ALLAN FRASER
& associates

Consulting Analytical Chemists and Geochemists

THE USE OF A TOP DOWN (NORDTEST) APPROACH IN THE ESTIMATION OF MEASUREMENT OF UNCERTAINTY IN THE DETERMINATION OF THE MOLARITY OF SULPHURIC ACID USING SODIUM CARBONATE

Allan Fraser

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ABSTRACT

A top down Nordtest 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. The within-laboratory reproducibility represents the uncertainty due to the analytical process which is combined with the uncertainty of verification of traceability to give a combined uncertainty for the molarity of sulphuric acid.

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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 'top-down' modelling approach (also referred to as Nord-Test), is to be used to estimate the combined uncertainty associated with the determined molarity of sulphuric acid.

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"*

3 PROCEDURE IN ESTIMATION OF MEASUREMENT UNCERTAINTY

The procedure in the Nordtest approach is:

- State the measurand, *i.e.,* what is being measured?
- State or outline the analytical method.
- Imitate the routine conditions used in the laboratory over a workweek (*e.g.,* 6 days) using the same analysts that would typically perform the titration over this time period.

- Determine the molarity of a standard reference material of sulphuric acid at not less than six replicates.
- Combine the estimates of bias uncertainty and within-laboratory reproducibility.
- Expanded the combined uncertainty to a 95 % level of confidence.

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:

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

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

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

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

An example of the calculation of the molarity ($M_{H_2SO_4}$) of the sulphuric acid is:

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

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

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

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 3.

3.3 Identification of Sources of Uncertainties

In the Nordtest approach the uncertainties considered are:

- The contribution due to bias.
- The contribution due to within-laboratory reproducibility which is the uncertainty contribution from the analytical procedure.

3.4 ESTIMATION OF UNCERTAINTIES

3.4.1 Uncertainty of Verification of Traceability

A certified reference material of sulphuric acid lot number BCCC8287 (Figure 1), was obtained and titrated with standard sodium carbonate to give the results as shown in Table 1.

The uncertainty of verification of traceability u_{trac} is:

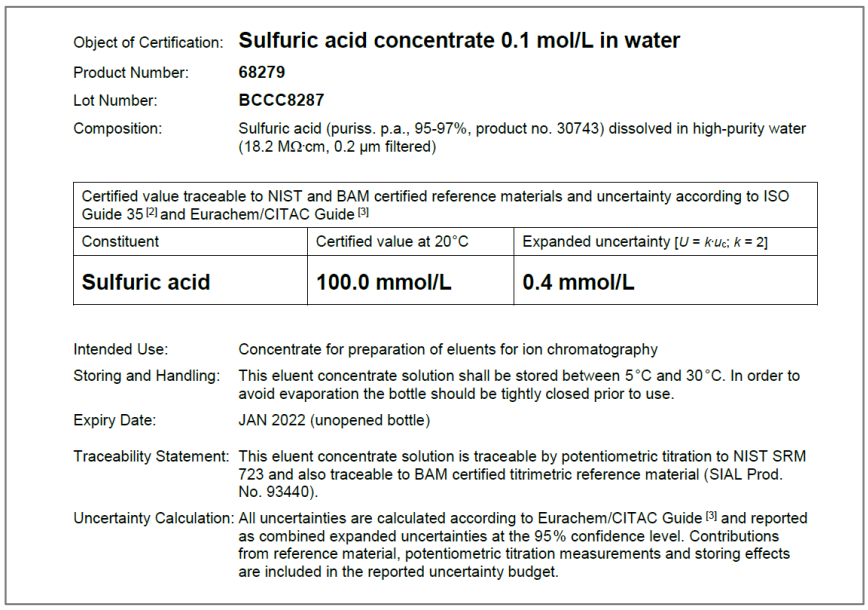
$$u_{trac} = \sqrt{u_{\mu}^2 + \frac{s^2}{n}} \quad [1]$$

Where, u_{μ} is the stated expanded uncertainty as per the certificate of analysis of the reference material used, divided by the coverage factor, *k* (if *k* is not given, default to $\sqrt{3}$), and s is the standard deviation of *n* measurements.

Substituting into [1]:

$$u_{trac} = \sqrt{0.00020^2 + \frac{0.00029^2}{7}}$$

$$u_{trac} = 0.000227$$



Object of Certification: **Sulfuric acid concentrate 0.1 mol/L in water**

Product Number: **68279**

Lot Number: **BCCC8287**

Composition: Sulfuric acid (puriss. p.a., 95-97%, product no. 30743) dissolved in high-purity water (18.2 MΩ·cm, 0.2 µm filtered)

Certified value traceable to NIST and BAM certified reference materials and uncertainty according to ISO Guide 35 [2] and Eurachem/CITAC Guide [3]

Constituent	Certified value at 20°C	Expanded uncertainty [$U = k \cdot u_c$; $k = 2$]
Sulfuric acid	**100.0 mmol/L**	**0.4 mmol/L**

Intended Use: Concentrate for preparation of eluents for ion chromatography

Storing and Handling: This eluent concentrate solution shall be stored between 5 °C and 30 °C. In order to avoid evaporation the bottle should be tightly closed prior to use.

Expiry Date: JAN 2022 (unopened bottle)

Traceability Statement: This eluent concentrate solution is traceable by potentiometric titration to NIST SRM 723 and also traceable to BAM certified titrimetric reference material (SIAL Prod. No. 93440).

Uncertainty Calculation: All uncertainties are calculated according to Eurachem/CITAC Guide [3] and reported as combined expanded uncertainties at the 95% confidence level. Contributions from reference material, potentiometric titration measurements and storing effects are included in the reported uncertainty budget.

Figure 1. Sigma Aldrich certificate of analysis Lot no. BCCC8287 for 0.1 mole/dm^3 sulphuric acid.

Table 1. Molarity values of Lot no. BCCC8287 H_2SO_4 certified reference material for six replicate titrations and the mean and standard deviation.

Molarity H_2SO_4 (mole/dm^3) CRM						
0.1004	0.09990	0.1001	0.1005	0.09970	0.09990	0.1001
Mean	**s**	***n***				
0.10009	0.00029	7				

3.4.2 Uncertainty in the Analytical Procedure

The uncertainty in the determination of the molarity of sulphuric acid, u_{proc} is the within-laboratory reproducibility, therefore:

$$u_{proc} = s_{total} \quad [2]$$

Where, s_{total} is the within-laboratory reproducibility obtained from ANOVA of replicate H_2SO_4 molarity data generated over time and under typical laboratory conditions (Table 2). s_{total} is found by firstly calculating the repeatability standard uncertainty, s_r from the Mean Squares Within, MSw

$$s_r = \sqrt{MSw} \quad [3]$$

$$s_r = \sqrt{6.2146 \text{ x } 10^{-7}}$$

$$s_r = 0.000788$$

followed by the between group uncertainty:

$$s_s = \sqrt{\frac{|MSw - MSb|}{n}} \quad [4]$$

Where, $MSw\ and\ MSb,$ are the mean squared within, mean squared between (both obtained from ANOVA). If *n* is the same for all groups, *n* will be the number of values in a single row. If n varies per column, take the average of the number of values per group the mean number of replicates.

$$s_s = \sqrt{\frac{|6.2146\ x\ 10^{-7} - 5.7379 \text{ x } 10^{-7}|}{7}}$$

$$s_s = 0.0000825$$

Within-laboratory reproducibility s_{total} is:

$$s_{Total} = \sqrt{{s_r}^2 + {s_s}^2} \quad [5]$$

$$s_{Total} = \sqrt{0.000788^2 + 0.0000825^2}$$

$$s_{Total} = 0.000793$$

Calculating the combined uncertainty

$$u_c = \sqrt{{u_{trac}}^2 + {s_{Total}}^2} \quad [6]$$

Therefore,

$$s_{Total} = \sqrt{0.000227^2 + 0.000793^2}$$

$$s_{Total} = 0.000825$$

Table 2. Six replicate molarity results for a 0.025 mole/dm^3 solution of H_2SO_4 as determined over a period of six days by six different analysts.

Molarity H_2SO_4	**Molarity H_2SO_4**	**Molarity H_2SO_4**	**Molarity H_2SO_4**	**Molarity H_2SO_4**	**Molarity H_2SO_4**
Day 1	***Day 2***	***Day 3***	***Day 4***	***Day 5***	***Day 6***
0.02498	0.02499	0.02469	0.02467	0.025	0.02502
0.02489	0.0249	0.02408	0.02445	0.02478	0.02489
0.02487	0.02535	0.02503	0.02511	0.02502	0.02501
0.02503	0.02545	0.02506	0.0298	0.02504	0.02489
0.0250	0.02522	0.02535	0.02502	0.02504	0.02556
0.02501	0.02506	0.02507	0.02577	0.02507	0.02504
0.02501	0.02509	0.02511	0.02502	0.02502	0.02509

Table 3. Results of a single-factor ANOVA from which the within-lab reproducibility is determined.

Source of Variation	***MS***	$\mathbf{F_{calc}}$	***p***	$\mathbf{F_{crit}}$
Between Days variance	5.7379×10^{-7}	0.923	0.477	2.48
Within Days variance	6.2146×10^{-7}			
Repeatability uncertainty s_r	0.000788			
Within-lab group uncertainty	0.0000825			
Within-lab Reproducibility	0.000793			

3.4.3 Combined Uncertainty

Calculating the combined uncertainty is the square root of the sum of squares of the uncertainty due to traceability and the within-laboratory reproducibility:

$$u_c = \sqrt{{u_{trac}}^2 + {s_{Total}}^2} \quad [7]$$

Therefore,

$$u_c = \sqrt{0.000227^2 + 0.000793^2}$$

$$u_c = 0.000825$$

3.4.4 Expanded Uncertainty

The expanded uncertainty, *U* at a 95% level of confidence is:

$$U = 2u_c \quad [8]$$

Therefore,

$$U = 2\ x\ 0.000825 = 0.001649$$

$$U = 0.002$$

Table 4 gives a breakdown of equations [1] and [5] and the associated data.

Table 4. Itemised symbols and values representing equation [1] and [5].

µCRM	0.10
U_{μ}	0.00040
u_{μ}	0.00020
u^2_{μ}	0.000000040
Mean	0.100086
s	0.00029
s^2	0.000000081
n	7
s^2/n	0.000000012
u_{trac}	0.000227
u^2_{trac}	0.000000052
u_{proc}	0.000793
u^2_{proc}	0.000000628
$u_{combined}$	0.000825
U at *k*=2	0.001649
±U at *k*=2	0.0016
±U at *k*=2 (rounded)	0.002

3.4.5 Reporting the Expanded Uncertainty

The expanded uncertainty is reported as:

$$Mean \pm U$$

The mean used is that of the Grand Mean for six replicates over six days *i.e.*, 0.02513 mole/dm^3 (Table 2)

$$0.02513 \pm 0.002\ mole/dm^3$$

4 CONCLUSION

Replicate determinations of the molarity of a sulphuric acid certified reference standard provided the uncertainty of verification of traceability. From an ANOVA of the replicates of a sulphuric acid sample over six days gave the uncertainty in the analytical procedure. The combined uncertainty was calculated from the sum of the squares of uncertainty of verification of traceability and the uncertainty in the analytical procedure.

The expanded uncertainty at k=2, 95 % level confidence is $0.02513 \pm 0.002\ mole/dm^3$

REFERENCES

EURACHEM / CITAC Guide CG 4. (2012). Quantifying uncertainty in analytical measurement. 3rd Edition. Editors: Ellison, S. L. R., Williams, A. 4-121.

CITATION

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