Ultraviolet/Visible Spectroscopy

1 Explain the underlying principles of UV/VIS spectroscopy. Details of instrumentation are not required.

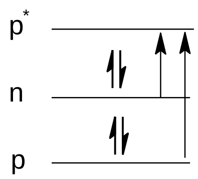
When a photon of UV light is absorbed by a molecule, an electron gains the photon's energy and is promoted to a higher energy orbital.

The lowest energy electronic transition is that between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).

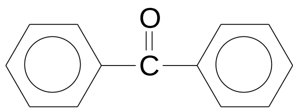
Absorption in the UV/VIS region corresponds to $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ transitions.

2 Organic molecules, such as propanone, $(CH_3)_2CO$, absorb energy in the uv/visible region of the spectrum as a result of electronic transitions.

(a) Draw an energy level diagram to show the electronic transitions which cause absorptions in propanone.



(b) Diphenylmethanone, shown below, also absorbs in the uv/visible region of the spectrum.



Predict where, relative to the absorptions shown by propanone, diphenylmethanone will absorb energy. Explain your answer.

Conjugation of π bonds from the two benzene rings **reduces the energy gap** between the π and the π* orbitals and between n and the π* orbitals, and **hence shifts the absorption towards longer wavelength** for diphenylmethanone as compared with propanone.

3 **(a)** A solution of guanine of concentration 2×10^{-4} mol dm^{-3} in a 1.00 cm path length cell has an absorbance of 1.56 at 275 nm. What is the molar extinction coefficient of guanine at this wavelength?

Using Beer's Law,

$A_{275nm} = \varepsilon_{275nm} lc$

$\varepsilon_{275nm} = A_{275nm} \div lc$

$= 1.56 \div (1 \text{ cm} \times 2 \times 10^{-4} \text{ mol dm}^{-3})$

$= 7800 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$

(b) A solution of quinone (molar extinction coefficient of quinone = 24 000 dm^3 mol^{-1} cm^{-1}) had an absorbance of 0.574 in a 1.0 cm cell at 242 nm. What is the concentration of the solution?

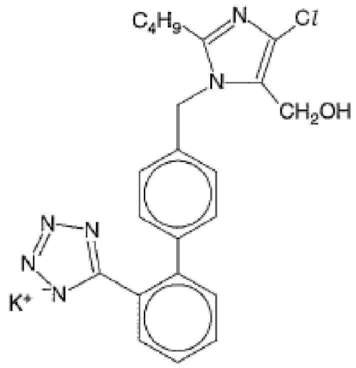
Using Beer's Law, $A_{242nm} = \varepsilon_{242nm} lc$

[Quinone] $= A_{242nm} \div (\varepsilon_{242nm} \times l)$

$= 0.574 \div 24000$

$= 2.39 \times 10^{-5}$ mol dm^{-3}

4 The amount of losartan ($C_{22}H_{22}KN_6ClO$) in a tablet may be estimated by UV spectroscopy. The molar extinction coefficient for losartan should be taken as 1980 $dm^3\ mol^{-1}\ cm^{-1}$ at a wavelength of 254 nm. The absorbance A of a solution is given by the expression $A = \varepsilon c l$.



losartan

(a) Explain why losartan absorbs UV radiation.

Losartan absorbs UV radiation due to the following electronic transitions between MOs with energy gap that coincides with energy of UV radiation:

- Losartan shows $n \rightarrow \sigma^*$ transitions since it contains atoms like Cl and O with lone pair of electrons in saturated bonds.
- Losartan shows $n \rightarrow \pi^*$ transitions since it contains atoms like N with lone pairs of electrons that form unsaturated bonds with C or N.
- Losartan shows $\pi \rightarrow \pi^*$ transitions as it has unsaturated N=N, C=N and C=C bonds. Furthermore, the presence of conjugated π bonds reduces the energy gap between the π and the π^* MOs. This shifts the absorption towards longer wavelength.

(b) One tablet of losartan, from another supplier, is dissolved in distilled water and the solution made up to 100 cm^3 in a volumetric flask. This is solution X.

5.00 cm^3 of solution X is diluted to 100 cm^3 in a second volumetric flask, giving solution Y.

Using a cell with a pathlength of 1 cm, the absorbance of solution Y was measured at 254 nm and found to be 0.217.

Calculate the mass of losartan in the tablet.

Using Beer's Law, $A = \varepsilon\, l\, c$
$[\text{Losartan}]_{\text{solution Y}} = 0.217 \div (1980 \times 1) = 0.0001095\ mol\ dm^{-3}$

$[\text{Losartan}]_{\text{solution X}} = 0.0001095 \times (100/5) = 0.002191\ mol\ dm^{-3}$

n(Losartan) in the tablet = 0.002191 x 0.100= 0.0002191 mol

Mass of Losartan = 0.0002191 x 460.6 = **<u>0.101 g</u>**

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5 A patient's blood serum level of diazepam is monitored by measuring the absorbance of diazepam at 240 nm in a spectrophotometer. It was found that the steady state absorbance of the serum was 0.018. The absorbances of four standard solutions of diazepam were also measured, using a path length of 1 cm, and the following results were obtained.

Concentration (mg dm^{-3})	**absorbance**
1.00	0.450
0.82	0.369
0.55	0.248
0.35	0.158

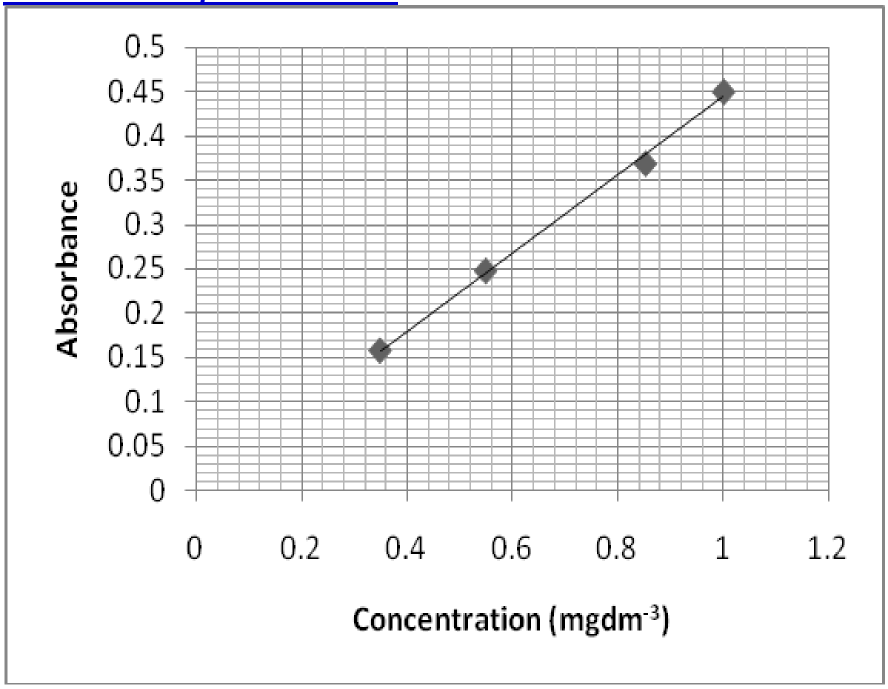
(a) Use the data provided to determine whether Beer's law is obeyed for diazepam at 240 nm.

Method 1: Calculate A/c ratio

Concentration (mg dm^{-3})	**absorbance**	**A/c**
1.00	0.450	0.450
0.82	0.369	0.450
0.55	0.248	0.451
0.35	0.158	0.451

Since A/c is a **constant**, at 240 nm, Beer's Law is **obeyed** by diazepam.

Method 2: Graphical Method



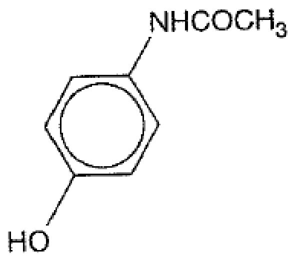
Since the **plot of absorbance against concentration is linear, absorbance is directly proportional to concentration**. Hence, Beer's law is obeyed by diazepam.

(b) Calculate the steady state concentration of diazepam in mg dm^{-3} of serum.

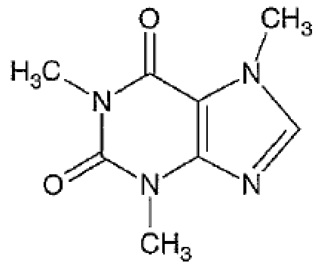
Since A/c = 0.450

Steady state concentration of diazepam = 0.018 / 0.450
= 0.0400 mg dm^{-3}

6 Paracetamol pills often contain small amounts of caffeine.



paracetamol



caffeine

The relative amounts in moles of caffeine and paracetamol in a pill may be estimated by making a solution of the pill, amd measuring the UV absorbance of the solution at a suitable wavelength for each compound.

The molar extinction coefficient, ε, should be taken as
- 18200 dm^3 mol^{-1} cm^{-1} at wavelength of 275 nm for caffeine
- 151100 dm^3 mol^{-1} cm^{-1} at wavelength of 245 nm for paracetamol.

(a) For a particular pill solution, the measured absorbances are 275 nm and 245 nm were 0.19 and 0.39 respectively.
Calculate the ratio of the relative amounts in moles of the two compounds in the pill.

Assume that the absorption at 275 nm is only due to caffeine, and that the absorption at 245 nm is only due to paracetamol.

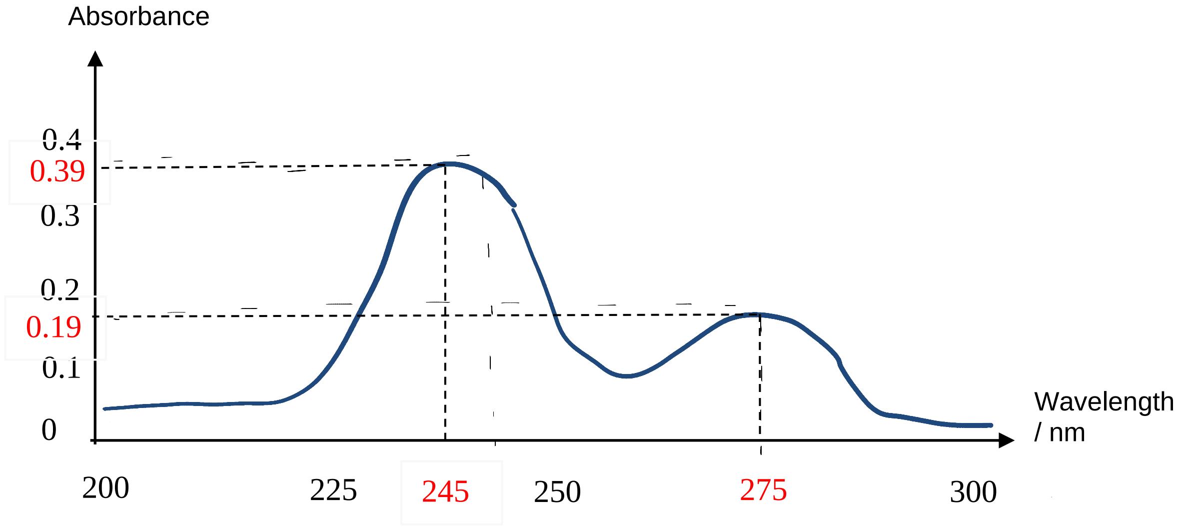
Using Beer's Law $A = \varepsilon c l$

At 275 nm, 0.19 = 18200 x [caffeine] x 1.0
[caffeine] = 1.044 x 10^{-5} mol dm^{-3}

At 245 nm, 0.39 = 151100 x [paracetamol] x 1.0
[paracetamol] = 2.581 x 10^{-6} mol dm^{-6}

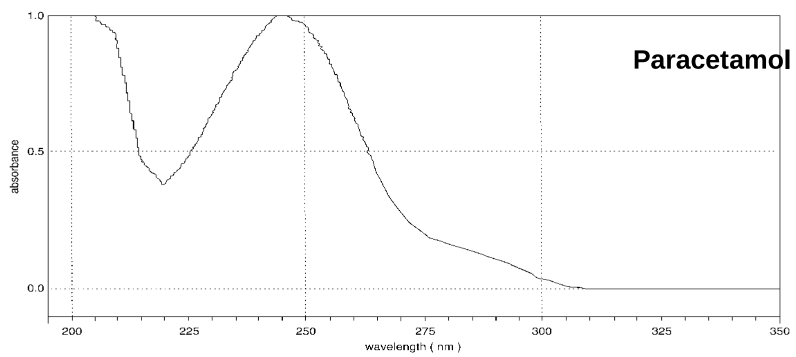
Ratio of [caffeine] : [paracetamol] = 4.04 : 1

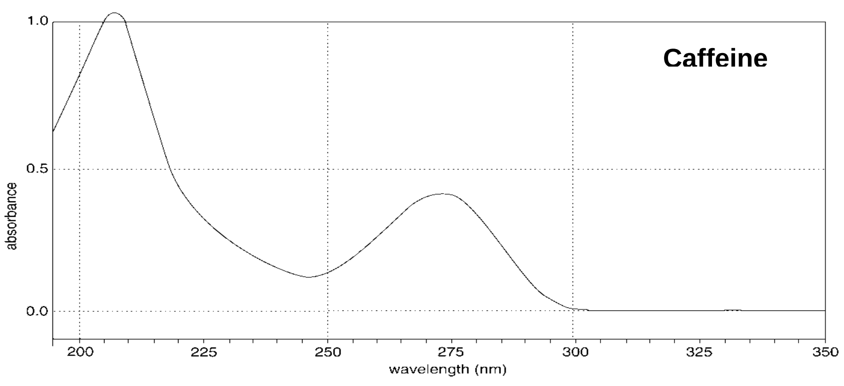
(b) Sketch the spectrum that you would expect for the pill solution between 200 nm and 300 nm.
Use your sketch to suggest why the ratio calculated in (ii) might be inaccurate.



The λ_{max} values for caffeine and paracetamol are similar in value, hence each compound has some absorption at both wavelengths. The assumption that the absorption at 275 nm is only due to caffeine, and that the absorption at 245 nm is only due to paracetamol is not valid.

Note: A graph showing sharp and separate absorption curves without overlap is incorrect.





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