M.Sc Chemistry
Inorganic Chemistry
Semester-IV

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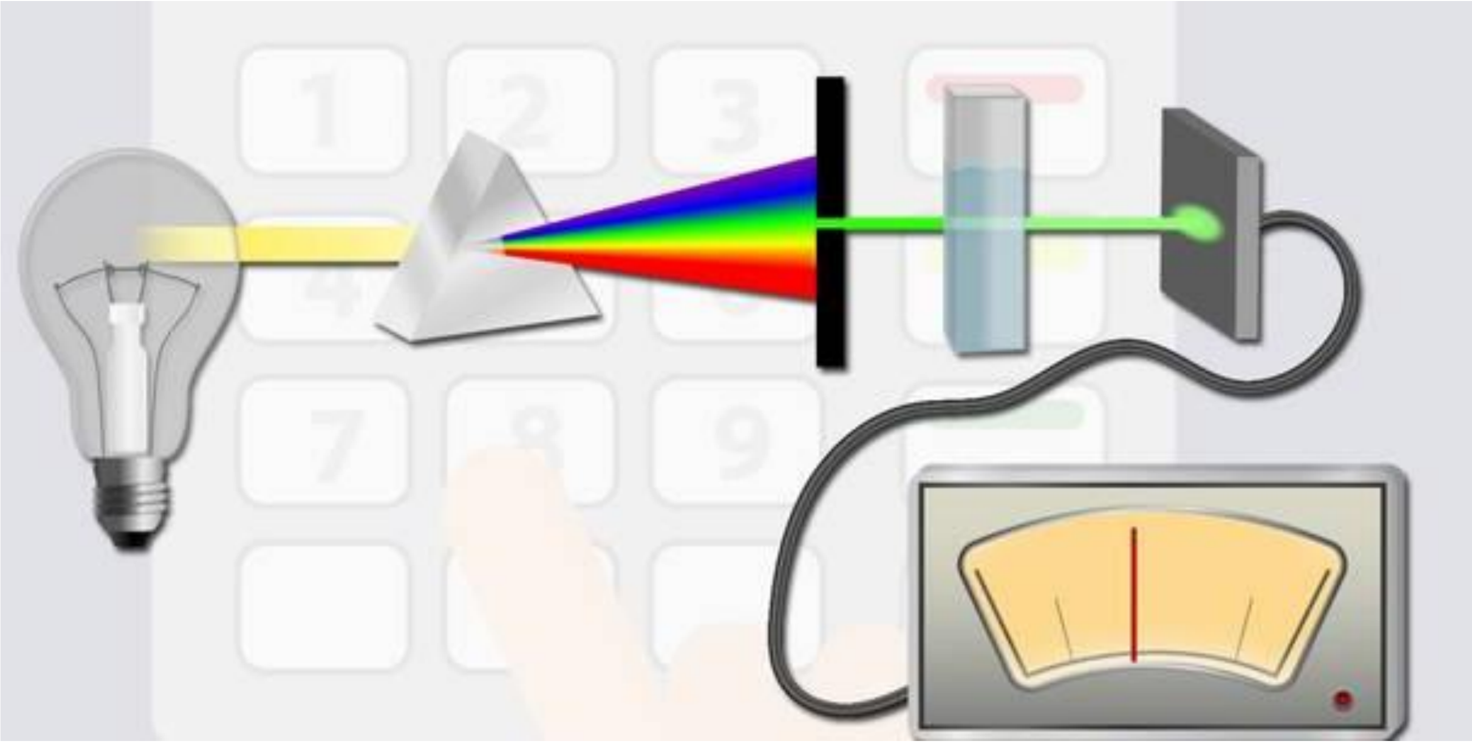
Inorganic Group 1

REFERENCE BOOKS:

1. Vogel's Quantitative inorganic analysis, 6th edition
Quantitative Chemical Analysis, 9th edition, D.C. Harris.
3. Fundamentals of Analytical Chemistry, 9th edition, Douglas A. Skoog, D.M. West, F.J. Holler, S. R. Crouch.

Spectrophotometric Methods

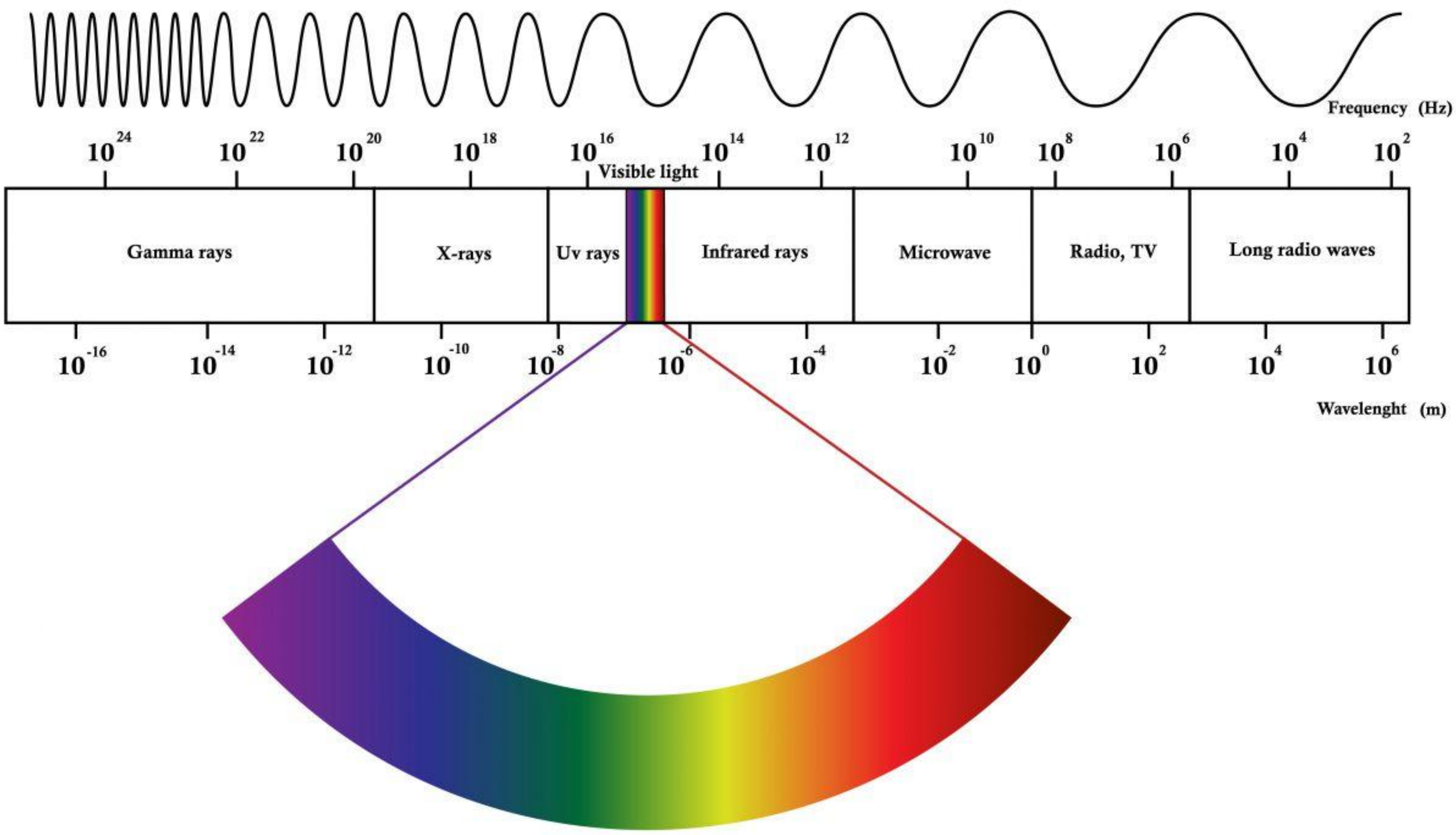


Basics of spectrophotometry and its applications

Introduction

- Spectroscopy is related to the interaction of light with matter.
- Every chemical compound absorbs, transmits, or reflects light (electromagnetic radiation) over a certain range of wavelength.
- Spectrophotometry is a measurement of how much a chemical substance absorbs or transmits.
- Spectrophotometry is widely used for quantitative analysis in various areas (e.g., chemistry, physics, biology, biochemistry, material and chemical engineering, clinical applications, industrial applications, etc).

Electromagnetic Spectrum



Spectrophotometer

- A spectrophotometer is an instrument that measures the amount of photons (the intensity of light) absorbed after it passes through sample solution. With the spectrophotometer, the amount of a known chemical substance (concentrations) can also be determined by measuring the intensity of light detected.

UV-visible spectrophotometer

- Uses light over the ultraviolet range (185 - 400 nm) and visible range (400 - 700 nm) of electromagnetic radiation spectrum.

UV-Visible Spectroscopy

- Ultraviolet-visible spectroscopy is considered an important tool in analytical chemistry.
- its main use is for the quantitative determination of different organic and inorganic compounds in solution.
- The absorption of visible light or ultraviolet light by a chemical compound will produce a distinct spectrum.
- When ultraviolet radiations are absorbed, this results in the excitation of the electrons from the ground state towards a higher energy state. The theory revolving around this concept states that the energy from the absorbed ultraviolet radiation is actually equal to the energy difference between the higher energy state and the ground state.

Basis of light absorption – Lambert Beer's law

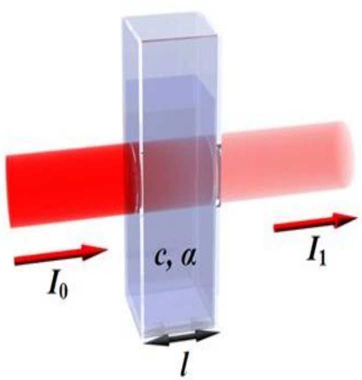
Beer-Lambert Law

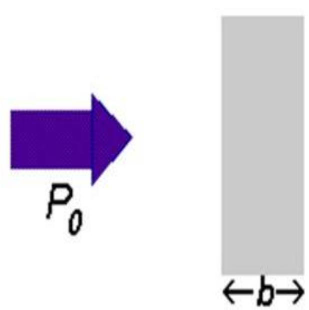
$$A = \varepsilon\, b\, C$$

Where A = absorbance, ε = molar extinction coefficient, b = path length (1cm), and C = concentration.

A = – Log (T) (Note 0<T<1)

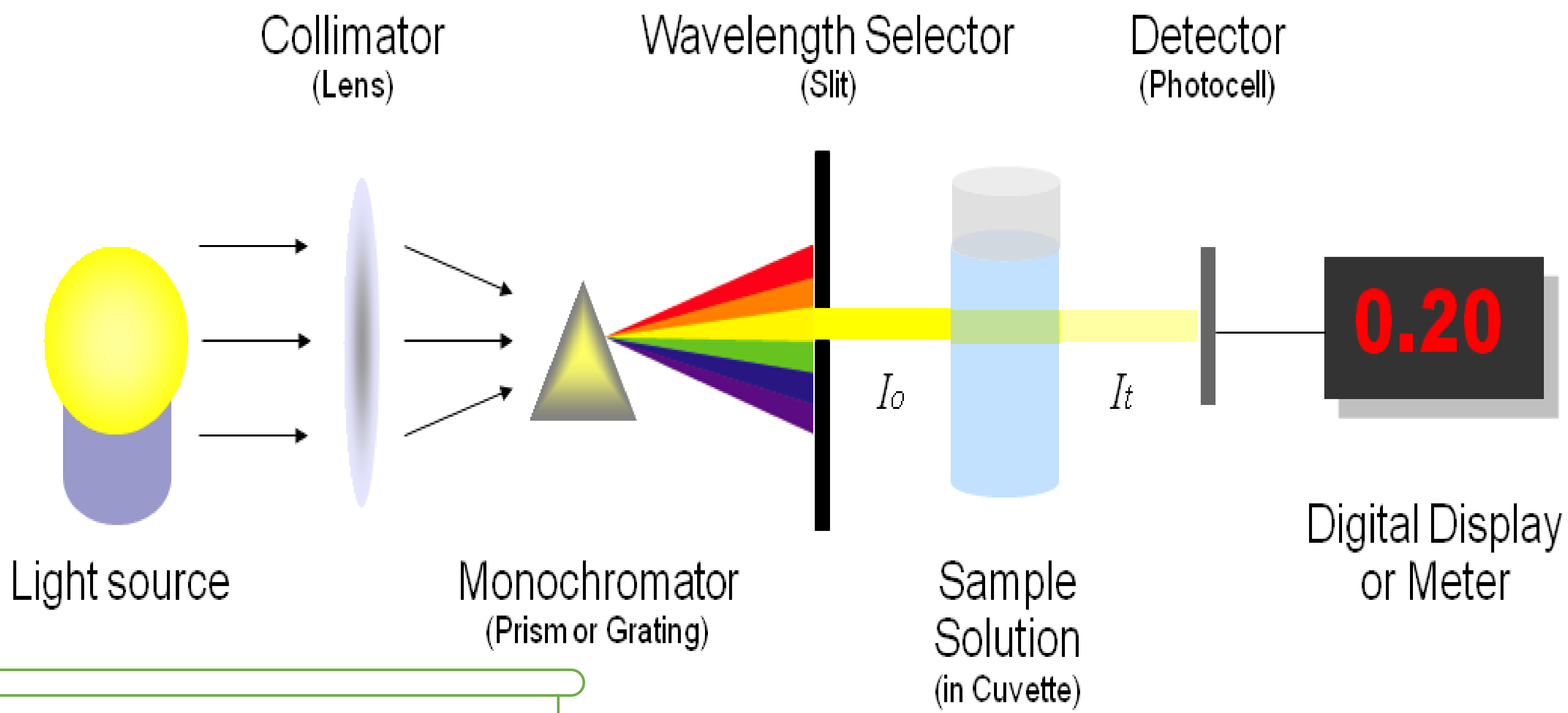
$$T = I_1/I_0$$





- **This law states that whenever a beam of monochromatic light is passed through a solution with an absorbing substance, the decreasing rate of the radiation intensity along with the thickness of the absorbing solution is actually proportional to the concentration of the solution and the incident radiation.**
- **Obeyed only in dilute solutions**

Components of UV-Visible Spectrophotometer



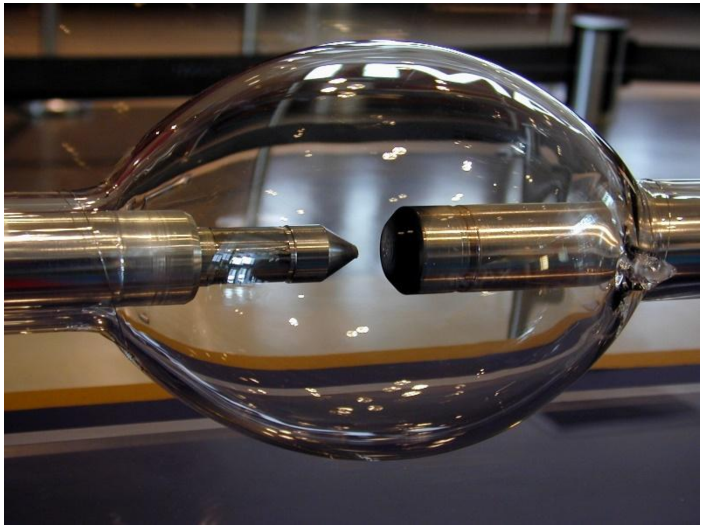
Ref : Vogel Pages 608-626

A spectrophotometer, in general, consists of two devices; a spectrometer and a photometer. A spectrometer is a device that produces, typically disperses and measures light. A photometer indicates the photoelectric detector that measures the intensity of light.

Light Source of a UV-Visible Spectrophotometer

TUNGSTEN FILAMENT
(300–2500 nm)

A DEUTERIUM ARC LAMP, which is continuous over the ultraviolet region (190–400 nm)

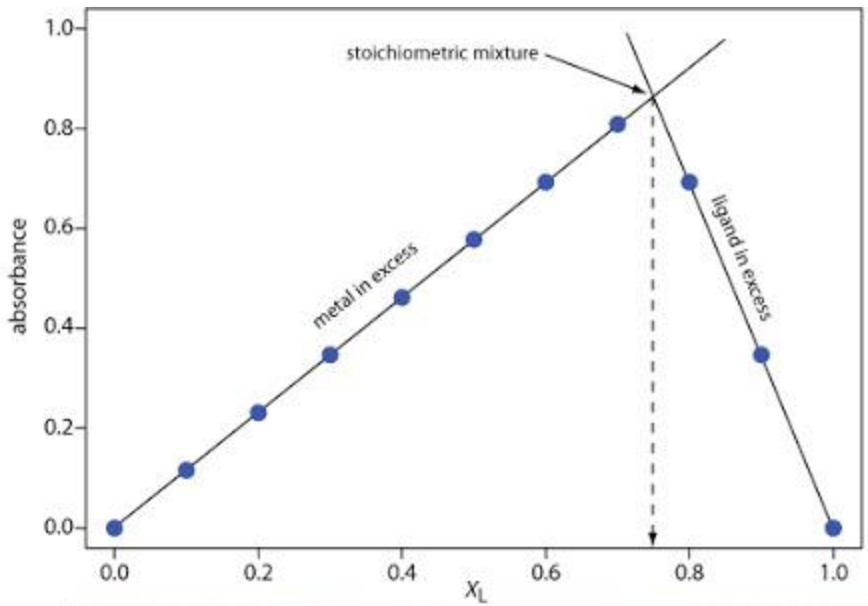


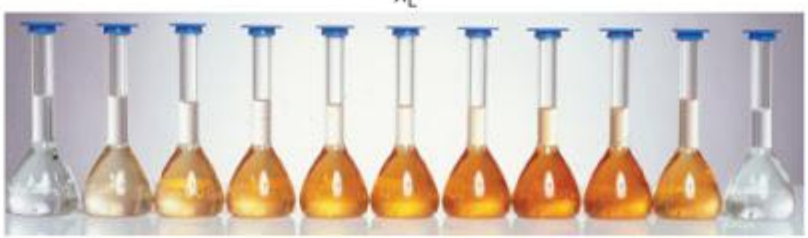
XENON ARC LAMP, which is continuous from 160 to 2,000 nm

List of Experiments

- Determine λ_{max} and molar extinction coefficient of $KMnO_4$ using UV-Visible Spectrophotometry.
- Determine λ_{max} and molar extinction coefficient of $K_2Cr_2O_7$ using UV-Visible Spectrophotometry.
- Verify Beer's Law for $KMnO_4$ using UV-Visible Spectrophotometric method.
- Verify Beer's Law for $K_2Cr_2O_7$ UV-Visible Spectrophotometric method.
- Determine the concentration of $KMnO_4$ and $K_2Cr_2O_7$ in a mixture using spectrophotometric method.
- Determine λ_{max} of Fe-phenanthroline complex using spectrophotometric method.
- Determine composition of Iron-phenanthroline complex using Job's Method.
- Determine composition of Iron-phenanthroline complex using Mole Ratio Method.

Job's Method of Continuous Variation





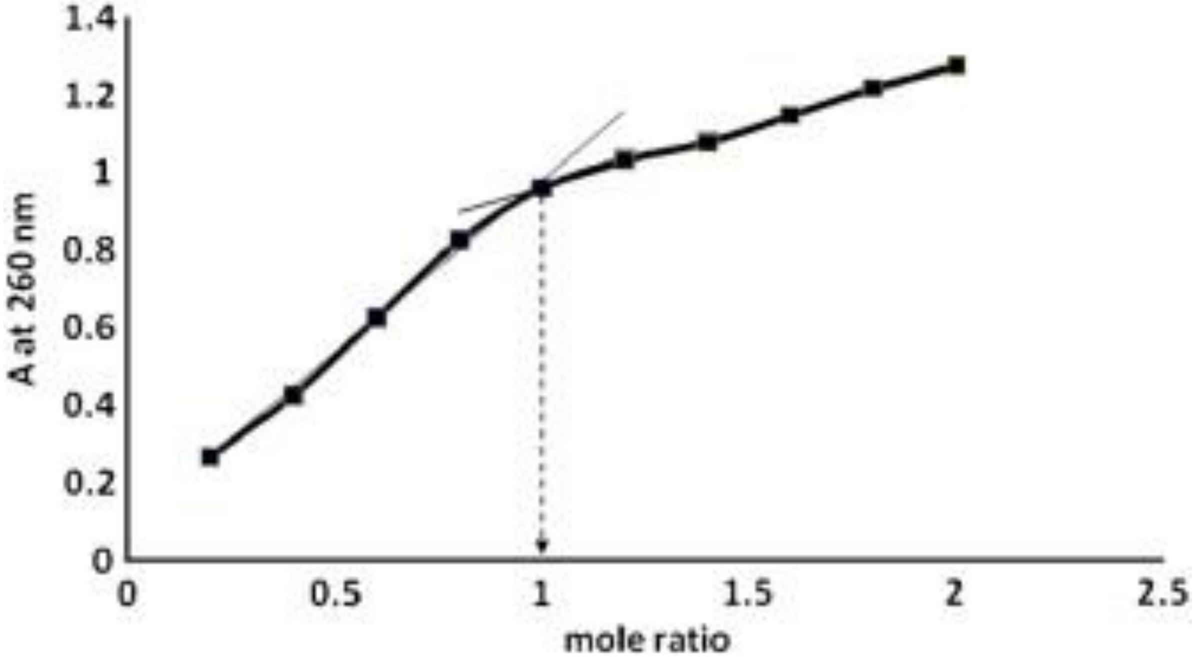
If only one species ML_n is formed then,
$n = \chi max / 1 - \chi max$

- Method of continuous variation, which was designed by Paul Job.

- In this method, concentration of both the reactants (metal ion and ligand) is varied, keeping total concentration constant.
- Absorbance of the solutions is measured.

Mole Ratio Method

- The principle of this method is that a series of solutions is prepared in which concentration of one of the reactants (usually Cm) is kept constant and the other is varied.
- Absorbance of the solutions are measured at suitable wavelength and plotted vs mole ratio.
- If only one stable complex is formed which has selective light absorption then absorbance increases approximately linearly with the mole ratio and then becomes constant.



Determine the concentration of $KMnO_4$ and $K_2Cr_2O_7$ in a mixture using spectrophotometry.

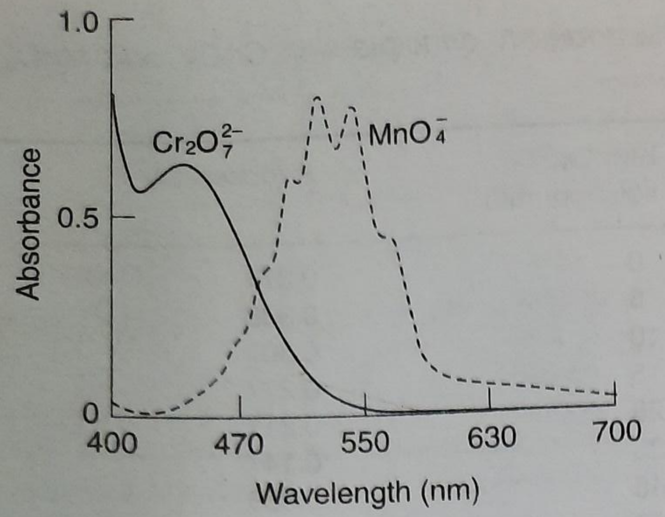


Figure 17.22 Visible spectra of $Cr_2O_7^{2-}$ and MnO_4^-

$$A_{\lambda_2} = {}_{\lambda_2}\varepsilon_1 c_1 + {}_{\lambda_2}\varepsilon_2 c_2 \qquad (17.20)$$

Solution of these simultaneous equations gives

$$c_1 = \frac{{}_{\lambda_2}\varepsilon_2 A_{\lambda_1} - {}_{\lambda_1}\varepsilon_2 A_{\lambda_2}}{{}_{\lambda_1}\varepsilon_1\, {}_{\lambda_2}\varepsilon_2 - {}_{\lambda_1}\varepsilon_2\, {}_{\lambda_2}\varepsilon_1} \qquad (17.21)$$

$$c_2 = \frac{{}_{\lambda_1}\varepsilon_1 A_{\lambda_2} - {}_{\lambda_2}\varepsilon_1 A_{\lambda_1}}{{}_{\lambda_1}\varepsilon_1\, {}_{\lambda_2}\varepsilon_2 - {}_{\lambda_1}\varepsilon_2\, {}_{\lambda_2}\varepsilon_1} \qquad (17.22)$$

For complete details, refer to Vogel's Quantitative inorganic analysis, 6th edition, Pages 662-664

References

1. Vogel's Quantitative inorganic analysis, 6th edition
2. Quantitative Chemical Analysis, 9th edition, D.C. Harris.
3. Fundamentals of Analytical Chemistry, 9th edition, Douglas A. Skoog, D.M. West, F.J. Holler, S. R. Crouch.
4. For Job's Method and Mole Ratio Method (general theory), ref to Analytical Applications of Complex Equilibria by J. Inczedy.