

## **Chemical Analysis and Working**

### **Definition:**

Chemical analysis, which relies on the use of measurements, is divided into two categories depending on the manner in which the assays are performed. Classical analysis, also termed wet chemical analysis, consists of those analytical techniques that use no mechanical or electronic instruments other than a balance.

For example, the product could be coloured or could be a solid that precipitates from a solution.

### **Introduction**

Most chemical analysis falls into the second category, which is instrumental analysis. It involves the use of an instrument, other than a balance, to perform the analysis. A wide assortment of instrumentation is available to the analyst. In some cases, the instrument is used to characterize a chemical reaction between the analyte and an added reagent; in others, it is used to measure a property of the analyte. Instrumental analysis is subdivided into categories on the basis of the type of instrumentation employed.

Both classical and instrumental quantitative analyses can be divided into gravimetric and volumetric analyses.

### **Gravimetric analysis**

It relies on a critical mass measurement. As an example, solutions containing chloride ions can be assayed by adding an excess of silver nitrate. The reaction product, a silver chloride precipitate, is filtered from the solution, dried, and weighed. Because the product was formed by an exhaustive chemical reaction with the analyte (i.e., virtually all of the analyte was precipitated), the mass of the precipitate can be used to calculate the amount of analyte initially present.

## **Volumetric analysis**

It relies on a critical volume measurement. Usually a liquid solution of a chemical reagent (a titrant) of known concentration is placed in a buret, which is a glass tube with calibrated volume graduations. The titrant is added gradually, in a procedure termed a titration, to the analyte until the chemical reaction is completed. The added titrant volume that is just sufficient to react with all of the analyte is the equivalence point and can be used to calculate the amount or concentration of the analyte that was originally present.

### **Principal Steps;**

The main steps that are performed during a chemical analysis are the following:

- Sampling
- Field sample pretreatment
- Laboratory treatment
- Laboratory assay,
- Calculations
- Results presentation.

Each must be executed correctly in order for the analytical result to be accurate. Some analytical chemists distinguish between an analysis, which involves all the steps, and an assay, which is the laboratory portion of the analysis.

### **Sampling**

During this initial step of analysis, a portion of a bulk material is removed in order to be assayed. The portion should be chosen so that it is representative of the bulk material. To assist in this, statistics is used as a guide to determine the sample size and the number of samples.

When selecting a sampling program, it is important that the analyst has a detailed description of the information required from the analysis, an estimate of the accuracy to

be achieved, and an estimate of the amount of time and money that can be spent on sampling. It is worthwhile to discuss with the users of the analytical results the type of data that is desired. Results may provide needless or insufficient information if the sampling procedure is either excessive or inadequate.

Generally the accuracy of an analysis is increased by obtaining multiple samples at varying locations (and times) within the bulk material. As an example, analysis of a lake for a chemical pollutant will likely yield inaccurate results if the lake is sampled only in the centre and at the surface. It is preferable to sample the lake at several locations around its periphery as well as at several depths near its centre. The homogeneity of the bulk material influences the number of samples needed. If the material is homogeneous, only a single sample is required. More samples are needed to obtain an accurate analytical result when the bulk material is heterogeneous. The disadvantages of taking a larger number of samples are the added time and expense. Few laboratories can afford massive sampling programs.

### **Sample preparation**

After the sample has been collected, it may be necessary to chemically or physically treat it at the sampling site. Normally this treatment is done immediately after the sample has been collected. The nature of the treatment is dependent on the sample and the substances for which it is being analyzed.

**For example**, natural water samples that are assayed for dissolved oxygen generally are placed in containers that are sealed, stored, and transported in a refrigerated compartment. Sealing prevents a change in oxygen concentration owing to exposure to the atmosphere, and refrigeration slows changes in oxygen levels caused by microscopic organisms within the sample.

This process eliminates the need to assay each of the individual specimens. In other instances, the sample must be chemically or physically treated in order to place it in a form that can be assayed.

For example, ore samples normally must be first dissolved in acidic solutions. Sometimes it is necessary to change the concentration of the analyte prior to performing the assay so that it will fall within the range of the analytical method. Once the specimen is prepared, enough laboratory assays are completed to allow the analyst to estimate the amount of random error. Typically a minimum of three assays are performed on each sample.

### **Equation of results**

After the assays have been completed, quantitative results are mathematically manipulated, and both qualitative and quantitative results are presented in a meaningful manner. In most cases, two values are reported for quantitative analyses. The first value is an estimate of the correct value for the analysis, and the second value indicates the amount of random error in the analysis. The most common way of reporting the best value is to give the mean (average) of the results of the laboratory assays.

In specific cases, however, it is better to report either the median (central value when the results are arranged in order of size) or the mode (the value obtained most often).

Accuracy is the degree of agreement between the experimental result and the true value. Precision is the degree of agreement among a series of measurements of the same quantity; it is a measure of the reproducibility of results rather than their correctness. Errors may be either systematic (determinant) or random (indeterminant).

Systematic errors cause the results to vary from the correct value in a predictable manner and can often be identified and corrected. An example of a systematic error is improper calibration of an instrument.

The most frequently reported error estimate is the standard deviation of the results; however, other values, such as the variance, the range, the average deviation, or confidence limits at a specified probability level are sometimes reported. For the relatively

small number of replicate samples that are used during chemical assays, the standard deviation ( $s$ ) is calculated by using equation (1) where  $\Sigma$  represents summation,  $x_i$  represents each of the individual analytical results,  $a$  is the average of the results, and  $N$  is the number of replicate assays.

$$s = \left( \frac{\Sigma(x_i - a)^2}{N - 1} \right)^{1/2} \quad (1)$$

The standard deviation is a popular estimate of the error in an analysis because it has statistical significance whenever the results are normally distributed. Most analytical results exhibit normal (Gaussian) behaviour, following the characteristic bell-shaped curve. If the results are normally distributed, 68.3 percent of the results can be expected to fall within the range of plus or minus one standard deviation of the mean as a result of random error. The units of standard deviation are identical to those of the individual analytical results.

The variance ( $V$ ) is the square of the standard deviation and is useful because, in many cases, it is additive throughout the several steps of the chemical analysis. Consequently, an estimate of the total random error in the analysis can be obtained by adding the variances for each of the individual steps in the analysis. The standard deviation for the overall analysis can then be calculated by taking the square root of the sum of the variances.

### **Preliminary laboratory methods**

A summary, though not comprehensive, of the common laboratory measurements that can be performed to supplement information obtained by another analytical procedure is provided in this section. Many of the methods can be used in the field or in process control apparatus as well as in the laboratory.

Some physical measurements that do not require instrumentation other than an accurate balance can be useful in selected circumstances. Density, specific gravity,

viscosity, and pH measurements are among the more useful measurements in this category.

### **Density measurements**

This property is defined as the ratio of mass to volume of a substance. Generally the mass is measured in grams and the volume in millilitres or cubic centimetres. Density measurements of liquids are straightforward and sometimes can aid in identifying pure substances or mixtures that contain two or three known components; they are most useful in assays of simple mixtures whose components differ significantly in their individual densities. Densities can be used, for example, as an aid in the quantitative analysis of aqueous sugar solutions. Liquid densities usually are measured by using electronic instruments called density meters or pycnometers.

### **Specific gravity measurements**

Specific gravity is a related quantity that is defined as the ratio of the density of the analyte to the density of water at a specified temperature. The procedure used to measure specific gravity often employs an instrument called a hydrometer, which is a glass tube that is sealed at both ends and can float when placed in a liquid. The hydrometer has a graduated scale on the side that allows one to measure specific gravity by observing where the surface of the liquid falls on the scale. Electronic density meters can also be used to measure specific gravity.

### **Viscosity measurements**

Measurements of this kind also provide limited analytical information. Viscosity is a measure of the resistance of a substance to change of shape. Often it is defined as the resistance to flow of a fluid. It is measured in units of poises (dyne-seconds per square centimetre) or a subdivision of poises.

For liquids viscosity is measured with an instrument called a viscometer, of which there are various types. One type of viscometer is a calibrated glass vessel. After inversion, the upper glass bulb is filled to the lower calibration mark by applying suction

with a rubber bulb and drawing the liquid analyte into the apparatus. The device is stoppered at the end near the lower bulb, inverted to its upright position, and placed in a constant-temperature bath. After temperature equilibrium has been established, the stopper is removed. The time required for the volume of liquid between the two marks to drain from the bulb is measured. The time elapsed is used in conjunction with a table supplied by the manufacturer of the bulb to determine the viscosity. The tube at the lower end of the upper bulb has a fixed length and radius that is used along with the pressure differential between the upper and lower ends of the apparatus to measure the viscosity.

### **pH determinations**

The pH of a solution is the negative logarithm (base 10) of the activity (the product of the molar concentration and the activity coefficient) of the hydrogen ions ( $H^+$ ) in the solution. In solutions of low ionic strength, pH can be defined as the negative logarithm of the molar concentration of the hydrogen ions because activity and concentration are nearly identical in these solutions.

One method for determining pH is by use of a chemical acid-base indicator, which consists of a dye that is either a weak acid or a weak base. The dye has one color in its acidic form and a second color in its basic form. Because different dyes change from the acidic to the basic form at different pH values, it is possible to use a series of dyes to determine the pH of a solution. A small portion of the dye or dye mixture is added to the analyte, or a portion of the analyte is added to the dye mixture (often on a piece of paper that is permeated with the indicator).

By comparing the color of the indicator or indicator mixture that is in contact with the sample to the colors of the dyes in their acidic and basic forms, it is possible to determine the pH of the solution. Although this method is rapid and inexpensive, it rarely is used to determine pH with an accuracy greater than about 0.5 pH units.

### **Interference removal**

Regardless of whether a classical or instrumental method is used, it may be necessary to remove interferences from an analyte prior to an assay. An interference is a substance, other than the assayed material, that can be measured by the chosen

analytical method or that can prevent the assayed material from being measured. Interferences cause erroneous analytical results.

Several methods have been devised to enable their removal. The most popular of such separatory methods include distillation, selective precipitation, filtration, complexation, osmosis, reverse osmosis, extraction, electrogravimetry, and chromatography. Some of these methods can be used not only to remove interferences but also to perform the assay.

## **Distillation**

During distillation a mixture of either liquid or liquid and solid components is placed in a glass vessel, called a pot (or boiling flask), and heated. The more volatile components—i.e., those with the lower boiling points—are converted to a gaseous state and exit the pot through a cooling tube, called a condenser, that is located above the pot. The condensed liquids, termed the distillate, are collected in a receiving flask and thereby separated from the less volatile components.

Separation is based on relative boiling points of the components. Normally the efficiency of the separation is increased by inserting a column between the pot and the condenser. A distillation column is a tube that provides surfaces on which condensations and vaporizations can occur before the gas enters the condenser in order to concentrate the more volatile liquid in the first fractions and the less volatile components in the later fractions. The analyte typically goes through several vaporization-condensation steps prior to arriving at the condenser.

## **Selective precipitation**

In some cases, selective precipitation can be used to remove interferences from a mixture. A chemical reagent is added to the solution, and it selectively reacts with the interference to form a precipitate. The precipitate can then be physically separated from the mixture by filtration or centrifugation.

## **Filtration**



This operation can be used to separate particles according to their dimensions. One application is the removal of the precipitate after selective precipitation. Such solid-liquid laboratory filtrations are performed through various grades of filter paper (i.e., those differing in pore size). The mixture is poured either onto a filter paper that rests in a funnel or onto another filtering device.

The liquid passes through the filter while the precipitate is trapped. When the filter has a small pore size, the normal filtration rate is slow but can be increased by filtering into a flask that is maintained under a partial vacuum. In that instance, fritted glass or glass fibre filters often are used in place of paper filters. Solid-gas filtrations are carried out in the laboratory as well.

## **Complexation**

This is another method used to prevent a substance from interfering with an assay. A chemical complexing agent is added to the analyte mixture for the purpose of selectively forming a complex with the interference. A complex is a combination of the two substances and normally remains dissolved. Because the chemical nature of the complex is different from that of the original interference, the complex does not interfere with the assay.

## **Osmosis**

This is a separation technique in which a semipermeable membrane is placed between two solutions containing the same solvent. The membrane allows passage of small solution components (usually the solvent) while preventing passage of larger molecules. The natural tendency is for the solvent to flow from the side where its concentration is higher to the side where its concentration is lower.

Reverse osmosis occurs when pressure is applied to the solution on the side of the membrane that contains the lower solvent concentration. The pressure forces the solvent to flow from a region of low concentration to one of high concentration. Reverse osmosis often is used for water purification. Osmosis or reverse osmosis can be utilized in certain instances to perform separations prior to a chemical assay.

## **Extraction**

Extraction takes advantage of the relative solubilities of solutes in immiscible solvents. If the solutes are in an aqueous solution, an organic solvent that is immiscible with water is added. The solutes will dissolve either in the water or in the organic solvent. If the relative solubilities of the solutes differ in the two solvents, a partial separation occurs. The upper, less dense solvent layer is physically separated from the lower layer. The separation is enhanced if the process is repeated on each of the separated layers.

## **Electrogravimetry**

This method employs an electric current to deposit a solid on an electrode from a solution. Normally the deposit is a metallic plate that has formed from the corresponding metallic ions in the solution; however, other electrode coatings also can be formed.

## **Chromatography**

Chromatography consists of a large group of separatory methods in which the components of a mixture are separated by the relative attraction of the components for a stationary phase (a solid or liquid) as a mobile phase (a liquid or gas) passes over the stationary phase. Chromatography usually is divided into two categories depending on the type of mobile phase that is used. If the mobile phase is a liquid, the technique is liquid chromatography; if it is a gas, the technique is gas chromatography.

In a simple liquid chromatographic apparatus the stationary phase is held in place either in a column or on a plane (such as a plate of glass, metal, or plastic or a sheet of paper). In the case of a column, the lower end is loosely plugged, often with glass wool or a sintered glass disk. Prior to the separation, the column is filled with the mobile phase to a level that is slightly above the level of the stationary phase. The mixture to be separated is added to the top of the column and is allowed to drain onto the stationary phase.

## **Classical methods**

The majority of the classical analytical methods rely on chemical reactions to perform an analysis. In contrast, instrumental methods typically depend on the measurement of a physical property of the analyte.

### **Classical qualitative analysis**

Classical qualitative analysis is performed by adding one or a series of chemical reagents to the analyte. By observing the chemical reactions and their products, one can deduce the identity of the analyte. The added reagents are chosen so that they selectively react with one or a single class of chemical compounds to form a distinctive reaction product. Normally the reaction product is a precipitate or a gas, or it is coloured. Take for example copper(II), which reacts with ammonia to form a copper-ammonia complex that is characteristically deep blue. Similarly, dissolved lead(II) reacts with solutions containing chromate to form a yellow lead chromate precipitate. Negative ions (anions) as well as positive ions (cations) can be qualitatively analyzed using the same approach. The reaction between carbonates and strong acids to form bubbles of carbon dioxide gas is a typical example.

Prior to the qualitative analysis of any given compound, the analyte generally has been identified as either organic or inorganic. Consequently, qualitative analysis is divided into organic and inorganic categories. Organic compounds consist of carbon compounds, whereas inorganic compounds primarily contain elements other than carbon. Sugar ( $C_{12}H_{22}O_{11}$ ) is an example of an organic compound, while table salt (NaCl) is inorganic.

### **Classical quantitative analysis**

Classical quantitative analysis can be divided into gravimetric analysis and volumetric analysis. Both methods utilize exhaustive chemical reactions between the analyte and added reagents. As discussed above, during gravimetric analysis an excess of added reagent reacts with the analyte to form a precipitate. The precipitate is filtered, dried, and weighed. Its mass is used to calculate the concentration or amount of the assayed substance in the analyte.

Volumetric analysis is also known as titrimetric analysis. The reagent (the titrant) is added gradually or stepwise to the analyte from a buret. The key to performing a successful titrimetric analysis is to recognize the equivalence point of the titration (the point at which the quantities of the two reacting species are equivalent), typically observed as a color change. If no spontaneous color change occurs during the titration, a small amount of a chemical indicator is added to the analyte prior to the titration.

Chemical indicators are available that change color at or near the equivalence point of acid-base, oxidation-reduction, complexation, and precipitation titrations. The volume of added titrant corresponding to the indicator color change is the end point of the titration. The end point is used as an approximation of the equivalence point and is employed, with the known concentration of the titrant, to calculate the amount or concentration of the analyte.