CHAPTER 1
INTRODUCTION TO ANALYTICAL CHEMISTRY

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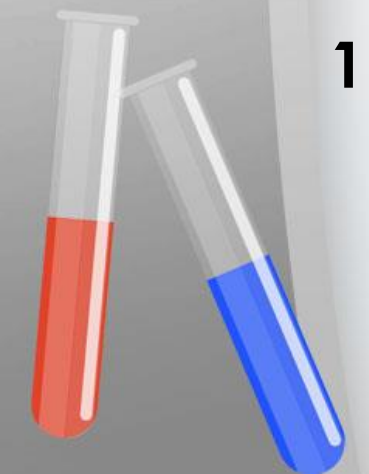
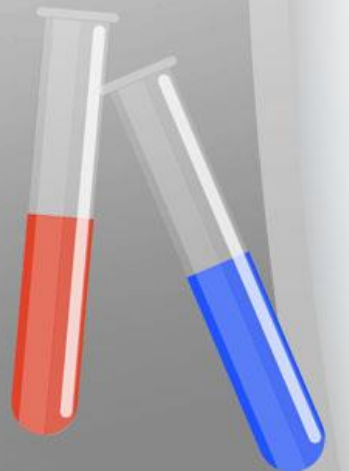


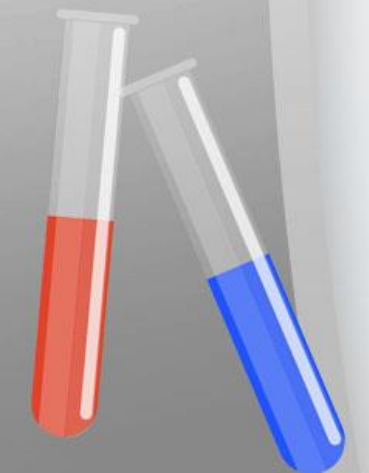
- Chemistry is the study of matter, including its composition and structure, its physical properties, and its reactivity.

- There are many ways to study chemistry, but, we traditionally divide it into five fields: (1) organic chemistry (2) inorganic chemistry (3) biochemistry (4) physical chemistry (5) **analytical chemistry**.



1.1: What is Analytical Chemistry

- Like all fields of chemistry, analytical chemistry is too broad and too active a discipline for us to define completely.
- **Analytical chemistry** is often described as the **area of chemistry responsible for characterizing the composition of matter**, **BOTH qualitatively** (Is there any lead in this sample?) and **quantitatively** (How much lead is in this sample?).
- The techniques of this science are used to **identify the substances which may be present** in a material and **determine the exact amounts** of the identified substances

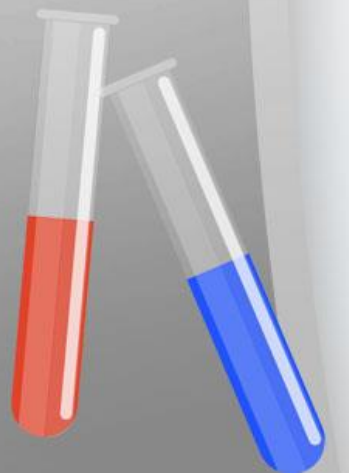


The Role of Analytical Chemistry

- Analytical chemists work to **improve** the reliability of existing techniques to meet the demands for **better** chemical measurements which arise constantly in our society

- They **adapt proven methodologies** to new kinds of materials or to answer new questions about their composition.

- They **carry out research** to discover completely new principles of measurements and at the forefront of the utilization of major discoveries for practical purposes (**R &D**)



The Role of Analytical Chemistry

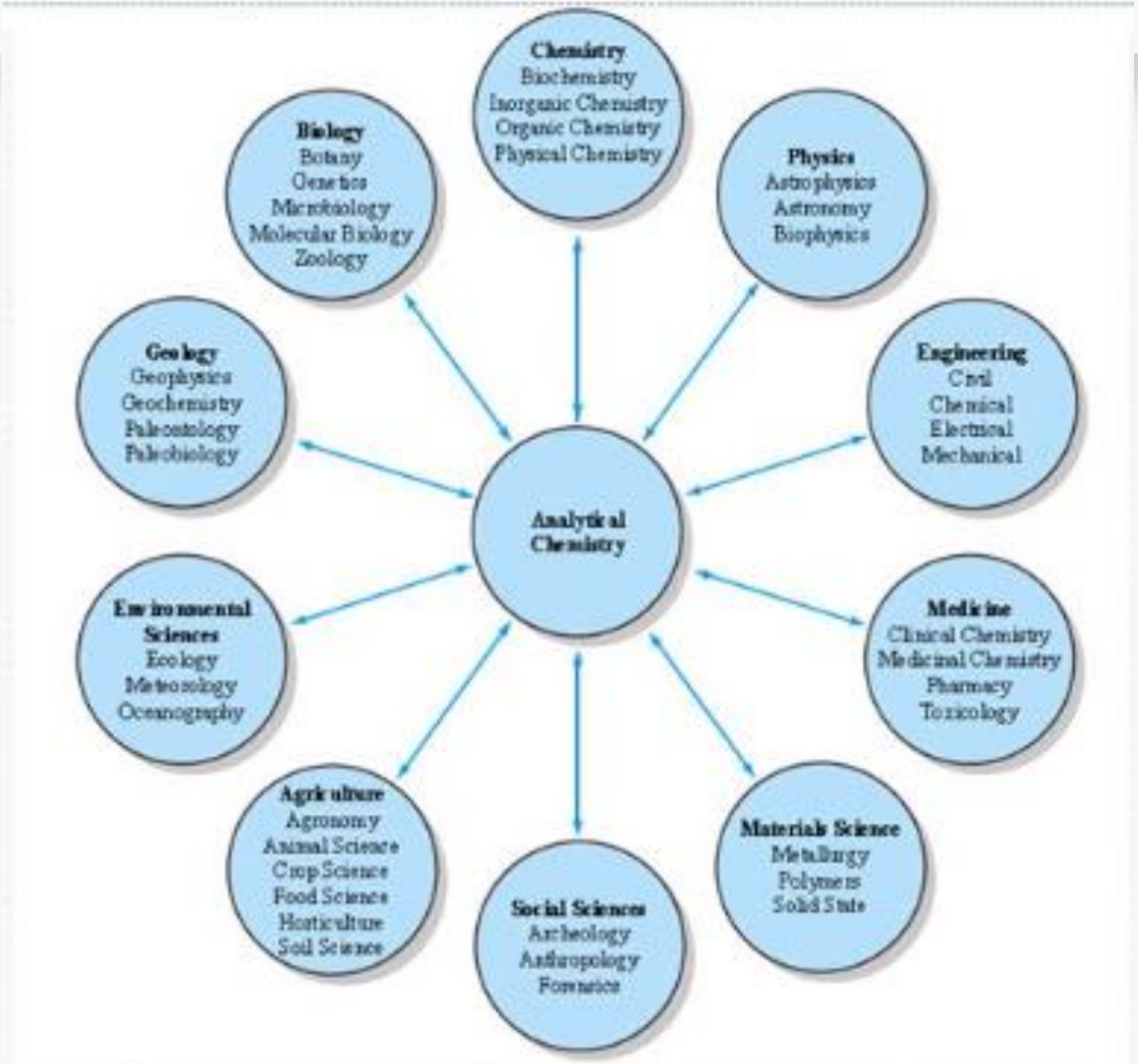
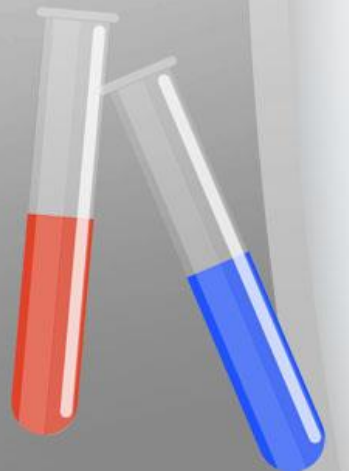


Figure 1-1 The relationship between analytical chemistry, other branches of chemistry, and the other sciences. The central location of analytical chemistry in the diagram signifies its importance and the breadth of its interactions with many other disciplines.

Qualitative Analysis vs Quantitative Analysis

- **Qualitative analysis** reveals the identity (identification) of the elements and compounds in a sample

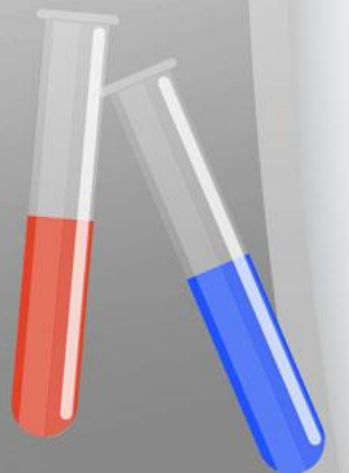
- **Quantitative analysis** indicates the amount (numerical) of each substance in a sample.



1.2: Classifying Quantitative Analytical Methods

- **Classical Methods**: Wet chemical methods such as precipitation, extraction, distillation, boiling or melting points, gravimetric and titrimetric measurements.

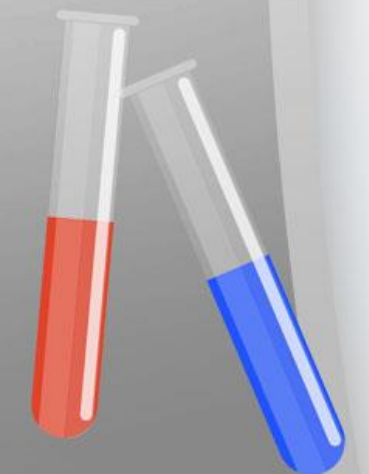
- **Instrumental Methods**: Analytical measurements (conductivity, electrode potential, light absorption or emission, mass to charge ratio, fluorescence etc.) are made using instrumentation.



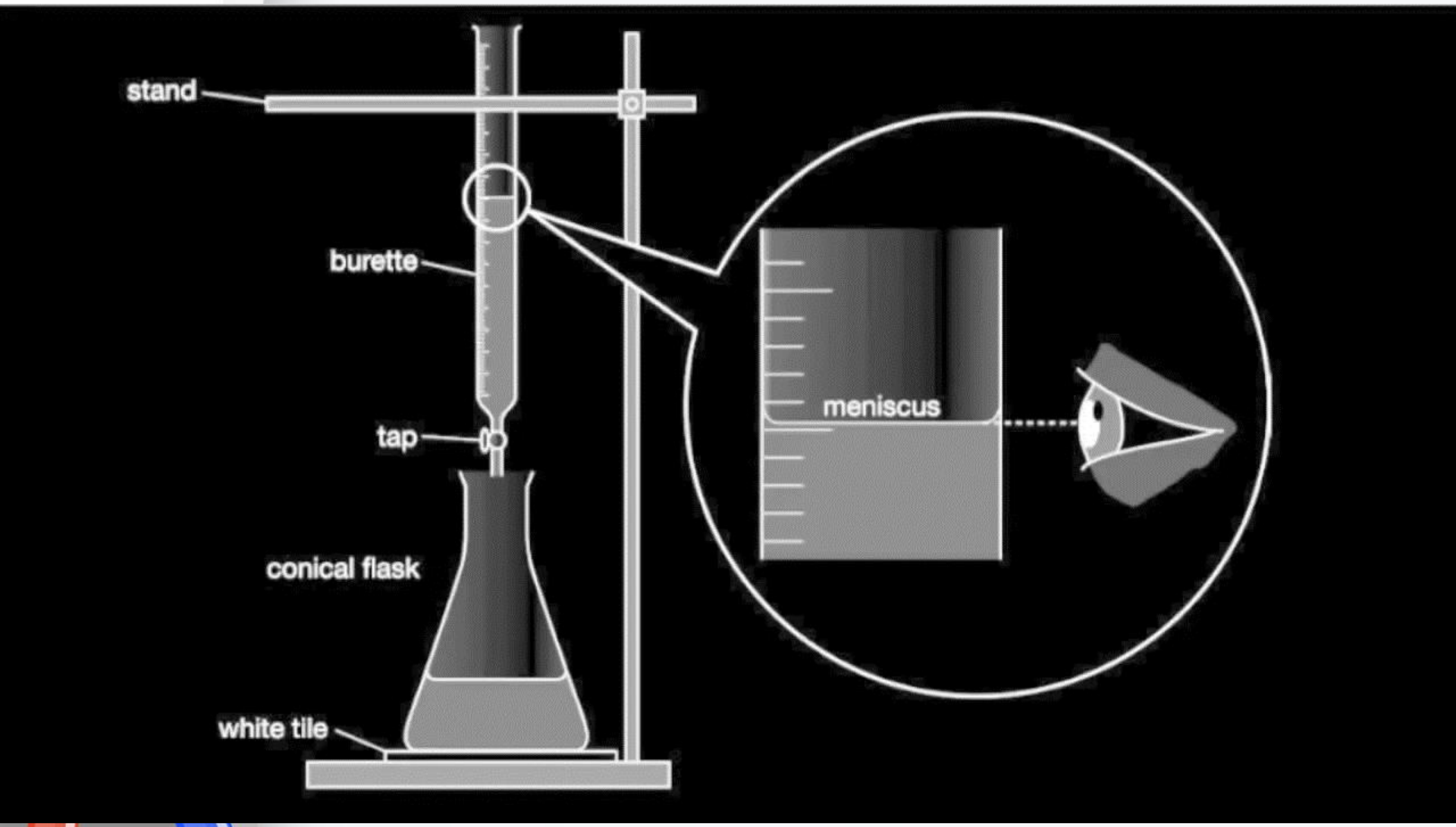
Classical Methods/ Wet chemical methods

- ✓ **Qualitative**: recognized by observation of color, boiling point, melting point, solubility, taste, physical appearance

- ✓ **Quantitative**: gravimetric or titrimetric/volumetric measurements

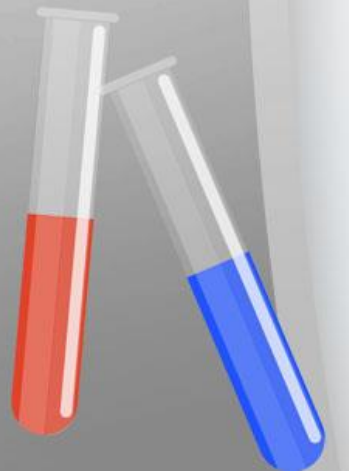


TITRIMETRIC/TITRATION



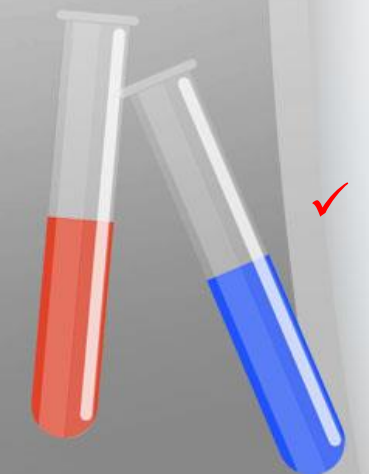
Instrumental Methods

- Newer technology, faster, more efficient
- Analytical measurements (conductivity, electrode potential, light absorption or emission, mass-to-charge ratio, fluorescence etc.) are made using instrumentation.



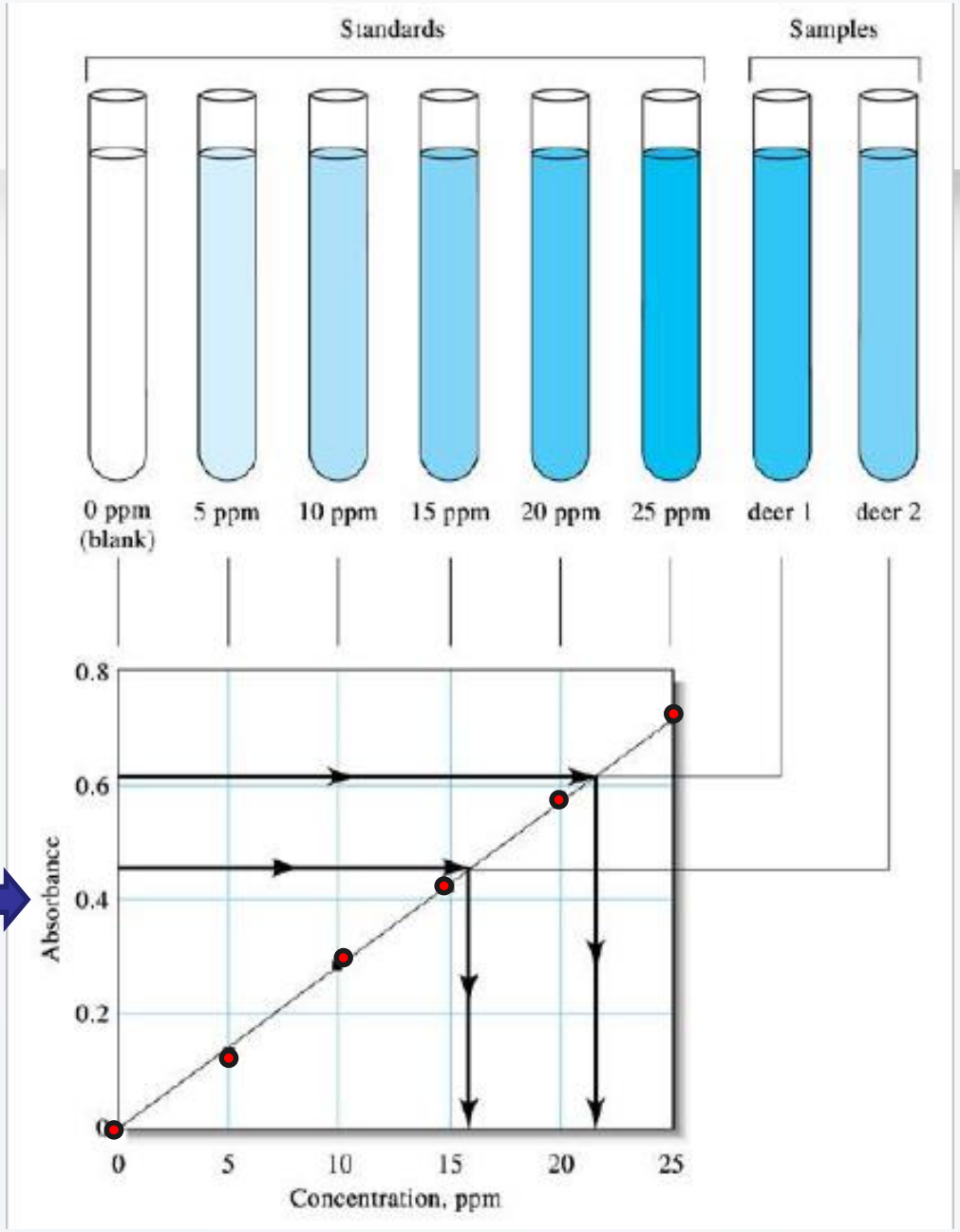
Instrumental Methods

- ✓ The presence of many chemical substances can often be found by their **response** to some external signal.
- ✓ The magnitude of this response is **proportional** to the amount of substance present.
- ✓ Because **electronic equipment** is often necessary to **generate the external signal and/or to detect the chemical response**, these methods of quantitative analysis are called **instrumental methods**.
- ✓ Instrumental methods are indirect, so the detecting instrument requires **calibration (refer next slide)** to measure the response initially from a **sample with a known concentration of analyte**.
- ✓ This is necessary to **relate the response**, which is often electrical, to the **quantity of chemical substance**.



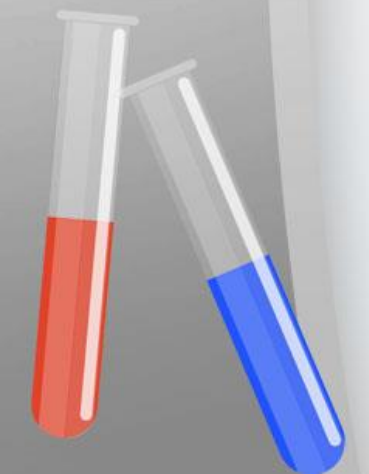
Calibration curve

response



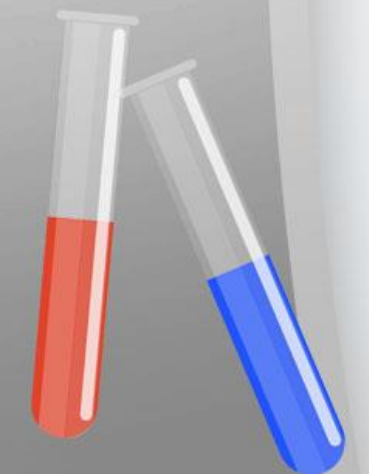
Instrumental Methods

- **Spectroscopic Methods**: Based on **measurement** of the interaction between electromagnetic radiation and analyte atoms or molecules. (UV-Vis, FTIR)
- **Chromatographic Methods**: **Separation** techniques and quantitation is based on calibration curve (GC, LC)



Spectroscopic Methods

- based on **measurement of the interaction between electromagnetic radiation** and **analyte atoms or molecules.**
- Spectroscopic analytical methods are based on **measuring the amount of radiation produced or absorbed** by **molecular or atomic species of interest**.
- The spectroscopic methods can be classified according to the region of the electromagnetic spectrum involved in the measurement. The regions **include γ–ray, X-ray, ultraviolet (UV), visible, infrared (IR), microwave, and radio frequency (RF).**



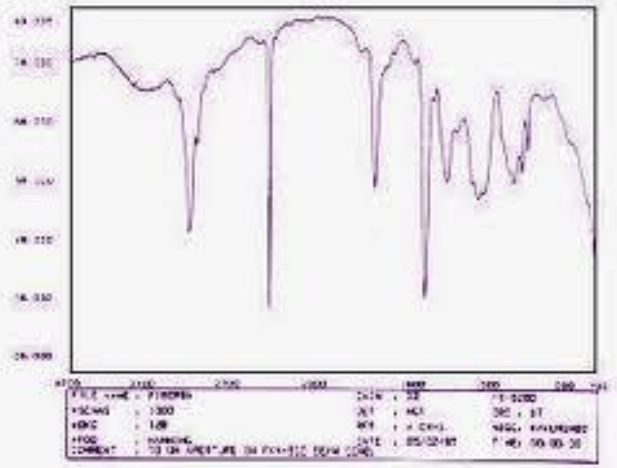
Electromagnetic radiation

TABLE 24-2

Regions of the UV, Visible, and IR Spectrum

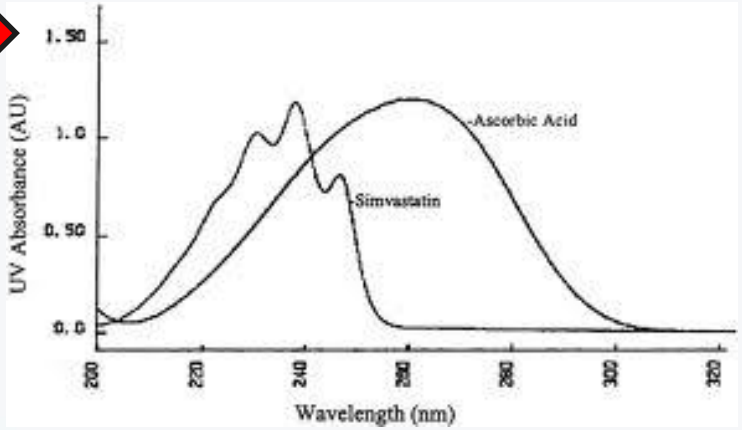
Region	Wavelength Range
UV	180–380 nm
Visible	380–780 nm
Near-IR	0.78–2.5 μm
Mid-IR	2.5–50 μm

Fourier Transform Infrared (FTIR)



FTIR spectrum

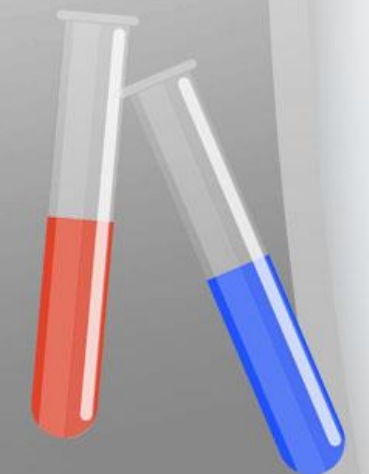
Ultraviolet Visible (UV-VIS)



UV VIS spectrum

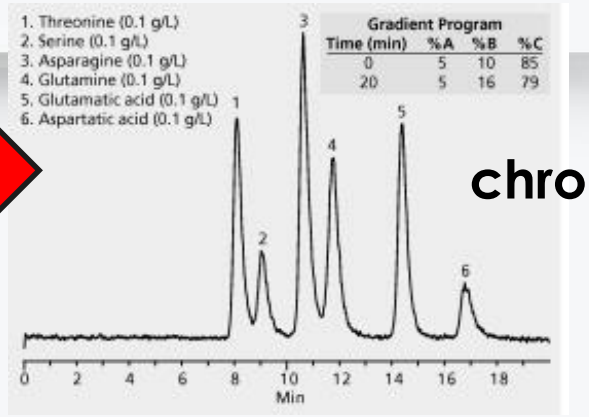
Chromatographic Methods

- **separation techniques and quantitation** is based on **calibration curve**.
- Chromatography is the science which is studies **the separation of molecules based on differences in their structure and/or composition**.
- Chromatographic separations can be carried out using a variety of supports, including **immobilized silica on glass plates (thin layer chromatography), volatile gases (gas chromatography), paper (paper chromatography), and liquids which may incorporate hydrophilic, insoluble molecules (liquid chromatography).**



Chromatography

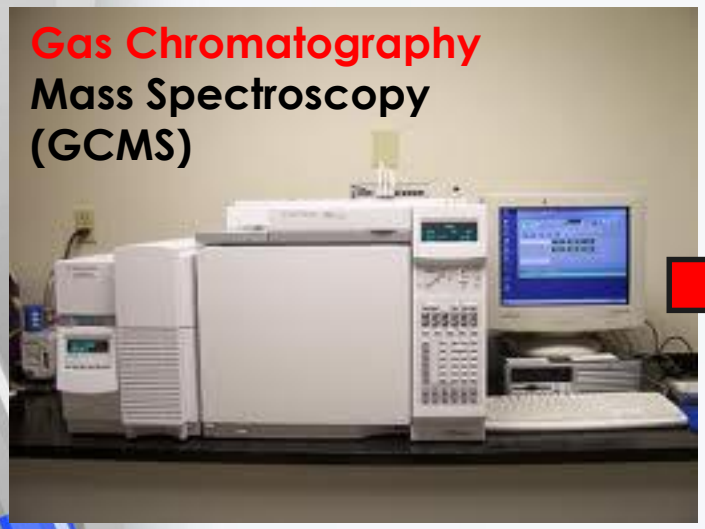
High performance
liquid chromatography
(HPLC)



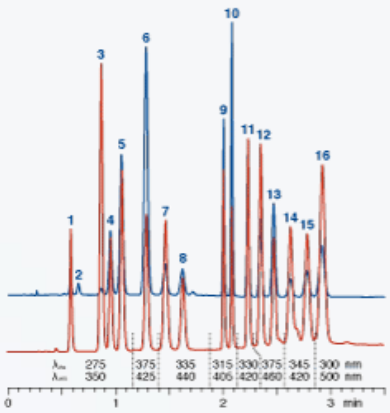
HPLC chromatogram

*head space -convert liquid to gas

Gas Chromatography
Mass Spectroscopy
(GCMS)



Colum: 100 x 4 mm NUCLEODUR® C18 PAH, 3 µm
Eluents: A) methanol – water (80:20, v/v)
B) acetonitrile
Gradient: 2 – 20 % B in 1.2 min, 20 – 100 % B in 0.5 min, 100 % B for 2.5 min, 100 – 2 % B in 0.4 min
Flow rate: 2.5 ml/min
Temperature: 35 °C
Detection: UV, 254 nm
fluorescence (see chromatogram)

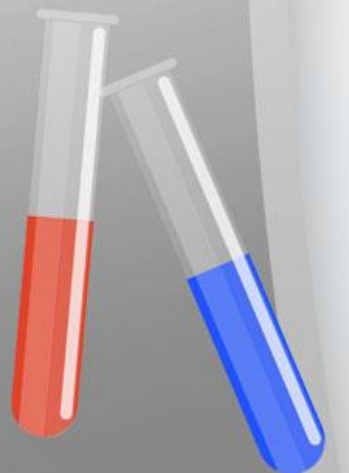


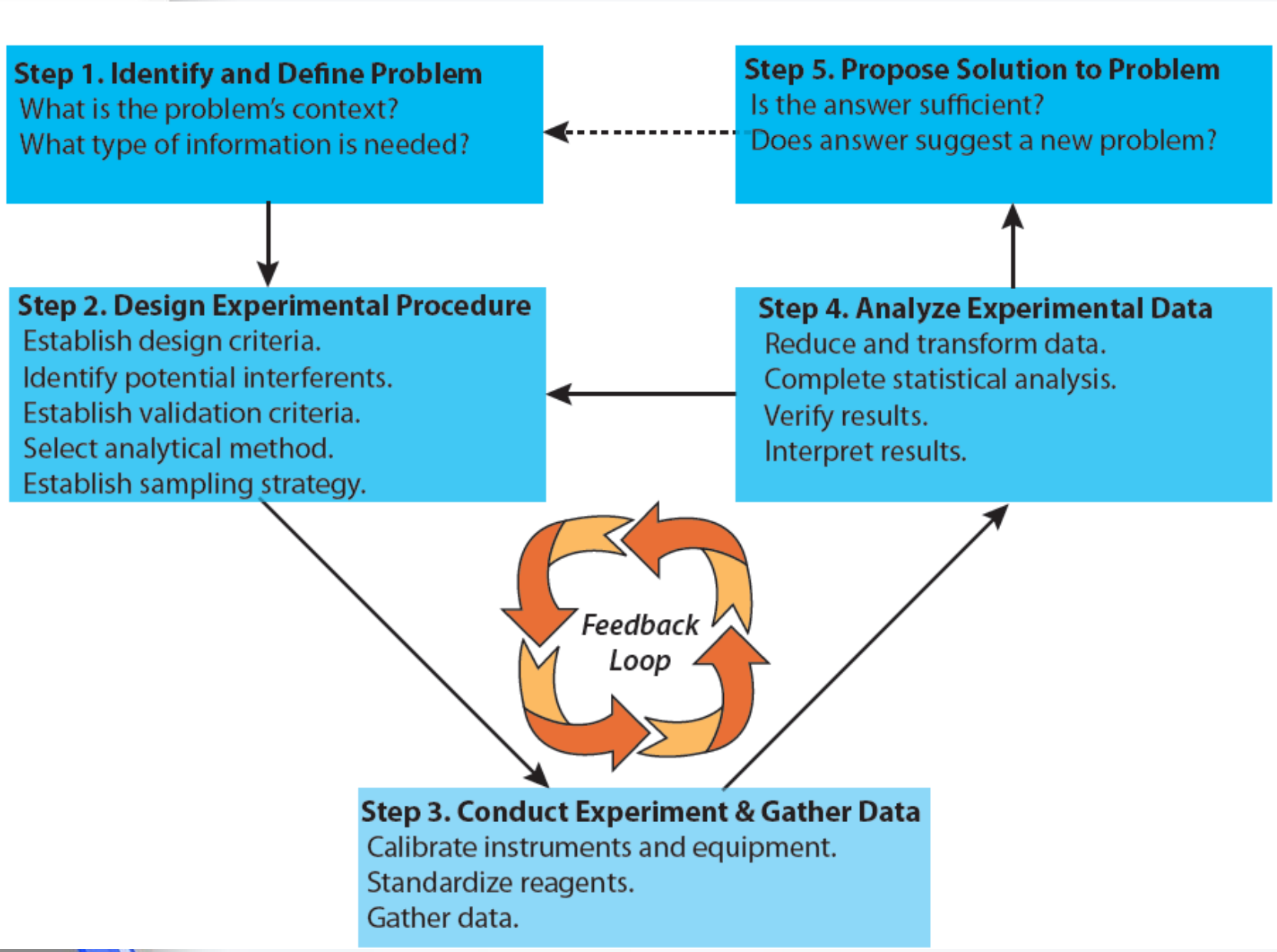
GCMS chromatogram

Peaks:
1. Naphthalene
2. Acenaphthylene (not detectable by fluorescence)
3. Acenaphthene
4. Fluorene
5. Phenanthrene
6. Anthracene
7. Fluoranthene
8. Pyrene
9. Benz[a]anthracene
10. Chrysene
11. Benzo[b]fluoranthene
12. Benzo[k]fluoranthene
13. Benzo[a]pyrene
14. Dibenz[ah]anthracene
15. Benzo[ghi]perylene
16. Indeno[1,2,3-cd]pyrene

MN Appl. No. 123820

1.3: STEPS IN A QUANTITATIVE ANALYSIS




Step 1. Identify and Define Problem
What is the problem's context?
What type of information is needed?
Step 5. Propose Solution to Problem
Is the answer sufficient?
Does answer suggest a new problem?
Step 2. Design Experimental Procedure
Establish design criteria.
Identify potential interferents.
Establish validation criteria.
Select analytical method.
Establish sampling strategy.
Step 4. Analyze Experimental Data
Reduce and transform data.
Complete statistical analysis.
Verify results.
Interpret results.
Feedback Loop
Step 3. Conduct Experiment & Gather Data
Calibrate instruments and equipment.
Standardize reagents.
Gather data.

Define and Identify problem

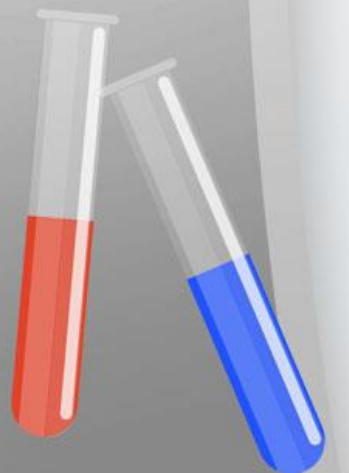
Select Method

Sampling

Sample Preservation

Sample Preparation

Analysis



Problem : Metals pollution in river water

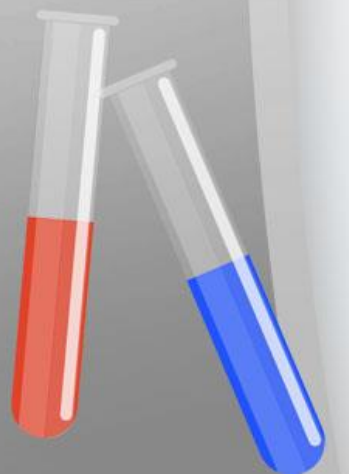
Method : Determination of metals in river water

Sampling : grab sampling, sampling at certain depth

Sample Preservation : Below $4^{o}C$

Sample Preparation : Digestion, Extraction

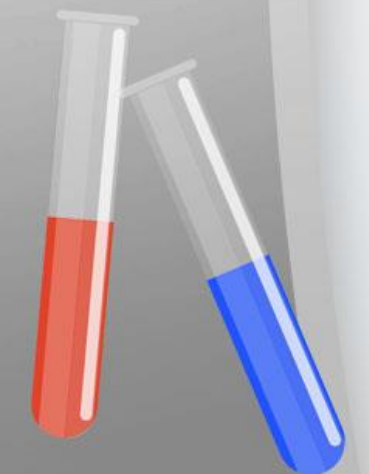
Analysis : Atomic absorption spectrometry, ICP MS



Step in a quantitative analysis

1) Select a Method: The first step is the selection of a method. Factors need to be considered in the selection process are:

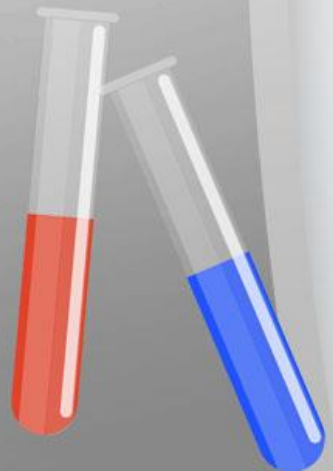
1. Accuracy required
2. Cost of analysis (total investment)
3. Number of sample to be analyzed
4. Time required for analysis
5. Skill required
6. Complexity of the sample
7. Number of components in the sample



Step in a quantitative analysis

2) Acquiring the Sample: Sampling and sample preservation

- Sampling is the process of **collecting a small mass of a material** whose composition accurately represents the bulk of the material from which it was taken.
- To produce meaningful information, an analysis must be performed on a representative sample.
- For large heterogeneous sample, great effort is required to get a representative sample.
- Sometime proper sampling is the most difficult step in an analysis and the source of greatest error.
- The final result of an analysis will never be any more reliable than the reliability of the sampling step.



Step in a quantitative analysis

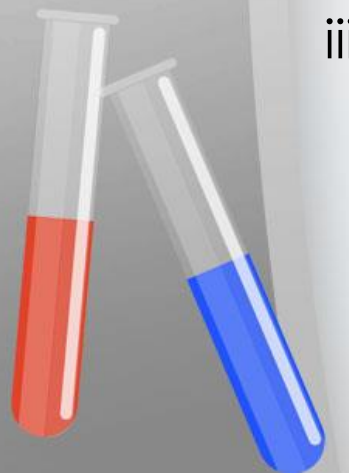
3) Processing the sample: Sample preparation

- Sometimes no sample processing is required prior to the measurement step such as pH of water sample can be measured directly.
- Under most circumstances, sample need to be processed in a variety of different ways.

i. Preparing a Laboratory Sample

ii. Defining Replicate Samples

iii. Preparing Solutions: Physical and Chemical Changes



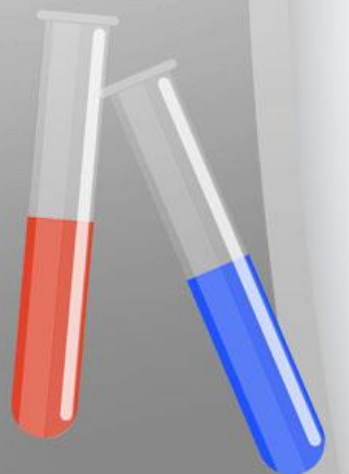
Analytes	Sample Preparation	Instrument[a]
Organics	Extraction, concentration, cleanup, derivatization	GC, HPLC, GC/MS, LC/MS
Volatile organics	Transfer to vapor phase, concentration	GC, GC-MS
Metals	Extraction, concentration, speciation	AA, GFAA, ICP, ICP/MS
Metals	Extraction, derivatization, concentration, speciation	UV-VIS molecular absorption spectrophotometry, ion chromatography
Ions	Extraction, concentration, derivatization	IC, UV-VIS
DNA/RNA	Cell lysis, extraction, PCR	Electrophoresis, UV-VIS, florescence
Amino acids, fats carbohydrates	Extraction, cleanup	GC, HPLC, electrophoresis
Microstructures	Etching, polishing, reactive ion techniques, ion bombardments, etc.	Microscopy, surface spectroscopy

[a]GC, gas chromatography; HPLC, high-performance liquid chromatography; MS, mass spectroscopy; AA, atomic absorption; GFAA, graphite furnace atomic absorption; ICP, inductively coupled plasma; UV-VIS, ultraviolet–visible molecular absorption spectroscopy; IC, ion chromatography.

Step in a quantitative analysis

4) Eliminating Interferences:

- Need to eliminate substances from the sample that may interfere with the measurement step.
- Species other than the analyte that affect the final measurement are called interferences.
- An interference causes an error in an analysis by enhancing or attenuating the quantity being measured.
- A scheme must be devised to isolate the analytes from interferences before the final measurement is made.

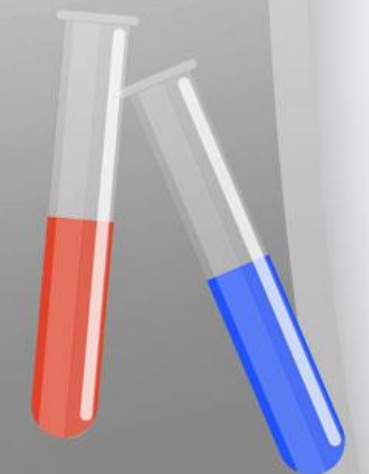


Step in a quantitative analysis

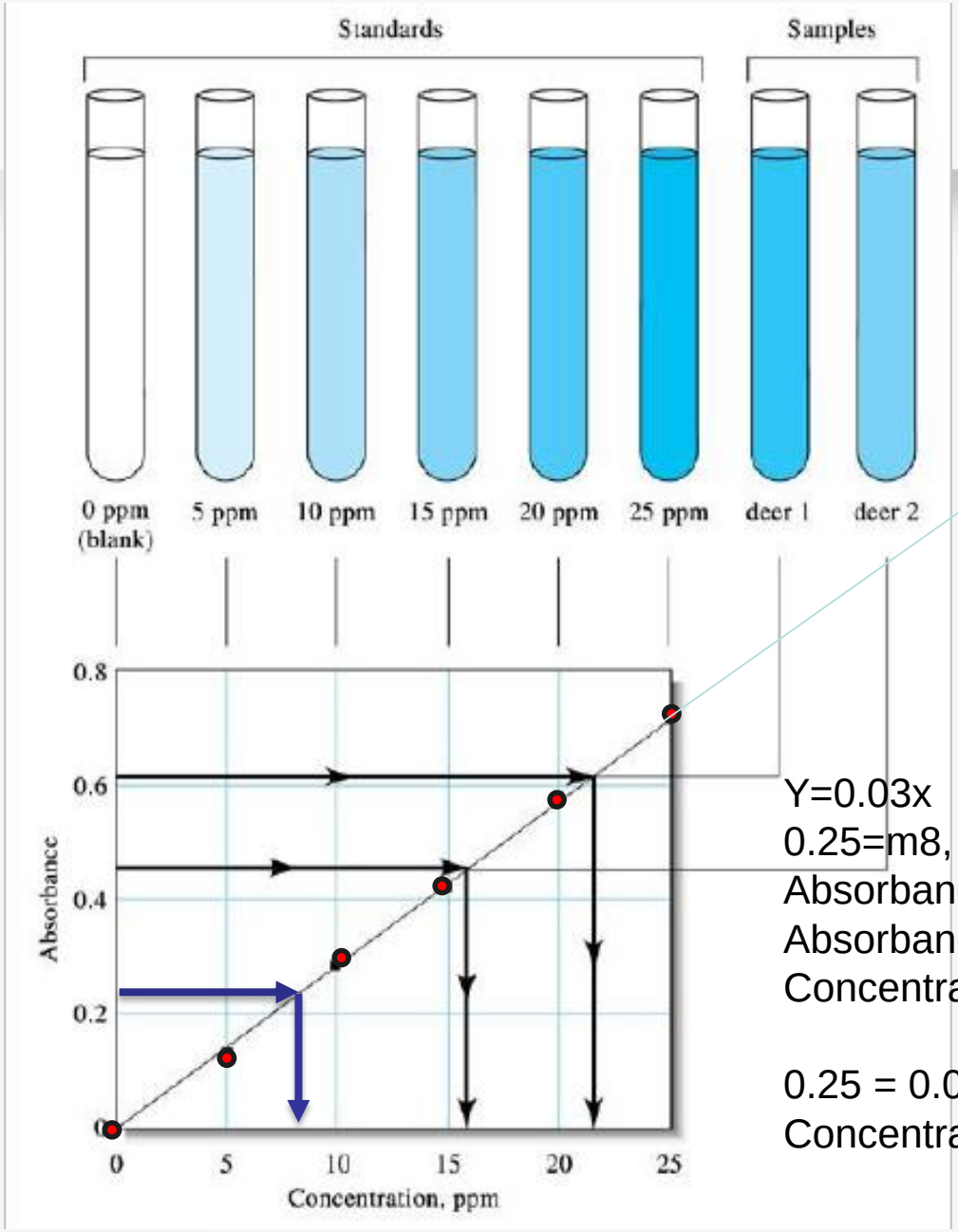
5) Calibration and Measurement: An analytical results depend on a final measurement of a physical or chemical property (X). Ideally, the measurement of the property is directly proportional to the concentration (CA).

$$CA = kX$$

where, k is a proportionality constant. The process of determining k is an important step in most analyses. This step is called a **calibration**.



Calibration curve



Y=0.03x
0.25=m8, m=0.03
Absorbance =3.4(concentration)
Absorbance sample = 0.25
Concentration =?

0.25 = 0.03 (concentration)
Concentration = 0.25/0.03 = 8

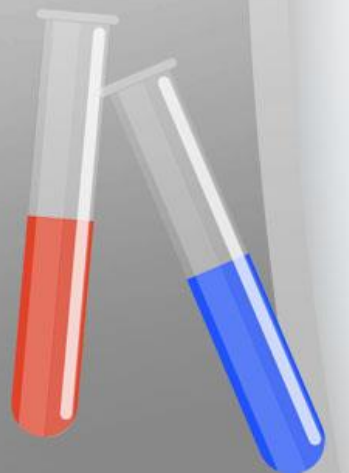
Step in a quantitative analysis

6) Calculating Results:

Analyte concentrations from experimental data need to be calculated. These computation are based on the raw experimental data collected in the measurement steps, the characteristics of the measurement instruments and the stoichiometry of the analytical reaction.

7) Evaluating Results by Estimating Their Reliability:

Analytical results are incomplete without an estimate of their reliability. Some measure of the uncertainties associated with computed results need to be provided.



1.4: VOCABULARY IN ANALYTICAL CHEMISTRY

Analysis, Determination and Measurement

- An **ANALYSIS** provides chemical or physical information about a sample. The **component of interest in the sample** is called the **analyte**, and the **remainder of the sample** is the **matrix**.
- In an analysis we **DETERMINE** the identity, concentration, or properties of an analyte.
- To make this determination we **MEASURE** one or more of the analyte's chemical or physical properties.

1.4: VOCABULARY IN ANALYTICAL CHEMISTRY

- **Techniques, Methods, Procedures, and Protocols**

- A **TECHNIQUE** is **any chemical or physical principle we can use to study an analyte.** Example : There are many techniques for determining the concentration of lead in drinking water.- AAS/ICP MS/Gravimetric analysis
- A **METHOD** is the application of a technique for a **specific analyte in a specific matrix.**
- A **PROCEDURE** is a **set of written directions telling us how to apply a method to a particular sample**, including information on obtaining samples, handling interferents, and validating results.
- Finally, a **PROTOCOL** is a **set of stringent guidelines specifying a procedure that must be followed if an agency is to accept the results.** Protocols are common when the result of an analysis supports or defines public policy. When determining the concentration of lead in water under the Safe Drinking Water Act, for example, labs must use a protocol specified by the **Environmental Protection Agency.**