CALCULATION OF UNCERTAINTIES IN STACK MONITORING

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Acknowledgements

- This lecture is based largely on the previous lecture prepared by Dr Andrew Clarke
- It has been updated by Rod Robinson and includes an example based on the CEN/TS 17021 Stationary source emissions - Determination of the mass concentration of sulphur dioxide by instrumental techniques

Literature - Standards

Overarching :

- **ISO/IEC 98-3:2008 / ENV 13005:1999** – Guide to the expression of uncertainty in measurement (GUM)

https://www.bipm.org/en/publications/guides/gum.html

- **BS EN ISO 14956:2002** Air quality - Evaluation of the suitability of a measurement procedure by comparison with a required measurement

- **BS EN ISO 20988: 2007** Air quality – Guidelines for estimating measurement uncertainty

  (Esp. Annex E dealing with AMS)

Standards for individual SRMs

General guidance

- EURACHEM / CITAC Guide CG 4 : Quantifying Uncertainty in Analytical Measurement

https://www.eurachem.org/images/stories/Guides/pdf/QUAM2012_P1.pdf

- NPL offer some free guides on uncertainties

https://www.npl.co.uk/resources/gpgs/all-gpgs

- NPL run some e-learning courses:

https://training.npl.co.uk/

Literature - STA

- *“Guidance on assessing measurement uncertainty in stack emissions monitoring”*

  2nd Edn 2004 by Jonathan Pullen and Rod Robinson

  Source Testing Association QGN001-r1

- Particles by 13284-1 (QGN001-01) but see new standard BS EN 13284-1 2017

- Example spreadsheets – for most SRMs including flow

  BS EN ISO 16911-1:2013

Literature – Environment Agency

- **Technical Guidance Note M2**
  Monitoring of stack emissions to air V12, 2017

  Section 4.10 - pages of general guidance relating to measurement uncertainty

  Section 6 - a more detailed treatment of the principles and practice of uncertainty calculation.

  Section 7 - Table of *maximum permissible measurement uncertainties* covering species of pollutant beyond those in EU standards.

  Used in assessing compliance of measurements with ELVs. Uncertainty subtracted from measured value before comparison with ELV.

https://www.gov.uk/government/publications/m2-monitoring-of-stack-emissions-to-air

Overall Uncertainties for Standard Reference Methods

Pollutant	BS EN Standard	Uncertainty Requirement
H_2O Manual	14790:2017*	±20% of measured value
SO_2 Manual	14791:2017*	±20% relative at daily ELV
NO_x Chemiluminescence	14792: 2017*	±10% relative at daily ELV
O_2 Paramagnetic	14789:2017*	±6% of measured value
CO Infra Red	15058:2017*	±6% relative at daily ELV
HCl Manual	1911:2010	±30% relative at daily ELV (for LCP and WID plant)
SO_2 Instrumental	TS 17021:2017	±15% relative at daily ELV

* or the lowest limit value specified for the plant by the local authorities

O_2 6% relative or 0.3% absolute.

Note uncertainty requirement is generally expressed as relative to ELV on a dry basis before correction to the oxygen reference

Uncertainties for SRMs

- Overall uncertainties incorporating all possible significant sources of variation

- **Expanded** uncertainties with 95% confidence limits

- H_2O, O_2 relative to the actual measured concentration whilst the rest are relative to the daily Emission Limit Value (ELV)

- Note – must report expanded uncertainty on reported value – but requirement in standard to check requirement is met is before oxygen correction.

General Approach

1. Specify what is being measured and the parameters on which it depends - *model equation*

2. Identify possible sources of uncertainty for each parameter

3. Quantify the component standard uncertainties u i.e.. prepare the **uncertainty budget**

   Calculate all component uncertainties in same way – either as percentage (relative) uncertainties or in units of reported value (standard)

   Recommend to use units of reported value.

General Approach

4. Determine the <u>combined</u> standard uncertainty of the measured value u_c

Then determine the <u>expanded</u> uncertainty $\mathbf{U_c}$

Concentration = X ± $\mathbf{U_c}$

where $\mathbf{U_c}$ is the **overall uncertainty** at a confidence level of 95%.

1. Problem Specification

Manual Methods - gases or particles

Specify the “model equation” relating input quantities to the required concentration:-

Mass Concentration in flue gas

= (Mass collected) ÷ (Sample gas volume)

Mass of particles = (Weight Filter +Particles) – Filter weight

also include washing weight if significant

Mass of Gas = (Solution Concentration) x (Solution Volume)

Sample gas vol = (Meas. Sample gas vol) (T_{ref} / T_{act}) (P_{act} / P_{ref})

(at ref. T and P) (at actual T,P)

1. Problem Specification

Manual methods – gases or particles

- Uncertainty of weighing particles
- Uncertainty of chemical analysis of solution
- Uncertainty of measurement of sample gas volume or liquid solution volume
- Uncertainty of meter temperature or pressure

\+ Efficiency of sampling bottles in collecting the measurand, leakage and losses in train etc.

1. Problem Specification

- Manual methods –
- Full treatment is included in the newest standards for

Particles   EN 13284-1, (Annex G)

$H2O$ EN 14790

HCl   EN 1911

SO_2 EN 14791

VOC (Speciated) CEN/TS 13649

1. Problem Specification

Instrumental Gas Analysers

- Simple model equation, instrument is calibrated using certified gas

Conc = Instr reading*factor + ∑ influences

  - Factor = calibration factor
  - Influences = whatever may affect reading which is not included in calibration e.g. temp, drift, interfering gases

- Sensitivities of output to factors which may influence it determined experimentally
- Information from manufacturers and performance characteristics determined during MCERTS testing

2. Identify possible sources of uncertainty for each parameter

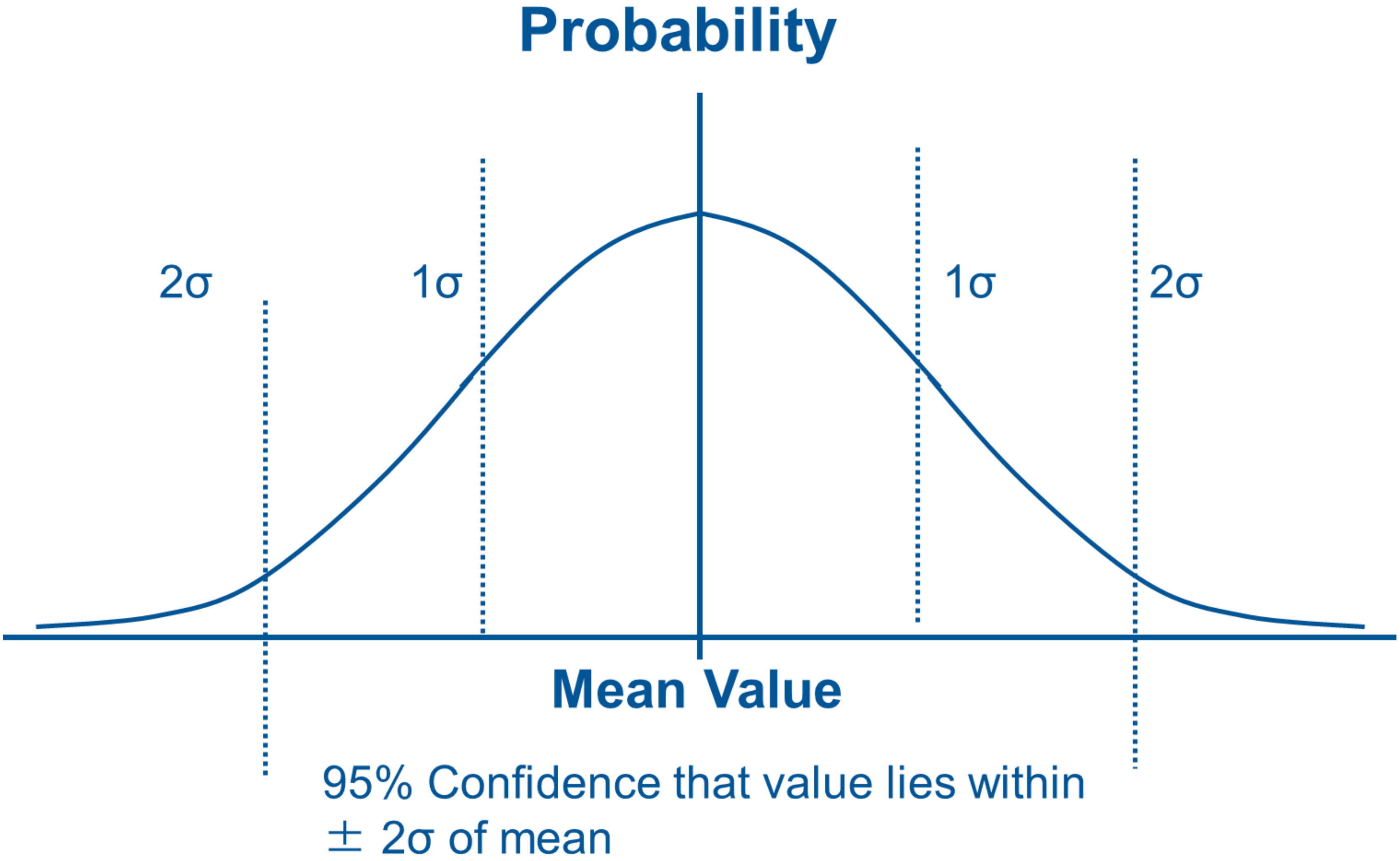
Instrumental Gas Analysers

- Lack of fit (linearity)
- Zero drift
- Span drift
- Sensitivity to sample volume flow
- Sensitivity to atmospheric pressure
- Sensitivity to ambient temperature
- Sensitivity to electrical voltage
- Interferences from other gaseous components present in the flue gas
- Repeatability standard deviation in lab at span level*
- Calibration gas
- (*Repeatability standard deviation at zero is not included)

3. Quantify the component standard uncertainties

- **Standard uncertainties u** – those which are obtained from experimental data and thus lead directly to a standard deviation. ("Type A" uncertainties)
- Assuming normal distribution of points around the mean then, with 95% confidence, the uncertainty is ± 2 times the standard deviation.
- The exact factor is 1.96 which is sometimes called the **coverage factor k**.
- When quoting the values, we must be very clear whether we are giving the **standard uncertainty** (u=1 SD) or the **expanded uncertainty U (where U=k.u)** for a particular degree of confidence such as 95% when k=2.

Probability Distributions A



95% Confidence that value lies within ± 2σ of mean

3. Quantify the component standard uncertainties

Uncertainties from influence quantities

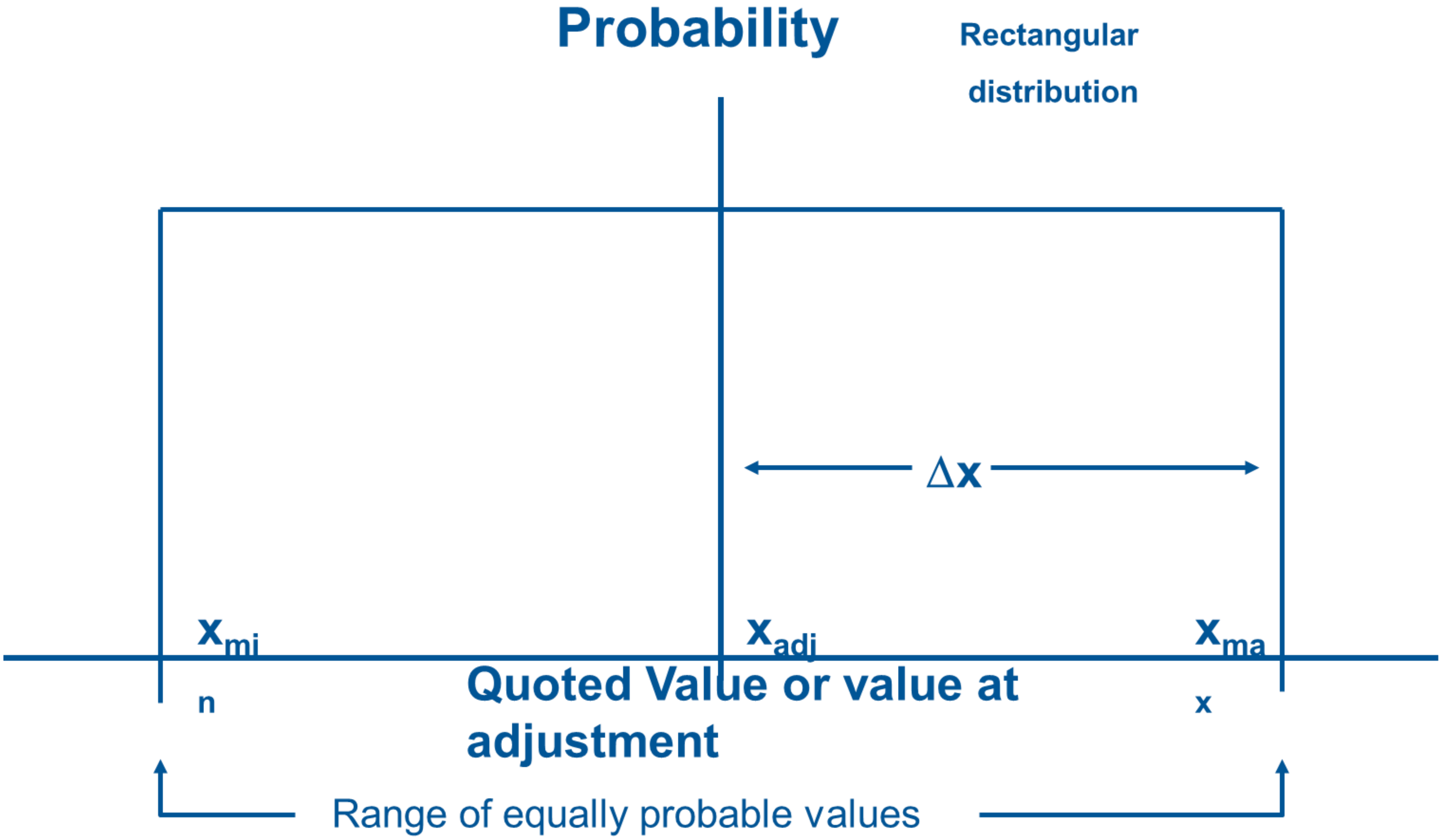
where a parameter of influence has a range of values compared to the value at instrument calibration
e.g. Ambient temp at cal = 298.
Ambient temp during measurement =290 to 303.

Other examples

- uncertainty of a physical dimension (e.g. nozzle size)
- uncertainty of voltage during the experimental work

converted to a **standard uncertainty** assuming all values within the range are equally likely (rectangular distribution)

Probability Distributions



Conversion Factors for Type B Uncertainties (see M2)

- . If x_{adj} is halfway between x_{min} and x_{max} then defining

$$\Delta x = (x_{adj} - x_{min}) = (x_{max} - x_{adj})$$

The standard uncertainty is

$$\mathbf{u_x = \Delta x / (\sqrt{3})}$$

- If the value of x_{adj} is offset from the centre of the range then

$$\mathbf{u_x^2 = [\, (x_{max} - x_{adj})^2 + (x_{min} - x_{adj})(x_{max} - x_{adj}) + (x_{max} - x_{adj})^2 \,] \,/\, 3}$$

Estimating Component Standard Uncertainties

Example

a) Atmospheric pressure variation:

- Measured value   75 mg/m3
- Sensitivity of concentration to atmospheric pressure
  0.8% per kPa
- Variation during measurement 99-100 kPa
  $\Delta x = 0.5$
- Standard Uncertainty in concentration units
  $=(0.8/100) \times 75 \times 0.5 / \sqrt{3}$
  $=0.17$mg/m3

Estimating Component Standard Uncertainties

Example b) Calibration Gas

An error in the cal gas affects the reported measured concentration directly and proportionately

- Cal gas conc 75mg/m^3
- Specified uncertainty 2%
- Type B uncertainty - true concentration 73.5 - 76.5mg/m^3

- Standard uncertainty (2/100) x 75/ $\sqrt{3}$ = 0.87mg/m^3

Rules for Combining Uncertainties

- The mathematical approach is to combine as partial differentials – but there are simple rules for usual cases:
- X obtained by *addition* or *subtraction* – absolute values of component uncertainties combined

$$X = (a \pm u_a) + (b \pm u_b) + (c \pm u_c)$$

$$u_X = \sqrt{u_a^{\,2} + u_b^{\,2} + u_c^{\,2}}$$

Rules for Combining Uncertainties

- X obtained by *multipliplication* or *division* -
- relative or percentage values of component uncertainties combined

$$X = \frac{(a \pm u_a)(b \pm u_b)}{(c \pm u_c)}$$

$$\frac{u_X}{X} = \sqrt{\left(\left(\frac{u_a}{a}\right)^2 + \left(\frac{u_b}{b}\right)^2 + \left(\frac{u_c}{c}\right)^2\right)}$$

Rules for Combining Uncertainties

- *Powers and roots* – multiply component uncertainty by value of power (2, 3, 0.5, 0.333, etc)
- Eg $u(x^2) = 2\ u(x)$

Neglecting Minor Component Uncertainties.

- When one component uncertainty is much smaller than the others then the smaller one can effectively be neglected
- A factor of four is generally sufficient
- European standards state:
  ignore a component uncertainty <5% of the largest

The Expanded Uncertainty U_c

- Combining all the component standard uncertainties we obtain the *combined uncertainty* u_c

- Multiply by the coverage factor k to obtain the *expanded uncertainty* ***U_c***

$$U_c = k\, u_c$$

with k = 2 for 95% confidence.

The Expanded Uncertainty U_c

- U_c may be calculated in concentration units and then expressed as a percentage by dividing by the ELV

  OR the whole calculation may be done in percentages of the ELV.

- Examples in standards are done assuming measured value is at ELV. This is a special case to show performance of the method – most of the time you will calculate the uncertainty at the measured value – and then check this against requirement as a percentage of the ELV

Example: Instrumental SO_2

- Example based on Annex A of CEN TS 17021:2017

(A similar example is give in Annex B of the CO standard BS EN 15058:2017)

- This calculation is based on an ELV of 50 mg.m^{-3}

SO_2 site specific conditions

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Table 1

Specific conditions	Value/range
Range of analyser	0-26 ppm (0-75 mg/$m_0$3)
Studied concentration of SO_2 : limit value of SO_2 for the site	50 mg/$m_0$3
	corresponding to 17 ppm at O2,ref
Conditions on the field	
Sample flow during adjustment	60 l.h^{-1}
Sample flow variation during monitoring	55 – 65 l.h^{-1}
Sample pressure during adjustment	100 kPa
Sample pressure variation during monitoring	97.5 – 102.5 kPa
Ambient temperature during adjustment	285 K
Ambient temperature variation during monitoring	283 to 308 K
Voltage during adjustment[a]	110 V
Voltage variation during monitoring	107 – 115.5 V
O2 reference concentration : O2,ref	11 % volume
Calibration gas	26 ppm ± 2 %, k = 2
Reading of calibration gas during checking of sampling system	25.7ppm
SO_2 in N2, without interferent	

Uncertainty Sources

Number Source of uncertainty Assigned symbol	Number Source of uncertainty Assigned symbol	Number Source of uncertainty Assigned symbol
1	Precision of analyser	uread
2	Repeatability standard deviation at span point	ur
3	Lack of fit	ulof
4	Short-term zero drift	ud,z
5	Short-term span drift	ud,s
6	Influence of ambient temperature	uat
7	Influence of electrical voltage	uv
8	Influence of vibration	uvib
9	Influence of sample gas pressure	up
10	Influence of sample gas flow	uf
11	Cross-sensitivity	uint
12	Losses in sample line	uloss
13	Calibration gas	ucal

Symbol	Source of uncertainty	Value	Probability distribution	Divisor d	c_i	$c_i u(x_i)$
u_r	Repeatability standard deviation at span point	0,35 %	normal	1	$\frac{R}{100}$	$c_r \frac{0{,}35}{d_r}$
u_{lof}	Lack of fit	0,4 %	rectangular	$\sqrt{3}$	$\frac{R}{100}$	$c_{lof} \frac{0{,}4}{d_{lof}}$
$u_{d,z}$	Zero drift	0,01 %	rectangular	$\sqrt{3}$	$\frac{R}{100}$	$c_{d,z} \frac{0{,}01}{d_{d,z}}$
$u_{d,s}$	Span drift	0,5 %	rectangular	$\sqrt{3}$	$\frac{R}{100}$	$c_{d,s} \frac{0{,}5}{d_{d,s}}$
u_{at}	Influence of ambient temperature	0,2 % / 10 K	rectangular	$\sqrt{3}$	$\frac{1}{10}\frac{R}{100}$	$c_{at} \frac{0{,}2\sqrt{\begin{matrix}(t_{max}-t_{adj})^2 \\ +(t_{min}-t_{adj})(t_{max}-t_{adj}) \\ +(t_{min}-t_{adj})^2\end{matrix}}}{d_{at}}$
u_v	Influence of electrical voltage	0,12 % / 10 V	rectangular	$\sqrt{3}$	$\frac{1}{10}\frac{R}{100}$	$c_v \frac{0{,}12\sqrt{\begin{matrix}(v_{max}-v_{adj})^2 \\ +(v_{min}-v_{adj})(v_{max}-v_{adj}) \\ +(v_{min}-v_{adj})^2\end{matrix}}}{d_v}$
u_{vib}	Influence of vibration	0,4 %	rectangular	$\sqrt{3}$	$\frac{R}{100}$	$c_{vib} \frac{0{,}4}{d_{vib}}$
u_p	Influence of sample gas pressure	1,0 % / 3 kPa	rectangular	$\sqrt{3}$	$\frac{1}{3}\frac{R}{100}$	$c_p \frac{1{,}0(P_{max}-P_{adj})}{d_p}$

u_f	Influence of sample gas flow	0,2 % / 10 l.h^{-1}	rectangular	$\sqrt{3}$	$\frac{1}{10}\frac{R}{100}$	$c_f \frac{0{,}2\left(f_{max}-f_{adj}\right)}{d_f}$
u_{int}	Cross-sensitivity	1,4 %	rectangular	$\sqrt{3}$	$\frac{R}{100}$	$c_{int} \frac{1{,}4}{d_{int}}$
u_{loss}	Losses and leakage in the sampling system	0,3 ppm	rectangular	$\sqrt{3}$	1	$c_{loss} \frac{loss_{max}-loss_{min}}{d_{loss}}$
u_{CRM}	Calibration gas	0,5 ppm , k = 2	normal	2	1	$c_{CRM} \frac{0{,}5}{d_{CRM}}$
$\boldsymbol{u_c}$	Combined standard uncertainty		normal			$\sqrt{\sum_{i=1}^{N} c_i^2 u_i^2(x_i)}$
$\boldsymbol{U_{95}}$	Expanded uncertainty		t-distribution			$k_{95} u_c$

Symbol	Source of uncertainty	Value	Probability distribution	Divisor d	c_i	$c_i u(x_i)$
u_r	Repeatability standard deviation at span point	0,35 %	normal	1	$\frac{26}{100} = 0,260$	$0,260 \frac{0,35}{1} = 0,091$
u_{lof}	Lack of fit	0,4 %	rectangular	$\sqrt{3}$	$\frac{26}{100} = 0,260$	$0,260 \frac{0,4}{\sqrt{3}} = 0,060$
$u_{d,z}$	Zero drift	0,01 %	rectangular	$\sqrt{3}$	$\frac{26}{100} = 0,260$	$0,260 \frac{0,01}{\sqrt{3}} = 0,002$
$u_{d,s}$	Span drift	0,5 %	rectangular	$\sqrt{3}$	$\frac{26}{100} = 0,260$	$0,260 \frac{0,5}{\sqrt{3}} = 0,075$
u_{at}	Influence of ambient temperature	0,2 % / 10 K	rectangular	$\sqrt{3}$	$\frac{1}{10} \frac{26}{100} = 0,026$	$0,026 \frac{0,2 \sqrt{\begin{array}{c}(308-285)^2 \\ +(283-285)(308-285) \\ +(283-285)^2\end{array}}}{\sqrt{3}} = 0,066$
u_v	Influence of electrical voltage	0,12 % / 10 V	rectangular	$\sqrt{3}$	$\frac{1}{10} \frac{26}{100} = 0,026$	$0,026 \frac{\sqrt{\begin{array}{c}(115,5-110)^2 + \\ (107-110)(115,5-110) \\ +(107-110)^2\end{array}}}{\sqrt{3}} = 0,009$
u_{vib}	Influence of vibration	0,4 %	rectangular	$\sqrt{3}$	$\frac{26}{100} = 0,260$	$0,260 \frac{0,4}{\sqrt{3}} = 0,060$
u_p	Influence of sample gas pressure	1,0 % / 3 kPa	rectangular	$\sqrt{3}$	$\frac{1}{3} \frac{26}{100} = 0,087$	$0,087 \frac{1,0(102,5-100)}{\sqrt{3}} = 0,125$

u_f	**Influence of sample gas flow**	**0,2 % / 10 l. h^{-1}**	**rectangular**	$\sqrt{3}$	$\frac{1}{10}\frac{26}{100} = 0{,}026$	$0{,}026\frac{0{,}2(65-60)}{\sqrt{3}} = 0{,}015$
u_{int}	Cross-sensitivity	1,4 %	rectangular	$\sqrt{3}$	$\frac{26}{100} = 0{,}260$	$0{,}260\frac{1{,}4}{\sqrt{3}} = 0{,}210$
u_{loss}	Losses and leakage in the sampling system	0,3 ppm	rectangular	$\sqrt{3}$	1	$1\frac{0{,}3}{\sqrt{3}} = 0{,}173$
u_{CRM}	Calibration gas	0,5 ppm, k = 2	normal	2	1	$1\frac{0{,}5}{2} = 0{,}250$
$\boldsymbol{u_c}$	Combined standard uncertainty (ppm)		normal			0,419
$\boldsymbol{U_{95}}$	Expanded uncertainty (ppm)		k = 2			0,838

Calculation of Combined and Expanded Uncertainty

The **combined uncertainty u_c** is obtained as the square root of the sum of the squares of all the component uncertainty u values in the right hand column, converted to mass concentration from which:

$$u_c = 1.20\ \mathrm{mg.m^{-3}}$$

The **Expanded uncertainty $U_c = 2 \cdot u_c$**

$$U_c = \underline{\pm 2.40\ \mathrm{mg.m}}^{-3}$$

with level of confidence of 95%.

ELV = 50 mg.m^{-3} so this represents **4.8% of the ELV**

QUESTIONS?

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