SIGNIFICANT FIGURES

Significant figures are digits necessary to express the result of a measurement to the precision with which measurement is made, ie The number which expresses the result of a measurement such that only a last digit is in doubt. Eg, in the reading of a 50ml burette the small graduation is 0.1ml. Thus an analyst can be estimate the reading upto 0.01ml by mentally dividing the smallest division into 10 equal parts thus getting in figure 1, the reading around 1.42ml approximately . Thus in this value there are 3 significant figure, 2 certain and 1 uncertain (last digit).

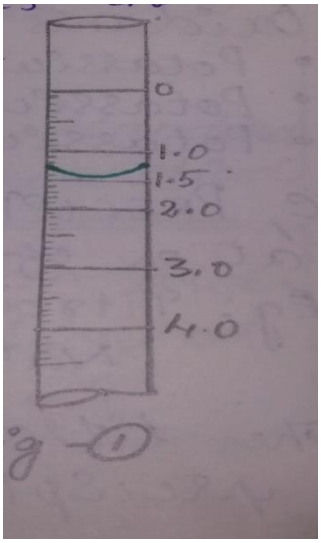


Fig. 1. Reading showing the burette reading to the approximate value.

4 RULES IN SIGNIFICANT FIGURES.

Rule 1.

All non zero digits are significant

- 2.345 in this there are 4 significant figures
- -9.66 In this there are 3 significant figures.

Rule 2.

Final zeros right to the decimals are significant

- 2.0 km :- 2 significant figures.
- 6.300 cm ;- 4 significant figures.

Rule 3.

Zeroes found between 2 significant figures

- 17.008m :- 5 significant figures.
- 28.0005 :- 6 significant figures.

Rule 4 .

Zeroes as place holders left to the decimal are not significant

- 0.00038 m: - 2 significant figures.
- 42 g :- 2 significant figures.

Rules for computation of significant figures.

1, Rounding off the numerical figures

In this all the digits to be rounded off are removed together and not one at a time. Eg-

A, 76.8437 → 76.8

All the numbers following the last figure to be retained is less than 5.

B, 59.873 →59.9

If the figure following the last digit to be retained is greater than 5, the last digit retained is increased by 1.

C, 69.752 →69.8

If the figure following the last digit to be retained is 5 and at least one of the other digit is non ero, the last digit retained is increased by 1.

D, 68.250 →68.2
68.350 → 68.4
In the figure, following the last digit to be retained if 5, all the other digits to be removed are zero, the last digit retained is not changed if it is even but it is increased by 1 if it is odd.

2, Addition And Subtraction

In addition and subtraction only as many decimal places are kept as occur in the number which has fewest decimal. Eg -15.23 + 9.145 – 4.6758 +121.4

The final answer should be expressed in only one decimal place. The number may be first rounded off to 2 decimal places, then find out the answer.

15.23 +
9.145 –
4.6758 +
121.4

rounded off to 2 decimal point →

15.23 +
9.14–
4.68 +
121.4

141.09

3, Multiplication And Division

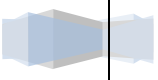
In this the number of significant figures in the result is the same as the least reliable measurement. Eg. 0.165 m^3 X 10.487 kg/m^{3+} = 1.730355 kg/m^3

= 1.73 kg/m^3

4, Logarithms

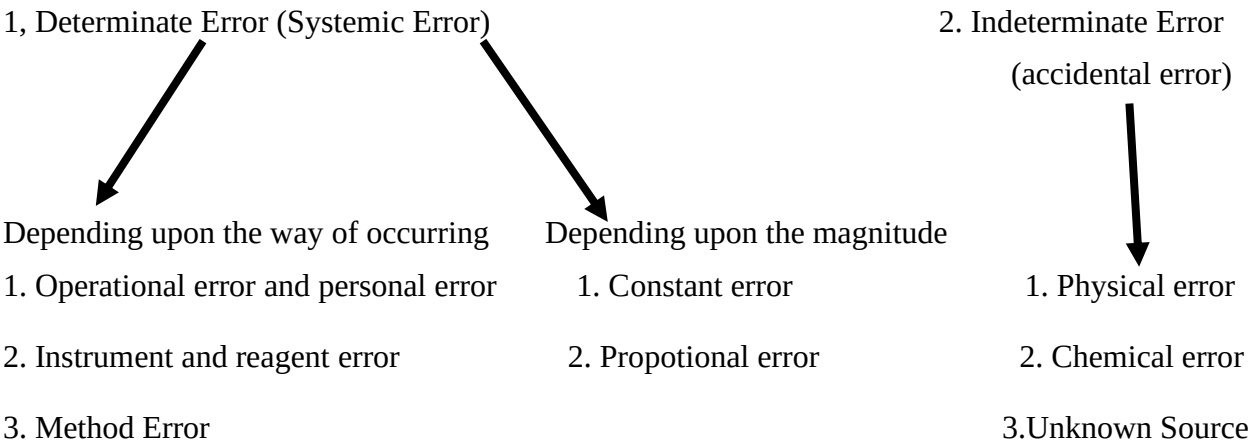
Its made of 2 parts, a whole number and a decimal fraction. The whole number is not considered as the significant figure but the decimal fraction (mantissa) all digits are considered as significant. Eg. 2.4 x 10^5

From the log table .mantissa is 0.3802, the characteristic is 5 ,hence value is 5.38



ERRORS

Error is defined as the numerical difference between a measured value and a true value of an analytical determination. It can be classified as,



1,. **DETERMINATE ERROR-** those errors which can be avoided or whose magnitude can be determined.

a. Operational And Personal Error

Due to the factor for which the experimenter is personally responsible and donot depend on method or procedure

- They arise from erractic personel judjement ,prejudice or biased, inability
    1. Eg- judgement of a colourof the solution at the end point
    2. Estimation of position of pointer in balance.
    3. Level of meniscus on a burette/pipette.
    4. Insufficient cooling of a crucible before weighing
    5. Allowing hygroscopic material to absorb moisture before /during weighing

Such errors can be varied from person to person and can be minimized by experienced and careful physical manipulation.

b. Instrumental And Reagent Error

These arise from the imperfections in measuring devices. Electronic devices are much prone to this because of voltage fluctuations

1. Eg. Unadjusted chemical balance

2. Uncalibrated weight's usage
3. Usage of uncalibrated glasswares
4. Reactions between chemicals and porcelien resulting in introduction of new undesirable material.
5. Usage of low grade chemicals.

c. Method Error

These errors arise from incorrect sampling and incomplete rezctions involved in the determination

1. Eg .In volumetric analysis, errors arise due to failure of reaction to proceed to completion, occurance of side reactions etc
2. In iodometric, determination of Cu,I gets adsorbed on starch which is difficult to remove completely

The determinate errors are further classified into **Constant Errors** And **Propotional Errors**

A, Constant error (Depends on Magnitude) – Independent of magnitude of measured quantity and becomes less significant as magnitude increases, also independent on concentration.

Error value remains same, its magnitude changes.

For example- In a number of titration if there is a constant error of 0.10 ml, then this indicates 1 % of 10 ml titrant and 0.2% or a 50 ml of titrant .

ie, Constant Error decreases with increases in a measured quantity.

B, Proportional Error – Most common errors, because of presence of interfering impurities in sample. Here its magnitude will remain constant with the change in concentration.

Eg- In Iodometric titration of copper, if the sample is contaminated with Fe(III) impurity, it will also liberate I_2 from KI along with copper; hence resulting in a false result of high copper concentration. And if the concentration of sample is doubled, the error will also get doubled.

INDETERMINATE ERROR

Random errors arises from uncertainties which are associated with physical or chemical measurements. Such errors cannot be attributed to any known source or cause.

- They are random or accidental in nature .
- Lead to both high and low results with equal propability
- Cannot be eliminated or corrected
- And are the ultimate limitation on the measurement.

Minimization of errors –

They can be minimized by

- Calibration of apparatus and application of corrections.
- Analysis of standard samples.
- Running a blank determination
- Independent analysis- ie strength of HCl can be determined by titration with Na OH and again it can be determined by gravimetric precipitation with AgNO3 as AgCl. If the 2 results obtained are concordant, high propablity of correct values.

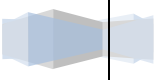
ACCURACY AND PRECISION

- There are certain basic concepts in analytical chemistry that are helpful to the analyst when treating analytical data. This section will address accuracy, precision, mean, and deviation as related to chemical measurements in the general field of analytical chemistry.

ACCURACY

- In analytical chemistry, the term 'accuracy' is used in relation to a chemical measurement. It can be defined as"closeness of the agreement between the result of a measurement and a true value." In theory, true value is that value that would be obtained by a perfect measurement.
- Accuracy is how close a measurement is to its desired or theoretical value.
- For example, if we need to dispense 25.0 mL of dilute HCl, then dispensing 24.9 mL is more accurate than dispensing 25.7 mL.
- Accuracy usually is reported as a percent error

$$\%\text{Error} = \frac{\text{actual value} - \text{expected value}}{\text{expected value}} \times 100$$



expected value

For analytical methods there are two methods for determining accuracy.

1. ABSOLUTE METHOD – In this Sample containing known amount is used. Various concentration of known amount is made and proceeded according to specified instructions
   The amount of constituent should be varied, because the determinate error is considered as a function

   Eg 1, 100% known + 5% added ---------- 105%
   2, 100% known + 6% added ---------- 106%
   } Accurate

   1, 100% known + 5% added ---------- 105%
   2, 100% known + 6% added ---------- 105%
   } Not Accurate

2. COMPARATIVE METHOD – sometimes when primary samples unavailable and are impossible to prepare it for analyst. In those cases a secondary standard is used in a same method. But this method is not usefull in analytical purpose.

PRECISSION

Precision is the reproducibility of a set of measurements. For example, Three identically prepared solutions with pH values of **6.76, 6.73,** and **6.78** are more precise than a duplicate set with pH values of **6.76, 6.54,** and **6.92**.

Precision usually is reported as a standard deviation,s,

which we define as $S = \sqrt{\frac{\sum(xi - \bar{x})^2}{2n-1}}$

Where '$\bar{x}$' is the average, or mean result, and 'xi' is one of the 'n' different results.

Another example - 2 analyst performing analysis for an accurate value 70%.

Analyst 1

70.07
70.18
70.14
70.08
70.02
} NOT PRECISE

Analyst 2

70.20
70.21
70.23
70.21
70.20

MORE PRECISE

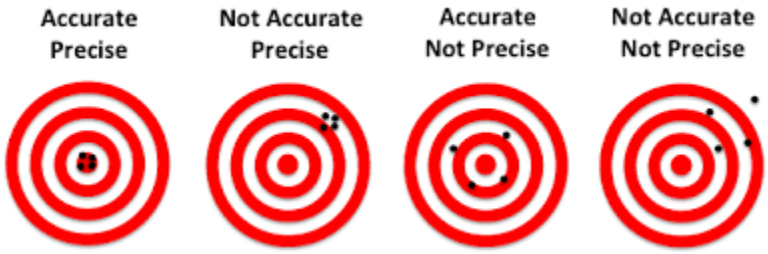


Figure 2: Clusters of five rifle shots illustrating the difference between accuracy and precision