An acid/base titration

This is the example A3 of the EURACHEM / CITAC Guide "Quantifying Uncertainty in Analytical Measurement", Second Edition.

A solution of hydrochloric acid (HCl) is standardised against a solution of sodium hydroxide (NaOH) with known content. The standardisation of the NaOH solution is similar to example A2.

Model Equation:

{calculation of the uncertainty of V_{T2}}

$V_{T2} = V_{T2\ nominal} * f_{VT2\text{-}calibration} * f_{VT2\text{-}temperature}$;

{calculation of the uncertainty of V_{T1}}

$V_{T1} = V_{T1\ nominal} * f_{VT1\text{-}calibration} * f_{VT1\text{-}temperature}$;

{calculation of the uncertainty of V_{HCl}}

$V_{HCl} = V_{HCl\ nominal} * f_{VHCl\text{-}calibration} * f_{VHCl\text{-}temperature}$;

{molar mass of KHP}

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

{calculation of the the HCl concentration}

$c_{HCl} = (k_{mL} * m_{KHP} * P_{KHP} * V_{T2}) / (V_{T1} * M_{KHP} * V_{HCl}) * f_{repeatability}$;

List of Quantities:

Quantity	Unit	Definition
V_{T2}	mL	Volume of NaOH for HCl titration
$V_{T2\ nominal}$	mL	Nominal volume of NaOH for HCl titration
$f_{VT2\text{-}calibration}$		Uncertainty contribution to V_{T2} due to instrument calibration
$f_{VT2\text{-}temperature}$		Uncertainty contribution to V_{T2} due to temperature variation
V_{T1}	mL	Volume of NaOH for KHP titration
$V_{T1\ nominal}$	mL	Nominal volume of NaOH for KHP titration
$f_{VT1\text{-}calibration}$		Uncertainty contribution to V_{T1} due to instrument calibration
$f_{VT1\text{-}temperature}$		Uncertainty contribution to V_{T1} due to temperature variation
V_{HCl}	mL	HCl aliquot for NaOH titration
$V_{HCl\ nominal}$	mL	Nominal volume of HCl for NaOH titration
$f_{VHCl\text{-}calibration}$		Uncertainty contribution to V_{HCl} due to pipette calibration
$f_{VHCl\text{-}temperature}$		Uncertainty contribution to V_{HCl} due to temperature variation
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
c_{HCl}	mol/L	HCl solution concentration

Quantity	Unit	Definition
k_{mL}	mL/L	Conversion factor 1000 mL = 1 L
m_{KHP}	g	Weight of KHP
P_{KHP}		Purity of KHP
$f_{repeatability}$		Uncertainty contribution attributed to repeatability

$V_{T2\ nominal}$: Constant
Value: 14.89 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. No further uncertainty contributions are introduced to cover the bias of the end-point detection.

$f_{VT2\text{-}calibration}$: Type B triangular distribution
Value: 1
Halfwidth of Limits: =0.03/14.89

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 $f_{VT2\text{-}calibration}$ 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 / 14.89 mL).

$f_{VT2\text{-}temperature}$: Type B rectangular distribution
Value: 1
Halfwidth of Limits: =2.1e-4*4

The laboratory temperature can vary by ±4°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}. This leads to a possible volume variation of $\pm(15 \cdot 4 \cdot 2.1 \cdot 10^{-4})$ mL. A rectangular distribution is assumed for the temperature variation Since $f_{VT2\text{-}temperature}$ 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 the possible volume variation divided by the volume dispensed.

$V_{T1\ nominal}$: 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. No further uncertainty contributions are introduced to cover the bias of the end-point detection.

$f_{VT1\text{-}calibration}$: Type B triangular distribution
Value: 1
Halfwidth of Limits: =0.03/18.64

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 $f_{VT1\text{-}calibration}$ 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 / 18.64 mL).

$f_{VT1\text{-}temperature}$: Type B rectangular distribution
Value: 1
Halfwidth of Limits: =2.1e-4*4

The laboratory temperature can vary by ±4°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 $2.1\cdot10^{-4}{}^{\circ}C^{-1}$. This leads to a possible volume variation of $\pm(19 \cdot 4 \cdot 2.1\cdot10^{-4})$ mL. A rectangular distribution is assumed for the temperature variation Since $f_{VT1\text{-}temperature}$ 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 the possible volume variation divided by the volume dispensed.

$V_{HCl\ nominal}$: Constant
Value: 15 mL

The nominal volume is not associated with any uncertainties. The uncertainty of the real volume of the pipette 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, $f_{repeatability}$.

$f_{VHCl\text{-}calibration}$: Type B triangular distribution
Value: 1
Halfwidth of Limits: =0.02/15

The uncertainty stated by the manufacturer for a 15 mL pipette is ±0.02 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 $f_{VHCl\text{-}calibration}$ 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. 0.02 mL / 15 mL).

$f_{VHCl\text{-}temperature}$: Type B rectangular distribution
Value: 1
Halfwidth of Limits: =2.1e-4*4

The laboratory temperature can vary by ±4°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 pipette, so only the volume expansion of the liquid is considered. The coefficient of volume expansion for water is $2.1\cdot10^{-4}{}^{\circ}C^{-1}$. This leads to a possible volume variation of $\pm(15 \cdot 4 \cdot 2.1\cdot10^{-4})$ mL. A rectangular distribution is assumed for the temperature variation Since $f_{VHCl\text{-}temperature}$ 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 the possible volume variation divided by the volume dispensed.

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.

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

m_{KHP}: Type B normal distribution
Value: 0.3888 g
Expanded Uncertainty: =sqrt(2*sqr(0.00015/sqrt(3)))
Coverage Factor: 1

Repeatability of the wheighing is taken into account via the combined repeatability term, $f_{repeatability}$. 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 accounted for twice, once for the tare and once for the gross mass.

P_{KHP}: Type B rectangular distribution
Value: 1
Halfwidth of Limits: 0.05 %

In the supplier's catalogue, the purity of the KHP is given as 100%±0.05%. No further information concerning the uncertainty is given. Therefore this value is assumed to be of rectangular distribution.

$f_{repeatability}$: Type B normal distribution
Value: 1
Expanded Uncertainty: 0.1 %
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 volumes delivered by the burette and the pipette. 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 0.1%. Since $f_{repeatability}$ 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 0.1%.

Interim Results:

Quantity	Value	Standard Uncertainty
V_{T2}	14.89000 mL	0.01422 mL
V_{T1}	18.64000 mL	0.01522 mL
V_{HCl}	15.00000 mL	0.01094 mL
M_{KHP}	204.221200 g/mol	$3.765 \cdot 10^{-3}$ g/mol

Uncertainty Budgets:

c_{HCl}: HCl solution concentration

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
V_{T2}	14.89000 mL	0.01422 mL				
$V_{T2\ nominal}$	14.89 mL					
$f_{VT2\text{-}calibration}$	1.0000000	$822.5 \cdot 10^{-6}$	triangular	0.10	$83 \cdot 10^{-6}$ mol/L	20.5 %
$f_{VT2\text{-}temperature}$	1.0000000	$485.0 \cdot 10^{-6}$	rectangular	0.10	$49 \cdot 10^{-6}$ mol/L	7.1 %
V_{T1}	18.64000 mL	0.01522 mL				
$V_{T1\ nominal}$	18.64 mL					
$f_{VT1\text{-}calibration}$	1.0000000	$657.1 \cdot 10^{-6}$	triangular	-0.10	$-67 \cdot 10^{-6}$ mol/L	13.1 %
$f_{VT1\text{-}temperature}$	1.0000000	$485.0 \cdot 10^{-6}$	rectangular	-0.10	$-49 \cdot 10^{-6}$ mol/L	7.1 %
V_{HCl}	15.00000 mL	0.01094 mL				
$V_{HCl\ nominal}$	15.0 mL					
$f_{VHCl\text{-}calibration}$	1.0000000	$544.3 \cdot 10^{-6}$	triangular	-0.10	$-55 \cdot 10^{-6}$ mol/L	9.0 %
$f_{VHCl\text{-}temperature}$	1.0000000	$485.0 \cdot 10^{-6}$	rectangular	-0.10	$-49 \cdot 10^{-6}$ mol/L	7.1 %
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	$-2.0 \cdot 10^{-3}$	$-340 \cdot 10^{-9}$ 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 %
k_{mL}	1000.0 mL/L					
m_{KHP}	0.3888000 g	$122.5 \cdot 10^{-6}$ g	normal	0.26	$32 \cdot 10^{-6}$ mol/L	3.0 %
P_{KHP}	1.0000000	$288.7 \cdot 10^{-6}$	rectangular	0.10	$29 \cdot 10^{-6}$ mol/L	2.5 %
$f_{repeatability}$	1.000000	$1.000 \cdot 10^{-3}$	normal	0.10	$100 \cdot 10^{-6}$ mol/L	30.4 %
c_{HCl}	0.1013872 mol/L	$184.0 \cdot 10^{-6}$ mol/L				

Results:

Quantity	Value	Expanded Uncertainty	Coverage factor	Coverage
c_{HCl}	0.10139 mol/L	$370 \cdot 10^{-6}$ mol/L	2.00	95% (t-table 95.45%)