10 Appendix – Measurements

Useful terms

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.

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

Precision is the closeness of agreement between independent measurements obtained under the same conditions. It depends only on the distribution of random errors (*i.e.* the spread of measurements) and does not relate to the true value.

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, *i.e.* if the uncertainty is great; the measurement is not very reliable.

How accurate are measurements?

When using a digital measuring device (such as a modern top pan balance or ammeter),

- record *all* the digits shown.

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.

As a general rule, the uncertainty is often taken to be half a division on either side of the smallest unit on the scale you are using. However, the accuracy of measurements does also depend on the quality of the apparatus used, such as a balance, thermometer or glassware.
For example, a 100 cm^3 measuring cylinder is graduated in divisions every 1 cm^3.

- A Class A measuring cylinder has a maximum error of half a division or 0.5 cm^3
- A Class B measuring cylinder has a maximum error of a whole division or 1 cm^3.

Because of this variability, assessed Tasks will state the **maximum error** in any measurement that is being made.

Examples of maximum errors

When glassware is manufactured there will always be a maximum error. This is usually marked on the glassware.

Some examples are shown below. Note that the actual maximum error on a particular item of glassware may differ from the values given below.

Volumetric or standard flask (Class B)

- A 250 cm^3 volumetric flask has a maximum error of 0.2 cm^3 or 0.08%.

Pipette (Class B)

- A 25 cm^3 pipette has a maximum error of 0.06 cm^3 or 0.24%.

Burette (Class B)

- A pipette has a maximum error of 0.05 cm^3 in each measurement.

Some examples

The significance of the maximum error in a measurement depends upon how large a quantity is being measured. It is useful to quantify this error as a percentage error.

$$\text{Percentage error} = \frac{\text{maximum error}}{\text{quantity measured}} \times 100\%$$

For example, a two-decimal place balance may have a maximum error of 0.005 g.
For a mass measurement of 2.56 g,

- percentage error = $\frac{0.005}{2.56} \times 100\%$ = 0.20%

- For a mass measurement of 0.12 g, the percentage error is much greater:

  Percentage error = $\frac{0.005}{0.12} \times 100\%$ = 4.2%

Multiple measurements

For multiple measurements using the same two-decimal place balance, there will be a maximum error of 0.005 g for each measurement.
For two mass measurements that give a resultant mass by difference, there are two maximum errors:

$$\text{Percentage error} = \frac{2 \times \text{maximum error in each measurment}}{\text{quantity measured}} \times 100\%$$

For example, using the same two-decimal place balance,

Mass of crucible + crystals before heat = 23.45 g	maximum error = 0.005 g
Mass of crucible + crystals after heat = 23.21 g	maximum error = 0.005 g
Mass lost = 0.23 g	maximum overall error = 2 x 0.005 g

There is a negligible percentage error in each mass measurement but the overall error in mass loss is much greater:

Percentage error in mass loss = $\frac{2 \times 0.005}{0.23} \times 100\%$ = 4.3%

Reading burettes

A burette is graduated in divisions every 0.1 cm^3.
A burette is a non-digital device, so we record all figures that are known for certain plus one that is estimated.
Using the half-division rule, the estimation is one of 0.05 cm^3. We therefore record burette measurements to two decimal places with the last figure either ‘0’ or ‘5’.
The maximum error in each measurement = 0.05 cm^3.

The overall maximum error in any volume measured always comes from two measurements, so the overall maximum error = 2 x 0.05 cm^3 = 0.1 cm^3.
In a titration, a burette will typically deliver about 25 cm^3 so the percentage error is small.

- Percentage error = $\frac{2 \times 0.05}{25.00} \times 100\% = 0.4\%$

For small volumes, the percentage error becomes more significant
For delivery of 2.50 cm^3,

- percentage error = $\frac{2 \times 0.05}{2.50} \times 100\% = 4\%$

Recording volumes during titrations

As shown above, each burette measurements should be recorded to two decimal places with the last figure either '0' or '5'.

During a titration, it is expected that students will record both initial and final burette readings from which a titre is calculated by difference. It is usual practice to record titration results in a table of the type shown below.

	trial	**1**	**2**	**3**
final burette reading / cm^3				
initial burette reading / cm^3				
titre / cm^3				
titres used to calculate mean (tick)				
mean titre / cm^3				

When recording the titre, it is normal practice to use two decimal places. This is what will be expected within the assessment Tasks.

Mean titres

When recording a mean titre, is usual practice to take an average of the concordant titres, *i.e.* those that agree to within 0.10 cm^3. Where this is not possible, the two titres that have the closest agreement should be used.

For example, three recorded titres are 25.80 cm^3, 25.30 cm^3 and 25.20 cm^3.
The mean titre is the average of the 2nd and 3rd titres which agree to within 0.1 cm^3.

- The mean titre is $\frac{25.30 + 25.20}{2}$ cm^3 = 25.25 cm^3

The overall maximum error is 2 x 0.05 = 0.1 cm^3.

There is a case for arguing that the accumulated errors indicate that one decimal place is more appropriate but this should **not** be used. The maximum error is the worst-case scenario and it is likely that the actual titre will in reality be more accurate than one decimal place.

A student obtaining concordant titres within 0.05 cm^3 of one another may encounter a problem when calculating the mean titre. For example, a student may obtain three recorded titres of 25.80 cm^3, 25.25 cm^3 and 25.20 cm^3.

The mean titre is $\frac{25.25 + 25.20}{2}$ cm^3 = 25.225 cm^3

This mean titre has a value that is more accurate than the burette can measure. The value of 25.225 cm^3 should more correctly be 'rounded' to 25.25 cm^3.

It would seem very unfair not to credit a mean titre of 25.225 cm^3 in this case, especially as this student has carried out the titration better than the first student.

What is acceptable in assessed Tasks?

As there are clearly problems with both the accumulated errors argument (leading to a one-decimal place titre) and titres that differ by 0.05 cm^3 (leading to a three-decimal place mean titre), the Mark Schemes of assessment Tasks will allow some licence for what is acceptable in the calculation of a mean titre.

- For example, the mean of two titres of 25.25 cm^3 and 25.20 cm^3 will be allowed as 25.2, 25.20, 25.25 or 25.225 cm^3.
- These values are not all equally valid but the policy will be to give the student the benefit of the doubt so long as the mean has been calculated from the appropriate values.

How many significant figures should be used?

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

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.

Rounding off

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

For example, the number 350.99 rounded to:

4 sig fig is 351.0
3 sig fig is 351
2 sig fig is 350
1 sig fig is 400

Notice that when rounding you only look at the one figure beyond the number of figures to which you are rounding, *i.e.* to round to three sig fig you only look at the fourth figure.

How do we know the number of significant figures?

In the example above, 351 has been rounded to the 2 sig fig value of 350.
However, if seen in isolation, it would be impossible to know whether the final zero in 350 is significant (and the value to 3 sig figs) or insignificant (and the value to 2 sig figs).
In such cases, standard form should be used and is unambiguous:

- 3.5×10^2 is to 2 sig figs
- 3.50×10^2 is to 3 sig figs

When to round off

It is important to be careful when rounding off in a calculation with two or more steps.

- Rounding off should be left until the very end of the calculation.
- Rounding off after each step, and using this rounded figure as the starting figure for the next step, is likely to make a difference to the final answer. This introduces a **rounding error**.

Students often introduce rounding errors in multi-step calculations.

Example
When 6.074 g of a carbonate is reacted with 50.0 cm^3 of 2.0 mol dm^{-3} HCl(aq) (which is an excess), a temperature rise of 5.5 °C is obtained. The specific heat capacity of the solution is 4.18 J g^{-1} K^{-1},
The heat produced = $50.0 \times 4.18 \times 5.5$ for which a calculator gives 1149.5 J = 1.1495 kJ

> *Since the least certain measurement (the temperature rise) is only to 2 significant figures the answer should also be quoted to 2 significant figures.*

Therefore, the heat produced = 1.1 kJ

- *It should be noted however, that if this figure is to be used subsequently to calculate the enthalpy change per mole then the rounding off should* ***not*** *be applied until the final answer has been obtained.*

For example, if the carbonate has a molar mass of 84.3 g mol^{-1}, the enthalpy change per mole of carbonate can be calculated from the value above.

Using the calculator value of 1.1495 kJ for the heat produced,

- enthalpy per mole = 15.95371255 kJ mol^{-1}.
- rounding to 2 sig figs gives 16 kJ mol^{-1}

Using the rounded value of 1.1 kJ for the heat produced,

- enthalpy per mole = 15.26671057 kJ mol^{-1}.
- rounding to 2 sig figs gives 15 kJ mol^{-1} and we have a ‘rounding error’.

Errors in procedure

The accuracy of a final result also depends on the procedure used. For example, in an enthalpy experiment, the measurement of a temperature change may be precise but there may be large heat losses to the surroundings which affect the accuracy of overall result.

Anomalous readings

Where an experiment uses repeated measurements of the same quantity, such as repeated titration readings, anomalous readings should be identified. If a titre is clearly outside the range of all other readings, it can be judged as being anomalous and should be ignored when the mean titre is calculated.

Similarly, if a plotted graph reveals that a value is anomalous, then it should be ignored.

References

The Royal Society of Chemistry has produced several very helpful documents on measurements and errors, see:

www.rsc.org/education/teachers/learnnet/pdf/learnnet/RSCmeasurements_teacher.pdf

www.rsc.org/pdf/amc/brief13.pdf