Activity: Spectroscopy

Read: Kenkel (p 149 - 237) and Harris, (Chp 17 - 21)

For all spectral analysis, show your complete analysis and provide evidence for your proposed structure.

Basic Spectroscopy

i. Determine the index of hydrogen deficiency for the following-
   a) \( \text{C}_8\text{H}_7\text{NO} \)
   b) \( \text{C}_4\text{H}_4\text{BrNO}_2 \)
   c) \( \text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_2 \)

ii. Calculate the molecular formulas for possible compounds with molecular masses of 136, using the Rule of Thirteen.
   You may assume that the only other atoms present in each molecule are carbons and hydrogens.
   a) A compound with two oxygen atoms
   b) A compound with two nitrogen atoms and one oxygen atom
   c) A compound with five carbon atoms and our oxygen atoms

UV-Vis Molecular Absorption Spectroscopy

Reference: Google search key words: UV chromophores table

iii. Draw the structural formulas that show a UV maximum at-
   a) An acid, \( \text{C}_7\text{H}_4\text{O}_2\text{Cl}_2 \) shows a UV with \( \lambda_{\text{max}} = 242 \text{ nm} \).
   b) An aldehyde \( \text{C}_8\text{H}_12\text{O} \), absorbs in the UV with \( \lambda_{\text{max}} = 244 \text{ nm} \).

iv. Predict the UV maximum for each of the following substances-

   a) ![Structural formula](image1)
   b) ![Structural formula](image2)

Infra-Red Spectroscopy

v. In each of the following part of the molecular formula is given. Deduce the structure that is consistent with the infrared spectrum.
   There may be more than one answer.

   a) ![Infra-Red Spectroscopy](image3)
   b) ![Infra-Red Spectroscopy](image4)
Nuclear Magnetic Resonance Spectroscopy

vi. Determine the organic structure for the following. Provide as much evidence as possible for the structure you proposed.

a) The following NMR spectra are of mono-substituted aromatic hydrocarbon compound with the formula C\textsubscript{10}H\textsubscript{14}. The chemical shift in the aromatic region is found between 7.1 and 7.3 ppm. Proposed reasonable structures.

b) Below are the NMR spectra of two isomeric carboxylic acids, C\textsubscript{3}H\textsubscript{5}ClO\textsubscript{2}. Proposed reasonable structures.

vii. Using a correlation table for \(^{13}\text{C}\) chemical shifts, calculate the \(\delta\) for the carbons for the following chemicals.

\[
\begin{array}{c}
\text{CH}_3 \\
\text{b)} \\
\text{CH}_3 \\
\end{array}
\]

Mass Spectroscopy

viii. The mass spectrum of an unknown halo-organic liquid shows a molecular ion peak at m/e = 78 with a relative intensity of 23.6. Suggest a reasonable chemical formula and structure given the relative intensities of the isotopic peaks are as follow:

\[
\begin{array}{ccc}
m/e: & 79 & 80 & 81 \\
Relative intensities: & 0.79 & 7.55 & 0.25 \\
\end{array}
\]
Atomic Absorption Spectroscopy

The chromium in an aqueous sample was determined by pipetting 10.0mL of the unknown into each of five 50.0-mL volumetric flasks. Various volumes of a standard containing 12.2 ppm Cr were added to the flask, followed by diluting each solution to volume.

<table>
<thead>
<tr>
<th>Unknown, mL</th>
<th>Standard, mL</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.0</td>
<td>0.0</td>
<td>0.201</td>
</tr>
<tr>
<td>10.0</td>
<td>10.0</td>
<td>0.292</td>
</tr>
<tr>
<td>10.0</td>
<td>20.0</td>
<td>0.378</td>
</tr>
<tr>
<td>10.0</td>
<td>30.0</td>
<td>0.467</td>
</tr>
<tr>
<td>10.0</td>
<td>40.0</td>
<td>0.554</td>
</tr>
</tbody>
</table>

a) Plot the data
b) Derive an equation for the relationship between absorbance and volume of standard.
c) Calculate the standard deviation for the slope and the standard deviation about regression in (b)
d) Calculate the ppm Cr in the sample
e) Calculate the standard deviation of the results in (d)

Fluorescence Spectroscopy

Quinine is one of the best known fluorescent molecules. The sensitivities of fluorescence are often specified in terms of the detection limit for this molecule. The structure of quinine is given below. Predict the part of the molecule that is most likely to behave as the chromophore and fluorescence center.

![Quinine structure](image)

xi. The reduced form of nicotinamide adenine dinucleotide (NADH) is an important and highly fluorescent coenzyme. It has an absorption maximum at 340nm and an emission maximum at 465 nm. Standard solutions of NADH gave the following fluorescence intensities:

- Conc NADH, (umol/L) = 0.100, 0.200, 0.300, 0.400, 0.500, 0.600, 0.700, 0.800
- Relative intensities, I = 2.24, 4.74, 6.59, 8.98, 10.93, 14.01, 15.49, 18.02

a) Construct a calibration curve for NADH.
b) Compute the least-squares regression parameters of a linear equation for the plot in part (a)
c) Calculate the standard deviation of the slope and the intercept.
d) An unknown exhibits a relative fluorescence of 12.16. Calculate the concentration of NADH
e) Calculate the relative standard deviation for the result in part (d)
f) Calculate the relative standard deviation for the result in part (d) if the reading of 12.16 was the mean of three measurements.

xii. Why is spectrofluorimetry potentially more sensitive than spectrophotometry?
Spectroscopy Combination Spectral Analysis

xiii) Use the information provided to propose a reasonable organic structure for the halogenated alkane.
xiv) The compound has the formula $C_4H_8O$.

The $^1H$ NMR spectrum shows a triplet at 9.8 ppm and the signal at 2.4 ppm is a triplet of doublet. Suggest a reasonable structure for the compound.

Error formula should be $C_4H_8O$.

xv) The compound has the formula $C_3H_6O_2$.

The UV spectrum of the compound shows no maximum above 205 nm. The carbon NMR spectrum shows peaks at 14, 60 and 161 ppm. The peak at 161 ppm appears as a possible peak in the DEPT-90 spectrum.