Uncertainty Calculation in Analytical Chemistry

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Introduction

- **A Few Definitions**
- **Procedure in Measurement Uncertainty Estimation**
- **Example of Uncertainty Estimation in the Using of External Calibration Curve**
- **Conclusion**

Definitions (ISO/BIPM Guide)

1. Measurand

"Particular quantity subject to a measurement" or "the result of a measurement."

2. Uncertainty

"A parameter, associated with the result of a measurement, that characterises the dispersion of the values that could reasonable be attributed to the measurand."

The number after the "

3. Standard Uncertainty -- u_{x_i}

"Uncertainty of the result x_i of a measurement expressed as a standard deviation."

Definitions (ISO/BIPM Guide)

4. Combined Standard Uncertainty -- u_c(y)

"Standard uncertainty of the result y of a measurement when the result is obtained from the values of a number of other quantities."

$$u_c^{\,2}(y) = \sum_{i=1}^{N}\left(\frac{\partial f}{\partial x_i}\right)^2 u^2(x_i) + 2\cdot\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\left(\frac{\partial f}{\partial x_i}\right)\cdot\left(\frac{\partial f}{\partial x_j}\right)\cdot u(x_i, x_j)$$

Where y = $f(x_1, x_2, \ldots, x_N)$ and is conveniently referred to as *the law of propagation of uncertainty*. The partial derivatives $\partial f/\partial x_i$ are often referred to as *sensitivity coefficients*, $u(x_i)$ is the standard uncertainty associated with the input x_i, and $u(x_i, x_j)$ is the estimated covariance associated with x_i and x_j.

$$u_c^{\,2}(y) = \sum_{i=1}^{N}\left(\frac{\partial f}{\partial x_i}\right)^2 u^2(x_i) + 2\cdot\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\left(\frac{\partial f}{\partial x_i}\right)\cdot\left(\frac{\partial f}{\partial x_j}\right)\cdot u(x_i)\cdot u(x_j)\cdot r_{(i,j)}$$

$r_{(i,j)}$ is correlation coefficient, $-1 \leq r_{(i,j)} \leq 1$.

$$u_c(y)^2 = \sum_{i=1}^{N}\left(\frac{\partial f}{\partial x_i}\right)^2 u_{x_i}^{\,2}$$

When $x_1, x_2, \ldots, x_N$ are independent parameters.

Definitions (ISO/BIPM Guide)

5. Expanded Uncertainty -- *U*

"Quantity defining an interval about the result of a measurement that may be expected to encompass a large fraction of the distribution of values that could reasonably be attributed to the measurand."

U is obtained by multiplying u_c(y), the combined standard uncertainty, by a coverage factor k."

6. Coverage Factor-- *k*

"Numerical factor used as a multiplier of the combined standard uncertainty in order to obtain an expanded uncertainty."
k=2~3 (depends on the level of confidence desired)

Uncertainty Types

Type A

"Uncertainties are evaluated by the statistical analysis of a series of observations."

- **Calculating the standard deviation of the mean of a series of independent observations**

Absorbance: 0.500, 0.510, 0.490

A = 0.500 S_i = 0.010

$$u_A = \left(\frac{S_i}{\sqrt{n}}\right) = \left(\frac{0.01}{\sqrt{3}}\right) = 0.00577$$

Type B

"Uncertainties are evaluated by means other than the statistical analysis of a series of observations."

- **Manufacturer's specifications**
- **experience**

99.90±0.05 % (95% confidence interval) pure Cu

$$u_{purity} = \frac{0.0005}{1.960} = 0.000255$$

Procedure of Measurement Uncertainty Estimation

1. **Specify the Measurand**
   - **Write down complete equation**

2. **Identify all Uncertainty Sources**

3. **Quantify Uncertainty Components**
   - **Using Type A or Type B method to calculate individual standard uncertainty of all parameters**

4. **Calculate Combined Uncertainty**
   - **Using partial differential method**

$$u_c^{\,2}(y) = \sum_{i=1}^{N}\left(\frac{\partial f}{\partial x_i}\right)^2 u^2(x_i) + 2\cdot\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\left(\frac{\partial f}{\partial x_i}\right)\cdot\left(\frac{\partial f}{\partial x_j}\right)\cdot u(x_i, x_j)$$

   - **Using approximate numerical differentiation method**

$$u_c^{\,2}(y) \approx \sum\left(f(x_i + u(x_i)) - f(x_i)\right)^2 + 2\cdot\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\left(f(x_i + u(x_i)) - f(x_i)\right)$$
$$\cdot\left(f(x_j + u(x_j)) - f(x_j)\right)\cdot r_{(i,j)}$$

When y= *f*($x_1, x_2, \ldots, x_n$) is either linear in x_i or *u*(x_i) is small compared to x_i.

Procedure of Measurement Uncertainty Estimation

4. Calculate Combined Uncertainty

- **Using simple method**

$$\left(\frac{u_y}{y}\right)^2 = \left(\frac{u_a}{a}\right)^2 + \left(\frac{u_b}{b}\right)^2 + \left(\frac{u_c}{c}\right)^2 + \left(\frac{u_d}{d}\right)^2$$

When $y = k \cdot \frac{a \cdot b}{c \cdot d}$ **, where k is a constant, and a, b, c, d are independent parameters**.

$$(u_y)^2 = (k_a \cdot u_a)^2 + (k_b \cdot u_b)^2 + (k_c \cdot u_c)^2 + (k_d \cdot u_d)^2$$

When $y = k + k_a \cdot a - k_b \cdot b + k_c \cdot c - k_d \cdot d$ **, where k,** k_a**,** k_b**,** k_c**,** k_d **are constants, and a, b, c, d are independent parameters**.

5. Reporting Uncertainty

- **Expanded uncertainty   Result: mean " U**
- **Check reported uncertainty (re-evaluation?)**

Choices in Combined Uncertainty Calculation Methods

1. Partial Differential Method

$$u_c^{\,2}(y) = \sum_{i=1}^{N}\left(\frac{\partial f}{\partial x_i}\right)^2 u^2(x_i) + 2\cdot\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\left(\frac{\partial f}{\partial x_i}\right)\cdot\left(\frac{\partial f}{\partial x_j}\right)\cdot u(x_i, x_j)$$

- **Universal**
- **No limitation**

2. Approximate Numerical Differentiation Method

$$u_c^{\,2}(y) \approx \sum\left(f(x_i + u(x_i)) - f(x_i)\right)^2 + 2\cdot\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\left(f(x_i + u(x_i)) - f(x_i)\right)$$
$$\cdot\left(f(x_j + u(x_j)) - f(x_j)\right)\cdot r_{(i,j)}$$

- **Adequate in most practice**

Requirements:

- ***u*(x_i) <<x_i True in almost all situations**

  Or
- **y and x_i has linear relationship**

3. Simple Method

$$\left(\frac{u_y}{y}\right)^2 = \left(\frac{u_a}{a}\right)^2 + \left(\frac{u_b}{b}\right)^2 + \left(\frac{u_c}{c}\right)^2 + \left(\frac{u_d}{d}\right)^2$$ **When** $y = k\cdot\frac{a\cdot b}{c\cdot d}$.

$$(u_y)^2 = (k_a\cdot u_a)^2 + (k_b\cdot u_b)^2 + (k_c\cdot u_c)^2 + (k_d\cdot u_d)^2$$

When $y = k + k_a\cdot a - k_b\cdot b + k_c\cdot c - k_d\cdot d$ **, where k, k_a, k_b, k_c, k_d are constants and a, b, c, d are independent parameters.**

- **Adequate in some cases**

Requirements:

- **All parameters in measurement equation have to be independent**

Choices in Combined Uncertainty Calculation Methods

$$C = \frac{C_{spiked} \cdot A_{unspiked}}{(A_{spiked} - A_{unspiked})} - C_{blank}$$

Measurement equation

Parameter	Typical Value	u_{xi}
C_{spiked}, (ng/g)	100.0	0.0447
$A_{unspiked}$	0.500	0.0058
A_{spiked}	1.500	0.0115
C_{blank} (ng/g)	0.40	0.0577

- **Simple Method -- Not adequate**
  u_C **= 0.862 ng/g**

- **Approximate Numerical Differentiation Method -- OK**
  u_C **= 1.045 ng/g**

- **Partial Differential Method -- OK**
  u_C **= 1.045 ng/g**

Example 1 -- Lead determination in a tap water by AA using an external calibration curve

Parameter	Typical Value	A_i
C_{std1}, (ng/g)	10.00	0.100, 0.105, 0.095
C_{std2}, (ng/g)	50.00	0.500, 0.507, 0.490
C_{std3}, (ng/g)	100.0	1.000, 1.010, 0.990
$A_{sample1}$	0.500	0.500, 0.510, 0.490
$A_{sample2}$	0.505	0.505, 0.504, 0.506
$A_{sample3}$	0.495	0.498, 0.492, 0.495
C_{blank} (ng/g)	0.40, 0.30, 0.50	

E1.1 Step 1: Specify the Measurand

Aim of Step 1-describe the measurement procedure and write complete measurement equation

Preparation of 10.00, 50.00, 100.0 ng/g standards
↓
Determination
↓
Result

The measurand is the concentration of Pb in the tap water.

Equations:

$$A_i = a \cdot C_i + b$$

$$C_{sample} = \frac{A_{sample} - b}{a}$$ **Calibration equation**

$$C = \frac{A_{sample} - b}{a} - C_{blank}$$ **Measurement equation**

Example 1 - Lead determination in a tap water by AA using an external calibration

E1.2 Step 2: Identify all Uncertainty Sources

$u_{A_{sample}}$ **– Standard uncertainty of measured absorbance in sample (A_{sample})**

u_a **– Standard uncertainty of the slop of the external calibration curve**

u_b **– Standard uncertainty of the intercept of the external calibration curve**

$u_{C_{blank}}$ **– Standard uncertainty of concentration in sample blank (C_{blank})**

E1.3 Step 3: Quantify Uncertainty Components

E1.3.1 $u_{A_{sample}}$ Calculation

Parameter	Typical Value	A_i
C_{std1}, (ng/g)	10.00	0.100, 0.105, 0.095
C_{std2}, (ng/g)	50.00	0.500, 0.507, 0.490
C_{std3}, (ng/g)	100.0	1.000, 1.010, 0.990
$A_{sample1}$	0.500	0.500, 0.510, 0.490
$A_{sample2}$	0.505	0.505, 0.504, 0.506
$A_{sample3}$	0.495	0.498, 0.492, 0.495
C_{blank} (ng/g)	0.40, 0.30, 0.50	

A_{sample} = 0.500 **S_i = 0.01**

$$u_{A_{sample}} = \left(\frac{S_i}{\sqrt{n}}\right) = \left(\frac{0.01}{\sqrt{3}}\right) = 0.00577$$

Type A

E1.3 Step 3: Quantify Uncertainty Components

E1.3.2 and E1.3.3 u_a and u_b Calculation

Slope: a = 0.0100008 **Intercept: b = -0.000377**

u_a = 0.000068267 **u_b = 0.00442418 Type B**

A_i	C_i (ppb)
0.100	10.00
0.105	10.00
0.095	10.00
0.500	50.00
0.507	50.00
0.490	50.00
1.000	100.0
1.010	100.0
0.990	100.0

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.999836955
R Square	0.999673937
Adjusted R Square	0.999627357
Standard Error	0.00754029
Observations	9

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	1.220200008	1.2202	21461.2462	1.82197E-13
Residual	7	0.000397992	5.7E-05		
Total	8	1.220598			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*
Intercept	-0.000377049	0.00442418	-0.0852	0.93446912	-0.010838565
X Variable 1	0.0100008	6.82666E-05	146.497	1.822E-13	0.009839395

E1.3 Step 3: Quantify Uncertainty Components

E1.3.4 $u_{c_{blank}}$ Calculation

Parameter	Typical Value	A_i
C_{std1}, (ng/g)	10.00	0.100, 0.105, 0.095
C_{std2}, (ng/g)	50.00	0.500, 0.507, 0.490
C_{std3}, (ng/g)	100.0	1.000, 1.010, 0.990
$A_{sample1}$	0.500	0.500, 0.510, 0.490
$A_{sample2}$	0.505	0.505, 0.504, 0.506
$A_{sample3}$	0.495	0.498, 0.492, 0.495
C_{blank} (ng/g)	0.40, 0.30, 0.50	

C_{blank} = 0.40 ng/g **S_i = 0.10 ng/g**

$$u_{C_{blank}} = \left(\frac{S_i}{\sqrt{n}}\right) = \left(\frac{0.1}{\sqrt{3}}\right) = 0.0577 \ ng/g$$ **Type A**

E1.4 Step 4: Calculate Combined Uncertainty
Approximate Numerical Differentiation Method – OK

$$u_c^{\,2}(y) \approx \sum \big(f(x_i + u(x_i)) - f(x_i) \big)^2 + 2 \cdot \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \big(f(x_i + u(x_i)) - f(x_i) \big) \cdot \big(f(x_j + u(x_j)) - f(x_j) \big) \cdot r_{(i,j)}$$

$$C = \frac{A_{sample} - b}{a} - C_{blank}$$ **Measurement equation**

$$u_c^{\,2}(y) \approx \sum \big(f(x_i + u(x_i)) - f(x_i) \big)^2 + 2 \cdot \big(f(a + u(a)) - f(a) \big) \cdot \big(f(b + u(b)) - f(b) \big) \cdot r_{(a,b)}$$

$$r_{(a,b)} = \frac{-\overline{C}_{std} \cdot u_a}{u_b} = \frac{-53.333 \cdot 0.0000683}{0.004424} = -0.8230$$

Example 1 -- Lead determination in a tap water by AA using an external calibration curve

- **Approximate Numerical Differentiation Method – OK**

$$C = \frac{A_{sample} - b}{a} - C_{blank}$$

Measurement equation

Parameter	Typical value	u_i	$A_{sample} + u_{Asample}$	$a + u_a$	$b + u_b$	$C_{blank} + u_{Cblank}$
A_{sample}	0.500	0.00577	0.50577	0.500	0.500	0.500
a	0.01000082	0.0000683	0.01000082	0.0100691	0.01000082	0.010000820
b	-0.000377	0.004424	-0.000377	-0.000377	0.00405	-0.000377
C_{blank}	0.40	0.0577	0.40	0.40	0.40	0.4577

r	-0.8230					
C	49.63	$f(x_i)=$	49.63	49.63	49.63	49.63
		$f(x_i+u_i)=$	50.21	49.29	49.19	49.58
		$(\partial f/\partial x_i)\, u_{xi} = f(x_i+u_i) - f(x_i) =$	0.57695	-0.33922	-0.44238	-0.05770
		$(f(a+u_a)-f(a)),\ (f(b+u_b)-f(b)) =$		-0.33922	-0.44238	
		$(f(x_i+u_i)-f(x_i))^2 =$	0.33287	0.11507	0.19570	0.00333

$u_C^2 = \mathrm{Sum}(f(x_i+u_i)-f(x_i))^2 + 2\,(f(a+u_a)-f(a))(f(b+u_b)-f(b))\, r_{(a,b)} = 0.39998$

$u_C = 0.632$

$$u_C = 0.632 \ \textbf{ng/g}$$

E1.5 Step 5: Reporting Results

Example 1 -- Lead determination in a tap water by AA using An External Calibration

Table 1. Summary of Results for Pb in Tap Water.

Elements	Pb
Recommended value, ng/g	49.6
Combined uncertainty, u_c	0.632
Coverage factor, k	2
Expanded uncertainty, ng/g	1.3
Average, ng/g	49.6
Standard deviation (n=3), S_i	0.50

Table 2. Components of Uncertainty for Pb in Tap Water

Parameter	Typical value	Type A/B	u_{xi}	$c_i = \partial f/\partial x_i$	$c_i\, u_{xi}$
A_{sample}	0.500	A	0.00577	99.99	0.57695
a	0.0100008	B	0.00006826	-4969.1	-0.33922
b	-0.000377	B	0.004424	-99.99	-0.44238
C_{blank} (ng/g)	0.40	A	0.0577	-1	-0.0577
Combined uncertainty (ng/g) u_c					0.650

Conclusion

- **Analysts need to make careful choices to ensure the proper estimation of uncertainty associated with a measurand**

- **Approximate Numerical Differentiation Method for Combined Uncertainty Calculation**

$$u_c^{2}(y) \approx \sum \left(f(x_i + u(x_i)) - f(x_i) \right)^2 + 2 \cdot \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \left(f(x_i + u(x_i)) - f(x_i) \right) \cdot \left(f(x_j + u(x_j)) - f(x_j) \right) \cdot r_{(i,j)}$$

  - **Adequate in almost all cases under conditions of *u*(x_i) <<x_i Or y and x_i has linear relationship**

  - **Sensitivity coefficient of each parameter can be estimated**

$$c_i = \frac{\partial f}{\partial x_i} \approx \frac{f(x_i + u(x_i)) - f(x_i)}{u(x_i)}$$