Preparation of a calibration standard

This is the example A1 of the EURACHEM / CITAC Guide "Quantifying Uncertainty in Analytical Measurement", Second Edition.

A calibration standard of ca. 1000 $mg \cdot L^{-1}$ is prepared from a high purity metalic cadmium.

After cleaning the surface of the high purity metal it is weighed and dissolved in nitric acid in a volumetric flask.

Model Equation:

{Calculation of the uncertainty of the volume}

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

{Calculation of the uncertainty of the calibration standard}

$c_{Cd} = (k_{mL} * m * P) / V$;

List of Quantities:

Quantity	Unit	Definition
V	mL	Volume of the flask
$V_{nominal}$	mL	Nominal volume of the flask
$f_{V\text{-}calibration}$		Uncertainty contribution to the volume due to uncertainty in calibration of the flask
$f_{V\text{-}temperature}$		Uncertainty contribution to the volume due to temperature variation
$f_{V\text{-}repeatability}$		temperaturabhängige Widerstandsänderung des zu kalibrierenden Widerstandes
c_{Cd}	mg/L	Concentration of the calibration standard
k_{mL}	mL/L	Conversion factor 1000 mL = 1 L
m	mg	Mass of the metal
P		Purity of the metal

$V_{nominal}$: Constant
Value: 100 mL

The nominal volume is not associated with any uncertainties. The uncertainty of the real volume of the flask has three components, calibration, temperature and repeatability. These are included in the uncertainty budget as separate factors.

$f_{V\text{-}calibration}$: Type B triangular distribution
Value: 1
Halfwidth of Limits: 0.001

The manufacturer of the flask quotes the volume of the flask as 100 mL ±0.1 mL, measured at a temperature of 20°C. 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. 0.1 mL / 100 mL).

$f_{V\text{-}temperature}$: Type B rectangular distribution
Value: 1
Halfwidth of Limits: 0.00084

The flask has been calibrated at 20°C (manufacturer statement). The laboratory temperature varies by ±4°C around this value. 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 flask, 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 nitric acid solution. This leads to a possible volume variation of $\pm(100 \cdot 4 \cdot 2.1 \cdot 10^{-4})$ mL = ±0.084 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. The halfwidth of limits corresponds to the possible volume variation as calculated above.

$f_{V\text{-repeatability}}$: Type A summarized
Mean: 1
Standard Uncertainty: 0.0002
Degrees of Freedom: 9

The uncertainty due to the repeatability of the filings can be estimated from a repeatability experiment on a typical example of the flask used. The flask was filled and weighed ten times. For the 100 mL flask this resulted in a standard deviation of 0.02 mL. This is used directly as the standard uncertainty. Since $f_{V\text{-repeatability}}$ is a multiplicative factor to the nominal volume, which is only used to introduce the repeatability uncertainty, it has the value 1 ± 0.0002.

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

m: Type B normal distribution
Value: 100.28 mg
Expanded Uncertainty: 0.05 mg
Coverage Factor: 1

The mass of the cadmium is determined by a tared weighing. The literature of the balance's manufacturer identifies three uncertainty sources for the tared weighing: the repeatablility, the readability (digital resolution) of the balance scale and the contribution due to the uncertainty in the calibration function of the scale. This calibration function has two potential sources of uncertainty, identified as the sensitivity of the balance and the linearity. The sensitivity can be neglected because the mass by difference is done on the same balance over a very narrow range. Bouyance correction is not considered here. Using data from the calibration certificate of the balance and following the manufacturer's recommendations on uncertainty estimation, the uncertainty associated with the mass of the cadmium is estimated as 0.05 mg.

P: Type B rectangular distribution
Value: 0.9999
Halfwidth of Limits: 0.0001

The purity of the metal is quoted in the suppliers certificate as 99.99 ±0.01%. P is expressed as mass fraction (g/g), and its value is therefore 0.9999±0.0001. There is no additional information about the uncertainty. A rectangular distribution is assumed.

If the manufacturers procedure for cleaning the surface is strictly followed, there should be no additional uncertainty contribution. There is no information available about the completeness of the dissolution. Therefore one has to check with a repeated preparation experiment that this contribution can be neglected.

Interim Results:

Quantity	Value	Standard Uncertainty
V	100.00000 mL	0.06647 mL

Uncertainty Budgets:

c_{Cd}: Concentration of the calibration standard

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
V	100.00000 mL	0.06647 mL				
$V_{nominal}$	100.0 mL					
$f_{V\text{-}calibration}$	1.0000000	$408.2 \cdot 10^{-6}$	triangular	-1000	-0.41 mg/L	24.0 %
$f_{V\text{-}temperature}$	1.0000000	$485.0 \cdot 10^{-6}$	rectangular	-1000	-0.49 mg/L	33.9 %
$f_{V\text{-}repeatability}$	1.0000000	$200.0 \cdot 10^{-6}$	normal	-1000	-0.20 mg/L	5.8 %
k_{mL}	1000.0 mL/L					
m	100.28000 mg	0.05000 mg	normal	10	0.50 mg/L	35.8 %
P	0.99990000	$57.74 \cdot 10^{-6}$	rectangular	1000	0.058 mg/L	0.5 %
c_{Cd}	1002.6997 mg/L	0.8352 mg/L				

Results:

Quantity	Value	Expanded Uncertainty	Coverage factor	Coverage
c_{Cd}	1002.7 mg/L	1.7 mg/L	2.00	manual