

Making measurements and manipulating experimental results

Many students and, perhaps, some teachers, have difficulty with the ideas of accuracy, precision and uncertainty when dealing with experimental measurements and with the appropriate use of significant figures and units when carrying out mathematical manipulations. This material presents a brief guide to these concepts suitable for post-16 level. The three main parts of the material, *Accuracy, precision and uncertainty*, *Significant figures* and *Units*, are aimed mainly at the teacher but teachers may wish to select sections to be given to students. Sets of questions (with answers) related to *Significant figures* and *Units* are provided to help students practise working with these ideas. A simplified version of this material aimed at post-16 students is also available at:

www.chemsoc.org/networks/learnnet/RSCmeasurements.htm

Accuracy, precision and uncertainty

There is often some confusion about a number of terms used when dealing with experimental measurements in science, including the chemical sciences. In particular the words *accuracy* and *precision* are often, wrongly, used interchangeably.

Some definitions

The following are formal definitions of some of the terminology used.

Trueness is a measure of the closeness of agreement between the average value obtained from a large series of measurements and the accepted reference value. Note that in many real life situations there is no accepted reference value, for example in the case of measuring the purity of a newly-synthesised compound. In this sort of situation, the same experimental set up is used to measure a value that is known in order to obtain an estimate of the trueness of the procedure.

Bias of a method of measurement is a measure of trueness, it is the difference between the average of a number of measurements and the reference value. (For example a 250 cm³ volumetric flask that consistently holds 250.3 cm³ due to imperfections in manufacture may be said to be biased by 0.3 cm³.) It is a measure of the overall systematic error of the method.

Precision is the closeness of agreement between independent measurements obtained under the same conditions. It depends only on the distribution of random errors (*ie* the spread of measurements) and does not relate to the true value. This means that a set of measurements may be precise but not true.

Error (of measurement) is the difference between an individual measurement and the **true** value (or accepted reference value) of the quantity being measured.

Accuracy is a measure of the closeness of agreement between an individual test result and the accepted reference value. If a test result is **accurate**, it is in close agreement with the accepted reference value, *ie* is precise and unbiased.

Uncertainty is an estimate attached to a measurement which characterises the range of values within which the true value is asserted to lie. This is normally expressed as a range of values such as 44.0 ± 0.4.

Reliability is the opposite of uncertainty, *ie* if the uncertainty is great, the measurement is not very reliable.

The analogy between experimental results and the grouping of shots on a dartboard is often used to help explain some of these terms. Here the true value is represented by the bull (centre of the board) and the fall of the darts is analogous to the experimental results. Some situations are shown in Figure 1.

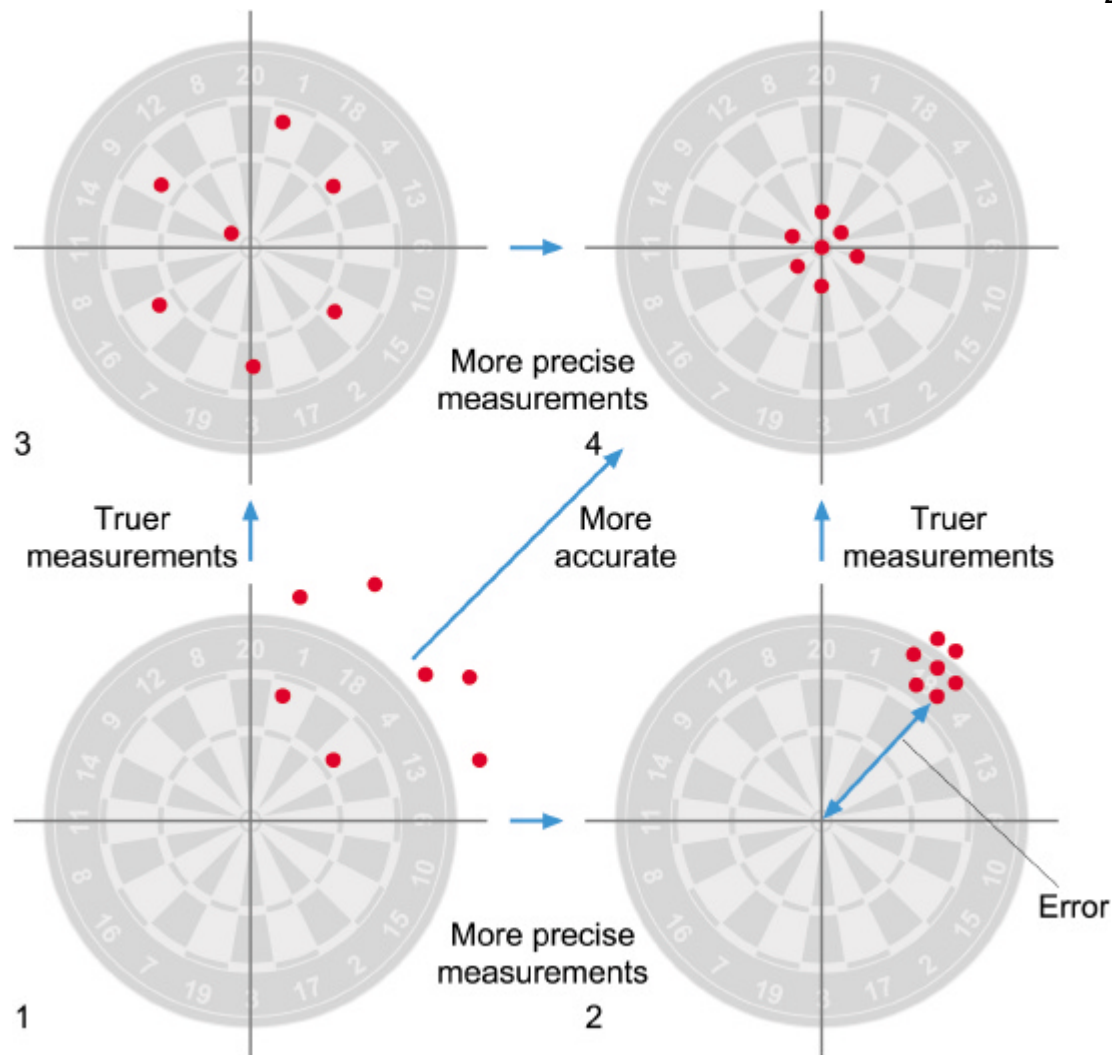


Figure 1 The dartboard analogy for experimental results

In situation 1, the darts are relatively spread out and it is clear that the average position is some way from the bull. The results are neither **precise** (closely grouped) nor **true** (centred on the bull).

In 2, the darts are grouped more closely together, but the average position is the same as in 1. In this situation, the **precision** is greater but the **trueness** is the same compared with 1.

In 3, the darts are relatively spread out but the average position is close to the bull. Here the **precision** is low, as in 1, but the **trueness** is better.

In 4, the darts are grouped closely together and their average position is close to the bull. The position of the darts is both **more precise** and closer to being **true** than in 1. The individual points in 4 are also more accurate than those in 1.

In case 2 the magnitude of the error for one of the results is shown.

Calibration

Before use, measuring instruments must be calibrated to ensure that the readings they give are accurate as defined above. For a balance this would involve weighing a standard mass and comparing the value obtained with the reference value of the standard. (In practice this would actually involve weighing a number of standard masses of different sizes derived from reference standards to get a range of

calibration points across the operating range of the balance.) This is how all balances are calibrated by (indirect) reference to the international standard kilogram mass held in a vault at Sèvres, in France. In reality, of course, this is done indirectly by means of secondary standards (copies of the original). If the balance is consistently giving readings that vary from the known value of the standard (*ie* the results are not true) then either the balance must be adjusted or a correction applied to the results displayed.

Random and systematic errors

If a scientist makes a measurement of the same thing several times, following exactly the same procedure, he will not get the same result each time (although it may look the same because of over-rounding or because the instrument displays only a limited number of digits). This is due to so-called **random errors**. For example, if a chemist repeatedly dispenses 10 cm³ water from the same pipette and weighs the aliquots in grams on a balance to 4 decimal places, all the results will be slightly different. This scatter is random because the readings will be either side of the true value and it is not possible to predict their size. Precision is a measure of this scatter – the smaller the scatter, the more precise is the result.

Systematic errors are predictable in that they are the same every time and their size can be worked out. For example a 250 cm³ volumetric flask may actually hold 250.3 cm³ when it is filled to the mark because of the way it was manufactured. Every time this flask is used, this error will be the same. In other words, there will be bias in the measurements.

Significant figures

When making a numerical measurement, we should indicate its degree of uncertainty by the appropriate use of significant figures. If the uncertainty of the final result (appropriate sum of all uncertainties) has not been calculated we can still indicate the uncertainty of measured values by the correct use of significant figures. If we measure a reading of length as 5 cm, for example, we mean that our measuring device reads to the nearest centimetre, *ie* the length is somewhere between 4.5 cm and 5.5 cm. If we report the length as 5.0 cm it means that our ruler reads to the nearest 0.1 cm, *ie* the true value lies between 4.95 cm and 5.05 cm. A value of 5.00 cm means that we have measured to 0.01 cm and so on. So the measurements 5 cm, 5.0 cm and 5.00 cm have different meanings. We say that they have different numbers of **significant figures**.

In a measurement, the number of significant figures is the number of digits that we know *for certain* plus the *first uncertain one*. A top pan balance that reads to two decimal places (of a gram) is a good example. We may get a reading such as 32.5? g, the ? meaning that the last figure fluctuates between, say, 6 and 8. We would therefore report the weight as 32.57 g. We know the first three figures for certain but we cannot be sure of the final one so there are four significant figures. It is important not to delete or round off the last figure because this gives us a measure of the uncertainty of the reading. See the section on *Rounding off* below.

A useful rule for making measurements is:

- When using a digital measuring device (such as a modern top pan balance or ammeter), record *all* the digits shown, see Figure 2.
- When using a non-digital device (such as a ruler or a burette) record all the figures that are known for certain plus one that is estimated, see Figure 3.

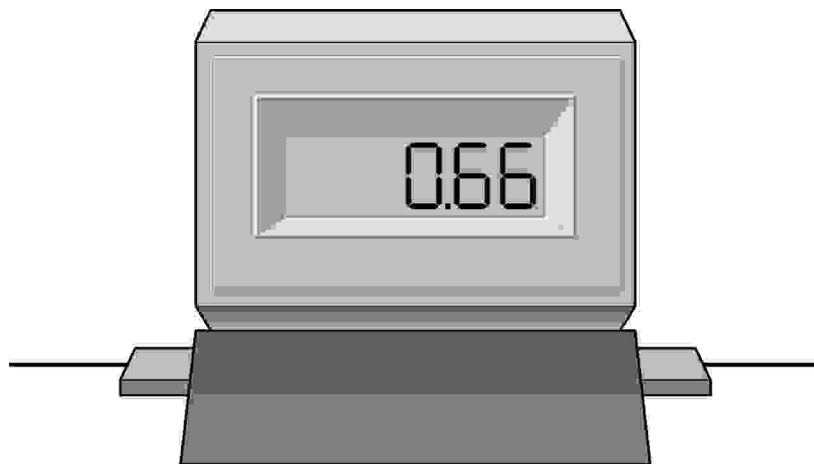


Figure 2 When using a digital measuring device, record *all* the digits

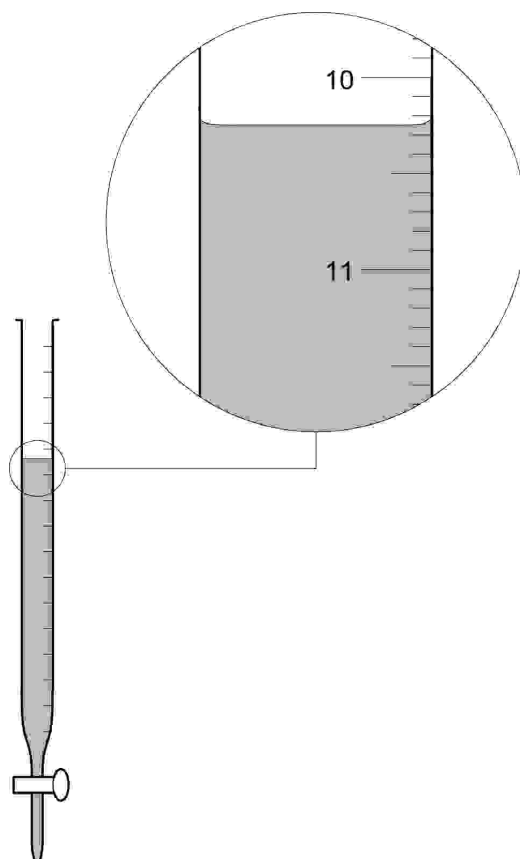


Figure 3 When using a non-digital device record all the figures that are known for certain plus one that is estimated. This burette is reading estimated as 10.25 cm^3

When a number contains zeros, some confusion can arise. The rules for working out the number of significant figures are given below:

- Zeros between digits are significant. For example 2004 has four significant figures.
- Zeros to the left of the first non-zero digit are not significant (even when there is a decimal point in the number). For example 0.002 has one significant figure.

- When a number with a decimal point ends in zeros to the right of the decimal point these zeros are significant. For example 2.0040 has five significant figures.
- When a number with no decimal point ends in several zeros, these zeros may or may not be significant. The number of significant figures should then be stated. For example: 20 000 (to 3 sf) means that the number has been measured to the nearest 100 while 20 000 (to 4 sf) means that the number has been measured to the nearest 10.

The following examples of the number of significant figures should help you work out the number of significant figures in your data.

1. The number 14.33 has four significant figures - all non-zero digits are significant.
2. The number 2000. We cannot tell the number of significant figures. Since there is no decimal point, the zeros may or may not be significant. With numbers with zeroes at the end we must state the number of significant figures.
3. The number 2000.0 has five significant figures - the decimal point implies that we have measured to the nearest 0.1.
4. The number 1.045 has four significant figures - zeros between digits are significant.
5. The number 0.025 has two significant figures - zeros to the left of the decimal point only fix the position of the decimal point. They are not significant.
6. The rules are the same when dealing with numbers expressed in standard form so 6×10^{23} has one significant figure, 6.022×10^{23} has four.

Significant figures in calculations

The result of a calculation that involves measured quantities cannot be more certain than the *least* certain of the information you used. So the result should contain the same number of significant figures as the measurement that has the *smallest* number of them.

A common mistake by students is to simply copy down the final answer from the display of a calculator. This often has far more significant figures than the measurements justify.

Example

From a single measurement and volume, 81.04 g (4 significant figures) of iron has a volume of 10.1 cm^3 (3 significant figures). What is its density?

$$\text{Density} = \frac{\text{mass}}{\text{volume}} = \frac{81.04 \text{ g}}{10.1 \text{ cm}^3}$$

Doing this division on a calculator gives the result $8.023762376 \text{ g cm}^{-3}$. This apparently has 10 significant figures.

Since our least certain measurement was to 3 significant figures, the answer cannot be more certain than this and we should give the best estimate of density to three significant figures.

$$\text{Density} = 8.02 \text{ g cm}^{-3}$$

Note that we do not know how the measurements were made so we cannot comment on the accuracy of the result

Rounding off

When we round off a number that has more significant figures than are justified (as in the example above), we round up if the last figure is between 5 and 9 inclusive and round down if it is between 0 and 4 inclusive.

For example, the number 360.99 rounded to:

4 sig fig is 361.0 (rounded up – the fifth figure is 9)

3 sig fig is 361 (rounded up – the fourth figure is 9)

2 sig fig is 360 (rounded down – the third figure is 0)

1 sig fig is 400 (rounded up – the second figure is 6)

Notice that when rounding you only look at the one figure beyond the number of figures to which you are rounding, *ie* to round to three sig fig you only look at the fourth figure. 'Sig fig' and 'sf' are both acceptable abbreviations for significant figures'.

If the answer to the density calculation above had been 7.97644094, we would have rounded up to 7.98 as the fourth significant figure is between 5 and 9.

The other point to be careful about is *when* to round off in calculation with two or more steps. This is best left to the very end of the calculation. Rounding off after each step and using this rounded figure as the starting figure for the next step could make a difference to the final answer.

Units

All measured quantities have units which almost without exception in scientific work, will be SI (Système International) ones. The base units from which all other units can be derived are:

metre, m, length

kilogram, kg, mass

second, s, time

ampère, A, electric current

kelvin, K, temperature

mole, mol, amount of substance

candela, cd, luminous intensity

Derived units are formed from the base units by multiplication or division. For example speed is defined as distance travelled \div time taken, so the unit of speed is m / s, often written as m s^{-1} . Some derived units have their own names. For example electric charge is calculated from the equation

electric charge = electric current \times time

and so is measured in A s (ampère seconds). The A s has the name coulomb, C.

Frequency is a measure of the number of vibrations per second has thus has the units s^{-1} . This unit is given the name hertz, symbol Hz

Note. Despite being named after people, units such as coulomb, hertz, newton, pascal, *etc* are written with a lower case initial letter.

When doing calculations it is good practice to include the units along with the numerical quantity. The units multiply and cancel in just the same way as do numbers. So the units of the quantity being calculated are derived from those of the quantities used to calculate it.

Example 1

$$\text{Density} = \frac{\text{mass}}{\text{volume}}$$

So if 2 m^3 of aluminium has a mass of 5400 kg, what is the density of aluminium?

$$\text{Density} = \frac{5400 \text{ kg}}{2 \text{ m}^3} = 2700 \text{ kg m}^{-3}$$

Example 2

The rate expression for the acid catalysed reaction of iodine with propanone is

Rate = $k [\text{CH}_3\text{COCH}_3] [\text{H}^+]$, where k is the rate constant and the square brackets represent the concentration of the species inside them in mol dm^{-3} .

$$k = \frac{\text{rate}}{[\text{CH}_3\text{COCH}_3][\text{H}^+]}$$

Reaction rates are measured in $\text{mol dm}^{-3} \text{ s}^{-1}$ and concentrations in mol dm^{-3} , so the units of the rate constant are

$$\frac{\text{mol dm}^{-3} \text{ s}^{-1}}{\text{mol dm}^{-3} \text{ mol dm}^{-3}}$$

These cancel

$$\frac{\text{mol dm}^{-3} \text{ s}^{-1}}{\text{mol dm}^{-3} \text{ mol dm}^{-3}}$$

to give the units of k as $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

Writing and cancelling units in equations should make sure that you get the correct units for the quantity you are calculating. To make sure that you can cancel units correctly, you may need to convert derived units back into base units.

Example 3

The frequency, f , of electromagnetic radiation is linked to its wavelength, λ , by the equation

$$c = f \lambda$$

where c is the speed of light, $3 \times 10^8 \text{ m s}^{-1}$. The frequency of red light is $5 \times 10^{14} \text{ Hz}$; what is its wavelength?

Rearranging the equation gives

$$\lambda = \frac{c}{f} = \frac{3 \times 10^8 \text{ m s}^{-1}}{5 \times 10^{14} \text{ Hz}}$$

It is not possible to cancel the units when expressed in this way but if Hz is converted to the base unit, s^{-1} , it is possible to cancel and the units of wavelength are expressed correctly as m.

$$\lambda = \frac{3 \times 10^8 \text{ m s}^{-1}}{5 \times 10^{14} \text{ s}^{-1}}$$

$$\lambda = 6 \times 10^{-7} \text{ m}$$

Prefixes

Prefixes are often used with units. The most common ones are shown in the Table.

Prefix	Factor	Symbol
tera	10^{12}	T
giga	10^9	G
mega	10^6	M
kilo	10^3	k
deci	10^{-1}	d
centi	10^{-2}	c
milli	10^{-3}	m
micro	10^{-6}	μ
nano	10^{-9}	n
pico	10^{-12}	p

Notes

1. The base unit of mass, the kilogram already has a prefix. This is for historical reasons. We do not add extra prefixes to this. So 1×10^{-6} kg is 1 milligram (1 mg), *not* 1 microkilogram.
2. The prefixes deci- and centi- are not used very often except for the decimetre, dm, (and hence dm^3) and the centimetre, cm.

When using data expressed in units with prefixes in calculations it is better to convert back to the base units to prevent numerical errors and to allow the units to be cancelled. The preferred way to do this is to express the number in standard form, *ie* as a number multiplied by 10 raised to the appropriate power, the number being written with the decimal point to the right of the first digit.

Examples

1. The covalent radius of iodine is 0.133 nm. This is 0.133×10^{-9} m or 1.33×10^{-8} m.
2. The speed of light is $299\,792 \text{ km s}^{-1}$. This is $299\,792 \times 10^3 \text{ m s}^{-1}$ or $2.997\,92 \times 10^8 \text{ m s}^{-1}$.

Questions - significant figures and rounding

- Q1. What is the number of significant figures in each of the following?
- a) 12.45
 - b) 1200
 - c) 1200.0
 - d) 1.204
 - e) 0.024
- Q 2. Write the following numbers to the stated number of significant figures remembering to round up or down correctly.
- a) 34 561.22 to 4 sig fig
 - b) 4.278 to 3 sig fig
 - c) 523 to 1 sig fig
 - d) 542.45 to 4 sig fig
- Q 3. 50.00 g of sodium hydroxide were mixed with 50.00 g of hydrochloric acid and the temperature rose by 11.1 K. Use the equation
- $$?H = m s T$$
- to work out much heat (?H) was produced in the reaction stating your answer to the appropriate number of significant figures.
- m is the total mass of the solutions, T is the temperature rise. Take s (the specific heat capacity of the solution) to be $4.18 \text{ J g}^{-1} \text{ K}^{-1}$.

Questions - units

- Q 1. The rate expression for the reaction of 2-bromo-2-methylpropane, C_4H_9Br , with hydroxide ions is: $\text{Rate} = k [C_4H_9Br]$. Work out the units for the rate constant, k .
- Q 2. The frequency, f , of electromagnetic radiation is linked to its wavelength, λ , by the equation
 $c = f \lambda$
 where c is the speed of light, $3 \times 10^8 \text{ m s}^{-1}$. Blue/green light has a wavelength of $5 \times 10^{-7} \text{ m}$. Work out the frequency of this light and give the correct units.
- Q 3. The equilibrium law expression for the dissociation of water
 $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$
 is $K_c = \frac{[H^+(aq)]_{\text{eqm}} [OH^-(aq)]_{\text{eqm}}}{[H_2O(l)]_{\text{eqm}}}$
 where the square brackets [] represent the concentration of the species within them in mol dm^{-3} .
 What are the units of the equilibrium constant, K_c ?
- Q 4. The amount of heat (enthalpy) given out when two dilute solutions are mixed is given by the expression
 $Q = m s \Delta T$
 where m is the total mass of the solution in grams, s is the specific heat capacity of the solutions in $\text{J g}^{-1} \text{ K}^{-1}$ and T the temperature rise in K. Confirm by cancelling the units of m , s and T that this gives the correct units for enthalpy - joules.
- Q 5. The ionic radius of Cl^- is 0.180 nm. Express this in
 a) m
 b) pm
- Q 6. ΔH for the decomposition of ammonia into its elements is 92 kJ mol^{-1} . Express this in J mol^{-1} in standard form.

Answers

Significant figures and rounding

1.
 - a) 4 – all non-zero digits are significant
 - b) 2 (but it could be 2, 3, or 4). As the number has no decimal point, we cannot tell whether the zeros are significant or not. In cases such as this it is better to state the number of significant figures (eg 1200 to 2 sig fig).
 - c) 5. The decimal point makes the number of significant figures clear.
 - d) 4. Zeros *between* digits are significant.
 - e) 2. Zeros before the decimal point are not significant, they merely fix the position of the decimal point.
2.
 - a) 34 560
 - b) 4.28
 - c) 500
 - d) 542.5
3. A calculator gives the answer as 4639.8 J, but this has 5 significant figures. The smallest number of significant figures in the data is 3 (4.18 and 11.1) so we can give the answer to no more than 3 sig fig which is 4640 J.

Units

1. s^{-1}
2. $6 \times 10^{14} \text{ s}^{-1}$. (or Hz)
3. $\text{mol}^2 \text{ dm}^{-6}$.
4. Yes it does –the units are given by $\text{g} \times \text{J} \text{ g}^{-4} \text{ K}^{-4} \times \text{K}$.
5. a) $1.80 \times 10^{-10} \text{ m}$
 b) 180 pm.
6. $9.2 \times 10^4 \text{ J mol}^{-1}$.

Note – examinations

As indicated in the introduction there is sometimes inconsistency about how some of the ideas in this material are used and interpreted. When preparing students for external examinations, it would be advisable to check the interpretation used by the particular Awarding Body so that students can be made aware of what their particular Specification requires and to ensure that they are not unnecessarily penalised.

Further information

The LGC (Laboratory of the Government Chemist) has produced an excellent booklet, specifically targeted at students of post-16 chemistry: Vicki Barwick & Elizabeth Prichard, *Introducing measurement uncertainty*, London: LGC, 2003. A further booklet from LGC covers in detail much of the terminology used in measurement: Elizabeth Prichard, *Introduction to measurement terminology*, London: LGC, 2004.

These can be ordered from LGC.

Further details are available at.

http://www.vam.org.uk/training/training_school_resources.asp. (Accessed Nov 2004)

A simpler treatment of many of the above ideas suitable for use with pre-16 students is given in D. Warren, *The Nature of Science*, London: Royal Society of Chemistry, 2001, pp15-26. Student worksheets relating to this publication are available at www.chemsoc.org/networks/learnnet/nature.htm. (Accessed Nov 2004)

Some useful material about experimental error in chemistry and, in particular, combining experimental errors can be found at www.rod.beavon.clara.net/err_exp.htm. (Accessed Nov 2004)

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