

Definition of Significant Figure

Significant figure in a number may be defined as all the certain digits plus one doubtful (or uncertain) digit.

For example volume of 12.6 ml & 12.60 ml are numerically the same. But from the analytical point of view 12.6 ml containing three figures (1, 2, 6) is significant. When one burette is graduated to 0.1 ml whereas actual volume is 12.6 ± 0.1 , 12.60 ml containing 4 figures (1, 2, 6, 0) when burette is graduated to 0.01 ml, actual volume is 12.60 ± 0.01 .

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Rules for determining Significant Figures.

Nonzero integers: All nonzero integers are significant.
e.g. 5.231 has four significant figures. 2.45 has three significant figures.

Recognition of zero as significant numbers.

The digit zero may or may not be significant.

In the burette graduated to 0.01 ml, let burette reading be 20.05 ml. This contains four significant figures.

Here both zeros are treated as significant figures. If the above burette reading is expressed in a litre, it could be

0.02005 lt. Since the number of significant number figure

can not change just by changing the unit, this should have only four significant numbers.

a volume of 2 lt \approx 2000 ml has one significant figure

Number	Expression	Significant figure	Remark
0.612	612×10^{-3}	3	→ 0 is not significant
70.9	709×10^{-1}	3	→ 0 significant
0.007	7×10^{-3}	1	→ 0 not significant
	6.023×10^{23}	4	→ 0 significant figure
	1.03×10^{-13}	3	→ 0 significant

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Leading zeros: zeros that precede all the non-zero digits are called leading zero. These are not counted as significant figures. They merely indicate the position of decimal point. 0.007, the zeros are leading zero so that 0.007 has one significant figure.

Captive zeros: zeros between two non-zero digits are called captive zeros. These are always counted as significant figures. E.g. 70.9, 0 is captive zero & taken as significant figure. 70.9 has three significant figures.

Trailing zeros: the zeros at the right-end of the number are called trailing zero. They are significant if the number contains a decimal point. 900.00, the zeros are example of trailing zero and are significant as these are present after the decimal point.

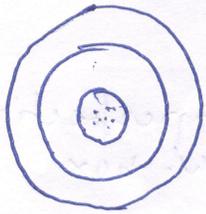
When the number ends in zeros that are not to the right of the decimal point, the zeros are not necessarily significant. For e.g. 240 can have two or three significant figures.

Accuracy: Accuracy is the degree of agreement between the measured value & the true value.

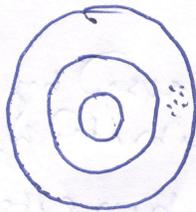
Precision: precision is defined as the degree of agreement between the replicate measurements of the same quantity.

That is, it is the repeatability of a result.

good precision does not assure good accuracy.



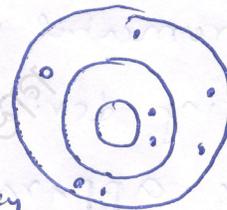
High accuracy
high precision



Low accuracy
high precision



High accuracy
low precision



Low accuracy
low precision

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Ways of Expressing Accuracy

Absolute Error: The difference between the ^{measured} ~~true~~ value & the ~~measured~~ ^{true} value, with regard to the sign, is the absolute error. It is reported in same unit.

If a 2.62 g sample of material analysed to be ~~2.59~~ 2.59 g

$$\text{absolute error} = 2.62 - 2.59 =$$

$$\text{absolute error} = 2.59 - 2.62 = -0.03 \text{ g}$$

$$E = (x_m - x_t)$$

Relative Error: It is the value obtained by dividing the absolute error by the accepted or true value.

$$E_r = \frac{(x_m - x_t)}{x_t}$$

E_r is expressed in percentage or in parts per thousand (ppt)

$$E_r = \frac{x_m - x_t}{x_t} \times 100 \%$$

Classification of Errors

- 1) Determinate errors or constant errors or systematic errors
- 2) Indeterminate errors or unsystematic errors or random errors

Determinate errors: Source of error can be identified.

Thus this error can easily be identified by an analytical chemist & can be avoided.

1) Instrumental error: This is caused by imperfections in measuring devices such as uncalibrated weight box, volumetric apparatus like pipette, burette etc. faulty chemical balance & pH meter. Electronic instruments are subject to this error due to voltage fluctuations. This is also considered as reagent error due to attack of reagents on graduated glassware, porcelain etc.

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2) Methodic error: These errors arise from incorrect sampling & incomplete reactions involved in a particular analytical procedure or non-ideal behavior of reagents or reactions. The non-ideal behavior arises from the slowness of reactions, instability of reactions, involvement of side reactions that interfere with main measurements.

3) Operational & personal errors: This depends on the personal judgement of individual analyst & not connected to the method or procedure followed.

Standard deviation (σ or s)

The standard deviation σ of an infinite set of experimental data is theoretically the square root of the mean of square of the difference betⁿ the individual measured value (x_i) & the mean (μ) of infinite no of measurement.

$$\sigma = \sqrt{\frac{\sum (x_i - \mu)^2}{N}} \quad \text{Where } N \rightarrow \infty$$

In practice, it is only possible to calculate the individual deviation from the mean (\bar{x}) of a limited number of measurement. i.e. $x_i - \bar{x}$. Hence it is desirable to define a quantity which is called the estimated standard deviation (s) which is applicable to a finite set of data & is given by

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

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Where N is the number of measurement & the number ($N-1$) is called the number of degrees of freedom or independent measurement.

For a set of N measurements, it is possible to calculate N independently variable deviations from the some reference no. But if the reference no chosen is the estimated mean \bar{x} , the sum of the individual deviations must necessarily add upto zero. So values $N-1$ deviations are adequate to define the N th value. Restricted to $N \geq 30$ values applicable

Relative standard deviation:

Relative standard may be expressed relative to mean as per % of ...