University of Malta
Department of Chemistry

CH033 - Mathematics for Chemists
CH130 - Chemistry Practicals

ERRORS IN QUANTITATIVE ANALYSIS

1. Introduction

The purpose of a quantitative chemical 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. In the discussion of errors, one must distinguish between two main types of errors: systematic and random errors.

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 $20^{o}C$. 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 $20^{o}C$.

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 as a range of values $X \pm \Delta X$ in which we have a 95% level of confidence. The quantity ΔX may be referred to as the **tolerance** in the value of X. (Note that in some cases, it may be necessary to quote results at a higher/lower confidence level.)

2. Quantifying errors

There are several approaches that can be used to determine associated 'random error' with an experimentally measured quantity. We shall consider two scenarios:

(1) When the main source of error may be traced back to errors arising from equipment (including chemicals) limitations – e.g. the 'Instrument Limit of Error (ILE)', errors in the initial concentration of solutions, etc.. We shall henceforth refer to these errors as **ILE**s.

(2) Errors from other sources which when repeated readings are taken, then the result in the observed value follow a normal or Gaussian distribution. We shall henceforth refer to these errors as **RE**s (random errors). These errors may be:

- *Accidental:* due to changes in environmental conditions, e.g. draughts, temperature changes
- *Personal:* e.g. parallax error when reading a scale
- *Variations in quantities to be measured:* e.g. diameter of a pendulum bob.

Both of these types of errors will need to be included in the calculation.

2.1 Errors from equipment limitations (ILE)

2.1.1 Introduction

The *least count* is the smallest division that is marked on the equipment. Thus for example, a 50mL burette will have a least count of 0.1mL, and an electronic chemical balance giving up to three decimal places of a gram (e.g. 1g reads weights as 1.000 g) will have a least count of 0.001 g, i.e. 1mg.

2.1.2 The instrument limit of error (ILE)

The instrument limit of error (ILE), is the precision to which a measuring device can be read, and is always equal to or smaller than (i.e. a fraction of) the least count (unless the manufacturers specify some other value). The use of a fraction of the least count as the ILE rather that the least count itself is justified when the space between the scale divisions is large, in which case we may for example use ½ of the least count at the ILE instead of the least count itself. However, in some cases, we are recommended by the manufacture to use an ILE (usually referred to as tolerance) which is higher than the value suggested from a 'least count' point of view. In such cases, the value for the ILE specified by the manufacturer should be used in the calculation.

We may illustrate these statements by considering the ILE in a burette reading. Although the least count in a 50mL burette is 0.1mL, one may usually distinguish up to 0.05mL, and hence the ILE for such a burette should be taken as ±0.05mL. This value for the ILE is usually true for Grade A burettes. However, the suppliers of more economical burettes sometimes specify an ILE which is higher than ±0.05mL. For example, the 50mL economy-grade burettes sold by Aldrich have a tolerance of ±0.06mL, i.e. 0.01mL higher than expected from a 'least count' point of view.

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). For example volumetric glassware that is permanently marked 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.

2.1.3 Errors due to purity

The purity of the reagents should also 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 $(99 \pm 1)\%$ pure, then we should use 59.03g of NaCl rather than 58.44g since:

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

The $\pm 1\%$ uncertainty in the composition should be combined the ILE*s* from weight and volume measurements (see propagation of errors) in computing the acceptable range the NaCl concentration.

Note that these types of errors can be (and should be) reduced by carrying out a quantitative analysis of the substance against primary standards.

2.1.4 Estimated uncertainties

Sometimes, experimental limitations are such that we encounter uncertainties which are larger than the ILE. If for example in a physics experiment, we try to balance a simple beam balance with masses that have an ILE of 0.01 grams, but find that we can vary the mass on one pan by as much as 3 grams without seeing a change in the indicator. In such case, quoting masses as ± 0.01 grams would of course be inappropriate. Instead we have to use an estimated uncertainty, given by half of the 3g as the estimated uncertainty, thus getting uncertainty of $\pm 1.5g$.

2.2 Errors from other sources which may be corrected by taking repeated readings (RE)

If one were to repeat a measurement several times, the values obtained 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, ..., x_N, of the same quantity x, the mean value $\bar{x}$ may be given by:

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

Note that:

$$x = \lim_{N \to \infty} \left(\bar{x} \right)$$

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, ..., x_N) is the **standard deviation**, σ (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:

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

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

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

In reporting uncertainties in mean values it is becoming more and more common to follow the practice of reporting the 95 percent confidence limits. These confidence limits are determined by recognizing firstly for an infinite set of measurements, where only random error enters, an ideal Gaussian distribution will be observed.

For such a distribution:
- o 68% of all observations fall within $\pm\sigma$ of the mean;
- o 95% of all observations fall within $\pm1.96\sigma$ of the mean;
- o 96% of all observations fall within $\pm2\sigma$ of the mean;
- o 99.7% of all observations fall within $\pm3\sigma$ of the mean;
- o 99.9% of all observations fall within $\pm3.29\sigma$ of the mean;

When applied to our situation, we can say that at a 95% confidence limit, for a given N, the accepted value for x will lie in within the range:

$$x = \bar{x} \pm \frac{ts}{\sqrt{N}}$$

where $t=t(\alpha,\nu)$ may be read from statistical tables (Student's t-distribution, see Table 2) for given values of a (which relates to the confidence level, CL) and n (the number of degrees of freedom, which depends on N) where:

$$\alpha = \frac{1}{2}\left(\frac{100-CL}{100}\right)$$

and:

$$\nu = N-1$$

Thus, for example, for a titre value averaged from 3 repeated titrations (i.e. $N=3$, $n=2$), we may say that at a 95% confidence level (i.e. a = 0.025) that the accepted value of the titre value is given by:

$$x = \bar{x} \pm 4.303\frac{s}{\sqrt{N}}$$

| α	0.10	0.05	0.025	0.01	0.005	0.001
$\nu = 1$	3.078	6.314	12.706	3.1621	63.657	318.310
2	1.886	2.920	4.303	6.965	9.925	22.327
3	1.638	2.353	3.182	4.541	5.841	10.215
4	1.533	2.132	2.776	3.747	4.604	7.173
5	1.476	2.015	2.571	3.365	4.032	5.893
6	1.440	1.943	2.447	3.143	3.707	5.208
7	1.415	1.895	2.365	2.998	3.499	4.785
8	1.397	1.860	2.306	2.896	3.355	4.501
9	1.383	1.833	2.262	2821	3.250	4.297
10	1.372	1.812	2.228	2764	3.169	4.144
11	1.363	1.796	2.201	2.718	3.106	4.025
12	1.356	1.782	2.179	2.681	3.055	3.930
13	1.350	1.771	2.160	2.650	3.012	3.852
14	1.345	1.761	2.145	2.624	2.977	3.787
15	1.341	1.753	2.131	2.602	2.947	3.733
16	1.337	1 .746	2120	2.583	2.921	3.686
17	1.333	1.740	2.110	2.567	2.898	3.646
18	1.330	1.734	2.101	2.552	2.878	3.610
19	1.328	1.729	2.093	2.539	2.861	3.579
20	1.325	1.725	2.086	2.528	2.845	3.552
21	1.323	1.721	2.080	2.518	2.831	3.527
22	1.321	1.717	2.074	2.508	2.819	3.505
23	1.319	1.714	2.069	2.500	2.807	3.485
24	1.318	1.711	2.064	2.492	2.797	3.467
25	1.316	1.708	2.060	2.485	2.787	3.450
26	1.315	1.706	2.056	2479	2.779	3.435
27	1.314	1.703	2.052	2.473	2.771	3.421
28	1.313	1.701	2.048	2.467	2.763	3.408
23	1.311	1.699	2.045	2.462	2.756	3.396
30	1.310	1.697	2.042	2.457	2.750	3.385
40	1.303	1.684	2.021	2423	2.704	3.307
60	1.296	1.671	2.000	2.390	2.660	3.232
120	1.289	1.658	1.980	2.358	2.617	3.160
∞	1.282	1.645	1.960	2.326	2.576	3.090
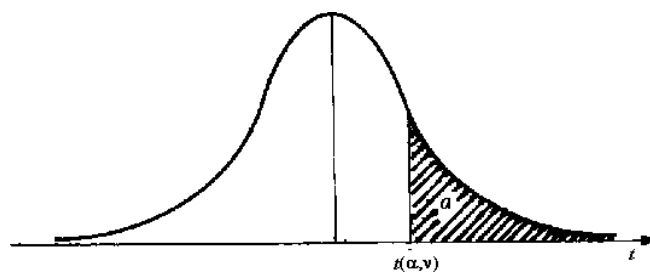
Table 1: Percentage points of the Student's t-distribution *(Taken from The University of Malta booklet of Mathematical Formulae, Malta University Press, 1987)*

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. mol L^{-1}) is given by:

$$C = \left(\frac{1000\rho}{\text{RMM}}\right)\left(\frac{P}{100}\right)\left(\frac{V_S}{1000}\right)\left(\frac{V_T}{1000}\right)^{-1} = \left(\frac{10\rho}{\text{RMM}}\right)\frac{PV_S}{V_T}$$

(eqn 1.)

where:

- ρ is the specific density (in kg L^{-1}) of the substance, i.e. 1000ρ is the specific density in 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 tolerance 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 tolerance. In this case we may assume that r and the RMM are constants, hence leaving P, V_S and V_T as variables. Let us assume that the tolerance for the values of these three variables be ΔP, ΔV_S and ΔV_T respectively, i.e. the true value of P is likely to be within the range of $P \pm \Delta P$, etc.

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 ΔC in terms of ΔP, ΔV_S and ΔV_T:

$$\Delta C \approx \left(\frac{\partial C}{\partial P}\right)\Delta P + \left(\frac{\partial C}{\partial V_S}\right)\Delta V_S + \left(\frac{\partial C}{\partial V_T}\right)\Delta V_T$$

Squaring[i] this equation and recognising that the 'ΔX_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 an expression for the most likely error in the value of C by:

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

i.e. <u>in this case</u>:

$$(\Delta C)^2 = \left[\left(\frac{10\rho}{RMM}\right)\frac{V_s}{V_T}\right]^2 (\Delta P)^2 + \left[\left(\frac{10\rho}{RMM}\right)\frac{P}{V_T}\right]^2 (\Delta V_S)^2 + \left[-\left(\frac{10\rho}{RMM}\right)\frac{PV_S}{V_T^2}\right]^2 (\Delta V_T)^2$$

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

A table summarising the different errors for the more common types of functions used in volumetric analysis is given in Appendix 1. **Note that there is no need to derive these equations in your reports.**

4. Example: Standardisation 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.

---

[i] This 'squaring', etc. is required to make ΔC the 'statistically most likely value for the error in C', i.e.

strictly speaking we should say that $\overline{\Delta C} = \sqrt{\left(\frac{\partial C}{\partial P}\right)^2 (\Delta P)^2 + \left(\frac{\partial C}{\partial V_S}\right)^2 (\Delta V_S)^2 + \left(\frac{\partial C}{\partial V_T}\right)^2 (\Delta V_T)^2}$. Some authors prefer

to make use of the 'maximum value for the error in C' which is given by:

$\Delta C_{max} = \left|\frac{\partial C}{\partial P}\right| |\Delta P| + \left|\frac{\partial C}{\partial V_S}\right| |\Delta V_S| + \left|\frac{\partial C}{\partial V_T}\right| |\Delta V_T|$

Results and Calculations:

1. The accurate 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-$38.0\% = 37.25 \pm 0.75\%$
$V_T \pm \Delta V_T$, the total volume of final solution: 250.00 ± 0.24mL
RMM of HCl: 36.46 ρ, density of HCl: 1.19 kg L^{-1}

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

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

and:

$$\Delta C = C \left\{ \left(\frac{\Delta P}{P} \right)^2 + \left(\frac{\Delta V_S}{V_S} \right)^2 + \left(\frac{\Delta V_T}{V_T} \right)^2 \right\}^{1/2} = ... = 0.021\text{M}$$

i.e. the concentration $C \pm \Delta C$ of the HCl is given by (1.001 ± 0.021)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, ±0.06mL)	27.20	29.30	28.70
Initial reading, V_i (mL, ±0.06mL)	2.10	4.30	3.70
Titre value, V_u, (mL, ± ΔV_u mL)	25.10	25.00	25.00

The mean titre value may be computed by through:

$$\overline{V_u} = \frac{V_{u,1} + V_{u,2} + V_{u,3}}{3}$$

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

$$\overline{V_u} = \frac{25.10 + 25.00 + 25.00}{3} = 25.033\text{mL}$$

The error in this value is due to **ILE**s and **RE**s, i.e.:

$$\Delta \overline{V_u} = \Delta \overline{V_u}^{\text{ILE}} + \Delta \overline{V_u}^{\text{RE}}$$

To calculate the errors due to **ILE**s in we shall first calculate the error 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:

$$(\Delta V_u)^2 = \left(\frac{\partial V_u}{\partial V_f}\right)^2 (\Delta V_f)^2 + \left(\frac{\partial V_u}{\partial V_i}\right)^2 (\Delta V_i)^2$$

$$= (1)^2 (\Delta V_f)^2 + (-1)^2 (\Delta V_i)^2$$

$$= (\Delta V_f)^2 + (\Delta V_i)^2$$

i.e.:

$$(\Delta V_u)^2 = (0.1\text{mL})^2 + (0.1\text{mL})^2 = 2(0.1\text{mL})^2$$

$$\Rightarrow \Delta V_u = \sqrt{2}\ 0.06\text{mL}$$

Similarly, the errors due to ILEs in the mean titre values may be computed by recalling that:

$$\overline{V_u} = \frac{V_u^1 + V_u^2 + V_u^3}{3}$$

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

$$\left(\Delta \overline{V_u}^{\textbf{ILE}}\right)^2 = \left(\frac{\partial \overline{V_u}}{\partial V_{u,1}}\right)^2 (\Delta V_{u,1})^2 + \left(\frac{\partial \overline{V_u}}{\partial V_{u,2}}\right)^2 (\Delta V_{u,2})^2 + \left(\frac{\partial \overline{V_u}}{\partial V_{u,3}}\right)^2 (\Delta V_{u,3})^2$$

$$= \left(\frac{1}{3}\right)^2 (\Delta V_u)^2 + \left(\frac{1}{3}\right)^2 (\Delta V_u)^2 + \left(\frac{1}{3}\right)^2 (\Delta V_u)^2$$

$$= 3\left(\frac{1}{3}\right)^2 (\Delta V_u)^2 = \frac{1}{3}(\Delta V_u)^2$$

i.e.:

$$\Delta \overline{V_u}^{\textbf{ILE}} = \frac{1}{\sqrt{3}} \Delta V_u = \sqrt{\frac{2}{3}}\ 0.06\ \text{mL} \approx 0.049\text{mL}$$

However, over and above this error due to ILE's of the burette, there are also the other random errors which may be corrected statistically. Because we have three readings of the titre value, then at a 95% confidence limit we may say that:

$$\overline{V_u} \pm \Delta \overline{V_u}^{\textbf{RE}} = \overline{V_u} \pm 4.303 \frac{s}{\sqrt{N}}$$

where s is the standard deviation given by:

$$s = \sqrt{\frac{\sum_{i=1}^{N}(\overline{x} - x_i)^2}{N-1}} = \sqrt{\frac{(25.033 - 25.1)^2 + (25.033 - 25.0)^2 + (25.033 - 25.0)^2}{3-1}} = 0.058\text{mL}$$

i.e. the error due **RE** is given by:

$$\Delta\overline{V_u}^{\text{RE}} = 4.303\frac{s}{\sqrt{N}} = 4.303\frac{0.058}{\sqrt{3}} = 0.143\text{mL}$$

Thus, the titre value with its associated errors is given by:

$$\overline{V_u} \pm \Delta\overline{V_u} = \overline{V_u} \pm \left(\Delta\overline{V_u}^{\text{ILE}} + \Delta\overline{V_u}^{\text{RE}}\right)$$

$$= 25.033 \pm (0.049 + 0.143)$$

$$= \underline{(25.033 \pm 0.192)\ \text{mL}}$$

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 ± 0.224) mL and that the concentration of the HCl used is (1.001 ± 0.021) 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 $\dfrac{\overline{V_u}}{1000}C$ moles of NaOH, i.e.

the concentration of NaOH is given by:

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

i.e.:

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

The final error in this concentration is given by:

$$\Delta C_{NaOH} = C_{NaOH}\left\{\left(\frac{\Delta\overline{V_u}}{\overline{V_u}}\right)^2 + \left(\frac{\Delta\overline{V_{\text{NaOH}}}}{\overline{V_{\text{NaOH}}}}\right)^2 + \left(\frac{\Delta C}{C}\right)^2\right\}^{1/2}$$

where $\Delta \overline{V_{\text{NaOH}}}$ may be assumed to be given by:

$$\Delta \overline{V_{\text{NaOH}}} = \frac{1}{\sqrt{3}} \times \left(\text{tolerance of a 25mL pipette} \right) = \frac{1}{\sqrt{3}} \left(0.05 \right) \text{mL} \approx 0.029 \text{mL}$$

i.e.:

$$\Delta C_{NaOH} = C_{NaOH} \left\{ \left(\frac{\Delta \overline{V_u}}{\overline{V_u}} \right)^2 + \left(\frac{\Delta \overline{V_{\text{NaOH}}}}{V_{\text{NaOH}}} \right)^2 + \left(\frac{\Delta C}{C} \right)^2 \right\}^{1/2}$$

$$= 1.002 \sqrt{\left(\frac{0.192}{25.033} \right)^2 + \left(\frac{0.029}{25.000} \right)^2 + \left(\frac{0.021}{1.001} \right)^2}$$

$$= 0.022 \text{M}$$

i.e. the concentration of the NaOH solution is given by: (1.002 ± 0.022) M, or since the error in the NaOH concentration starts appears in the second decimal places, we are more justified in saying that the concentration of NaOH is **1.00 ± 0.02 M** .

Notes: (1) In your calculation you should work with one decimal place more than in the final result. (2) For your reports, there is no need to re-derive the expressions for the propagation of errors from first principles and instead you may start from the equations in Appendix 1.

Appendix 1: Formulae for the mean error Δf in terms of Δx, Δy, and Δz for $f=f(x,y,z)$

$f = f(x,y,z)$	$df = \left(\dfrac{\partial f}{\partial x}\right)dx + \left(\dfrac{\partial f}{\partial y}\right)dy + \left(\dfrac{\partial f}{\partial z}\right)dz$	$(\Delta f)^2 = \left(\dfrac{\partial f}{\partial x}\right)^2 (\Delta x)^2 + \left(\dfrac{\partial f}{\partial y}\right)^2 (\Delta y)^2 + \left(\dfrac{\partial f}{\partial z}\right)(\Delta z)^2$	Δf
Addition / subtraction $f = x \pm y \pm z$	$df = (\pm 1)dx + (\pm 1)dy + (\pm 1)dz$	$(\Delta f)^2 = (\pm 1)^2 (\Delta x)^2 + (\pm 1)^2 (\Delta y)^2 + (\pm 1)^2 (\Delta z)^2$ $= (\Delta x)^2 + (\Delta y)^2 + (\Delta z)^2$	$\Delta f = \sqrt{(\Delta x)^2 + (\Delta y)^2 + (\Delta z)^2}$
Multiplication / division $f = \dfrac{xy}{z} = xy.z^{-1}$	$df = \left(\dfrac{y}{z}\right)dx + \left(\dfrac{x}{z}\right)dy + \left(-\dfrac{xy}{z^2}\right)dz$	$(\Delta f)^2 = \left(\dfrac{y}{z}\right)^2 (\Delta x)^2 + \left(\dfrac{x}{z}\right)^2 (\Delta y)^2 + \left(-\dfrac{xy}{z^2}\right)^2 (\Delta z)^2$ $= \left(\dfrac{f}{x}\right)^2 (\Delta x)^2 + \left(\dfrac{f}{y}\right)^2 (\Delta y)^2 + \left(-\dfrac{f}{z}\right)^2 (\Delta z)^2$	$\Delta f = \dfrac{1}{f}\sqrt{\left(\dfrac{\Delta x}{x}\right)^2 + \left(\dfrac{\Delta y}{y}\right)^2 + \left(\dfrac{\Delta z}{z}\right)^2}$
Mean: $f = \dfrac{\sum\limits_{i=1}^{N} x_i}{N}$ where $\forall i, \; \Delta x_i = \Delta x$	$df = \dfrac{(1)dx_1 + (1)dx_2 + ... + (1)dx_N}{N}$	$(\Delta f)^2 = \left(\dfrac{1}{N}\right)^2 (\Delta x_1)^2 + \left(\dfrac{1}{N}\right)^2 (\Delta x_2)^2 + ... + \left(\dfrac{1}{N}\right)^2 (\Delta x_N)^2$ $= \left(\dfrac{1}{N}\right)^2 (\Delta x)^2 + \left(\dfrac{1}{N}\right)^2 (\Delta x)^2 + ... + \left(\dfrac{1}{N}\right)^2 (\Delta x)^2$ $= N\left(\dfrac{1}{N}\right)^2 (\Delta x)^2 = \dfrac{(\Delta x)^2}{N}$	$\Delta f = \dfrac{1}{\sqrt{N}}\Delta x$

Note: The Δf presented here is the 'statistically most likely value for the error in f', i.e. strictly speaking we should use the notation $\overline{\Delta f}$ rather than Δf. Some authors prefer to make use of the 'maximum value for the error in f' which is given by: $\Delta f_{max} = \left|\dfrac{\partial f}{\partial x}\right||\Delta x| + \left|\dfrac{\partial f}{\partial y}\right||\Delta y| + \left|\dfrac{\partial f}{\partial z}\right||\Delta z|$.