

# Errors and Uncertainty

## Reporting results: Significant figures

- The number of figures reported for a particular quantity tells us how accurately the quantity has been measured. These are called significant figures.
- You should quote your results to an appropriate number of significant figures. Calculators display lots of numbers but many of them will be meaningless. When deciding how many significant figures to quote a result to, you must consider the various stages of the method and their uncertainties, e.g. the accuracy of the analytical balance or the readability of a burette.
- Remember to use the number of significant figures that is appropriate to the accuracy of the measuring equipment you have used.

## Glossary of key terms

A glossary of key terms to help you when carrying out experimental procedures and looking at your results objectively.

- **STANDARD DEVIATION** - A measure of the spread of data. It is used to estimate the precision of measurements and give an estimate of the likely spread of results about the average value.
- **PRECISION** - A measure of the spread of results. Precision is estimated by calculating the standard deviation of the results from a set of repeated measurements. Methods that give results that are close together are said to be precise. The size of the random errors will determine the precision.
- **REPEATABILITY** - The estimate of precision that is obtained if repeated measurements are made by the same person, using the same equipment, in the same location over a short period of time.
- **REPRODUCIBILITY** - The estimate of precision that is obtained if repeated measurements are made by different people, using different equipment, in different locations over a long period of time.
- **BIAS** - A measure of the difference between the average of repeated measurements and the true value (the 'right' answer). Methods that give results that are very close to the true value are said to be unbiased. Systematic errors cause results to be biased.
- **ACCURACY** - A property of a single result. It tells us how close the results are to the true value. A result that is precise and unbiased is said to be accurate.
- **MEASUREMENT UNCERTAINTY** - The range of values within which we expect the true value to lie, with a stated level of confidence. Both random and systematic errors contribute to measurement uncertainty.

For more information on measurement terminology see, Introduction to Measurement Terminology, E Prichard, LGC, Teddington, 2004, ISBN 0 948926 21 X.



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## What is measurement uncertainty?

- Measurement uncertainty is the range of values within which the value of the quantity being measured is expected to lie.
- It indicates how sure or unsure you are of your measurement results.
- Example - The concentration of a hydrochloric acid solution has been determined as  $0.102 \text{ mol dm}^{-3}$ . The uncertainty has been estimated as  $\pm 0.0016 \text{ mol dm}^{-3}$ . This means that the actual concentration of the acid is somewhere between  $0.1004$  and  $0.1036 \text{ mol dm}^{-3}$ .

## Why is measurement uncertainty important?

- Measurement uncertainty tells us something about the reliability of a measurement.
- Every day, many decisions are made, based on the results of measurements. People making these decisions need to be sure that the results are reliable. If the results are not reliable then the wrong decision may be made.
- This could result in, for example, a patient being given the wrong treatment or a poor quality product being sold.

## Sources of measurement uncertainty

- Even the most careful and experienced analyst rarely gets exactly the same results every time.
- Uncertainty in results is not due to the analyst making mistakes during the analysis. Results vary due to factors outside the control of the analyst.
- Some examples of where sources of measurement uncertainty in chemical analysis can arise are shown opposite.
- In any experiment there will be a number of causes of error that will contribute to the measurement uncertainty.
- When thinking about measurement uncertainty there are two general sources of uncertainty that we need to consider - random and systematic errors.

If the meniscus of a liquid lies between two graduation marks on a burette, it is difficult to accurately determine the volume.



Judging the position of the end point (colour change) of a titration by eye is difficult.



A volumetric flask may contain slightly more than the stated volume when filled to the calibration mark, due to permitted variation in the manufacture of the flask.



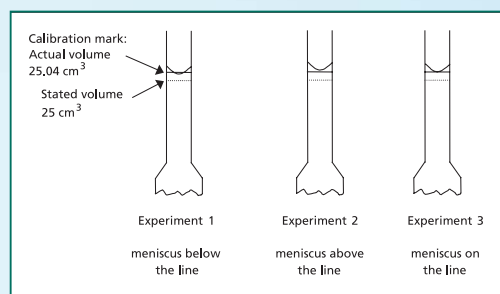
The balance display will only show the mass to a certain number of decimal places.



## Sources of error

- Every measurement you make in an experiment is subject to some degree of error or doubt. These errors lead to uncertainty in the final result that you quote. Understanding how errors happen can help you find ways to reduce them and therefore have greater confidence in your results.
- The main sources of error in an experiment are random errors and systematic errors.
- Random error - A random error causes variation in results from one measurement to the next in an unpredictable way. Random errors are always with us and cannot be corrected for, but they can be reduced by making more measurements and calculating the average of the results.
- Systematic error - Systematic errors cause results to differ from the true value (the 'right' answer) by the same amount, each time a measurement is made. These errors make the result always higher or lower each time. Sometimes it is possible to correct results to remove systematic errors.
- The choice of equipment used to make a measurement will influence the size of the errors.
- Volumetric glassware (pipettes, burettes etc) is calibrated so that when it is filled to the calibration line at a specific temperature it will contain a stated amount of liquid. However it is impossible for the manufacturer to produce a large amount of glassware (e.g. pipettes) which will all contain exactly the stated amount of liquid when filled to the calibration mark. The manufacturer is therefore allowed a range around the target value (e.g.  $\pm 0.06 \text{ cm}^3$  for a  $25 \text{ cm}^3$  Class B pipette). This range is called a tolerance.
- For example a  $25 \text{ cm}^3$  Class B pipette has a tolerance of  $\pm 0.06 \text{ cm}^3$ , whereas a  $25 \text{ cm}^3$  Class B measuring cylinder has a tolerance of  $\pm 0.5 \text{ cm}^3$ . If you were to measure  $25 \text{ cm}^3$  of liquid with both a  $25 \text{ cm}^3$  Class B pipette and a  $25 \text{ cm}^3$  Class B measuring cylinder, the volume of liquid dispensed from the measuring cylinder would have a larger uncertainty, due to it having a larger tolerance. Therefore to reduce the uncertainty you should measure  $25 \text{ cm}^3$  of the liquid using a  $25 \text{ cm}^3$  Class B pipette.

### BOTH SYSTEMATIC AND RANDOM ERRORS NEED TO BE CONSIDERED WHEN THINKING ABOUT MEASUREMENT UNCERTAINTY



### The figure illustrates both random and systematic errors, using the example of a $25 \text{ cm}^3$ Class B pipette

**Systematic error** - The pipette has a stated volume of  $25 \text{ cm}^3$ . However, due to the manufacturing process the actual volume of liquid, when the pipette is filled to the calibration mark is  $25.04 \text{ cm}^3$ . This is well within the permitted tolerance for a class B pipette. As the calibration mark will always be  $0.04 \text{ cm}^3$  higher than the stated volume (dotted line), this is a systematic error.

**Random error** - Every time you use the pipette, lining up the meniscus with the calibration mark will vary slightly. This is a random error as the position of the meniscus varies unpredictably.

- Errors are often wrongly referred to as mistakes, but in scientific measurements errors and mistakes are very different. When mistakes happen in your practical work they can have a large effect on your results, whereas errors often have only a small effect and are difficult to detect.
- For any method there are many sources of error that will contribute to the uncertainty in the results.

### Sources of uncertainty for the determination of hydrochloric acid concentration by titration

- The concentration of hydrochloric acid is determined by titration with sodium hydroxide solution, that has been standardised against a solution of potassium hydrogen phthalate (KHP).
- Errors are present even when the method has been carried out correctly and you have worked carefully.
- Typical uncertainty estimates are shown in the table below.

Concentration of KHP standard solution	Value	Uncertainty	Uncertainty expressed as a % *
Purity of KHP	99.5 %	0.14 %	0.14 %
Weighing out KHP <ul style="list-style-type: none"><li>▪ Calibration of balance</li><li>▪ Readability of balance</li><li>▪ Precision (random variability in using the balance)</li></ul>	5.105 g	0.0016 g	0.031 %
Making solution up to volume <ul style="list-style-type: none"><li>▪ Calibration of volumetric flask (manufacturing tolerance)</li><li>▪ Precision (variability in judging when the meniscus is lined up with the calibration mark)</li></ul>	250.0 cm <sup>3</sup>	0.18 cm <sup>3</sup>	0.072 %
Concentration of the NaOH solution			
Volume of KHP standard solution <ul style="list-style-type: none"><li>▪ Calibration of the pipette (manufacturing tolerance)</li><li>▪ Precision (variability of pipette delivery)</li></ul>	25.0 cm <sup>3</sup>	0.042 cm <sup>3</sup>	0.17 %
Volume of NaOH <ul style="list-style-type: none"><li>▪ Calibration of the burette</li><li>▪ Readability of the burette (judging the position of the meniscus in relation to the calibration marks)</li><li>▪ Precision (variability in judging the endpoint)</li></ul>	25.15 cm <sup>3</sup>	0.13 cm <sup>3</sup>	0.52 %
Transferring HCl solution			
Volume of HCl <ul style="list-style-type: none"><li>▪ Calibration of the pipette</li><li>▪ Precision (variability of pipette delivery)</li></ul>	25.0 cm <sup>3</sup>	0.042 cm <sup>3</sup>	0.17 %
Carrying out titration			
Volume of NaOH solution <ul style="list-style-type: none"><li>▪ Calibration of the burette</li><li>▪ Readability of the burette</li><li>▪ Precision (variability in judging the endpoint)</li></ul>	25.65 cm <sup>3</sup>	0.13 cm <sup>3</sup>	0.51 %

\* Uncertainty expressed as a % =  $\frac{\text{Uncertainty} \times 100}{\text{Value}}$

NOTE: The relative uncertainty, calculated using the equation above, has no units as it is a ratio of two values with the same units.

For more on measurement uncertainty see, *Introducing Measurement Uncertainty*, V Barwick and E Prichard, LGC, Teddington, 2003, ISBN 0 948926 19 8.