use the retention data given in the following table to calculate the retention index of 1-hexene.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Retention Time, min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>0.571</td>
</tr>
<tr>
<td>n-pentane</td>
<td>2.16</td>
</tr>
<tr>
<td>n-hexane</td>
<td>4.23</td>
</tr>
<tr>
<td>1-hexene</td>
<td>3.15</td>
</tr>
</tbody>
</table>

$t_R'\ (\text{n-pentane}) = 2.16 - 0.571 = 1.589$

$log\ t_R'\ (\text{n-pentane}) = 0.20112$

$I\ (\text{n-pentane}) = 500$

$t_R'\ (\text{n-hexane}) = 4.23 - 0.571 = 3.659$

$log\ t_R'\ (\text{n-hexane}) = 0.56336$

$I\ (\text{n-hexane}) = 600$

Slope $= (0.56336 - 0.20112)/(600 - 500) = 3.622 \times 10^{-3}$

$Y = b + mx$, substitution for pentane gives:

$0.20112 = 3.622 \times 10^{-3} \times 500 + b$

$b = -1.609$

Now, work for 1-hexene:

$t_R'\ (\text{1-hexene}) = 3.15 - 0.571 = 2.579$

$log\ t_R'\ (\text{1-hexene}) = 0.4115$

Substitution in the derived equation gives:
0.4115 = 3.622 \times 10^{-3} \times I_{1\text{-hexene}} - 1.609

I_{1\text{-hexene}} = 558

27-19. A GC column was operated under the following conditions:
- column: 1.10 m x 2.0 mm, packed with Chromosorb P
- weight of stationary liquid added, 1.40 g
- density of liquid, 1.02 g/mL
- measured outlet flow rate: 25.3 mL/min
- temperature: room, 21.2°C; column, 102.0°C
- retention times: air, 18.0 s; methyl acetate, 1.98 min; methyl propionate, 4.16 min; methyl n-butyrate, 7.93 min
- peak widths of esters at base: 0.19, 0.39, and 0.79, respectively

Calculate
(a) the retention factor \( k \) for each component.
(b) selectivity factor, for each adjacent pair of compounds.
(c) the average number of theoretical plates and plate height for the column.
(d) the resolution for each adjacent pair of compounds.

. a. \( k' = (t_R - t_M)/t_M \)

\( k'_{\text{MA}} = (1.98 - 0.3)/0.3 = 5.6 \)

\( k'_{\text{MP}} = (4.16 - 0.3)/0.3 = 12.9 \)

\( k'_{\text{MB}} = (7.93 - 0.3)/0.3 = 25.4 \)

b. \( \alpha_{\text{MP/MA}} = k'_{\text{MP}}/k'_{\text{MA}} \)

\( \alpha_{\text{MP/MA}} = 12.9/5.6 = 2.3 \)

\( \alpha_{\text{MB/MA}} = 25.4/5.6 = 4.54 \)

\( \alpha_{\text{MB/MP}} = 25.4/12.9 = 1.97 \)

c. \( N = 16 \left( \frac{t_R}{W} \right)^2 \)

\( N_{\text{MA}} = 16(1.98/0.19)^2 = 1738 \)

\( N_{\text{MP}} = 16(4.16/0.39)^2 = 1820 \)

\( N_{\text{MB}} = 16(7.93/0.79)^2 = 1612 \)

\( \bar{N} = (1738 + 1820 + 1612)/3 = 1723 \)

\( H = L/N = 110/1723 = 0.064 \text{ cm} \)
d. $R_{2,1} = 2(t_{R2} - t_{R1})/(W_1 + W_2)$

$R_{MP,MA} = 2(4.16-1.98)/(0.19+0.39) = 7.5$

$R_{MB,MP} = 2(7.93-4.16)/(0.39+0.79) = 6.4$

27-20. The stationary-phase liquid in the column described in previous problem was didecylphthalate, a solvent of intermediate polarity. If a nonpolar solvent such as a silicone oil had been used instead, would the retention times for the three compounds be larger or smaller? Why?

The esters have an intermediate polarity like the didecylphthalate stationary phase. If a nonpolar stationary phase is used, the retention times of esters will decrease.

7-21. Corrected retention times for ethyl-, n-propyl- and n-butyl alcohols on a column employing a packing coated with silicone oil are 0.69, 1.51, and 3.57 min, respectively. Predict the retention times for the next two members of the homologous series (n-pentyl and n-hexyl alcohols).

Plot the logarithm of the retention time versus the number of carbons of alcohols and extend the graph to get the retention times of the unknown alcohols:

For pentanol (5 carbons) first find $Y$ which is the log of $t_R$, then find the retention time:

$Y = -0.879 + 0.357 \times 5$
\[ t'_R = 8.1 \]

For hexanol (6 carbons) first find Y which is the log of \( t'_R \) then find the retention time:

\[ Y = -0.879 + 0.357 \times 6 \]

\[ t'_R = 18.3 \]

27-22. What would be the effect of the following on the plate height of a column?
(a) Increasing the weight of the stationary phase relative to the packing weight.
(b) Decreasing the rate of sample injection.
(c) Increasing the injection port temperature.
(d) Increasing the flow rate.
(e) Reducing the particle size of the packing.
(f) Decreasing the column temperature.

a. Increasing the weight of stationary phase will increase the stationary phase film thickness which will increase \( H_S \) and thus decrease efficiency.

b. Decreasing rate of sample injection will result in broader peaks due to increased \( H \).

c. Effect of increasing injection port temperature depends on the initial value of the injector. If the initial value was inadequately low, increasing the injection port temperature will very much improve efficiency and decrease \( H \). However, if the injector temperature was high enough, further increase in temperature of the injector will have little or no effect on efficiency or \( H \).

d. Increasing flow rate above optimum will increase \( H \) while increasing flow rates towards optimum will decrease \( H \).

e. Reducing \( d_p \) will decrease \( H \) and improves efficiency.

f. Decreasing column temperature will decrease the \( C \) term and increase the \( B \) term of van Deemter equation. Usually, \( H \) will increase as column temperature is decreased.
27-23. Calculate the retention index of the following compounds:

<table>
<thead>
<tr>
<th>Compound</th>
<th>( T_R - t_M )</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Propane</td>
<td>1.29</td>
</tr>
<tr>
<td>n-Butane</td>
<td>2.21</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>4.10</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>7.61</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>14.08</td>
</tr>
<tr>
<td>n-Octane</td>
<td>26.11</td>
</tr>
<tr>
<td>Toluene</td>
<td>16.32</td>
</tr>
<tr>
<td>2-Butene</td>
<td>2.67</td>
</tr>
<tr>
<td>n-Propanol</td>
<td>7.60</td>
</tr>
<tr>
<td>Methylethylketone</td>
<td>8.40</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>6.94</td>
</tr>
<tr>
<td>n-Butanol</td>
<td>9.83</td>
</tr>
</tbody>
</table>

First plot the log \( t_R' \) versus the number of carbons in n-alkanes as required by Kovat’s retention index determination. Then find the retention index of the different compounds:

From the assumption of Kovat, the retention index for each compound is equal to the number of carbons times 100.

Sample calculation for toluene: applying the straight line equation, we get:

We know the adjusted retention time, therefore find log \( t_R' \) and substitute for \( Y \) then find \( x \). The retention index is equal to \( x \times 100 \)

\[
1.213 = -0.697 + 0.264 \times x
\]

\[
x = 7.23
\]
\[ I_{\text{toluene}} = 7.23 \times 100 = 723 \]

Other compounds are calculated in the same manner:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Retention Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Propane</td>
<td>300</td>
</tr>
<tr>
<td>n-Butane</td>
<td>400</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>500</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>600</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>700</td>
</tr>
<tr>
<td>n-Octane</td>
<td>800</td>
</tr>
<tr>
<td>Toluene</td>
<td>723</td>
</tr>
<tr>
<td>2-Butene</td>
<td>426</td>
</tr>
<tr>
<td>n-Propanol</td>
<td>598</td>
</tr>
<tr>
<td>Methyl ethyl ketone</td>
<td>614</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>583</td>
</tr>
<tr>
<td>n-Butanol</td>
<td>640</td>
</tr>
</tbody>
</table>