WEEK 5: ANALYTICAL CHEMISTRY OF ORGANIC COMPOUNDS (CHAPTER 15)

Midterm 1: It's over, but not graded yet. Will be returned in labs.

3) SEPARATION/PURIFICATION

Methods:
1) Crystallization (if solid)
2) Distillation (if liquid & each component has substantially different bp)
3) Chromatography
   TLC (thin layer chromatography) - you've done this in lab.
   Column
   HPLC
   Gas (GC)

4a) Column Chromatography: larger scale than possible w/ TLC.

Apply mixture of compounds (A/B/C)
Stationary phase (silica gel)
Mobile phase (eluent) solvent
Mobile phase carries A, B+C through stationary phase. A, B, C "stick" to stationary phase w/ different affinities \(\Rightarrow\) separation

3b) HPLC (High Performance Liquid Chromatography)

Same thing, but
1) Pumps deliver mobile phase
2) Columns are smaller
3) Attach a detector
4) Computer driven
   \(\text{INJECTOR} \rightarrow \text{PUMP} \rightarrow \text{COLUMN} \rightarrow \text{DETECTOR}\)

\(\text{Collector} \rightarrow \text{Student} \equiv \text{Automated Spectrophotometer (need a "chromophore")}

Plot:

Good for larger, more polar molecules.
Gas Chromatography (GC)

1. Mobile phase = gas (He or H₂)
2. Stationary phase = silicone polymers
3. Heat the column

Injectors, Heaters/Ovens, Columns, Collect after cooling.

~good for hydrophobic (greasy) small molecules.

Once pure, how do you figure out what it is? Lots of options, usually need >1.

Elemental - Combustion Analysis

Derive Empirical Formula by "burning" the compound.

\[ \text{Unknown} + O_2 \rightarrow H_2O + CO_2 \]

**Step 1:**
1. Derive C content of unknown from weight of CO₂ produced.
2. Derive H content from weight of H₂O.
3. Oxygen content by a "difference calculation" (Subtraction).

10 mg Unknown \( \rightarrow \) 29.3 mg CO₂.

\[ wt(C) = \frac{MW(C) \times wt(CO_2)}{MW(CO_2)} \]

\[ = \frac{12.011 g/mol \times 29.31 mg}{44.009 g/mol} \]

\[ = 8 \text{ mg C} \]

Hydrogen Content:

\[ wt(H) = \frac{2\times MW(H) \times wt(H_2O)}{MW(H_2O)} \]

\[ = \frac{2 \times (1.008 g/mol) \times 5.99 mg}{18.015 g/mol} \]

\[ = 0.67 \text{ mg H} \]

\[ \% C = \frac{8.0 \text{ mg C} \times 100}{10.0 \text{ mg}} = 80\% \text{ C} \]

\[ \% H = \frac{0.67 \text{ mg H} \times 100}{10 \text{ mg}} = 6.7\% \text{ H} \]

\[ \% O = 100 - 80 - 6.7 = 13.3\% \text{ O} \]

**Step 2:** Derive Empirical Formula from \( \% \) values:

Calculate # moles of each element (assuming we have 100 g):

\[ C = 80 g \times \frac{1 \text{ mol}}{12.019 g} = 6.66 \text{ mol} \]

\[ H = 6.67 g \times \frac{1 \text{ mol}}{1.01 g} = 6.63 \text{ mol} \]

\[ O = 13.3 g \times \frac{1 \text{ mol}}{16.0 g} = 0.831 \text{ mol} \]

Empirical Formula is

\[ C_{6.66}H_{6.63}O_{0.831} \]

What?!
Step 3: Determine degrees of unsaturation (for common organic species)
- Convert Actual Molecular formula to Hydrocarbon Formula (HCF).

**Rules:**
- Each atom of: 
  - F, Cl, Br, I  → replaced by H
  - O, S  → ignored
  - N, P, B, Al  → one H removed also replaced by C
  - Si

**Example:** C₈H₈O → C₈H₈

End of Term.

Mass Spectrometry
- Determination of Molecular Weight (p. 69 for good picture)
  - How? M = molecule
  1) Bombard M w/ an e⁻ (70eV)
     \[ M + e^- \rightarrow 2e^- + M^{+}\]
     (e⁻ is ejected from M)
  2) Radical cation (M⁺) is accelerated towards plate of opposite charge.

**Parent ion:** mass of the molecule
**pH peak:** results from relative abundance of isotopes of elements
Here: Carbon

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Relative Abundance</th>
<th>Atomic Wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>¹²C</td>
<td>98.9</td>
<td>12.00</td>
</tr>
<tr>
<td>¹³C</td>
<td>1.1</td>
<td>13.00</td>
</tr>
</tbody>
</table>

For ¹²C, ¹³C's, all w/ 1.1% probability of being ¹³C, so...
1²C x 1.1 ≈ 7% chance that mass of □ will be one unit higher.
Here: pH peak 7% parent ion peak.
Daughter Ions: Charged Species resulting from fragmentation

fragment → smaller ions

*fragmentation results in most stable (+) ions.

ex: \[ \text{CH}_3 \] \[ \text{H} \] + 70eV → \[ \text{CH}_3 \] \[ \text{CH} \] \[ \text{H} \] + \[ \text{CH}_3 \] (neutral, not observed)

parent = 106

more stable cation

Fragmentation can involve rearrangements:

ex: McLafferty Rearrangement

- occur w/ carbonyl compounds containing a \( \delta^- \) hydrogen

ex: \[ \text{CH}_3 \] \[ \text{H} \] \[ \text{H} \] \[ \text{CH} \] \[ \text{D} \] \[ \text{O} \] + 70eV \[ \text{CH}_3 \] \[ \text{H} \] \[ \text{H} \] \[ \text{O} \] \[ \text{H} \] \[ \text{CH}_3 \] 140

11 \[ \text{CH}_3 \] + \[ \text{CH}_3 \] \[ \text{O} \] = 98 (neutral)

Resonance stabilized

INFRARED SPECTROSCOPY (IR)

Process:

IR Source \[ \text{IR Radiation} \] \[ \text{Sample} \] \[ \text{Molecule absorbs energy} \]

IR radiation: \( \lambda \) is \( 1 \times 10^{-4} \text{ to } 1 \times 10^{-2} \text{ cm} \), or \( \nu = \frac{1}{\lambda} \text{ cm}^{-1} \).

Absorbed energy (energy is quantized)

(a) Molecular Rotations & (b) Molecular Vibrations (stretching & bending)

Wavelength of Absorption depends on:

(a) relative masses of atoms in molecule

(b) force constant (strength) of bonds connecting the atoms.
25
Instrument:

LAMP

reference(solvent)

sample + solvent

DETECTOR

1 plotted

If a molecule only absorbs 500 cm⁻¹

Absorbance

1000

\( \tilde{\nu} (\text{cm}^{-1}) \)

500

100

28

IR spectra of organic molecules are complex!

Every bond that vibrates affects the vibrations of all other bonds in the molecule.

Use IR to

1. Fingerprint molecules (ex: drug testing)
2. Identify characteristic absorptions of common functional groups.

Table 15.3 in book (will be given on exam)

Sample Spectra (overhead)
Unknown 2
IR Spectrum

#2

No O-H

C-H

C=C

C=O
1680 cm⁻¹
(Strong peak)
#3

\[ \text{C} = \text{N} \quad \text{CH}_3 \]

\[ \text{C} - \text{H} \]

\[ \text{C} = \text{C} \]

\[ \text{C} = \text{N} \quad 2210 \text{ cm}^{-1} \]

\[ \text{NO} 0 - \text{H} \]