Analytical Chemistry

ERRORS IN CHEMICAL ANALYSES

Sawa University

College of Pharmacology

First Stage

جامعـــــة ســـــــاوة الأهلية

كلية الصيدلة

المرحلـــــــــــة الاولى

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المحاضرة الثالثة : الجانب النظري

Introduction

- Measurements invariably involve **errors** and **uncertainties**.
- Only a few of these are due to **mistakes** on the part of the **experimenter.**
- More commonly, **errors** are caused by **faulty calibrations** or standardizations or by **random variations and uncertainties** in results.
- However, **measurement errors are an inherent part of the quantized world in which we live**.
- Because of this, it is impossible to perform a chemical analysis that is totally free of errors or uncertainties.
- We can only **hope to minimize errors** and estimate their size with acceptable **accuracy**.

Some important terms

1. **The Mean and the Median**

- **The mean: The mean** of two or more measurements **is** their **average value**.

$$\bar{X} = \frac{\sum x_i}{N}$$

- **The median: The median is the middle value** in a set of data that has been arranged in numerical order.
- **Note:** The median is used when **there is an outlier value**.

Some important terms

Example: Calculate the mean and median for the data below?

19.6 , 19.4 , 19.5 , 20.1 , 20.3 ,19.8

Solution: The Mean

$$Mean = \bar{x} = \frac{\sum x_i}{N} = \frac{19.6 + 19.4 + 19.5 + 20.1 + 20.3 + 19.8}{6} = 19.78$$

The Median

- If the number of data is even (19.4 , 19.5 , 19.6 , 19.8 , 20.1 , 20.3)

$$Median = \frac{19.6 + 19.8}{2} = 19.7$$

- If the number of data is odd (19.4 , 19.5 , 19.6 , 19.7 , 19.8 , 20.1 , 20.3)

$$Median = 19.7$$

Some important terms

- **Precision: Precision is the closeness of results to others obtained in exactly the same way**.
- Precision describes the **reproducibility** of measurements.
- Three terms are widely used to describe the precision of a set of replicate data:

- **Standard deviation.**

$$S = \sqrt{\frac{\sum(x_i - \bar{x})^2}{N-1}}$$

- **Variance, and**

$$S^2 = \frac{\sum(x_i - \bar{x})^2}{N-1}$$

- **Coefficient of variation**.

$$\boldsymbol{CV = RSD\% = \frac{S}{\bar{X}} * 100}$$

Note: The precision measured by Coefficient of variation and the good precision when Coefficient of variation between ∓ 5 (larger than -5 and smaller than +5) (good precision : $-5 < RSD\% < +5$)

Some important terms

- **Accuracy**: **Accuracy is the closeness of a measured value to the true or accepted value**.

- **Absolute Error:** The absolute error E in the measurement of a quantity x is given by the equation.

$$E = X_i - X_t$$

- **Relative Error**: The relative error E% is often a more useful quantity than the absolute error. The percent relative error is given by the expression.

$$E\% = \frac{X_i - X_t}{X_t} * 100$$

Note: the accuracy measured by Relative Error and the good accuracy when Relative Error between ∓ 5

Example. In the experiment estimating iron in a water sample containing 20 parts per million, and repeating the experiment six times under the same conditions, the measured values for iron were 19.4, 19.5, 19.6, 19.8, 20.1 and 20.3, respectively. **Calculate the accuracy and precision**?

1. Accuracy

$$\text{Measured value}(x_i) = \bar{X} = \frac{\sum x_i}{N} = \frac{19.4 + 19.5 + 19.6 + 19.8 + 20.1 + 20.3}{6} = 19.8$$

$$E\% = \frac{X_i - X_t}{X_t} * 100 = \frac{19.8 - 20}{20} * 100 = \frac{0.2}{20} * 100 = 1\%$$

E% is smaller than 5% therefore, the method has high accuracy.

2. Precision

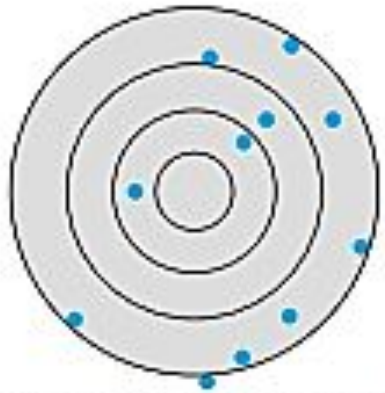
$$s = \sqrt{\frac{\sum(x_i - \bar{x})^2}{N-1}}$$

$$S = \sqrt{\frac{(19.4-19.8)^2 + (19.5-19.8)^2 + (19.6-19.8)^2 + (19.8-19.8)^2 + (20.1-19.8)^2 + (20.3-19.8)^2}{6-1}}$$

$$S = \sqrt{\frac{0.16 + 0.09 + 0.04 + 0 + 0.09 + 0.25}{5}} = \sqrt{\frac{0.63}{5}} = \sqrt{0.126} = 0.355$$

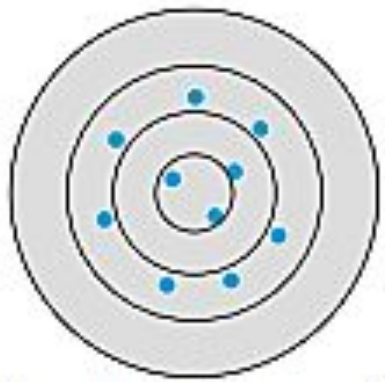
$$RSD\% = \frac{S}{\bar{X}} * 100 = \frac{0.355}{19.8} * 100 = 0.018 * 100 = 1.8\ \%$$

$RSD\%$ is smaller than 5% therefore, the method has high precision



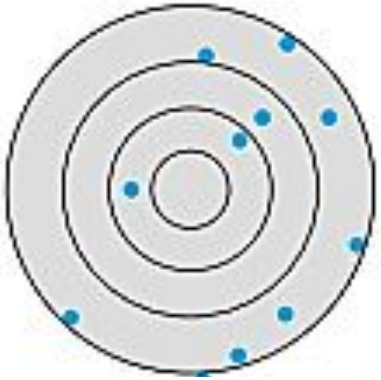
Low accuracy, low precision

Low accuracy, high precision



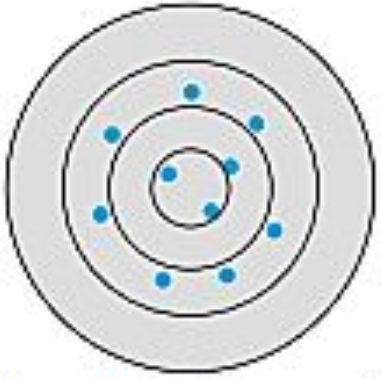
High accuracy, low precision

High accuracy, high precision

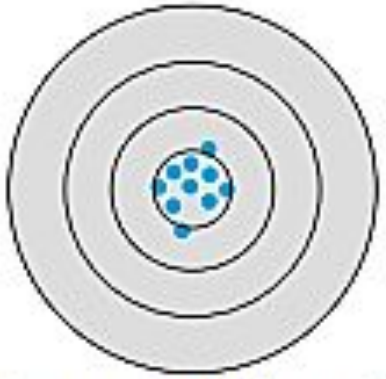


Q/ What you think about the accuracy and precision to that method and is the method is rejected or accepted

Q/ What you think about the accuracy and precision to that figure



Q/ What you think about the accuracy and precision to that figure

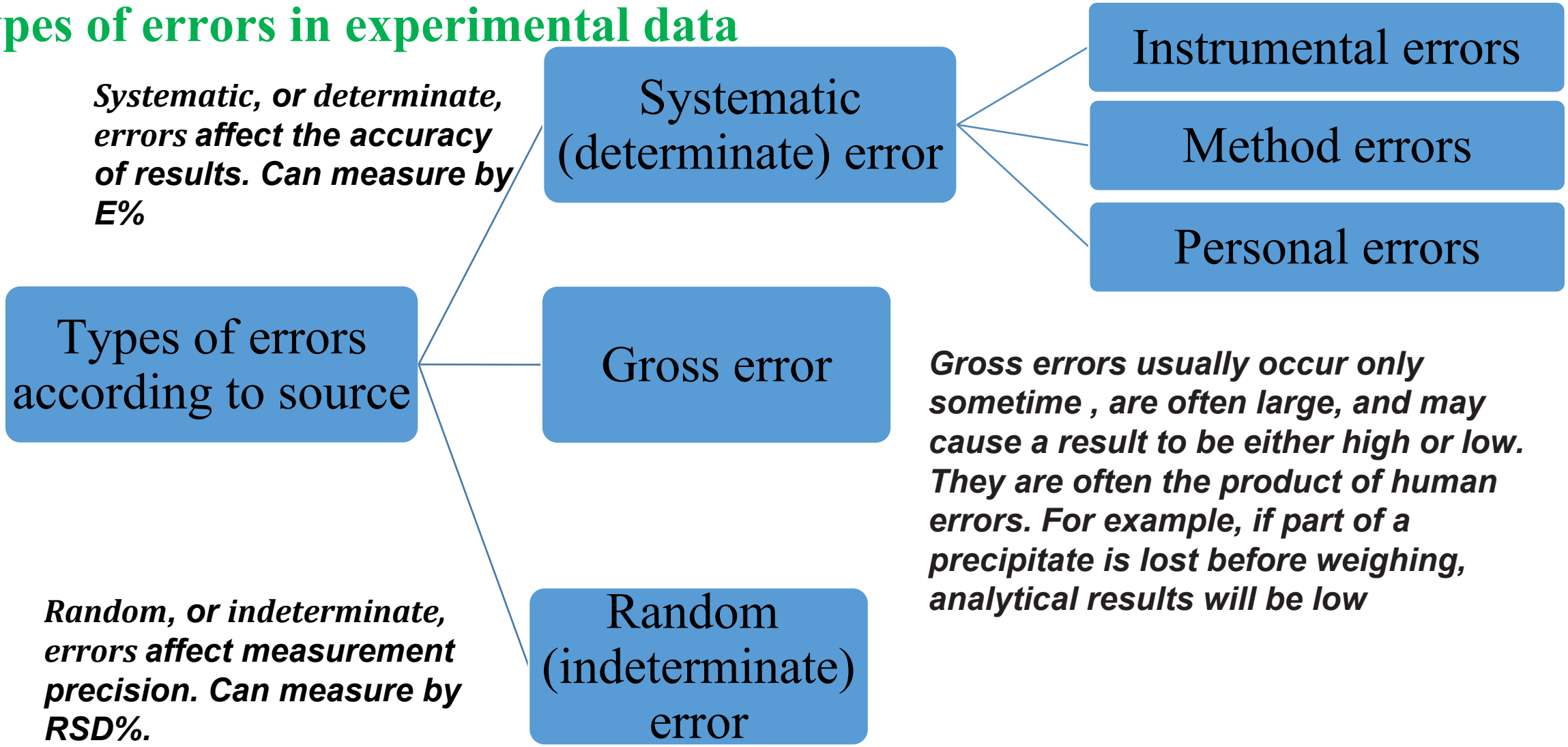


Q/ What you think about the accuracy and precision to that figure

Other important terms

- **Limit of detection (LOD)**: The limit of detection **is the lowest concentration level that can be determined** to be statistically different from an analyte blank.
- **Limit of quantitation (LOQ)**: The limit of quantitation **is the lowest concentration of analyte that can be measured** in the sample matrix **at an acceptable level of precision and accuracy**.
- **Specificity**: Specificity is the ability of an analytical method to **discriminate between similar substances** being analyzed.
- **Sensitivity**: Sensitivity is the ability of an analytical method to **measure the minimum quantities** of analytes under consideration.

Types of errors in experimental data



Systematic, or determinate, errors affect the accuracy of results. Can measure by E%

Gross errors usually occur only sometime , are often large, and may cause a result to be either high or low. They are often the product of human errors. For example, if part of a precipitate is lost before weighing, analytical results will be low

Random, or indeterminate, errors affect measurement precision. Can measure by RSD%.

Detection of systematic instrument error

- The response of most instruments changes with time as a result
  - **Component aging**
  - **Corrosion**
  - **Mistreatment**
- **Periodic calibration** of equipment is always desirable.

Detection of systematic personal error

- Most personal errors can be minimized by
  - **Careful laboratory work.**
  - **Check instrument readings**
  - **Using notebook**
  - **Calculations systematically.**
  - **Using an automated procedure.**

Detection of systematic method errors

- It is difficult to detect the systematic method errors in an analytical method. One or more of the following steps can be taken to recognize and adjust for a systematic error.

1. Analysis of standard reference materials (SRMs)

- Standard reference materials (SRMs) is materials that contain one or more analytes at known concentration levels.
- The first step, is analysis the SRMs by the propose method to know the amount the analyte.
- In step two, E% is calculated. if E% less than 5% , that mean the method has high accuracy and free from the affect systematic error.

Detection of systematic method errors

Example:

In the analyses of RSMs for serum number 909b for knowing the amount of cholesterol (146.4 mg/dL) was found the measured value is 145.5 mg/dL. If we suppose the method free from the instrumental and personal error, find if the method has an effect methodic error or not?

Solution:

$$E\% = \frac{X_i - X_t}{X_t} * 100 = \frac{145.5 - 146.4}{146.4} * 100 = \frac{-0.9}{146.4} * 100 = -0.61\%$$

So as E% is larger than -5% therefore, the method has high accuracy and free from an effect methodic error.

Detection of systematic method errors

2. Independent Analysis

- If standard samples are not available, a second independent and reliable analytical method can be used in parallel with the method being evaluated.

3. Blank Determinations

- **A blank solution: is the solution contains the reagents and solvents used in a determination, but no analyte**. Often, many of the sample constituents are added to simulate the analyte environment, which is called the sample matrix. In a blank determination, all steps of the analysis are performed on the blank material. The results are then applied as a correction to the sample measurements. Blank determinations reveal errors due to interfering contaminants from the reagents and vessels employed in the analysis. Blanks are also used to correct titration data for the volume of reagent needed to cause an indicator to change color.

The laboratory errors may also be grouped into

Types of error according to time

Pre-analytical errors

It is arise before the analysis of sample takes place. Common examples are ***mismatch of sample and laboratory data, error in presentation of analyzed results.***

Analytical errors

It is arise during analytical methods and include errors related to ***expired or spoiled reagents, use of controls or calibrators that have expired, sampling errors, and changes in analyzer's measuring unit***

Post-analytical errors

It is arise after the analysis include errors related to the ***mistake during transmission of data from analyzers, result validation, and communicating results to physicians or patients***

Methods to Minimize the Laboratory Errors

- The routinely used methods being performed in a laboratory should be monitored continuously for any change in **precision** or **accuracy**. The **quality control techniques** must be used regularly to detect such changes and to follow corrective measures.

1. Internal Quality Control

- The internal quality control involves internal processes followed for monitoring of experimental protocols and checking of the resultant data systematically.
  - The correlation of clinical test being used with the diagnosis of disease.
  - The analysis of the same sample should be performed two times, and identical. results must be obtained if no error exists.
  - The reproducibility of samples must be checked frequently.
  - If a test is conducted on patient the second time, then the results obtained from such test may be compared with the previous results. The values may be increased with progression of disease or vice versa.

Methods to Minimize the Laboratory Errors

2. External Quality Control

- The external quality control involves monitoring the resultant outcome of clinical tests by using controls or reference samples provided from other sources.
- The quality control methods are performed at regular intervals by the laboratory personnel by using the controls/standards of an external referral laboratory, without having any idea of resultant value.
- It is helpful to check primarily the accuracy of analytical methods of any laboratory.
- If the results for any methods which are followed in a laboratory show deviation from other established methods, then the methods should be replaced immediately by another after revaluation of other parameters such as the use of calibration standards, reagents, pipettes, and instruments used for measurements.