Estimation of uncertainty

Introduction

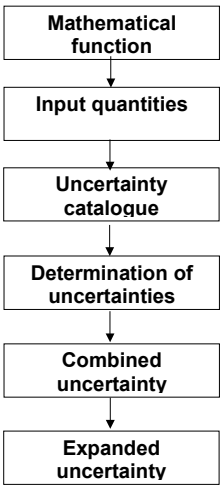
As specified in the European daughter directives, uncertainty shall be evaluated according to the method of the „Guide for the expression in measurement evaluation (GUM). The GUM provides a general concept for the estimation of measurement uncertainties by assessing and combining all potential sources of uncertainty.

General procedure

The first step in uncertainty calculation is to define a mathematical relationship between the measurand and the input quantities.

The estimated value of input quantity is determined and the standard uncertainty of each in input estimate is evaluated.

A catalogue of the possible sources of uncertainty associated with the input quantities has to be assembled. The quantification of uncertainty takes places by statistical analysis of a series of observations (type A) or by scientific judgement (type B.) If correlations are present, they should also be taken into account, to avoid double-counting of uncertainties.



The individual uncertainties are combined.

The combined uncertainty is expanded by a coverage factor to express expanded uncertainty at stated level of confidence, usually 95%.

Evaluation of uncertainty

The following measurement equation has been used to calculate uncertainty

$$C_u = \frac{m_d - m_b}{SR \cdot t}$$

C_u:	ambient concentration	[µg/m^3]
m_d:	mass of desorbed analyte	[µg]
m_b:	blank of analyte	[µg]
SR:	diffusive uptake rate	[ml/min]
t:	exposure time	[min]

The input quantities and their and their uncertainties are:

u_{md}: analytical determination of the mass of absorbed analyte.
The standard uncertainty can be characterised by the standard deviation of the calibration function.

u_b: The variation of blank value has to be added to u_{md} in absolute terms .

u_{SR}: The main term influencing the standard uncertainty is u_{md}
The variation of this term is given by the standard deviation of repeated verification experiments in standard atmospheres.

u_t: This term is in general negligible at exposure times of more than one week. At shorter times, this term has be taken into account.

An additional term has been introduced, which coveres the uncertainties budgets of repeated measurements, microenvironmental factors, variations in the geometry of samplers etc.

u_p The size of this term is estimated by the median of triplicate samplers in the field.

u_{ext}: This term has to be taken into account, if the samplers are used in extreme conditions.
This term has to be estimated

Catalogue of error sources

A general list of uncertainties which are covered by the main factors is given in the following table

sources of uncertainties	uncertainty term
Sampling rate	**U_{SR}**
weight loss of permeation tube	**x**
flow measurement	**x**
absorption on chamberwalls	x
precision of measurement	
Repeatability (repeatet verification)	**xxx**
Sampling	**U_P**
length of tube	**x**
area of tube	**x**
precision of measurement	**xx**
Laboratory analysis	**U_{md}**
calibration function	**xxx**
standard solutions	**x**
Dispenser	**x**
volumetric flasks	**x**
pipettes	**x**
microliter syringe	**x**
analytical equipment	**x**
operator	
balance	**x**
Reproducibility	**x**
Blanks	**U_{mb}**
laboratory blanks	**x**
field blancs	**x**
storability after use	**x**
shelf life	**x**
leak test	**x**
Exposure time	**U_t**
Zeitnahme	**x**
external influences	**U_{ext}**
temperature	**x**
humidity	**x**
windspeed	**xx**
Interferences	

The uncertainty budgets are categorized:

x: u < 1%
xx: u 1- 5 %
xxx: u > 5%

Calculation of uncertainty

The combined uncertainty U_k is calculated as follows:

$$U_k = \sqrt{u^2_{SR} + (u^2_{md} + u^2_{mb}) + u^2_P + u^2_t + u^2_{ext}}$$

The expanded uncertainty is calculated by using a coverage factor of 2.

$$U_e = 2 \bullet \sqrt{u^2_{SR} + (u^2_{md} + u^2_{mb}) + u^2_P + u^2_t + u^2_{ext}}$$

Uncertainty of passam tubes

Pollutant	Range of concentration µg/m^3	Expanded uncertainty
NO_2	< 10 20 – 40 > 40	26.0% 22.6 % 21.9 %
Ozone	<10 40 – 80 > 80	32.8 % 22.8 % 21.2 %
SO_2	< 10 20 - 40 > 40	38.8 % 29.6 % 25.4
BTX	1 – 4	20.2 %

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Remark

The uncertainty depend both s of the laboratory performance as well as of field application. There fore it can vary from year to year as well as from study to study.

The uncertainity estimation depends also from the assumptions and terms which are considered.

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