Gas Chromatography

- Used to separate components of a mixture
- Mixture is injected, vaporized and carried by an inert gas
- Compounds separate when they interact with the column at different times. Retention times are based on the polarity of the substance compared to the column
- Components then pass into a mass spectrometer where they are ionized, fragmented, and detected
Mass Spectrometry

- Vaporized substance is ionized to form a positive ion
- Passes through ion accelerator that propels the ion through a thin slit
- Narrow beam of positive ions passed into a magnetic field which deflects ions according to mass to charge ratio
- All mass spectrometers consist of 3 regions:
  - Ionizer
  - Mass Analyzer
  - Detector
Ionizer – electron impact (EI)

- A high energy beam excites gas molecules by ejecting electrons which strikes molecules to remove an electron.
Ionizer – chemical ionization (CI)

- Ions are produced through the collision of the analyte (sample) with the ions of the reagent (or ionizing) gas that are present in the ion source
  - Fragments the molecule to a lower degree than the hard ionization of EI
  - Benefit of CI the mass fragment closely corresponds to the molecular weight of the analyte in interest
Mass Analyzer - quadrupole

- Sorts the ions according to their mass/charge (m/z) ratio
- Electric field generated by charged rods is modulated by controlled AC and DC voltage sources
- Incoming ions whose m/z meets resonate criteria will pass through quadrupole filter
- A mass spectrum is obtained by monitoring the ions passing through the quadrupole filter as the voltages on the rods are varied
Ion detector

- Counts the ions and a signal is generated that is proportional to the total number of ions
Why use GCMS data

- Each mixture component is fragment uniquely by the mass spectrometer
- Information can be used to identify compounds or compare samples
- Quantitatively measure subtle differences
- Can be used for characterizing complicating mixtures such as fuel
GCMS Applications

• Data may be viewed, processed, or analyzed
  – Total Ion Chromatogram, Single Ion Chromatogram, or Mass Spectra
• Graphs respond to user interaction – clicking, adjust, contrast
Fragmentation patterns in the mass spectra

- The tallest line in the mass spectra (in this case at m/z = 246) is called the **base peak**
  - The height of everything else is measured relative to this
  - The base peak is the tallest peak because it represents the commonest fragment ion to be formed
Mass Spectra – the molecular ion (M+) peak

• In the mass spectrum, the heaviest ion (the one with the greatest m/z value) is likely to be the molecular ion
  – Example: DDE mass spectrum
  – Because the largest m/z value is 318, that represents the largest ion going through the mass spectrometer - and you can reasonably assume that this is the molecular ion
The effect of chlorine atoms on the mass spectrum

- The lines in the molecular ion region (at m/z values of 318) arise because of the various combinations of chlorine isotopes that are possible.
- Chlorine can be either of the two chlorine isotopes, 35Cl and 37Cl.
- Chlorine contains 3 times as much of the 35Cl isotope as the 37Cl one.
- The carbons and hydrogens add up to 176 - so the various possible molecular ions could be:
  - 176 + 37 + 37 + 37 + 37 = 324
  - 176 + 35 + 37 + 37 + 37 = 322
  - 176 + 35 + 35 + 37 + 37 = 320
  - 176 + 35 + 35 + 35 + 37 = 318
  - 176 + 35 + 35 + 35 + 35 = 316
Internal standard

- A known concentration of a substance that is present in every sample (standards, blanks, QA/QC, unknown) that is analyzed
  - Dibromobiphenyl
  - Tetrabromobephenyl
  - Anthracene-d10
- Signal from analyte is compared with signal from the internal standard to find out how much analyte is present
Deuterium (D)

- Stable isotope of hydrogen
  - Mass 2.014 (common H = 1.007)
  - Contains one proton and one neutron (common hydrogen contains no neutron)
- Behaves similarly to ordinary hydrogen
- Distinguished easily from ordinary H by its mass using mass spectrometry
  - Example- Anthracene

\[
\begin{array}{c}
\text{H} & \text{H} & \text{H} & \text{H} \\
\text{H} & \text{H} & \text{H} & \text{H} \\
\end{array}
\quad \text{Mass = 178}
\]
\[
\begin{array}{c}
\text{D} & \text{D} & \text{D} & \text{D} \\
\text{D} & \text{D} & \text{D} & \text{D} \\
\end{array}
\quad \text{Mass = 188}
\]
Recovery surrogates (RS)

- Monitors extraction efficiency

<table>
<thead>
<tr>
<th>Recovery surrogates</th>
<th>5E-SO G1S1 (A); ng/g</th>
<th>Spike; ng</th>
<th>% recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCMX</td>
<td>176.48</td>
<td>400</td>
<td>44.12</td>
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<tr>
<td>PCB 30</td>
<td>318.97</td>
<td>400</td>
<td>79.74</td>
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<td>PCB 112</td>
<td>367.87</td>
<td>400</td>
<td>91.97</td>
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<tr>
<td>PCB 198</td>
<td>496.84</td>
<td>400</td>
<td>124.21</td>
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</table>

- Acceptance range = 70-130%
Matrix spikes (MS)

- Determines the effect of the matrix on analyte recovery

\[
RSD = \left(\frac{\text{STDEV}(\text{MS1}, \text{MS2}) \times 100}{\text{AVERAGE}(\text{MS1}, \text{MS2})}\right)
\]

- % recovery acceptance range = 70-130%
- RSD Acceptance < 30%

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Matrix Spike 1</th>
<th></th>
<th></th>
<th></th>
<th>Matrix Spike 2</th>
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<tbody>
<tr>
<td></td>
<td>Net</td>
<td>Spike Amt</td>
<td>% Recovery</td>
<td>Net</td>
<td>Spike Amt</td>
<td>% Recovery</td>
<td>RSD</td>
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<tr>
<td>PCB 008</td>
<td>89.10</td>
<td>160</td>
<td>55.69</td>
<td>88.65</td>
<td>160</td>
<td>55.41</td>
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<td>PCB 018</td>
<td>112.77</td>
<td>160</td>
<td>70.48</td>
<td>123.49</td>
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<td>77.18</td>
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<tr>
<td>PCB 028</td>
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<td>160</td>
<td>57.29</td>
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<tr>
<td>PCB 031</td>
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<td>160</td>
<td>73.29</td>
<td>124.03</td>
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<td>3.97</td>
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<tr>
<td>PCB 033</td>
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<td>59.63</td>
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<td>68.65</td>
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<tr>
<td>PCB 052</td>
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<td>160</td>
<td>65.24</td>
<td>117.26</td>
<td>160</td>
<td>73.29</td>
<td>8.22</td>
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</table>
Standard Reference Material (SRM)

- Homogeneous material where analyte values have been well established to validate lab and analytical methods
  - Lake Michigan Fish Tissue (SRM 1947)
  - Sediments (1944)
  - Acceptance range = 70 - 130%

<table>
<thead>
<tr>
<th>Certified PCB congeners</th>
<th>Net µg/kg, ww</th>
<th>Spike Amt µg/kg, ww</th>
<th>% Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCB 28</td>
<td>13.85</td>
<td>14.1 ± 1.0</td>
<td>98.2</td>
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<td>PCB 31</td>
<td>10.68</td>
<td>10.4 ± 1.4</td>
<td>102.7</td>
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<tr>
<td>PCB 52</td>
<td>35.85</td>
<td>36.4 ± 4.3</td>
<td>98.5</td>
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<tr>
<td>PCB 49</td>
<td>27.43</td>
<td>27.3 ± 3.8</td>
<td>100.5</td>
</tr>
<tr>
<td>PCB 44</td>
<td>21.42</td>
<td>20.4 ± 1.7</td>
<td>105.0</td>
</tr>
<tr>
<td>PCB 63</td>
<td>NA</td>
<td>4.75 ± 0.60</td>
<td>NA</td>
</tr>
<tr>
<td>PCB 74</td>
<td>32.40</td>
<td>33.7 ± 3.1</td>
<td>96.1</td>
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