國立清華大學 102 學年度碩士班考試入學試題

系所班組別：生醫工程與環境科學系 乙組(環境分子科學組)

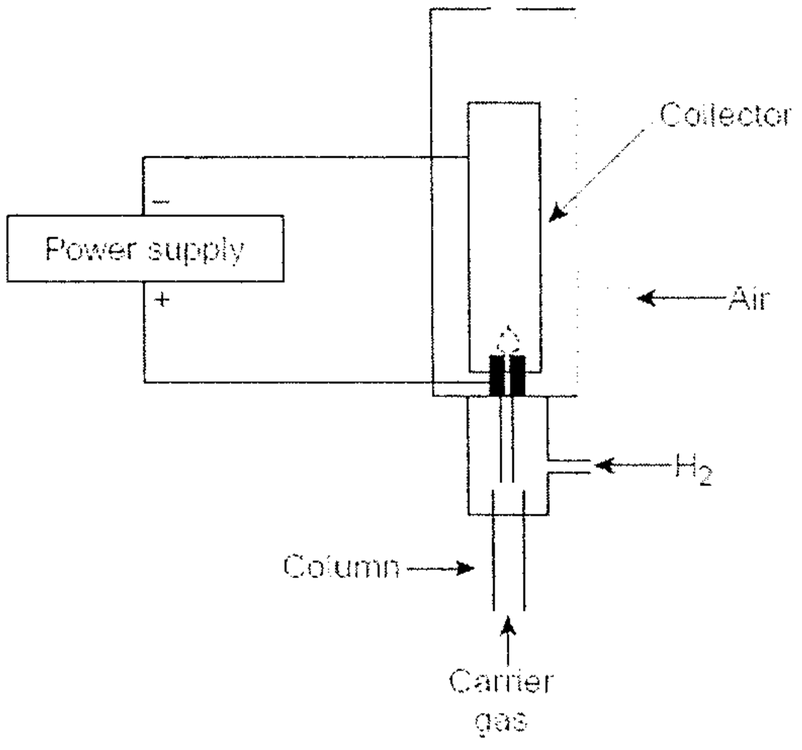
考試科目（代碼）：分析化學 (2303)

1. (10%) (1) Following Figure (a) indicates the schematic diagram of flame ionization detector (FID). Please state the working principle of FID.

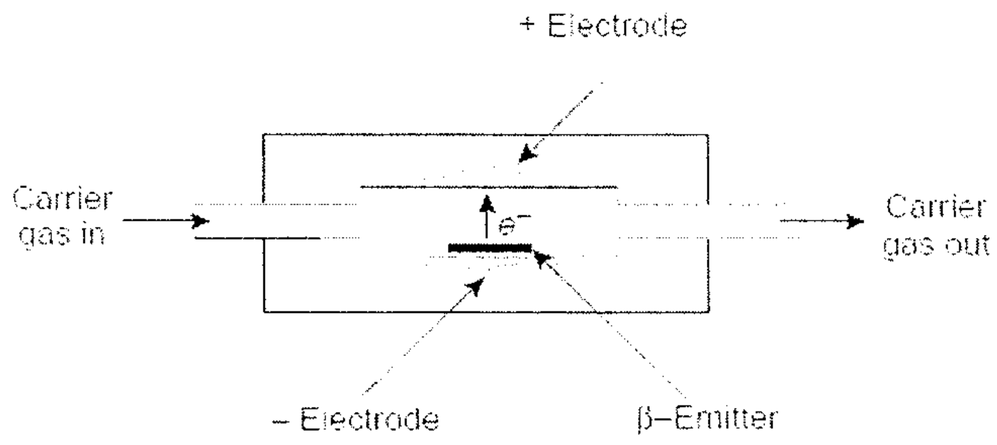
   (2) Please state the reason why the FID is considered as an almost universal detector for the measurement of organic compounds by GC.

   (3) Following Figure (b) indicates the schematic diagram of electron capture detector (ECD). Please state the working principle of ECD.

   (4) Please state the reason why the ECD is considered as the best detector for the measurement of polychlorinated biphenyls (PCBs) and organo-halogen pesticides by GC.



(a)Flame ionization detector



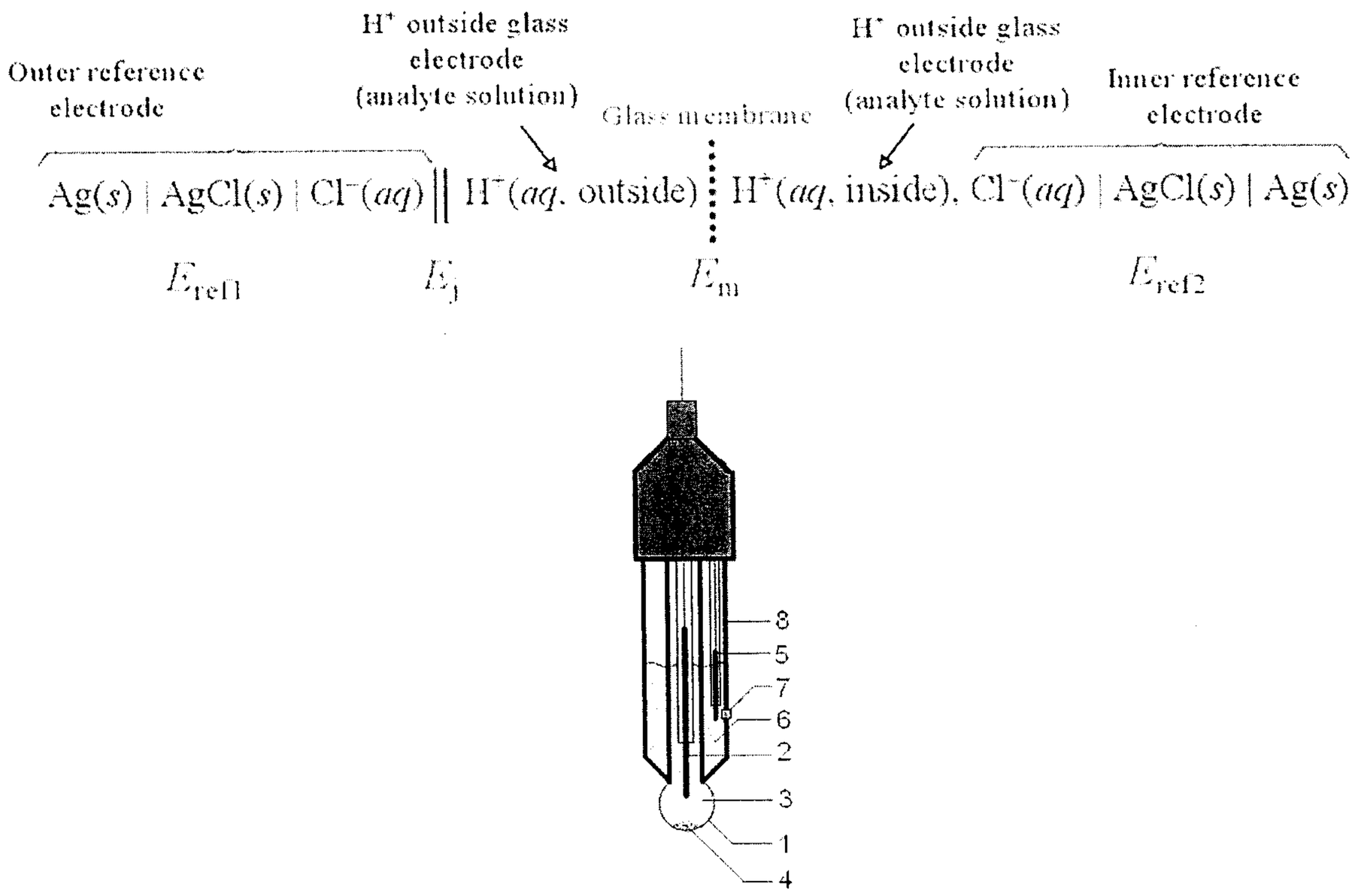
(b) electron capture detector

2. (10%) (1) A typical modern pH probe is a combination electrode, which combines both the glass and reference electrodes into one body. Please give the name of the following parts of a combination electrode shown below.

   (2) Please define asymmetry potential

   (3) Based on following diagram of glass cell, please illustrate the principle of glass

electrode for the measurement of pH.



3. (10%)The following data are for a liquid chromatographic column:

Length of Packing	24.7 cm
Flow rate	0.313 mL/min
V_M	1.37 mL
V_S	0.164 mL

A chromatogram of a mixture of species A, B, C, and D provided the following data:

	Retention time, min	Width of peak base(W), mm
Noretained	3.1	--
A	5.4	0.41
B	13.3	1.07
C	14.1	1.16
D	21.6	1.72

Calculate

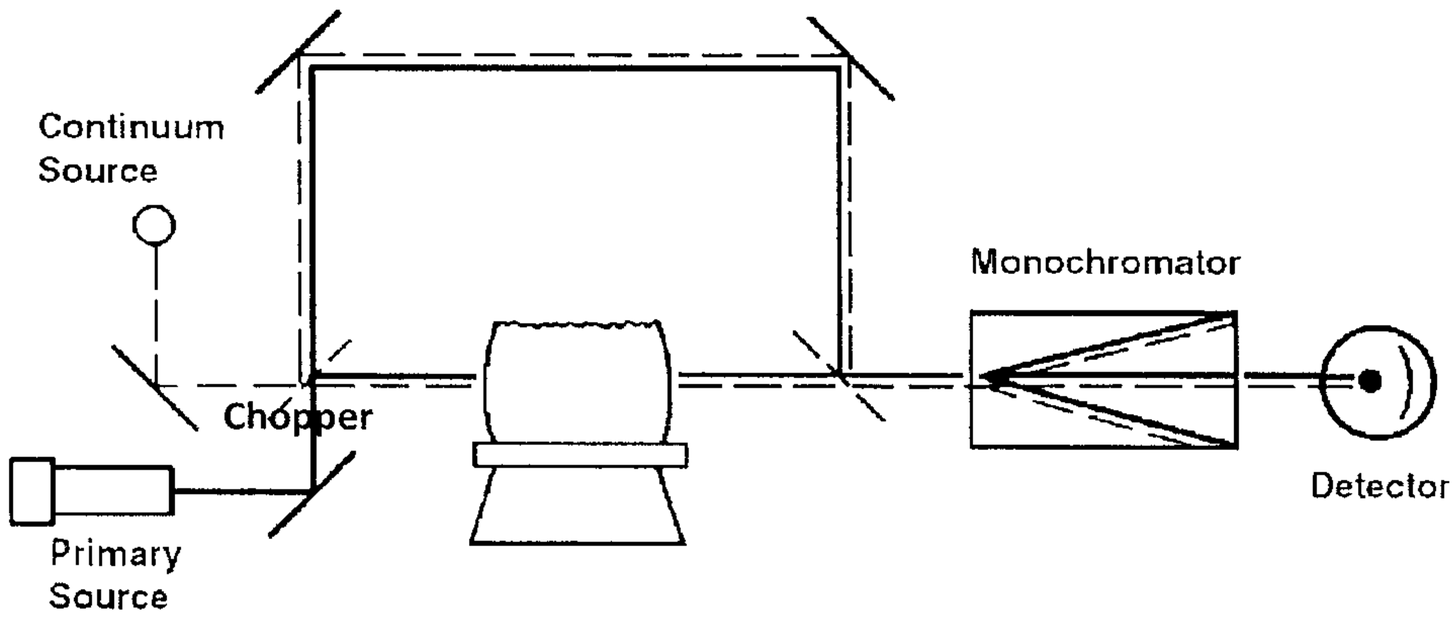
(a) the number of plates from each peak

(b) the selectivity factor for species B and C

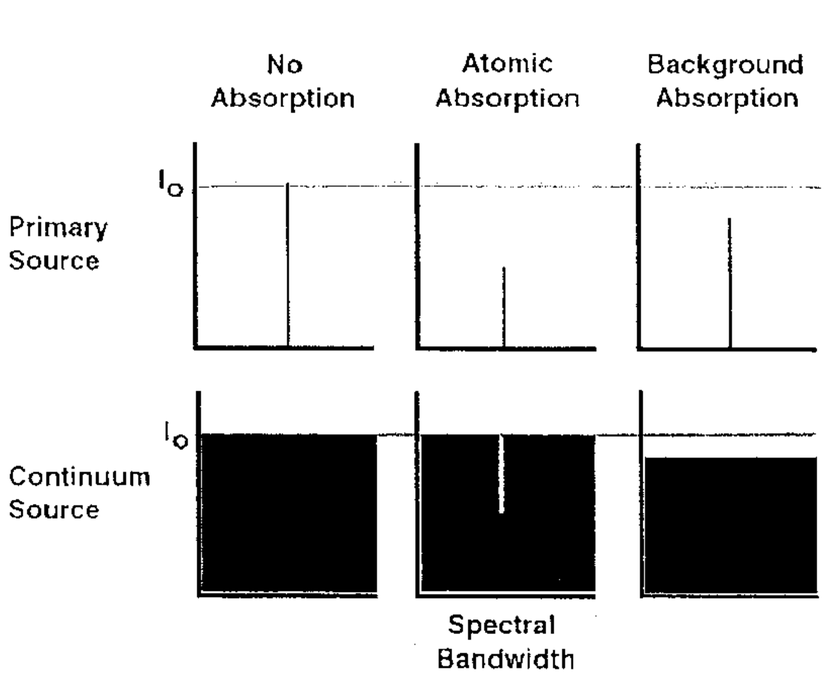
(c) the resolution for species C and D

the length of column necessary to separate species B and C with a resolution of 1.5

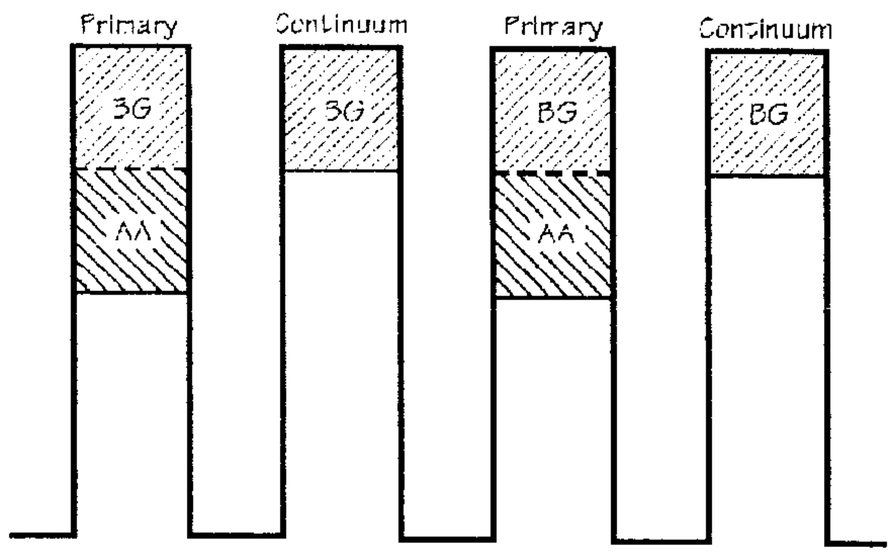
4. (10%) Atomic absorption spectroscopy (AAS) is fundamentally a very simple technique. Light at the resonance wavelength of an element can be absorbed by atoms of that element in the vapor phase. This reduction in light from the source is the AAS signal. It is correlated with the number of atoms through which the light must pass. If anything else in the sample (the matrix) can reduce the intensity of radiation from the source, by scattering or molecular absorption, it will be indistinguishable from the analyte. This nonanalyte signal is called background absorption, whether the cause of the signal is scattering or absorption. Continuum source background correction (Deuterium Background Correction) is a technique for automatically measuring and compensating for any background component which might be present in an atomic absorption measurement. This method incorporates a continuum light source in a modified optical system, illustrated in following Figure.



In this background correction technique, a separate source (a deuterium lamp) with broad emission is used to measure the background absorption over the entire width of the exit slit of the spectrometer. Referring to following Figures, please state the principle of background correction with the deuterium-lamp technique.



Atomic and background absorption with a primary (line) source and a continuum source



Simplified timing diagram

5. (10%) FT-IR stands for Fourier Transform InfraRed, the preferred method of infrared spectroscopy. In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular

absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint no two unique molecular structures produce the same infrared spectrum. This makes infrared spectroscopy useful for several types of analysis.

(a) Does an FT-IR instrument record a signal in the time domain or the frequency domain? (choice question)

(b) What does the Michelson interferometer do? (choice question)

(1) Split a polychromatic beam of radiation into its component wavelengths

(2) Selectively filter certain wavelengths from a beam of I.R. radiation

(3) Modulate the I.R. signal at a lower frequency, so that it can be observed by a detector

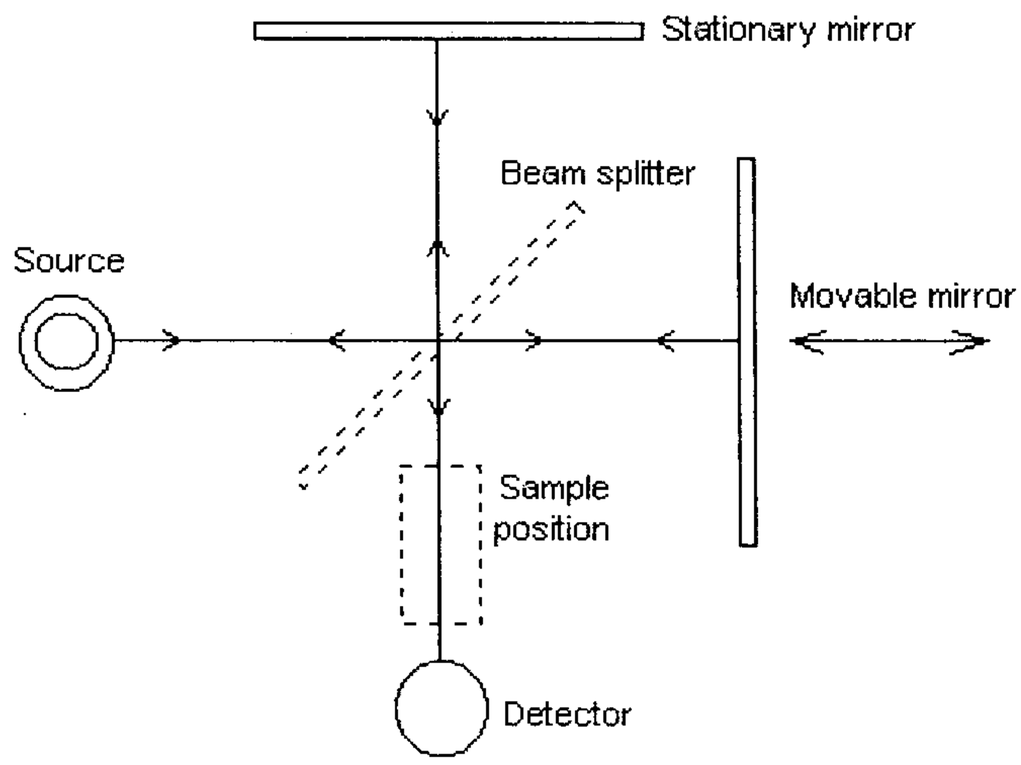
(c) How do you turn a signal recorded in the time domain into a frequency domain signal? (choice question)

(1) Fourier transformation

(2) Measurement of peak areas

(3) By use of a Michelson interferometer

(d) FT-IR instruments employ single beam optics. True or false? (choice question)



The Michelson interferometer

6. (10%) In spectrometry, the Beer–Lambert law, also known as Beer's law relates the absorption of light to the properties of the material through which the light is travelling. The diagram below shows a beam of monochromatic radiation of radiant power I_0, directed at a sample solution. Absorption takes place and the beam of radiation leaving the sample has radiant power I. The absorbance of a sample can be related to the concentration of the absorbing species through Beer's law:

Transmittance, $T = I / I_0$

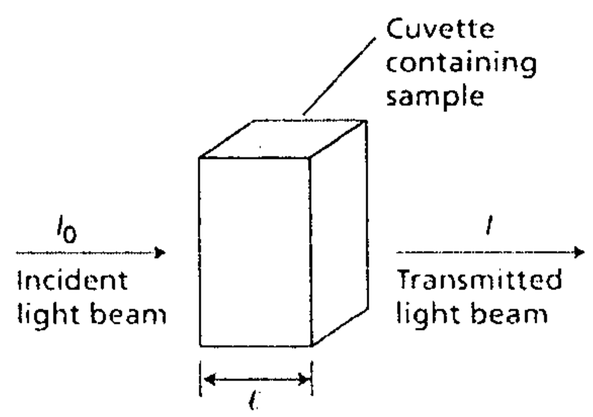
$A=\varepsilon bc$

Where A is absorbance (no units, since $A = log(I_0 / I)$

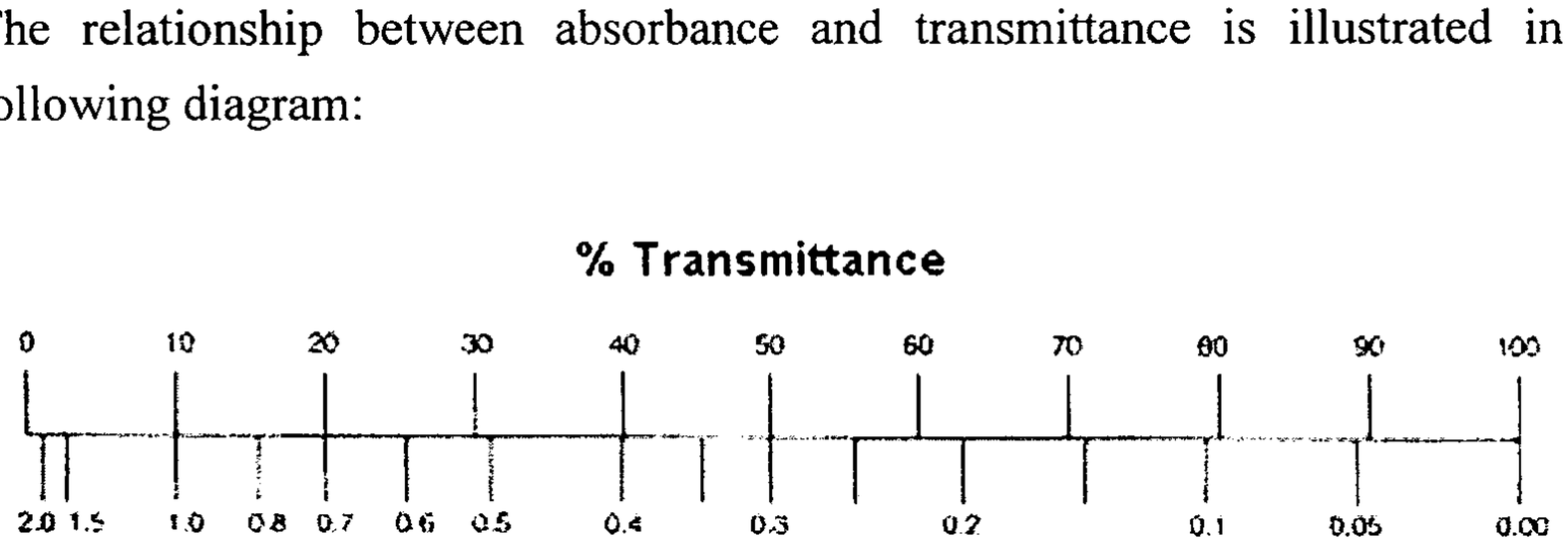
ε is the molar absorbtivity with units of L mol^{-1} cm^{-1}

b is the path length of the sample - that is, the path length of the cuvette in which the sample is contained. We will express this measurement in centimetres.

c is the concentration of the compound in solution, expressed in mol L^{-1}



(a) The relationship between absorbance and transmittance is illustrated in the following diagram:

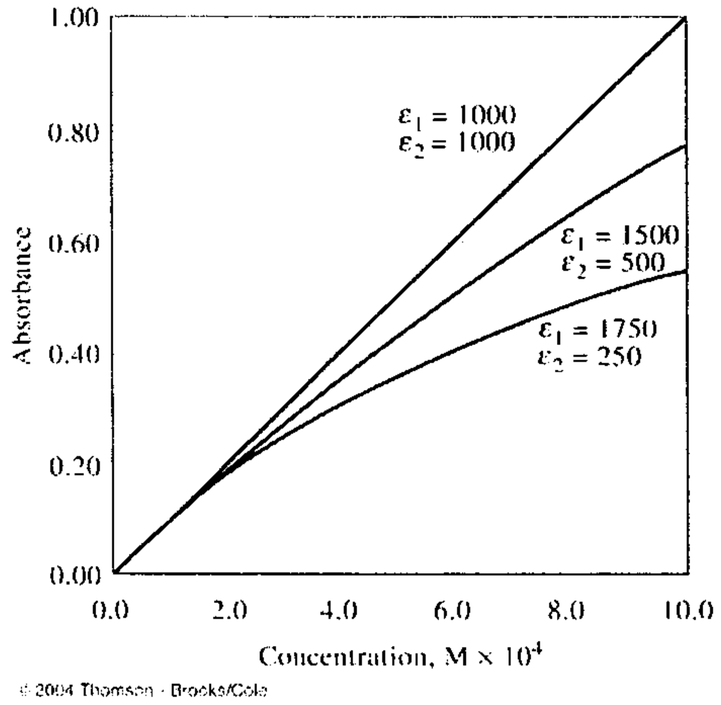


Why do we prefer to express the Beer-Lambert law using absorbance as a measure of the absorption rather than %T ?

(b) What is the significance of the molar absorptivity, ε ?

(c) In following Figure, it shows the effect of polychromatic radiation on Beer's law. Consider a light beam consisting of just two wavelength, λ' and λ". Based on those equations given in this question, please derive an equation and describe the reason why the relationship between A and concentration is no longer linear when the molar absorptivities differ.

$A = \log_{10} I_0 / I$



7. (10%) (1) Please define buffer capacity and indicate which buffer shown below has greater buffer capacity. (a) a mixture containing 0.100 mol of NH_3 and 0.200 mol of NH_4Cl, (b) a mixture containing 0.0500 mol of NH_3 and 0.100 mol of NH_4Cl.

(2) What volume of 0.200 M HCl must be added to 250.0 mL of 0.300 M sodium mandelate to produce a buffer solution with a pH of 3.37? (K_a of mandelate $=4.0\times10^{-4}$)

8. (10%) Iron(III) forms a complex with thiocyanate ion that has the formula $Fe(SCN)^{2+}$. The complex has an absorption maximum at 580 nm. A sample of well water was assayed according to the scheme shown in the table below. Calculate the concentration of iron in parts per million in the well water.

Sample	Volumes, mL					Absorbance, 580 nm (1.00-cm cell)
	Sample volume	Oxidizing reagent	Fe(II) 2.75 ppm	KSCN 0.050 M	H_2O	
1	50.00	5.00	5.00	20.00	20.00	0.549
2	50.00	5.00	0.00	20.00	25.00	0.231

9. (10%) Calculate the % relative error in solubility by using concentrations instead of activities for the following compounds in 0.0500 M KNO_3 using thermodynamic Ksp shown below.

(1) CuCl ($Ksp=1.9\times10^{-7}$)

(2) $Fe(OH)_3$ ($Ksp=2\times10^{-39}$)

(3) Ag_3AsO_4 ($Ksp=6\times10^{-23}$)

(4) Based on above calculations, please illustrate the effect of charges of ionic participants on equilibrium when the effect of electrolyte is ought to be take into consideration.

10. (10%) The solubility-product for a series of iodides are

CuI $K_{sp}=1\times10^{-12}$, AgI $K_{sp}=8.3\times10^{-17}$, PbI_2 $K_{sp}=7.1\times10^{-9}$, BiI_3 $K_{sp}=8.1\times10^{-19}$

List these four compounds in order of decreasing molar solubility in

(1) water

(2) 0.10 MNaI

(3) a 0.010 M solution of the solute cation.