

University of Malta  
Department of Chemistry

CHE1332 - Mathematics for Chemists  
CHE1302 - Chemistry Practicals

## UNCERTAINTIES IN QUANTITATIVE ANALYSIS

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### 1. Introduction

The purpose of quantitative chemistry analysis is the quantitative characterization of matter. The very nature of quantitative experimental observation is such that it always involves some uncertainty, hence strictly speaking, no measurement made is ever exact.

Uncertainties are sometimes linked to errors, although the two terms refer to two completely different properties. Errors can be subdivided in three categories:

- systematic errors
- random errors
- spurious errors or blunders

A **systematic error** is the result of a mis-calibrated device, or a measuring technique which always makes the measured value larger (or smaller) than the "true" value. For example, all volumetric glassware is usually calibrated at 20°C. Thus, when this equipment is used at any other temperature, a systematic error is introduced. Careful design of an experiment will allow us to eliminate or to correct for systematic errors. For example, in our example, we may choose to run the experiments in an 'air-conditioned' laboratory maintained at a constant temperature of 20°C.

Even when systematic errors are eliminated there will remain a second type of variation in measured values of a single quantity. These remaining deviations are known as **random errors**, and can be dealt with in a statistical manner. In view of this, it is standard procedure to report any experimentally measured quantity,  $X$  with its associated standard uncertainties, or sometimes as a range  $X \pm \Delta X$  in which we have a 95% level of confidence.

A further type of error is a **spurious error or blunder**. Errors of this type invalidate a measurement and typically arise through human failure or instrument malfunction. Transposing digits in a number while recording data, an air bubble lodged in a spectrophotometer flow-through cell, or accidental cross-contamination of test items are common examples of this type of error. Uncertainties estimated using this guide are not intended to allow for the possibility of spurious errors/blunders.

## 2. Procedure for calculating uncertainties

The process of measurement uncertainty estimation involves the following steps:

### 1 - Specify measurand

Write down a clear statement of what is being measured, including the relationship between the measurand and the parameters (*e.g.* measured quantities, constants, calibration standards *etc.*) upon which it depends. Where possible, include corrections for known systematic effects. The specification information should be given in the method description.

### 2 - Identify uncertainty sources

List the possible sources of uncertainty. This will include sources that contribute to the uncertainty on the parameters in the relationship specified in step 1, but may include other sources and must include sources arising from chemical assumptions.

> For more details click here.

### 3 - Quantify uncertainty components

Measure or estimate the size of the uncertainty component associated with each potential source of uncertainty identified.

### 4 - Calculate combined uncertainty

The information obtained in step 3 will consist of a number of quantified contributions to overall uncertainty, whether associated with individual sources or with the combined effects of several sources. The contributions have to be expressed as standard deviations, and combined according to the appropriate rules, to give a combined standard uncertainty. At the end, the standard uncertainty may be transformed to a range of values acceptable at 95% confidence level using the appropriate coverage factor.

## 3. Quantifying uncertainties in single measurements

Very good measuring tools are calibrated against standards maintained by the National Institute of Standards and Technology (NIST), the British Standards (BS) or more commonly, the American Society For Testing and Materials (ASTM). At this level, we shall discuss the uncertainties in:

1. measurements of volume
2. measurements of mass
3. chemical purity.

### 3.1 Measurement of volume

The three main pieces of analytical equipment that are used in measuring volumes are volumetric flasks, burettes and pipettes. Such equipment is calibrated at 20<sup>0</sup>C and hence, its use at temperatures different than 20<sup>0</sup>C will result in a systematic error.

However, even at 20<sup>0</sup>C, it is not possible to have the volume measured exactly and there is always some uncertainty associated with the measured volume. In fact, volumetric glassware is permanently marked to state the uncertainties in the volume measured. For example, volumetric glassware that is permanently marked to Class "A" is guaranteed to comply with volumetric tolerances prescribed in ASTM E694, and latest revisions. It is also supplied with a serialized certificate of precision. Volumetric glassware that is permanently marked Class "B" has a tolerance that is twice as large as Class "A". (Note that Grade B equipment is sometimes referred to as 'economical' or 'general use'.

Volumetric equipment that is usually provided calibrated to a single mark (e.g. volumetric flasks), are always permanently marked as Grade A or Grade B, or should have a stated tolerance limit. The tolerance values as regulated by the ASTM for volumetric flasks of various sizes are given in Table 1.

Size of Flask (mL)	Tolerance (mL)		Size of Flask (mL)	Tolerance (mL)	
	Grade A	Grade B		Grade A	Grade B
10	0.02	0.04	250	0.12	0.24
25	0.03	0.06	500	0.2	0.4
50	0.05	0.1	1000	0.3	0.6
100	0.08	0.16	2000	0.5	1
200	0.1	0.2	5000	1.1	2.2

**Table 1:** Accepted tolerances for volumetric flasks according to the ASTM standards.

This means that a 100mL Grade A flask will have a tolerance of 0.08mL. This means that at 20<sup>0</sup>C (the temperature at which volumetric flasks are calibrated), the flask may contain anything between 99.92mL to 100.08mL. This is a description of a rectangular distribution function with a semi-range of  $\alpha = 0.08\text{mL}$ , and it can be shown that for a rectangular distribution, an estimate of the standard uncertainty (or standard deviation) can be calculated using<sup>1</sup>:

$$u(V) = \frac{\alpha}{\sqrt{3}}$$

i.e. in this case, we may say that the volume contained in a 100mL Grade A flask at 20<sup>0</sup>C is 100.00mL with a standard uncertainty of  $(0.08 / 3^{1/2})$  mL.

If a certificate of specification (or marks on the actual equipment cannot be found), one may assume that the tolerance of the equipment is given by the *least count* (or a fraction of the least count) of the equipment. The *least count* is the smallest division that is

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<sup>1</sup> This method for calculating the standard uncertainty from the tolerance of the equipment (i.e. by dividing with  $\sqrt{3}$ ) should also be used when the equipment certificate or other specification gives limits without specifying a level of confidence, or when an estimate is made in the form of a maximum range ( $\pm\alpha$ ) with no knowledge of the shape of the distribution. The only exception is when although the tolerance are given without a confidence level, there is reason to expect that extreme values are unlikely. In such cases, it is normally appropriate to assume a triangular distribution, with a standard deviation of  $\alpha/\sqrt{3}$ .

marked on the equipment. Thus for example, a 50mL burette will have a least count of 1.0mL, The use of a fraction of the least count as the tolerance rather than the least count itself is justified when the space between the scale divisions is large, in which case we may use for example use  $\frac{1}{2}$  of the least count instead of the least count itself. For example, the least count for a 50mL burette is usually 0.1mL, but as it possible to distinguish between a 0.10mL and a 0.15mL, then the  $\frac{1}{2}$  of the least count (i.e. 0.05mL) should be used as the tolerance of the burette.

Note that if a certificate of specification is found, you will find that the tolerance quoted is higher than the least count or the fraction of the least count. In other words, the least count / fraction of the least count should be the lower bound of the possible uncertainty in the measurement).

In addition to the uncertainty discussed above, other factors should be considered, such as uncertainties that arise from variations in temperature, etc. However, at this level, this will not be considered.

### 3.2 Measurement of mass

Mass is normally measured using digital analytical balances that can measure mass up to four decimal places of a gram (e.g. 1g reads weights as 1.0000 g). Analytical balances should also be calibrated and a certificate of specification should be available which should give the uncertainty associated with the measurement. If this certificate is unavailable, then the least count should be used, recalling that the standard uncertainty from a least count of  $\alpha$  is given by:

$$u(m) = \frac{\alpha}{\sqrt{3}}$$

Once again, in addition to the uncertainty discussed above, other factors should be considered, such as uncertainties that arise from lack of repeatability, etc. However, at this level, this will not be considered.

### 3.2 Purity of reagents

Analytical reagents are also supplied with a certificate of analysis which will state the purity of the reagents and the standard uncertainty in the purity. This should be taken into consideration in quantitative analysis. For example, if we need to prepare 1L of 1M NaCl (RMM: 58.44), then if the NaCl is supplied as 99% pure, then we should use 59.03g of NaCl rather than 58.44g since:

$$\text{mass}(\text{NaCl}) = \frac{100 \times 58.44}{99} = 59.03 \text{g}$$

Generally, uncertainties arising from purity can be reduced by using chemicals of higher standards or by carrying out a quantitative analysis of the substance using primary standards.

### 3. The issue of repeatability

Repeated measurements of the same quantity through the same method sometimes (and in practice, very often) result in slightly different readings. This ‘lack of repeatability’ may be due to:

1. Instrument limitation errors when performing the different steps of the experiment;
2. Other errors, such as inhomogeneity of the samples, etc.

The values obtained from repeated readings could be averaged and this average or mean value could be taken as the best value of the quantity in question. For measurements  $x_1, \dots, x_N$ , of the same quantity  $x$ , the mean value  $\bar{x}$  may be given by:

$$\bar{x} = \frac{x_1 + x_2 + \dots + x_n}{N} = \frac{\sum_{i=1}^N x_i}{N}$$

Note that:

$$x = \lim_{N \rightarrow \infty} (\bar{x})$$

In practice, repeated readings cost time and money, and in general, for quantitative analysis,  $N$  is 3-5. When only a finite number of measurements are recorded, we should also state a meaningful measure of the reliability of the mean value. In most work it is assumed that a given group of repeated measurements is a sample from a normal or Gaussian distribution. This distribution represents, for a large number of measurements, the relation between the *number of times* that readings of a given magnitude  $x$  are obtained and the *magnitude* of  $x$  itself.

A measure of the spread of observed values of  $x$  (i.e.  $x_1, \dots, x_N$ ) is the **standard deviation**,  $\sigma$  (valid when  $N > 30$ ) where the range  $\bar{x} \pm \sigma$  covers about 68% of all observations when repeated many times and is given by:

$$\sigma = \sqrt{\frac{(\bar{x} - x_1)^2 + (\bar{x} - x_2)^2 + \dots + (\bar{x} - x_N)^2}{N}} = \sqrt{\frac{\sum_{i=1}^N (\bar{x} - x_i)^2}{N}}$$

In practice, the number of observations is less than 30 (i.e.  $N \leq 30$ ) then we make use of  $s$  rather than  $\sigma$  where  $s$  is given by:

$$s = \sqrt{\frac{(\bar{x} - x_1)^2 + (\bar{x} - x_2)^2 + \dots + (\bar{x} - x_N)^2}{N - 1}} = \sqrt{\frac{\sum_{i=1}^N (\bar{x} - x_i)^2}{N - 1}}$$

Note that in practice, most of the calculations that are required under to calculate the mean and the standard deviation can be performed through a spreadsheet package such as MS Excel, see fig. 1.

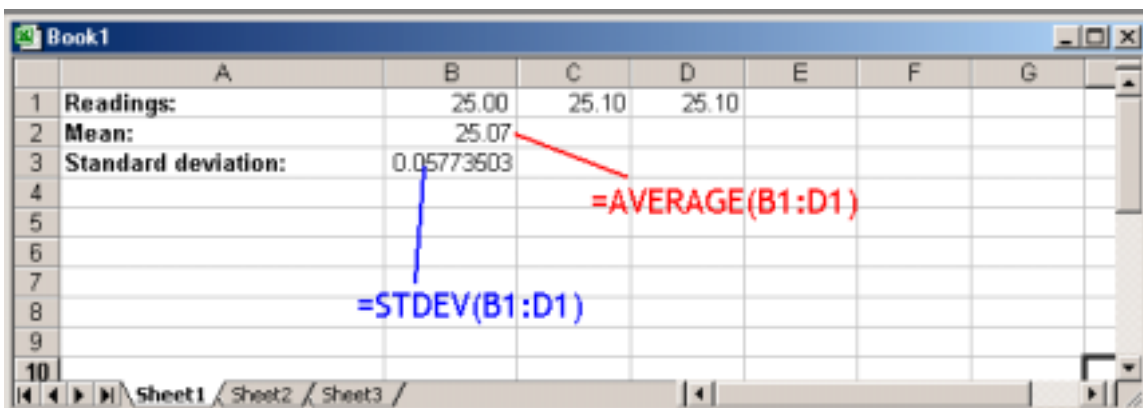


Fig. 1: The use of MS Excel to calculate means and standard deviations.

### 3. Propagation of Errors - Exemplified through the problem of finding the tolerance in volumetric solutions

We shall consider the case when the original substance is a liquid of  $(P \pm \Delta P)\%$  purity.

The concentration  $C$  (in M, i.e.  $\text{mol L}^{-1}$ ) is given by:

$$C = \left( \frac{1000\rho}{\text{RMM}} \right) \left( \frac{P}{100} \right) \left( \frac{V_s}{1000} \right) \left( \frac{V_T}{1000} \right)^{-1} = \left( \frac{10\rho}{\text{RMM}} \right) \frac{PV_s}{V_T} \quad (\text{eqn 1.})$$

where:

- $\rho$  is the specific density (in  $\text{kg L}^{-1}$ ) of the substance, i.e.  $1000\rho$  is the specific density in  $\text{g L}^{-1}$
- $P$  is the percentage purity, i.e.  $P/100$  represents the purity expressed as a fraction (maximum 1, minimum 0)
- $V_s$  is the volume of the substance in mL, i.e.  $V_s / 1000$  represents the volume of substance in L
- $V_T$  is the total volume of the final solution in mL, i.e.  $V_T / 1000$  represents the total volume in L. Note that this is the volume of the volumetric flask.

Let us now derive an expression for the standard uncertainty in  $C$ .

We must first check that the equation that we shall be using is unit consistent, as in this case.

We must then identify which quantities may be treated as ‘errorless constants’, leaving the rest as ‘variables’ each with a respective standard uncertainty. In this case we may assume that  $\rho$  and the RMM are constants, hence leaving  $P$ ,  $V_s$  and  $V_T$  as variables. Let us assume that the uncertainties in the values of these three variables be  $u(P)$ ,  $u(V_s)$  and  $u(V_T)$  respectively.

From eqn. 1 and the above we may deduce that:

$$C = \left( \frac{10\rho}{\text{RMM}} \right) \frac{PV_s}{V_T} = C(P, V_s, V_T)$$

i.e.:

$$dC = \left( \frac{\partial C}{\partial P} \right) dP + \left( \frac{\partial C}{\partial V_s} \right) dV_s + \left( \frac{\partial C}{\partial V_T} \right) dV_T$$

from which we may write an approximate value of  $\Delta C$  in terms of  $\Delta P$ ,  $\Delta V_s$  and  $\Delta V_T$ :

$$\Delta C = \left( \frac{\partial C}{\partial P} \right) \Delta P + \left( \frac{\partial C}{\partial V_s} \right) \Delta V_s + \left( \frac{\partial C}{\partial V_T} \right) \Delta V_T$$

Squaring this equation and recognising that the ' $\Delta X_i$ ' pairs other than  $(\Delta P)^2$ ,  $(\Delta V_s)^2$  and  $(\Delta V_T)^2$  may be assumed to be zero since  $P$ ,  $V_s$  and  $V_T$  are independent variables, then we may write:

$$(\Delta C)^2 = \left( \frac{\partial C}{\partial P} \right)^2 (\Delta P)^2 + \left( \frac{\partial C}{\partial V_s} \right)^2 (\Delta V_s)^2 + \left( \frac{\partial C}{\partial V_T} \right)^2 (\Delta V_T)^2$$

or in terms of standard uncertainties:

$$[u(C)]^2 = \left( \frac{\partial C}{\partial P} \right)^2 [u(P)]^2 + \left( \frac{\partial C}{\partial V_s} \right)^2 [u(V_s)]^2 + \left( \frac{\partial C}{\partial V_T} \right)^2 [u(V_T)]^2$$

i.e. in this case:

$$\begin{aligned} [u(C)]^2 &= \left[ \left( \frac{10\rho}{\text{RMM}} \right) \frac{V_s}{V_T} \right]^2 [u(P)]^2 + \left[ - \left( \frac{10\rho}{\text{RMM}} \right) \frac{P}{V_T} \right]^2 [u(V_s)]^2 + \left[ - \left( \frac{10\rho}{\text{RMM}} \right) \frac{PV_s}{V_T^2} \right]^2 [u(V_T)]^2 \\ &= C^2 \left\{ \frac{[u(P)]^2}{P^2} + \frac{[u(V_s)]^2}{V_s^2} + \frac{[u(V_T)]^2}{V_T^2} \right\} \end{aligned}$$

#### 4. Example: Titration of an NaOH(aq) solution through titration against 1M HCl(aq)

##### Method:

1. 1M HCl was prepared from ACS reagent grade concentrated HCl (Sigma, ACS reagent grade, 36.5-38.0%) by topping 20.6±0.1 mL of concentrated acid to 250 mL in a Grade B volumetric flask (tolerance = 0.24mL).
2. 25mL of the NaOH(aq) solution was transferred into a clean conical flask using a Grade B 25mL pipette (tolerance = ±0.08mL) and titrated against the 1M HCl solution prepared in (1) using a Grade B burette (ILE = ±0.06mL) using phenolphthalein as an indicator. This step was repeated three times.

##### Results and Calculations:

## 1. The concentration of the HCl solution:

$V_S \pm \Delta V_S$ , the volume of HCl used: (20.6±0.1) mL

$P \pm \Delta P$ , the purity of HCl used: 36.5-38.0% = (37.25±0.75)%

$V_T \pm \Delta V_T$ , the total volume of final solution: (250.00±0.24) mL

RMM of HCl: 36.46

$\rho$ , density of HCl: 1.19 kg L<sup>-1</sup>

Given this information we can use the equations derived above to calculate the concentration  $C \pm \Delta C$  of the HCl solution by:

$$C = \left( \frac{10\rho}{\text{RMM}} \right) \frac{PV_S}{V_T} = \dots = 1.002\text{M}$$

The standard uncertainty is given by:

$$u(C) = C \left\{ \frac{[u(P)]^2}{P^2} + \frac{[u(V_s)]^2}{V_s^2} + \frac{[u(V_T)]^2}{V_T^2} \right\}^{1/2}$$

where:

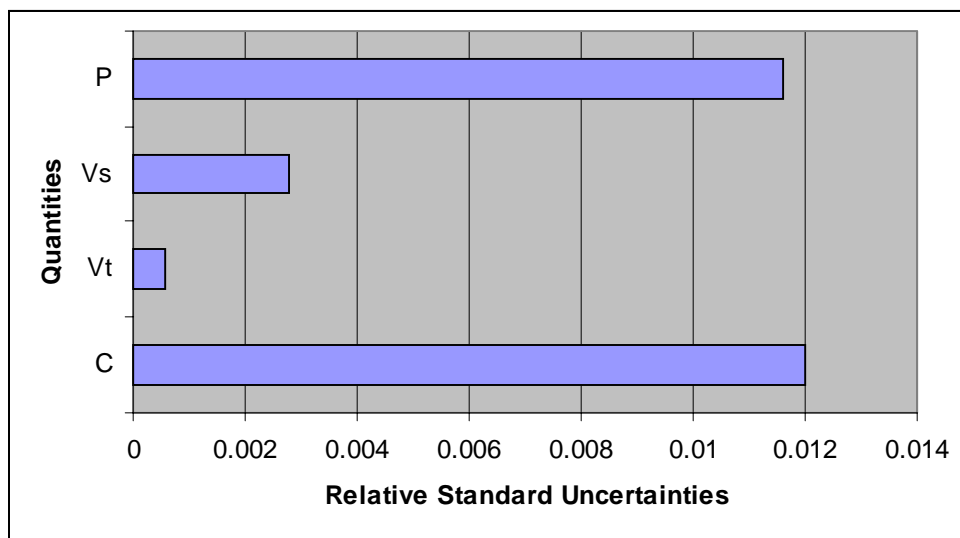
Quantity, X	Quoted uncertainty (rectangular distribution)	Standard uncertainty, u(X) (rectangular distribution)
P	0.75 %	$u(P) = \left( \frac{0.75}{\sqrt{3}} \right) \%$
$V_s$	0.1 mL	$u(V_s) = \left( \frac{0.1}{\sqrt{3}} \right) \text{mL}$
$V_T$	0.24 mL	$u(V_T) = \left( \frac{0.24}{\sqrt{3}} \right) \text{mL}$

which give a standard uncertainty of:

$$u(C) = C \left\{ \frac{[u(P)]^2}{P^2} + \frac{[u(V_s)]^2}{V_s^2} + \frac{[u(V_T)]^2}{V_T^2} \right\}^{1/2} = \dots = 0.012 \text{ M}$$

Given this information, it is possible to plot the relative standard uncertainties (i.e.  $\frac{u(X)}{X}$ ) of P,  $V_s$ ,  $V_T$  and C as in Fig. 1. This plot shows that main source on uncertainty is the purity of the HCl.





**Fig. 1: A plot of the relative standard uncertainties for  $P$ ,  $V_s$ ,  $V_T$  and  $C$ .**

It is also possible to use this information to state a value of the concentration at a 95% confidence level.

The information can also be used to state the concentration of HCl at a 95% confidence. Assuming that the concentration calculated and the associated standard deviation can be related to a Gaussian or normal distribution, i.e. a distribution where 95% of all observations fall within  $\pm 1.96 \sigma$  of the mean; then at 95% confidence we may say that:

$$C \pm \Delta C = (1.002 \pm 1.96 \times 0.012) \text{M}$$

$$= (1.002 \pm 0.024) \text{M}$$

or more appropriately:

$$C \pm \Delta C = (1.00 \pm 0.02) \text{M}$$

## 2. The results of the titration:

The results from the titration were as follows:

	1st reading	2nd reading	3rd reading
Final reading $V_f$ , (mL, $\pm 0.06 \text{mL}$ )	2.10	4.30	3.70
Initial reading, $V_i$ , (mL, $\pm 0.06 \text{mL}$ )	27.20	29.30	28.70
Titre value, $V_u$ , (mL)	25.10	25.00	25.00

The mean titre value may be computed by through:

$$\bar{V}_u = \frac{V_{u,1} + V_{u,2} + V_{u,3}}{3}$$

where  $V_{u,1}$ ,  $V_{u,2}$  and  $V_{u,3}$  are the titre values from the 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> reading respectively, i.e.:

$$\bar{V}_u = \frac{25.1 + 25.0 + 25.0}{3} = 25.033\text{mL}$$

The uncertainties in this case will arise from two sources (at this level):

- $u_a(V_u)$  : The standard uncertainty that results from the tolerance of the burette (recall that the burette readings are  $\pm 0.06$  mL).
- $u_b(V_u)$  : The standard uncertainty that results from the spread of the titre values.

which can be combined to give the total standard uncertainty:

$$u(V_u) = \sqrt{[u_a(V_u)]^2 + [u_b(V_u)]^2}$$

To calculate  $u_a(V_u)$  we shall first calculate the uncertainty in each reading of the titre values.

Since the titre value  $V_u$  is given by:

$$V_u = V_f - V_i$$

then applying the rule of the combinations of errors, we have:

$$\begin{aligned} [u(\Delta V_u)]^2 &= \left(\frac{\partial V_u}{\partial V_f}\right)^2 [u(\Delta V_f)]^2 + \left(\frac{\partial V_u}{\partial V_i}\right)^2 [u(\Delta V_i)]^2 \\ &= (1)^2 [u(\Delta V_f)]^2 + (-1)^2 [u(\Delta V_i)]^2 \\ &= [u(\Delta V_f)]^2 + [u(\Delta V_i)]^2 \end{aligned}$$

i.e. assuming a rectangular distribution for the burette readings  $u(V)$

$$\begin{aligned} [u(\Delta V_u)]^2 &= \left(\frac{0.06\text{mL}}{\sqrt{3}}\right)^2 + \left(\frac{0.06\text{mL}}{\sqrt{3}}\right)^2 \\ \Rightarrow [u(\Delta V_u)] &= 0.05 \text{ mL} \end{aligned}$$

Similarly, the standard uncertainty  $u_a(\Delta V_u)$  that results from the tolerance of the burette may be computed by recalling that:

$$\bar{V}_u = \frac{V_u^1 + V_u^2 + V_u^3}{3}$$

and applying the rule of the combinations of errors, we have:

$$\begin{aligned}
 [u_a(\bar{V}_u)]^2 &= \left(\frac{\partial \bar{V}_u}{\partial V_{u,1}}\right)^2 [u(V_{u,1})]^2 + \left(\frac{\partial \bar{V}_u}{\partial V_{u,2}}\right)^2 [u(V_{u,2})]^2 + \left(\frac{\partial \bar{V}_u}{\partial V_{u,3}}\right)^2 [u(V_{u,3})]^2 \\
 &= \left(\frac{1}{3}\right)^2 [u(V_{u,1})]^2 + \left(\frac{1}{3}\right)^2 [u(V_{u,2})]^2 + \left(\frac{1}{3}\right)^2 [u(V_{u,3})]^2 \\
 &= 3\left(\frac{1}{3}\right)^2 [u(V_u)]^2 = \frac{1}{3}[u(V_u)]^2
 \end{aligned}$$

i.e.:

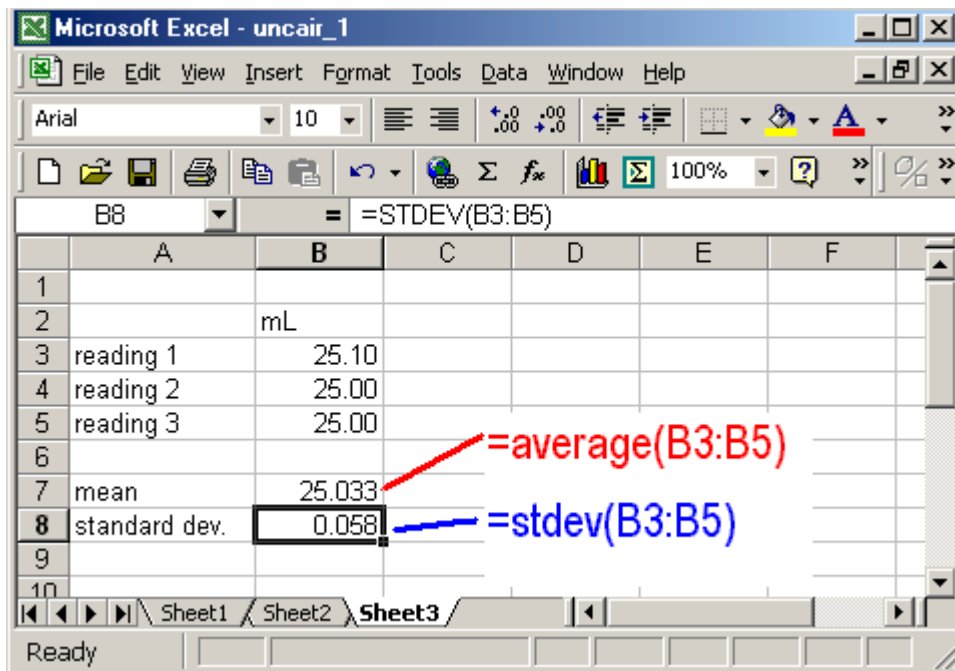
$$u_a(\bar{V}_u) = \frac{1}{\sqrt{3}} u(V_u) = \sqrt{\frac{1}{3}} 0.01 \text{ mL} \approx 0.029 \text{ mL}$$

The calculation of  $u_b(V_u)$ , i.e. the standard deviation of the 3 titre values assuming that these are taken from a normal distribution, can be carried out using MS Excel (see Fig. 2) to get:

$$u_b(V_u) = 0.058 \text{ mL}$$

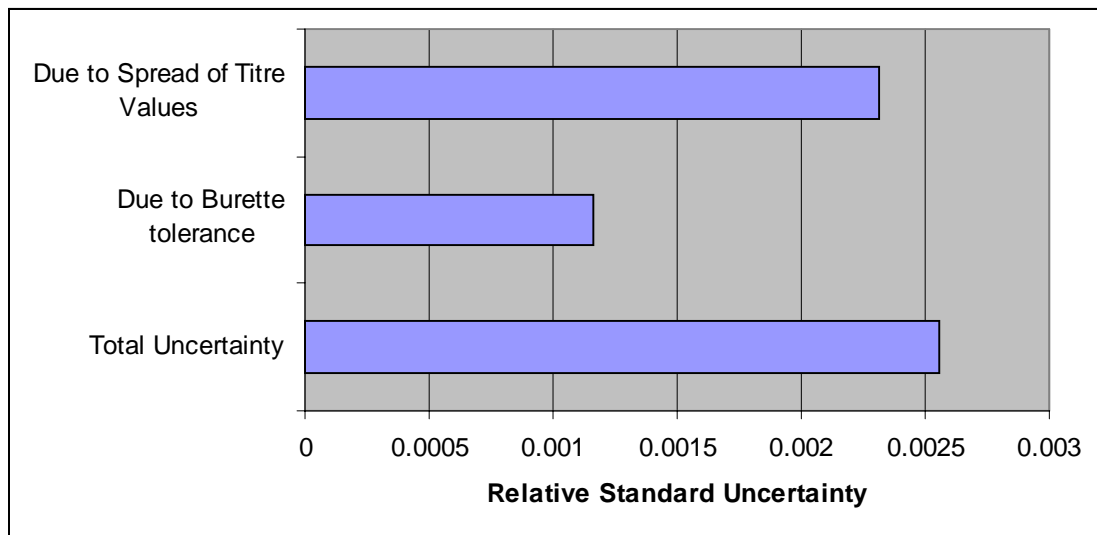
and hence the combined stands uncertainty in the titre value is given by:

$$\begin{aligned}
 u(V_u) &= \sqrt{[u_a(V_u)]^2 + [u_b(V_u)]^2} \\
 &= \sqrt{0.029^2 + 0.058^2} = 0.065 \text{ mL}
 \end{aligned}$$



**Fig. 2:** The use of MS Excel to calculate the standard deviation of the three titre values

Once again, we can plot the relative standard uncertainties and we realise that in this case, the main source of uncertainty is due to the spread of titre values.



**Fig. 3:** A plot of the relative standard uncertainties that relate to the titre values

### 3. The number of moles of HCl used in the reaction and the molarity of the NaOH solution.

Since we know that the average titre value is 25.033 mL (standard uncertainty 0.065 mL) and that the concentration of the HCl used is 1.001 M (standard uncertainty 0.012 M), then we may calculate the average number of moles of HCl required to neutralise 25.0 mL of NaOH by:

$$n(\text{HCl}) = \frac{\overline{V}_u}{1000} C$$

Also, since the reaction between NaOH and HCl has a 1:1 stoichiometry, then we may conclude that in 25mL of NaOH, there are  $\frac{\overline{V}_u}{1000} C$  moles of NaOH, i.e.

the concentration of NaOH is given by:

$$C_{\text{NaOH}} = \left[ \frac{\overline{V}_u}{1000} C \right] \div \left[ \frac{V_{\text{NaOH}}}{1000} \right] = \frac{\overline{V}_u}{V_{\text{NaOH}}} C$$

i.e.:

$$C_{\text{NaOH}} = \frac{\overline{V}_u}{V_{\text{NaOH}}} C = \frac{25.033 \text{ mL}}{25.000 \text{ mL}} \times 1.001 \text{ M} = 1.002 \text{ M}$$

The uncertainty in this concentration is given by:

$$u(C_{NaOH}) = C_{NaOH} \left\{ \left( \frac{u(\overline{V}_u)}{\overline{V}_u} \right)^2 + \left( \frac{u(\overline{V}_{NaOH})}{\overline{V}_{NaOH}} \right)^2 + \left( \frac{u(C_{HCl})}{C_{HCl}} \right)^2 \right\}^{1/2}$$

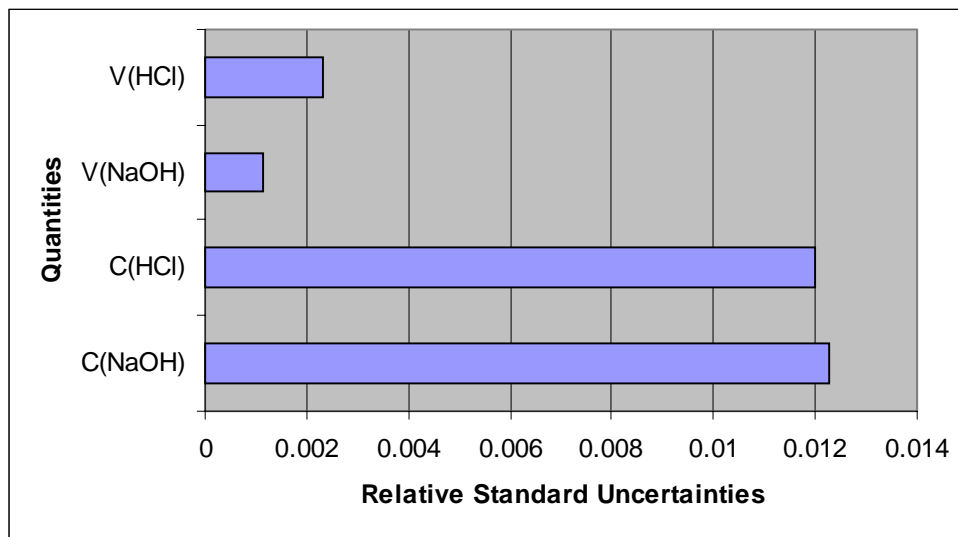
where  $u(\overline{V}_{NaOH})$  may be assumed to be given by:

$$u(\overline{V}_{NaOH}) = \frac{1}{\sqrt{3}} \times (\text{tolerance of a 25mL pipette}) = \frac{1}{\sqrt{3}} (0.05) \text{ mL} \approx 0.029 \text{ mL}$$

i.e.:

$$\begin{aligned} u(C_{NaOH}) &= C_{NaOH} \left\{ \left( \frac{u(\overline{V}_u)}{\overline{V}_u} \right)^2 + \left( \frac{u(\overline{V}_{NaOH})}{\overline{V}_{NaOH}} \right)^2 + \left( \frac{u(C_{HCl})}{C_{HCl}} \right)^2 \right\}^{1/2} \\ &= 1.002 \left\{ \left( \frac{0.058}{25.033} \right)^2 + \left( \frac{0.029}{25.000} \right)^2 + \left( \frac{0.012}{1.002} \right)^2 \right\} \\ &= 0.012 \text{ M} \end{aligned}$$

Once again, we can plot the relative standard uncertainties (Fig. 4) and we realise that the main source of uncertainty is the concentration of HCl. Also, a comparison of all the three plots of the relative standard uncertainties, we will realise the main source of uncertainty was the uncertainty in the purity of the HCl.



**Fig. 4:** A plot of the relative standard uncertainties that relate to the final calculation.

Once again, we may state a value of the concentration of NaOH at a 95% confidence level. Assuming that the concentration calculated and the associated standard deviation can be related to a Gaussian or normal distribution, i.e. a distribution where 95% of all observations fall within  $\pm 1.96 \sigma$  of the mean; then at 95% confidence we may say that:

$$\begin{aligned} C \pm \Delta C &= (1.002 \pm 1.96 \times 0.012) \text{M} \\ &= (1.002 \pm 0.024) \text{M} \end{aligned}$$

or more appropriately:

$$C \pm \Delta C = (1.00 \pm 0.02) \text{M}$$

*NOTE: If the main source of uncertainty was due to repeated readings in the titre values, then the factor of 1.96 should be replaced by the appropriate value from the two-tailed student t-distribution.*