

## Quadrant II – Transcript and Related Materials

**Programme:** Bachelor of Science (Third Year)

**Subject:** Chemistry

**Course Code:** CHD103 (SECTION B)

**Course Title:** Selected Instrumentation in Chemistry

**Unit:** 1 UV-Visible Spectroscopy

**Module Name:** Photometric Titrations

**Name of the Presenter:** Dr. Sachin B. Kakodkar

---

### Notes

#### PHOTOMETRIC TITRATIONS

##### Introduction

Titration in which the absorbance changes of a solution are used to determine the end point are called photometric titrations. The method is based on the fact that the absorbance of a solution is directly proportional to the concentration. During the course of a titration the concentration of the solution being titrated, changes and the absorbance of the solution will also change. The shape of a photometric titration curve will be dependent upon the optical properties of the reactant, titrant and products of the reaction at the wavelength used.

A photometric titration involves the measurement of the absorbance values when a sample solution is titrated against a suitable titrant. The absorbance value of the solution varies with the concentration of the absorbing species present in the solution. These changing absorbance values are plotted against the volume of the titrant.

The titration can be represented as: **Reactant + Titrant  $\rightarrow$  Product**

The end point can be determined by plotting a graph of absorbance versus volume of titrant. It is necessary that the solvent used should not absorb any light during the course of the titration.

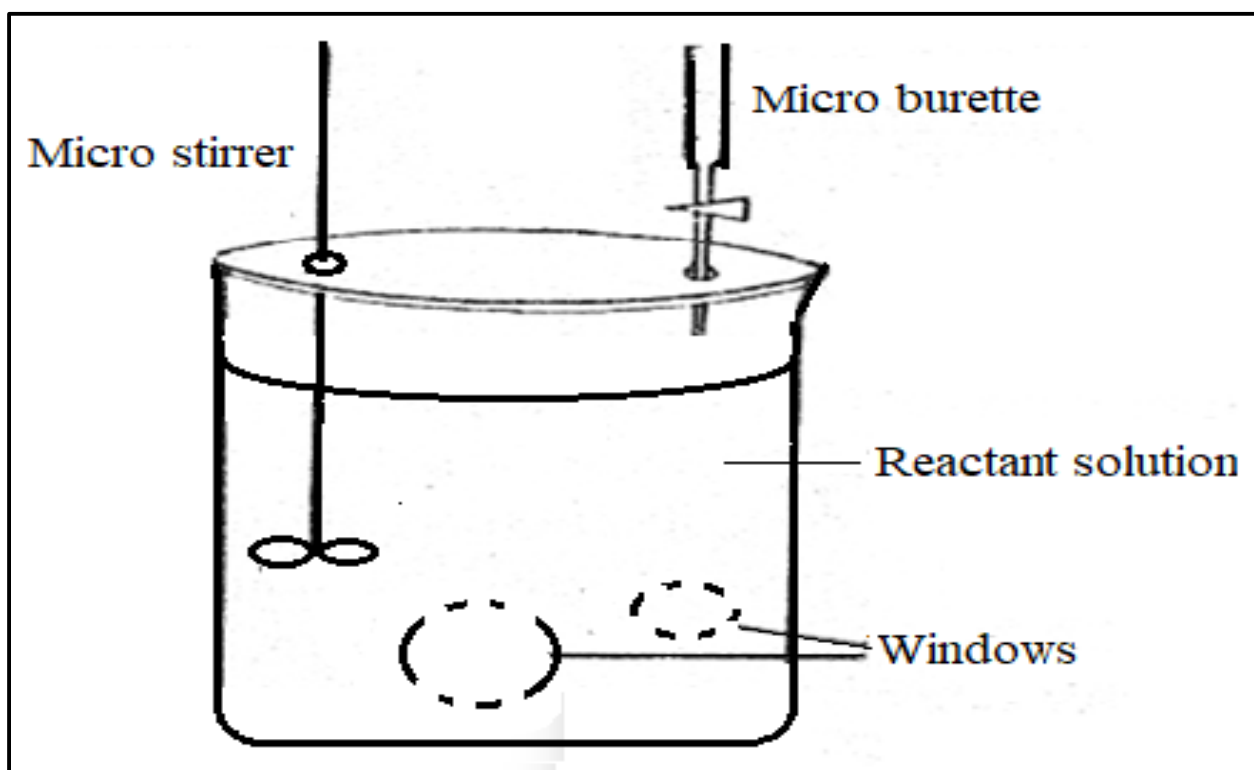
##### Significance of Photometric Titrations

Photometric titrations are resorted to when the end point is not sharp enough to be detected visually; i.e. there is a gradual colour change and the two colours at the end point do not have a

sharp contrast. The technique is also used for the titration of highly coloured solutions where the usual visual indicators cannot be used.

### **Titration Cell for Photometric Titration**

Photometric titrations are carried out using a cylindrical titration cell which can be inserted in the path of light in a spectrophotometer. The cell has two circular windows through which the incident light enters the solution to be titrated and the transmitted light passes out into the photocell. Barring these two windows, the cell is covered with black paper to prevent the entry of any external light into the solution. The cell has openings for the tip of a micro burette and a micro stirrer. The reactant solution is first taken in the cell and the cell is kept in the path of light in a spectrophotometer.



**Titration Cell for Photometric Titration**

### **Photometric Titration Procedure**

The absorbance values are determined after successive installments of the titrant have been added. The absorbance values are then plotted against the volume of the titrant added, and, from the graph, the end point of the titration is determined. In order to avoid errors due to dilution of the solution during titration, titrant should be more concentrated than the solution.

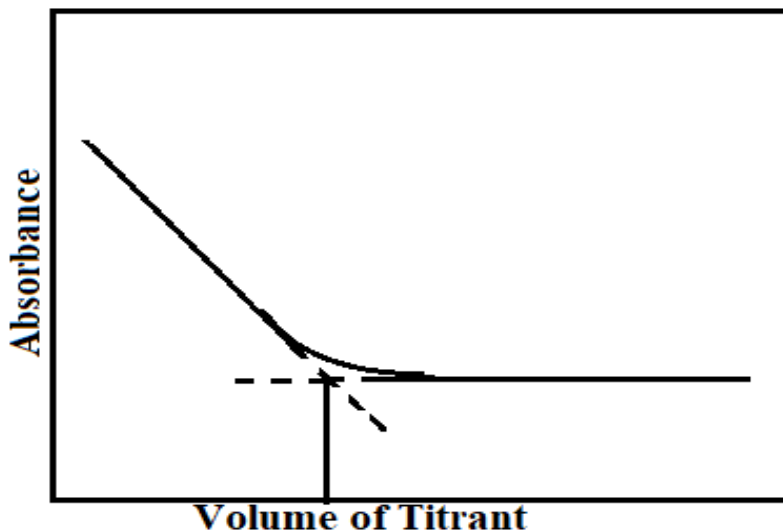
## Types of Photometric Titrations

Photometric titrations are of four types:

**1. The reactant is the absorber while the titrant and product do not absorb at all.**

The absorbance decreases during the titration and remains constant after the end point is reached.

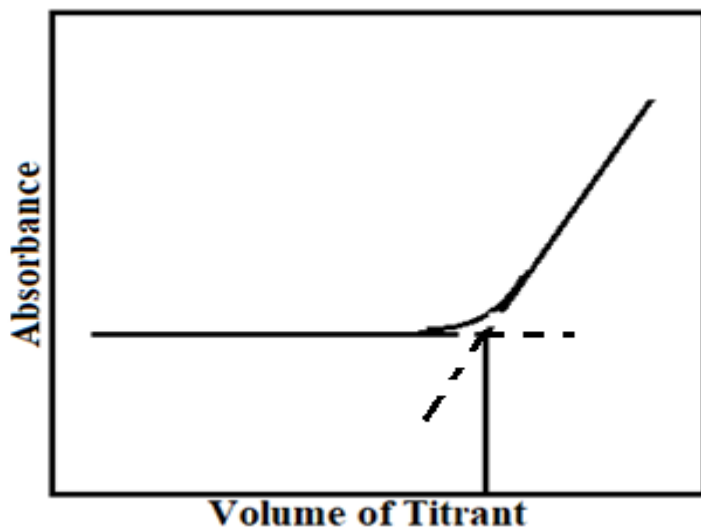
Eg. Photometric titration of p-toluidine in butanol solvent with perchloric acid ( $\text{HClO}_4$ )



**2. The titrant is the absorber while the reactant and product do not absorb at all.**

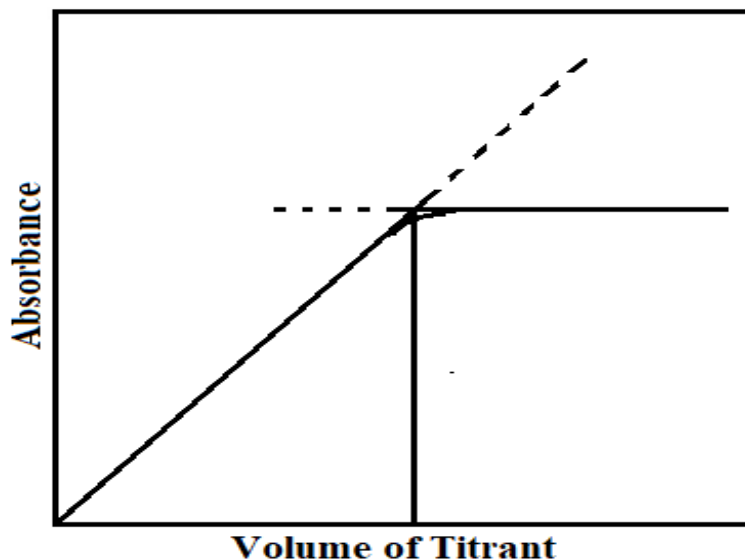
Initially the absorbance remains constant but increases once the end point is reached due to the accumulation of titrant in the reacting solution.

Eg. Titration of  $\text{AsCl}_3$  with  $\text{KBr} + \text{KBrO}_3$  mixture



3. **The product is the absorber while the reactant and the titrant do not absorb at all.** The absorbance increases steadily as the titration proceeds but remains constant once the end point is reached.

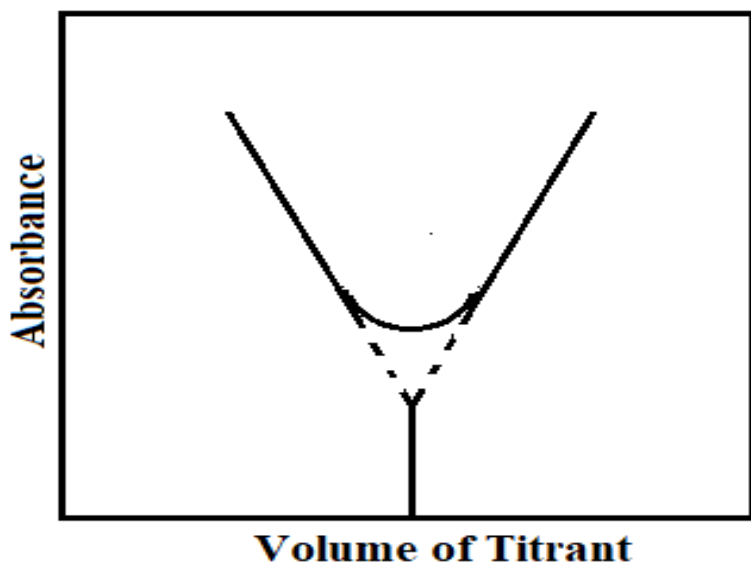
**Eg.** Titration of Cu(II) or Ni(II) with EDTA. In this case the product Cu-EDTA or Ni-EDTA complex is the absorber of light.



4. **Both the reactant and the titrant absorb but to different extents.**

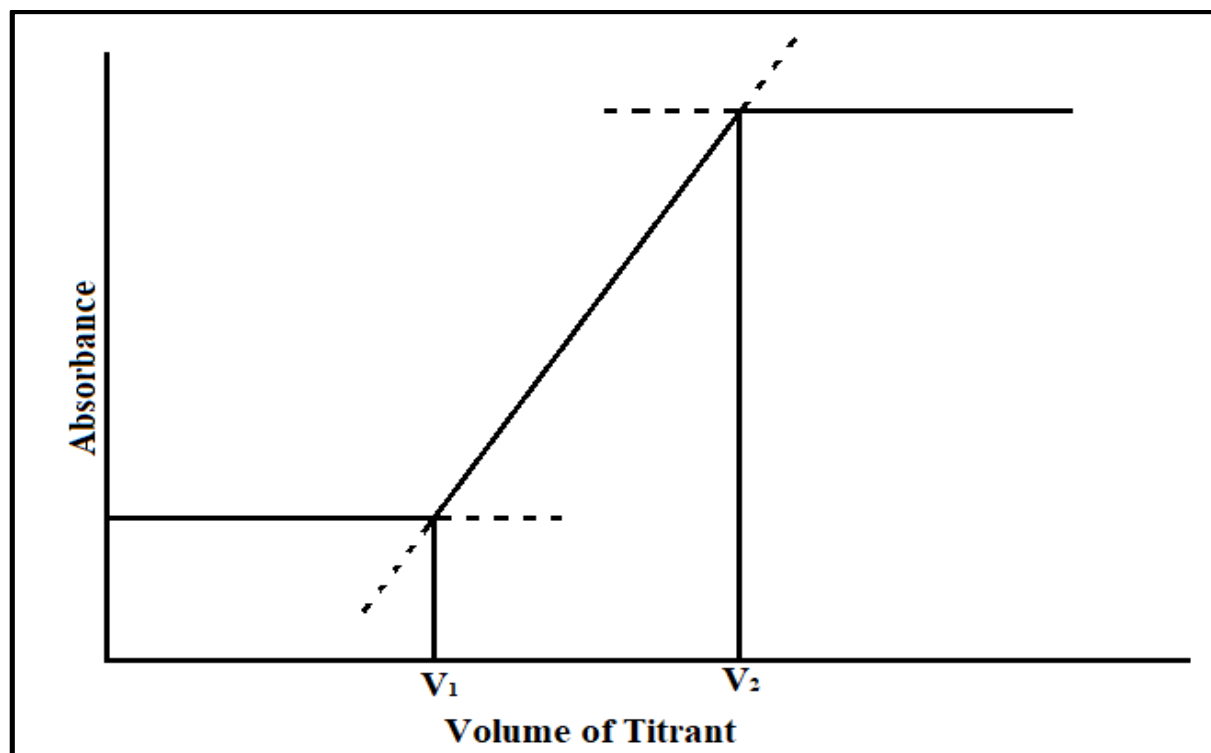
Here a coloured reactant is converted into a colourless product (non-absorber) by a coloured titrant. The absorbance first decreases and then increases after equivalence point is reached.

**Eg.** Bromination of a red dye.



### Estimation of metals in a mixture

Photometric titrations are used to estimate metals in a mixture. Copper and bismuth can be estimated in a mixture by a photometric titration against EDTA at 745 nm. At 745 nm,  $\text{Cu}^{2+}$ ,  $\text{Bi}^{3+}$  and EDTA titrant do not absorb light. The Bi-EDTA complex too does not absorb light at 745 nm. Hence during titration, the titre solution does not show any absorbance till all the bismuth has reacted with EDTA. The absorbance starts increasing when copper reacts with EDTA to form Cu-EDTA complex which is a strong absorber of light. The absorbance rises till copper is fully titrated. If excess titrant is added the absorbance remains constant. Thus the photometric curve shows two distinct end points, i.e. first one ( $V_1$ ) for bismuth and second one ( $V_2$ ) for copper.



Photometric Titration Curve for Bi-Cu mixture

### Deviations

The obedience of the Beer-Lambert's law is a strict requirement for such titrations. Both mechanical and chemical deviations are observed from Beer's law. To overcome the chemical deviation sufficient data should be recorded even after the equivalence point. For eliminating mechanical deviation, which otherwise yield impure curves, extremely narrow band of radiation needs to be employed.

**Dilution Correction**

The effect of dilution is rendered negligible either by the use of a sufficiently concentrated titrant or by applying a correction to the absorbance. For this absorbance is multiplied by the factor  $(V+v)/V$  where  $V$  is the volume of solution being titrated and  $v$  is volume of titrant.