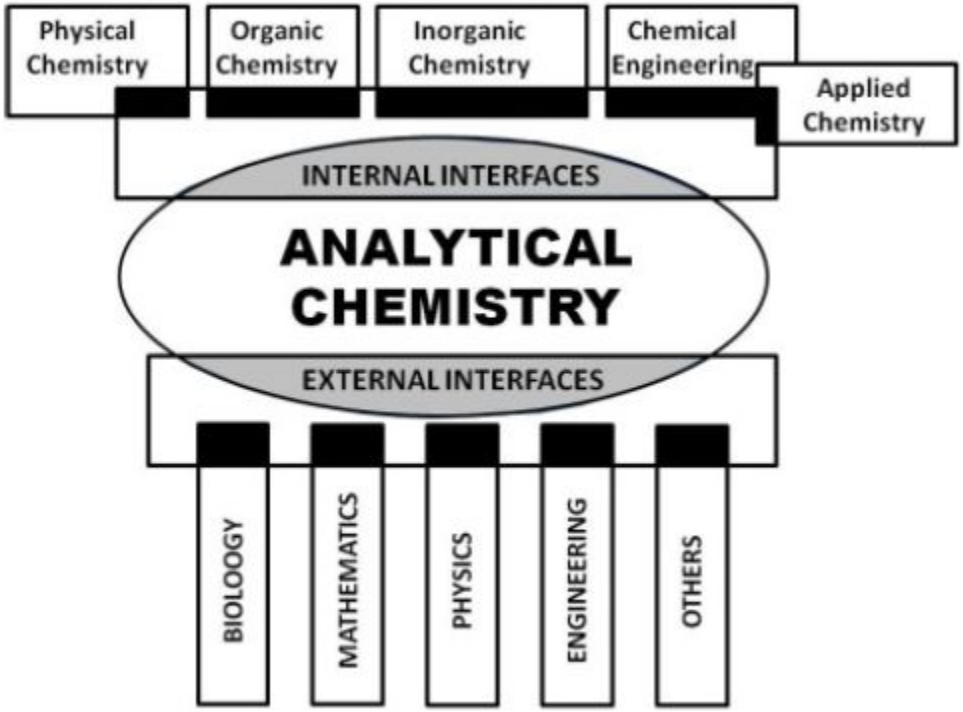
Classification of Analytical Methods

Internal and interdisciplinary interfaces in the realm of Chemistry

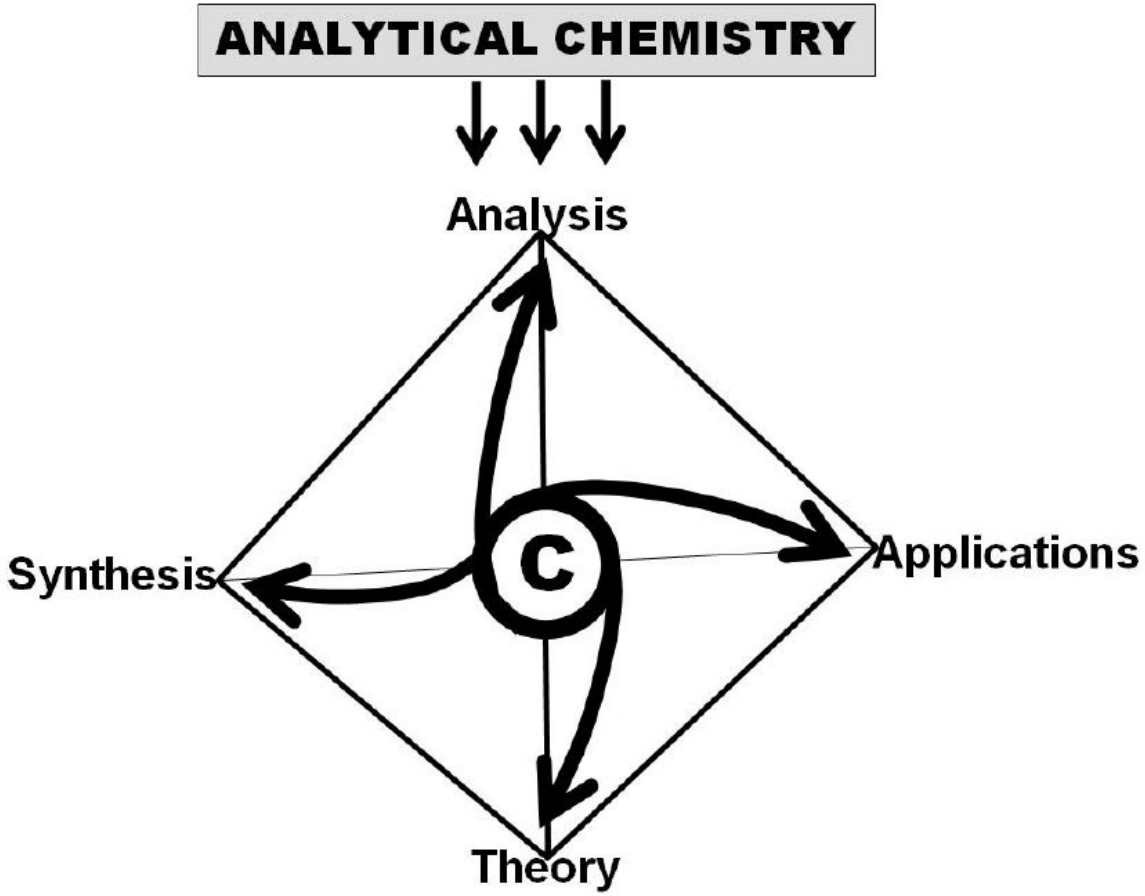


Analytical Chemistry

- *Internal interfaces* with other chemical areas (e.g. organic, inorganic, physical and applied chemistry, chemical engineering).
- *External interfaces* with other scientific and technical disciplines such as biology, biochemistry, mathematics, physics or engineering, where Analytical Chemistry can play an active role (e.g. in the determination of enzyme activities or that of drugs of abuse in biological fluids) or a passive one (e.g. in chemometric developments for data processing or the use of immobilized enzymes in analytical processes).

Analytical Chemistry

- the discipline in charge of “Analysis” (the fourth component of Chemistry in addition to Theory, Synthesis and Applications, all of which are mutually related via the vertices of the tetrahedron in Figure
- the discipline in charge of the production of so named “(bio)chemical information” or “analytical information”; the discipline of (bio)chemical measurements; and the chemical metrological discipline, which is related to the previous definition.


ANALYTICAL CHEMISTRY
Analysis
Synthesis
C
Applications
Theory

Definitions:

- "*Analytical Chemistry is a scientific discipline that develops and applies methods, instruments and strategies to obtain information on the composition and nature of matter in space and time*" (Working Party on Analytical Chemistry of the European Federation of ChemicalSocieties).
- "*Analytical Chemistry is a metrological discipline that develops, optimizes and applies measurement processes intended to produce quality (bio)chemical information of global and partial type from natural and artificial objects and systems in order to solve analytical problems derived from information needs*".

Analytical Chemistry has two essential aims.

- the obtainment of as high metrological quality as possible (i.e. of as true as possible nalytical information with as low as possible uncertainty).
- solving analytical problems derived from (bio)chemical information needs posed by “clients” engaged in a great variety of activities (health, general and agrifood industries, the environment).

Quality indicators

Top or capital analytical properties

- *Accuracy*
- *Reliability*
- *Representativeness*

Basic analytical properties

- *Precision*
- *Sensitivity*
- *Selectivity*

Productivity-related properties

- *Expeditiousness*
- *Cost-effectiveness*
- *Personnel-related factors*

Classification of techniques

- by the type of analytical technique – ***classical*** or ***instrumental*** techniques;
- by the nature of the measurement data generated – ***single-channel*** or ***multi-channel*** techniques;
- by the quantitation method (by which the analyte concentration is calculated) – ***relative*** or ***absolute*** techniques.

Basic Equipment and Instrumentation

Photo of a typical electronic balance.

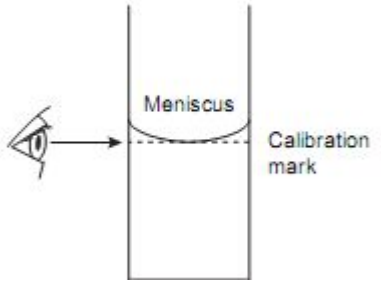
beaker

graduated cylinder

Basic Equipment and Instrumentation

volumetric flask

dropping pipet



Proper means of reading the meniscus on a volumetric flask or pipet.

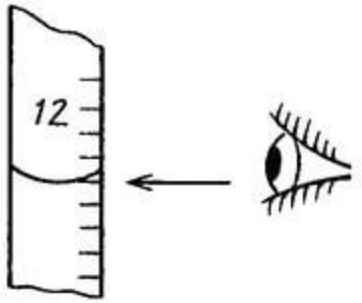
Classical Methods:

- Separation of analytes by precipitation, extraction, or distillation.
- Qualitative analysis by reaction of analytes with reagents that yielded products that could be recognized by their colors, boiling or melting points, solubilities, optical activities, or refractive indexes.
- Quantitative analysis by gravimetric or by titrimetric techniques.

In the early years of chemistry, most analyses were carried out by separating components of interest in a sample by precipitation, extraction, or distillation. For quantitative analyses, the separated components were then treated with reagents that yielded products that could be recognized by their colors, boiling points or melting points, their solubility in a series of solvents, their odors, their optical activities, or their refractive indexes. For quantitative analyses, the amount of analyte was determined by gravimetric or by titrimetric measurement.

- Gravimetric Methods – the mass of the analyte or some compound produced from the analyte was determined.
- Titrimetric Methods – the volume or mass of a standard reagent required to react completely with the analyte was measured.

Titrimetric Analysis



The term **titrimetric analysis** refers to quantitative chemical analysis carried out by determining the volume of a solution of accurately known concentration which is required to react quantitatively with a measured volume of a solution of a substance to be determined. The solution of accurately known concentration is called standard solution

For use in titrimetric analysis a reaction must have the following conditions

1- There must be **a simple reaction** which can be expressed by a chemical equation; the substance to be determined should react completely with the reagent instoichiometric or equivalent properties.

2- The reaction should **be relatively fast**. (Most ionic reaction satisfy this condition.) In some cases the addition of a catalyst may be necessary to increase the speed of areaction.

3- There must be an **alteration in some physical or chemical property** of the solution at the equivalence point.

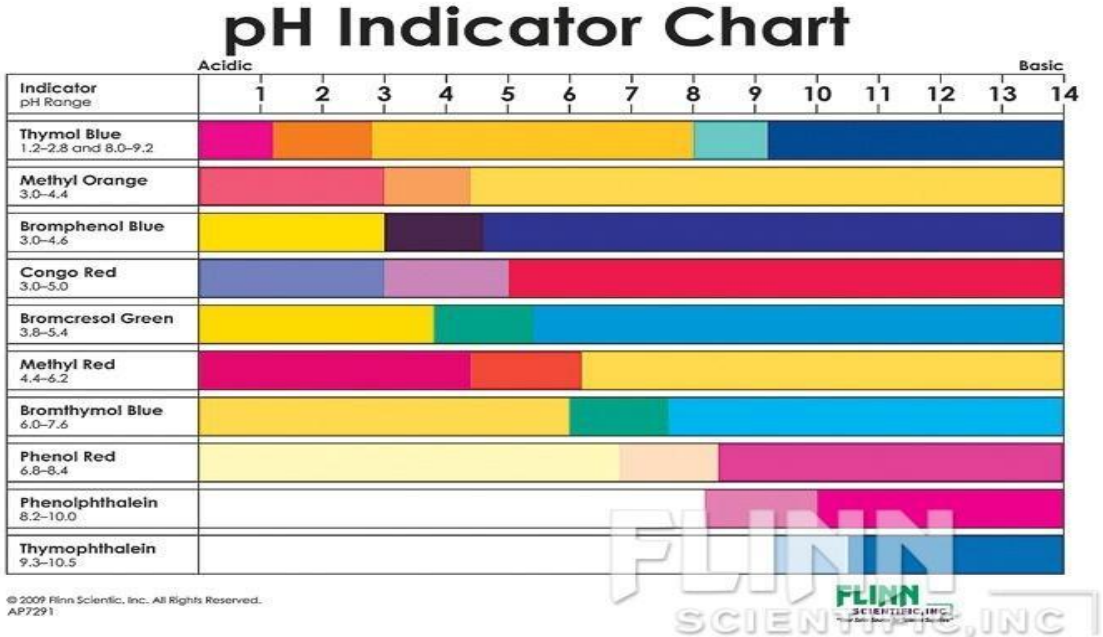
4- An **indicator should be available** which, by a change in physical properties (color or formation of a precipitate), should sharply define the end point of the reaction.

Definition of some terms

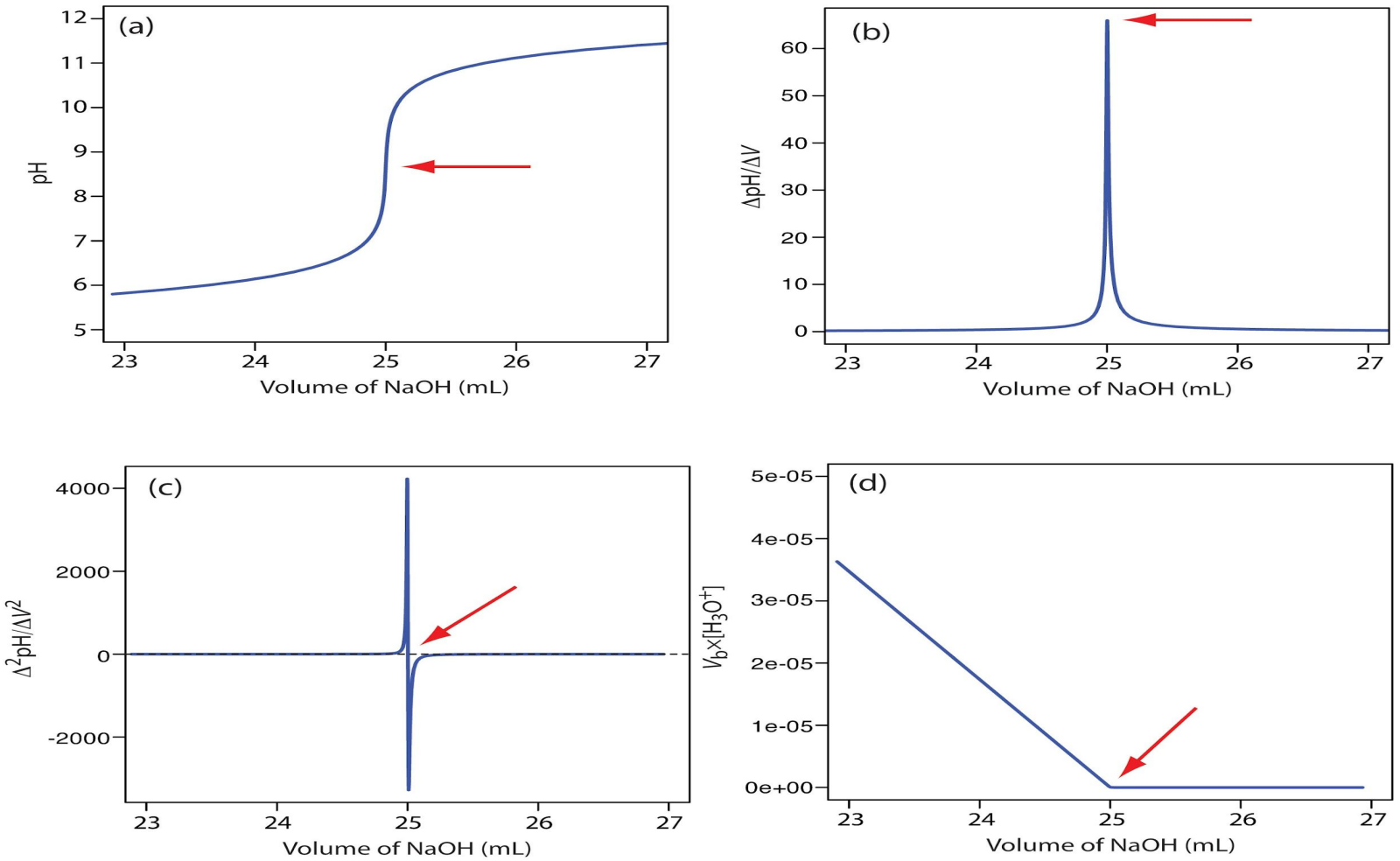
- **Titration is the process in which the standard reagent is added to a solution of ananalyte until the reaction between the analyte and reagent is complete.**
- **Equivalence point and End point** - The equivalence point of a titration is a theoretical point that can not be determine experimentally. Instead, we can only estimate its position by observing some physical change associated with the condition of equivalence. This change is called the end point for titration.
- Titration error - The difference between the observed end point and the true equivalence point in a titration.

Indicators

- Indicators are often added to analyte solution in order to give an observable physical change (end point) at or near the equivalence point. In other wards indicator is a compound having a physical property (usually color) that changes abruptly near thee quivalence point of a chemical reaction.



Titrimetric curve



Classification of reaction in titrimetric analysis

1. **Neutralization reaction**, or acidimetry and alkalimetry. These include thetitration of free bases, or those formed from salts of weak acids by hydrolysis with astandard acid (acidimetry), and the titration of free acids, or those formed by thehydrolysis of salts or weak bases, with a standard base (alkalimrtry). The reactioninvolve the combination of hydrogen and hydroxide ions to form water. Also under this heading must be included titrations in non-aqueous solvents, most of whichinvolve organic compounds.

2. **Precipitation reaction.**

These depend upon the combination of ions to form asimple precipitate as in the titration of silver ion with solution of chloride. No changein oxidation state occurs.

3. **Complex formation reaction**.

These depend upon the combination of ions, other than hydrogen or hydroxide ion, to form a soluble slightly dissociated ion or compound, as in the titration of a solution af a cyanide with silver nitrate.Ethylendiaminetera-acetic acid, largely as the disodium salt of EDTA, is a veryimportant reagent for complex formation titration and has become on of the mostimportant reagents used in titrimetric analysis.

4. **Oxidation-reduction reaction**.

Under this heading are included all reactionsinvolving change in oxidation number or transfer of electrons among the reactivesubstance. The standard solutions are either oxidizing or reducing agents.

Instrumental Methods:

Measurements of physical properties of analytes, such as
- conductivity,
- electrode potential,
- light absorption,
- or emission, mass to charge ratio,
- and fluorescence,

began to be used for quantitative analysis of a variety of inorganic, organic, and biochemical analyte. Highly efficient chromatographic and electrophoretic techniques began to replace distillation, extraction, and precipitation for the separation of components of complex mixtures prior to their qualitative or quantitative determination. These newer methods for separating and determining chemical species are known collectively as instrumental methods of analysis.

The advantages of instrumental methods over classical methods include:

1. The ability to perform *trace analysis*, as we have mentioned.
2. Generally, large numbers of samples may be analyzed very quickly.
3. Many instrumental methods can be automated.
4. Most instrumental methods are multi-channel techniques (we will discuss these shortly).
5. Less skill and training is usually required to perform instrumental analysis than classicalanalysis.

Instrumental analysis can be further classified according to the principles by which the measurement signal is generated

- ***Electrochemical*** methods of analysis
- ***Spectrochemical*** methods of analysis
- ***mass spectroscopy***
- ***chromatography*** and ***electrophoresis***.
- ***electrogravimetry***, and ***potentiostatic amperostatic coulometry***

Lists the names of instrumental methods that are based upon various analytical signals.

Signal	Instrumental Methods
Emission of radiation	Emission spectroscopy (X-ray, UV, visible, electron, Auger); fluorescence, phosphorescence, and luminescence (X-ray, UV, and visible)
Absorption of radiation	**Spectrophotometry and photometry** (X-ray, UV, visible, IR); photoacoustic spectroscopy; nuclear magnetic resonance and electron spin resonance spectroscopy
Scattering of radiation	Turbidimetry; nephelometry; Raman spectroscopy
Refraction of radiation	Refractometry; interferometry
Diffraction of radiation	X-Ray and electron diffraction methods
Rotation of radiation	Polarimetry; optical rotary dispersion; circular dichroism
Electrical potential	**Potentiometry**; chronopotentiometry
Electrical charge	Coulometry
Electrical current	Polarography; amperometry
Electrical resistance	Conductometry
Mass-to-charge ratio	Mass spectrometry
Rate of reaction	Kinetic methods
Thermal properties	Thermal conductivity and enthalpy
Radioactivity	Activation and isotope dilution methods

Electrochemical methods of analysis

- in which the analyte participates in a redox reaction or other process.

In potentiometric analysis, the *analyte is part of a galvanic cell*, which generates a voltage due to a drive to thermodynamic equilibrium. The magnitude of the voltage generated by the galvanic cell depends on the concentration of analyte in the sample solution.

In voltammetric analysis, the *analyte is part of an electrolytic cell*. Current flows when voltage is applied to the cell due to the participation of the analyte in a redox reaction; the conditions of the electrolytic cell are such that the magnitude of the current is directly proportional to the concentration of analyte in the sample solution.

Spectrochemical methods of analysis

- in which the analyte interacts with electromagnetic radiation. Most of the methods in this category are based on the measurement of the amount of light absorbed by a sample; such *absorption-based* techniques include atomic absorption, molecular absorption, and nmr methods.
- The rest of the methods are generally based on the measurement of light emitted or scattered by a sample; these *emission-based* techniques include atomic emission, molecular fluorescence, and Raman scatter methods.

The technique of ***mass spectroscopy***

- in which the analyte is ionized and subsequently detected. Although in common usage, the term “spectroscopy” is not really appropriate to describe this method, since electromagnetic radiation is not usually involved in mass spectroscopy. Perhaps the most important use of mass spectrometers in quantitative analysis is as a gas or liquid chromatographic detector. A more recent innovation is the use of an inductively coupled plasma (ICP) as an ion source for a mass spectrometer; this combination (ICP-MS) is a powerful tool for elemental analysis.

Single-Channel *vs* Multi-Channel Techniques

- ***single-channel*** techniques will generate but a single number for each analysis of the sample. Examples include gravimetric and potentiometric analysis. In the former, the signal is a singlemass measurement (e.g., mass of the precipitate) and in the latter method the signal is a single voltage value.
- • ***multi-channel*** techniques will generate a series of numbers for a single analysis. Multi-channel techniques are characterized by the ability to obtain measurements while changing some independently controllable parameter. For example, in a molecular absorption method, an absorption *spectrum* may be generated, in which the absorbance of a sample is monitored as a function of the avelength of the light transmitted through the sample. Measurement of the sample thus produces a series of absorbance values.

Multi-channel methods have two important advantages over their single-channel counterparts:

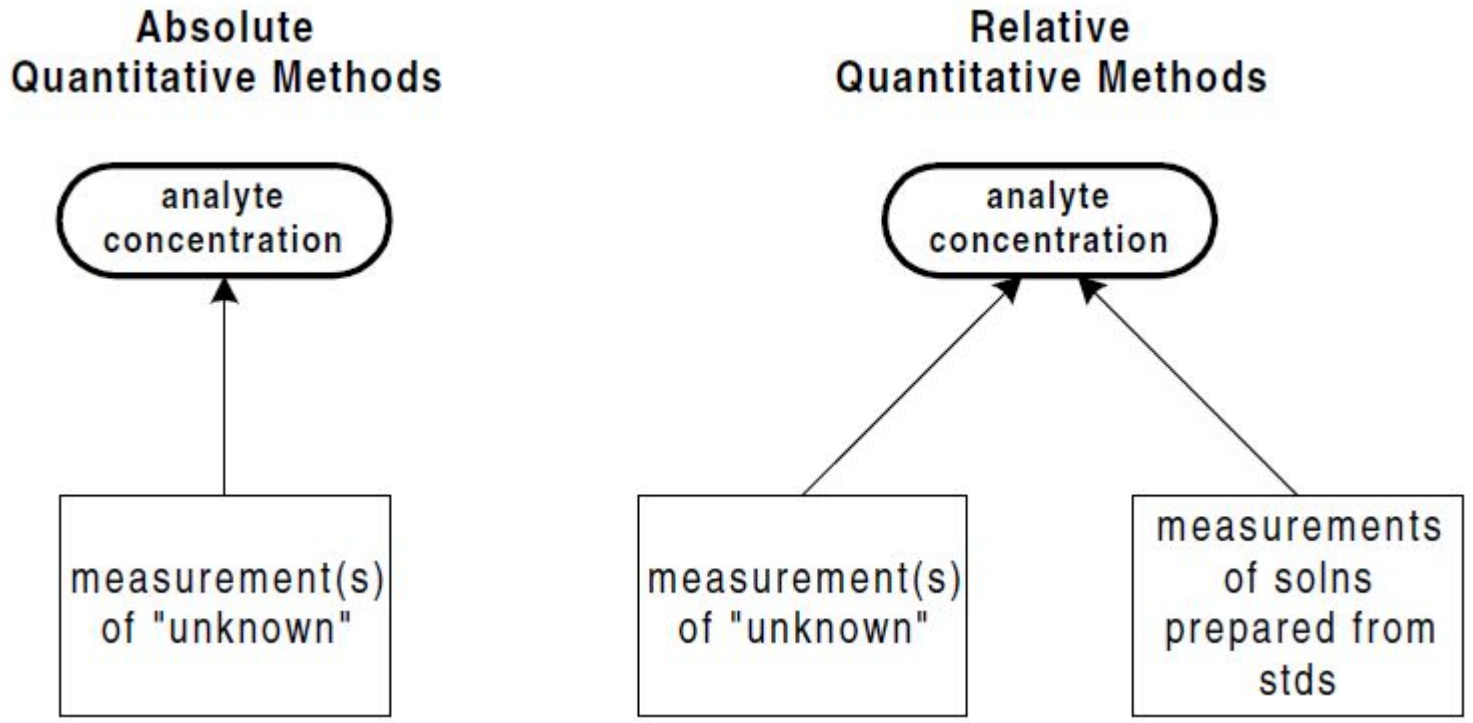
1. They provide the ability to perform *multicomponent analysis*. In other words, the concentrations of more than one analyte in a single sample may be determined.

2. Multi-channel methods can detect, and sometimes correct for, the presence of a number of types of interferences in the sample. If uncorrected, the presence of the interference will result in biased estimates of analyte concentration.

Relative vs Absolute Techniques

- Another way of classifying analytical techniques is according to the method by which the analyte concentration is calculated from the data:
- in absolute analytical techniques, the analyte concentration can be calculated directly from measurement of the sample. No additional measurements are required (other than ameasurement of sample mass or volume).
- in relative analytical techniques, the measurement of the sample must be compared to measurements of additional samples that are prepared with the use of analyte standards (e.g.,solutions of known analyte

The difference between *absolute* and *relative* techniques is that the latter requires
additional measurements in order to obtain an estimate of the analyte concentration.



Characterization of analytical techniques

Technique	Quantity Measured	Single- or multi-channel? (*independent parameter*)	Theoretical Principle
Classical Techniques – all absolute methods[a]			
gravimetry	mass	single-channel	complete/selective rxn of analyte; composition of weighing form is known
electrogravimetry	mass	single-channel	
titrimetry (chemical indicator)	endpoint volume/mass	single-channel	complete/selective rxn of analyte; known stoichiometry of titration reaction
titrimetry (instrum endpt detection)	instrument signal	multi-channel (*volume/mass of titrant solution*)	
amperostatic coulometry	time	single-channel	complete/selective rxn of analyte; Faraday's Law, and the known stoichiometry of titration reaction
potentiostatic coulometry	current	multi-channel (*time*)	
Instrumental Techniques – all relative methods[b]			
potentiometry	potential	single-channel	thermodynamic drive to equilibrium (Nernst)
voltammetry	current	multi-channel (*working electrode potential*)	analyte diffusion controls signal (Fick's Law)
atomic absorption	attenuation of light intensity	single-channel[c]	Beer's Law
molecular absorption	attenuation of light intensity	multi-channel (*wavelength*)	
atomic emission	emitted light intensity	multi-channel (*wavelength*)	signal is proportional to excited-state concentration
molecular fluorescence	fluorescence light intensity	multi-channel[d] (*excitation wavelength* and *emission wavelength*)	

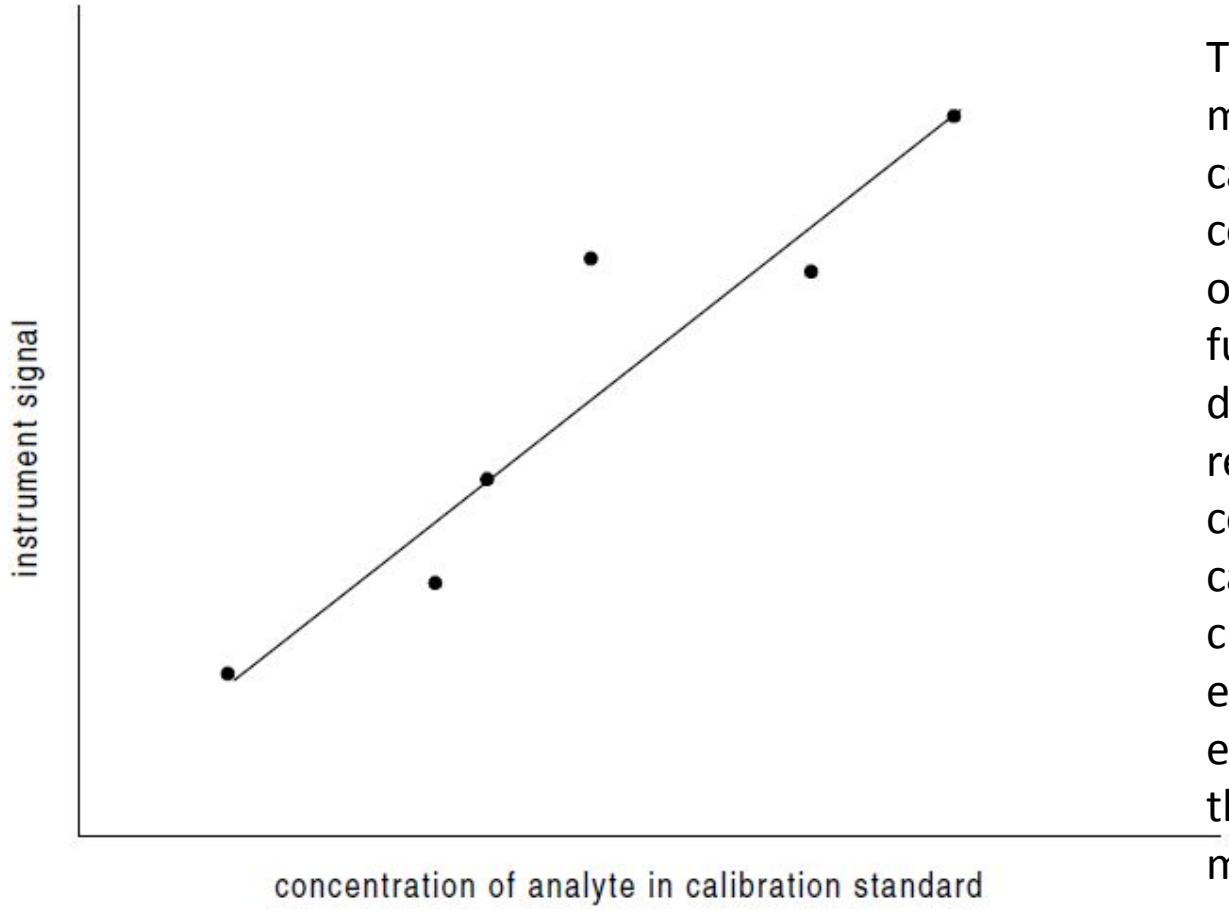
Calibration Curve Method

For any instrumental method used for quantitative chemical analysis, there is some functional relationship between the instrument signal, *r*, and the analyte concentration, *C*A:

$$r = f(C\text{A})$$

The calibration curve approach to quantitation is an attempt to estimate the nature of this functional relationship. A series of ***calibration standards*** are analyzed, and a "best-fit" line or curve is used to describe the relationship between the analyte concentration in the calibration standards and the measured signal. The following figure demonstrates the concept.

Typical calibration curve



The instrument response is measured for a series of calibration standards, which contain a known concentration of analyte. The curve is a function that
describes the functional relationship between signal and concentration. Note that the calibration
curve should never be extrapolated (i.e., never extended beyond the range of the calibration measurements).

The following points should be made about this method of quantitation:

- The central philosophy of the calibration curve method is this: *the function that describes the relationship between signal and concentration for the calibration standards* ***also applies*** *to any other sample* that is analyzed. Any factor that changes this functional relationship will result in a biased estimate of analyte concentration.
- A linear relationship between signal and concentration is desirable, generally resulting in the best accuracy and precision using the fewest number of calibration standards.
- Ideally, the analyte concentration should only be calculated by *interpolation*, not by *extrapolation*. In other words, the analyte concentration should be within the range of concentrations spanned by the calibration standards. If the analyte concentration in thesample is too great, then the sample may be diluted. If the analyte concentration is too small, then additional calibration standards can be prepared. For best precision, the concentration is close to the mean concentration of the calibration standards.

Electroanalytical methods

- **Electroanalytical methods** are a class of techniques in analytical chemistry which study an analyte by measuring the potential (volts) and/or current (amperes) in an electrochemical cell containing the analyte. These methods can be broken down into several categories depending on which aspects of the cell are controlled and which are measured. The three main categories are potentiometry (the difference in electrode potentials is measured), coulometry (the cell's current is measured over time), and voltammetry (the cell's current is measured while actively altering the cell's potential).

Potentiometry

- Potentiometry passively measures the potential of a solution between two electrodes, affecting the solution very little in the process. The potential is then related to the concentration of one or more analytes. The cell structure used is often referred to as an electrode even though it actually contains *two* electrodes: an *indicator electrode* and a *reference electrode* (distinct from the reference electrode used in the three electrode system). Potentiometry usually uses electrodes made *selectively* sensitive to the ion of interest, such as a fluoride-selective electrode. The most common potentiometric electrode is the glass-membrane electrode used in a pH meter.