University of Stuttgart
Germany
Institute for Sanitary Engineering,
Water Quality and Solid Waste Management
AQS Baden-Württemberg

INTERNATIONAL STANDARD **ISO 11352**

First edition
2012-07-01

Water quality — Estimation of measurement uncertainty based on validation and quality control data

Excel tool for estimation of measurement uncertainty from validation and quality control according to ISO 11352

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Principle of ISO 11352 and the NORDTEST technical report

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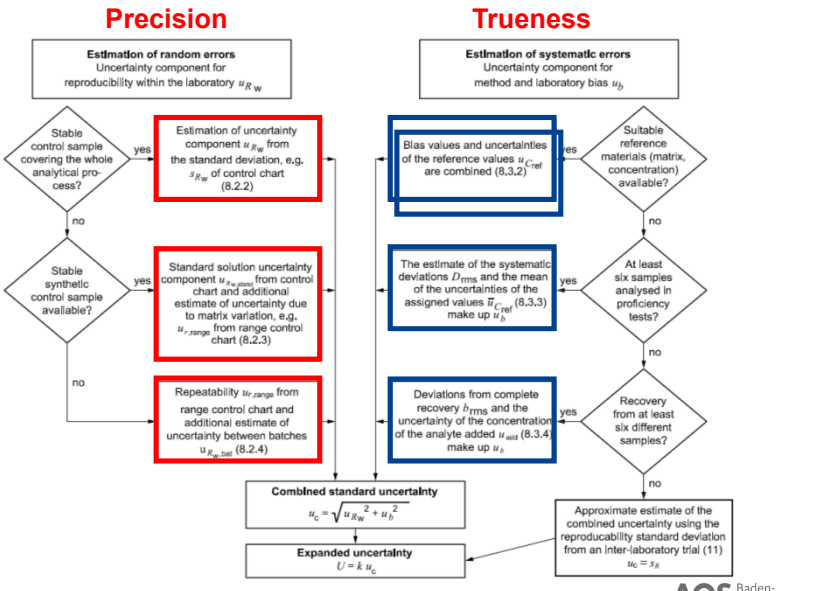

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General

- The idea of these EXCEL® sheets is to fully reflect the ISO standard ISO 11352
- Their design is intended to allow not only the estimation, but also use it for documentation

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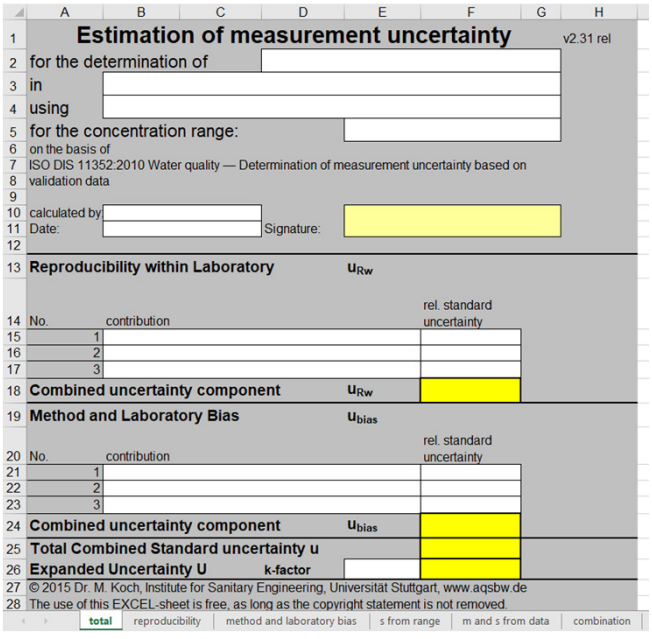
Sheet „total“



	A	B	C	D	E	F	G	H
1	**Estimation of measurement uncertainty**							v2.31 rel
2	for the determination of							
3	in							
4	using							
5	for the concentration range:							
6	on the basis of							
7	ISO DIS 11352:2010 Water quality — Determination of measurement uncertainty based on							
8	validation data							
9								
10	calculated by							
11	Date:			Signature:				
12								
13	**Reproducibility within Laboratory**				u_{Rw}			
14	No.	contribution				rel. standard uncertainty		
15	1							
16	2							
17	3							
18	**Combined uncertainty component**				u_{Rw}			
19	**Method and Laboratory Bias**				u_{bias}			
20	No.	contribution				rel. standard uncertainty		
21	1							
22	2							
23	3							
24	**Combined uncertainty component**				u_{bias}			
25	**Total Combined Standard uncertainty u**							
26	**Expanded Uncertainty U**			**k-factor**				
27	© 2015 Dr. M. Koch, Institute for Sanitary Engineering, Universität Stuttgart, www.aqsbw.de							
28	The use of this EXCEL-sheet is free, as long as the copyright statement is not removed.							

total | reproducibility | method and laboratory bias | s from range | m and s from data | combination

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Sheet „total“

1	**Estimation of measurement uncertainty**						v2.31 rel
2	for the determination of		mass concentration of Cd				
3	in		aqua regia extract of soil				
4	using		microwave digestion and ICP-OES				
5	for the concentration range:				X to Y mg/l		
6	on the basis of						
7	ISO DIS 11352:2010 Water quality — Determination of measurement uncertainty based on						
8	validation data						
9							
10	calculated by:	John Smith					
11	Date:	05 Jan 2019	Signature:				
12							
13	**Reproducibility within Laboratory**			u_{Rw}			
14	No.	contribution				rel. standard uncertainty	
15	1	X-Chart 03-178				5,46%	
16	2						
17	3						
18	**Combined uncertainty component**			u_{Rw}		**5,46%**	
19	**Method and Laboratory Bias**			u_{bias}			
20	No.	contribution				rel. standard uncertainty	
21	1	CRM BCR-142R				3,15%	
22	2						
23	3						
24	**Combined uncertainty component**			u_{bias}		**3,15%**	
25	**Total Combined Standard uncertainty u**					**6,30%**	
26	**Expanded Uncertainty U**			k-factor	2	**12,60%**	
27	© 2015 Dr. M. Koch, Institute for Sanitary Engineering, Universität Stuttgart, www.aqsbw.de						
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total | reproducibility | method and laboratory bias | s from range | m and s from data | combination

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Sheet „reproducibility“

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1	**Reproducibility within laboratory**				u_{Rw}						
2	**A) Control sample, covering the whole analytical process**										
3	Standard deviation:										
4	at concentration:										
5	rel standard deviation:				transfer to sheet "Total"						
6											
7	Remarks:										
8											
9											
10	**B) Control sample, not covering the whole analytical process**										
11	B.1 result from the control sample										
12	Standard deviation:										
13	at concentration:										
14	rel standard deviation:										
15	B.2 component from changing matrices and concentrations (from range)										
16	Mean rel. range:						sheet "s from range", cell M4				
17	Number of measurements for the range (2, 3, 4 or 5)										
18	rel. standard deviation:										
19	Combination:						transfer to sheet "Total"				
20											
21	Remarks:										
22											
23											
24	**C) Unstable control samples**										
25	C.1 Repeatability										
26	Mean rel. range:						sheet "s from range", cell M4				
27	Number of measurements for the range (2, 3, 4 or 5)										
28	Standard deviation:										
29	C.2 "Long term" component										
30	Estimation for standard deviation										
31	based on										
32	Combination:						transfer to sheet "Total"				
33											
34	Remarks:										
35											

In this sheet three approaches are given to quantify the uncertainty contribution caused by the imprecision.
Please choose the most appropriate one.

For more details see ISO DIS 11352:2010 Water quality — Determination of measurement uncertainty based on validation data.

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Sheet „reproducibility“

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	A	B	C	D	E	F	G	H	I	J	K
1	**Reproducibility within laboratory**				u_{Rw}						
2	**A) Control sample, covering the whole analytical process**										
3	Standard deviation:		0,04								
4	at concentration:		0,41								
5	rel standard deviation:		9,76%	transfer to sheet "Total"							
6											
7	Remarks:	30 results from X-Chart 03-178 Jul-Dec 2018									
8											
9											
10	**B) Control sample, not covering the whole analytical process**										
11	B.1 result from the control sample										
12	Standard deviation:										
13	at concentration:										
14	rel standard deviation:										
15	B.2 component from changing matrices and concentrations (from range)										
16	Mean rel. range:					sheet "s from range", cell M4					
17	Number of measurements for the range (2, 3, 4 or 5)										
18	rel. standard deviation:										
19	Combination:					transfer to sheet "Total"					
20											
21	Remarks:										
22											
23											
24	**C) Unstable control samples**										
25	C.1 Repeatability										
26	Mean rel. range:					sheet "s from range", cell M4					
27	Number of measurements for the range (2, 3, 4 or 5)										
28	Standard deviation:										
29	C.2 "Long term" component										
30	Estimation for standard deviation										
31	based on										
32	Combination:					transfer to sheet "Total"					
33											
34	Remarks:										
35											

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Please choose the most appropriate one.

For more details see ISO DIS 11352:2010 Water quality — Determination of measurement uncertainty based on validation data.

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Sheet „reproducibility“

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	A	B	C	D	E	F	G	H	I	J	K
1	**Reproducibility within laboratory**				u_{Rw}						
2	**A) Control sample, covering the whole analytical process**										
3	Standard deviation:										
4	at concentration:										
5	rel standard deviation:			transfer to sheet "Total"							
6											
7	Remarks:										
8											
9											
10	**B) Control sample, not covering the whole analytical process**										
11	B.1 result from the control sample										
12	Standard deviation:		0,45								
13	at concentration:		19,5								
14	rel standard deviation:		2,31%								
15	B.2 component from changing matrices and concentrations (from range)										
16	Mean rel. range:				5,61%	sheet "s from range", cell M4					
17	Number of measurements for the range (2, 3, 4 or 5)				2						
18	rel. standard deviation:				4,97%						
19	Combination:				5,48%	transfer to sheet "Total"					
20											
21	Remarks:	30 results X-Chart 03-178 Jul-Dec 2018 / 50 results from, R-Chart 01-143 2018									
22											
23											
24	**C) Unstable control samples**										
25	C.1 Repeatability										
26	Mean rel. range:					sheet "s from range", cell M4					
27	Number of measurements for the range (2, 3, 4 or 5)										
28	Standard deviation:										
29	C.2 "Long term" component										
30	Estimation for standard deviation										
31	based on										
32	Combination:					transfer to sheet "Total"					
33											
34	Remarks:										
35											

In this sheet three approaches are given to quantify the uncertainty contribution caused by the imprecision.
Please choose the most appropriate one.

For more details see ISO DIS 11352:2010 Water quality — Determination of measurement uncertainty based on validation data.

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Sheet „reproducibility“

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	A	B	C	D	E	F	G	H	I	J	K
1	**Reproducibility within laboratory**				u_{Rw}						
2	**A) Control sample, covering the whole analytical process**										
3	Standard deviation:										
4	at concentration:										
5	rel standard deviation:				transfer to sheet "Total"						
6											
7	Remarks:										
8											
9											
10	**B) Control sample, not covering the whole analytical process**										
11	B.1 result from the control sample										
12	Standard deviation:										
13	at concentration:										
14	rel standard deviation:										
15	B.2 component from changing matrices and concentrations (from range)										
16	Mean rel. range:				sheet "s from range", cell M4						
17	Number of measurements for the range (2, 3, 4 or 5)										
18	rel. standard deviation:										
19	Combination:				transfer to sheet "Total"						
20											
21	Remarks:										
22											
23											
24	**C) Unstable control samples**										
25	C.1 Repeatability										
26	Mean rel. range:				2,13%	sheet "s from range", cell M4					
27	Number of measurements for the range (2, 3, 4 or 5)				2						
28	Standard deviation:				1,89%						
29	C.2 "Long term" component										
30	Estimation for standard deviation				0,5%						
31	based on	Observed variations in the daily calibration									
32	Combination:				1,95%	transfer to sheet "Total"					
33											
34	Remarks:	50 results from, R-Chart 01-143 2018									
35											

In this sheet three approaches are given to quantify the uncertainty contribution caused by the imprecision.
Please choose the most appropriate one.

For more details see
ISO DIS 11352:2010 Water quality — Determination of measurement uncertainty based on validation data.

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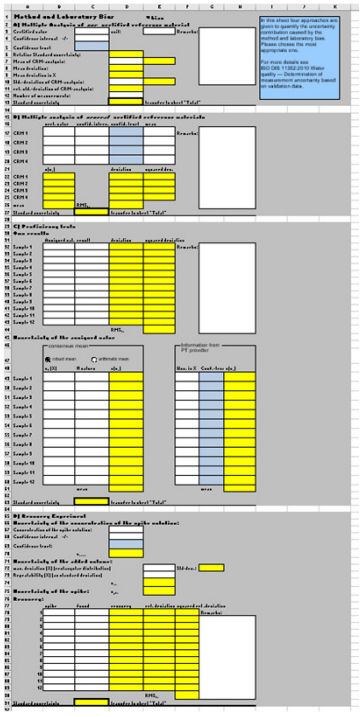

1 CRM

several CRMs

PT results

Recovery experiments

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Sheet „method and laboratory bias“

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Sheet „method and laboratory bias“ CRM part

	A	B	C	D	E	F	G	H	I	J	K
1	**Method and Laboratory Bias**			u_{bias}							
2	**A) Multiple Analysis of *one* certified reference material**										
3	Certified value			unit:		Remarks:					
4	Confidence interval +/-										
5	Confidence level										
6	Relative Standard uncertainty:										
7	Mean of CRM-analysis:										
8	Mean deviation:										
9	Mean deviation in %										
10	Std.-deviation of CRM-analysis:										
11	rel. std.-deviation of CRM-analysis:										
12	Number of measurements:										
13	Standard uncertainty				transfer to sheet "Total"						
14											
15	**B) Multiple analysis of *several* certified reference materials**										
16		cert. value	confid. interval	confid. level	mean						
17	CRM 1					Remarks:					
18	CRM 2										
19	CRM 3										
20	CRM 4										
21		$u(c_{ref})$		deviation	squared dev.						
22	CRM 1										
23	CRM 2										
24	CRM 3										
25	CRM 4										
26	mean		RMS_{bias}								
27	Standard uncertainty			transfer to sheet "Total"							

In this sheet four approaches are given to quantify the uncertainty contribution caused by the method and laboratory bias. Please chosse the most appropriate one.

For more details see ISO DIS 11352:2010 Water quality — Determination of measurement uncertainty based on validation data.

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Sheet „method and laboratory bias“ CRM part

	A	B	C	D	E	F	G	H	I	J	K
1	**Method and Laboratory Bias**			u_{bias}							
2	**A) Multiple Analysis of *one* certified reference material**										
3	Certified value		0,249	unit:	mg/kg	Remarks:	10 measurements of BCR 142R in 2018				
4	Confidence interval +/-		0,01								
5	Confidence level		95%								
6	Relative Standard uncertainty:			2,05%							
7	Mean of CRM-analysis:			0,2337	mg/kg						
8	Mean deviation:			-0,0153							
9	Mean deviation in %			-6,14%							
10	Std.-deviation of CRM-analysis:			0,0112	mg/kg						
11	rel. std.-deviation of CRM-analysis:			4,79%							
12	Number of measurements:			10							
13	Standard uncertainty			6,65%	transfer to sheet "Total"						
14											
15	**B) Multiple analysis of *several* certified reference materials**										
16		cert. value	confid. interval	confid. level	mean						
17	CRM 1					Remarks:					
18	CRM 2										
19	CRM 3										
20	CRM 4										
21		$u(c_{ref})$		deviation	squared dev.						
22	CRM 1										
23	CRM 2										
24	CRM 3										
25	CRM 4										
26	mean		RMS_{bias}								
27	Standard uncertainty			transfer to sheet "Total"							

In this sheet four approaches are given to quantify the uncertainty contribution caused by the method and laboratory bias. Please chosse the most appropriate one.

For more details see ISO DIS 11352:2010 Water quality — Determination of measurement uncertainty based on validation data.

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Sheet „method and laboratory bias“ CRM part

Method and Laboratory Bias u_{bias}

A) Multiple Analysis of *one* certified reference material

Certified value		unit:		Remarks:
Confidence interval +/-				
Confidence level				
Relative Standard uncertainty:				
Mean of CRM-analysis:				
Mean deviation:				
Mean deviation in %				
Std.-deviation of CRM-analysis:				
rel. std.-deviation of CRM-analysis:				
Number of measurements:				
Standard uncertainty		transfer to sheet "Total"		

In this sheet four approaches are given to quantify the uncertainty contribution caused by the method and laboratory bias. Please chosse the most appropriate one.

For more details see ISO DIS 11352:2010 Water quality — Determination of measurement uncertainty based on validation data.

B) Multiple analysis of *several* certified reference materials

	cert. value	confid. interval	confid. level	mean	
CRM 1	11,5	0,5	95%	11,9	Remarks:
CRM 2	22,6	0,8	95%	22,4	
CRM 3	34,3	1,0	95%	35,2	
CRM 4					

	$u(c_{ref})$		deviation	squared dev.
CRM 1	2,22%		3,48%	0,0012
CRM 2	1,81%		-0,88%	0,0001
CRM 3	1,49%		2,62%	0,0007
CRM 4				
mean	1,84%	RMS_{bias}	2,57%	
Standard uncertainty		3,16%	transfer to sheet "Total"	

10 measurements of BCR 142R in 2018

15 measurements of FTZ 364 in 2018

12 measurements of JTU 284 in 2018

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Sheet „method and laboratory bias“ PT part

C) Proficiency tests

Own results

	Assigned val.	result	deviation	squared deviation	
Sample 1					Remarks:
Sample 2					
Sample 3					
Sample 4					
Sample 5					
Sample 6					
Sample 7					
Sample 8					
Sample 9					
Sample 10					
Sample 11					
Sample 12					
			RMS_{bias}		

Uncertainty of the assigned value

consensus mean: ◉ robust mean ○ arithmetic mean

	s_R (%)	N values	$u(c_{ref})$	Information from PT provider: Unc. in %	Conf.-level	$u(c_{ref})$
Sample 1						
Sample 2						
Sample 3						
Sample 4						
Sample 5						
Sample 6						
Sample 7						
Sample 8						
Sample 9						
Sample 10						
Sample 11						
Sample 12						
		mean			mean	

Standard uncertainty: transfer to sheet "Total"

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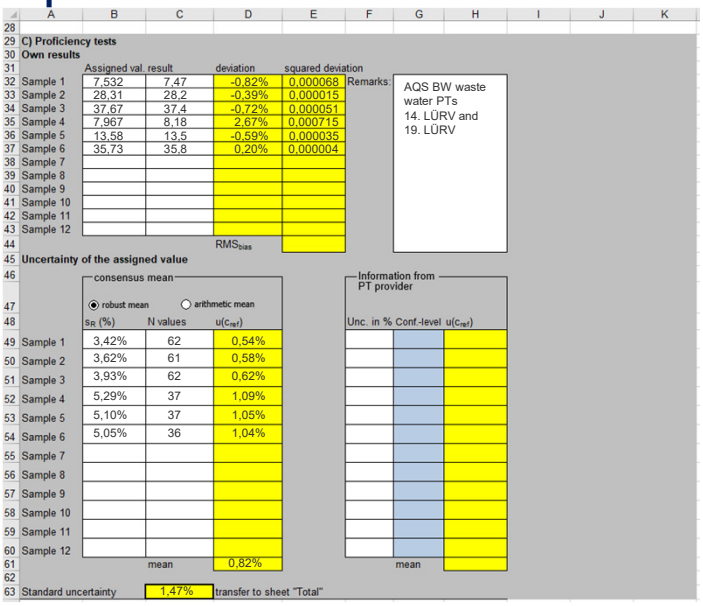
Sheet „method and laboratory bias“ PT part



C) Proficiency tests
Own results

	Assigned val.	result	deviation	squared deviation
Sample 1	7,532	7,47	-0,82%	0,000068
Sample 2	28,31	28,2	-0,39%	0,000015
Sample 3	37,67	37,4	-0,72%	0,000051
Sample 4	7,967	8,18	2,67%	0,000715
Sample 5	13,58	13,5	-0,59%	0,000035
Sample 6	35,73	35,8	0,20%	0,000004
Sample 7				
Sample 8				
Sample 9				
Sample 10				
Sample 11				
Sample 12				
			RMS_{bias}	

Remarks: AQS BW waste water PTs 14. LÜRV and 19. LÜRV

Uncertainty of the assigned value

consensus mean: (•) robust mean ( ) arithmetic mean

	s_R (%)	N values	$u(c_{ref})$
Sample 1	3,42%	62	0,54%
Sample 2	3,62%	61	0,58%
Sample 3	3,93%	62	0,62%
Sample 4	5,29%	37	1,09%
Sample 5	5,10%	37	1,05%
Sample 6	5,05%	36	1,04%
Sample 7			
Sample 8			
Sample 9			
Sample 10			
Sample 11			
Sample 12			
	mean		0,82%

Information from PT provider

Unc. in %	Conf.-level	$u(c_{ref})$
mean		

Standard uncertainty: 1,47% transfer to sheet "Total"

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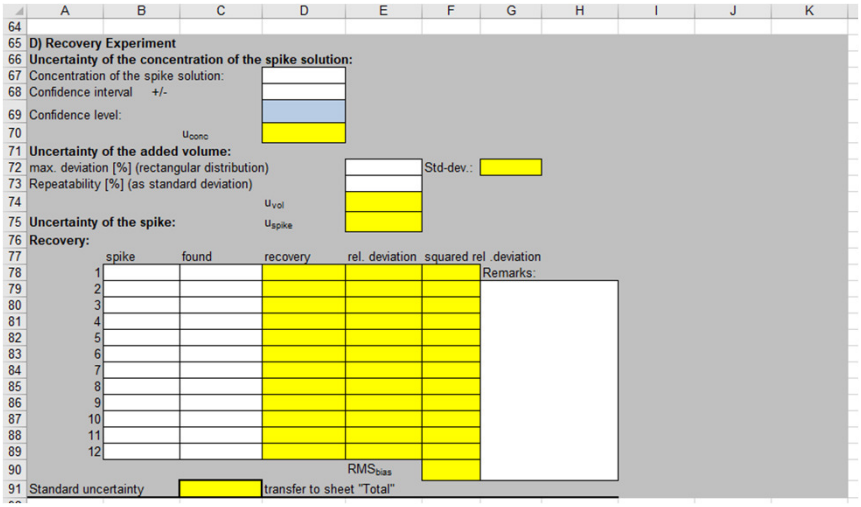
Sheet „method and laboratory bias“ Recovery experiment part



D) Recovery Experiment
Uncertainty of the concentration of the spike solution:
Concentration of the spike solution:
Confidence interval +/-
Confidence level:
u_{conc}
Uncertainty of the added volume:
max. deviation [%] (rectangular distribution)
Repeatability [%] (as standard deviation)
Std-dev.:
u_{vol}
Uncertainty of the spike: u_{spike}
Recovery:

	spike	found	recovery	rel. deviation	squared rel .deviation
1					
2					
3					
4					
5					
6					
7					
8					
9					
10					
11					
12					
				RMS_{bias}	

Remarks:

Standard uncertainty: transfer to sheet "Total"

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Sheet „method and laboratory bias“ Recovery experiment part

64											
65	**D) Recovery Experiment**										
66	**Uncertainty of the concentration of the spike solution:**										
67	Concentration of the spike solution:		125								
68	Confidence interval +/-		0,82								
69	Confidence level:		1 s								
70		u_{conc}	0,66%								
71	**Uncertainty of the added volume:**										
72	max. deviation [%] (rectangular distribution)				1,00%	Std-dev.:	0,58%				
73	Repeatability [%] (as standard deviation)										
74		u_{vol}			0,64%						
75	**Uncertainty of the spike:**	u_{spike}			0,91%						
76	**Recovery:**										
77		spike	found	recovery	rel. deviation	squared rel .deviation					
78	1	94,2	100,1	106,26%	6,26%	0,39%	Remarks:				
79	2	94,2	89,5	95,01%	-4,99%	0,25%					
80	3	94,2	103,3	109,66%	9,66%	0,93%					
81	4	94,2	101,3	107,54%	7,54%	0,57%					
82	5	94,2	90,4	95,97%	-4,03%	0,16%					
83	6	94,2	97,8	103,82%	3,82%	0,15%					
84	7	94,2	93	98,73%	-1,27%	0,02%					
85	8	94,2	88	93,24%	-6,58%	0,43%					
86	9	94,2	88,8	94,27%	-5,73%	0,33%					
87	10	94,2	100,1	100,85%	0,85%	0,01%					
88	11										
89	12										
90					RMS_{bias}	5,69%					
91	Standard uncertainty		5,76%	transfer to sheet "Total"							

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Support-sheet „m and s from data“

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	A	B	C	D	E
1		values			
2	1		mean:		
3	2		standard deviation		
4	3		rel. standard deviation		
5	4				
6	5				
7	6		Remarks:		
8	7				
9	8				
10	9				
11	10				
12	11				
13	12				
14	13				
15	14				
16	15				
17	16				
18	17				
19	18				
20	19				
21	20				
22	21				
23	22				
24	23				
25	24				
26	25				
27	26				
28	27				
29	28				
30	29				
31	30				
32	31				
33	32				
34	33				
35	34				

This sheet is a tool to calculate the arithmetic mean and the standard deviation from a data set.

If you need more than one calculation of this kind just copy the whole sheet "m and s from data"

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Support-sheet „m and s from data“

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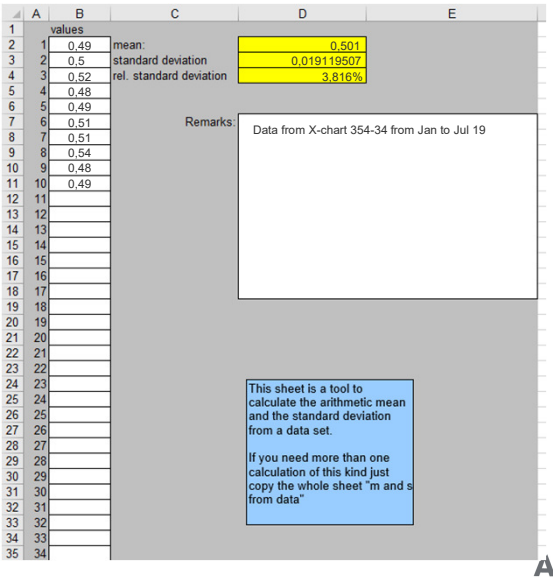

	A	B	C	D	E
1		values			
2	1	0,49	mean:	0,501	
3	2	0,5	standard deviation	0,019119507	
4	3	0,52	rel. standard deviation	3,816%	
5	4	0,48			
6	5	0,49			
7	6	0,51	Remarks:	Data from X-chart 354-34 from Jan to Jul 19	
8	7	0,51			
9	8	0,54			
10	9	0,48			
11	10	0,49			
12	11				
13	12				
14	13				
15	14				
16	15				
17	16				
18	17				
19	18				
20	19				
21	20				
22	21				
23	22				
24	23				
25	24				
26	25				
27	26				
28	27				
29	28				
30	29				
31	30				
32	31				
33	32				
34	33				
35	34				

This sheet is a tool to calculate the arithmetic mean and the standard deviation from a data set.

If you need more than one calculation of this kind just copy the whole sheet "m and s from data"

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Support-sheet „s from range“

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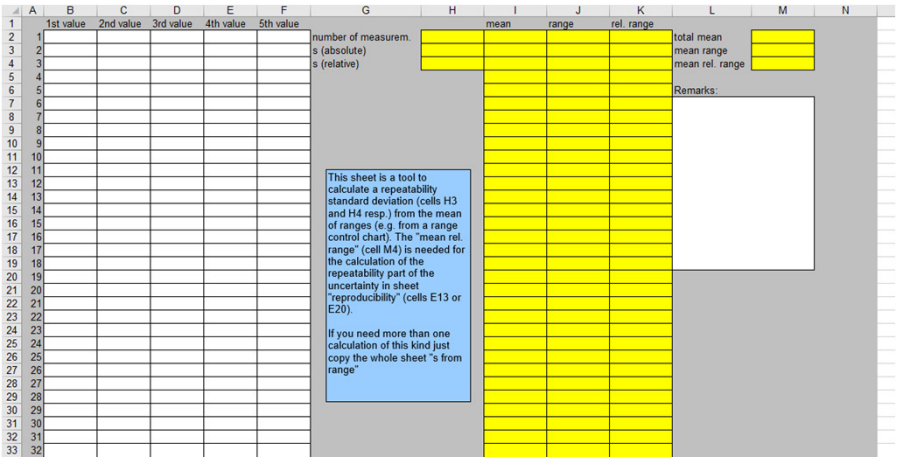

	A	B	C	D	E	F	G	H	I	J	K	L	M	N
1		1st value	2nd value	3rd value	4th value	5th value			mean	range	rel. range			
2	1						number of measurem.					total mean		
3	2						s (absolute)					mean range		
4	3						s (relative)					mean rel. range		
5	4													
6	5											Remarks:		
7	6													
8	7													
9	8													
10	9													
11	10													
12	11													
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26	25													
27	26													
28	27													
29	28													
30	29													
31	30													
32	31													
33	32													

This sheet is a tool to calculate a repeatability standard deviation (cells H3 and H4 resp.) from the mean of ranges (e.g. from a range control chart). The "mean rel. range" (cell M4) is needed for the calculation of the repeatability part of the uncertainty in sheet "reproducibility" (cells E13 or E20).

If you need more than one calculation of this kind just copy the whole sheet "s from range"

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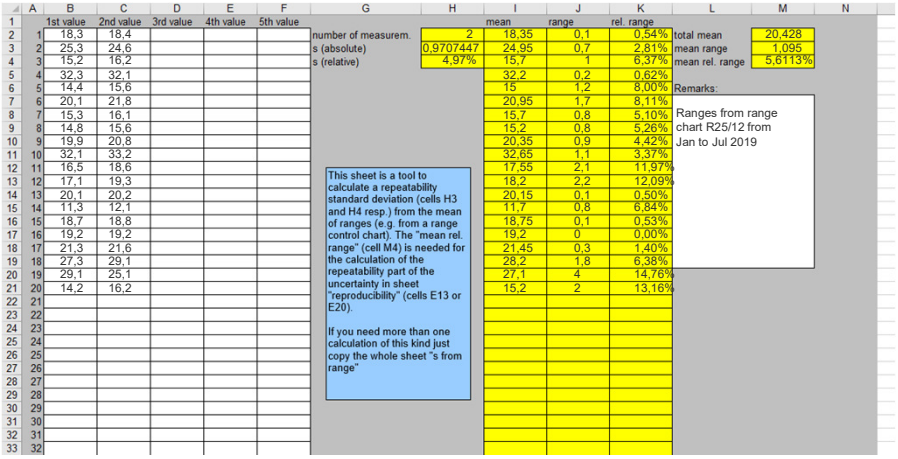
Support-sheet „s from range“



	1st value	2nd value	3rd value	4th value	5th value			mean	range	rel. range		
1	18,3	18,4				number of measurem.	2	18,35	0,1	0,54%	total mean	20,428
2	25,3	24,6				s (absolute)	0,9707447	24,95	0,7	2,81%	mean range	1,095
3	15,2	16,2				s (relative)	4,97%	15,7	1	6,37%	mean rel. range	5,6113%
4	32,3	32,1						32,2	0,2	0,62%		
5	14,4	15,6						15	1,2	8,00%	Remarks:	
6	20,1	21,8						20,95	1,7	8,11%		
7	15,3	16,1						15,7	0,8	5,10%	Ranges from range	
8	14,8	15,6						15,2	0,8	5,26%	chart R25/12 from	
9	19,9	20,8						20,35	0,9	4,42%	Jan to Jul 2019	
10	32,1	33,2						32,65	1,1	3,37%		
11	16,5	18,6						17,55	2,1	11,97%		
12	17,1	19,3						18,2	2,2	12,09%		
13	20,1	20,2						20,15	0,1	0,50%		
14	11,3	12,1						11,7	0,8	6,84%		
15	18,7	18,8						18,75	0,1	0,53%		
16	19,2	19,2						19,2	0	0,00%		
17	21,3	21,6						21,45	0,3	1,40%		
18	27,3	29,1						28,2	1,8	6,38%		
19	29,1	25,1						27,1	4	14,76%		
20	14,2	16,2						15,2	2	13,16%		

This sheet is a tool to calculate a repeatability standard deviation (cells H3 and H4 resp.) from the mean of ranges (e.g. from a range control chart). The "mean rel. range" (cell M4) is needed for the calculation of the repeatability part of the uncertainty in sheet "reproducibility" (cells E13 or E20).

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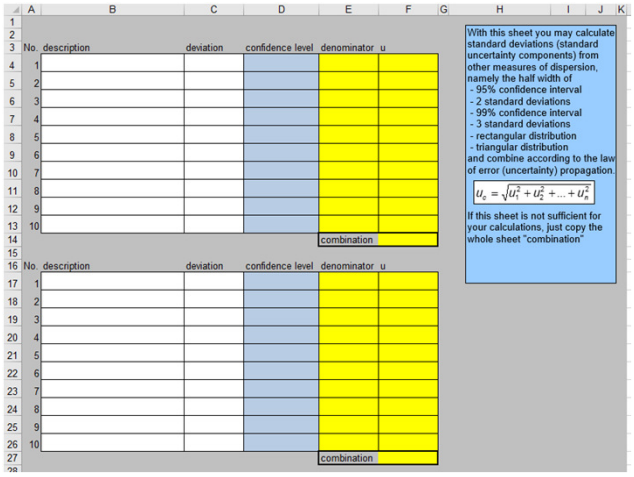
Support-sheet „combination“



No.	description	deviation	confidence level	denominator	u
1					
2					
3					
4					
5					
6					
7					
8					
9					
10					
				combination	

No.	description	deviation	confidence level	denominator	u
1					
2					
3					
4					
5					
6					
7					
8					
9					
10					
				combination	

With this sheet you may calculate standard deviations (standard uncertainty components) from other measures of dispersion, namely the half width of
- 95% confidence interval
- 2 standard deviations
- 99% confidence interval
- 3 standard deviations
- rectangular distribution
- triangular distribution

and combine according to the law of error (uncertainty) propagation.

$$u_c = \sqrt{u_1^2 + u_2^2 + \ldots + u_n^2}$$

If this sheet is not sufficient for your calculations, just copy the whole sheet "combination"

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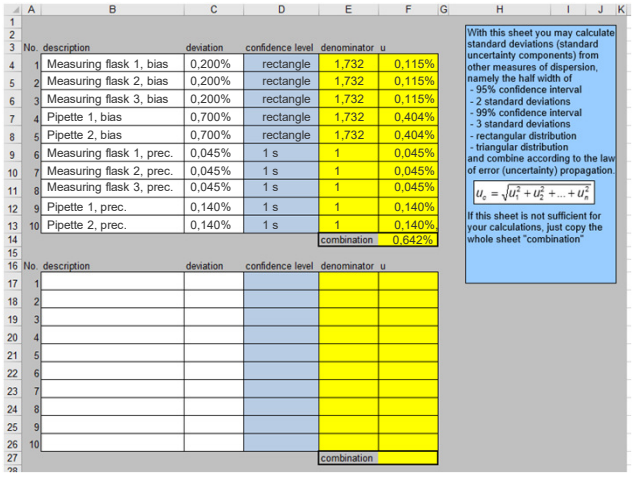
Support-sheet „combination“



No.	description	deviation	confidence level	denominator	u
1	Measuring flask 1, bias	0,200%	rectangle	1,732	0,115%
2	Measuring flask 2, bias	0,200%	rectangle	1,732	0,115%
3	Measuring flask 3, bias	0,200%	rectangle	1,732	0,115%
4	Pipette 1, bias	0,700%	rectangle	1,732	0,404%
5	Pipette 2, bias	0,700%	rectangle	1,732	0,404%
6	Measuring flask 1, prec.	0,045%	1 s	1	0,045%
7	Measuring flask 2, prec.	0,045%	1 s	1	0,045%
8	Measuring flask 3, prec.	0,045%	1 s	1	0,045%
9	Pipette 1, prec.	0,140%	1 s	1	0,140%
10	Pipette 2, prec.	0,140%	1 s	1	0,140%
				combination	0,642%

No.	description	deviation	confidence level	denominator	u
1					
2					
3					
4					
5					
6					
7					
8					
9					
10					
				combination	

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Availability

- The Excel sheets are available from
  - www.aqsbw.de/en -> download -> software -> freeware programmes in English
  - www.aqsbw.de -> Download -> Software -> Freeware-Programme in German
- Thank you for your attention

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