ANALYTICAL CHEMISTRY

INTRODUCTION

The Scope of Analytical Chemistry

- Analytical chemistry has bounds which are amongst the widest of any technological discipline.
- An analyst must be able to design, carry out, and interpret measurements within the context of the fundamental technological problem with which he or she is presented.
- The selection and utilization of suitable chemical procedures requires a wide knowledge of chemistry, whilst familiarity with and the ability to operate a varied range of instruments is essential.
- Finally, analysts must have a sound knowledge of the statistical treatment of experimental data to enable them to gauge the meaning and reliability of the results that they obtain.
- When an examination is restricted to the identification of one or more constituents of a sample, it is known as *qualitative analysis*, while an examination to determine how much of a particular species is present constitutes a *quantitative analysis*.
- Sometimes information concerning the spatial arrangement of atoms in a molecule or crystalline compound is required or confirmation of the presence or position of certain organic functional groups is sought. Such examinations are described as *structural analysis* and they may be considered as more detailed forms of analysis.
- Any species that are the subjects of either qualitative or quantitative analysis are known as *analytes*.

The Function of Analytical Chemistry

(a) Fundamental Research

- The first steps in unravelling the details of an unknown system frequently involve the identification of its constituents by qualitative chemical analysis.
- Follow-up investigations usually require structural information and quantitative measurements.
- This pattern appears in such diverse areas as the formulation of new drugs, the examination of meteorites, and studies on the results of heavy ion bombardment by nuclear physicists.

(b)Product Development

- The design and development of a new product will often depend upon establishing a link between its chemical composition and its physical properties or performance.
- Typical examples are the development of alloys and of polymer composites.

(c)Product Quality Control

- Most manufacturing industries require a uniform product quality.
- To ensure that this requirement is met, both raw materials and finished products are subjected to extensive chemical analysis.
- On the one hand, the necessary constituents must be kept at the optimum levels, while on the other impurities such as poisons in foodstuffs must be kept below the maximum allowed by law.

(d)Monitoring and Control of Pollutants

- Residual heavy metals and organo-chlorine pesticides represent two well-known pollution problems.
- Sensitive and accurate analysis is required to enable the distribution and level of a pollutant in the environment to be assessed and routine chemical analysis is important in the control of industrial effluents.

(e)Assay

- In commercial dealings with raw materials such as ores, the value of the ore is set by its metal content.
- Large amounts of material are often involved, so that taken overall small differences in concentration can be of considerable commercial significance.

(f)Medical and Clinical Studies

- The levels of various elements and compounds in body fluids are important indicators of physiological disorders.
- A high sugar content in urine indicating a diabetic condition and lead in blood are probably the most well-known examples.

Analytical Problems and Their Solution

The solutions of all analytical problems, both qualitative and quantitative, follow the same basic pattern. This may be described under seven general headings.

(1)Choice of Method

- The selection of the method of analysis is a vital step in the solution of an analytical problem.

- A choice cannot be made until the overall problem is defined, and where possible a decision should be taken by the client and the analyst in consultation.
- Inevitably, in the method selected, a compromise has to be reached between the sensitivity, precision and accuracy desired of the results and the costs involved.
- For example, X-ray fluorescence spectrometry may provide rapid but rather imprecise quantitative results in a trace element problem. Atomic absorption spectrophotometry, on the other hand, will supply more precise data, but at the expense of more time-consuming chemical manipulations.

(2)Sampling

- Correct sampling is the corner stone of reliable analysis.
- The analyst must decide in conjunction with technological colleagues how, where, and when a sample should be taken so as to be truly representative of the parameter that is to be measured.

(3)Preliminary Sample Treatment

- For quantitative analysis, the amount of sample taken is usually measured by mass or volume.
- Where a homogeneous sample already exists, it may be subdivided without further treatment.
- With many solids such as ores, however, crushing and mixing are prior requirements.
- The sample often needs additional preparation for analysis, such as drying, ignition and dissolution.

(4)Separations

- A large proportion of analytical measurements is subject to interference from other constituents of the sample.
- Newer methods increasingly employ instrumental techniques to distinguish between analyte and interference signals.

(5)Final Measurement

- The fundamental necessity is a known proportionality between the magnitude of the measurement and the amount of analyte present.

(6)Method Validation

- It is pointless carrying out the analysis unless the results obtained are known to be meaningful.
- This can only be ensured by proper validation of the method before use and subsequent monitoring of its performance.

- The analysis of validated standards is the most satisfactory approach. Validated standards have been extensively analysed by a variety of methods, and an accepted value for the appropriate analyte obtained.
- A standard should be selected with a matrix similar to that of the sample. In order to ensure continued accurate analysis, standards must be re-analysed at regular intervals.

(7)The Assessment of Results

- Results obtained from an analysis must be assessed by the appropriate statistical methods and their meaning considered in the light of the original problem.

The Nature of Analytical Methods

It is common to find analytical methods classified as *classical* or *instrumental*, the former comprising 'wet chemical' methods such as gravimetry and titrimetry. Such a classification is historically derived andlargely artificial as there is no fundamental difference between the methods in the two groups. All involve the correlation of a physical measurement with the analyte concentration. Indeed, very few analytical methods are entirely instrumental, and most involve chemical manipulations prior to the instrumental measurement. A more satisfactory general classification is achieved in terms of the physical parameter that is
measured

A general classification of important analytical techniques

Group	**:**	**Property measured**
Gravimetric		weight of pure analyte or of a stoichiometric compound containing it
volumetric	**:**	volume of standard reagent solution reacting with the analyte
Spectrometric	**:**	intensity of electromagnetic radiation emitted or absorbed by the analyte.
Electrochemical	**:**	electrical properties of analyte solutions
Radiochemical	**:**	intensity of nuclear radiations emitted by the analyte
Mass spectrometric	**:**	abundance of molecular fragments derived from the analyte
Chromatographic	**:**	physico-chemical properties of individual analytes after separation
Thermal	**:**	physico-chemical properties of the sample as it is heated and cooled

Trends in Analytical Methods and Procedures

- Better instrument design and a fuller understanding of the mechanics of analytical processes enable steady improvements to be made in sensitivity, precision, and accuracy.
- These same changes contribute to more economic analysis as they frequently lead to the elimination of time-consuming separation steps.
- The ultimate development in this direction is a non-destructive method, which not only saves time but leaves the sample unchanged for further examination or processing.

The Language of Analytical Chemistry

- **Analysis**

An **analysis** provides chemical or physical information about a sample. The components of interest in the sample are called **analytes,** and the remainder of the sample is the **matrix.**

- **Determination**

In an analysis we determine the identity, concentration, or properties of the analytes. To make this **determination** we measure one or more of the analyte's chemical or physical properties.

- **Measurement**

An experimental determination of an analyte's chemical or physical properties.

- **Techniques**

A **technique** is any chemical or physical principle that can be used to study an analyte. Many techniques have been used to determine lead levels. For example, in graphite furnace atomic absorption spectroscopy lead is atomized, and the ability of the free atoms to absorb light is measured; thus, both a chemical principle (atomization) and a physical principle (absorption of light) are used in this technique.

- **Methods**

A **method** is the application of a technique for the determination of a specific analyte in a specific matrix. As shown in (Figure 2), the graphite furnace atomic absorption spectroscopic method for determining lead levels in water is different from that for the determination of lead in soil or blood. Choosing a method for determining lead in water depends on how the information is to be used and the established design criteria (Figure 3). For some analytical problems the best method might use graphite furnace atomic absorption spectroscopy,

whereas other problems might be more easily solved by using another technique, such as anodic stripping voltammetry or potentiometry with a lead ion-selective electrode.

Techniques	Graphite furnace atomic absorption spectroscopy		
Methods	Pb in Soil	Pb in Water	Pb in Blood
Procedures	APHA (American Public Health Association) ASTM (American Society for Testing Materials)		
Protocols	EPA (Environmental Protection Agency)		

(Figure 3)

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1. Identify the problem: Determine type of information needed (qualitative, quantitative, or characterization) Identify context of the problem
2. Design the experimental procedure: Establish design criteria (accuracy, precision, scale of operation, sensitivity, selectivity, cost, speed)
    - Identify interferents
    - Select method
    - Establish validation criteria
    - Establish sampling strategy

➢ **Procedures**

A **procedure** is a set of written directions detailing how to apply a method to a particular sample, including information on proper sampling, handling of interferents, and validating results. A method does not necessarily lead to a single procedure, as different analysts or agencies will adapt the method to their specific needs. As shown in Figure 3.2, the American Public Health Agency and the American Society for Testing Materials publish separate procedures for the determination of lead levels in water.

➢ **Protocols**

A **protocol** is a set of stringent written guidelines detailing the procedure that must be followed if the agency specifying the protocol is to accept the results of the analysis.

Protocols are commonly encountered when analytical chemistry is used to support or define public policy. For purposes of determining lead levels in water under the Safe Drinking Water Act, labs follow a protocol specified by the Environmental Protection Agency.

Classifying Analytical Techniques

- Analyzing a sample generates a chemical or physical **signal** whose magnitude is proportional to the amount of analyte in the sample.
- The signal may be anything we can measure; common examples are mass, volume, and absorbance.
- For our purposes it is convenient to divide analytical techniques into two general classes based on whether this signal is proportional to an absolute amount of analyte or a relative amount of analyte.

  Consider two graduated cylinders, each containing 0.01 M $Cu(NO_3)_2$ (Figure 4). Cylinder 1 contains 10 mL, or 0.0001 mol, of Cu^{2+}; cylinder 2 contains 20 mL, or 0.0002 mol, of Cu^{2+}.
- If a technique responds to the absolute amount of analyte in the sample, then the signal due to the analyte, S_A, can be expressed as

$$S_A = kn_A \qquad \text{----------1}$$

where n_A is the moles or grams of analyte in the sample, and k is a proportionality constant. Since cylinder 2 contains twice as many moles of Cu^{2+} as cylinder 1, analyzing the contents of cylinder 2 gives a signal that is twice that of cylinder 1.

Graduated cylinders containing 0.01 M $Cu(NO_3)_2$. (a) Cylinder 1 contains 10 mL, or 0.0001 mol, of Cu^{2+}. (b) Cylinder 2 contains 20 mL, or 0.0002 mol, of Cu^{2+}.

(Figure 4)

- A second class of analytical techniques are those that respond to the relative amount of analyte; thus

$$S_A = kC_A \qquad \text{----------2}$$

where C_A is the concentration of analyte in the sample. Since the solutions in both cylinders have the same concentration of Cu^{2+}, their analysis yields identical signals.

Selecting an Analytical Method

A method is the application of a technique to a specific analyte in a specific matrix. Methods for determining the concentration of lead in drinking water can be developed using any of the techniques mentioned in the previous section. Insoluble lead salts such as $PbSO_4$ and $PbCrO_4$ can form the basis for a gravimetric method.

1. Lead forms several soluble complexes that can be used in a complexation titrimetric method or, if the complexes are highly absorbing, in a spectrophotometric method.
2. Lead in the gaseous free-atom state can be measured by an atomic absorption spectroscopic method.
3. Finally, the availability of multiple oxidation states (Pb, Pb^{2+}, Pb^{4+}) makes coulometric, potentiometric, and voltammetric methods feasible.

The requirements of the analysis determine the best method. In choosing a method, consideration is given to some or all the following design criteria: accuracy, precision, sensitivity, selectivity, robustness, ruggedness, scale of operation, analysis time, availability of equipment, and cost. Each of these criteria is considered in more detail in the following sections.

Accuracy

- **Accuracy** is a measure of how closely the result of an experiment agrees with the expected result.
- The difference between the obtained result and the expected result is usually divided by the expected result and reported as a percent relative error

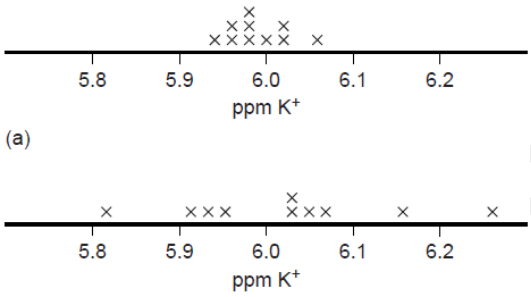
$$\%\ \text{Error} = \frac{\text{obtained result} - \text{expected result}}{\text{expected result}} \times 100$$

- Analytical methods may be divided into three groups based on the magnitude of their relative errors.
- When an experimental result is within 1% of the correct result, the analytical method is highly accurate. Methods resulting in relative errors between 1% and 5% are moderately accurate, but methods of low accuracy produce relative errors greater than 5%.

The magnitude of a method's relative error depends on how accurately the signal is measured, how accurately the value of *k* in equations 1 or 2 is known, and the ease of handling the sample without loss or contamination.

Precision

- When a sample is analyzed several times, the individual results are rarely the same. Instead, the results are randomly scattered.
- Precision is a measure of this variability. The closer the agreement between individual analyses, the more precise the results.
- For example, in determining the concentration of K+ in serum, the results shown in Figure 5(a) are more precise than those in Figure 5(b).
- It is important to realize that precision does not imply accuracy. That the data in Figure 5(a) are more precise does not mean that the first set of results is more accurate. In fact, both sets of results may be very inaccurate.
- As with accuracy, precision depends on those factors affecting the relationship between the signal and the analyte (equations 1 and 2).



Two determinations of the concentration of K^+ in serum, showing the effect of precision. The data in (a) are less scattered and, therefore, more precise than the data in (b).

(Figure 5)

Sensitivity

- The ability to demonstrate that two samples have different amounts of analyte is an essential part of many analyses.
- The **detection limit** is the smallest amount of analyte that can be determined with confidence. The detection limit, therefore, is a statistical parameter.
- Sensitivity is the change in signal per unit change in the amount of analyte and is equivalent to the proportionality constant, *k*, in equations 1 and 2.
- If ΔSA is the smallest increment in signal that can be measured, then the smallest difference in the amount of analyte that can be detected is

$$\Delta nA = \frac{\Delta SA}{k}$$ (total analysis method)

$$\Delta CA = \frac{\Delta SA}{k}$$ (concentration method)

Selectivity

An analytical method is selective if its signal is a function of only the amount of analyte present in the sample. In the presence of an interferent, equations 1 and 2 can be expanded to include a term corresponding to the interferent's contribution to the signal, S_I,

$S_{samp} = S_A + S_I = k_A n_A + k_I n_I$ (total analysis method) **-------3**

$S_{samp} = S_A + S_I = k_A C_A + k_I C_I$ (concentration method) **------4**

where S_{samp} is the total signal due to constituents in the sample; k_A and k_I are the sensitivities for the analyte and the interferent, respectively; and n_I and C_I are the moles (or grams) and concentration of the interferent in the sample.

The **selectivity** of the method for the interferent relative to the analyte is defined by a **selectivity coefficient,** $K_{A,I}$

$$KA, I = \frac{kI}{kA}$$ **------5**

which may be positive or negative depending on whether the interferent's effect on the signal is opposite that of the analyte. A selectivity coefficient greater than +1 or less than –1 indicates that the method is more selective for the interferent than for the analyte. Solving equation 5 for *k*I

$$k_I = K_{A,I} \times k_A$$ **-------6**

substituting into equations 3.3 and 3.4, and simplifying gives

*S*samp = *k*A(*n*A + *K*A,I ´ *n*I) (total analysis method) **---------7**

*S*samp = *k*A(*C*A + *K*A,I ´ *C*I) (concentration method) **-------- 8**

The selectivity coefficient is easy to calculate if k_A and k_I can be independently determined. It is also possible to calculate $K_{A,I}$ by measuring *S*samp in the presence and absence of known amounts of analyte and interferent.

Knowing the selectivity coefficient provides a useful way to evaluate an interferent's potential effect on an analysis. An interferent will not pose a problem as long as the term

$K_{A,I} \times nI$ in equation (7) is significantly smaller than nA, or $K_{A,I} \times C_I$ in equation(8) is significantly smaller than C_A.

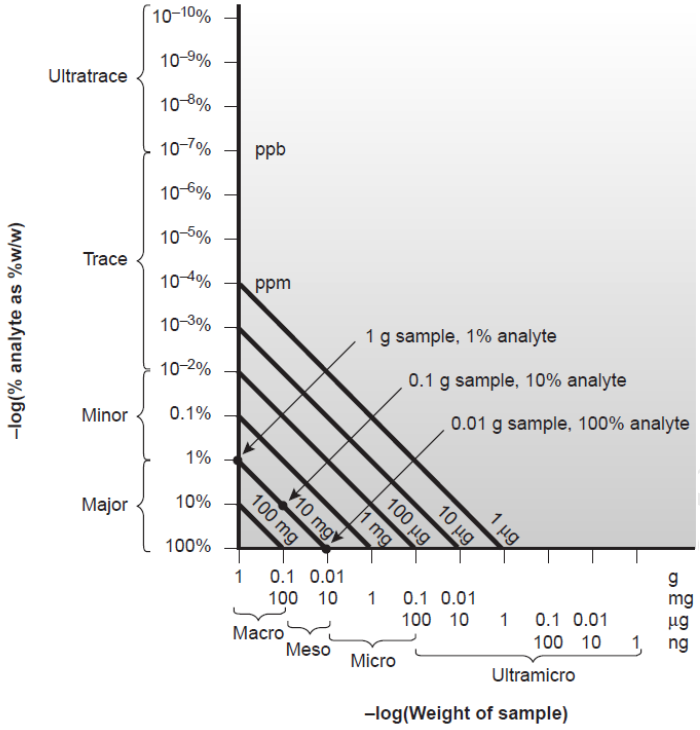
Robustness and Ruggedness

- Methods are subject to a variety of chemical and physical interferences that contribute uncertainty to the analysis.
- When a method is relatively free from chemical interferences, it can be applied to the determination of analytes in a wide variety of sample matrices. Such methods are considered **robust.**
- Random variations in experimental conditions also introduce uncertainty.
- If a method's sensitivity is highly dependent on experimental conditions, such as temperature, acidity, or reaction time, then slight changes in those conditions may lead to significantly different results.
- A **rugged** method is relatively insensitive to changes in experimental conditions.

Scale of Operation

- Another way to narrow the choice of methods is to consider the scale on which the analysis must be conducted.
- The scale of operations in Figure 6 shows the analyte's concentration in weight percent on the *y*-axis and the sample's size on the *x*-axis.
- For convenience, we divide analytes into
    a) major (>1% w/w)
    b) minor (0.01% w/w – 1% w/w)
    c) trace (10^{-7} % w/w – 0.01% w/w) and
    d) ultra trace (< 10–7% w/w) components
- we divide samples into
    a) macro (>0.1 g)
    b) meso (10 mg – 100 mg)
    c) micro (0.1 mg – 10 mg) and
    d) ultra micro (<0.1 mg) sample sizes.
- Note that both the *x*-axis and the *y*-axis use a logarithmic scale.
- The analyte's concentration and the amount of sample used provide a characteristic description for an analysis.
- For example, samples in a macro–major analysis weigh more than 0.1 g and contain more than 1% analyte.

Diagonal lines connecting the two axes show combinations of sample size and concentration of analyte containing the same absolute amount of analyte. As shown in Figure 6, for example, a 1-g sample containing 1% analyte has the same amount of analyte (0.010 g) as a 100-mg sample containing 10% analyte or a 10-mg sample containing 100% analyte.



Scale of operation for analytical methods.

(Figure 6)

Equipment

Finally, analytical methods can be compared in terms of their need for equipment, the time required to complete an analysis, and the cost per sample.

- Methods relying on instrumentation are equipment-intensive and may require significant operator training.
- For example, the graphite furnace atomic absorption spectroscopic method for determining lead levels in water requires a significant capital investment in the instrument and an experienced operator to obtain reliable results.

Time

- The time needed to complete an analysis for a single sample is often fairly similar from method to method.
- This is somewhat misleading, however, because much of this time is spent preparing the solutions and equipment needed for the analysis.

- Once the solutions and equipment are in place, the number of samples that can be analyzed per hour differs substantially from method to method.
- This is a significant factor in selecting a method for laboratories that handle a high volume of samples.

Cost

- The cost of an analysis is determined by many factors, including the cost of necessary equipment and reagents, the cost of hiring analysts, and the number of samples that can be processed per hour.
- In general, methods relying on instruments cost more per sample than other methods.

Making the Final Choice

- Attempts to minimize cost and analysis time may decrease accuracy.
- Selecting a specific method requires a careful balance among these design criteria. Usually, the most important design criterion is accuracy, and the best method is that capable of producing the most accurate results.
- When the need for results is urgent, as is often the case in clinical labs, analysis time may become the critical factor.
- The best method is often dictated by the sample's properties. Analyzing a sample with a complex matrix may require a method with excellent selectivity to avoid interferences.
- Samples in which the analyte is present at a trace or ultratrace concentration usually must be analyzed by a concentration method.
- If the quantity of sample is limited, then the method must not require large amounts of sample.

Determining the concentration of lead in drinking water requires a method that can detect lead at the parts per billion concentrations. Selectivity is also important because other metal ions are present at significantly higher concentrations. Graphite furnace atomic absorption spectroscopy is a commonly used method for determining lead levels in drinking water because it meets these specifications. The same method is also used in determining lead levels in blood, where its ability to detect low concentrations of lead using a few microliters of sample are important considerations.

ERRORS & TREATMENT OF ANALYTICAL DATA

Two main classes of errors can affect the accuracy or precision of a measured quantity,

1. Determinate error/ systematic/ constant error.
2. Indeterminate error/ random error.

1. Determinate error/ systematic/ constant error:

- Are those that, as the name implies, are determinate and that presumably can be either avoided or corrected.
- Determinate errors are often reproducible, and in many cases they can be predicted by person who thoroughly understands all the aspects of the measurement.

Ex: sources of determinate errors are incorrectly calibrated instruments, such as a burette, balances or PH meter and impurities in the reagent, a side reaction in a titration and heating a sample at too high a temperature

Determinate errors have been classified as:

1. Methodical error.
2. Operative error/personal error.
3. Instrumental error.

Methodical error:

These are the most serious errors of an analysis. Most of the above errors can be minimized or corrected for, but errors that are inherent in a method cannot be changed unless the conditions of the determination are altered. some sources of methodical errors includes, *co precipitation of impurities, slightly solubility of a precipitate, side reactions, incomplete reactions, impurities in reagents.*

Operative error/personal error:

These includes personal error and can be reduced by experience and care of the analyst in the physical manipulations involved, operations in which these errors may occur include, *transfer of solutions, effervescences & bumping of samples, incomplete drying of samples, improper washing of ppt., errors in reading burette, allowing hygroscopic materials to absorb moisture, errors in calculations.*

Instrumental error:

These includes faulty equipment, un calibrated weights, un calibrated glass wares, failure of measuring devices to perform in accordance with required standards.

Determinate errors can also be classified as

- ***Constant errors***: a constant error is independent of a magnitude of the measured quantity and becomes less significant as the magnitude.

  Ex: if a constant end point error of 0.10ml is made in a series of titrations, these represents a relative error of 1% for a sample requiring 10ml of titrant, but only 0.2% if 50 ml of titrant is used
- ***Proportional errors;*** the absolute value of this type of error varies with sample size in such a way that the relative error remains constant. A substance that interferes in an analytical method may lead to such an error if present in the sample.

Ex: in the iodometric determination of an oxidant like chlorate, another oxidizing agent such as bromate would cause high results if its presence were unsuspected and not corrected for. Taking larger samples would increase the absolute error, but the relative error would remain constant provided the sample was homogeneous.

2. Indeterminate error/ random error:

Indeterminate errors, as the name implies, cannot be attributed to any known cause, but they inevitably attend measurements made by human beings. They are random in nature and lead to both high and low results with equal probability. They cannot be eliminated or corrected and are the ultimate limitation on the measurement. They can be treated by statistics, & repeated measurement of the same variable can have the effect of reducing their importance.

Minimization of errors:

Detection of Systematic Instrument and Personal Errors

- Some systematic instrument errors can be found and corrected by calibration.
- Periodic calibration of equipment is always desirable because the response of most instruments changes with time as a result of wear, corrosion, or mistreatment.
- Many systematic instrument errors involve interferences in which a species present in the sample affects the response of the analyte.
- Most personal errors can be minimized by care and self-discipline.
- It is a good habit to check instrument readings, notebook entries, and calculations systematically.
- Errors due to limitations of the experimenter can usually be avoided by carefully choosing the analytical method.

Detection of Systematic Method Errors:

- ***Analysis* of *Standard Samples***

The best way of estimating the bias of an analytical method is by the analysis of **standard reference materials,** materials that contain one or more analytes at known concentration levels. Standard reference materials are obtained in several ways

- Standard reference material can be purchased from a number of governmental and industrial sources. For example, the National Institute of Standards and Technology (NIST) (formerly the National Bureau of Standards) offers more than 1300 standard reference materials, including rocks and minerals, gas mixtures, glasses, hydrocarbon mixtures, polymers, urban dusts, rain waters, and river sedirnents."

- ***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.

- ***Blank Determinations***

A **blank** 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, often called the **sample matrix.**

- ***Variation in Sample Size***

The size of a measurement increases, the effect of a constant error decreases. Thus, constant errors can often be detected by varying the sample size.

Characterizing Measurements and Results

Let's begin by choosing a simple quantitative problem requiring a single measurement.

Measures of Central Tendency

Two common ways to report this estimate of central tendency are the mean and the median.

Mean

- The **mean,** $\bar{x}$, is the numerical average obtained by dividing the sum of the individual measurements by the number of measurements

$$\bar{x} = \frac{\sum_{i=1}^{n} X_i}{n}$$

where X_i is the i^{th} measurement, and n is the number of independent measurements.

- The mean is the most common estimator of central tendency. It is not considered a robust estimator, however, because extreme measurements, those much larger or smaller than the remainder of the data, strongly influence the mean's value.

Median:

The **median,** X_{med}, is the middle value when data are ordered from the smallest to the largest value. When the data include an odd number of measurements, the median is the middle value. For an even number of measurements, the median is the average of the $n/2$ and the $(n/2) + 1$ measurements, where n is the number of measurements.

Measures of Spread

Although spread is often defined relative to a specific measure of central tendency, its magnitude is independent of the central value. Changing all measurements in the same direction, by adding or subtracting a constant value, changes the mean or median, but will not change the magnitude of the spread.

Three common measures of spread are range, standard deviation, and variance.

Range:

The **range,** w, is the difference between the largest and smallest values in the data set.

$$\text{Range} = w = X_{\text{largest}} - X_{\text{smallest}}$$

The range provides information about the total variability in the data set, but does not provide any information about the distribution of individual measurements.

Standard Deviation:

The absolute **standard deviation,** s, describes the spread of individual measurements about the mean and is given as

$$\mathbf{s} = \sqrt{\frac{\sum_{i=1}^{n}(Xi - \bar{x})^2}{n-1}} \quad \text{----------1}$$

where X_i is one of n individual measurements, and $\bar{x}$ is the mean.

Frequently, the relative standard deviation, s_r, is reported.

$$s_r = \frac{s}{\bar{x}}$$

The percent relative standard deviation is obtained by multiplying s_r by 100%

Variance:

Another common measure of spread is the square of the standard deviation, or the **variance.** The standard deviation, rather than the variance, is usually reported because the units for standard deviation are the same as that for the mean value.