Determination of Cadmium Release from Ceramic Ware by Atomic Absorption Spectrometry

This is the example A5 of the EURACHEM / CITAC Guide "Quantifying Uncertainty in Analytical Measurement", Second Edition.

The amount of released cadmium from ceramic ware is determined using atomic absorption spectrometry. The procedure employed is the empirical method BS 6748.

The item to be tested is filled with a 4 % v/v acetid acid solution for a given lenght of time, the amount of cadmium released from the item is then calculated from the measured cadmium concentration in the leach solution and the volume of the leach solution. Parameters such as leaching time, temperature, acid concentration etc. are specified in the empirical method.

Model Equation:

{calculation of the uncertainty of volume V_L}

$V_L = V_{L\ nominal} * f_{VL\text{-}filling} * f_{VL\text{-}temperature} * f_{VL\text{-}reading} * f_{VL\text{-}calibration}$;

{calculation of the uncertainty of the surfache area}

$a_V = a_{V\ nominal} * f_{aV\text{-}length1} * f_{aV\text{-}lenght2} * f_{aV\text{-}area}$;

{calculation of the mass of cadmium leached}

$r = c_0 * V_L / a_V * d * f_{acid} * f_{time} * f_{temperature}$;

List of Quantities:

Quantity	Unit	Definition
V_L	L	Volume of the leachate
$V_{L\ nominal}$	L	Nominal volume of the leachate
$f_{VL\text{-}filling}$		Uncertainty contribution of V_L due to filling of the vessel
$f_{VL\text{-}temperature}$		Uncertainty contribution of V_L due to temperature variation
$f_{VL\text{-}reading}$		Uncertainty contribution of V_L due to reading of the measuring cylinder
$f_{VL\text{-}calibration}$		Uncertainty contribution of V_L due to calibration of the measuring cylinder
a_V	dm^2	Surface area of the vessel
$a_{V\ nominal}$	dm^2	Nominal surface area of the vessel
$f_{aV\text{-}length1}$		Uncertainty contribution to a_V of first length measurement (i.e. height)
$f_{aV\text{-}lenght2}$		Uncertainty contribution to a_V of second length measurement (i.e. lenght)
$f_{aV\text{-}area}$		Uncertainty contribution to a_V due to imperfect geometry
r	mg/dm^2	Mass of cadmium leached per unit area
c_0	mg/L	Content of cadmium in the extraction solution
d		Dilution factor (if used)
f_{acid}		Influence of the acid concentration
f_{time}		Influence of the duration
$f_{temperature}$		Influence of the temperature

$V_{L\ nominal}$: Constant
Value: 0.332 L

The nominal volume is not associated with any uncertainties. Four different factors contribute to the uncertainty of the real volume, filling, temperature, reading and calibration. These are introduced in the uncertainy budget through the factors $f_{VL\text{-}filling}$, $f_{VL\text{-}temperature}$, $f_{VL\text{-}reading}$ and $f_{VL\text{-}calibration}$.

$f_{VL\text{-}filling}$: Type B triangular distribution
Value: 0.995
Halfwidth of Limits: 0.005

The method requires the vessel to be filled 'to within 1mm from the brim'. For a typical drinking or kitchen utensil, this represents about 1% of the total height. The vessel will therefore be 99.5% ± 0.5% filled.

$f_{VL\text{-}temperature}$: Type B rectangular distribution
Value: 1
Halfwidth of Limits: =2.1e-4*2

The temperature of the acetic acid has to be 22 ±2°C, according to the method. This range leads to an uncertainty in the measured volume, due to a considerably larger volume expansion of the liquid compared to the vessel. The coefficient of volume expansion for water is $2.1 \cdot 10^{-4} °C^{-1}$. This leads to a possible volume variation of $\pm(332 \cdot 2 \cdot 2.1 \cdot 10^{-4})$ mL. A rectangular distribution is assumed for the temperature variation of the volume. Since $f_{VL\text{-}temperature}$ 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.

$f_{VL\text{-}reading}$: Type B triangular distribution
Value: 1
Halfwidth of Limits: 0.01

$f_{VL\text{-}calibration}$: Type B triangular distribution
Value: 1
Halfwidth of Limits: =2.5/332

The volume is calibrated within ±2.5 mL for a 500 mL measuring cylinder. 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 $f_{VL\text{-}calibration}$ 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. 2.5 mL / 332 mL).

$a_{V\ nominal}$: Constant
Value: 2.37 dm^2

The nominal surface are is not associated with any uncertainties. Three different factors contribute to the uncertainty of the real surface area, that are the two length measurements required to calculate the surface area, and an area-factor, covering the imperfect geometry of any real vessel.

$f_{aV\text{-}length1}$: Type B normal distribution
Value: 1
Expanded Uncertainty: =0.01/1.45
Coverage Factor: 1

Typically, two length measurements are required to calculate the surface area of a vessel. In this case, the item was approximated by a cylindrical geometry. Typical dimensions are between 1.0 and 2.0 dm, leading to an estimated uncertainty of 1 mm. The two length measurements required for this vessel were 1.45 and 1.64 dm.

$f_{aV\text{-}lenght2}$: Type B normal distribution
Value: 1
Expanded Uncertainty: =0.01/1.64
Coverage Factor: 1

Typically, two length measurements are required to calculate the surface area of a vessel. In this case, the item was approximated by a cylindrical geometry. Typical dimensions are between 1.0 and 2.0 dm, leading to an estimated uncertainty of 1 mm. The two length measurements required for this vessel were 1.45 and 1.64 dm.

$f_{aV\text{-}area}$: Type B normal distribution
Value: 1
Expanded Uncertainty: =0.05/1.96
Coverage Factor: 1

The item is not a perfect geometric shape (cylinder in this case). Therefore the real surface area may deviate from the caluclated one. This deviation was estimated to be 5% at 95% confidence level. To obtain the standard uncertainty the possible deviation is divided by 1.96.

c_0: Type B normal distribution
Value: 0.26 mg/L
Expanded Uncertainty: 0.018 mg/L
Coverage Factor: 1

The content of cadmium in the extraction solution is calculated using a calibration curve. For the calibration curve five calibration standards were prepared and measured 3 times each. Using a linear least square fit, the slope and intercept of the calibration curve have been calculated. Using this data, the concentration c_0 was calculated from a duplicate measurement of the actual leach solution. The calculation of the uncertianty of the least square fit is described in Appendix E3 of the EURACHEM / CITAC Guide. Only the final result of this calculation is used here.

d: Type B normal distribution
Value: 1
Expanded Uncertainty: 0
Coverage Factor: 1

For this sample, no dilution of the leach solution was necessary, therefore no uncertainty needs to be introduced here.

f_{acid}: Type B normal distribution
Value: 1
Expanded Uncertainty: =0.008*0.1
Coverage Factor: 1

Data from two study on the effect of acid concentration on lead release was used to estimate this factor. One study showed that lead release was increased by approximately 0.1 when the acid concentration was increased from 4 to 5% v/v. Another study reported a 50% increase of the lead release for a change of acid concentration from 2 to 6% v/v. Assuming a liner effect, on can estimate a change of f_{acid} of 0.1 per 1% v/v change of acid concentration. In another experiment the concentration of the acetic acid and its standard uncertainty have been established using titration with standardised NaOH solution, resulting in an acetic acid concentration of 3.996 % v/v with a standard uncertainty of 0.008% v/v. The uncertainty of f_{acid} can then be calculated as $0.008 \cdot 0.1$.

f_{time}: Type B rectangular distribution
Value: 1
Halfwidth of Limits: =0.5*0.003

For a relatively slow process such as leaching, the amount leached will be approximately proportional to the leaching time for small changes in that time. In a study, a mean change of concentration over the last six hours of leaching of approximately $1.8\ \mathrm{mg} \cdot \mathrm{L}^{-1}$ (=0.3% / h) was found. The leaching time is specified in the method as 24 ±0.5 h, the content of Cd in the extraction solution therefore needs to be corrected by a factor of $1 \pm (0.5 \cdot 0.003)$. A rectangular distribution is assumed for this factor.

$f_{temperature}$: Type B rectangular distribution
Value: 1
Halfwidth of Limits: 0.1

A number if studies on the effect of temperature on metal release from ceramic ware have been undertaken. The temperature effect is substantial, and a near-exponential increase in metal release with temperature is observed until limiting values are reached. Nevertheless, only one study gives information for the temperature range 20-25°C. The metal release approximately linear wit temperature in this temperature range, with a gradient of approximately 5% $°C^{-1}$. For the ±2°C range allowed by the empirical method, this leads to a factor $f_{temperature}$ of 1 ± 0.1. A rectangular distribution is assumed for this factor.

Interim Results:

Quantity	Value	Standard Uncertainty
V_L	0.330340 L	$1.821 \cdot 10^{-3}$ L
a_V	2.37000 dm^2	0.06428 dm^2

Uncertainty Budgets:

r: **Mass of cadmium leached per unit area**

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
V_L	0.330340 L	$1.821 \cdot 10^{-3}$ L				
$V_{L\ nominal}$	0.332 L					
$f_{VL\text{-}filling}$	0.995000	$2.041 \cdot 10^{-3}$	triangular	0.036	$74 \cdot 10^{-6}$ mg/dm^2	0.0 %
$f_{VL\text{-}temperature}$	1.0000000	$242.5 \cdot 10^{-6}$	rectangular	0.036	$8.8 \cdot 10^{-6}$ mg/dm^2	0.0 %
$f_{VL\text{-}reading}$	1.000000	$4.082 \cdot 10^{-3}$	triangular	0.036	$150 \cdot 10^{-6}$ mg/dm^2	0.2 %
$f_{VL\text{-}calibration}$	1.000000	$3.074 \cdot 10^{-3}$	triangular	0.036	$110 \cdot 10^{-6}$ mg/dm^2	0.1 %
a_V	2.37000 dm^2	0.06428 dm^2				
$a_{V\ nominal}$	2.37 dm^2					
$f_{aV\text{-}length1}$	1.000000	$6.897 \cdot 10^{-3}$	normal	-0.036	$-250 \cdot 10^{-6}$ mg/dm^2	0.5 %
$f_{aV\text{-}lenght2}$	1.000000	$6.098 \cdot 10^{-3}$	normal	-0.036	$-220 \cdot 10^{-6}$ mg/dm^2	0.4 %
$f_{aV\text{-}area}$	1.00000	0.02551	normal	-0.036	$-930 \cdot 10^{-6}$ mg/dm^2	7.3 %
c_0	0.26000 mg/L	0.01800 mg/L	normal	0.14	$2.5 \cdot 10^{-3}$ mg/dm^2	53.9 %
d	1.0	0.0	normal	0.0	0.0 mg/dm^2	0.0 %
f_{acid}	1.0000000	$800.0 \cdot 10^{-6}$	normal	0.036	$29 \cdot 10^{-6}$ mg/dm^2	0.0 %
f_{time}	1.0000000	$866.0 \cdot 10^{-6}$	rectangular	0.036	$31 \cdot 10^{-6}$ mg/dm^2	0.0 %
$f_{temperature}$	1.00000	0.05774	rectangular	0.036	$2.1 \cdot 10^{-3}$ mg/dm^2	37.5 %
r	0.036240 mg/dm^2	$3.418 \cdot 10^{-3}$ mg/dm^2				

Results:

Quantity	Value	Expanded Uncertainty	Coverage factor	Coverage
r	0.0362 mg/dm^2	6.8·10^{-3} mg/dm^2	2.00	95% (t-table 95.45%)