



# Chemistry 4632

**Instrumental Analysis**

**Lab Lecture 1**

**Stats UV-vis Labs**

# Statistics/Laboratory

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

**If you want to put equations for calculations 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, $s$	$s = \sqrt{\frac{\sum_{i=1}^N (x_i - \bar{x})^2}{N - 1}}$
Relative standard deviation (RSD)	$\text{RSD} = \frac{s}{\bar{x}}$
Standard deviation of the mean, $s_m$	$s_m = s/\sqrt{N}$
Coefficient of variation, CV	$\text{CV} = \frac{s}{\bar{x}} \times 100\%$
Variance	$s^2$

\* $x_i$  = numerical value of the  $i$ th measurement.

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

# Bias

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

$\mu$  – population mean

$x_t$  – true concentration

# Bias

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

**The sample is a fraction of the infinite number of observations possible. (i.e. 50 measurements).**

**This infinite number of observations (measurements) is called the population or universe of data.**

# Sensitivity

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

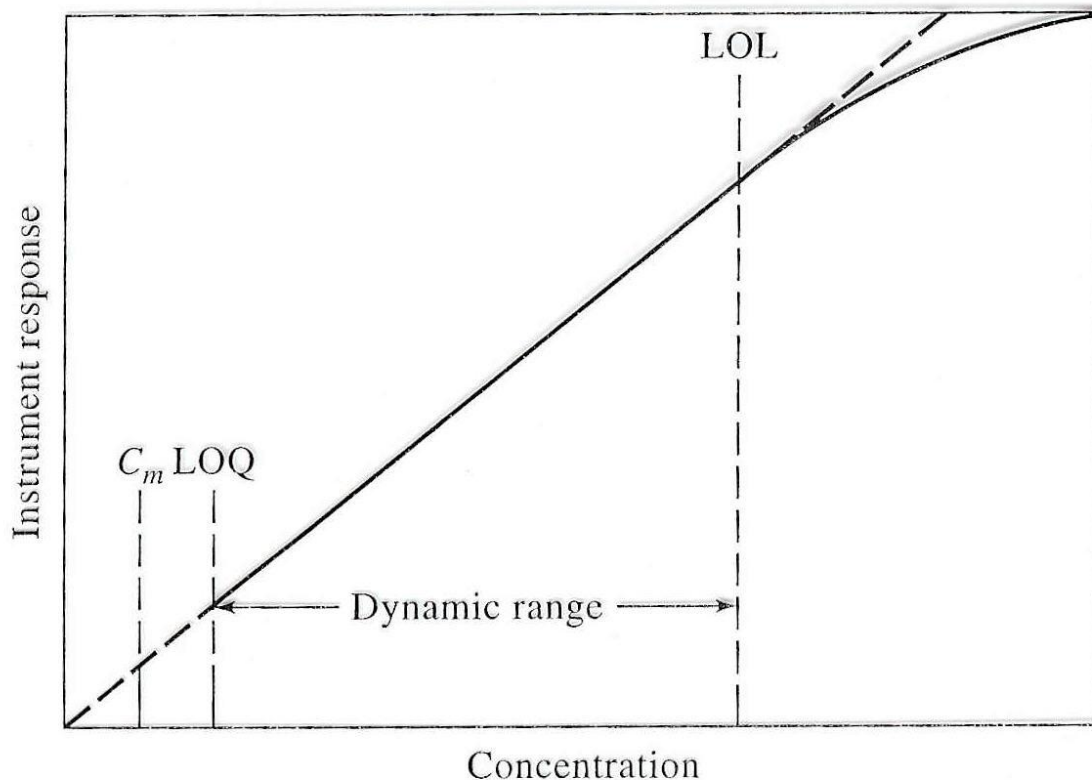
# Selectivity

**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

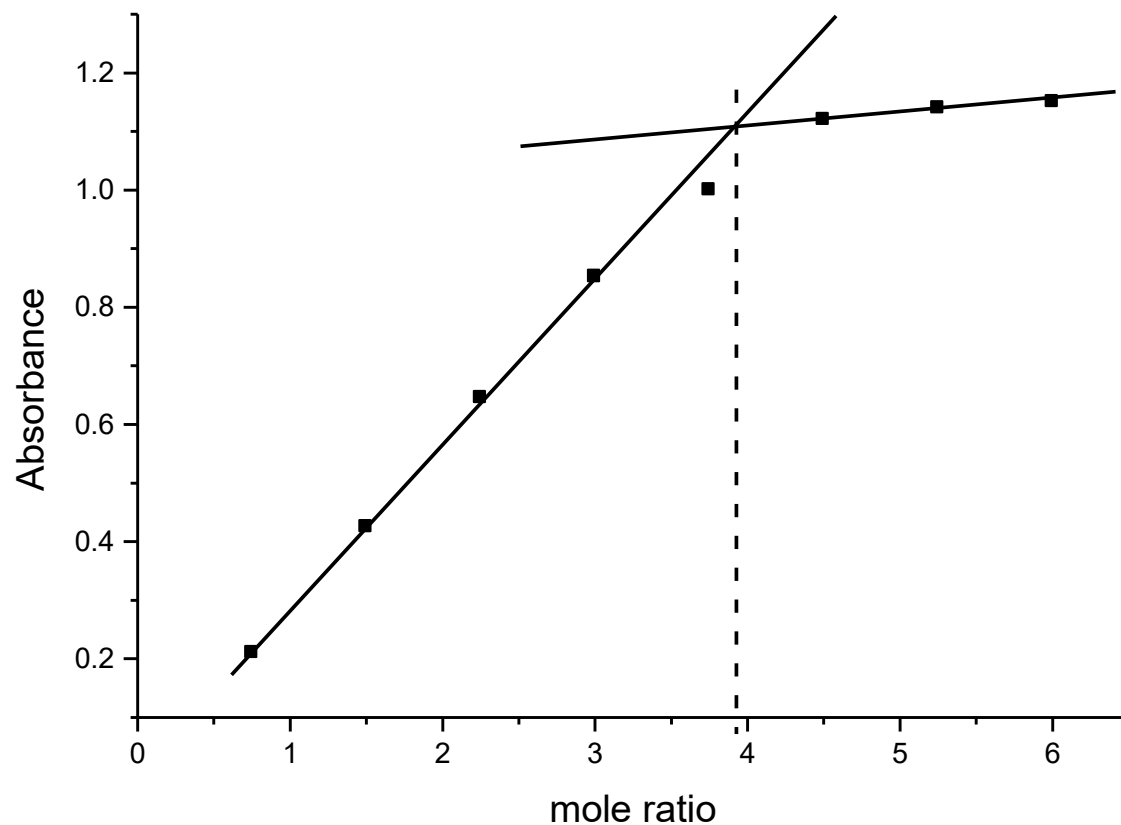
### Mole-ratio procedure

**Example: What is the number of  $\text{CN}^-$  ions attached to  $\text{Cd}^{3+}$  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



# 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

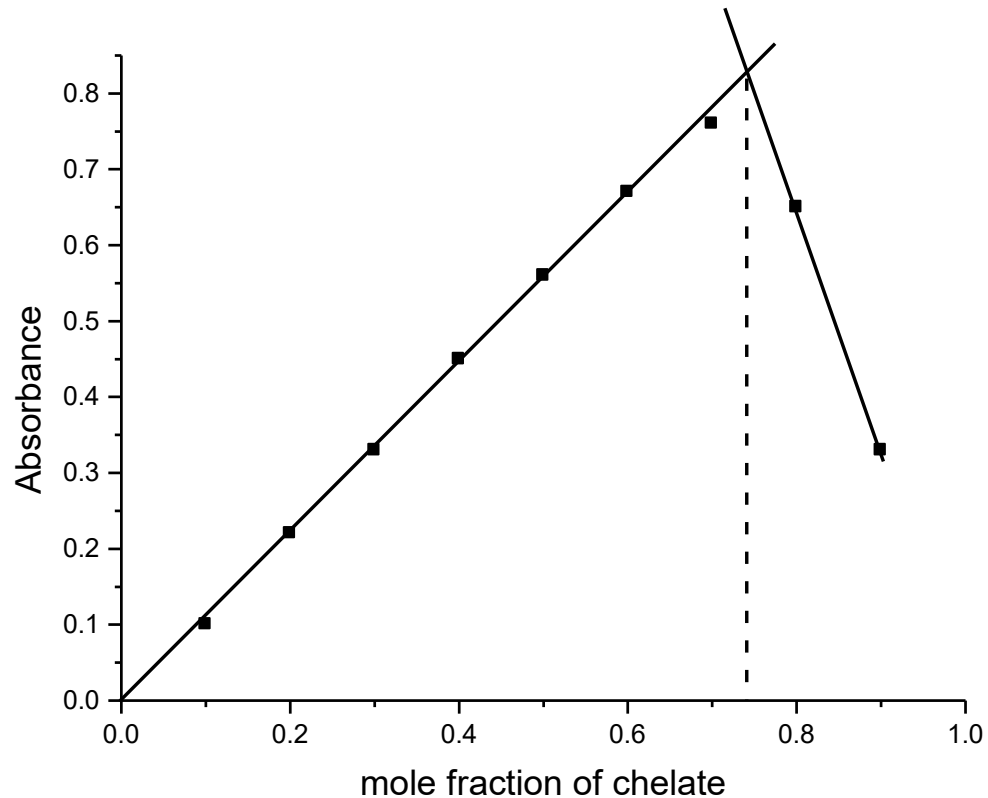
#### Example:

Determine the ratio of ligand to metal for the  $\text{Fe}^{2+}$ -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  $\text{Fe}^{2+}$

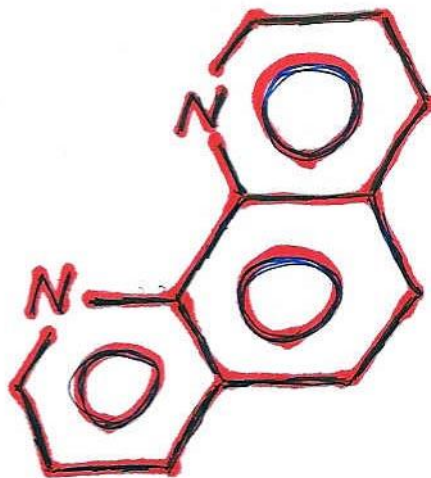
# Data Analysis

## Determination of Stoichiometry of Complex Ions

### Method of continuous variation

Coordination number = 6

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



# Assignment

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

