MUkit - Measurement Uncertainty kit

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Eurachem/CITAC Scientific Workshop
Measurement uncertainty evaluation based on in-house validation data
25-26 October 2022

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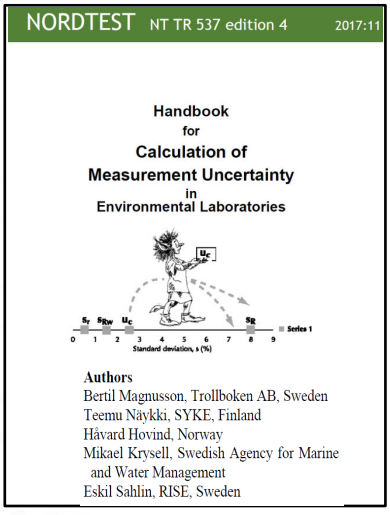
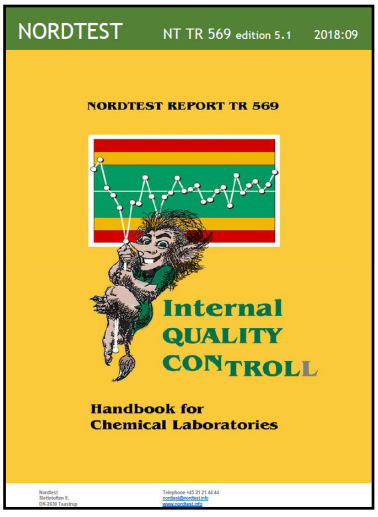
Popular Nordtest guides

www.nordtest.info





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http://www.nordtest.info/wp/2017/11/29/handbook-for-calculation-of-measurement-uncertainty-in-environmental-laboratories-nt-tr-537-edition-4/

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MUkit – measurement uncertainty program

- It is mainly 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 program, 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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Example: Total nitrogen in waste water

- Step 1: Specify measurand
- Total nitrogen mass concentration in waste water measured according to standard method EN ISO 11905-1.
- Uncertainty is evaluated using the results of:
  - routine sample replicates at different concentration levels
  - certified reference material

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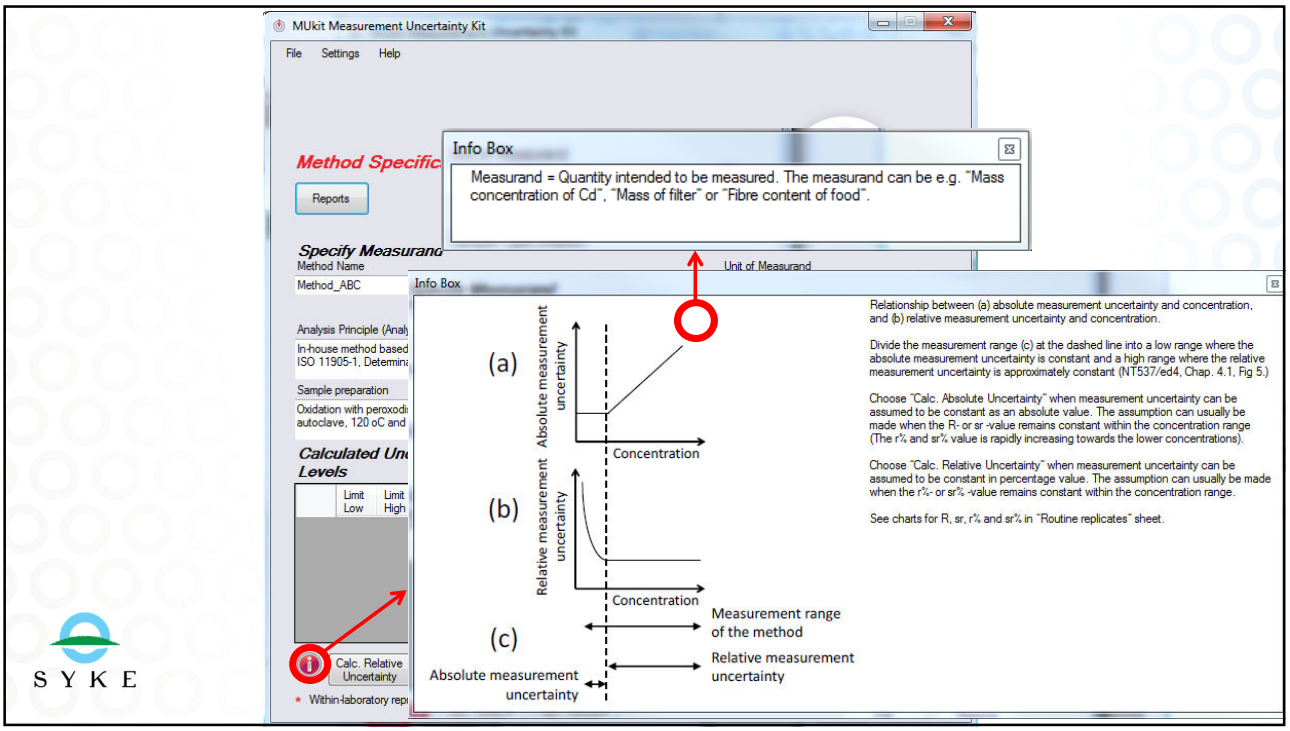
MUkit Measurement Uncertainty Kit
File
Settings
Help
Method Specific
Reports
Specify Measurand
Method Name
Method_ABC
Analysis Principle (Anal
In-house method based
ISO 11905-1, Determina
Sample preparation
Oxidation with peroxodi
autoclave, 120 oC and
Calculated Un
Levels
Limit Low
Limit High
Calc. Relative Uncertainty
Within-laboratory repr
Info Box
Measurand = Quantity intended to be measured. The measurand can be e.g. "Mass concentration of Cd", "Mass of filter" or "Fibre content of food".
Unit of Measurand
Info Box
(a)
Absolute measurement uncertainty
Concentration
(b)
Relative measurement uncertainty
Concentration
(c)
Measurement range of the method
Relative measurement uncertainty
Absolute measurement uncertainty
Relationship between (a) absolute measurement uncertainty and concentration, and (b) relative measurement uncertainty and concentration.
Divide the measurement range (c) at the dashed line into a low range where the absolute measurement uncertainty is constant and a high range where the relative measurement uncertainty is approximately constant (NT537/ed4, Chap. 4.1, Fig 5.)
Choose "Calc. Absolute Uncertainty" when measurement uncertainty can be assumed to be constant as an absolute value. The assumption can usually be made when the R- or sr -value remains constant within the concentration range (The r% and sr% value is rapidly increasing towards the lower concentrations).
Choose "Calc. Relative Uncertainty" when measurement uncertainty can be assumed to be constant in percentage value. The assumption can usually be made when the r%- or sr%- value remains constant within the concentration range.
See charts for R, sr, r% and sr% in "Routine replicates" sheet.
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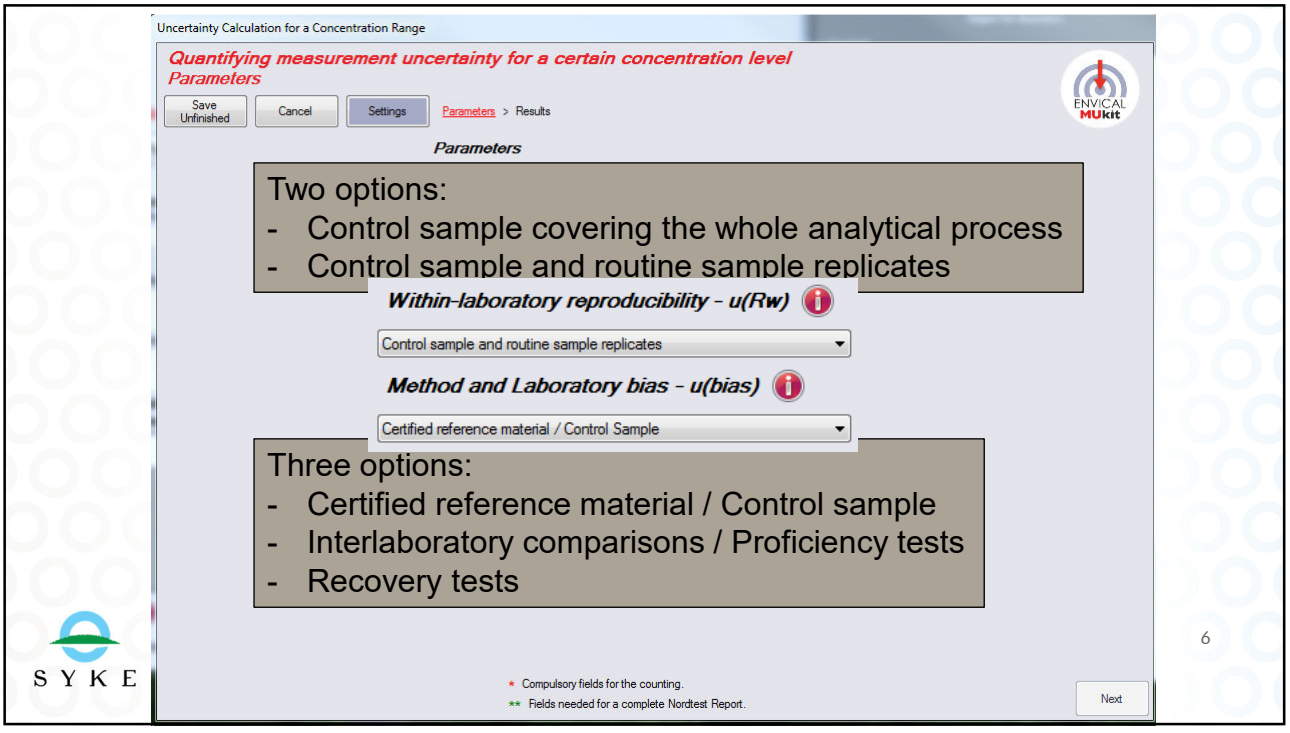
Uncertainty Calculation for a Concentration Range
Quantifying measurement uncertainty for a certain concentration level
Parameters
Save Unfinished
Cancel
Settings
Parameters > Results
ENVICAL MUkit
Parameters
Two options:
- Control sample covering the whole analytical process
- Control sample and routine sample replicates
Within-laboratory reproducibility - u(Rw)
Control sample and routine sample replicates
Method and Laboratory bias - u(bias)
Certified reference material / Control Sample
Three options:
- Certified reference material / Control sample
- Interlaboratory comparisons / Proficiency tests
- Recovery tests
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* Compulsory fields for the counting.
** Fields needed for a complete Nordtest Report.
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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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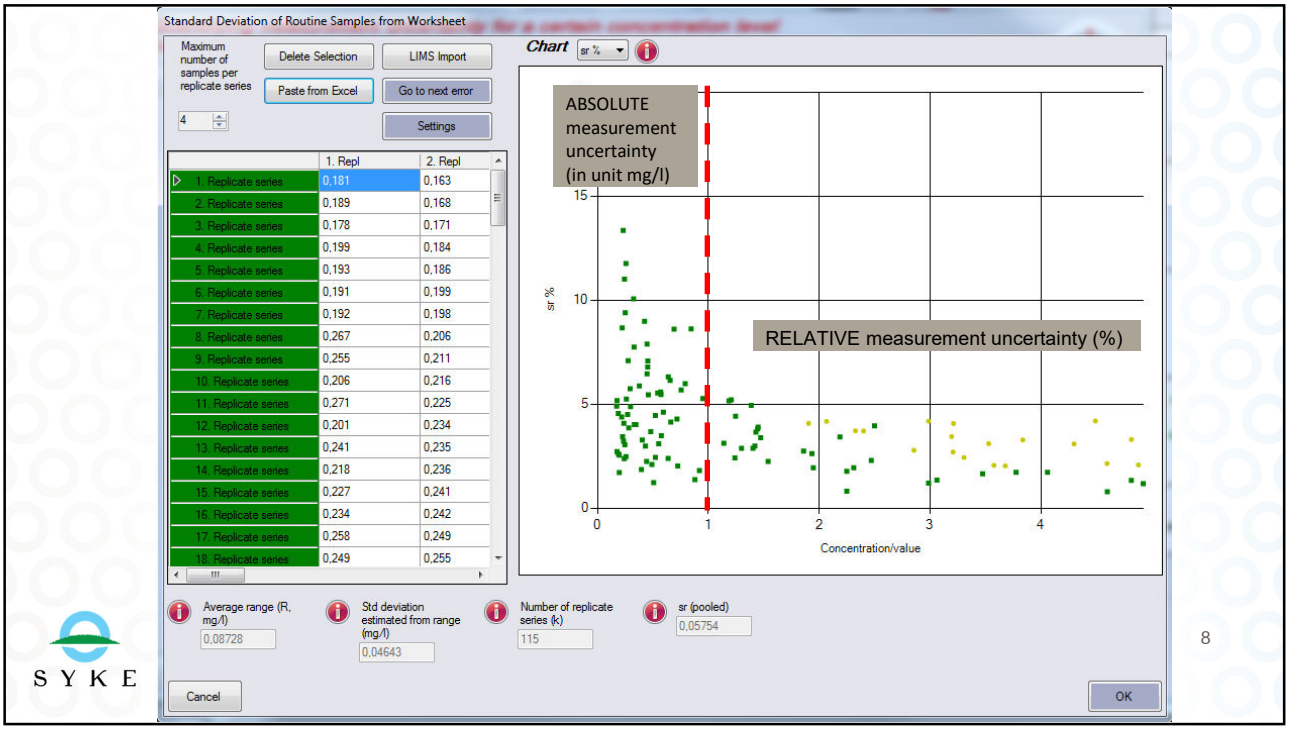

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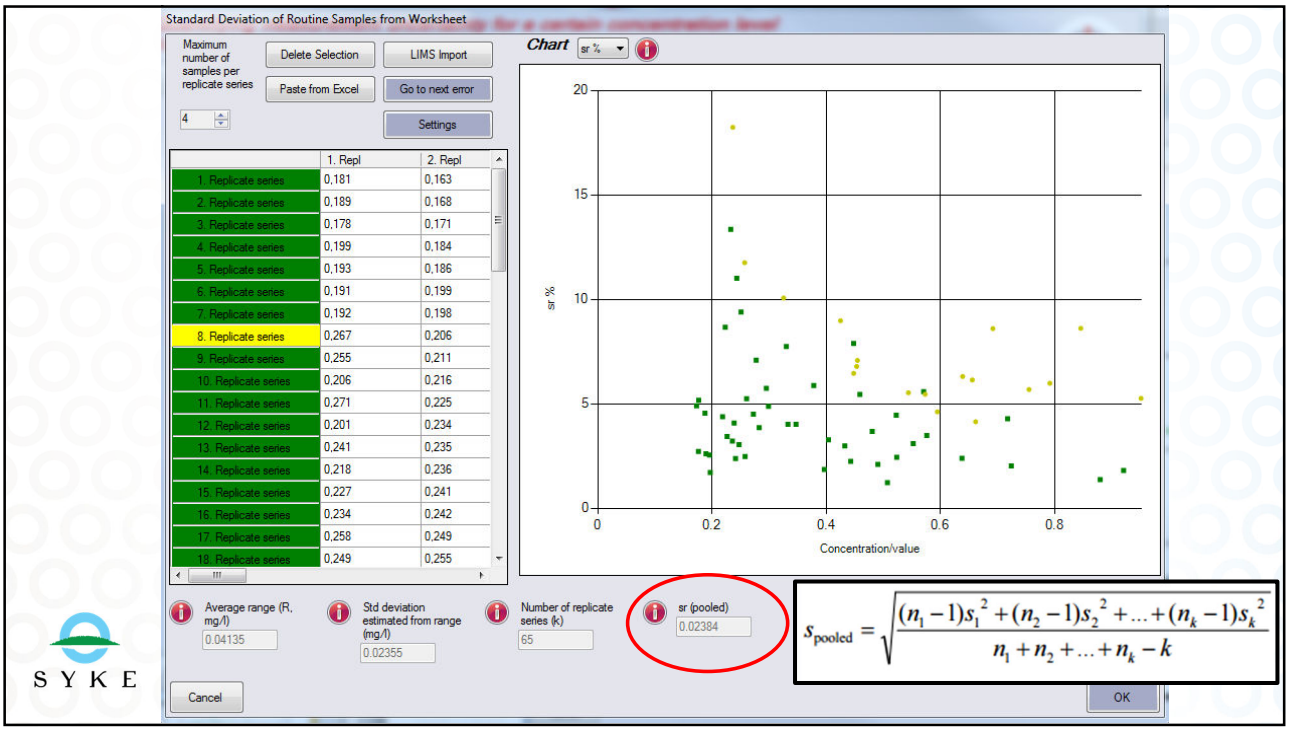

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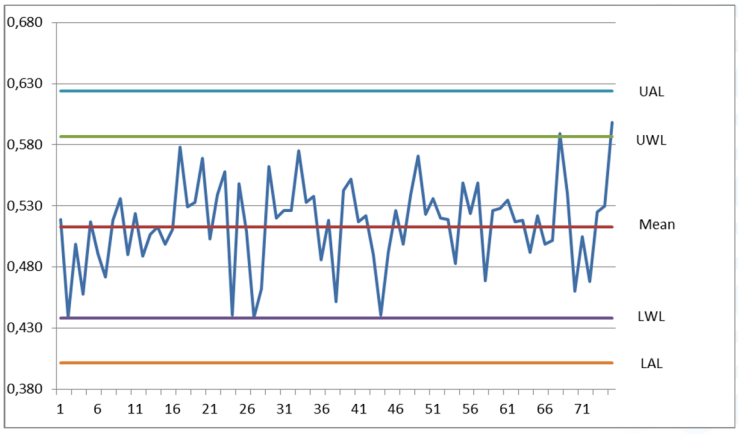
Meas. Number	Date	Measurement result (mg/L)
1	3.1.2018	0,519
2	5.1.2018	0,439
3	9.1.2018	0,499
4	11.1.2018	0,458
5	13.1.2018	0,517
6	15.1.2018	0,491
7	17.1.2018	0,472
8	19.1.2018	0,518
9	23.1.2018	0,536
10	26.1.2018	0,490
11	29.1.2018	0,524
12	1.2.2018	0,489
...	...	...
65	26.9.2018	0,522
66	2.10.2018	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

CRM 0.5 mg/L is used as control sample.



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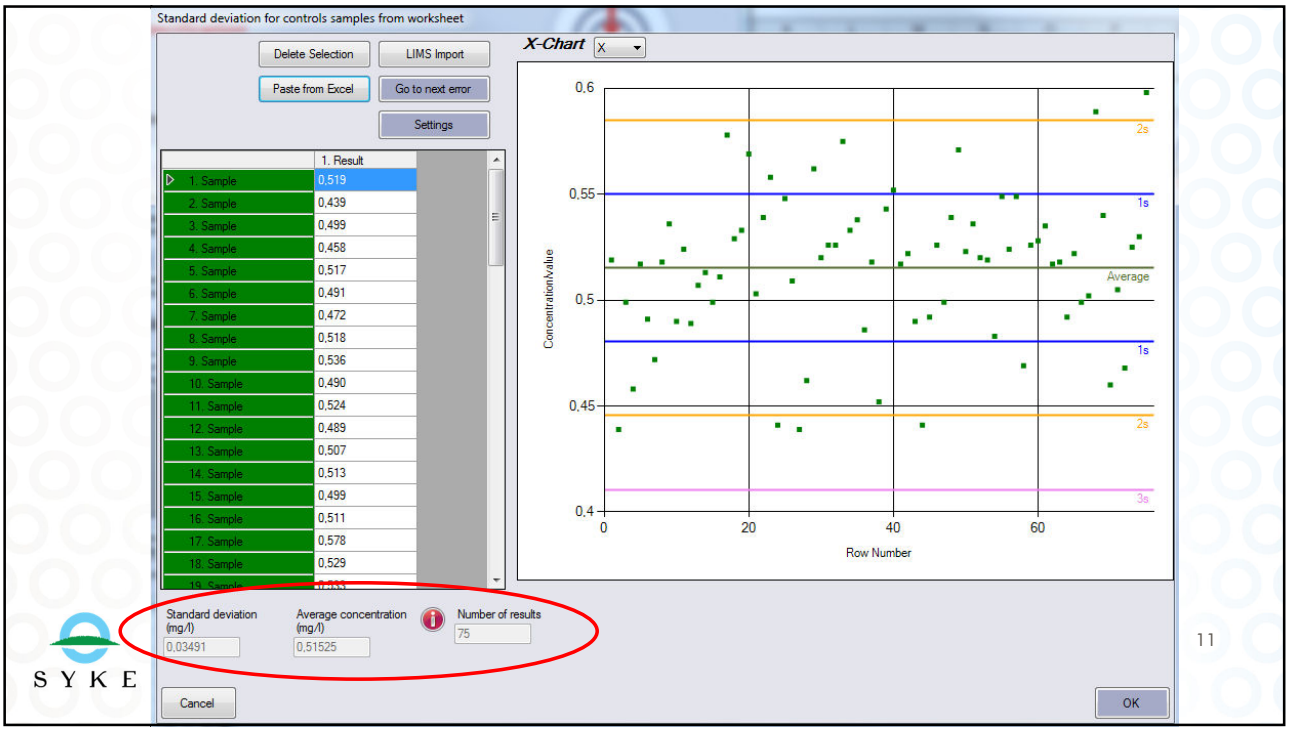
Standard deviation for controls samples from worksheet
Delete Selection
LIMS Import
Paste from Excel
Go to next error
Settings
X-Chart
1. Result
1. Sample 0,519
2. Sample 0,439
3. Sample 0,499
4. Sample 0,458
5. Sample 0,517
6. Sample 0,491
7. Sample 0,472
8. Sample 0,518
9. Sample 0,536
10. Sample 0,490
11. Sample 0,524
12. Sample 0,489
13. Sample 0,507
14. Sample 0,513
15. Sample 0,499
16. Sample 0,511
17. Sample 0,578
18. Sample 0,529
Concentration/value
Row Number
2s
1s
Average
1s
2s
3s
Standard deviation (mg/l) 0,03491
Average concentration (mg/l) 0,51525
Number of results 75
Cancel
OK
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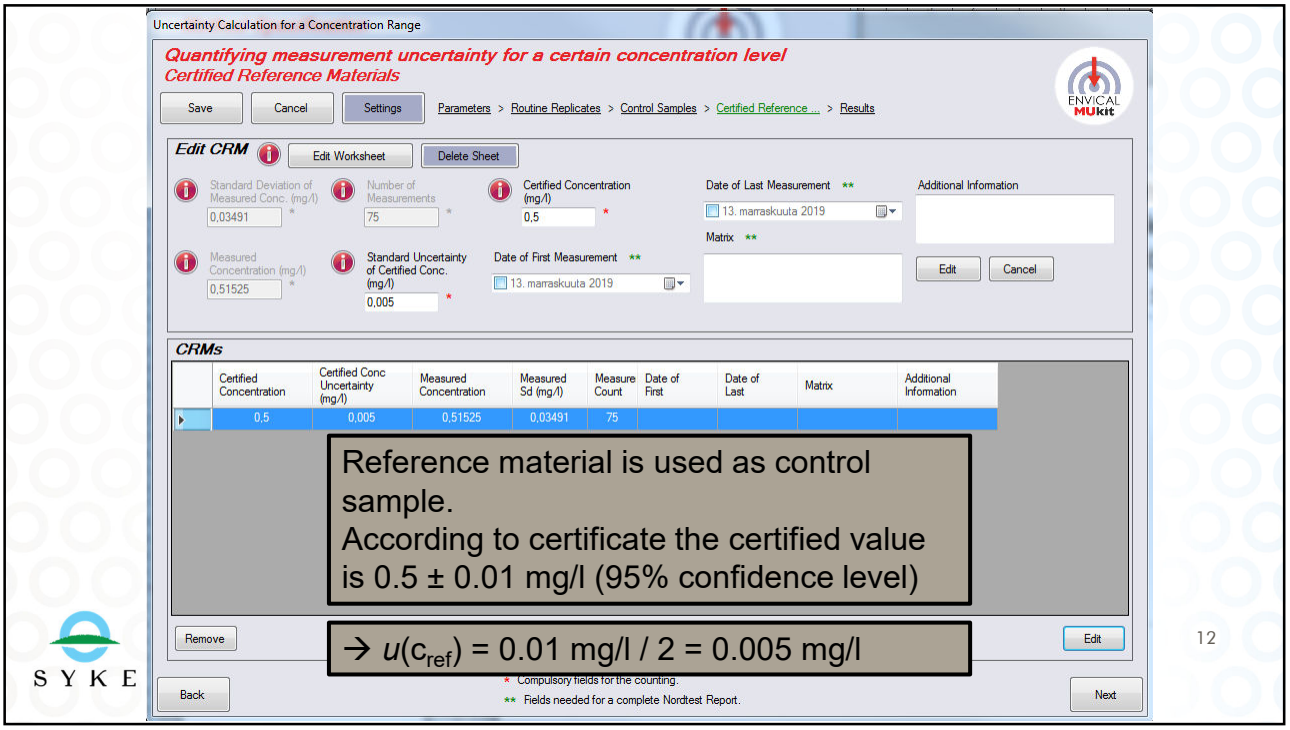
Uncertainty Calculation for a Concentration Range
Quantifying measurement uncertainty for a certain concentration level
Certified Reference Materials
Save
Cancel
Settings
Parameters > Routine Replicates > Control Samples > Certified Reference ... > Results
ENVICAL MUkit
Edit CRM
Edit Worksheet
Delete Sheet
Standard Deviation of Measured Conc. (mg/l) 0,03491
Number of Measurements 75
Certified Concentration (mg/l) 0,5
Date of Last Measurement ** 13. marraskuuta 2019
Additional Information
Measured Concentration (mg/l) 0,51525
Standard Uncertainty of Certified Conc. (mg/l) 0,005
Date of First Measurement ** 13. marraskuuta 2019
Matrix **
Edit
Cancel
CRMs
Certified Concentration
Certified Conc Uncertainty (mg/l)
Measured Concentration
Measured Sd (mg/l)
Measure Count
Date of First
Date of Last
Matrix
Additional Information
0,5 0,005 0,51525 0,03491 75
Reference material is used as control sample.
According to certificate the certified value is 0.5 ± 0.01 mg/l (95% confidence level)
→ u(cref) = 0.01 mg/l / 2 = 0.005 mg/l
Remove
Edit
Back
* Compulsory fields for the counting.
** Fields needed for a complete Nordtest Report.
Next
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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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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

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

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

ABSOLUTE MEASUREMENT UNCERTAINTY ESTIMATION

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MEASUREMENT UNCERTAINTY ESTIMATION

RELATIVE 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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for your attention
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$u(R_w) = \sqrt{s_{Rw}^2 + s_r}$
Method and laboratory bias fr
Different certified reference materials
i
Certified concentration, $c_{ref\,i}$
Standard uncertainty of certified concentration, $u(c_{ref\,i})$
Measured concentration, c_i
Standard deviation of measured concentration, s_{bias}
Number of Measurements, n_i
$bias_i = c_i - c_{refi}$
Period of measurements
Sample Type (Matrix)
Additional information
$u(bias) = \sqrt{bias_1^2 + \left(\frac{s_{bias}}{\sqrt{n_i}}\right)^2 + u\left(c_{ref_1}\right)^2}$
od and laboratory bias,
ents to standard
andard
$u(R_w)$ = 0.461 µg/l
$u(bias)$ = 0.117 µg/l
$u_c = \sqrt{u(Rw)^2 + u(bias)^2}$ = 0.47
$U = 2 \cdot u_c$ = 1.0 µg/l

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