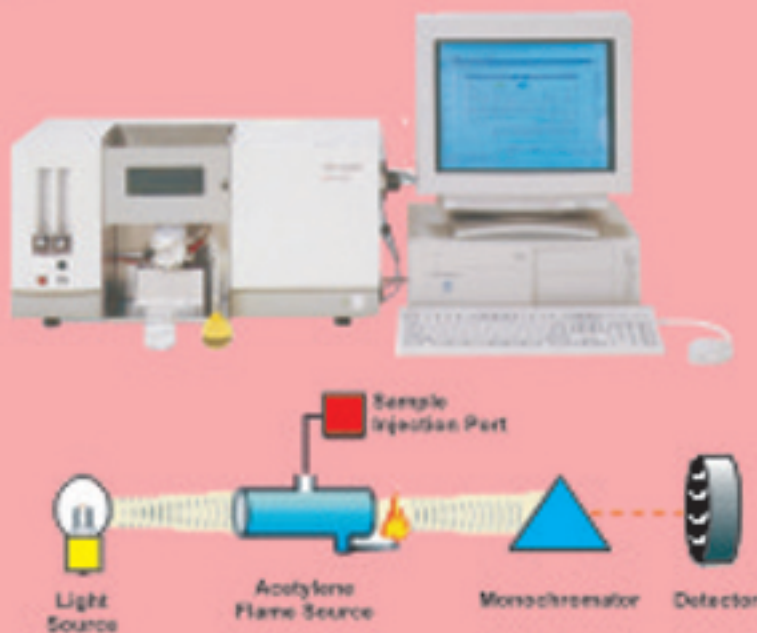


**New Syllabus 2010**

**A Text Book of**

# **ANALYTICAL CHEMISTRY**

**T. Y. B.Sc. • CHEMISTRY CH-334 • SEMESTER III**



**Dr. A. V. NAGWADE**

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**NIRALI PRAKASHAN**

A TEXT BOOK OF

# ANALYTICAL CHEMISTRY

For

**T. Y. B. Sc. (CH - 364)**

**Semester - VI**

**According to New Revised Syllabus of  
North Maharashtra University, Jalgaon, w.e.f. June 2017**

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## PREFACE

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We have a great pleasure in presenting this book on '**Analytical Chemistry**' for T.Y.B.Sc. students of Semester VI.

This book is written according to the revised syllabus and guidelines of the North Maharashtra University, Jalgaon in force from June 2017.

The aim of this book is to provide a concise and simple information of topic included in the syllabus given wherever necessary to illustrate the concept. A large number of exercises have been given at the end of each topic.

We expect that the book will be helpful to the students as well as teachers.

The authors will welcome and appreciate any suggestions and criticism from the teachers and students for the improvement of this book.

We are grateful to our publisher Mr. Dineshbhai Furia and Mr. Jignesh Furia for their keen interest and constant encouragement to make this book an ideal one. We are also thankful to the staff of Nirali Prakashan, especially Mr. Ilyas Shaikh, Mr. Kiran Velankar and Miss Chaitali Takle for completing the publication of the book as early as possible.

**- Authors**

# SYLLABUS

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## 1. SPECTROMETRY (20 L, 20 M)

Interaction of electromagnetic radiation with matter, Electromagnetic Spectrum, The Absorption of Radiation, Absorption by Inorganic Compounds, Solvents for Spectrometry, Quantitative Calculations, Beer's Law, Principles of Instruments - Sources, Monochromators (Prism, Diffraction gratings, Optical filters), Cells, Detectors, Slit Width, Single Beam Spectrometer, Spectrometric Errors, Deviation from Beer's law - Chemical deviation, Instrumental deviation.

## 2. EMISSION SPECTROMETRY (08 L, 08 M)

Flame Emission Spectroscopy, Plasma Emission Spectrometry, Distribution between Ground and Excited States,

## 3. ATOMIC ABSORPTION SPECTROMETRY (10 L, 10 M)

Principles, Instrumentation - Sources, Burners, Flames, Interferences - Spectral Interferences, Ionization Interferences, Refractory Compound Formation, Physical Interferences, Use of Organic Solvents, Sample Preparation.

## 4. NEPHELOMETRY AND TURBIDIMETRY (10 L, 10 M)

Introduction, Turbidimetry and Colorimetry, Nephelometry and Fluorimetry, Choice between Nephelometry and Turbidimetry, Theory, Instrumentation, Comparison of Spectrometry, Turbidimetry and Nephelometry, Applications of Turbidimetry and Nephelometry.

## 5. THERMAL METHODS (12 L, 12 M)

General Discussion.

**Thermogravimetry:** Instruments for Thermogravimetry, Applications of Thermogravimetry.

**Differential Techniques:** Differential Thermal Analysis (DTA) and Differential Scanning Colorimetry (DSC), Instruments for DTA and DSC, Experimental and Instrumental Factors, Applications of DTA and DSC.



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1. SPECTROMETRY	1.1 – 1.40
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# Chapter 1

## SPECTROMETRY

### 1.1 INTRODUCTION

- The spectroscopy deals with the studies involving entire electromagnetic radiation and some other techniques that do not involve electromagnetic radiation. The spectrometry which deals with the visible region of the electromagnetic radiation is most widely used as an analytical technique in all branches of chemistry as well as chemical and environmental laboratories. This technique is simple, readily available and less expensive. The visible spectrometry is also called as spectrophotometry.

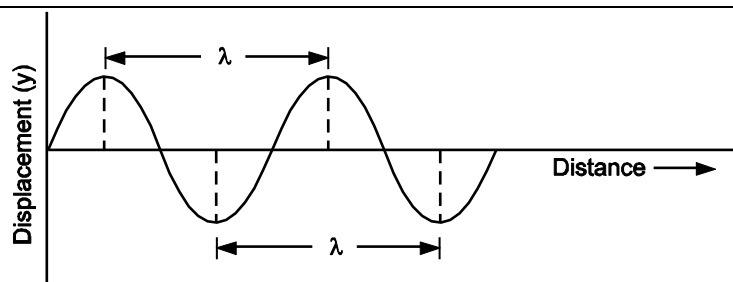
#### 1.1.1 Electromagnetic Radiation and its Interactions

- The spectrometric methods of analysis depend on the absorption of electromagnetic radiation from the source and the amount of radiation absorbed is related to the concentration of the solution of analyte. This method is based on absorption of light and called as absorption spectrometry. We will first study the different regions of electromagnetic spectrum and its absorption by the molecules of the test solution.

### 1.2 ELECTROMAGNETIC RADIATION AND ITS CHARACTERIZATION

- Electromagnetic radiation consists of energy associated with electric and magnetic fields resulting from the acceleration of electric charge. The electric and magnetic field which require no supporting medium and can be propagated through space or vacuum are at right angles to each other and to the direction of propagation. The electromagnetic radiation possesses properties of both waves and discrete particles which are termed as photons. The electromagnetic radiation is considered as a simple harmonic wave propagated from a source and travelling in a straight line.

(1.1)



**Fig. 1.1 : Simple Harmonic Wave**

**Wavelength :** We define a characteristic property of the wave called wavelength. The wavelength is defined as *the distance travelled during a complete cycle*. Also defined as the number of cycles passing a fixed point per unit time. It is *the distance between two successive maxima or minima*. It is represented by  $\lambda$ .

**Frequency :** It is defined as the *number of vibrations per second*. It is represented by  $\nu$ .

**Wave number :** It is defined as the *number of waves in unit length or distance per cycle*. It is reciprocal of wavelength. It is represented by  $\bar{\nu}$ .

**Relation Between Wavelength, Frequency and Wave Number :**

$$(i) \quad \lambda = \frac{c}{\nu} \quad \dots(1.1)$$

where,  $\lambda$  – Wavelength in cm  
 $\nu$  – Frequency in  $\text{second}^{-1}$  or Hertz (Hz)  
 $c$  – Velocity of light in cm per second

$$(ii) \quad \bar{\nu} = \frac{1}{\lambda} \quad \dots(1.2)$$

where  $\bar{\nu}$  – Frequency in  $\text{cm}^{-1}$

$$(iii) \quad \bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} \quad \dots(1.3)$$

$$\text{Or} \quad \nu = \frac{c}{\lambda} \quad \dots(1.4)$$

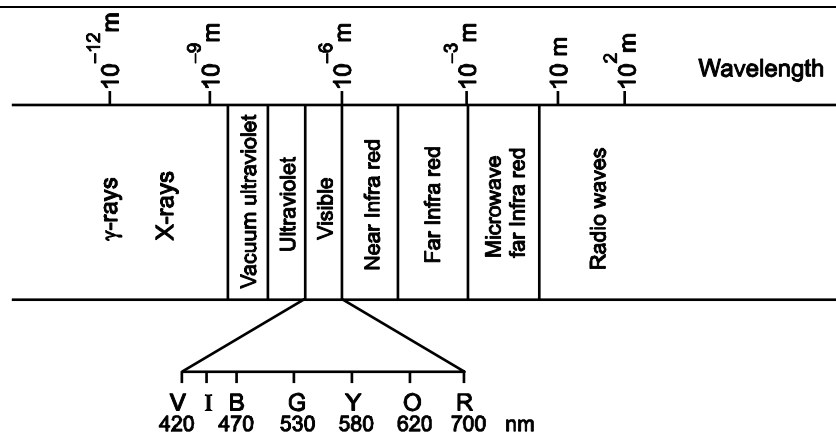
**Different Units of Wavelength :** The wavelength is expressed in different units. The unit is chosen for particular range of electromagnetic radiation such that it does not involve large power of ten.

**Table 1.1 : Units of Wavelengths**

Sr. No.	Unit	Symbol	Value	Region
1.	Metre	m	$10^2$ cm	Radio frequency
2.	Centimeter	cm.	-	Radio frequency
3.	Angstrom	$\text{A}^\circ$	$10^{-8}$ cm $= 10^{-10}$ metre	X - rays, ultraviolet, visible
4.	Nanometer (SI unit)	nm	$10^{-9}$ metre $= 10 \text{ A}^\circ$	Ultraviolet and visible, near infrared
5.	Micron or micrometer	$\mu\text{m}$	$10^{-6}$ metre	Infrared and microwave
6.	Millimicron	$\text{m}\mu$	$10^{-3}$ micron $= 10^{-9}$ metre = nm	Ultraviolet and visible
7.	Picometer	pm	$10^{-12}$ meter	X - ray region

### 1.2.1 Regions of Electromagnetic Spectrum

The electromagnetic spectrum is the range of frequencies over which the electromagnetic radiations are propagated. Fig. 1.2 gives the electromagnetic spectrum. The spectrum is split into different regions according to wavelength as shown in Fig. 1.2.



**Fig. 1.2 : Electromagnetic Spectrum and Extended Visible Region**

The ultraviolet and visible regions are most important in spectrometry. The near ultraviolet region which extends from 200-380 nm to 780 nm which can be seen by human eye. The infra red region extends from 0.75  $\mu\text{m}$  to 300  $\mu\text{m}$ .

### 1.2.2 Energy of Electromagnetic Radiation

The energy possessed by the electromagnetic radiation is given in terms of a unit called photon. The energy of the photon of frequency  $\nu$  is given by,

$$E = h\nu \quad \dots (1.5)$$

where,

$E$  – Energy in joule

$h$  – Planck's constant

$$= 6.626 \times 10^{-34} \text{ Js}$$

$\nu$  – frequency in Hz

Substituting the value of  $\nu$  in the equation (1.5), we get

$$E = \frac{hc}{\lambda} \dots (1.6)$$

It is clear from the equation that greater the frequency (or shorter the wavelength), greater is the energy. Therefore, ultraviolet radiation has higher energy than visible.

## 1.3 ABSORPTION OF RADIATION BY MATTER

- When electromagnetic radiation passes through a layer of solid, liquid or gas, certain frequencies (or wavelength) may be selectively removed by the process of absorption. The electromagnetic energy is transferred to the atoms or molecules of the sample. We will consider the absorption of light in the visible region. When white light which contains whole spectrum of wavelength in visible region is passed through the sample, it will absorb certain wavelengths and radiation of unabsorbed wavelength is transmitted. The colour of sample is complementary to the colour of absorbed wavelengths. e.g. The sample of copper sulphate appears blue because it absorbs wavelength 580-595 (yellow colour) and transmits the wavelength 435-492 corresponding to the blue colour. Table 1.2 gives the colours and their complementary colours in visible region.

**Table 1.2 : Colours and their Complementary Colours**

Approximate wavelength/nm	Colour of the solution (Transmitted colour)	Complementary colour (Absorbed colour)
400 - 435	Violet	Yellowish - green
435 - 482	Blue	Yellow
482 - 490	Greenish - blue	Orange
490 - 500	Bluish - green	Red
500 - 560	Green	Purple
560 - 580	Yellowish - green	Violet
580 - 595	Yellow	Blue
595 - 615	Orange	Greenish blue
615 - 755	Red	Bluish green

**1.3.1 Absorption of Radiation by Inorganic Substances**

- We will consider here the absorption of ultraviolet and visible radiation by inorganic substances. The metal ions and complexes are very important part of inorganic substances and many of them are coloured.
- When ultraviolet or visible radiation is absorbed by a metal complex, excitation of the metal ion in a complex is not useful for analysis since molar absorptivity is low (1 to 100).
- The complex is formed when ligands and metal salts react with each other. The ligands used are generally organic compounds which exhibit absorption properties and undergo  $\pi \rightarrow \pi^*$  [ $C = O$  (ketone)  $\rightarrow C^+ - O^-$ ] and  $n \rightarrow \pi^*$  [ $C = O$  (ketone)  $\rightarrow C^- = O^+$ ] transitions. Complexation will result slight change in wavelength and intensity of absorption.
- The metal chelates are intense coloured inorganic compounds. The colour is due to charge transfer transitions in which electron moves from metal ion to the ligand or vice versa. During this transition oxidation-reduction reaction occurs between metal ion and ligand. The wavelength of maximum absorption depends on ease with which the transition occurs. Mostly the metal ion is reduced and legand is oxidised.
- Some metal complexes are extremely intense coloured due to charge transfer transitions and hence high absorption in UV and visible regions. The coloured complexes are suited for quantitative analysis. The molar absorptivity ranges from  $10^4$  to  $10^5$ .

## 1.4 FUNDAMENTAL LAWS OF COLORIMETRY

- Bouger (1729) and Lambert (1760) gave relationship between the fraction of radiant energy transmitted with thickness of medium called Lambert law. Beer and Bernard (1952) gave the relationship between fraction of radiant energy transmitted and concentration of the solution called Beer's law. The combined law Beer-Bouger Lambert law is commonly known as Beer's law.
- We will define some important terms before considering the laws of photometry in detail.

**(i) Radiant Power (P) (Old Name Intensity) :** Energy transmitted per unit time is called power. Radiant power is the rate at which energy is transported in a beam of radiant energy. This quantity is detected by photocell or thermocouple. It is represented by symbol P. The radiant power of incident beam is  $P_o$  and that of transmitted beam is P.

**(ii) Transmittance (T) :** It is the fraction of the incident power transmitted by a sample. It is the ratio of radiant power transmitted by a sample to the radiant power incident upon the sample.

$$T = \frac{P}{P_o} \quad \dots(1.7)$$

It is generally expressed in %.

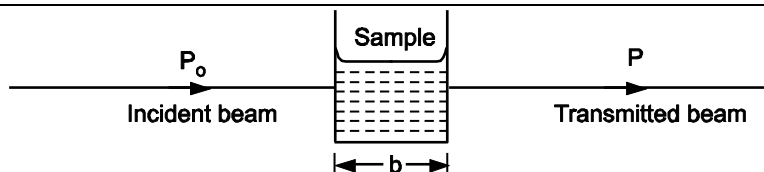
$$\% T = \frac{P}{P_o} \times 100 \quad \dots(1.8)$$

**(iii) Absorbance (Old Name Optical Density) :** It is the logarithm to the base 10 of reciprocal of transmittance. It can also be defined as the logarithm to the power 10 of the ratio of radiant power of incident beam to the radiant power of transmitted beam by a sample.

$$A = \log \frac{1}{T} = -\log T = -\log \frac{P}{P_o}$$

$$A = \log \frac{P_o}{P} \quad \dots(1.9)$$

Consider a beam of monochromatic light of radiant power  $P_o$  incident upon a homogeneous medium of thickness  $b$ . The part of incident beam is absorbed by the medium and  $P$  is radiant power of the transmitted beam.



**Fig. 1.3 : Absorption of Radiation by a Sample**

#### 1.4.1 Lambert's Law

The fraction of the radiant energy transmitted (transmittance of the sample) decays exponentially with path length. The law can be given in the form of equation as,

$$T = \frac{P}{P_o} = 10^{-k'b} \quad \dots(1.10)$$

where,  $k'$  – Constant  
 $b$  – Path length  
 $T$  – Transmittance

Taking log of both sides of equation (1.10)

$$\log T = \log \frac{P}{P_o} = -k'b$$

$$\boxed{-\log T = k'b} \quad \dots(1.11)$$

#### 1.4.2 Beer's Law

The fraction of the radiant energy transmitted decays exponentially with the concentration of the sample.

$$T = \frac{P}{P_o} = 10^{-kC} \quad \dots(1.12)$$

where,  $k$  – Constant  
 $C$  – Concentration of the sample

Taking log of both sides,

$$\log T = \log \frac{P}{P_o} = -kC$$

$$\boxed{-\log T = kC} \quad \dots(1.13)$$

### 1.4.3 Beer – Lambert's Combined Law

Combining equations (1.11) and (1.13), we get combined law,

$$-\log T = \log \frac{P}{P_0} = k'k bC$$

$$\text{Or} \quad -\log T = \log \frac{P}{P_0} = ab C \quad \dots(1.14)$$

where,  $a = k'k = \text{Constant}$

We can write the equation as,

$$A = abC$$

where,  $A = -\log T = \log \frac{P}{P_0} = \text{Absorbance}$

$a$  – Constant called absorptivity which depends on wavelength and nature of the sample.

$b$  – Path length in cm

$C$  – Concentration in gram per litre.

- The absorptivity is defined as the *absorbance of the solution when path length is low and concentration is one gm per litre*. Units of  $a$  are  $\text{Lg}^{-1} \text{cm}^{-1}$ . When the concentration is expressed in moles per litre, we can write the combined law as

$$A = \epsilon bC$$

where,  $\epsilon$  – molar absorptivity which is the product of absorptivity and molecular weight. It is defined as the absorbance when the path length is one cm and concentration is one mole per litre. The units of  $\epsilon$  are  $\text{L mol}^{-1} \text{cm}^{-1}$ . The path length is generally 1 cm in colorimetry or spectrophotometry.

#### SOLVED EXAMPLES

**Example 1.1 :** The absorbance of  $1.5 \times 10^{-3} \text{ M}$  solution of a sample was found to be 0.163 at 440 nm in a cell of 1 cm path length. Find (i) % transmittance and (ii) molar extinction co-efficient.

**Solution : Data :**

$A = 0.163,$   
 $b = 1 \text{ cm},$   
 $A = \epsilon bC$

**Formula :**

$$\varepsilon = \frac{A}{bC}$$

$$\varepsilon = \frac{0.163}{1 \times 1.5 \times 10^{-3}}$$

$$\varepsilon = 1.088 \times 10^2 \text{ L mol}^{-1} \text{ cm}^{-1}$$

$$A = \log \frac{1}{T}$$

$$\log \frac{1}{T} = 0.163$$

$$\frac{1}{T} = \text{Antilog } 0.163 = 1.455$$

$$T = \text{Reciprocal of } 1.455 = 0.6870$$

$$\% T = 0.6870 \times 100$$

**Result :**

$$\%T = 68.7\%$$

**Example 1.2 :** The solution has absorbance 0.22 in a cell of 1 cm path length and molar absorptivity is  $4 \times 10^{-3} \text{ L mol}^{-1} \text{ cm}^{-1}$  at 450 nm. Calculate the concentration of the solution.

**Solution : Data :**

$$A = 0.22,$$

$$\varepsilon = 4 \times 10^{-3} \text{ L mol}^{-1} \text{ cm}^{-1},$$

$$A = \varepsilon b C$$

**Formula :**

$$C = \frac{A}{\varepsilon b}$$

$$= \frac{0.22}{4 \times 10^{-3} \times 1}$$

**Result :**

$$C = 5.5 \times 10^{-5} \text{ M}$$

**Example 1.3 :** Find the concentration of the solution which transmits 65% light when placed in 1 cm cell at certain wavelength. The absorptivity of the substance is  $2.5 \text{ L g}^{-1} \text{ cm}^{-1}$ .

**Solution : Data :**

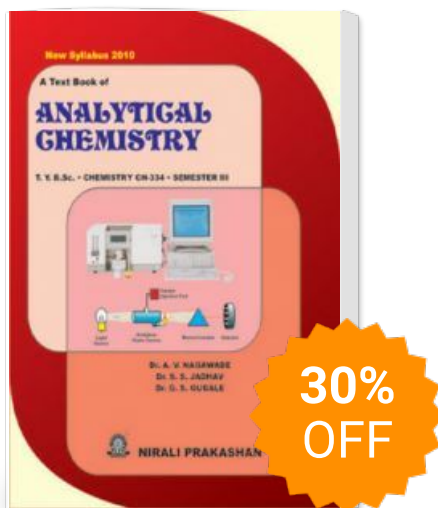
$$a = 2.5 \text{ L g}^{-1} \text{ cm}^{-1},$$

$$b = 1 \text{ cm},$$

$$P_o = 100\%,$$

$$P = 65\%$$

# Analytical Chemistry



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