VSL

National Metrology Institute

Evaluation of measurement uncertainty in the preparation of the proficiency test items in the project MetrIAQ

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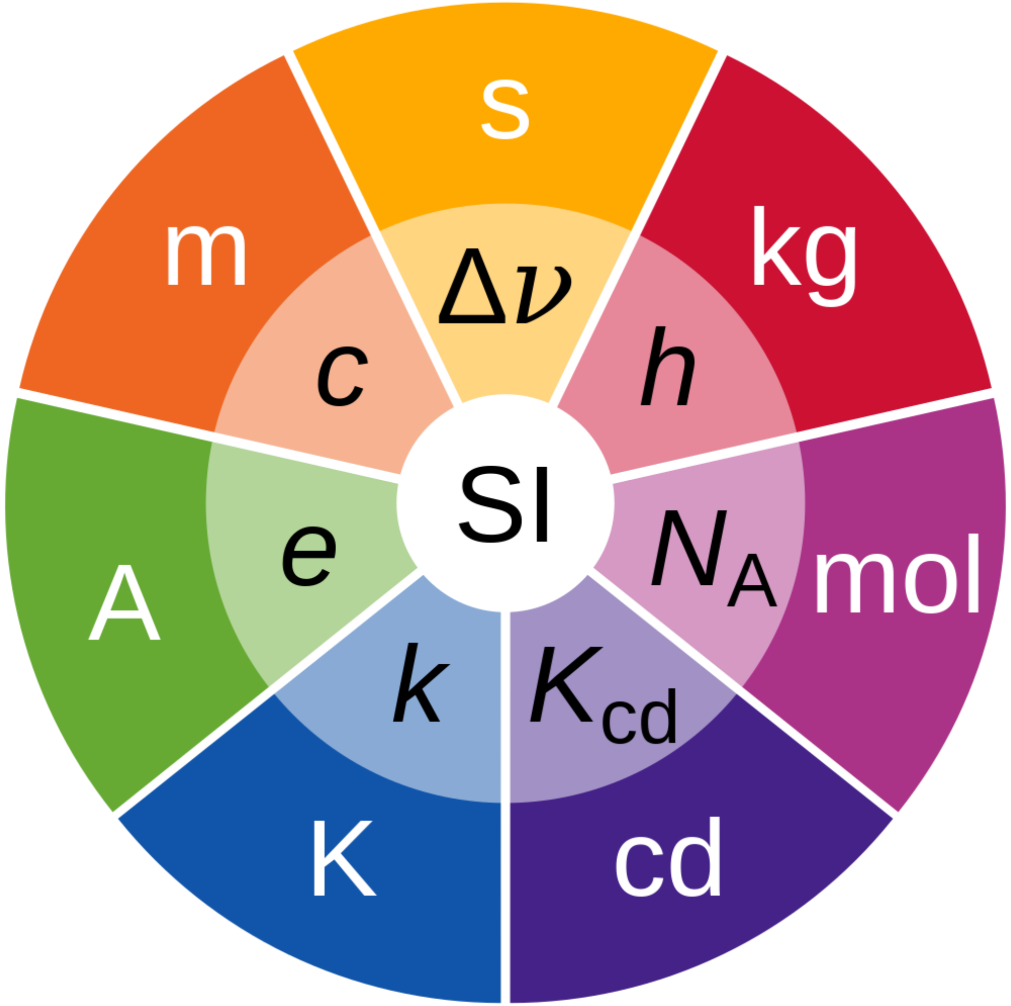
Preamble

Why measurement?

- A *measurement* is performed to learn about a *quantity*, the *measurand*
- Usually, our knowledge about the (unknown) ‘true value’ has increased after making a measurement
- However, *after* the measurement, there is still *doubt* about the true value
- Measurement uncertainty is this *doubt* about the ‘true value’
- Measurement uncertainty can be expressed in many ways

[JCGM GUM-1:2023]



Measurement uncertainty

measurement uncertainty
uncertainty of measurement

doubt about the true value of the measurand that remains after making a measurement

NOTE 1 Measurement uncertainty can be described fully and quantitatively by a probability distribution on the set of possible values of the measurand. It can be described summarily and approximately by a quantitative indication of the dispersion (or scatter) of such distribution.

NOTE 2 For scalar measurands, measurement uncertainty can be described summarily by, for example, the standard uncertainty, a coverage interval with specified coverage probability, or by selected quantiles of the probability distribution in Note 1. For multivariate measurands, measurement uncertainty can be described, for example, by the covariance matrix or by a coverage region, with specified coverage probability.

NOTE 3 When a quantitative expression is impractical, measurement uncertainty can be expressed using an ordinal scale of levels of confidence in the assigned value.

[JCGM WG1]

Uses of measurement uncertainty

- *comparison* of measurement results,
- comparison of a measured value with specification *limits* (*conformity assessment*),
- establishing *metrological traceability*,
- applying a *decision rule*,
- calculating risks and performing *risk assessment*,
- comparison of *model outputs* and *experiments*,
- evaluating the *validity of models*,
- setting *limits for the values of physical quantities*,
- validating or developing *scientific theories*, and
- *propagation of uncertainty* from one measurement to another.

[JCGM GUM-1:2023]

The process

- Specify the measurand
- Model the measurement principle
- Add effects arising from the measurand
- Evaluate the input quantities
- Evaluate any dependencies between input quantities
- Propagate the measurement uncertainty
- Calculate the expanded uncertainty

A simple case

- we are reading the water level as 102 cm
- the scale resolution is 1 cm
- the height of the waves is ± 10 cm
- what is the measurement uncertainty?

Water level (continued)

- uncertainty of the indication (h_{ind}): modelled using a rectangular distribution with location 102 cm and half-width the resolution of the scale
- uncertainty of the waves (δ_{waves}): rectangular distribution with location 0 cm (no net correction) and half-width 10 cm
- uncertainty of the scale (δ_{waves}): according to Rijkswaterstaat ± 3 cm
- modelled using an rectangular distribution with location 0 cm and half-width 3 cm

Uncertainty budget (water level, continued)

- Measured value is 102 cm
- Standard uncertainty is 6 cm
- Assuming the normal distribution, using a coverage factor of 2, the expanded uncertainty is 12 cm
- Our result would hence be 102 cm ± 12 cm ($k = 2$)
- Largest contributor to the measurement uncertainty is the weather!

Propagation of measurement uncertainty

- Law of propagation of uncertainty
  - Mostly used
  - Requires computing the sensitivity coefficients (= partial derivatives)
  - Good for (approximately) linear measurement models and small relative uncertainties (≤ 5 %)
- Monte Carlo method
  - Works for non-linear models and larger relative uncertainties
  - Works with the probability density functions identified for the input quantities
  - Provides a sample of the probability density function for the measurand
- Both methods are implemented in open source and commercial software

Measurand and measurement models

Measurand

- Quantity *intended* to be measured
- Usually not the quantity on which we obtain data during the measurement
- Is preparing sorption tubes a measurement? Sure, the data gathered in the process are used to compute the measurand
- Measurand: mass of a component on the sorption tube

Measurement principle

- Basically, the recipe to arrive at the measured value
- We compute the mass from
  - Flow rate of the gas(es) used when sampling the tube
  - Composition of the calibration gas mixture used with respect to the component(s) of interest
  - Measured sampling time

$$m_i = x_i \frac{M_i}{V_m} q_{v(sample)}\, \Delta t$$

Effects arising from the measurement

- Calibration of instruments
- Repeatability effects
- Reproducibility effects
- Resolution of the instruments
- Variability of environmental conditions
- Conversion from actual to standard conditions
- Absorption efficiency
- …

Elaborating the measurement model

- Different approaches:
  a) Write submodels for each of the input quantities in the measurement model describing the measurement principle
  b) Incorporate all effects in the measurement model
  c) … or use a combination of both!
- In this instance, option a) is probably the most practical one
  - We can evaluate the sub models one by one
  - We can use the outcomes in the measurement model on the left-hand side

$$m_i = x_i \frac{M_i}{V_m} q_{v(sample)} \Delta t$$

Molar mass

- Computed from the standard atomic weights
- For n-hexane, the equation reads as $M = 6A_\mathrm{C} + 14A_\mathrm{H}$
- There is no correlation between the standard atomic weights
- IUPAC table provides the standard atomic weights as intervals
  - Carbon
  - Hydrogen
- Intervals to be interpreted using the rectangular distribution
- Using the law of propagation of uncertainty,

$$u^2(M) = 36u^2(A_\mathrm{C}) + 196u^2(A_\mathrm{H})$$

Molar volume of air (at reference conditions)

- Calculation:

$$V_\mathrm{m} = \frac{RTZ}{p}$$

- At reference conditions, temperature and pressure are without uncertainty
- Gas constant is without uncertainty (according to the SI)
- What is the uncertainty of Z?
- Suppose, we assume that the air behaves like an ideal gas ($Z = 1$)
- The error we make is -0.000355
- We model it using the rectangular distribution with the (absolute) value of the error as the half-width of the interval $\rightarrow u_\mathrm{rel}(Z) = 0.000205 \approx 0.021\%$
- So, $u_\mathrm{rel}(V_m) = 0.000205 \approx 0.021\%$

Flow rate

- We need to consider (at minimum!)
  - Fluctuations in the flow rate
  - Effects of actual conditions (on the flowrate)
  - Calibration of the mass flow controller(s)
- Generally, a mass flow controller is read at *standard conditions*
- Let us start simple …

$$q_V = q_{\mathrm{ind}} + \delta q_{\mathrm{cal}}$$

- Fluctuations in the environmental conditions are in included in q_{ind}
- Evaluation of the uncertainty of q_{ind} can be done by calculating the standard deviation of the indications …

Flow rate (continued)

- … but these indications are not necessarily independent → $u(\bar{q}) \neq \frac{s}{\sqrt{n}}$
- A cautious approach is to use just the standard deviation …

- Calibration results of a flow meter are often given as a relative error and associated expanded uncertainty, say -0.2 % with an expanded uncertainty of 0.4 % (*k* = 2)
- These values are relative to the *flow rate*
- So, our model could be reformulated as $q_V = q_{\mathrm{ind}}(1 + \delta e_{\mathrm{cal}})$ in which $\delta e_{\mathrm{cal}} = -0.2\% = 0.002$

Amount fraction

- Obtained from the preparation/analysis of the calibration gas mixture
- It takes a separate hour to go into details …
- … but that is not what the GUM requires!

Fraction (expanded uncertainty (k = 2))				
	nmol mol^{-1}	nmol mol^{-1}	nmol mol^{-1}	nmol mol^{-1}
n-hexane	46.308 (0.006)	46.813 (0.006)	46.569 (0.006)	46.627 (0.006)
MIBK	50.131 (0.007)	50.677 (0.007)	50.412 (0.007)	50.476 (0.007)
Toluene	49.694 (0.007)	50.236 (0.007)	49.974 (0.007)	50.036 (0.007)
Butyl acetate	50.307 (0.006)	50.855 (0.006)	50.590 (0.007)	50.653 (0.006)
Cyclohexanone	49.735 (0.006)	50.277 (0.006)	50.015 (0.007)	50.077 (0.006)
o-Xylene	50.427 (0.007)	50.976 (0.007)	50.710 (0.007)	50.774 (0.007)
Phenol	48.926 (0.006)	49.459 (0.006)	49.201 (0.006)	49.262 (0.006)
1,3,5-TMB	48.694 (0.006)	49.224 (0.006)	48.967 (0.007)	49.029 (0.006)

Uncertainty of the time measurement

- Resolution of the clock
- Calibration of the clock
- **Reaction time**
- **Effects of starting/stopping**

- The latter two effects are probably the most important ones …
- They are hard to evaluate directly …
- … but a validation experiment of some sort can highlight what the magnitude of these effects are
- Validation and knowing the performance of your method is a requirement of ISO/IEC 17025

Law of propagation of uncertainty

Measurement model

- Mass of a component is given by

$$m_i = x_i \frac{M_i}{V_m} q_{v(sample)}\, \Delta t$$

- As this model is purely multiplicative, the relative standard uncertainties can be combined, viz.,

$$\frac{u^2(m_i)}{m_i^2} = \frac{u^2(x_i)}{x_i^2} + \frac{u^2(M_i)}{M_i^2} + \frac{u^2(V_\mathrm{m})}{V_\mathrm{m}^2} + \frac{u^2(q_{v(sample)})}{q_{v(sample)}^2} + \frac{u^2(\Delta t)}{(\Delta t)^2}$$

- As the quantities are mutually independent, there are no covariance terms to consider at this stage

Reference values and benchmarking of results

Results (expanded uncertainty)

Cylinders	**Dynamic gas mixture**	**VSL114044**	**VSL114045**	**VSL187546**	**VSL187555**
$q_{v(sample)}$ **(mL min^{-1})**	50.17	50.16	50.16	50.16	50.16
t (min)	14.0	12.0	12.0	12.0	12.0
Mass (U (k = 2)) (ng)					
n-hexane	127 (6)	99.9 (1.0)	100.9 (1.0)	100.4 (1.0)	100.5 (1.0)
MIBK	128 (6)	125.6 (1.3)	127.0 (1.3)	126.3 (1.3)	126.5 (1.3)
Toluene	127 (6)	114.6 (1.1)	115.8 (1.2)	115.2 (1.2)	115.4 (1.2)
Butyl acetate	128 (6)	146.2 (1.5)	147.8 (1.5)	147.0 (1.5)	147.2 (1.5)
Cyclohexanone	124 (6)	122.1 (1.2)	123.5 (1.2)	122.8 (1.2)	123.0 (1.2)
o-Xylene	129 (6)	134.0 (1.3)	135.4 (1.4)	134.7 (1.3)	134.9 (1.3)
Phenol	128 (6)	146.4 (1.5)	116.5 (1.2)	115.9 (1.2)	116.0 (1.2)
1,3,5-TMB	121 (6)	115.2 (1.2)	148.0 (1.5)	147.3 (1.5)	147.5 (1.5)

Benchmarking of results

- Use of ζ-scores

$$\zeta_i = \frac{X_i - X_{\mathrm{PT}}}{\sqrt{u^2(X_i) + u^2(X_{\mathrm{PT}})}}$$

- Interpretation:
  - $|\zeta_i| \leq 2$ satisfactory performance
  - $2 < |\zeta_i| \leq 3$ questionable performance
  - $|\zeta_i| > 3$ unsatisfactory performance
- Results benchmarked in view of the uncertainty of the result of the participant and the reference value

Finale

Concluding remarks

- Framework of the GUM (Guide to the expression of Uncertainty in Measurement) applied to evaluating measurement uncertainty
- Modular approach used
- Use of submodels allows for simple mathematics and the application of simple “rules” for propagating measurement uncertainty
- Main model multiplicative → allows for combining directly the relative standard uncertainties
- Especially the time measurement requires some validation work
- Application of the law of propagation of uncertainty is at the brink of being safe to use …

Metrology for the determination of emissions of dangerous substances from building materials into indoor air
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