Gas Chromatography

Rosa Yu, David Reckhow
CEE772 Instrumental Methods in Environmental Analysis

Contents

• The primary components to a GC system
  1. Carrier Gas System (including Gas Clean Filters)
     • The concept of theoretical plates and van Deemter curves
     • Selection of proper carrier gas
  2. Sample Introduction System
     • Split & splitless injection
  3. Column (most critical component)
     • Column configurations: packed vs. open tubular/capillary
     • Stationary phase
  4. Detection System/GC Detectors
     • Types of detectors and their specific applications
  5. Computer ChemStation/Integrator
The Basic Components to a GC System

Carrier Gas
Gas Clean Filter
Injection Port
Detector
GC Column
Integrator

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I. Carrier Gas System

- Type of carrier gas effect on column efficiency and resolution
  - H₂/He/N₂

- Selection of carrier gas linear velocity/column flow rate

- Gas clean filter

Type of Carrier Gas Effect on Column Efficiency and Resolution

<table>
<thead>
<tr>
<th>Carrier Gas</th>
<th>Column Efficiency (HEpT) (mm)</th>
<th>Resolution (R)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>12.4</td>
<td>1.17</td>
</tr>
<tr>
<td>Helium</td>
<td>10.4</td>
<td>1.37</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>8.4</td>
<td></td>
</tr>
</tbody>
</table>

Efficiency curves for a 25 m x 0.25 mm id WCOT column with 0.4 um of OV-101

Selection of carrier gas:
- H₂ > He > N₂ (> Argon)
- H₂ should be applied with safety precautions
Optimizing Linear Velocity/Flow Rate for High Column Efficiency

\[ \text{HETP} = A + \frac{B}{m} + C m \]

- Efficiency is a function of the carrier gas linear velocity or flow rate.
- HETP (height equivalent to theoretical plates) is defined as the length of the column divided by the number of theoretical plates (L/N).
- Plot of HETP vs. linear velocity is known as the Van Deemter plot.
- The minimum of the curve represents the smallest HETP (or largest plates per meter) and thus the best efficiency.
- The linear velocity value at the minimum of the curve is the optimum value for achieving the best efficiency.

\[ \text{Average Linear Velocity} \]

van Deemter Plot

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\[ \text{Average Linear Velocity} \]

van Deemter Plot
Gas Clean Filter

- Significant damages can be done to the column if it is heated above 70°C with even trace amounts of O₂ in the column
- Use carrier gas that meets the 99.9995% specification (UHP grade)
- Use O₂ & moisture traps

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II. Sample Introduction

- The sample must be of a suitable size (especially for WCOT/capillary columns) and introduced *instantaneously* as a **PLUG OF VAPOR**

  Slow injection/oversize causes peak broadening and poor resolution

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**Types of GC samples and injection methods**

- **Liquid**
- **Gas**
- **Solid**
Auto Sampler

- Automation
- Up to 150 samples
- Instantaneous injection
- Same amount of sample injected every time

Injection Port

Packed Column Injector
**Split vs. Splitless Injection**

**• Splitless injection**

For example, a liquid sample is injected into the port, it is quickly volatilized at the end of the microsyringe and at the head of the column; the solutes are then taken by the carrier gas into the column.

**• Split injection**

Open tubular/capillary columns usually have a much smaller cross-section area than that of packed columns. This makes them more subject to extra-column band-broadening, requiring that special low volume injection techniques be used with them.

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**Sample Splitter**

**• The sample is first placed into the injection port and is vaporized**

**• As the sample leaves the inject port, only a small portion of the vaporized samples is applied to the column (usually 1/50 to 1/500), with the remainder going to waste (by opening the purge valve/split vent).**
**Cold On-Column Injector**

- Cold on-column injectors involve **direct injection** of a sample **onto a column** at low temperature.

- No heated injection port is used. The low initial column temperature increases the retention of all solutes and concentrates them at the top of the column in a narrow plug. The column temperature is then increased, allowing the solutes to volatilize and be separated.

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**Programmed temperature vaporizer (PTV)**

- A programmed temperature vaporizer involves placing sample into a **cold injection port**, where it is then heated and applied to column at any desired temperature.

- A "universal" injector for open-tubular columns since its temperature program may be changed so that it can be used either in cold injectors, splitless injectors, or split injectors.
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III. GC Column (heart of a GC system)

• Column configurations: packed vs. open tubular/capillary columns
• Stationary phase
• Film thickness and column efficiency
The Heart of GC

2. Injection

The Heart of GC

3. Column Separation
1. Types of GC columns (GLC)

Packed

Capillary

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23

1. Types of GC columns (GLC)

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24
Packed GC Columns

- Less ubiquitous application: fixed gas analysis
- Lower column efficiency than that of capillary columns (smaller in length)
- Larger sample capacity

The efficiency of a gas chromatographic column increases rapidly with decreasing particle diameter of the packing. The pressure difference (head loss) required to maintain an acceptable flow rate of carrier gas, however, varies inversely as the square of the particle diameter; the latter relationship has placed lower limits on the size of particles used in GC because it is not convenient to use pressure differences that are greater than 50 psi.
Open Tubular/Capillary GC Columns

• Most widely used
• High column efficiency (large number of theoretical plates due to long column length, up to 100 m)
• Small sample capacity (split sample inside inlet)

Open Tubular/Capillary GC Columns

Fused silica—pure form of glass that is very inert but fragile

Polyamide—provides great mechanical strength and flexibility
Open Tubular/Capillary Columns

WCOT-wall coated open tubular
Length 5 to 100 meters

Polymer coating
Fused Silica

100, 180, 200, 250, 320, 530 μm

Typical liquid phase 0.5 to 5 μm

Packed vs. Capillary

Packed Column Analysis:
5% OV101
on 80/100 Chromosorb

Capillary Column Analysis:
30 m × 0.53 mm × 0.88 μm

Capillary Column Analysis:
30 m × 0.32 mm × 0.25 μm
Packed vs. Capillary

<table>
<thead>
<tr>
<th></th>
<th>Packed</th>
<th>Capillary</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Megabore</td>
</tr>
<tr>
<td>Length (meters)</td>
<td>0.5–10</td>
<td>5–100</td>
</tr>
<tr>
<td>I.D. (mm)</td>
<td>2–4</td>
<td>0.530</td>
</tr>
<tr>
<td>Flow Rate (ml/min.)</td>
<td>10–60</td>
<td>4–30</td>
</tr>
<tr>
<td>Operating Pressure</td>
<td>10–90 PSI</td>
<td>5–15 PSI</td>
</tr>
<tr>
<td>Sample Capacity</td>
<td>100 ng/peak</td>
<td>10 ng/peak</td>
</tr>
</tbody>
</table>

2. Stationary Phase

Important Attributes

1. Low volatility (boiling point at least 100 °C higher than max. column operating temperature)
2. Thermo stability (wide temperature operating range)
3. Chemical inertness (non-reactive to both solutes and carrier gas)
4. Solvent characteristics (differential solvent for different components)
Qualitative Guidelines for Stationary Phase Selection

- **Sources:**
  Literature review, Internet search, prior experience, advice from a vendor of chromatographic equipment and supplies

- **General rule: “like dissolves like”**
  - “Like” refers to the POLARITIES of the analyte and the immobilized liquid
  - The polarity of a molecule, as indicated by its dipole moment, is a measure of the electric field produced by separation of charge within the molecule
  - **Polar functional groups:** -CN, -CO, -OH, -COOH, -NH₂, -CHO, -X, etc.
  - **Nonpolar function groups:** saturated alkane –CH₂, etc.

Types and Polarities of Stationary Phase

- **Polydimethyl siloxane backbone**
- **Phenyl substitution of methyl groups**

<table>
<thead>
<tr>
<th>Structures</th>
<th>Polarity</th>
<th>Temperature range (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nonpolar</td>
<td>-60° - 320°</td>
<td></td>
</tr>
<tr>
<td>Intermediate polarity</td>
<td>-70° - 280°</td>
<td></td>
</tr>
<tr>
<td>Strongly polar</td>
<td>46° - 250°</td>
<td></td>
</tr>
<tr>
<td>Strongly polar</td>
<td>0° - 250°</td>
<td></td>
</tr>
</tbody>
</table>

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33
Types and Polarities of Stationary Phase

Table 2.4
Characteristic properties of some poly(siloxane) liquid phases used for packed column gas chromatography

<table>
<thead>
<tr>
<th>Name</th>
<th>Structure</th>
<th>Viscosity (cP)</th>
<th>Average molecular weight</th>
<th>Temperature operating range (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OV-1</td>
<td>Dimethylsiloxane</td>
<td>gum</td>
<td>&gt; 10^6</td>
<td>100</td>
</tr>
<tr>
<td>OV-101</td>
<td>Dimethylsiloxane</td>
<td>1500</td>
<td>30,000</td>
<td>&lt;20</td>
</tr>
<tr>
<td>OV-7</td>
<td>Phenylmethyl(dimethylsiloxane 80 % methyl and 20 % phenyl)</td>
<td>500</td>
<td>10,000</td>
<td>&lt;20</td>
</tr>
<tr>
<td>OV-17</td>
<td>Phenylmethylsiloxane</td>
<td>1300</td>
<td>40,000</td>
<td>&lt;20</td>
</tr>
<tr>
<td>OV-25</td>
<td>Phenylmethylidiphenylsiloxane 25 % methyl and 75 % phenyl</td>
<td>&gt;100,000</td>
<td>10,000</td>
<td>&lt;20</td>
</tr>
<tr>
<td>OV-210</td>
<td>Trifluoropropyl(dimethylsiloxane 50 % methyl and 50 % 3,3,3-trifluoropropyl)</td>
<td>10,000</td>
<td>200,000</td>
<td>&lt;20</td>
</tr>
<tr>
<td>OV-225</td>
<td>Cyanopropyl(dimethylphenylmethylsiloxane 50 % methyl, 25 % phenyl and 25 % 3-cyanopropyl)</td>
<td>9000</td>
<td>8,000</td>
<td>&lt;20</td>
</tr>
<tr>
<td>Silar 7CP</td>
<td>Cyanopropyl(dimethylsiloxane 75 % 3-cyanopropyl and 25 % phenyl)</td>
<td>50</td>
<td>250</td>
<td></td>
</tr>
<tr>
<td>OV-275</td>
<td>Diarylidicyanomethylsiloxane 70 % 3-cyanopropyl and 30 % 2-cyanomethyl</td>
<td>20,000</td>
<td>5,000</td>
<td>250</td>
</tr>
<tr>
<td>Silar 10CP</td>
<td>Di(3-Cyanopropyl)dimethylsiloxane</td>
<td>50</td>
<td>250</td>
<td></td>
</tr>
</tbody>
</table>

3. Effect of Film Thickness on Column Efficiency

Stationary phase—thick films

≥1.0 µm

Advantages:
- Increased retention for volatiles
- Increased capacity for GC/MS, GC/IR

Disadvantages:
- Less efficient
- Higher temperatures required—Leads to noise
- Higher bleed
3. Effect of Film Thickness on Column Efficiency

Stationary phase—thin films

- ≤ 0.5 μm
- Advantages:
  - Highest efficiency
  - Lower elution temperature (less bleed)
  - Fast analysis
- Disadvantages:
  - Low capacity
  - Limited trace analysis

Peak Fronting

Packed vs. Capillary

Packed Column Analysis:
5% OV101
on 80/100 Chromosorb

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IV. GC Detection Systems/Detectors
 Characteristics of the Ideal Detector

1. Adequate sensitivity (application specific, i.e. adequate for certain tasks)

![Graph showing signal to noise ratio (S/N) > 3]

2. Good stability and reproducibility
3. A linear response to solutes that extends over several orders of magnitude (calibration purposes)
4. A wide temperature range
5. A short response time independent of flow rate
6. High reliability and ease of use (unfortunately, usually not the case)
7. Similarity in response toward all solutes/most classes of solutes
8. The detector should be nondestructive

Typical GC Detectors

<table>
<thead>
<tr>
<th>Table 15.5 Properties of Selected Gas Chromatography Detectors</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Type</strong></td>
</tr>
<tr>
<td>-------------------------------</td>
</tr>
<tr>
<td>Thermal conductivity (TCD)</td>
</tr>
<tr>
<td>Flame ionization (FID)</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Universal detectors</td>
</tr>
<tr>
<td>Electron capture (EC or ECD)</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Flame photometric (FPD)</td>
</tr>
<tr>
<td>Nitrogen-phosphorus</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Photodissociation (PD)</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Hall Detector</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Mass spectrometer (MS)</td>
</tr>
<tr>
<td>Fourier-transform infrared (FTIR)</td>
</tr>
</tbody>
</table>

* a. Varies, depending on the type of mass spectrometer as well as the kinds of compounds being analyzed.
1. Flame Ionization Detector (FID)

- Most common detector for GC
- In an FID, effluent from the column is directed into a small air-hydrogen flame. Most carbon atoms (except C=O) produce radicals (CHO+) in the flame:
  \[ \text{CH} + \text{O} \rightarrow \text{CHO}^+ + e^- \]
- Electrons are used to neutralize the CHO+ atoms and the ions are collected at an electrode to create a current to be measured. This current is proportional to the number of molecules present.
- The ionization of carbon compounds in the FID is not fully understood, although the number of ions produced is roughly proportional to the number of reduced carbon atoms in the flame.

Pros and Cons of FID

- **Advantages:**
  1. universal detector for organics
  2. does not respond to common inorganic compounds
  3. mobile phase impurities not detected
  4. carrier gases not detected
  5. limit of detection: FID is 1000x better than TCD
  6. linear and dynamic range better than TCD
- **Disadvantage:**
  destructive detector
2. Thermal Conductivity Detector (TCD)

- One of the earliest detectors of GC
- The device contains an electrically heated source whose temperature at constant electrical power depends on the thermal conductivity of the surrounding gas.
- Twin detectors are usually used, one being located ahead of the sample-injection chamber and the other immediately beyond the column. The bridge (Wheatstone bridge) circuit is arranged so that the thermal conductivity of the carrier gas is canceled.

The thermal conductivities of helium and hydrogen (commonly used carrier gases for TCD) are roughly 6~10 times greater than those of most organic compounds. Thus, even small amounts of organic species cause relatively large decreases in the thermal conductivity of the column effluent, which results in a marked rise in the temperature of the detector.

Advantages:
- Simplicity, large linear dynamic range, nondestructive

Disadvantages:
- Low sensitivity (precludes their use with WCOT columns with small amounts of sample)
3. Electron Capture Detector (ECD)

- Radioactive decay-based detector
- Selective for compounds containing electronegative atoms, such as halogens, peroxides, quinones, and nitro groups
- The sample effluent from a column is passed over a radioactive β emitter, usually $^{63}$Ni. An electron from the emitter causes ionization of the carrier gas (often N$_2$) and the production of a burst of electrons.
- In the absence of organic species, a constant standing current between a pair of electrode results from this ionization process. The current decreases significantly in the presence of organic molecules containing electron negative functional groups that tend to capture electrons.

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3. Electron Capture Detector (ECD)

- Ionization of carrier gases:
  \[ N_2 + \beta^- \rightarrow N_2^+ + e^- \quad \text{Ar}_2 + \beta^- \rightarrow \text{Ar}_2^+ + e^- \]
- Advantages:
  - useful for environmental testing
  - detection of chlorinated pesticides or herbicides; polynuclear aromatic carcinogens, organometallic compounds
  - selective for halogen- (I, Br, Cl, F), nitro-, and sulfur-containing compounds
  - detects polynuclear aromatic compounds, anhydrides and conjugated carbonyl compounds
- Disadvantages:
  - could be affected by the flow rate
4. Thermionic Detector/Nitrogen-Phosphorous Detector (NPD)

- A NPD is based on the same basic principles as an FID.
- However, a small amount of alkali metal vapor in the flame, which greatly enhances the formation of ions from nitrogen and phosphorus-containing compounds.
- The NPD is about 500-fold more sensitive that an FID in detecting phosphorous-containing compounds, and 50-fold more sensitive to nitrogen-containing compounds.
- Applications: Organophosphate in pesticides and in drug analysis for determination of amine-containing or basic drugs.

5. Electrolytic Conductivity Detector

- Element-selective detector for halogen-, sulfur- and nitrogen-containing compounds.
- Compounds containing halogens, sulfur, or nitrogen are mixed with a reaction gas in a small reactor tube, usually made of Ni. The products from the reaction tube are then dissolved in a liquid, which produces a conductive solution. The change in conductivity as a result of the ionic species is then measured.
Other GC Detectors

- Photoionization Detector
  aromatic hydrocarbons
  organosulfur/organophosphorous

- Atomic Emission Detector
  element-selective detector

- Flame Photometric Detector
  sulfur and phosphorous containing compounds

Comparison of GC Detector Sensitivity and Dynamic Range
*Mass Spectrometry Detector (MS)*

- One of the most powerful detectors for gas chromatography

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V. Quantitative Chromatographic Analysis

• Quantitative Analysis
  Based on a comparison of either the height or the area of the analyte peak with that of one or more standards

• Peak height vs. Peak area
  Peak heights are inversely related to peak width. Thus, accurate results are obtained with peak heights only if variations in column conditions do not alter the peak width during the period required to obtain chromatograms for samples and standards.
  Peak areas are independent of broadening effects, which are usually the preferred method of quantitation.
  * most modern chromatographic instruments are equipped with computers or digital electronic integrators that permit precise estimation of peak areas

Questions?

Rosa Yu
Email: victorosa1212@gmail.com
• To next lecture