

Chapter

1

Introduction to Analytical Chemistry

UGC Syllabus

Introduction to analytical chemistry and its interdisciplinary nature. Concept of sampling. Importance of accuracy, precision and sources of error in analytical measurements. Presentation of experimental data and results, from the point of view of significant figures.

INTRODUCTION

Analytical chemistry is a branch of chemistry which uses several methods and instruments to identify an unknown chemical substance quantitatively as well as qualitatively. Qualitative analysis gives the idea of chemical identity of the substance, whereas the quantitative analysis measures the relative quantities of the substances in numerical value. Analytical measurements are applied to solve the real problems in wide areas of science such as in biology, geology, medicine, environmental sciences, agriculture, material science, medicine, etc.

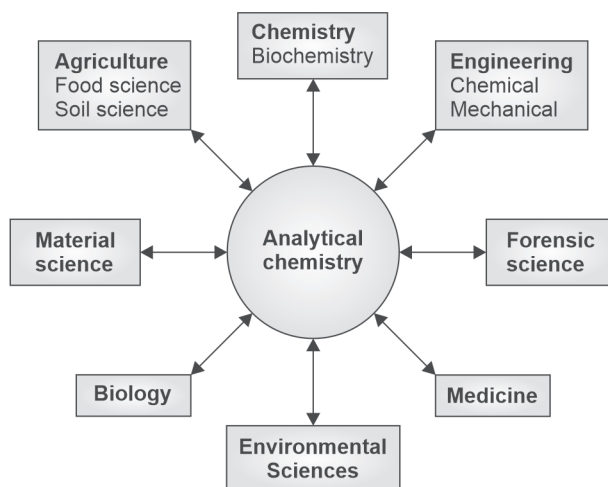


Fig. 1.1: Interdisciplinary nature of analytical chemistry

Interdisciplinary nature: The interdisciplinary nature of analytical chemistry promotes it as an essential tool for all kinds of laboratory (Fig. 1.1). An analytical chemist uses it to solve the real practical problems. Scientific analysis cannot be completed without the help of analytical chemistry.

- (i) Analytical chemistry has huge applications in agricultural field. Such as, for obtaining maximum production, a farmer needs to know first the nature of soil (soil pH), the availability of essential nutrients, etc. Thorough analysis of the soil is performed using the knowledge of analytical chemistry. Fertilizers are also analysed before their administration to the soil.
- (ii) The food items and many other consumable products (cosmetics and medicines) are analysed by different techniques of analytical chemistry such as gravimetric and volumetric analysis (complexometric titrations, acid–base titrations), various types of chromatographic methods, spectroscopic techniques, etc.
- (iii) The medicinal science is also dependent on analytical chemistry. Not only the composition analysis of medicine, but also the examination of different samples like blood, serum, urine, etc. is done using various analytical methods.
- (iv) This branch of chemistry is an indispensable part of metallurgy. Analysis of ores, extraction of metal ions and their quality checking is performed by analytical chemistry.
- (v) Analytical chemistry is also employed in forensic sciences where different chemicals and instrumental methods are used to prove a criminal act.

1.1 ANALYTICAL METHODS

The most important step of any analysis is choice of proper analytical methods. The analytical method is selected depending on the number and nature of samples, desired accuracy, etc. Analytical methods are mainly classified into three types.

- (i) *Classical method*: It is the simplest and cheapest method of analysis where the required chemicals and apparatus are readily available in any chemical laboratory. Calibration of known sample is not required in this method. Titrimetry and gravimetry are two classical methods of analysis.
- (ii) *Instrumental method*: This method is more expensive and faster than classical method. The instruments used in this method are very sophisticated, expensive and sensitive. These instruments are capable of determining very low concentrations (trace, substrate and ultratrace analysis) of a chemical substance. Colorimetry, potentiometry, spectrophotometry, voltammetry, chromatography, etc. are examples of instrumental methods.
- (iii) *Non-destructive method*: The non-destructive methods of analysis are very costly and speed of analysis depends on the selected method. This method produces results with moderate to high accuracy. The example of this type of method includes X-ray fluorescence spectroscopy.

1.2 CONCEPT OF SAMPLING

In analytical chemistry, sampling or sample preparation is a method of collecting or extracting an optimum amount of sample as representative of a larger amount of substance which is to be analysed.

Sampling is the most crucial step in analysis as the result and its accuracy depends on it. Depending up on the state of a substance, i.e. heterogeneous or homogeneous, solid, liquid or gas, the sampling procedure is different. Following are some important terminologies which readers should know about the sampling procedure in analytical chemistry.

- **Homogeneous substance**: For homogeneous material, a *gross sample* is taken for the analysis such as in clinical laboratory blood, urine, etc. are analysed directly.

- **Heterogeneous substance:** For heterogeneous material, a combination of materials is collected to make a *gross sample*.
- **Gross sample:** It contains several portion of the substance to be analysed. The amount of the sample is within the range of few grams to kilograms.
- **Laboratory sample:** It contains a small portion of homogeneous **gross sample**. The amount of the sample is taken as few grams.
- **Analysis sample:** It is the actual amount of sample that is analysed. The amount of the sample is taken as few milligrams or millilitre.

The sampling techniques involving solid, liquid and gas samples are discussed briefly.

Solid sampling: Sampling of the solid sample is most difficult due to its less homogeneous nature. For this reason, solids are crushed or ground into smaller particles to a homogenized sample. Depending on the hardness of the material automated or manual crusher or grinder is used. Polymer pellets are treated with liquid nitrogen, which freezes the polymer to make it brittle in nature and then these polymers are easily grinded to obtain the powder form. Soft materials cannot be easily grinded as they just deform rather than crushing. Therefore, soft materials are often dried before grinding using oven to remove any adsorbed liquids in order to get the representative sample. A large number of analytical techniques employing grinding, blending and pulverizing instruments are used for sampling the solid substances such as soil, cement, ceramics, food, textile and other solid materials.

Liquid sampling: For sampling a liquid, portions of the same are collected from the sources and treated according to the nature of analysis. In general, liquid samples are first stirred or shaken well before considering it as a *grab sample*. For the preparation of a *representative sample* from big sources (such as analysis of lake water or river water), samples are collected from different locations or layers. Then these samples are either analysed separately or they can be blended together to obtain a representative sample. To analyse the normal river water, the samples are collected away from contaminates such as floating froth, river banks, municipal waste treatment sites and industrial waste disposal areas. Sometimes, centrifugation or filtration is performed to remove solid particles present in liquid sample. For liquid samples having two immiscible layers, either separate layer analysis or emulsification method is adopted for sampling. Liquid suspensions like milk, orange juice, antacids are sampled as it is without the removal of the suspended solids.

Gas sampling: Gas samples are homogeneous in nature but they may often form separate layers of different density. Therefore, gas samples are needed to be stirred prior to analysis. Gas samples are collected either at a particular point at a time or a batch of samples are collected at different locations over a certain time period and then mixed together to obtain the average representative sample. For collection of gas samples, containers like balloons, gas tight syringes, plastic bags, etc. can be used. Suitable PPE (personal protective equipment) should be used for sampling of toxic or flammable gases. Gas samples can also be collected by absorbing the gas into a solid or liquid adsorbent. This process is called 'scrubbing of gas'. Scrubbing also reduces the sample size which makes it easy to carry. For example, organic pollutant vapour present in air can be collected in an activated charcoal bead of size as small as a ball

point pen. The gas samples can often be filtered to remove any undesirable solid particles present in the sample.

1.3 ERRORS IN CHEMICAL ANALYSIS

Almost every measurement in chemical analysis involves some uncertainties, which is defined as errors. The error can be classified into two principal types such as *determinate* or *systematic error* and *indeterminate* or *random error*.

(I) **Determinate or systematic error:** This type of errors is mainly caused by the design of an improper analytical procedure or faults in the equipment used in the analysis. The name determinate suggests that this type of error may be determined and hence it is either avoided or corrected through the proper analysis. Determinate errors influence the accuracy of the measurement.

Depending upon the *relative magnitude of the error with respect to the size of the sample*, the determinate errors are of two types:

- **Constant errors:** The magnitude of constant error does not change with the change in sample size. Thus, the effect of this type of error is more prominent when the sample size is decreased. Let us consider three samples 20, 35 and 50 mg/L of analyte for which the measured values are 25, 40 and 55 mg/L, respectively. This analysis has a constant positive error of 5 mg/L with the relative percentages of constant errors 25%, 14% and 10%, respectively, for the three measured values. Therefore, the effect of constant error can be reduced by increasing the sample size.
- **Proportional errors:** The magnitude of proportional error varies depending upon the size of the sample. With this type of errors, the absolute error changes with the size of the sample, but the relative error remains constant. Let us consider the same three samples 20, 35 and 50 mg/L of analyte where the measured values are 21.6, 37.8 and 54 mg/L, respectively. This analysis has a proportional positive error of 1.6, 2.8, 4 mg/L, respectively. The method results in a constant relative error of 8% for the three measured values.

Based on the *sources*, the determinate or systematic errors are mainly of three types:

- **Instrumental errors:** The effect of improper calibration or the environmental factors on the instrument or equipment causes the instrumental error. Such as measuring equipment like burette, pipet, measuring cylinder, volumetric flask, etc. does not provide the correct volume in all environmental condition. An electronic instrument gives this error due to fluctuation of current voltage, incorrect calibration, changes in temperature, etc.
- **Methodical errors:** The imperfect chemical or physical behaviour of the reagents and reactions such as very slow reaction rate, low specificity of reagents, contaminated or low-grade reagents, instability of some products, unwanted side reactions, etc. affect the analysis and produces the systematic method errors. For example, in titrimetric method an excess (though very small) volume of titrant is required for the colour change of indicator used.
- **Personal or analyst error:** This type of errors is introduced in the analysis results due to carelessness, ignorance or inattention of the analyst or the person who is performing the analysis. Knowingly or unknowingly, use of an incorrect setting in an instrument or the wrong operating condition may lead to the analyst error.

However, with proper setting, an analyst also can do some common errors like transcription errors (by noting down the wrong data on lab notebook) and calculation error.

Minimizing the systematic errors in analytical methods: The complete elimination of the systematic error is very challenging task. However, this type of error can be identified and minimized with proper choice of the analytical methods and operating conditions. The following measures can be taken to identify and reduce systematic errors in an analytical method:

- a. **Calibration of instruments:** Systematic error can often be detected by comparison to theoretical model or someone else's result. However, in such case, it is difficult to tell which one is accurate. Calibration (if feasible) is the most trustworthy approach to decrease systematic errors. A reference quantity, for which the actual result is already known, can be used to calibrate the analytical procedure. However, if possible, it is always better to calibrate the whole procedure and apparatus, on a known quantity of sample of similar size to your unknown quantities.
- b. **Analysis of standard samples:** The best way to measure the error originating in an analytical method is to analyse standard reference materials (SRMs). The SRMs contain one or more analytes in known concentration. The standard reference materials can either be commercially purchased or synthetically produced in the laboratory. For preparation of SRMs, utmost care should be taken so that the overall composition of the synthetic standard material closely approaches the composition of the samples to be analysed.
If results of analysis on the SRMs differ from the accepted value, one should check with the random error (if any) associated with the analytical method.
- c. **Variation in sample size:** The extent of determinate error is dependent on the sample size. With increase in the size of sample, the effect of constant error decreases. Hence, multiple measurements with varying sample size can often be helpful in determination of constant error.
- d. **Blank determinations:** Blank comprises of all the reagents except the analyte in the same solvent used in a determination. Often some reagents are added to the sample to create the analyte environment, which is known as sample matrix. In a blank measurement, all steps of the analysis are executed on the matrix without the analyte. The results of blank determination are then applied for correction of the analyte measurement in order to remove errors originating from unwanted contaminants present in the reagents and vessels used for analysis.
- e. **Independent analysis:** To compare the results and to avoid some common sources of errors, a second independent analytical method which differs significantly from the existing method can be performed in parallel. Generally, it is very much useful in case of non-availability of SRMs.

(II) **Indeterminate or random error:** This type of errors originates from the uncontrollable variables in the analysis. It is generally small but irregular and cannot be corrected. A better measurement can help to reduce it yet. Indeterminate errors influence the precision of the measurement.

Minimizing random errors in analytical methods: The occurrence of random error in a measurement is very irregular and has no preferred direction. Therefore, it cannot

be eliminated from the measurement, however, following measures can be taken in order to minimize the effect of random error:

- Large number of measurements can be performed to obtain an average value. This method reduces the effect of random error.
- Imprecision, i.e. the impact of random error can be reduced by large sample sizes.
- Maintaining appropriate experimental method can also be helpful in reducing the effect of random error.

1.4 ACCURACY AND PRECISION

- Accuracy:** Accuracy is defined as the nearness of a measured value to the actual value. It signifies the parity between a result and the accepted value. The smaller the difference between these two values, the greater is the accuracy (Fig. 1.2). The greater is the value of accuracy, the more correct is the analysis or measurement. In most of the cases actual true value is not known, it is difficult to determine the accuracy and accepted true value is used in place of true value.

Accuracy can be mathematically expressed by two terms—**absolute error** and **relative error**.

- **Absolute error (E_a):** It is the difference between the measured or experimental value and the true value of a quantity and it is expressed as: $E_a = x_i - x_t$, where x_i is the measured and x_t is the true value. The E_a has the unit dependent on the type of measurement.

Example: Let, the 28.31 cm is the true value of a length measurement and 28.46 cm is the experimental value. Therefore, absolute error = $(28.46 - 28.31)$ cm = 0.15 cm.

- **Relative error (E_r):** It is described as the ratio of the absolute error (E_a) of the measurement to the true value and it is expressed as $E_r = \frac{x_i - x_t}{x_t}$.

Example: The relative error of the above example will be 0.0053.

The E_r is dimensionless and it is more significant or better measurement than absolute error. The percent relative error can be expressed by multiplying the fractional error by 100.

- **Precision:** It is referred to the extent of closeness between the results of two or more replicate measurements on the same system using identical method of analysis. It indicates the reproducibility of the method (Fig. 1.2).

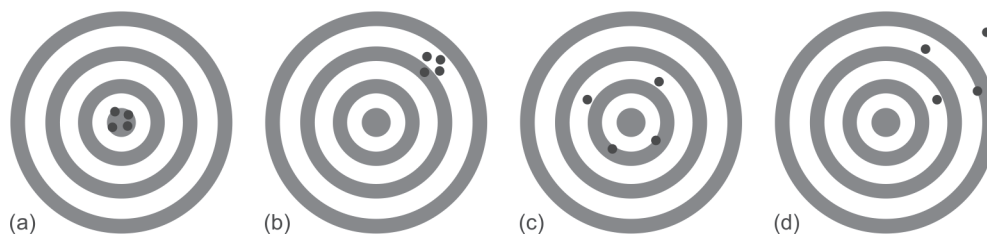


Fig. 1.2: (a) High accuracy and precision, (b) low accuracy but high precision, (c) high accuracy but low precision, (d) low accuracy and precision

For example, if replicate measurements of a data by method A gives the values 5.35, 5.32 and 5.36 while method B gives the values 6.32, 6.38 and 6.42, precision of method A is better than that of method B.

The precision of a result obtained in a set of measurement is expressed in terms of the *average deviation of the mean*, *relative average deviation (RAD)*, *standard deviation (SD)* and *relative standard deviation (RSD)*.

- **Average deviation of the mean:** Let N numbers of measurements are performed for quantity 'a'. The measured values are $x_1, x_2, x_3, \dots, x_N$ and the mean value is $\bar{x}$. Then the deviations of the individual values from the mean values are $(x_1 - \bar{x}), (x_2 - \bar{x}), (x_3 - \bar{x}), \dots, (x_N - \bar{x})$.

Then the mean deviation

$$= \frac{|x_1 - \bar{x}| + |x_2 - \bar{x}| + |x_3 - \bar{x}| + \dots + |x_N - \bar{x}|}{N} = \frac{\sum_{i=1}^N |x_i - \bar{x}|}{N}$$

The average deviation of the mean is obtained by dividing the mean deviation by square root of the number of measurements.

Therefore, the average deviation of the mean

$$= \frac{\text{Mean deviation}}{\sqrt{N}} = \frac{\sum_{i=1}^N |x_i - \bar{x}| / N}{\sqrt{N}}$$

- **Relative average deviation:** It is expressed in either of the three following terms:

I. Relative average deviation (%)

$$= \frac{\sum_{i=1}^N |x_i - \bar{x}|}{\bar{x} \cdot N} \times 100$$

II. Relative average deviation (parts per thousand or ppt)

$$= \frac{\sum_{i=1}^N |x_i - \bar{x}|}{\bar{x} \cdot N} \times 1000$$

III. Relative average deviation (parts per million or ppm)

$$= \frac{\sum_{i=1}^N |x_i - \bar{x}|}{\bar{x} \cdot N} \times 10^6$$

- **Standard deviation:** The precision of a measurement is generally expressed in terms of standard deviation. It is defined as the square root of the mean of the squares of individual deviation from their mean value. Generally, it is expressed by the following equation:

Standard deviation

$$= \sqrt{\frac{(x_1 - \bar{x})^2 + (x_2 - \bar{x})^2 + (x_3 - \bar{x})^2 + \dots + (x_N - \bar{x})^2}{N}}$$

- I. **Population standard deviation (σ):** It measures the precision of the population (when $N \rightarrow \infty$), and expressed as

$$\sigma = \sqrt{\frac{\sum_{i=1}^N (x_i - \mu)^2}{N}}$$

where $\mu = \frac{\sum_{i=1}^N x_i}{N}$ is called the *population mean* and N is the total number of measurements in the population. The μ can never be measured but as N increases, μ approaches to $\bar{x}$.

- II. *Sample standard deviation (s)*: With small number of sample data (N is small) the extent of precision is measured by the value of sample standard deviation. It is expressed as:

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

where $\bar{x}$ is the sample mean and $(N - 1)$ is called the number of degrees of freedom.

- *Relative standard deviation (RSD)*: The relative standard deviation of a measurement is calculated by dividing the standard deviation value with the mean value of all the measurements.

Relative standard deviation (RSD)

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

Percent relative standard deviation (% RSD) or coefficient of variation

$$= \frac{s}{\bar{x}} \times 100\%$$

Relative standard deviation input

$$= \frac{s}{\bar{x}} \times 1000 \text{ ppt}$$

- **%Variance**: The square of the standard deviation value is known as variance (σ^2 or s^2).

Importance of accuracy and precision: To achieve the best quality of measurement, accuracy and precision both are equally important. For a set of measurement, where the true value is not so important, the precise value is more meaningful as they are grouped throughout the series of measurement. On the other hand, where the true value is more important, the accuracy is valued over precision, as it is more useful in measuring the needed value. However, to maintain a measurement system, it should be checked for precision and accuracy regularly, as they are equally important.

1.5 PRESENTATION OF EXPERIMENTAL RESULTS: CONCEPT OF SIGNIFICANT FIGURES

Significant figures: The concept of significant figures is very much important in writing a numerical value of an analytical experimental result. It is defined by all the certain digits in addition with the first uncertain digit in a number. For example, if an analytical balance capable of measuring nearest milligram accurately shows the mass of a sample to be 42.04672 g, then only the first four digits after decimal is meaningful. The last digit known with certainty is 6. The fourth digit 7 is uncertain and it only indicates that the mass is greater than 42.045 g but less than 42.047 g. The fifth or the last digit 2 is meaningless. In another example, while recording a burette reading of a 50 mL burette as shown in Fig. 1.3, one can easily tell that the liquid level is between

30.2 to 30.3 mL. The analyst can also assess the liquid mark between the graduations to about 0.02 mL and report the volume as 30.24 mL. The reported value 30.24 has four significant numbers where first three digits (3, 0, 2) are certain and fourth digit 4 is uncertain.

Rules for significant figures:

- (i) *All non-zero digits are significant.* For example, the number 35 has two significant figures, 45.2 has three significant figures, 30.45 has four significant figures, 2.5403 has five significant figures.
- (ii) A zero becomes significant if it appears in between two non-zero digits. For example, the number 5.034 has four significant figures and 407 has three significant figures.
- (iii) When zero appears at first or before non-zero digits, it becomes insignificant. The numbers 0.35 and 0.0035 both have two significant figures.
- (iv) Zeros following non-zero digits or placed right to the decimal are significant. For example, 25.0 has three, 25.00 has four, 25.000 has five significant numbers, respectively.
- (v) Zero at the end of a whole number becomes significant when it is followed by a decimal. For example, writing 630 means the trailing zero is not significant whereas '630'. Indicates the trailing zero is significant.
- (vi) For a number ($M \times 10^n$), all digits included in M are significant according to the above five rules but '10' and n are insignificant. For example, 2.35×10^6 has three significant figures (2, 3, 5).

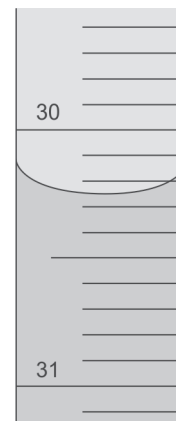


Fig. 1.3: Graduated burette reading

Rounding off a number: In different analytical methods, the results are generally rounded off to express it to a desired number of significant figures. Before rounding off a number let us know about the different significant figures in detail. The left most digit (do not count a leading zero) is called the most significant digit. If a number is to be rounded off to n significant digits then the n th digit from the most significant digit is called least significant digit. The least significant could be zero. The $(n + 1)$ th digit is the first non-significant digit.

Following rules are to be taken care of while rounding off a number.

- (i) While rounding off a number, all non-significant digits are dropped.
- (ii) When the first non-significant digit is less than 5, the least significant digit remains unchanged.
- (iii) When the first non-significant digit is greater than 5, the least significant digit is increased by 1.
- (iv) If the first non-significant digit is 5, the least significant number is rounded off to an even digit. While rounding off, zero is considered to be even number.

Example 1: Let us round off 54.2364 to four significant figures. The fifth digit (6) is the first non-significant number which is greater than 5. Therefore, for rounding off, we will drop every figure after the fourth digit (3) and increase it by 1. So, the original number rounds off to 54.24.

Example 2: Let us round off 2.7626 to three significant figures. The fourth digit (2) is the first non-significant figure which is less than 5. Hence we will simply remove all the figures after third digit and the original number rounds off to 2.76.

Example 3: Rounding off 26.235 to four significant figures. The fifth or the first non-significant digit is itself 5. Thus, the fourth digit will be rounded off to an even number and the original number rounds up to 26.24.

Example 4: Rounding off 26.8513 to three significant figures. The fourth or first non-significant digit is 5. The third or last significant digit is 8 which is an even number. So, it will be 26.8 after rounding off.

Rules of rounding off in mathematics:

- (i) *For addition or subtraction*, the result is expressed up to the same decimal places as it is in the number with least number of decimal places.
For example, the addition of numbers 125.7, 5.8, 0.637 gives a value of 132.137. Here the number with least decimal place is 5.8. Hence the result should be expressed up to one decimal place. Therefore, the correct answer is 132.1.
Similarly, subtracting 24.36 from 475.264 we get 450.904. So, by the above rule the correct answer will be 450.90.
- (ii) *For multiplication or division*, the result is expressed with same number of significant figures as it is in the number with least number of significant figures.
For example, if we multiply 3.425 (four significant figures) with 6.23 (three significant figures), we get 21.33775. By considering the above rule, the result must be reported to three significant figures. Hence, 21.3 is the correct answer. Similarly, when we divide 8.24534 (six significant figures) by 3.52 (three significant figures), we get 2.34242. By the above rule, the correct result is 2.34.

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QUESTIONS

Multiple Choice Questions

1. Analytical chemistry is employed for:
(a) Quantitative analysis (b) Qualitative analysis
(c) Both a and b (d) None of these
2. Qualitative analysis gives information about:
(a) Amount of the sample (b) Nature of the sample
(c) Both a and b (d) None of these
3. Instrumental error is which type of the following errors?
(a) Determinate (b) Indeterminate
(c) Random (d) None of these
4. The proper way to minimize the random error is:
(a) Changing the instrument
(b) Taking repeated measurements to get an average value

- (c) Taking help from other analyst
(d) None of these
5. The nearness of a measured value to the true value is called:
(a) Mean (b) Median
(c) Accuracy (d) Precision
6. Standard deviation is a measure of:
(a) Error (b) Accuracy
(c) Precision (d) None of these
7. The number of significant figures in 0.0065 and 65.00 are and, respectively.
(a) 2, 4 (b) 4, 2
(c) 5, 2 (d) 5, 4
8. After rounding off to three significant figures the number 26.8513 will be:
(a) 26.9 (b) 26.8
(c) 26.7 (d) 26.85

Answers

1. (c); 2. (b); 3. (a); 4. (b); 5. (c); 6. (c); 7. (a); 8. (b)

Practice Questions

1. What is analytical chemistry? Discuss its interdisciplinary nature.
2. Discuss different types of analytical methods.
3. What do you mean by sampling? Briefly discuss the sampling for solid and liquid substances.
4. Based on the sources classify the systematic errors and briefly discuss about them.
5. What is the difference between precision and accuracy? Which is more important?
6. What is meant by standard deviation? Derive the mathematical formula for calculating standard deviation.
7. Briefly discuss the concept of significant figures.
8. State and explain the rules for rounding of numerical expression with example.
9. Write down the rules for rounding of while performing mathematical programme.
10. Calculate the standard deviation for the percentage of copper in a sample: 6.23, 6.25, 6.26, 6.24, 6.28 and 6.30.
11. Round of the following numbers to four significant figures: 28.6824, 45.5832, 62.590 and 39.56.
12. What are the absolute and relative errors of the approximation 3.14 to the value of π ?
[Hint: $E_a = |3.14 - \pi| \approx 0.0016$ and $E_x = |3.14 - \pi| / |\pi| \approx 0.00051$]