Chemistry 4631

Instrumental Analysis
Lab Lecture 1
Stats UV-vis Labs

Theory for UV/vis Spectrometry

- Be ready to do statistical anlaysis on your results and data for each lab this semester.

- If you want to put equations for calculatations in your notebook to remember – there are several in this lecture you can use.

- Properly setting up and obtaining a calibration curve will be required in each lab.

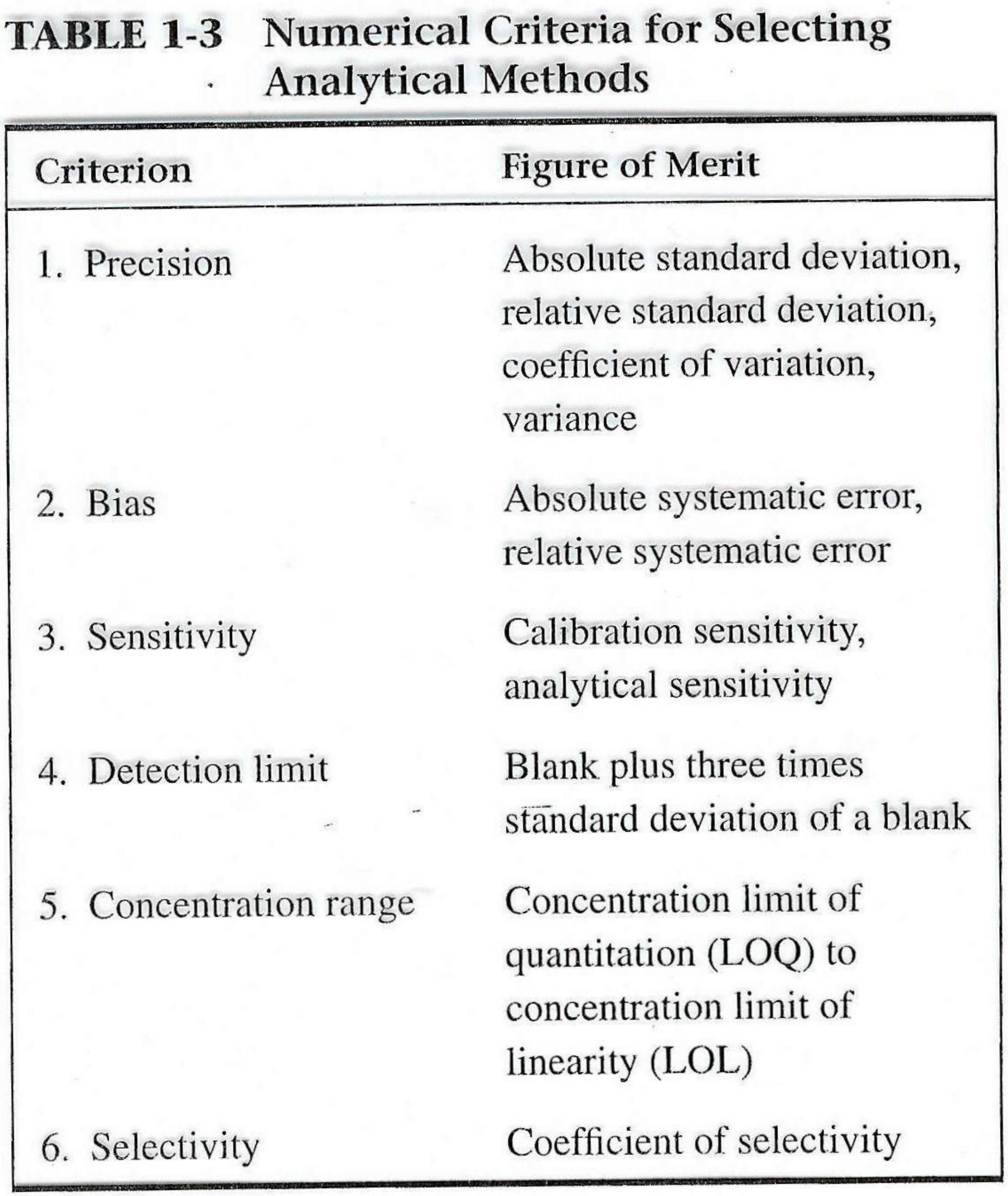


TABLE 1-3 Numerical Criteria for Selecting Analytical Methods

Criterion	Figure of Merit
1. Precision	Absolute standard deviation, relative standard deviation, coefficient of variation, variance
2. Bias	Absolute systematic error, relative systematic error
3. Sensitivity	Calibration sensitivity, analytical sensitivity
4. Detection limit	Blank plus three times standard deviation of a blank
5. Concentration range	Concentration limit of quantitation (LOQ) to concentration limit of linearity (LOL)
6. Selectivity	Coefficient of selectivity

Precision

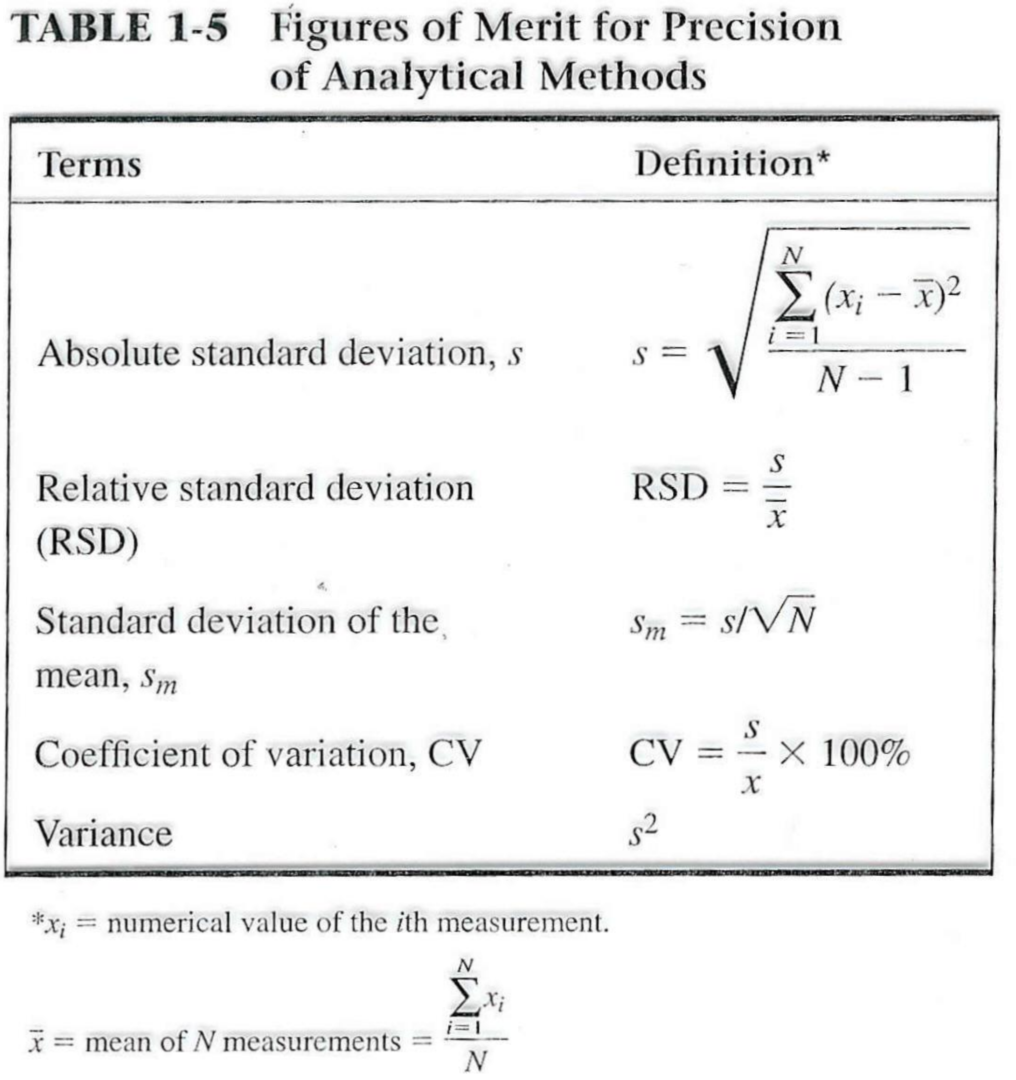


TABLE 1-5 Figures of Merit for Precision of Analytical Methods

Terms	Definition*
Absolute standard deviation, s	$s = \sqrt{\dfrac{\sum_{i=1}^{N}(x_i - \bar{x})^2}{N-1}}$
Relative standard deviation (RSD)	$\mathrm{RSD} = \dfrac{s}{\bar{x}}$
Standard deviation of the mean, s_m	$s_m = s/\sqrt{N}$
Coefficient of variation, CV	$\mathrm{CV} = \dfrac{s}{\bar{x}} \times 100\%$
Variance	s^2

*x_i = numerical value of the ith measurement.

$\bar{x}$ = mean of N measurements $= \dfrac{\sum_{i=1}^{N} x_i}{N}$

Bias

$\text{Bias} = \mu - x_t$

μ – population mean

x_t – true concentration

Bias

Sample – finite number of experimental observations (all the replicate).

The <u>sample</u> is a fraction of the infinite number of observations possible. (i.e. 50 measurements).

This infinite number of observations (measurements) is called the <u>population</u> or <u>universe</u> of data.

Sensitivity

Instruments or methods ability to discriminate between small differences in analyte concentration.

Selectivity

Degree to which the method is free from interference by other species contained in the sample matrix.

Detection Limit

Minimum concentration or mass of analyte that can be detected at a known confidence level.

Dynamic Range

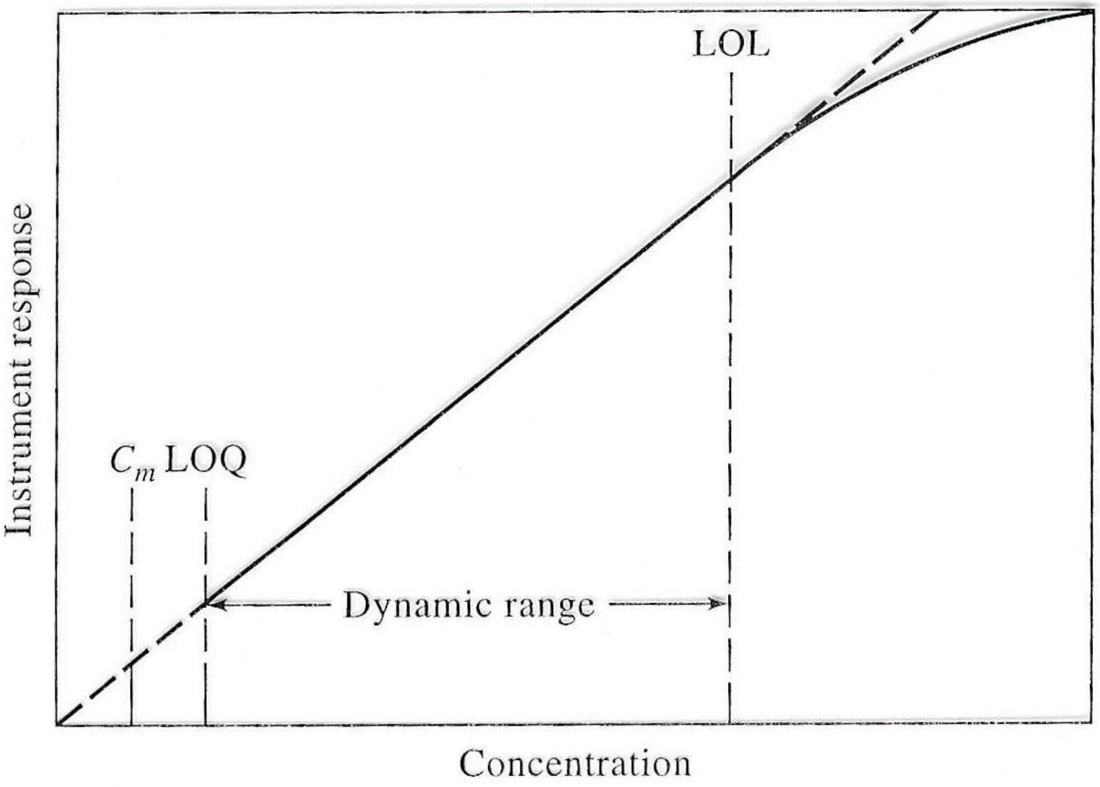


Figure 1-7 Useful range of an analytical method. LOQ = limit of quantitative measurement; LOL = limit of linear response.

Applications of UV/vis Spectrometry

Calibration curve

Calibration standards need to approximate the composition of sample to be analyzed

If cannot match the matrix – best to use the standard addition method (Chapter 1).

Calibration

- **Standard Addition Method**
- **Internal Standard**

Data Analysis

Standard addition method

Add one or more increments of a standard solution to sample aliquots of the same size.

Each solution is diluted to a fixed volume and absorbance is measured.

Plot Absorbance versus Volume Standard Solution, mL.

Data Analysis

Determination of Stoichiometry of Complex Ions

- Mole-ratio method
- Method of continuous variation

Data Analysis

Mole-ratio Procedure

- A known concentration of central atom is prepared
- A known concentration of ligand is prepared at the same concentration
- Add complexing ligand in increments and measure absorbance after each addition
- Plot absorbance versus mole ratio (ligand:metal)

Data Analysis

Determination of Stoichiometry of Complex Ions

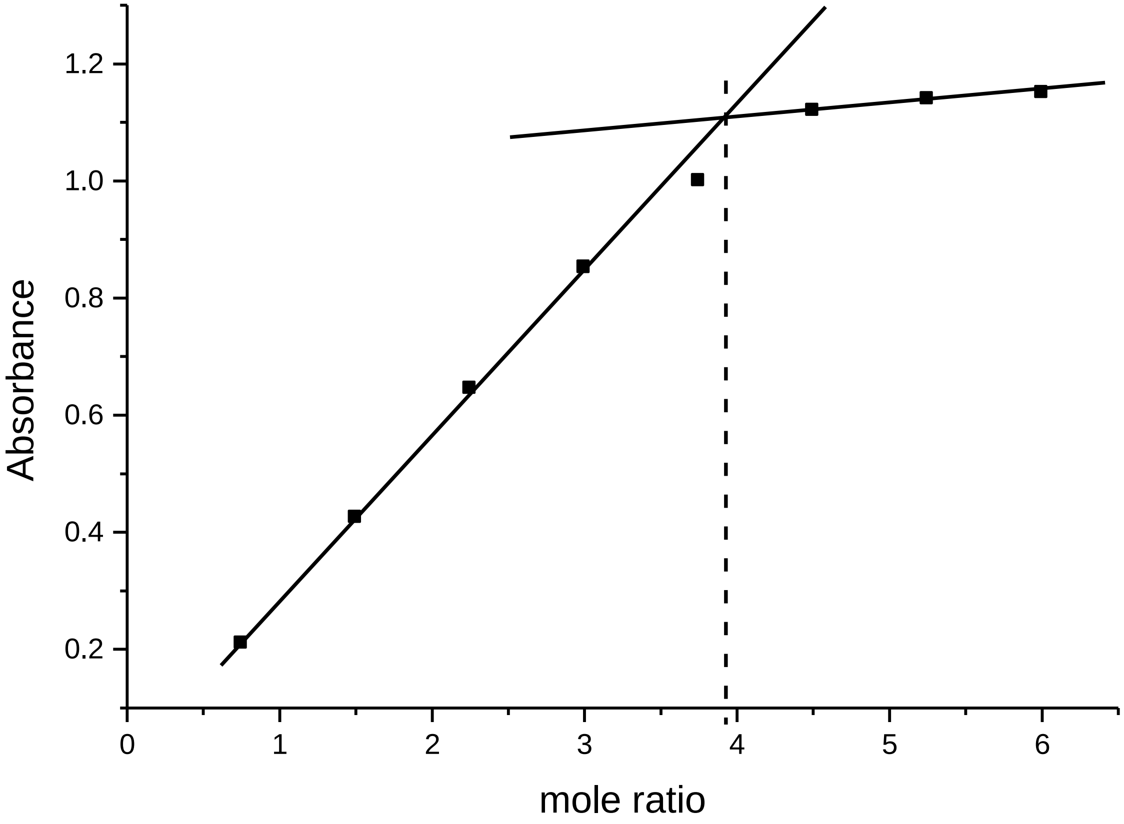
Mole-ratio procedure

Example: What is the number of CN- ions attached to Cd^{3+} in basic solution?

Absorbance	Mole ratio
0.210	0.75
0.425	1.50
0.645	2.25
0.852	3.00
1.00	3.75
1.12	4.50
1.14	5.25
1.15	6.00

Data Analysis

Determination of Stoichiometry of Complex Ions



Data Analysis

Determination of Stoichiometry of Complex Ions

Mole-ratio procedure

There are four ligands to one metal ion

$[Cd(CN)_4]^{2-}$

Data Analysis

Determination of Stoichiometry of Complex Ions

Method of Continuous Variation

Total number of moles of ligands + moles of M^{n+} is constant.

Data Analysis

Determination of Stoichiometry of Complex Ions

Method of continuous variation

Procedure:

- Mix 2.0 mL of one solution (0.01 M) and 8.0 mL of the other (0.01 M) (must use 10 mL for all other measurements)
- Measure absorbance of each mixture
- Plot absorbance versus mole fraction of ligand

(moles of ligand/moles of ligand + moles of metal)

Data Analysis

Determination of Stoichiometry of Complex Ions

Method of Continuous variation

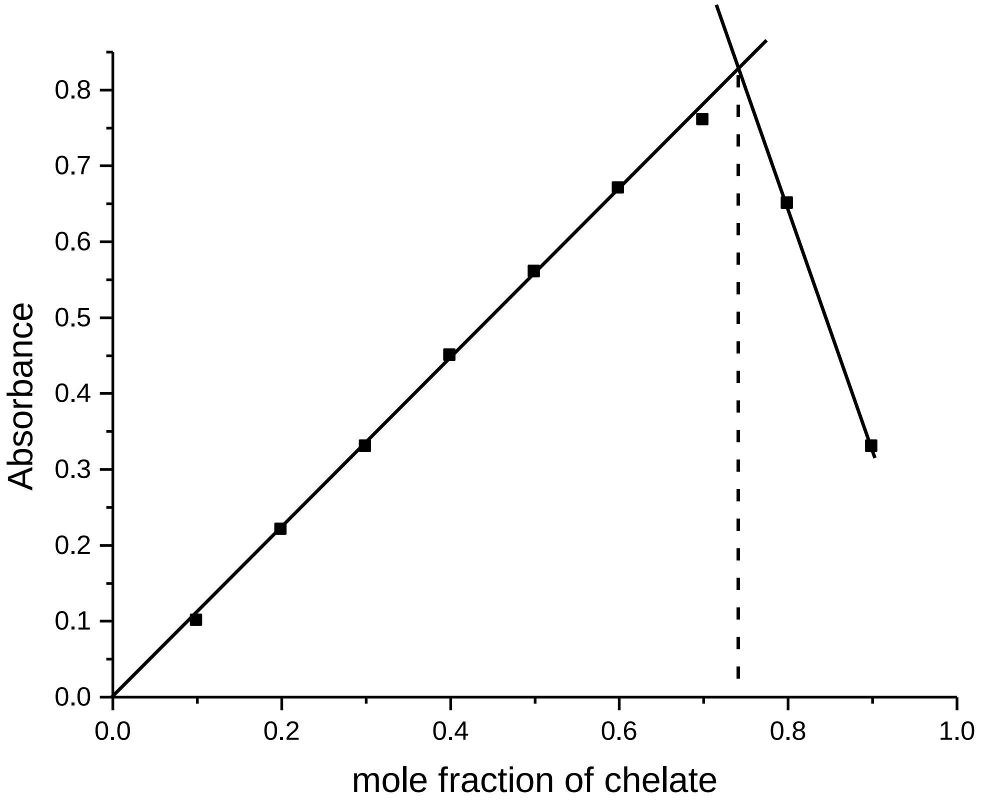
Example:

Determine the ratio of ligand to metal for the Fe^{2+}-phenanthroline system, if a continuous variation gave the following:

Absorbance	Mole fraction
0.10	0.1
0.22	0.2
0.33	0.3
0.45	0.4
0.56	0.5
0.67	0.6
0.76	0.7
0.65	0.8
0.33	0.9

Data Analysis

Determination of Stoichiometry of Complex Ions
Method of continuous variation



Data Analysis

Determination of Stoichiometry of Complex Ions
Method of continuous variation

0.75 = (0.75)/(0.75 +0.25)

0.75 – mole fraction of chelate
0.25 – mole fraction of metal

3 times as much ligand as metal ion

Data Analysis

Determination of Stoichiometry of Complex Ions
Method of continuous variation

Very low ligand concentrations give low absorbance on the first side of the curve.
On the second side you have high ligand concentrations but low Fe^{2+}

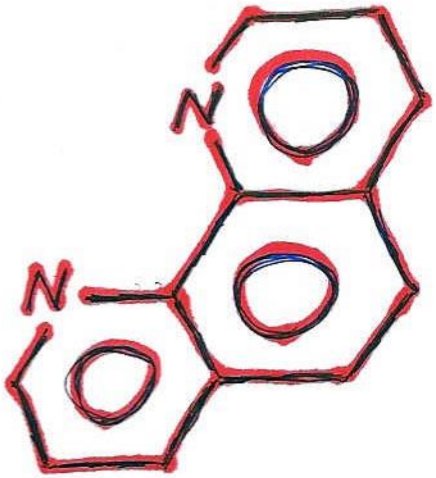
Data Analysis

Determination of Stoichiometry of Complex Ions

Method of continuous variation

  Coordination number = 6

  (ligand binds twice to Fe^{2+}, bidentate ligand)



Assignment

- Review Quantitative Analysis Stats Chapters if needed
- Read Chapter 1
- Read Appendix 1