

Analytische Qualitätssicherung Baden-Württemberg

Proficiency Tests UKWIR 1/20 to 5/20
priority substances in surface water -

benzo[a]pyrene, fluoranthene, perfluorooctane sulfonic acid,
perfluorooctanoic acid, cypermethrin, hexabromocyclodecane,
nonylphenol, octylphenol

Stuttgart, July 2020

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 three rounds the following determinands were to be measured:

- UKWIR 1/20
 - benzo[a]pyrene
 - fluoranthene
- UKWIR 2/20
 - perfluorooctane sulfonic acid (PFOS)
 - perfluorooctanoic acid (PFOA)
- UKWIR 3/20
 - cypermethrin
- UKWIR 4/20
 - hexabromocyclododecane (HBCDD)
- UKWIR 5/20
 - nonylphenol
 - octylphenol

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

PT design

Each participant received the following samples for the PT rounds UKWIR 1/20-4/20:

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

For the PT round UKWIR 5/20 the participants received following samples:

- 3 spiked samples for the determination of the respective determinands based on a filtered and pasteurised effluent of a waste water treatment plant in 1000 ml glass bottles with ground glass plug
- 1 blank sample of the filtered and pasteurised waste water

The concentrations of the analytes 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 limits of quantification were required:

| Determinand | Required LOQ in µg/l |
|----------------|----------------------|
| benzo[a]pyrene | 0.0005 |
| fluoranthene | 0.0018 |
| PFOS | 0.002 |
| PFOA | 0.002 |
| cypermethrin | 0.0004 |
| HBCDD | 0.0092 |
| nonylphenol | 0.05 |
| octylphenol | 0.01 |

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 with the combined estimator Hampel/Q-method, a method of robust statistics.

For the PT 1/20 the assigned value x_{pt} was derived from participants' results using the Hampel estimator, for the PTs 3/20 to 4/20 due to the low number of results in UKWIR PT 7/19 we used an arithmetic mean after exclusion of the gross outliers.

The uncertainty of the assigned value was calculated according to ISO 13528:

$$u(x_{pt}) = \frac{1,25 \times s^*}{\sqrt{p}}$$

s^* : standard deviation calculated from the results using the Q-method

p : number of results

For PT 2/20 the assigned value was calculated from the formulation of the sample, the spiked amount plus the median of the blank analyses of the participating laboratories. In this case the uncertainty was calculated from the uncertainties of the weighings plus the uncertainty of the median of blank analyses.

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:

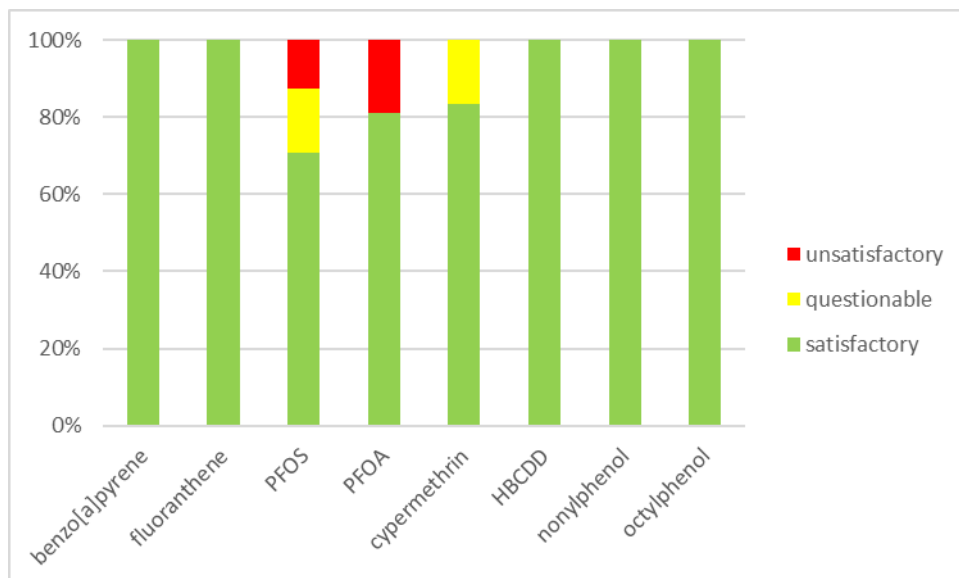
- |z| ≤ 2.0 satisfactory
- 2.0 < |z| < 3.0 questionable
- |z| ≥ 3.0 unsatisfactory

Results of evaluation

Number of participants:

| PT round | determinands | number of participants | number of participants reporting results |
|------------|---|------------------------|--|
| UKWIR 1/20 | benzo[a]pyrene fluoranthene | 7 | 6 |
| UKWIR 2/20 | perfluorooctane sulfonic acid (PFOS) perfluorooctanoic acid (PFOA) | 8 | 8 |
| UKWIR 3/20 | cypermethrin | 6 | 6 |
| UKWIR 4/20 | HBCDD | 7 | 5 |
| UKWIR 5/20 | nonylphenol octylphenol | 8 | 4 |

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 µg/l
- expanded uncertainty of the assigned value in %
- standard deviation of the data set in µg/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 µg/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 µg/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.

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.

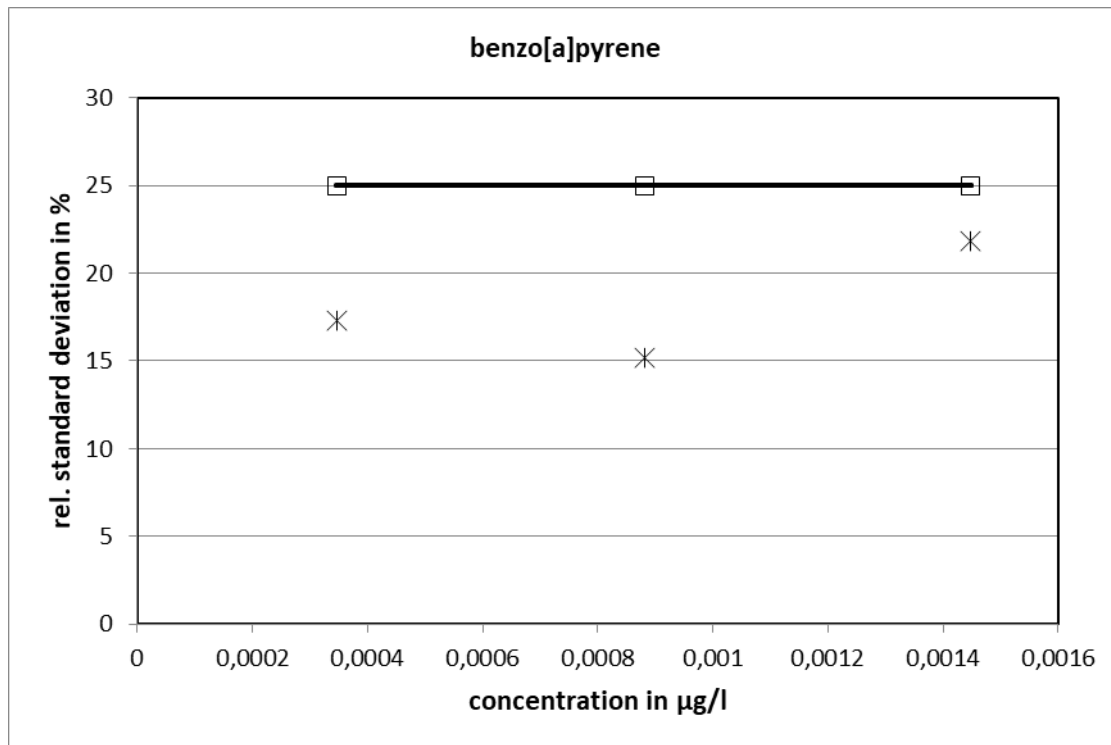
ζ -score graphs

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

UKWIR 1/20

| benzo[a]pyrene | | | | | | | | | | | | | | |
|-----------------------|-----------------------|--|---|--|---|------------------------------|------------------------------|---------------------------|---------------------------|-------------------|-----------|-----------|---------|-----|
| 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 | 0,0009 | 15,49 | 0,0001 | 0,0002 | 25,00 | 0,0013 | 0,0004 | 50,00 | -50,00 | 6 | 0 | 0 | 0,0 | |
| 2 | 0,0003 | 19,32 | 0,0001 | 0,0001 | 25,00 | 0,0005 | 0,0002 | 50,00 | -50,00 | 5 | 0 | 0 | 0,0 | |
| 3 | 0,0014 | 22,28 | 0,0003 | 0,0004 | 25,00 | 0,0022 | 0,0007 | 50,00 | -50,00 | 6 | 0 | 0 | 0,0 | |
| | | | | | | | | | | sum | 17 | 0 | 0 | 0,0 |

Relative standard deviation

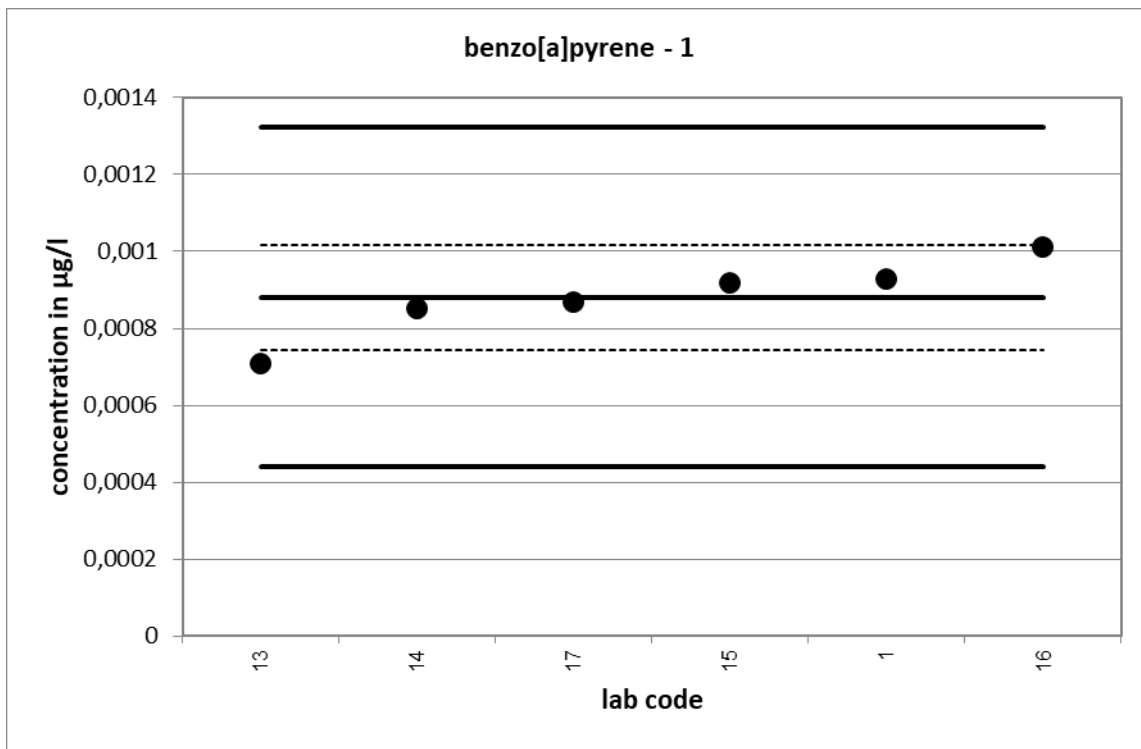


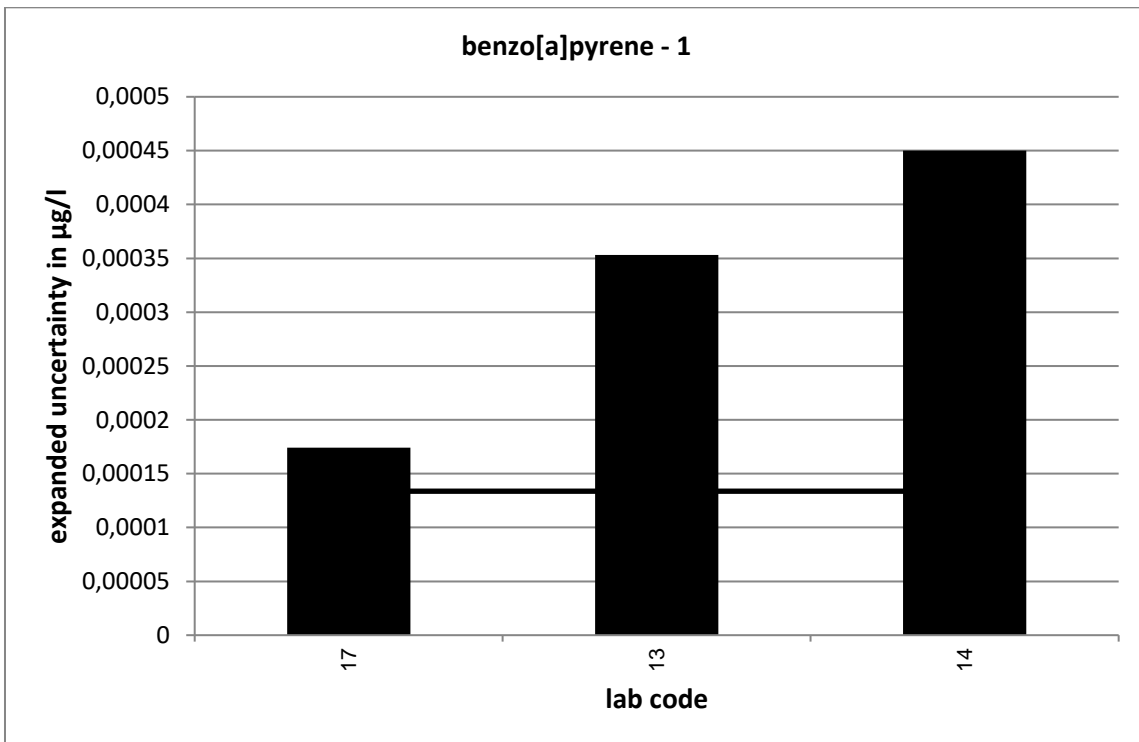
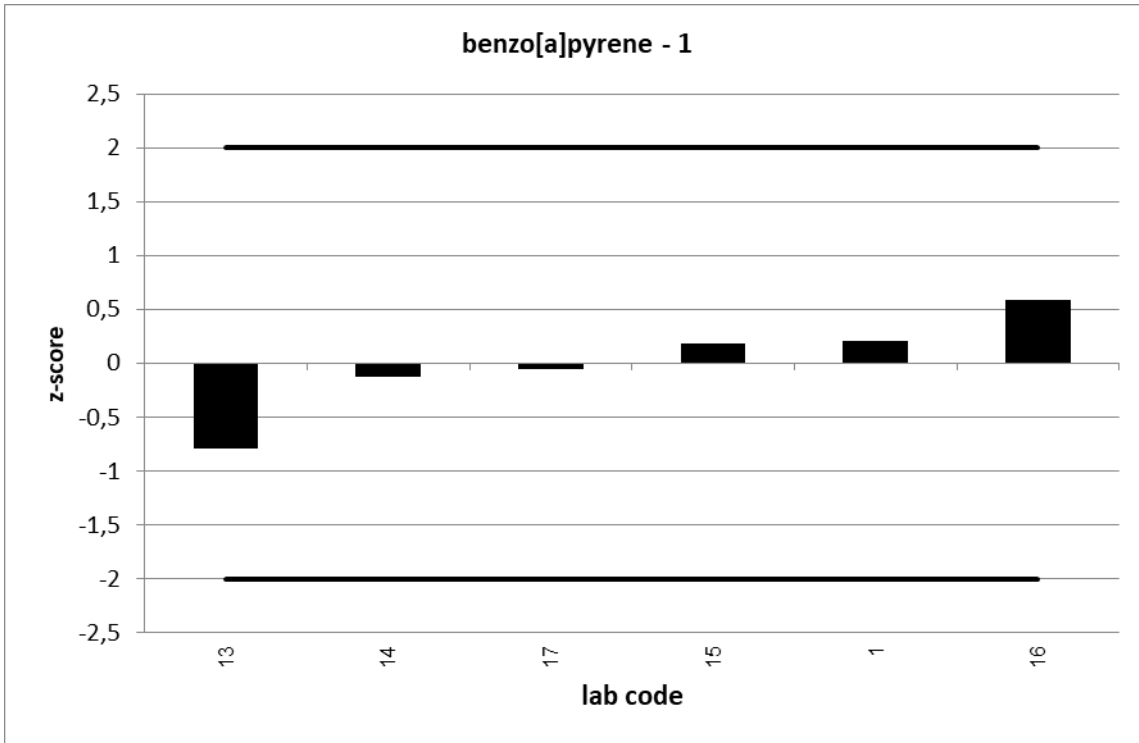
25 % is the value used as standard deviation for proficiency assessment.

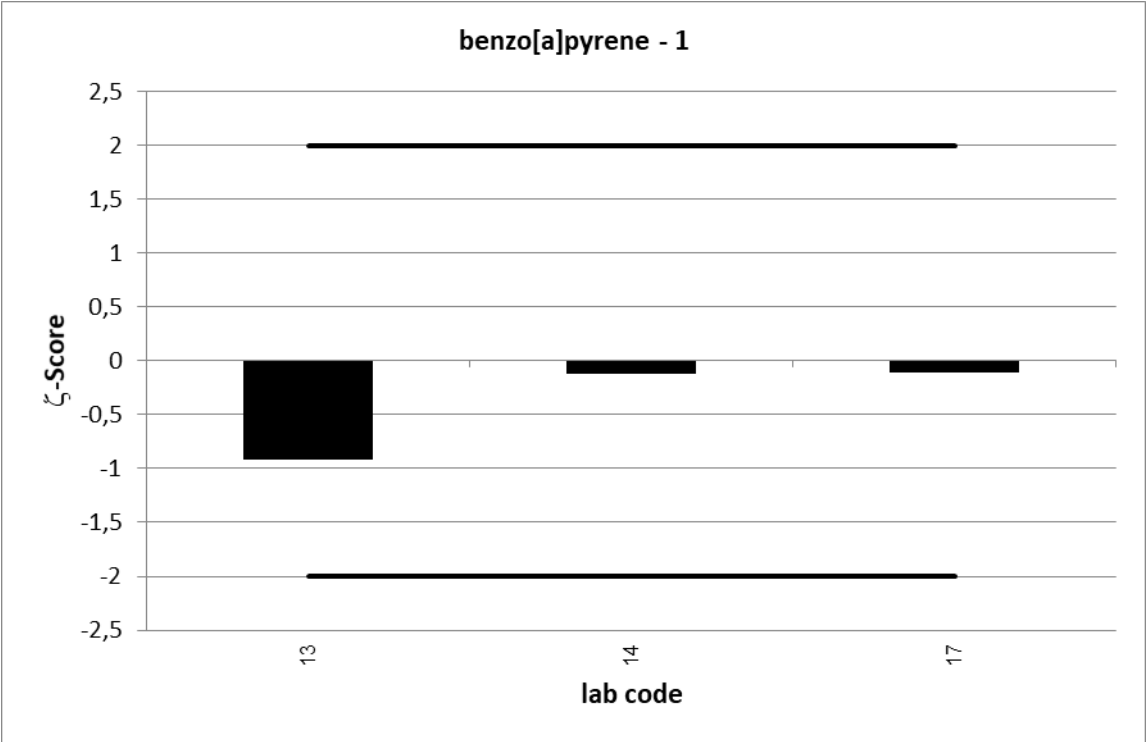
| UKWIR PT 1/20 | | benzo[a]pyrene - 1 | | | |
|---|----------------------------|--------------------------|----------------|---------|------------|
| assigned value [$\mu\text{g/l}$]* | | 0,000881 \pm 0,0001365 | | | |
| upper tolerance limit [$\mu\text{g/l}$] | | 0,001322 | | | |
| lower tolerance limit [$\mu\text{g/l}$] | | 0,0004405 | | | |
| lab code | result [$\mu\text{g/l}$] | \pm | ζ -score | z-score | assessm.** |
| 1 | 0,000927 | | | 0,2 | s |
| 13 | 0,000707 | 4E-04 | -0,9 | -0,8 | s |
| 14 | 0,000853 | 5E-04 | -0,1 | -0,1 | s |
| 15 | 0,00092 | | | 0,2 | s |
| 16 | 0,00101 | | | 0,6 | s |
| 17 | 0,000869 | 2E-04 | -0,1 | -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



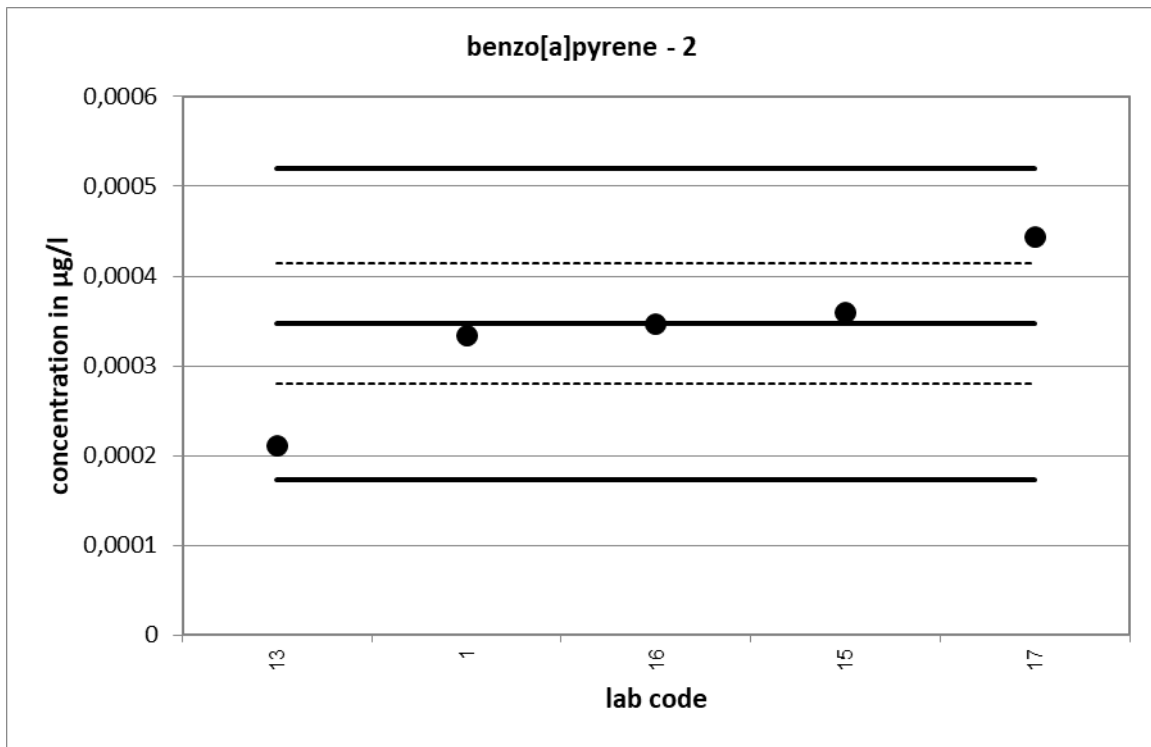


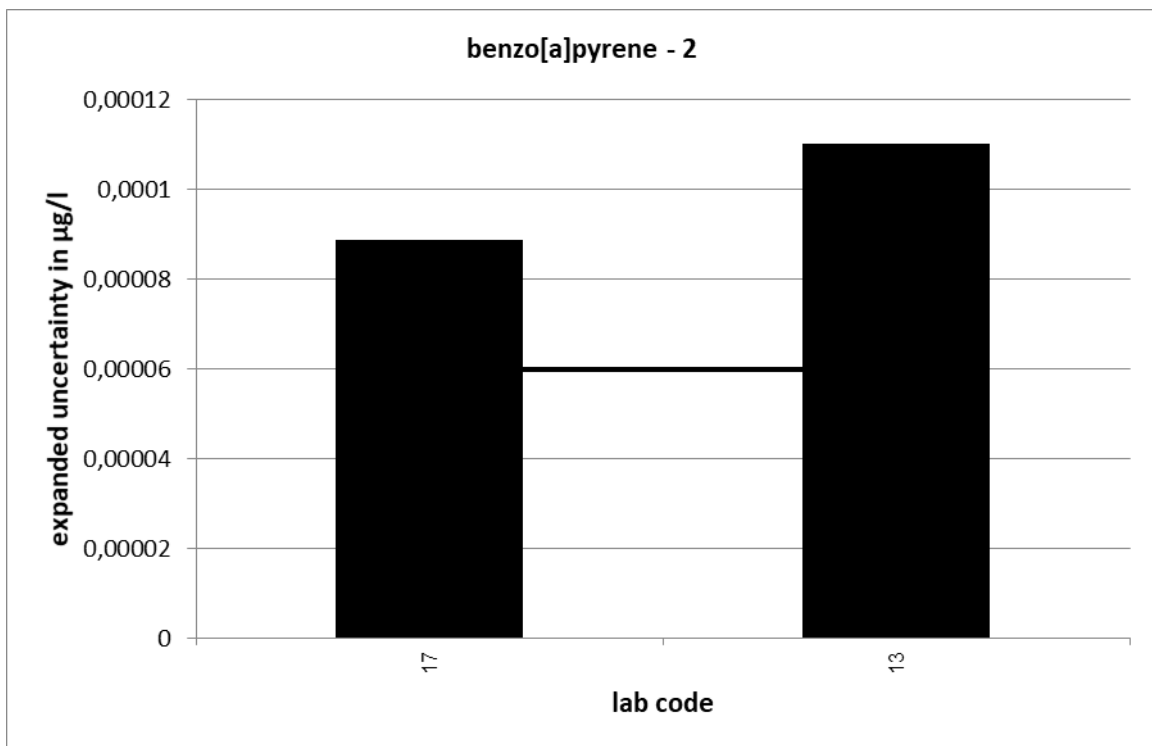
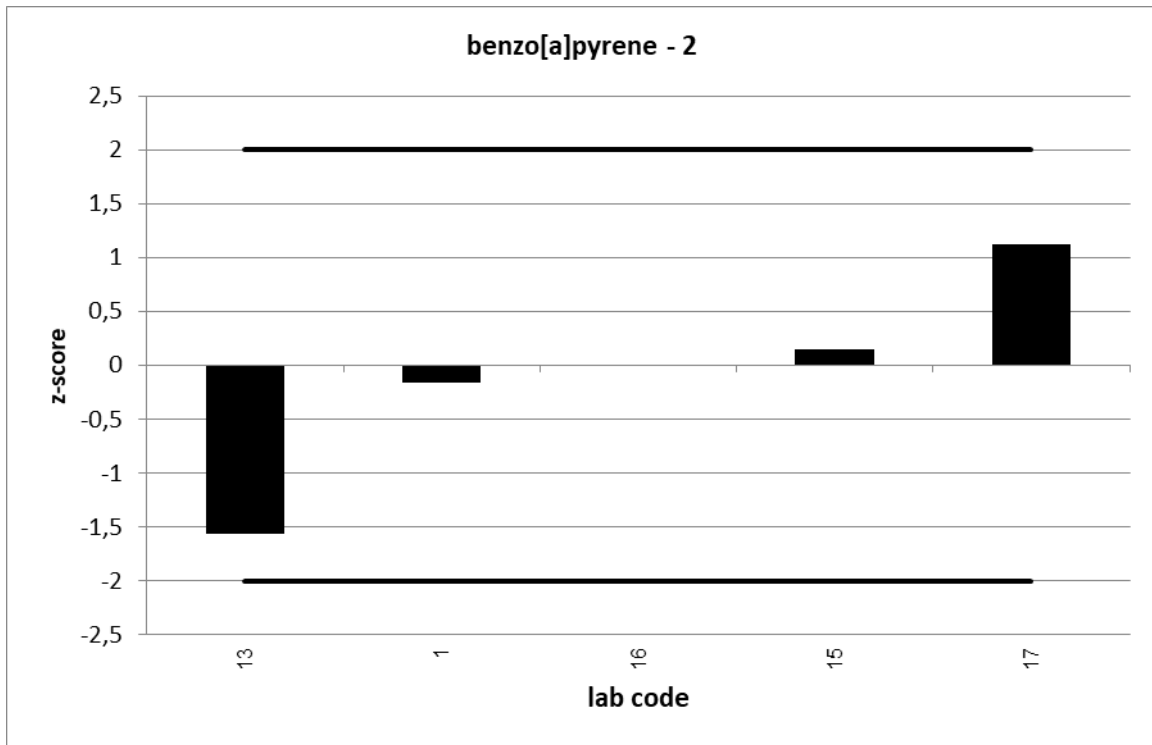


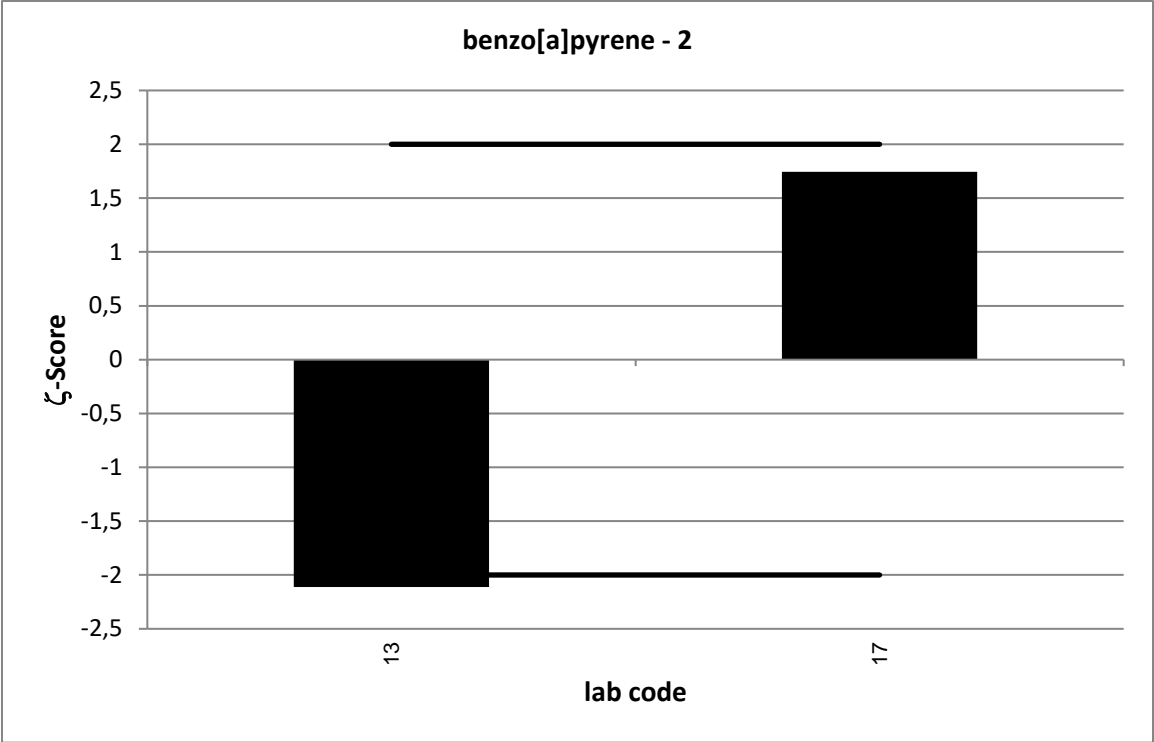
| UKWIR PT 1/20 | | benzo[a]pyrene - 2 | | | |
|---|----------------------------|-------------------------|----------------|---------|------------|
| assigned value [$\mu\text{g/l}$]* | | 0,000347 \pm 0,000067 | | | |
| upper tolerance limit [$\mu\text{g/l}$] | | 0,0005205 | | | |
| lower tolerance limit [$\mu\text{g/l}$] | | 0,0001735 | | | |
| lab code | result [$\mu\text{g/l}$] | \pm | ζ -score | z-score | assessm.** |
| 1 | 0,000333 | | | -0,2 | s |
| 13 | 0,000211 | 1E-04 | -2,1 | -1,6 | s |
| 15 | 0,00036 | | | 0,1 | s |
| 16 | 0,000347 | | | 0,0 | s |
| 17 | 0,000444 | 9E-05 | 1,7 | 1,1 | 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



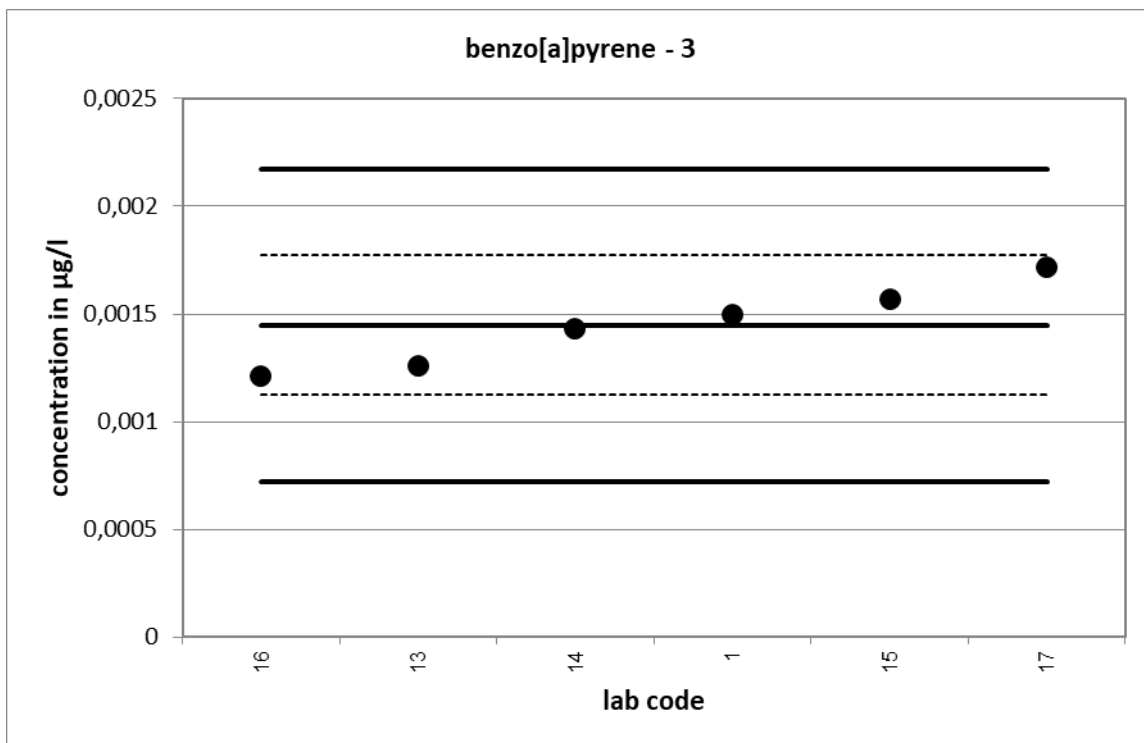


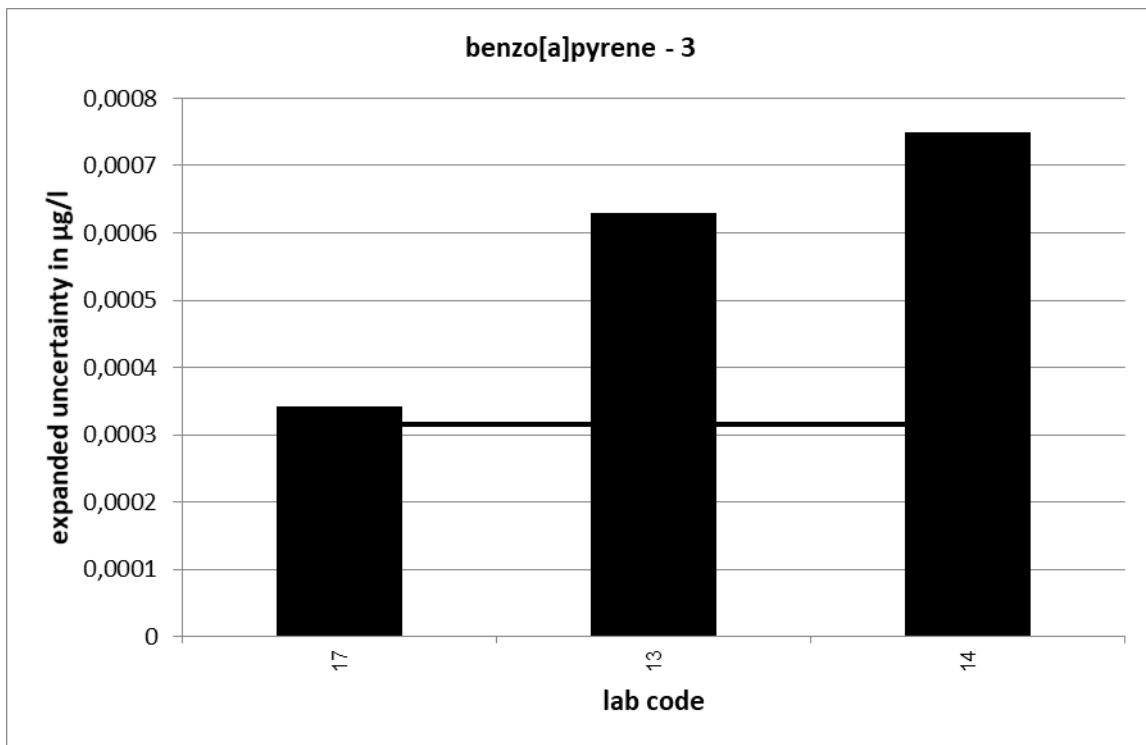
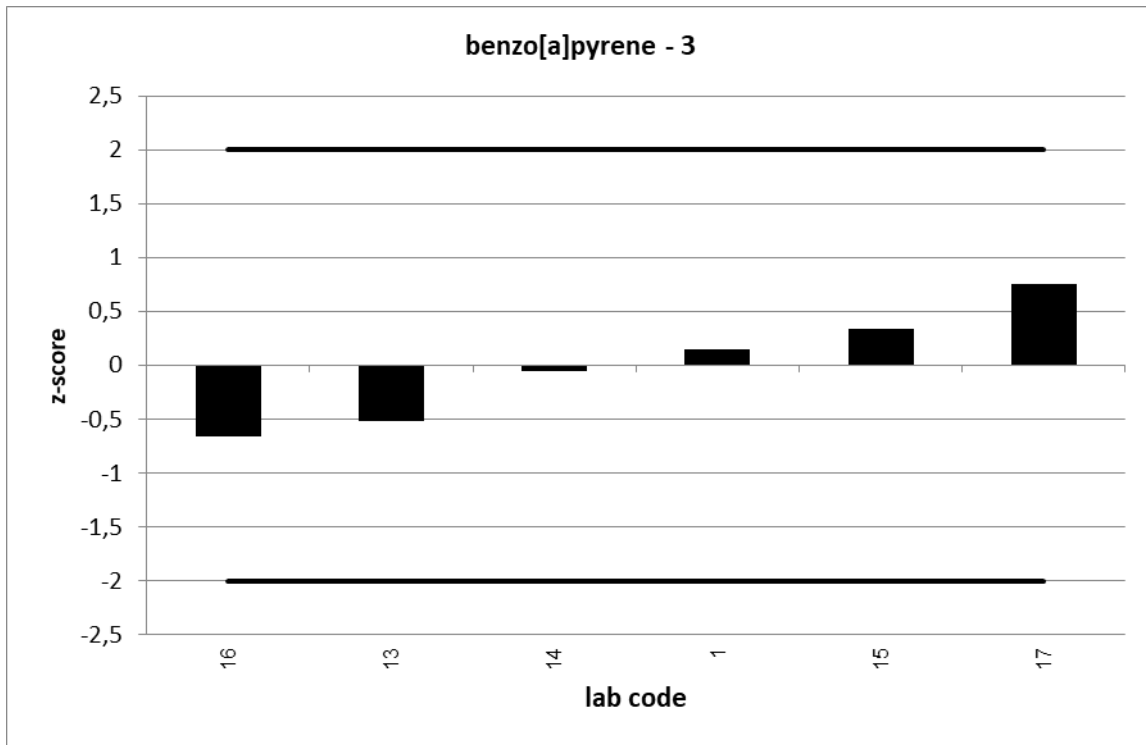


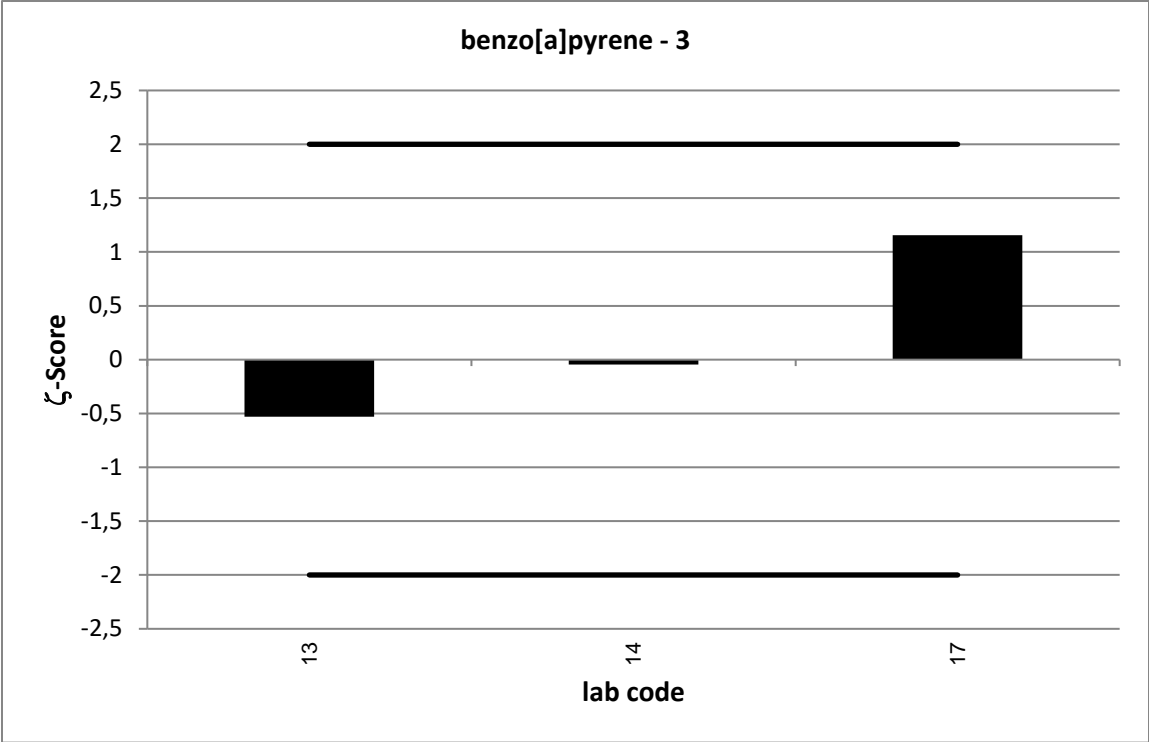
| UKWIR PT 1/20 | | benzo[a]pyrene - 3 | | | |
|---|----------------------------|-------------------------|----------------|---------|------------|
| assigned value [$\mu\text{g/l}$]* | | 0,001448 \pm 0,000323 | | | |
| upper tolerance limit [$\mu\text{g/l}$] | | 0,002172 | | | |
| lower tolerance limit [$\mu\text{g/l}$] | | 0,000724 | | | |
| lab code | result [$\mu\text{g/l}$] | \pm | ζ -score | z-score | assessm.** |
| 1 | 0,0015 | | | 0,1 | s |
| 13 | 0,00126 | 6E-04 | -0,5 | -0,5 | s |
| 14 | 0,00143 | 8E-04 | 0,0 | 0,0 | s |
| 15 | 0,00157 | | | 0,3 | s |
| 16 | 0,00121 | | | -0,7 | s |
| 17 | 0,00172 | 3E-04 | 1,2 | 0,8 | 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

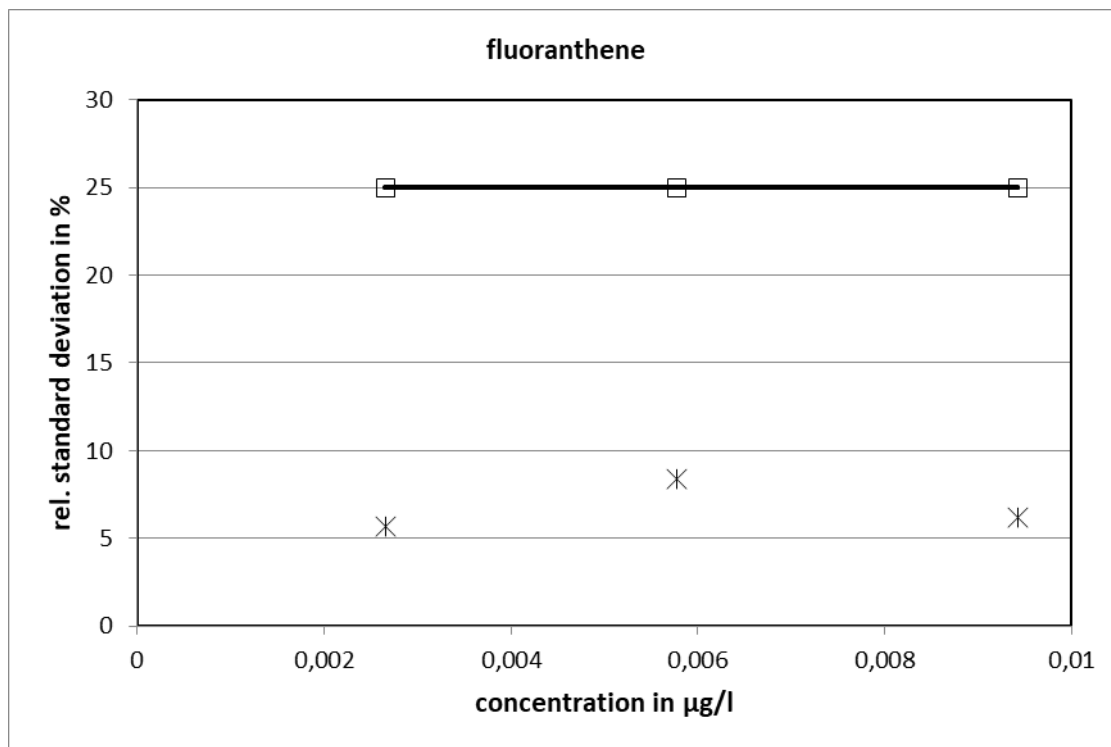






| fluoranthene | | | | | | | | | | | | | |
|--------------|-----------------------|--|---|--|---|------------------------------|------------------------------|---------------------------|---------------------------|-------------------|-----------|-----------|---------|
| level | assigned value [µg/l] | 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 | 0,0027 | 5,83 | 0,0002 | 0,0007 | 25,00 | 0,0040 | 0,0013 | 50,00 | -50,00 | 6 | 0 | 0 | 0,0 |
| 2 | 0,0058 | 8,56 | 0,0005 | 0,0014 | 25,00 | 0,0087 | 0,0029 | 50,00 | -50,00 | 6 | 0 | 0 | 0,0 |
| 3 | 0,0094 | 6,31 | 0,0006 | 0,0024 | 25,00 | 0,0141 | 0,0047 | 50,00 | -50,00 | 6 | 0 | 0 | 0,0 |
| | | | | | | | | | | sum | 18 | 0 | 0,0 |

Relative standard deviation

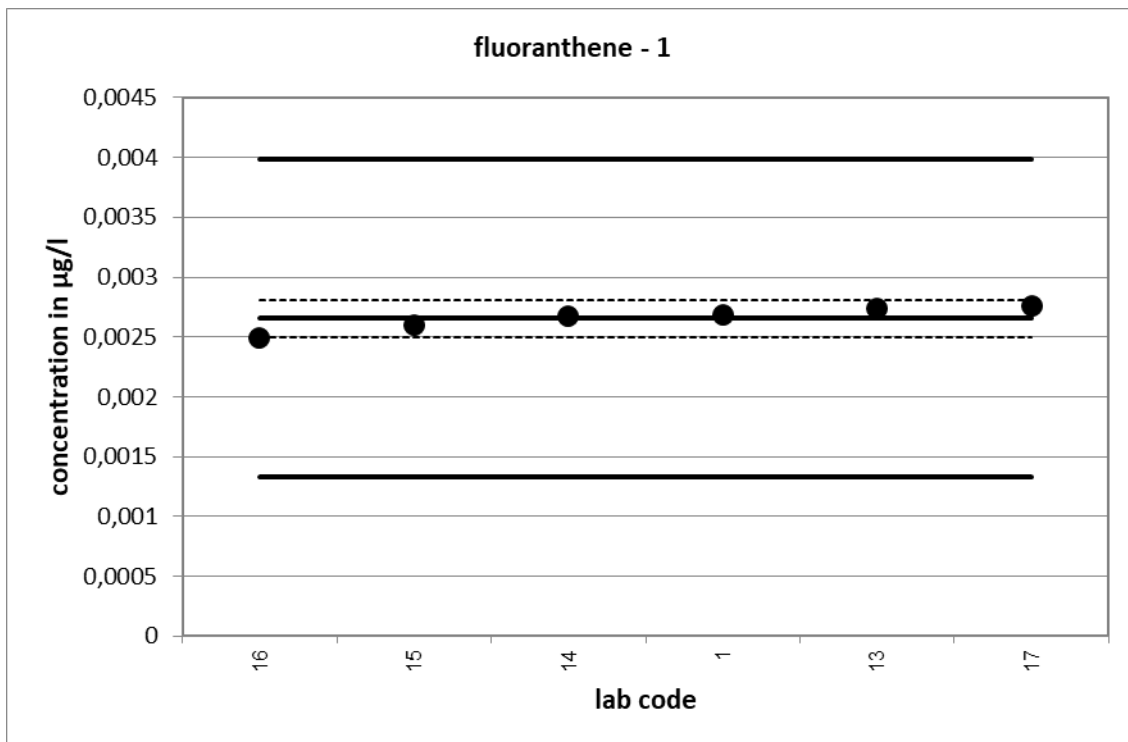


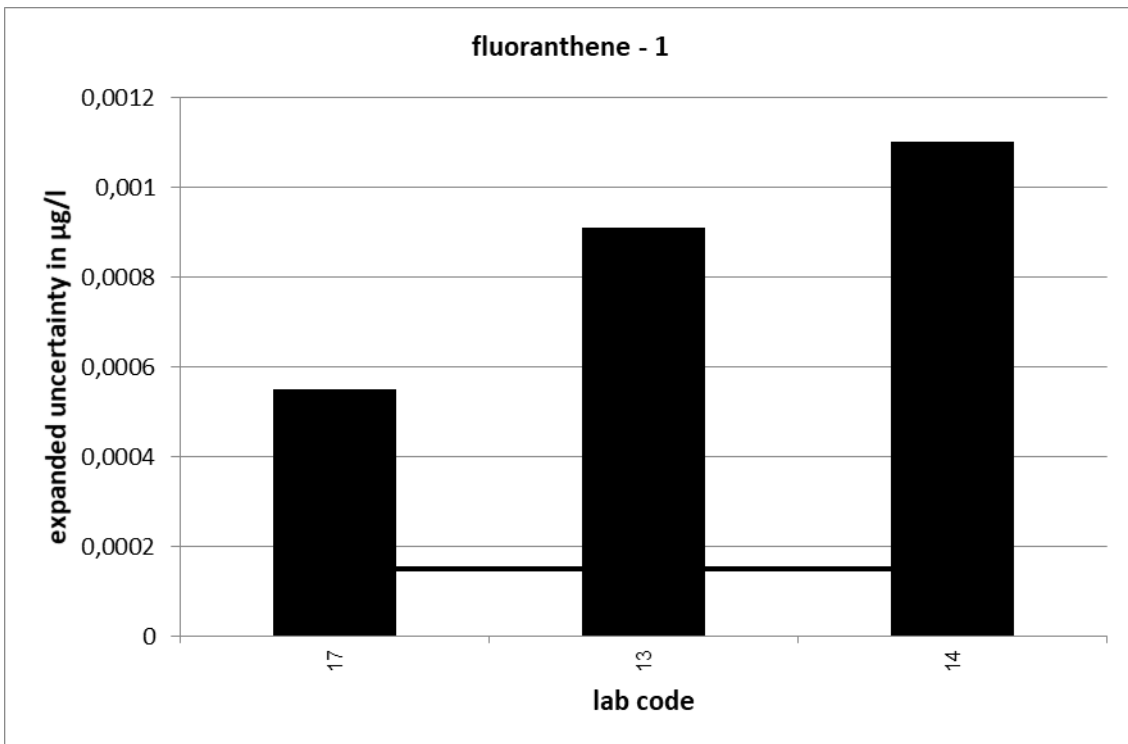
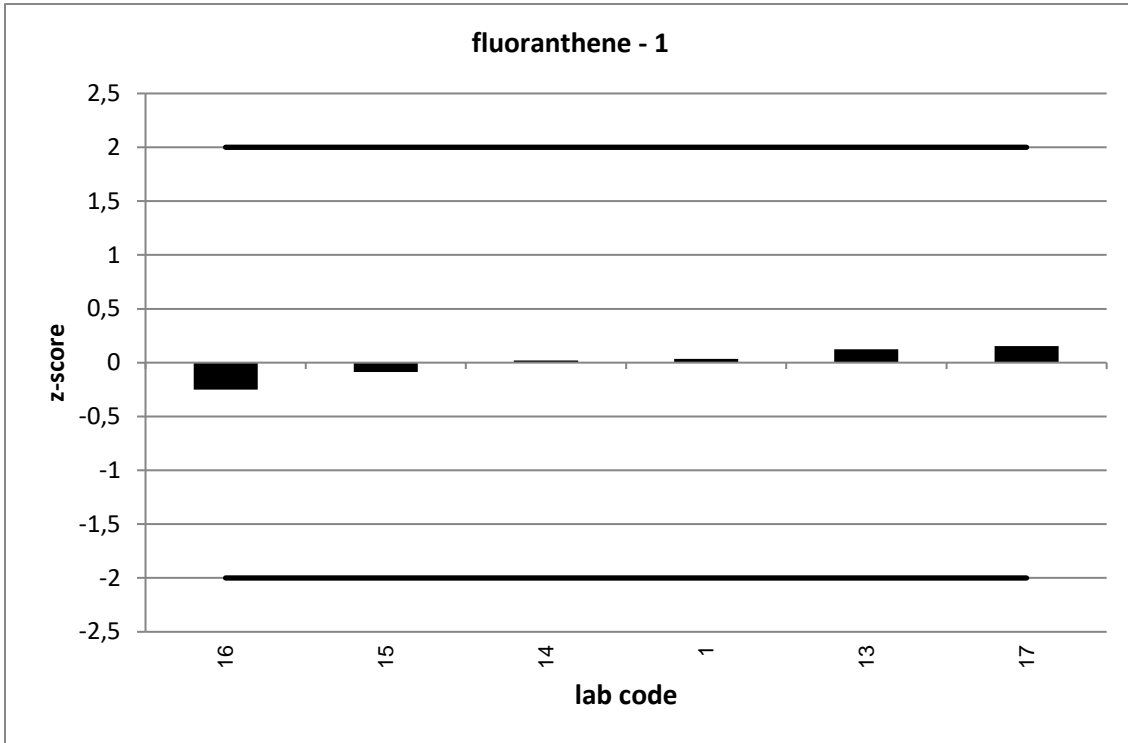
25 % is the value used as standard deviation for proficiency assessment.

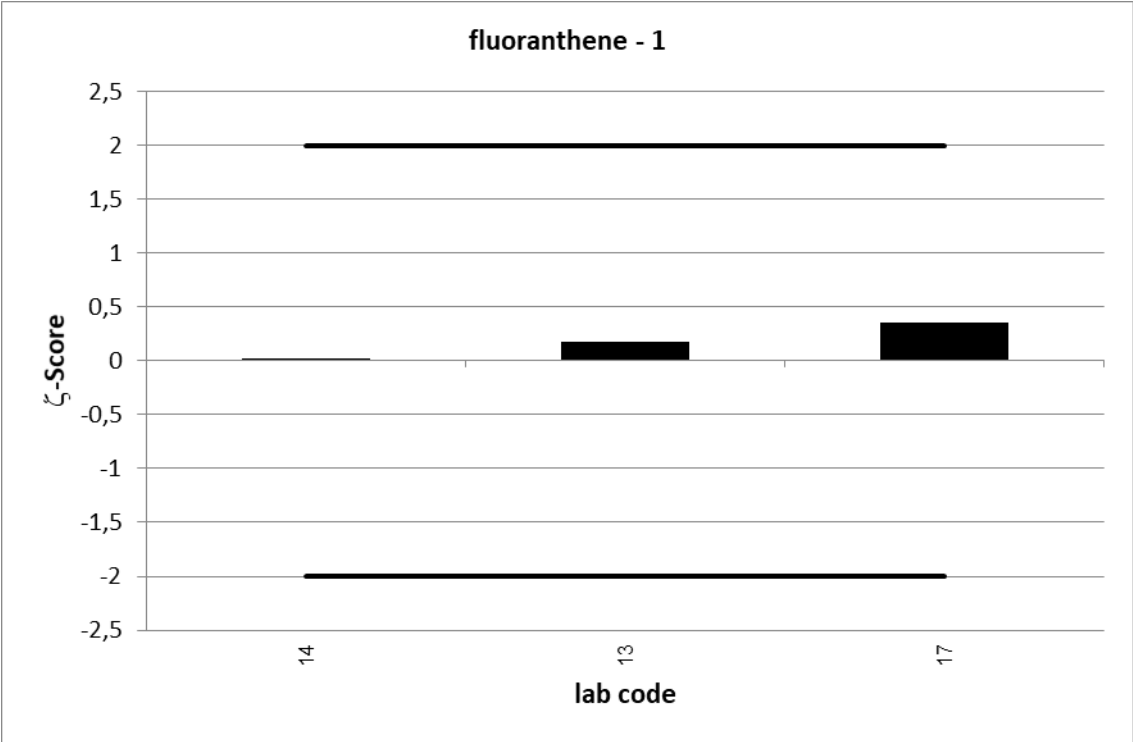
| UKWIR PT 1/20 | | fluoranthene - 1 | | | |
|---|----------------------------|------------------|----------------|----------------|------------|
| assigned value [$\mu\text{g/l}$]* | | 0,002657 | | $\pm 0,000155$ | |
| upper tolerance limit [$\mu\text{g/l}$] | | 0,003986 | | | |
| lower tolerance limit [$\mu\text{g/l}$] | | 0,001329 | | | |
| lab code | result [$\mu\text{g/l}$] | \pm | ζ -score | z-score | assessm.** |
| 1 | 0,00268 | | | 0,0 | s |
| 13 | 0,00274 | 9E-04 | 0,2 | 0,1 | s |
| 14 | 0,00267 | 0,001 | 0,0 | 0,0 | s |
| 15 | 0,0026 | | | -0,1 | s |
| 16 | 0,00249 | | | -0,3 | s |
| 17 | 0,00276 | 6E-04 | 0,4 | 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



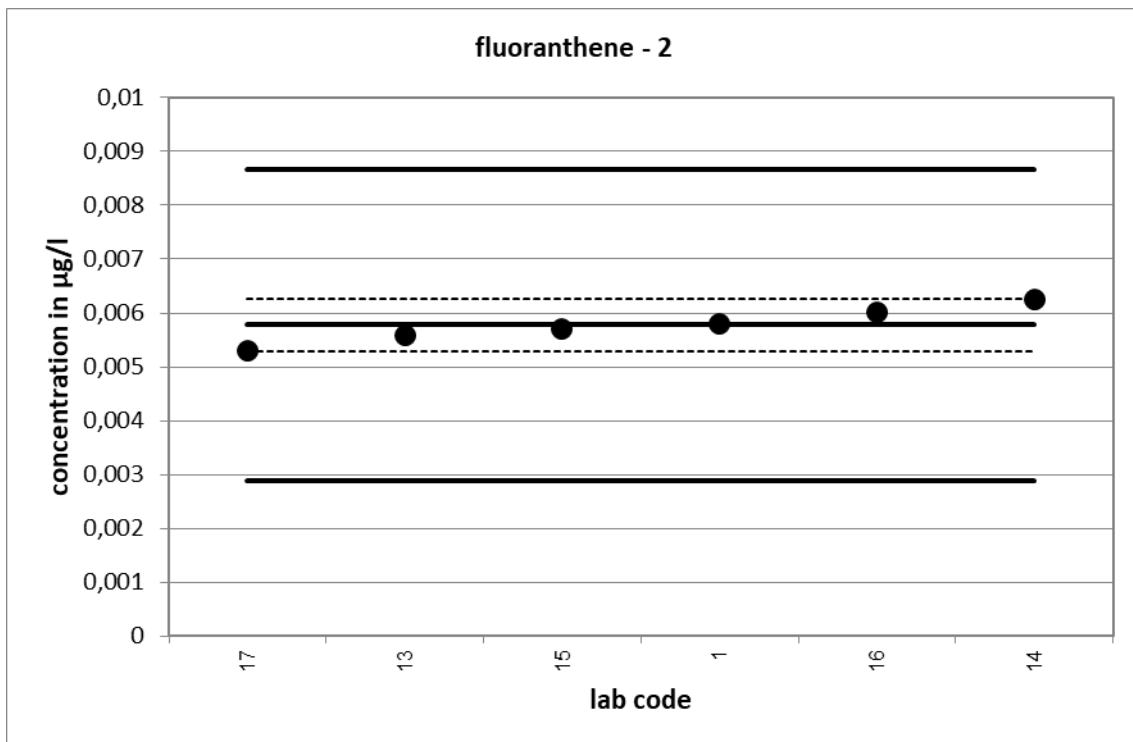


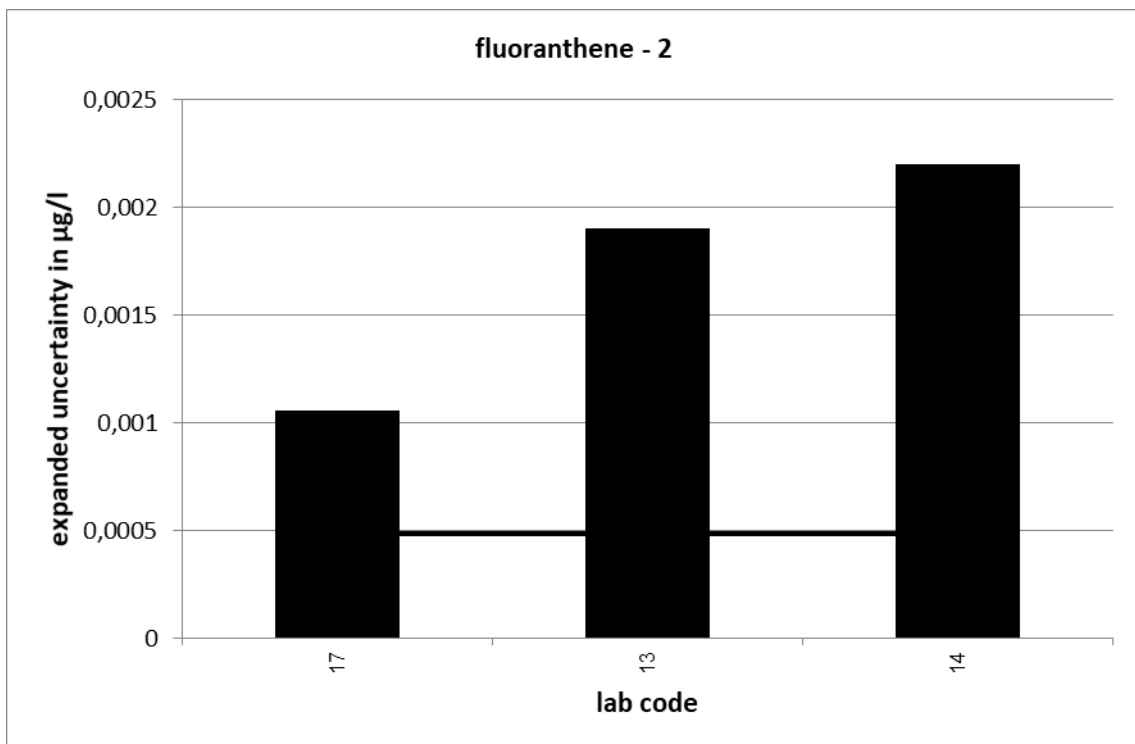
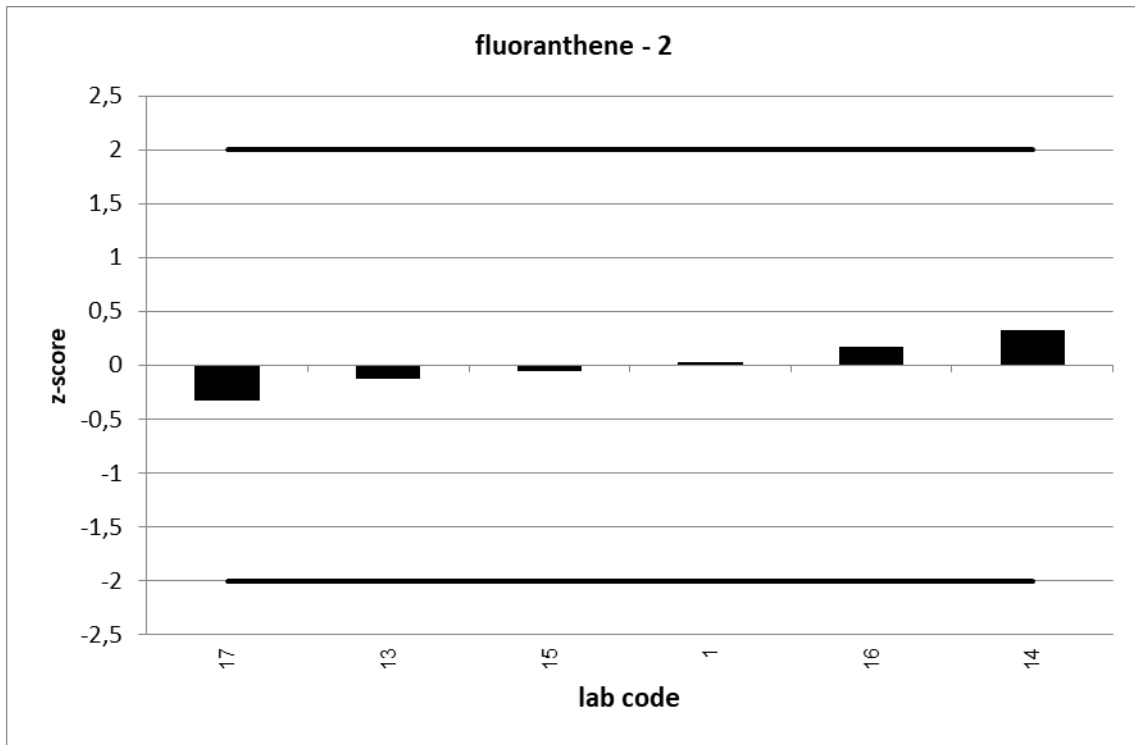


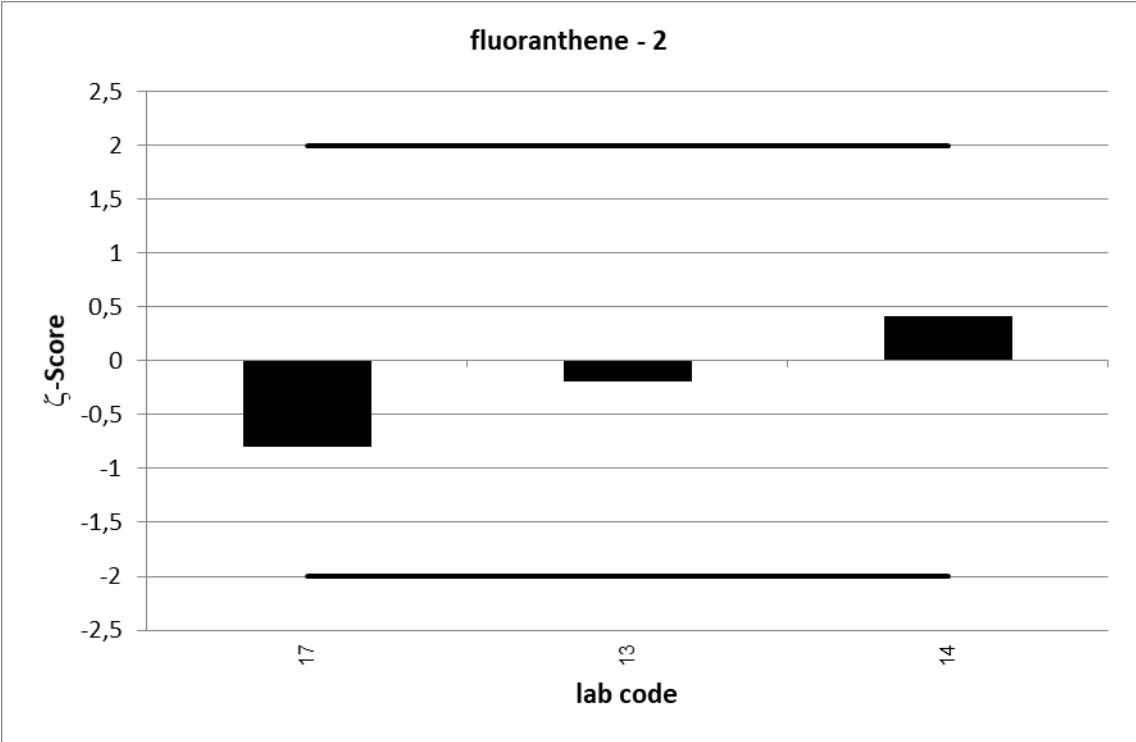
| UKWIR PT 1/20 | | fluoranthene - 2 | | | |
|---|----------------------------|-------------------------|----------------|---------|------------|
| assigned value [$\mu\text{g/l}$]* | | 0,005778 \pm 0,000495 | | | |
| upper tolerance limit [$\mu\text{g/l}$] | | 0,008667 | | | |
| lower tolerance limit [$\mu\text{g/l}$] | | 0,002889 | | | |
| lab code | result [$\mu\text{g/l}$] | \pm | ζ -score | z-score | assessm.** |
| 1 | 0,00581 | | | 0,0 | s |
| 13 | 0,00559 | 0,002 | -0,2 | -0,1 | s |
| 14 | 0,00624 | 0,002 | 0,4 | 0,3 | s |
| 15 | 0,0057 | | | -0,1 | s |
| 16 | 0,00602 | | | 0,2 | s |
| 17 | 0,00531 | 0,001 | -0,8 | -0,3 | 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



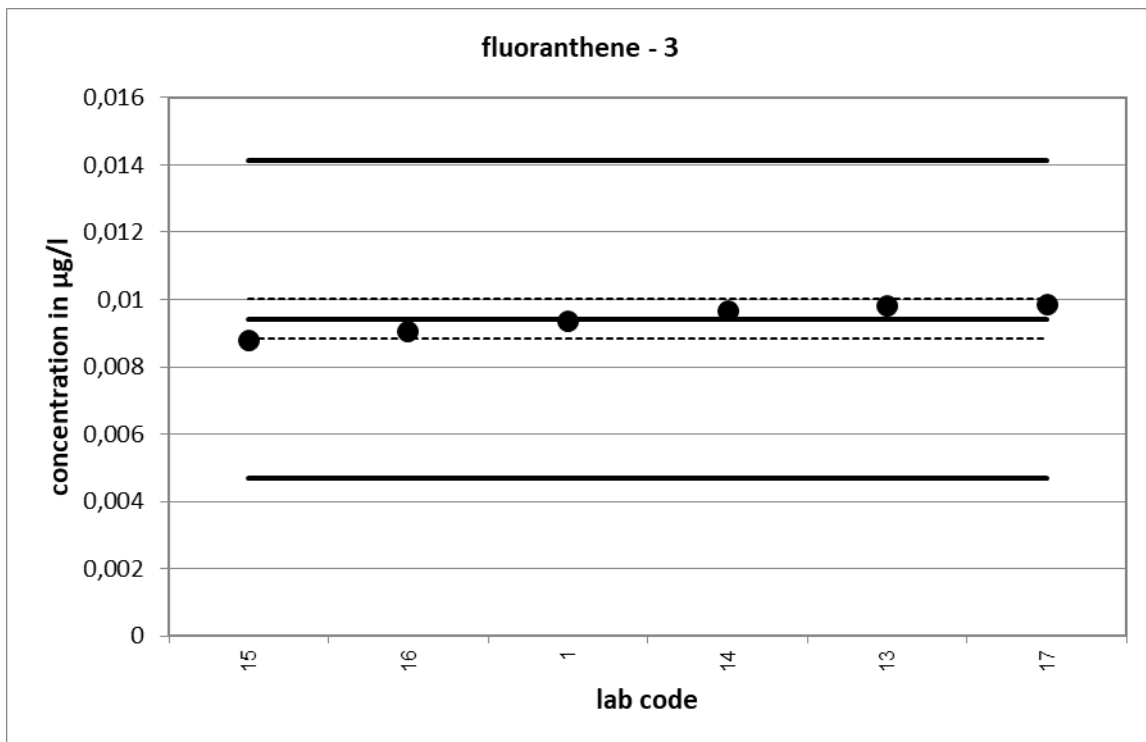


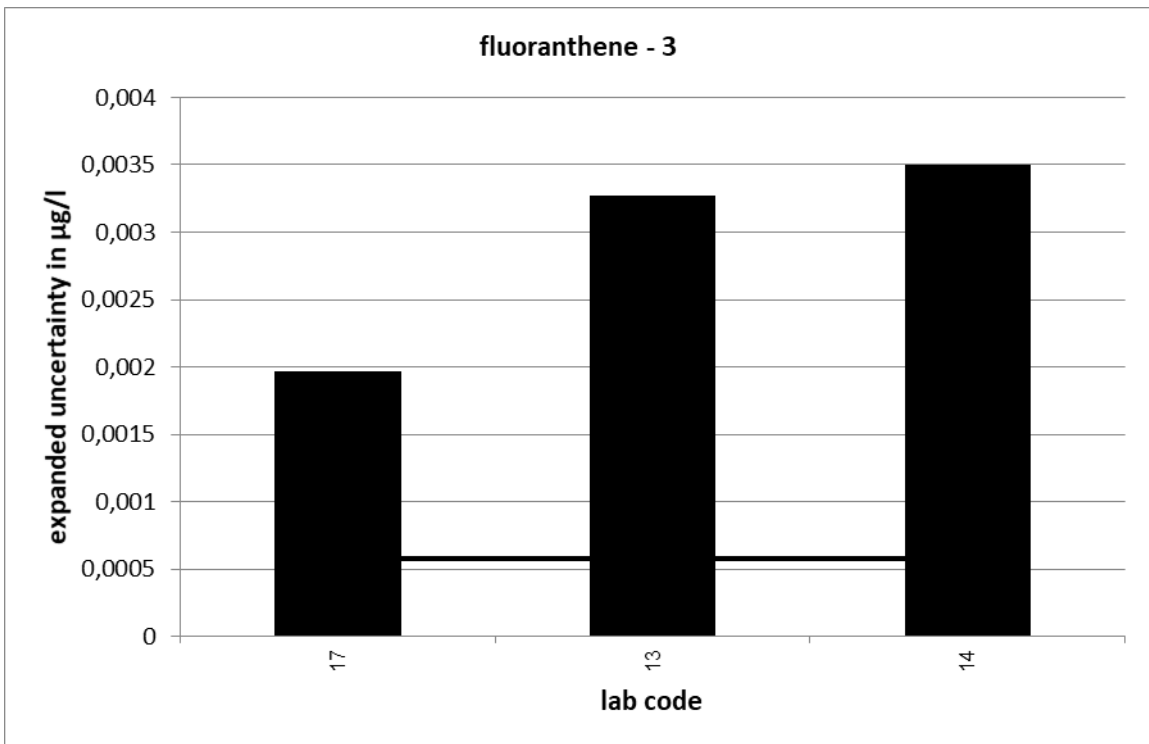
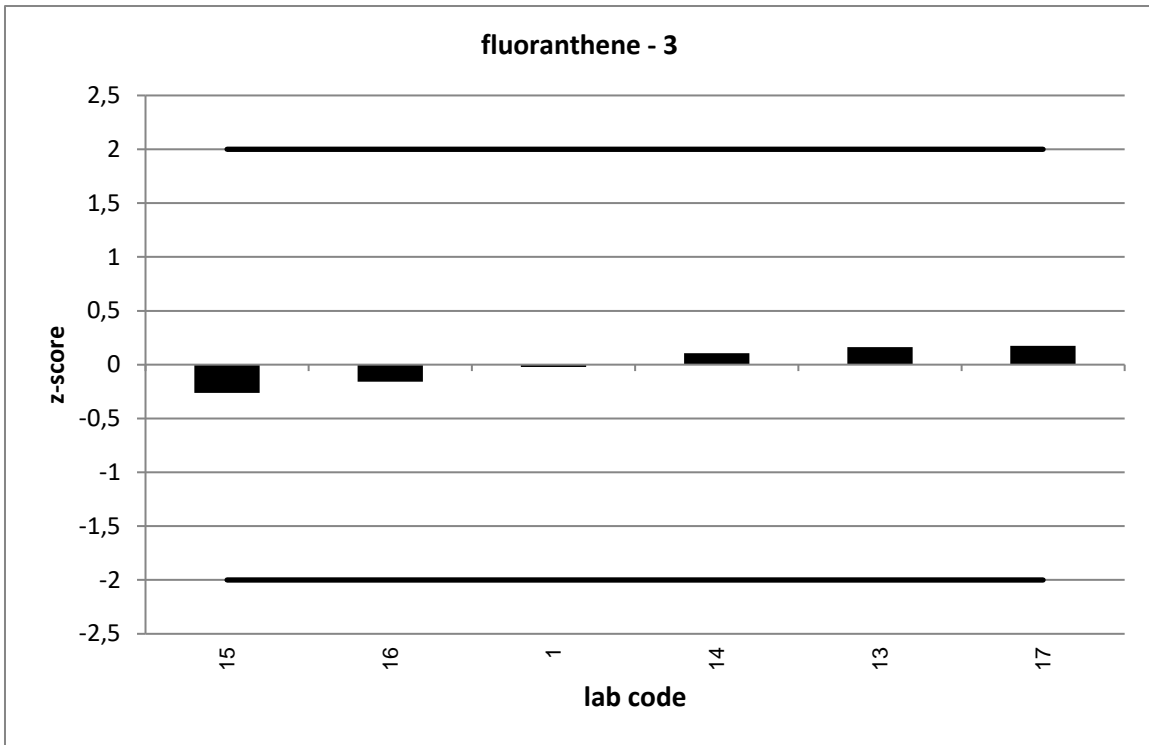


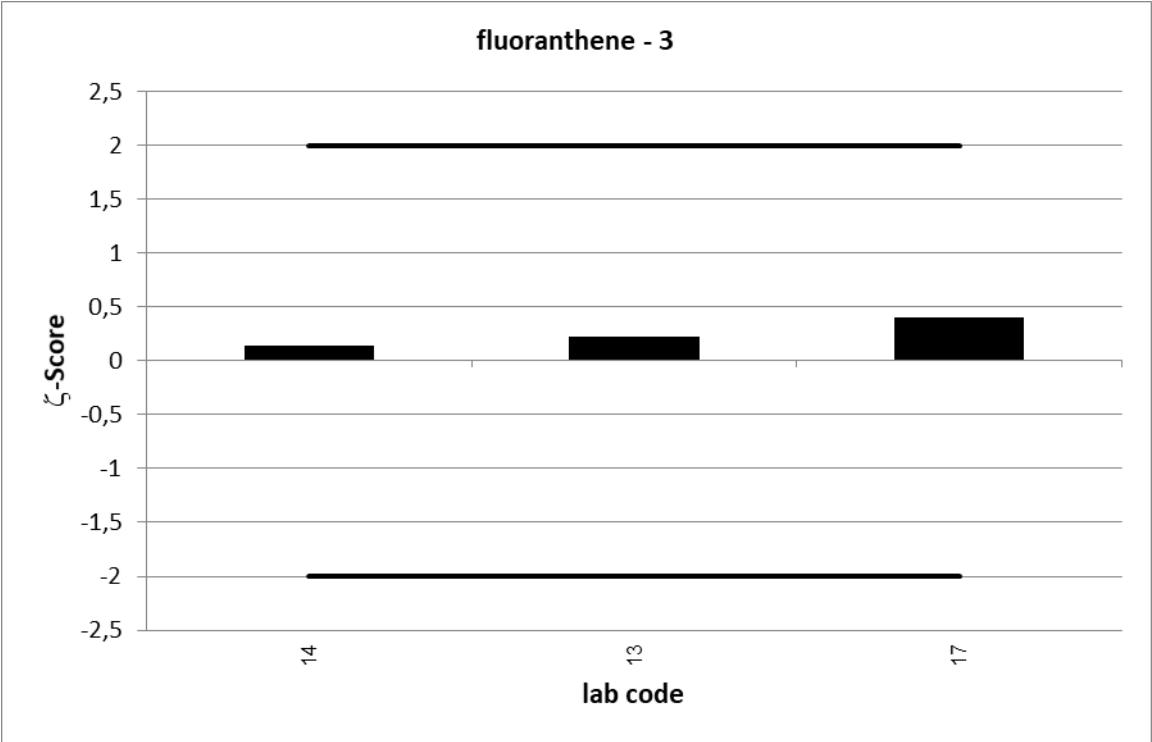
| UKWIR PT 1/20 | | fluoranthene - 3 | | | |
|---|----------------------------|------------------------|----------------|---------|------------|
| assigned value [$\mu\text{g/l}$]* | | 0,00942 \pm 0,000595 | | | |
| upper tolerance limit [$\mu\text{g/l}$] | | 0,01413 | | | |
| lower tolerance limit [$\mu\text{g/l}$] | | 0,00471 | | | |
| lab code | result [$\mu\text{g/l}$] | \pm | ζ -score | z-score | assessm.** |
| 1 | 0,00937 | | | 0,0 | s |
| 13 | 0,0098 | 0,003 | 0,2 | 0,2 | s |
| 14 | 0,00967 | 0,004 | 0,1 | 0,1 | s |
| 15 | 0,0088 | | | -0,3 | s |
| 16 | 0,00905 | | | -0,2 | s |
| 17 | 0,00983 | 0,002 | 0,4 | 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



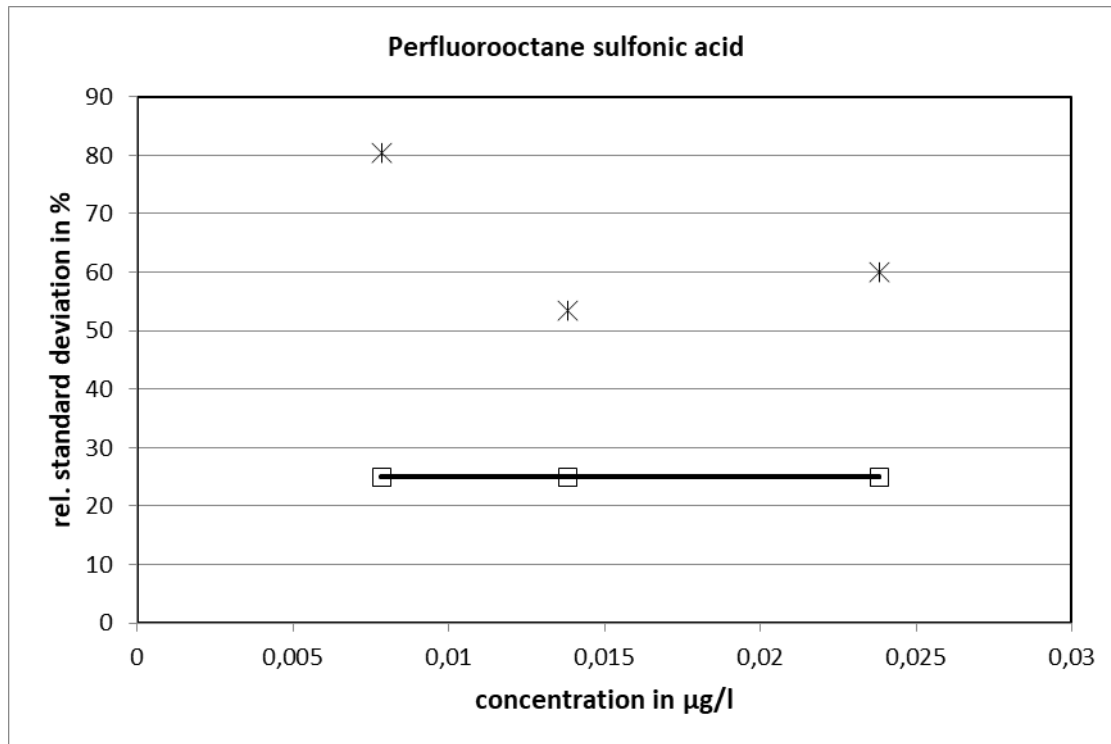




UKWIR 2/20:

| Perfluorooctane sulfonic acid | | | | | | | | | | | | | | |
|-------------------------------|-----------------------|--|---|--|---|------------------------------|------------------------------|---------------------------|---------------------------|-------------------|-----------|-----------|---------|------|
| 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 | 0,0078 | 13,05 | 0,0063 | 0,0020 | 25,00 | 0,0118 | 0,0039 | 50,00 | -50,00 | 8 | 1 | 2 | 37,5 | |
| 2 | 0,0138 | 7,04 | 0,0074 | 0,0035 | 25,00 | 0,0208 | 0,0069 | 50,00 | -50,00 | 8 | 1 | 1 | 25,0 | |
| 3 | 0,0238 | 4,74 | 0,0143 | 0,0060 | 25,00 | 0,0357 | 0,0119 | 50,00 | -50,00 | 8 | 2 | 0 | 25,0 | |
| | | | | | | | | | | sum | 24 | 4 | 3 | 29,2 |

Relative standard deviation

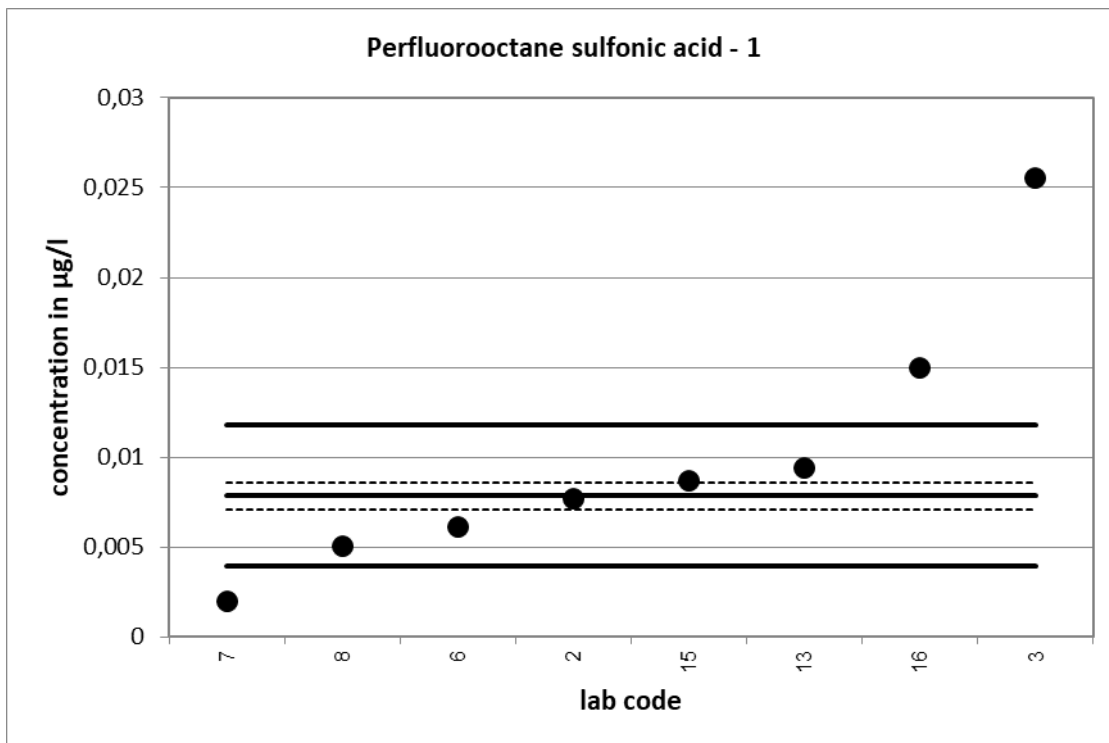


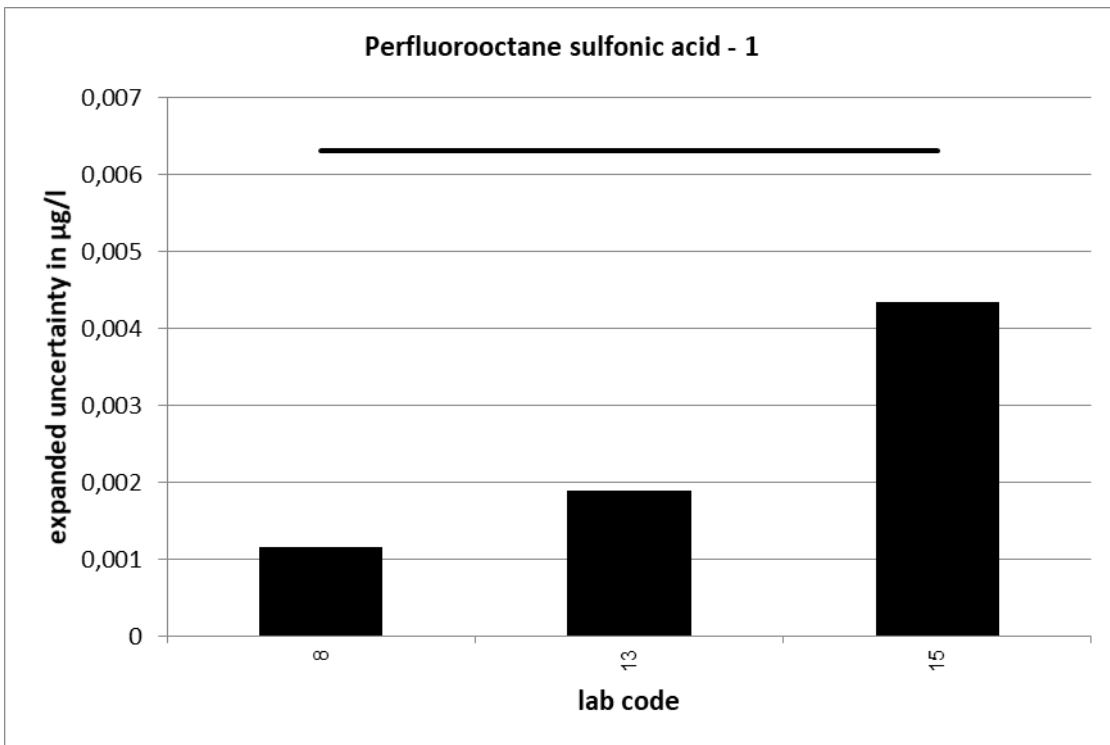
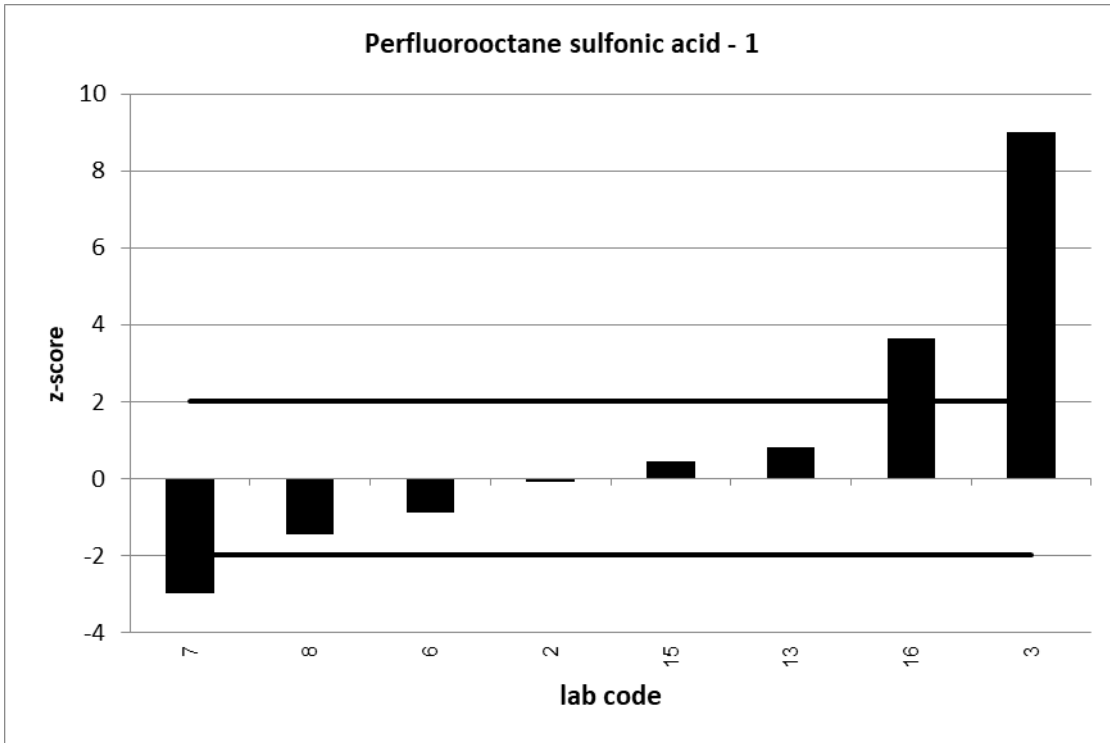
25 % is used as standard deviation for proficiency assessment.

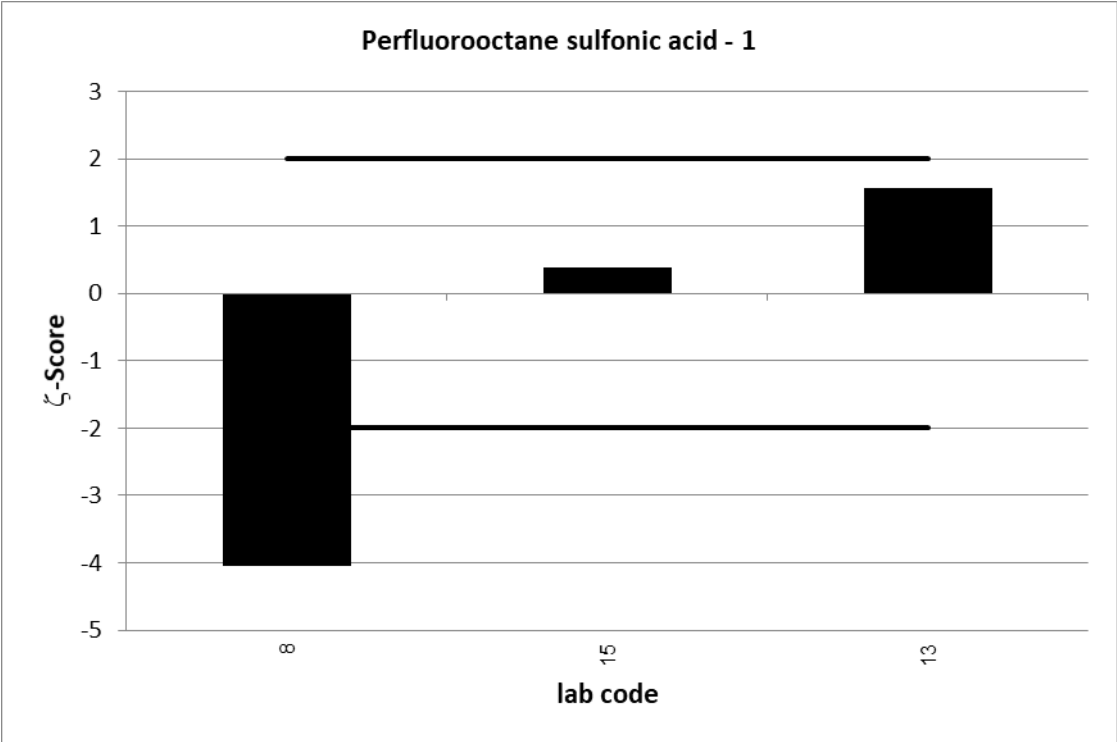
| UKWIR PT 2/20 | | Perfluorooctane sulfonic acid - 1 | | | |
|------------------------------|---------------|-----------------------------------|---------|---------|------------|
| assigned value [µg/l]* | | 0,007843 ± 0,000754 | | | |
| upper tolerance limit [µg/l] | | 0,01176 | | | |
| lower tolerance limit [µg/l] | | 0,003922 | | | |
| lab code | result [µg/l] | ± | ζ-score | z-score | assessm.** |
| 2 | 0,00769 | | | -0,1 | s |
| 3 | 0,0255 | | | 9,0 | u |
| 6 | 0,0061 | | | -0,9 | s |
| 7 | 0,002 | | | -3,0 | u |
| 8 | 0,00502 | 0,001 | -4,1 | -1,4 | s |
| 13 | 0,00943 | 0,002 | 1,6 | 0,8 | s |
| 15 | 0,0087 | 0,004 | 0,4 | 0,4 | s |
| 16 | 0,015 | | | 3,7 | 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



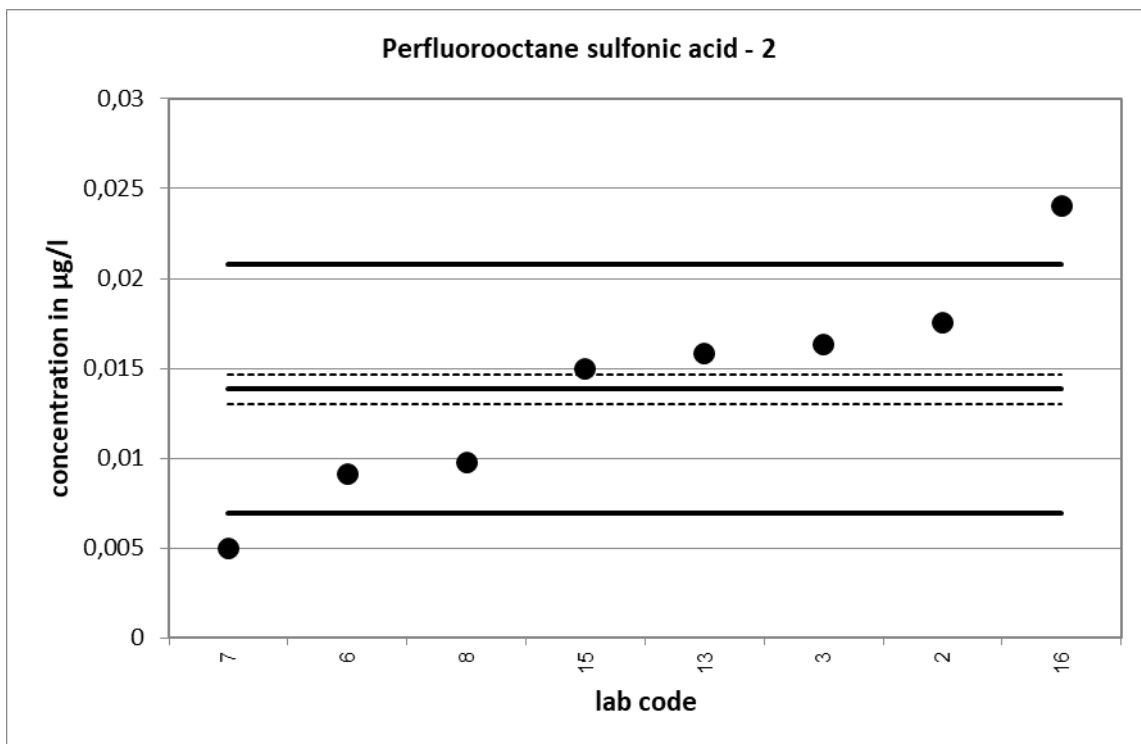


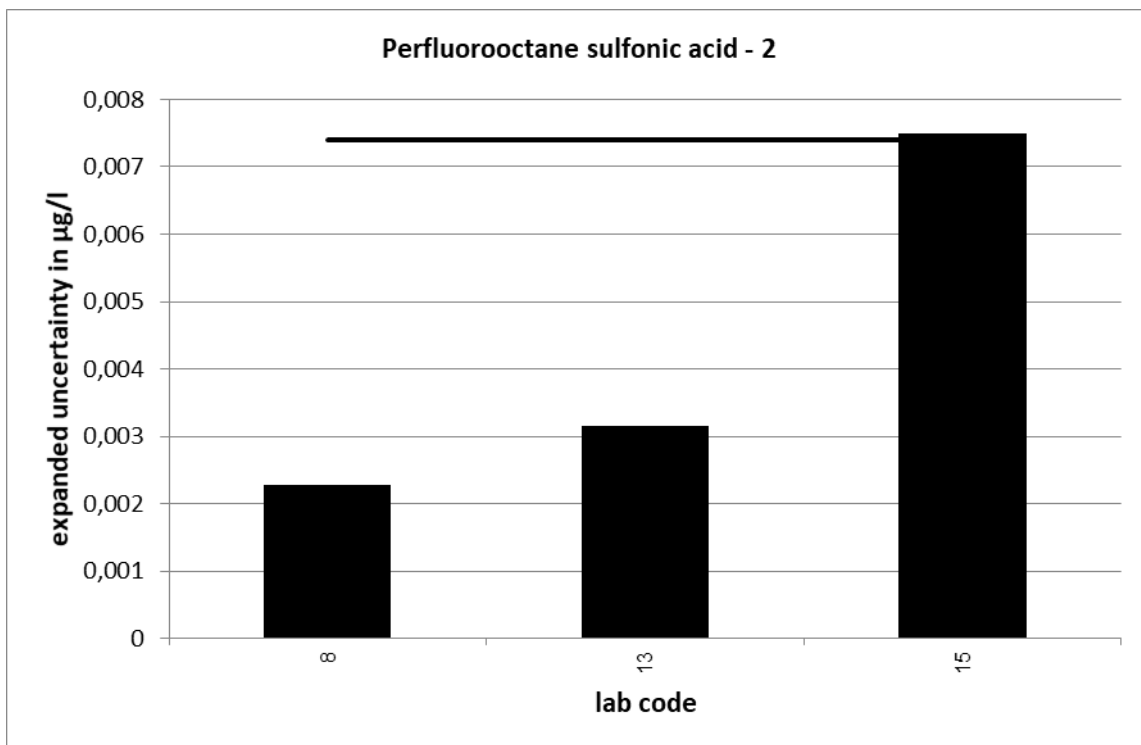
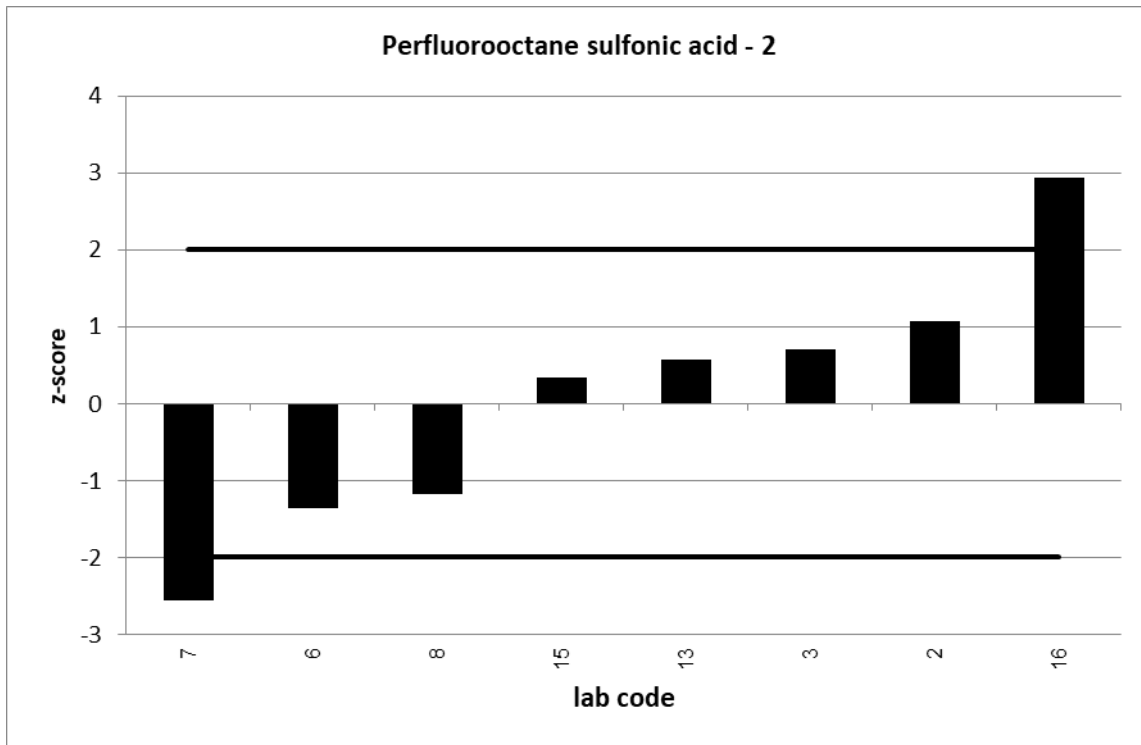


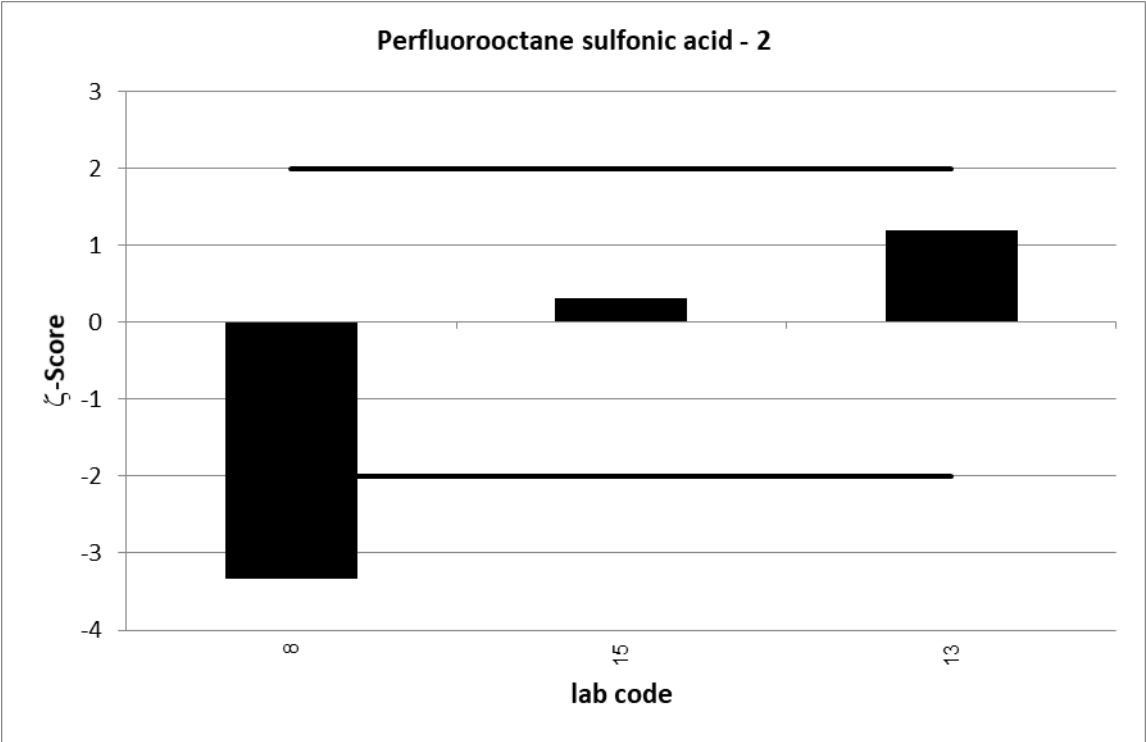
| UKWIR PT 2/20 | | Perfluorooctane sulfonic acid - 2 | | | |
|---|----------------------------|-----------------------------------|----------------|---------|------------|
| assigned value [$\mu\text{g/l}$]* | | 0,01384 \pm 0,00083 | | | |
| upper tolerance limit [$\mu\text{g/l}$] | | 0,02076 | | | |
| lower tolerance limit [$\mu\text{g/l}$] | | 0,00692 | | | |
| lab code | result [$\mu\text{g/l}$] | \pm | ζ -score | z-score | assessm.** |
| 2 | 0,01755 | | | 1,1 | s |
| 3 | 0,0163 | | | 0,7 | s |
| 6 | 0,00912 | | | -1,4 | s |
| 7 | 0,005 | | | -2,6 | q |
| 8 | 0,00979 | 0,002 | -3,3 | -1,2 | s |
| 13 | 0,0158 | 0,003 | 1,2 | 0,6 | s |
| 15 | 0,015 | 0,008 | 0,3 | 0,3 | s |
| 16 | 0,024 | | | 2,9 | q |

* 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



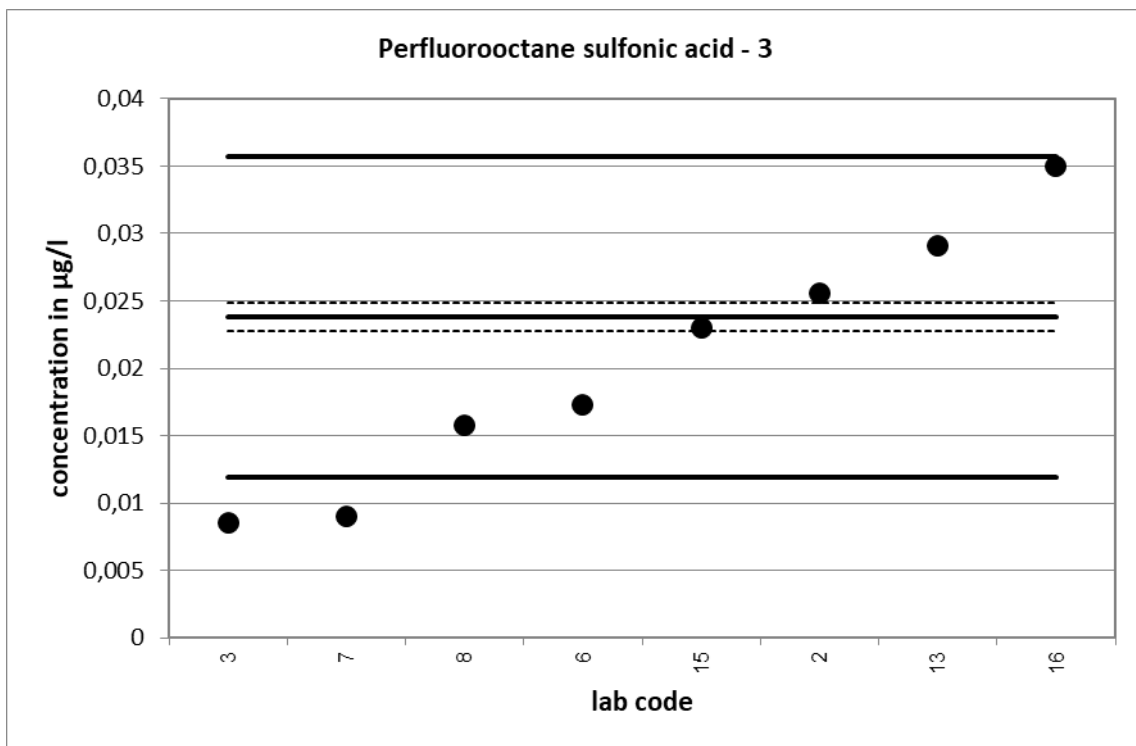


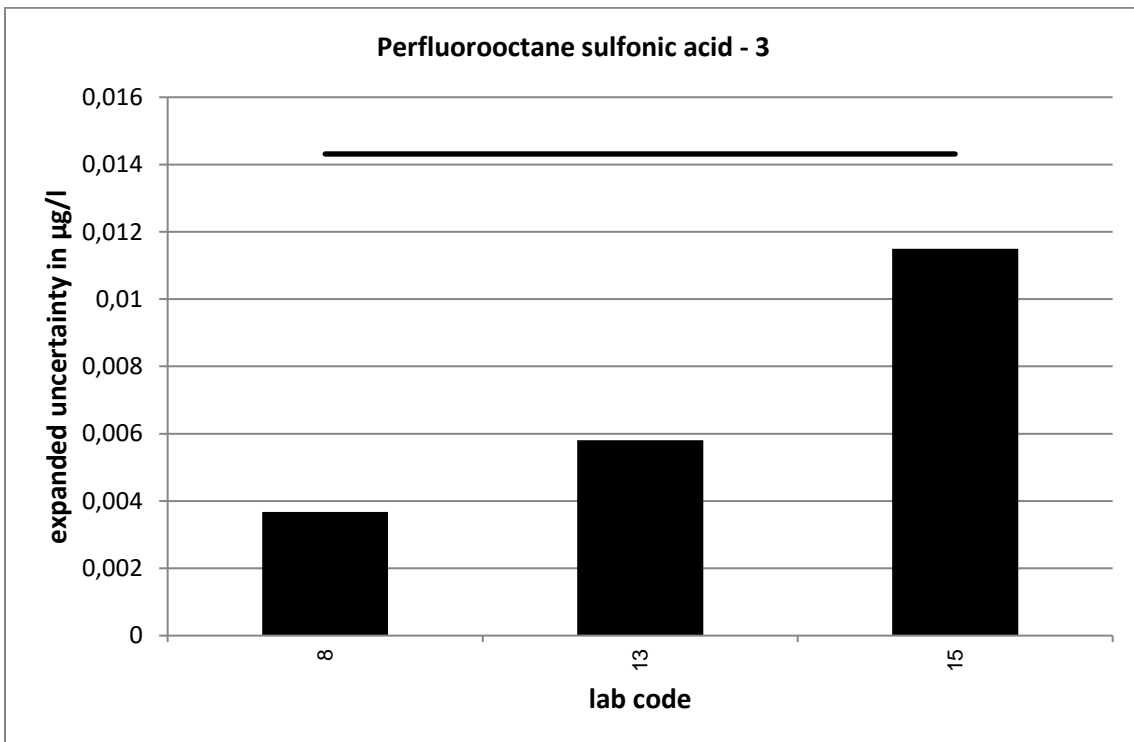
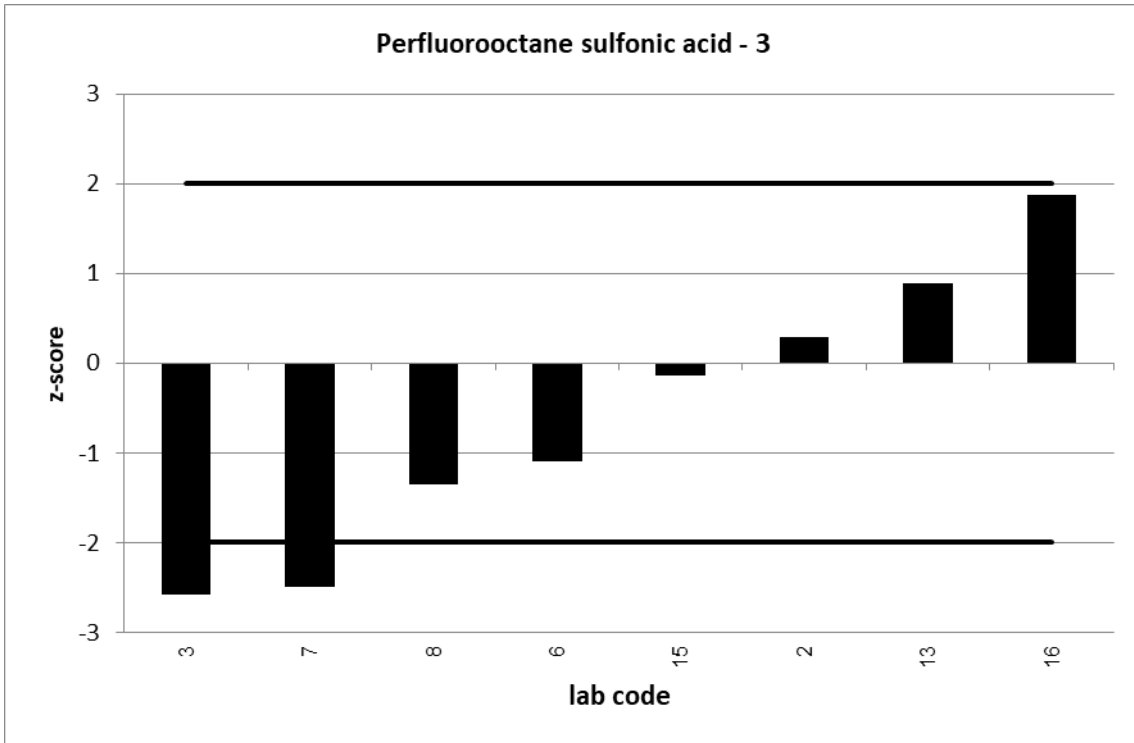


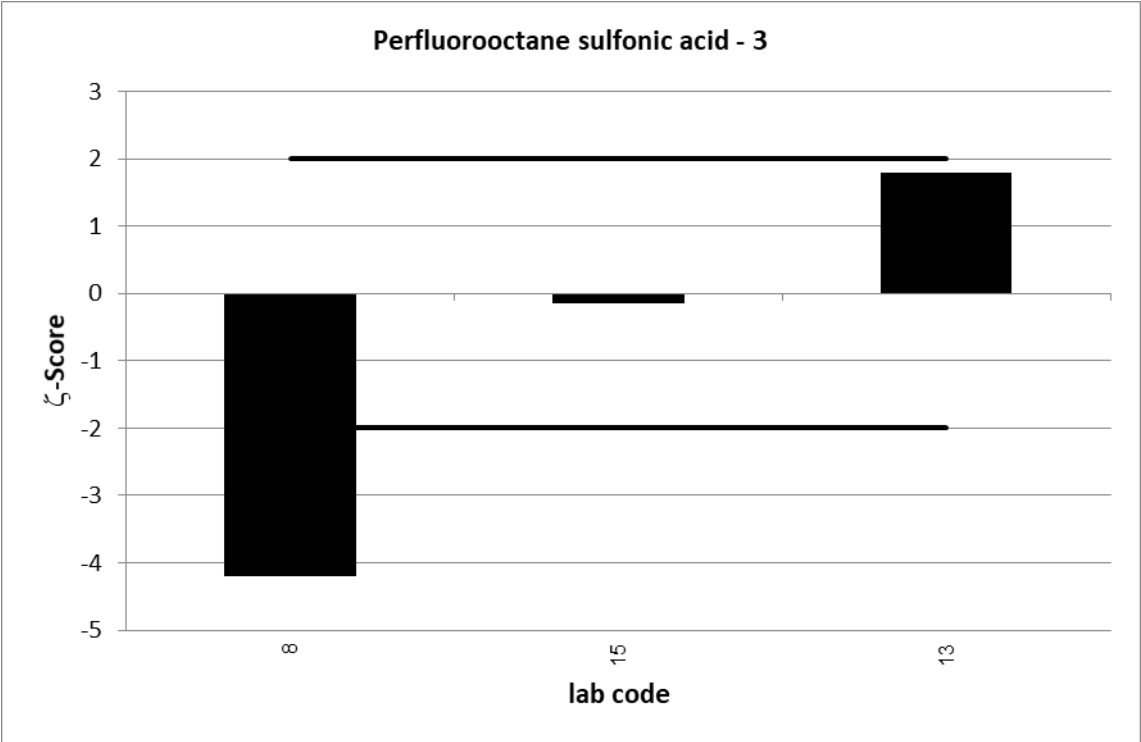
| UKWIR PT 2/20 | | Perfluorooctane sulfonic acid - 3 | | | |
|------------------------------|---------------|-----------------------------------|---------|---------|------------|
| assigned value [µg/l]* | | 0,02382 ± 0,00103 | | | |
| upper tolerance limit [µg/l] | | 0,03573 | | | |
| lower tolerance limit [µg/l] | | 0,01191 | | | |
| lab code | result [µg/l] | ± | ζ-score | z-score | assessm.** |
| 2 | 0,02558 | | | 0,3 | s |
| 3 | 0,0085 | | | -2,6 | q |
| 6 | 0,0173 | | | -1,1 | s |
| 7 | 0,009 | | | -2,5 | q |
| 8 | 0,0158 | 0,004 | -4,2 | -1,3 | s |
| 13 | 0,0291 | 0,006 | 1,8 | 0,9 | s |
| 15 | 0,023 | 0,012 | -0,1 | -0,1 | s |
| 16 | 0,035 | | | 1,9 | 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

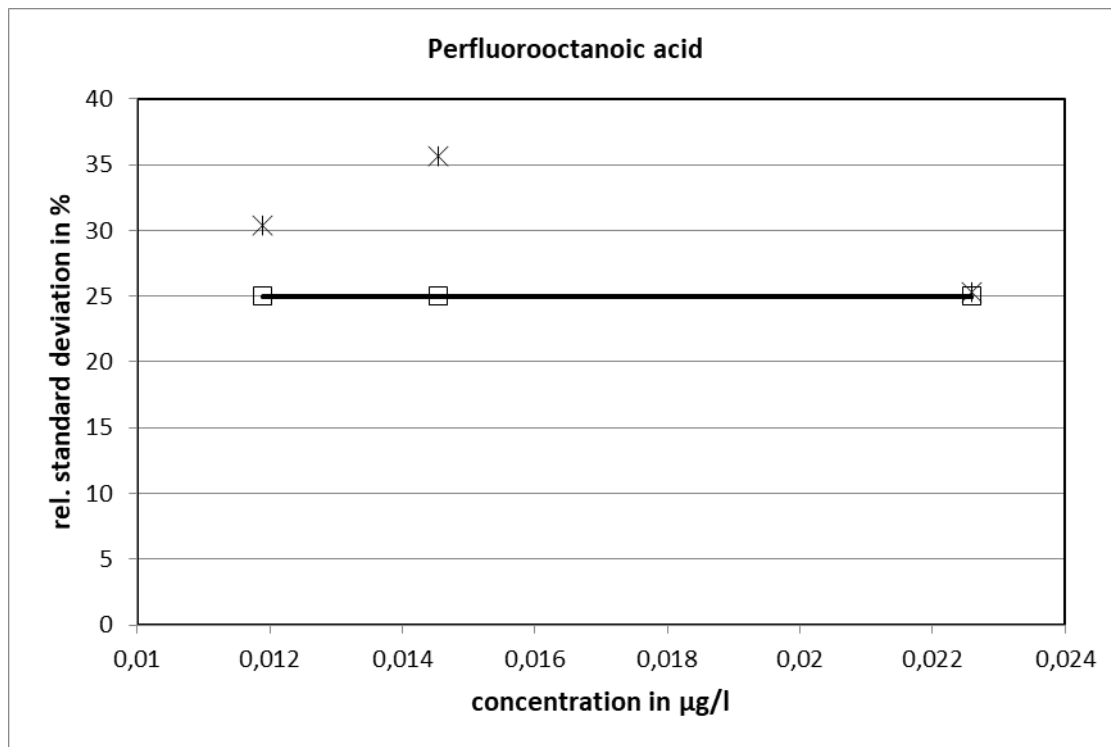






| Perfluorooctanoic acid | | | | | | | | | | | | | | |
|------------------------|-----------------------|--|---|--|---|------------------------------|------------------------------|---------------------------|---------------------------|-------------------|-----------|-----------|---------|------|
| 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 | 0,0119 | 19,99 | 0,0036 | 0,0030 | 25,00 | 0,0179 | 0,0060 | 50,00 | -50,00 | 7 | 0 | 1 | 14,3 | |
| 2 | 0,0145 | 14,69 | 0,0052 | 0,0036 | 25,00 | 0,0218 | 0,0073 | 50,00 | -50,00 | 7 | 0 | 2 | 28,6 | |
| 3 | 0,0226 | 8,48 | 0,0057 | 0,0056 | 25,00 | 0,0339 | 0,0113 | 50,00 | -50,00 | 7 | 0 | 1 | 14,3 | |
| | | | | | | | | | | sum | 21 | 0 | 4 | 19,0 |

Relative standard deviation

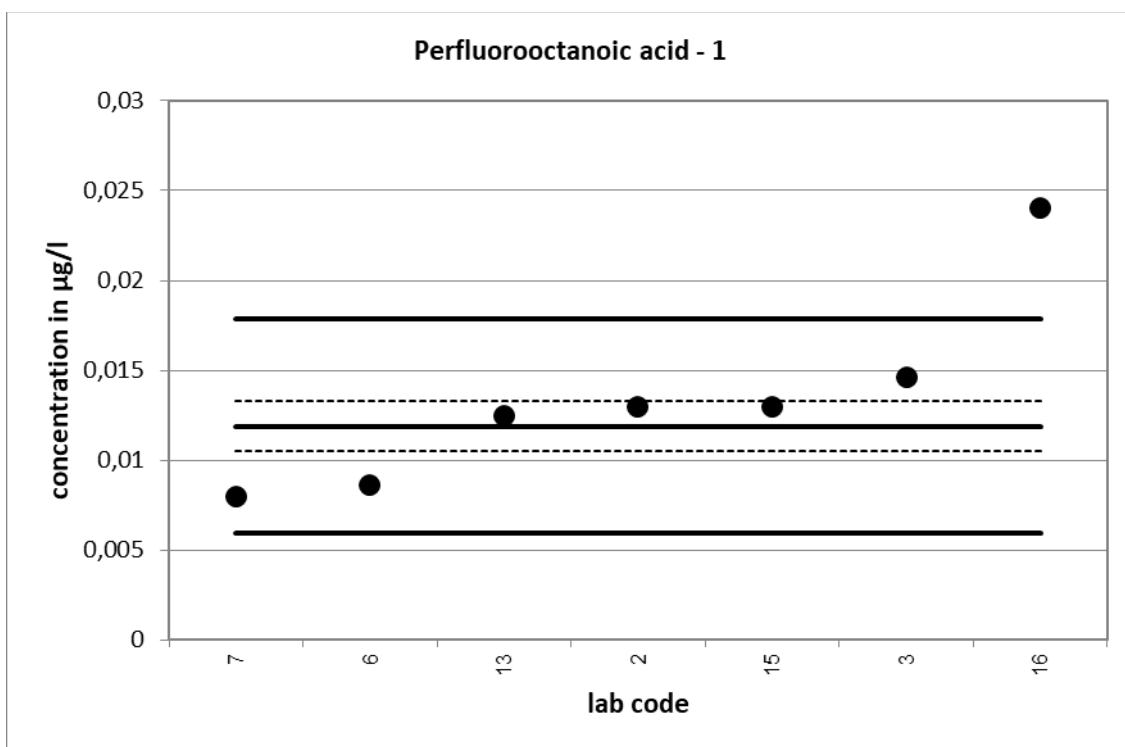


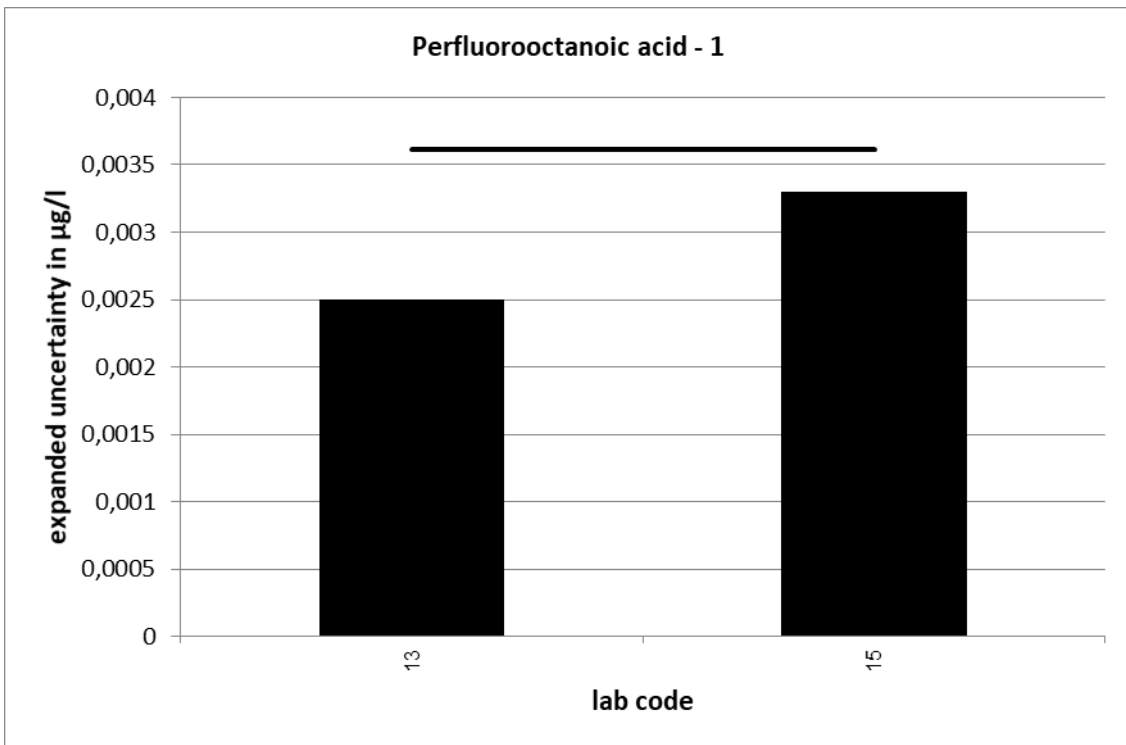
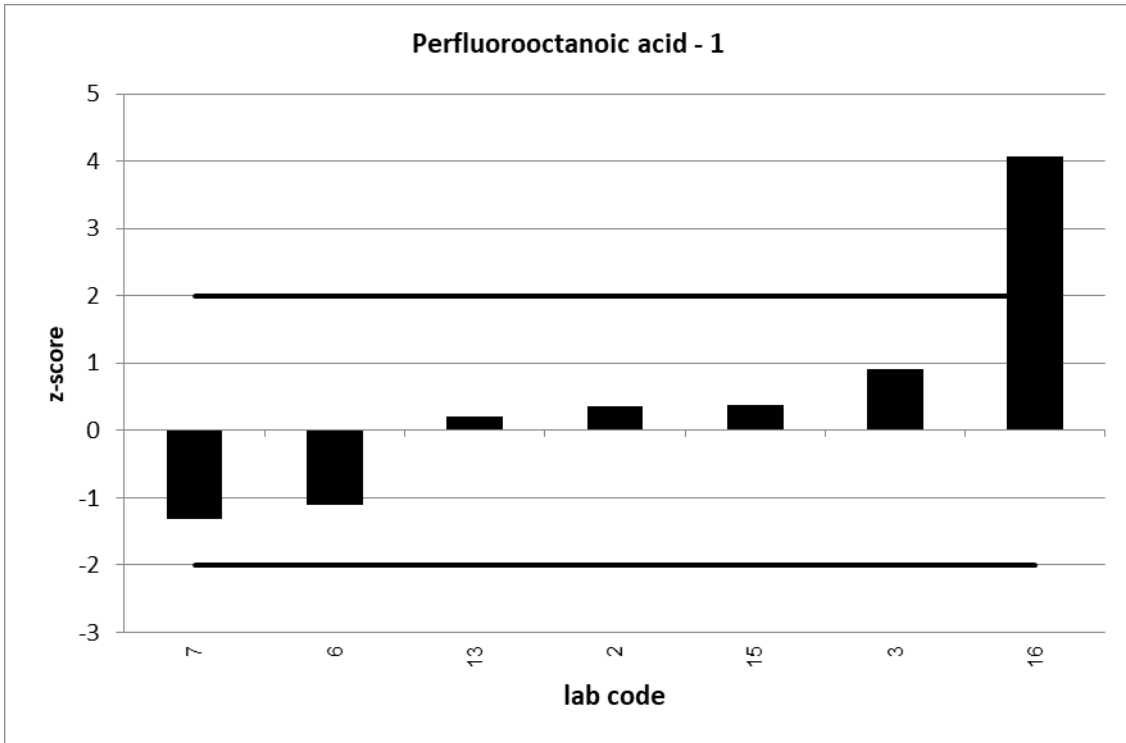
25 % is used as standard deviation for proficiency assessment.

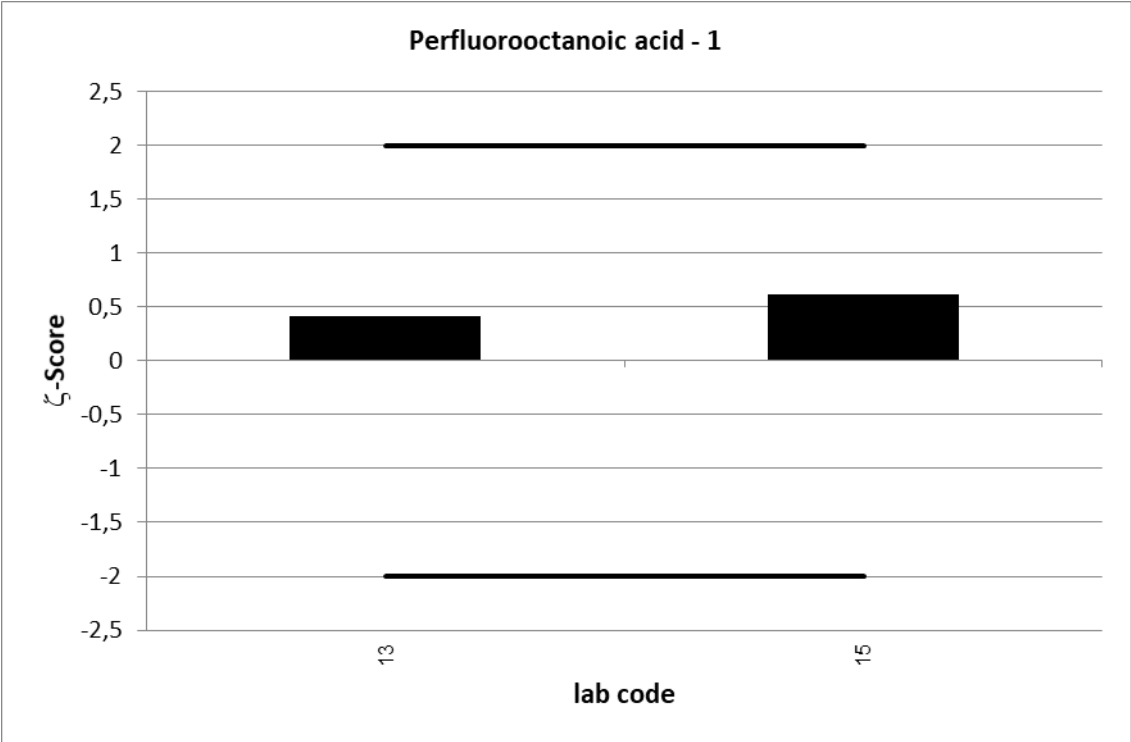
| UKWIR PT 2/20 | | Perfluorooctanoic acid - 1 | | | |
|---|----------------------------|----------------------------|----------------|---------|------------|
| assigned value [$\mu\text{g/l}$]* | | 0,0119 \pm 0,00139 | | | |
| upper tolerance limit [$\mu\text{g/l}$] | | 0,01785 | | | |
| lower tolerance limit [$\mu\text{g/l}$] | | 0,00595 | | | |
| lab code | result [$\mu\text{g/l}$] | \pm | ζ -score | z-score | assessm.** |
| 2 | 0,01296 | | | 0,4 | s |
| 3 | 0,0146 | | | 0,9 | s |
| 6 | 0,00859 | | | -1,1 | s |
| 7 | 0,008 | | | -1,3 | s |
| 13 | 0,0125 | 0,003 | 0,4 | 0,2 | s |
| 15 | 0,013 | 0,003 | 0,6 | 0,4 | s |
| 16 | 0,024 | | | 4,1 | 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



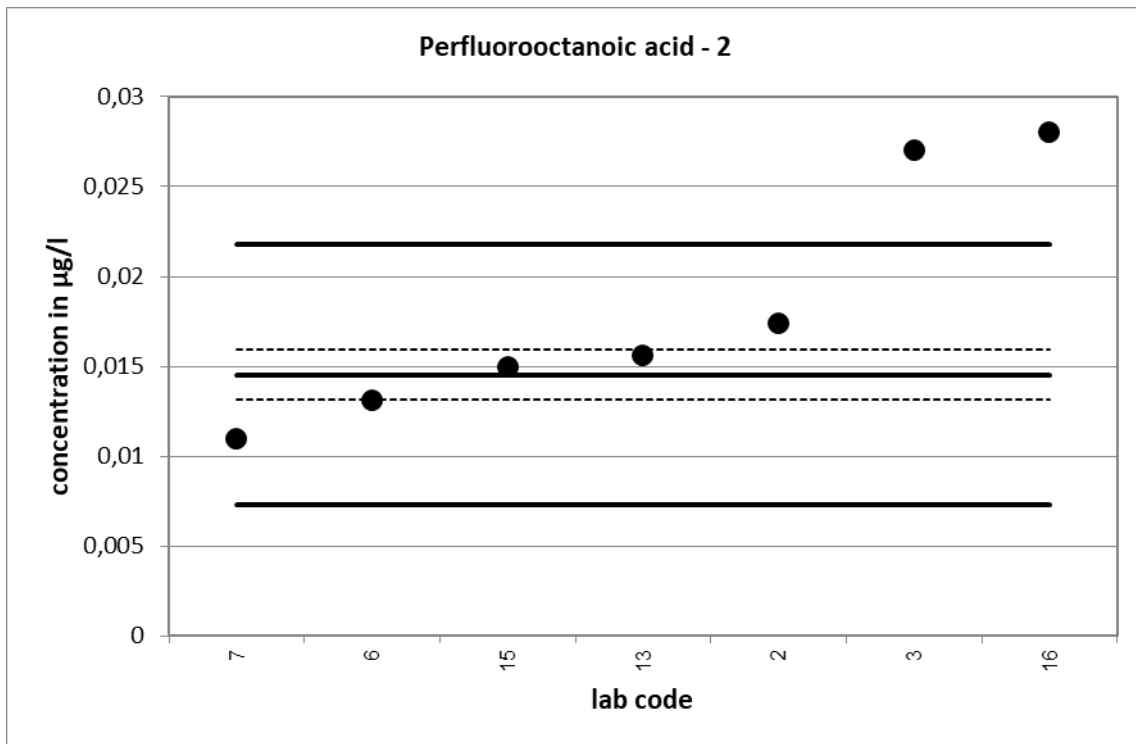


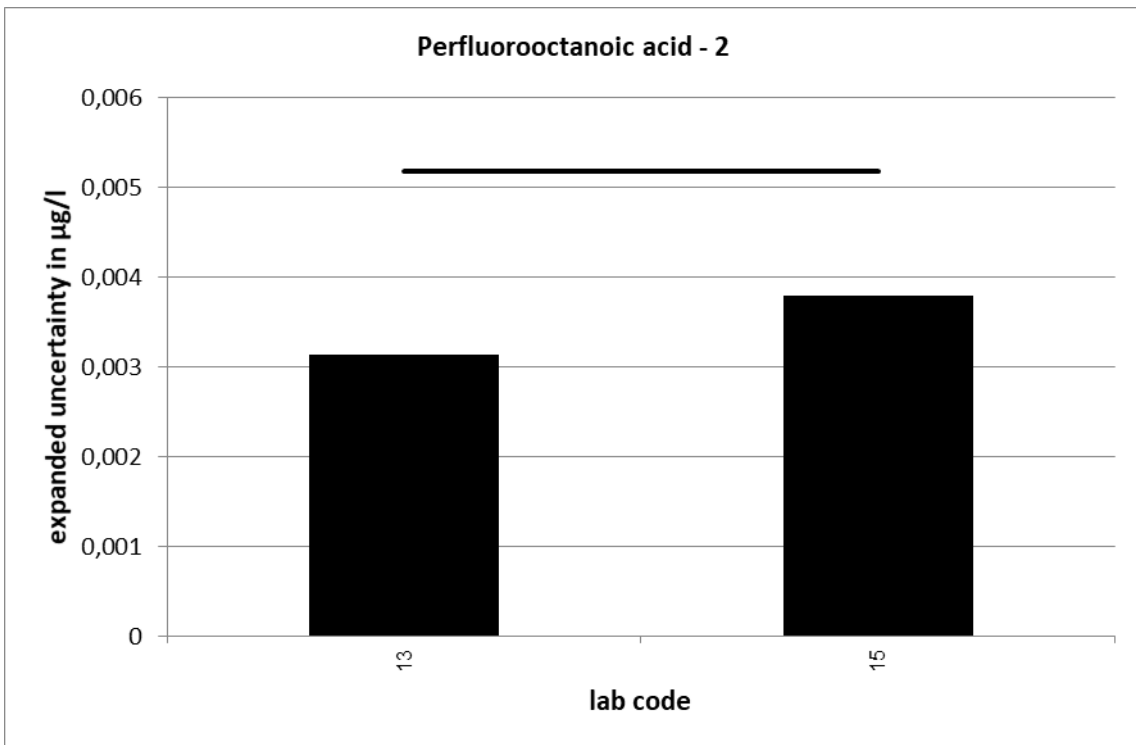
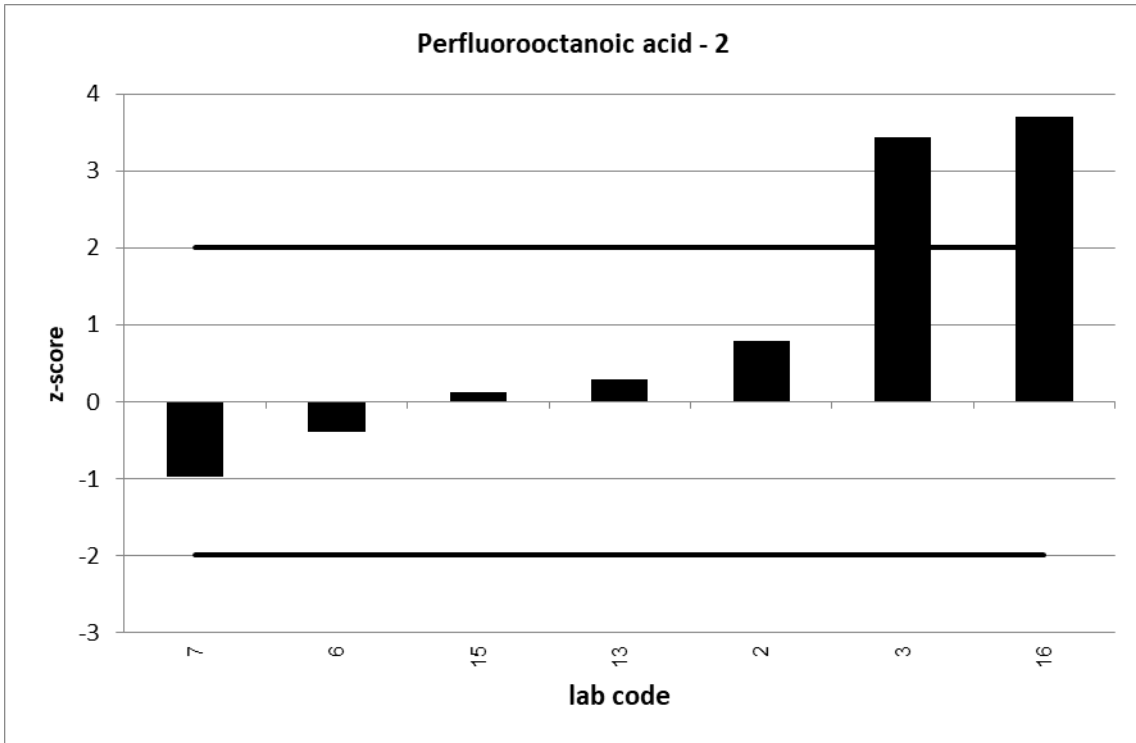


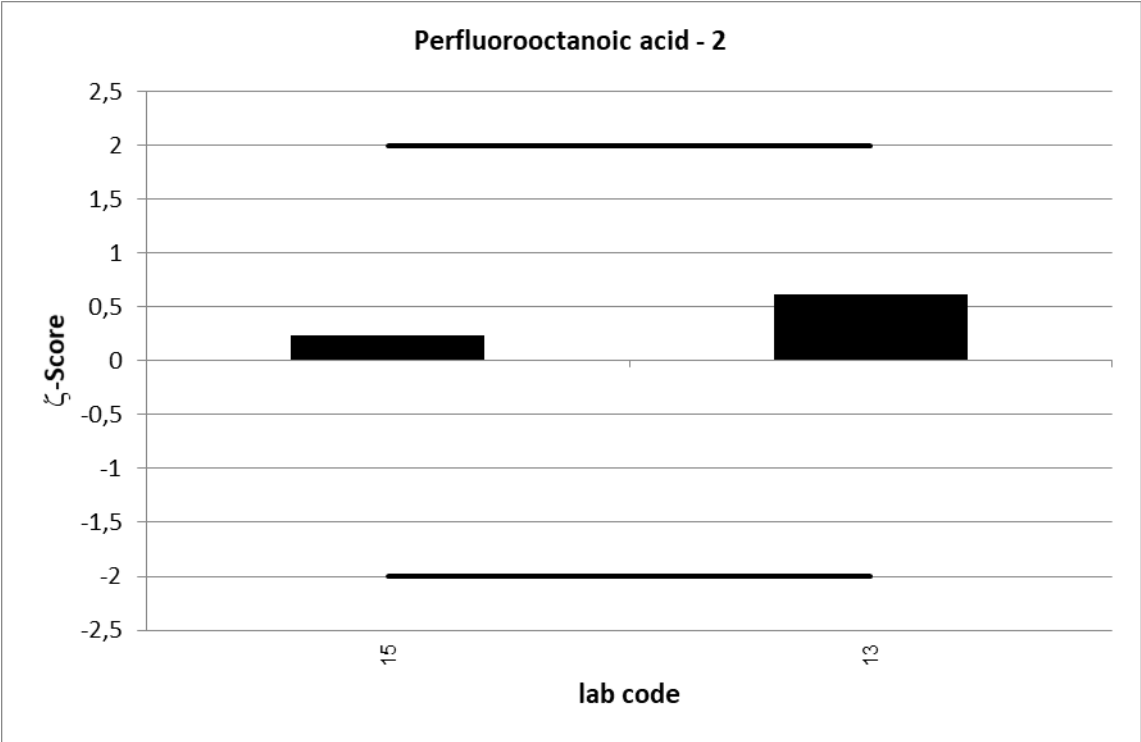
| UKWIR PT 2/20 | | Perfluorooctanoic acid - 2 | | | |
|---|----------------------------|----------------------------|----------------|---------|------------|
| assigned value [$\mu\text{g/l}$]* | | 0,01453 \pm 0,00141 | | | |
| upper tolerance limit [$\mu\text{g/l}$] | | 0,0218 | | | |
| lower tolerance limit [$\mu\text{g/l}$] | | 0,007267 | | | |
| lab code | result [$\mu\text{g/l}$] | \pm | ζ -score | z-score | assessm.** |
| 2 | 0,01741 | | | 0,8 | s |
| 3 | 0,027 | | | 3,4 | u |
| 6 | 0,0131 | | | -0,4 | s |
| 7 | 0,011 | | | -1,0 | s |
| 13 | 0,0156 | 0,003 | 0,6 | 0,3 | s |
| 15 | 0,015 | 0,004 | 0,2 | 0,1 | s |
| 16 | 0,028 | | | 3,7 | 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



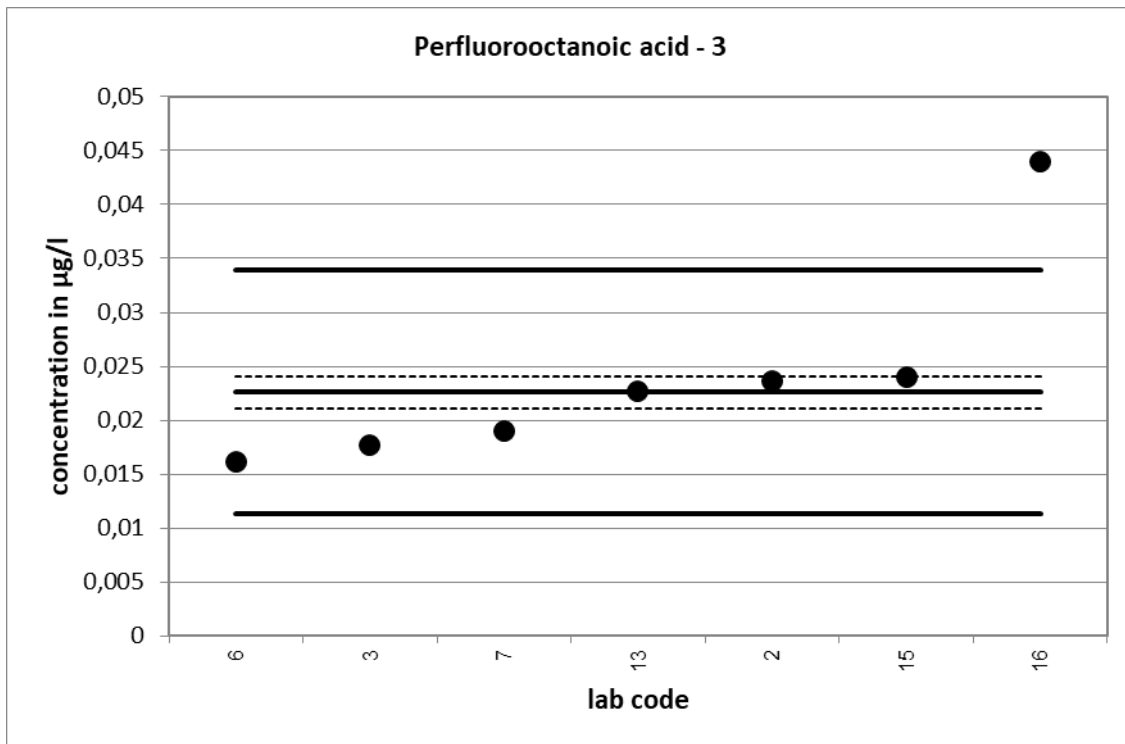


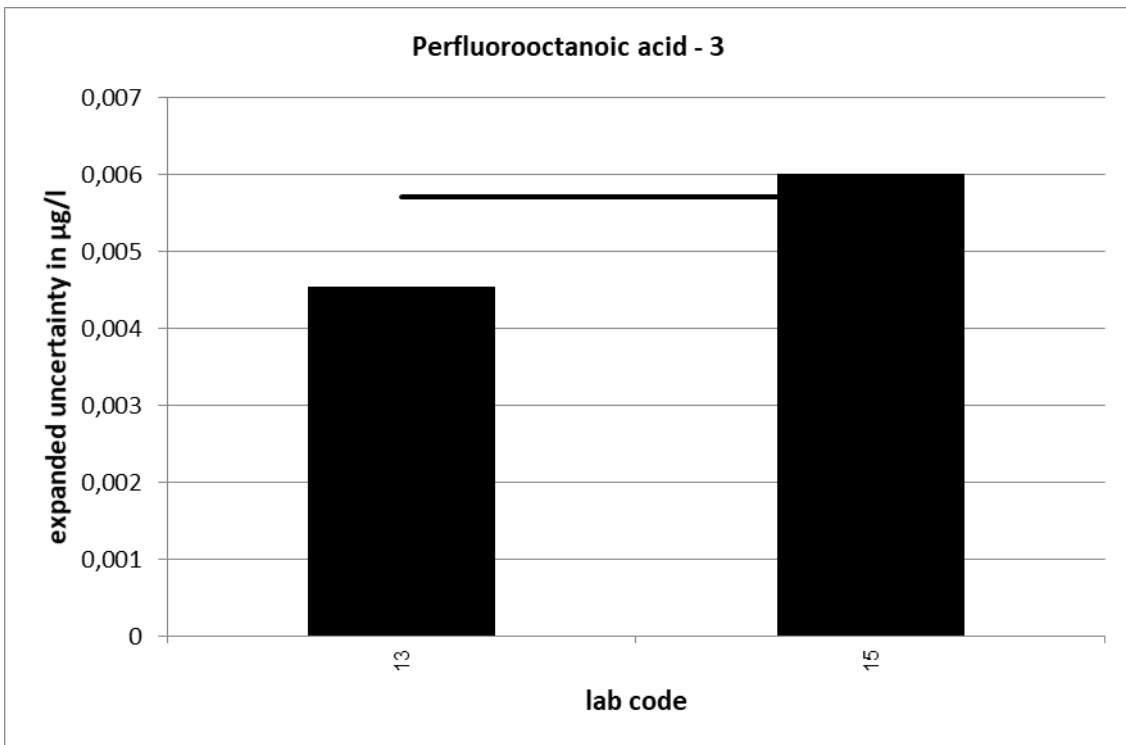
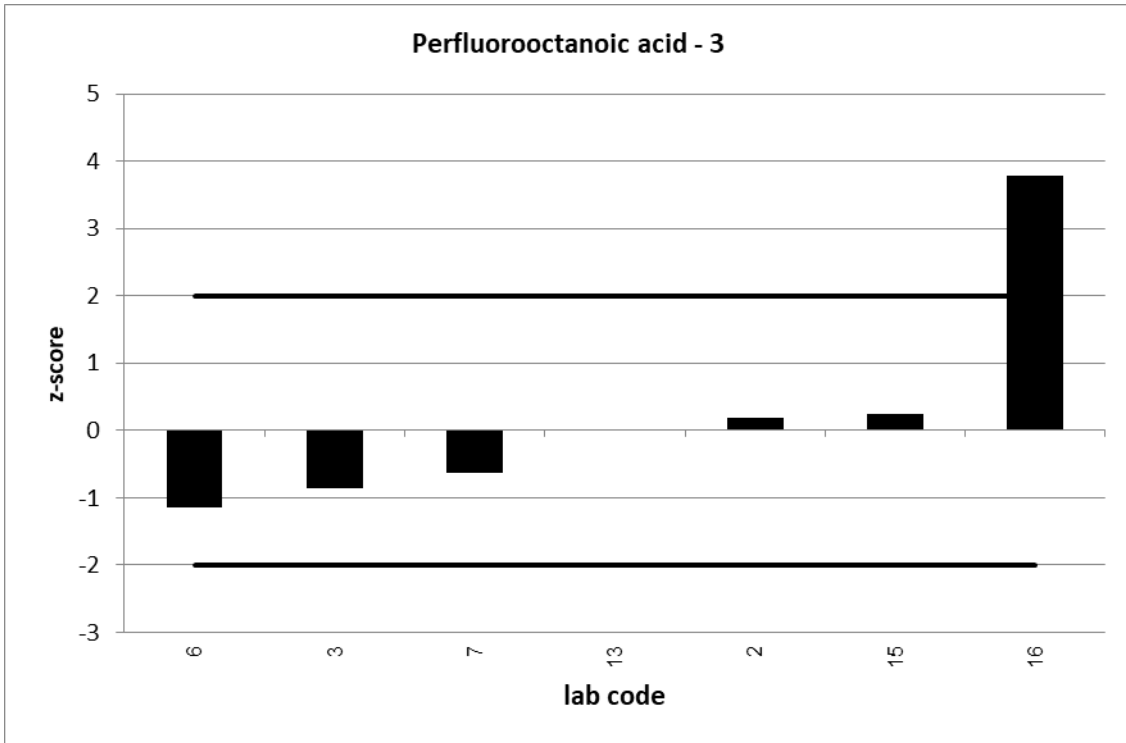


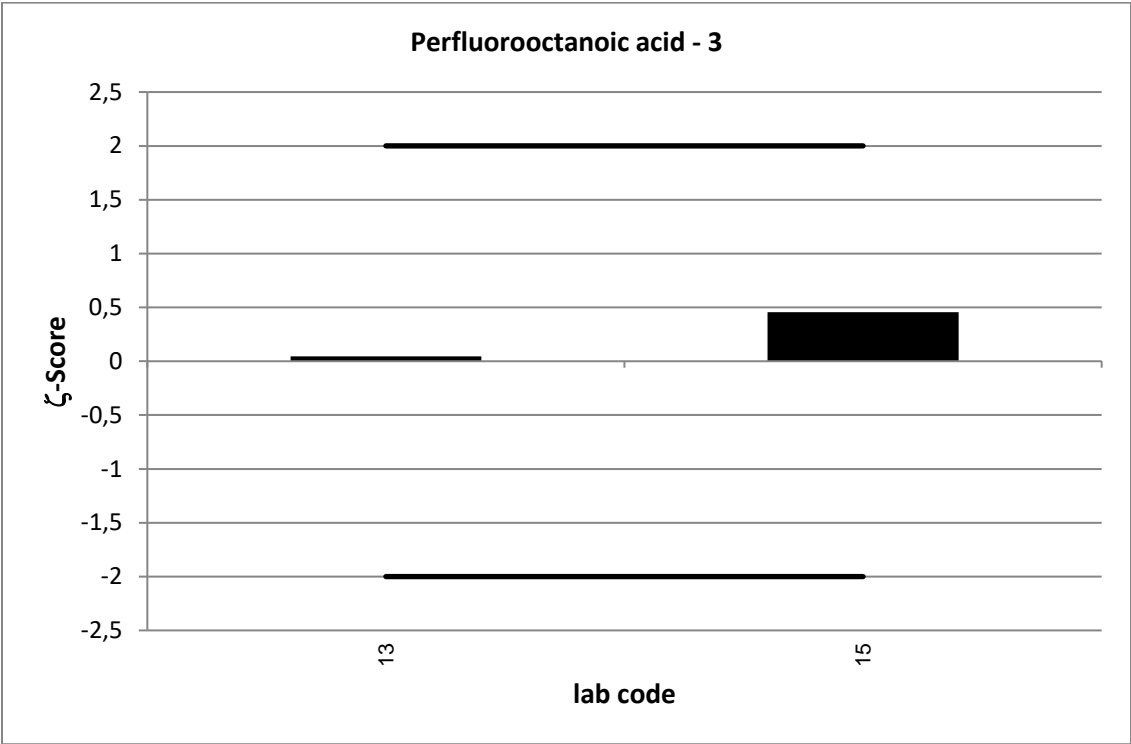
| UKWIR PT 2/20 | | Perfluorooctanoic acid - 3 | | | |
|---|----------------------------|----------------------------|----------------|---------|------------|
| assigned value [$\mu\text{g/l}$]* | | 0,02259 \pm 0,0015 | | | |
| upper tolerance limit [$\mu\text{g/l}$] | | 0,03389 | | | |
| lower tolerance limit [$\mu\text{g/l}$] | | 0,0113 | | | |
| lab code | result [$\mu\text{g/l}$] | \pm | ζ -score | z-score | assessm.** |
| 2 | 0,02368 | | | 0,2 | s |
| 3 | 0,0177 | | | -0,9 | s |
| 6 | 0,0161 | | | -1,1 | s |
| 7 | 0,019 | | | -0,6 | s |
| 13 | 0,0227 | 0,005 | 0,0 | 0,0 | s |
| 15 | 0,024 | 0,006 | 0,5 | 0,2 | s |
| 16 | 0,044 | | | 3,8 | 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



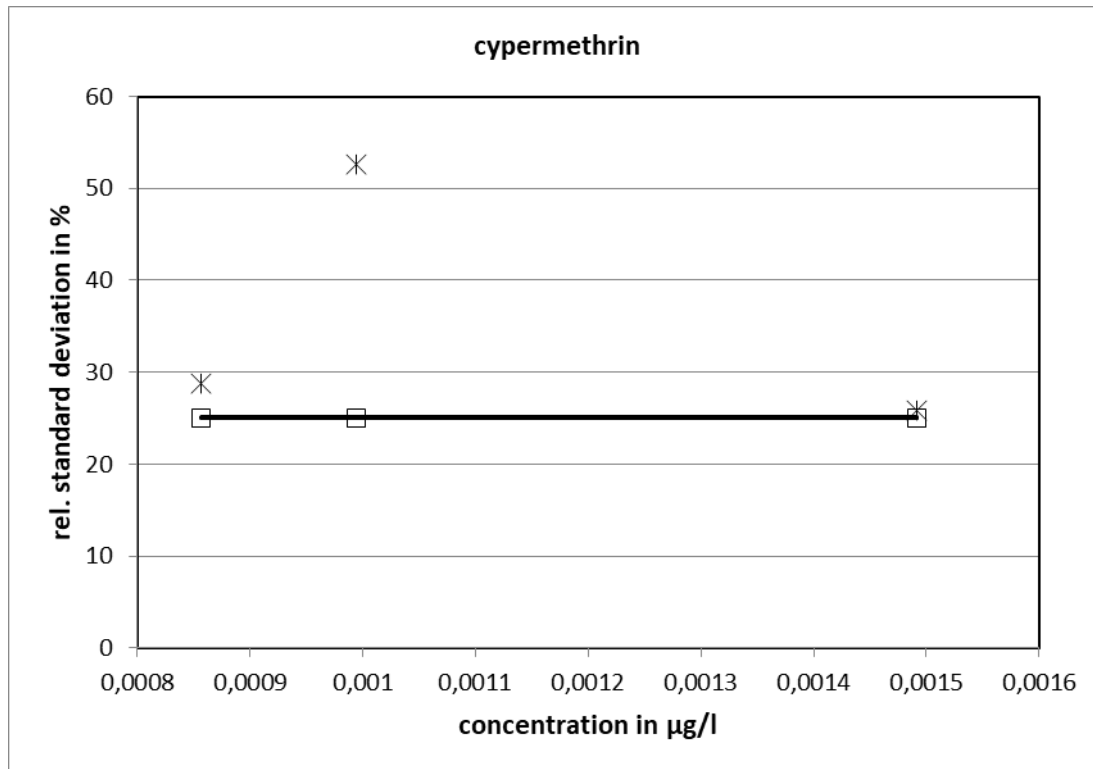




UKWIR 3/20:

| 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 | 0,0009 | 31,10 | 0,0002 | 0,0002 | 25 | 0,0013 | 0,0004 | 50 | -50 | 6 | 0 | 1 | 16,7 | |
| 2 | 0,0010 | 33,61 | 0,0005 | 0,0002 | 25 | 0,0015 | 0,0005 | 50 | -50 | 6 | 1 | 1 | 33,3 | |
| 3 | 0,0015 | 22,36 | 0,0004 | 0,0004 | 25 | 0,0022 | 0,0007 | 50 | -50 | 6 | 0 | 0 | 0,0 | |
| | | | | | | | | | | sum | 18 | 1 | 2 | 16,7 |

Relative standard deviation

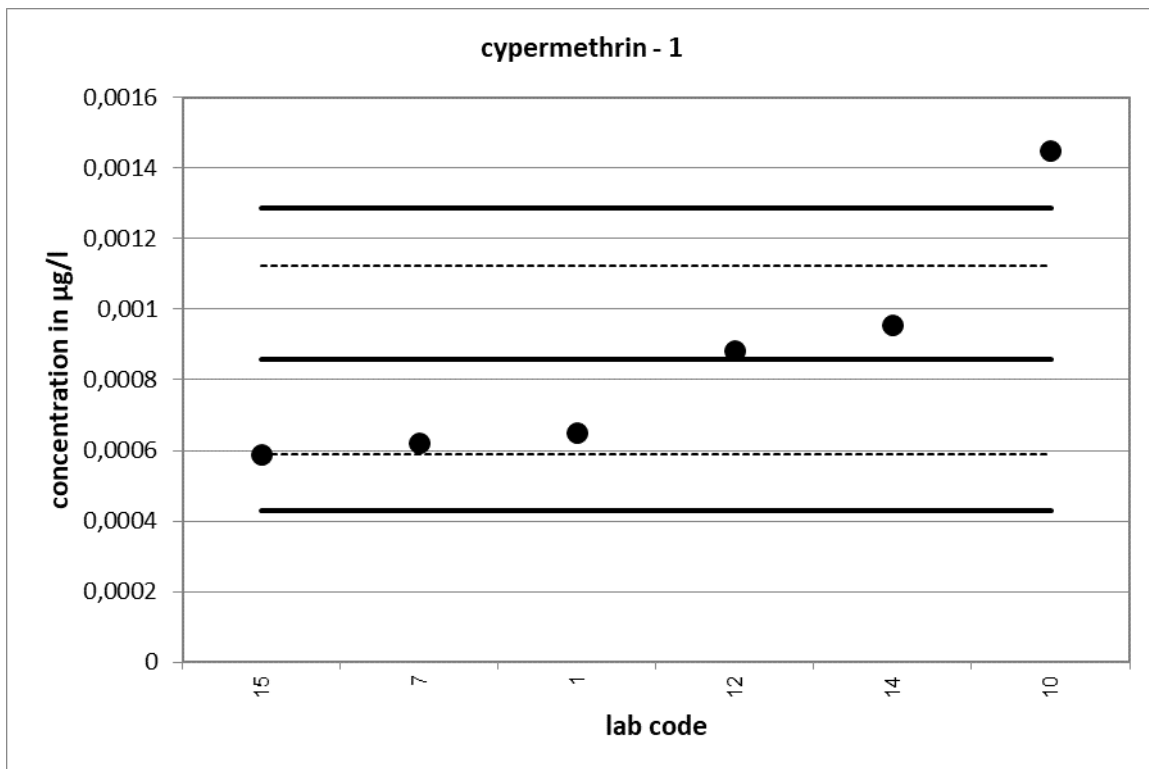


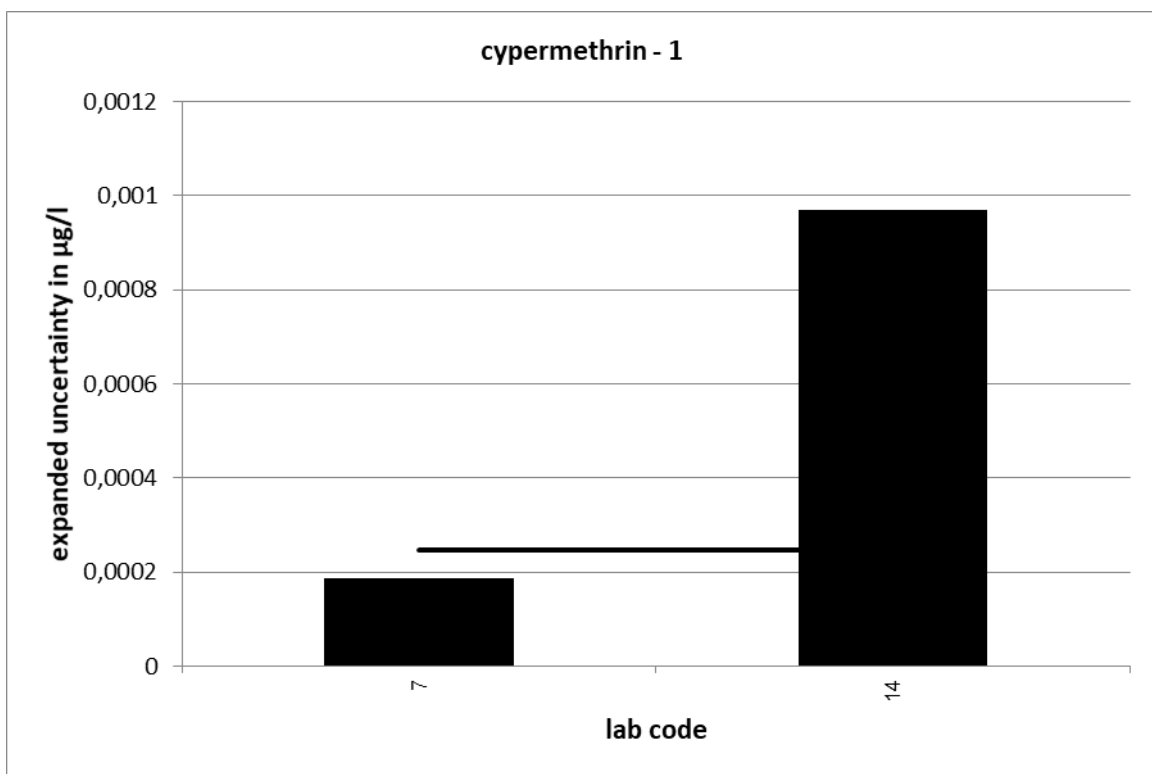
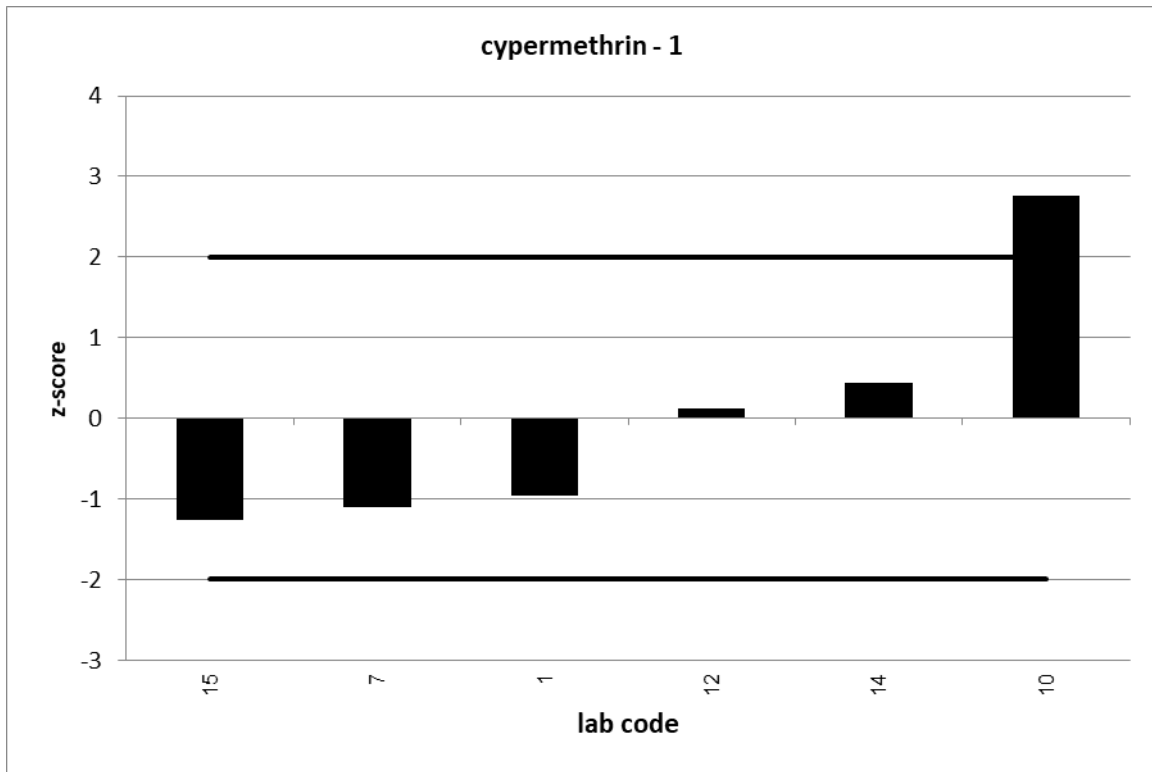
25 % is used as standard deviation for proficiency assessment.

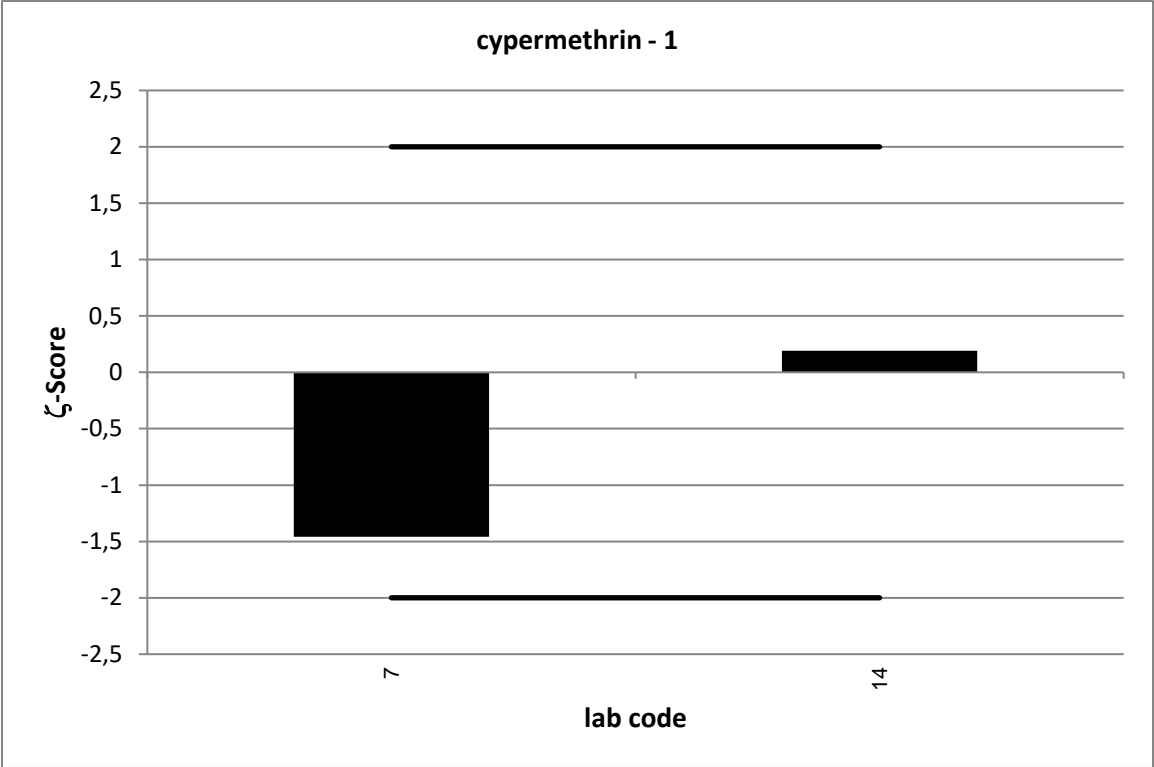
| UKWIR PT 3/20 | | cypermethrin - 1 | | | |
|---|----------------------------|---------------------------|----------------|---------|-------------|
| assigned value [$\mu\text{g/l}$]* | | 0,0008572 \pm 0,0002666 | | | |
| upper tolerance limit [$\mu\text{g/l}$] | | 0,001286 | | | |
| lower tolerance limit [$\mu\text{g/l}$] | | 0,0004286 | | | |
| lab code | result [$\mu\text{g/l}$] | \pm | ζ -score | z-score | assessm. ** |
| 1 | 0,00065 | | | -1,0 | s |
| 7 | 0,00062 | 0,000186 | -1,5 | -1,1 | s |
| 10 | 0,00145 | | | 2,8 | q |
| 12 | 0,0008821 | | | 0,1 | s |
| 14 | 0,000953 | 0,00097 | 0,2 | 0,4 | s |
| 15 | 0,0005878 | | | -1,3 | 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



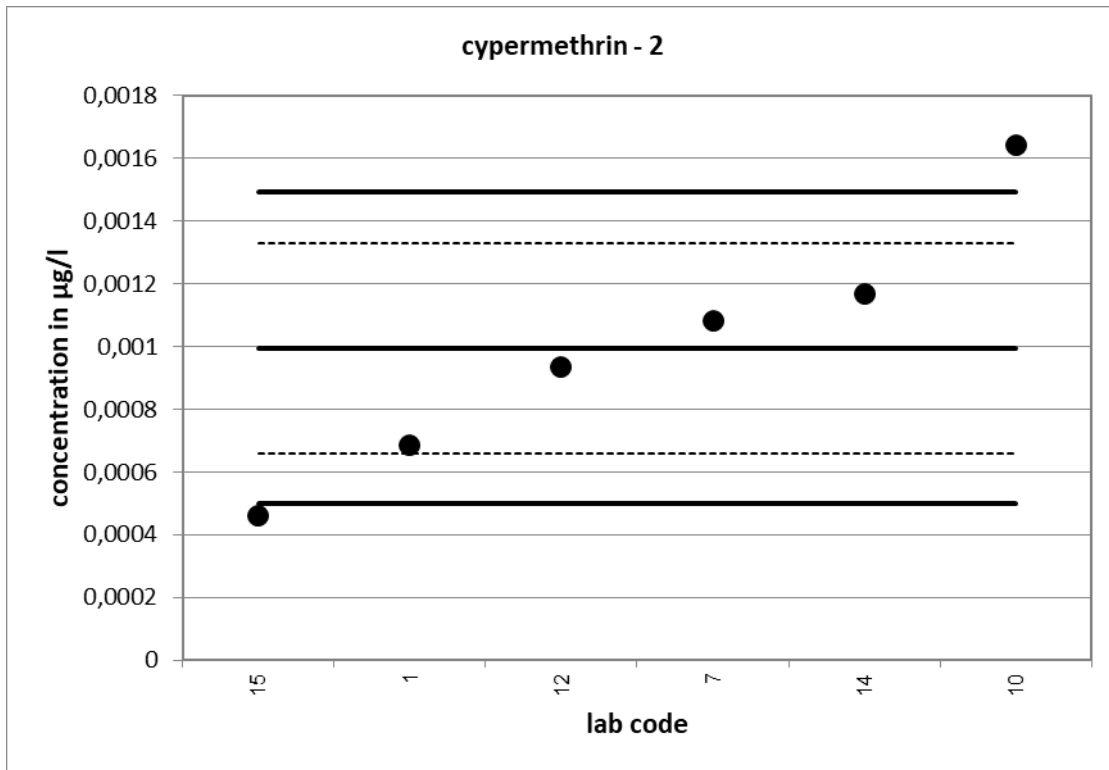


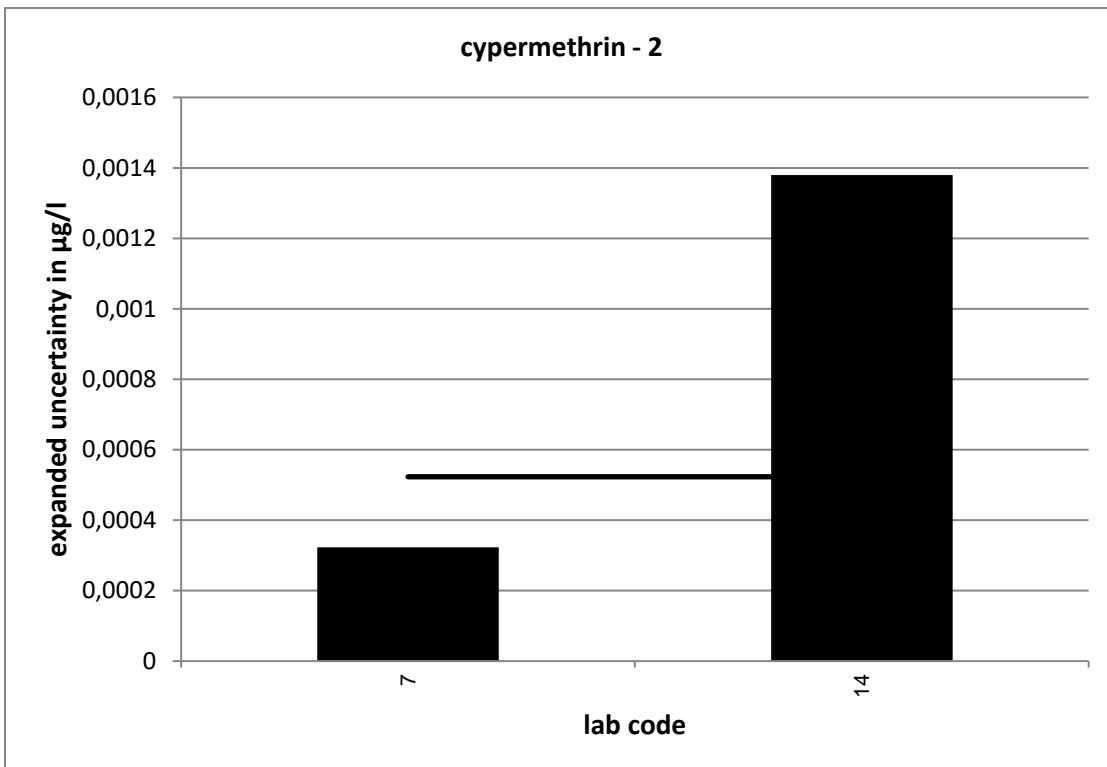
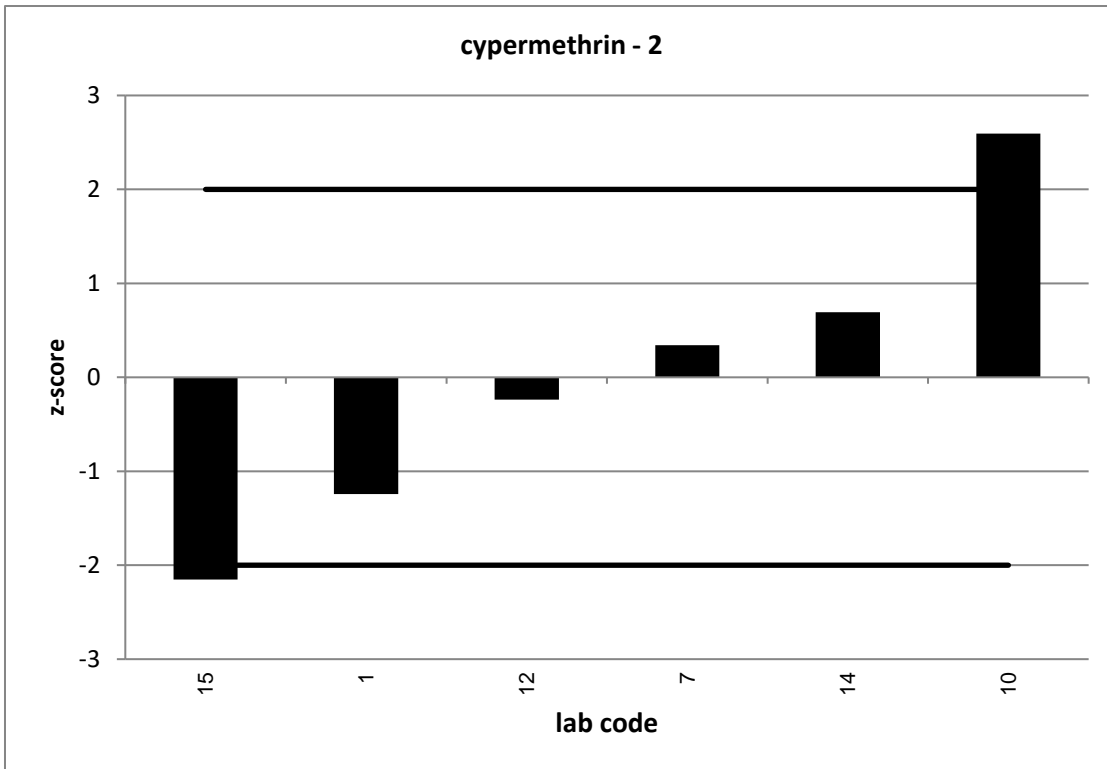


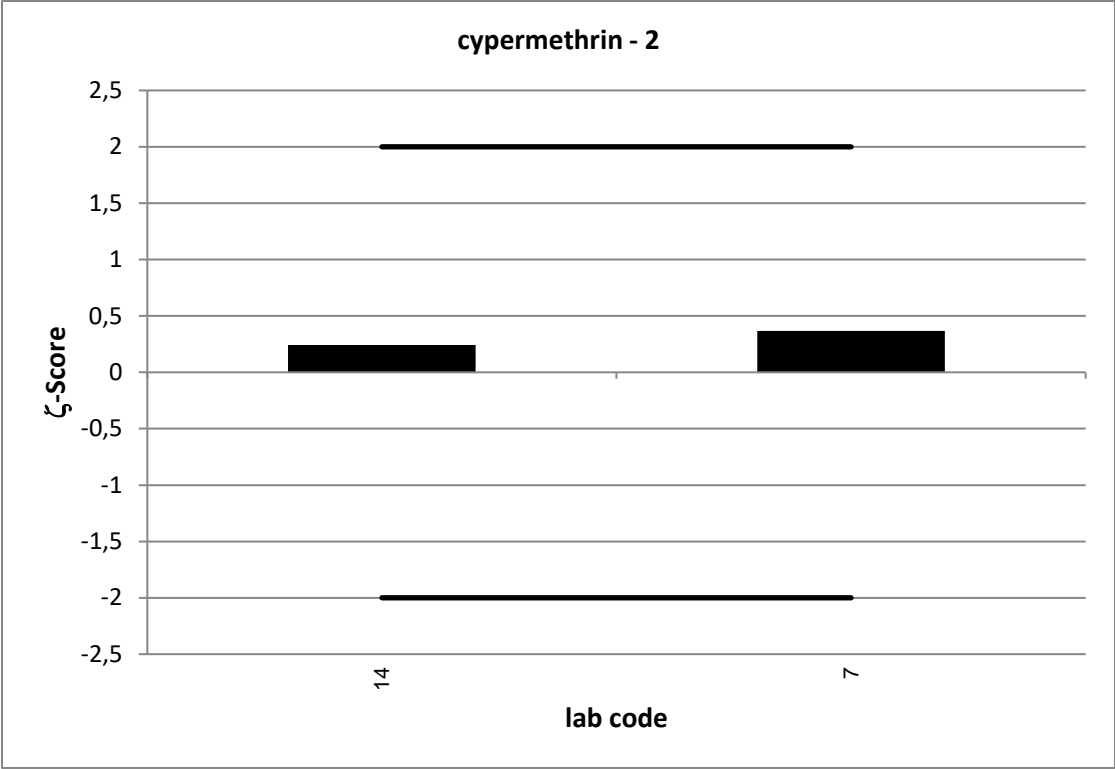
| UKWIR PT 3/20 | | cypermethrin - 2 | | | |
|---|----------------------------|---------------------------|----------------|---------|-------------|
| assigned value [$\mu\text{g/l}$]* | | 0,0009948 \pm 0,0003344 | | | |
| upper tolerance limit [$\mu\text{g/l}$] | | 0,001492 | | | |
| lower tolerance limit [$\mu\text{g/l}$] | | 0,0004974 | | | |
| lab code | result [$\mu\text{g/l}$] | \pm | ζ -score | z-score | assessm. ** |
| 1 | 0,000686 | | | -1,2 | s |
| 7 | 0,00108 | 0,0003 | 0,4 | 0,3 | s |
| 10 | 0,00164 | | | 2,6 | q |
| 12 | 0,000936 | | | -0,2 | s |
| 14 | 0,001167 | 0,0014 | 0,2 | 0,7 | s |
| 15 | 0,0004596 | | | -2,2 | q |

* 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



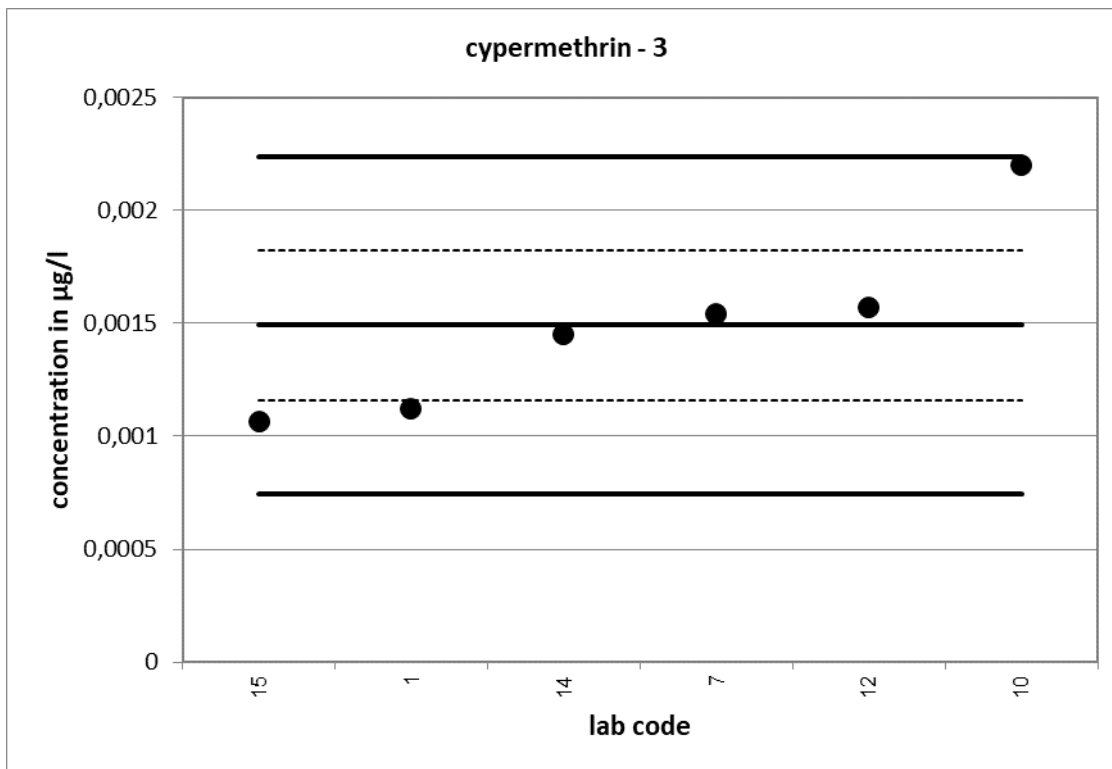


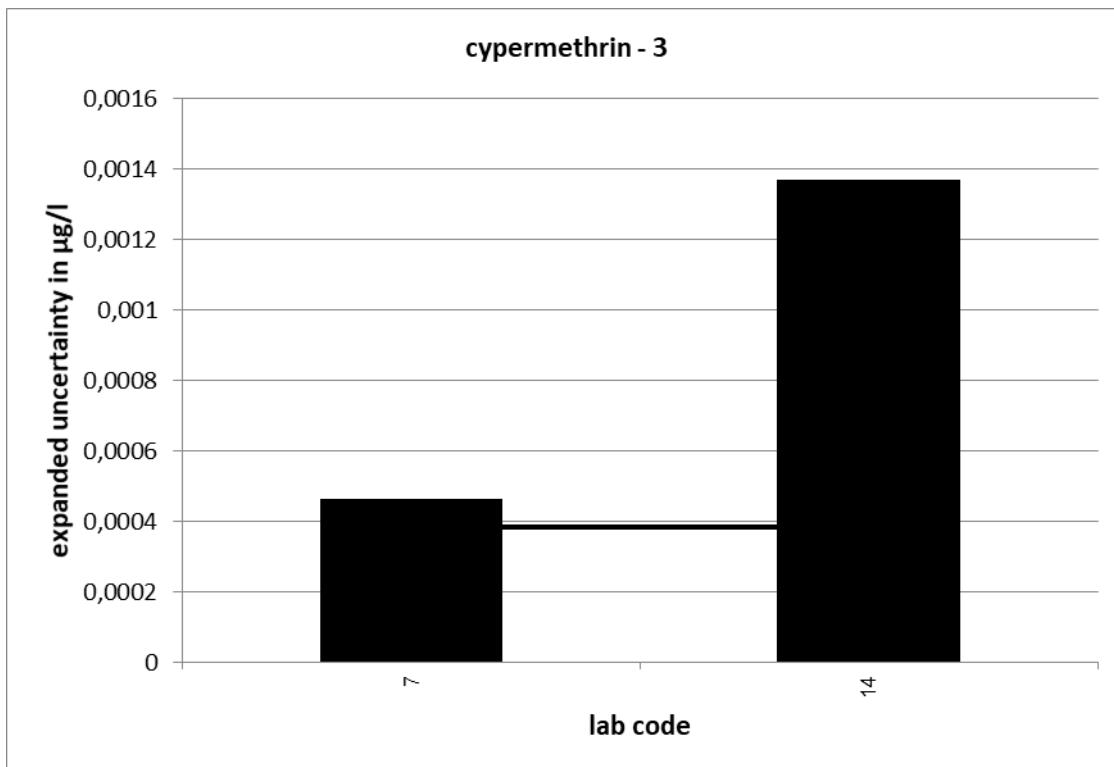
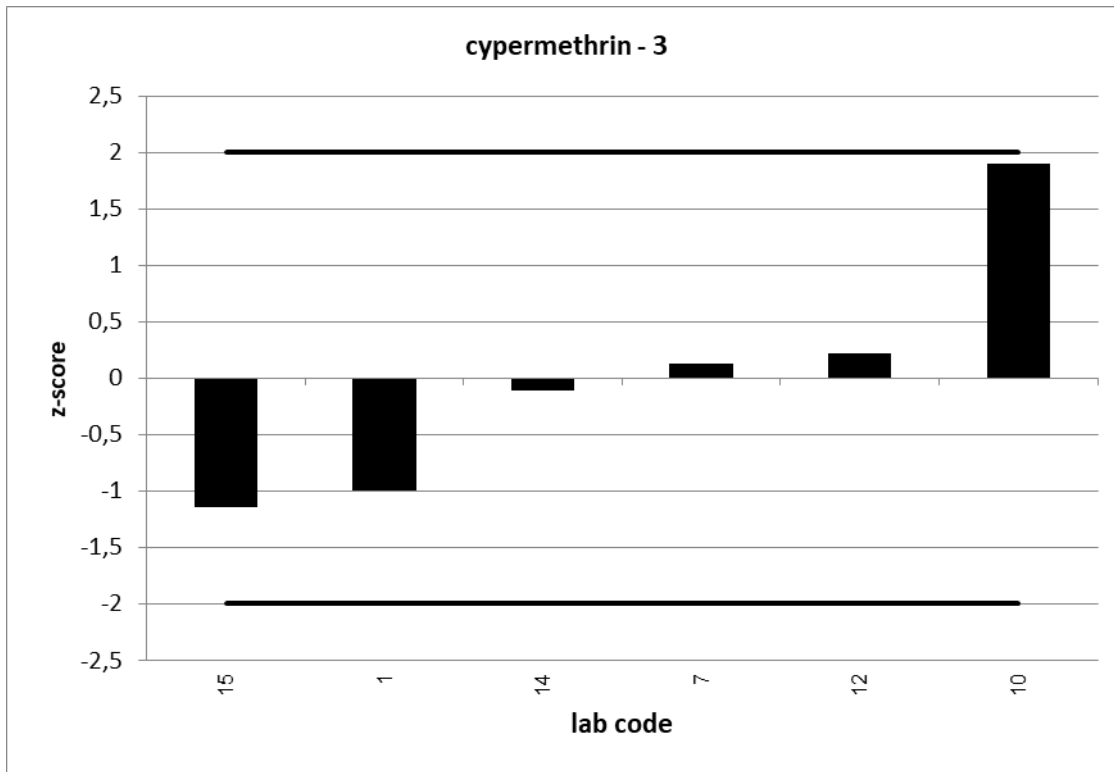


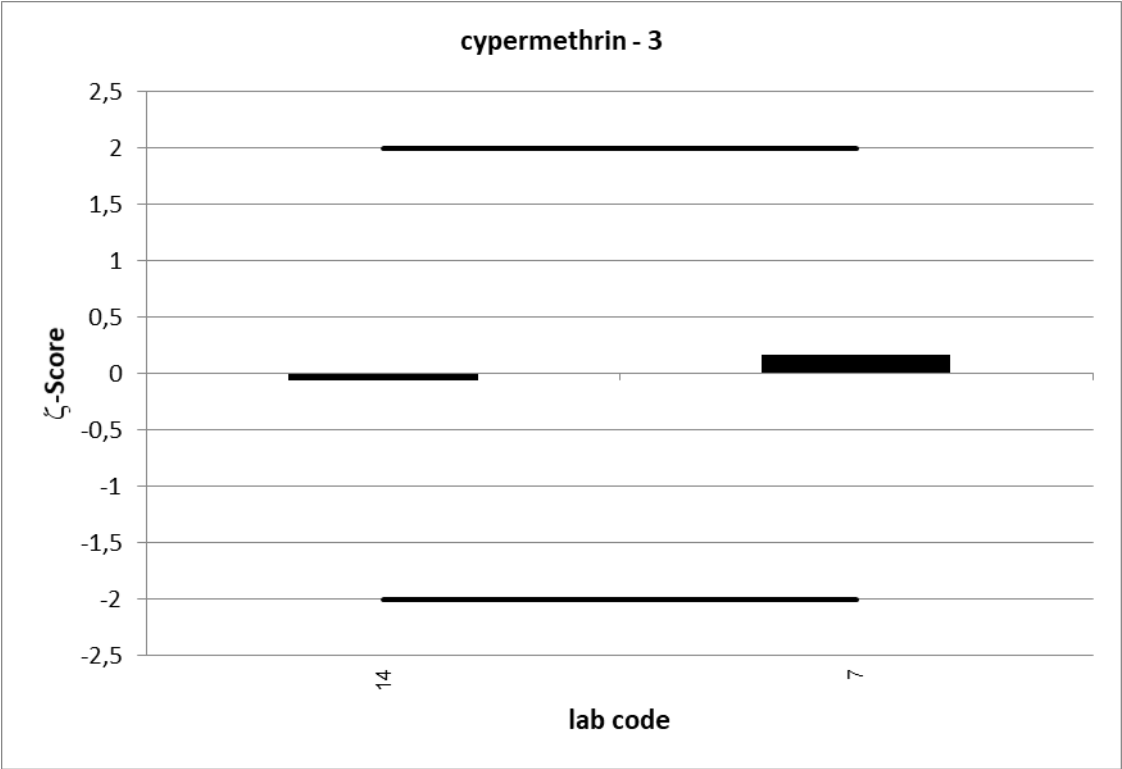
| UKWIR PT 3/20 | | cypermethrin - 3 | | | |
|----------------------------|---------------|---------------------|---------|---------|------------|
| assigned value [µg/l]* | | 0,001491 ± 0,000333 | | | |
| upper tolerance limit [µg/ | | 0,002237 | | | |
| lower tolerance limit [µg/ | | 0,0007457 | | | |
| lab code | result [µg/l] | ± | ζ-score | z-score | assessm.** |
| 1 | 0,00112 | | | -1,0 | s |
| 7 | 0,00154 | 0,0005 | 0,2 | 0,1 | s |
| 10 | 0,0022 | | | 1,9 | s |
| 12 | 0,0015723 | | | 0,2 | s |
| 14 | 0,001452 | 0,0014 | -0,1 | -0,1 | s |
| 15 | 0,0010635 | | | -1,1 | 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



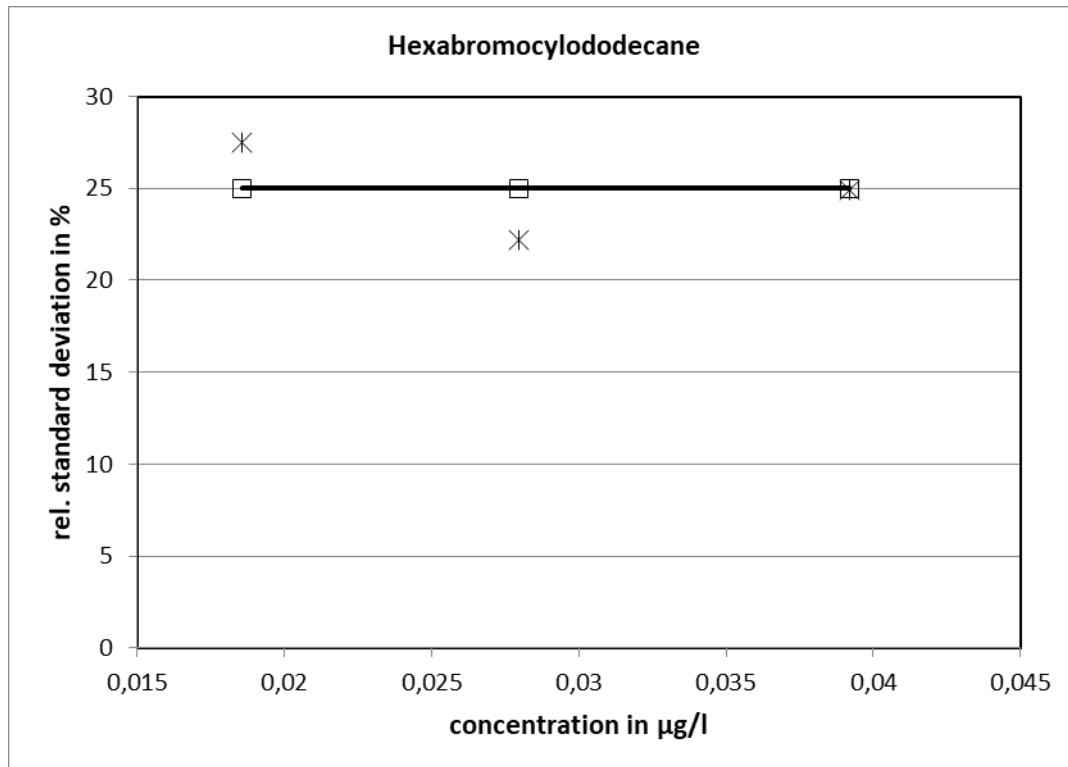




UKWIR 4/20:

| Hexabromocyclododecane | | | | | | | | | | | | | |
|-------------------------------|-----------------------|--|---|--|---|------------------------------|------------------------------|---------------------------|---------------------------|-------------------|-----------|-----------|---------|
| 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 | 0,0186 | 30,71 | 0,0051 | 0,0046 | 25 | 0,0279 | 0,0093 | 50 | -50 | 5 | 0 | 0 | 0,0 |
| 2 | 0,0280 | 24,85 | 0,0062 | 0,0070 | 25 | 0,0419 | 0,0140 | 50 | -50 | 5 | 0 | 0 | 0,0 |
| 3 | 0,0392 | 27,86 | 0,0098 | 0,0098 | 25 | 0,0588 | 0,0196 | 50 | -50 | 5 | 0 | 0 | 0,0 |
| | | | | | | | | | | sum | 15 | 0 | 0,0 |

Relative standard deviation

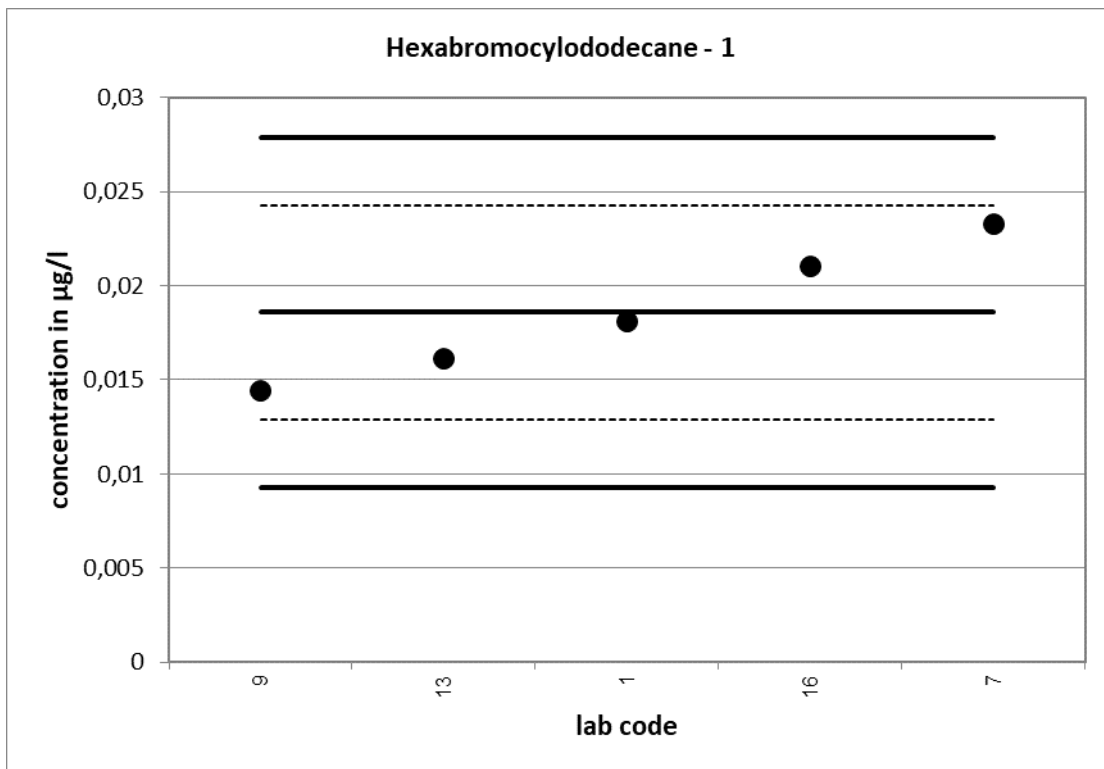


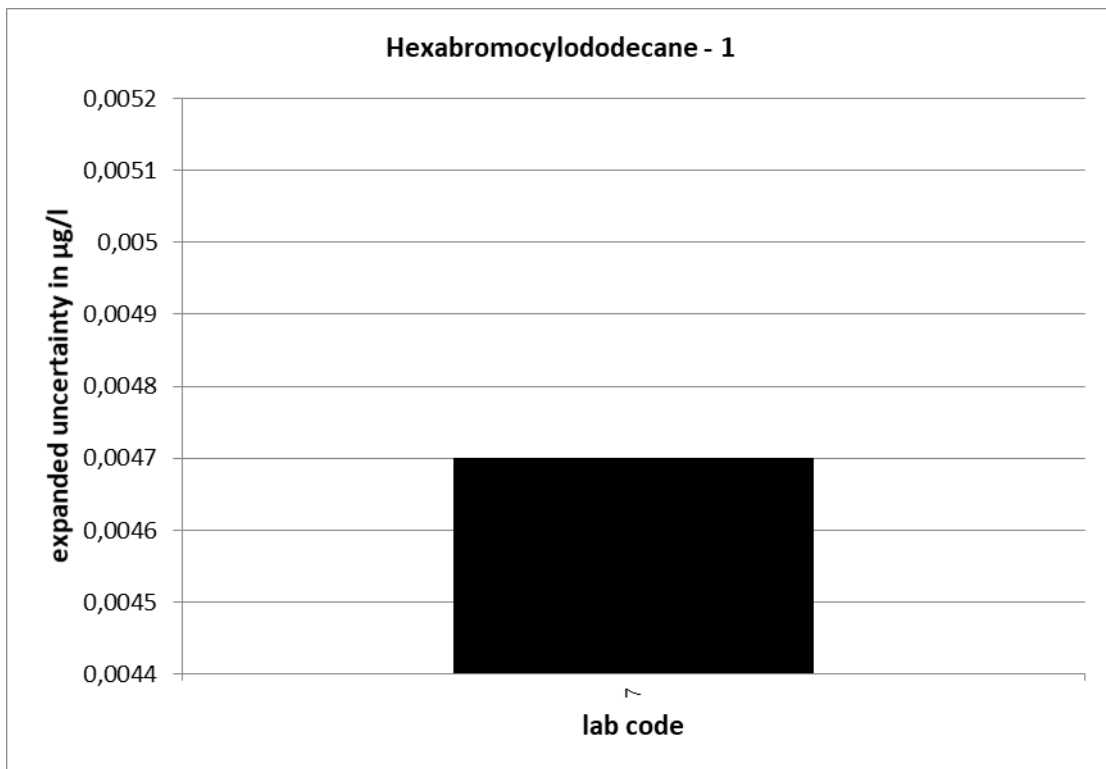
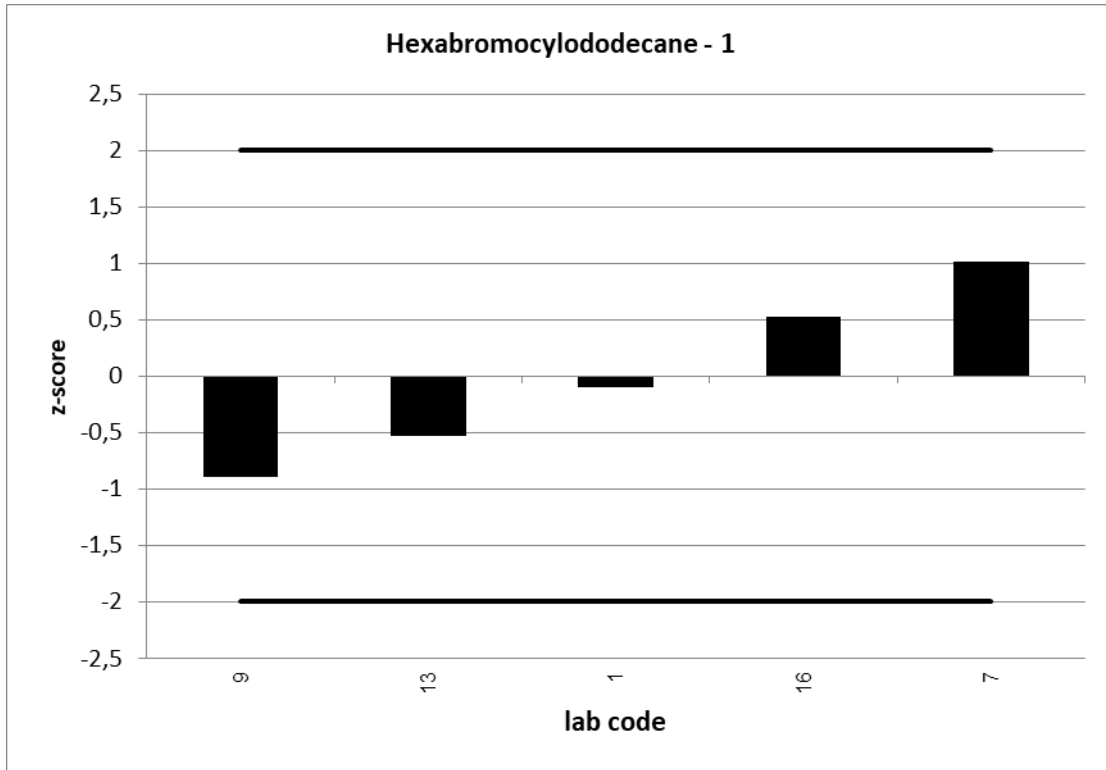
25 % is used as standard deviation for proficiency assessment.

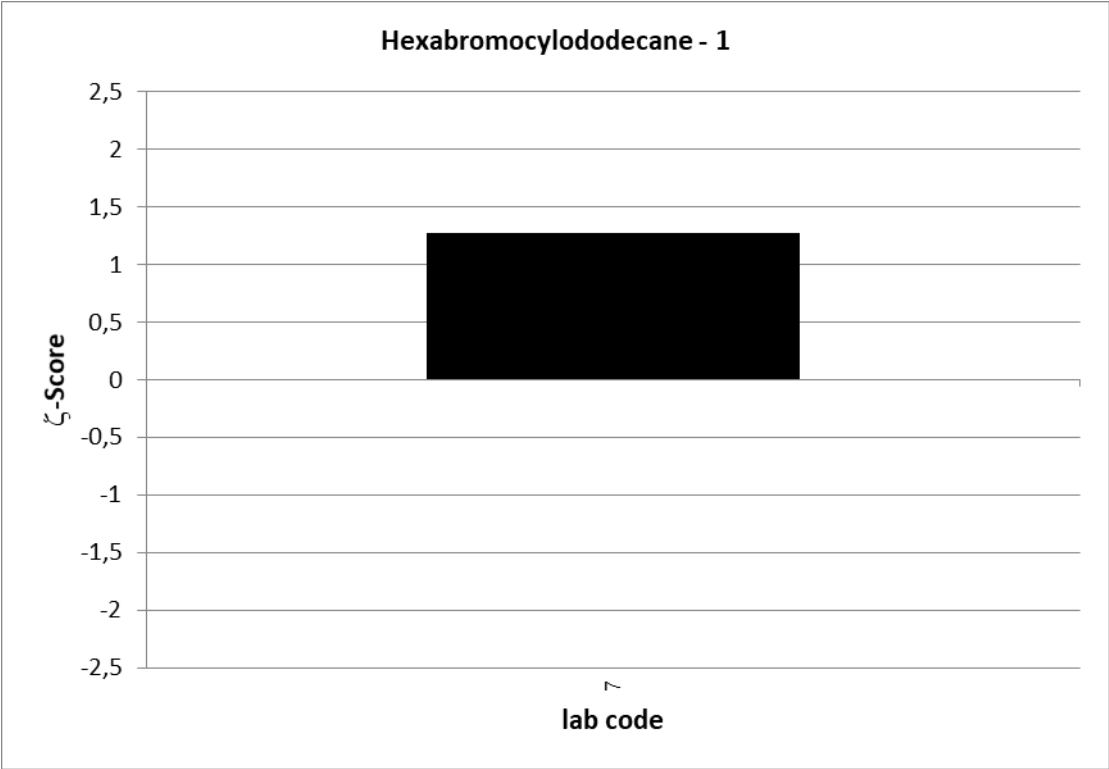
| UKWIR PT 4/20 | | Hexabromocyclododecane - 1 | | | |
|---|----------------------------|----------------------------|----------------|---------|------------|
| assigned value [$\mu\text{g/l}$]* | | 0,01858 \pm 0,00571 | | | |
| upper tolerance limit [$\mu\text{g/l}$] | | 0,02787 | | | |
| lower tolerance limit [$\mu\text{g/l}$] | | 0,00929 | | | |
| lab code | result [$\mu\text{g/l}$] | \pm | ζ -score | z-score | assessm.** |
| 1 | 0,0181 | | | -0,1 | s |
| 7 | 0,0233 | 0,005 | 1,3 | 1,0 | s |
| 9 | 0,0144 | | | -0,9 | s |
| 13 | 0,0161 | | | -0,5 | s |
| 16 | 0,021 | | | 0,5 | 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



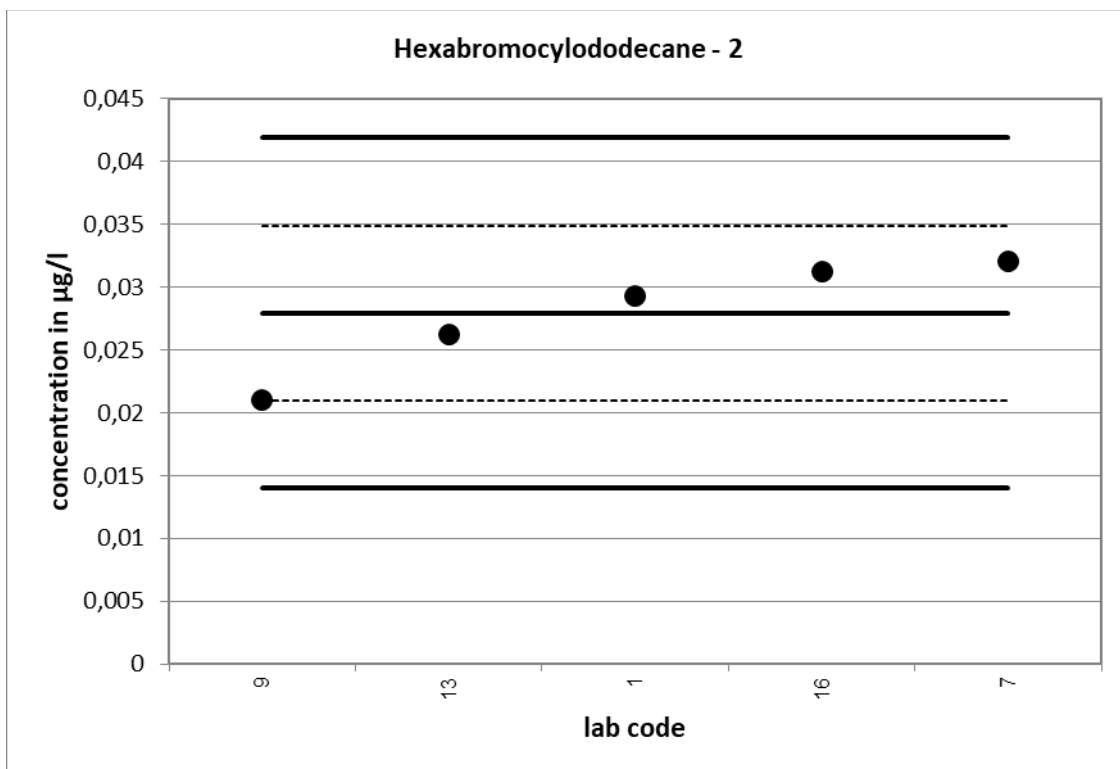


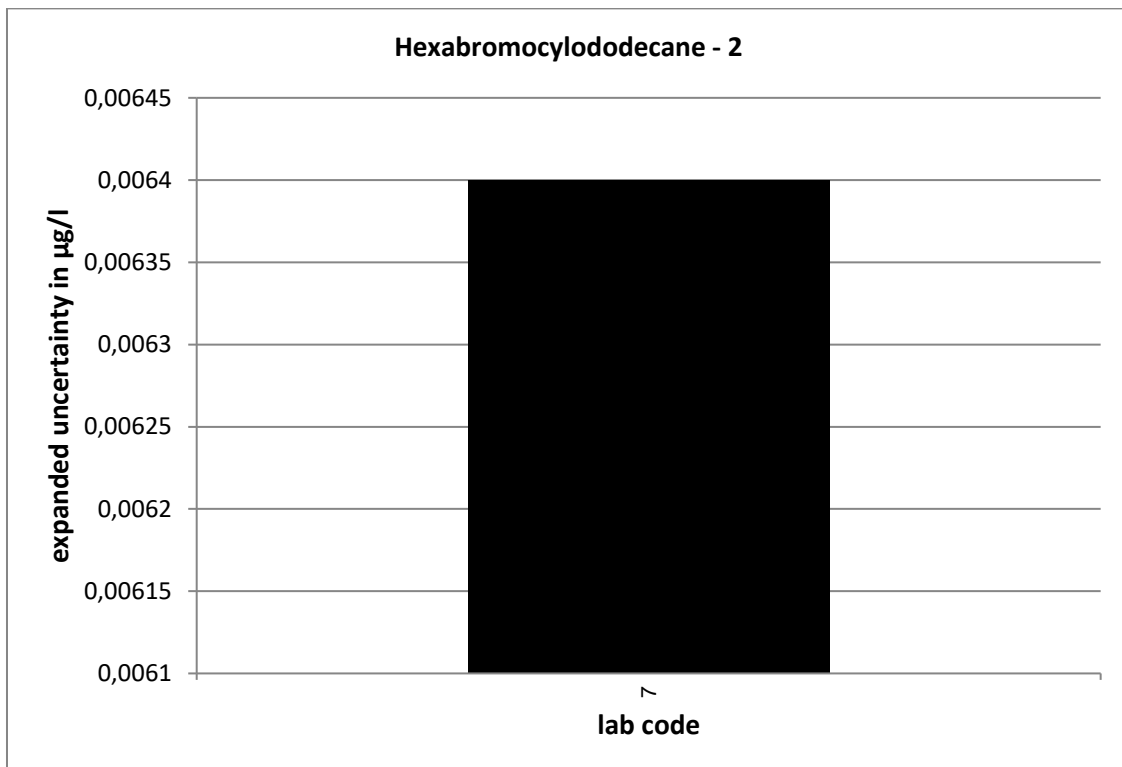
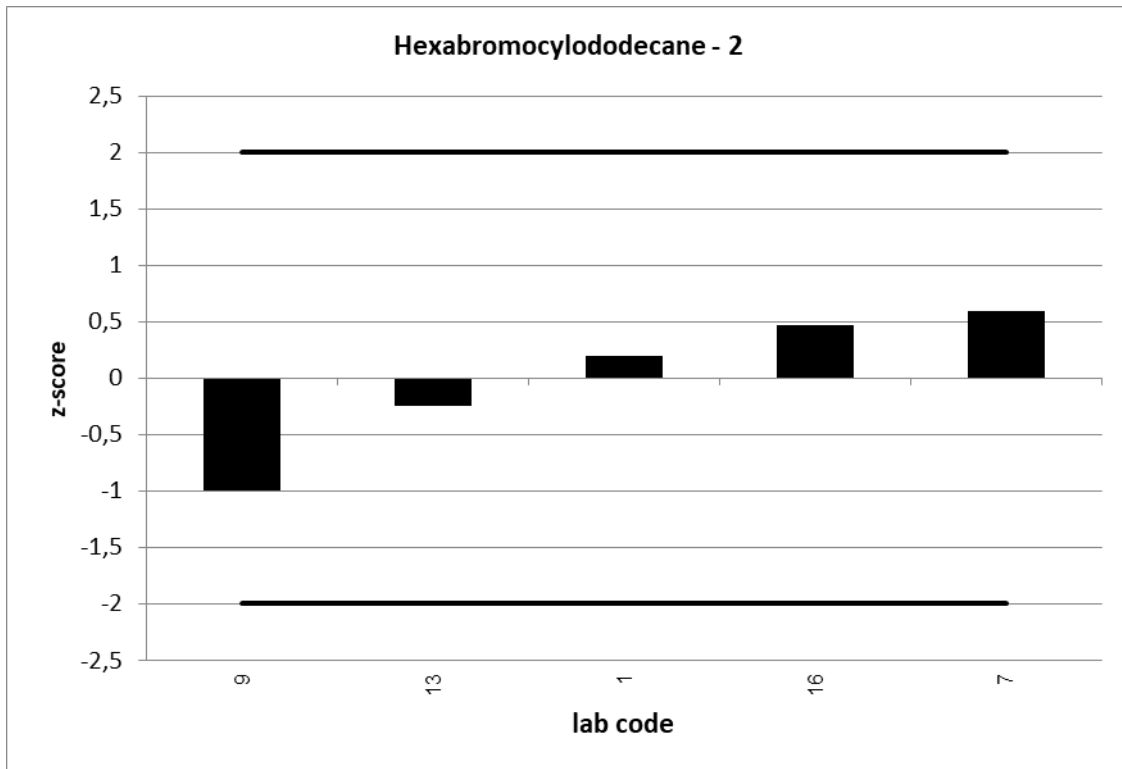


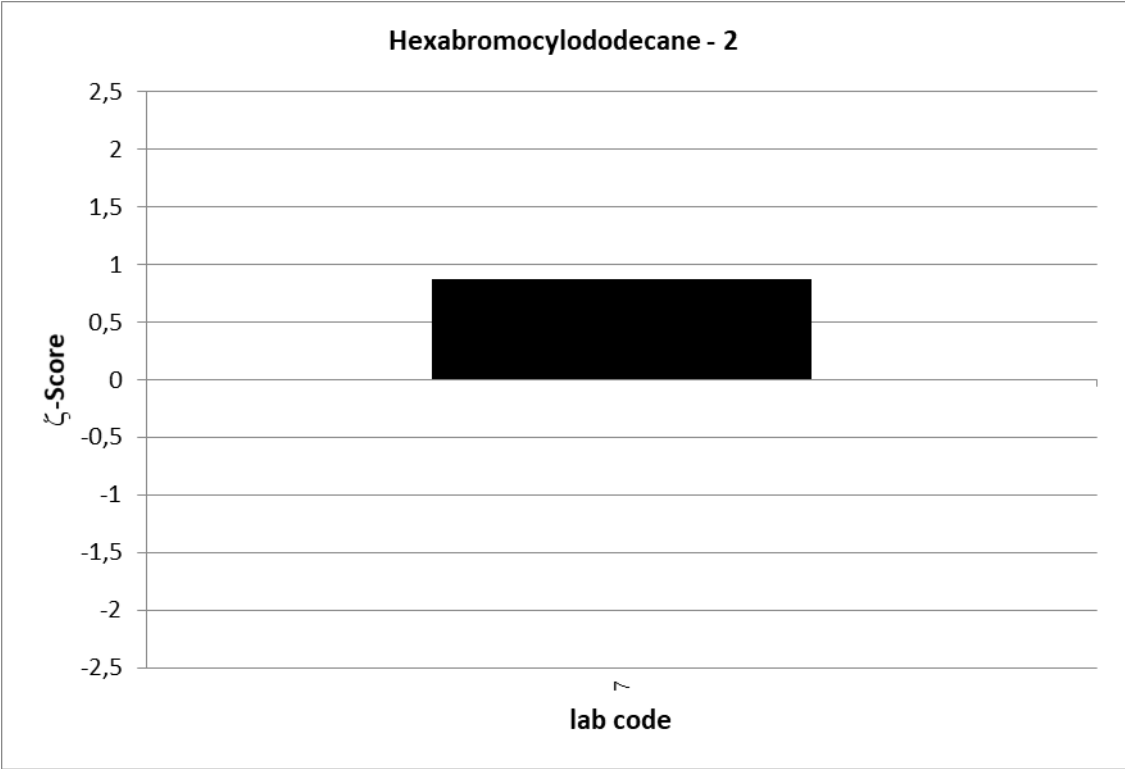
| UKWIR PT 4/20 | | Hexabromocyclododecane - 2 | | | |
|---|----------------------------|----------------------------|----------------|---------|------------|
| assigned value [$\mu\text{g/l}$]* | | 0,02796 \pm 0,00695 | | | |
| upper tolerance limit [$\mu\text{g/l}$] | | 0,04194 | | | |
| lower tolerance limit [$\mu\text{g/l}$] | | 0,01398 | | | |
| lab code | result [$\mu\text{g/l}$] | \pm | ζ -score | z-score | assessm.** |
| 1 | 0,0293 | | | 0,2 | s |
| 7 | 0,0321 | 0,006 | 0,9 | 0,6 | s |
| 9 | 0,021 | | | -1,0 | s |
| 13 | 0,0262 | | | -0,3 | s |
| 16 | 0,0312 | | | 0,5 | 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



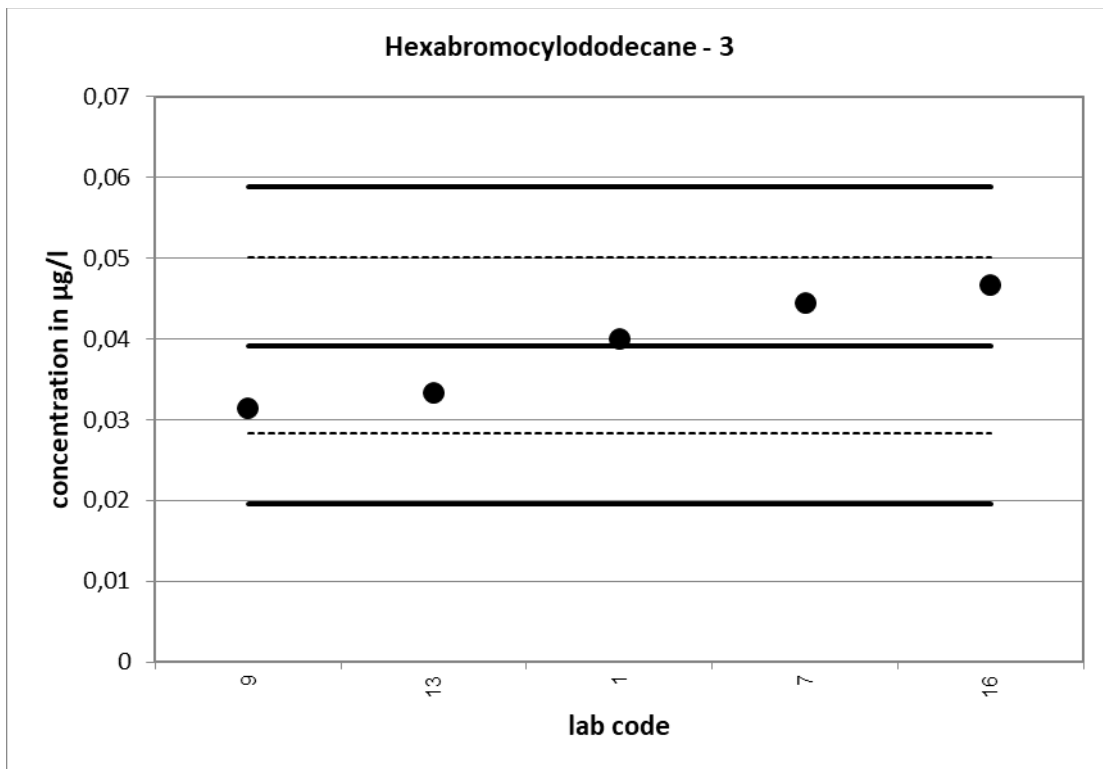


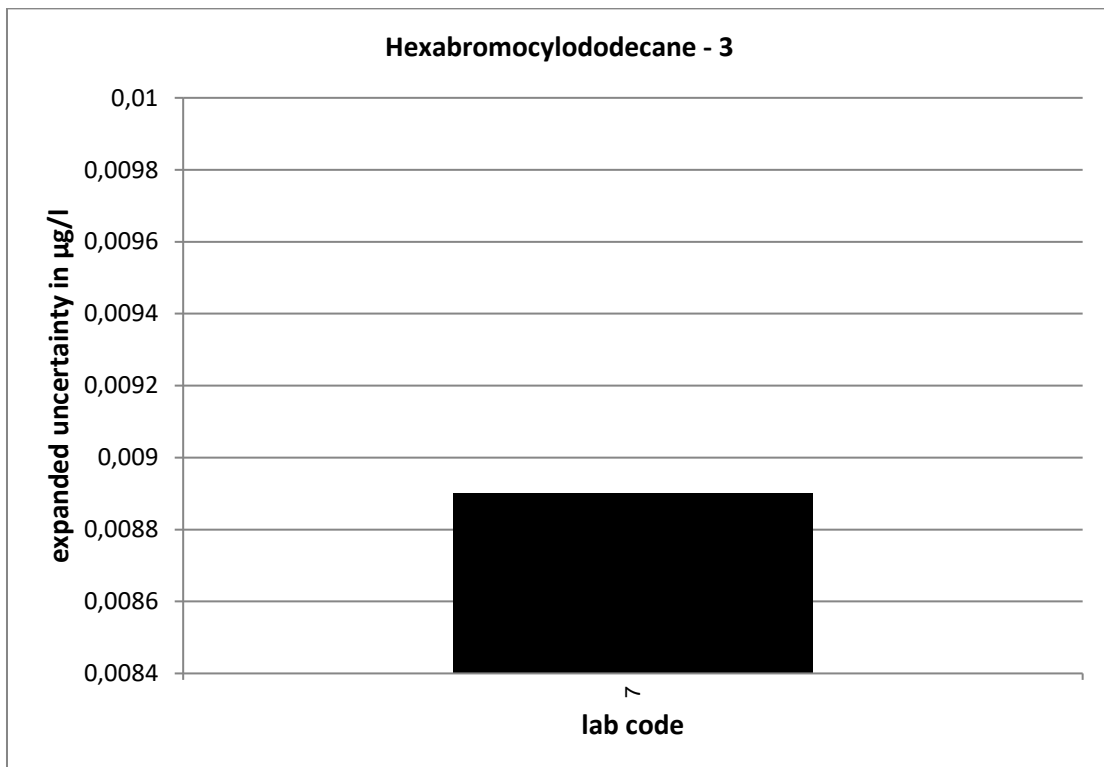
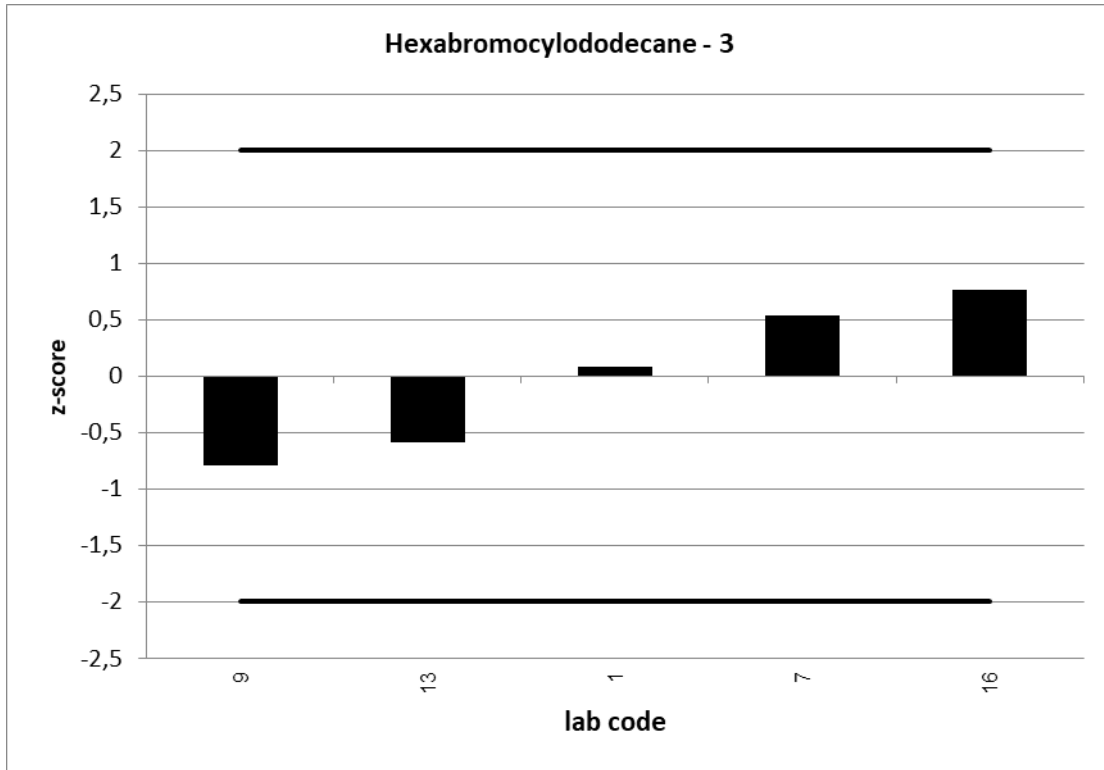


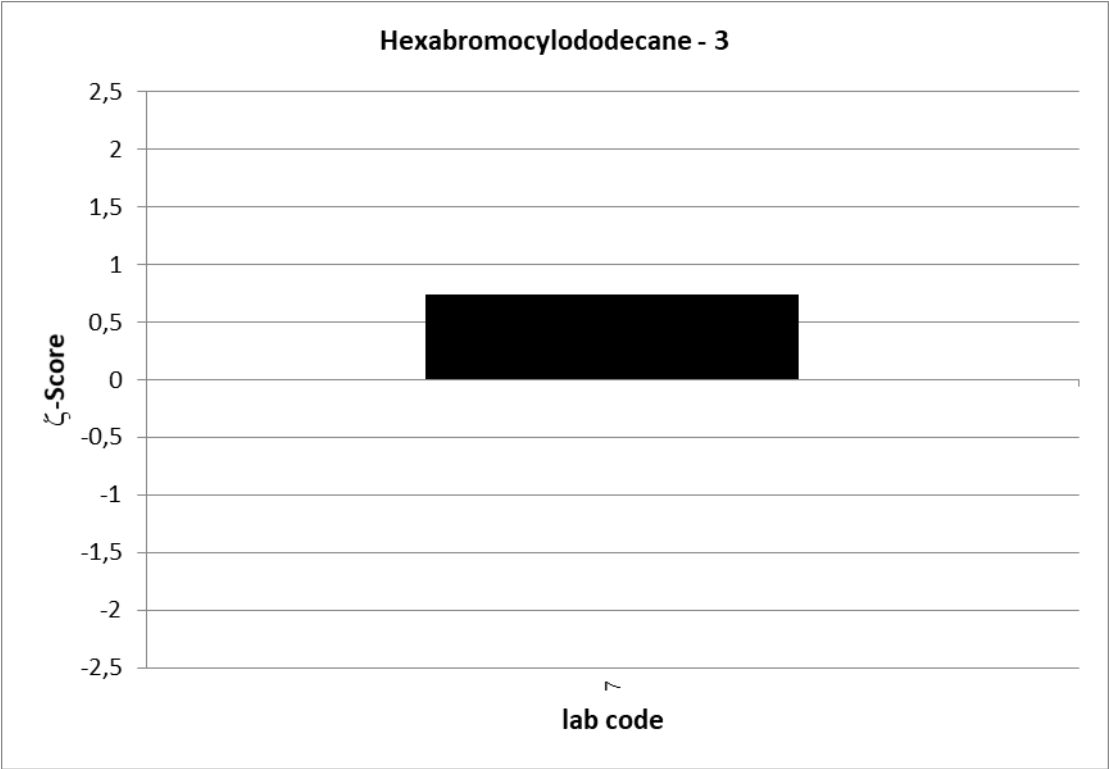
| UKWIR PT 4/20 | | Hexabromocyclododecane - 3 | | | |
|---|----------------------------|----------------------------|----------------|---------|------------|
| assigned value [$\mu\text{g/l}$]* | | 0,03918 \pm 0,01092 | | | |
| upper tolerance limit [$\mu\text{g/l}$] | | 0,05877 | | | |
| lower tolerance limit [$\mu\text{g/l}$] | | 0,01959 | | | |
| lab code | result [$\mu\text{g/l}$] | \pm | ζ -score | z-score | assessm.** |
| 1 | 0,04 | | | 0,1 | s |
| 7 | 0,0444 | 0,009 | 0,7 | 0,5 | s |
| 9 | 0,0314 | | | -0,8 | s |
| 13 | 0,0334 | | | -0,6 | s |
| 16 | 0,0467 | | | 0,8 | 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



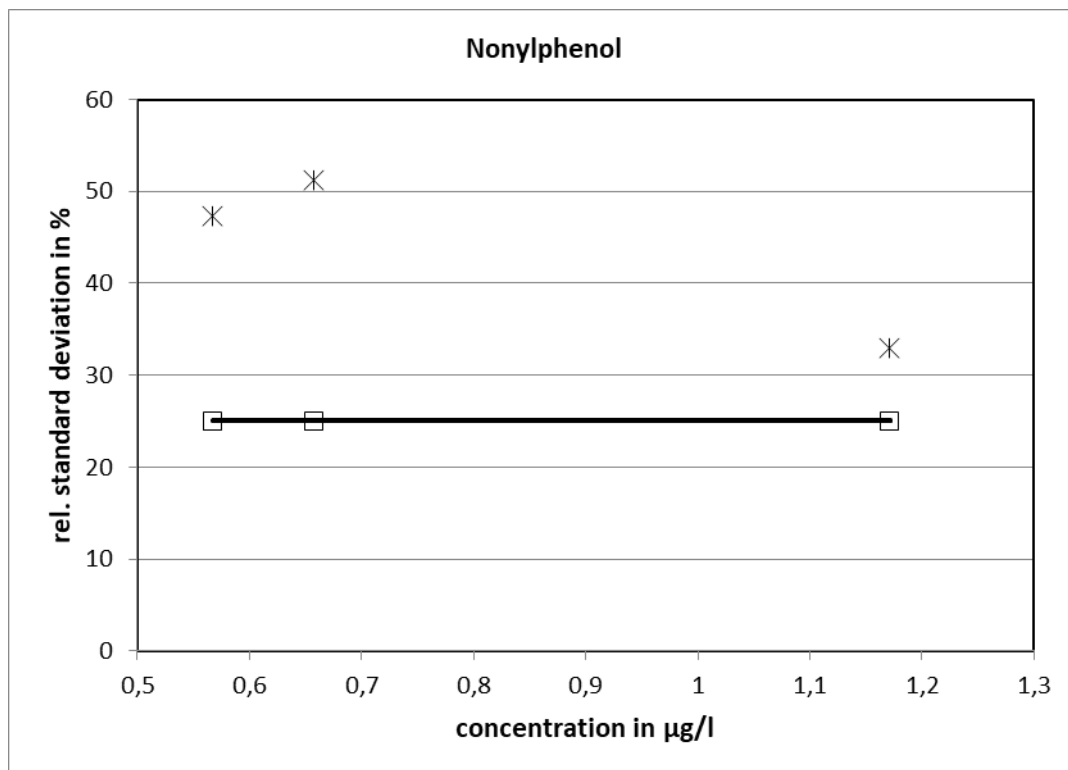




UKWIR 5/20:

| Nonylphenol | | | | | | | | | | | | | |
|--------------------|-----------------------|--|---|--|---|------------------------------|------------------------------|---------------------------|---------------------------|-------------------|-----------|-----------|---------|
| 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 | 0,5673 | 24,22 | 0,2685 | 0,1418 | 25 | 0,8509 | 0,2836 | 50 | -50 | 4 | 0 | 0 | 0,0 |
| 2 | 0,6580 | 25,34 | 0,3373 | 0,1645 | 25 | 0,9870 | 0,3290 | 50 | -50 | 4 | 0 | 0 | 0,0 |
| 3 | 1,171 | 16,80 | 0,3861 | 0,2928 | 25 | 1,757 | 0,5855 | 50 | -50 | 4 | 0 | 0 | 0,0 |
| | | | | | | | | | sum | 12 | 0 | 0 | 0,0 |

Relative standard deviation

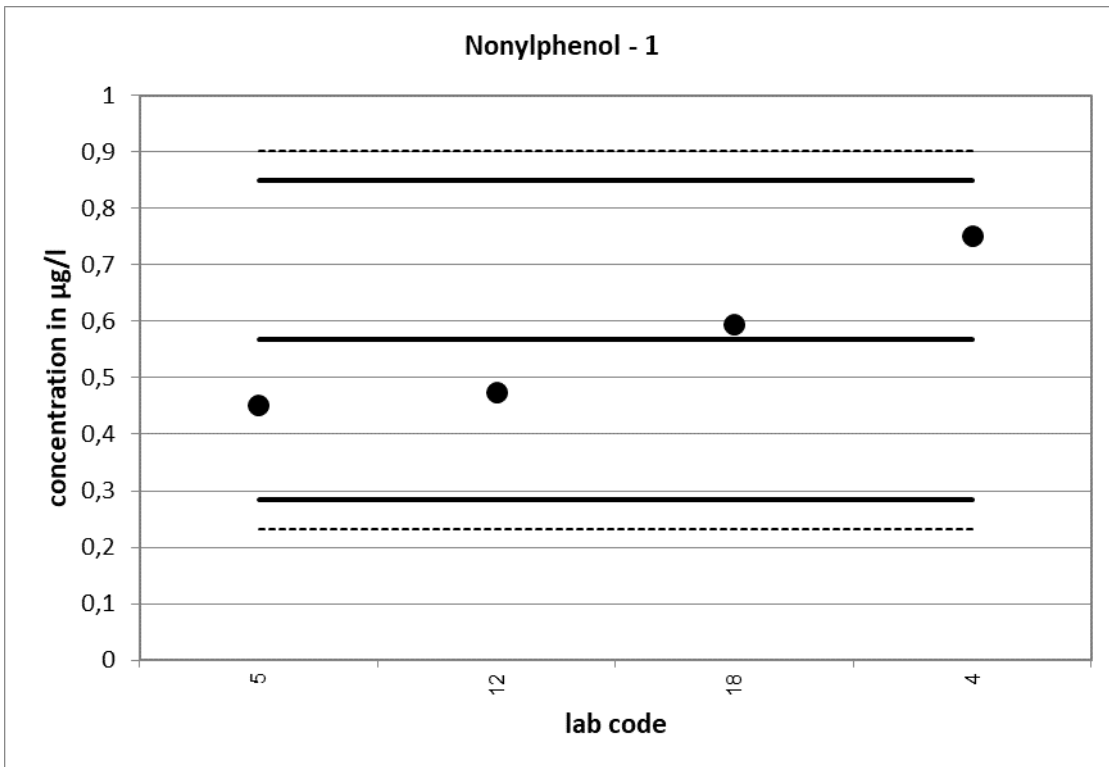


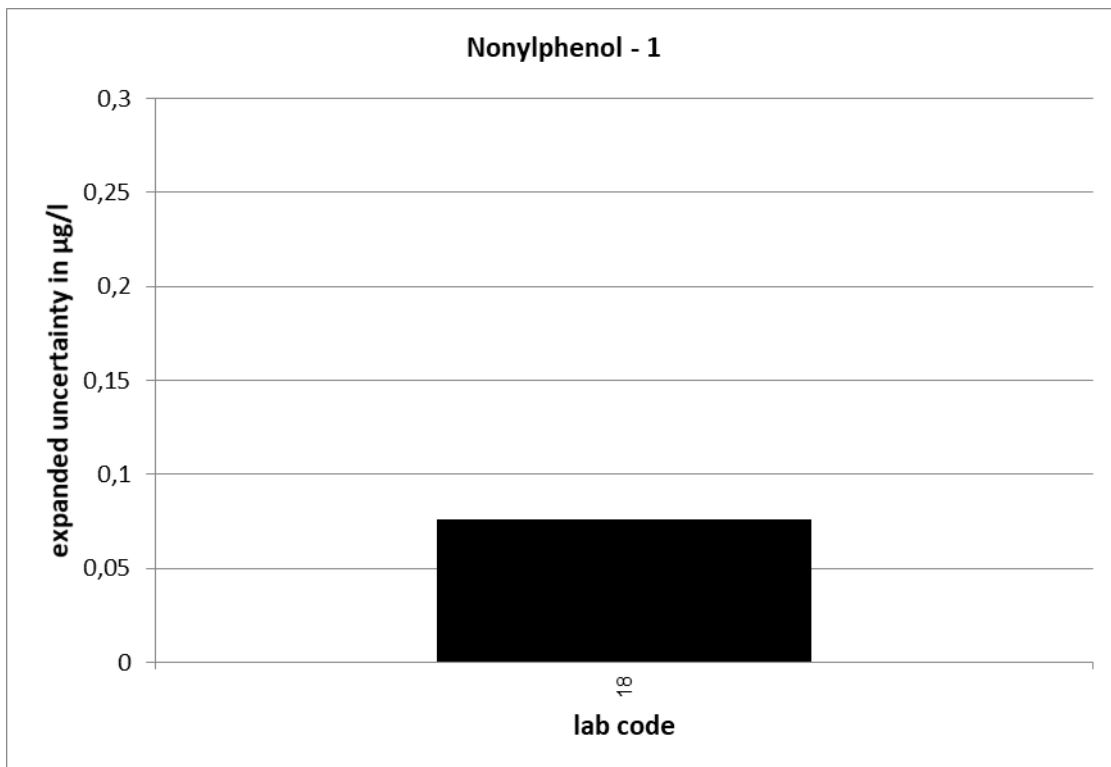
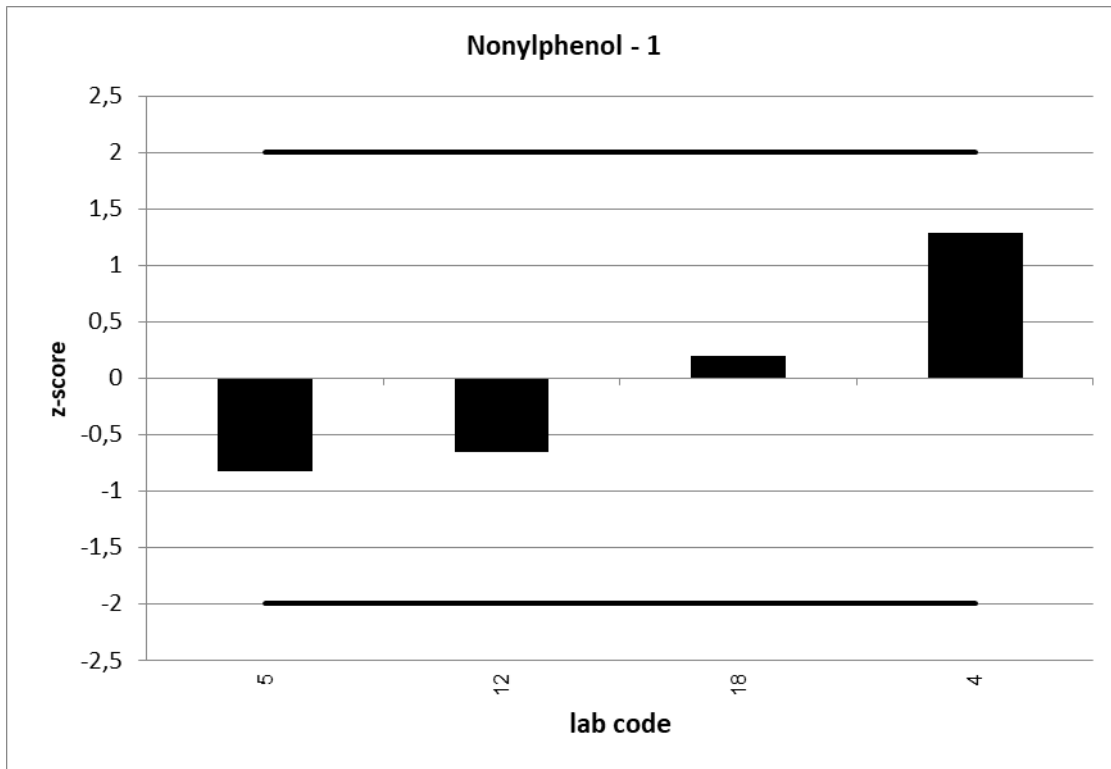
25 % is used as standard deviation for proficiency assessment.

| UKWIR PT 5/20 | | Nonylphenol - 1 | | | |
|---|----------------------------|---------------------|----------------|---------|-------------|
| assigned value [$\mu\text{g/l}$]* | | 0,5673 \pm 0,3356 | | | |
| upper tolerance limit [$\mu\text{g/l}$] | | 0,8509 | | | |
| lower tolerance limit [$\mu\text{g/l}$] | | 0,2836 | | | |
| lab code | result [$\mu\text{g/l}$] | \pm | ζ -score | z-score | assessm. ** |
| 4 | 0,75 | | | 1,3 | s |
| 5 | 0,45 | | | -0,8 | s |
| 12 | 0,474 | | | -0,7 | s |
| 18 | 0,595 | 0,0762 | 0,2 | 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



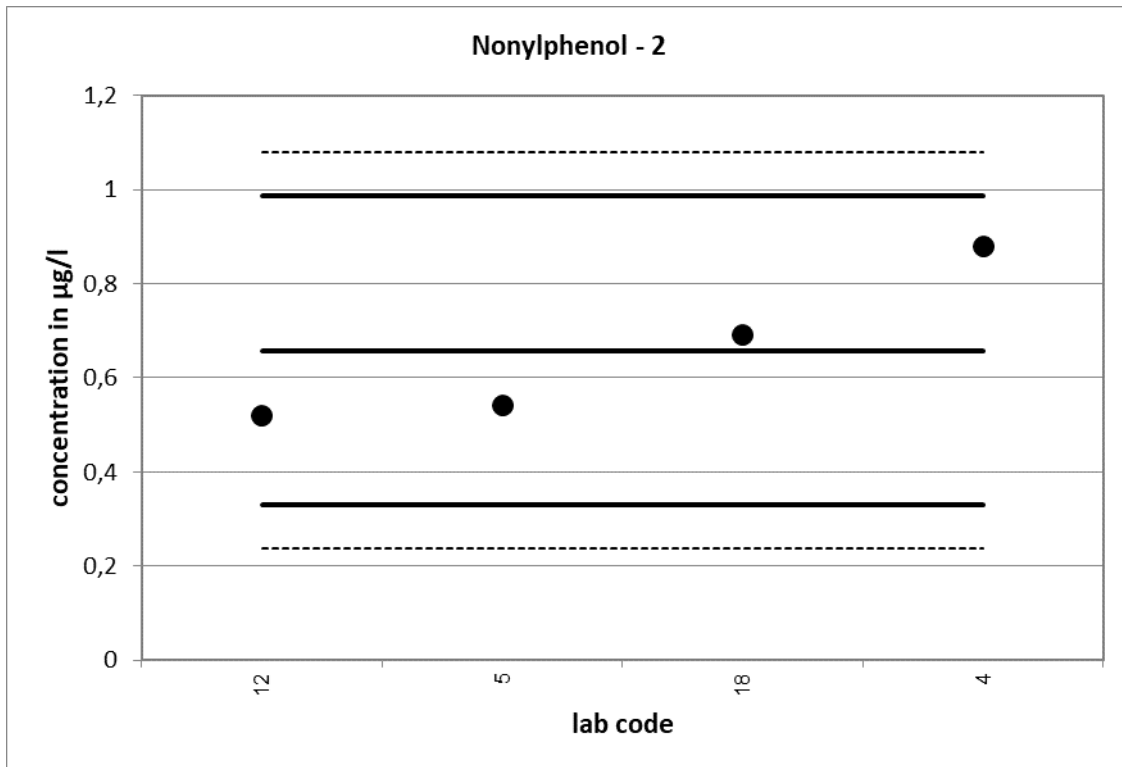


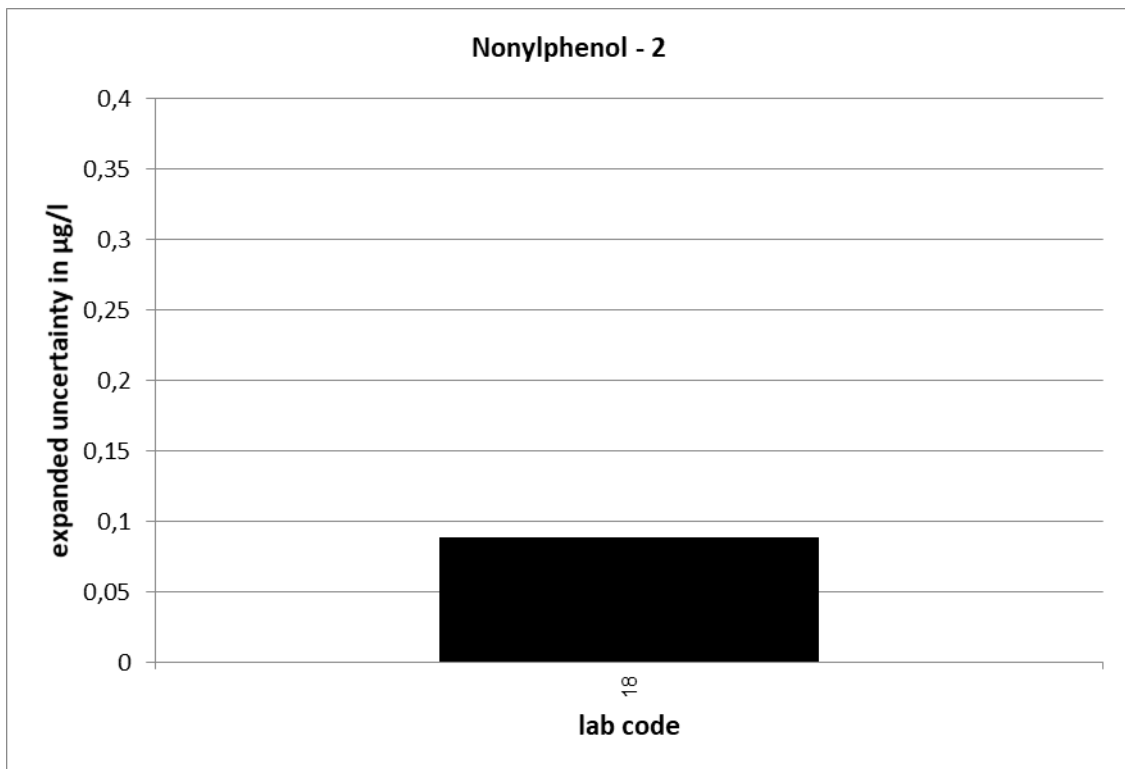
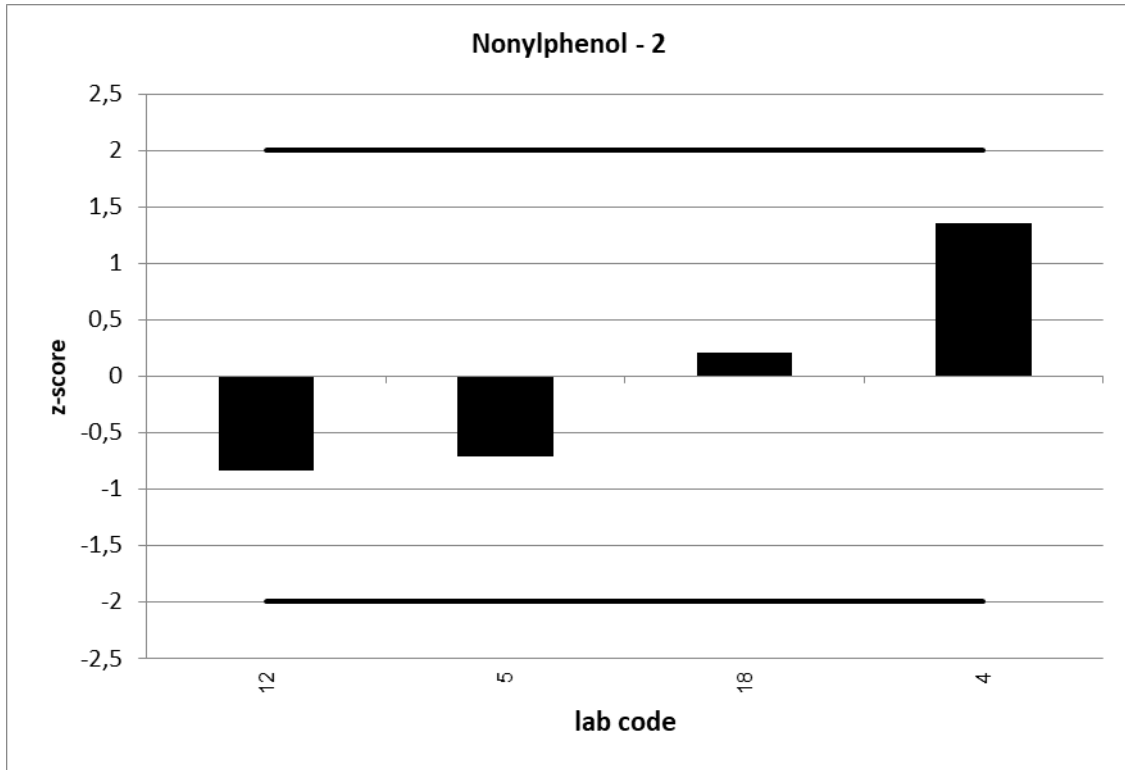


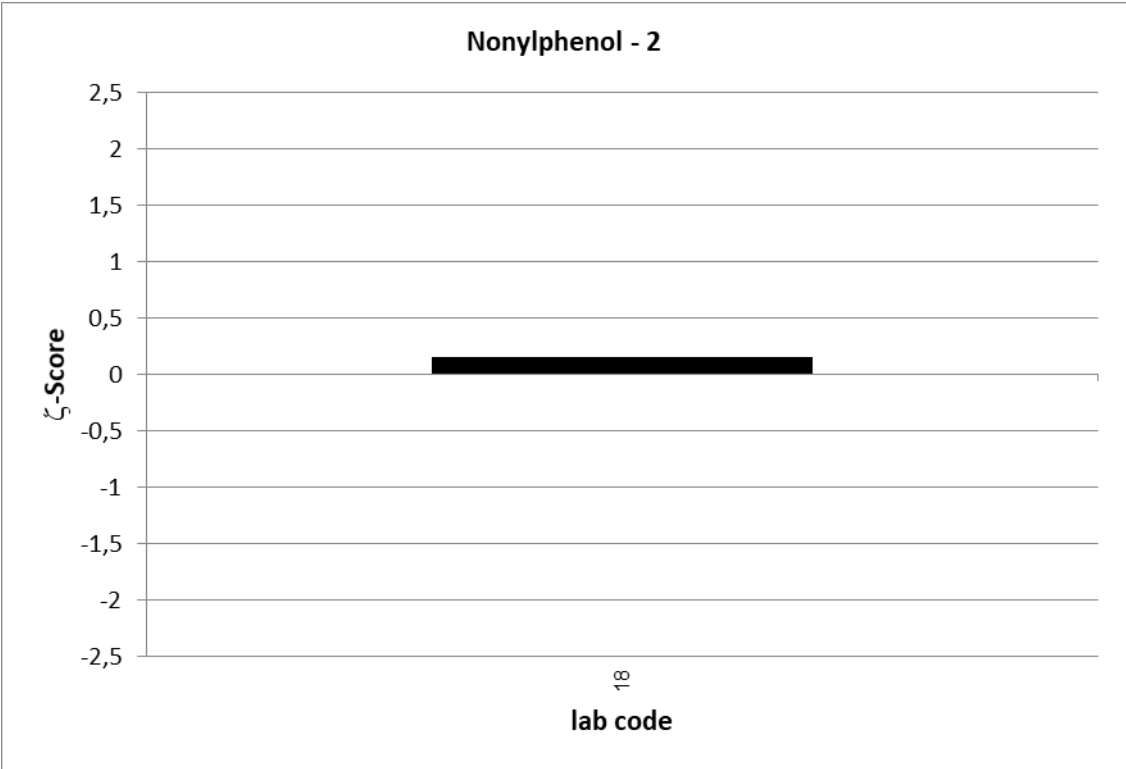
| UKWIR PT 5/20 | | Nonylphenol - 2 | | | |
|---|----------------------------|--------------------|----------------|---------|-------------|
| assigned value [$\mu\text{g/l}$]* | | 0,658 \pm 0,4216 | | | |
| upper tolerance limit [$\mu\text{g/l}$] | | 0,987 | | | |
| lower tolerance limit [$\mu\text{g/l}$] | | 0,329 | | | |
| lab code | result [$\mu\text{g/l}$] | \pm | ζ -score | z-score | assessm. ** |
| 4 | 0,88 | | | 1,3 | s |
| 5 | 0,54 | | | -0,7 | s |
| 12 | 0,52 | | | -0,8 | s |
| 18 | 0,692 | 0,0886 | 0,2 | 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



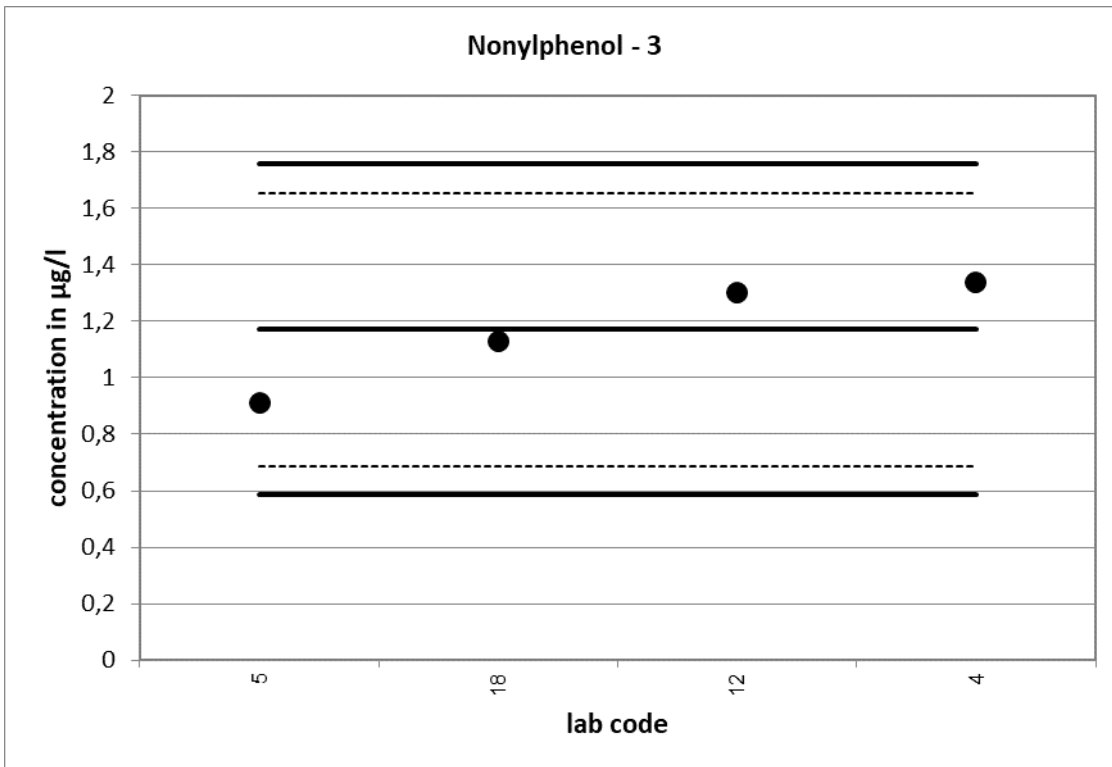


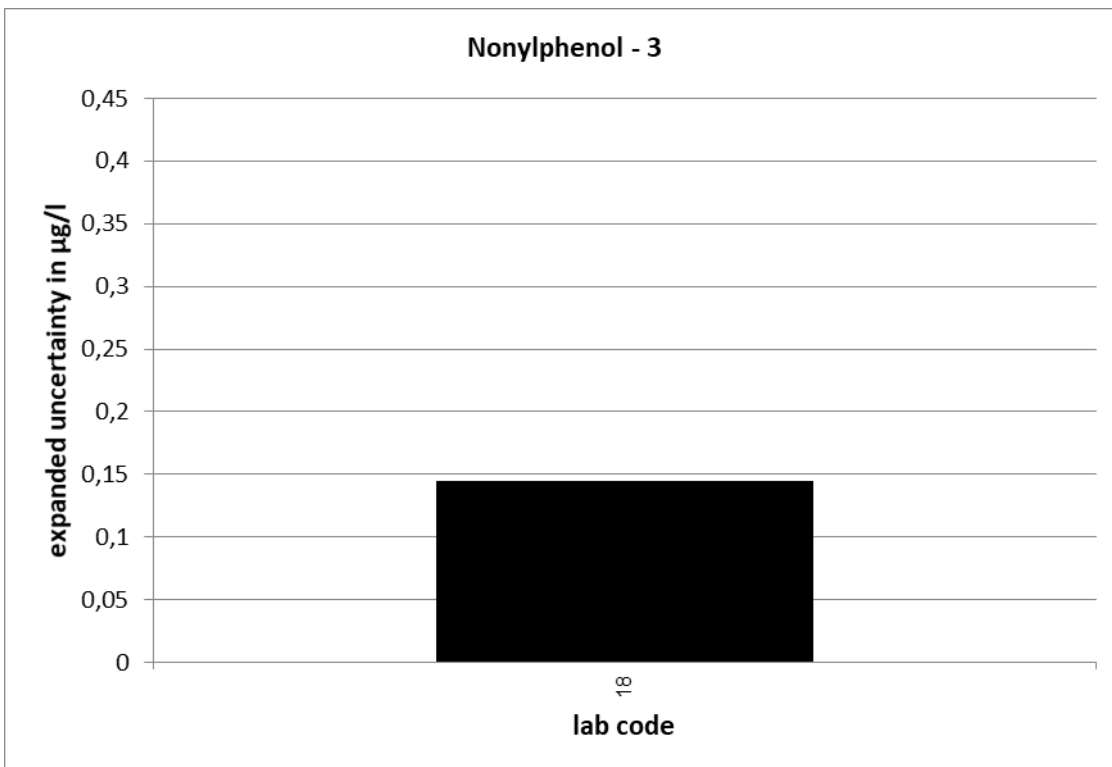
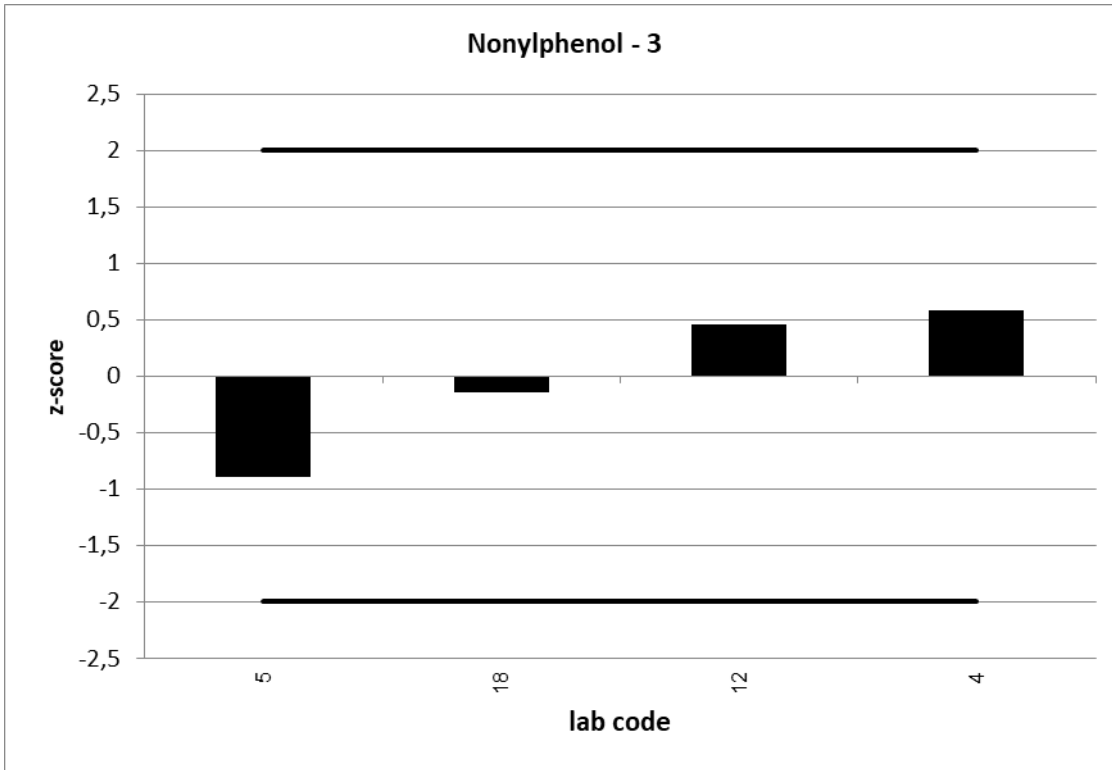


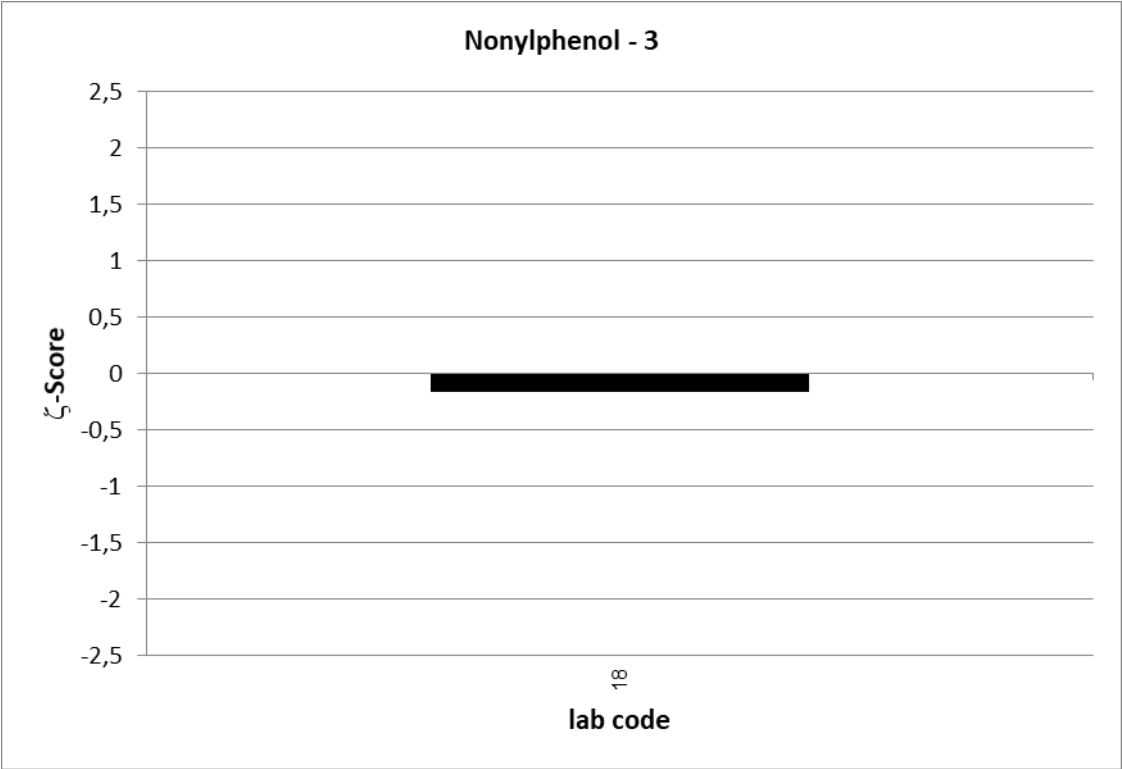
| UKWIR PT 5/20 | | Nonylphenol - 3 | | | |
|----------------------------|---------------|-----------------|---------|---------|-------------|
| assigned value [µg/l]* | | 1,171 ± 0,483 | | | |
| upper tolerance limit [µg/ | | 1,757 | | | |
| lower tolerance limit [µg/ | | 0,5855 | | | |
| lab code | result [µg/l] | ± | ζ-score | z-score | assessm. ** |
| 4 | 1,34 | | | 0,6 | s |
| 5 | 0,91 | | | -0,9 | s |
| 12 | 1,304 | | | 0,5 | s |
| 18 | 1,13 | 0,1446 | -0,2 | -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

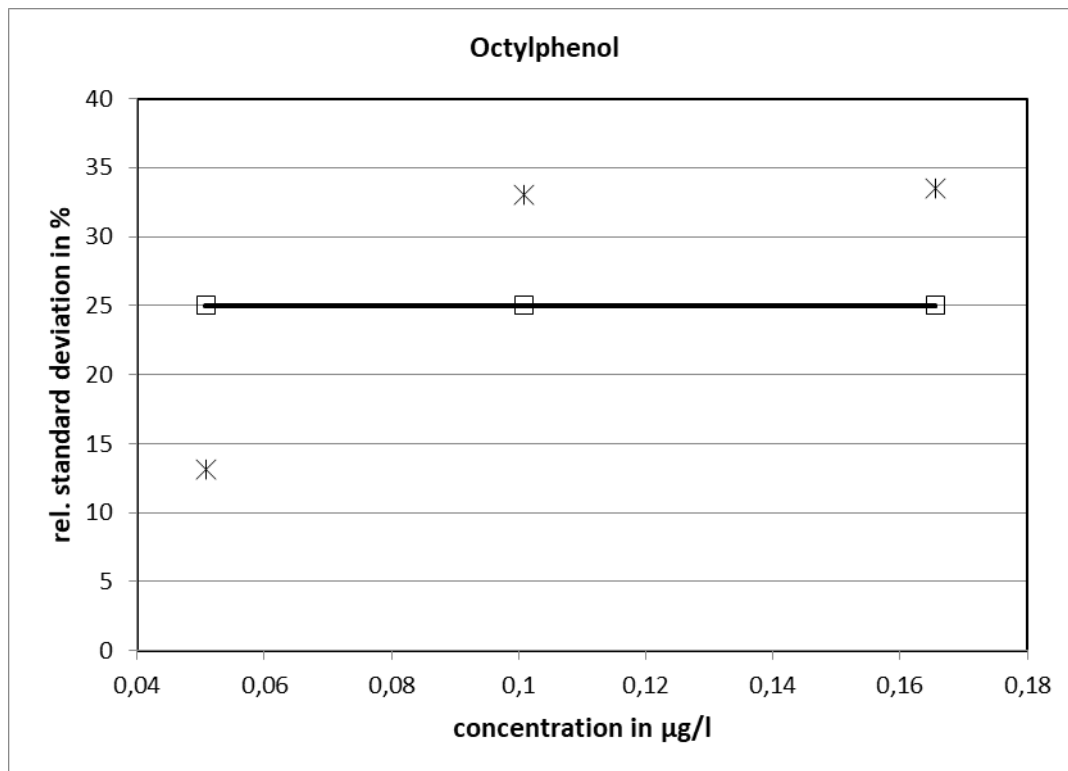






| Octylphenol | | | | | | | | | | | | | |
|-------------|-----------------------|--|---|--|---|------------------------------|------------------------------|---------------------------|---------------------------|-------------------|-----------|-----------|---------|
| level | assigned value [µg/l] | 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 | 0,0508 | 8,95 | 0,0067 | 0,0127 | 25 | 0,0762 | 0,0254 | 50 | -50 | 4 | 0 | 0 | 0,0 |
| 2 | 0,1009 | 22,87 | 0,0333 | 0,0252 | 25 | 0,1513 | 0,0504 | 50 | -50 | 4 | 0 | 0 | 0,0 |
| 3 | 0,1655 | 41,90 | 0,0555 | 0,0414 | 25 | 0,2483 | 0,0828 | 50 | -50 | 4 | 0 | 0 | 0,0 |
| | | | | | | | | | | sum | 12 | 0 | 0,0 |

Relative standard deviation

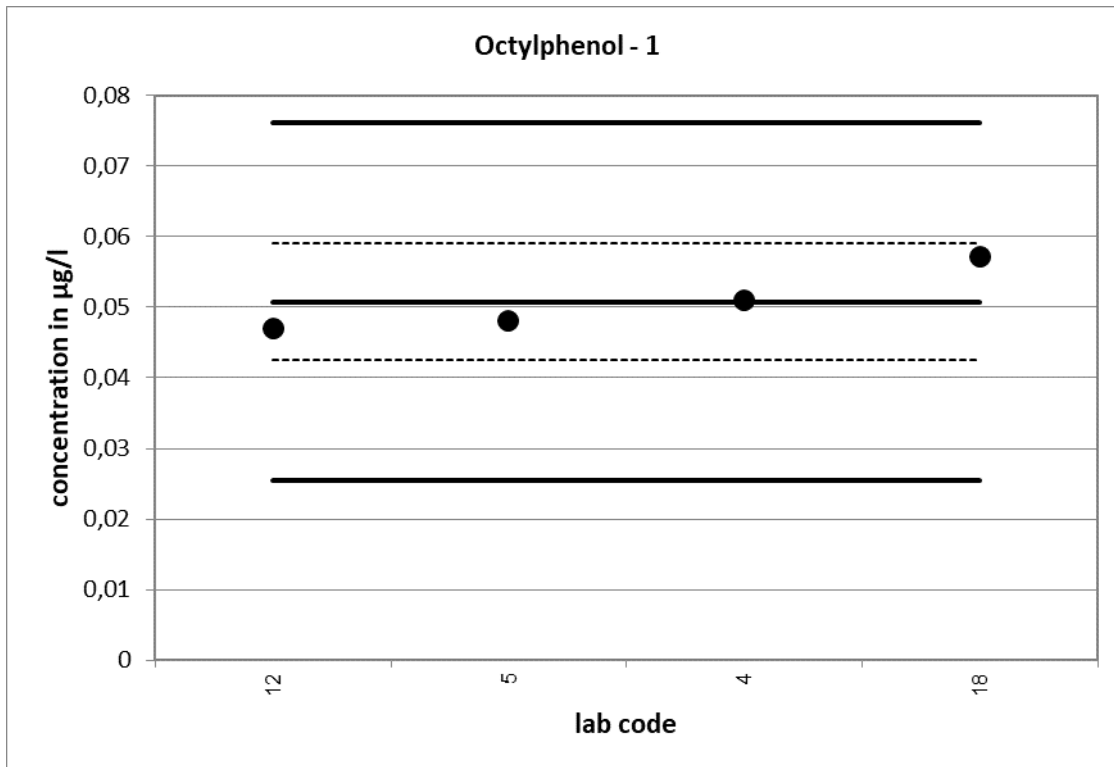


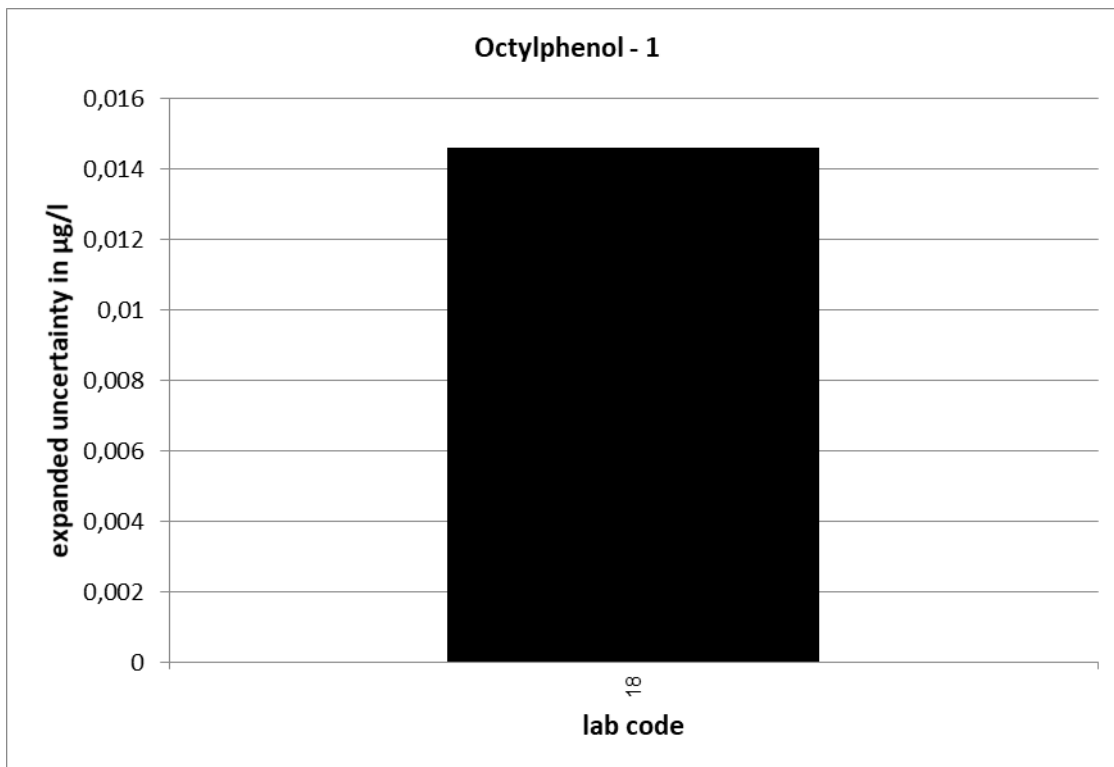
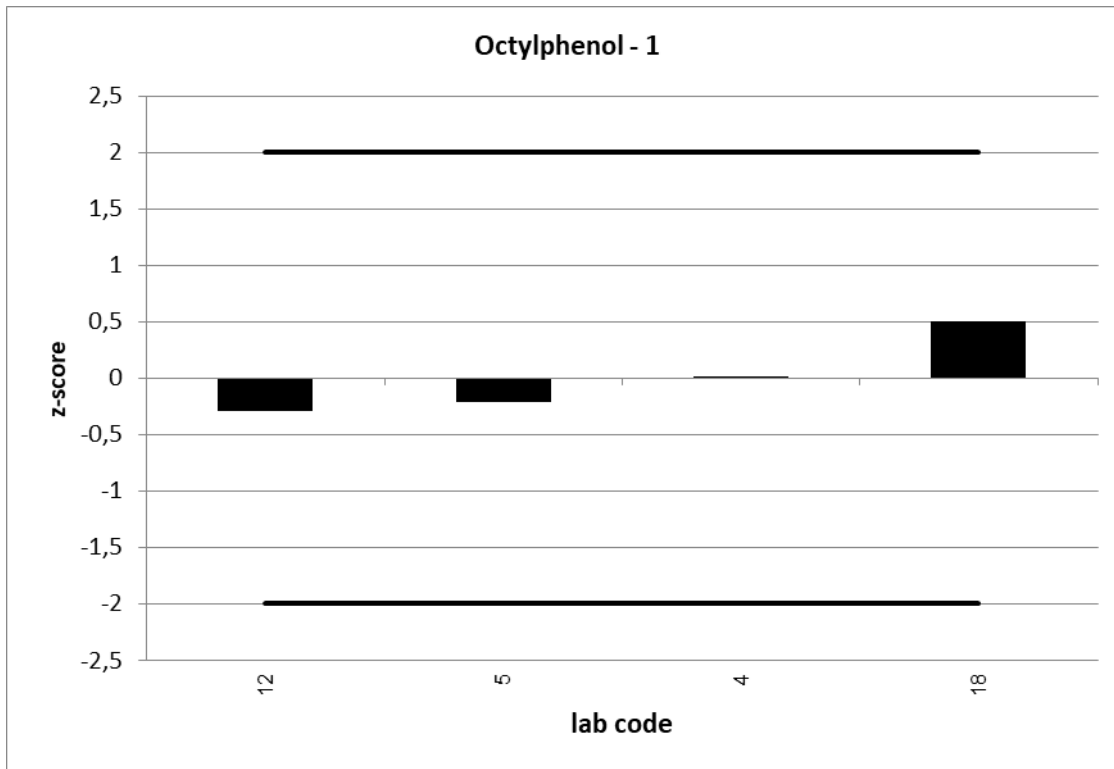
25 % is used as standard deviation for proficiency assessment.

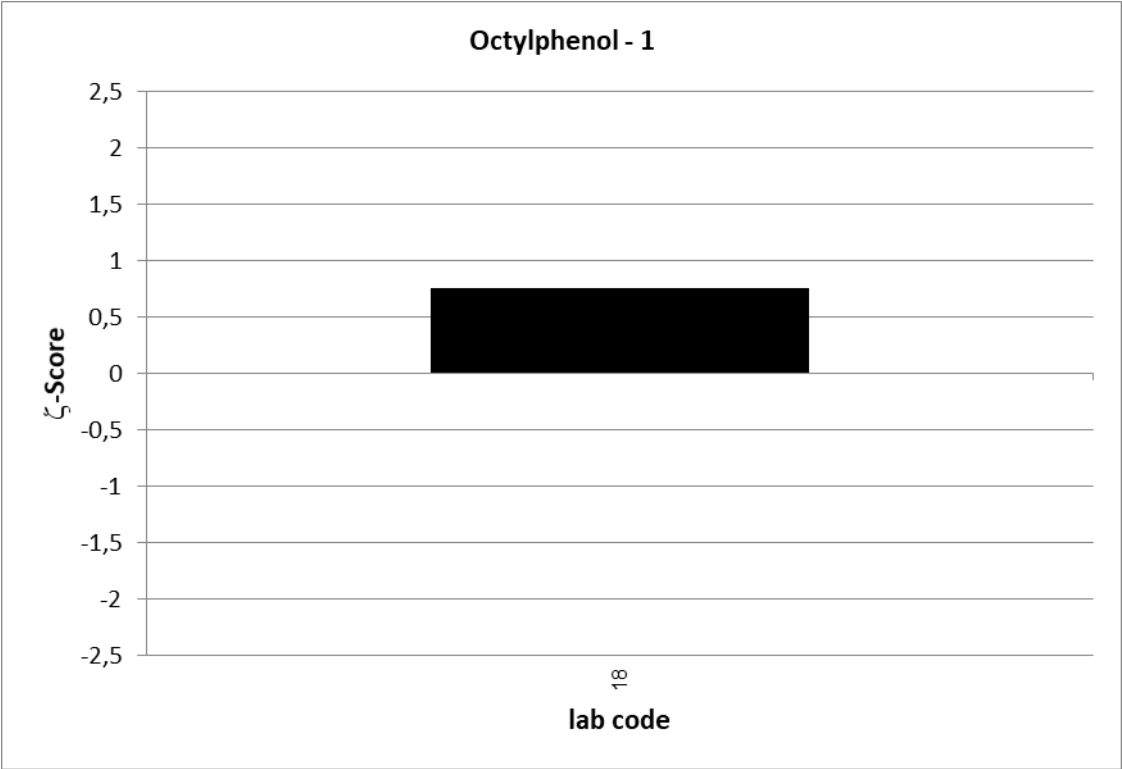
| UKWIR PT 5/20 | | Octylphenol - 1 | | | |
|----------------------------|---------------|-------------------|---------|---------|-------------|
| assigned value [µg/l]* | | 0,05078 ± 0,00832 | | | |
| upper tolerance limit [µg/ | | 0,07616 | | | |
| lower tolerance limit [µg/ | | 0,02539 | | | |
| lab code | result [µg/l] | ± | ζ-score | z-score | assessm. ** |
| 4 | 0,051 | | | 0,0 | s |
| 5 | 0,048 | | | -0,2 | s |
| 12 | 0,047 | | | -0,3 | s |
| 18 | 0,0571 | 0,0146 | 0,8 | 0,5 | 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



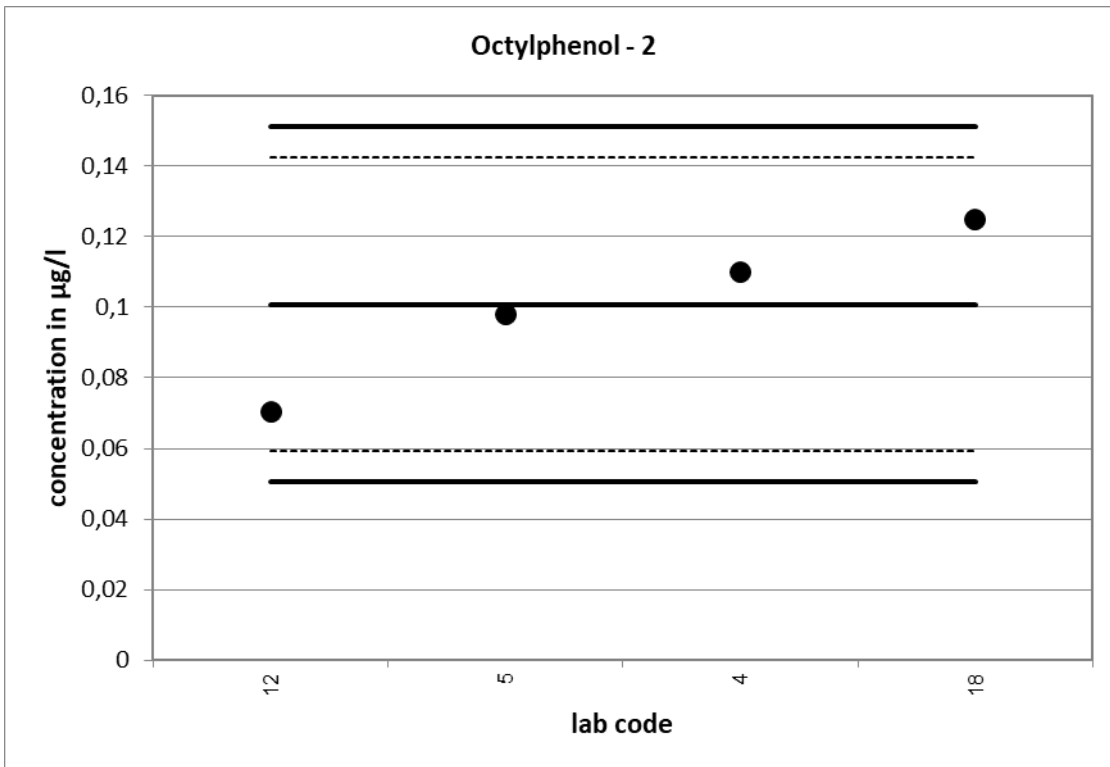


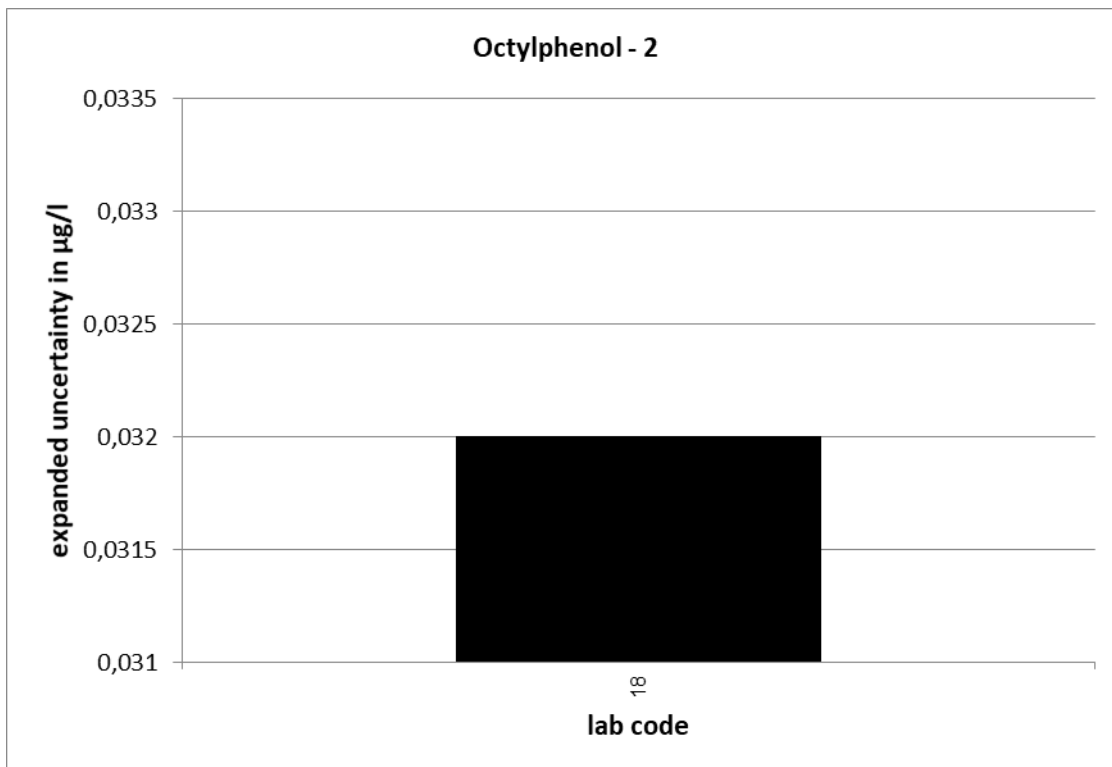
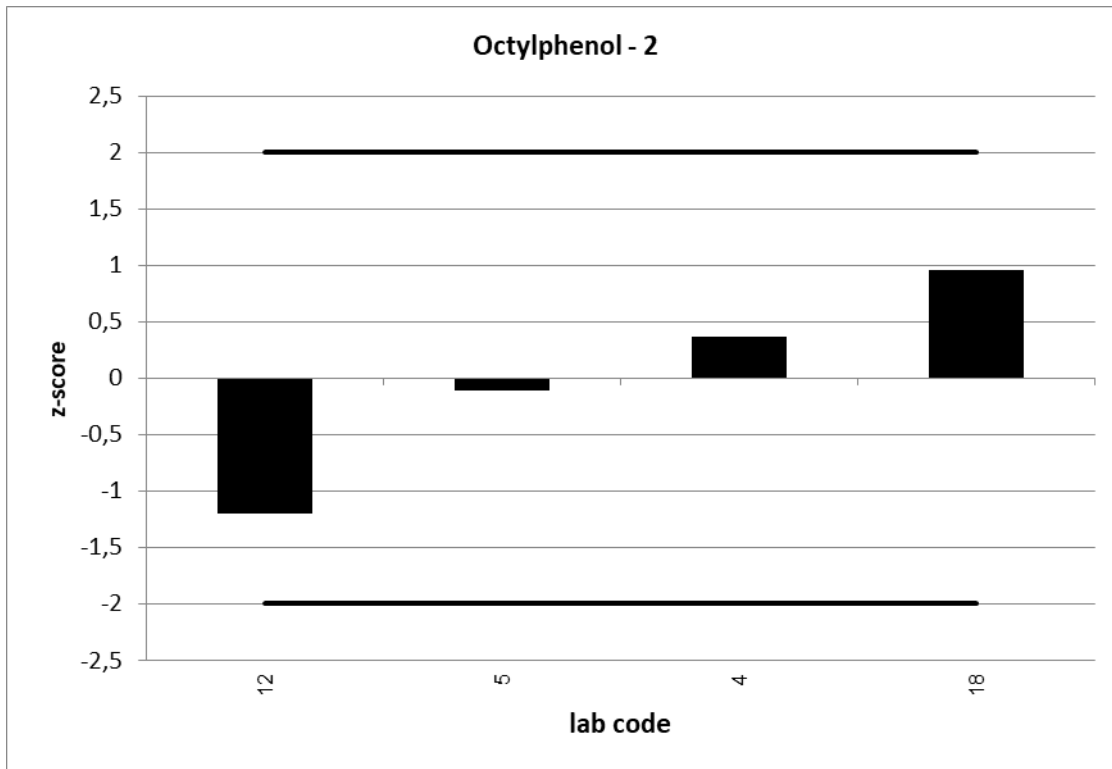


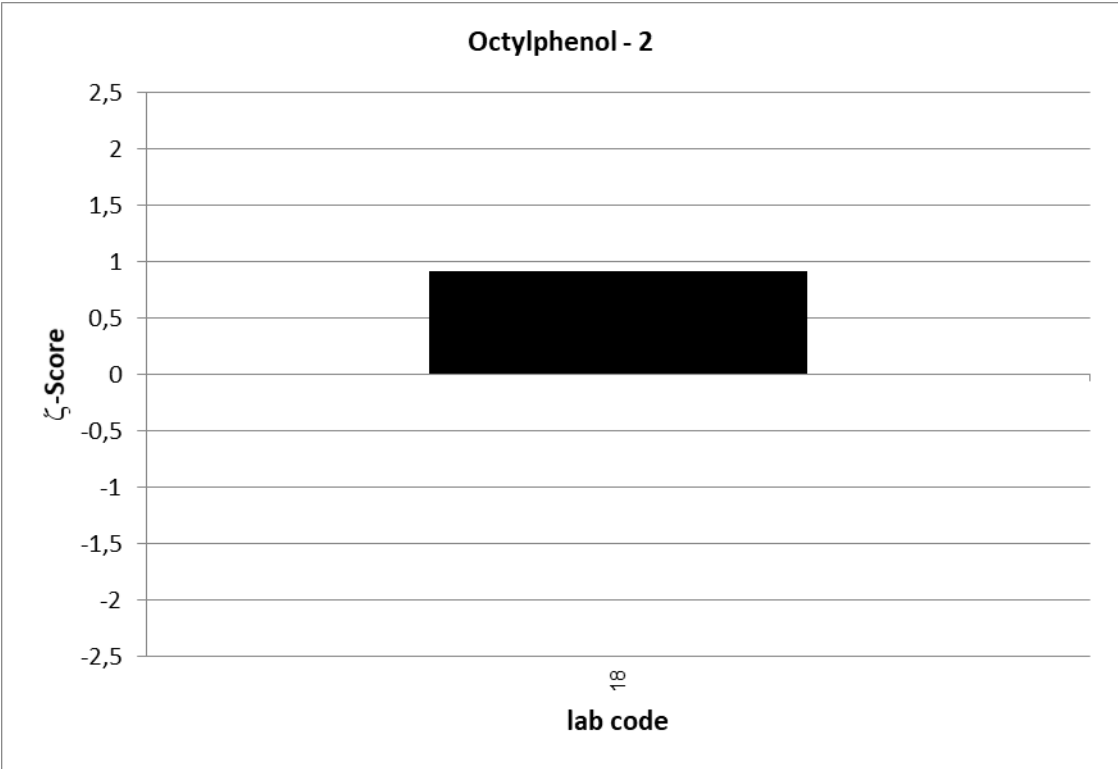
| UKWIR PT 5/20 | | Octylphenol - 2 | | | |
|---|----------------------------|---------------------|----------------|---------|-------------|
| assigned value [$\mu\text{g/l}$]* | | 0,1009 \pm 0,0416 | | | |
| upper tolerance limit [$\mu\text{g/l}$] | | 0,1513 | | | |
| lower tolerance limit [$\mu\text{g/l}$] | | 0,05044 | | | |
| lab code | result [$\mu\text{g/l}$] | \pm | ζ -score | z-score | assessm. ** |
| 4 | 0,11 | | | 0,4 | s |
| 5 | 0,098 | | | -0,1 | s |
| 12 | 0,0705 | | | -1,2 | s |
| 18 | 0,125 | 0,032 | 0,9 | 1,0 | 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 PT 5/20 | | Octylphenol - 3 | | | |
|---|----------------------------|---------------------|----------------|---------|------------|
| assigned value [$\mu\text{g/l}$]* | | 0,1655 \pm 0,0693 | | | |
| upper tolerance limit [$\mu\text{g/l}$] | | 0,2483 | | | |
| lower tolerance limit [$\mu\text{g/l}$] | | 0,08275 | | | |
| lab code | result [$\mu\text{g/l}$] | \pm | ζ -score | z-score | assessm.** |
| 4 | 0,177 | | | 0,3 | s |
| 5 | 0,156 | | | -0,2 | s |
| 12 | 0,127 | | | -0,9 | s |
| 18 | 0,202 | 0,0517 | 0,8 | 0,9 | 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

