Consulting Analytical Chemists and Geochemists

THE USE OF A MODELLING APPROACH IN THE ESTIMATION OF MEASUREMENT OF UNCERTAINTY IN THE DETERMINATION OF THE MOLARITY OF SULPHURIC ACID USING SODIUM CARBONATE

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ABSTRACT

A modelling approach is used to estimate the measurement of uncertainty expressed as an expanded uncertainty for the molarity of sulphuric acid as determined by titration with standard sodium carbonate. Each uncertainty is identified, quantified and combined. The largest contributor to the measurement uncertainty is that of repeatability in the determination followed by the volume of sulphuric acid and sodium carbonate.

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1 OBJECTIVE

The objective is to estimate the expanded uncertainty of the molarity of sulphuric determined by titration with a solution of sodium carbonate of known concentration. A 'bottom up' modelling approach is to be used to estimate the uncertainties identified and to apply an expanded uncertainty to the determined molarity.

2 ERROR AND UNCERTAINTY

It is important not to confuse the terms 'error' and 'uncertainty'. Error is the difference between the measured value and the 'true value' of the analyte being measured. Uncertainty is a *quantification of the doubt* about the measurement result. All individual contributors to the total uncertainty can be studied with a view to reducing those that can be reduced. Measurement Uncertainty therefore gives our limitations of the analytical method used.

2.1 DEFINITIONS FROM THE ISO GUIDE TO MEASUREMENT UNCERTAINTY

(EURACHEM / CITAC Guide CG 4. (2012), defines uncertainty as, *"a parameter associated with the result of a measurement that characterises the dispersion of the values that could reasonably be attributed to the "measurand"*

2.2 TYPES OF UNCERTAINTY

There are two sources to obtain information on uncertainty:

2.2.1 Type A

A Type A uncertainty is associated with repeated measurements, *e.g.*, standard deviation of a series of replicate analyses; Mean of 10 replicates = 0.2450 mole/dm^3 with a standard deviation, *s*, of 0.0023 mole/dm^3.

2.2.2 Type B

Type B is based on scientific judgement. Examples are:

- The stated uncertainty from a balance calibration certificate (±0.0002 g).
- The stated uncertainty from a certificate of analysis of a certified reference material (Copper =12.34 ±0.25%, where the ± value is the stated uncertainty).
- The internal volume uncertainty of a volumetric flask (±0.40 cm^3).

Three distribution models are used in a Type B uncertainty to convert an expanded uncertainty to a standard uncertainty. These are:

- Normal
- Rectangular
- Triangular

2.2.2.1 *Rules for Conversion to Standard Uncertainty*

All uncertainties identified and quantified are to be converted to a standard uncertainty so that they are all in the same state when a summation of the uncertainties is to done. Converting from a given uncertainty to a standard uncertainty follows these rules:

- Normal; divide the expanded uncertainty by 2, unless the certificate states otherwise, *e.g.,* 2.32.
- Example: the stated measurement of uncertainty for an analytical balance is 0.0002 grams, given with the statement, coverage factor (*k*=2) at 95% level of confidence. The standard uncertainty is: $\frac{0.0002\ g}{2} = 0.0001\ g.$
- Rectangular; divide the given expanded uncertainty by $\sqrt{3}$
  - Example: The calibration certificate for a 10±0.02 cm^3 pipette states that a rectangular distribution pertains. Therefore, the standard uncertainty is: $\frac{0.02}{\sqrt{3}}$
- Triangular; divide the given expanded uncertainty by $\sqrt{6}$
  - Example: The calibration certificate for a 10±0.02 cm^3 pipette states that a triangular distribution pertains. Therefore, the standard uncertainty is: $\frac{0.02}{\sqrt{6}}$
- An uncertainty is quoted; however, no distribution is given. In this situation, always revert to using $\sqrt{3}$

3 PROCEDURE IN ESTIMATION OF MEASUREMENT UNCERTAINTY

The procedure is:

- Determine the measurand, *i.e.*, what is being measured?
- State or outline the analytical method.
- Identify the sources of uncertainty.
- Estimate the uncertainties.
- Expanded the combined uncertainty to a 95 % level of confidence.
- Examine which uncertainties contribute significantly to the overall uncertainty and attempt to reduce these.

3.1 DETERMINATION OF MEASURAND

The measurand, or that which is to be determined, is the concentration in mole/dm^3 of sulphuric acid. The molarity ($M_{H_2SO_4}$) of the sulphuric acid is calculated from:

$$M_{H_2SO_4} = \frac{V_{Na_2CO_3}\, x M_{Na_2CO_3}}{V_{H_2SO_4}}$$

Where:

$V_{Na_2CO_3}\,(cm^3) = volume\ Na_2CO_3$

$M_{Na_2CO_3}\,(mole/dm^3) = molarity\ Na_2CO_3$

$V_{H_2SO_4}\,(cm^3) = volume\ H_2SO_4$

$M_{H_2SO_4}\,(mole/\ dm^3) = molarity\ H_2SO_4$

Using the measurements made in the titration (Table 1), the molarity ($M_{H_2SO_4}$) of the sulphuric acid is calculated using the equation above.

$$M_{H_2SO_4} = \frac{50.0\ cm^3 x\ 0.01960\ mole/dm^3}{39.21\ cm^3}$$

$$M_{H_2SO_4} = 0.02499\ mole/\ dm^3$$

$M_{H_2SO_4}$ is associated with an uncertainty since there are uncertainties in the measurements made to determine the molarity.

Table 1. Measurements made and results used to determine the concentration of sulphuric acid.

Component	**Symbol** (Standard Uncertainty)	**Value**
$Na_2CO_3\ molarity$ *Weighing* *Flask* *Reference value*	$uM_{Na_2CO_3}$	$0.01960\ mole/dm^3$
$Na_2CO_3\ volume\ (pipette)$	$uV_{Pipette}$	$50.0\ cm^3$
$H_2SO_4\ volume$ *Burette*	$uV_{Burette}$	$39.21\ cm^3$
$H_2SO_4\ molarity$	$uM_{H_2SO_4}$	$0.02499\ cm^3$

3.2 OUTLINE OF ANALYTICAL METHOD

Sodium carbonate reacts with sulphuric acid to give sodium sulphate, water and carbon dioxide.

$$H_2SO_4 + Na_2CO_3 = Na_2SO_4 + H_2O + CO_2$$

The endpoint of the reaction is sharp and quantitative and is therefore suitable as a means of quantification of the concentration of sulphuric acid.

Standard sodium carbonate is prepared by dissolving a known mass of the salt and diluting to 1000 cm^3. A 50.0 cm^3 volume is taken from the standard solution using a 50 cm^3 pipette and transferred to an Erlenmeyer flask. The sulphuric acid sample is transferred to a 50 cm^3 burette and added to the standard sodium carbonate with methyl orange as an indicator. The molarity of the sulphuric acid sample is calculated using the equation in 3.1, page 4.

3.3 IDENTIFICATION OF SOURCES OF UNCERTAINTIES

The uncertainties identified are:

- Uncertainty in the molarity of Na_2CO_3
  - *Volumetric uncertainties:* For the volumetric flask and pipette consider the temperature of the environment compared to 20°C, the internal volume uncertainty, repeatability in filling to the calibration mark and expansion of glass due to temperature (very small and can be ignored) are to be considered.
  - *Mass Uncertainty:* uncertainty in the balance used to weigh the Na_2CO_3.
  - *Uncertainty in the molecular mass* of Na_2CO_3.
- Uncertainty in the volume of H_2SO_4
  - *Volumetric Uncertainty: Burette:* as with the pipette and the volumetric flask, the temperature of the environment compared to 20°C, the internal volume uncertainty, the repeatability in draining the burette to the 50 cm^3 calibration mark and expansion of glass due to temperature (very small and can be ignored) are to be considered.
- *Uncertainty in the repeatability* of the determination of molarity of H_2SO_4

3.4 ESTIMATION OF UNCERTAINTIES

3.4.1 Uncertainty in Molarity of Na_2CO_3

A mass of 1.0386 g of NIST Na_2CO_3 standard reference material 351a lot number 124ANE was weighed out into a beaker and dissolved in about 100 cm^3 of deionised water. Once dissolved it was transferred into a calibrated A-grade volumetric flask of 1000 cm^3 and made up to the calibration mark with water.

The uncertainties are from the balance used to weigh the Na_2CO_3, the 1000 cm^3 flask, and from the Na_2CO_3, NIST reference material.

3.4.1.1 *Weighing*

The uncertainty taken from the balance calibration certificate, gives an uncertainty of ±0.0001 g, however no distribution is given. Therefore, the default distribution used is that of rectangular, *i.e.*, $\sqrt{3}$. The standard uncertainty (u_{Bal}) of the balance is:

$$u_{Bal} = \frac{Stated\ uncertianty}{Distribution}$$

$$u_{Bal} = \frac{0.0001\ g}{\sqrt{3}} = 5.774\ x\ 10^{-5}$$

In using the balance, it is first tared to zero, and then the NIST Na_2CO_3 is weighed out. This process has two uncertainties, *i.e.,* in taring and weighing. The combined standard uncertainty (u_{Mass}) is thus:

$$u_{Mass} = \sqrt{(u_{tare\ weight}^2) + (u_{gross\ weight}^2)}$$

$$u_{Mass} = \sqrt{(5.774\ x\ 10^{-5} g)^2 + (5.774\ x\ 10^{-5}\ g)}$$

$$u_{Mass} = 8.165\ x\ 10^{-5} g$$

The standard relative uncertainty of mass 1.0386 g is:

$$u_{relative} = \frac{u_{Mass}}{Mass}$$

$$u_{relative} = \frac{8.165\ x\ 10^{-5}}{1.0386\ g} = 7.862\ x\ 10^{-5}$$

$$u_{relative} = \left(\frac{8.165\ x\ 10^{-5}}{1.0386\ g}\right)^2 = 6.1804\ x\ 10^{-5}$$

The relative uncertainty as a function of mass is given in Table 2.

Table 2. Summary of uncertainty for mass of 1.0386 g of Na_2CO_3.

Device	**Mass**	***u***	u_c	**Relative *u*** $\frac{u_c}{Mass}$	**Relative u^2** $[\frac{u_c}{Mass}]^2$
Balance	1.0386 g	$8.165\ x\ 10^{-5}$	$8.165\ x\ 10^{-5}$	$7.862\ x\ 10^{-5}$	$\mathbf{6.1804\ x\ 10^{-9}}$

3.4.1.2 *1000 cm³ Volumetric Flask*

The volumetric flask has three uncertainties:

- Internal volume uncertainty
- Temperature
- Repeatability of filling to the calibration mark.

3.4.1.2.1 *Internal volume uncertainty*

The 1000 cm^3 volumetric flask has a stated internal volume uncertainty of ±0.30 cm^3 with a triangular distribution as per the flask's certificate. This is a B Type uncertainty.

$$u_{volume\ 1000} = \frac{Stated\ Uncertainty}{\sqrt{6}}$$

$$u_{volume\ 1000} = \frac{0.30\ cm^3}{\sqrt{6}} = 0.12247 cm^3$$

3.4.1.2.2 *Solution Temperature Uncertainty*

The temperature of the environment where standard solutions are prepared was measured twice per day over a period of 7 days. The mean temperature was found to be 23 ^oC, which is 3 degrees different from 20 ^oC, therefore Δ Temp., in [6] is 3 ^oC.

$$u_{Temp} = \frac{Thermal\ Expansion\ Coefficient\ of\ Water\ x\ \Delta\ Temp.x\ volume\ flask}{Rectangular\ Distribution}$$

$$u_{Temp} = \frac{2.1\ x\ 10^{-4}\ Deg.C/cm^3\ x\ 3^O C\ x\ 1000cm^3}{\sqrt{3}}$$

$$u_{Temp} = 0.3637\ ^{o}\mathrm{C}$$

3.4.1.2.3 *Repeatability of filling to the calibration mark*

The standard deviation of four repeated filling to the calibration mark for an A-grade volumetric flask gave a standard deviation of 0.3705 g.

The relative standard uncertainty in the repeats:

$$u_{rep} = \frac{s}{\sqrt{n}}$$

Where, *s*= standard deviation of repeat filling to the calibration mark at *n* measurements. This is a Type A uncertainty as it is associated with repeated measurements.

Therefore,

$$u_{rep} = \frac{0.3705}{\sqrt{4}} = 0.2139\ cm^3$$

Table 3. Mass of water measured at calibration mark for 1000 cm^3 volumetric flask.

Mass 1	**Mass 2**	**Mass 3**	**Mass 4**	***s***
998.2963	998.9477	998.9276	998.7239	0.3705

3.4.1.2.4 *Combined Uncertainty in the volume of Na_2CO_3 standard solution*

The combined uncertainty in the volume is:

$$u_{Volume\ 1000} = \sqrt{u_{vol}^2 + u_{Temp}^2 + u_{rep}^2}$$

$$u_{Volume\ 1000} = \sqrt{0.12247^2 + 0.36373^2 + 0.2139^2}$$

$$u_{Volume\ 1000} = 0.4394$$

$Calculating\ relative\ standard\ uncertainty$:

$$Rel\ u = \frac{u_{Volume\ 1000}}{Volume_{1000}}$$

$$Rel\ u = \frac{0.4394}{1000} = 0.0004394$$

$$Rel\ u^2 = \left(\frac{0.4394}{1000}\right)^2 = 1.9307\ x\ 10^{-7} cm^3$$

Table 4. Summary of uncertainty for volume of Na_2CO_3.

Device	**Value**	$\boldsymbol{u_{vol}}$	$\boldsymbol{u_{temp}}$	**Combined *u*** $\frac{u_c}{Volume}$	**Relative u^2** $[\frac{u_c}{Volume}]^2$
Flask	1000 cm^3	0.1225 cm^3	0.3637 ºC	0.0004394 cm^3	$\mathbf{1.9307\ x\ 10^{-7} cm^3}$

3.4.1.3 *Uncertainty Imported from Reference Material*

The certificate of analysis supplied of NIST Na_2CO_3 standard reference material 351a lot number 124ANE gives the purity as 99.97 % with an expanded uncertainty *U*, of 0.014 % and coverage factor, *k*, of 2.08.

$$u_{CRM} = \frac{U}{k}$$

$$u_{CRM} = \frac{0.014}{2.08} = 0.006731\ \%$$

$$Rel\ u_{CRM} = \frac{u_{CRM}}{Purity\ Na_2CO_3}$$

$$Rel\ u_{CRM} = \frac{0.00631\ \%}{99.97\ \%} = 6.733\ x\ 10^{-5}\ \%$$

$$Rel\ u^2CRM = 4.533 \text{ x } 10^{-9}\ \%$$

Table 5. Summary data of uncertainties used to calculate the relative squared standard uncertainty.

Device	**Cert %**	***U***	***k***	***u***	**Rel *u***	**Rel u^2**
COA	99.970	0.014	2.08	0.006731	6.733 x 10^{-5}	4.533 x 10^{-9}

3.4.1.4 *Uncertainty Molecular Mass Na_2CO_3*

Table 6 gives the atomic mass of Na, C and O and uncertainty as per IUPAC (2006). It is not clear from the quoted IUPAC uncertainties if they are standard or expanded uncertainties, therefore the default $\sqrt{3}$ is used to calculate the standard uncertainty (Table 6). Table 7 gives the atomic mass of Na, C and O, and the calculations for the combined uncertainty for the molar mass of Na_2CO_3. The molar mass Na_2CO_3 is 105.9884 g/mole and standard uncertainty $u(Na_2CO_3)$ is 0.000695 g/mole.

Table 6. Atomic weights and quoted IUPAC uncertainty as per IUPAC.

Element	**Atomic Mass**	**Quoted IUPAC Uncertainty**	***(u)*** $\frac{quoted}{\sqrt{3}}$
Na	22.98976928(2)	$2\ x\ 10^{-8}$	$1.1547\ x\ 10^{-8}$
C	12.01107(8)	0.00008	$4.6188 \text{ x } 10^{-4}$
O	15.9994(3)	0.0003	$1.7321 \text{ x } 10^{-4}$

Table 7. Molar mass and calculated uncertainty of Na, C and O.

Element	Mass calculation	Mass	u	u^2
Na x 2	2 x 22.9898	45.97954	$2.309\ x\ 10^{-8}$	$5.33\ \ x\ 10^{-16}$
C	1 x 12.01707	12.01707	0.00046188	$2.13\ \ x\ 10^{-7}$
O x 3	3 x 15.9994	47.9982	0.00051962	$2.7\ \ x\ 10^{-7}$
			Sum	4.83 x 10^{-7}
			$\sqrt{Sum}$	0.000695

Table 8. Data for calculation of relative standard uncertainty of molar mass.

Molar Mass Na_2CO_3	Combined u	Rel. u $\frac{\mathrm{u}}{Molar\ Mass}$	Rel u^2 $[\frac{\mathrm{u}}{Molar\ Mass}]^2$
105.9884386 g/mole	0.000695222	6.5594 x10^{-6}	4.3026 x 10^{-11}

3.4.1.5 *Combined Uncertainty in Molarity of Na_2CO_3*

To calculate the combined uncertainty (u_c) of the molarity of Na_2CO_3, each uncertainty component from the preparation of the standard solution of Na_2CO_3 are summed as relative uncertainties in quadrature.

$$u_c = \sqrt{\left(\frac{u_{bal}}{Mass}\right)^2 + \left(\frac{u_{V\ 1000}}{Vol}\right)^2 + \left(\frac{u_{CRM}}{CRM}\right)^2 + \left(\frac{u_{Molar\ Mass}}{Molar\ Mass}\right)^2}$$

$$u_c = \sqrt{6.180\ x\ 10^{-9} + 1.473\ x\ 10^{-7} + 4.533\ x\ 10^{-9} + \ 4.303\mathrm{x}10^{-11}}$$

$$u_c = \sqrt{1.58056\ x\ 10^{-7}}$$

$$u_c = 0.000397568$$

Table 9. Summation of each uncertainty component from the preparation of the standard Na_2CO_3 solution.

Device	$\frac{u_c}{Value}$	$\left(\frac{u_c}{Value}\right)^2$
Balance	$7.86\ x\ 10^{-5}$	$6.180\ x\ 10^{-9}$
1000 cm^3 flask	$3.838\ x\ 10^{-4}$	$1.473\ x\ 10^{-7}$
Imported from Reference Material	$6.733\ x\ 10^{-5}$	$4.533\ x\ 10^{-9}$
Molar Mass	$6.559\ x\ 10^{-6}$	$4.303\ x\ 10^{-4}$
	Sum	$1.5806\ x\ 10^{-7}$
	$u_c=\sqrt{Sum}$	0.000397568

3.4.1.6 *50 cm^3 Pipette*

In the determination of the molarity of the sulphuric acid, a volume of 50.0 cm^3 was transferred using an A-grade calibrated pipette with internal volume uncertainty of 0.05 cm^3 and a quoted triangular distribution. There are three uncertainties associated with the volume of the 50 cm^3 pipette:

- Internal volume uncertainty
- Temperature
- Repeatability of filling to the calibration mark

3.4.1.7 *Uncertainty in pipette volume*

3.4.1.7.1 *Internal volume uncertainty:*

$$u_{int.vol} = \frac{0.05\ cm^3}{\sqrt{6}}$$

$$u_{int.vol} = 0.0204$$

3.4.1.7.2 *Temperature*

$$u_{Temp} = \frac{Thermal\ Expansion\ Coefficient\ of\ Water\ x\ \Delta\ Temp.x\ volume\ flask}{Rectangular\ Distribution}$$

$$u_{Temp} = \frac{2.1\ x\ 10^{-4}\ Deg.C/cm^3\ x\ 3^O C\ x\ 50.0\ cm^3}{\sqrt{3}}$$

$$u_{Temp} = 0.0182\ ^{o}\mathrm{C}$$

3.4.1.7.3 *Calibration Mark*

The standard deviation of the mass of water measured at calibration mark in repeated filling to the mark for the 50.0 cm^3 pipette is 0.0057445 (Table 10).

$$u_{rep} = \frac{0.0057445}{\sqrt{4}} = 0.002873cm^3$$

3.4.1.7.4 *Combined standard uncertainty for pipette*

$$u_{Volume} = \sqrt{u_{int.vol}^2 + u_{Temp}^2 + u_{rep}^2}$$

$$u_{Volume} = \sqrt{0.0204^2 + 0.0182^2 + 0.002873^2}$$

$$u_{Volume} = 0.027489$$

$$Rel\ u_{Volume} = \frac{Combined\ u}{Volume\ pipette}$$

$$Rel\ u_{Volume} = \frac{0.027489}{50.0} = 0.00054979$$

$$Rel_{u_{Volume}}^2 = 2.9889\ \mathrm{x}\ 10^{-7}$$

Table 10. Mass of water measured at calibration mark in repeated filling to the mark for 50.0 cm^3 pipette.

Mass 1	**Mass 2**	**Mass 3**	**Mass 4**	***s***
49.957	49.945	49.955	49.957	0.0057445

Table 11. Summary of data for calculation of the relative standard uncertainty for the 50.0 cm^3 pipette.

Device	**Volume**	u_{volume}	u_{temp}	u_c	***Rel u***	***Rel*** u^2
Pipette	50	0.0204	0.01819	0.027489	0.00054979	2.9889×10^{-7}

3.4.2 Uncertainty in Volume of H_2SO_4

To determine the molarity sulphuric acid was added from a A-grade burette of 50.0 cm^3 capacity and internal volume uncertainty of 0.05 cm^3 (triangular distribution) to standard Na_2CO_3. The endpoint was found at 39.21 cm^3. There are three uncertainties associated with the volume of burette:

- Internal volume uncertainty
- Temperature
- Repeatability of filling to the calibration mark

3.4.2.1 *Internal volume uncertainty*

The 50 cm^3 burette has a stated internal volume uncertainty of 0.05 cm^3 of triangular distribution, as per the burette certificate. Calculating the standard uncertainty of the burette:

$$u_{volume\ 50} = \frac{Stated\ Uncertainty}{\sqrt{6}}$$

$$u_{volume\ 50} = \frac{0.05\ cm^3}{\sqrt{6}} = 0.020412\ cm^3$$

3.4.2.2 *Temperature*

The temperature of the environment where standard solutions are prepared was measured twice per day over a period of 7 days. The mean temperature was found to be 23 °C, which is 3 degrees different from 20 °C, therefore Δ Temp., in is 3 °C.

$$u_{Temp} = \frac{Thermal\ Expansion\ Coefficient\ of\ Water\ x\ \Delta\ Temp.x\ volume\ titre}{Rectangular\ Distribution}$$

$$u_{Temp} = \frac{2.1\ x\ 10^{-4}\ Deg.C/cm^3\ x\ 3^{O}C\ x\ 39.21\ cm^3}{\sqrt{3}}$$

$$u_{Temp} = 0.014258\ ^{o}\text{C}$$

3.4.2.3 *Calibration Mark*

A burette was filled with water to the 0.0 cm^3, mark, and allowed to drain to 50.0 cm^3 mark. The mass of water at 50 cm^3 was weighed. This was repeated an additional three times. The obtained masses and standard deviation are shown in Table 12.

The standard uncertainty in the repeated draining of the burette to 50 cm^3 is:

$$u_{rep} = \frac{u}{\sqrt{n}}$$

Where, *s*= standard deviation of repeat draining of the burette to the 50 cm^3 mark with *n* measurements. This is a Type A uncertainty as it is associated with repeated measurements.

Therefore,

$$u_{rep} = \frac{0.005188}{\sqrt{4}} = 0.002594\ cm^3$$

Table 12. Repeatability measured by draining the burette to 50 cm^3.

Mass 1	Mass 2	Mass 3	Mass 4	*s*
50.001	49.991	49.995	50.002	0.005188

3.4.3 Uncertainty in titrated H_2SO_4 volume

The combined uncertainty (u_c) in the volume of H_2SO_4 titrated is given by:

$$u_c = \sqrt{u_{vol}^2 + u_{Temp}^2 + u_{rep}^2}$$

$$u_c = \sqrt{0.0204^2 + 0.01426^2 + 0.005188^2}$$

$$u_c = 0.025423\ cm^3$$

The relative uncertainty in the volume delivered by the burette is found using:

$$Rel\ u_{Volume} = \frac{u_c}{Volume\ Titrated}$$

$$Rel\ u_{Volume} = \frac{0.025423\ cm^3}{39.21\ cm^3}$$

$$Rel\ u_{Volume} = 0.00064838$$

Table 13. Summation of each uncertainty component from the titrated volume delivered by the burette and relative standard uncertainty.

Device	Value	u_c	u_{Temp}	u_{rep}	Rel u	Rel u^2
Burette	39.21 cm^3	0.02542 cm^3	0.014258 °C	0.002594 cm^3	0.00064838	$\mathbf{4.204\ x10^{-9}}$

3.4.4 Uncertainty in Repeat Measurements of H_2SO_4 Standardisation

To determine the standard deviation (random uncertainty) a series of repeated titrations were done on the H_2SO_4 (Table 15). A summary of the uncertainty components from the titrated volume delivered by the burette are shown in Table 15.

3.4.4.1 *Standard uncertainty of repeated determinations*

Calculating the standard uncertainty of the repeats:

$$u_{rep} = \frac{s}{\sqrt{n}}$$

$$u_{rep} = \frac{0.000047}{\sqrt{7}}$$

$$u_{rep} = 1.77 \; x \; 10^{-5}$$

$$Rel \; u_{Rep} = \frac{1.77425 \; x \; 10^{-5}}{0.02499}$$

$$Rel \; u_{Rep} = 0.000709984$$

Table 14. Summation of each uncertainty components from the repeated measurement of molarity.

Parameter	Value	s	n	u_{rep}	Rel u_{Rep}	$Rel \; u^2_{Rep}$
Repeat	0.02499 mol/dm^3	0.00004694	7	0.000017742	0.000709984	$\mathbf{5.04077 \; x \; 10^{-7}}$

Table 15. Mean and standard deviation in the molarity of H_2SO_4 determined in a series of repeat titrations.

Measurement No.	**Molarity H_2SO_4**
1	0.02498
2	0.02489
3	0.02502
4	0.02503
5	0.02500
6	0.02501
7	0.02501
s =	0.00004694
Mean molarity	0.02499

3.4.5 Uncertainty of Molarity of H_2SO_4

$(Note\ M_{H_2SO_4}$ abbreviated here to: $M_2)$

The relative standard uncertainties squared $e.g., Rel\ u_{Rep}^2$ are summed in quadrature:

$$\frac{uM_2}{M_2} = \sqrt{1.581\ x\ 10^{-7} + 1.9307\ \mathrm{x}10^{-7} + 4.032\ x\ 10^{-7} + 5.04077\ x\ 10^{-7}}$$

Multiplying both sides by M_2

$$\frac{uM_2}{M_2}\ x\ M_2 = M_2\sqrt{1.581\ x\ 10^{-7} + 1.9307\ \mathrm{x}10^{-7} + 4.032\ x\ 10^{-7} + 5.04077\ x\ 10^{-7}}$$

gives the combined standard uncertainty of the molarity of the sulphuric acid:

$$uM_2 = 0.02499\sqrt{1.581\ x\ 10^{-7} + 1.9307\ \mathrm{x}10^{-7} + 4.032\ x\ 10^{-7} + 5.04077\ x\ 10^{-7}}$$

$$uM_2 = 0.02499\sqrt{1.581\ x\ 10^{-7} + 1.9307\ \mathrm{x}10^{-7} + 4.032\ x\ 10^{-7} + 5.04077x\ 10^{-7}}$$

$$uM_2 = 0.02499\ x\ 0.001121805$$

Therefore, the combined standard uncertainty for the molarity of H_2SO_4 is:

$$uM_2 = 2.80339 \ x \ 10^{-5}$$

Expanding the standard uncertainty to a 95% level of confidence, (k=2):

$$Expanded \ uncertainty \ U = 2 \ x \ uM_2$$

$$U = 2 \ x \ 2.08339 \ x \ 10^{-5}$$

$$M_2 = 0.02499 \pm 0.0000560678 \ mole/dm^3$$

Rounding to 1 significant figure:

$$M_2 = 0.02499 \pm 0.00006 \ mole/dm^3$$

Or, in %:5.60678E-05

$$\% \ Expanded \ U = \frac{0.0000560678 \ mole/dm^3}{0.02499 \ mole/dm^3} x \ 100$$

$$\% \ Expanded \ U = 0.22\%$$

$$M_2 = 0.02499 \pm 2.2\%$$

Table 16. Summary of components in calculation of the expanded uncertainty of the molarity of H_2SO_4.

Symbols	Input	$(\frac{u_c}{Value})^2$
$uM_{Na_2CO_3}$	Uncertainty Na_2CO_3 molarity	$1.581\ x\ 10^{-7}$
$uV_{Na_2CO_3}$	Uncertainty in Na_2CO_3 volume	1.9307×10^{-7}
$uV_{H_2SO_4}$	Uncertainty in H_2SO_4 volume	$4.032\ x\ 10^{-7}$
u_{Rep}	Uncertainty in repeatability	$5.04077 x\ 10^{-7}$
$\sum(\frac{u_c}{Value})^2$	Sum of relative uncertainties	1.25845×10^{-6}
$\sqrt{\sum(\frac{u_c}{Value})^2}$	Square root of sum of relative uncertainties	0.001121805
$uM_{H_2SO_4}\ x\ M_{H_2SO_4}$	Combined standard uncertainty	2.80339×10^{-5}
U	Expanded Uncertainty	$5.600678\ x\ 10^{-5}$
U	Expanded Uncertainty (rounded)	0.00006
$Mean \pm U$		0.02499 ± 0.00006
$Mean \pm U\%$	$\frac{U}{M_2} x\ 100$	$0.02499 \pm 2.2\%$

Table 17. The significance of the contribution of each task in the method to combined uncertainty in the determination of the molarity of H_2SO_4.

Device/Measurement	Standard Relative Uncertainty	% Contribution
1000 cm^3 Volumetric Flask	$4.394\ x\ 10^{-4}$	17.6
Balance	$7.862\ x\ 10^{-5}$	3.14
Imported from CRM Na_2CO_3	6.733×10^{-5}	2.69
Volume Na_2CO_3	5.4979×10^{-4}	22.0
Volume H_2SO_4	6.4838×10^{-4}	25.9
Repeatability of determination of molarity	$7.09984\ x\ 10^{-4}$	28.4
Molecular mass Na_2CO_3	6.5594×10^{-6}	0.26
Sum	2.50×10^{-3}	**100**

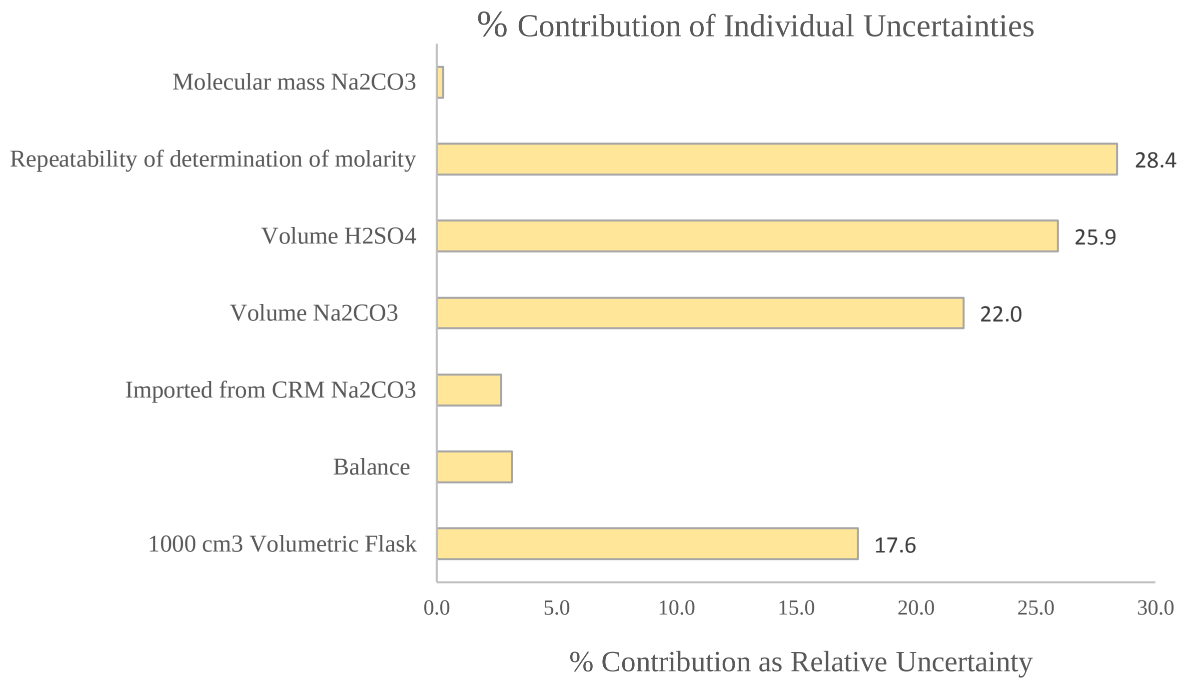

Figure 1. The most significant contributor to the combined uncertainty in the determination of molarity of H_2SO_4 is the repeatability in the determination.

4 Conclusion

The measurement of uncertainty expressed as an expanded uncertainty for the H_2SO_4 molarity is $0.02499 \pm 0.00006\ mole/dm^3$ at a 95 % level of confidence (k=2). Expressed as a percentage, it is $0.02499 \pm 2.2\%$.

The largest contributor to the measurement uncertainty in the determination of H_2SO_4 with standard Na_2CO_3 is that of repeatability in the determination. The volume of H2SO4, Na2CO3 are also major contributors. On this basis, the laboratory may require an automated titrator to improve the precision in repeated measurements. However, a value of 0.22\% expanded uncertainty may be fit for purpose.

REFERENCES

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