CHAPTER 1

THE NATURE OF ANALYTICAL CHEMISTRY

Analytical chemistry is a measurement science :

- ✓ consisting of a set of powerful ideas and methods that are useful in all fields of science, engineering, and medicine.
- ✓ determines the identity and amounts of major, minor, and trace elements and detects hydrated minerals.
- ✓ demonstrates both qualitative and quantitative information required in an analysis.
- ✓ applied throughout industry, medicine, and all the sciences.

We will explore quantitative methods of **analysis**, **separation methods**, and **the principles** behind their operation.

- **Qualitative analysis** establishes the chemical identity of the species in the sample.

- **Quantitative analysis** determines the relative amounts of these species, or **analytes,** in numerical terms.

A **qualitative analysis** is often an integral part of the separation step, and determining the identity of the analytes is an essential adjunct to **quantitative analysis**.

Examples for Quantitative Measurements

- ✓ The concentrations of oxygen and of carbon dioxide are determined in millions of blood samples every day and used to diagnose and treat illnesses.
- ✓ Quantities of hydrocarbons, nitrogen oxides, and carbon monoxide present in automobile exhaust gases are measured to determine the effectiveness of emission-control devices.
- ✓ Ionized calcium in blood serum help diagnose parathyroid disease in humans.
- ✓ Quantitative determination of nitrogen in foods establishes their protein content and thus their nutritional value.

- ✓ Analysis of steel during its production permits adjustment in the concentrations of such elements as carbon, nickel, and chromium to achieve a desired strength, hardness, corrosion resistance, and ductility.

- ✓ The mercaptan content of household gas supplies is monitored continually to ensure that the gas has a sufficiently obnoxious odor to warn of dangerous leaks.

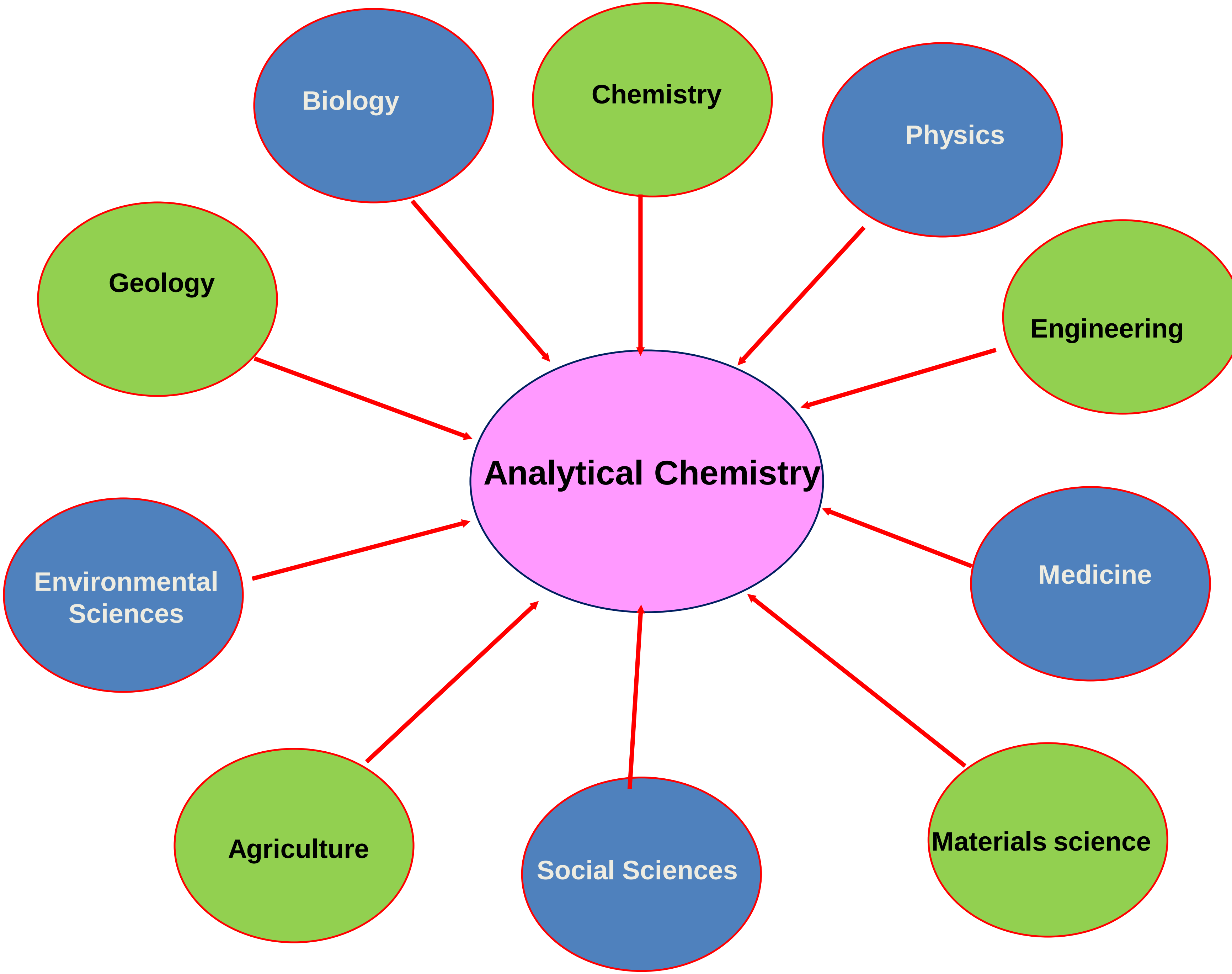
- ✓ Farmers tailor fertilization and irrigation schedules to meet changing plant needs during the growing season, gauging these needs from quantitative analyses of plants and soil.

- ✓ Chemistry is often called *the central science; its top* center position and the central position of analytical chemistry emphasize this importance.

- ✓ All branches of chemistry draw on the ideas and techniques of analytical chemistry.

- ✓ Quantitative analytical measurements also play a vital role in many research areas in **chemistry, biochemistry, biology, geology, physics**, and the other sciences.

- ✓ The interdisciplinary nature of chemical analysis makes it a vital tool in **medical, industrial, government,** and **academic laboratories** throughout the world.

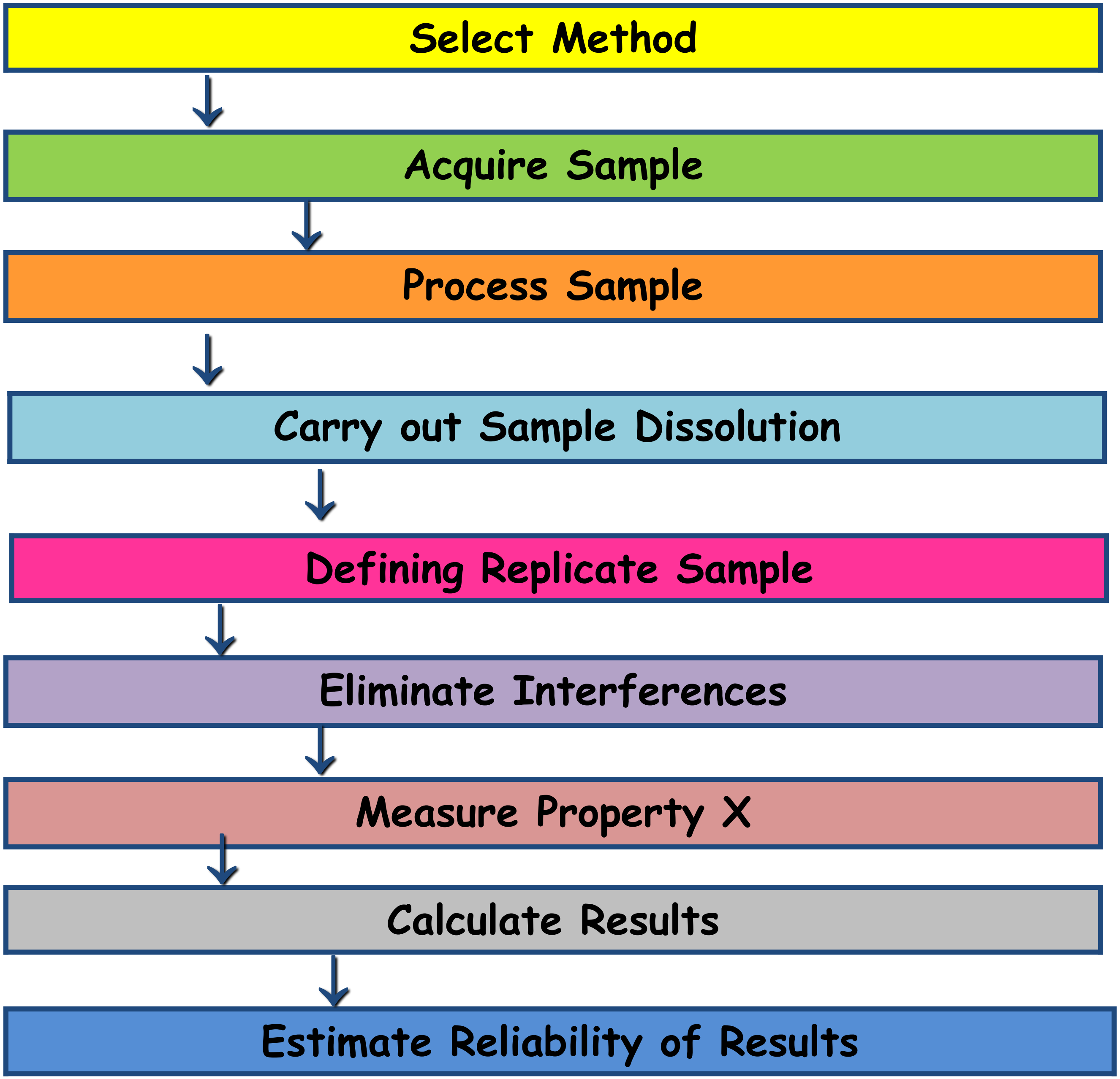

Biology
Chemistry
Physics
Geology
Engineering
Analytical Chemistry
Environmental Sciences
Medicine
Agriculture
Social Sciences
Materials science

Quantitative Analytical Methods

The results of a typical quantitative analysis are computed from two measurements.

- the mass or the volume of sample being analyzed.
- some quantity that is proportional to the amount of analyte in the sample such as mass, volume, intensity of light, or electrical charge.

This second measurement usually completes the analysis, and we usually classify analytical methods according to the nature of this final measurement.



The sequence of steps included in a typical quantitative analysis.

In **gravimetric methods**, we determine the mass of the analyte or some compound chemically related to it.

In **volumetric method**, we measure the volume of a solution containing sufficient reagent to react completely with the analyte.

In **electroanalytical methods**, we measure electrical properties such as potential, current, resistance, and quantity of electrical charge.

In **spectroscopic methods**, we explore the interaction between electromagnetic radiation and analyte atoms or molecules or the emission of radiation by analytes.

Finally, in **a group of miscellaneous methods**,

- quantities as mass-to-charge ratio of ions by mass spectrometry,
- rate of radioactive decay,
- heat of reaction,
- rate of reaction,
- sample thermal conductivity,
- optical activity,
- refractive index

were measured.

We *analyze samples, and we determine substances.*

For example, **a blood sample is analyzed** **to determine the concentrations of various substances** such as blood gases and glucose.

We, therefore, speak of the determination of blood gases or glucose, *not the analysis* of blood gases or glucose.

1. Choosing a Method

The essential **first step** in any quantitative analysis is the selection of a method.

The choice is **sometimes difficult** and requires **experience** as well as intuition.

Questions to be considered in the selection process of a method are:

1st question:

the level of accuracy required: Unfortunately, high reliability nearly always requires a large investment of time.

selected method must represent a compromise between **the accuracy required and the time and money available** for the analysis.

2nd question:

related to economic factors (the number of samples that will be analyzed):

If there are many samples, we can afford to spend a significant amount of time in preliminary operations such as assembling and calibrating instruments and equipment and preparing standard solutions.

If we have only a single sample or just a few samples, it may be more appropriate to select a procedure that avoids or minimizes such preliminary steps.

Final question:

the complexity of the sample and the number of components in the sample:

They always influence the choice of method to some degree.

2. Acquiring the Sample

❖To produce meaningful information, an analysis must be performed on a sample that has the same composition as the bulk of material from which it was taken.

❖When the bulk is **large** and **heterogeneous**, great effort is required to get **A REPRESENTATIVE SAMPLE**.

❖**Sampling is the process of collecting a small mass of a material whose composition accurately represents** the bulk of the material being sampled.

The **analyst must be sure** that the **laboratory sample is representative** of the whole before proceeding.

Sampling is frequently **the most difficult step** in an analysis and the source of greatest error.

The final analytical result will never be any more reliable than the reliability of the sampling step.

3. Processing the Sample

Under certain circumstances, no sample processing is required prior to the measurement step.

For example, once a water sample is withdrawn from a stream, a lake, or an ocean, the pH of the sample can be measured directly.

Under most circumstances, we must process the sample in one of several different ways.

✓ The first step in processing is often the preparation of a laboratory sample.

Preparing a Laboratory Sample

- **A solid laboratory sample is**
  - ground to decrease particle size,
  - mixed to ensure homogeneity,
  - stored for various lengths of time before analysis begins.
  - kept dry just before starting an analysis or the moisture content of the sample can be determined at the time of the analysis in a separate analytical procedure.

- **Liquid samples** present a slightly different but related **set of problems** during the preparation step. **IF**
  - samples are allowed to stand in open containers, the solvent may evaporate and change the concentration of the analyte.
  - the analyte is a gas dissolved in a liquid, as in our blood gas example, the sample container must be kept inside a second sealed container to prevent contamination by atmospheric gases.

Preparing Solutions: Physical and Chemical Changes

- Most analyses are performed on solutions of the sample made with a suitable solvent.
- The solvent should dissolve the entire sample, including the analyte, rapidly and completely.

- Unfortunately, many materials that must be analyzed are insoluble in common solvents. Converting the analyte into a soluble form is often the most difficult and time-consuming task in the analytical process.
- The sample may require heating with aqueous solutions of strong acids, strong bases, oxidizing agents, reducing agents, or some combination of such reagents.

- Once the analyte is made soluble, we then ask whether the sample has a property that is proportional to analyte concentration and that we can measure.
- If it does not, other chemical steps may be necessary to convert the analyte to a form that is suitable for the measurement step.

4. Defining Replicate Samples

- Most chemical analyses are performed on **replicate samples** **whose masses or volumes** have been determined by careful measurements with an analytical balance or with a precise volumetric device.

- Replication improves the quality of the results and provides a measure of their reliability.

- Quantitative measurements on replicates are usually averaged, and various statistical tests are performed on the results to establish their reliability.

Replicate samples, or replicates, **are** portions of a material of approximately the same size that are carried through an analytical procedure at the same time and in the same way.

5. Calibrating and Measuring Concentration

- All analytical results depend on a final measurement *X of a physical or chemical* property of the analyte. This property must vary in a known
- and reproducible way with the concentration C_A *of the analyte.*

- *The measurement* of the property is directly proportional to the concentration, that is, $C_A = kX$ where *k is a proportionality constant.*

- The process of determining *k is thus an important step in most analyses; this step is* called a **calibration** **(**the process of determining the proportionality between analyte concentration and a measured quantity**)**.

The **matrix**, or **sample matrix**, is the collection of all of the components in the sample containing an analyte.

Techniques or reactions that work for only one analyte are said to be **specific.** Techniques or reactions that apply to only a few analytes are **selective.**

6. Eliminating Interferences

- Once we have the sample in solution and converted the analyte to an appropriate form for measurement, the next step is to eliminate substances from the sample that may interfere with measurement.

- Few chemical or physical properties of importance in chemical analysis are unique to a single chemical species.

- The reactions used and the properties measured are characteristic of a group of elements of compounds.

- **A scheme must be devised to isolate** the analytes from interferences before the final measurement is made.

An **interference** or **interferent** is a species that causes an error in an analysis by enhancing or attenuating (making smaller) the quantity being measured.

7. Calculating Results

Computing analyte concentrations from experimental data is usually relatively easy, particularly with computers.

These computations are based on

- the raw experimental data collected in the measurement step,
- the characteristics of the measurement instruments,
- the stoichiometry of the analytical reaction.

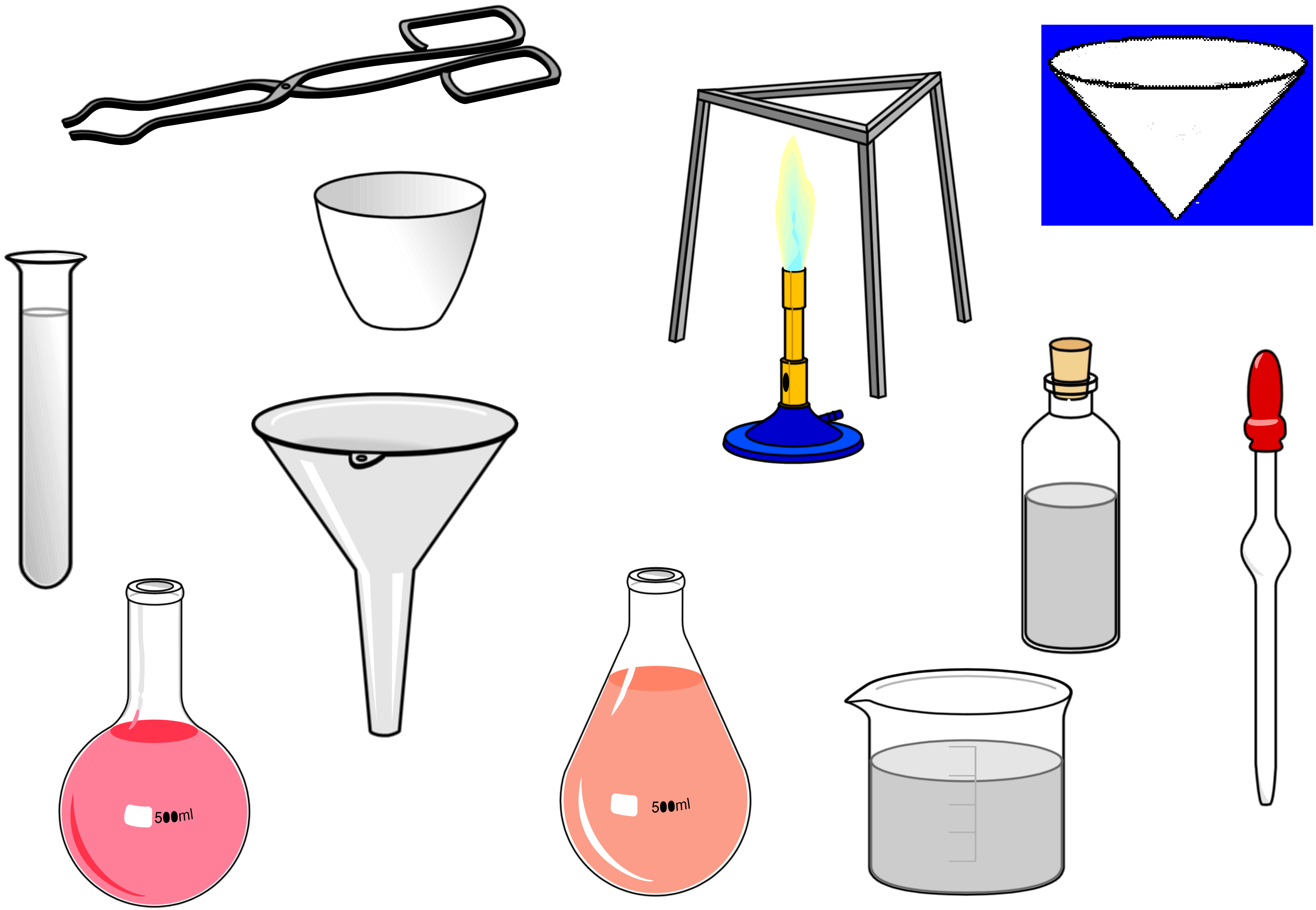
8. Evaluating Results by Estimating Reliability

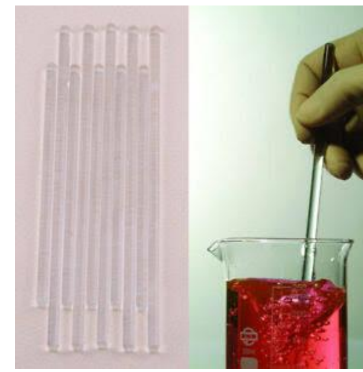
The final step: analytical results are complete only when their reliability has been estimated.

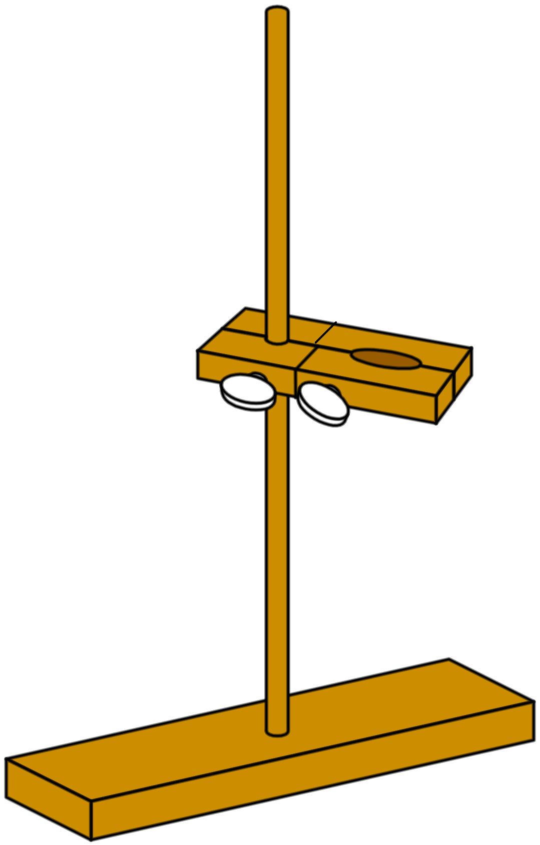
The experimenter must provide some measure of the **uncertainties** associated with computed results if the data are to have any value.

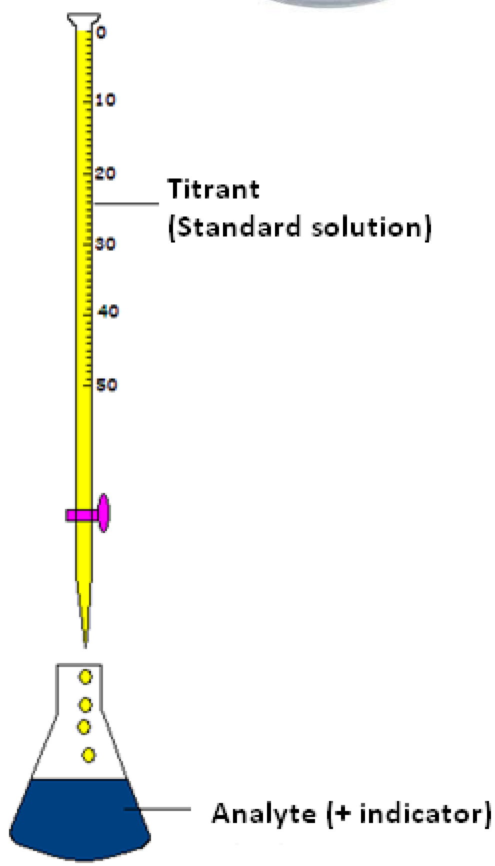
An analytical result without an estimate of reliability is of no value.

Examples of Laboratory Equipments








0
10
20
30
40
50
Titrant
(Standard solution)
Analyte (+ indicator)