Procedure for evaluating Uncertainty according to the GUM

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Motivation (1)

***International Vocabulary of Basic and General Terms in Metrology* (VIM), 3rd Edition**

2.24

(6.10)

metrological traceability

property of a measurement result relating the result to a stated metrological reference through an unbroken chain of calibrations of a measuring system or comparisons, **each contributing to the stated measurement uncertainty**

Motivation (2)

When reporting the result of a measurement of a physical quantity, it is obligatory that some **quantitative indication of the quality of the result** be given so that those who use it can assess its reliability. Without such an indication, measurement results cannot be compared, either among themselves or with reference values given in a specification or standard.

uncertainty (of measurement)

parameter, associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measurand [2]

Guide to the Expression of Uncertainty in Measurement, ISO, 1993

GUM

„History“

- 1978 CIPM asks BIPM to compile recommendations for uncertainty calculations
- 1979 feedback from 21 NMIs
- 1980 WG presents INC-1
- CIPM asks ISO to develop an uncertainty guide with the collaboration of BIPM, ISO, IEC, IFCC, IUPAC, IUPAP, OIML
- 1993 „**G**uide to the expression of **u**ncertainty in **m**easurement (GUM)“
- 1995 „Leitfaden zur Angabe der Unsicherheit beim Messen“ (seit 1999 DIN V ENV 13005)
- 1995 EURACHEM/CITAC-Guide „**Q**uantifying **u**ncertainty in **a**nalytical **m**easurement“ (QUAM)

Procedure („recipe“)

(1) Formulate the model of measurement $Y = f(X_1, X_2, \ldots X_i, \ldots X_N)$

(2) Determine the estimates x_i of the input quantity X_i and their associated standard uncertainties $u(x_i)$

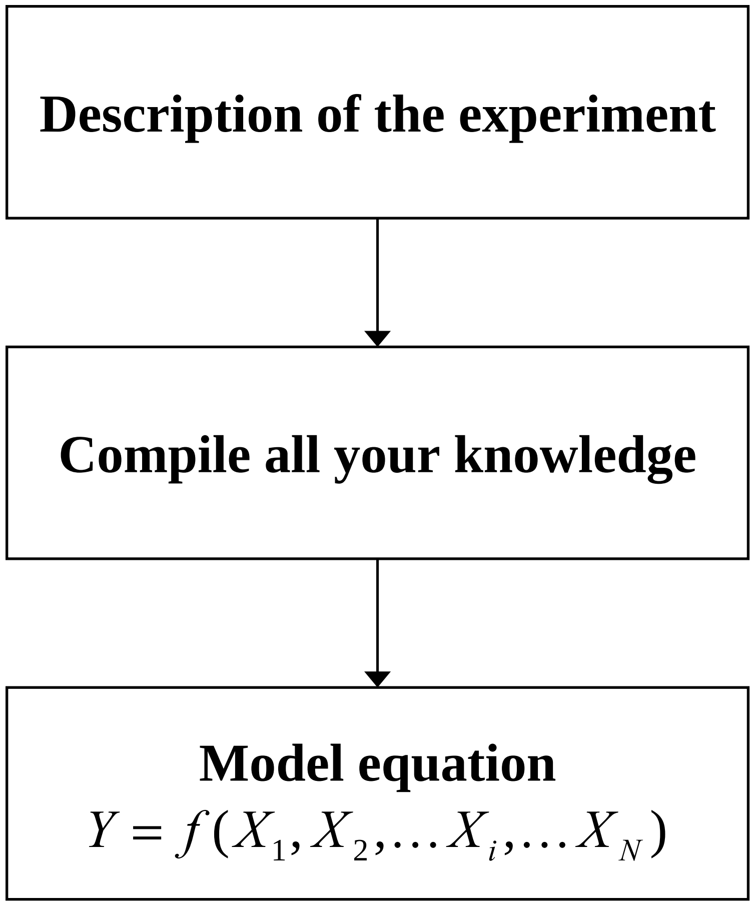
(3) Determine the estimate y of the measurand Y

(4) Calculate the combined standard uncertainty $u_c(y)$

(5) Calculate the expanded uncertainty U

(6) Report the result and its uncertainty $Y = y \pm U$

1) Model equation



2) Determination of x_i and $u(x_i)$

Best estimate x_i **of the input quantity** X_i

$$x_i = \mathrm{E}\left[X_i\right] = \int_{-\infty}^{+\infty} g(\xi_i)\xi_i \, d\xi_i$$

Associated standard uncertainty $u(x_i)$ **of the input quantity** X_i

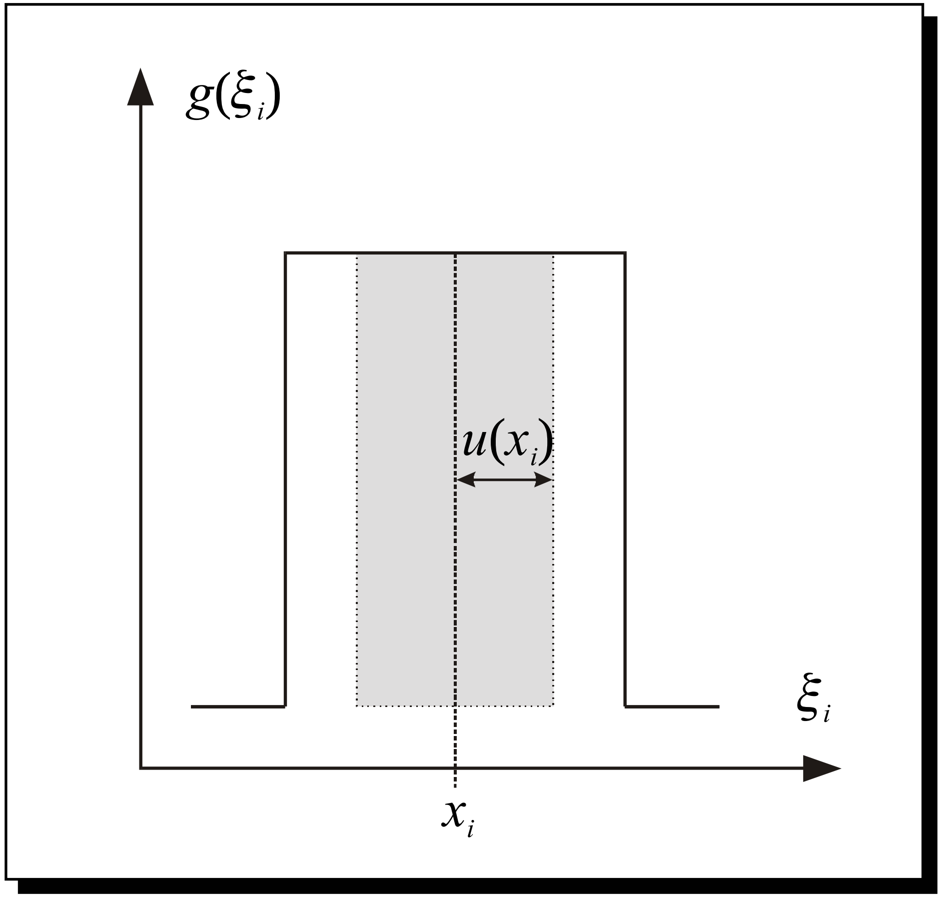
$$u^2(x_i) = \mathrm{E}\left\{\left(X_i - \mathrm{E}\left[X_i\right]\right)^2\right\} = \mathrm{E}\left[\left(X_i - x_i\right)^2\right]$$

$$= \int_{-\infty}^{+\infty} g(\xi_i)\left(\xi_i - x_i\right)^2 d\xi_i = \mathrm{VAR}\left[X_i\right]$$

$$x_i = \mathrm{E}\left[X_i\right] \qquad u(x_i) = \left(\mathrm{VAR}\left[X_i\right]\right)^{1/2}$$

2) Determination of x_i and $u(x_i)$ - supplement

Probability density function (pdf)



2.1) Type A evaluation

Evaluation of repeated observations
(statistical knowledge)

- n observation of the measurand q used to determine the input quantity x_i
- arithmetic average is the best estimate of the input quantity
- experimental standard deviation of the mean is the standard uncertainty

$$s(q_k) = \sqrt{\frac{1}{n-1}\sum_{k=1}^{n}(q_k - \overline{q})^2} \qquad s(\overline{q}) = \frac{1}{\sqrt{n}} s(q_k)$$

$$x_i = \overline{q} = \frac{1}{n}\sum_{k=1}^{n} q_k \qquad u(x_i) = s(\overline{q}) = \sqrt{\frac{1}{n(n-1)}\sum_{k=1}^{n}(q_k - \overline{q})^2}$$

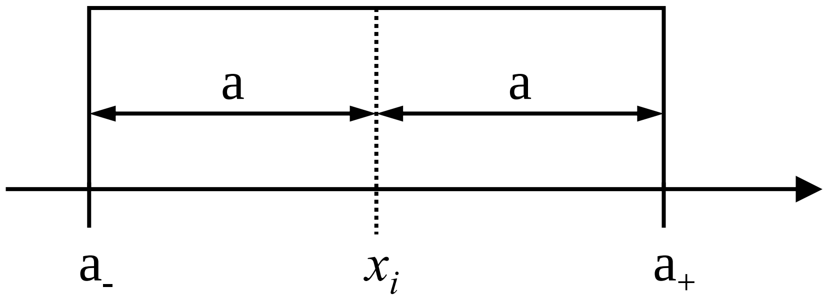
2.2) Type B evaluation

Information, not derived from repeated observations (non-statistical knowledge)

- previous measurement data
- manufacturer’s specifications
- data provided in calibration and other certificates
- uncertainties assigned to reference data taken from handbooks
- experience with (or general knowledge of) the behavior and properties of relevant materials and instruments

2.2) Type B evaluation – example 1

Trace impuritiy in a reference material that can not be determined (rectangular pdf, upper/lower limit)



$$x_i = \frac{a_+ + a_-}{2} \qquad u(x_i) = \frac{a}{\sqrt{3}} = \frac{a_+ - a_-}{2\sqrt{3}}$$

Derivation of the rectangular pdf (I)

Probability density function (pdf) *f*(*x*)

$$\int_{-\infty}^{+\infty} f(x)\,dx \equiv 1$$

$$\int_{-\infty}^{+\infty} f(x)\,dx = \underbrace{\int_{-\infty}^{a_-} f(x)\,dx}_{=0} + \int_{a_-}^{a_+} f(x)\,dx + \underbrace{\int_{a_+}^{+\infty} f(x)\,dx}_{=0}$$

$$f(x) = \frac{1}{a_+ - a_-}$$

$$\int_{a_-}^{a_+} f(x)\,dx = \int_{a_-}^{a_+} \frac{1}{a_+ - a_-}\,dx = \frac{1}{a_+ - a_-}\int_{a_-}^{a_+} dx$$

$$\int_{a_-}^{a_+} f(x)\,dx = \frac{1}{a_+ - a_-}\left[x\right]_{a_-}^{a_+} = \frac{1}{a_+ - a_-}\left(a_+ - a_-\right) = 1 \quad \text{q.e.d.}$$

Derivation of the rectangular pdf (II)

Expectation (best estimate of the input quantity) x_i

$$\mathrm{E}(X) = \int_{-\infty}^{+\infty} x\, f(x)\, dx = \int_{a_-}^{a_+} x\, f(x)\, dx$$

$$= \int_{a_-}^{a_+} x \frac{1}{a_+ - a_-} dx = \frac{1}{a_+ - a_-} \int_{a_-}^{a_+} x\, dx$$

$$= \frac{1}{a_+ - a_-} \left[\frac{1}{2} \cdot x^2 \right]_{a_-}^{a_+} = \frac{1}{2} \cdot \frac{1}{a_+ - a_-} \cdot \left(a_+^2 - a_-^2 \right)$$

$$= \frac{1}{2} \cdot \frac{1}{a_+ - a_-} \cdot \left(a_+ + a_- \right) \cdot \left(a_+ - a_- \right)$$

$$x_i = \mathrm{E}(X) = \frac{a_+ + a_-}{2}$$

Derivation of the rectangular pdf (III)

standard uncertainty *u*(*x_i*)

$$u^2(x) = \int_{-\infty}^{+\infty} (x - \mathrm{E}[X])^2 f(x)dx = \mathrm{E}\left\{(X - \mathrm{E}[X])^2\right\} = \mathrm{E}\left[X^2\right] - (\mathrm{E}[X])^2$$

$$= \left(\int_{a_-}^{a_+} x^2 f(x)dx\right) - \left(\frac{a_+ + a_-}{2}\right)^2 = \frac{1}{a_+ - a_-} \cdot \left[\frac{1}{3} \cdot x^3\right]_{a_-}^{a_+} - \frac{1}{4} \cdot \left(a_+^2 + 2a_+a_- + a_-^2\right)$$

$$= \frac{1}{a_+ - a_-} \cdot \frac{1}{3} \cdot \left(a_+^3 - a_-^3\right) - \frac{1}{4} \cdot \left(a_+^2 + 2a_+a_- + a_-^2\right)$$

$$= \frac{4a_+^3 - 4a_-^3 - 3 \cdot \left(a_+^2 + 2a_+a_- + a_-^2\right) \cdot (a_+ - a_-)}{12 \cdot (a_+ - a_-)} = \frac{a_+^3 - 3a_+^2a_- + 3a_+a_-^2 - a_-^3}{12 \cdot (a_+ - a_-)} = \frac{(a_+ - a_-)^3}{12 \cdot (a_+ - a_-)}$$

$$u^2(x) = \frac{(a_+ - a_-)^2}{12} = \frac{(a_+ - a_-)^2}{3 \cdot 4} = \frac{a^2}{3} \qquad \text{mit} \quad a = \frac{a_+ - a_-}{2}$$

$$u(x_i) = \frac{a}{\sqrt{3}}$$

2.2) Type B evaluation – example 2

Data provided in a manufacturer's certificate

This Standard Reference Material (SRM) is certified as a chemical of known purity. It is intended primarily for use in the calibration and standardization of procedures for potassium (K) and chloride (Cl) determinations employed in clinical analysis and for routine critical evaluation of the daily working standards used in these procedures. SRM 918a is supplied in crystallinc form as a 30 g unit.

Certified Purity

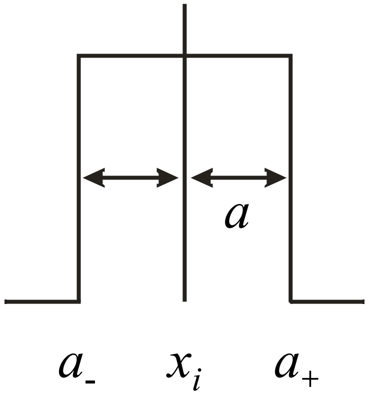
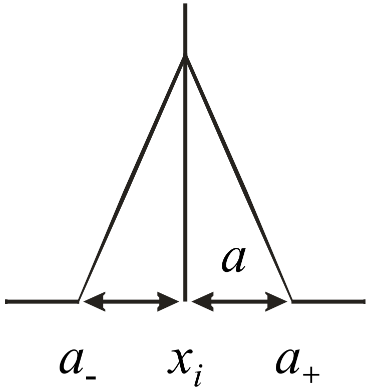
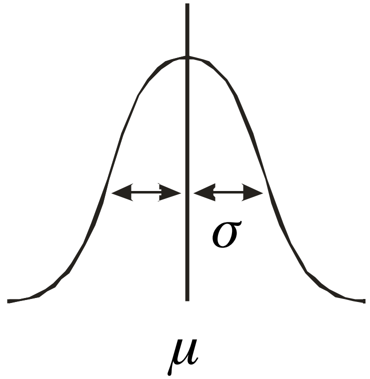
Potassium Chloride, mass fraction	99.9817 (±0.0084) %
Potassium, mass fraction	52.4354 (±0.0044) %
Chloride, mass fraction	47.5463 (± 0.0040) %

This certified purity is based on the results of independent coulometric assays as described in this Certificate of Analysis. Each uncertainty interval represents the expanded uncertainty, U, calculated according to the ISO Guide [1] with a coverage factor of 2 and represents the 95% level of confidence. The percent K and percent Cl are calculated by multiplying the KCL assay by the mass relationship (gravimetric factors for K to KCL and Cl to KCL). The factors are

$$x_i = y \qquad u(x_i) = \frac{U}{k}$$

2.3) Type B evaluation

most common pdfs

	rectangular	triangular	normal
pdf			
$\boldsymbol{x_i}$	$(a_+ + a_-)/2$	$(a_+ + a_-)/2$	μ
$\boldsymbol{u(x_i)}$	$a/\sqrt{3}$	$a/\sqrt{6}$	σ

2) Evaluation methods - remark

Random error **= Type A-uncertainty?**

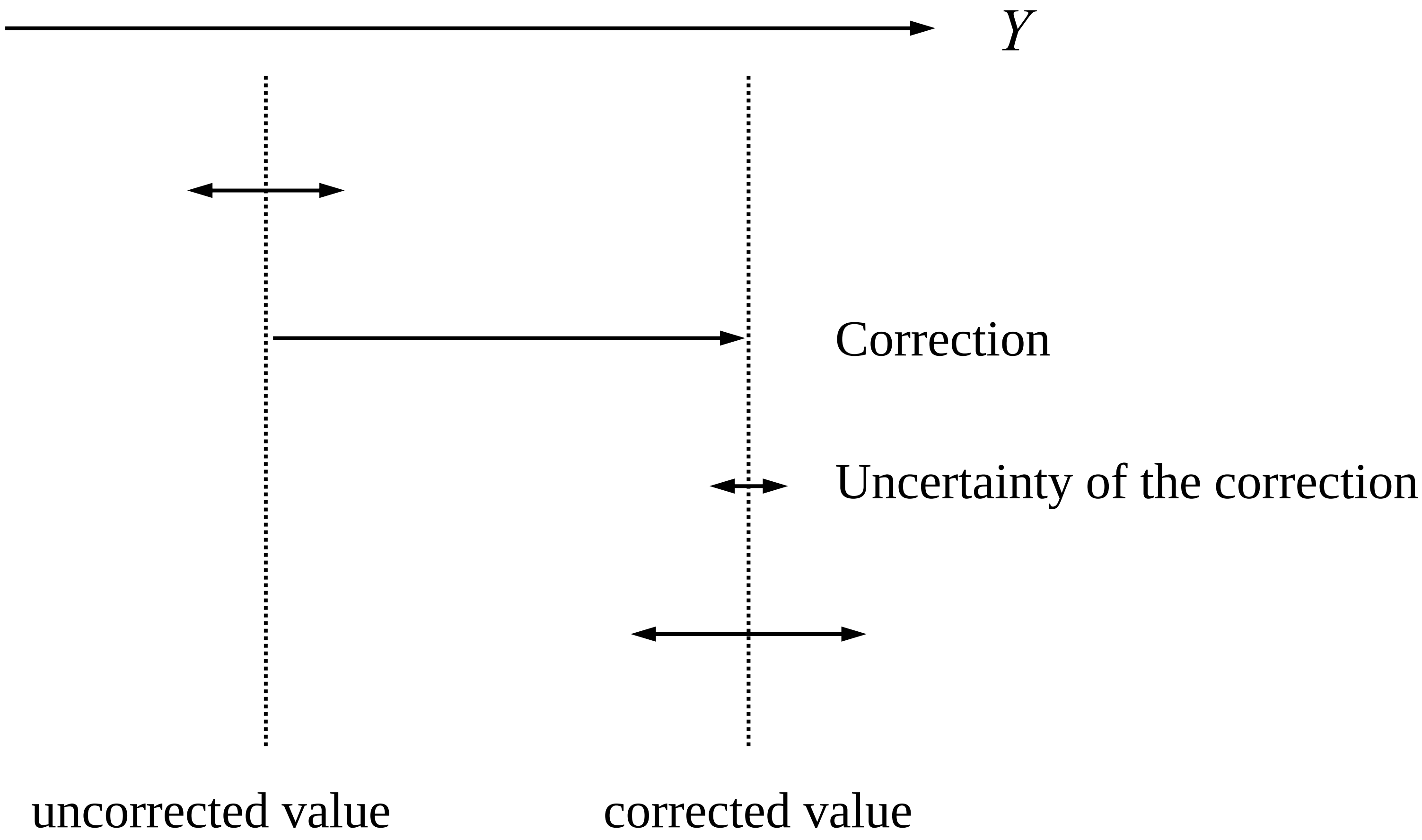
Systematic error **= Type B-uncertainty?**

NO!!!

Examples:

- Blank
- Recovery
- Moisture correction

2) Evaluation methods – remark (2)



3) Best estimate *y* of the measurand *Y*

in general

$$y = \mathrm{E}[Y]$$

$$y = \int_{-\infty}^{+\infty} h(\eta)\,\eta\, d\eta$$

(sufficiently) linear model equation

$$y = f(x_1, x_2, x_3, \dots x_N)$$

$$x_1 = \mathrm{E}[X_1] \quad x_2 = \mathrm{E}[X_2] \quad x_3 = \mathrm{E}[X_3] \quad \dots \quad x_N = \mathrm{E}[X_N]$$

non-linear model equation

$$y = \frac{1}{n}\sum_{k=1}^{n} Y_k = \frac{1}{n}\sum_{k=1}^{n} f(X_{1,k}, X_{2,k}, X_{3,k}, \dots X_{N,k})$$

$$y = f(x_1, x_2, x_3, \dots x_N)$$

4) Combined standard uncertainty (I)

Calculation of the combined standard uncertainty $u_c(y)$ associated with the measurand Y (uncertainty propagation)

- in general

$$u_c^2(y) = \int_{-\infty}^{+\infty} h(\eta)(\eta - y)^2 \, d\eta$$

- (sufficiently) linear model equation

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

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

- uncorrelated input quantities

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

4) Combined standard uncertainty (II)

Definitions

- Sensitivity coefficient c_i

$$c_i \equiv \frac{\partial f}{\partial x_i} = \left.\frac{\partial f}{\partial X_i}\right|_{X_1=x_1, X_2=x_2, \ldots X_N=x_N}$$

- Component $u_i(y)$ of combined standard uncertainty generated by x_i

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

$$u_c^2(y) = \sum_{i=1}^{N} \left[c_i\, u(x_i)\right]^2 \equiv \sum_{i=1}^{N} u_i^2(y)$$

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

4) Combined standard uncertainty (III)

Basic model equations

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

Additive model	$Y = X_1 \pm X_2$ $\Rightarrow \quad u_\mathrm{C}(y) = \sqrt{u^2(x_1) + u^2(x_2)}$
Multiplicative model	$Y = X_1 \cdot X_2^{\pm 1}$ $\Rightarrow \quad \frac{u_\mathrm{C}(y)}{y} = \sqrt{\frac{u^2(x_1)}{x_1^2} + \frac{u^2(x_2)}{x_2^2}}$

4) Combined standard uncertainty (IV)

Derivation of the simplification of the additive model

$$Y = f\left(X_1, X_2\right) = X_1 \pm X_2$$

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

$$\frac{\partial f}{\partial x_1} = \frac{\partial}{\partial x_1}\left(x_1 \pm x_2\right) = 1 \qquad \frac{\partial f}{\partial x_2} = \frac{\partial}{\partial x_2}\left(x_1 \pm x_2\right) = \pm 1$$

$$u_\mathrm{c}^2(y) = \left(\frac{\partial f}{\partial x_1}\right)^2 u^2\left(x_1\right) + \left(\frac{\partial f}{\partial x_2}\right)^2 u^2\left(x_2\right)$$

$$u_\mathrm{c}^2(y) = (1)^2 u^2\left(x_1\right) + (\pm 1)^2 u^2\left(x_2\right) = u^2\left(x_1\right) + u^2\left(x_2\right)$$

$$u_\mathrm{c}(y) = \sqrt{u^2\left(x_1\right) + u^2\left(x_2\right)} \quad \text{für} \quad Y = X_1 \pm X_2$$

4) Combined standard uncertainty (V)

Derivation of the simplification of the multiplicative model (1)

$$Y = f\left(X_1, X_2\right) = X_1 \cdot X_2^{\pm 1}$$

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

$$\frac{\partial f}{\partial x_1} = \frac{\partial}{\partial x_1}\left(x_1 \cdot x_2^{\pm 1}\right) = 1 \cdot x_2^{\pm 1} \qquad \frac{\partial f}{\partial x_2} = \frac{\partial}{\partial x_2}\left(x_1 \cdot x_2^{\pm 1}\right) = \begin{cases} x_1 \cdot 1 \\ x_1 \cdot (-1) x_2^{-2} \end{cases}$$

$$u_c^2(y) = \left(\frac{\partial f}{\partial x_1} \right)^2 u^2\left(x_1\right) + \left(\frac{\partial f}{\partial x_2} \right)^2 u^2\left(x_2\right) = \begin{cases} \left(x_2\right)^2 u^2\left(x_1\right) + \left(x_1\right)^2 u^2\left(x_2\right) \\ \left(x_2^{-1}\right)^2 u^2\left(x_1\right) + \left(- x_1 \cdot x_2^{-2}\right)^2 u^2\left(x_2\right) \end{cases}$$

$$u_c^2(y) = \begin{cases} x_2^2 u^2\left(x_1\right) + x_1^2 u^2\left(x_2\right) \\ x_2^{-2} u^2\left(x_1\right) + x_1^2 x_2^{-4} u^2\left(x_2\right) \end{cases}$$

4) Combined standard uncertainty (VI)

Derivation of the simplification of the multiplicative model (2)

$$y = \begin{cases} x_1 \cdot x_2 & \Rightarrow \quad x_2^2 = y^2 / x_1^2 \quad \text{und} \quad x_1^2 = y^2 / x_2^2 \\ x_1 / x_2 & \Rightarrow \quad 1/x_2^2 = y^2 / x_1^2 \quad \text{und} \quad x_1^2 / x_2^4 = x_1^2 / x_2^2 \cdot 1/x_2^2 = y^2 / x_2^2 \end{cases}$$

$$u_c^2(y) = \begin{cases} x_2^2 u^2(x_1) + x_1^2 u^2(x_2) \\ x_2^{-2} u^2(x_1) + x_1^2 x_2^{-4} u^2(x_2) \end{cases}$$

$$u_c^2(y) = \frac{y^2}{x_1^2} u^2(x_1) + \frac{y^2}{x_2^2} u^2(x_2) \quad \Rightarrow \quad \frac{u_c^2(y)}{y^2} = \frac{u^2(x_1)}{x_1^2} + \frac{u^2(x_2)}{x_2^2}$$

$$\frac{u_c(y)}{y} = \sqrt{\frac{u^2(x_1)}{x_1^2} + \frac{u^2(x_2)}{x_2^2}} \quad \text{für} \quad Y = X_1 \cdot X_2^{\pm 1}$$

5) Calculation of the expanded uncertainty *U*

Coverage factor *k*

$$k = k(p) = t_p(\nu_{\text{eff}})$$

Effective degrees of freedom ν_{eff} (Welch-Satterthwaite)

$$\nu_{\text{eff}} = \frac{u_c^4(y)}{\sum_{i=1}^{N} \frac{u_i^4(y)}{\nu_i}} = \frac{u_c^4(y)}{\sum_{i=1}^{N} \frac{\left[\frac{\partial f}{\partial x_i} u(x_i)\right]^4}{\nu_i}}$$

Expanded uncertainty *U*

$$U = k \cdot u_c(y) \qquad k = 2 \quad \text{with} \quad p = 0.95 \text{ and } \nu_{\text{eff}} \geq 50$$

6) Reporting uncertainty (I)

Uncertainty budget (in table form)

- Definition of the measurand Y (model equation)
- Uncertainty components (input quantities X_i)
- Knowledge about input quantities (source,… ν_i,…pdf)
- Estimates x_i of the input quantities and their associated standard uncertainties $u(x_i)$
- Sensitivity coefficients c_i
- Components of the combined standard uncertainty $u_i(y)$
- Combined standard uncertainty $u_\mathrm{c}(y)$
- Effective degree of freedom ν_eff
- Coverage factor k and level of confidence p

6) Reporting uncertainty (II)

Supplemental

- Methods used to calculate the result and its uncertainty arising from observations and other contributions
- Documentation of the evaluation
- Comprehensive calculations
- References to all sources, corrections, constants, ….

Result of the measurement

$$Y = y \pm U$$

6) Reporting uncertainty (III)

Rounding

- Expanded uncertainty two significant digits
- Round result (estimate of the measurand) accordingly
- For intermediate results a larger number of digits is reasonable

Example

$$w(\mathrm{Pb}) = (0.0275 \pm 0.0013)\,\mu\mathrm{g/g}$$

$$w(\mathrm{Pb}) = 0.0275\,\mu\mathrm{g/g} \pm 0.0013\,\mu\mathrm{g/g}$$

References

(1) Guide to the expression of uncertainty in measurement. International Organization for Standardization, 1995, ISBN 92-67-10188-9.

(2) DIN V ENV 13005. Leitfaden zur Angabe der Unsicherheit beim Messen. 1999.

(3) EURACHEM/CITAC Guide. Quantifying uncertainty in analytical measurement. http://www.measurementuncertainty.org/mu/QUAM2000-1.pdf

(4) EURACHEM/CITAC Leitfaden. Ermittlung der Messunsicherheit bei analytischen Messungen.2004. http://www.eurolabd.bam.de/eurachem_dokumente/Ermittlung%20der%20Messunsicherheit%20bei%20analytischen%20Messungen,.pdf

(5) P. de Bievre, H. Günzler. Measurement Uncertainty in Chemical Analysis. Springer. ISBN 3-540-43990-0. 2003.

(6) K. Weise, W. Wöger. Meßunsicherheit und Meßdatenauswertung. Wiley-VCH. 1999.

(7) http://www.analytik-news.de/Links/Qualitaetskontrolle/Messunsicherheit.html

(8) B.R.L. Siebert, K.-D. Sommer. Weiterentwicklung des GUM und Monte-Carlo-Techniken. Technisches Messen 71 (2004) 2.

(9) Oto Mestek et al. Computer simulation of the uncertainty of analytical results. Fresenius J Anal Chem (1999) 364:203-207.

Definitions, terms (selection)

Zeichen	deutsche Bezeichnung	englische Bezeichnung
Y	Meßgröße, Ausgangsgröße	measurand
y	Ausgangsschätzwert, Meßergebnis	result of a measurement, output estimate
X_i	i-te Eingangsgröße	ith input quantity on which measurand Y depends
x_i	Schätzwert der i-ten Eingangsgröße	estimate of input quantity X_i
f	Funktionsbeziehung zwischen Y und X_i	functional relationship between Y and X_i
N	Anzahl der Eingangsgrößen	number of input quantities
n	Anzahl der Beobachtungen	number of repeated observations
$u(x_i)$	Standardunsicherheit von x_i	standard uncertainty of input estimate x_i
$u^2(x_i)$	geschätzte Varianz von x_i	estimated variance associated with input estimate x_i
$u(x_i, x_j)$	geschätzte Kovarianz von x_i und x_j	estimated covariance associated with x_i and x_j
$r(x_i, x_j)$	geschätzter Korrelationskoeffizient von x_i und x_j	estimated correlation coefficient associated with x_i and x_j
q	zufällig schwankende Größe	randomly varying quantity
$u_c(y)$	kombinierte Standardunsicherheit von y	combined standard uncertainty associated with y
$u_c^2(y)$	kombinierte Varianz von y	combined variance associated with output estimate y
$u_i(y)$	Komponente von $u_c(y)$	component of combined standard uncertainty $u_c(y)$
c_i	Empfindlichkeitskoeffizient, partielle Ableitung	sensitivity coefficient, partial derivative
p	Grad des Vertrauens, Wahrscheinlichkeit	level of confidence, probability
k	Erweiterungsfaktor	coverage factor
U	erweiterte Unsicherheit von y	expanded uncertainty of output estimate y
$s(q_k)$	empirische Standardabweichung	experimental standard deviation
$s(\bar{q})$	empirische Standardabweichung des Mittelwertes	experimental standard deviation of the mean

Summary „GUM-procedure“

(1) Formulate the model of measurement $Y = f(X_1, X_2, \ldots X_i, \ldots X_N)$

(2) Determine the estimates x_i of the input quantity X_i and their associated standard uncertainties $u(x_i)$

(3) Determine the estimate y of the measurand Y

(4) Calculate the combined standard uncertainty $u_{\mathrm{c}}(y)$

(5) Calculate the expanded uncertainty U

(6) Report the result and its uncertainty $Y = y \pm U$

Thank you very much for your attention!