INTRODUCTION

The environmental scientists are generally concerned with the identification, characterization and quantification of materials present in the environment, both polluting and non-polluting. In other words, we can say that the important task for an environmental analyst in this context is finding out what and how much of the materials present in the environment. You might know that this task is accomplished by chemical and instrumental analysis done using a number of analytical techniques. In view of the objective of learning the use and significance of analytical techniques generally related to the environment, in the first unit of this course you will be introduced to the various types of analytical techniques available and used by the analysts. The basic principles involved in the process of analysis will be explained. The unit also deals with the criteria for evaluating that includes sampling and measurement. A brief about evaluation of the analytical data would be given along with an introduction to the concepts of errors, accuracy, precision and significant figures. The unit ends with the ways of reporting the results of analysis.

OBJECTIVES

After studying this unit, you should be able to:
Analytical Techniques in Environmental Chemistry

- enlist and explain the analytical techniques used by the environmental scientists for the analysis of polluting and non-polluting components,
- describe in brief the principles involved in the analytical techniques,
- explain the procedure of sampling of environmental materials,
- describe the method of measurement during environmental analysis,
- explain the concept of errors, accuracy, precision and significant figures,
- differentiate between accuracy and precision, and
- state the procedure of reporting the analytical results.

12.2 ANALYTICAL TECHNIQUES: IMPORTANCE

You would agree with the fact that chemicals are part and parcel of our day-to-day life. These include the food we eat, the clothes we wear, the medicines we take, the radiations produced and the wide variety of facilities in the form of latest machines that we use. All of us know that the use of chemicals in excess and without proper knowledge has been responsible for the contamination of our environment in various ways. This has led to various types of pollution and all of us are the victims in some or the other ways. The need of the hour is to assess the levels of pollution and take precautionary measures to combat it.

An environmental analyst analyses the type of chemical and the amount of the chemical present as a pollutant or otherwise in the given sample. The constituents to be analysed may be elements, ions, radicals, functional groups or compounds. The methods or the techniques for chemical analysis are developed by analytical scientists or analysts to accomplish this task and are called analytical techniques. In the process of developing these techniques the analysts try to use the principles from many fields of science viz. chemistry, physics, biology, biochemistry, geology, engineering and computers, etc. The development of new and improved analytical techniques permits separation, detection, structure elucidation and quantification of much lower levels of chemical species, multi-component analysis and a much short duration for analysis.

A substance can be determined by a number of techniques, and the analytical chemist has to select the most advantageous technique available in the laboratory. For choosing a suitable technique, the analyst has to keep in mind the following objectives:

- **Type** of samples to be analysed
- **Information** sought
- **Purpose** of the analysis
- **Accuracy, sensitivity** and **selectivity** of the instrument

The performance of an analysis will depend on the following:

- **Experience** of the analyst

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Sample: A sample is the part of the material, which is examined during analysis.
• Availability of the equipment
• Preparation of the sample for analysis
• Time and Cost involved in the analysis

While choosing an instrumental technique one should be aware of the fact that most instrumental methods are relative methods. Therefore, these must be calibrated with standards. Usually an analytical calibration curve of instrument response versus concentration or amount of the substance is prepared prior to analysis of unknowns.

Let us understand the way the analytical techniques are classified.

### 12.3 CLASSIFICATION OF ANALYTICAL TECHNIQUES

A method to be called as an analytical technique should be based on the measurement of a property, which is related to either the nature or the amount of the substance under examination. The property, which depends on the nature of the substance is helpful in **qualitative** analysis, whereas the property which depends on the amount of the substance is useful in **quantitative** analysis. You will read about both the types in the subsections coming ahead.

As mentioned above the analytical methods depend on the measurement of some physical property. Various physical properties, which are characteristics of a particular substance or its constituent, can be made the basis of an analytical technique. In the broader sense the analytical techniques can be classified on the basis of type of properties in the following way.

i) Chemical methods of analysis
ii) Electrical methods of analysis
iii) Optical methods of analysis
iv) Nuclear radiation methods of analysis
v) Thermal methods of analysis
vi) Separation methods

These methods can further be classified into different techniques depending on the measurement of a characteristic property based on either the nature or the amount of the desired constituent of the sample. We will briefly outline the principles involved in the important and relevant methods under each type in the following subsections. For the sake of an overview the classification is given in Fig. 1.1. The basic principle of the techniques is given in brief thereafter as you would be studying the details in the other units of this course dealing with the specific technique.
Chemical Methods of Analysis

The chemical methods of analysis belong to the broad type of analysis called the quantitative analysis. As mentioned earlier, these methods are based on the measurement of quantity. In one case it is the mass of the substance while in the other the volume is taken into consideration. The corresponding methods are known as gravimetry and volumetry. Both of these being developed at early stages are also known as classical methods of analysis.

i) Gravimetry
Gravimetry is an accurate macro-analysis procedure which mainly depends upon precipitation of an ionic or molecular substance on the basis of a chemical reaction. In gravimetric analysis, the component to be estimated is converted into an insoluble precipitate, which is filtered, dried, ignited and weighed accurately. Knowing the stoichiometry of the chemical reaction involved in precipitation the mass of the precipitate is used to determine the amount of the component in the substance. At undergraduate level you might have estimated barium as barium sulphate following gravimetric analysis.

ii) Volumetry
The amount of the analyte can also be determined by measurement of the volume. The method based on accurate measurement of volume of a reagent solution of accurately known concentration, taken for a reaction is known as volumetric analysis. The measurement of volume saves time to a considerable extent. The greater speed of volumetric analysis is an important advantage over gravimetry.
The volumetric analysis is characterized by a titration; hence the method is also known as **titrimetry**.

You will be learning these chemical techniques while performing the experiments included in the course.

### 1.3.2 Electrical Methods of Analysis

An electrical method of analysis also known as electroanalytical method can be defined as one, in which an electrochemical property of a solution is measured. The electrical quantities, such as, potential, current, quantity of current, resistance and dielectric constant are considered under this class. These methods have been categorised into following briefly explained five types.

Analytical method based on the measurement of potential difference across an electrochemical cell is called **potentiometry**. The result of the analysis can be computed directly from the voltage of the cell, or the equivalence point of a titration known as **potentiometric titration**. In potentiometric titrations we discuss redox titration curves based on half-cell potentials.

A special class of potentiometry where the potential of an indicator electrode is measured as a function of hydrogen ion concentration is called **pHmetry**. By suitably modifying the common voltmeter to high impedance mV meter and usually making use of a glass electrode as a hydrogen ion indicator electrode suitable pHmeters can be designed to measure pH instantaneously.

Amperometry involves current measurements. The term **amperometry** is derived from the word “ampere” which is the unit of current. Amperometry methods are generally applied to the detection of equivalence point of titration and method is known as **amperometric titration**.

i) **Voltammetry**

In voltammetry an electroactive species is consumed (oxidized or reduced) only at the surface layer of the indicator electrode in an electrolytic cell. The resulting current, due to electron transfer process, is measured as a function of applied potential. The current versus potential curves are plotted. In voltammetry we study the relationship between the current and electrode potential and its application to chemical analysis.

ii) **Coulometry**

Analytical methods based on the measurement of the quantity of electricity are designated by the term **coulometry**. The term is derived from “coulomb”, which is one of the units used for quantity of current. A fundamental requirement of all coulometric methods is that the species determined interacts with 100% current efficiency.

iii) **Conductometry**

The measurement of conductance (the reciprocal of the resistance) can sometimes be useful in chemical analysis. Methods based on electrical conductance measurements are grouped under the term **conductometry**. The analysis can be computed directly...
from conductance measurements or by the determination of equivalence point of titrations (conductometric titrations).

1.3.3 Optical Methods of Analysis

The optical methods are called as spectroscopic methods of analysis. These are based on the interaction of electromagnetic radiation (emr) with the quantised energy states of the matter. Here we study the measurement of a quantity based on emission, absorption, scattering or change in some property of electromagnetic radiation depending on the nature or the amount of the constituents of the sample. The classification may be based on either the type of effect (emission, absorption or scattering) or the type of the emr (x-ray, uv-vis, IR etc.) used. The important spectroscopic methods are mentioned below.

i) Emission Spectroscopy

These methods depend on the electromagnetic radiation produced when the analyte is excited by thermal, electrical or radiant energy. Each element has a characteristic emission spectrum, this is applied to qualitative analysis. Quantitative determinations are also possible, as during the burning of the sample under controlled conditions the energy emitted for a given spectral line of an element is proportional to the number of atoms that are excited and consequently to the concentration of element in the sample.

ii) Absorption Spectrometry

This method is based on the measurement of the absorption of electromagnetic radiation by matter. Absorption refers to a process by which a chemical species in a transparent medium selectively absorbs the photons of certain electromagnetic radiation. The absorption varies with the wavelength of incident radiation. Absorbance is easily measured in each spectral region and is of great utility in analytical studies.

iii) Ultraviolet and Visible Absorption Spectroscopy

Analytical method, which involves the measurement of absorption of ultraviolet and visible radiation (wavelength range from 180 to 780 nm) by an atomic, ionic or molecular species, is known as ultraviolet and visible spectroscopic method (UV-VIS). UV and visible spectroscopy involve transitions between electronic levels of absorbing chemical species. These methods find application in qualitative as well as quantitative analysis.

iv) Infrared Absorption Spectroscopy

Infrared absorption spectroscopy (IR) involves the absorption of infrared radiation (wavelength range from 0.78 to 1000 μm) depending on increasing the energy of vibration or rotation associated with a covalent bond, provided that such an increase results in a change in the dipole moment of the molecule. IR spectroscopy finds widespread application in qualitative and quantitative analyses. However, its most important use has been for the functional group identification of organic compounds.
v) **Fluorophotometry**

The energy of the photons of incident radiation absorbed and changes the absorbing species to excited state. Certain chemical substances (known as photoluminiscient) after excitation can re-emit radiation. Re-emission of radiation can be immediately ($< 10^{-8}$ sec) after the absorption and is known as **fluorescence**. The fluorescence intensity is practically proportional to the concentration of fluorescent substance. The measurement of the intensity of fluorescence serves useful analytical purposes and the technique is known as **fluorophotometry**.

When re-emission of radiation takes longer time (minutes, hours or days) the phenomenon is known as **phosphorescence** and the related technique as **phosphorimetry**.

vi) **Turbidimetry and Nephelometry**

Analytical methods where determinations are made by measuring opacity of suspension of small particles with the help of measuring intensity of transmitted light is known as **turbidimetry**.

The analytical method, which is based upon the measurement of intensity of light scattered by a suspension of small particles, is designated as **nephelometry**.

vii) **Raman Spectroscopy**

*Raman spectroscopy* involves the scattering of electromagnetic radiation by a liquid (solution) following **Raman effect** (scattering with change of wavelength). Raman and infrared techniques concern vibrational energy change and they are complimentary to each other. An important advantage of Raman spectra over IR spectra lies in the fact that water does not interfere in Raman spectroscopy and aqueous solutions can be handled very well.

Some other optical methods, namely, flame photometry, refractometry and polarimetry find applications in analytical laboratory but are not considered due to their less importance.

### 1.3.4 Nuclear Methods

These methods can provide analytical information based on nuclear properties. Some of the types of the nuclear methods are given below.

i) Radiochemical Methods

ii) Mossbauer Spectroscopy

iii) Nuclear Magnetic Resonance Spectroscopy

iv) Mass Spectrometry

Table 1.1 lists these methods along with the property measured and the mechanism involved.
Table 1.1: Nuclear methods of analysis with the property measured and the mechanism involved

<table>
<thead>
<tr>
<th>S.N</th>
<th>Name of the method</th>
<th>Property measured</th>
<th>Mechanism involved</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Radiochemical methods</td>
<td>Radioactivity</td>
<td>Radioactive disintegration of radioisotopes can be measured with high sensitivity and specificity.</td>
</tr>
<tr>
<td>2.</td>
<td>Mossbauer spectroscopy</td>
<td>Rasonance absorption of γ-rays</td>
<td>Resonance fluorescence of γ-rays and involves intranuclear energy levels.</td>
</tr>
<tr>
<td>3.</td>
<td>Nuclear magnetic resonance spectroscopy</td>
<td>Position of signals (chemical shift) and their intensity in NMR spectrum</td>
<td>Interaction of quantized nuclear spin with an applied magnetic field</td>
</tr>
<tr>
<td>4.</td>
<td>Mass spectrometry</td>
<td>Position and intensity of signals of mass spectrum</td>
<td>Mass to charge ratio of ionized atoms or molecules</td>
</tr>
</tbody>
</table>

1.3.5 Thermal Methods of Analysis

In thermal methods of analysis some property of the system is measured as a function of temperature. In some of these methods the temperature is used as an independent variable while in some others as a dependent variable say time. The recorded curves are helpful in interpreting the thermal behaviour of the sample.

Thermal methods are classed into nearly a dozen varieties. Out of these some commonly used methods are:

i) Thermogravimetric Analysis (TGA)

ii) Derivative Thermogravimetry (DTG)

iii) Differential Thermal Analysis (DTA)

iv) Differential Scanning Calorimetry (DSC)

v) Thermometric Enthalpy Titrations (TET)

Property measured and instrument used for these methods are given in Table 1.2.

Table 1.2: Thermal Methods

<table>
<thead>
<tr>
<th>S.N</th>
<th>Name of the method</th>
<th>Property measured</th>
<th>As a function of</th>
<th>Instrument</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Thermogravimetric Analysis (TGA)</td>
<td>Change in weight</td>
<td>Temp.</td>
<td>Thermobalance</td>
</tr>
<tr>
<td>2.</td>
<td>Derivative thermogravimetry (DTG)</td>
<td>Rate of change in weight</td>
<td>Temp.</td>
<td>Thermobalance</td>
</tr>
<tr>
<td>3.</td>
<td>Differential Thermal Analysis (DTA)</td>
<td>Heat absorbed or evolved</td>
<td>Temp.</td>
<td>DTA apparatus</td>
</tr>
</tbody>
</table>
### Separation Methods

In the previous subsections 1.3.1 – 1.3.5 you have learnt that the determination of a substance which is free from interfering substances can be accurately made by the direct application of the suitable technique. However, in natural samples because of the complex nature there is always a presence of interfering substances. Extremely few methods may be specific or even selective and accuracy by most methods is affected by the interfering substances. It is, therefore, frequently necessary to perform quantitative separations with the objective either for isolation of the analyte or to remove the interfering substances. Therefore, separation is a prerequisite procedure for such determinations. Though separation is not a purely analytical technique but it is commonly required prior to many analyses.

You will know about some methods of separations in this subsection. In separations, in general by appropriate reactions, the desired constituent is brought into one phase and interfering elements are brought into another and the phases being separated by physical processes. Some methods of separation are the following:

#### A. Classical methods
1. Precipitation
2. Distillation
3. Sublimation
4. Formation of complexes

#### B. Modern methods
1. Chromatography
2. Solvent extraction
3. Ion-Exchange
4. Electrophoresis

You are well aware about the classical methods and only the modern methods will be defined here briefly and you will learn these methods in details in other unit.

#### i) Chromatography

Chromatography is a multistage separation process in which the sample is applied on a stationary phase over which a mobile phase is percolated. Various solutes present in the sample are separated on the basis of differential migration. Chromatography can be classified into various kinds depending on the nature of stationary and mobile phases and the mechanism of distribution involved. These kinds are named as paper chromatography, thin-layer chromatography, liquid chromatography, high performance liquid chromatography, gas chromatography, gel chromatography, partition chromatography, adsorption chromatography, ion exchange chromatography, electrochromatography etc.
Chromatography has been used with remarkable success in the separations of inorganic, organic and biochemical substances. The separations of vitamins, hormones, natural pigments, fission products of uranium and steroids etc. are some good examples of its scope and success.

ii) **Solvent Extraction**

In solvent extraction, a desired solute can be isolated/extracted by distributing it between two immiscible liquids. It exploits the differential solubility of a given solute in two immiscible solvents to separate it from the given mixture. Solvent extraction can be applied as a single stage procedure or a multistage procedure (counter current extraction).

iii) **Ion Exchange**

*Ion exchange* is a stoichiometric process in which a solid (insoluble) material, known as ion exchanger, when comes in contact with an electrolyte solution takes either positive or negative ions (known as counter ions) and releases the ions of like charge (to maintain the stoichiometry) to the solution. The solid materials having cations as exchangeable ions are known as *cation exchangers* and having anions as exchangeable ions are known as *anion exchangers*. Ion exchange is a reversible process. The exchanged ions can be replaced by other ions of like charge. Ion exchangers find great utility in separating the ionic species of similar nature. Some separations of common interest are of rare earth elements and of amino acids.

iv) **Electrophoresis**

The movement of charged particles in the influence of an electric field, in general, is known as *electrophoresis*. If the components of a mixture have different velocities under the influence of the electric field, it is possible to separate them. This method has been used with remarkable success for the separation and characterization of polysaccharides, nucleic acids, haemoglobins and other high-molecular-weight compounds. Small organic and inorganic ions can also be separated with the help of this technique (known as *ionophoresis*).

**SAQ 1**

What is the essential feature of a method to be called as an analytical technique?

**SAQ 2**

Name the methods that are now known as classical methods.

**SAQ 3**

Define polarography.

**SAQ 4**

Is chromatography a single stage or a multistage separation process?

**12.4 CRITERIA FOR EVALUATING**

Analytical chemistry is of enormous importance in science and industry. It deals with the development of methods for chemical analysis which are utilized in detection, determination and separation of chemical constituents and structure elucidation.
of chemical compounds. For example, the chemical formula of an unknown substance is ascertained from the percentage contents of its constituents found by analysis. Today, with the help of newer techniques, such as mass spectrometry, NMR spectroscopy, high performance liquid chromatography, etc., the structure elucidation has become more perfect.

Utility of analytical techniques is to be found in various fields as the key to the solution of a variety of scientific problems and of industrial problems. It is a chemical discipline with interdisciplinary character providing valuable information in many branches of science and technology. All fundamental laws are based on analysis. Mechanisms in so many chemical reactions are developed as a result of analysis. Much of what is known of the mechanisms by which chemical reactions occur has been learned through kinetic studies employing quantitative measurements of the rates at which reactants are consumed or products are formed. You understand the importance of rates in an industrial process to decide the cost of the products coming out of an industry.

The results of a typical quantitative analysis are based upon two series of measurements, one of which is related to the amount of sample taken, and the second to the relative amount of the desired constituent present in the sample. On the basis of the amount of the sample taken the methods are named as macro, meso, micro, and ultramicro methods. On the basis of the relative amount of the desired constituent the results take the form of numerical data in suitable units such as percent, parts per million, parts per billion or some other form.

In order to understand the criteria for evaluating the utility of the analytical techniques, it is useful to identify the several steps in performing quantitative analyses. A complete analysis actually consists of the following main steps:

i) Sampling
ii) Dissolution of the sample
iii) Separation of interfering substances
iv) Measurement
v) Interpretation of the measurements

**Sampling**
The heart of the quantitative analysis is to carry a sample with great care through a number of manipulations without accidental losses and without introducing foreign material, since the sample is representative of all components and their amounts as contained in the bulk material. Conclusions will be drawn about the composition of the bulk material from the analysis of a very small portion of the material. Knowledge of statistics is of considerable importance as an aid to establishing sampling programmes so that data obtained may be subjected to statistical treatment when necessary.

Sampling techniques may be quite different in different cases. Each type of material has its own special sampling instructions, which take into account the specific characteristics of the material, the quantity taken, its purpose, etc.
Dissolution of the Sample
Most analyses are performed on solutions of the sample. Therefore, suitable solvent is required to dissolve the sample rapidly and under conditions in which there is no loss of the analyte. The dissolution process depends on the nature of the sample material.

Two most common methods employed in dissolving inorganic sample are (1) treatment with hydrochloric acid, nitric acid, mixture of hydrochloric and nitric acids, sulphuric acid or perchloric acid, and (2) fusion with an acidic or basic flux followed by treatment with water or an acid.

Organic solvents are preferentially taken to dissolve the samples of organic nature. However, special methods are to be developed to dissolve a silicate material, a high molecular weight polymer or a specimen of animal tissue.

Separation of Interfering Substances
The interfering substances are the compounds or elements that prevent the direct measurement of the species being determined. Therefore, before an analytical measurement can be made it is usually necessary to solve the problem of interferences by their separation from the analyte.

There may be two ways in general to achieve separation (i) by isolating the desired constituent in a measurable form or (ii) by removing the interfering substances from the desired constituent.

In most of the separation techniques the substance of interest is transferred from one phase to another. Therefore the separation procedures can be classified depending on the type of phases involved in these procedures. There may be four such combinations: solid-liquid, liquid-liquid, solid-gas and liquid-gas.

Measurement
The way of measurement depends upon the type of analytical technique being used. A gravimetric method involves the measurement of weight of a suitable form of the analyte. In a volumetric method the measurement is of the volume of a solution of known concentration which is required to react with the analyte. A characteristic feature of most instrumental methods is the necessity for finding empirically the value of the intensity factor corresponding to the mass or concentration of a given constituent. The majority of these methods therefore, require calibration by the use of a standard containing a known amount of constituent, which serves as a basis for comparison in the measurement.

The established procedure must be followed carefully in individual quantitative determinations. Equal care must be taken in the choice of suitable technique for the desired determination. The success or failure of an analysis is often critically dependent upon the proper selection of method.

The analytical chemistry can save much time and improve the accuracy of results by a critical comparison of the various methods on the basis of certain criteria.
Although no simple rule can be prescribed but some essential characteristics of a method which must always be considered are the following:

a) The complexity of the materials to be analysed
b) The probable concentration of the species of interest
c) Accuracy
d) Sensitivity and detection limit
e) Selectivity
f) Duration of an analysis
g) Cost of equipment

**Interpretation of the Measurement**

The result of an analytical measurement after proper calculation is usually reported in relative terms, that is, in some way that expresses the quantity of the analyte present per unit weight or volume of the sample. Thus the results take the form of numerical data in suitable units such as percent, parts per million or some other.

The methods of statistics are commonly used and are especially useful in expressing the analytical results. You should remember that the analytical results can be reliable only if all the conditions for which the particular method was developed and verified are strictly obeyed. Any deviation from these conditions leads to error and loss in accuracy.

**SAQ 5**
Name any two criteria helpful in comparing the analytical methods.

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**12.5 EVALUATION OF ANALYTICAL DATA**

A chemical analysis is usually more than a simple measurement. In a measurement the operator mainly takes care of three components: the system, some property being measured, and the instrument. Errors originate in all three components and need to be considered in a measurement. It is a real fact that no single physical measurement is perfectly accurate. The question of accuracy must, in general, receive attention both before and after an analysis. The aspect which can answer the quality assurance is the evaluation of analytical data.

The purpose of this unit is to provide sufficient information to the student to enable him to examine the factors affecting the reliability of results and understand the contributions of errors, their types, their minimization for accuracy and precision of the measurement and the proper use of significant figures.

**1.5.1 Errors and detection of Errors**

The data obtained by a physical measurement should always raise the question of errors and their nature. Various types of errors are caused in quantitative chemical
analysis. It is, therefore, worthwhile to account for these errors. Now first understand what are error and its types.

**Error**

The error is an inverse measure of the accuracy of a result. Less the error, more accurate the result is. Error is mathematically defined as the difference between the observed value and the true value:

\[ E = O - T \quad (2.1) \]

where \( E \) is the error (absolute error), \( O \) is the observed value of a measurement, and \( T \) is the true value. It is with regard to sign, and it is reported in the same units as the measurements. Let us consider, for example, for the capacity of a measuring flask whose true value, as given by standard measurements, is 250 ml. For a series of 5 measurements done by an analyst the error is represented in Table 1.3.

**Table 1.3: Expression of Error in Measurements in Volume of a Flask**

<table>
<thead>
<tr>
<th>Serial Number of observations</th>
<th>Observed value (ml)</th>
<th>True value (ml)</th>
<th>Error (E) (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>249</td>
<td>250</td>
<td>-1</td>
</tr>
<tr>
<td>2</td>
<td>247</td>
<td>250</td>
<td>-3</td>
</tr>
<tr>
<td>3</td>
<td>250</td>
<td>250</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>248</td>
<td>250</td>
<td>-2</td>
</tr>
<tr>
<td>5</td>
<td>251</td>
<td>250</td>
<td>1</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td></td>
<td><strong>-5 ml</strong></td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td></td>
<td></td>
<td><strong>-1 ml</strong></td>
</tr>
</tbody>
</table>

The error represented in the above table is the absolute error and the average

\[ \text{Error} = \frac{\text{Total error}}{\text{Number of Observations}} = \frac{-5 \text{ ml}}{5} = -1 \text{ ml} \]

However, the absolute error is of little practical significance for a quantitative analysis. It is the relative error, that is, the error relative to the true value \( (E/T) \) expressed in suitable units, is of the practical importance as a measure of inaccuracy (or as an inverse measure of accuracy). It is convenient to express relative error in terms of percentage (parts per hundred), or parts per thousand (ppt), preferably.

To understand the importance of relative error let us consider the measurement of the capacities of three standard flasks of 10, 100 and 1000 ml by three analysts A, B and C respectively represented as follows:

**Table**

<table>
<thead>
<tr>
<th>Analyst</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>T =</td>
<td>10 ml</td>
<td>100 ml</td>
<td>1000 ml</td>
</tr>
<tr>
<td>O =</td>
<td>11 ml</td>
<td>101 ml</td>
<td>1001 ml</td>
</tr>
<tr>
<td>E =</td>
<td>1 ml</td>
<td>1 ml</td>
<td>1 ml</td>
</tr>
<tr>
<td>Relative Error = ( E/T )</td>
<td>1/10 = 0.1</td>
<td>1/100 = 0.01</td>
<td>1/1000 = 0.001</td>
</tr>
<tr>
<td>% R.E. = ((E\times100)/T)</td>
<td>10%</td>
<td>1%</td>
<td>0.1%</td>
</tr>
</tbody>
</table>
You see that the absolute error in all the three cases is the same (1 ml), but the comparison of the relative errors tells that the error (inaccuracy) in case of the analyst C is the least and hence his result is the most reliable out of all the three.

However, for a finite measurement the true value is, usually, not known and the scatter is measured in terms of deviation which is the difference between the observed value and the mean of the given set of data. You will study about the deviation in detail in the next unit (Unit 3) of this block.

**Types of Errors**

For a practical point of view, it is useful to classify errors into two categories: (i) determinate errors, and (ii) indeterminate errors.

i) **Determinate Errors**
As the name implies, determinate errors are those whose magnitude can be determined after assigning a definite cause and thereby they can be corrected for. For example, weighing of a hygroscopic salt like calcium chloride. Its weight will vary according to water absorbed by it from atmosphere if it were weighed in open. The error caused due to absorption of water by the salt can be corrected for if the salt were weighed after drying and keeping in a desiccator.

The determinate errors may be constant or variable. When the determinate error possessed the same value from one measurement to another under a variety of conditions, is called a constant error, for example, error due to uncalibrated weights. On the other hand, in certain cases the determinate errors may vary in magnitude with conditions, for example, the errors caused due to expansion or contraction of volumetric solutions with a change in temperature. The magnitude of the change in volume can be determined by noting the temperature. These variable determinate errors are sometimes called systematic errors. Commonly people do not use this designation of systematic error only for variable errors but frequently call both types of determinate errors (constant or variable) as systematic errors and we shall also follow the same nomenclature.

**Indeterminate Errors**

Indeterminate errors are the errors for those no exact cause can be assigned, hence they cannot be corrected. The sources of these errors may be similar to those for the determinate errors but no definite causes out of these can be assigned for indeterminate errors. Even after applying every correction for the possible determinate errors the replicate observations may vary. Such a variation in observations is due to the indeterminate errors. These errors follow the rules of chance or the laws of probability and are also known as Random Errors. These errors, which accompany every determination, are quite irregular and generally small.

Indeterminate errors cannot be prevented or eliminated by corrections. However, they can be considerably reduced by increased care in work, and increase of the number of replicate determinations. Their pattern of occurrence can be analysed by the techniques of statistics in order to secure a worthwhile insight into their magnitudes, frequencies of occurrence, and effects on the final expression of
results. A plot of the normal distribution of occurrence of indeterminate errors can be prepared.

**Sources of Determinate Errors**
Determinate errors may be caused by numerous sources. It is not needed to enumerate them all but more important ones are given as follows:

- Errors due to reagents: The quality of the reagents is very important in the quantitative analysis. Certain reagents may possess impurities that will interfere in a particular quantitative analysis. Errors are also caused by the use of incorrectly standardized solutions for titration.

  a) **Personal errors**: These errors are caused due to constitutional inability of an analyst to make certain observations accurately, that is, they are caused due to some natural weakness of the analyst. For example, some persons always detect the end point a little past in titration because their inability to judge colour changes exactly. Personal errors also include the so called psychological errors, due to certain bias often met within students, for example, some students often tend to choose in a burette reading the division which is closer to the previous determination or even to those found by his fellow students rather than the actual one. Obviously, this makes the results less accurate.

  b) **Operational errors**: The operational errors are associated with the operation of an analysis. These errors are independent of the instrument and the apparatus employed, also these errors are not related to the chemical properties of the system in hand. Their magnitude depends more upon the analyst himself than on any other factor. They are mainly caused by carelessness of the operator in a quantitative work, for example, loss in bumping of uncovered solution while heating, failure to remove precipitate quantitatively from vessels, underwashing or overwashing of precipitate, etc.

  c) **Methodic errors**: Sometimes a particular method for the determination of a particular constituent in the given sample may not be accurate because of improper selection of the procedure in the required range and will give the inaccurate result. For example, in the determination of iron (present in traces) in water, the gravimetric method will not give the correct result, and a method suitable for trace contents, say, a spectrophotometric method should be selected. The methodic errors are inherent in the method, and cannot be corrected unless the correct method is applied.

**SAQ 6**
In an analysis the observed value is 5.24 g compared with the accepted (true) value of 5.28 g. What is the relative error in parts per thousand?
1.5.2 Accuracy and Precision

You have experienced that a single measurement cannot be taken as an accurate result. A single result could be in error of one kind or the other. Our confidence in an analytical result is increased by increasing the number of parallel determinations (replicate determinations). When assessing the final results it is necessary to judge (i) their accuracy, and (ii) their precision. It will be worthwhile to understand the meanings of these two terms while evaluating the analytical data.

Accuracy

The term accuracy is defined as the nearness of a measurement to its true value (or accepted value). It is expressed in terms of error. Error (defined in section 2.2) is an inverse measure of accuracy. Less the error greater is the accuracy. Thus, after knowing the relative error the loss in accuracy can be estimated.

There are various ways and units to express the accuracy of a measurement. The most common being either in terms of percent relative error or in terms of relative accuracy in percentage. Consider the illustration.

Example 2.1

A sample was analyzed for desired constituent having 2.62 g as the true value. The results of three measurements were 2.50 g, 2.54 g, and 2.52 g. Find the error of the mean (mean error), the percent relative error and the relative accuracy of the mean of the measurements.

Solution

<table>
<thead>
<tr>
<th>Measurement (O)</th>
<th>True Value (T)</th>
<th>Error (O-T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.50 g</td>
<td>2.62 g</td>
<td>– 0.12 g</td>
</tr>
<tr>
<td>2.54 g</td>
<td>2.62 g</td>
<td>– 0.08 g</td>
</tr>
<tr>
<td>2.52 g</td>
<td>2.62 g</td>
<td>– 0.10 g</td>
</tr>
<tr>
<td>Total 7.56</td>
<td>Total – 0.30 g</td>
<td>Mean Error = –0.10 g</td>
</tr>
<tr>
<td>Mean 7.56/3 = 2.52 g</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

% Relative Error = $\frac{\text{Mean Error}}{\text{True Value}} \times 100 = \frac{-0.10}{2.62} \times 100 = -3.8%$

Relative Accuracy (%) = $\frac{\text{Mean}}{\text{True Value}} \times 100 = \frac{2.52}{2.62} \times 100 = 96.2%$

Also it can be calculated from % R.E. as = 100 – 3.8 = 96.2%

Precision

Precision is defined as the reproducibility of measurements. It tells an agreement between the numerical values of replicate measurements. The magnitude of random errors determines the precision of the analytical results. It follows that the closer the results of replicate determinations are to each other, the more precise is the analysis considered to be. Precision in a common way is expressed in terms of deviation. Less the deviation more precise the result is. Deviation or apparent error is defined as the difference between the measured value and the mean (average) of the series of measurements.
The deviation bears a relationship to the mean value of a series similar to that which exists between the absolute error and the true value. Mathematically,

\[ d = K - \bar{x} \quad (2.2) \]

where, \( d \) is the deviation, \( x_i \) is the observation, and \( \bar{x} \) is the mean of series of measurements, \( \bar{x} = \frac{x_1 + x_2 + \ldots + x_n}{n} = \frac{\sum x_i}{n} \) where symbol \( \sum \) represents summation (add all). Deviation is, generally, taken without regard to sign.

It is more informative to express the precision in terms of relative deviation which is deviation relative to the mean expressed in suitable units.

Thus, average deviation (a.d.) = \( \frac{d_1 + d_2 + d_n}{n} = \frac{\sum(x_i - \bar{x})}{n} \)

and \% a.d. = \( \frac{\text{a.d.}}{\bar{x}} \times 100 \)

The most important measures of precision are the standard deviation and the variance. The standard deviation \( s \) of a measurement is theoretically given by:

\[ s = \sqrt{\frac{d_1^2 + d_2^2 + \ldots + d_n^2}{n-1}} \quad (2.3) \]

where, \( n \) is the number of observations and \((n-1)\) is known as the degree of freedom.

Variance \( V \) is the square of the standard deviation,

\[ V = s^2 = \frac{\sum d^2}{n-1} \quad (2.4) \]

**Distinction between Accuracy and Precision**

The accuracy should not be confused with the precision. Good agreement in parallel determinations signifies that the determinations have been made under closely similar conditions, it does not guarantee the accuracy of the results. A method may be precise but may not be accurate if a large systematic error is made. On the other hand it is nearly impossible to have accuracy without good precision. The difference of the terms accuracy and precision can be illustrated by considering the shooting of series of bullets on the targets by three riflemen (A, B, C), shown in Figure 2.1.
Rifleman A has the ideal marksmanship. His all hits are in centre. His results are both accurate and precise. The shooting by rifleman B shows a good grouping of hits which indicate that the marksman is undoubtedly consistent, but in this target the grouping is centered at 3 O’clock hence cannot be considered as representing accurate shooting. His results agree well mutually means precise, but the final result (obtained as their mean value) differs somewhat from the actual value, therefore not accurate. This illustrates the effect of a constant error such as poorly adjusted sights and, since precise marksmanship is evidenced, it is reasonable to assume that if the source of error can be located and corrected, accurate shooting should be forthcoming.

The shooting by rifleman C shows that the hits are spotted all over the face of the target in a display of poor reproducibility. It seems that the rifleman has no experience of shooting, his hits result only as an accident. We say that the mean value is of low reliability. Hence, these results are neither precise nor accurate. Also we see that good precision is needed for good accuracy.

Of course the most favourable methods are those which give precise and at the same time accurate results. In practice results that are precise but subject to small systematic error are often more useful than results with an accurate mean value but low precision, since in first case we can actually find out how much they differ from the true value, while in the second case we know nothing but that the mean value is of low reliability. In the following example you can see the difference of accuracy and precision for the results of burette reading of a titration.

**Example 2.2**
The burette readings of titrations carried out by three students A, B and C are given below. Compare the accuracy and precision of the three students, if the true reading is 22.22 ml.

<table>
<thead>
<tr>
<th>Student</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Burette readings</td>
<td>ml</td>
<td>ml</td>
<td>ml</td>
</tr>
<tr>
<td>22.22</td>
<td>22.28</td>
<td>22.38</td>
<td></td>
</tr>
<tr>
<td>22.24</td>
<td>22.27</td>
<td>22.12</td>
<td></td>
</tr>
<tr>
<td>22.23</td>
<td>22.29</td>
<td>22.32</td>
<td></td>
</tr>
<tr>
<td>22.21</td>
<td>22.28</td>
<td>22.30</td>
<td></td>
</tr>
</tbody>
</table>
You can understand from the observed values and calculated mean values of titrations of three students that the results of student A are reproducible and the mean value resembles the true value. Hence the results of student A are both precise and accurate. A look of the titration results of student B shows that his results are reproducible but the mean value is slightly on the higher side than the true value. May be he might be taking the end point (colour change) on the higher side. Therefore, the results of student B are precise but not accurate. The readings of students C are spread in a wide range with a poor reproducibility. Hence his results are neither precise nor accurate.

**SAQ 7**
Define accuracy and precision.

### 12.6 REPORTING OF RESULTS

An analytical result is reported in two parts: (i) chemical, and (ii) numerical.

#### 1.6.1 Chemical Expression of Results

As far as possible, the result of the element determined should be reported in the chemical form in which it is present in the sample analyzed. For example, in reporting the result of a determination of nitrogen, it should be reported as nitrate, nitrite or ammonia depending upon the chemical form in which the element (nitrogen) is present. The analysis of a solution of electrolytes is generally expressed in terms of the ions present (as Fe$^{3+}$, Ca$^{2+}$, Cl$^{-}$, CO$_3^{2-}$, etc.).

However, when the actual form is not known or some other specific purpose is to be solved, the expression may be modified. Often the purpose for the analysis decides the form in which the constituents are reported. For example, when limestone is used for the purpose of manufacture of lime, its calcium content is expressed as calcium oxide. The hardness of water is usually expressed in terms of calcium carbonate (although a number of ions other than calcium are present in water).

#### 1.6.2 Numerical Expression of Results

In most of the analyses, it is the relative amount of the constituent in a sample that is of importance. Therefore, the numerical expression represents the amount of the desired constituent as parts of the amount of the sample in suitable units. Thus, if $W_i$ is the amount of the constituent of interest, $W_s$ is the amount of the sample, and $C$ is a factor required to express the results in suitable units, the expression

$$\frac{W_i}{W_s} \times C$$

is useful for the numerical expression of results of an analysis.
For example, if $W_i$ and $W_s$ are in grams and $C$ is 100, the result is given in percent (%) by weight of the constituent in the sample. If $C$ is set equal to 1000 and $W_i$ and $W_s$ in same units, the answer is in parts per thousand (ppt) by weight of the constituent in the sample. And if $C$ is set equal to 1,000,000 the answer is in parts per million (ppm) by weight of the constituent in the sample, and so on. The quantities $W_i$ and $W_s$ may also be expressed in volume units. Way of numerical expression of the results also depends on the physical state (solid, liquid, or gas) of the constituent and of the sample.

**Solids**

In case of the solid sample, usually, the weight constituent of interest and that of sample are taken in the same weight units and the result is expressed as percentage by weight ($\text{weight of constituent} \times 100/\text{weight of sample}$) to give the number of parts of analyte in 100 parts of the sample.

**Liquids**

The percentage in liquid samples is expressed in three ways:

i) **Weight percentage**: It is expressed in the same way as in solids and gives the number of parts of the desired constituent in 100 parts of the sample. Both weights are taken in same units.

ii) **Weight-volume percentage**: $\frac{\text{Weight of constituent in g} \times 100}{\text{Volume of sample in mL}}$ gives the number of parts by weight of constituent in 100 parts by volume of the sample. The temperature should be mentioned.

iii) **Volume percentage**: $\frac{\text{Volume of constituent}}{\text{Volume of sample}} \times 100$ gives the number of parts of volume of desired constituent in 100 volumes of the sample. Both the volumes should be taken in the same units and the temperature should be specified.

**Gases**

The composition of a gaseous mixture is usually expressed in percentage by volume, that is, $\frac{\text{Volume of constituent}}{\text{Volume of sample}} \times 100$. Both the volumes should be taken in the same units and the temperature should be specified.

The percentage representation is very common, but it is useful mainly for major constituents. When the constituent is in traces, it is advantageous to express in parts per million by weight or volume. For further lower amounts, parts per billion or parts per trillion may also be used.

### 1.6.3 Significant Figures

In the preceding section you learnt how to report the results of measurements of an analysis. In this section you will learn about the use of correct number of significant figures. The correct number of significant figures in measurement and calculations is critical in giving the proper significance to an analysis.
You know that a *number* is a mathematical expression of a quantity. A *figure*, or *digit*, is any one of the characters 0, 1, 2, ..., 9 which, alone or in combination, serves to express a number. *The digits of a number which are needed to express the precision of the measurement from which the number was derived are known as significant figures.*

Digits from 1 to 9 are always a part of significant figures, while 0 may or may not be a significant figure. A digit signifies the amount of the quantity in the place in which it stands. In case of the number 542, the figures signify that there are five hundreds, four tens, and two units and are therefore all significant.

The character zero (0) is used in two ways, it may be used as a significant figure or it may be used merely to locate the decimal place. When zero is the part of the measurement it is significant. For example, the weight of a crucible is found to be 12.610 g. The terminal zero is significant meaning that the weight can be measured correctly up to third place of decimal. The zero after 1 is significant because this is the part of the measurement. Similarly, expressing the concentration of a copper sulphate solution as 0.1000 N, the three zeros after 1 are all significant.

Consider the number 107.2 cm. The zero between 1 and 7 is significant because zero placed between two significant figures is significant. This number has four significant figures regardless of where the decimal point is placed, say 1072 mm, 10.72 dm, 1.072 m and 0.001072 km all have four significant figures, they simply represent the result in different units. In the last number 0.001072 km, the zeros before 1 are just to locate the decimal point and therefore are not significant.

To write a result with some degree of certainty the correct use of significant figures must be made, which depends on various rules for computation. The student should be familiar about these (the rules have got the limited validity), i.e.:

i) **Observed quantities should be recorded with one uncertain figure retained.**

That is, there must be as many significant figures in a result or in any data as will give only one uncertain figure. Thus, in most analyses represent the last retained significant figure by ±1. For example, a value 22.6 ml represented as 22.6±1 means that this is known to be between 22.5 ml and 22.7 ml.

ii) **In rounding off quantities to desired number of significant figures by dropping the superfluous figures, increase the last retained figure by one if the following figure (which is dropped) is greater than 5.**

For example, the number 46.2368 rounded off to four significant figures becomes 46.24.

If the dropped digit is exactly 5 (not ... 51, 524, etc. which are treated as greater than 5), the last retained figure is rounded off to the nearest even digit.

Thus,

- 3.55 is rounded off to two significant figures = 3.6
- 3.65 is rounded off to two significant figures also = 3.6
- 14.75 rounded off to one decimal place = 14.8
- 2.652 rounded off to one decimal place = 2.7

If the dropped figure is less than 5 the last retained figure is not changed.
Thus, 26.4332 rounded off to four significant figures = 26.43.

iii) *In addition or subtraction* the answer is rounded off to the significant figures in terms of the least significant unit. It is mainly for decimal places in the numbers and the number having the fewest decimals is thus the least significant unit. Thus, the result of sum or difference should have the number of decimals equal to the number of decimals present in the least significant unit (means the number having the fewest decimals). Although, all numbers being added or subtracted can be rounded off to the least significant unit. But again for the consistency in the answer in practice we keep an extra figure during stepwise calculations and then the final result is rounded off to one less figure. For example, summing the numbers: 26.234 + 3.223 + 143.4 + 2.2260, the third number 143.4 is the least significant unit which contains only one decimal place. Therefore, all other numbers are rounded off to two decimal places and the final result is then rounded off to one decimal place (equal to the number having least decimal places).

26.234 is rounded off to 26.23  
3.223 is rounded off to 3.22  
143.4 is retained as 143.4  
2.2260 is rounded off to 2.23  
Sum = 175.08

Finally rounded to one decimal place the sum = 175.1 Answer

In *multiplication or division* you can retain in each factor one more significant figure than that of a factor having the least significant figures (that is significant figures contained in the least precise factor). After calculations the answer is rounded off to the number of significant figures contained in the least precise factor. For example, in the multiplication

\[
7.0783 \times 0.00305 \times 6.602
\]

the middle factor has got the least (=3) significant figures hence the values will be written as

\[
7.078 \times 0.00305 \times 6.602 = 0.1425233
\]

The answer rounded off to 3 significant figures is = 0.143

iv) If a calculation involves addition / subtraction and multiplication /division then the individual steps must be treated separately. As good practice one extra figure may be retained in the intermediate calculations and the final result is then rounded off by dropping the superfluous figures.

v) When a *calculator* or computer is used, insert all available digits in the calculation. The final result is rounded off as desired.

vi) One extra figure may be included in the average.
vii) In logarithm calculations as you understand a logarithm of a given number is composed of two parts (i) the characteristic which is a whole number and is indicative of the position of the decimal in the given number and hence is not a significant figure, (ii) the mantissa which is a decimal fraction and is the same regardless of the position of decimal in the given number. For example, to express properly the logarithm of \(2.4 \times 10^4\), characteristic is 4 and mantissa is 0.3802 and the logarithm is 4.3802. The result is rounded to 4.38 since the given number (\(2.4 \times 10^4\)) has only two significant figures.

**Example**
Calculate the pH of a \(4.0 \times 10^{-3}\) M solution of hydrochloric acid.

**Solution**
\[
pH = -\log [H^+] = -\log 4.0 \times 10^{-3}
\]
The – 3 is the characteristic (from \(10^{-3}\)). The mantissa is 0.6010 (from the logarithm of 4.0). But the concentration is known only upto two significant figures, hence
\[
pH = -(– 3 + 0.6010) = 3 – 0.60 = 2.40
\] Answer.

**SAQ 8**
List the proper number of significant figures in the following numbers
i) 0.162  ii) 10.06  iii) 200.0  iv) 0.0260

**12.7 LET US SUM UP**
Let us summarise the key points dealt in this unit.
The classical as well as instrumental analytical techniques are very important to an environmental analyst; the reason being the increasing levels of many types of pollutants day by day across the globe. This helps in monitoring of various pollutants and hence in applying some of the corrective measures.

In a broad sense the analytical techniques can be grouped into qualitative and quantitative types. The classification of these techniques is based also on the physical properties of the analytes. On the basis of these properties the types are divided into chemical, electrical, optical, nuclear radiation, thermal and separation methods. All the methods are further divided into many types. Thus chemical methods are divided into gravimetric and volumetric analysis. Electrical methods have potentiometry, voltammetry, coulometry, amperiometry and conductometry. Emission, absorption, ultraviolet-visible absorption, IR absorption, fluorophotometry, turbidimetry and nephelometry and Raman spectroscopy are the parts of optical methods. Nuclear methods include radiochemical spectroscopy, Mossbauer spectroscopy, nuclear magnetic resonance spectroscopy and mass spectrometry. Thermal methods are thermogravimetric analysis, derivative thermogravimetry, differential thermal analysis, differential scanning calorimetry and thermometric enthalpy titrations. Separation methods have classical and modern methods wherein chromatography and electrophoresis are parts of the latter one.
A complete analysis actually consists of the many steps. These include sampling, dissolution of the sample, separation of interfering substances, measurement and interpretation of the measurements. Evaluation of analytical data includes errors, detection of errors and the concept of accuracy and precision. There are chemical and numerical methods of reporting the results where the concept of significant figures is very important.

12.8 TERMINAL QUESTIONS

1. What is the essential feature of a method to be called as an analytical technique?

2. Name the methods that are now known as classical methods.

3. Define accuracy and precision with suitable examples.