Quadrant II – Transcript and Related Materials

Programme: Bachelor of Science (Third year)

Subject: Chemistry

Course Code: CHD 103

Course Title: Selected Instrumentation in Chemistry

Unit: 05

Module Name: Types of instruments - Photoelectric colorimeters and Spectrophotometers: Single and double beam, Comparison between colorimeter and spectrophotometer

Name of the Presenter: Ms. Shubhlaxmi K. Naik

Notes

Photoelectric Colorimeters and Spectrophotometers

The absorption of radiation by absorbing media like solutions is quantitatively measured by using photoelectric colorimeters and spectrophotometers.

Photoelectric Colorimeters

In photoelectric colorimeters photocell is introduced in the instruments and its function is to convert intensity of light into electric signal. Thus the amount of radiation absorbed or transmitted by the sample is converted into absorbance or % transmittance.

There are two types Photoelectric colorimeters.

They are:

1. Single beam colorimeter
2. Double beam colorimeter

1. Single beam colorimeter

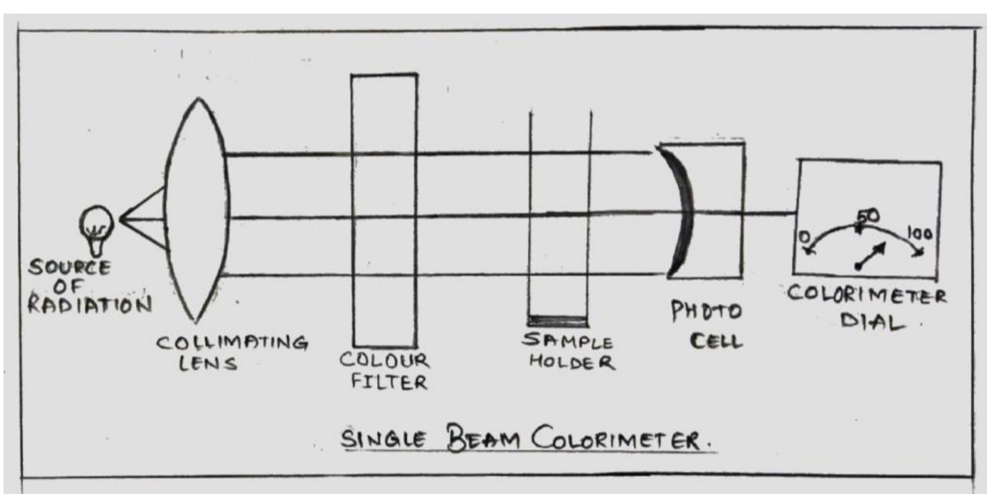
In a single beam colorimeter, a narrow band of wavelengths is incident on the absorbing sample. The absorbance (or percentage transmittance) of the sample is determined after adjusting absorbance of the solvent (blank) to 0 (or 100 % for the same wavelengths). All measurements are done using a single optical path for the beam of light.

A Photoelectric Colorimeter has the following components:

1. A source of visible light e.g. an incandescent lamp with a tungsten filament. The beam is collimated by a convex lens.
2. A colour filter which selects a narrow band of wavelengths which enters a fine slit and is then incident on the sample.

Colour filters are of two types:

1. **Glass filters**: It is a solid sheet of glass which is coloured by a suitable pigment dissolved or dispersed in the glass.
2. **Interference filters**: An interference filter consists of two thin films of silver separated by a film of transparent material of low refractive index. Light undergoes interference at the silver surface. The unwanted wavelengths are removed by selective reflection and only required wavelengths pass out of the filter.
3. A **sample holder** called cuvette. It is a rectangular transparent container of glass or quartz.
4. A **photocell** which converts the transmitted beam emerging from the sample into an electrical current. This electrical pulse is due the emission of electrons from the photoelectrode surface caused by the transmitted beam falling on the photoelectrode.
5. A **dial** on which the absorbance or percentage transmittance be directly read.

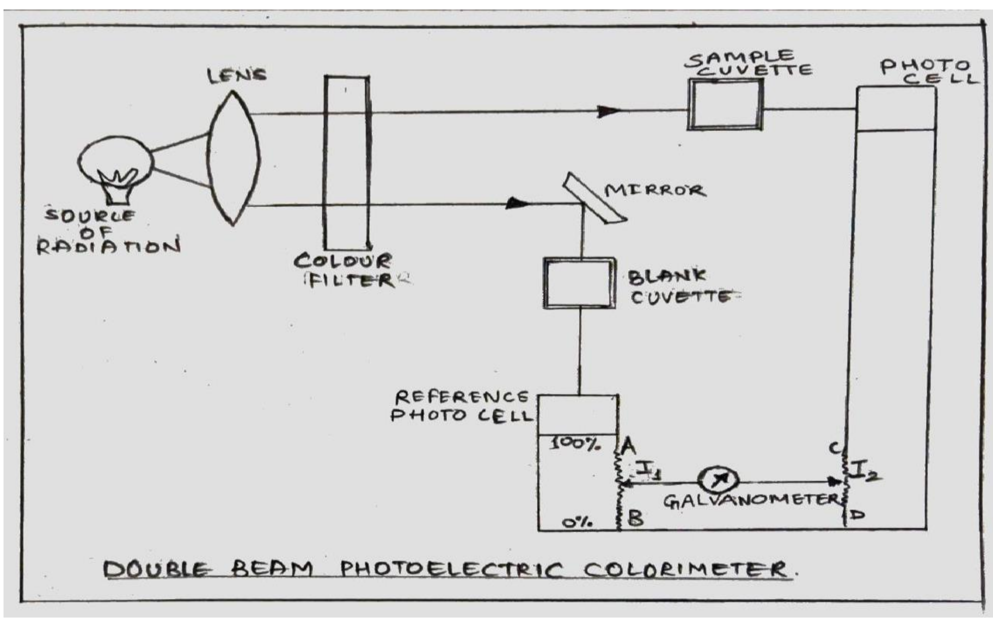


Working

The cuvette is first filled with the solvent and the adjusted to 100% (or A is adjusted to 0). Then the cuvette is filled the sample solution and its % T or A is determined. The concentration of the sample can then be determined using Beer-Lambert's equation.

2. Double Beam Photoelectric colorimeter

A beam of visible light from an incandescent tungsten lamp passes through a colour filter which selects narrow band of wavelengths. A mirror splits this narrow band into two beams - one passing through the sample and the other passing through the solvent (blank) hence the name double beam colorimeter. The sample absorbs a part of the beam whereas the solvent transmits it completely. The two beams then fall on respective photocells where photoelectrons are emitted. The two currents thus produced pass through the variable resistances resistance AB for the current coming from the solvent side and resistance CD for the current coming from the sample side. A potential is set up across AB and CD depending on the two currents. AB is calibrated to read % T. A galvanometer connected across the two resistances serves as the null indicator.



SPECTROPHOTOMETERS

Spectrophotometer is a device containing spectrometer and photometer. Spectrometer produces a narrow band width or a monochromatic beam of light. Therefore the results are accurate as compared to photoelectric colorimeter.

Spectrophotometer obeys Beer-Lambert's law in principle whereas colorimeter are not perfectly obeying Beer-Lambert's law. General spectrophotometer when have a band width of 20-30nm are available for the routine work. The spectrophotometer having a band width of 5-10nm are most accurate instead but they are costly. The spectrophotometers are designed as UV spectrophotometer, Visible spectrophotometer and IR spectrophotometer. For analytical work the spectrophotometer with smallest band width are used.

Spectrophotometers are of two types:

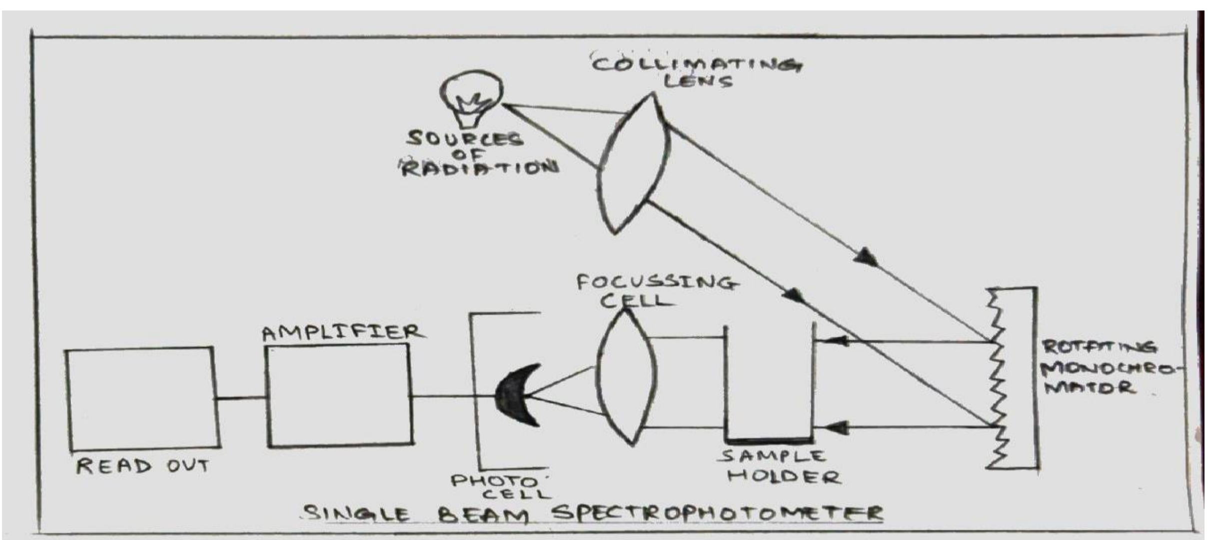
1. Single beam spectrophotometer

2. Double beam spectrophotometer

1. Single beam spectrophotometer

In this instrument a monochromator i.e. prism or diffraction grating produces a monochromatic beam which is then made incident in the sample. The optical density (or % T) of the simple solution is determined for different wavelengths after adjusting the absorbance of the blank to **0** (or %T to 100%) for each of the wavelengths. All measurements are done using a single optical path for the monochromatic beam of light.

A single beam spectrophotometer has the following components.



i) Source of radiation

A tungsten lamp is used for obtaining visible light. U.V. light is obtained from a hydrogen or deuterium discharge lamp. A Nernst glower which is a rod containing a mixture of Zirconium, yttrium and erbium oxides, when heated to 1500 - 2000^oC emits I.R. light. A Globar rod of silicon carbide when heated to 1300-1700^oC produces I.R. light.

ii) Monochromator

A monochromator, either a prism or diffraction grating disperses the light into its constituent wavelengths. By rotating the monochromator, the different wavelengths are focussed one by one on the sample.

iii) Sample holder (Sample cell)

Glass cuvettes are used in the Visible region. Quartz cuvettes are used in the U.V. region since glass absorbs U.V. light. Both glass and quartz absorb strongly in the I.R. region hence they cannot be used for I.R. absorption studies. In the I.R. region, metal halide cells of NaCl, KBr CsBr and CsI are used.

iv) Photocell

The transmitted beam emerging from the sample falls on the photocell. An electric current is produced due to the photoemission of electrons at the photocathode. If this current is small, it can be amplified using an electronic amplifier.

v) Read out device

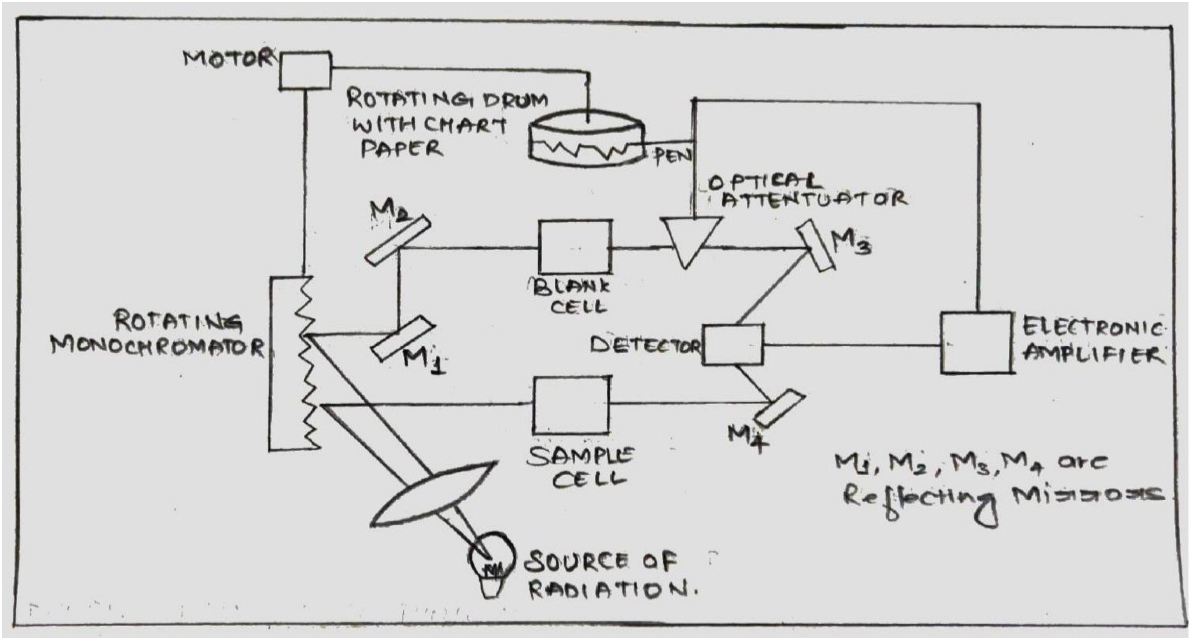
It may be a dial on which absorbance A or %T can be directly read or a digital display.

Working

The sample holder is filled with the solvent (blank). The A value (or % T) of the solvent is adjusted to 0 (or 100 %) for a particular wavelength; obtained by the rotation of the monochromator. The sample is then taken in the sample holder and its A value (or % T) determined for the same wavelength. The procedure is repeated for different wavelengths obtained by the rotation of the monochromator. The A (or % T) values can be read either on a dial or a digital display. The λ_{max} *values for the* sample can thus be found out.

2. Double Beam Spectrophotometer

In the double beam spectrophotometer, the monochromatic beam coming from the diffraction grating monochromator is split into two beams by means of mirror M_1. The reference beam is reflected by mirror M_2 into the blank cell containing the solvent and the sample passes into the sample cell. An optical attenuator mounted in the path of the reference beam reduces its intensity to match that of the sample beam i.e. the amount of transmitted light coming from the blank is decreased so that its intensity is equal to that of the transmitted light coming from the sample. The attenuator is connected to a recorder pen which moves across the chart paper wound on a rotating drum. The two beams are then reflected by mirrors M_3 and M_4 onto a suitable detector.



Photocells are used as detectors in the U.V. and Visible regions. In the IR region thermal detectors like thermocouple or bolometer are used.

The electric current is magnified by use of an electronic amplifier and the electric signal is sent to the recorder pen. A motor synchronises the speed of the rotating monochromator with that of the rotating drum carrying the chart paper. As a result, the wavelength marked on the chart is identical with that received by the detector.

Working

The monochromator is rotated to allow different wavelengths to fall on the blank and sample. The process is called scanning. The recorder pen plots a graph of absorbance or % T versus wavelength (λ), frequency *(v)* or wave number on the rotating drum. The wavelengths at which maximum absorption or minimum transmission occurs are noted from the respective spectra and the groups responsible for these absorptions or transmissions are identified. Thus the structure of the sample can be elucidated from spectrum analysis.

Comparison between Colorimeter and Spectrophotometer

1. Colorimeters work in visible region while spectrophotometers work in U.V. visible and IR regions.

2. Colorimeters use colour filters which allow a band of a wavelengths of the complementary colour of the sample to be incident on the sample. Spectrophotometers employ monochromators (prisms or diffracting gratings) which produce perfectly monochromatic beams hence spectrophotometric analysis is more accurate as the band width of the light beam is minimum.

3. Beer Lambert's law is strictly obeyed for the monochromatic beam used in spectrophotometers.

4. Colorimeters are generally used for quantitative analysis of coloured compounds whereas spectrophotometers are used for structure determination of colourless as well as coloured compounds in addition to quantitative analysis.

5. Spectrophotometers are much more costly than colorimeter.