MUkit – Software for uncertainty calculations from validation and QC data according to Nordtest TR537

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Eurachem Workshop –
Uncertainty from sampling and analysis for accredited laboratories
Berlin 20.11.2019

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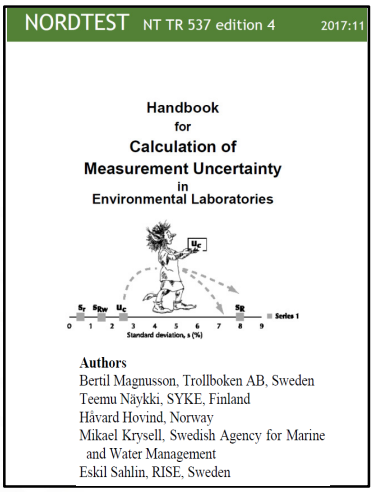
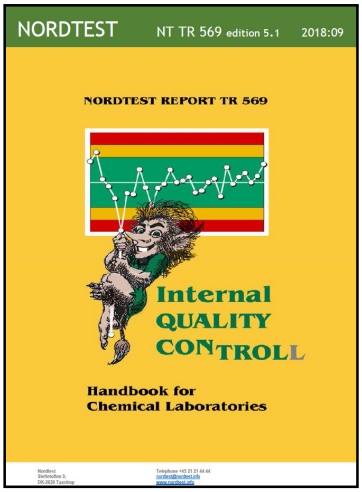
Popular Nordtest guides

www.nordtest.info





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www.nordtest.info/index.php/nordtest/41-calculation-of-measurement-uncertainty-4.html

Aims of the Nordtest TR 537

- To provide a practical, understandable and common way of measurement uncertainty calculations, mainly based on already existing quality control and validation data
- To present and explain practical examples, taken directly from the everyday world of environmental laboratories
  - However, the approach is very general and should be applicable to most testing laboratories in the chemical field
- The handbook covers all steps in the analytical chain from the arrival of the sample in the laboratory until the data has been reported.
  - NOTE: Vital parts of the total measurement uncertainty are not included, e.g. sampling, sample transportation and possible gross errors during data storage/retrieval.

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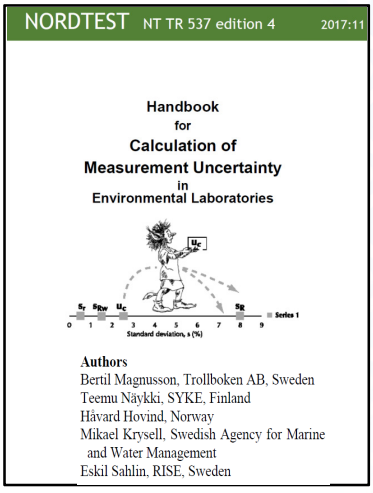
History of Nordtest TR537

- **Edition 1.0 2003**
- **Edition 1.2 2003**
- **Edition 1.3 2003**
- **Edition 2 2004**
- **Edition 3 2008**
- **Edition 3.1 2012**
- **Edition 4 2017**



- **Available in…**
  - **English, Danish, Greek, Serbian, Turkish, Finnish, Russian…**

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Nordtest TR 537 Edition 4 - Updates

- Uncertainty over the measurement range
  - Separate section on estimating measurement uncertainty over the measurement range, in either absolute units or relative units
- Estimating standard deviation from routine sample replicates
  - Pooled standard deviation is used instead of a factor applied to the mean range.
- Use of control chart limits for the within-lab reproducibility component *u*(Rw) is pointed out more clearly
- Harmonisation of the terminology with ISO 11352
  - Water quality — Estimation of measurement uncertainty based on validation and quality control data

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Nordtest TR537 uncertainty estimation

- Basic principle

Within-laboratory reproducibility

Long-term random effects

$$u_c = \sqrt{u(R_w)^2 + u(bias)^2}$$

Laboratory and method bias

Long-term systematic effects

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Data sources for uncertainty estimation accoring to Nordtest TR537

- Within-laboratory reproducibility, $u(R_w)$
  - Two options
    - Control sample covering the whole analytical process
    - Control sample and routine sample replicates
- Bias, u(bias)
  - Three options
    - Certified reference material / Control sample
    - Interlaboratory comparisons / Proficiency tests
    - Recovery tests

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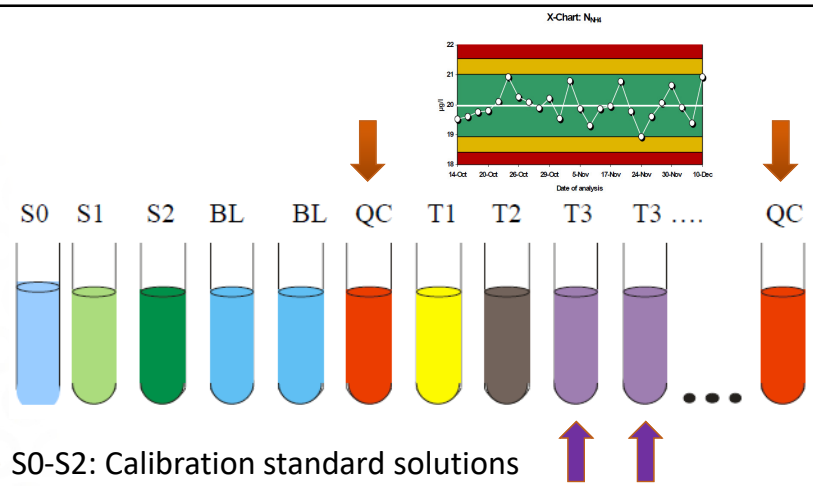

- S0-S2: Calibration standard solutions
- BL: Blank samples
- QC: Quality control samples
- T1…: Test samples

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Modified from Nordtest TR 569

MUkit – measurement uncertainty software

- It is based on the
  - Nordtest TR 537 *(Handbook for Calculation of Measurement Uncertainty in Environmental Laboratories)* and on the
  - Standard ISO 11352 *(Water quality -- Estimation of measurement uncertainty based on validation and quality control data)*.
- Using the software, the laboratories can easily calculate measurement uncertainties using
  - Quality control samples,
  - Repeated results from routine samples,
  - Results from proficiency tests and
  - Results from recovery tests

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History of MUkit software

- Version 1.0
  - Only relative uncertainty estimation possible
  - Open source code under BSD license
- Version 1.9.5
  - Test version including absolute uncertainty estimation
- Version 3.0
  - The software calculates the repeatability component using the pooled standard deviation as presented in the latest edition (Ed.4) of Nordtest TR537 guide
  - Software info texts have been updated to match the chapters in the Nordtest guide
  - In addition to relative measurement uncertainty, also absolute measurement uncertainty calculation is available
  - Software can still be downloaded and used for free of charge, but the program source code will not be open anymore.

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Example: Total nitrogen in waste water

- Step 1: Specify measurand
- Total nitrogen mass concentration in waste water measured according standard method EN ISO 11905-1.
- Uncertainty is estimated using the results of control charts (X-chart and R-chart)

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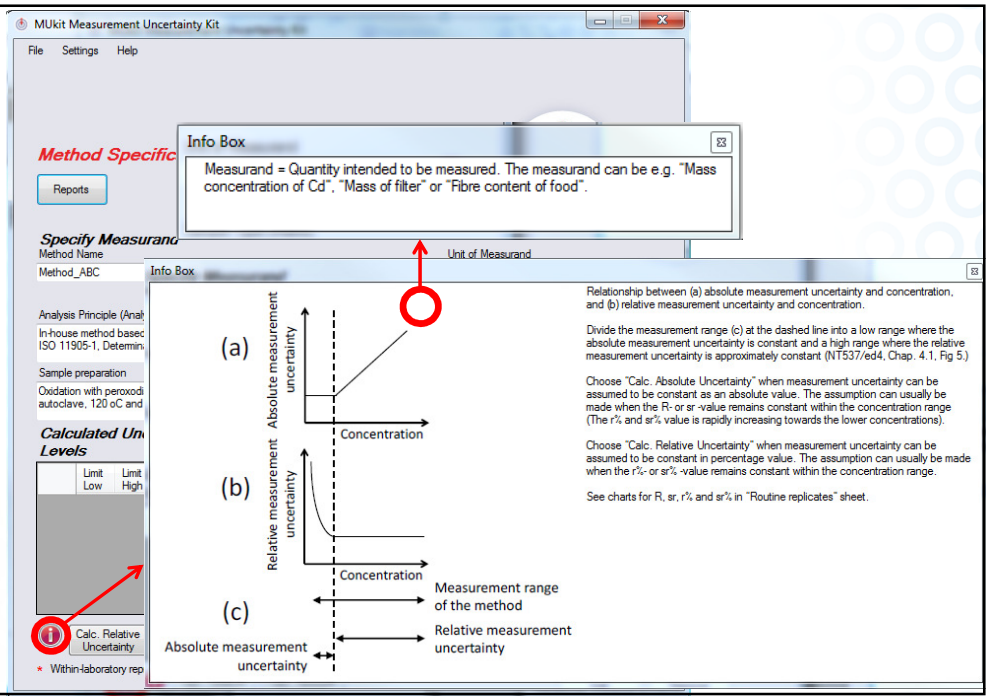

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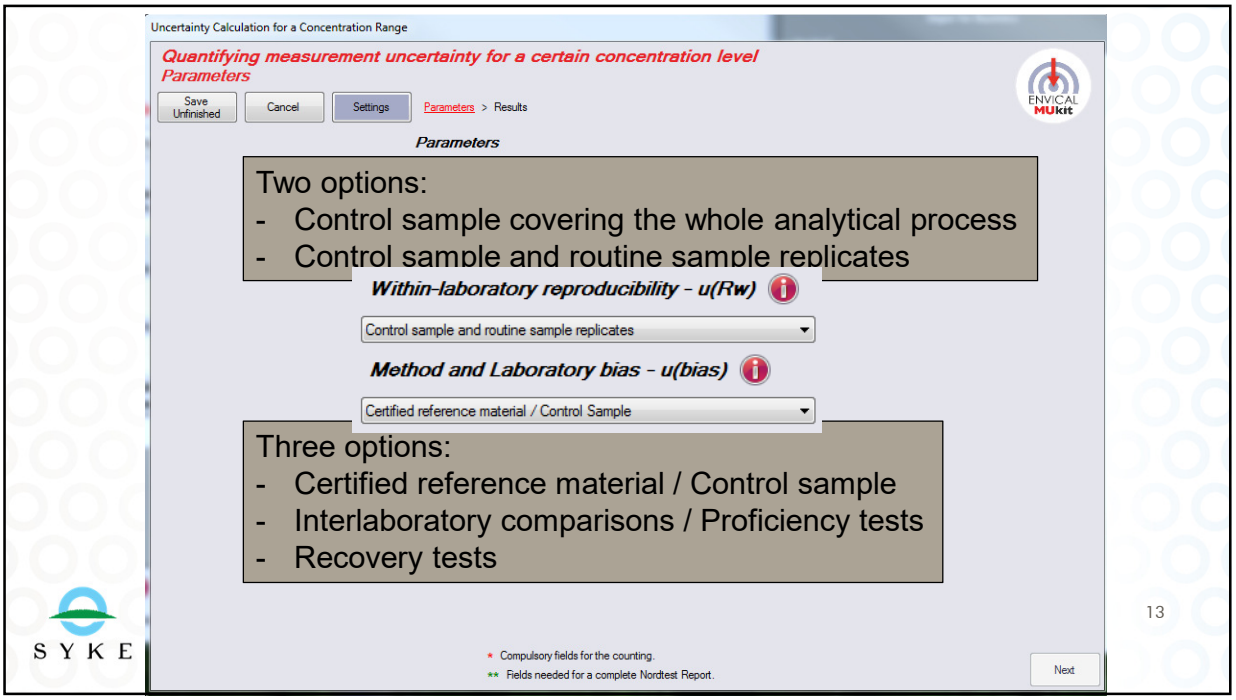

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Routine sample replicates

Replicate series N:o	Replicate result 1 (mg/L)	Replicate result 2 (mg/L)	Replicate result 3 (mg/L)	Replicate result 4 (mg/L)	Date measured
1	0,181	0,163	0,169	0,179	30.9.2018
2	0,189	0,168	0,172	0,178	21.12.2018
3	0,178	0,171	0,174	0,182	10.10.2018
4	0,199	0,184	0,179	0,189	1.8.2018
5	0,193	0,186			7.12.2018
6	0,191	0,199	0,201	0,192	27.11.2018
7	0,192	0,198	0,199	0,199	11.1.2018
8	0,267	0,206			7.1.2018
9	0,255	0,211			26.4.2018
10	0,206	0,216	0,226	0,226	27.7.2018
11	0,271	0,225	0,257		2.10.2018
...					
105	3,84	3,78	3,71		13.11.2018
106	3,72	3,99	3,89	3,75	17.6.2018
107	4,01	4,12	3,99	4,12	20.2.2018
108	4,44	4,31	4,12	4,33	11.11.2018
109	4,71	4,51	4,52	4,65	10.12.2018
110	4,31	4,65	4,66	4,35	3.4.2018
111	4,64	4,59	4,57		24.10.2018
112	4,95	4,67	4,69	4,96	7.12.2018
113	4,93	4,73	4,95	4,91	3.2.2018
114	4,89	4,77	4,79		5.7.2018
115	4,99	4,89	4,89		10.10.2018

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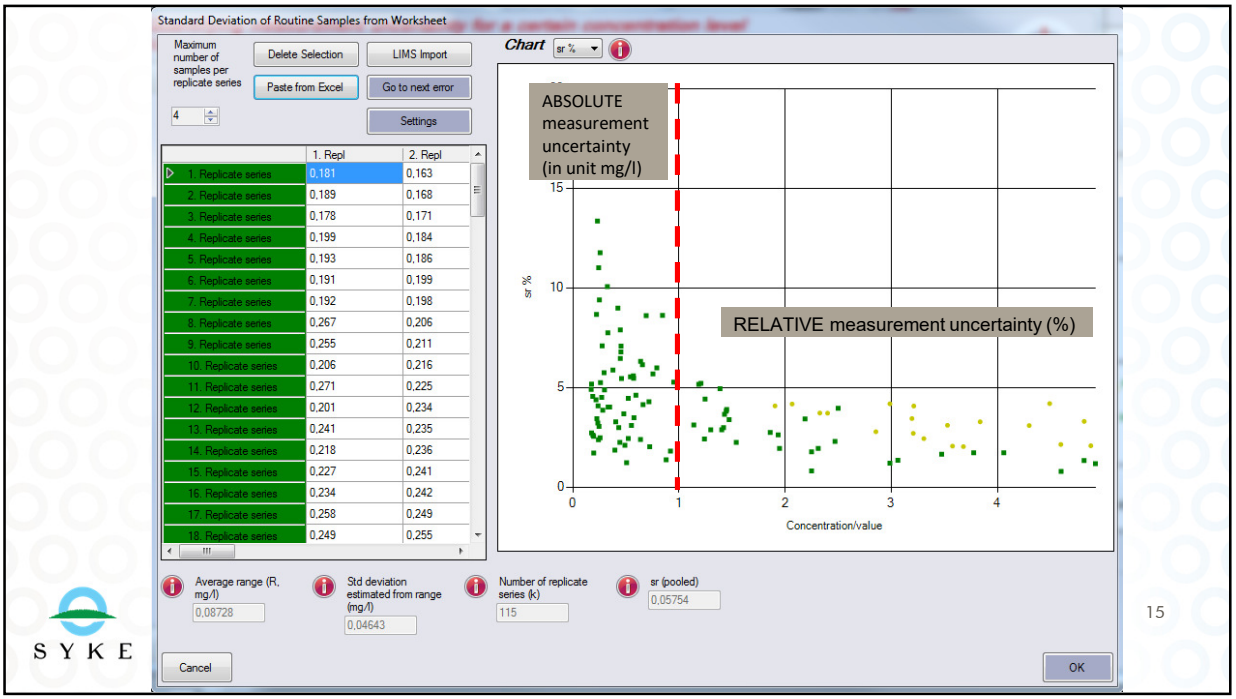
Standard Deviation of Routine Samples from Worksheet
Maximum number of samples per replicate series
Delete Selection
LIMS Import
Paste from Excel
Go to next error
Settings
Chart
sr %
ABSOLUTE measurement uncertainty (in unit mg/l)
RELATIVE measurement uncertainty (%)
Concentration/value
Average range (R, mg/l)
Std deviation estimated from range (mg/l)
Number of replicate series (k)
sr (pooled)
Cancel
OK
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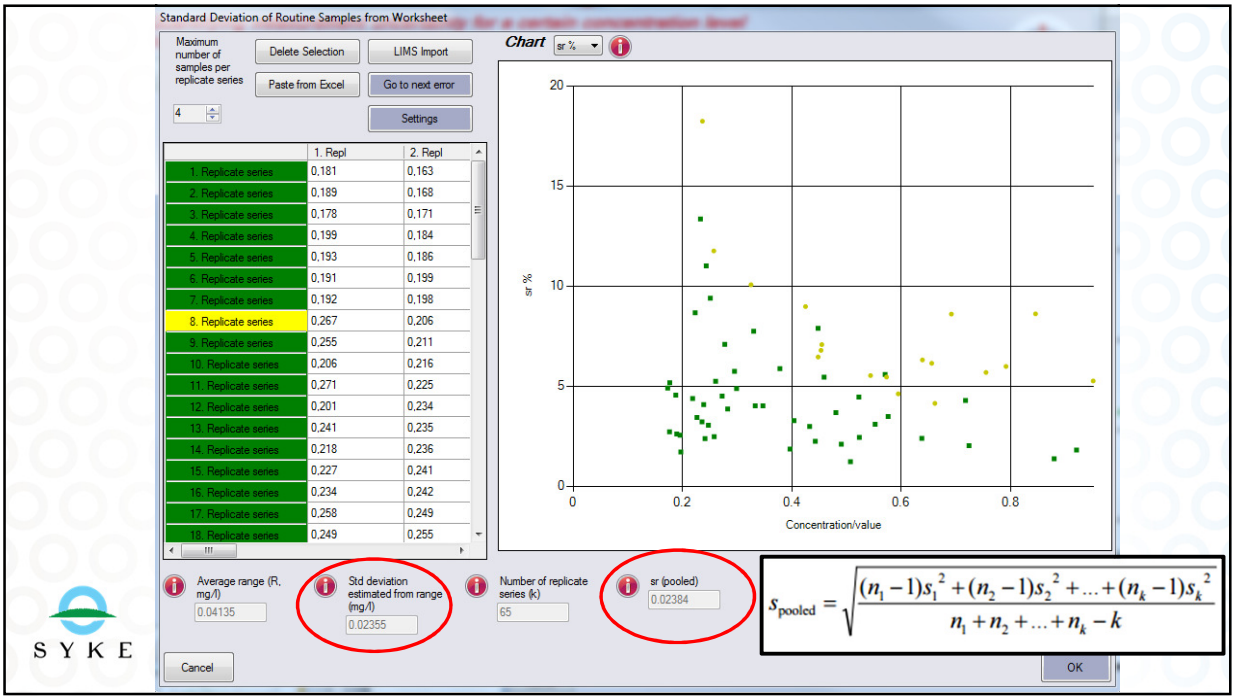
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Settings
Chart
sr %
Concentration/value
Average range (R, mg/l)
Std deviation estimated from range (mg/l)
Number of replicate series (k)
sr (pooled)
$s_{pooled} = \sqrt{\frac{(n_1-1)s_1^2+(n_2-1)s_2^2+\ldots+(n_k-1)s_k^2}{n_1+n_2+\ldots+n_k-k}}$
Cancel
OK
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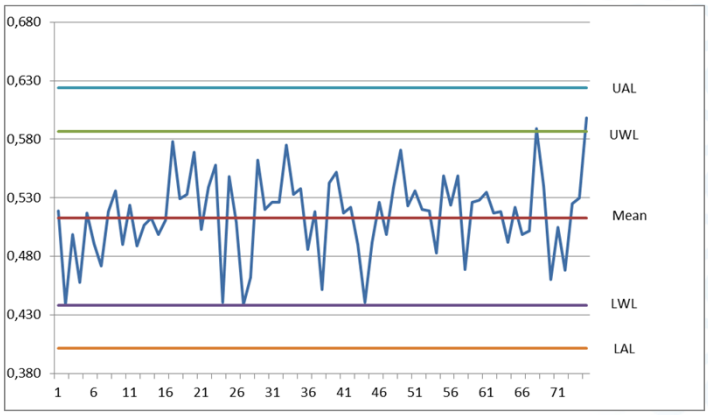
Meas. Number	Date	Measurement result (mg/L)
1	3.1.2018	0,519
2	5.1.2018	0,439
3	9.1.2018	0,499
4	11.1.2018	0,458
5	13.1.2018	0,517
6	15.1.2018	0,491
7	17.1.2018	0,472
8	19.1.2018	0,518
9	23.1.2018	0,536
10	26.1.2018	0,490
11	29.1.2018	0,524
12	1.2.2018	0,489
↓		↓
65	26.9.2018	0,522
66	2.10.2018	0,499
67	11.10.2018	0,502
68	16.10.2018	0,589
69	24.10.2018	0,540
70	12.11.2018	0,460
71	15.11.2018	0,505
72	27.11.2018	0,468
73	7.12.2018	0,525
74	17.12.2018	0,530
75	21.12.2018	0,598

Reference material is used as control sample.



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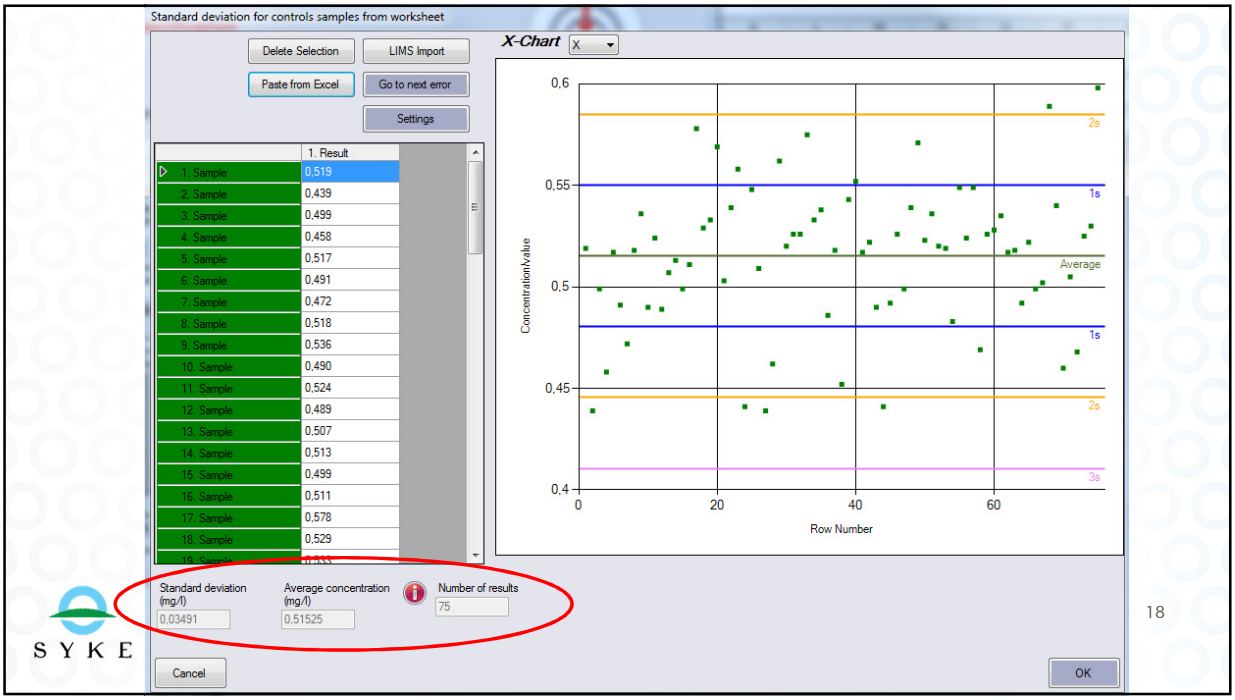

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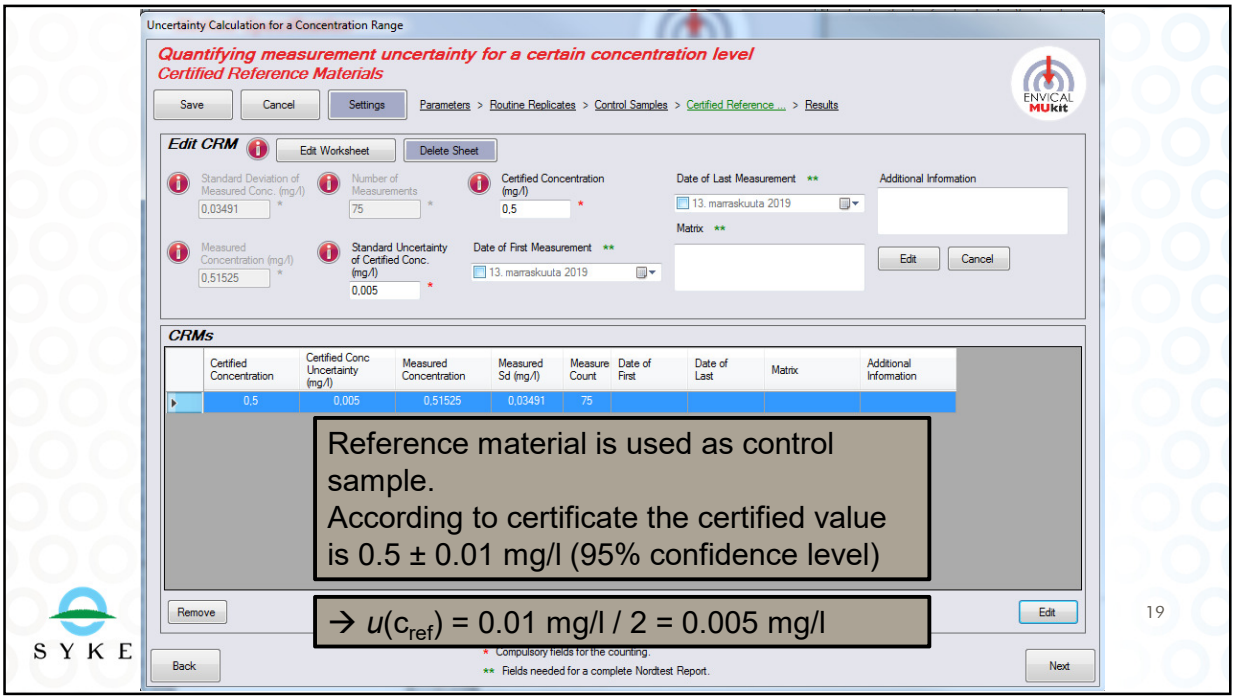

15.11.2019

Summary of the method's measurement uncertainties

Method information

Method name	Method_ABC
Measurand	Total nitrogen (Ntot) mass concentration
Sample Type (Matrix)	Waste water
Analysis Principle (Analyzer etc.)	In-house method based on standard EN ISO 11905-1, Determination of nitrogen -- Part 1: Method using oxidative digestion with peroxodisulfate
Sample preparation	Oxidation with peroxodisulfate in autoclave, 120 oC and 30 minutes
Additional information	Limit of quantification (LOQ): 0.15 mg/l Range of detection: up to 5 mg/l

Calculated Uncertainties at Different Measurand Levels

Concentration range (mg/l)	Within-lab Reproducibility Data	u (Rw)	Bias Data	u (bias)	Combined standard uncertainty	Expanded uncertainty
0,15-1	Control sample and routine sample replicates	0,042 mg/l	Certified reference material / Control Sample	0,017 mg/l	0,045 mg/l	0,10 mg/l

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ABSOLUTE MEASUREMENT UNCERTAINTY ESTIMATION

MEASUREMENT UNCERTAINTY ESTIMATION

Step	Action	Method_ABC	15.11.2019
1	Specify Measurand	Measurand: Total nitrogen (Ntot) mass concentration Concentration range: 0,15 - 1 mg/l Sample Type (Matrix): Waste water Analysis Principle (Analyzer etc.): In-house method based on standard EN ISO 11905-1, Determination of nitrogen -- Part 1: Method using oxidative digestion with peroxodisulfate Sample preparation: Oxidation with peroxodisulfate in autoclave, 120 oC and 30 minutes Additional information: Limit of quantification (LOQ): 0,15 mg/l Range of detection: up to 5 mg/l	
2	Quantify within-laboratory reproducibility, $u(R_w)$ A: Control sample B: Possible steps not covered by control sample	**A: Control samples:** Number of control samples: 75 Average concentration: 0,52 mg/l Standard deviation, s_{Rw} : 0,035 mg/l **B: Routine replicate samples :** Number of routine replicate series: 65 Number of parallell measurements: 3 - 4 Concentration range: 0,17 - 0,95 mg/l Pooled standard deviation, s_r : 0,024 mg/l $u(R_w) = \sqrt{{s_{Rw}}^2 + {s_r}^2}$ = 0,042 mg/l	
3	Quantify method and laboratory bias, $u(bias)$	**Method and laboratory bias from certified reference material:** Different certified reference materials count, N : 1	
4	Convert components to standard uncertainty	$u(R_w)$ = 0.042 mg/l $u(bias)$ = 0.017 mg/l	
5	Calculate combined standard uncertainty, u_c	$u_c = \sqrt{u(Rw)^2 + u(bias)^2}$ = 0.045 mg/l	
6	Calculate expanded uncertainty, U	$U = 2 \cdot u_c$ = 0.10 mg/l	

i	1
Certified concentration, $c_{ref\,i}$	0.5 mg/l
Standard uncertainty of certified concentration, $u(c_{ref\,i})$	0.005 mg/l
Measured concentration, c_i	0.52 mg/l
Standard deviation of measured concentration, s_{bias}	0.035 mg/l
Number of Measurements, n_i	75
$bias_i = c_i - c_{ref\,i}$	0.015 mg/l
Period of measurements	-
Sample Type (Matrix)	
Additional information	

$u(bias) = \sqrt{{bias_1}^2 + \left(\frac{s_{bias_1}}{\sqrt{n_1}}\right)^2 + u\left(c_{ref_1}\right)^2}$ = 0.017 mg/l

RELATIVE MEASUREMENT UNCERTAINTY ESTIMATION

MEASUREMENT UNCERTAINTY ESTIMATION

Step	Action	Method_ABC	11/15/2019
1	Specify Measurand	Measurand: Total nitrogen (Ntot) mass concentration Concentration range: 1 - 5 mg/l Sample Type (Matrix): Waste water Analysis Principle (Analyzer etc.): In-house method based on standard EN ISO 11905-1, Determination of nitrogen -- Part 1: Method using oxidative digestion with peroxodisulfate Sample preparation: Oxidation with peroxodisulfate in au minutes Additional information: Limit of quantification (LOQ): 0.1 up to 5 mg/l	
2	Quantify within-laboratory reproducibility, $u(R_w)$ A: Control sample B: Possible steps not covered by control sample	**A: Control samples:** Number of control samples: 123 Average concentration: 2.55 mg/l Standard deviation, s_{Rw} : 4.7 % **B: Routine replicate samples :** Number of routine replicate series: 50 Number of parallell measurements: 2 - 4 Concentration range: 1.14 - 4.92 mg/l Pooled standard deviation, s_r : 3.1 % $u(R_w) = \sqrt{{s_{Rw}}^2 + {s_r}^2}$ = 5.6 %	
3	Quantify method and laboratory bias, $u(bias)$	**Method and laboratory bias from certified reference material:** Different certified reference materials count, N : 2	
4	Convert components to standard uncertainty	$u(R_w)$ = 5.6 % $u(bias)$ = 1.9 %	
5	Calculate combined standard uncertainty, u_c	$u_c = \sqrt{u(Rw)^2 + u(bias)^2}$ = 5.9 %	
6	Calculate expanded uncertainty, U	$U = 2 \cdot u_c$ = 12 %	

i	1	2
Certified concentration, $c_{ref\,i}$	2.5 mg/l	4 mg/l
Standard uncertainty of certified concentration, $u(c_{ref\,i})$	0.8 %	0.6 %
Measured concentration, c_i	2.55 mg/l	3.95 mg/l
Standard deviation of measured concentration, s_{bias}	4.7 %	2.9 %
Number of Measurements, n_i	123	75
$bias_i = \frac{c_i - c_{ref\,i}}{c_{ref\,i}} 100\%$	2.1 %	-1.3 %
Period of measurements	-	-
Sample Type (Matrix)		
Additional information		

$u(c_{ref}) = \frac{\sum_{i=1}^{N} u(c_{ref\,i})}{N}$ = 0.7 %

$RMS_{bias} = \sqrt{\frac{\sum_{i=1}^{N} {bias_i}^2}{N}}$ = 1.7 %

$u(bias) = \sqrt{{RMS_{bias}}^2 + u(c_{ref})^2}$ = 1.9 %

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Calibration and contract laboratory

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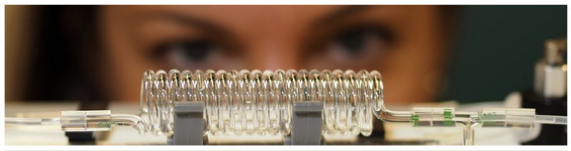

CURRENT

ENVICAL SYKE has released new version (v3.0) of the MUkit measurement uncertainty software. Major updates in the new version are as follows:

- The software calculates the repeatability component using the pooled standard deviation as presented in the latest edition (Ed.4) of Nordtest TR537 guide
- Software info texts have been updated to match the chapters in the Nordtest guide
- In addition to relative measurement uncertainty, also absolute measurement uncertainty calculation is available
- Software can still be downloaded and used for free of charge, but the program source code will not be open anymore.

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New version (v3.0) has now been released!

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MUkit
Measurement Uncertainty Kit

- About the program
- System requirements
- End User License Agreement
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- Authors & Acknowledgements

About the program

MUkit (Measurement Uncertainty Kit) is a measurement uncertainty software application, where calculations are based on the Nordtest TR537 handbook. By introducing the MUkit software, ENVICAL SYKE presents for chemical laboratories a user-friendly tool, which can be utilized for measurement uncertainty estimations often appearing to be a laborious task to perform. The traceability and comparability of analytical results require knowledge of the measurement uncertainty associated with a result. A uniform procedure for the estimation of measurement uncertainty is expected to improve the comparability of analysis results between laboratories.

The software allows laboratories to easily evaluate the measurement uncertainties utilizing:

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