Standardising a sodium hydroxide solution

This is the example A2 of the EURACHEM / CITAC Guide "Quantifying Uncertainty in Analytical Measurement", Second Edition.

A solution of sodium hydroxide (NaOH) is standardised against the titrimetric standard potassium hydrogen phtalate (KHP).

The titrimetric standard KHP is dried and weighed. After the preparation of the NaOH solution a sample of the KHP is dissolved and then titrated using the NaOH solution.

Model Equation:

{Molar mass of KHP}

$M_{KHP} = 8 * M_C + 5 * M_H + 4 * M_O + M_K$;

{Volume delivered by the piston burette, excluding repeatability}

$V_T = V_{nominal} * f_{V\text{-}calibration} * f_{V\text{-}temperature}$;

{mass of KHP weighed, excluding repeatability}

$m_{KHP} = m_{container\ and\ KHP} - m_{container\ less\ KHP}$;

{calculation of the concentration of the NaOH solution}

$c_{NaOH} = (k_{mL} * m_{KHP} * P_{KHP}) / (M_{KHP} * V_T) * f_{repeatability}$;

List of Quantities:

Quantity	Unit	Definition
M_{KHP}	g/mol	Molar mass of KHP
M_C	g/mol	Atomic weight of carbon
M_H	g/mol	Atomic weight of hydrogen
M_O	g/mol	Atomic weight of oxygen
M_K	g/mol	Atomic weight of potassium
V_T	mL	Volume delivered by piston burette
$V_{nominal}$	mL	Volume indicated by burette
$f_{V\text{-}calibration}$		Uncertainty contribution to the volume due to uncertainty in calibration of the burette
$f_{V\text{-}temperature}$		Uncertainty contribution to the volume due to temperature variation
m_{KHP}	g	Mass of KHP weighed
$m_{container\ and\ KHP}$	g	Mass of container and KHP
$m_{container\ less\ KHP}$	g	Mass of container less KHP
c_{NaOH}	mol/L	Concentration of the sodium hydroxide solution
k_{mL}	mL/L	Conversion factor 1000 ml = 1L
P_{KHP}		Purity of the KHP
$f_{repeatability}$		Repeatability of the titration

M_C:
Type B rectangular distribution
Value: 12.0107 g/mol
Halfwidth of Limits: 0.0008 g/mol

The atomic weight of carbon and its uncertainty are taken from data listed in the latest IUPAC table of atomic weights. The IUPAC quoted data is considered to be of rectangular distribution.

M_H: Type B rectangular distribution
Value: 1.00794 g/mol
Halfwidth of Limits: 0.00007 g/mol

The atomic weight of hydrogen and its uncertainty are taken from data listed in the latest IUPAC table of atomic weights. The IUPAC quoted data is considered to be of rectangular distribution.

M_O: Type B rectangular distribution
Value: 15.9994 g/mol
Halfwidth of Limits: 0.0003 g/mol

The atomic weight of oxigen and its uncertainty are taken from data listed in the latest IUPAC table of atomic weights. The IUPAC quoted data is considered to be of rectangular distribution.

M_K: Type B rectangular distribution
Value: 39.0983 g/mol
Halfwidth of Limits: 0.0001 g/mol

The atomic weight of potassium and its uncertainty are taken from data listed in the latest IUPAC table of atomic weights. The IUPAC quoted data is considered to be of rectangular distribution.

$V_{nominal}$: Constant
Value: 18.64 mL

The nominal volume is not associated with any uncertainties. The uncertainty of the real volume of the burette has three components, repeatability, calibration and temperature. The latter two are included in the uncertainty budget as separate factors. Repeatability of the volume delivery is taken into account via the combined repeatability term for the experiment, $f_{repeatability}$. Another factor influencing the result of the titration, which can also be attributed to the automatic titration system, of which the burette is one part, is the bias of the end-point detection. The titration is performed under a protective atmosphere (Ar) to prevent absorption of CO_2, which would bias the titration. There are no indications that the end-point determined from the shape of the pH-curve does not correspond to the equivalence-point, because a strong acid is titrated with a strong base. No further uncertainty contributions are introduced to cover the bias of the end-point detection.

$f_{V\text{-}calibration}$: Type B triangular distribution
Value: 1
Halfwidth of Limits: 0.0015

The limits of accuracy for a 20 mL piston burette are indicated by the manufacturer as typically ±0.03 ml. No further statement is made about the level of confidence or the underlying distribution. An assumption is necessary to work with this uncertainty statement. In this case a triangular distribution is assumed. Since $f_{V\text{-}calibration}$ is a multiplicative factor to the nominal volume, which is only used to introduce the calibration uncertainty, it has the value 1. The halfwidth of limits corresponds to the relative uncertainty as stated by the manufacturer (i.e. 0.03 mL / 20 mL).

$f_{V\text{-}temperature}$: Type B normal distribution
Value: 1
Expanded Uncertainty: 0.0003
Coverage Factor: 1

The laboratory temperature can vary by ±3°C. The uncertainty of the volume due to temperature variations can be calculated from the estimate of the possible temperature range and the coefficient of the volume expansion. The volume expansion of the liquid is considerably larger than that of the burette, so only the volume expansion of the liquid is considered. The coefficient of volume expansion for water is $2.1 \cdot 10^{-4} °C^{-1}$, which is used here also for the NaOH solution. This leads to a possible volume variation of $\pm(19 \cdot 3 \cdot 2.1 \cdot 10^{-4}/1.96)$ mL = ±0.006 mL. A rectangular distribution is assumed for the temperature variation Since $f_{V\text{-temperature}}$ is a multiplicative factor to the nominal volume, which is only used to introduce the temperature uncertainty, it has the value 1. Its uncertainty is calculated as 0.006 mL / 19 mL.

$m_{\text{container and KHP}}$: Type B rectangular distribution
Value: 60.5450 g
Halfwidth of Limits: 0.00015 g

Repeatability of the wheighing is taken into account via the combined repeatability term, $f_{\text{repeatability}}$. Any systematic offset across the scale will also cancel due to the wheighing by difference. The only contributing source of uncertainty is the linearity of the balance. The calibration certficate of the balance quotes ±0.15 mg for the linearity. The manufacturer recommends using a rectangular distribution to convert this linearity contribution into a standard uncertatiny. This uncertainty is not correlated with the uncertainty of $m_{\text{container less KHP}}$, since they are independent observations and the linearity effects are not correlated.

$m_{\text{container less KHP}}$: Type B rectangular distribution
Value: 60.1562 g
Halfwidth of Limits: 0.00015 g

Repeatability of the wheighing is taken into account via the combined repeatability term, $f_{\text{repeatability}}$. Any systematic offset across the scale will also cancel due to the wheighing by difference. The only contributing source of uncertainty is the linearity of the balance. The calibration certficate of the balance quotes ±0.15 mg for the linearity. The manufacturer recommends using a rectangular distribution to convert this linearity contribution into a standard uncertatiny. This uncertainty is not correlated with the uncertainty of $m_{\text{container and KHP}}$, since they are independent observations and the linearity effects are not correlated.

k_{mL}: Constant
Value: 1000 mL/L

P_{KHP}: Type B rectangular distribution
Value: 1
Halfwidth of Limits: 0.0005

In the supplier's catalogue, the purity of the KHP is given as 1.0000±0.0005. No further information concerning the uncertainty is given. Therefore this value is assumed to be of rectangular distribution.

$f_{\text{repeatability}}$: Type B normal distribution
Value: 1
Expanded Uncertainty: 0.0005
Coverage Factor: 1

All uncertainty contributions due to repeatability of one of the operations are combined in this factor. It includes at least the repeatability of the wheighings and of the volume delivered by the burette. The magnitude of this uncertainty contribution is assessed during the method validation stage. The data shows that the overall repeatability of the titration experiment is 0.05%. Since $f_{\text{repeatability}}$ is a multiplicative factor to the result, which is only used to introduce the repeatability uncertainty, it has the value 1 with an uncertainty of 0.0005.

Interim Results:

Quantity	Value	Standard Uncertainty
M_{KHP}	204.221200 g/mol	$3.765\cdot10^{-3}$ g/mol
V_T	18.64000 mL	0.01271 mL
m_{KHP}	0.3888000 g	$122.5\cdot10^{-6}$ g

Uncertainty Budgets:

c_{NaOH}: Concentration of the sodium hydroxide solution

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
M_{KHP}	204.221200 g/mol	$3.765 \cdot 10^{-3}$ g/mol				
M_C	12.0107000 g/mol	$461.9 \cdot 10^{-6}$ g/mol	rectangular	$-4.0 \cdot 10^{-3}$	$-1.8 \cdot 10^{-6}$ mol/L	0.0 %
M_H	1.00794000 g/mol	$40.41 \cdot 10^{-6}$ g/mol	rectangular	$-2.5 \cdot 10^{-3}$	$-100 \cdot 10^{-9}$ mol/L	0.0 %
M_O	15.9994000 g/mol	$173.2 \cdot 10^{-6}$ g/mol	rectangular	$-2.0 \cdot 10^{-3}$	$-350 \cdot 10^{-9}$ mol/L	0.0 %
M_K	39.09830000 g/mol	$57.74 \cdot 10^{-6}$ g/mol	rectangular	$-500 \cdot 10^{-6}$	$-29 \cdot 10^{-9}$ mol/L	0.0 %
V_T	18.64000 mL	0.01271 mL				
$V_{nominal}$	18.64 mL					
$f_{V\text{-}calibration}$	1.0000000	$612.4 \cdot 10^{-6}$	triangular	-0.10	$-63 \cdot 10^{-6}$ mol/L	41.8 %
$f_{V\text{-}temperature}$	1.0000000	$300.0 \cdot 10^{-6}$	normal	-0.10	$-31 \cdot 10^{-6}$ mol/L	10.0 %
m_{KHP}	0.3888000 g	$122.5 \cdot 10^{-6}$ g				
$m_{container\ and\ KHP}$	60.54500000 g	$86.60 \cdot 10^{-6}$ g	rectangular	0.26	$23 \cdot 10^{-6}$ mol/L	5.5 %
$m_{container\ less\ KHP}$	60.15620000 g	$86.60 \cdot 10^{-6}$ g	rectangular	-0.26	$-23 \cdot 10^{-6}$ mol/L	5.5 %
k_{mL}	1000.0 mL/L					
P_{KHP}	1.0000000	$288.7 \cdot 10^{-6}$	rectangular	0.10	$29 \cdot 10^{-6}$ mol/L	9.3 %
$f_{repeatability}$	1.0000000	$500.0 \cdot 10^{-6}$	normal	0.10	$51 \cdot 10^{-6}$ mol/L	27.8 %
c_{NaOH}	0.10213616 mol/L	$96.78 \cdot 10^{-6}$ mol/L				

Results:

Quantity	Value	Expanded Uncertainty	Coverage factor	Coverage
c_{NaOH}	0.10214 mol/L	$190 \cdot 10^{-6}$ mol/L	2.00	95% (t-table 95.45%)