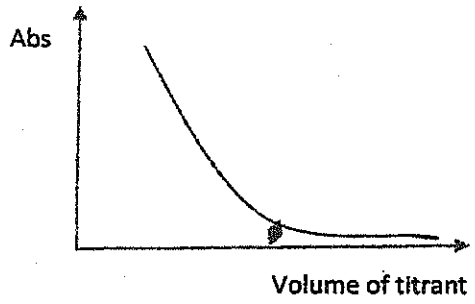
THE OPEN UNIVERSITY OF SRI LANKA
BSc Degree Programme/ Stand Alone Courses in Chemistry
Level 5- Home Assignment I- 2019/2020
CYU5308- INSTRUMENTAL METHODS OF CHEMICAL ANALYSIS

ANSWER GUIDE

1. (a)(i) Briefly explain the basis of photometric titration for the determination of an analyte.

It uses the fact that intensity of a particular color can be measured as absorbance. A color change in the titration can be monitored by measuring the change in absorbance at a λ. Absorbance varies linearly with the concentration (Beer-Lambert law) which changes with the volume of titrant as the titration proceeds. So the plot of absorbance (corrected) vs. volume of titrant is a straight line.

(ii) In a determination of concentration of an analyte, X (λ_{max}= 580 nm), a photometric titration of 25.0 cm^3 of X was carried out at 580 nm against a titrant Y. Draw and label the titration curve, if Y does not absorb light at 580 nm. Briefly explain the titration curve. (Assume that the product of the reaction does not absorb light at 580 nm)



As the titration proceeds with the addition of Y, X + Y → Product, products are formed. As the titration proceeds, concentration of X decreases, the absorbance decreases until the end point is reached when all X has been used up. Since only X absorbs, the absorbance nears zero and does not change with further addition of Y after the end point.

(iii) Why do you need to make correction for the plot? How do you do it?

Correction is made for the change in volume. Absorbance is α concentration. When titrant is added (during titration), volume increases, concentration decreases and this affects absorbance measurements. Hence correction is needed. Must calculate absorbance if volume remained constant.

$A_{corr} = A_{meas}\frac{V_i + V_t}{V_i}$ where V_i is the initial volume of the sample solution

V_t is the volume of titrant added

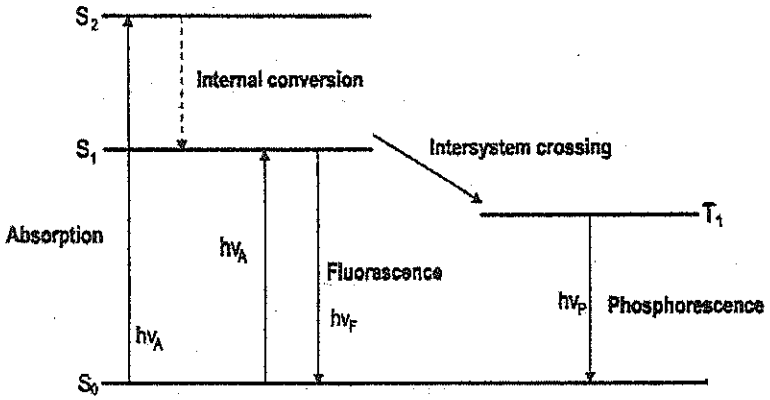
Alternatively, we can use a fairly concentrated titrant, so that V_t <<.

(iv) List two advantages of photometric titrations. (25 marks)

Easy to locate equivalence point – from change in absorbing pattern (Absorbance vs Volume)- from the intersection of two straight lines. All data valuable, even those away from equivalence point. Even if color change is not sharp (curvature near equivalence point). Can use the linear portion of data to locate equivalence point. Only one absorbing species need to be present. Even if other absorbing species are present, they will not interfere (will not absorb at the λ measured).

(b) *Phosphorescence* and *fluorescence* are collectively known as *photoluminescence* and have found applications in analytical chemistry.

(i) Drawing a suitable energy level diagram, compare *phosphorescence* and *fluorescence.*



Fluorescence involves electron transition from singlet excited state to singlet ground state while phosphorescence involves transition from triplet excited state to singlet ground state

(ii) A few large aromatic molecules with several fused rings fluoresce well and are said to have a high *quantum efficiency (*or *yield).*

(α) Define quantum efficiency.

$$\text{Quantum efficiency} = \frac{\text{number of fluorescing molecules}}{\textit{Total number of excited moleculess}}$$

$$= \frac{No.\,of\ photons\ emitted\ by\ fluorescence}{Total\ No\ of\ photons\ \ absorbed}$$

(β) What will be the quantum efficiency of molecules that do not fluoresce? 0 (Zero)

(iii) In an effort to determine the quality of quinine tablet used as an anti-malarial tablet, a suitable solution was prepared following standard protocols. The fluorescent intensity measured at 347 nm was found to be 276 in arbitrary units. Under identical conditions, a 100 ppm sample of quinine gave a reading of 180. Determine the strength (in ppm) of quinine in the prepared solution? (50 marks)

Fluorescence intensity, Fα C; F= KC
For the sample of known concentration, 180= K(100 ppm)
For the prepared solution of Quinine tablet, 276= Kc

$$\frac{180}{276} = \frac{K\,(100\,ppm)}{K\,.C}$$

C= $\frac{276}{180} \times 100\ ppm$
= 153 ppm

(c)(i) Explaining the principles underlying Flame Emission Spectroscopy (FES), briefly describe the method of analysis using Flame photometer.

The elements in a sample are converted to excited atoms in a flame. When the excited atoms return to their ground state, they emit light of characteristic wavelength. The intensity of light (no of photons) emitted is proportional to the no. of atoms in the flame α concentration of analyte in the sample.
F= KC.
Instrument is calibrated by plotting graph: F vs C of a series of standard solutions. From the intensity of unknown, its concentration is read off from the graph.

(ii) Compare FES and Atomic Absorption Spectrophotometer (AAS).

Similarities:
Both use flame to atomize sample. Instrument is calibrated using a set of standards Intensity of emitted light, F vs C for FES; A vs C in AAS (is linear). Both can be used to detect elements. Have comparable accuracies

Differences:
Basic principles underlying the two methods are different.
FES: Flame itself is the source of light. A filter is used to remove unwanted λ. Intensity of emitted light is measured directly. Simple, less expensive. Significant fraction of atoms must be in the excited state in the flame. Therefore not widely applied.
Hollow Cathode Lamp (HCL) is the source of light; monochromatic light from HCL is passed through the flame. Absorbance is measured. To distinguish between light passing through flame and that emitted by the excited atoms in the flame, complicated modulation techniques used. AAS depends on whether there is a large number of atoms in the ground state in the flame.

They complement one another. FES is more sensitive to alkali and alkaline earth metals while AAS is for others (metals and metalloids). (25 marks)

2. (a)(i) Write down the shorthand description of the cell comprising an anode made up of a cadmium rod immersed in a Cd^{2+} solution and a cathode made up of a piece of silver wire (Ag) coated with Ag_2SO_4, immersed in a 1 M H_2SO_4 solution.

$Cd/\ Cd^{2+}_{(aq)}\ //\ H_2SO_4\ (1M)\ /\ Ag_2SO_{4\ (s)}\ /Ag$

Write equations for the half- reactions and a balanced equation for the cell reaction. (20 marks)

$$Cd\ (s) \longrightarrow Cd^{2+}_{(aq)} + 2e$$
$$Ag_2SO_{4\ (s)} + 2e \longrightarrow 2Ag\ (s) + SO^{2-}_{(aq)}$$
$$Cd\ (s) + Ag_2SO_{4\ (s)} \longrightarrow Cd^{2+}_{(aq)} + 2Ag\ (s) + SO_4^{2-}{}_{(aq)}$$

(b)(i) Stating the basic principles involved, briefly describe each of the following analytical techniques for the determination of analyte concentration.

Coulometry

Current is passed through an electrolytic cell- electrochemical reaction is carried out to completion at the electrode. From the knowledge of charge passed, amount of reactant/ product formed is calculated.

Voltammetry

Potential of a working electrode (of a 3- electrode system) immersed in an analyte solution (+ supporting electrolyte) w.r.t. reference electrode is varied over time and resultant current is monitored. Current increases with potential (V), when reaction takes place; $i_D \alpha$ concentration.

(ii) Indicate the type of measurement(s) made and whether a calibration using a standard solution is required or not. (40 marks)

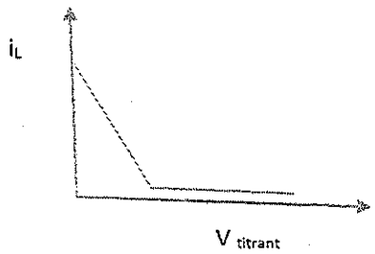
Coulometry – Total charge passed	Calibration not required
Voltammetry- Current	Required

(c) To determine the concentration of Pb^{2+} in a given solution, an amperometric titration of 25.0 cm^3 of the Pb^{2+} solution was carried out with a solution of SO_4^{2-}.

(i) Draw and explain the expected amperometric titration curve. (Assume volume change in the flask is negligible).

i_L vs. $V_{titrant}$

Pb^{2+} is reducible; when SO_4^{2-} is added from the burrete $PbSO_4$ is precipitated:



$Pb^{2+}{}_{(aq)} + SO_4^{2-}{}_{(aq)} \longrightarrow PbSO_4\,(s)$
Pb^{2+} concentration in the bulk decreases and so does i_L. i_L decreases linearly with $V_{titrant}$. At equivalence point i_L drops to ~0 after which no further change takes place because SO_4^{2-} does not get reduced. So another straight line is obtained.

(ii) Compare amperometric titrations with photometric titrations. (40 marks)

Similarity- Carried out in the same way. No indicator is used. Correction for volume increase is the same or concentrated titrant solution ($10 \times analyte$) is used.
Both are accurate.

Differences

Amperometric	Photometric
i_L measured at a suitable potential	Absorbance at λ
Analyte/reagent/ both must be reducible or oxidable	Analyte/reagent/ both must absorb at λ

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