

Analytische Qualitätssicherung Baden-Württemberg

Proficiency Tests UKWIR 5/18
priority substances in surface water

cypermethrin

Stuttgart, July 2018

provided by
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General

This PT was provided by AQS Baden-Württemberg as a subcontractor for wca environment limited, Brunel House, Volunteer Way, Faringdon, Oxfordshire SN7 7YR, United Kingdom on behalf of United Kingdom Water Industry Research (UKWIR).

In one round the following determinand was to be measured:

- UKWIR 5/18
 - Cypermethrin

The PTs were executed and evaluated according to the requirements of ISO 13528: 2015.

PT design

Each participant received the following samples:

- 3 spiked samples for the determination of the respective determinand based on a filtered surface water sample in 1000-ml-ground bottles with ground-in stopper
- 1 blank sample of the filtered surface water

The concentrations of the analyte of the spiked samples were chosen according to the requirements of UKWIR based on the European Regulation for Environmental Quality Standard (Directive 2008/105/EG on environmental quality standards in the field of water policy).

The samples were cooled directly after preparation and dispatched with freezer packs added to the packages by express service (TNT). Participants were requested to start with the analysis one day after receipt of the samples at the latest.

Analytical methods

The participants were free to choose a suitable method, but the following limit of quantification was required:

Determinand	Required LOQ
cypermethrin	0.0004 µg/l

The samples had to be analysed in duplicate over the complete method (sample preparation and measurement). The participants were asked to submit the results as average values in µg/l with three significant digits.

Evaluation procedure

The statistical evaluation was executed according to ISO 13528:2015.

The assigned value x_{pt} was derived from the median of the participants' results. The uncertainty of the assigned values was calculated according to ISO 13528 from the standard deviation derived from the MAD (median absolute deviation):

$$u(x_{pt}) = 1.25 * \frac{s^*}{\sqrt{p}} \quad (s^* = 1,483 * MAD).$$

The standard deviation for proficiency assessment σ_{pt} was calculated in accordance with the European QA/QC Directive: $\sigma_{pt} = 0,25 * x_{pt}$.

A z-score was calculated for each measurement result derived from the assigned value x_{pt} and the standard deviation for proficiency assessment σ_{pt} :

$$z = \frac{x - x_{pt}}{\sigma_{pt}}$$

The assessment of the results was as follows:

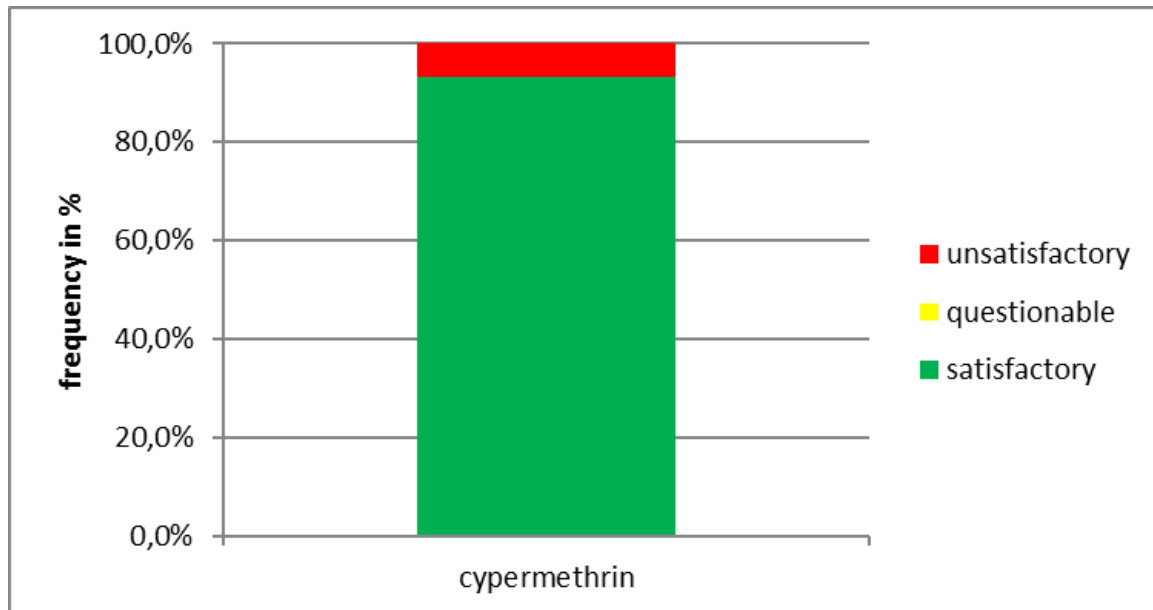
$ z \leq 2.0$	satisfactory
$2.0 < z < 3.0$	questionable
$ z \geq 3.0$	unsatisfactory

Results of evaluation

Number of participants:

PT round	Determinands	Number of participants	Number of participants reporting results
UKWIR 5/18	cypermethrin	6	5

In the following figure the percentage of satisfactory, questionable and unsatisfactory results are illustrated.



Explanation of tables and graphs in the appendix

The appendix contains the PT data for all parameters and all samples in tables and graphs. For each parameter the following illustrations are given:

Parameter table

In these tables the following values for each concentration level are listed:

- assigned value in $\mu\text{g/l}$
- expanded uncertainty of the assigned value in %
- standard deviation of the data set in $\mu\text{g/l}$, calculated using the Q-method (due to the often low number of participants this standard deviation estimate is not very reliable)
- standard deviation for proficiency assessment in $\mu\text{g/l}$ for the calculation of z-scores (25 % of the assigned value)
- rel. standard deviation for proficiency assessment in %
- tolerance limits above and below in $\mu\text{g/l}$ and % (limit for assessment as 'satisfactory')
- number of values in this level
- number of not satisfactory values ('questionable' or unsatisfactory') below and above the assigned value and the percentage of these values in total

Relative standard deviation

The diagrams for the rel. standard deviation vs. the assigned value show the values compared to the fixed standard deviation for proficiency assessment (horizontal line at 25%) and the concentration dependence.

Used methods

The percentage of analytical techniques used are shown here.

Sample table

In this table all results of the participants are noted together with uncertainties (where reported). For these uncertainties ζ -scores (zeta-scores) are calculated according to the formula

$$\zeta = \frac{x - x_{pt}}{\sqrt{u_{lab}^2 + u_{x_{pt}}^2}}$$

With

x = result of the participant

x_{pt} = assigned value

u_{lab} = participant's standard uncertainty

$u_{x,pt}$ = standard uncertainty of the assigned value

ζ -scores can be used for the plausibility check of measurement uncertainties. The type of assessment is equivalent to that of z-scores, i.e. an absolute value of $\leq 2,0$ can be regarded as 'satisfactory'.

ζ -scores above this value indicate an underestimation of the measurement uncertainty. This table also contains the assigned value and its uncertainty as well as the tolerance limits ($z = \pm 2,0$).

Sample graphs of concentrations

All participants' results, sorted for values, are shown here versus the laboratory codes. The assigned value and its uncertainty as well as the tolerance limits are also included.

z-score graphs

In a similar way the z-scores attributed to the participants' results are shown here versus the laboratory codes.

Graphs of expanded uncertainty

The expanded uncertainty is shown if laboratories reported uncertainties.

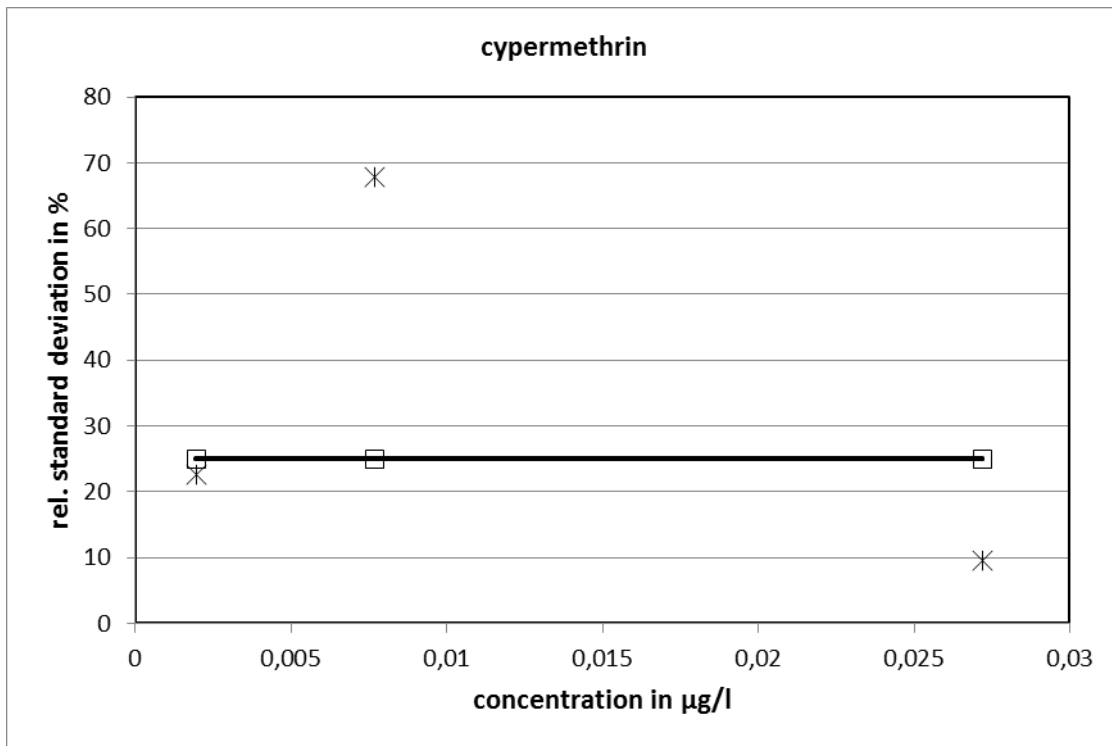
ζ -score graphs

If laboratories reported uncertainties, ζ -scores were calculated and are shown versus the laboratory codes.

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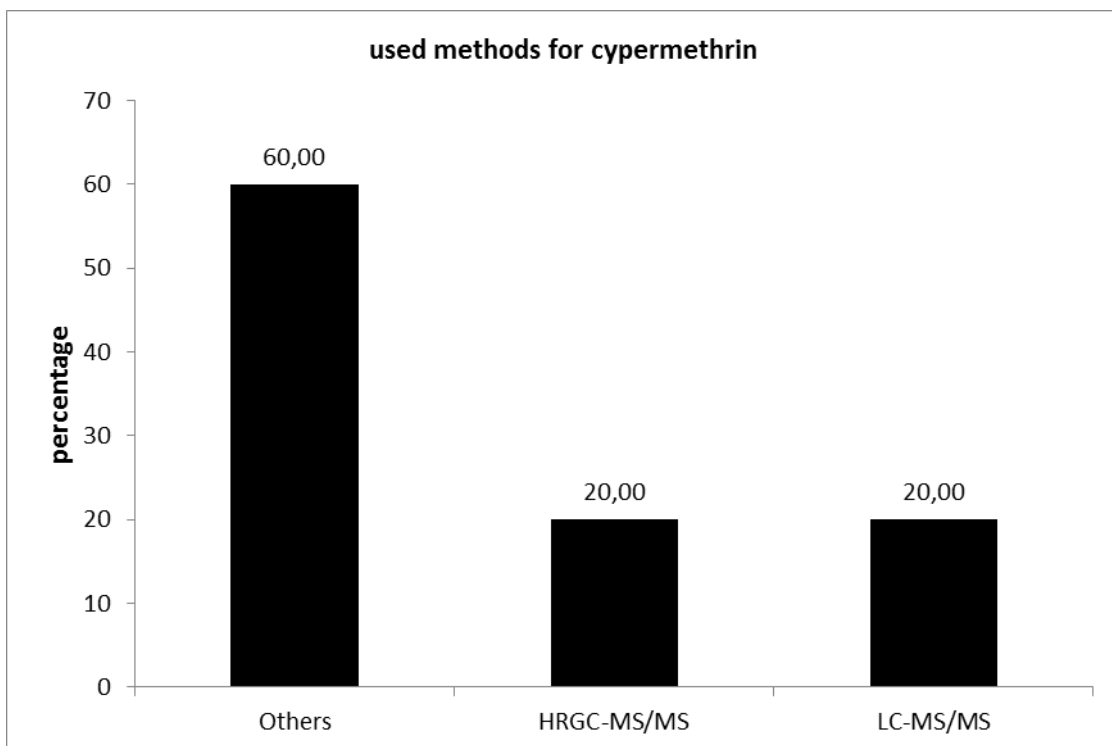
cypermethrin													
level	assigned value [µg/l]	expanded uncertainty of the assigned value [%]	standard deviation, calculated using robust statistics [µg/l]	standard deviation for proficiency assessment [µg/l]	standard deviation for proficiency assessment [%]	upper tolerance limit [µg/l]	lower tolerance limit [µg/l]	upper tolerance limit [%]	lower tolerance limit [%]	number of results	out below	out above	out [%]
1	0,0020	19,46	0,0004	0,0005	25,00	0,0029	0,0010	50,00	-50,00	5	0	0	0,0
2	0,0077	50,67	0,0052	0,0019	25,00	0,0115	0,0038	50,00	-50,00	5	0	1	20,0
3	0,0272	7,19	0,0026	0,0068	25,00	0,0408	0,0136	50,00	-50,00	5	0	0	0,0
									sum	15	0	1	6,7

Relative standard deviation



25 % is the value used as standard deviation for proficiency assessment.

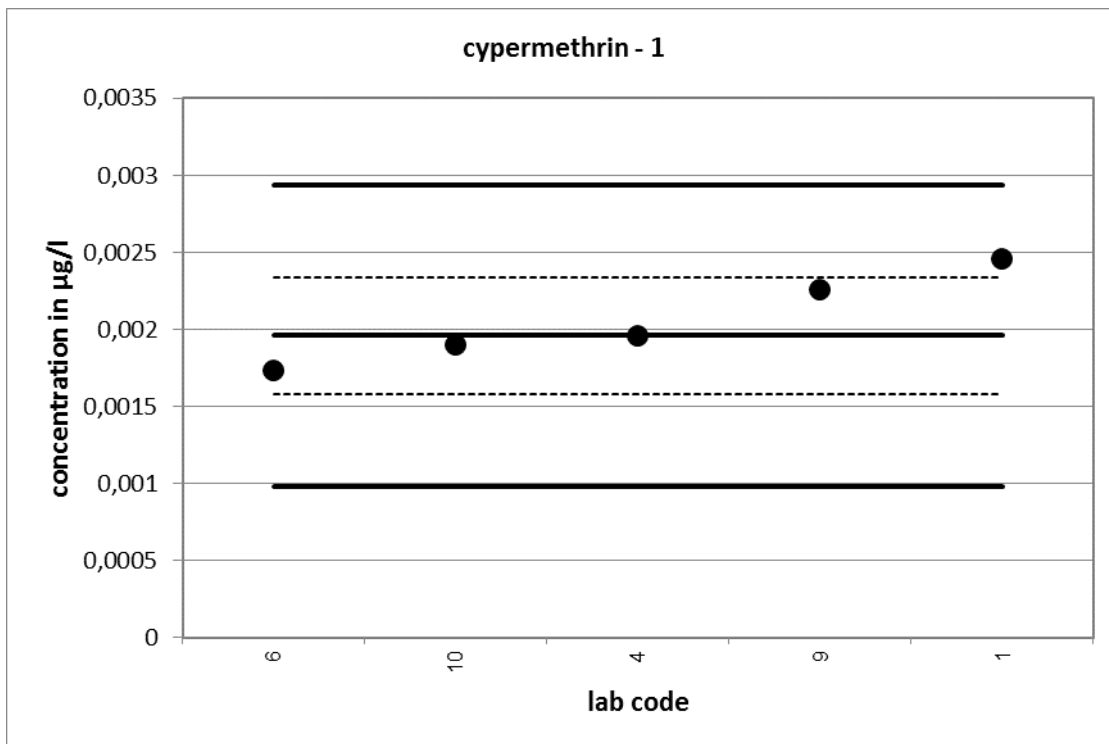
Used methods

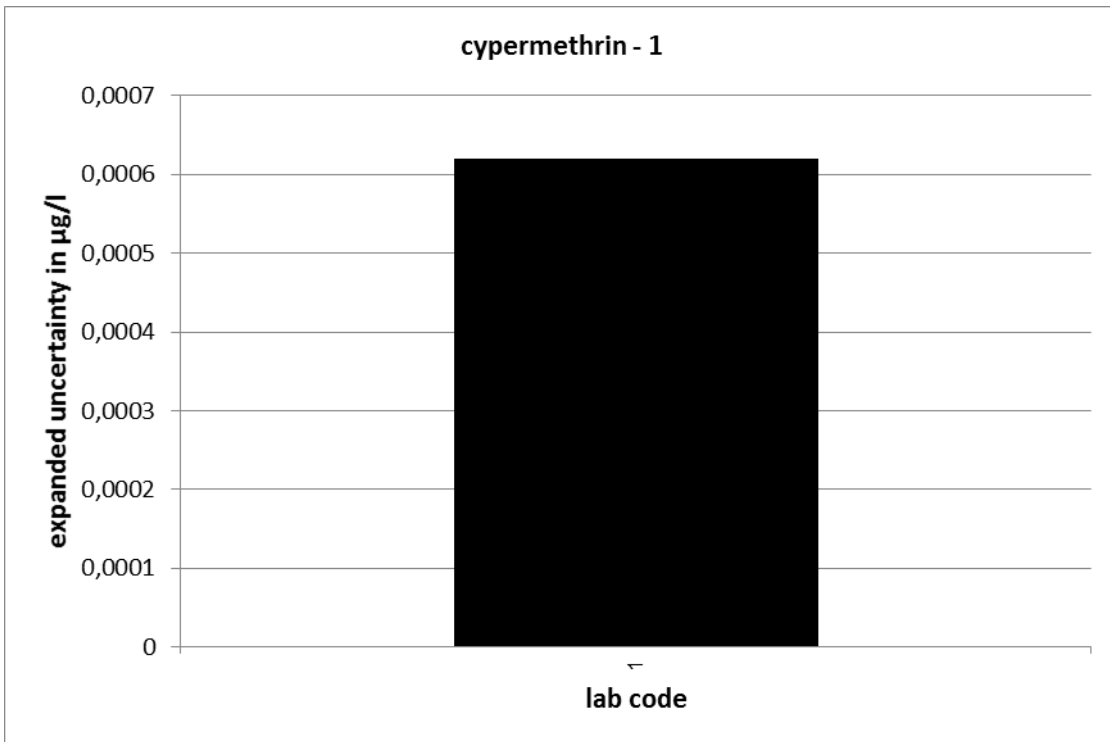
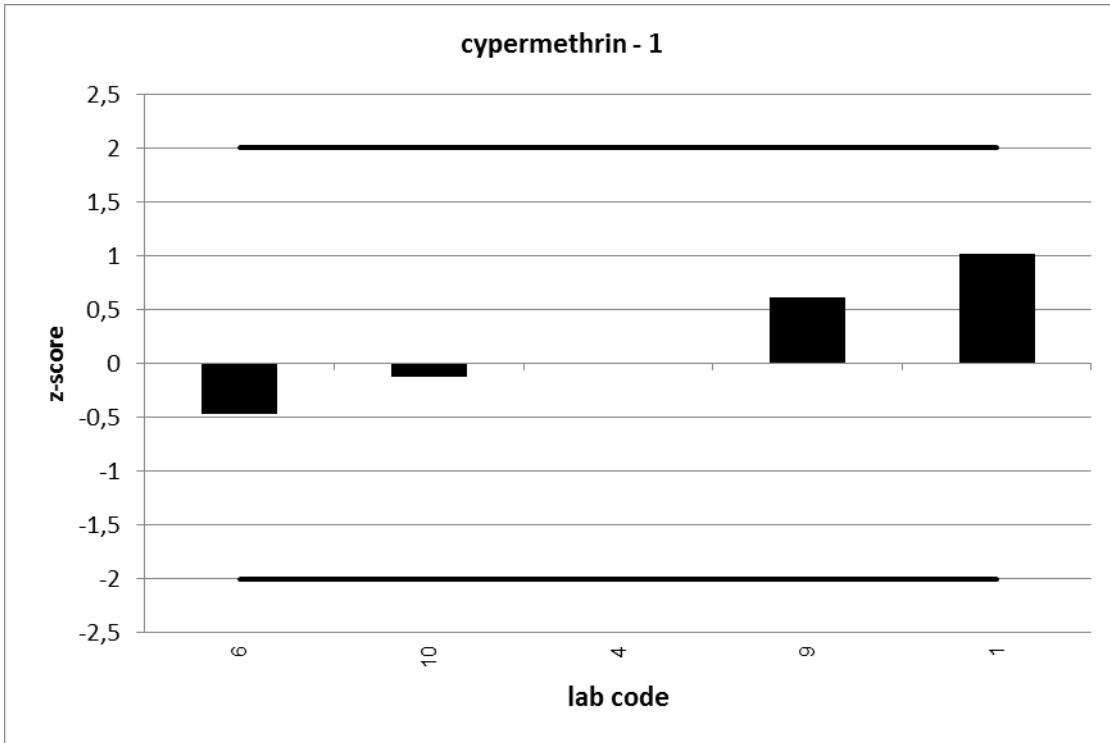


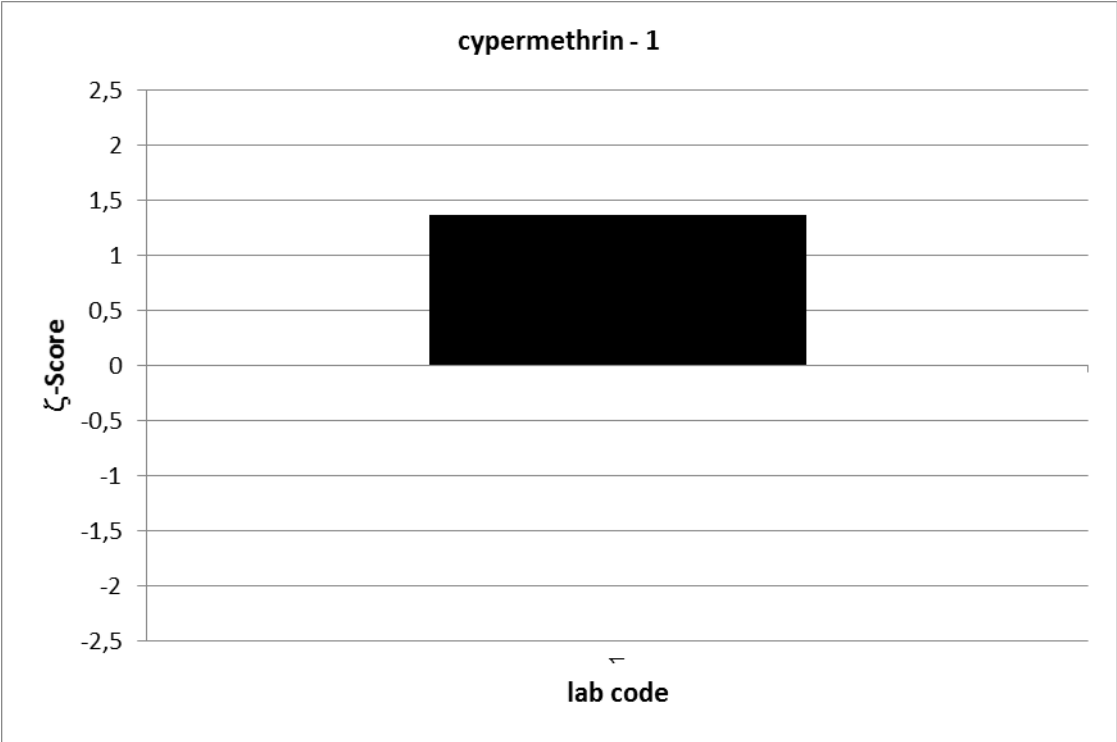
UKWIR 5/18		cypermethrin - 1			
assigned value [$\mu\text{g/l}$]*		0,00196 \pm 0,000381			
upper tolerance limit [$\mu\text{g/l}$]		0,00294			
lower tolerance limit [$\mu\text{g/l}$]		0,00098			
lab code	result [$\mu\text{g/l}$]	\pm	ζ -score	z-score	assessm.*
1	0,00246	6E-04	1,4	1,0	s
4	0,00196			0,0	s
6	0,00173			-0,5	s
9	0,00226			0,6	s
10	0,0019			-0,1	s

* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor $k=2$ corresponding to a confidence level of about 95%

** s = satisfactory, q = questionable, u = unsatisfactory



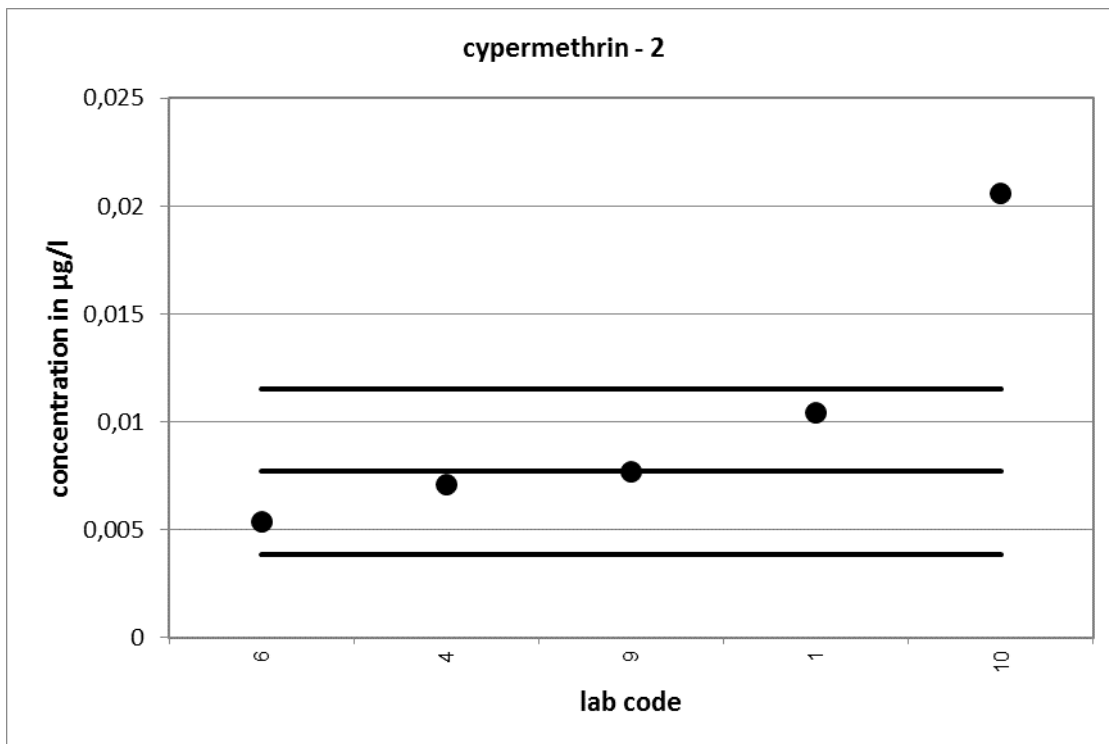


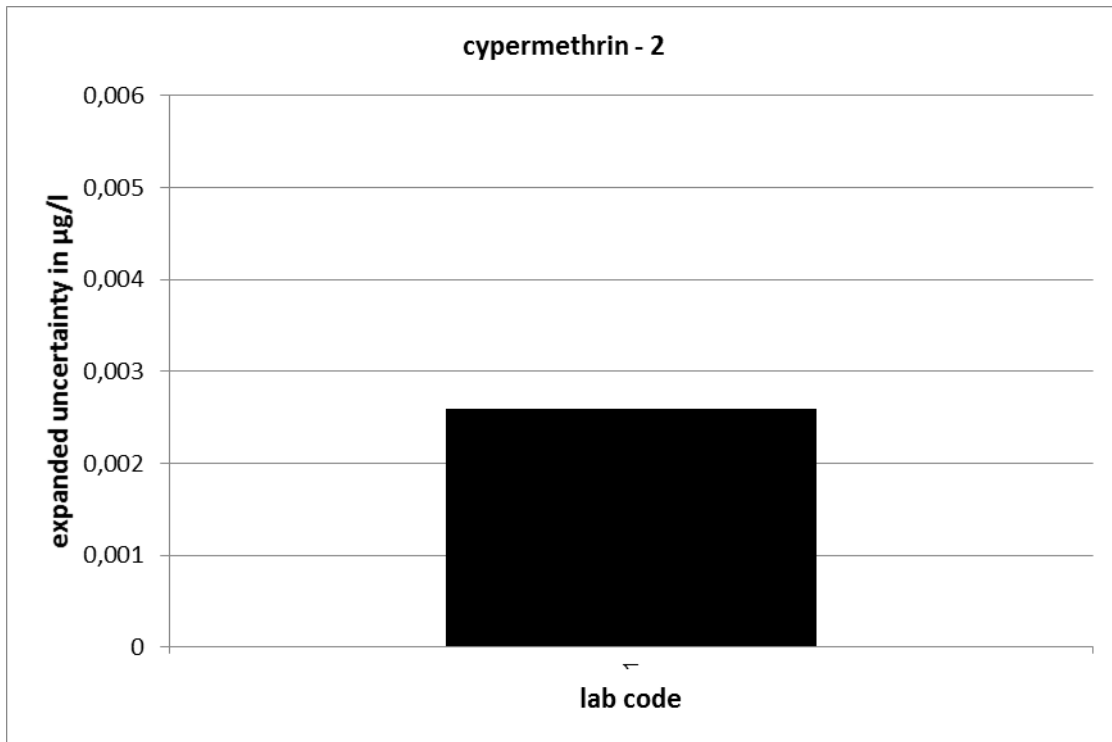
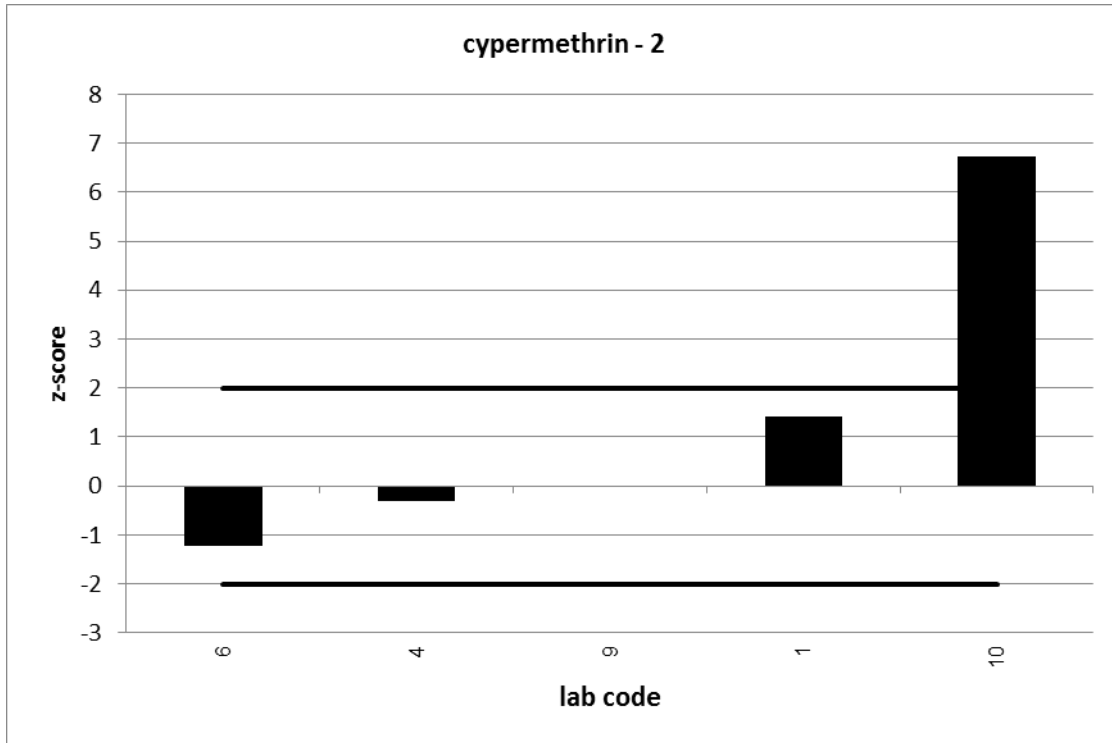


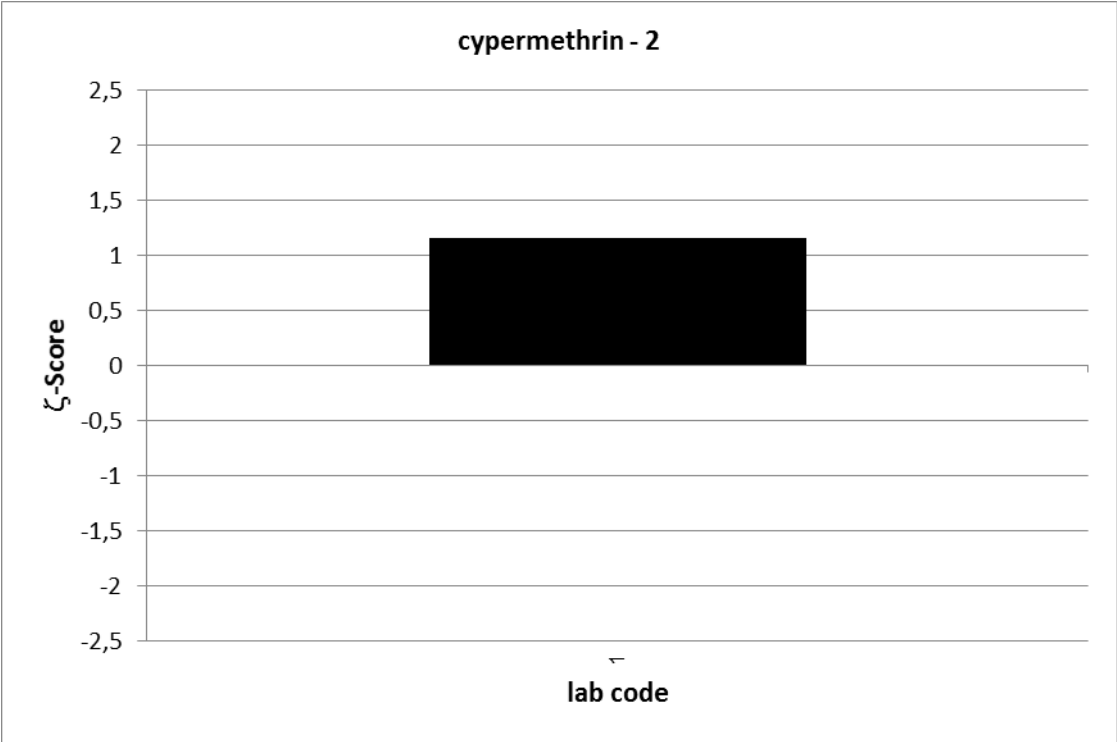
UKWIR 5/18		cypermethrin - 2			
assigned value [$\mu\text{g/l}$]*		0,00769 \pm 0,003896			
upper tolerance limit [$\mu\text{g/l}$]		0,01154			
lower tolerance limit [$\mu\text{g/l}$]		0,003845			
lab code	result [$\mu\text{g/l}$]	\pm	ζ -score	z-score	assessm.*
1	0,0104	0,003	1,2	1,4	s
4	0,00711			-0,3	s
6	0,00534			-1,2	s
9	0,00769			0,0	s
10	0,0206			6,7	u

* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor $k=2$ corresponding to a confidence level of about 95%

** s = satisfactory, q = questionable, u = unsatisfactory







UKWIR 5/18		cypermethrin - 3			
assigned value [$\mu\text{g/l}$]*		0,0272 \pm 0,00196			
upper tolerance limit [$\mu\text{g/l}$]		0,0408			
lower tolerance limit [$\mu\text{g/l}$]		0,0136			
lab code	result [$\mu\text{g/l}$]	\pm	ζ -score	z-score	assessm.*
1	0,0292	0,007	0,5	0,3	s
4	0,0272			0,0	s
6	0,02602			-0,2	s
9	0,015			-1,8	s
10	0,0283			0,2	s

* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor $k=2$ corresponding to a confidence level of about 95%

** s = satisfactory, q = questionable, u = unsatisfactory

