DLA
Dienstleistung
Lebensmittel
Analytik GbR

Evaluation-Report
proficiency test

DLA 18/2014

Ergot-Alkaloids in cereal product

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Contents

1 Introduction

The participation in proficiency testing schemes is an essential element of the quality-management-system of every laboratory testing food and feed, cosmetics and food contact materials. The implementation of proficiency tests enables the participating laboratories to prove their own analytical competence under realistic conditions. At the same time they receive valuable data regarding the validity of the particular testing method.
The purpose of DLA is to offer proficiency tests for selected parameters in concentrations with practical relevance.
Realisation and evaluation of the present proficiency test follows the technical requirements of DIN EN ISO/IEC 17043 (2010) and DIN ISO 13528:2009.

2 Evaluation

2.1 Assigned value

Because the analysed material was no certified reference material the robust mean of the submitted results was used as assigned value X. The distribution of submitted results showed no hint for bimodal distribution or other reasons for a higher variability.

2.2 Standard deviation

For comparison to the target standard deviation a robust standard deviation (Sx) was calculated.

2.3 Outliers

Statistical outliers were determined by Mandel´s-H-Statistic (95% significance). Detected outliers were stated for information only, when z-score was < -2 or > 2.

2.4 Target standard deviation

The target standard deviation of the assigned value is determined according to the following methods.

2.4.1 General model (Horwitz / Thompson)

The relative target standard deviation in % of the assigned value was derived from following equation (Horwitz)

$$\sigma_{(\%)} = 2^{(1-0,5\log X)} .$$

From the result the target standard deviation was calculated

$$\sigma = X * \sigma_{(\%)} / 100.$$

For analytes with a content below 120 µg/kg after the evaluation of a lot of mycotoxin- proficiency testing schemes after 1997 it was suggested for the target standard deviation a steady value of 22 % (Thompson), analogical:

$$\sigma = 0,22\ C / mr;$$

with σ = Target standard deviation for contents < 120 µg/kg
C = assigned content, expressed as a dimensionless mass ratio
mr = dimensionless mass ratio.

2.4.2 Precision experiment

Using the reproducibility standard deviation σ_R and the repeatability standard deviation σ_r of a precision experiment the between-laboratories standard deviation (σ_L) can be calculated :

$$\sigma_L = \sqrt{(\sigma_R^2 - \sigma_r^2)} .$$

And then, using the number of replicate measurements n, each participant is to perform, the standard deviation for proficiency assessment is calculated :

$$\sigma = \sqrt{(\sigma_L^2 + (\sigma_r^2 / n))} .$$

If available, the precision data from official methods for each parameter are used to calculate the target standard deviation.

2.5 z-Score

To assess the results of the participants the z-score is used. It indicates about which multiple of the target standard deviation (σ) the result (x) of the participant is deviating from the assigned value (X).

Participants' z-scores are derived as:

$$z = (x - X) / \sigma \quad ;$$

the requirements for the analytical performance are generally considered as fulfilled if

$$-2 \leq z \leq 2 \ .$$

2.6 z'-Score

The z'-Score can be used to assess the results of the participants in case the standard uncertainty must be considered (s. 2.8).

The calculation is carried out as follows (3)

$$z' = (x - X) / \sqrt{\hat{\sigma}^2 + u_X^2}$$

For the following evaluation $\sqrt{\hat{\sigma}^2 + u_X^2}$ is defined as $\hat{\sigma}'$, the target standard deviation considering the standard uncertainty of the results.

The requirements for the analytical performance are considered as fulfilled then, if

$$-2 \leq z' \leq 2 \ .$$

2.7 Quotient S^x/σ

Following the Horrat-value the results of a proficiency-test (PT) can be considered convincing, if the quotient of robust standard deviation and target standard deviation does not exceed the value of 2.
A value > 2 means an insufficient precision, i.e. the analytical method is too variable, or the variation between the test participants is higher than estimated. Thus the comparability of the results is not given.

2.8 Standard uncertainty

The assigned value X has a standard uncertainty u_X that depends on the analytical method, differences between the analytical methods used, the test material, the number of participant laboratories and perhaps on other factors. The standard uncertainty u_X for this PT is calculated as follows

$$u_X = 1{,}25 * S^x / \sqrt{(p)} \quad .$$

If $u_X \leq 0{,}3 * \sigma$ the standard uncertainty of the assigned value needs not be included in the interpretation of the results of the PT. The quotient u_X / σ is given in the evaluation.

3 Realisation

3.1 Test material

The test material was a mixture of rye flours, positively tested for ergot alkaloids. The material was ground, sieved, homogenized, packaged lightproof in portions to approximately 40 g and tested for homogeneity. The portions were numbered chronologically.

3.1.1 Homogeneity

The calculation of the repeatability standard deviation of the participants for ergometrine, ergotamine and total ergot alkaloids was used as an indicator of homogeneity. The results are in the same magnitude as specified in a recent evaluation of the analytical methods to determine ergot alkaloids. The repeatability standard deviation of the participants is given in the documentation. In the documentation the portion numbers are graphically assigned to the results of ergometrine and total ergot alkaloids. There is no trend recognizable in the results which could suggest inhomogeneity.

3.2 Tests

The test samples were sent to every participating laboratory in the 11th week of 2014. The test method was optional. The tests should be finished at 28.04.2014.

3.3 Results and statistic evaluation

The participants submitted their results in standard forms, which have been handed out with the samples.
The statistical evaluation was carried out if at least 7 results were submitted. In this PT all 13 parameters were evaluated. The evaluation was always carried out according to Horwitz/Thompson.
Queried and documented were single results and the testing method applied. Two participants did not submit any results, one participant submitted his results delayed and the other participants submitted their results in time.

4 Results

All following tables are anonymized. With the delivering of the evaluation-report the participants are informed about their individual evaluation-number.

In the upper table the characteristics are listed:

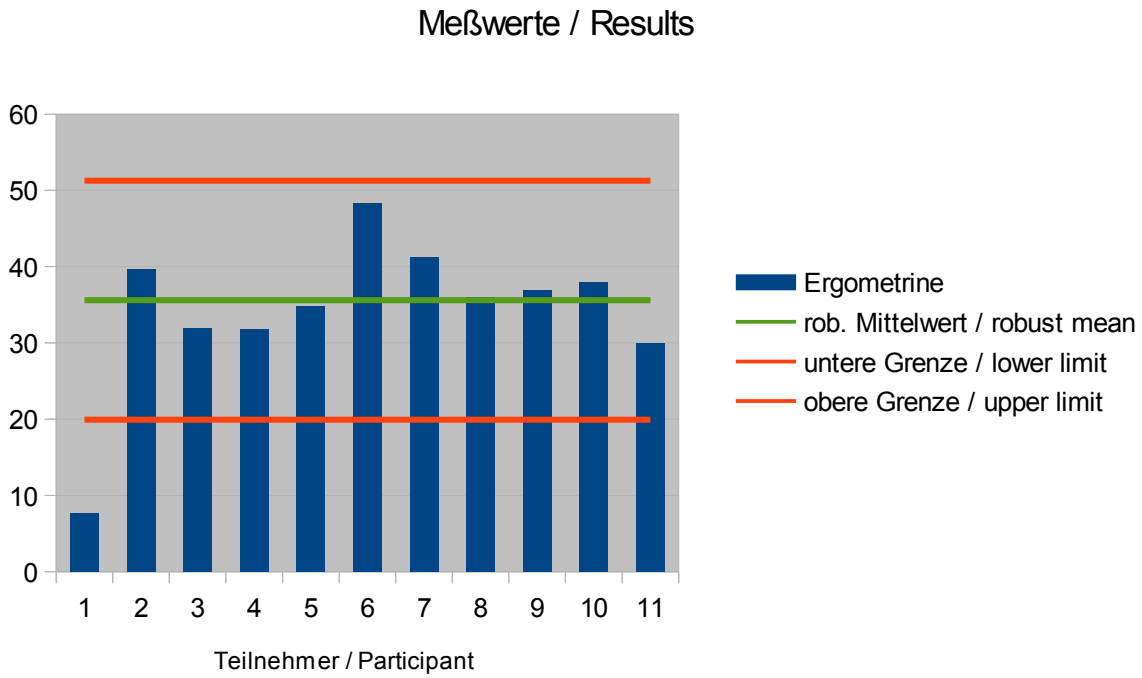
number of the results
number of outliers
mean
median
robust mean (X)
robust standard deviation(S^x)
target standard deviation (σ) or (σ´)
lower limit of target range (X – 2σ) or (X – 2σ´)
upper limit of target range (X + 2σ) or (X + 2σ´)
quotient S^x/σ
standard uncertainty u_x
quotient u_X/σ
results in target range.

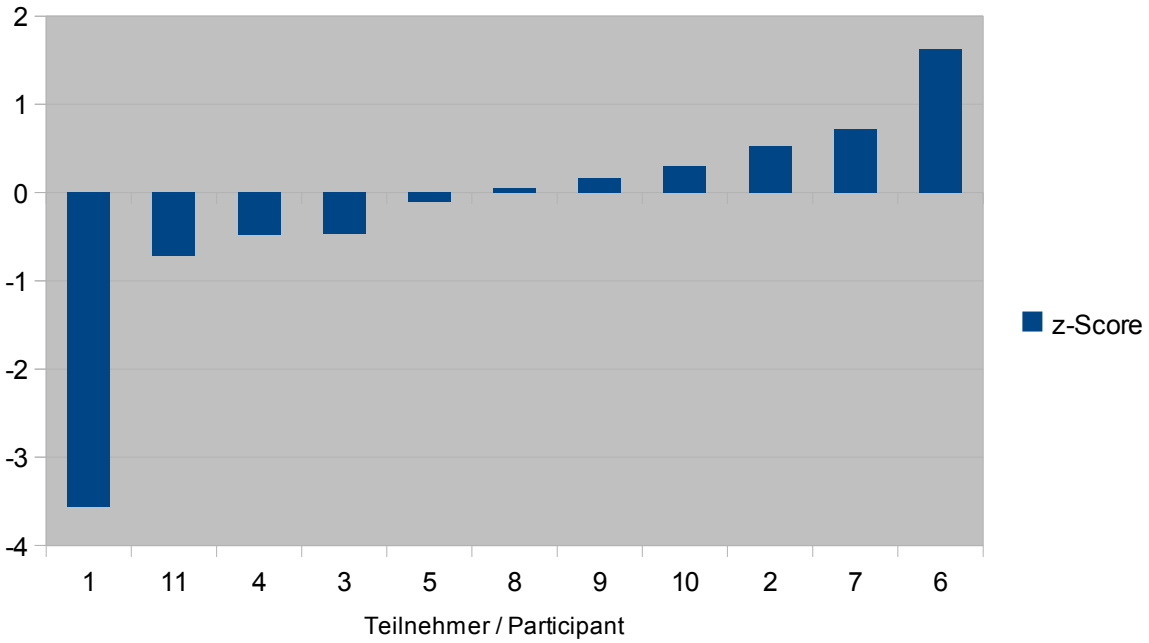
In the lower table -laboratories- the individual results of the participating laboratory are listed:

evaluation number	test result	deviation from assigned value	Z-Score (σ)	remarks

4.1 Ergometrine in µg/kg

Statistic Data	
number of the results	11
number of outliers	1
mean	34,2
median	36,0
robust mean (X)	35,6
robust standard deviation (S^x)	5,95
target standard deviation (σ)	7,83
lower limit of target range	19,9
upper limit of target range	51,3
quotient S^x/σ	0,8
standard uncertainty U^x	2,2
quotient U^x/σ	0,3
results in target range	10
percent in target range	91

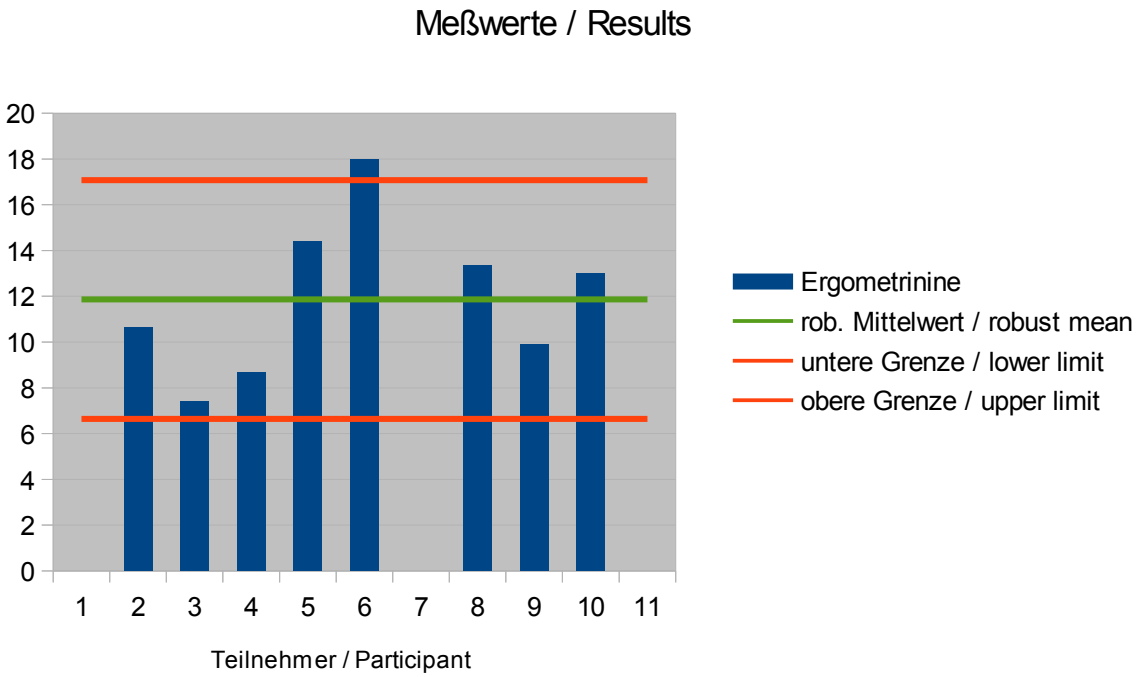


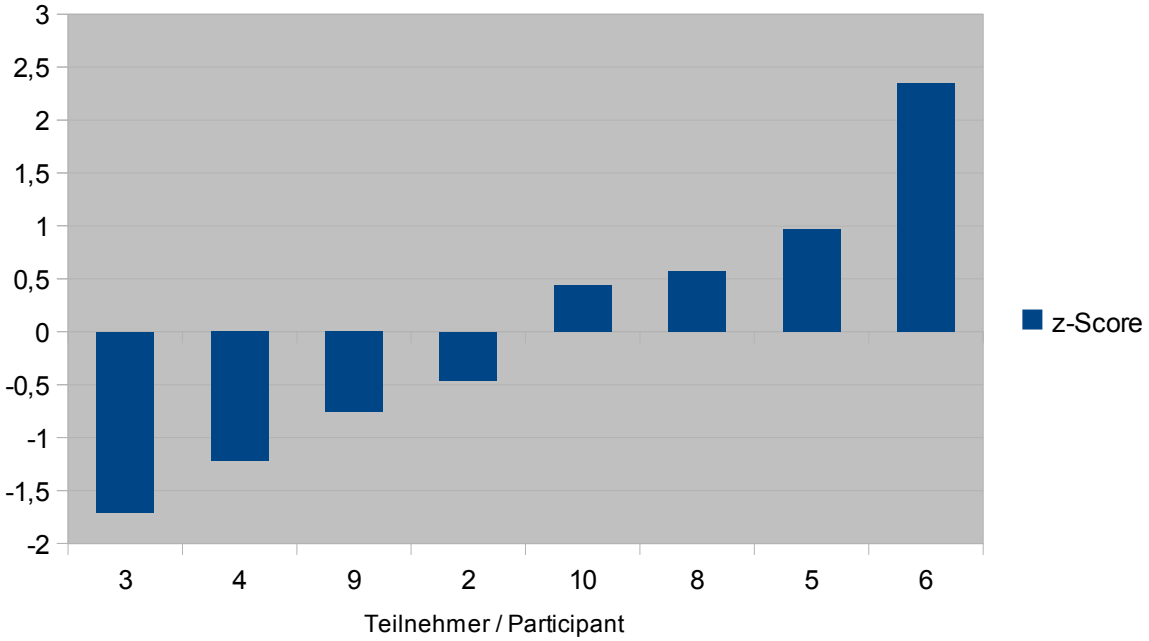


Auswerte nummer / Evaluation number	Ergometrine	Abweichung / Deviation	z-Score	Hinweis / Remark
1	7,7	-27,9	-3,6	Ausreisser / Outlier
2	39,69	4,1	0,5	
3	31,91	-3,68	-0,5	
4	31,8	-3,8	-0,5	
5	34,8	-0,8	-0,1	
6	48,3	12,7	1,6	
7	41,2	5,6	0,7	
8	36,03	0,43	0,1	
9	36,93	1,33	0,2	
10	38	2,4	0,3	
11	30	-5,6	-0,7	

4.2 Ergometrinine in µg/kg

Statistic Data	
number of the results	8
number of outliers	0
mean	11,9
median	11,8
robust mean (X)	11,9
robust standard deviation (S^x)	3,77
target standard deviation (σ)	2,61
lower limit of target range	6,64
upper limit of target range	17,1
quotient S^x/σ	1,4
standard uncertainty U^x	1,7
quotient U^x/σ	0,6
results in target range	7
percent in target range	88

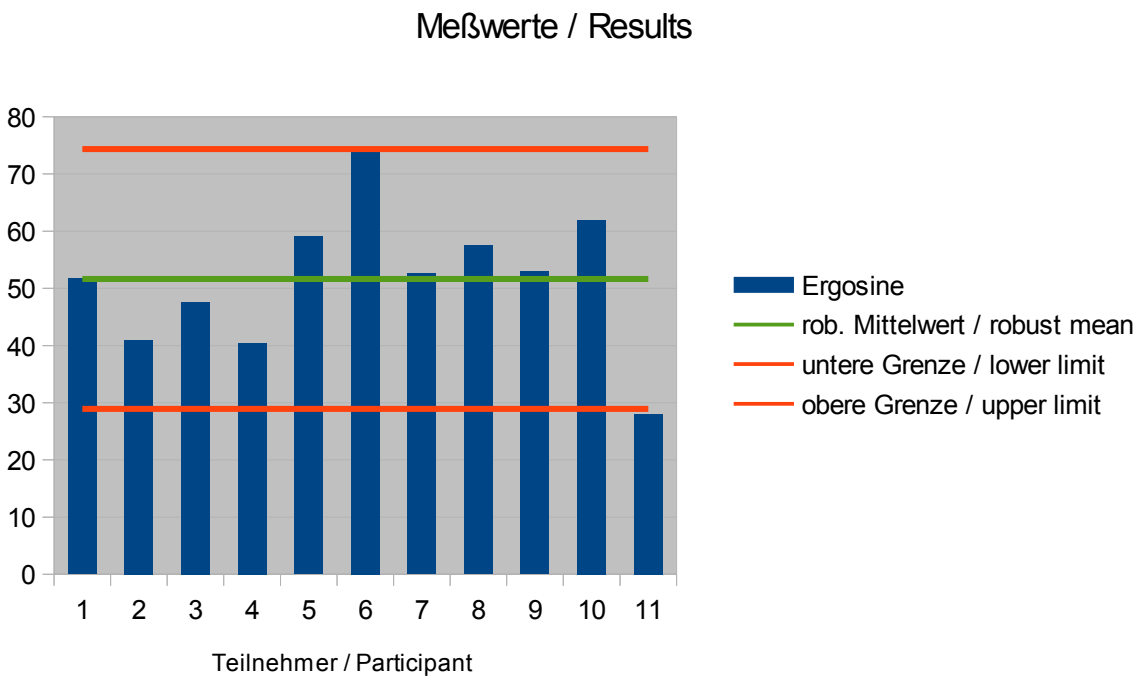


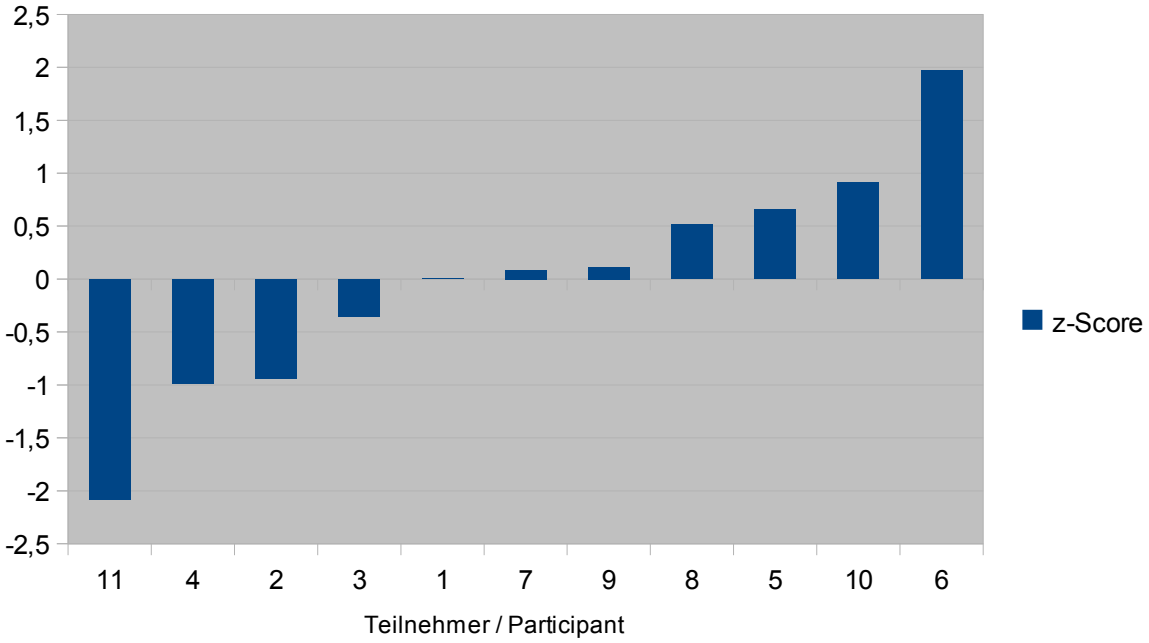


Auswerte nummer / Evaluation number	Ergometrinine	Abweichung / Deviation	z-Score	Hinweis / Remark
1				
2	10,66	-1,2	-0,5	
3	7,4	-4,46	-1,7	
4	8,67	-3,19	-1,2	
5	14,4	2,54	1,0	
6	18	6,14	2,4	
7				
8	13,36	1,5	0,6	
9	9,88	-1,98	-0,8	
10	13	1,14	0,4	
11				

4.3 Ergosine in µg/kg

Statistic Data	
number of the results	11
number of outliers	1
mean	51,5
median	52,6
robust mean (X)	51,6
robust standard deviation (S^x)	11,8
target standard deviation (σ)	11,4
lower limit of target range	28,9
upper limit of target range	74,4
quotient S^x/σ	1,0
standard uncertainty U^x	4,5
quotient U^x/σ	0,4
results in target range	10
percent in target range	91

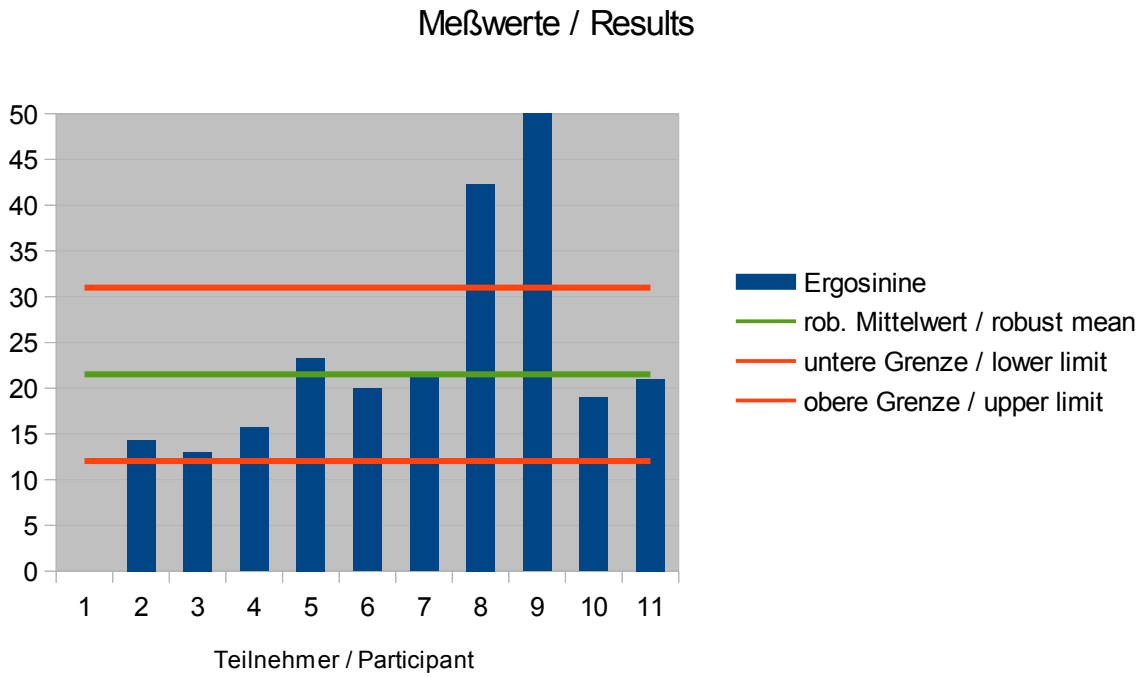


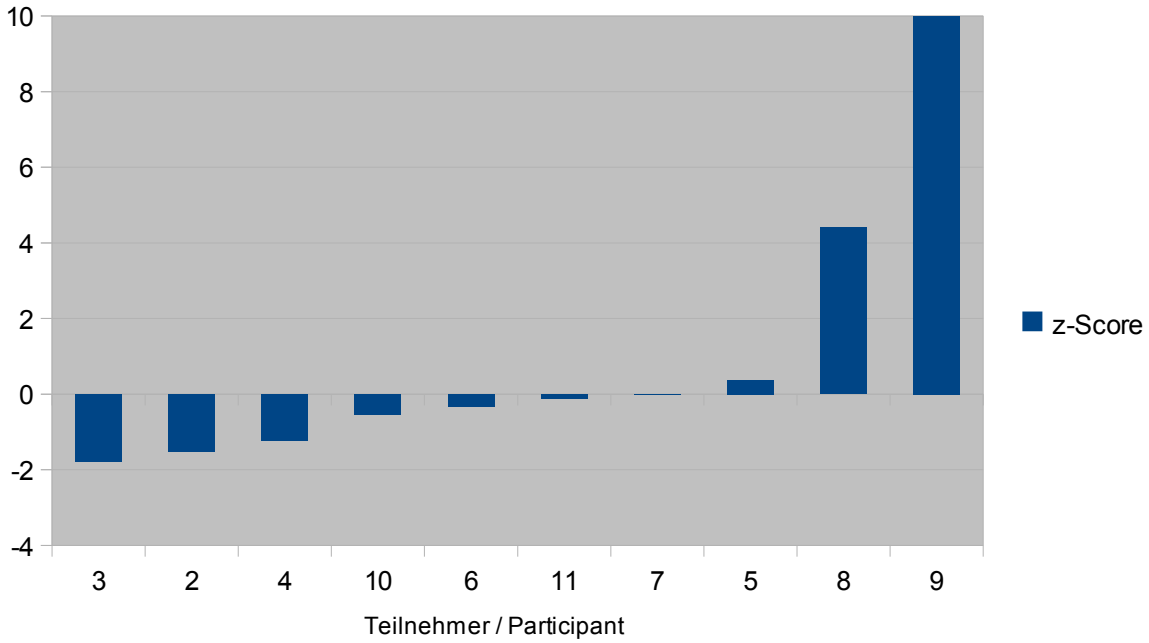


Auswerte nummer / Evaluation number	Ergosine	Abweichung / Deviation	z-Score	Hinweis / Remark
1	51,71	0,06	0,0	
2	40,93	-10,71	-0,9	
3	47,61	-4,04	-0,4	
4	40,4	-11,24	-1,0	
5	59,1	7,46	0,7	
6	74	22,36	2,0	
7	52,6	0,96	0,1	
8	57,54	5,89	0,5	
9	52,92	1,28	0,1	
10	62	10,36	0,9	
11	28	-23,64	-2,1	Ausreisser / Outlier

4.4 Ergosinine in µg/kg

Statistic Data	
number of the results	10
number of outliers	2
mean	37,6
median	20,5
robust mean (X)	21,5
robust standard deviation (S^x)	8,14
target standard deviation (σ)	4,73
lower limit of target range	12,0
upper limit of target range	31,0
quotient S^x/σ	1,7
standard uncertainty U^x	3,2
quotient U^x/σ	0,7
results in target range	8
percent in target range	80

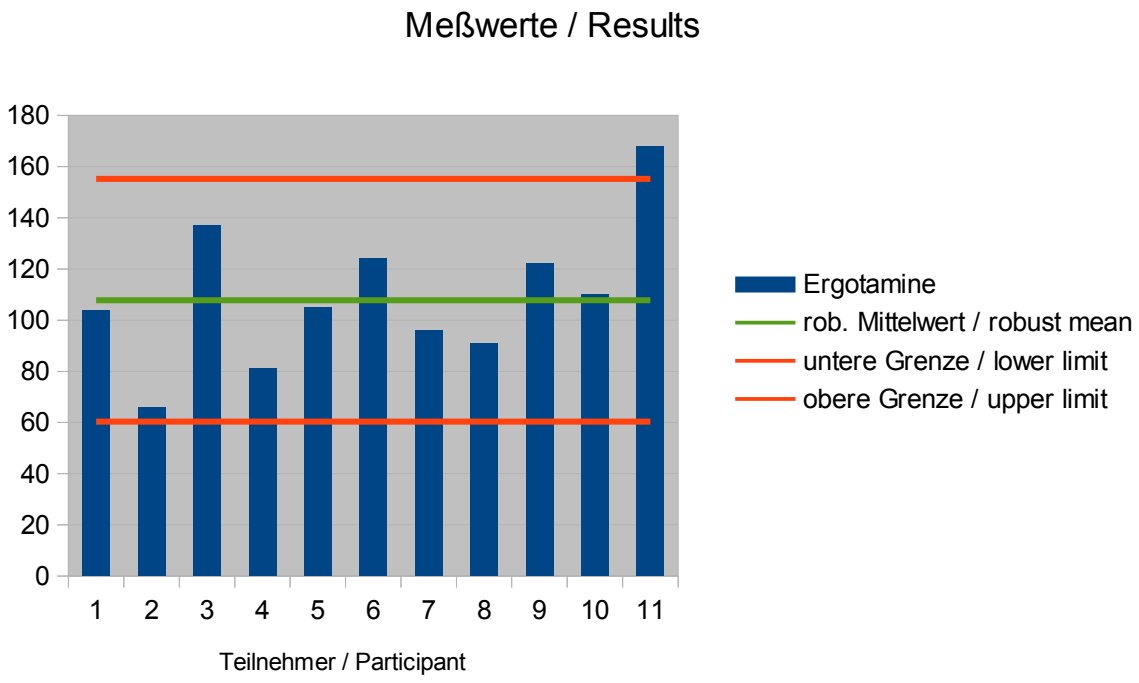


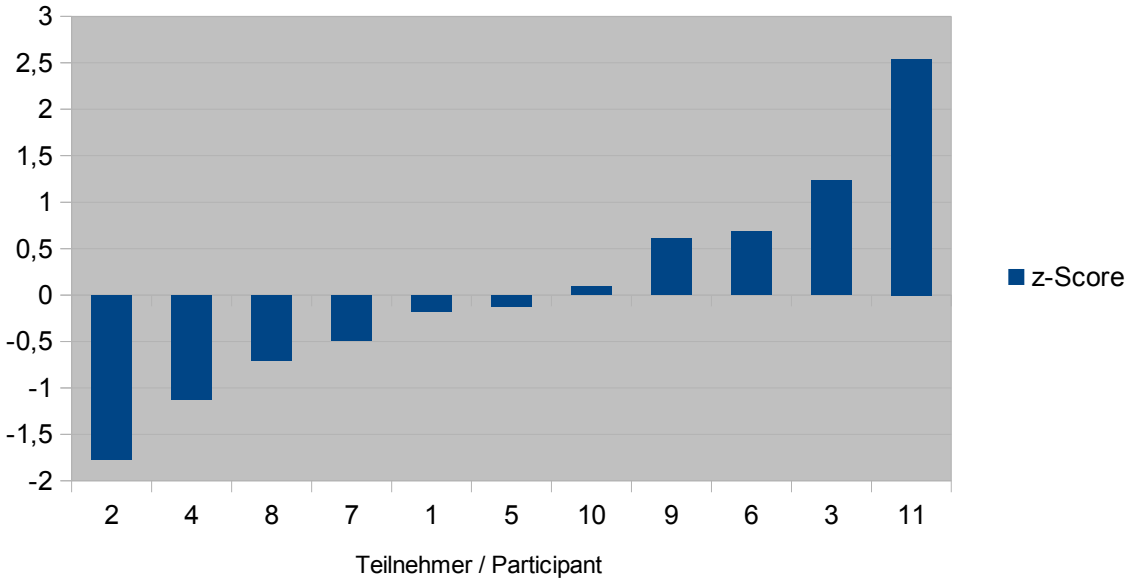


Auswerte nummer / Evaluation number	Ergosinine	Abweichung / Deviation	z-Score	Hinweis / Remark
1				
2	14,35	-7,16	-1,5	
3	13,04	-8,47	-1,8	
4	15,7	-5,81	-1,2	
5	23,3	1,79	0,4	
6	20	-1,51	-0,3	
7	21,4	-0,11	0,0	
8	42,32	20,81	4,4	Ausreisser / Outlier
9	185,64	164,12	34,7	Ausreisser / Outlier
10	19	-2,51	-0,5	
11	21	-0,51	-0,1	

4.5 Ergotamine in µg/kg

Statistic Data	
number of the results	11
number of outliers	1
mean	109
median	105
robust mean (X)	108
robust standard deviation (S^x)	27,6
target standard deviation (σ)	23,7
lower limit of target range	60,3
upper limit of target range	155
quotient S^x/σ	1,2
standard uncertainty U^x	10,4
quotient U^x/σ	0,4
results in target range	10
percent in target range	91

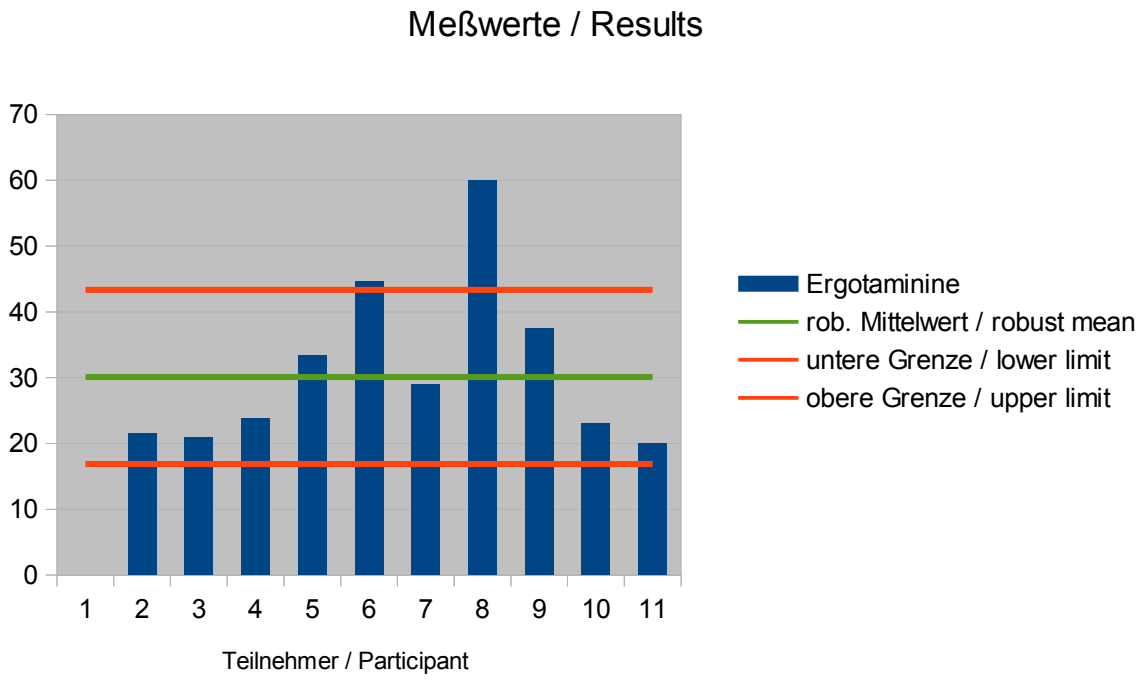


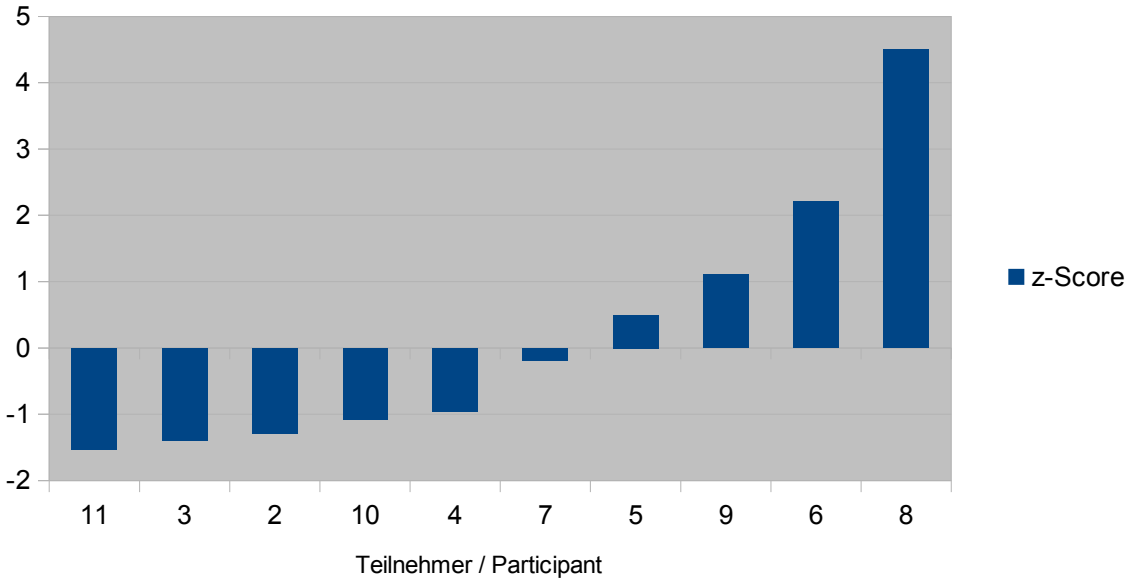


Auswerte nummer / Evaluation number	Ergotamine	Abweichung / Deviation	z-Score	Hinweis / Remark
1	103,68	-4,09	-0,2	
2	65,86	-41,9	-1,8	
3	137,1	29,33	1,2	
4	81,1	-26,67	-1,1	
5	104,8	-2,97	-0,1	
6	124	16,23	0,7	
7	96,1	-11,67	-0,5	
8	90,94	-16,83	-0,7	
9	122,17	14,41	0,6	
10	110	2,23	0,1	
11	168	60,23	2,5	Ausreisser / Outlier

4.6 Ergotaminine in µg/kg

Statistic Data	
number of the results	10
number of outliers	1
mean	31,4
median	26,4
robust mean (X)	30,1
robust standard deviation (S^x)	11,5
target standard deviation (σ)	6,62
lower limit of target range	16,9
upper limit of target range	43,4
quotient S^x/σ	1,7
standard uncertainty U^x	4,6
quotient U^x/σ	0,7
results in target range	8
percent in target range	80

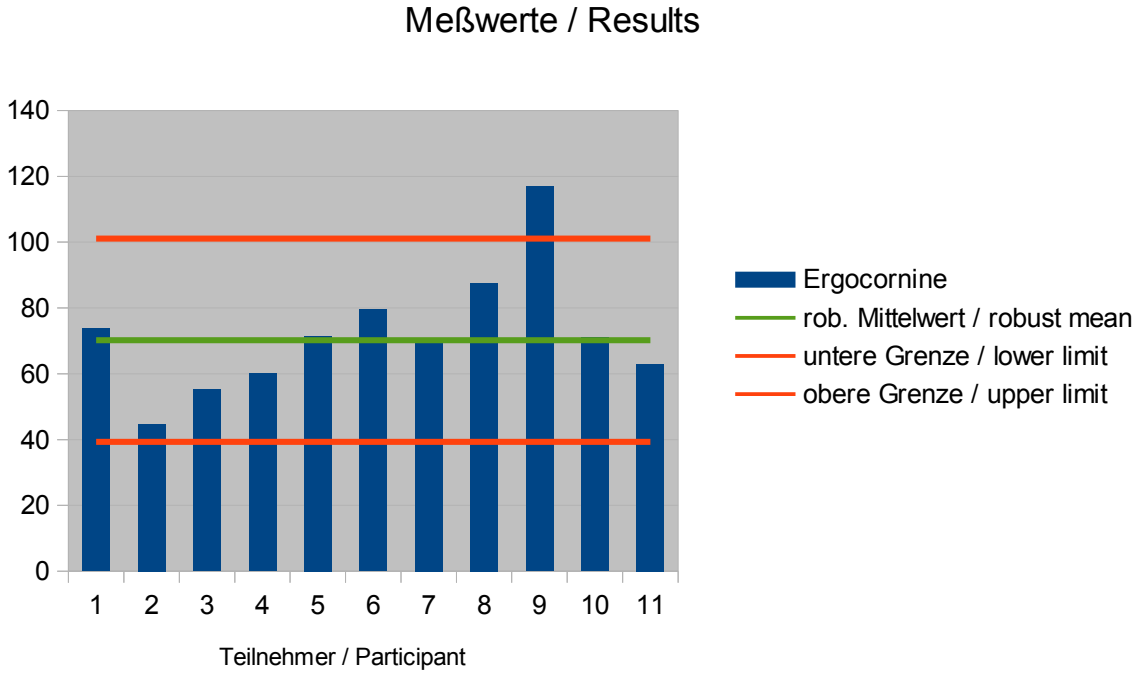


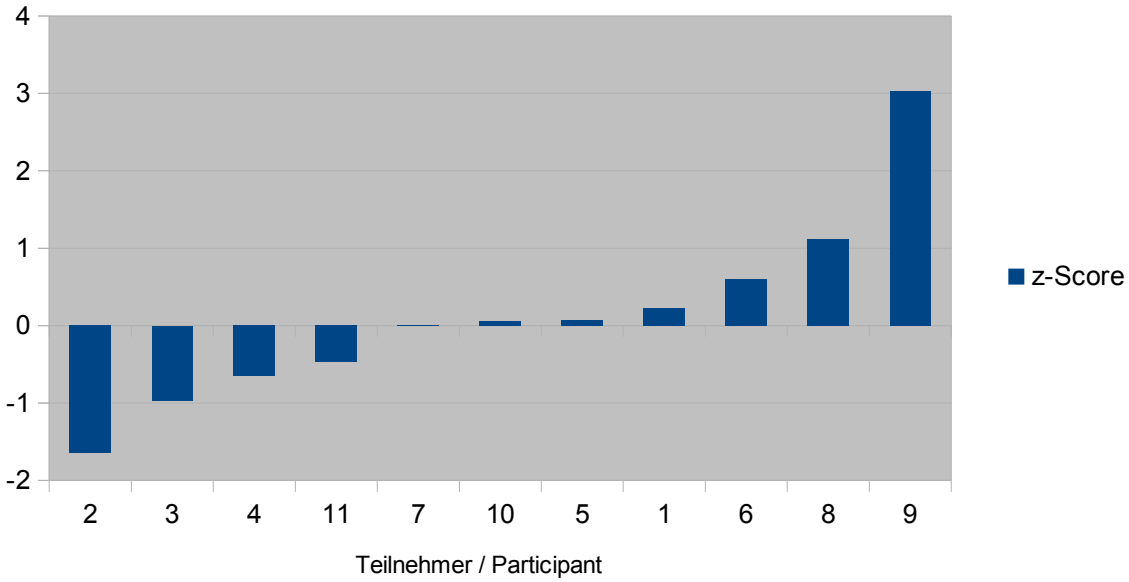


Auswerte nummer / Evaluation number	Ergotaminine	Abweichung / Deviation	z-Score	Hinweis / Remark
1				
2	21,55	-8,56	-1,3	
3	20,87	-9,24	-1,4	
4	23,8	-6,31	-1,0	
5	33,4	3,29	0,5	
6	44,7	14,59	2,2	
7	28,9	-1,21	-0,2	
8	59,94	29,82	4,5	Ausreisser / Outlier
9	37,49	7,38	1,1	
10	23	-7,11	-1,1	
11	20	-10,11	-1,5	

4.7 Ergocornine in µg/kg

Statistic Data	
number of the results	11
number of outliers	1
mean	72,2
median	71,0
robust mean (X)	70,2
robust standard deviation (S^x)	15,4
target standard deviation (σ)	15,4
lower limit of target range	39,3
upper limit of target range	101
quotient S^x/σ	1,0
standard uncertainty U^x	5,8
quotient U^x/σ	0,4
results in target range	10
percent in target range	91

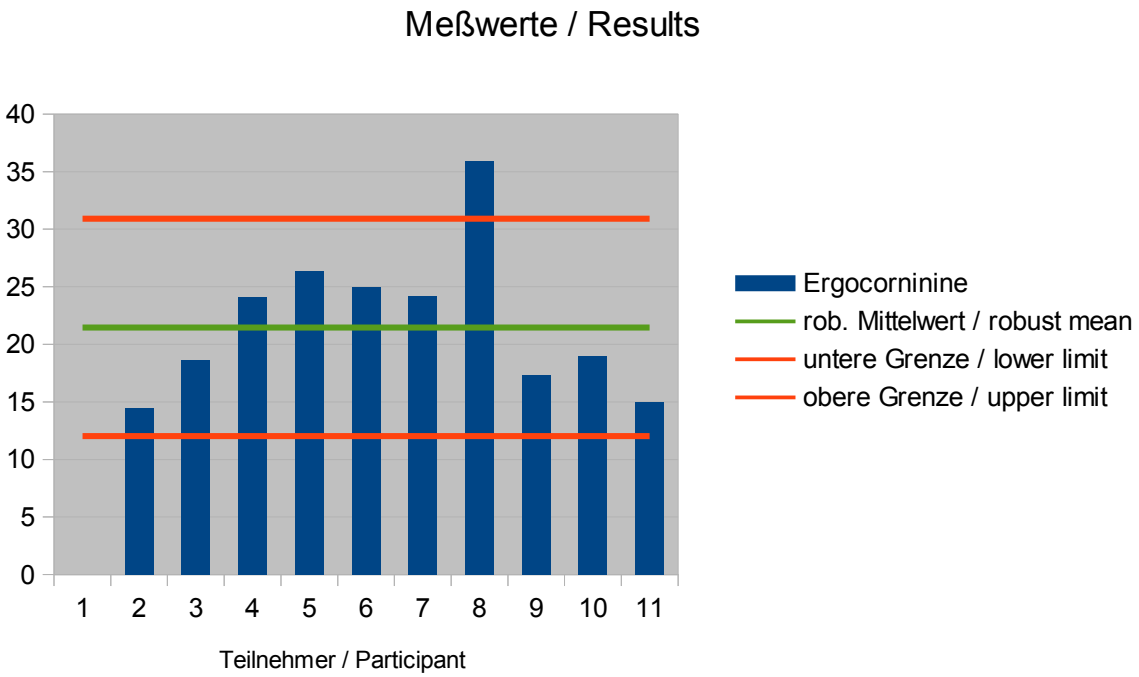


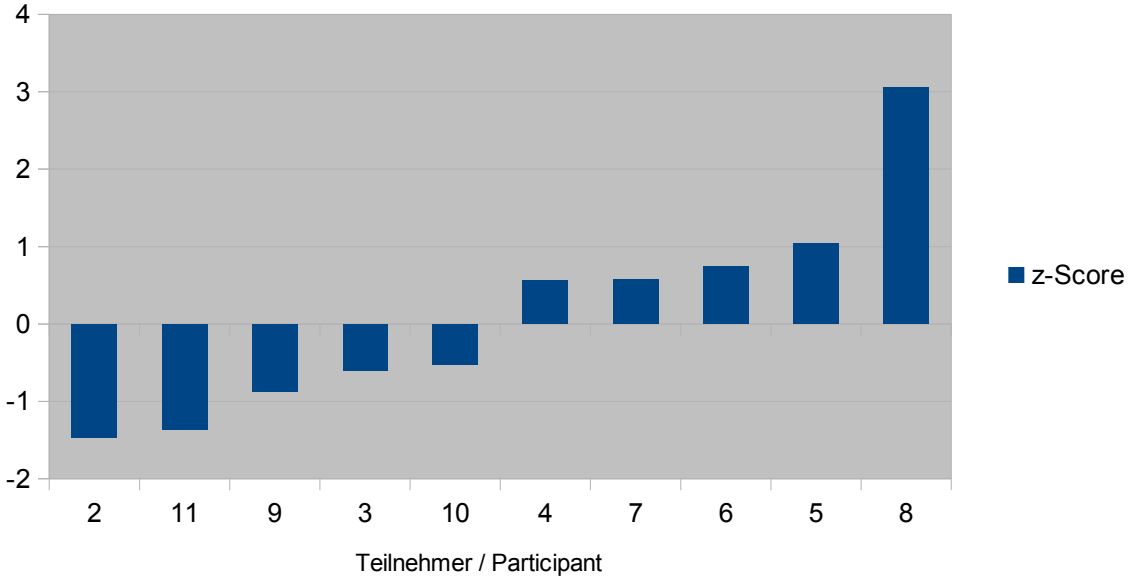


Auswerte nummer / Evaluation number	Ergocornine	Abweichung / Deviation	z-Score	Hinweis / Remark
1	73,69	3,47	0,2	
2	44,74	-25,48	-1,6	
3	55,31	-14,91	-1,0	
4	60,2	-10,02	-0,6	
5	71,4	1,18	0,1	
6	79,5	9,28	0,6	
7	70,3	0,08	0,0	
8	87,58	17,36	1,1	
9	117,02	46,8	3,0	Ausreisser / Outlier
10	71	0,78	0,1	
11	63	-7,22	-0,5	

4.8 Ergocorninine in µg/kg

Statistic Data	
number of the results	10
number of outliers	1
mean	22
median	21,6
robust mean (X)	21,5
robust standard deviation (S^x)	6,03
target standard deviation (σ)	4,72
lower limit of target range	12,0
upper limit of target range	30,9
quotient S^x/σ	1,3
standard uncertainty U^x	2,4
quotient U^x/σ	0,5
results in target range	9
percent in target range	90

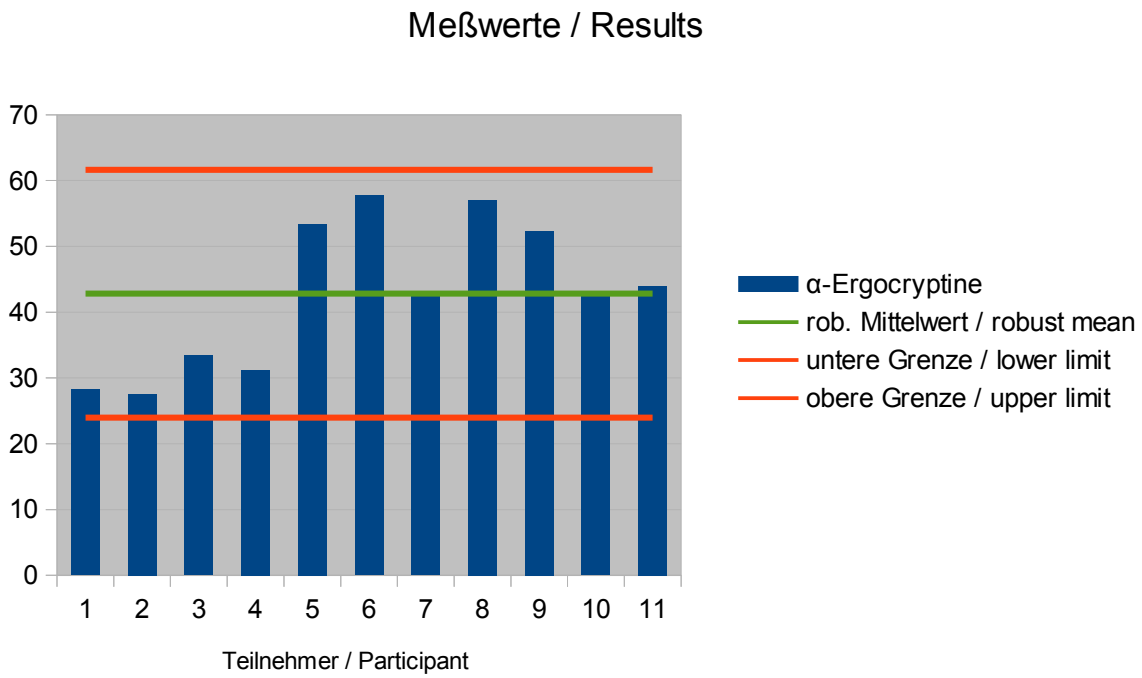


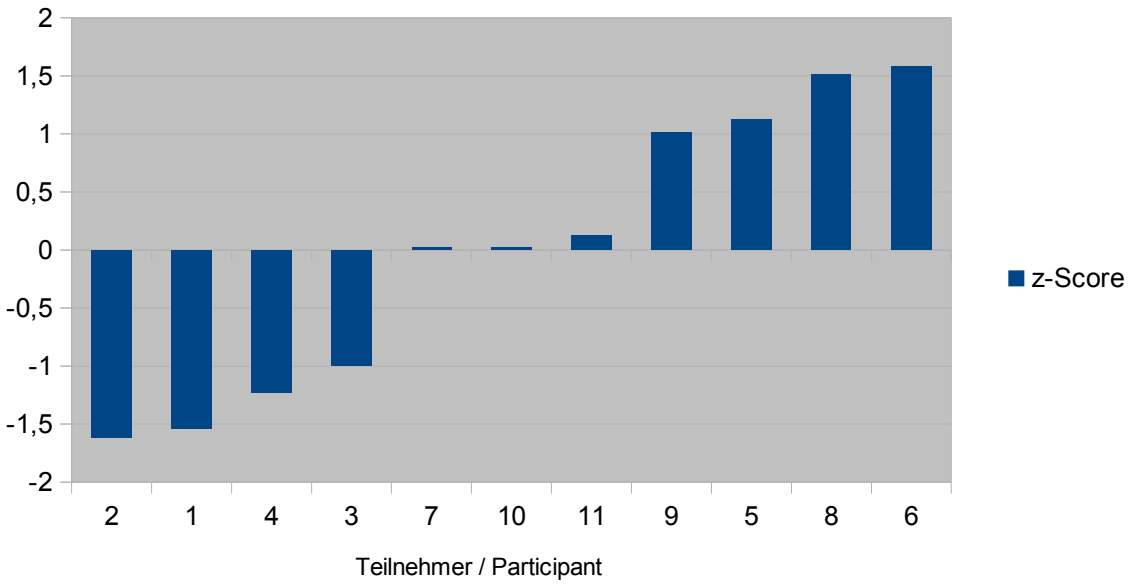


Auswerte nummer / Evaluation number	Ergocorninine	Abweichung / Deviation	z-Score	Hinweis / Remark
1				
2	14,52	-6,95	-1,5	
3	18,62	-2,85	-0,6	
4	24,1	2,63	0,6	
5	26,4	4,93	1,0	
6	25	3,53	0,7	
7	24,2	2,73	0,6	
8	35,88	14,42	3,1	Ausreisser / Outlier
9	17,32	-4,15	-0,9	
10	19	-2,47	-0,5	
11	15	-6,47	-1,4	

4.9 α-Ergocryptine in µg/kg

Statistic Data	
number of the results	11
number of outliers	0
mean	42,8
median	43
robust mean (X)	42,8
robust standard deviation (S^x)	12,9
target standard deviation (σ)	9,42
lower limit of target range	24,0
upper limit of target range	61,6
quotient S^x/σ	1,37
standard uncertainty U^x	4,86
quotient U^x/σ	0,52
results in target range	11
percent in target range	100

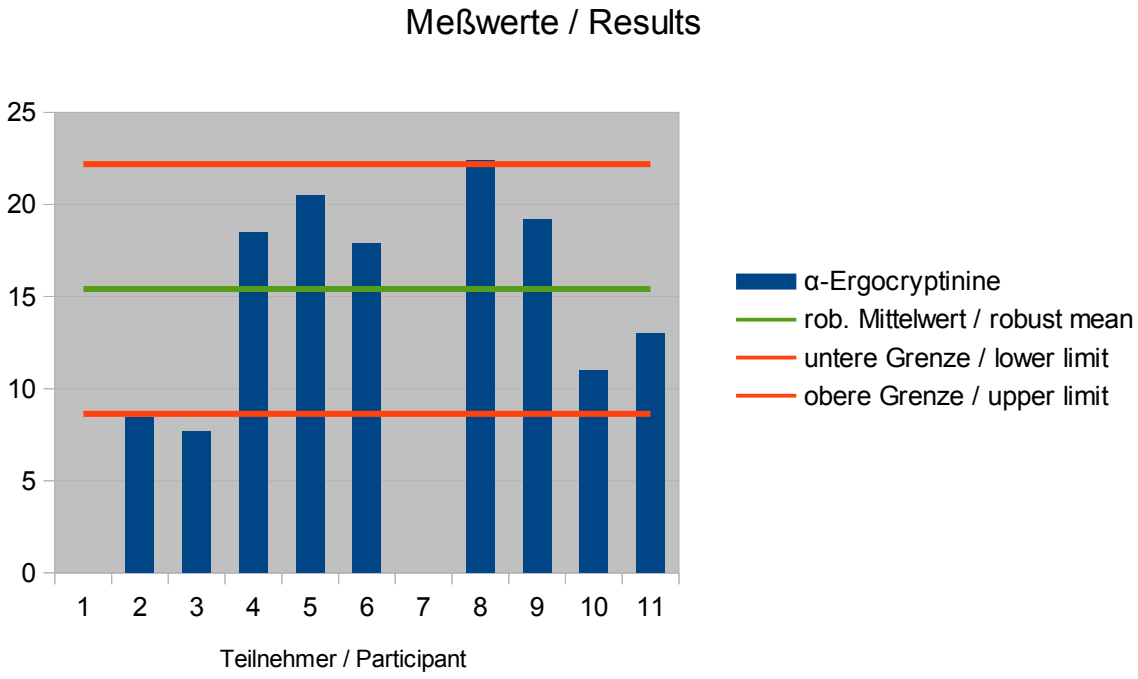


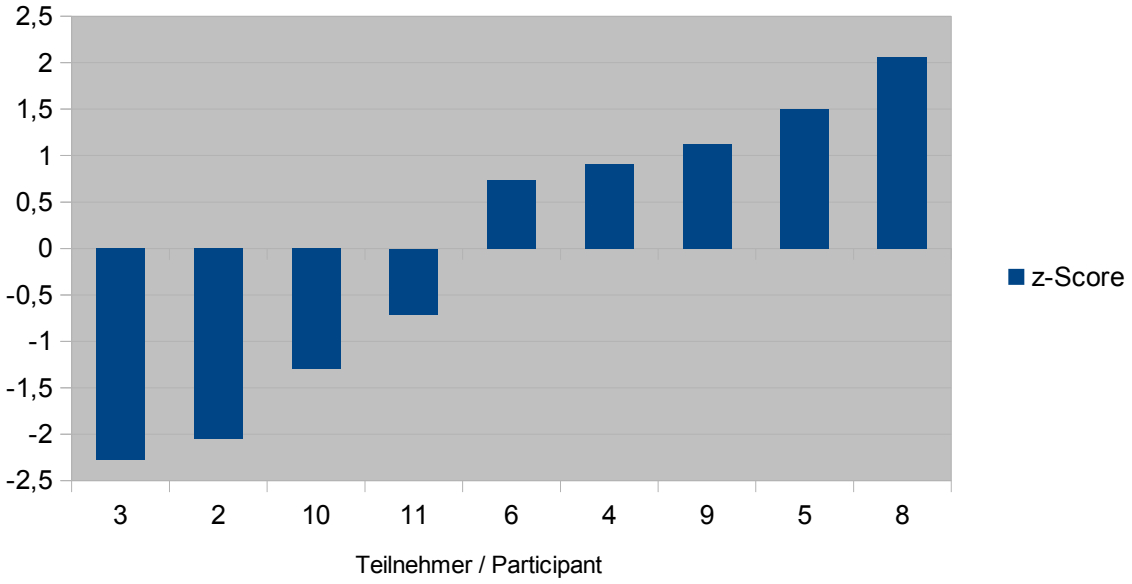


Auswerte nummer / Evaluation number	A-Ergocryptine	Abweichung / Deviation	z-Score	Hinweis / Remark
1	28,28	-14,53	-1,5	
2	27,57	-15,24	-1,6	
3	33,41	-9,4	-1,0	
4	31,2	-11,61	-1,2	
5	53,4	10,59	1,1	
6	57,7	14,89	1,6	
7	43	0,19	0,0	
8	57,04	14,23	1,5	
9	52,32	9,51	1,0	
10	43	0,19	0,0	
11	44	1,19	0,1	

4.10 α-Ergocryptinine in µg/kg

Statistic Data	
number of the results	9
number of outliers	0
mean	15,4
median	17,9
robust mean (X)	15,4
robust standard deviation (S^x)	6,19
target standard deviation (σ)	3,39
target standard deviation (σ, for information)	3,39
lower limit of target range	8,63
upper limit of target range	22,2
quotient S^x/σ	1,8
standard uncertainty U^x	2,6
quotient U^x/σ	0,8
results in target range	7
percent in target range	67

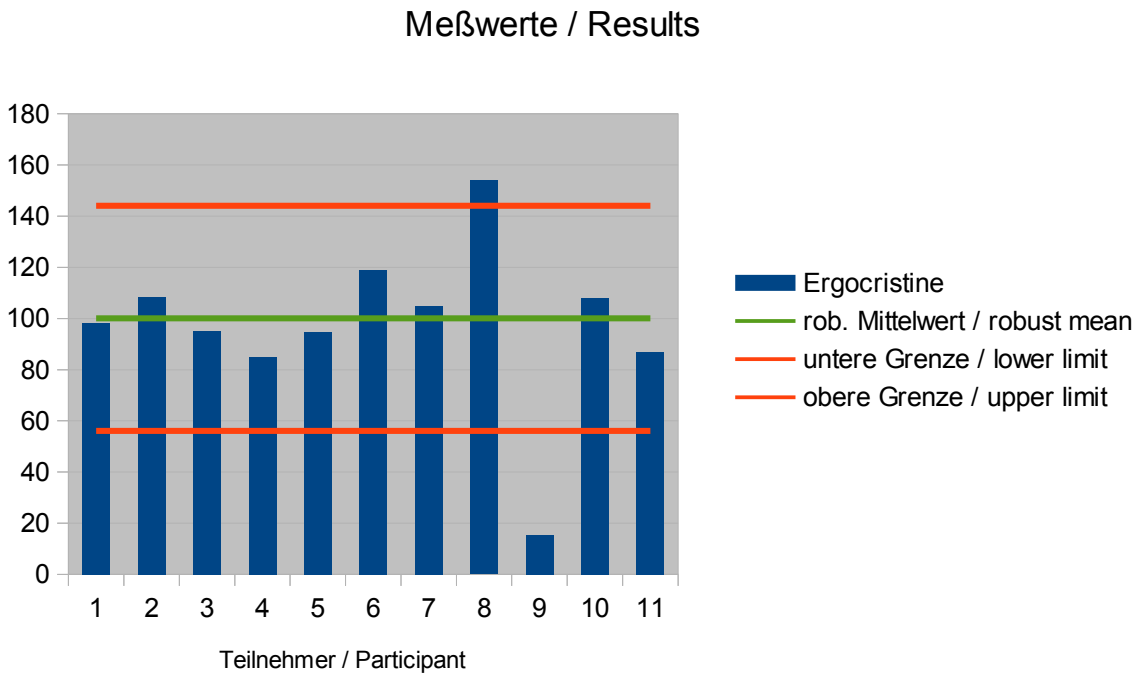


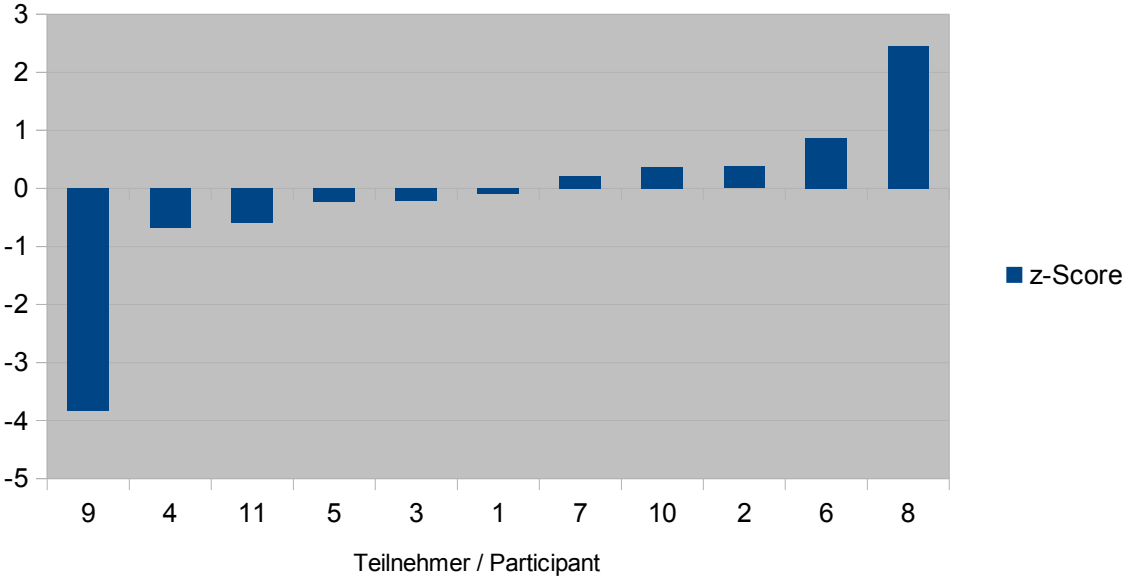


Auswerte nummer / Evaluation number	α-Ergocryptinine	Abweichung / Deviation	z-Score	Hinweis / Remark
1				
2	8,46	-6,94	-2,0	
3	7,67	-7,74	-2,3	
4	18,5	3,1	0,9	
5	20,5	5,1	1,5	
6	17,9	2,5	0,7	
7				
8	22,39	6,98	2,1	
9	19,22	3,82	1,1	
10	11	-4,4	-1,3	
11	13	-2,4	-0,7	

4.11 Ergocristine in µg/kg

Statistic Data	
number of the results	11
number of outliers	1
mean	97,2
median	98,0
robust mean (X)	100
robust standard deviation (S^x)	17,1
target standard deviation (σ)	22,0
lower limit of target range	56,0
upper limit of target range	144
quotient S^x/σ	0,8
standard uncertainty U^x	6,5
quotient U^x/σ	0,3
results in target range	9
percent in target range	82

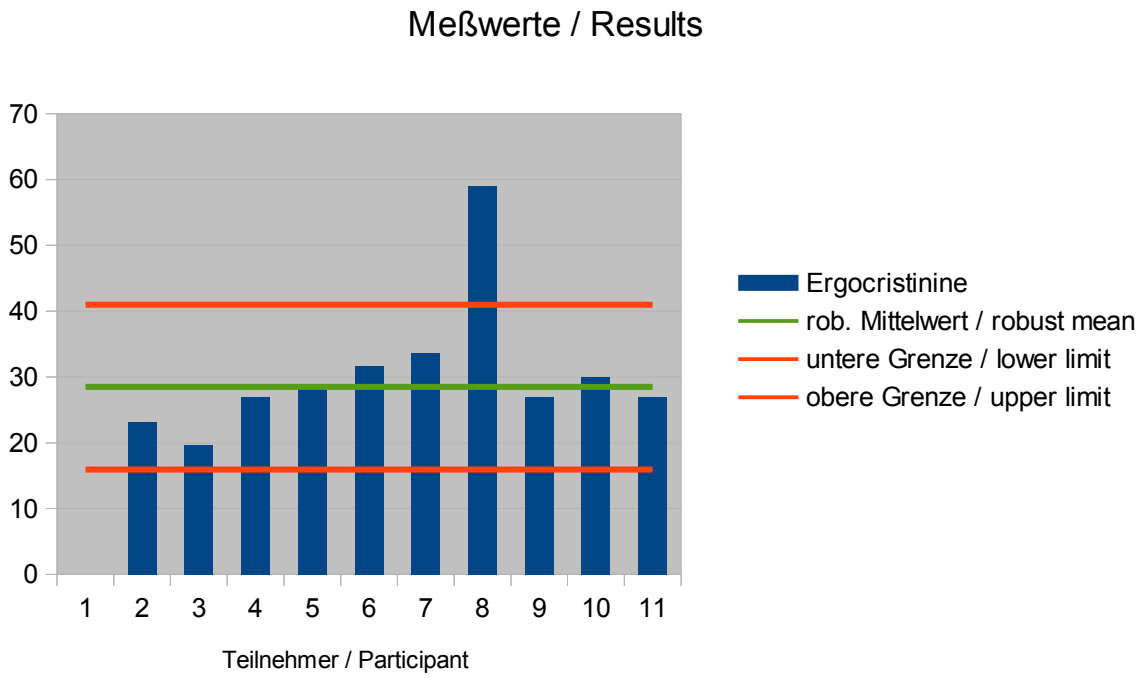


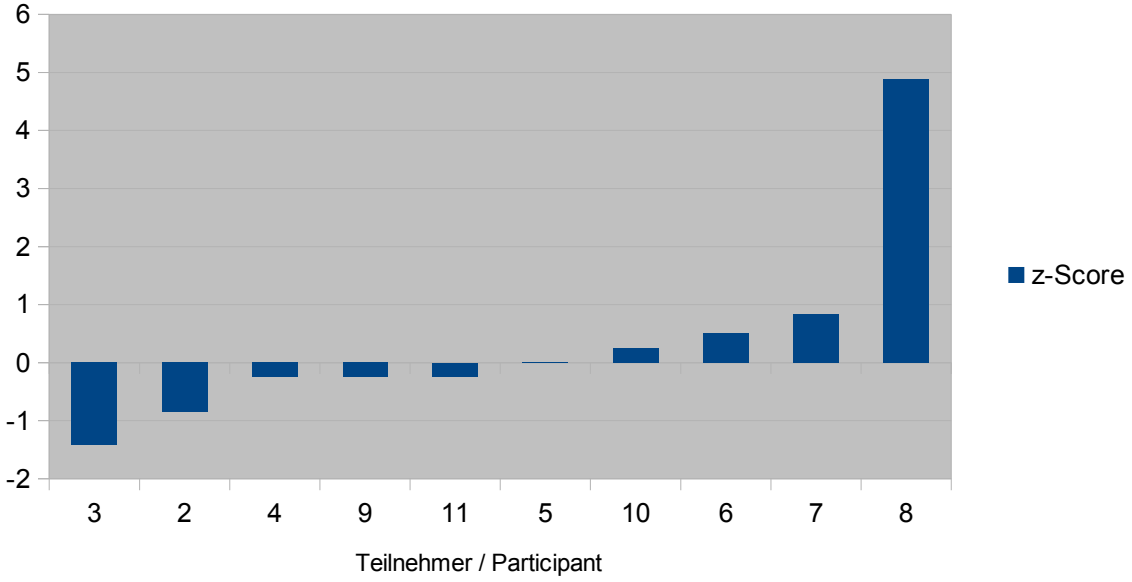


Auswerte nummer / Evaluation number	Ergocristine	Abweichung / Deviation	z-Score	Hinweis / Remark
1	98,04	-2	-0,1	
2	108,28	8,24	0,4	
3	95,18	-4,85	-0,2	
4	85,1	-14,93	-0,7	
5	94,8	-5,23	-0,2	
6	119	18,97	0,9	
7	104,9	4,87	0,2	
8	153,93	53,89	2,4	
9	15,53	-84,5	-3,8	Ausreisser / Outlier
10	108	7,97	0,4	
11	87	-13,03	-0,6	

4.12 Ergocristinine in µg/kg

Statistic Data	
number of the results	10
number of outliers	1
mean	30,6
median	27,8
robust mean (X)	28,5
robust standard deviation (S^x)	5,47
target standard deviation (σ)	6,26
lower limit of target range	15,9
upper limit of target range	41
quotient S^x/σ	0,9
standard uncertainty U^x	2,2
quotient U^x/σ	0,3
results in target range	9
percent in target range	90

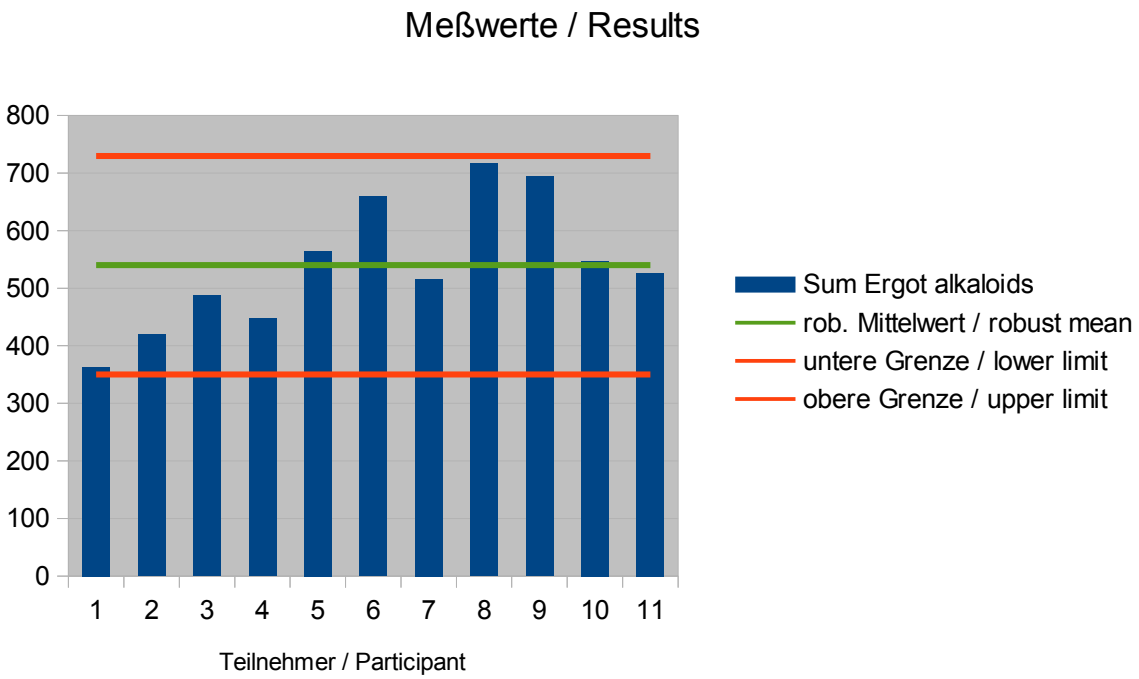


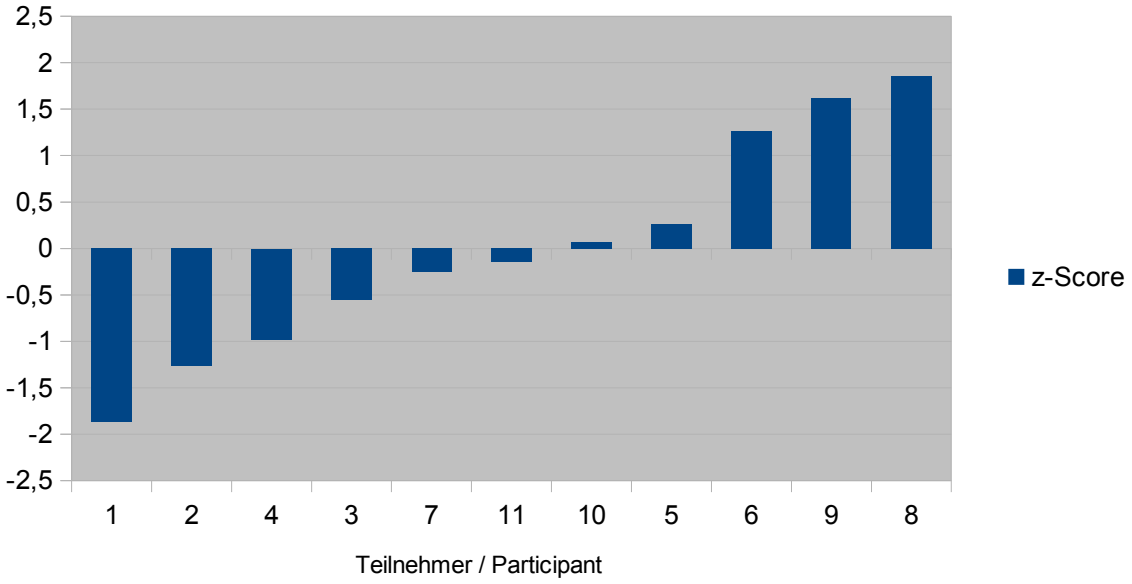


Auswerte nummer / Evaluation number	Ergocristinine	Abweichung / Deviation	z-Score	Hinweis / Remark
1				
2	23,14	-5,33	-0,9	
3	19,61	-8,86	-1,4	
4	26,9	-1,57	-0,3	
5	28,5	0,03	0,0	
6	31,6	3,13	0,5	
7	33,7	5,23	0,8	
8	59,07	30,6	4,9	Ausreisser / Outlier
9	26,93	-1,54	-0,2	
10	30	1,53	0,2	
11	27	-1,47	-0,2	

4.13 Sum Ergot alkaloids in µg/kg

Statistic Data	
number of the results	11
number of outliers	0
mean	540
median	526
robust mean (X)	540
robust standard deviation (S^x)	128
target standard deviation (σ)	94,8
lower limit of target range	350
upper limit of target range	730
quotient S^x/σ	1,4
standard uncertainty U^x	48,2
quotient U^x/σ	0,5
results in target range	11
percent in target range	100





Auswerte nummer / Evaluation number	Sum Ergot alkaloids	Abweichung / Deviation	z-Score	Hinweis / Remark
1	363,08	-176,94	-1,9	
2	419,76	-120,26	-1,3	
3	487,74	-52,29	-0,6	
4	447	-93,02	-1,0	
5	564,6	24,58	0,3	
6	659,7	119,68	1,3	
7	516	-24,02	-0,3	
8	716,02	175,99	1,9	
9	693,37	153,35	1,6	
10	547	6,98	0,1	
11	526	-14,02	-0,1	

5 Documentation

5.1 *Primary data*

Teilnehmer / participant	Probe / sample A	Probe / sample B	Einheit / unit	Ergometrin (e)	Ergebnis / result A incl. recovery	Ergebnis / result B incl. recovery	Wiederfindungsrate / recovery
							in %
1	25	43	µg/kg		7,7	7,7	
2	2	34	µg/kg	39,7	43,3	36,1	26
3	7	20	µg/kg	31,9	33,0	30,9	94
4	18	41	µg/kg	31,8	35,2	28,4	95
5	10	45	µg/kg	34,8	35,8	33,8	
6	6	29	µg/kg	48,3	48,9	47,7	82
7	11	30	µg/kg	41,2	42,4	40,0	164
8	32	48	µg/kg	36,0	33,7	38,4	91
9	21	55	µg/kg	36,9	37,0	36,9	99
10	19	33	µg/kg	38,0	37,0	39,0	80-120
11	22	50	µg/kg	30,0	29,0	31,0	

Teilnehmer / participant	Ergometrinin(e)	Ergebnis / result A incl. recovery	Ergebnis / result B incl. recovery	Wiederfindungsrate / recovery	Ergosin(e)	Ergebnis / result A incl. recovery	Ergebnis / result B incl. recovery	Wiederfindungsrate / recovery
				in %				in %
1						51,4	52,0	
2	10,7	11,0	10,4	34	40,9	47,2	34,7	34
3	7,4	7,8	7,0	104	47,6	50,5	44,7	94
4	8,7	9,3	8,0	100	40,4	38,1	42,7	101
5	14,4	14,5	14,3		59,1	65,4	52,8	
6	18,0	18,7	17,2	113	74,0	78,6	69,4	102
7	<20	<20	<20	113	52,6	49,6	55,5	119
8	13,4	12,5	14,2	91	57,5	58,8	56,2	79
9	9,9	10,1	9,6	110	52,9	53,2	52,6	116
10	13,0	12,0	13,0	80-120	62,0	61,0	62,0	80-120
11	<10	<10	<10		28,0	27,0	28,0	

Teilnehmer / participant	Ergosinin(e)	Ergebnis / result A incl. recovery	Ergebnis / result B incl. recovery	Wiederfindungsrate / recovery	Ergotamin(e)	Ergebnis / result A incl. recovery	Ergebnis / result B incl. recovery	Wiederfindungsrate / recovery
				in %				in %
1						103,7	103,7	
2	14,4	16,4	12,3	52	65,9	78,2	53,5	41
3	13,0	13,5	12,6	115	137,1	134,4	139,8	93
4	15,7	15,5	15,9	103	81,1	73,5	88,8	97
5	23,3	25,5	21,0		104,8	107,5	102,1	
6	20,0	19,7	20,0	107	124,0	132,0	115,0	94
7	21,4	20,0	22,7	111	96,1	92,1	100,0	120
8	42,3	43,6	41,0	74	90,9	92,0	89,8	84
9	185,6	188,7	182,6	93	122,2	119,4	125,0	83
10	19,0	18,0	19,0	80-120	110,0	95,0	125,0	80-120
11	21,0	20,0	21,0		168,0	166,0	170,0	

Teilnehmer / participant	Ergotaminin (e)	Ergebnis / result A incl. recovery	Ergebnis / result B incl. recovery	Wiederfindungsrate / recovery	Ergocornin(e)	Ergebnis / result A incl. recovery	Ergebnis / result B incl. recovery	Wiederfindungsrate / recovery
				in %				in %
1						74,3	73,1	
2	21,6	23,9	19,2	46	44,7	50,8	38,7	39
3	20,9	19,6	22,2	115	55,3	55,8	54,9	113
4	23,8	21,8	25,8	104	60,2	64,2	56,2	102
5	33,4	34,1	32,7		71,4	73,2	69,5	
6	44,7	46,6	42,7	170	79,5	87,0	71,9	106
7	28,9	27,5	30,2	120	70,3	65,7	74,8	109
8	59,9	60,2	59,7	65	87,6	81,2	94,0	57
9	37,5	36,4	38,5	108	117,0	117,2	116,9	116
10	23,0	22,0	23,0	80-120	71,0	74,0	68,0	80-120
11	20,0	20,0	20,0		63,0	67,0	59,0	

Teilnehmer / participant	Ergocorninin (e)	Ergebnis / result A incl. recovery	Ergebnis / result B incl. recovery	Wiederfindungsrate / recovery	α -Ergocryptin(e)	Ergebnis / result A incl. recovery	Ergebnis / result B incl. recovery	Wiederfindungsrate / recovery
				in %				in %
1						28,4	28,2	
2	14,5	15,3	13,7	61	27,6	29,5	25,6	40
3	18,6	18,4	18,9	98	33,4	33,2	33,6	110
4	24,1	24,9	23,2	100	31,2	32,3	30,1	104
5	26,4	26,9	25,9		53,4	52,8	53,9	
6	25,0	25,6	24,3	102	57,7	61,1	54,2	102
7	24,2	23,2	25,2	113	43,0	43,9	42,0	116
8	35,9	34,0	37,8	93	57,0	52,9	61,2	57
9	17,3	16,6	18,0	119	52,3	52,0	52,7	112
10	19,0	20,0	18,0	126	43,0	44,0	41,0	80-120
11	15,0	14,0	16,0		44,0	44,0	44,0	

Teilnehmer / participant	α -Ergo-cryptinin(e)	Ergebnis / result A incl. recovery	Ergebnis / result B incl. recovery	Wiederfindungsrate / recovery	Ergocristin(e)	Ergebnis / result A incl. recovery	Ergebnis / result B incl. recovery	Wiederfindungsrate / recovery
				in %				in %
1						102,0	94,1	
2	8,5	9,9	7,0	54	108,3	124,4	92,2	41
3	7,7	7,6	7,7	104	95,2	93,1	97,2	109
4	18,5	19,5	17,6	112	85,1	83,0	87,3	96
5	20,5	21,4	19,7		94,8	99,9	89,7	
6	17,9	18,4	17,4	94	119,0	124,0	114,0	108
7	<20	<20	<20	116	104,9	111,0	98,7	121
8	22,4	21,1	23,6	86	153,9	147,3	160,6	51
9	19,2	18,9	19,6	105	15,5	15,3	15,7	119
10	11,0	11,0	10,0	125	108,0	101,0	115,0	80-120
11	13,0	12,0	13,0		87,0	85,0	88,0	

Teilnehmer / participant	Ergocristinin (e)	Ergebnis / result A incl. recovery	Ergebnis / result B incl. recovery	Wiederfindungsrate / recovery	Sum(me) Ergot Alkaloide(s)	Ergebnis / result A incl. recovery	Ergebnis / result B incl. recovery	Wiederfindungsrate / recovery
				in %				in %
1						367,4	358,8	
2	23,1	26,2	20,0	57	419,8	476,1	363,4	
3	19,6	18,6	20,6	102	487,7	485,4	490,0	
4	26,9	26,7	27,0	114	447,0	444,0	451,0	entfällt
5	28,5	29,8	27,3		564,6	586,7	542,5	
6	31,6	31,8	31,4	106	659,7	692,4	625,2	106
7	33,7	35,3	32,0	92	516,0	511,0	521,0	
8	59,1	56,5	61,6	79	716,0	694,0	738,1	-
9	26,9	26,1	27,8	92	693,4	690,8	695,9	106
10	30,0	29,0	30,0	80-120	547,0	522,0	562,0	
11	27,0	26,0	28,0		526,0	520,0	528,0	

5.2 Homogeneity

5.2.1 *Repeatability standard deviation of results*

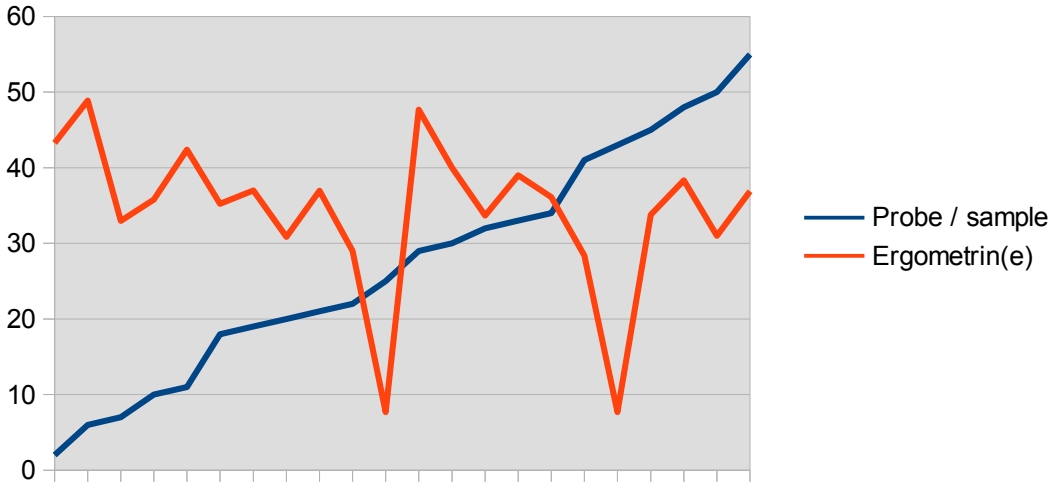
The Repeatability standard deviation of duplicate tests of the participants was calculated from the data documented in 5.1.

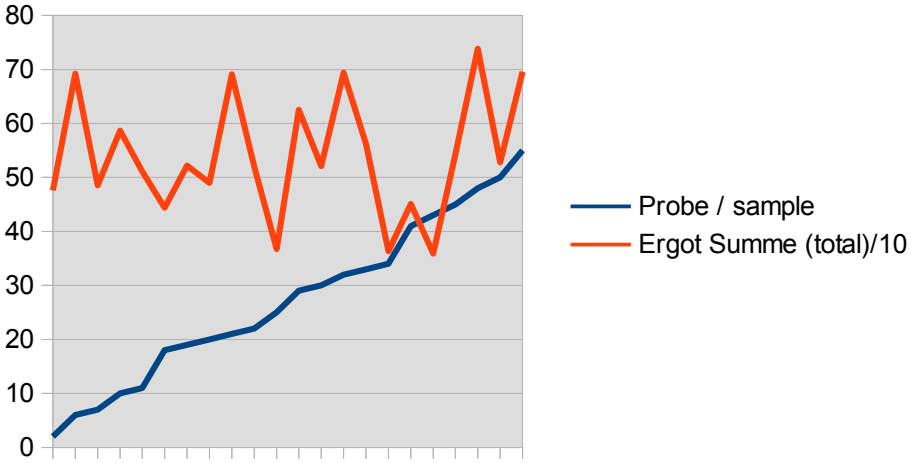
It is 3,56 µg/kg = 10,0% of X (Ergometrine).

It is 10,8 µg/kg = 10,0 % of X (Ergotamine).

It is 28,0 µg/kg = 5,2 % of X (Sum ergot alkaloids)

5.2.2 *Comparison of sample number / test result*





5.3 Analytical methods

Details from the participants

Teilnehmer / participant	Methodenbeschreibung, wie in einem regulären Prüfbericht angegeben / method description	Extraktion / extraction	Basisch / sauer / basic / acidic	Probenaufreinigung / cleanup	Trennmethode / chromatography
1	Romer Labs HPLC	AcN/ $(NH_4)_2CO_3$		Mycosep 150 Ergot	HPLC
2	20g weight and 100 ml Ethylacetate:Methanole:Ammonia 25%:Isopropanole - 75:5:7:7	Ultraturrax 1 min and shaking 45 min	basic	SepPak Al2O3	Gemini C6 Phenyl 150x2 with precolumn, water with Amm.Carb and ACN
3	Ergot alkaloids: extraction and clean up with SPE. Determination with HPLC/FLD	Ethylacetate/Methanole/NH3 25%/2-Propanole 75/5/7/7		SPE	HPLC
4	In house method LC-MS/MS	Ammoniumcarbonate-buffer /MeCN	basic	PSA	HPLC
5					
6	PV 3458 (§64 LFGB L 15.01/02 5)	Ethylacetate, Methanole, Ammoniumhydroxide	basic	Sep-Pak Plus Al B Cartridge Waters	HPLC
7	UHPLC	Acetonitrile/ammonium carbonate solution (200 mg/l) (84/16 v/v)	basic	Mycosep Ergot	UHPLC
8	Following ASU L15.01/02-5 2012-02	Ethylacetate : Methanole : Ammoniumhydroxide : 2-Propanole = 75 : 5 : 7 : 7	basic	SPE, basic Aluminiumoxide	HPLC
9	§64 LFGB 15.01/02-5 mod. HPLC-FL	organic	basic	SPE	RP8
10	§ 64 LFGB L 1501/02-5				
11	In house method		basic	none	

Teilnehmer / participant	Detektion / detection	Standard material	Konzentration und Alter der Standardlösungen / concentration and age of std	Referenz material / reference material	Wiederfindung wurde mit gleicher Matrix bestimmt / recovery with same matrix	Methode ist akkreditiert / method accredited	Sonstige Hinweise / remarks
1	RI	Mix (6 Ergotakaloids)	50ppb and 100 ppb fresh	In house reference	yes	no	A=25,B=43
2	LC-MS	Biopure, aliquot and concentrated	100,6 µg/ml	Wheat	no	no	A=02, B=34
3	FLD				yes	yes	A=07, B=20
4	MS/MS	Ergometrine	2,5 - 150 ng/g	Dinkel wheat whole grain flour	yes	yes	A=18, B=41
5							A=10, B=45
6	HPLC-FLD	Biopure	2,5ng-50ng/ml /25.03.14	DLA 16/2013	no	yes	A=06, B=29
7	Fluorescence	Biopure	100 µg/ml; 08/07/2013	spiked wheat	yes	yes	
8	MS/MS	LGC Standards	1 - 120 ng/ml; fresh	none, extract spiking	yes	yes	
9	FL	Sigma	0,25 ng/µL / max. 2 weeks	rye flour	yes	yes	
10						yes	
11	LC-MS/MS	biopure				yes	

6 Index of participant laboratories

Participant	Location	Country
		Austria
		France
		Germany
		Germany
		Germany
		Germany
		Belgium
		Germany
		Swiss
		Germany
		Germany
		Germany
		Canada

[The address data of the participants were deleted for publication of the evaluation report.]

7 Index of literature

1. DIN EN ISO/IEC 17043:2010; Konformitätsbewertung – Allgemeine Anforderungen an Eignungsprüfungen / Conformity assessment – General requirements for proficiency testing
2. Verordnung / Regulation 882/2004/EU; Verordnung über amtliche Kontrollen / Regulation on official controls
3. DIN EN ISO/IEC 17025:2005; Allgemeine Anforderungen an die Kompetenz von Prüf- und Kalibrierlaboratorien / General requirements for the competence of testing and calibration laboratories
4. Richtlinie / Directive 1993/99/EU; über zusätzliche Maßnahmen im Bereich der amtlichen Lebensmittelüberwachung / on additional measures concerning the official control of foodstuffs
5. ASU §64 LFGB : Planung und statistische Auswertung von Ringversuchen zur Methodenvalidierung
6. DIN ISO 13528:2009; Statistische Verfahren für Eignungsprüfungen durch Ringversuche
7. The International Harmonised Protocol for the Proficiency Testing of Ananlytical Laboratories ; J.AOAC Int., 76(4), 926 – 940 (1993)
8. The International Harmonised Protocol for the Proficiency Testing of Ananlytical Chemistry Laboratories ; Pure Appl Chem, 78, 145 – 196 (2006)
9. Evaluation of analytical methods used for regulation of food and drugs;W. Horwitz; Analytical Chemistry, 54, 67-76 (1982)
10. A Horwitz-like funktion describes precision in proficiency test; M. Thompson, P.J. Lowthian; Analyst, 120, 271-272 (1995)
11. Recent trends in inter-laboratory precision at ppb and sub-ppb concentrations in relation to fitness for purpose criteria in proficiency testing; M. Thompson; Analyst, 125, 385-386 (2000)
12. Protocol for the design, conduct and interpretation of method performance studies; W. Horwitz; Pure & Applied Chemistry, 67, 331-343 (1995)