Chapter 1: Overview of Analytical Techniques

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Definition of Analytical Chemistry

- Analytical chemistry is the branch of chemistry concerned with studying the <u>properties of materials</u> and <u>development of tools</u> <u>used to analyze materials</u>. It is the science of sampling, defining, isolating , concentrating and preserving samples.

Textbook to follow:

 Fundamentals of Analytical Chemistry, Douglas A. Skoog, Donald M. West, F. James Holler, Stanley R. Crouch Any one of the 7 th, 8th and 9 th editions.

Analytical Terminology

- **Qualitative analysis:** An analysis in which we determine the <u>identity of the constituent</u> species in a sample.

- **Quantitative analysis:** An analysis in which we determine <u>how much of a constituent</u> species is present in a sample.

- **Precision** describes the <u>reproducibility</u> of a result. If you measure a quantity several times and the <u>values agree closely</u> with one another, your measurement is precise. If the values vary widely, your measurement is not very precise.

- **Accuracy** describes <u>how close a measured value is to the "true" value</u>. If a known standard is available, accuracy is how close your value is to the known value.
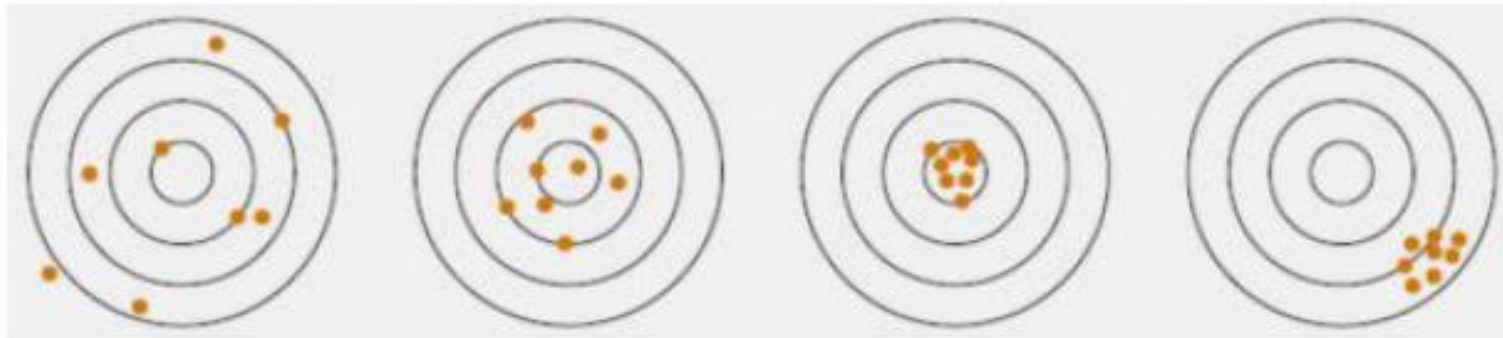
Difference between Precision and Accuracy

Precision

- Precision describes the <u>agreement among several results</u> obtained in the same way.
- Describes the <u>reproducibility</u> of measurements.
- Precision is <u>readily determined by</u> simply <u>repeating</u> the measurement on replicate samples.
- Precision of a set of replicate data may be <u>expressed as</u> <u>standard deviation</u>, <u>variance</u>, and <u>coefficient of variation</u>.

* d_i, deviation from mean, is how much x_i, the individual result, deviates from the mean.

$$d_i = |x_i - \bar{x}|$$

Accuracy

- Accuracy indicates the <u>closeness of the measurement to the true</u> or accepted value and is expressed by the error.
- Accuracy measures <u>agreement</u> between a result and the accepted value.
- Accuracy is often more <u>difficult to determine</u> because the true value is usually unknown. An accepted value must be used instead.
- Accuracy is <u>expressed in</u> terms of either absolute or relative error

Role of Analytical Chemistry

- Analytical chemistry used in many fields:

- In *medicine*, analytical chemistry is the basis for clinical laboratory tests which help physicians diagnosis disease and chart progress in recovery.

- In *industry*, analytical chemistry provides the means of testing raw materials and for assuring the quality of finished products whose chemical composition is critical.

- Many household products, fuels, paints, pharmaceuticals, etc. are analysed by the procedures developed by analytical chemists before being sold to the consumer.

- *Environmental quality* is often evaluated by testing for suspected contaminants using the techniques of analytical chemistry.

- The nutritional value of *food* is determined by chemical analysis for major components such as protein and carbohydrates and trace components such as vitamins and minerals. Indeed, even the calories in a food are often calculated from the chemical analysis.

- *Forensic analysis* - analysis related to criminology; DNA finger printing, finger print detection; blood analysis.

- *Bioanalytical chemistry and analysis* - detection and/or analysis of biological components (i.e., proteins, DNA, RNA, carbohydrates, metabolites, etc.).

Steps in a Chemical Analysis

- Define the problem.

- Select a method.

- Sampling (obtain sample).

- Sample preparation (prepare sample for analysis).

- Perform any necessary chemical separations

- Analysis (perform the measurement).

- Calculate the results and report.

- The first question to be considered in the selection process is the level of accuracy.

- Second is the economical factor for the analysis of the samples.

- Sampling involves obtaining a small mass of a material whose composition accurately represents the bulk of the material being sampled. It is the most difficult step in an analysis and the source of the greatest error.

- An assay is the process of determining how much of a given sample is the material indicated by its name.

- In this the sample is analyse and determine the substance.

Preparation of the samples

- Solid Sample: A solid sample is ground to decrease particle size, mixed to ensure homogeneity, and stored for various lengths of time before analysis.

- Liquid samples are subject to solvent evaporation.

- If the analyte is a gas dissolved in a liquid, analyte must be kept inside a second sealed container to prevent contamination by atmospheric gases.

- Species other than the analyte that affect the final measurement are called interferences, or interferents.

Classifying Analytical Techniques

Classical techniques

Mass, volume, and charge are the most common signals for classical techniques,

and the corresponding techniques are:

1- Gravimetric techniques: the substance being determined is converted into an insoluble precipitate which is collected and weighed or in the special case of electrogravimetry electrolysis is carried out and the material deposited on one of the electrodes is weighed.

2- Volumetric/Titrimetric techniques: the substance to be determined is allowed to react with an appropriate reagent added as a standard solution, and the volume of solution needed for complete reaction is determined. The common types of reaction which are used in titrimetry are (a) neutralisation (acid-base) reactions; (b) complex-forming reactions; (c) precipitation reactions; (d) oxidation-reduction reactions.

3- Coulometeric techniques: (i) voltammetry (measurement of current at a micro-electrode at a specified voltage); (ii) coulometry (measurement of current and time needed to complete an electrochemical reaction or to generate sufficient material to react completely with a specified reagent); (iii) potentiometry (measurement of the potential of an electrode in equilibrium with an ion to be determined); (iv) conductimetry (measurement of the electrical conductivity of a solution).

Instrumental techniques

Optical methods of analysis are dependent either upon (i) measurement of the amount of radiant energy of a particular wavelength absorbed by the sample, or (ii) the emission of radiant energy and measurement of the amount of energy of a particular wavelength emitted. Absorption methods are usually classified according to the wavelength involved as (a) visible spectrophotometry (colorimetry), (b) ultraviolet spectrophotometry, and (c) infrared spectrophotometry.

1- Spectroscopic methods - measuring the interaction between the analyte and electromagnetic radiation (or the production of radiation by an analyte).

2- Electro-analytic methods - measure an electrical property (i.e., potential, current, resistance, amperes, etc.) chemically related to the amount of analyte.

Disadvantage of Instrumental methods

1. The apparatus required for classical procedures is <u>cheap</u> and readily available in all laboratories, but many instruments are <u>expensive</u> and their use will only be justified if numerous samples have to be analysed, or when dealing with the determination of substances present in <u>minute quantities</u> (trace, subtrace or ultratrace analysis).

2. With instrumental methods it is necessary to carry out a <u>calibration operation</u> using a sample of material of known composition as reference substance.

 3. Whilst an instrumental method is ideally suited to the performance of a <u>large number of routine determinations</u>, for an occasional, non-routine, analysis it is often simpler to use a classical method than to go to the trouble of preparing requisite standards and carrying out the calibration of an instrument.

FACTORS AFFECTING THE CHOICE OF ANALYTICAL METHODS

- The type of analysis required: elemental or molecular, routine or occasional.

- Problems arising from the nature of the material to be investigated, e.g. radioactive substances, corrosive substances, substances affected by water.

- Possible interference from components of the material other than those of interest. (d) The concentration range which needs to be investigated.

- The accuracy required.

- The facilities available; this will refer particularly to the kinds of instrumentation which are at hand.

- The time required to complete the analysis

- The number of analyses of similar type which have to be performed

Standard Solution

- A standard solution is a <u>solution of</u> <u>accurately known concentration</u> <u>prepared from</u> <u>a primary standard</u> (a compound which is <u>stable</u>, of <u>high purity</u>, <u>highly soluble</u> in water and of a <u>high molar mass</u> to allow for accurate weighing) that is weighed accurately and made up to a <u>fixed volume</u>.

https://youtu.be/iPYyRNjXkgY

Type of Standard solution

- Primary standard solutions are solutions made out of primary standard substances. A primary standard is a substance of known high purity (99.9% pure) which may be dissolved in a known volume of solvent to give a primary standard solution.

Examples of Primary Standard Solutions and their Applications

(i)   Potassium bromate ($KBrO_3$):Used for the standardization of sodium thiosulfate solutions.

(ii) Sodium chloride (NaCl): Used as a primary standard for silver nitrate

(iii) Zinc powder: Used to standardize EDTA solutions

Secondary Solution

A secondary standard solution is a solution that is made specifically for a certain analysis. A secondary standard is a substance whose active agent contents have been found by comparison against a primary standard. This means it is usually standardized against a primary standard.

Example: (i) Anhydrous sodium hydroxide is a secondary standard. It is highly hygroscopic. (ii) Potassium permanganate is another compound that is often used as a secondary standard. It is less stable and is reactive. Therefore when a Potassium permanganate solution is being prepared, it has to be standardized with a primary standard.

Calculating Concentration of a Primary Standard

You should know:

- the <u>name</u>, and <u>formula</u>, of the compound you used as a primary standard

- m, the <u>mass</u> of this compound that you weighed out and transferred to volumetric flask

- V, the <u>volume</u> of the volumetric flask that you used to make the primary standard solution
(Note that this volume is probably in <u>milliltres</u>, mL)

You will need to calculate:

• M, the molar mass of the compound used as the primary standard

M(compound) = sum of the molar mass of each element multiplied by the number of atoms present in the formula

n, the amount in moles of the compound used to make standard solution

$n = m \div M$

V, the volume of solution in litres

c, the concentration in mol L^{-1} of the primary standard solution

$c = n \div V$

- For the preparation of the sodium carbonate primary standard solution above:

- formula: Na_2CO_3

- $M(Na_2CO_3) = (2 \times 22.99) + 12.01 + (3 \times 16.00) = 105.99$ g mol-1

- $m(Na_2CO_3(s)) = 1.300$ g

- $n(Na_2CO_3(s)) = m \div M = 1.300 \div 105.99 = 0.012265$ mol

- $V(Na_2CO_3(aq)) = 250.00$ mL

  convert volume in mL to volume in L: 250.00 mL $\div 1000$ mL/L $= 0.25000$ L

- $c(Na_2CO_3) = n \div V = 0.012265 \div 0.25000 = 0.04906$ mol L^{-1}

Q: 0.800 g of anhydrous sodium carbonate, Na2CO3(s), is transferred to a 150.0 mL volumetric flask and made up to the mark with distilled water. What is the concentration of the aqueous sodium carbonate solution in mol L⁻¹ in the flask?

0.0503 mol L-1

Q: What mass of potassium hydrogen phthalate, $KH(C_8H_4O_4)$, in grams, must be weighed out in order to make 200.0 mL of 0.250 mol L⁻¹ KH(C8H4O4)(aq) ?
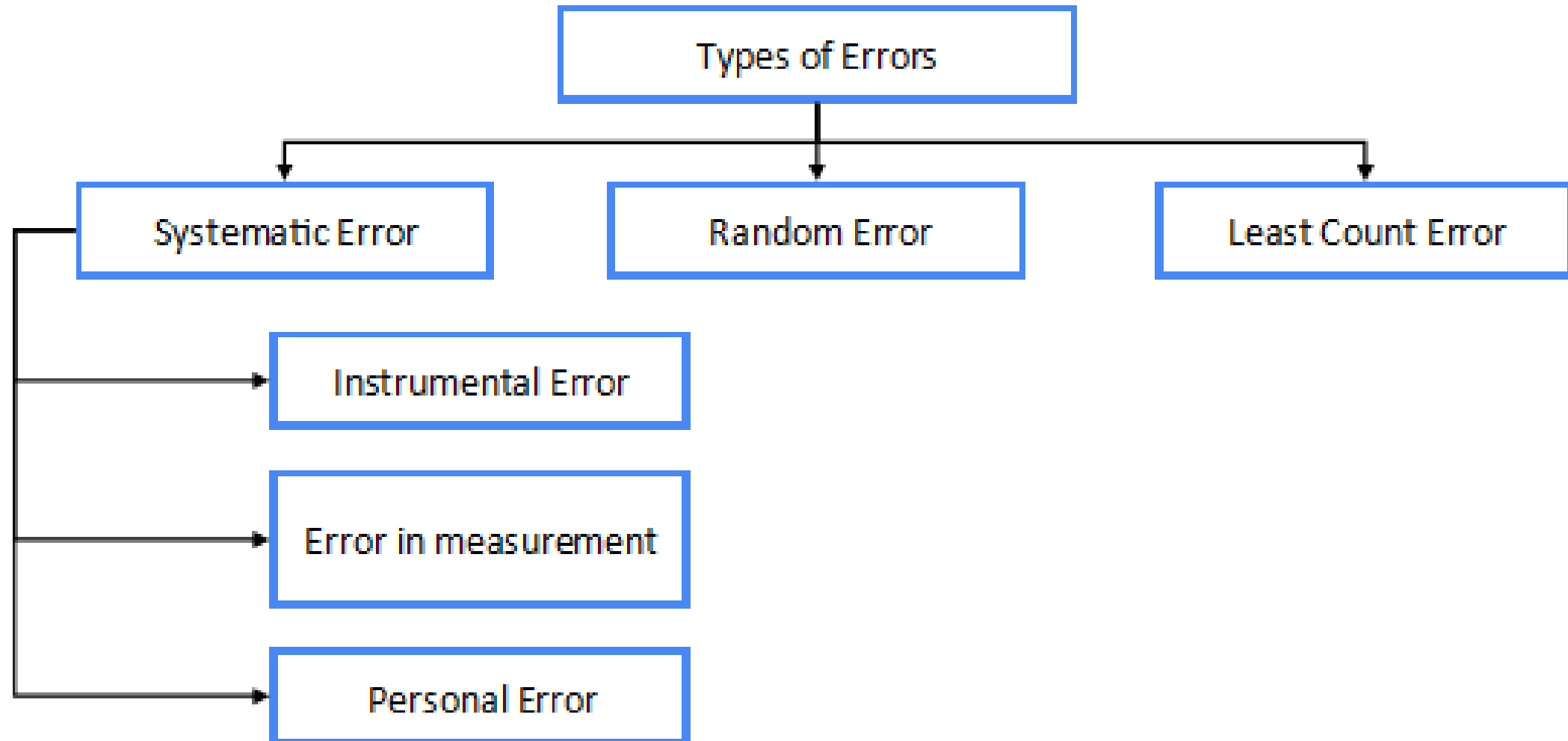
10.2 gm

Types of Errors in Chemical Analysis

The term error has two slightly different meanings.

1) error refs to the difference between a <u>measured value</u> and the <u>"true" or "known" value</u>.

2) error often denotes the <u>estimated uncertainty</u> in a measurement or experiment.

"We can only hope to minimize errors and <u>estimate their size</u> with <u>acceptable accuracy</u>"

Absolute Error

* The absolute error of a measurement is the difference between the measured value and the true value. If the measurement result is low, the sign is negative; if the measurement result is high, the sign is positive.

$$E = x_i - x_t$$

(Should always be positive)

Relative Error

The relative error of a measurement is the absolute error divided by the true value.

Relative error may be expressed in percent, parts per thousand, or parts per million, depending on the magnitude of the result.

$$E_r = \frac{x_i - x_t}{x_t} \times 100\%$$

Chemical analyses are affected by at least two types of errors:

1. Systematic (or determinate) error, causes the <u>mean of a data set to differ from the accepted value.</u>

2. Random (or indeterminate) error, causes data to be scattered more or <u>less symmetrically around a mean value.</u>

A third type of error is **gross error.**

➤ These differ from indeterminate and determinate errors.

➤ They usually occur only occasionally, are often <u>large,</u> and may cause a result to be either high or low.

➤ They are often the <u>product of human errors.</u>

➤ Gross errors lead to <u>outliers,</u> results that appear to differ markedly from all other data in a set of replicate measurements.

Systematic Errors/ Determinate Error

Systematic error is <u>predictable</u> and either <u>constant</u> or else <u>proportional to the measurement</u>.

Typical causes of systematic error include <u>observational error</u>, <u>imperfect instrument calibration</u>, and <u>environmental interference</u>. For example:

- Forgetting to tare or zero a balance produces mass measurements that are <u>always "off" by the same amount</u>. An error caused by not setting an instrument to zero prior to its use is called an **offset error**.
- Not reading the <u>meniscus</u> at eye level for a volume measurement will always result in an inaccurate.
- Measuring length with a <u>metal ruler</u> will give a different result at a cold temperature than at a hot temperature, due to thermal expansion of the material.
- An <u>improperly calibrated thermometer</u> may give accurate readings within a certain temperature range, but become inaccurate at higher or lower temperatures.
- Measured distance is different using a new cloth measuring tape versus an older, stretched one. Proportional errors of this type are called **scale factor errors**.
- **Drift** occurs when <u>successive readings</u> become consistently lower or higher over time. <u>Electronic equipment</u> tends to be susceptible to drift. Many other instruments are affected by (usually positive) drift, as the device warms up.

Instrumental Errors

✓ are caused by nonideal instrument behavior, by faulty calibrations, or by use under inappropriate conditions

✓ Pipets, burets, and volumetric flasks may hold or deliver volumes slightly different from those indicated by their graduations.

✓ Calibration eliminates most systematic errors of this type.

✓ Electronic instruments can be influenced by noise, temperature, pH and are also subject to systematic errors.

✓ Errors of these types usually are detectable and correctable.

Can be corrected by calibration or proper instrumentation maintenance.

Method Errors

❑ The nonideal chemical or physical behavior of the reagents and reactions on which an analysis is based often introduce systematic method errors.

❑ Such sources of nonideality include the slowness of some reactions, the incompleteness of others, the instability of some species, the lack of specificity of most reagents, and the possible occurrence of side reactions that interfere with the measurement process.

❑ Errors inherent in a method are often difficult to detect and hence, these errors are usually the most difficult to identify and correct.

Can be corrected with proper method development

Personal Errors

➤ result from the carelessness, inattention, or personal limitations of the experimenter.

➤ Many measurements require personal judgments.

➤Examples include estimating the position of a pointer between two scale divisions, the color of a solution at the end point in a titration, or the level of a liquid with respect to a graduation in a pipet or buret.

➤Judgments of this type are often subject to systematic, unidirectional errors.

➤A universal source of personal error is prejudice, or bias.

> ➤Number bias is another source of personal error that varies considerably from person to person.

> ➤The most frequent number bias encountered in estimating the position of a needle on a scale involves a preference for the digits 0 and 5.

> ➤ Also common is a prejudice favoring small digits over large and even numbers over odd.

> ➤ Digital and computer displays on ph meters, laboratory balances, and other electronic instruments eliminate number bias because no judgment is involved in

Can be minimized or eliminated with proper training and experience.

Random Error/ Indeterminate Error

Random error primarily affects precision. Typically, random error affects the last significant digit of a measurement.

The main reasons for random error are limitations of instruments, environmental factors, and slight variations in procedure. For example:

•When weighing yourself on a scale, you position yourself slightly differently each time.

•When taking a volume reading in a flask, you may read the value from a different angle each time.

•Measuring the mass of a sample on an analytical balance may produce different values as air currents affect the balance or as water enters and leaves the specimen.

•Measuring your height is affected by minor posture changes.

•Measuring wind velocity depends on the height and time at which a measurement is taken. Multiple readings must be taken and averaged because gusts and changes in direction affect the value.

•Readings must be estimated when they fall between marks on a scale or when the thickness of a measurement marking is taken into account.